Quantum Chemistry and Surface Hopping Dynamics of Azobenzenes: Free and Constrained Models

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Abstract

This cumulative doctoral dissertation, based on three publications, is devoted to the investigation of several aspects of azobenzene molecular switches, with the aid of computational chemistry. In the first paper, the isomerization rates of a thermal cis → trans isomerization of azobenzenes for species formed upon an integer electron transfer, i.e., with added or removed electron, are calculated from Eyring’s transition state theory and activation energy barriers, computed by means of density functional theory. The obtained results are discussed in connection with an experimental study of the thermal cis → trans isomerization of azobenzene derivatives in the presence of gold nanoparticles, which is demonstrated to be greatly accelerated in comparison to the same isomerization reaction in the absence of nanoparticles.

The second paper is concerned with electronically excited states of (i) dimers, composed of two photoswitchable units placed closely side-by-side, as well as (ii) monomers and dimers adsorbed on a silicon cluster. A variety of quantum chemistry methods, capable of calculating molecular electronic absorption spectra, based on density functional and wave function theories, is employed to quantify changes in optical absorption upon dimerization and covalent grafting to a surface. Specifically, the exciton (Davydov) splitting between states of interest is determined from first-principles calculations with the help of natural transition orbital analysis, allowing for insight into the nature of excited states.

In the third paper, nonadiabatic molecular dynamics with trajectory surface hopping is applied to model the photoisomerization of azobenzene dimers, (i) for the isolated case (exhibiting the exciton coupling between two molecules) as well as (ii) for the constrained case (providing the van der Waals interaction with environment in addition to the exciton coupling between two monomers). For the latter, the additional azobenzene molecules, surrounding the dimer, are introduced, mimicking a densely packed self-assembled monolayer. From obtained results it is concluded that the isolated dimer is capable of isomerization likewise the monomer, whereas the steric hindrance considerably suppresses trans → cis photoisomerization.

Furthermore, the present dissertation comprises the general introduction describing the main features of the azobenzene photoswitch and objectives of this work, theoretical basis of the employed methods, and discussion of gained findings in the light of existing literature. Also, additional results on (i) activation parameters of the thermal cis → trans isomerization of azobenzenes, (ii) an approximate scheme to account for anharmonicity of molecular vibrations in calculation of the activation entropy, as well as (iii) absorption spectra of photoswitch–silicon composites obtained from time-demanding wave function-based methods are presented.
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1. Introduction

Molecular switches—molecules capable of reversible conformational change between two or more (meta)stable states—continue to attract attention of researchers due to the possibility to cause and govern various important transformations on nano and micro scales. Being molecular analogues of conventional switches, used ubiquitously in everyday life, they can become an indispensable part of molecular machines of the future, for synthesis and design of prototypes of which the Nobel Prize in chemistry has been awarded in this year (2016). Some of the molecular switches can be shifted between different states (isomers) by using light illumination, and are therefore called molecular photoswitches. Examples of the molecular photoswitches are azobenzenes, stilbenes, spiropyrans, fulgides, etc.

The focus of this dissertation is on azobenzene-containing molecules, which can be isomerized between trans (also called $E$) and cis ($Z$) forms (Fig. 1). The existence of the cis isomer of azobenzene (AB) was proposed by Hartley in 1937. Since that time numerous investigations of the AB isomerization have been carried out, and this remarkable reaction has been utilized in multiple applications, such as image storage, molecular machines, responsive surfaces, reversible conformational changes of macromolecules, in particular biopolymers (for example, DNA).

The $trans$ isomer of AB corresponds to the lower energy minimum on the ground-state potential energy surface (PES) in comparison to the cis isomer (Fig. 1). The energy barrier between the isomers can be overcome by using photoexcitation of specific energy (in the ultraviolet/visible (UV/Vis) range), which, in turn, induces the excited-state nuclear dynamics resulting (with some probability) in the isomerization. Moreover, the cis $\rightarrow$ trans isomerization can occur also without external photoexcitation, due to relatively low barrier ($\sim 1$ eV/molecule) on the ground-state PES, when coming from the cis isomer side. This barrier is the difference between energies of the cis isomer and a so-called transition state (TS) for the isomerization reaction—a first-order saddle point on the PES, being a minimum for all vibrational normal modes except one (reaction coordinate), leading to the thermal cis $\rightarrow$ trans isomerization. Recently, it has also been reported on mechanically-induced AB isomerization, caused with sonication.

On metallic surfaces the isomerization of AB and its derivatives can be stimulated with tunneling electrons, electric field, or X-ray.

The isomers of AB have different shape, molecular length, dipole moment, and some other properties. The $trans$-AB possesses the planar equilibrium geometry belonging to the $C_{2h}$ symmetry point group, whereas the cis-AB is bent, having lower $C_2$ symmetry (cf. Fig. 1). The $trans$ isomer has no permanent dipole moment. However, by introducing appropriate substituents one can bring a permanent dipole to the $trans$ form. The cis isomer of nonsubstituted AB has a permanent dipole of about 3 D. The change in the dipole moment upon isomerization along with the change in geometry is very crucial for intermolecular interactions, particularly, for self-assembly.

The mechanism of azobenzene isomerization has been a subject of many
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Figure 1. Schematic view on the lowest singlet potential energy surfaces (PESs) of azobenzene (AB), namely $S_0$, $S_1$, and $S_2$. The trans and cis isomers (the optimized B3LYP/6-31G* structures) are depicted along with excitations usually employed for isomerizations (illumination with ultraviolet (UV) light of the trans isomer and with visible (Vis) light of the cis isomer) and the ground-state barrier for the back ($cis \rightarrow trans$) isomerization (which is equal to 1.1 eV at the B3LYP/6-31G* level of theory).

investigations. Two main pathways of the $trans \rightarrow cis$ isomerization have been originally widely discussed: (i) out-of-plane rotation around the central NN bond and (ii) in-plane inversion through variation of one or both CNN angles. More recent works, employing nonadiabatic molecular dynamics, show more involved mechanisms of the photoisomerization, such as inversion-assisted rotation or pedal-like motion of the azo group. We note, however, that the precise mechanism of isomerization is still an open question. The thermal back ($cis \rightarrow trans$) isomerization is supposed to proceed mostly through an inversion mechanism on $S_0$, which is supported by linearization of one of the CNN angles in the TS. Also, the possibility of a nonadiabatic route for the thermal back isomerization due to $S_0/T_1$ crossings (of ground singlet and triplet states) has been proposed.

The environment can play a dramatic role in the switching process. It has been observed that the $trans \rightarrow cis$ photoisomerization is suppressed for bare AB deposited on a gold surface (the molecules “lie” on the surface) and for densely packed self-assembled monolayers (SAMs) of thiolated AB derivatives, again on a gold surface (the AB-containing molecules “stand” on the surface). The mentioned factors which are supposed to hinder isomerization are steric hindrance, photoswitch–substrate and photoswitch–photoswitch couplings. We note, though, that for terminally thiolated azobiphenyl SAMs on gold the cooperative light-induced switching has been observed.

Despite a large number of works devoted to the investigation of AB, its isomerization and omnifarious applications, there are still questions to be answered. Some of them
we address in this dissertation. For example, recently it has been experimentally observed that the thermal back isomerization of azobenzenes is greatly accelerated in the presence of gold nanoparticles in solution.\textsuperscript{34–37} As a possible reason for this \textit{rapid} thermal isomerization an electron transfer mechanism has been proposed.\textsuperscript{35} However, to clarify this phenomenon, theoretical insight into the problem is highly desired.

Another challenging task is the switching (or lack thereof) of AB-containing molecules in tightly packed ensembles. As already mentioned above, isomerization is suppressed for \textit{densely packed} SAMs of certain AB-containing molecules on surfaces.\textsuperscript{31,32} In ref.\textsuperscript{38}, it has been pointed out, that for switching to occur, an area occupied by a single AB group should be larger than $\sim 0.4 \text{ nm}^2$. In other words, for isomerization to take place, one needs grafting densities smaller than $\sim 2.5$ molecules per $\text{nm}^2$. In addition to the free volume (or steric hindrance) factor, it has been proposed that the sizable exciton coupling between AB chromophores (when the latter are tightly packed) leads to ultrafast excitation transfer in the SAM, and thus, quenches excitation, preventing a switch from isomerization.\textsuperscript{31} The excitation energy transfer time has been estimated to be on the order of several femtoseconds,\textsuperscript{31,39} whereas hundreds of femtoseconds\textsuperscript{40} or even several picoseconds (see ref. \textsuperscript{41} and references therein) are usually required for the isomerization reaction. However, a deep insight into the details of isomerization possibility in densely packed SAMs is still an open question. In this dissertation we use models tractable by means of quantum chemical methods to clarify effects of inter-photoswitch couplings. In particular, we study the effect of dimerization on optical properties and switching of azobenzenes.

Taking into account said above, we put forward the following questions, to be addressed in the present dissertation:

- Why do naked gold nanoparticles accelerate the thermal back isomerization of azobenzenes? How can quantum chemical computations help to elucidate proposed hypotheses, explaining the increased thermal isomerization rate?

- What are the effects of dimerization on optical absorption of azobenzenes? In particular, what is the magnitude of the \textit{exciton (Davydov) splitting} and the spectral shift?

- What quantum chemical methods can be used to calculate absorption and the exciton splitting properly?

- What are the effects of covalent grafting to a silicon surface on UV/Vis absorption spectra of monomers and dimers?

- How does the dimerization affect isomerization dynamics of AB? Specifically, how does the switching quantum yield change with respect to the monomeric reference? What are the effects on the excited-state lifetimes and product geometries?

- What occurs with above mentioned observables in SAM-like densely packed model imposing the steric constraint on motion of switchable AB units?

The present dissertation is based on three papers, in which we explore the raised problems. Briefly, the first paper\textsuperscript{42} deals with the recently reported phenomenon of
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great acceleration of the thermal $\text{cis} \rightarrow \text{trans}$ AB isomerization in the presence of gold nanoparticles in a solution.\textsuperscript{34–37} For the computational part of our investigation we have considered a set of AB-containing molecules in the initial (reference) state and upon electron attachment and withdrawal, since an electron-transfer mechanism is expected to be responsible for rapid back isomerization in the vicinity of gold nanoparticles. Aiming at obtaining theoretical insight into this problem we have applied density functional theory calculations in conjunction with Eyring’s transition state theory\textsuperscript{43} to get the corresponding activation energy barriers and rates of isomerization. In this publication the transformations of the electronic ground state with adding/removing an electron to/from ABs have been investigated.

The second\textsuperscript{44} and the third\textsuperscript{45} publications are concerned with electronically excited states of ABs. Specifically, in the second paper, we have performed stationary quantum chemical calculations to elucidate the problem of exciton coupling in a dimer and determine the exciton splitting from first-principles calculations. Also, the change in optical absorption upon covalent grafting of a single molecule and a dimer to a silicon surface has been analyzed.

In the third paper nonadiabatic molecular dynamics with trajectory surface hopping has been performed for an AB dimer and the dimer embedded in the “classical” (molecular mechanics) environment of additional ABs, mimicking the arrangement in a SAM, to obtain the quantum yield of photoisomerization and track the influence of electronic and steric effects on this reaction. Both these studies contribute to the understanding of inter-chromophore interactions and isomerization at intermolecular distances smaller than the size of the chromophore itself, which can be realized when adsorbing molecules on surfaces forming SAMs, or in various self-assembled structures in solution, such as micelles.

The dissertation is organized as follows. The next chapter (chapter 2) concisely describes the indispensable theoretical basis of performed investigations. Summaries of publications, composing this cumulative dissertation, are presented in chapter 3. The reprints of the published papers (main texts and supporting information parts) constitute chapter 4. Chapter 5 provides a discussion of the obtained results and draws conclusions. Moreover, in appendices, we report additional results, which complement the findings of the presented publications.
2. Theoretical basis

In this chapter the theoretical approaches and computational methods used in the dissertation are outlined.

2.1. Time-independent non-relativistic Schrödinger equation. Adiabatic and Born–Oppenheimer approximations

The time-independent non-relativistic Schrödinger equation (SE) for a molecule reads:

\[ \hat{H}\Psi(r, R) = E_{tot}\Psi(r, R). \] (2.1)

The solution of this equation gives the total energy of the molecule \( E_{tot} \) and its wave function \( \Psi(r, R) \), the latter is a function of all electronic \( r \) and all nuclear \( R \) spatial coordinates. If \( N \) is the number of electrons and \( \tilde{N} \) is the number of nuclei in the molecule, then \( r = \{\vec{r}_1, \ldots, \vec{r}_N\} \) is a 3\(N\)-dimensional vector and \( R = \{\vec{R}_1, \ldots, \vec{R}_{\tilde{N}}\} \) is a 3\(\tilde{N}\)-dimensional vector (where \( \vec{r}_i \) \((i = 1, \ldots, N) \) and \( \vec{R}_A \) \((A = 1, \ldots, \tilde{N}) \) denote 3-dimensional vectors of coordinates of individual electrons and nuclei, respectively). The molecular Hamiltonian \( \hat{H} \) in (2.1) is a sum of operators of kinetic energy of nuclei \( \hat{T}_n \) and electrons \( \hat{T}_e \) and potential energy of their interaction: Coulomb repulsion of nuclei \( \hat{V}_{nn} \), Coulomb repulsion of electrons \( \hat{V}_{ee} \), and Coulomb attraction of nuclei and electrons \( \hat{V}_{ne} \):

\[ \hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne}. \] (2.2)

In atomic units the operators are given as follows:

\[
\begin{align*}
\hat{T}_n &= -\frac{1}{2} \sum_{A=1}^{\tilde{N}} \frac{1}{M_A} \Delta_A, \\
\hat{T}_e &= -\frac{1}{2} \sum_{i=1}^{N} \Delta_i, \\
\hat{V}_{nn} &= \frac{1}{2} \sum_{A=1}^{\tilde{N}} \sum_{B=1}^{\tilde{N}} Z_A Z_B \frac{1}{|\vec{R}_A - \vec{R}_B|}, \\
\hat{V}_{ee} &= \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|}, \\
\hat{V}_{ne} &= -\sum_{A=1}^{\tilde{N}} \sum_{i=1}^{N} \frac{Z_A}{|\vec{R}_A - \vec{r}_i|}.
\end{align*}
\] (2.3)
Here, $M_A$ and $Z_A$ are the nuclear masses and atomic numbers, respectively.

Inspecting (2.3) one can note that $\hat{T}_n$ contains nuclear masses, which are much larger than the mass of an electron. Even the lightest nucleus—the proton, the nucleus of a hydrogen atom—is about 1836 times heavier than the electron. Thus, to simplify the problem it is reasonable to consider the limit of infinite nuclear masses, in which we obtain the following equation:

$$\hat{H}_{cn}\Phi(r; R) = \mathcal{E}(R)\Phi(r; R) ,$$

(2.4)

where $\hat{H}_{cn} = \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ee} + \hat{V}_{ne}$ is a clamped-nuclei electronic Hamiltonian, and nuclear coordinates $R$ are viewed as parameters. Further, $\Phi(r; R)$ is the electronic wave function. Eq. (2.4) is called an electronic Schrödinger equation. The spectrum of $\hat{H}_{cn}$ has both discrete and continuous parts at lower and higher energies, respectively. We will consider only bound states, corresponding to the lower-energy part of the spectrum. Such states can be normalized to unity, i.e.:

$$\int \Phi^*(r; R)\Phi(r; R)dr = 1 \quad \forall \quad R .$$

(2.5)

Here and in what follows $\int dr$ denotes the integral taken over the whole space of all the electronic coordinates.

The solution to the original SE (2.1) we will seek in the form:

$$\Psi(r, R) = \Phi(r, R)X(R) ,$$

(2.6)

where $\Phi(r; R)$ is one of the solutions to the clamped-nuclei Hamiltonian (corresponding to the discrete part of the $\hat{H}_{cn}$ spectrum) and $X(R)$ is some function of only nuclear coordinates. One can substitute (2.6) in (2.1), multiply from the left by $\Phi^*(r; R)$ and integrate over electronic coordinates:

$$\int \Phi^*(r; R) \left[ \hat{T}_n + \hat{H}_{cn} \right] \Phi(r; R)X(R)dr = \int \Phi^*(r; R)E_{tot}\Phi(r; R)X(R)dr ,$$

(2.7)

and further taking into account (2.3)–(2.5):

$$\left[ \hat{T}_n + \mathcal{E}(R) + \int \Phi^*(r; R)\hat{T}_n\Phi(r; R)dr \right] X(R) -$$

$$- \sum_{A=1}^{N} \frac{1}{M_A} \nabla_A X(R) \int \Phi^*(r; R)\nabla_A \Phi(r; R)dr = E_{tot}X(R) .$$

(2.8)

If functions $\Phi(r; R)$ are real then $\int \Phi^*(r; R)\nabla_A \Phi(r; R)dr = 0$ (that can be shown by applying $\nabla_A$ to normalization (2.5)) and we arrive at a nuclear Schrödinger equation in the adiabatic approximation:

$$\left[ \hat{T}_n + \mathcal{E}(R) + \int \Phi(r; R)\hat{T}_n\Phi(r; R)dr \right] X(R) = E_{tot}X(R) .$$

(2.9)
The integral \[ \int \Phi(r; R) \hat{T}_n \Phi(r; R) dr \] is called the diagonal Born–Oppenheimer correction (DBOC) or the Born–Oppenheimer diagonal correction (BODC). The Born–Oppenheimer approximation corresponds to dropping in (2.9) the DBOC term:

\[ \left[ \hat{T}_n + \mathcal{E}(R) \right] X(R) = E_{\text{tot}} X(R) . \] (2.10)

From (2.10) one can see that \( \mathcal{E}(R) \) serves as an effective potential in which nuclei move. The \( \mathcal{E}(R) \) function is termed therefore potential energy surface (PES). There are multiple PESs, corresponding to different eigenvalues of \( H_{cn} \) Hamiltonian, the lowest-valued of them is the ground-state PES and the others are the excited-state PESs.

We note that in the approach presented above, the center-of-mass motion of nuclei is retained, and the corresponding plane-wave exponential factor should arise in the \( X(R) \) function, when considering the problem of nuclear motion.

### 2.2. Hartree–Fock method

The clamped-nuclei electronic SE (2.4) for many-electron systems (which most molecules are) cannot be solved exactly. Thus, approximate methods should be used. We note that at fixed nuclear configuration \( R \) the nuclear–nuclear repulsion term \( \hat{V}_{nn} \) is a constant (see (2.3)), and, thus, does not affect electronic wave functions (eigenfunctions) and shifts eigenvalues by a constant. Hence, we can drop this term and consider a purely electronic SE of the following form:

\[ \hat{H}_e \Phi = E \Phi , \]
\[ \hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ne} . \] (2.11)

In the Hartree–Fock (HF) method the electronic wave function \( \Phi \) is represented by a single Slater determinant:

\[ \Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \chi_2(\vec{x}_1) & \ldots & \chi_N(\vec{x}_1) \\ \chi_1(\vec{x}_2) & \chi_2(\vec{x}_2) & \ldots & \chi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \chi_2(\vec{x}_N) & \ldots & \chi_N(\vec{x}_N) \end{vmatrix} . \] (2.12)

Here \( \{\chi_i\} \) are single-electron functions, each of these functions depends on three spatial coordinates \( \vec{r}_j \) and a spin variable \( \sigma_j \) of an electron, collected in a single vector \( \vec{x}_j = (\vec{r}_j, \sigma_j) \). Such functions are called spin-orbitals. We note that now the many-electron wave function \( \Phi \) depends also on spin variables, which we had neglected so far.

The "right" spin-orbitals (within this single-determinant ansatz) can be found, following the variational principle of minimization of the energy functional \( \int \Phi^* \hat{H}_e \Phi d\vec{x}_1 \ldots d\vec{x}_N, \) from the system of canonical Hartree–Fock equations:

\[ \hat{F} \chi_i(\vec{x}) = \varepsilon_i \chi_i(\vec{x}) , \quad i = 1, \ldots, N . \] (2.13)
\( \hat{F} \) stands here for the Fock operator (Fockian), which is a single-electron operator and has the following form:

\[
\hat{F} = \hat{\mathcal{H}} + \sum_{j=1}^{N} (\hat{J}_j - \hat{K}_j),
\]

\[
\hat{\mathcal{H}} \chi_i(\vec{x}) = \begin{bmatrix}
-\frac{1}{2} \Delta - \sum_{A=1}^{\tilde{N}} \frac{Z_A}{|\vec{R}_A - \vec{r}|}
\end{bmatrix} \chi_i(\vec{x}),
\]

\[
\hat{J}_j \chi_i(\vec{x}) = \int \chi^*_j(\vec{x}') \frac{1}{|\vec{r} - \vec{r}'|} \chi_j(\vec{x}') d\vec{x}' \chi_i(\vec{x}),
\]

\[
\hat{K}_j \chi_i(\vec{x}) = \int \chi^*_j(\vec{x}') \frac{1}{|\vec{r} - \vec{r}'|} \chi_i(\vec{x}') d\vec{x}' \chi_j(\vec{x}).
\]

(2.14)

\( \hat{J}_j \) is a multiplicative operator, called Coulomb operator and \( \hat{K}_j \) is an integral operator, called exchange operator. In (2.13), \( \varepsilon_i \) is the molecular orbital energy.

For a closed-shell case spin-orbitals may be given as

\[
\chi_{2i-1} = \varphi_i(\vec{r})^\alpha, \quad \chi_{2i} = \varphi_i(\vec{r})^\beta, \quad i = 1, \ldots, N/2,
\]

(2.15)

where \( \alpha \) and \( \beta \) are spin functions corresponding to “spin up” and “spin down” cases, respectively. The Hartree-Fock equations for spatial orbitals \( \varphi_i \) read (so-called restricted Hartree–Fock (RHF) method):

\[
\hat{F}^{RHF} \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r}), \quad i = 1, \ldots, N/2,
\]

(2.16)

where

\[
\hat{F}^{RHF} = \hat{\mathcal{H}} + \sum_{j=1}^{N/2} (2\hat{J}_j^{RHF} - \hat{K}_j^{RHF}),
\]

\[
\hat{\mathcal{H}}^{RHF} \varphi_i(\vec{r}) = \begin{bmatrix}
-\frac{1}{2} \Delta - \sum_{A=1}^{\tilde{N}} \frac{Z_A}{|\vec{R}_A - \vec{r}|}
\end{bmatrix} \varphi_i(\vec{r}),
\]

\[
\hat{J}_j^{RHF} \varphi_i(\vec{r}) = \int \varphi^*_j(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \varphi_j(\vec{r}') d\vec{r}' \varphi_i(\vec{r}),
\]

\[
\hat{K}_j^{RHF} \varphi_i(\vec{r}) = \int \varphi^*_j(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \varphi_i(\vec{r}') d\vec{r}' \varphi_j(\vec{r}).
\]

(2.17)

In general, each of the spatial molecular orbitals \( \varphi_i^\alpha \) of \( \alpha \) electrons may differ from each of the molecular orbitals \( \varphi_i^\beta \) of \( \beta \) electrons. The approach, accounting for this difference, is referred to as the unrestricted Hartree–Fock (UHF) method. The UHF method can describe an open-shell ground state (as for radicals) or an excited state, represented by a single Slater determinant. The UHF equations for a molecule
2.3. Density functional theory

with \( N_{\alpha} \) \( \alpha \) electrons and \( N_{\beta} \) \( \beta \) electrons are the following:

\[
\hat{F}^{\alpha}_i \varphi_i^{\alpha}(\vec{r}) = \varepsilon_i^{\alpha} \varphi_i^{\alpha}(\vec{r}) , \quad i = 1, \ldots, N_{\alpha} , \tag{2.18a}
\]

\[
\hat{F}^{\beta}_i \varphi_i^{\beta}(\vec{r}) = \varepsilon_i^{\beta} \varphi_i^{\beta}(\vec{r}) , \quad i = 1, \ldots, N_{\beta} . \tag{2.18b}
\]

Here Fock operators \( \hat{F}^{\alpha} \) and \( \hat{F}^{\beta} \) take the following form:

\[
\hat{F}^{\alpha} = \hat{h} + \sum_{j=1}^{N_{\alpha}} (\hat{J}^{\alpha}_j - \hat{K}^{\alpha}_j) + \sum_{j=1}^{N_{\beta}} \hat{J}^{\beta}_j , \tag{2.19a}
\]

\[
\hat{F}^{\beta} = \hat{h} + \sum_{j=1}^{N_{\beta}} (\hat{J}^{\beta}_j - \hat{K}^{\beta}_j) + \sum_{j=1}^{N_{\alpha}} \hat{J}^{\alpha}_j , \tag{2.19b}
\]

with the \( \hat{h} \) operator being the same as in (2.17) and \( \hat{J}^{\alpha(\beta)}_j \) and \( \hat{K}^{\alpha(\beta)}_j \) corresponding to \( \hat{J}^{RHF}_j \) and \( \hat{K}^{RHF}_j \) of (2.17), provided that \( \varphi_j \) is replaced with \( \varphi_j^{\alpha(\beta)} \).

Usually, in practice, the spatial molecular orbitals \( \varphi_i \) are constructed as linear combinations of atomic orbitals \( \eta_\mu \) (such molecular orbitals are referred to as LCAO MOs, Linear Combination of Atomic Orbitals Molecular Orbitals):

\[
\varphi_i(\vec{r}) = \sum_\mu c_i^\mu \eta_\mu(\vec{r}) . \tag{2.20}
\]

For a closed-shell ground state one can arrive, starting from (2.16) and utilizing the expansion (2.20), at the Roothaan equations:\(^{52}\)

\[
F c_i = \varepsilon_i S c_i . \tag{2.21}
\]

Here \( F \) is the Fock matrix, composed of \( \int \eta_\mu^* \hat{F}^{RHF} \eta_\nu \, d\vec{r} \) matrix elements (\( \hat{F}^{RHF} \) from (2.17)), and \( S \) is the overlap matrix, composed of \( \int \eta_\mu^* \eta_\nu \, d\vec{r} \) elements. Further, \( c_i \) is the MO (column) eigenvector, \( c_i = (c_{i1} \, c_{i2} \, \ldots)^T \).

The Roothaan equations (2.21) can be generalized to treat separately molecular orbitals of \( \alpha \) and \( \beta \) electrons. The corresponding equations (called the Pople–Nesbet–Berthier equations) read:\(^{53}\)

\[
F^{\alpha} c_i^{\alpha} = \varepsilon_i^{\alpha} S c_i^{\alpha} , \tag{2.22a}
\]

\[
F^{\beta} c_i^{\beta} = \varepsilon_i^{\beta} S c_i^{\beta} , \tag{2.22b}
\]

with matrices \( F^{\alpha} \) and \( F^{\beta} \) consisting of matrix elements computed on \( \hat{F}^{\alpha} \) and \( \hat{F}^{\beta} \) operators of (2.19a) and (2.19b), respectively.

2.3. Density functional theory

Another approach to deal with the electronic SE (2.11) is the density functional theory (DFT). The electron (number) density of an \( N \)-electron system described by a wave
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function \( \Phi(\vec{x}, \vec{x}_2, \ldots, \vec{x}_N) \) is given by the formula:

\[
\rho(\vec{r}) = N \int |\Phi(\vec{x}, \vec{x}_2, \ldots, \vec{x}_N)|^2 d\vec{x}_2 \ldots d\vec{x}_N.
\] (2.23)

When integrated over the whole (3D) space this results in the total number of electrons:
\[
\int \rho(\vec{r}) d\vec{r} = N.
\] (2.24)

The electron density depends only on 3 coordinates in contrast to the electron wave function, which is a function of \( 3N \) variables (or \( 4N \) if one counts spin). The electron density is a key quantity of DFT. The latter is based on two Hohenberg–Kohn theorems.\(^{54}\) The first theorem states that the external (for the electrons) potential is a unique functional of the electron density (apart from an additive constant). Hence, the whole electronic Hamiltonian \( \hat{H}_e \), and thus the wave function \( \Phi \), are uniquely determined by the ground-state electron density. If we consider an isolated molecule with fixed nuclei in the absence of external fields then the external potential is the potential of nuclear–electron attraction and reads:

\[
v_{\text{ext}}(\vec{r}) = -\sum_{A=1}^{\tilde{N}} \frac{Z_A}{|\vec{R}_A - \vec{r}|}.
\] (2.25)

The electron energy functional (a functional of the electron density) for a given external potential is then:
\[
E[\rho(\vec{r})] = T[\rho(\vec{r})] + V_{ee}[\rho] + \int \rho(\vec{r}) v_{\text{ext}}(\vec{r}) d\vec{r}.
\] (2.26)

The second theorem states that the correct ground-state density provides a minimum for the energy functional (2.26).

The \( V_{ee}[\rho] \) functional can be written as a sum of a Coulomb part \( J[\rho] \) and a nonclassical part, which includes electron exchange and correlation contributions:

\[
V_{ee}[\rho] = J[\rho] + \text{nonclassical part},
\]

\[
J[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'.
\] (2.27)

There were early attempts to write a functional for the kinetic energy.\(^{55}\) In particular, Thomas and Fermi derived the kinetic energy expression for the uniform electron gas. However, this model was not successful to correctly describe the kinetic energy of electrons in molecules.

The practical use of DFT is based on the approach proposed by Kohn and Sham.\(^{56}\) They decided to consider a fictitious system of \( N \) non-interacting electrons yielding the same ground-state density as that for the real system of \( N \) interacting electrons. The fictitious system has then its own kinetic energy, which we denote \( T_S[\rho] \). The energy
2.3. Density functional theory

The functional \( E[\rho] \) can be rewritten as:

\[
E[\rho] = T_S[\rho] + \frac{1}{2} \int \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + \int \rho(\vec{r}) v_{\text{ext}}(\vec{r}) d\vec{r} + E_{\text{xc}}[\rho].
\]

Here, the \( E_{\text{xc}}[\rho] \) term stands for the exchange–correlation functional, which includes the nonclassical part of \( V_{\text{ee}}[\rho] \) and a residual of the kinetic energy.

The system of \( N \) non-interacting electrons is described by the following Hamiltonian:

\[
\hat{H}_S = -\frac{1}{2} \sum_{i=1}^{N} \Delta_i + \sum_{i=1}^{N} \hat{v}_S(\vec{r}_i),
\]

where \( \hat{v}_S \) is an effective Kohn–Sham potential.

The exact ground-state wave function for this fictitious system is a Slater determinant composed of the Kohn–Sham (KS) spin-orbitals \( \{\chi_{KS}^i\} \):

\[
\Phi_S = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\chi_1^{KS}(\vec{x}_1) & \chi_2^{KS}(\vec{x}_1) & \cdots & \chi_N^{KS}(\vec{x}_1) \\
\chi_1^{KS}(\vec{x}_2) & \chi_2^{KS}(\vec{x}_2) & \cdots & \chi_N^{KS}(\vec{x}_2) \\
\vdots & \vdots & \ddots & \vdots \\
\chi_1^{KS}(\vec{x}_N) & \chi_2^{KS}(\vec{x}_N) & \cdots & \chi_N^{KS}(\vec{x}_N)
\end{vmatrix}.
\]

The orbitals themselves are found from the single-particle equations (the Kohn–Sham equations):

\[
\left[ -\frac{1}{2} \Delta + v_S(\vec{r}) \right] \chi_i^{KS}(\vec{x}) = \varepsilon_i^{KS} \chi_i^{KS}(\vec{x}), \quad i = 1, \ldots, N.
\]

The electron density is then obtained from the spin-orbitals as

\[
\rho(\vec{r}) = \sum_{i=1}^{N} \int |\chi_i^{KS}(\vec{x})|^2 d\sigma,
\]

and the kinetic energy \( T_S[\rho] \) reads:

\[
T_S[\rho] = \sum_{i=1}^{N} \int \chi_i^{KS*}(\vec{x}) \left( -\frac{1}{2} \Delta \right) \chi_i^{KS}(\vec{x}) d\vec{x}.
\]

The main remaining question is what effective potential \( v_S(\vec{r}) \) one should take to ensure the same electron densities for the fictitious and the real systems. The answer can be obtained applying a variational principle for the energy functional (2.28). Thus, the effective potential for the motion of a single electron reads:

\[
v_S(\vec{r}) = v_{\text{ext}}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{\text{xc}}(\vec{r}),
\]

where the exchange–correlation potential is \( v_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \) (the functional derivative of
2. Theoretical basis

the exchange–correlation energy functional).

If we deal with a closed-shell case, we can choose the spin-orbitals similarly to (2.15), and then:

$$\rho(\vec{r}) = 2 \sum_{i=1}^{N/2} |\varphi_{i}^{KS}(\vec{r})|^2$$  \hspace{1cm} (2.35)

and

$$T_S[\rho] = 2 \sum_{i=1}^{N/2} \int \varphi_{i}^{KS}(\vec{r}) \left( -\frac{1}{2} \Delta \right) \varphi_{i}^{KS}(\vec{r}) \, d\vec{r} \, ,$$  \hspace{1cm} (2.36)

where \{\varphi_{i}^{KS}\} are the KS spatial molecular orbitals.

The Kohn–Sham formalism can be generalized introducing separate densities for \(\alpha\) and \(\beta\) electrons. This is necessary for systems with external magnetic fields, and, moreover, can be applied to treat an open-shell case for molecules. For the latter we then obtain the unrestricted KS-DFT equations (an analogue of the UHF method):

$$\begin{bmatrix} -\frac{1}{2} \Delta + v_S^{\alpha}(\vec{r}) \end{bmatrix} \varphi_{i}^{KS,\alpha}(\vec{r}) = \varepsilon_{i}^{KS,\alpha} \varphi_{i}^{KS,\alpha}(\vec{r}) , \quad i = 1, \ldots , N_{\alpha} \, ,$$  \hspace{1cm} (2.37a)

$$\begin{bmatrix} -\frac{1}{2} \Delta + v_S^{\beta}(\vec{r}) \end{bmatrix} \varphi_{i}^{KS,\beta}(\vec{r}) = \varepsilon_{i}^{KS,\beta} \varphi_{i}^{KS,\beta}(\vec{r}) , \quad i = 1, \ldots , N_{\beta} \, .$$  \hspace{1cm} (2.37b)

Here the effective \(\alpha\) and \(\beta\) potentials take the following form:

$$v_S(\vec{r}) = v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}' + v_{xc}^{\alpha}(\vec{r}) \, ,$$  \hspace{1cm} (2.38a)

$$v_S(\vec{r}) = v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}' + v_{xc}^{\beta}(\vec{r}) \, ,$$  \hspace{1cm} (2.38b)

$$v_{xc}^{\alpha}(\vec{r}) = \left. \frac{\delta E_{xc}[\rho^\alpha, \rho^\beta]}{\delta \rho^\alpha} \right| , \quad v_{xc}^{\beta}(\vec{r}) = \left. \frac{\delta E_{xc}[\rho^\alpha, \rho^\beta]}{\delta \rho^\beta} \right| .$$  \hspace{1cm} (2.38c)

The \(\rho^\alpha\) and \(\rho^\beta\) densities (summing up to the total density \(\rho(\vec{r}) = \rho^\alpha(\vec{r}) + \rho^\beta(\vec{r})\)) can be calculated from the corresponding KS orbitals:

$$\rho^\alpha(\vec{r}) = \sum_{i=1}^{N_{\alpha}} |\varphi_{i}^{KS,\alpha}(\vec{r})|^2 \, ,$$  \hspace{1cm} (2.39a)

$$\rho^\beta(\vec{r}) = \sum_{i=1}^{N_{\beta}} |\varphi_{i}^{KS,\beta}(\vec{r})|^2 \, .$$  \hspace{1cm} (2.39b)

The next step is to establish the suitable approximation to the exchange–correlation functional \(E_{xc}[\rho]\). The simplest form used is the so-called local (spin) density approximation (L(S)DA), where the expression for \(E_{xc}[\rho]\) depends only on the electron density \(\rho\) (or \(\rho^\alpha\) and \(\rho^\beta\)). A further improvement may be achieved by including in an exchange–correlation functional gradient-dependence, on \(\nabla \rho\) (so-called generalized gradient approximation (GGA)), dependence on \(\Delta \rho\) and non-interacting kinetic energy.
2.4. LR-TD-DFT and LR-TD-HF

density (meta-GGA), admixture of exact exchange (hybrid functionals). 57

2.4. Linear response time-dependent density functional theory and Hartree–Fock method

The DFT has been extended to account for time-dependent external potentials. The foundation of the time-dependent density functional theory (TD-DFT) is provided by the Runge–Gross theorem. 58 The huge practical use of TD-DFT is based on the linear response (LR) approach and the resulting Casida equation, which will be outlined in this section.

We consider a time-dependent external potential:

\[ v_{\text{ext}}(\vec{r}, t) = v_0(\vec{r}) + v_1(\vec{r}, t) , \]  

(2.40)

where \( v_1(\vec{r}, t) \) is a small (in comparison to \( v_0(\vec{r}) \)) time-dependent perturbation, caused, e.g., by a weak time-dependent electric field. This perturbation will induce the change in the density:

\[ \rho(\vec{r}, t) = \rho_0(\vec{r}) + \rho_1(\vec{r}, t) + \ldots , \]  

(2.41)

where \( \rho_1(\vec{r}, t) \) depends linearly on \( v_1(\vec{r}, t) \), and higher-order terms are denoted by three dots. In the frequency domain one can then write: 59

\[ \rho_1(\vec{r}, \omega) = \int \chi(\vec{r}, \vec{r}', \omega) v_1(\vec{r}', \omega) d\vec{r}' . \]  

(2.42)

Here \( \chi \) is a so-called linear response function (not to be confused with spin-orbitals).

Due to the Runge–Gross theorem it is possible to calculate the change in the density \( \rho_1 \) employing the fictitious KS system of non-interacting electrons:

\[ \rho_1(\vec{r}, \omega) = \int \chi_{\text{KS}}(\vec{r}, \vec{r}', \omega) v_{S,1}(\vec{r}', \omega) d\vec{r}' . \]  

(2.43)

The linear response function for the system of non-interacting electrons reads: 60

\[ \chi_{\text{KS}}(\vec{r}, \vec{r}', \omega) = \lim_{\eta \to 0^+} \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} (f_k - f_j) \frac{\varphi_{j,KS}(\vec{r}) \varphi_{j,KS}^*(\vec{r}') \varphi_{k,KS}(\vec{r}') \varphi_{k,KS}^*(\vec{r})}{\omega - (\omega_j - \omega_k) + i\eta} , \]  

(2.44)

where \( f_l \) is the occupation number of the \( l \)th KS orbital for the ground state with the corresponding frequency \( \omega_l \). The change in the KS potential \( v_{S,1} \) can be calculated using the time-dependent analogue of (2.34):

\[ v_{S,1}(\vec{r}, t) = v_1(\vec{r}, t) + \int \frac{\rho_1(\vec{r}', t)}{|\vec{r} - \vec{r}'|} d\vec{r}' + \int \int \frac{\delta v_{xc}(\vec{r}, t)}{\delta \rho(\vec{r}', t')} \rho_1(\vec{r}', t') d\vec{r}' dt' , \]  

(2.45)

where \( \frac{\delta v_{xc}(\vec{r}, t)}{\delta \rho(\vec{r}', t')} \) is the so-called exchange–correlation kernel, usually denoted as \( f_{xc} \).
Further, transforming to the frequency space and using (2.43), we obtain:

\[ \rho_1(\vec{r}, \omega) = \int \chi_{KS}(\vec{r}, \vec{r}', \omega) v_1(\vec{r}', \omega) d\vec{r}' + \]
\[ + \int \chi_{KS}(\vec{r}, \vec{r}', \omega) \int \frac{\rho_1(\vec{r}'', \omega)}{|\vec{r}' - \vec{r}''|} d\vec{r}'' d\vec{r}' + \]
\[ + \int \chi_{KS}(\vec{r}, \vec{r}', \omega) \int f_{xc}(\vec{r}'', \vec{r}''', \omega) \rho_1(\vec{r}'', \omega) d\vec{r}'' d\vec{r}'. \]

(2.46)

Inserting (2.42) into (2.46), we are able to establish the relation between interacting \( \chi \) and non-interacting \( \chi_{KS} \) linear response functions:

\[ \chi(\vec{r}, \vec{r}', \omega) = \chi_{KS}(\vec{r}, \vec{r}', \omega) + \]
\[ + \int \int \chi(\vec{r}, \vec{r}'', \omega) \left( \frac{1}{|\vec{r}'' - \vec{r}'|} + f_{xc}(\vec{r}'', \vec{r}''', \omega) \right) \chi_{KS}(\vec{r}'', \vec{r}', \omega) d\vec{r}'' d\vec{r}'. \]

(2.47)

Thus, we get the equation for the linear response function \( \chi \) of the real system, which should be solved self-consistently. The poles of the \( \chi \) function are the excitation frequencies of the molecule.

Equation (2.47) can be transformed into a matrix eigenvalue problem—the so-called Casida equation:

\[
\begin{pmatrix}
A & B \\
B^* & A^*
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix} = \omega
\begin{pmatrix}
I & 0 \\
0 & -I
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix},
\]

(2.48)

where elements of the matrices \( A \) and \( B \) in adiabatic approximation (assuming that the time-dependent exchange–correlation potential can be approximated with the exchange–correlation potential from the ground-state DFT, and the exchange–correlation kernel is thus \( f_{xc} = \frac{\delta^2 E_{xc}}{\delta \rho(\vec{r}) \delta \rho(\vec{r})} \)) are given as follows:

\[ A_{ia,jb} = \delta_{ij} \delta_{ab} (\omega_a^{KS} - \omega_i^{KS}) + \]
\[ + \int \int \varphi_i^{KS*}(\vec{r}) \varphi_a^{KS}(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \varphi_j^{KS*}(\vec{r}') \varphi_b^{KS}(\vec{r}') \ d\vec{r} d\vec{r}' + \]
\[ + \int \int \varphi_i^{KS*}(\vec{r}) \varphi_a^{KS}(\vec{r}) \frac{\delta^2 E_{xc}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}') \delta \rho(\vec{r}'')} \varphi_j^{KS*}(\vec{r}'') \varphi_b^{KS}(\vec{r}'') \ d\vec{r} d\vec{r}' \]

(2.49)

and

\[ B_{ia,jb} = \int \int \varphi_i^{KS*}(\vec{r}) \varphi_a^{KS}(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \varphi_j^{KS*}(\vec{r}') \varphi_b^{KS}(\vec{r}') d\vec{r} d\vec{r}' + \]
\[ + \int \int \varphi_i^{KS*}(\vec{r}) \varphi_a^{KS}(\vec{r}) \frac{\delta^2 E_{xc}}{\delta \rho(\vec{r}) \delta \rho(\vec{r}') \delta \rho(\vec{r}'')} \varphi_j^{KS*}(\vec{r}'') \varphi_b^{KS}(\vec{r}'') \ d\vec{r} d\vec{r}'', \]

(2.50)

where indices \( i, j \) denote occupied and \( a, b \) unoccupied ground-state molecular orbitals.

The linear response Hartree–Fock method can also be represented in the form (2.48),
2.5. Approximate coupled cluster CC2 model

with the following matrix elements: \(^{62}\)

\[
A_{ia,jb} = \delta_{ij} \delta_{ab} (\omega_a - \omega_i) + \]
\[
+ \int \int \varphi_i^*(\vec{r}) \varphi_a(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \varphi_b^*(\vec{r}') \varphi_j(\vec{r}') \, d\vec{r} \, d\vec{r}' - \int \int \varphi_i^*(\vec{r}) \varphi_j(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \varphi_b^*(\vec{r}') \varphi_a(\vec{r}') \, d\vec{r} \, d\vec{r}'
\]

(2.51)

and

\[
B_{ia,jb} = \int \int \varphi_i^*(\vec{r}) \varphi_a(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \varphi_j^*(\vec{r}') \varphi_b(\vec{r}') \, d\vec{r} \, d\vec{r}' - \int \int \varphi_i^*(\vec{r}) \varphi_b(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \varphi_j^*(\vec{r}') \varphi_a(\vec{r}') \, d\vec{r} \, d\vec{r}'
\]

(2.52)

The oscillator strength \(f_I\) of an electronic transition from the ground to the \(I\)th excited state: \(^{64}\)

\[
f_I = \frac{2m_e \Delta E_I \mu_I^2}{3\hbar^2 e^2} \tag{2.53}
\]

can be calculated from \(X\) and \(Y\) vectors. \(^{62}\) In (2.53) \(\Delta E_I\) is the excitation energy of the \(I\)th transition and \(\mu_I\) the absolute value of the corresponding transition dipole moment, \(\hbar\) is the reduced Planck constant, \(m_e\) and \(e\) are the mass and the charge of the electron, respectively (here we explicitly write fundamental physical constants, leaving the atomic units, for the sake of clarity).

We note that the described above approach can be extended to hybrid functionals as well.

### 2.5. Approximate coupled cluster CC2 model

Another way to calculate an excitation (absorption) spectrum is to use post-Hartree–Fock wave function theory (WFT) methods. For medium-sized molecules, however, calculations with highly accurate WFT methods become hard feasible. The approximate coupled cluster CC2 model represents a good compromise between accuracy and computational effort.

In coupled-cluster theory the electronic wave function \(\Phi_{CC}\) is written as follows: \(^{65,66}\)

\[
\Phi_{CC} = e^\hat{T} \Phi_{HF} = \left( \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \ldots \right) \Phi_{HF} = \left( \sum_{q=0}^{\infty} \frac{1}{q!} \hat{T}^q \right) \Phi_{HF}, \tag{2.54}
\]
2. Theoretical basis

where \( \Phi_{HF} \) is the Hartree–Fock wave function and \( \hat{T} \) is the cluster operator, given by:

\[
\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots + \hat{T}_N ,
\]

\[
\hat{T}_1 = \sum_i^{\text{occ}} \sum_a^{\text{vir}} t_i^a \Phi_i^a ,
\]

\[
\hat{T}_2 = \sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{vir}} t_{ij}^{ab} \Phi_{ij}^{ab} ,
\]

\[
\hat{T}_3 = \sum_{i<j<k}^{\text{occ}} \sum_{a<b<c}^{\text{vir}} t_{ijk}^{abc} \Phi_{ijk}^{abc} ,
\]

\[
\ldots ,
\]

where \( \Phi_i^a \), \( \Phi_{ij}^{ab} \), \( \Phi_{ijk}^{abc} \) are the singly, doubly, triply excited determinants, respectively (this sequence is, in general, extended up to \( N \) (number of electrons) excitations) and coefficients \( t_i^a \), \( t_{ij}^{ab} \), \( t_{ijk}^{abc} \), etc. are the corresponding cluster amplitudes.

The \( \hat{T}_p \) terms are referred to as connected. The exponential operator (also called the wave operator\(^{66}\)) may be rewritten as follows:

\[
e^\hat{T} = \hat{1} + \hat{T}_1 + \left( \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \right) + \left( \hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3 \right) + \left( \hat{T}_4 + \hat{T}_3 \hat{T}_1 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{2} \hat{T}_2 \hat{T}_1^2 + \frac{1}{24} \hat{T}_1^4 \right) + \ldots .
\]

(2.56)

Here the \( \hat{1} \) operator generates the HF reference, \( \hat{T}_1 \) all singly excited determinants, \( \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 \) all doubly excited contributions, \( \hat{T}_3 + \hat{T}_2 \hat{T}_1 + \frac{1}{6} \hat{T}_1^3 \) all triply excited states, and so on. The terms of the type \( \frac{1}{2} \hat{T}_1^2 \) or \( \hat{T}_2 \hat{T}_1 \) are called disconnected.

Truncation of the cluster operator such that \( \hat{T} = \hat{T}_1 + \hat{T}_2 \) yields the coupled cluster singles and doubles (CCSD) model.\(^{67}\) The coupled cluster energy can be expressed, multiplying the electronic Schrödinger equation from the left by \( \Phi_{HF}^* \) and integrating over electronic degrees of freedom:

\[
E_{CCSD} = \int \Phi_{HF}^* \hat{H}_e \Phi_{CCSD} \, dx = \int \Phi_{HF}^* \hat{H}_e e^{\hat{T}_1 + \hat{T}_2} \Phi_{HF} \, dx ,
\]

(2.57)

and equations for cluster amplitudes can be obtained by projecting onto the singly and doubly excited determinants:

\[
\int \Phi_i^a(x) \hat{H}_e e^{\hat{T}_1 + \hat{T}_2} \Phi_{HF}(x) \, dx = E_{CCSD} \int \Phi_i^a(x) e^{\hat{T}_1 + \hat{T}_2} \Phi_{HF}(x) \, dx ,
\]

\[
\int \Phi_{ij}^{ab}(x) \hat{H}_e e^{\hat{T}_1 + \hat{T}_2} \Phi_{HF}(x) \, dx = E_{CCSD} \int \Phi_{ij}^{ab}(x) e^{\hat{T}_1 + \hat{T}_2} \Phi_{HF}(x) \, dx .
\]

(2.58)

These coupled equations should be then solved self-consistently. To decouple equations for the amplitudes from the energy expression one can first multiply the
2.5. Approximate coupled cluster CC2 model

electronic Schrödinger equation by \( e^{-(\hat{T}_1 + \hat{T}_2)} \) and then project onto the reference and excited determinants;\(^{68,69}\)

\[
E_{\text{CCSD}} = \int \Phi^*_H(x) e^{-(\hat{T}_1 + \hat{T}_2)} \hat{H}_e \hat{T}_1 + \hat{T}_2 \Phi_H(x) dx ,
\]

and

\[
\int \Phi^a_i(x) e^{-(\hat{T}_1 + \hat{T}_2)} \hat{H}_e \hat{T}_1 + \hat{T}_2 \Phi_H(x) dx = 0 ,
\]

\[
\int \Phi^b_{ij}(x) e^{-(\hat{T}_1 + \hat{T}_2)} \hat{H}_e \hat{T}_1 + \hat{T}_2 \Phi_H(x) dx = 0 .
\]

The operator \( e^{-(\hat{T}_1 + \hat{T}_2)} \hat{H}_e \hat{T}_1 + \hat{T}_2 \) is known as the similarity-transformed Hamiltonian. In general, finding the cluster amplitudes by solving (2.60) allows to find the CCSD wave function and the energy.

To obtain the equations of the CC2 model\(^7\) we first introduce the \( \hat{T}_1 \) transformed Hamiltonian \( \hat{H}_{\hat{T}_1} \) as:

\[
\hat{H}_{\hat{T}_1} = e^{-\hat{T}_1} \hat{H}_e e^{\hat{T}_1} .
\]

The CCSD amplitude equations then read:

\[
\int \Phi^a_i(x) \left( \hat{H}_{\hat{T}_1} + \left[ \hat{H}_{\hat{T}_1}, \hat{T}_2 \right] \right) \Phi_H(x) dx = 0 ,
\]

\[
\int \Phi^b_{ij}(x) \left( \hat{H}_{\hat{T}_1} + \left[ \hat{H}_{\hat{T}_1}, \hat{T}_2 \right] + \frac{1}{2} \left[ \left[ \hat{H}_{\hat{T}_1}, \hat{T}_2 \right], \hat{T}_2 \right] \right) \Phi_H(x) dx = 0 ,
\]

where square brackets with comma inside denote commutators. Partitioning the electronic Hamiltonian \( \hat{H}_e \) into a Fock operator \( \hat{F} \) and a fluctuation operator \( \hat{U} \), \( \hat{H}_e = \hat{F} + \hat{U} \), one might approximate the equation for doubles as:

\[
\int \Phi^b_{ij}(x) \left( \hat{H}_{\hat{T}_1} + \left[ \hat{F}, \hat{T}_2 \right] \right) \Phi_H(x) dx = 0 .
\]

The CC2 model is defined through equations for singles (2.62a) and equations for doubles (2.63).

Using a linear response approach one can arrive at an eigenvalue problem for the CC2 excitation energies. These energies are obtained as the eigenvalues of the CC2 Jacobian matrix:\(^7\)

\[
A_{\text{CC2}} = \left( \begin{array}{cc}
\int \Phi^a_i \left[ \hat{H}_{\hat{T}_1} + \left[ \hat{H}_{\hat{T}_1}, \hat{T}_2 \right], \hat{\tau}_k \right] \Phi_H dx & \int \Phi^a_i \left[ \hat{H}_{\hat{T}_1}, \hat{\tau}_{kd} \right] \Phi_H dx \\
\int \Phi^b_{ij} \left[ \hat{H}_{\hat{T}_1}, \hat{\tau}_k \right] \Phi_H dx & \int \Phi^b_{ij} \left[ \hat{F}, \hat{\tau}_{kd} \right] \Phi_H dx
\end{array} \right),
\]

where \( \hat{\tau}_k \) and \( \hat{\tau}_{kd} \) are single and double replacement operators, respectively. We note that each of four symbolic integrals of (2.64) represents a block.

In practical calculations of medium-sized molecules the resolution of the identity (RI) approximation for two-electron integrals is used to reduce computational time.\(^72,73\)
Theoretical basis

The calculation of transition moments for the CC2 model is described in ref. 73.

2.6. Nonadiabatic molecular dynamics

In this section we will briefly describe an approach to model dynamics of molecules with accounting for electronic transitions. The central assumption for what follows is that the nuclear movement is described by a classical trajectory $R(t)$ (here denotes time). The electronic part, in contrast, is treated quantum mechanically, i.e., the electronic wave function obeys the time-dependent Schrödinger equation:

$$i \frac{d \Phi(r, R, t)}{dt} = \hat{H}_{cn} \Phi(r, R, t).$$

(2.65)

The electronic time-dependent wave function can be represented in terms of a linear combination of electronic orthonormal wave functions $\{\Phi_j(r; R)\}$ (which depend parametrically on $R$) with time-dependent coefficients $\{c_j(t)\}$:

$$\Phi(r, R, t) = \sum_j c_j(t) \Phi_j(r; R).$$

(2.66)

Substituting (2.66) into (2.65), multiplying by $\Phi_k^*(r; R)$ from the left, and integrating over all electronic coordinates, one obtains:

$$\frac{dc_k}{dt} = - \sum_j c_j \left( i \mathcal{E}_{kj} + \left( d_{kj}, \frac{dR}{dt} \right) \right),$$

(2.67)

where parentheses with comma inside denote a scalar product, $\mathcal{E}_{kj}$ are the matrix elements of the clamped-nuclei Hamiltonian:

$$\mathcal{E}_{kj} = \int \Phi_k^*(r; R) \hat{H}_{cn} \Phi_j(r; R) dr,$$

(2.68)

and $d_{kj}$ are the nonadiabatic coupling vectors:

$$d_{kj}(R) = \int \Phi_k^*(r; R) \nabla_R \Phi_j(r; R) dr.$$

(2.69)

Here $\nabla_R$ is a vector composed of first derivatives with respect to the nuclear coordinates, $\nabla_R = \left( \frac{\partial}{\partial R_{ix}}, \frac{\partial}{\partial R_{iy}}, \frac{\partial}{\partial R_{iz}}, \cdots, \frac{\partial}{\partial R_{N_{ix}}}, \frac{\partial}{\partial R_{N_{iy}}}, \frac{\partial}{\partial R_{N_{iz}}} \right)$.

If functions $\Phi_j(r; R)$ are chosen to be eigenstates of $\hat{H}_{cn}$ (adiabatic states), then $\mathcal{E}_{kj} = \mathcal{E}_k \delta_{kj}$, where $\mathcal{E}_k = \mathcal{E}_k(R)$ are the PESs.

For the modeling of classical nuclear dynamics, i.e., for obtaining $R(t)$ there are two main approaches. In the first one, known as Ehrenfest or mean-field dynamics, one constructs the potential for the nuclear motion as:

$$V(R) = \int \Phi^*(r, R, t) \hat{H}_{cn} \Phi(r, R, t) dr = \sum_k \sum_l c_k^* c_l \mathcal{E}_{kl}.$$

(2.70)
Another approach is the *surface hopping* dynamics. In this treatment at each time point the nuclei move on the PES of a certain state \( k \), i.e., the potential for the nuclear motion is:

\[
V(R) = \mathcal{E}_{kk}(R)
\] (2.71)

but the molecule can experience transitions (hops) to other states, depending on the state probabilities \( P_k(t) = |c_k(t)|^2 \). When a switch of an electronic state should occur (and to which new state the molecule should hop) is determined by a stochastic algorithm. A very widely used method is Tully’s *fewest switches* algorithm.\(^7^4\) This algorithm minimizes the number or surface hops, providing the correct distribution of state populations, i.e., spreading the trajectories among electronic states in accord with the state probabilities.

Using (2.67) we can derive the expression for the time-derivative of the state probability:

\[
\frac{dP_k}{dt} = \sum_j \left\{ 2 \text{Im} (c^*_k c_j \mathcal{E}_{kj}) - 2 \text{Re} \left( c^*_k c_j \left( d_{kj} \cdot \frac{dR}{dt} \right) \right) \right\}.
\] (2.72)

The probability to hop from the current state \( k \) to another state \( j \) is calculated using the expression:

\[
g_{kj} = \frac{\Delta t}{P_k} \left\{ 2 \text{Im} (c^*_k c_j \mathcal{E}_{kj}) - 2 \text{Re} \left( c^*_k c_j \left( d_{kj} \cdot \frac{dR}{dt} \right) \right) \right\}.
\] (2.73)

If \( g_{kj} < 0 \) then it is set equal to zero. Next, a random number \( \xi \) is drawn, such that \( 0 < \xi < 1 \). If \( g_{kj} > \xi \) a hop \( k \to j \) occurs, otherwise the \( k \)th electronic state is retained. If a hop occurs and \( \mathcal{E}_{kk}(R) \neq \mathcal{E}_{jj}(R) \) then nuclear velocities are re-scaled to conserve total energy. This is usually done along the nonadiabatic coupling vector.

The classical trajectory of the nuclear motion is computed integrating Newton’s second law, which reads:

\[
M_A \frac{d^2 \vec{R}_A}{dt^2} = -\nabla_A V(R), \quad A = 1, \ldots, \bar{N}.
\] (2.74)

The PESs may be either pre-calculated or computed “on the fly”. The latter approach is used in this work, in paper 3 (ref. 45). In general, the PESs and nonadiabatic couplings can be computed by means of first-principles (*ab initio* and DFT) methods or semiempirical methods.\(^7^6\) In paper 3 (ref. 45) we have employed the configuration interaction (CI) approach with floating occupation number molecular orbitals (FOMO)\(^7^7-7^9\) obtained by using the semiempirical AM1 method\(^8^0\) (specially reparameterized for azobenzene\(^8^1\)).
3. Summary of publications

3.1. Paper 1. Thermal cis-to-trans isomerization of azobenzene-containing molecules enhanced by gold nanoparticles: An experimental and theoretical study

In this work we have investigated the phenomenon of drastically enhanced (relative to the case in gas phase or solution) thermal cis $\rightarrow$ trans isomerization (also called back isomerization) of azobenzenes in the presence of gold nanoparticles, which has been recently experimentally observed and reported in a series of publications. The hypothesis of a charge transfer between an azobenzene molecule and a gold nanoparticle as a key step leading to the acceleration of switching has been taken as a basis for the computational study. Having a priori no solid evidence for the preferred direction of the charge transfer we have considered both possibilities, i.e., (i) an electron transfer from the cis isomer to a gold nanoparticle with formation of a cation and (ii) an electron transfer from a gold nanoparticle to the cis isomer with formation of an anion. Using a density functional theory approach (specifically, restricted (for closed-shell cases) and unrestricted (for open-shell situations) B3LYP/6-31G* calculations), we have performed optimizations of the trans and cis isomers as well as transition states for the set of small azobenzenes in neutral and ionic states. Apart from the parent AB molecule derivatives with electron donating (–CH$_3$, –OCH$_3$, –NH$_2$) and withdrawing (–CF$_3$, –NO$_2$) groups in para position of one of the two phenyl rings have been considered. Moreover, we have explored a cationic surfactant molecule, containing azobenzene in the tail part of its structure. This molecule has served as a DNA compaction agent in the previous research of photoreversible DNA compaction. In our work the neutral and doubly positively charged forms of this surfactant have been assumed to be a result of the charge transfer. For the optimizations the isolated-molecule model has been used throughout the paper.

The calculation of activation energy for the thermal cis $\rightarrow$ trans isomerization, which is the difference between energies of the TS and the cis isomer, allows one to obtain the corresponding rate of the reaction. We have applied Eyring’s transition state theory, which relates the absolute isomerization rate $k$ with the activation Gibbs free energy $\Delta G = G(\text{TS}) - G(\text{cis})$ (the ideal gas state has been assumed for calculation of $G$) as follows:

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta G}{k_B T}\right).$$

(3.1)

Here $k_B$ and $h$ are the Boltzmann and Planck constants, respectively, and $T$ is the temperature.

In our work we have found that both the electron attachment to and withdrawal from the studied molecules lead to pronounced reduction in the activation barrier of the thermal back isomerization. This reduction, in turn, results in a large increase in the isomerization rate $k$, due to the exponential dependence of $k$ on $\Delta G$. 

29
Further, we have made an attempt to estimate the formation energies of ions from the neutrals for small AB derivatives in the presence of gold nanoparticles. The approach is based on calculation of electron affinities (which correspond to an anion formation) and ionization potentials (cation formation) and accounts, in addition, for the work function of the gold surface and the ion–image charge interaction. Applying this approach, lesser “energy costs” have been found for cation formation in comparison with those for anion formation, suggesting that the rapid isomerization proceeds through the cationic pathway.

**Contribution of E. Titov:**

E. Titov has performed all quantum chemical calculations, analyzed the obtained results, designed and assembled all figures (except for Fig. 1) and tables, written the first version of the manuscript, actively participated in the discussion and writing a reply to the comments of the reviewers.

### 3.2. Paper 2. Exciton splitting of adsorbed and free 4-nitroazobenzene dimers: A quantum chemical study

This study\(^{44}\) has been devoted to understanding of the electronically excited states of azobenzenes, in particular when molecules interact with each other and/or with a surface, as it is the case for the azobenzene-containing SAMs. Specifically, excitonic effects arising from the presence of a second chromophore have been addressed.

Experimentally, a pronounced blue shift of the intense absorption band (corresponding to the \(\pi \rightarrow \pi^*\) transition) for densely packed SAMs of certain AB-containing thiols formed on a gold surface has been observed when compared to molecules in solution.\(^{31}\) This blue shift has been related to the sizable exciton coupling between AB units in the SAM. Further, it has been suggested that this exciton coupling causes the ultrafast delocalization of optical excitation and can be responsible for the suppression of isomerization.\(^{31}\)

For our study (paper 2\(^{44}\)), a 4-nitroazobenzene molecule has been chosen as a photoswitch. Applying of first-principles methods is limited to relatively moderate systems in terms of the number of atoms. Therefore in our study we have considered a monomer (a single isolated molecule), a non-covalent dimer (thus accounting for the interaction of the chromophores), as well as the monomer and the dimer chemisorbed on a silicon nanocluster (thus considering the effect of a surface). In case of dimers the chosen supermolecular models allow also for a comparison to simpler monomer-based models, such as the point–dipole coupling model.

The molecular exciton theory\(^{84,85}\) predicts for the isolated dimer the splitting of a bright state (corresponding to a \(\pi \rightarrow \pi^*\) transition) in two states, the upper of which is allowed and the lower forbidden (in the case of two identical monomers located side by side, forming an H-like aggregate)—the so-called **exciton** or Davydov splitting. The excitation energies of the split states in the dimer are expressed as

\[
\Delta E_{\pm,\text{dimer}} = \Delta E_{\text{monomer}} \pm \frac{\Delta E_{\text{exciton}}}{2} + \Delta D.
\]

Here \(\Delta E_{\text{monomer}}\) is the excitation energy of the bright transition for the monomer, \(\Delta E_{\text{exciton}}\) the exciton splitting in the dimer, \(\Delta D\) the van der Waals (vdW) correction. Usually \(\Delta D < 0\), that leads
to the red shift of the splitting origin relative to the monomer excitation energy. To obtain the spectral shift ($\Delta E_{\text{shift}} = \Delta E_{\text{bright dimer}} - \Delta E_{\text{bright monomer}}$) and exciton splitting ($\Delta E_{\text{exciton}} = \Delta E_{+ \text{dimer}} - \Delta E_{- \text{dimer}}$), we have employed and assessed various quantum chemical methods, ranging from wave function-based methods without (HF) and with (CC2) electron correlation, to density functional methods containing exact exchange, either global hybrids (B3LYP, X3LYP, BMK, BHandH, BHandHLYP, M06-2X, M06-HF) or range-separated methods (CAM-B3LYP, LC-ωPBE, M11, ωB97, ωB97X, ωB97X-D).

Applying the natural transition orbital (NTO) analysis we have been able to get insight into the nature of the electronically excited states in the monomer and the dimer, and thus, identify the states which correspond to the Davydov pair of the bright transition, and hence, the exciton splitting itself. It has turned out that at the distance of $\sim 3.6 \text{ Å}$ which corresponds to the nearest-neighbor separation upon attachment to the silicon nanocluster, the spectral shift $\Delta E_{\text{shift}}$ is small (ca. 0.05 eV), but the exciton splitting is sizable, amounting to about 0.3 eV. Thus, the vdW correction $\Delta D$ is relatively large and should be accounted for at small intermolecular separations. Moreover, we have related the determined exciton splitting to an excitation transfer time by using a simple Rabi-type model. The obtained time (from this purely electronic Davykov splitting) is found to be very short, on the order of several femtoseconds.

Further, we have found that upon attachment to a silicon nanocluster the lowest bright ($\pi \rightarrow \pi^*$) transition shifts to the red, both for the monomer and the dimer. Moreover, for molecules attached to a silicon cluster higher absorption intensity has been observed than for the isolated species. This implies that the direct covalent grafting of an azobenzene chromophore to a silicon surface will change the absorption of the photoswitch.

**Contribution of E. Titov:**

E. Titov has performed all quantum chemical calculations, analyzed the obtained results, designed and assembled all figures and tables, written the first version of the manuscript, actively participated in the discussion and writing a reply to the comments of the reviewers.

### 3.3. Paper 3. Dynamics of azobenzene dimer photoisomerization: Electronic and steric effects

The large exciton splitting of excited states of azobenzenes in aggregates might lead to a fast excitation transfer. In fact, such an electronic quenching mechanism has been suggested as a reason for the experimentally observed suppression of optical $\text{trans} \rightarrow \text{cis}$ isomerization of azobenzenes on surfaces at high grafting densities, alternative or in addition to steric hindrance.

However, a dynamical exploration should be performed to unravel the details of the isomerization reaction of azobenzenes in densely packed environments. We have therefore carried out a study (paper 3) by means of nonadiabatic molecular dynamics with trajectory surface hopping—the method which allows for the electronic transitions during molecular dynamics and, thus, is suitable for the modeling of photoisomerization.
3. Summary of publications

The photodynamics of the \( \text{trans} \rightarrow \text{cis} \) isomerization after excitation into the \( \pi \rightarrow \pi^* \) absorption band (which corresponds to the usual way to convert ABs from the \textit{trans} to the \textit{cis} isomer) has been conducted for an AB dimer, both molecules of which have been treated quantum-mechanically (QM), and a dimer surrounded by other (treated by virtue of molecular mechanics (MM)) AB molecules, as it is the case in the SAMs. The QM part has been treated by means of configuration interaction (CI) procedure with floating occupation number molecular orbitals (FOMO)\textsuperscript{77–79} obtained by using the semiempirical AM1 method,\textsuperscript{80} reparameterized for azobenzene.\textsuperscript{81} For the MM part, frozen in the present study, the MM3-2000 force field\textsuperscript{99,100} has been employed. With these models we have accounted for the electronic coupling between two molecules of the AB dimer as well as steric hindrance, introducing the vdW interaction of the central QM dimer with the surrounding MM molecules.

From the theoretical side, the modeling of photoisomerization dynamics of a \textit{non-covalent} AB dimer is a novel step in investigation of AB isomerization. Previously, surface hopping calculations have been performed to simulate the photoisomerization reaction of an AB monomer (as well as monomers of several AB derivatives) in gas phase,\textsuperscript{11,23,24,101–114} in solution,\textsuperscript{102,103,115} in liquid state,\textsuperscript{23,24} and on sterically confining surfaces.\textsuperscript{116,117} Moreover, \textit{covalently} connected dimeric molecular systems, comprising two AB units, have been considered either in QM/MM\textsuperscript{79} or purely QM\textsuperscript{118} (regarding the electronic structure) frameworks.

Our simulations reveal that in comparison to the single molecule the quantum yield of the \( \text{trans} \rightarrow \text{cis} \) photoisomerization is similar for the isolated (free) dimer, but greatly reduced in the sterically constrained situation (still remaining non-zero though). We conclude that in the present model system at least (which has both strong exciton coupling and large steric hindrance), steric effects are the main reason why switching is suppressed in densely packed monolayers of AB-containing molecules on surfaces. We have further found that the excited-state lifetimes are affected by dimerization and the vdW interaction with surrounding MM molecules, and the end-to-end distance of the \textit{cis} isomer, formed after photoisomerization, is on average larger for the “SAM” model, suggesting that the steric confinement can also lead to different product geometries.

In addition, the supporting information of paper 3 (ref. 45) contains extensive benchmarks of absorption spectra and exciton splittings obtained by using variety of quantum chemical methods. We note that in paper 3\textsuperscript{45} as well as in paper 2\textsuperscript{44} we have been concerned with a regime of small intermolecular distances, namely, smaller than the size of the chromophore (concretely, the considered distances between AB molecules are \( \sim 3.5 \) Å, whereas the length of \textit{trans}-AB is \( \sim 11 \) Å). Thus, our investigations assess the inter-photoswitch couplings and isomerization behaviour corresponding to tight packing of molecules—an important case for self-assembled molecular arrangements.

\textit{Contribution of E. Titov:}

E. Titov has constructed models and performed all dynamical as well as quantum chemical (except for DFT/MRCI) computations, analyzed the obtained results, designed and assembled all figures and tables, written the first version of the manuscript, actively participated in the discussion and writing a reply to the comments of the reviewers.
At the end of this chapter we mention that apart described above papers, which are included in this dissertation (referred to as papers 1–3 throughout this work), E. Titov has also contributed to manuscripts 4–8, presented in the list of publications on page 201. Publications 4\textsuperscript{82} and 5\textsuperscript{83} are devoted to a study of DNA compaction by AB-containing cationic surfactants. Contributions of E. Titov to these two manuscripts (4 and 5) have been made during the Master’s studies and consist of experimental results. Contributions to papers 6–8 have been made during the PhD studies of E. Titov and comprise quantum chemical investigations. Namely, paper 6\textsuperscript{119} deals with excited states of xanthene derivatives, in manuscript 7\textsuperscript{120} DFT calculations are performed to complement Kelvin probe experimental findings on AB-containing SAMs on a silicon surface, and in manuscript 8\textsuperscript{121} DFT calculations of ground-state activation energies are carried out to elucidate electrochemical experiments on azobenzenes.
4. Reprints
4. Reprints

4.1. Paper 1


Thermal Cis-to-Trans Isomerization of Azobenzene-Containing Molecules Enhanced by Gold Nanoparticles: An Experimental and Theoretical Study

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Abstract

We report on the experimental and theoretical investigation of a considerable increase in the rate for thermal cis $\rightarrow$ trans isomerization of azobenzene-containing molecules in the presence of gold nanoparticles. Experimentally, by means of UV-Vis spectroscopy, we studied a series of azobenzene-containing surfactants and 4-nitroazobenzene. We found that in the presence of gold nanoparticles the thermal lifetime of the cis isomer of the azobenzene-containing molecules was decreased by up to 3 orders of magnitude in comparison to the lifetime in solution without nanoparticles. The electron transfer between azobenzene-containing molecules and a surface of gold nanoparticles is a possible reason to promote the thermal cis $\rightarrow$ trans switching. To investigate the effect of electron attachment to, and withdrawal from, the azobenzene-containing molecules on the isomerization rate, we performed density functional theory calculations of activation energy barriers of the reaction together with Eyring’s transition state theory calculations of the rates for azobenzene derivatives with donor and acceptor groups in para position of one of the phenyl rings, as well as for one of the azobenzene-containing surfactants. We found that activation barriers are greatly lowered for azobenzene-containing molecules, both upon electron attachment and withdrawal, which leads, in turn, to a dramatic increase in the thermal isomerization rate.
1 Introduction

The catalytic activity of gold nanoparticles (Au NPs) has received considerable attention in many organic and inorganic reactions such as selective oxidation/reduction of organic compounds, carbon-carbon coupling, or synthesis of organic materials.\textsuperscript{1–5} In heterogeneous catalysis, the reacting molecules adsorb on the catalytically active solid surface followed by breaking and formation of chemical bonds on the surface and eventually desorption of newly formed products back into the liquid or gas phase. One of the explanations for the catalytic activity of gold nanoparticles is related to a charge transfer between the adsorbed molecule and the gold particle.\textsuperscript{6–8}

One of prominent cases of Au NPs catalytic activity involves azobenzene molecules, which are known to offer light-controlled isomerization yielding a variety of applications in light-triggered switching of polymers, surface-modified materials, protein probes, molecular machines, holographic recording devices and metal ion chelators etc.\textsuperscript{9,10} The azobenzene molecule consists of two phenyl rings linked by azo group (N=N) and can be reversibly switched between \textit{trans} (more stable) and \textit{cis} (less stable) isomers. The \textit{trans} $\rightarrow$ \textit{cis} isomerization in solution is induced by light illumination with appropriate wavelength in the UV range. The \textit{cis} $\rightarrow$ \textit{trans} isomerization, the back isomerization, can be achieved by illumination with light of longer wavelength (in the blue range). Back isomerization also occurs readily at room temperature in the dark due to relatively low activation energy barrier $\approx 95 \text{ kJ mol}^{-1} \approx 1 \text{ eV/molecule}$.\textsuperscript{9} The thermal back isomerization typically takes several hours or days. However, the presence of gold nanoparticles was found to accelerate the back isomerization of azobenzene down to several minutes.\textsuperscript{11–14} This phenomenon was reported for azobenzene-derivatized sulfides adsorbed and spatially confined in gold nanoparticle aggregates,\textsuperscript{11} for azobenzene-oligoglycerol conjugates on cyclodextrin-coated gold nanoparticles,\textsuperscript{12} and finally for aqueous azobenzene solutions under the addition of Au NPs.\textsuperscript{13} An efficient interaction of azobenzene with gold in the latter case was possible due to the pseudo-naked surface of Au NPs (only Cl$^{-}$ left on the surface),\textsuperscript{13,15} conditioned by
laser irradiation of chemically synthesized NPs in a small droplet. Hallett-Tapley et al. suggested that the rapid thermal $cis \rightarrow trans$ isomerization is due to an electron transfer from azobenzene to the gold nanoparticles. The charge transfer results in the formation of an azobenzene radical cation, which isomerizes far more readily than neutral azobenzene, probably, through rotation about the N=N bond. No striking evidence for the formation of an azobenzene radical cation could however be given. In this context it is interesting to note, though, that earlier spectrophotometrical and electrochemical investigations revealed that indeed, a $cis$ azobenzene radical anion isomerizes very fast to the $trans$ isomer.

We recently explored interactions of azobenzene-modified cationic surfactants with Au-based nanomaterials. The incorporation of an azobenzene moiety into the hydrophobic tail of a surfactant, having a charged head group, enables one to light-trigger the hydrophobicity of the surfactant in order to control the strength of interactions with other charged compounds with a variety of promising applications in photoreversible DNA compaction, remote control of the size of microgel particles triggered by light, and light-controlled structuring of polymer brushes. Profiting from electrostatic interactions between the positively charged surfactant head and negatively charged bare Au nanoparticles prepared by methods of laser ablation in deionized water, we have created novel plasmonic nanoarchitectures based on azobenzene-modified cationic surfactants – Au nanoparticle complexes. In this case, a light-tunable azobenzene unit in the surfactant can be used to initiate light-controlled nanoclustering of Au NPs, yielding a switch in the plasmonic absorption band and a related change in the solution color. Despite the different materials used (bare Au NPs and azobenzene-modified surfactants) and the different nature of involved chemical interactions, we also could observe a drastic acceleration of back $cis \rightarrow trans$ isomerization of azobenzene in the formed azobenzene-modified cationic surfactant – Au nanoparticle complexes.

This paper is conceived as an attempt to clarify the nature of the observed acceleration of back $cis \rightarrow trans$ isomerization of azobenzene in the presence of Au NPs. In our tests, we vary
the nature of the head group starting from toxic cationic trimethylammonium to less toxic polyamines,\textsuperscript{34} as well as the length of the hydrophobic tail. To gain theoretical insight into this phenomenon we perform density functional theory (DFT) calculations of the activation energy barriers for isolated azobenzene-containing molecules in differently charged states and apply Eyring’s transition state theory to calculate isomerization rates. We also estimate the influence of a gold surface on the formation energies of ions of azobenzene derivatives. Since the direction of charge transfer between molecular switches and Au nanoparticles in solution is not known with certainty, we consider both (radical) anions and cations.

The paper is organized as follows. In Section 2 the studied molecules, experimental and computational details are described. In Section 3 we present our results and discuss them. Section 4 concludes the work.

2 Materials and Methods

2.1 Studied molecules

The chemical structure of the molecules investigated in this work along with used substituents and abbreviations as well as atom labelling, are presented in Table 1.

Table 1: Chemical structure of the studied molecules, the used substituents, abbreviations and atom labelling.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>R’</th>
<th>R</th>
</tr>
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<tbody>
<tr>
<td>4-R-AB</td>
<td>H</td>
<td>H, CH₃, OCH₃, NH₂, CF₃, NO₂</td>
</tr>
<tr>
<td>AzoCₙ</td>
<td>(CH₂)₃CH₃</td>
<td>O[CH₂]ₙN⁺(CH₃)₃, n = 6, 8, 10, 12</td>
</tr>
<tr>
<td>AzoEAₙ</td>
<td>(CH₂)₃CH₃</td>
<td>O(CH₂)₆[NH(CH₂)₂]ₙNH₂, n = 1, 2</td>
</tr>
</tbody>
</table>

The experiments were carried out with neutral 4-nitroazobenzene molecule (4-NO₂-AB) and cationic AzoCₙ and AzoEAₙ surfactant molecules, whereas the calculations were done
for all the 4-R-AB molecules and the AzoC₆ surfactant molecule (as a representative of a class of surfactants studied experimentally). The cationic azobenzene-containing surfactants have not been studied before in the context of acceleration of thermal $cis \rightarrow trans$ isomerization by gold nanoparticles in contrast to small azobenzenes (similar to 4-R-AB molecules considered here) which were investigated experimentally in Ref. 13,14 and were found to undergo rapid thermal back isomerization upon addition of Au NPs. However, the calculations have not been done before neither for small neutral molecules nor for long cationic surfactants.

In the case of the 4-R-AB molecules substituents $R$ which are either electron donors ($CH_3$, OCH$_3$, NH$_2$) or acceptors (CF$_3$, NO$_2$) were considered in calculations. Hereafter the parent azobenzene molecule 4-H-AB is denoted as AB. For the 4-R-AB molecules we calculated the neutral, anionic and cationic states, whereas for the AzoC₆ surfactant molecule which is initially cationic, the cationic, neutral (one electron added) and dicationic (one electron removed) states were investigated. The choice of cationic azobenzene-containing trimethylammonium and polyamine surfactants was motivated by their important role in remote control of the size and properties of soft objects as mentioned above. The selection of molecules for theoretical investigation serves the same purpose (for AzoC₆), but also to elucidate substituent effects for small azobenzenes similar to Ref. 13.

### 2.2 Experimental details

The cationic azobenzene-containing surfactants were synthesized according to the published procedure.$^{19,34}$ At first, azocoupling of $p$-buthylaniline with phenol and subsequent reaction with appropriate dibromoalkane was carried out. The next step was quaternization with trimethylamine (AzoCₙ) or the reactions with ethylenediamine (AzoEA₁) and diethylenetriamine (AzoEA₂).

For the trimethylammonium surfactants the length of the spacer between a charged head and azobenzene ring ranges between 6 CH$_2$ and 12 CH$_2$ groups (Table 1). The azobenzene-containing polyamines AzoEAₙ differ in the number of amine groups in the head to be
2 (AzoEA₁) and 3 (AzoEA₂). The surfactants were dissolved in water (MilliQ) and kept in the dark for several days to ensure complete relaxation to the trans isomer state. 4-nitroazobenzene (4-NO₂-AB) was purchased from Sigma Aldrich and dissolved in methanol (Sigma Aldrich). No effect on its thermal relaxation has been revealed when the solution in methanol was slightly diluted with water, as to be the reference for the solution in methanol with added gold nanoparticles aqueous colloid.

Bare Au NPs were prepared by femtosecond laser ablation from a gold target in deionized water. To homogenize the size dispersion of Au NPs, in some cases we additionally applied the technique of femtosecond laser fragmentation from already formed bare Au colloids. The final Au NPs were of 10 ± 3 nm in diameter (as measured using TEM). Gold nanoparticles are partially oxidized with atomic percentages estimated as 88.7 % for Au⁰, 6.6 % for Au⁺, and 4.7 % for Au³⁺. Those gold atoms that are bound to oxygen on the particle surface tend to accumulate positive or negative charge depending on the pH of the surrounding media. At basic conditions (pH ≈ 8 in a solution together with AzoCₙ surfactants) the nanoparticles are negatively charged. The colloids just produced were stored in darkness at 4 °C. Before mixing with the azobenzene-containing compounds the gold nanoparticles were sonicated in order to destroy possible aggregates.

UV-Vis absorption spectroscopy (Cary 5000, Varian Inc.) was used to experimentally estimate the changes in the rate of the thermal cis → trans isomerization. In the experiments, a droplet of gold nanoparticles aqueous colloid was added into solutions of azobenzene-containing molecules previously irradiated with UV light (365 nm, VL-4.L, Vilber Lourmat) for 10 minutes.

2.3 Computational details

Quantum chemical calculations were done using density functional theory (DFT) (see, e.g., Ref. 37). The B3LYP hybrid functional and the 6-31G* basis set were employed. For the calculations the Gaussian 09 program (Revisions A.02 and D.01) was used. The
neutral singlet 4-R-AB species were calculated with restricted B3LYP (RB3LYP), whereas for charged doublet 4-R-AB species unrestricted B3LYP (UB3LYP) was used. In the case of the AzoC₆ molecule, RB3LYP was applied to treat the cationic singlet state and UB3LYP for neutral and dicationic doublet states, respectively.

In a first step, geometry optimizations of the cis and trans isomers were performed. Only real frequencies were obtained for both isomers by normal mode analysis showing that optimized geometries correspond to minima on the potential energy surface. In a next step, transition states (TS) for the cis ↔ trans reaction were located by the synchronous transit-guided quasi-Newton method (QST2 and QST3)⁴³,⁴⁴ and/or optimization to a transition state using the Berny algorithm as implemented in Gaussian 09. Normal mode analysis showed a single imaginary frequency for the TS.

The activation parameters of the cis → trans isomerization (activation energy ΔE at 0 K and activation Gibbs free energy ΔG at 298.15 K) were calculated as a difference between values of corresponding parameters for TS and cis isomer:

\[ \Delta B = B(\text{TS}) - B(\text{cis}), \]

\[ B = E, G. \]

(1)

Note that the energy E is the point on the potential energy surface, i.e., the sum of the electronic energy and the energy of nuclear-nuclear repulsion. The isomerization rate k of the cis → trans reaction was calculated from the activation Gibbs free energy ΔG according to Eyring’s transition state theory:⁴⁵

\[ k = \frac{k_B T}{h} \exp \left( -\frac{\Delta G}{k_B T} \right). \]

(2)

Here \( k_B \) and \( h \) are the Boltzmann and Planck constants, respectively; T is the temperature.

All the thermochemical calculations were done under ideal gas conditions at the temperature of 298.15 K and the pressure of 1 atm.
3 Results and Discussion

3.1 Experimental results

A series of azobenzene-containing trimethylammonium surfactants, differing in the length of the hydrophobic tail, as well as azobenzene-containing polyamine surfactants, differing in the number of amine groups, were examined with respect to the kinetics of the thermal $\text{cis} \rightarrow \text{trans}$ isomerization in the presence of Au NPs. The absorption spectra of all used surfactants are similar, since the ring substituent groups near the azobenzene unit are the same for all molecules. Figure 1a shows characteristic absorption spectra of azobenzene molecules illustrated by the cationic surfactant AzoC$_8$ containing 8 CH$_2$ groups in the spacer between the cationic head and the azobenzene unit.

The photoisomerization behavior of the surfactant is described in detail elsewhere.$^{19}$ In short, all surfactants in the dark state are characterized by an absorption band ($\pi \rightarrow \pi^*$ transition of the azobenzene unit in the $\text{trans}$ conformation) with a maximum at 353 nm (black curve in Figure 1a). Irradiation with UV light induces $\text{trans} \rightarrow \text{cis}$ photoisomerization accompanied by changes in absorption spectra (red curve in Figure 1a). The spectrum of the $\text{cis}$ isomer is characterized by two absorption bands with maxima at 313 nm ($\pi \rightarrow \pi^*$ transition) and at 437 nm ($n \rightarrow \pi^*$ transition). The band with maximum at $\approx 240$ nm presented in the spectra of both isomers corresponds to the absorption of the $\pi$-conjugated benzene rings.

The back $\text{cis} \rightarrow \text{trans}$ isomerization of azobenzene occurs either via spontaneous thermal relaxation or can be driven by irradiation with visible light. In this work we studied spontaneous thermal $\text{cis} \rightarrow \text{trans}$ isomerization of azobenzene-containing compounds. The characteristic time of the thermal relaxation is referred to as the lifetime of the $\text{cis}$ isomer, denoted as $\tau_0$ in the absence of Au NPs in what follows. The lifetime of the $\text{cis}$ isomer of the surfactant molecules in an aqueous solution is $\approx 62$ hours (see SI, Figure 1). However, the lifetime of the $\text{cis}$ isomer of the azobenzene-containing surfactants shortens significantly
in the presence of Au NPs. Figure 1b shows the evolution of absorption spectra of the UV-irradiated surfactant in the presence of Au NPs. The solution of the azobenzene-containing compound was first irradiated with UV light for 10 minutes in order to convert the\textit{trans} isomer to the \textit{cis} isomer. The irradiation time was chosen to get a so-called steady state at which a maximally achievable concentration of the \textit{cis} isomer is obtained. For AzoC$_6$ \approx 90\% of the surfactant molecules are in the \textit{cis} conformation at the steady state.$^{20}$ The absorption spectroscopy measurements were started immediately after Au NPs had been added into the UV-irradiated solutions of azobenzene-containing compounds.

Figure 1b shows, for AzoC$_8$, the spectrum change with time, revealing the transition
from the initial cis to the final trans conformation. At the same time the gold plasmon peak located at 527 nm (523 nm for free Au NPs, grey curve) does not change significantly. The plots of the optical density at a fixed wavelength $D_\lambda$ versus time $t$ were used to estimate the thermal lifetime of the cis isomer. Specifically, the value of the optical density at $\lambda = 376$ nm was chosen for the azobenzene-containing surfactants. In the case of 4-NO$_2$-AB, the optical density at $\lambda = 360$ nm was used. To estimate the lifetime an exponential fit of the optical density as a function of time was performed using the following equation:

$$D_\lambda(t) = D_0 + D_1 \exp\left(-\frac{t}{\tau_0}\right) + D_2 \exp\left(-\frac{t}{\tau}\right) + ...$$  \hspace{1cm} (3)

In the case of Au NP solutions a reliable fit was achieved using a sum of two exponents in Eq. (3) for the representation of optical density time dependencies, yielding two lifetimes. One lifetime is comparable with the lifetime of the cis isomer without gold, $\tau_0$ and, therefore, can refer to the thermal cis $\rightarrow$ trans relaxation of the free azobenzene-containing molecules. Being orders of magnitude shorter than $\tau_0$, the second lifetime, $\tau$, shows the Au NP-enhanced isomerization of azobenzene-containing molecules near a gold surface. The lifetimes $\tau_0$ and $\tau$ of the cis isomers, the corresponding isomerization rates $k_0 = 1/\tau_0$ and $k = 1/\tau$, and the acceleration factor $\tau_0/\tau = k/k_0$ are shown in Table 2.

**Table 2: The thermal cis isomer lifetimes, cis $\rightarrow$ trans isomerization rates for free compounds in solution without gold, ($\tau_0$, $k_0$), and in the presence of gold nanoparticles, ($\tau$, $k$), and the acceleration factor $\tau_0/\tau = k/k_0$.**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\tau_0$ (min)</th>
<th>$\tau$ (min)</th>
<th>$k_0$ ($10^{-4}$ s$^{-1}$)</th>
<th>$k$ ($10^{-4}$ s$^{-1}$)</th>
<th>$\tau_0/\tau = k/k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-NO$_2$-AB</td>
<td>144</td>
<td>3.5</td>
<td>1.2</td>
<td>48</td>
<td>41</td>
</tr>
<tr>
<td>AzoC$_n$ ($n = 6, 8, 10, 12$)$^a$</td>
<td>3720</td>
<td>3.0</td>
<td>0.045</td>
<td>56</td>
<td>1240</td>
</tr>
<tr>
<td>AzoEA$_n$ ($n = 1, 2$)$^a$</td>
<td>3720</td>
<td>9.5</td>
<td>0.045</td>
<td>18</td>
<td>392</td>
</tr>
</tbody>
</table>

$^a$ The lifetimes for the series of AzoC$_n$ and AzoEA$_n$ surfactants were averaged, since they are approximately the same for each $n$.

In the presence of Au NPs azobenzene-containing surfactants undergo cis $\rightarrow$ trans relaxation far more readily than free cis isomers. The lifetime $\tau$ does not depend markedly on the number $n$ of CH$_2$ groups in the spacer. Azobenzene-containing polyamines show the
same trend, the gold-enhanced cis $\rightarrow$ trans relaxation of AzoEA$_2$ is approximately as fast as in Au NPs-containing AzoEA$_1$ solution. In contrast to the cationic surfactants, 4-NO$_2$-AB in solution is not expected to form ionic bonds with Au NPs. However, its thermal cis $\rightarrow$ trans relaxation is also enhanced by gold nanoparticles. At this point, we can hypothesize that the azobenzene unit can interact with the gold particle via the N=N bond, which can accumulate or give away an electron. Interestingly, the lifetime of the cis isomer of the azobenzene-containing polyamines is longer than that of trimethylammonium surfactants, probably due to stronger ionic interaction of the former with the gold surface via its charged head, which inhibits the competitive interaction via the azobenzene N=N bond, which, in turn, is responsible for the possible electron transfer.

3.2 Computational results and discussion

A possible hypothesis to explain the experimental findings is that an electron transfer between azobenzene-containing molecules and the surface of gold nanoparticles with the following formation of the state, different in charge from the initial, is the reason to promote thermal switching. To test this possibility, we investigated various charged states of azobenzene-containing molecules, treated as gas phase species, considering neither the metal surface nor the solution, and compared the activation parameters and isomerization rates of the thermal cis $\rightarrow$ trans reaction with calculated ones for a state of reference. Specifically, we studied all 4-R-AB compounds of Table 1 with the neutral molecules being the reference, as well as AzoC$_6$ for which the cation is the reference state. Single electrons were removed from or attached to these references, as outlined above.

The energetic picture of location of the isomers and the TS is shown in Figure 2. The energy values of the isomers and the TS, shown in Figure 2, were calculated as described in Section 2.3 and then recalculated relative to the value for the trans isomer in the state of reference, i.e., $E = 0$ for the trans isomer of neutral 4-R-AB species, and the cationic state of AzoC$_6$. The values of activation parameters ($\Delta E$, $\Delta G$) and absolute $k$
Figure 2: Energies of the cis and trans isomers as well as the TSs of the studied molecules, relative to the energy of the corresponding trans isomer in the state of reference \((E = 0\) for the trans isomer of the neutral state of 4-R-AB and cationic state of AzoC\(_6\)). The chemical groups on the bottom axis are the used substituents R. The inset shows the location of both isomers and the TS in the figure. Symbols are the data. Lines are merely shown to clarify the figure.

and relative \(k_{rel}\) (which is the ratio \(k(ion)/k(neutral)\)) isomerization rates calculated for 4-R-AB molecules are presented in Table 3. The activation parameters and isomerization rates for the AzoC\(_6\) molecule are shown in Table 4. In the case of AzoC\(_6\) we defined \(k_{rel}\) as \(k(neutral\ or\ dication)/k(cation)\). Note that for AzoC\(_6\) the number of stable conformations, which are the minima on the potential energy surface, is most likely large due to the presence of carbon chain substituents, capable to adopt various conformations. The geometries considered in our work are shown in the SI, Table 4.

From Figure 2, Table 3, and Table 4 it is seen that both, the electron attachment to and withdrawal from the studied azobenzene-containing molecules lead to significant reduction in activation barriers of thermal cis \(\rightarrow\) trans isomerization in comparison with species of reference (neutral 4-R-AB and cationic AzoC\(_6\)), which is in agreement with previous findings for other azobenzenes.\(^{46,47}\) In particular for AB, \(\Delta E = 0.26\) eV in the anionic form and \(\Delta E = 0.15\) eV in the cationic form, while the barrier for the thermal isomerization in the neutral form is \(\Delta E = 1.10\) eV (here and below the values of activation energies are given per molecule). Thus, the activation energy is \(\approx 4\) times smaller in the anionic form and \(\approx 7\)
Table 3: Activation parameters and isomerization rates for neutral, anionic and cationic states of the 4-R-AB molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta E$ (eV)</th>
<th>$\Delta G$ (eV)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$k_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>1.10</td>
<td>0.99</td>
<td>$1.1 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>4-CH$_3$-AB</td>
<td>1.08</td>
<td>0.98</td>
<td>$1.7 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>4-OCH$_3$-AB</td>
<td>1.06</td>
<td>0.98</td>
<td>$1.7 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>4-NH$_2$-AB</td>
<td>1.04</td>
<td>0.96</td>
<td>$3.7 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>4-CF$_3$-AB</td>
<td>0.98</td>
<td>0.92</td>
<td>$1.7 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>4-NO$_2$-AB</td>
<td>0.83</td>
<td>0.79</td>
<td>$2.8 \times 10^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta E$ (eV)</th>
<th>$\Delta G$ (eV)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$k_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>0.26</td>
<td>0.22</td>
<td>$1.2 \times 10^{9}$</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>4-CH$_3$-AB</td>
<td>0.26</td>
<td>0.23</td>
<td>$8.0 \times 10^{8}$</td>
<td>$10^{12}$</td>
</tr>
<tr>
<td>4-OCH$_3$-AB</td>
<td>0.23</td>
<td>0.19</td>
<td>$3.8 \times 10^{9}$</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>4-NH$_2$-AB</td>
<td>0.21</td>
<td>0.18</td>
<td>$5.6 \times 10^{9}$</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>4-CF$_3$-AB</td>
<td>0.14</td>
<td>0.11</td>
<td>$8.6 \times 10^{10}$</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>4-NO$_2$-AB</td>
<td>0.05</td>
<td>0.06</td>
<td>$6.0 \times 10^{11}$</td>
<td>$10^{12}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta E$ (eV)</th>
<th>$\Delta G$ (eV)</th>
<th>$k$ (s$^{-1}$)</th>
<th>$k_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>0.15</td>
<td>0.10</td>
<td>$1.3 \times 10^{11}$</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>4-CH$_3$-AB</td>
<td>0.16</td>
<td>0.11</td>
<td>$8.6 \times 10^{10}$</td>
<td>$10^{15}$</td>
</tr>
<tr>
<td>4-OCH$_3$-AB</td>
<td>0.13</td>
<td>0.11</td>
<td>$8.6 \times 10^{10}$</td>
<td>$10^{15}$</td>
</tr>
<tr>
<td>4-NH$_2$-AB</td>
<td>0.09</td>
<td>0.08</td>
<td>$2.8 \times 10^{11}$</td>
<td>$10^{15}$</td>
</tr>
<tr>
<td>4-CF$_3$-AB</td>
<td>0.14</td>
<td>0.10</td>
<td>$1.3 \times 10^{11}$</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>4-NO$_2$-AB</td>
<td>0.12</td>
<td>0.09</td>
<td>$1.9 \times 10^{11}$</td>
<td>$10^{12}$</td>
</tr>
</tbody>
</table>

a Energies are given in eV/molecule.

Table 4: Activation parameters and isomerization rates for cationic, neutral and dicationic states of the AzoC$_6$ molecule.

<table>
<thead>
<tr>
<th>$\Delta E$ (eV)$^a$</th>
<th>$\Delta G$ (eV)$^a$</th>
<th>$k$ (s$^{-1}$)</th>
<th>$k_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.16</td>
<td>1.04</td>
<td>$1.6 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>neutral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.22</td>
<td>0.19</td>
<td>$3.8 \times 10^{9}$</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>dication</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.21</td>
<td>0.16</td>
<td>$1.2 \times 10^{10}$</td>
<td>$10^{15}$</td>
</tr>
</tbody>
</table>

$^a$ Energies are given in eV/molecule.

times smaller in the cationic form, relative to the value for neutral AB. This reduction in barrier leads to a large increase in the isomerization rate of AB in ionic forms: $\approx 10^{13}$ times higher in the anionic form and $\approx 10^{15}$ times higher in the cationic form in comparison with the isomerization rate of neutral AB. The values of $k_{rel}$ in Table 3 and Table 4 are given not
very precisely, but merely to show the order of magnitude of the enhancement effect.

While the computed isomerization rates for the reference states are of reasonable order of magnitude when compared to experiment (in particular for AzoC₆), we should stress that the calculated isomerization rates for species with an added/removed electron and hence enhancement factors $k_{rel}$, are much too large. This fact is not too surprising, since our calculations were done for isolated molecules and under ideal gas conditions. The experimental picture is much more complicated. Apart from the fact that the isomerization takes place in solution, one must also expect strong effects of the surface of Au NPs. While possible (integer) charge transfers to and from the surface are accounted for in our model calculations, steric hindrance by the surface and associated, altered energies and structures are not included. Also, the possible interaction of charged with other charged species or neutral molecules in solution is not taken care of. Nevertheless, we qualitatively reproduce the experimental finding of accelerated rates near Au NPs if we accept the hypothesis of the charge transfer from or to the surface. We also assume that trends due to different substituents should be meaningful (note that calculated $k_{rel}$ for AzoC₆ is bigger than the corresponding value for 4-NO₂-AB, which is in (qualitative) agreement with the experiment (see Table 2)).

From Table 3 one can then also conclude:

(1) For neutral species the substitution of hydrogen atoms in para position leads to a reduction in activation energies. The acceptors (CF₃, NO₂) reduce the barrier more than donors (CH₃, OCH₃, NH₂). Such a trend was revealed previously in Ref. 48. (Note that the activation energies of Ref. 48 and here are almost identical, but slight deviations in activation free energies and, hence, rates were obtained for the neutral species compared to the present work. In this context we note that in particular activation entropies are sensitive to restrictive computational settings (Gaussian keywords Opt=Tight, Integral(Grid=UltraFineGrid) were used here).) The most efficient in the reduction of barrier (lowering by $\approx 0.3$ eV the activation energy) is the acceptor NO₂. The isomerization rates do not change significantly
when substituents are donors. A slight increase, less than 10 times, is observed in the case of electron donating substituents. Acceptors in para position result in a more significant increase of the isomerization rate: \( \approx 10 \) times bigger for a CF\(_3\) group and \( \approx 10^3 \) times bigger for a NO\(_2\) group. (Note, however, that certain \( \sigma \)-acceptors like fluorine when in \textit{ortho} positions such as in \textit{o}-fluoroazobenzenes, can lead to exceptionally long-lived \textit{cis}-species.\(^{49}\)

(2) For \textit{anionic} species a strong decrease in barrier for all investigated molecules is observed. All the activation energies are less than 0.3 eV compared to about 1 eV for neutral molecules. This large drop in the value of the barrier in comparison with neutral species results in a dramatic increase (\( \approx 10^{12} \)–\( 10^{14} \) times) of the isomerization rate of the thermal \textit{cis} \( \rightarrow \text{trans} \) isomerization, relative to neutral azobenzene-containing molecules. As in the case of neutral molecules considered above, donors do not influence much the activation barriers and hence the isomerization rate in comparison with anionic AB. On the contrary, acceptors lower the barrier much more efficiently (as was observed for neutral species as well): the activation energy is only 0.14 eV in the case of a CF\(_3\) group and merely 0.05 eV in the case of a NO\(_2\) group.

(3) For \textit{cationic} species a strong decrease in barrier for all the molecules is found, too. All the activation energies are less than 0.2 eV. The isomerization rates for cationic forms of AB-containing molecules are \( \approx 10^{12} \)–\( 10^{15} \) times higher than for neutral molecules. We should note that donor and acceptor groups do not have much of an influence on the barrier relative to the value for parent cationic AB. Moreover, acceptors are not more efficient than donors in contrast to the situation observed for neutral and anionic species.

The acceleration of isomerization upon electron attachment to and withdrawal from azobenzene-containing molecules can be discussed in qualitative terms using frontier orbital arguments, by considering the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of neutral \textit{cis} AB (see Figure 3).

In an (unrelaxed) one-electron picture we expect that upon formation of an \textit{anion} the electron will occupy the LUMO of the neutral \textit{cis} isomer, which has N=N antibonding
character. Then we can suppose, that the rotation around N=N bond should happen to minimize the unfavourable antibonding interaction. Indeed, the found TS structures of azobenzene-containing molecules in the anionic state are rotation-type TSs with $\omega_{CN\text{N'C'}} \approx 90^\circ$ (see SI, Tables 1 and 2). Also, our calculations show that in the anionic state the N=N bond length in the cis isomer is typically elongated by about 0.1 Å compared to the neutral molecule. Remarkably, the weakening of the N=N bond of the azo group in the cis isomer in the vicinity of a gold nanoparticle was suggested in the literature based on the analysis of surface-enhanced Raman spectra.\textsuperscript{11} However, note that in Ref. 11 this was not discussed in connection with a possible electron transfer.

In the case of the cation formation we expect that the electron will escape from the HOMO of the neutral cis isomer, which has essentially N=N nonbonding character. Further inversion and/or rotation around the N=N bond can be possible ways to stabilize the cationic state. The TS structures obtained for cations differ from each other in the sense of TS type (inversion/rotation), that depends on the used substituents (see SI, Table 1). The N=N bond length for the cis isomer cations is only slightly affected (shortened by $\approx 0.02–0.05$ Å) in comparison to the neutral cis isomers (SI, Table 1), which is one reason why the HOMO can be characterized as nonbonding. The isomerization of the cation radical through rotational pathways was hypothesized to be a possible mechanism of the thermal
cis $\rightarrow$ trans isomerization of azobenzene-containing molecules in the presence of Au NPs.\textsuperscript{13} Since both situations with electrons attached to or removed from the switching molecules can lead to enhanced backward rates and since none of the two possibilities can be excluded \textit{a priori}, it is instructive to estimate the “energy costs” for formation of anions and cations from the neutral state of 4-R-AB, close to an Au NP. For this purpose, we consider first the relaxed electron affinities $EA = E_0 - E_-$ and ionization potentials $IP = E_+ - E_0$, where $E_0$ – the energy of neutral molecule, $E_-$ – the energy of anion and $E_+$ – the energy of cation (relaxed values mean that geometries of anions and cations were optimized). The obtained values are presented in Table 5 (and pictorially represented in Figure 2). (Note that we used the basis set without diffuse functions, namely 6-31G*. The employing of diffuse functions leads, in particular, to larger electron affinities.)

Table 5: Relaxed electron affinities and ionization potentials of cis isomers of 4-R-AB.

<table>
<thead>
<tr>
<th>Molecule (cis isomer)</th>
<th>$EA$ (eV)\textsuperscript{a}</th>
<th>$IP$ (eV)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>0.72</td>
<td>6.96</td>
</tr>
<tr>
<td>4-CH$_3$-AB</td>
<td>0.68</td>
<td>6.82</td>
</tr>
<tr>
<td>4-OCH$_3$-AB</td>
<td>0.61</td>
<td>6.62</td>
</tr>
<tr>
<td>4-NH$_2$-AB</td>
<td>0.48</td>
<td>6.34</td>
</tr>
<tr>
<td>4-CF$_3$-AB</td>
<td>1.16</td>
<td>7.24</td>
</tr>
<tr>
<td>4-NO$_2$-AB</td>
<td>1.66</td>
<td>7.47</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Energies are given in eV/molecule.

From Figure 2 and Table 5 it is seen that for the isolated species the ionization potentials are typically around 7 eV. The electron affinities for all studied 4-R-AB molecules are found to be positive, indicating that the formation of an anion from a neutral molecule is energetically favoured compared to formation of a cation. However, this conclusion is true for the species in the gas phase only.

On a metal surface the energetics can be most likely different, even if geometries were the same as in the gas phase (which they are not). The formation energies of an anion, $\Delta E^-_{\text{surf}} = E^-_{\text{surf}} - E_0^{\text{surf}}$, and cation, $\Delta E^+_{\text{surf}} = E^+_{\text{surf}} - E_0^{\text{surf}}$, on a surface can be roughly estimated, neglecting geometric distortions and chemical bonding, from the following
expressions (for an initially neutral surface):

\[ \Delta E_{\text{surf}}^- = -EA + \Phi + \Delta_{\text{im}}, \]
\[ \Delta E_{\text{surf}}^+ = IP - \Phi + \Delta_{\text{im}}. \] (4)

Here, \( \Phi \) is the work function of the surface and \( \Delta_{\text{im}} \) the image charge term (\( \Delta_{\text{im}} = -1/4z \) in atomic units, with \( z \) being the distance between ion and image plane). A positive \( \Delta E_{\text{surf}}^- \) value corresponds to an energetically unfavourable situation with a smaller tendency to enforce a charge transfer and form an ion. To estimate the formation energies \( \Delta E_{\text{surf}}^- \) and \( \Delta E_{\text{surf}}^+ \) on Au(111) surface the values of \( \Phi = 5.31 \) eV \(^{50}\) (note, most probably, the work function of nanoparticles is different from the value used here which is for planar surface) and \( \Delta_{\text{im}} = -1.50 \) eV (at \( z = 2.4 \) Å, as \( z \) we used the vertical distance between the surface and azo group as computed for azobenzene on an extended Au(111) surface in Ref. 51,52) were taken. The results are shown in Table 6.

Table 6: Estimated formation energies of anion \( \Delta E_{\text{surf}}^- \) and cation \( \Delta E_{\text{surf}}^+ \) of cis isomers of 4-R-AB on a gold surface.

<table>
<thead>
<tr>
<th>Molecule (cis isomer)</th>
<th>( \Delta E_{\text{surf}}^- ) (eV) (^{a})</th>
<th>( \Delta E_{\text{surf}}^+ ) (eV) (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>3.09</td>
<td>0.15</td>
</tr>
<tr>
<td>4-CH(_3)-AB</td>
<td>3.13</td>
<td>0.01</td>
</tr>
<tr>
<td>4-OCH(_3)-AB</td>
<td>3.20</td>
<td>-0.19</td>
</tr>
<tr>
<td>4-NH(_2)-AB</td>
<td>3.33</td>
<td>-0.47</td>
</tr>
<tr>
<td>4-CF(_3)-AB</td>
<td>2.65</td>
<td>0.43</td>
</tr>
<tr>
<td>4-NO(_2)-AB</td>
<td>2.15</td>
<td>0.66</td>
</tr>
</tbody>
</table>

\(^{a}\) Energies are given in eV/molecule.

It is seen that the formation energy of a cation on the gold surface is smaller than the formation energy of an anion, \( i.e. \), the tendency to form a cation is greater. For 4-OCH\(_3\)-AB and 4-NH\(_2\)-AB the values of \( \Delta E_{\text{surf}}^+ \) are even negative, indicating a possible spontaneous formation of a cation on the surface.

We should remark that it was observed experimentally with scanning tunneling microscopy, that AB does not photoisomerize on a planar gold surface.\(^{53}\) It is also interesting
to note that, as revealed by the already mentioned dispersion-corrected DFT calculations, the ground-state barrier of thermal $cis \rightarrow trans$ isomerization of AB along the rotational pathway is significantly reduced on Au(111) in comparison with the gas phase, to about 0.4 eV.\textsuperscript{52} Photoswitching of azobenzenes on an extended gold surface, however, can be achieved by spatial decoupling of the azo unit from the surface through, e.g., attaching tert-butyl groups to the phenyl rings of azobenzene,\textsuperscript{53} or complexation of AB-containing conjugates to a functionalized surface.\textsuperscript{12}

However, it is very important to note that the system studied here, with gold nanoparticles in solution and azobenzene-containing species interacting with them, is quite different from the case of photosensitive molecules on a surface in vacuum. Thus, our estimate of formation energies should be considered only as a qualitative guide. It is nevertheless a worthwhile guide, since the complete simulation of the physical system by first principles methods is currently out of reach.

## 4 Conclusions

In this work we studied the effect of gold nanoparticles on the thermal $cis \rightarrow trans$ isomerization of various azobenzene-containing molecules in aqueous solution. Experimentally, cationic azobenzene-containing trimethylammonium and polyamine surfactants were investigated. We have found a decrease of the thermal lifetime of the $cis$ isomer upon the addition of 10 nm gold nanoparticles to aqueous solutions of azobenzene-containing molecules. The thermal lifetime in the presence of Au NPs was found to be about 1000 times smaller for the trimethylammonium surfactants and 400 times smaller for polyamines. Also 4-nitroazobenzene was studied experimentally in methanol solution (partially containing water after addition of gold colloid), for which we observed a $\approx 40$ times decrease in the thermal lifetime.

Following the hypothesis of charge transfer between the azobenzene-containing molecules...
and gold nanoparticles, we performed DFT calculations of various charged states of azobenzene-containing molecules and found that both the electron attachment to, and withdrawal from, the azobenzene-containing molecules lead to a pronounced decrease in the activation energy barrier of the thermal back isomerization. Applying Eyring’s transition state theory, we calculated absolute rates for thermal \textit{cis} \rightarrow \textit{trans} isomerization and found that they are \( \approx 10^{12} - 10^{15} \) times larger for azobenzene-containing molecules upon electron attachment and withdrawal. Such large numbers are not in quantitative agreement with the obtained experimental values, however, that was also not expected due to differences of the experimental conditions and the idealized gas-phase type theoretical models as adopted here. Finally, we made a simple estimate of the 4-R-AB ion formation energies in the presence of a gold surface and revealed that the energy for cation formation is smaller than for anion formation; for some of the molecules the cation formation energy was even negative. This result suggests an easier cation formation and, thus, corroborates the possible electron transfer from the azobenzene-containing molecule to the gold nanoparticle surface, proposed by Hallet-Tapley \textit{et al.}\textsuperscript{13} Certainly, this is still a hypothesis, which should be verified.

\section*{Acknowledgements}

This research was done in the framework of the IMPRS on Multiscale Bio-Systems. P.S. acknowledges support through Sonderforschungsbereich 658, “Molecular switches at surfaces”. E.T. thanks Prof. Dr. A.D. Boese and M. Utecht for valuable advices. We also acknowledge a financial contribution of the French National Research Agency (ANR) (Grant LASERNANOBIIO, ANR-10-BLAN-919) and the A*MIDEX project (No. ANR-11-IDEX-0001-02) funded by the “Investissements d’Avenir” French Government program, managed by the ANR. Finally, we acknowledge support from “Plan Cancer” of the French Institute of Health and Medical Research (INSERM).
Supporting Information

Kinetics of isomerization in an aqueous solution and the geometries of isomers and transition states of the studied azobenzene-containing molecules.

References


4. Reprints


4.1. Paper 1


Supporting Information for
Thermal Cis-to-Trans Isomerization of Azobenzene-Containing Molecules Enhanced by Gold Nanoparticles: An Experimental and Theoretical Study

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Peter Saalfrank,*,‡ and Svetlana Santer*,†

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‡Theoretical Chemistry, Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany
¶Aix Marseille University, CNRS, LP3 UMR 7341, Campus de Luminy, Case 917, 13288, Marseille Cedex 9, France
Kinetics of Isomerization in an Aqueous Solution

![Figure 1: Kinetics of thermal cis → trans isomerization of AzoEA\(_2\) in an aqueous solution at room temperature. The inset shows the evolution of optical density at 376 nm with time (open circles), and the corresponding monoexponential fit (red curve).](image)

Geometries of Isomers and Transition States

Selected geometric parameters, which are the dihedral angle \(\omega_{CN'N'C'}\) of the rotation around NN bond, inversion angles \(\alpha_{CN'}\) and \(\alpha_{N'NC'}\), and the bond lengths \(r_{NN'}, r_{CN}\) and \(r_{N'C'}\) of the trans, cis isomers and the TS of 4-R-AB in neutral, anionic and cationic states are presented in Table 1.

From Table 1 one can see that:
(1) The \textit{trans} isomer of the studied molecules has a planar $CNN'C'$ moiety ($\omega_{CNN'C'} = 180^\circ$) (and the phenyl rings are located in the $CNN'C'$ plane (the optimized geometries of AB are presented in Table 2)) in neutral and anionic forms, whereas in the cationic form it is twisted ($\omega_{CNN'C'} \approx 155^\circ$). The nonplanarity of the \textit{trans} isomer of positively charged AB with a similar value of $\omega_{CNN'C'}$ obtained from DFT calculations was reported before in Ref. 1. Moreover, we found that the planar AB geometry (with $\omega_{CNN'C'} = 180^\circ$ and the phenyl rings located in the plane of $CNN'C'$ moiety) is the TS of the “\textit{trans} $\leftrightarrow$ \textit{trans}” reaction of AB in the cationic form with a corresponding energy barrier of $\Delta E = 0.07$ eV. The inversion angles are not much affected in the anionic form and bigger by near 13$^\circ$ in the cationic form, relative to the neutral species. The NN bond length becomes bigger by about 0.07 Å in the anionic form and smaller by about 0.03 Å for cations in comparison with neutral molecules. The CN bonds shorten by about 0.05 Å for both charged forms.

(2) The \textit{cis} isomer of the neutral species has $\omega_{CNN'C'} \approx 10^\circ$. The molecules in charged forms exhibit increased values of the dihedral angle: for AB $\omega_{CNN'C'} \approx 46^\circ$ in the anionic form and $\omega_{CNN'C'} \approx 39^\circ$ in the cationic one. The obtained value of $\omega_{CNN'C'}$ for the anionic form of AB is in agreement with a previously reported one.\textsuperscript{2} As for the \textit{trans} isomer, the inversion angles are not much affected in the anionic form and bigger by near 12$^\circ$ in the cationic form, relative to the neutral species, the NN bond length becomes bigger by about 0.09 Å in the anionic form and smaller by about 0.04 Å for cations, the CN bonds shorten by about 0.06 Å for both charged forms.

(3) The TS of \textit{neutral} azobenzene-containing molecules reveals linearization in either the $CNN'$ ($\alpha_{CNN'} = 180^\circ$) or the $NN'C'$ moiety ($\alpha_{NN'C'} = 180^\circ$) and so can be called “a linear TS”. At that, the donors (CH$_3$, OCH$_3$, NH$_2$) in para position lead to $\alpha_{NN'C'} \approx 180^\circ$ (linearization at nonsubstituted phenyl ring), whereas acceptors (CF$_3$, NO$_2$), opposite, to $\alpha_{CNN'} \approx 180^\circ$ (linearization at substituted phenyl ring) as was also reported in Ref. 3. The linear TS observed for neutral species indicates an inversion mechanism of isomerization. It should be noted that in the TS structure the phenyl rings are perpendicular to each other.
(see geometries of AB in Table 2). The CN bond (CN or N′C′) involved in linearization during isomerization shortens by ≈ 0.10 Å relative to the CN bond of cis and trans isomers, other bond lengths are affected much less.

(4) The TS of anionic azobenzene-containing molecules is not linear with an ω_{CNN′C′} angle of about 90°. The geometry of the TS indicates a rotation mechanism of isomerization. In the case of electron donating groups the inversion angle α_{CNN′} ≈ 116° (at the substituted phenyl ring) is smaller than α_{NN′C′} ≈ 125° (at the nonsubstituted ring). In the case of acceptors the opposite situation is realized.

(5) The found TS structures of cationic azobenzene-containing molecules differ from each other in the reaction type (inversion or rotation). The TS geometries of parent AB and the derivative with a CH₃ group are closer to inversion-type: in the case of AB one of the inversion angles is about 172° and α_{NN′C′} ≈ 162° (at the nonsubstituted phenyl ring) for 4-CH₃-AB. Donors OCH₃ and NH₂ give rise to rotation-type TSs (ω_{CNN′C′} of about 90°). Acceptors CF₃ and NO₂ lead to inversion-type TSs with α_{CNN′} (at the substituted phenyl ring) of about 170°.

The geometric parameters of the isomers and the TS of the AzoC₆ molecule in cationic, neutral and dicationic states are presented in Table 3 and the optimized geometries are shown in Table 4. The general trend in the variation of the parameters upon charging is similar to the one observed for 4-R-AB, as can be concluded from comparing Tables 1 and 3, taking into account the following correspondence: neutral 4-R-AB ∼ cationic AzoC₆, anionic 4-R-AB ∼ neutral AzoC₆, and cationic 4-R-AB ∼ dicationic AzoC₆.
### Table 1: Selected Geometric Parameters of the Isomers and the TS of 4-R-AB in Neutral, Anionic, and Cationic States

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \omega_{\text{CN}} )</th>
<th>( \alpha_{\text{C3N}} )</th>
<th>( \alpha_{\text{NC3}} )</th>
<th>( r_{\text{CN}} )</th>
<th>( r_{\text{C3N}} )</th>
<th>( r_{\text{NC3}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>180.0</td>
<td>114.8</td>
<td>114.8</td>
<td>1.26</td>
<td>1.32</td>
<td>1.42</td>
</tr>
<tr>
<td>4-CH$_3$-AB</td>
<td>180.0</td>
<td>114.9</td>
<td>114.8</td>
<td>1.26</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>4-CH$_2$-AB</td>
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<td>115.1</td>
<td>114.7</td>
<td>1.26</td>
<td>1.41</td>
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<tr>
<td>4-NH$_2$-AB</td>
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<td>114.6</td>
<td>1.26</td>
<td>1.41</td>
<td></td>
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<tr>
<td>4-CF$_3$-AB</td>
<td>179.9</td>
<td>114.5</td>
<td>115.0</td>
<td>1.26</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>4-NO$_2$-AB</td>
<td>180.0</td>
<td>114.3</td>
<td>115.1</td>
<td>1.26</td>
<td>1.42</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{Angles are given in } ^\circ \]. \[ \text{Bond lengths are given in } \text{Å} \].

4. Reprints
Table 2: Optimized Geometries of the Isomers and the TS of AB in Neutral, Anionic, and Cationic States

The molecules were visualized with Jmol, an open-source Java viewer for chemical structures in 3D (http://www.jmol.org/).

Table 3: Selected Geometric Parameters of the Isomers and the TS of AzoC₆ in Cationic, Neutral, and Dicationic States

<table>
<thead>
<tr>
<th></th>
<th>ωᵩ₅⁴°C&lt;sup&gt;a&lt;/sup&gt;</th>
<th>αᵩ₅₋₆&lt;sup&gt;a&lt;/sup&gt;</th>
<th>α₅₋₇&lt;sup&gt;a&lt;/sup&gt;</th>
<th>rₐ&lt;sup&gt;b&lt;/sup&gt;</th>
<th>rₐ&lt;sup&gt;b&lt;/sup&gt;</th>
<th>rₐ&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>trans</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>neutral</td>
<td>178.0</td>
<td>114.2</td>
<td>115.4</td>
<td>1.27</td>
<td>1.41</td>
<td>1.41</td>
</tr>
<tr>
<td>anion</td>
<td>179.8</td>
<td>113.2</td>
<td>114.0</td>
<td>1.34</td>
<td>1.38</td>
<td>1.38</td>
</tr>
<tr>
<td>cation</td>
<td>153.8</td>
<td>123.8</td>
<td>124.6</td>
<td>1.25</td>
<td>1.37</td>
<td>1.37</td>
</tr>
</tbody>
</table>

| **cis**         |                     |                     |                     |               |               |               |
| neutral         | 12.2                | 125.4               | 124.7               | 1.25          | 1.44          | 1.42          |
| anion           | 47.9                | 122.1               | 121.3               | 1.35          | 1.38          | 1.39          |
| cation          | 44.6                | 133.4               | 135.1               | 1.22          | 1.37          | 1.37          |

| **TS**          |                     |                     |                     |               |               |               |
| cation          | 172.8               | 178.1               | 118.0               | 1.23          | 1.34          | 1.43          |
| neutral         | 93.4                | 119.7               | 116.8               | 1.36          | 1.35          | 1.38          |
| dication        | 89.2                | 154.0               | 125.7               | 1.22          | 1.33          | 1.38          |

<sup>a</sup> Angles are given in °. <sup>b</sup> Bond lengths are given in Å.
Table 4: Optimized Geometries of the Isomers and the TS of AzoC₆ in Cationic, Neutral, and Dicationic States

<table>
<thead>
<tr>
<th>cation</th>
<th>neutral</th>
<th>dication</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans</td>
<td><img src="image1" alt="trans_cation" /></td>
<td><img src="image2" alt="trans_neutral" /></td>
</tr>
<tr>
<td>cis</td>
<td><img src="image4" alt="cis_cation" /></td>
<td><img src="image5" alt="cis_neutral" /></td>
</tr>
<tr>
<td>TS</td>
<td><img src="image7" alt="TS_cation" /></td>
<td><img src="image8" alt="TS_neutral" /></td>
</tr>
</tbody>
</table>

The molecules were visualized with Jmol, an open-source Java viewer for chemical structures in 3D (http://www.jmol.org/).

References


4. Reprints

4.2. Paper 2

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**Exciton Splitting of Adsorbed and Free 4-Nitroazobenzene Dimers: A Quantum Chemical Study**

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Abstract

Molecular photoswitches such as azobenzenes, which undergo photochemical trans $\leftrightarrow$ cis isomerizations, are often mounted for possible applications on a surface and/or surrounded by other switches, e.g., in self-assembled monolayers. This may suppress the isomerization cross section due to possible steric reasons, or, as recently speculated, by exciton coupling to neighbouring switches, leading to ultrafast electronic quenching (Gahl et al., J. Am. Chem. Soc. 2010, 132, 1831). The presence of exciton coupling has been anticipated from a blue shift of the optical absorption band, compared to molecules in solution. From the theory side the need arises to properly analyze and quantify the change of absorption spectra of interacting and adsorbed switches. In particular, suitable methods should be identified and effects of intermolecule and molecule–surface interactions on spectra disentangled. In this paper by means of time-dependent Hartree-Fock (TD-HF), various flavours of time-dependent density functional theory (TD-DFT), and the correlated wave function based coupled-cluster (CC2) method we investigated the 4-nitroazobenzene molecule as an example: The low-lying singlet excited states in the isolated trans monomer and dimer as well as their composites with a silicon pentamantane nanocluster, which serves also as a crude model for a silicon surface, were determined. As most important results we found that: (i) HF, CC2, range-separated density functionals or global hybrids with large amount of exact exchange are able to describe exciton (Davydov) splitting properly for free and adsorbed dimers, while hybrids with small amount of exact exchange fail producing spurious charge transfer. (ii) The exciton splitting in a free dimer would lead to a blue shift of the absorption signal, however, this effect is almost nullified or even overcompensated by the shift arising from van der Waals interactions between the two molecules. (iii) Adsorption on the Si “surface” leads to a further, strong red shift for the present system. (iv) At a next-nearest neighbour distance (of about 3.6 Å), the exciton splitting is around 0.3 eV, with or without “surface”, suggesting a rapid quenching of the molecular $\pi \rightarrow \pi^*$ excitation. At larger distances, exciton splitting decreases rapidly.
1 Introduction

Molecular photoswitches, capable of a light-driven reversible shift between at least two stable or meta-stable states, attract considerable attention due to potential applications in nanotechnology (see, e.g., reviews 1–4). One of the most widely studied molecular photoswitches is azobenzene, which can be reversibly switched between the thermodynamically more stable trans isomer and the less stable cis isomer. The $\text{trans} \rightarrow \text{cis}$ transition is enforced by UV light, and the $\text{cis} \rightarrow \text{trans}$ back isomerization by blue light, or thermally.\textsuperscript{5}

A possible route to implement this functionality for technical applications is to mount molecular photoswitches on a substrate. A particular promising substrate is silicon. In fact in recent years reversible photoisomerization was demonstrated for a series of self-assembled monolayers (SAMs) of azobenzene-containing molecules grafted on silicon.\textsuperscript{6–11} Recently, the reversible switching of a single azobenzene-containing molecule (namely, 4-anilino-4'-nitroazobenzene) adsorbed on a Si surface was also reported.\textsuperscript{12} In these cases intermolecular interactions were absent or at least expectedly small.

In contrast, photoisomerization was suppressed for densely packed SAMs of certain azobenzene-containing thiols formed on a gold surface.\textsuperscript{13,14} For this system, a blue shift for the $\pi \rightarrow \pi^*$ absorption band of the trans molecules in the close-packed molecular layer was observed when compared to molecules in solution.

The occurrence of this blue shift (hypsochromic shift) and its relation to quenching of localized excitations in interacting chromophores can be rationalized within the molecular exciton model.\textsuperscript{15,16} Being central to what follows, we wish to reiterate this model in some detail. Accordingly, when a molecule such as trans-azobenzene, say, has a ground state $|g\rangle$ and an excited state $|e\rangle$ – the lowest $\pi \rightarrow \pi^*$ excited state to be specific – one can write the eigenstates of a non-interacting dimer as $|gg\rangle$ (dimer ground state), $|ge\rangle$ and $|eg\rangle$ (single-exciton states), and $|ee\rangle$ (bi-exciton state), respectively. If the monomer ground state energy is $E_g$, and $E_e$ that of the excited state, then the lowest excitation energy
of both the monomer and the uncoupled dimer (here we consider a dimer composed of identical monomers) is \( \Delta E_{ge} = E_e - E_g \). If the two monomers are coupled by an operator \( \hat{V} \), the previously isolated, degenerate single-exciton states form symmetric and antisymmetric linear combinations, \( |\psi_\pm\rangle = \frac{1}{\sqrt{2}} (|eg\rangle \pm |ge\rangle) \), with energies

\[
E_\pm = E_e + E_g \pm \Delta .
\] (1)

Here, \( \Delta = \langle ge|\hat{V}|eg\rangle \) is the exciton coupling matrix element and \( 2\Delta \) the exciton (Davydov) splitting between the two states. In Eq. (1), van der Waals (vdW) corrections (terms of the type \( \langle ge|\hat{V}|ge\rangle \) and \( \langle eg|\hat{V}|eg\rangle \)) were neglected. Furthermore, strictly speaking, we neglect couplings between different states, \( i.e.\, \), terms of type \( \langle gg|\hat{V}|ge\rangle \), \( \langle gg|\hat{V}|ee\rangle \), and \( \langle ge|\hat{V}|ee\rangle \). Also note that \( |\psi_\pm\rangle = \frac{1}{\sqrt{2}} (|eg\rangle \pm |ge\rangle) \) are, in fact, eigenstates of uncoupled dimer with corresponding eigenvalue of \( E_e + E_g \) (the same value as for degenerate \( |eg\rangle \) and \( |ge\rangle \) states).

Thus, \( |\psi_\pm\rangle \) states are a zero-order approximation for eigenstates of coupled dimer. Further neglecting any couplings for the dimer ground state, such that \( |\psi_G\rangle = |gg\rangle \) with energy \( E_G = 2E_g \) serves as a zero-order model for the ground state of the combined system, excitation energies to single-exciton states \( |\psi_+\rangle \) and \( |\psi_-\rangle \) become \( \Delta E_\pm = E_\pm - E_G \), or

\[
\Delta E_\pm = E_e - E_g \pm \Delta .
\] (2)

Next, according to this theory the transition dipole moments for the dimer (with orientation of transition dipole moments of the monomers along the same direction) from the ground state \( |\psi_G\rangle = |gg\rangle \) to the \( |\psi_+\rangle \) and \( |\psi_-\rangle \) split final states are

\[
\mu_{G+} = \langle gg|\hat{\mu}|\psi_+\rangle = \sqrt{2} \mu_{ge} ,
\]
(3)

\[
\mu_{G-} = \langle gg|\hat{\mu}|\psi_-\rangle = 0 ,
\] (4)

where \( \hat{\mu} = \hat{\mu}^{(1)} + \hat{\mu}^{(2)} \) is the total dipole operator with contributions from both monomers 1
and 2. Eqs. (3) and (4) are obtained for the case of identical monomers, i.e., \( \mu^{(1)} = \mu^{(2)}(= \mu_{ge}) \), \( \mu_{ge} \) is the transition dipole moment of the monomer. Thus, the transition to the \( |\psi_{-}\rangle \) state is forbidden, while the one to the \( |\psi_{+}\rangle \) state is enhanced, by a factor of two in oscillator strengths. According to the well-known point-dipole model (henceforth PDM),

\[
\Delta = \frac{(\mu_{ge}^{(1)}, \mu_{ge}^{(2)})}{R^3} - 3 \frac{(\mu_{ge}^{(1)}, R)(\mu_{ge}^{(2)}, R)}{R^5} .
\]  

Here, \( R \) is the vector connecting the two transition dipoles. If the latter are (almost) parallel to each other standing side-by-side as is typically the case in SAMs, \( \Delta > 0 \) and Eq. (2) predicts a blue shift for the allowed transition.

\( \Delta \) is also related to the “quenching time” of a localized excitation, due to coupling to a neighbour molecule. For instance, considering a “left-localized” excitation \( |\psi_L\rangle = |eg\rangle = \frac{1}{\sqrt{2}}(|\psi_{+}\rangle + |\psi_{-}\rangle) \), this excitation is not an eigenstate of the coupled dimer and therefore will start oscillating from one monomer to the other, forming a right-localized state \( |\psi_R\rangle = |ge\rangle = \frac{1}{\sqrt{2}}(|\psi_{+}\rangle - |\psi_{-}\rangle) \) (multiplied by some phase factor), with a half-period

\[
\tau = \frac{\hbar \pi}{2\Delta} .
\]

This time can be interpreted as a “quenching time”, which, when short enough, hinders isomerization.

The above analysis of exciton-split states in coupled dimer can be refined by also taking vdw corrections into account, leading to

\[
\Delta E_{+} = E_e - E_g - D + \Delta
\]

for the allowed transition, where \( D \) is a vdw correction, \( D = \langle gg|\hat{V}|gg\rangle - \langle eg|\hat{V}|eg\rangle \), accounting for dipole–dipole, dipole–induced dipole and induced dipole–induced dipole interactions. Usually, \( D \) leads to a red-shift, i.e., \( D > 0 \). If \( D > \Delta \), even an overall
red shift (rather than blue shift) may arise. In general, \( D \neq 0 \) makes an estimate of the exciton splitting based on observed spectral shifts difficult. Moreover, also the interaction of the chromophores with the substrate will generally lead to a shift, which complicates things further.

In this work we wish to study optical properties of 4-nitroazobenzene, which is the functional part of the molecule employed in Ref. 12. We will consider a monomer and a dimer both in the gas phase, and when being adsorbed at a “surface”. More specifically, a nanocluster representing the hydrogen terminated 1D-isomer of silicon pentamantane (\( \text{Si}_{26}\text{H}_{32} \), we will denote this cluster as Penta) will be considered. The latter is composed of five fused sila-adamantane units (\( \text{Si}_{10} \) cages). The successful synthesis of the sila-adamantane (terminated by methyl and trimethylsilyl groups) was reported earlier.\(^{18}\) Our model will serve to study the effect of attaching one or two switching molecules on such a cluster, and also as a very crude model for adsorption on a real Si surface. We are aware, though, that the latter is typically reconstructed and may be unsaturated in vacuum, which is not the case here. An approach of the problem with a periodic model is outside the scope of this paper.

The “physical” questions we wish to answer below are as follows:

- What are the effects of a second molecule on optical properties of an 4-nitroazobenzene switch, in particular: What is the size of the exciton splitting (\( 2\Delta \) in the simple exciton model) and of the vdW shift (\( D \))?

- What is the effect of the “surface”?

The first question has already been addressed partially in Ref. 17, for a different system. There, linear response time-dependent hybrid density functional theory (TD-B3LYP) was used to determine exciton splittings in free-standing dimers and oligomers. For not too short intermolecular distances, this method was found to agree with expectations from simple exciton theory and the PDM. However, in particular when many excited states are present the problem arose of identifying the relevant transitions (\( i.e., \) the \( |\psi_+\rangle \) and \( |\psi_-\rangle \))
states). Further, in Refs. 19,20 the reliability of TD-B3LYP in general situations, including short intermolecular distances, has been questioned. Therefore, this paper also serves two “methodological” purposes, namely to answer the following questions:

- What is an appropriate quantum chemical method to determine exciton splittings in dimers of chromophores?
- How can we identify relevant exciton states leading to exciton splitting?

To address the first methodological question, we applied and assessed the linear response time-dependent Hartree-Fock and a large set of density functional theory methods, as well as the second-order approximate coupled-cluster singles-and-doubles model (CC2) (along with its spin-component scaled variant (SCS-CC2)) for low-lying singlet excited states. In order to tackle the second question which is necessary to unambiguously determine exciton splittings and associated delocalization (quenching) times, the natural transition orbitals (NTO) method was tested.

The paper is organized as follows. In Section 2 the computational methodology and the studied models are described. Then, in Section 3, we present our results and discuss them. Section 4 summarizes the findings and concludes our work.

2 Methods and Models

2.1 Calculation of absorption spectra

The calculation of vertical excitation energies and corresponding oscillator strengths for the models described in the next subsections was carried out with the linear response time-dependent Hartree-Fock (TD-HF) method (see, e.g., Refs. 21,22) and density functional theory (TD-DFT)\(^23\) as well as the second-order approximate coupled-cluster singles-and-doubles model (CC2)\(^24\) employing the resolution of the identity (RI)\(^25,26\) and the frozen core approximations. The spin-component scaled variant of CC2 (SCS-CC2)\(^27\) was also tested.
The selected methods cover wave function theory (WFT) methods without (TD-HF) and with (CC2, SCS-CC2) correlation energy included, as well as density-based (TD-DFT) methods with various amount of exact exchange and asymptotic behaviour. In particular for the latter, we used seven global hybrid functionals, B3LYP\textsuperscript{28,29} (20 % of exact exchange), X3LYP\textsuperscript{30} (21.8 %), BMK\textsuperscript{31} (42 %), BHandH (50 %) and BHandHLYP (50 %) (Gaussian 09 implementations, for “half-and-half” theory see Ref. 32), M06-2X\textsuperscript{33} (54 %), M06-HF\textsuperscript{34} (100 %), and six range-separated hybrid functionals, CAM-B3LYP,\textsuperscript{35} LC-\(\omega\)PBE,\textsuperscript{36} M11,\textsuperscript{37} \(\omega\)B97,\textsuperscript{38} \(\omega\)B97X,\textsuperscript{38} and \(\omega\)B97X-D.\textsuperscript{39} For TD-HF and TD-DFT calculations the 6-31G* basis set\textsuperscript{40,41} was employed. For CC2 calculations the aug-cc-pVDZ basis set\textsuperscript{42–44} (with corresponding auxiliary basis set for RI\textsuperscript{45}) was used, if not stated otherwise. Altogether, 16 different methods / model chemistries were employed. The focus of the main text will be on five “typical representatives” of them, namely HF, CC2, B3LYP, BMK and CAM-B3LYP, however, occasionally we will also refer explicitly to specific results for other methods. More results on all 16 methods will be presented in the Supporting Information (SI).

Vertical excitation energies and corresponding oscillator strengths were calculated for the lowest 20 singlet excited states of each system, using TD-HF, TD-DFT or CC2 methods. Absorption spectra were obtained from computed excitation wavelengths \(\lambda_i\) and oscillator strengths \(f_i\) as a sum over all signals broadened by unnormalized Gaussians:

\[
I(\lambda) = \sum_{i=1}^{20} f_i \exp \left( -\frac{1}{2\sigma^2} \left( \frac{1}{\lambda} - \frac{1}{\lambda_i} \right)^2 \right). \tag{8}
\]

Here, \(I\) is the absorbance (in arbitrary units), \(\lambda\) the wavelength, and \(\sigma\) a Gaussian broadening parameter (\(\sigma = 1500 \text{ cm}^{-1}\) in this work). Note that the broadening procedure is very crude but allows for a better comparability with experimental spectra (see below).

The TD-HF and TD-DFT calculations were done with Gaussian 09 (Revisions D.01 and A.02),\textsuperscript{46} while CC2 calculations were performed with TURBOMOLE (Version 6.5).\textsuperscript{47}
2.2 Free monomers of 4-nitroazobenzene and azobenzene

As a first model called “free monomer”, we used a single 4-nitroazobenzene molecules, denoted as 4-NO$_2$-AB in what follows. The geometries of the \textit{trans} and \textit{cis} isomers of 4-NO$_2$-AB are shown in Figure 1 (a), (b). The geometries of the isomers were fully optimized. Only real frequencies were obtained for both isomers of 4-NO$_2$-AB by vibrational frequency analysis showing that the structures are true minima. Geometries were optimized at the B3LYP/6-31G* level of theory and, for testing purposes, reoptimized within the respective methods (used for subsequent spectra calculations).

Also, apart from the 4-NO$_2$-AB molecule we considered the parent azobenzene (AB) molecule, for which the experimental gas phase spectra and accurate theoretical calculations are available. For simplicity, in this case we used always the geometries of the isomers optimized at B3LYP/6-31G* level of theory, without reoptimization.

2.3 Monomer and dimer of \textit{trans}-4-NO$_2$-AB on a Si nanocluster

In order to simulate the adsorption of 4-NO$_2$-AB on a Si cluster or “surface”, we used a silicon pentamantane (Si$_{26}$H$_{32}$) cluster as shown in Figure 1 (c). As mentioned above the Penta cluster consists of five fused Si adamantane units. By removing one or two H atoms from Penta and one H atom from each \textit{trans}-4-NO$_2$-AB molecule, we formed clusters with one (monomer) or two (dimer) molecules attached to the surface, in a way as shown in Figure 1 (d)–(f). We call these models “monomer on Penta” and “dimer on Penta” for short. In both cases Si–C bonds are formed. The dimer corresponds to a next-nearest neighbour arrangement of the two adsorbates.

Geometry optimizations of 4-NO$_2$-AB-Penta and [4-NO$_2$-AB]$\_2$-Penta composites were done at the B3LYP/6-31G* level. For the “dimer on Penta” model, two types of calculations were performed, one without dispersion correction (Figure 1 (e)) and one with dispersion correction included through Grimme’s D3 scheme ($\text{B3LYP}+\text{D3}/6-31G^*$), as shown in Figure 1 (f). Again, the minimum nature was proven by vibrational frequency analysis. The
Figure 1: Geometries of trans (a) and cis (b) isomers of 4-NO$_2$-AB, silicon pentamantane nanocluster (c), “monomer on Penta” (d) and “dimer on Penta” ((e), (f)) models, as well as free dimer (g) along with the numbering of the molecules. Figures (c)–(g) comprise side and top views. Geometries (a)–(e) were optimized at the B3LYP/6-31G* level of theory, geometry (f) at the B3LYP+D3/6-31G* level, for details on geometry of free dimer (g) see text.

A more detailed discussion of differences in geometries without and with dispersion correction is provided in SI A. We note that the geometry of the “monomer on Penta”, which is in near-perfect upright orientation (Figure 1 (d)), did not change much after including the D3 correction. The “monomer on Penta” structure obtained without D3
correction was used for spectra calculation.

2.4 Free dimer models

To track the effect of inter-molecule interaction only (without a surface), we also devised a model of the free trans dimer (Figure 1 (g)), in a geometry as found in the adsorbed state. To prepare the free dimer model, all atoms of the Penta cluster were removed from “dimer on Penta + D3” model (Figure 1 (f)), two H atoms were added to the C atoms previously involved in the C–Si bonds, and the corresponding C–H bond lengths reoptimized on the B3LYP/6-31G* level, keeping all other coordinates fixed. This model will be called the “free dimer” in what follows. Due to the construction protocol, in the resulting dimer both monomers have slightly different internal geometries, which are not ideally planar.

For test calculations, we also worked with a “totally symmetric” dimer model, consisting of two identical, fully planar monomers with molecular planes on top of each other and monomer separation of 3.6 Å (i.e., the fully optimized monomer geometry was taken for the first monomer and the second monomer was constructed by translating all atoms of the first monomer in the direction perpendicular to the molecular plane by 3.6 Å).

2.5 Natural Transition Orbitals

In order to facilitate the analysis of excitations beyond simple inspection of canonical orbitals, the natural transition orbitals (NTO) method\textsuperscript{51} was adopted. The analysis decomposes the electronic single-particle transition density matrix such that transition in question is described by pairs of occupied and virtual NTOs, corresponding to “hole” and “particle” contributions, respectively. Often, a single hole-particle pair dominates the transition, which is then characterized by an eigenvalue $\lambda$ of the pair close to 1. The NTOs (as well as molecular geometries) were visualized with Jmol: an open-source Java viewer for chemical structures in 3D (http://www.jmol.org/).
3 Results and Discussion

3.1 Free monomer

As a first step of theoretical analysis we calculated the electronic absorption spectra of the isolated monomers. In Figure 2 we show the broadened vertical absorption spectra (as well as corresponding stick spectra (oscillator strengths)) of trans and cis isomers of 4-NO₂-AB and AB obtained with HF, B3LYP, BMK, CAM-B3LYP, and CC2 methods. As mentioned above, we chose exemplarily B3LYP, BMK, and CAM-B3LYP functionals from the whole set of functionals to see the influence of exact exchange amount / range-separation on excited states. Excitation energies for trans-4-NO₂-AB monomer calculated with all used methods are shown in SI B. The spectra of 4-NO₂-AB, presented in Figures 2 (a) and 2 (b), were calculated using B3LYP/6-31G* geometries. To track the influence of geometry on absorption we also calculated vertical spectra for the 4-NO₂-AB isomers with geometries reoptimized within the respective methods used for spectra evaluation (Figures 2 (c) and 2 (d)). For AB we employed B3LYP-optimized geometries throughout (Figures 2 (e) and 2 (f)).

As a reference to judge on the quality of computed spectra for 4-NO₂-AB we used experimental UV/Vis spectra in chloroform solution, as described in SI C. For AB, experimental information from Ref. 48 (gas phase spectra) was taken as a reference. For trans-4-NO₂-AB, the experimental spectrum is dominated by the lowest $\pi \rightarrow \pi^*$ transition at 335 nm. For cis, the $n \rightarrow \pi^*$ transition becomes visible, at 426 nm. From Figure 2 it is seen that in every case HF (solid blue line) gives the expected blue-shifted absorption for the first bright transition when compared to experiment (the gray, vertical bars). In contrast, B3LYP (red solid line) is “too red” compared to experiment. The three other methods, which are either DFT methods with enhanced (BMK) or asymptotically attenuated (CAM-B3LYP) exact exchange, or a correlated wave function method (CC2) perform somewhat better. The BMK (dashed red line) gives an absorption band position of the trans isomer
Figure 2: Calculated broadened vertical absorption spectra of the trans ((a), (c)) and cis ((b), (d)) isomers of 4-NO$_2$-AB and trans (e) and cis (f) isomers of AB in gas phase. Figures (a) and (b) are for 4-NO$_2$-AB with B3LYP-optimized geometries. Figures (c) and (d) are for 4-NO$_2$-AB with reoptimized geometries. Figures (e) and (f) are for AB calculated using B3LYP-optimized geometries. Sticks show oscillator strengths $f_i$. Gray vertical bars show the experimental wavelengths of maximal absorption. For 4-NO$_2$-AB the experimental value corresponds to chloroform solution (this work), and for AB to gas phase (Ref. 48). Here and elsewhere, the scale for absorbance is in arbitrary units (arb. u.), chosen such, however, that it reflects the computed oscillator strengths.
close to experiment. However, the absorption band of the cis isomer is red-shifted similar to the one obtained with B3LYP. The range-separated hybrid CAM-B3LYP (dashed black line) provides a better description of the lowest excited state of the cis isomer than both global hybrids (BMK and B3LYP). The absorption obtained with CAM-B3LYP for trans is similar to the one for the BMK functional when a B3LYP-optimized geometry is employed, and shifts to blue for the reoptimized geometry. The performance of the computationally expensive CC2 method is as follows. From Figure 2 it is seen that CC2 describes the absorption of the cis isomer better than all other methods considered here. For the trans isomer, the CC2 method is close to experiment and in good agreement with BMK and CAM-B3LYP.

From Figure 2 it is also seen that the geometry affects absorption to some extent, especially in case of HF, CAM-B3LYP and CC2. For HF $-24$ nm, for BMK $+3$ nm, for CAM-B3LYP $-10$ nm and for CC2 $+13$ nm shifts of the maximal absorption of trans-4-NO$_2$-AB are observed when using reoptimized geometries compared to values obtained with the B3LYP geometry. For the cis isomer of 4-NO$_2$-AB, the corresponding shifts are $-19$ nm (HF), $-4$ nm (BMK), $-16$ nm (CAM-B3LYP), and $-28$ nm (CC2), respectively.

In conclusion, CC2/aug-cc-pVDZ followed by CAM-B3LYP/6-31G* performs overall best when compared to experiment. In the context of this statement, however, two remarks are in order: (i) The comparison of calculated spectra with experimental ones is of limited value because we determined vertical excitation energies without vibrational fine structure, and also the influence of a solvent (for 4-NO$_2$-AB) was neglected. However, in Ref. 17 it has been shown, at least for the $\pi \rightarrow \pi^*$ transition in trans-AB, that vibronic effects lead to practically no shift of the maximum. Concerning solvent effects, test calculations on 4-NO$_2$-AB using the Polarizable Continuum Model (PCM)$^{52}$ for chloroform, gave a red shift of the $\pi \rightarrow \pi^*$ transition for the trans form of 24 nm on the TD-B3LYP/6-31G* level of theory, and practically no change of the $n \rightarrow \pi^*$ signal of the cis isomer. Since CC2, CAM-B3LYP and BMK show an absorption spectrum for trans that is blue-shifted between 8–26 nm compared to experiment (Figure 2 (a), (c)), a solvent shift will make the agreement between theory
and experiment probably even better. (ii) In earlier works it has also been shown that the
effect of better basis sets for the DFT-based methods is comparatively small. However, this
may not be necessarily so for CC2. In SI D, a basis set convergence test is performed for the
first three excited states of trans-4-NO₂-AB, using CC2/aug-cc-pVXZ, where X=D, T, Q,
and 5. It is seen there that the excitation energy varies only weakly with increasing
basis. In particular the $\pi \rightarrow \pi^*$ transition (the $S_0 \rightarrow S_3$ transition in SI D, see also below)
changes only moderately from 3.946 eV (314 nm) for CC2/aug-cc-pVDZ to 3.905 eV (317
nm) for CC2/aug-cc-pV5Z.

When calculating the lowest-energy singlet excited states of trans-4-NO₂-AB and
applying the HF and B3LYP methods, the lowest bright transition (the mentioned $\pi \rightarrow \pi^*$)
is the $S_0 \rightarrow S_2$ excitation. In contrast, for BMK, CAM-B3LYP and CC2 methods it is
the $S_0 \rightarrow S_3$ transition. This can be seen from Table 1, where the energies and oscillator
strengths for the lowest three transitions are listed. In case of the cis isomer the lowest
bright transition is $S_0 \rightarrow S_1$ according to all methods used here. For the data shown in
Table 1 geometries optimized at the B3LYP/6-31G* level of theory were used. B3LYP/6-
31G* geometries will also be adopted for all other cases below if not stated otherwise. We do
so despite the mentioned dependencies of spectra on geometry changes, in order to directly
disentangle differences in the methods to evaluate excited states. (In case of “dimer on
Penta”, the D3 correction was adopted in addition for geometry optimization as outlined
above.)

For trans-AB the lowest bright transition is $S_0 \rightarrow S_2$ (Table 1) and for cis-AB it is
$S_0 \rightarrow S_1$ for all approaches (again at the B3LYP/6-31G* geometries). It is seen that
compared to trans-AB the $\pi \rightarrow \pi^*$ signal of trans-4-NO₂-AB is red-shifted by between
0.15 and 0.29 eV, depending on the method. Note that the obtained excitation energies and
oscillator strengths for AB isomers using the CC2 method are similar to previously reported
ones, calculated at the CC2/aug-cc-pVTZ level of theory. 49

To visualize electronic excitations and assign their character, we carried out NTO analysis
Table 1: Excitation energies and oscillator strengths for the first three low-lying singlet excited states of the trans isomers of 4-NO$_2$-AB and AB at the B3LYP/6-31G* geometries. Data for the lowest bright transitions are shown in bold.

<table>
<thead>
<tr>
<th>Transition</th>
<th>HF$^a$</th>
<th>B3LYP$^a$</th>
<th>BMK$^a$</th>
<th>CAM-B3LYP$^a$</th>
<th>CC2$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0 \rightarrow S_1$</td>
<td>3.1064</td>
<td>2.3910</td>
<td>2.4706</td>
<td>2.6242</td>
<td>2.7339</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_2$</td>
<td>4.2783</td>
<td>3.4842</td>
<td>3.8117</td>
<td>3.8706</td>
<td>3.7889</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_3$</td>
<td>4.7747</td>
<td>3.6213</td>
<td>3.8496</td>
<td>3.9462</td>
<td>3.9462</td>
</tr>
</tbody>
</table>

$^a$with 6-31G* basis set; $^b$with aug-cc-pVDZ basis set

Table 2: Dominant NTO pairs and associated eigenvalues $\lambda$ for the first three transitions in trans-4-NO$_2$-AB at the B3LYP/6-31G* geometry

<table>
<thead>
<tr>
<th>Transition</th>
<th>$S_0 \rightarrow S_1$</th>
<th>$S_0 \rightarrow S_2$</th>
<th>$S_0 \rightarrow S_3$</th>
</tr>
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<tbody>
<tr>
<td>Hole</td>
<td>Particle</td>
<td>Hole</td>
<td>Particle</td>
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<td><img src="image1" alt="" /></td>
<td>1</td>
<td><img src="image2" alt="" /></td>
</tr>
<tr>
<td>B3LYP</td>
<td><img src="image4" alt="" /></td>
<td>1</td>
<td><img src="image5" alt="" /></td>
</tr>
<tr>
<td>BMK</td>
<td><img src="image7" alt="" /></td>
<td>1</td>
<td><img src="image8" alt="" /></td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td><img src="image10" alt="" /></td>
<td>1</td>
<td><img src="image11" alt="" /></td>
</tr>
<tr>
<td>CC2</td>
<td><img src="image13" alt="" /></td>
<td>1</td>
<td><img src="image14" alt="" /></td>
</tr>
</tbody>
</table>

as mentioned above. The dominant NTO pairs corresponding to the first three electronic transitions in trans-4-NO$_2$-AB are shown in Table 2. It is seen that the first dark transition ($S_0 \rightarrow S_1$) has $n \rightarrow \pi^*$ character, for all methods: A single hole-particle pair dominates ($\lambda = 1$), with the “hole” being of $n$- and the “particle” of $\pi^*$-character. The first bright
transition \((S_0 \rightarrow S_2}\) for HF and B3LYP, and \(S_0 \rightarrow S_3\) for BMK, CAM-B3LYP and CC2) has \(\pi \rightarrow \pi^*\) character, as already anticipated above. The second dark transition \((S_0 \rightarrow S_3\) for HF and B3LYP, and \(S_0 \rightarrow S_2\) for BMK, CAM-B3LYP and CC2) exhibits some charge transfer from the oxygen atoms of the NO\(_2\) group to the \(\pi^*\)-system of the molecule, mostly the adjacent phenyl ring. From the excitation energies listed in SI B, one finds that similar characteristics arise also for other methods. Again, excitation energies can vary substantially with methods. Also, no clear correlation between the energetic location of, \textit{e.g.}, the partial charge-transfer state and the amount of exact exchange contained in the respective method, could be identified.

### 3.2 Free dimer

#### 3.2.1 Absorption spectra and spectral shift

Next we studied the isolated \textit{trans} dimer, however in a geometry reflecting the Si cluster, \textit{cf.} Figure 1 (g). The absorption spectra of the dimer (blue lines and sticks) along with the spectra of its monomeric components (red lines and sticks) are presented in Figure 3, again for the five selected model chemistries (HF, B3LYP, BMK, CAM-B3LYP, CC2). Excitation energies obtained with all 16 methods are shown in SI B.

First, we note that the monomers in the dimer have slightly different geometries, which are, moreover, slightly nonplanar, owing to the construction protocol. Therefore the monomers have slightly different absorption spectra from each other and compared to the planar monomer discussed in Section 3.1. The spectra of the two monomeric components of the dimer, as well as a corresponding NTO analysis, are discussed in some detail in SI E. There it is shown that individual excitation energies of the two monomers differ by 0.01–0.03 eV depending on state and method. Also the NTO pairs are similar but not identical to the ideally flat monomer.

More importantly, from Figure 3 one can see that the absorption spectrum of the dimer is different from those of the isolated monomers. There is also a clear dependence on methods.
Specifically, the global hybrids B3LYP (Figure 3 (b)) and BMK (Figure 3 (c)) predict a pronounced blue shift of the absorption maximum (of broadened spectra) by about 18 nm and 15 nm, respectively. The TD-HF method (Figure 3 (a)) predicts a much lower blue shift of about 5.5 nm. The range-separated CAM-B3LYP functional (Figure 3 (d)) results also in only a small blue shift, of about 3.5 nm. CC2, in contrast to all other methods, gives a small red shift of about 3 nm.

At this point we should say that it is known that local, semilocal and hybrid functionals with only a small fraction of exact exchange tend to produce spurious low energy charge-transfer excited states (or create an admixture of charge-transfer excitations to local ones) in molecular aggregates, large molecules and clusters and are not appropriate to describe excited states of dimers properly.\textsuperscript{19,20,55–59} Thus, the B3LYP and BMK functionals show most probably qualitatively wrong picture of dimer absorption.

The more suitable methods (CC2, CAM-B3LYP, HF) predict only a small shift with its sign being in fact disputable. The shift of the first bright excited state when going from the free monomer to the free dimer as obtained with the whole set of methods (B3LYP and X3LYP are not included due to completely wrong behaviour), is shown in SI F, Figure S3 (a). From there it is seen that the discussed shift (either blue (positive value) or red (negative value)) is in the order of about 0.05 eV.

From simple exciton theory without vdw shift \textit{D} (Section 1, in particular Eqs. (2) and (5)), we expect always a blue shift at least for a dimer consisting of two identical monomers oriented side-by-side with transition dipole moments being parallel. In this context we should remark that for a “totally symmetric” dimer consisting of two identical, fully planar monomers with molecular planes on top of each other, CC2 gives, at an intermolecular separation of 3.6 Å, also a small blue shift (of about 4 nm). This is demonstrated in SI G. In any case, the overall shift within a dimer at a geometry similar to the adsorbed state is small according to the more suitable methods. It will be argued shortly, that this does not automatically imply small exciton splittings at the intermolecular distances considered here.
Rather, the vdW shift $D$ plays also an important role.

Figure 3: Broadened vertical absorption spectra of the free dimer and its monomeric components calculated at various levels of theory: TD-HF/6-31G* (a), TD-B3LYP/6-31G* (b), TD-BMK/6-31G* (c), TD-CAM-B3LYP/6-31G* (d), and CC2/aug-cc-pVDZ (e). Sticks show oscillator strengths $f_i$. The free dimer geometry was obtained as described in Section 2.4 from a “dimer on Penta” cluster model, optimized at the B3LYP+D3/6-31G* level of theory.
The excitation energies and corresponding oscillator strengths for the first twelve transitions of the dimer are listed in Table 3. From the table it is seen that HF, CAM-B3LYP and CC2 give one strong transition \((f > 1)\), whereas B3LYP and BMK produce a number of transitions with non-vanishing but small \((f < 1)\) oscillator strengths of comparable size (see also Figure 3).

Table 3: Excitation energies and oscillator strengths for the first twelve low-lying singlet excited states of the trans-4-NO\(_2\)-AB dimer (the distance between monomeric centers of coordinates is \(d \approx 3.6\ \text{Å}\)). Data for the strongest bright transitions are shown in bold. The character of the first excited states (mostly exciton-split \(n \rightarrow \pi^*\), \(\pi \rightarrow \pi^*\), and charge-transfer states) is described in the text and graphically represented in SI B

<table>
<thead>
<tr>
<th>Transition</th>
<th>HF(^a)</th>
<th>B3LYP(^a)</th>
<th>BMK(^a)</th>
<th>CAM-B3LYP(^a)</th>
<th>CC2(^b)</th>
</tr>
</thead>
<tbody>
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<td>(S_0 \rightarrow S_1)</td>
<td>3.1034 0.0015</td>
<td>2.3850 0.0004</td>
<td>2.4641 0.0004</td>
<td>2.6198 0.0005</td>
<td>2.6912 0.0007</td>
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<tr>
<td>(S_0 \rightarrow S_2)</td>
<td>3.1111 0.0001</td>
<td>2.4097 0.0010</td>
<td>2.4748 0.0007</td>
<td>2.6288 0.0008</td>
<td>2.7080 0.0012</td>
</tr>
<tr>
<td>(S_0 \rightarrow S_3)</td>
<td>4.0595 0.0069</td>
<td>2.9220 0.0104</td>
<td>3.4959 0.0140</td>
<td>3.6068 0.0083</td>
<td>3.5766 0.0053</td>
</tr>
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<td>(S_0 \rightarrow S_4)</td>
<td>4.3460 1.5938</td>
<td>2.9845 0.0090</td>
<td>3.7506 0.5436</td>
<td>3.8531 0.0005</td>
<td>3.7487 0.0026</td>
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<td>(S_0 \rightarrow S_5)</td>
<td>4.7525 0.0006</td>
<td>3.0787 0.0207</td>
<td>3.7914 0.1305</td>
<td>3.8782 0.2221</td>
<td>3.7779 0.0364</td>
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<td>3.1409 0.1073</td>
<td>3.8268 0.0364</td>
<td>3.9204 1.0818</td>
<td>3.8912 1.4266</td>
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<td>5.0940 0.0001</td>
<td>3.5501 0.0429</td>
<td>4.0723 0.0057</td>
<td>4.3255 0.0091</td>
<td>4.1025 0.0002</td>
</tr>
<tr>
<td>(S_0 \rightarrow S_9)</td>
<td>5.2560 0.0025</td>
<td>3.5968 0.1675</td>
<td>4.1317 0.6338</td>
<td>4.3449 0.0101</td>
<td>4.1662 0.0195</td>
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<tr>
<td>(S_0 \rightarrow S_{10})</td>
<td>5.3326 0.0416</td>
<td>3.6071 0.0001</td>
<td>4.2210 0.0143</td>
<td>4.3603 0.1277</td>
<td>4.1976 0.0075</td>
</tr>
<tr>
<td>(S_0 \rightarrow S_{11})</td>
<td>5.3431 0.0016</td>
<td>3.6356 0.3641</td>
<td>4.2397 0.0030</td>
<td>4.4089 0.0157</td>
<td>4.2435 0.0083</td>
</tr>
<tr>
<td>(S_0 \rightarrow S_{12})</td>
<td>5.4036 0.0401</td>
<td>3.6770 0.5778</td>
<td>4.2492 0.0090</td>
<td>4.4245 0.0025</td>
<td>4.3102 0.1650</td>
</tr>
</tbody>
</table>

\(^a\)with 6-31G* basis set; \(^b\)with aug-cc-pVDZ basis set

The simple expectation of \(f_+ (\text{dimer}) = 2f (\text{monomer})\) as anticipated from Eq. (3) for a \(|\psi_+\rangle\) single-exciton state is thus not at all fulfilled for any of the first excited states of the dimer when calculated with B3LYP and BMK: In fact, in the dimer all states discussed have lower oscillator strengths than in the monomer according to Table 1. On the other hand, in particular HF and CC2 show clearly enhanced oscillator strengths relative to the monomer of Table 1 (by factors of 1.68 for HF and 1.36 for CC2) for one state. CAM-B3LYP behaves in between, with an enhancement factor of 1.11. We should note that other global hybrids (BHandH, BHandHLYP, M062-X and M06-HF), with bigger amount of exact exchange in comparison with BMK, produce only one strong \((f > 1)\) bright transition for the dimer; the oscillator strength for this transition is bigger than the oscillator strength for the bright
transition in the monomer.

### 3.2.2 Assignment of excited states and exciton splitting

To get insight into the character of the lowest excited states in the dimer we performed an NTO analysis. Table 4 gives the dominant NTO pairs for the first six transitions, obtained with B3LYP and CC2, respectively. The same information, however for the five selected methods is given in SI H.

From these tables one can see that the first two transitions are described similarly by all five methods. The $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions are $n \rightarrow \pi^*$ excitations, mainly localized on monomers. (In an ideally symmetric dimer, also delocalized $+ \text{ and } -$ linear combinations would be expected. That is the case for the “totally symmetric” dimer (see SI G, Table S6).) The exciton splitting between these states, which are near-dark, is small, in the order of 8–25 meV.

From Table 4 we see that for CC2, transitions $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_6$ correspond to exciton-split $\pi \rightarrow \pi^*$ excitations. More specifically, $S_0 \rightarrow S_3$ is the transition to the lower state $|\psi_-\rangle$, and $S_0 \rightarrow S_6$ to the higher state $|\psi_+\rangle$ of Section 1. The splitting and its method and distance dependence will be analyzed in more detail shortly. Note that $S_0 \rightarrow S_3$ transition has a much smaller oscillator strength (0.005) than the $S_0 \rightarrow S_6$ transition (1.43), as it should. Finally, for CC2, $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$ transitions are found to be localized on the monomers, exhibiting some intramonomeric charge transfer. Their oscillator strengths are small.

As shown in SI H, CAM-B3LYP behaves very similar to CC2 in qualitative terms. HF and BMK reveal the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ transitions as delocalized over the dimer. $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_6$ transitions for HF and BMK are mostly localized on monomers, with some charge transfer from oxygen atoms to the $\pi^*$-system of the molecule.
Table 4: Dominant B3LYP and CC2 NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_1$ to $S_0 \rightarrow S_6$ transitions in the free trans-4-NO$_2$-AB dimer

<table>
<thead>
<tr>
<th></th>
<th>Hole $S_0 \rightarrow S_1$</th>
<th>Particle $S_0 \rightarrow S_1$</th>
<th>Hole $S_0 \rightarrow S_2$</th>
<th>Particle $S_0 \rightarrow S_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>CC2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.88</td>
<td>0.89</td>
<td>0.84</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_3$</td>
<td>$S_0 \rightarrow S_3$</td>
<td>$S_0 \rightarrow S_4$</td>
<td>$S_0 \rightarrow S_4$</td>
</tr>
<tr>
<td>B3LYP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.96</td>
<td>0.94</td>
<td>0.84</td>
<td>0.99</td>
</tr>
<tr>
<td>CC2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.84</td>
<td>0.99</td>
<td>0.96</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_5$</td>
<td>$S_0 \rightarrow S_5$</td>
<td>$S_0 \rightarrow S_6$</td>
<td>$S_0 \rightarrow S_6$</td>
</tr>
<tr>
<td>B3LYP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.96</td>
<td>0.86</td>
<td>0.98</td>
<td>0.85</td>
</tr>
<tr>
<td>CC2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.98</td>
<td>0.85</td>
<td>0.98</td>
<td>0.85</td>
</tr>
</tbody>
</table>
According to Table 4 B3LYP, in contrast to other methods, leads to transitions exhibiting inter-monomeric charge transfer ($S_0 \rightarrow S_3$, $S_0 \rightarrow S_4$, $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_6$). We conclude from the NTO analysis and also from the fact that the oscillator strengths of the bright transitions in the dimer do in no way reflect expectations from the exciton model (see above), that B3LYP does not give a realistic description of excited states for the dimer, at a distance of about 3.6 Å as realized in Figure 1 (g). As noted earlier BMK has more exact exchange than B3LYP, which seems to “heal” some shortcomings of B3LYP. Thus, BMK behaves better than B3LYP, but not as good as the other three methods (HF, CAM-B3LYP, CC2).

The exciton splitting of the lowest bright ($\pi \rightarrow \pi^*$) transitions for the trans-4-NO$_2$-AB dimer is highlighted in Figure 4. The figure summarizes the results for all selected methods except for B3LYP, for which the splitting is not even qualitatively correct. The horizontal bars give as “m0” the state-energies (relative to the ground state) for the free trans monomer in its optimized geometry, “m1” and “m2” are those of the individual monomers in a geometry corresponding to the dimer, and “d” is the dimer result. Red bars are $\pi \rightarrow \pi^*$ excitations, blue bars denote intramonomeric charge-transfer excitations. (For BMK and CAM-B3LYP, for “m1” and “m2” two partially $\pi \rightarrow \pi^*$ transitions are found with reduced oscillator strengths, the corresponding states are denoted as black bars.) The green numbers aside the bars are state labels, e.g., 3 means $S_3$. The black numbers above or below the bars are oscillator strengths.

For CC2 (Figure 4 (d)), we see that states $S_3$ and $S_6$ of the dimer correspond to the exciton-split dark and bright states just mentioned, with other states $S_4$ and $S_5$ in between. (We also see that monomers 1 and 2 (in the dimer geometry) behave only slightly different compared to the ideally flat monomer “m0”. ) One further recognizes the exciton splitting of the $\pi \rightarrow \pi^*$ excited states ($S_4$ of monomers 1 and 2), i.e., $2\Delta^{CC2} = E^{CC2}_6 - E^{CC2}_3 = 0.31 \text{ eV}$. And we also observe that the most intense $\pi \rightarrow \pi^*$ transition in the dimer ($S_0 \rightarrow S_6$) is red-shifted compared to the monomer ($S_0 \rightarrow S_3$) transitions. This was already seen in Figure 3. This red shift is a result of the anticipated, strong downshift of the dimer states due to a
Figure 4: The splitting of excited states in the dimer as obtained by TD-HF/6-31G* (a), TD-BMK/6-31G* (b), TD-CAM-B3LYP/6-31G* (c), and CC2/aug-cc-pVDZ (d). The colours of bars correspond to different types of NTO pairs (see text). Green numbers are the state labels, black numbers are oscillator strengths. Further, “m0” denotes the free optimized monomer, “m1” and “m2” the monomers within the free dimer, and “d” the dimer.

The large vdW stabilization \( D \). The latter can be roughly estimated from the center of exciton-split states of the dimer. According to Figure 4 (d), for CC2 the center of the exciton-split states \( S_6 \) and \( S_3 \) is at around 3.75 eV. Compared to the monomeric-state energies of about 3.95 eV, therefore, \( D \approx 0.2 \text{ eV} \). According to the simple exciton theory, Eq. (7), the bright state \( |\psi_+\rangle \) should be shifted by \( -D + \Delta \approx -0.04 \text{ eV}, i.e., \) slightly to the red. We note that a counterpoise calculation for both monomers, i.e., employment of all basis functions used for the dimer calculation leads to negligible changes in excitation energies. Hence, the vdW shift is clearly not an artefact due to a basis set superposition error.

For HF (Figure 4 (a)), the vdW shift is much smaller (about 0.07 eV), and also only \( \pi \rightarrow \pi^* \) excitations are found in the relevant energy region. Here, the exciton-split, bright state \( |\psi_+\rangle (= S_4) \) is blue-shifted, by an amount of about 0.07 eV with respect to the monomer bright state. For BMK and CAM-B3LYP (Figures 4 (b) and 4 (c)) the situation is a bit more complicated, with the general observation, however, that vdW interaction is not negligible there either and an exciton splitting can be determined unambiguously.

For the four cases shown, the exciton splitting \( 2\Delta \) which corresponds to
the bright monomeric transitions is found to be 
\[ 2\Delta_{HF} = \Delta_{HF}^4 - \Delta_{HF}^3 = 0.29 \text{ eV}, \]
\[ 2\Delta_{CC2} = \Delta_{CC2}^6 - \Delta_{CC2}^3 = 0.31 \text{ eV} \text{ (vide supra)}, \]
\[ 2\Delta_{BMK} = \Delta_{BMK}^4 - \Delta_{BMK}^3 = 0.25 \text{ eV}, \]
and \[ 2\Delta_{CAM-B3LYP} = \Delta_{CAM-B3LYP}^6 - \Delta_{CAM-B3LYP}^3 = 0.31 \text{ eV}. \]
Thus, HF, CC2 and CAM-B3LYP give approximately the same value of \( 2\Delta \approx 0.3 \text{ eV} \), whereas BMK leads to somewhat smaller splitting of about 0.25 eV. The exciton splitting calculated with all used methods is shown in SI F, Figure S3 (d). It is seen there that the exciton splitting is indeed fairly method-independent. In contrast, the vdW shift \( D \) depends on the method: A large red shift for the correlated CC2 method, sizable shifts for BMK and CAM-B3LYP, and a small red shift for HF.

### 3.2.3 Distance dependence

Next, we tested the dependence of the exciton splitting on increasing distance between the monomers. Specifically, as a distance parameter the separation of the centers of the monomeric coordinates, \( d \), at the same, constant orientation of monomers with respect to each other as in Figure 1 (g) was chosen. In the initial dimer geometry of Figure 1 (g), \( d \approx 3.6 \text{ Å} \). In our tests we chose the \( d \) values to be 6.0 and 10.0 Å. Also, we performed calculations for a large distance of 100 Å to compare the transitions with monomeric limit cases. The excitation energies and oscillator strengths for the lowest transitions of these dimer models are collected in Table 5.

From this table we note that the B3LYP absorption picture for the dimers with \( d = 6 \) and 10 Å differs much from the case of small separation \( d \approx 3.6 \text{ Å} \) (compare with Table 3). Now, in contrast to previously, one strong transition with an oscillator strength \( f > 1 \) is found, namely \( S_0 \rightarrow S_8 \) (\( f_8 = 1.38 \) for \( d = 6 \text{ Å} \) and \( f_8 = 1.49 \) for \( d = 10 \text{ Å} \)). Based on analysis of NTOs it is possible to find a pair of delocalized transitions, \( \{S_0 \rightarrow S_8, S_0 \rightarrow S_7\} \), for \( d = 6 \text{ Å} \), corresponding to transitions into the \( |\psi_+\rangle \) and \( |\psi_-\rangle \) single-exciton states for \( \pi \rightarrow \pi^* \) excitations. The NTO analysis for three different methods (HF, B3LYP, CC2) and several transitions at \( d = 6 \text{ Å} \) is shown in SI I. For B3LYP, the lower exciton-split state \( S_7 \)
Table 5: Excitation energies and oscillator strengths for the first nine low-lying singlet excited states of the trans-4-NO$_2$-AB dimer at different monomer separations $d$. Data for the lowest bright transitions are shown in bold.

<table>
<thead>
<tr>
<th>Transition</th>
<th>HF$^a$</th>
<th>B3LYP$^a$</th>
<th>BMK$^a$</th>
<th>CAM-B3LYP$^a$</th>
<th>CC2$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0 \rightarrow S_1$</td>
<td>3.0948 0.0013 2.3899 0.0003</td>
<td>2.4668 0.0002 2.6203 0.0006</td>
<td>2.7257 0.0004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_2$</td>
<td>3.1055 0.0003 2.3965 0.0015</td>
<td>2.4672 0.0010 2.6204 0.0009</td>
<td>2.7303 0.0016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_3$</td>
<td>4.2005 0.0247 3.1456 0.0000</td>
<td>3.7640 0.0193 3.8103 0.0176</td>
<td>3.7804 0.0164</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_4$</td>
<td><strong>4.3240</strong> <strong>1.7135</strong> 3.2565 0.0000</td>
<td><strong>3.9196</strong> <strong>1.7036</strong> 3.9620 0.0058</td>
<td><strong>3.9940</strong> <strong>1.8810</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_5$</td>
<td>4.7737 0.0013 3.2841 0.0000</td>
<td>3.8373 0.0409 3.8960 0.0585</td>
<td>3.8746 0.0159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_6$</td>
<td>4.7965 0.0009 3.3608 0.0001</td>
<td><strong>3.9196</strong> <strong>1.7036</strong> 3.9620 0.0058</td>
<td><strong>3.9940</strong> <strong>1.8810</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_7$</td>
<td><strong>5.0835</strong> <strong>0.0003</strong> 3.4153 0.0158</td>
<td>4.2390 0.0000 4.3466 0.0002</td>
<td>4.2583 0.0055</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_8$</td>
<td>5.0911 0.0002 <strong>3.5465</strong> <strong>1.3824</strong> 3.6187 0.0476</td>
<td>4.2699 0.0002 4.3550 0.0002</td>
<td>4.2635 0.0024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_9$</td>
<td>5.3138 0.0015 3.6187 0.0476</td>
<td>4.2784 0.0002 4.4711 0.0105</td>
<td>4.3683 0.0030</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$with 6-31G* basis set; $^b$with aug-cc-pVDZ basis set

At $d = 10$ Å these artificial states are those from third to fifth and the seventh one.

is near-dark, as expected. Hence, at the larger distance of 6 Å, also B3LYP performs well with respect to treating exciton splittings. An exciton splitting can clearly be identified, in this case of $2\Delta_{B3LYP}(6 \text{ Å}) = E_8^{B3LYP}(6 \text{ Å}) - E_7^{B3LYP}(6 \text{ Å}) = 0.13$ eV. Similarly, for $d = 10$ Å we find transitions $\{S_0 \rightarrow S_8, S_0 \rightarrow S_6\}$ forming an exciton-split pair and determine the splitting as $2\Delta_{B3LYP}(10 \text{ Å}) = E_8^{B3LYP}(10 \text{ Å}) - E_6^{B3LYP}(10 \text{ Å}) = 0.05$ eV. The states from the third to the sixth at $d = 6$ Å are the spurious inter-monomeric charge-transfer states.
The calculated exciton splittings, obtained by analysis of oscillator strengths and dominant NTO pairs of the lowest transitions in dimers at different monomeric separations are summarized for the five selected methods in Table 6 along with corresponding state energy differences. The entry for $d \approx 3.6 \text{ Å}$ for B3LYP is left empty in the table, because we were not able to determine the splitting as outlined above by identifying a suitable pair of delocalized $\pi \rightarrow \pi^*$ excited states. The key to assigning relevant states in all cases, was the NTO analysis as shown in SI I (for $d = 6 \text{ Å}$). We see that the exciton splitting decreases with increasing separation in accord with expectation from the PDM.

Table 6: Exciton splitting $2\Delta$ (eV) corresponding to the $\pi \rightarrow \pi^*$ transitions in dependence on monomer separation $d$ as predicted by different methods. In parentheses the corresponding state energy differences are presented:

<table>
<thead>
<tr>
<th>Method</th>
<th>$d \approx 3.6 \text{ Å}$</th>
<th>$d = 6 \text{ Å}$</th>
<th>$d = 10 \text{ Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF*</td>
<td>0.2865 ($E_4 - E_3$)</td>
<td>0.1235 ($E_4 - E_3$)</td>
<td>0.0499 ($E_4 - E_3$)</td>
</tr>
<tr>
<td>B3LYP*</td>
<td>—</td>
<td>0.1312 ($E_8 - E_7$)</td>
<td>0.0502 ($E_8 - E_6$)</td>
</tr>
<tr>
<td>BMK*</td>
<td>0.2547 ($E_4 - E_3$)</td>
<td>0.1556 ($E_6 - E_4$)</td>
<td>0.0848 ($E_6 - E_3$)</td>
</tr>
<tr>
<td>CAM-B3LYP*</td>
<td>0.3136 ($E_6 - E_3$)</td>
<td>0.1517 ($E_6 - E_4$)</td>
<td>0.0819 ($E_6 - E_3$)</td>
</tr>
<tr>
<td>CC2b</td>
<td>0.3146 ($E_6 - E_3$)</td>
<td>0.1194 ($E_6 - E_5$)</td>
<td>0.0467 ($E_6 - E_5$)</td>
</tr>
</tbody>
</table>

*a with 6-31G* basis set; *b with aug-cc-pVDZ basis set

Finally, at $d = 100 \text{ Å}$ the first six excited states resemble the excited states of monomers 1 and 2 for all selected methods, except B3LYP, which produces inter-monomeric charge-transfer states even at this large separation: $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_6$ transitions (compare Table 5 and SI E, Table S2). B3LYP $S_0 \rightarrow S_7$ and $S_0 \rightarrow S_8$ transitions correspond to $S_0 \rightarrow S_3$ monomeric transitions, instead.

3.3 Monomer and dimer attached to a silicon nanocluster

In order to study effects of adsorption (here modelled by attaching the switches to a nanocluster), monomer and dimer in configurations shown in Figure 1 (d) (“monomer on Penta”) and Figure 1 (f) (“dimer on Penta”) were considered.
3.3.1 Monomer on silicon nanocluster

The spectra for the “monomer on Penta” model calculated with the selected methods are shown in Figure 5 (red lines). The spectra for the isolated monomer are presented for a comparison (black lines). Excitation energies and oscillator strengths for the lowest three singlet transitions are tabulated in Table 7. Excitation energies obtained with all used methods are shown in SI J.

All the applied methods show a clear red shift of the lowest $\pi \rightarrow \pi^*$ transition upon the attachment to the Penta cluster. The value of this red shift varies depending on the method used. When considering the broadened spectra of Figure 5, the CC2 method (Figure 5 (e)) provides the largest red shift of the absorption maximum of about 37 nm, or 0.42 eV. CAM-B3LYP (Figure 5 (d)) leads to a 18 nm shift and HF (Figure 5 (a)) to a 12 nm one. The global hybrids B3LYP (Figure 5 (b)) and BMK (Figure 5 (c)) give values of 28 and 27 nm, respectively. A special feature appears for the B3LYP method, where two bright transitions are observed, both of them red-shifted with respect to the monomeric $\pi \rightarrow \pi^*$ transition (Figure 5 (b) and Table 7). This is likely to be an artefact of B3LYP again, similar to those observed above for the free dimer at short distances.

The red shift upon adsorption is found also with all other methods as shown in SI F, Figure S3 (b). As another clear effect of adsorption, we see an enhanced intensity of absorption relative to the isolated molecule.

The origin of the red shift is not easy to analyze. It is found that the brightest transition is dominated by a HOMO ($\pi$) $\rightarrow$ LUMO ($\pi^*$) excitation (CAM-B3LYP, free monomer), and that the latter is only slightly affected by the Si cluster while the former interacts with occupied orbitals of the cluster. The HOMO hybridizes with Si molecular orbitals (in an antibonding manner), shifting upward in energy which results in a smaller HOMO–LUMO gap. On the CAM-B3LYP/6-31G* level of theory, for example, the gap reduces from 6.18 eV for the free molecule, to 5.67 eV.
Figure 5: The broadened vertical absorption spectra of “monomer on Penta” and isolated monomer calculated at various levels of theory: TD-HF/6-31G* (a), TD-B3LYP/6-31G* (b), TD-BMK/6-31G* (c), TD-CAM-B3LYP/6-31G* (d), and CC2/aug-cc-pVDZ (e). Sticks show oscillator strengths $f_i$. 
Table 7: Excitation energies and oscillator strengths for the first three low-lying singlet excited states of the “monomer on Penta” model. Data for the bright transitions are shown in bold.

<table>
<thead>
<tr>
<th>Transition</th>
<th>HF$^a$</th>
<th>B3LYP$^a$</th>
<th>BMK$^a$</th>
<th>CAM-B3LYP$^a$</th>
<th>CC2$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0 \rightarrow S_1$</td>
<td>3.0836 0.0000</td>
<td>2.3610 0.0000</td>
<td>2.4403 0.0000</td>
<td>2.5985 0.0000</td>
<td>2.6924 0.0000</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_2$</td>
<td>4.1091 1.5314</td>
<td>2.9876 0.3667</td>
<td>3.5449 1.3309</td>
<td>3.6878 1.5368</td>
<td>3.5294 1.2357</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_3$</td>
<td>4.7699 0.0000</td>
<td>3.2745 0.7469</td>
<td>3.8035 0.0000</td>
<td>3.8662 0.0000</td>
<td>3.7838 0.0000</td>
</tr>
</tbody>
</table>

$^a$with 6-31G* basis set; $^b$with aug-cc-pVDZ basis set.

For further clarity we summarize in Table 8 the excitation energies, wavelengths and oscillator strengths for the brightest transitions of the isolated monomer and “monomer on Penta” models. Clear red-shifts and intensity enhancements are seen for the HF, BMK, CAM-B3LYP and CC2 methods, while for B3LYP the intensity gain becomes visible only when all bright states are accounted for in a broadened spectrum.

Table 8: Excitation energies, wavelengths and oscillator strengths for the brightest, low-lying singlet excited states of various models and methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Free Monomer</th>
<th>Monomer on Penta</th>
<th>Free Dimer</th>
<th>Dimer on Penta</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF$^a$</td>
<td>E (eV)</td>
<td>E (eV)</td>
<td>E (eV)</td>
<td>E (eV)</td>
</tr>
<tr>
<td></td>
<td>λ (nm)</td>
<td>f</td>
<td>λ (nm)</td>
<td>f</td>
</tr>
<tr>
<td>B3LYP$^{a,c}$</td>
<td>E (eV)</td>
<td>4.2783</td>
<td>4.1091</td>
<td>4.3460</td>
</tr>
<tr>
<td></td>
<td>λ (nm)</td>
<td>290</td>
<td>302</td>
<td>285</td>
</tr>
<tr>
<td></td>
<td>f</td>
<td>0.9483</td>
<td>1.5314</td>
<td>1.5938</td>
</tr>
<tr>
<td>BMK$^{a,c}$</td>
<td>E (eV)</td>
<td>3.8496</td>
<td>3.5449</td>
<td>3.7506/4.1317</td>
</tr>
<tr>
<td></td>
<td>λ (nm)</td>
<td>322</td>
<td>350</td>
<td>331/300</td>
</tr>
<tr>
<td></td>
<td>f</td>
<td>0.9834</td>
<td>1.3509</td>
<td>0.5436/0.6338</td>
</tr>
<tr>
<td>CAM-B3LYP$^a$</td>
<td>E (eV)</td>
<td>3.8900</td>
<td>3.6878</td>
<td>3.9204</td>
</tr>
<tr>
<td></td>
<td>λ (nm)</td>
<td>318</td>
<td>336</td>
<td>316</td>
</tr>
<tr>
<td></td>
<td>f</td>
<td>0.9700</td>
<td>1.5368</td>
<td>1.0818</td>
</tr>
<tr>
<td>CC2$^b$</td>
<td>E (eV)</td>
<td>3.9462</td>
<td>3.5294</td>
<td>3.8912</td>
</tr>
<tr>
<td></td>
<td>λ (nm)</td>
<td>314</td>
<td>351</td>
<td>319</td>
</tr>
<tr>
<td></td>
<td>f</td>
<td>1.0501</td>
<td>1.2357</td>
<td>1.4266</td>
</tr>
</tbody>
</table>

$^a$with 6-31G* basis set; $^b$with aug-cc-pVDZ basis set; $^c$for B3LYP and BMK in certain cases several bright states occur (see text).

To get detailed insight into the character of the lowest electronic transitions in the 4-NO$_2$-AB–Penta composite, we again performed an NTO analysis. In Table 9 selected examples for B3LYP and CC2 are shown, while a more detailed analysis for the five selected methods and the first three excited states is given in SI K. From Table 9 and SI K, it is seen that B3LYP...
results in red-shifted bright excited states \( (S_0 \rightarrow S_2 \text{ and } S_0 \rightarrow S_3) \) with some charge transfer from the cluster to the molecule upon excitation. All other of the five selected methods favour a more localized picture, with the excitation being almost exclusively localized at the 4-nitroazobenzene molecule – Table 9 gives the example for CC2. This is particularly so for the \( S_0 \rightarrow S_2 \) transition, which corresponds to the bright \( \pi \rightarrow \pi^* \) transition. In passing we note that for BMK, CAM-B3LYP and CC2, a reordering in energy of the \( S_0 \rightarrow S_2 \) and \( S_0 \rightarrow S_3 \) transitions takes place in comparison to the isolated monomer. For other functionals, such as M06-HF, LC-\( \omega \)PBE, M11, and \( \omega \)B97, the order of states does not change upon attachment to the Si cluster (compare Figures S1 and S4). We also note that intramonomeric charge-transfer states are not sensitive to adsorption as can be seen from comparing Figures S1 and S4.

Table 9: Dominant NTO pairs and associated eigenvalues \( \lambda \) for the \( S_0 \rightarrow S_2 \) and \( S_0 \rightarrow S_3 \) transitions in the “monomer on Penta” model for B3LYP and CC2

<table>
<thead>
<tr>
<th></th>
<th>( S_0 \rightarrow S_2 )</th>
<th>( S_0 \rightarrow S_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hole</td>
<td>Particle</td>
</tr>
<tr>
<td>B3LYP</td>
<td>( \lambda )</td>
<td>1</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>1</td>
<td>0.97</td>
</tr>
<tr>
<td>CC2</td>
<td>( \lambda )</td>
<td>1</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>0.97</td>
<td>1</td>
</tr>
</tbody>
</table>
3.3.2 Dimer on silicon nanocluster

Finally, the spectra for the “dimer on Penta” model calculated with the five selected methods are shown in Figure 6 (blue lines). The spectra for the “monomer on Penta” are presented for comparison (red lines). Here we should note that calculation of the CC2 spectrum for the “dimer on Penta” model was not done by now because of its large computational needs. So, in this subsection we show results for the selected methods except for CC2. Excitation energies and oscillator strengths for the lowest twelve singlet transitions are tabulated in Table 10. Excitation energies obtained with all methods are shown in SI J.

The general picture is consistent with our previous observations, showing the two main effects: (i) Relative to the isolated dimer, there is a strong red shift upon “adsorption”; (ii) relative to the “monomer on Penta”, there is typically only a small shift for methods which are suitable for dimers, i.e., HF and CAM-B3LYP. It is seen that dimerization causes typically a small blue shift (for HF and CAM-B3LYP, cf. Figure 6 (a), (d)). See also the results for this shift obtained with other methods in SI F, Figure S3 (c).

To facilitate quantitative analysis, we refer to Table 8 again, where not only the brightest states of the free monomer and “monomer on Penta” are compared, but also the free dimer and the “dimer on Penta” models. There it is seen that for instance for CAM-B3LYP, the most intense transition for the free monomer is at 318 nm. Upon dimerization (free dimer), there is a very small blue shift to 316 nm. The “monomer on Penta” absorbs maximally at 336 nm, i.e., there is the mentioned strong red shift of above, by 18 nm. The “dimer on Penta” has its strongest transitions at 334 nm, i.e., there is the same red shift (of 18 nm) by the surface also for the dimerized system. For HF, the behaviour is qualitatively and also semi-quantitatively the same. The global hybrids B3LYP and BMK show an overall more complicated (most probably, wrong) behaviour again, due to the occurrence of several excited states with sizable oscillator strengths.
Figure 6: The broadened vertical absorption spectra of the “dimer on Penta” and “monomer on Penta” models calculated at various levels of theory: TD-HF/6-31G* (a), TD-B3LYP/6-31G* (b), TD-BMK/6-31G* (c), TD-CAM-B3LYP/6-31G* (d). Sticks show oscillator strengths $f_i$. 

4. Reprints
Table 10: Excitation energies and oscillator strengths for the first twelve low-lying singlet excited states of the “dimer on Penta” model. Data for the strongest bright transitions are shown in bold.

<table>
<thead>
<tr>
<th>Transition</th>
<th>HF&lt;sup&gt;a&lt;/sup&gt; E (eV)</th>
<th>f</th>
<th>B3LYP&lt;sup&gt;a&lt;/sup&gt; E (eV)</th>
<th>f</th>
<th>BMK&lt;sup&gt;a&lt;/sup&gt; E (eV)</th>
<th>f</th>
<th>CAM-B3LYP&lt;sup&gt;a&lt;/sup&gt; E (eV)</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;1&lt;/sub&gt;</td>
<td>3.0874</td>
<td>0.0023</td>
<td>2.3605</td>
<td>0.0005</td>
<td>2.4412</td>
<td>0.0006</td>
<td>2.6013</td>
<td>0.0008</td>
</tr>
<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.0962</td>
<td>0.0001</td>
<td>2.3833</td>
<td>0.0014</td>
<td>2.4504</td>
<td>0.0009</td>
<td>2.6092</td>
<td>0.0012</td>
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<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.9109</td>
<td>0.0176</td>
<td>2.7134</td>
<td>0.0323</td>
<td>3.2372</td>
<td>0.0312</td>
<td>3.4194</td>
<td>0.0209</td>
</tr>
<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;4&lt;/sub&gt;</td>
<td>4.1858</td>
<td>2.5686</td>
<td>2.8869</td>
<td>0.2999</td>
<td>3.5008</td>
<td>1.2343</td>
<td>3.7172</td>
<td>2.1012</td>
</tr>
<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;5&lt;/sub&gt;</td>
<td>4.7437</td>
<td>0.0003</td>
<td>2.9292</td>
<td>0.0166</td>
<td>3.7703</td>
<td>0.0742</td>
<td>3.8450</td>
<td>0.0028</td>
</tr>
<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;6&lt;/sub&gt;</td>
<td>4.7841</td>
<td>0.0008</td>
<td>3.0467</td>
<td>0.0018</td>
<td>3.8102</td>
<td>0.0004</td>
<td>3.8772</td>
<td>0.0146</td>
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<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;7&lt;/sub&gt;</td>
<td>5.0516</td>
<td>0.0003</td>
<td>3.1640</td>
<td>0.0104</td>
<td>3.8626</td>
<td>0.3228</td>
<td>4.1561</td>
<td>0.2914</td>
</tr>
<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;8&lt;/sub&gt;</td>
<td>5.0877</td>
<td>0.0001</td>
<td>3.2480</td>
<td>0.1092</td>
<td>3.9395</td>
<td>0.7052</td>
<td>4.2455</td>
<td>0.2015</td>
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<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;9&lt;/sub&gt;</td>
<td>5.2157</td>
<td>0.0004</td>
<td>3.2561</td>
<td>0.0002</td>
<td>3.9608</td>
<td>0.1010</td>
<td>4.3118</td>
<td>0.0017</td>
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<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;10&lt;/sub&gt;</td>
<td>5.2359</td>
<td>0.0017</td>
<td>3.4058</td>
<td>1.3357</td>
<td>4.0420</td>
<td>0.0125</td>
<td>4.3375</td>
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<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;11&lt;/sub&gt;</td>
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<td>3.5432</td>
<td>0.0158</td>
<td>4.0801</td>
<td>0.2004</td>
<td>4.3606</td>
<td>0.0055</td>
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<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt; → S&lt;sub&gt;12&lt;/sub&gt;</td>
<td>5.3125</td>
<td>0.0233</td>
<td>3.5658</td>
<td>0.0079</td>
<td>4.1730</td>
<td>0.0024</td>
<td>4.3892</td>
<td>0.0009</td>
</tr>
</tbody>
</table>

<sup>a</sup>with 6-31G* basis set

The dominant NTO pairs for the first six transitions are shown in SI L. Based on this NTO analysis, we can define the splitting of $\pi \rightarrow \pi^*$ excitations. For HF, BMK and CAM-B3LYP, the corresponding $|\psi_+\rangle$ and $|\psi_-\rangle$ combinations are states S<sub>4</sub> and S<sub>3</sub>, respectively, as shown exemplarily for CAM-B3LYP in Table 11. The corresponding exciton splitting is $2\Delta = E_4 - E_3$, giving $2\Delta = 0.27, 0.26$ and 0.30 eV for HF, BMK and CAM-B3LYP, respectively. These values are similar to those of the pure dimer, without the Si nanocluster. Thus, it appears that the attached cluster does not affect considerably the exciton splitting of the 4-NO<sub>2</sub>-AB dimer. This finding is supported by other methods (see SI F, Figure S3 (d), where the exciton splitting is plotted against all methods for free and adsorbed dimers).
Table 11: Dominant NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ transitions in the “dimer on Penta” model for CAM-B3LYP

<table>
<thead>
<tr>
<th></th>
<th>$S_0 \rightarrow S_3$</th>
<th></th>
<th>$S_0 \rightarrow S_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hole</td>
<td>0.81</td>
<td>Hole</td>
<td>0.86</td>
</tr>
<tr>
<td>Particle</td>
<td></td>
<td>Particle</td>
<td></td>
</tr>
</tbody>
</table>

4 Conclusions

In this paper we studied the low-lying singlet excited states in the 4-nitroazobenzene molecule, a dimer composed of two trans isomers, the trans monomer and dimer attached to a silicon pentamantane nanocluster, the latter also serving as a primitive model for a solid surface. We have extensively tested the performance of various methods, ranging from wave function-based methods without (HF) and with (CC2) correlation, to density functional methods containing exact exchange, either global hybrids (B3LYP, X3LYP, BMK, BHandH, BHandHLYP, M06-2X, M06-HF) or the range-separated methods (CAM-B3LYP, LC-\(\omega\)PBE, M11, \(\omega\)B97, \(\omega\)B97X, \(\omega\)B97X-D).

Returning to the four main questions originally posed in the Introduction, we can now answer them as follows, starting with the “methodological” questions first.

- What is an appropriate quantum chemical method to determine exciton splittings in dimers of chromophores?

The exciton splitting can be properly described by wave function-based methods (HF, CC2), range-separated density functionals or global hybrids with large amount of exact exchange (ca. \(\geq 50\%\)). There can be problems in particular at short intermolecular distances when using hybrid functionals such as BMK and especially B3LYP (or
X3LYP). At \( d \approx 3.6 \) Å, B3LYP produces spurious intermonomeric charge-transfer states instead of delocalized exciton transitions. At larger distances it becomes possible to determine the exciton splitting also by means of B3LYP. We should also stress that absolute values of excitation energies can differ quite a bit from each other depending on method: For example, the difference between bright state excitation energies for the free dimer obtained with CC2 and M06-HF, is about 0.6 eV. The same difference between CC2 and SCS-CC2 is about 0.2 eV.

- How can we identify relevant exciton states leading to exciton splitting?

The natural transition orbital (NTO) analysis is a reliable tool to identifying pairs of exciton-split states. It is to be preferred over simpler tools, such as contributions of dominant (Hartee-Fock or Kohn-Sham) orbitals in specific transitions, or oscillator strengths alone. Interestingly, dominant NTO pairs describing delocalized exciton transitions look differently for the cases of small and large monomer separations. In the latter case there are mainly two pairs with non-vanishing eigenvalues, each of them showing an excitation which is localized within one monomer. At small separation every pair is delocalized over the dimer. From a theoretical point of view it will be interesting to calculate charge-transfer numbers and make an attempt to establish the nature of these delocalized transitions (either classic Frenkel exciton or charge resonance state, or a mixture of both) at small separation based on an analysis proposed previously in the literature.\(^6\)

Returning to the “physical” questions of above, the following can be said.

- What are the effects of a second molecule on optical properties of a 4-nitroazobenzene switch, in particular: What is the size of the exciton splitting (\(2\Delta\) in the simple exciton model) and of the vdW shift (\(D\))? 

The exciton splitting of about 0.3 eV at \( d \approx 3.6 \) Å is largely independent of the method, as long as a reliable method is used. The exciton splitting decreases rapidly
with intermolecular distance, $d$, in rough agreement with the point-dipole model of simple exciton theory. The $\pi \to \pi^*$ excitations studied here form the expected + and − combinations, leading to an upper, bright state ($|\psi_+\rangle$) and a lower, dark state ($|\psi_-\rangle$). The spectral shifts when going from a monomer to a dimer are small (ca. 0.05 eV), much smaller than exciton splitting itself. Thus, the vdW shift $D$ is rather big, in the order of the exciton splitting parameter, $\Delta$.

- **What is the effect of the “surface”?**

Upon attachment to a pentamantane nanocluster the lowest bright ($\pi \to \pi^*$) transition shifts clearly to the red, both for monomer and dimer. The magnitude of the shift depends somewhat on the applied method, decreasing from CC2 (at least for the “monomer on Penta” model) through global hybrids and the range-separated functionals, to TD-HF. The attachment of a second molecule to the neighboring Si atom of the cluster leads to exciton splitting in the dimer. The presence of the silicon “surface” does not affect this splitting much, compared to the free dimer. Both for monomer and dimer adsorption, the surface leads to enhanced absorption signals.

Concerning these results, a few further statements should be made. First, an exciton splitting $2\Delta \approx 0.3$ eV suggests through Eq. (6) a delocalization time of about 7 fs. This is a very short “quenching time”, shorter than a typical isomerization time, and therefore isomerization in the adsorbates at finite coverages might indeed be hindered as speculated elsewhere. On the other hand, Eq. (6) is only a crude measure for quenching. Details of the post-excitation dynamics should be unravelled to account for a more accurate treatment of quenching and the role of steric effects. Work along these lines is in progress in our laboratory.

A second point refers to the shifts of absorption spectra of molecular switches due to aggregate formation, and the estimation of exciton splittings from these shifts. As mentioned above in Ref. 13, for example, a blue-shifted $\pi \to \pi^*$ absorption of *trans*-azobenzene-containing molecules forming SAMs on gold was observed and used as a semi-quantitative
measure for the exciton splitting. Indeed, according to the simple exciton model without vDW shift, Eq. (2), a blue shift of \( \Delta \) emerges which is half the exciton splitting. We have seen for the example studied in this work, however, that real life is more complicated due to a vDW shift within the dimer, suggesting that the allowed, exciton-split state can either be blue-shifted or red-shifted relative to the monomer. For example, for CC2, the absorption is slightly red-shifted in the dimer even without coupling to a surface. The surface, in this case the Penta Si cluster, introduces a further shift, here a strong shift to the red. We also expect clear system-dependencies (surface, switch, coverage), however, we conclude that a simple estimate of exciton splittings from spectral shifts is not straightforward. Here, theory can be of tremendous help.

**Acknowledgements**

This research was done in the framework of the IMPRS on Multiscale Bio-Systems. E.T. thanks Prof. Dr. Svetlana Santer and Dr. Nino Lomadze (Experimental Physics, University of Potsdam) for the assistance in experiment as well as Prof. Dr. Adrian Daniel Boese (Computational Physical Chemistry, University of Graz) and JProf. Dr. Thomas Körzdörfer (Computational Chemistry, University of Potsdam) for valuable advices regarding the computational study.

**Supporting Information**

The difference between geometries of “dimer on Penta” models with and without D3 correction; Excitation energies of \( \text{trans-4-NO}_2\text{-AB} \) monomer and dimer; Experimental spectra of 4-nitroazobenzene in solution; Basis set convergence test for CC2 for the monomer; Analysis of the two monomers in the free dimer; Method dependence of spectral shifts and exciton splitting; CC2 spectrum of the “totally symmetric” \( \text{trans-4-NO}_2\text{-AB} \) dimer at \( d = 3.6 \) Å; NTO analysis of the free “non-symmetric” dimer at \( d \approx 3.6 \) Å; NTO analysis of the free dimer at \( d = 6 \) Å; Excitation energies for “monomer on Penta” and “dimer on Penta” models;
NTO analysis of the “monomer on Penta”; NTO analysis of the “dimer on Penta”.

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Supporting Information for

“Exciton Splitting of Adsorbed and Free 4-Nitroazobenzene Dimers: A Quantum Chemical Study”

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SI A: The difference between geometries of dimer on Penta models with and without D3 correction

In this SI we study the influence of dispersion interactions on the geometry of the dimer of 4-NO$_2$-AB adsorbed on the Si nanocluster. From comparing Figures 1 (e) and (f) of the main text, one can conclude that dispersion interactions have a clear influence on the orientation of the molecules in the dimer on the cluster. The D3 correction leads to a “more parallel”, tilted orientation of the molecules, similar to one observed in real SAMs.$^1$ In contrast, the molecules are oriented away from each other when no dispersion correction is included. For the arrangement shown in Figure 1 (f) of the main text, the angles between the surface normal and the C–N(O$_2$) bonds in the 4-NO$_2$-AB molecules are about 18° and 13° for the first and the second molecules, respectively, resulting in an angle difference of 5°. The distance between the two adsorbed molecules (measured between the centers of coordinates (cocs) of the two molecules) is about 3.6 Å. (More precisely, 3.629 Å, obtained as a difference between two cocs, each coc is calculated using 25 atoms (no Si atoms were included in calculation).) This is a bit less than the distance between the two Si atoms to which the molecules are attached, which is 3.86 Å (for a model shown in Figure 1 (f) of the main text). The corresponding angles for the geometry obtained without dispersion correction (Figure 1 (e) of the paper) are about $-11°$ and $+11°$ for the first and the second molecules, respectively; the angle difference is 22° in this case. Moreover, apart from the change in a tilt one finds a rotation of the molecules when the D3 correction is used.
SI B: Excitation energies of trans-4-NO$_2$-AB monomer and dimer

Figure S1 shows excitation energies of 4-NO$_2$-AB monomer and dimer for all 16 model chemistries used in this work.

Figure S1: Excitation energies for optimized trans-4-NO$_2$-AB monomer (called “monomer 0” (or “m0”) here and in the main text), and the free dimer as obtained with different methods. Red bars show the lowest bright state of the monomer and the corresponding pair of the exciton-split states in the dimer. Blue bars show intramonomeric charge-transfer (CT) state(s) of m0 and corresponding exciton-split states of the dimer. Thin green bars are the first ($n \rightarrow \pi^*$) excited state (exciton-split states for the dimer). Thin gray bars represent other states. Thick black bars (for $\omega$B97, dimer) are states of mixed character: $\pi \rightarrow \pi^*$ plus intramonomeric CT. In the case of dimer for B3LYP and X3LYP all states (except for the first two) are shown in gray; it is not possible to find “red” states due to the CT problem.
SI C: Experimental spectra of 4-nitroazobenzene in solution

As a reference for judging on the quality of various methods in calculating excited states of 4-NO$_2$-AB, UV–vis absorption spectra of 4-NO$_2$-AB in chloroform solution were recorded experimentally. For this purpose, a concentration of 4-NO$_2$-AB of $4.4 \times 10^{-5}$ M was used and spectra were taken with a Cary 5000 spectrometer (Varian Inc.). Spectra were recorded before and after UV light illumination (365 nm) of the solution. The UV illumination was carried out with a VL-4.L lamp (Vilber Lourmat) for two minutes. 4-NO$_2$-AB and chloroform from Sigma-Aldrich were used.

![Figure S2: The experimental absorption spectra of 4-NO$_2$-AB in chloroform before and after illumination with UV light (365 nm).](image)

The UV–vis absorption spectra of 4-NO$_2$-AB in chloroform are shown in Figure S2. The initial spectrum (before illumination, solid line) corresponds to the state of the solution at which the molecules are mostly in *trans* form. The most intense absorption band in the considered wavelength region has its maximum at 335 nm, which is in agreement with a previously reported value. It corresponds to the well-known lowest $\pi \rightarrow \pi^*$ transition (see the main text). UV light illumination leads to *trans* $\rightarrow$ *cis* isomerization. The spectrum after UV light illumination (dotted line) has a characteristic band with maximum at 426 nm, which is the well-known $n \rightarrow \pi^*$ transition, while the $\pi \rightarrow \pi^*$ transition becomes weaker and is blue-shifted to about 325 nm.
SI D: Basis set convergence test for CC2 for the monomer

In Table S1, the basis set convergence of the CC2 method is demonstrated for the trans-4-NO$_2$-AB monomer.

Table S1: CC2 excitation energies (in eV) and corresponding oscillator strengths (in parentheses) for the first three low-lying singlet excited states of the trans isomer of 4-NO$_2$-AB calculated with various Dunning’s correlation consistent basis sets

<table>
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<th>Transition</th>
<th>Basis Set</th>
<th>aug-cc-pVDZ</th>
<th>aug-cc-pVTZ</th>
<th>aug-cc-pVQZ</th>
<th>aug-cc-pV5Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0 \rightarrow S_1$</td>
<td>2.7339 (0.0000)</td>
<td>2.6901 (0.0000)</td>
<td>2.6889 (0.0000)</td>
<td>2.6894 (0.0000)</td>
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</tr>
<tr>
<td>$S_0 \rightarrow S_2$</td>
<td>3.7889 (0.0000)</td>
<td>3.7604 (0.0000)</td>
<td>3.7643 (0.0000)</td>
<td>3.7672 (0.0000)</td>
<td></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_3$</td>
<td>3.9462 (1.0501)</td>
<td>3.9132 (1.0418)</td>
<td>3.9073 (1.0407)</td>
<td>3.9051 (1.0404)</td>
<td></td>
</tr>
</tbody>
</table>
SI E: Analysis of the two monomers in the free dimer

Tables S2, S3 and S4 analyze the absorption spectra of isolated monomers 1 and 2, in the (slightly asymmetric) dimer shown in Figure 1 (g) of the main text. Table S2 lists lowest excitation energies and oscillator strengths, for the five selected methods of this work. It is seen that in particular the $S_0 \rightarrow S_2$ transition evaluated with BMK and CAM-B3LYP becomes a bright transition with sizable oscillator strength comparable with the one for the $S_0 \rightarrow S_3$ transition. The CC2 $S_0 \rightarrow S_2$ transition in monomers 1 and 2 is also allowed but the oscillator strength is much smaller than in the case of BMK and CAM-B3LYP.

Table S2: Excitation energies and oscillator strengths for the first three low-lying singlet excited states of trans-4-NO$_2$-AB monomer 1 and monomer 2. Data for the strongest bright transitions are shown in bold

<table>
<thead>
<tr>
<th>Transition</th>
<th>$E$ (eV)</th>
<th>$f$</th>
<th>$E$ (eV)</th>
<th>$f$</th>
<th>$E$ (eV)</th>
<th>$f$</th>
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</thead>
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<tr>
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<td>3.1045</td>
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<td>2.3847</td>
<td>0.0004</td>
<td>2.4646</td>
<td>0.0003</td>
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<td>$S_0 \rightarrow S_2$</td>
<td>4.2481</td>
<td>0.9499</td>
<td>3.4591</td>
<td>0.8193</td>
<td>3.8009</td>
<td>0.4569</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_3$</td>
<td>4.7860</td>
<td>0.0011</td>
<td>3.6340</td>
<td>0.0098</td>
<td>3.8484</td>
<td>0.5225</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_1$</td>
<td>3.0924</td>
<td>0.0015</td>
<td>2.3861</td>
<td>0.0018</td>
<td>2.4617</td>
<td>0.0012</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_2$</td>
<td>4.2751</td>
<td>0.9482</td>
<td>3.4789</td>
<td>0.8250</td>
<td>3.8285</td>
<td>0.5160</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_3$</td>
<td>4.8103</td>
<td>0.0007</td>
<td>3.6598</td>
<td>0.0051</td>
<td>3.8680</td>
<td>0.4638</td>
</tr>
</tbody>
</table>

*with 6-31G* basis set; $^a$ with aug-cc-pVDZ basis set

Tables S3 and S4 give dominant NTO pairs for the three lowest transitions within the two isolated monomers. It is seen that NTO pairs of BMK and CAM-B3LYP $S_0 \rightarrow S_2$ transitions differ somewhat from the case of the isolated, ideally flat isomer of Section 3.1 of the paper. Apart from the oxygen atoms the hole occupies the $\pi$-system of the azobenzene unit. The hole of $S_0 \rightarrow S_3$ transition also changes, becoming similar on oxygen atoms to the $S_0 \rightarrow S_2$ hole.
Table S3: Dominant NTO pairs and associated eigenvalues $\lambda$ for the first three transitions in monomer 1 of *trans*-4-NO$_2$-AB

<table>
<thead>
<tr>
<th></th>
<th>$S_0 \rightarrow S_1$</th>
<th>$S_0 \rightarrow S_2$</th>
<th>$S_0 \rightarrow S_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hole</td>
<td>Particle</td>
<td>Hole</td>
</tr>
<tr>
<td>HF</td>
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<td>$\lambda$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>$\lambda$</td>
<td>1</td>
<td>$\lambda$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BMK</td>
<td>$\lambda$</td>
<td>1</td>
<td>$\lambda$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>$\lambda$</td>
<td>1</td>
<td>$\lambda$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC2</td>
<td>$\lambda$</td>
<td>1</td>
<td>$\lambda$</td>
</tr>
</tbody>
</table>
Table S4: Dominant NTO pairs and associated eigenvalues $\lambda$ for the first three transitions in monomer 2 of trans-4-NO$_2$-AB

<table>
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<th>Method</th>
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<th>$S_0 \rightarrow S_2$</th>
<th>$S_0 \rightarrow S_3$</th>
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</thead>
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<td>Particle</td>
<td>Hole</td>
</tr>
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<td>HF</td>
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<td>0.88</td>
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<tr>
<td>B3LYP</td>
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<td><img src="null" alt="Image" /></td>
<td><img src="null" alt="Image" /></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>BMK</td>
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<td><img src="null" alt="Image" /></td>
<td><img src="null" alt="Image" /></td>
</tr>
<tr>
<td>$\lambda$</td>
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<td>0.83</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
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<td><img src="null" alt="Image" /></td>
</tr>
<tr>
<td>$\lambda$</td>
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<td>0.81</td>
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<tr>
<td>CC2</td>
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<td><img src="null" alt="Image" /></td>
<td><img src="null" alt="Image" /></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>1</td>
<td></td>
<td>0.98</td>
</tr>
</tbody>
</table>
SI F: Method dependence of spectral shifts and exciton splitting

Figure S3 shows various optical properties of 4-NO$_2$-AB in free and adsorbed forms for all (up to 16) model chemistries used in this work.

Figure S3: (a) Difference between excitation energies of the lowest bright excited states in the free monomer (m0) and free dimer (“d”). (b) Difference between excitation energies of the lowest bright excited states in the free monomer (m0) and in the monomer on Penta (mop). (For B3LYP and X3LYP, two red-shifted bright states are found.) (c) Difference between excitation energies of the lowest bright excited states in the monomer on Penta (mop) and the dimer on Penta (dop). (d) Exciton splitting (for $\pi \rightarrow \pi^*$ transitions) in free and adsorbed dimers. (For some methods (M11, $\omega$B97) two values are presented for the same model meaning ambiguity in determining the dark exciton state of interest based on NTOs.) The lines in the graphs are a guide to the eye.
SI G: CC2 spectrum of the “totally symmetric” trans-4-NO\textsubscript{2}-AB dimer at $d = 3.6$ Å

In order to discriminate effects due to the slight geometric asymmetry of the adsorbed dimer from true dimerization effects, an ideal, “totally symmetric” dimer was considered as well. The geometry of the “totally symmetric” dimer was constructed by translating the geometry of the optimized, isolated monomer (monomer 0) in a direction perpendicular to molecular plane by 3.6 Å. The lowest eight calculated CC2/aug-cc-pVDZ transitions are presented in Table S5.

**Table S5:** CC2/aug-cc-pVDZ excitation energies and oscillator strengths for the first eight low-lying singlet excited states of the “totally symmetric” trans-4-NO\textsubscript{2}-AB dimer (at a distance between monomers of 3.6 Å). The bright transition is shown in bold

<table>
<thead>
<tr>
<th>Transition</th>
<th>$E$ (eV)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0 \rightarrow S_1$</td>
<td>2.6289</td>
<td>0.0000</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_2$</td>
<td>2.6915</td>
<td>0.0001</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_3$</td>
<td>3.3514</td>
<td>0.0000</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_4$</td>
<td>3.7205</td>
<td>0.0000</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_5$</td>
<td>3.7293</td>
<td>0.0000</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_6$</td>
<td>3.8430</td>
<td>0.0000</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_7$</td>
<td><strong>4.0031</strong></td>
<td><strong>1.7939</strong></td>
</tr>
<tr>
<td>$S_0 \rightarrow S_8$</td>
<td>4.0178</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

For this dimer a blue shift of about 0.05 eV (corresponding to about 4 nm) in comparison to the isolated monomer takes place: For the isolated monomer of Table 1 of the main text, the $\pi \rightarrow \pi^*$ excitation corresponds to the $S_0 \rightarrow S_3$ transition at about 3.95 eV, while for the symmetric dimer it is the $S_0 \rightarrow S_7$ transition at about 4.00 eV according to Table S5. Note that for the “non-symmetric” dimer described in Section 3.2 of the main text the $\pi \rightarrow \pi^*$ excitation corresponds to the $S_0 \rightarrow S_6$ transition instead (cf. Table 3 of the paper). Table S6 shows CC2 dominant NTO pairs for the transitions of “totally symmetric” dimer tabulated in Table S5. We see that $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_7$ are $\pi \rightarrow \pi^*$ transitions in question. The corresponding exciton splitting, $2\Delta = E_7 - E_3$, is equal to 0.65 eV, which is about 2.1 times...
larger than the splitting in the “non-symmetric” dimer.

Table S6: CC2 dominant NTO pairs and associated eigenvalues $\lambda$ for the first eight transitions in the free “totally symmetric” $\text{trans-4-NO}_2\text{-AB}$ dimer

<table>
<thead>
<tr>
<th>Hole</th>
<th>Particle</th>
<th>Hole</th>
<th>Particle</th>
<th>Hole</th>
<th>Particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0 \rightarrow S_1$</td>
<td><img src="image1" alt="Hole Particle" /></td>
<td>$S_0 \rightarrow S_2$</td>
<td><img src="image2" alt="Hole Particle" /></td>
<td>$S_0 \rightarrow S_3$</td>
<td><img src="image3" alt="Hole Particle" /></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.70</td>
<td>$\lambda$</td>
<td>0.30</td>
<td>$\lambda$</td>
<td>0.93</td>
</tr>
<tr>
<td>$S_0 \rightarrow S_4$</td>
<td><img src="image4" alt="Hole Particle" /></td>
<td>$S_0 \rightarrow S_5$</td>
<td><img src="image5" alt="Hole Particle" /></td>
<td>$S_0 \rightarrow S_6$</td>
<td><img src="image6" alt="Hole Particle" /></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.59</td>
<td>$\lambda$</td>
<td>0.36</td>
<td>$\lambda$</td>
<td>0.85</td>
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<tr>
<td>$S_0 \rightarrow S_7$</td>
<td><img src="image7" alt="Hole Particle" /></td>
<td>$S_0 \rightarrow S_8$</td>
<td><img src="image8" alt="Hole Particle" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.51</td>
<td>$\lambda$</td>
<td>0.45</td>
<td>$\lambda$</td>
<td>0.79</td>
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</tbody>
</table>
SI H: NTO analysis of the free “non-symmetric” dimer at $d \approx 3.6 \text{ Å}$

Tables S7, S8, and S9 give the dominant NTO pairs in the free (slightly asymmetric) dimer, for the lowest six transitions, for the five selected methods of this work.

Table S7: Dominant NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions in the free $\text{trans-4-NO}_2\text{-AB}$ dimer

<table>
<thead>
<tr>
<th>Method</th>
<th>$S_0 \rightarrow S_1$</th>
<th>$S_0 \rightarrow S_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hole</td>
<td>Particle</td>
</tr>
<tr>
<td>HF</td>
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<td></td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>BMK</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>CAM-B3LYP</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>CC2</td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>
Table S8: Dominant NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ transitions in the free trans-4-NO$_2$-AB dimer

<table>
<thead>
<tr>
<th>Method</th>
<th>$S_0 \rightarrow S_3$</th>
<th>$S_0 \rightarrow S_4$</th>
</tr>
</thead>
<tbody>
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<tr>
<td>B3LYP</td>
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<td>0.94</td>
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<tr>
<td>BMK</td>
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<td>1</td>
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<tr>
<td>CC2</td>
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</table>
Table S9: Dominant NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_6$ transitions in the free $trans$-4-NO$_2$-AB dimer

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<tr>
<th>Method</th>
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<tr>
<td>$\lambda$</td>
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<td>1</td>
</tr>
<tr>
<td>B3LYP</td>
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<td><img src="B3LYP_Hole_Particle.png" alt="Image" /></td>
</tr>
<tr>
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<td>0.86</td>
</tr>
<tr>
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</tr>
<tr>
<td>$\lambda$</td>
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<td>0.95</td>
</tr>
<tr>
<td>CAM-B3LYP</td>
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<td><img src="CAM-B3LYP_Hole_Particle.png" alt="Image" /></td>
</tr>
<tr>
<td>$\lambda$</td>
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<td>0.79</td>
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<tr>
<td>CC2</td>
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</tr>
<tr>
<td>$\lambda$</td>
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</table>
SI I: NTO analysis of the free dimer at $d = 6 \, \text Å$

Table S10: HF, B3LYP and CC2 dominant NTO pairs for delocalized transitions corresponding to exciton-split $\pi \rightarrow \pi^*$ transitions in the free dimer at $d = 6 \, \text Å$, and associated eigenvalues $\lambda$

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<td>$\lambda$</td>
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<td>0.34</td>
<td>![Image]</td>
<td>$\lambda$</td>
<td>0.34</td>
</tr>
<tr>
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<td>$\lambda$</td>
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### SI J: Excitation energies for monomer on Penta and dimer on Penta models

Figure S4 shows excitation energies of adsorbed 4-NO$_2$-AB monomer and dimer for all (up to 16) model chemistries used in this work.

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<th>Dimer on Penta</th>
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<td>X3LYP/6-31G*</td>
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<tr>
<td>M06-HF/6-31G*</td>
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<td></td>
</tr>
<tr>
<td>CAM-B3LYP/6-31G*</td>
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<td>ωB97X-D/6-31G*</td>
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</tbody>
</table>

Figure S4: Excitation energies for monomer on Penta (mop) and dimer on Penta (dop) models as obtained with different methods. Red bars show the lowest bright state of mop and the corresponding pair of the exciton-split states in dop. Blue bars show intramonomeric charge-transfer (CT) state(s) of mop and corresponding exciton-split states of dop. Thin green bars are the first ($n \rightarrow \pi^*$) excited state (exciton-split states for dop). Thin gray bars represent other states. Thick black bars (for M11, dop) are states of mixed character: $\pi \rightarrow \pi^*$ plus intramonomeric CT. In the case of dop for B3LYP and X3LYP all states (except for the first two) are shown in gray; it is not possible to find “red” states due to the CT problem.
**SI K: NTO analysis of the monomer on Penta**

Table S11: Dominant NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions in the monomer on Penta model

<table>
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<tr>
<th>Method</th>
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Table S12: Dominant NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_3$ transition in the monomer on Penta model

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### SI L: NTO analysis of the dimer on Penta

Table S13: Dominant NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions in the dimer on Penta model

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Table S14: Dominant NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ transitions in the dimer on Penta model

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Table S15: Dominant NTO pairs and associated eigenvalues $\lambda$ for the $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_6$ transitions in the dimer on Penta model.

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4. Reprints

References


Dynamics of Azobenzene Dimer

Photoisomerization: Electronic and Steric Effects

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Abstract

While azobenzenes readily photoswitch in solution, their photoisomerization in densely packed self-assembled monolayers (SAMs) can be suppressed. Reasons for this can be steric hindrance and/or electronic quenching, e.g., by exciton coupling. We address these possibilities by means of nonadiabatic molecular dynamics with trajectory surface hopping calculations, investigating the $\text{trans} \rightarrow \text{cis}$ isomerization of azobenzene after excitation into the $\pi\pi^*$ absorption band. We consider a free monomer, an isolated dimer and a dimer embedded in a SAM-like environment of additional azobenzene molecules, imitating in this way the gradual transition from an unconstrained over an electronically coupled to an electronically coupled and sterically hindered, molecular switch. Our simulations reveal that in comparison to the single molecule the quantum yield of the $\text{trans} \rightarrow \text{cis}$ photoisomerization is similar for the isolated dimer, but greatly reduced in the sterically constrained situation. Other implications of dimerization and steric constraints are also discussed.
The photoswitching of an azobenzene (AB) molecule between two different isomers, trans and cis, is a widely studied example of molecular switching which is of importance to potential applications in nanoscience. Readily accessible in gas phase or solution, the trans $\rightarrow$ cis photoisomerization can be hindered in densely packed self-assembled monolayers (SAMs), as has been observed for AB-containing thiols on a gold surface.\textsuperscript{1,2} As possible reasons for this suppression of the isomerization, steric hindrance and/or large exciton coupling between AB chromophores, leading to ultrafast excitation transfer in the SAM, have been mentioned.\textsuperscript{1} However, thorough insight into details of the problem is still elusive.

Since steric and electronic effects are hard to disentangle experimentally, theoretical modeling is worthwhile. Here in particular nonadiabatic molecular dynamics appears as a powerful tool to gain mechanistic insight into multi-mode, photoinduced molecular switching. So far, nonadiabatic molecular dynamics with trajectory surface hopping was applied to model single-molecule isomerization of AB in gas phase,\textsuperscript{3–12} in solution,\textsuperscript{5,6} and in the liquid state.\textsuperscript{10,11} The isomerization of (single) AB derivatives on sterically confining surfaces was also modeled showing a reduction of the quantum yield of reaction in comparison to the isolated-molecule case due to van der Waals (vdW) interaction with a surface and resulting steric hindrance.\textsuperscript{13,14} Furthermore, covalently connected dimeric molecular systems with two AB units, were considered either in quantum mechanics / molecular mechanics (QM/MM)\textsuperscript{15} or purely QM\textsuperscript{16} (regarding the electronic structure) setups.

In this work we make a step further, simulating by means of the surface hopping approach\textsuperscript{17,18} with QM and QM/MM models the trans $\rightarrow$ cis isomerization dynamics of a non-covalently bound AB dimer and the dimer in the environment of other AB molecules, imitating with the latter a densely packed SAM. Specifically, we studied three models of increasing sophistication: (i) an AB monomer as a reference, (ii) an isolated QM dimer (Fig. 1 (a)) and (iii) the QM dimer surrounded by ten frozen MM AB monomers, interacting with the QM central dimer through classical pairwise atomic vdW interactions only (Fig. 1 (b–d)). We will refer to the latter model as “SAM” or the vdW-constrained
Here, the initial geometry of a trans-AB molecule was determined at the B3LYP\textsuperscript{19,20}/6-31G*\textsuperscript{21,22} level of theory. Note that the “SAM” model is highly idealized, with upright (rather than tilted) molecules arranged in a rectangular unit cell, with lattice parameters \( a = 3.5 \) Å and \( b = 6.0 \) Å providing a high area density of \( \sim5 \) molecules per nm\(^2\). For comparison,
the densely packed molecular arrangement of Ref. 1 was \( \sim 4.2 \) molecules per nm\(^2\); in Ref. 23, a critical grafting density beyond which switching in AB-containing SAMs is suppressed of about 2.5 molecules per nm\(^2\) has been given. Further, the surface is only indirectly included in our proof-of-principle model, through a specific choice of lattice parameters and the fact that the two lowest atoms of the lower phenyl ring of each molecule of the QM dimer (for both models (ii) and (iii)) are kept fixed during the molecular dynamics runs, cf. Fig. 1. As such, model (i) represents a totally unconstrained switch, model (ii) an electronically coupled dimer with slight steric hindrance, and model (iii) an electronically coupled dimer with strong steric constraints imposed by an environment. We stress that in our third model (“SAM”) the MM perimeter molecules are frozen during dynamics allowing for regular molecular arrangement, which provides, in turn, the needed steric hindrance. However, with this we omit the vibrational energy transfer from the QM part to the MM one. These two factors are expected to affect a quantum yield in different directions.

Singlet excited states, gradients and nonadiabatic couplings required in the QM treatment and surface hopping dynamics were calculated “on the fly” by means of the semiempirical reparameterized AM1/FOMO-CI method. For all models, the same active space and CI procedure as previously employed for bisazobenzenes was used. Out of calculated excited states, the energetically lowest 14 singlet excited states (plus the ground state) were used for surface hopping dynamics. Note that these states include the singlet combinations of the two monomer triplets. However, we did not consider overall triplets and intersystem crossing transitions because the azobenzene \( T_1 \) and \( S_1 \) states are far enough in energy and share the same \( n\pi^* \) configuration, so they are expected to interact weakly by spin–orbit coupling, according to El-Sayed rules. For the “SAM” QM/MM model, vdW interactions with the surrounding AB molecules were described by the MM3-2000 force field. Further details on models and methods are presented in the SI.

First, we calculated vertical absorption spectra of the trans monomer and dimer (at \( T = 0 \) K) using various first-principles (DFT and wavefunction-based) methods to judge on the
performance of AM1/FOMO-CI for the systems under study. A detailed discussion of spectra and method dependencies is presented in the SI. Briefly, semiempirical (AM1/FOMO-CI) spectra are energetically close (in terms of a location of the $\pi\pi^*$ absorption band) to time-dependent Hartree-Fock (TD-HF) (see, e.g., Refs. 30, 31) ones, showing a blue shift with respect to other methods and to an available experimental gas-phase result\(^{32}\) (Fig. S2, Tabs. S1 and S2). The blue shift relative to modern range-separated functionals (e.g., M11\(^{33}\) or $\omega$B97\(^{34}\)) or SCS-CC2\(^{35}\) is rather moderate, $\sim$0.1–0.25 eV. Moreover, AM1/FOMO-CI shows the presence of several doubly excited states, as verified also by the so-called DFT/MRCI method\(^{36}\) which accounts for multiple-excitations as AM1/FOMO-CI. We also find, when going from monomer to the dimer, an expected blue shift (except for DFT/MRCI, which is not suitable for the dimers\(^{37}\)) and enhancement of the $\pi\pi^*$ signal. The blue shift is around 0.1–0.2 eV for most methods (Figs. S2 and S3). It is due to the fact that the $\pi\pi^*$ transition is split by exciton coupling into a red-shifted dark and a blue-shifted bright state, the so-called Davydov (or exciton) splitting.\(^{38,39}\) With the present short intermolecular distances and ideal upright orientation the exciton splitting $\Delta E_{exciton}$ between the two states is quite large and in the order of 0.6–0.7 eV, only moderately method-dependent (see Fig. S3). From these findings we conclude that the AM1/FOMO-CI method is sufficiently accurate to correctly account for excited-state properties of coupled AB dimers. The description of photoisomerization pathways and conical intersections obtained at the AM1/FOMO-CI level for the azobenzene is presented in Ref. 27.

In a second step, initial coordinates and velocities for subsequent photodynamics were sampled from Brownian trajectories\(^{40}\) on the ground state potential energy surface (PES), using the AM1/FOMO-CI method. Brownian dynamics were run once for each model (i)–(iii) for 10 ps at a temperature of 300 K. Initial structures for photoexcitation were selected after 1 ps. When computing vertical excitation energies (wavelengths) and transition dipole moments (and corresponding oscillator strengths) for each geometry along the Brownian trajectory and subsequently broadening the stick spectra by Gaussian functions (see SI for
details), we can estimate thermally broadened absorption spectra for the *trans*-AB species. The resulting spectra, averaged along the Brownian trajectories are presented in Fig. 2. Specifically, $\pi\pi^*$ and $n\pi^*$ bands are shown in plots (a) and (b), respectively, for all three models (*i.e.*, monomer, isolated dimer, and “SAM”).

![Figure 2: Averaged (along ground-state Brownian trajectories) broadened vertical absorption spectra for monomer (red solid lines), isolated dimer (blue), and “SAM” (black): (a) $\pi\pi^*$ band, (b) $n\pi^*$ band. Dashed lines in (a) show the boundaries of the energy windows to select initial PESs for the photodynamics: red for the monomer and blue for the isolated dimer and “SAM”. For details on the broadening procedure see SI.](image)

From Fig. 2 (a) we note also here the mentioned blue shift (by $\sim 0.2$ eV) and intensity enhancement (by a factor of about two) of the lowest bright $\pi\pi^*$ transition upon dimerization, compared to the monomer, in agreement with the Davydov model. The effect of constraining the dimer by a SAM-like environment on the $\pi\pi^*$ band is small. Due to thermal distortions the $n\pi^*$ transitions of the *trans* isomers become allowed (Fig. 2 (b)). Note that the spectral features of the $n\pi^*$ band behave differently than the $\pi\pi^*$ band as far as effects of dimerization and steric constraints are concerned (see SI for the discussion of the $n\pi^*$ band behaviour).

In what follows, however, we focus on excitations into the $\pi\pi^*$ band which is much more intense than the $n\pi^*$ one.

In a third step, we modeled the post-excitation dynamics (which may lead to
isomerization) of our three systems, after optical excitations of the thermalized \textit{trans} species into the $\pi\pi^*$ band. The corresponding energy windows selected for these excitations are shown with dashed lines in Fig. 2 (a). For all the models the size of the windows is 2 eV — we assigned a window of [3.8,5.8] eV for the monomer and [4.0,6.0] eV for the isolated dimer and “SAM”. Selecting the initial electronic states was done as described elsewhere\textsuperscript{40} based on the magnitudes of transition dipole moments from ground to the excited states which fall into the energy window. Moreover, we ensured that each single geometry selected from the Brownian trajectory was used only once as an initial geometry for photodynamics.

Next, multiple surface hopping trajectories, starting at the selected $\pi\pi^*$ states were launched. Examples of different kinds of trajectories, represented with CNN angles ($\alpha$) and CNNC dihedrals ($\omega$), are depicted in Fig. 3 (see also Fig. 1 (a) for definition of angles). Fig. 3 gives also information on which singlet potential energy surface the trajectory resides at a given moment. We find “reactive”, “unreactive”, and “undetermined” trajectories. The reactive trajectories shown in the left column of Fig. 3, \textit{i.e.}, those trajectories for which \textit{trans} $\rightarrow$ \textit{cis} isomerization took place, demonstrate after some time ($\lesssim$ 1 ps for the trajectories of Fig. 3) the change of the $\omega$-value from $\sim180^\circ$ (\textit{trans} isomer) to $\sim0^\circ$ (\textit{cis} isomer). Switching often occurs around the time when a $n\pi^* \rightarrow$ ground state transition happens. The mechanism of the isomerization is complex and involves the increase of $\alpha$ angles with subsequent rearrangement of the CNNC moiety to the \textit{cis} form. Note that in the dimeric models only one molecule is switched while the other stays in the \textit{trans} form (with $\omega$ about 180$^\circ$). This is true for all reactive trajectories on a timescale of 5 ps. The unreactive trajectories, \textit{i.e.}, the trajectories for which excited \textit{trans} models relaxed without reaching the \textit{cis} isomer are shown in the middle column of Fig. 3. For the dimeric models, in contrast to the monomer, some trajectories (Fig. 3, right column) demonstrate large-amplitude changes of dihedral angles during dynamics, and can be referred to as undetermined. On longer timescales, when including vibrational relaxation, these trajectories would eventually become reactive or unreactive, respectively.
Figure 3: Selected nonadiabatic trajectories for the three models under study: Shown are dihedral CNNC (ω₁, ω₂) and CNN (α₁₁, α₁₂, α₂₁, α₂₂) angles (cf. Fig. 1 (a)) (left scale) as well as PES numbers (right scale, the number n denoting state Sₙ) as a function of time. The left column represents reactive trajectories, middle — unreactive, and right — undetermined ones.

Counting reactive trajectories one can define the $\text{trans} \rightarrow \text{cis}$ quantum yield $\Phi$ as the ratio of the number of reactive trajectories, $N_{\text{reactive}}$, to the total number of reactive and unreactive trajectories, $N_{\text{total}}$, $\Phi = N_{\text{reactive}} / N_{\text{total}}$ (undetermined trajectories were not included in the analysis). The quantum yields along with bootstrap estimate of the standard error of the mean $\Delta \Phi = \sqrt{\Phi(1 - \Phi)} / N_{\text{total}}$ are presented in Tab. 1.
We first of all note that the quantum yield for the monomer is 0.21. [Note that in Ref. 16 the quantum yield of 0.12 ± 0.03 was reported for the AB monomer, obtained using the same method as we employed here. The discrepancy between the values can be explained as follows. Here we observed that some trajectories, after the molecule switched to the cis form and stayed in this form for hundreds of femtoseconds, exhibit the back isomerization to the trans form (being in the electronic ground state). All these back isomerizations happen before 3 ps — the time used in Ref. 16 as the landmark time to stop trajectories based on certain criteria (see section C.2 of Ref. 16 for further details). Excluding such trajectories from the reactive set in the present work will give a yield of 0.12. However, we believe that these back isomerizations are nonphysical and caused by the use of the AM1 method without an added potential (see Ref. 27).] This value agrees fairly well with the quantum yield of 0.25 found recently\textsuperscript{6} using corrected PESs\textsuperscript{27} and an energy based decoherence correction (EDC)\textsuperscript{18} (this latter correction was also applied in our calculations in the present work) for surface hopping. The quantum yield for the isolated dimer is very similar, 0.19. Thus, the switching probability for the free dimer is approximately as high as for the monomer. When restricting the dimer sterically within the “SAM” model, the quantum yield is greatly reduced, to 0.11. Since in the isolated dimer electronic coupling is present but steric hindrance is small while for the “SAM” dimer steric hindrance is large, we conclude that for the present model system at least steric hindrance appears as the dominating effect which suppresses the switching probability of densely packed monolayers of AB molecules.

Further, we compute state populations — fractions of trajectories being at a given time in...
a certain electronic state. For this analysis we considered all trajectories, reactive, unreactive,
and undetermined, for each of the studied models. We combined \( n\pi^* \) excited states in one
group and \( \pi\pi^* \) excited states in another one. Specifically, for the monomer \( n\pi^* \) corresponds
to \( S_1 \), and the \( \pi\pi^* \) group to \( S_2 \) and higher. For the isolated dimer and “SAM”, the \( n\pi^* \) group
includes three states \( S_1 \) to \( S_3 \), whereas \( \pi\pi^* \) includes \( S_4 \) and higher states. The populations
were fitted by using a two-step irreversible kinetics model (Fig. 4 (a)), giving lifetimes \( \tau_{\pi\pi^*} \)
and \( \tau_{n\pi^*} \) of the respective excited state manifolds: \(^{16}\)

\[
P_{\pi\pi^*} = e^{-t/\tau_{\pi\pi^*}}
\]

\[
P_{n\pi^*} = \frac{\tau_{n\pi^*}}{\tau_{n\pi^*} - \tau_{\pi\pi^*}} (e^{-t/\tau_{n\pi^*}} - e^{-t/\tau_{\pi\pi^*}})
\]

Figure 4: (a) Time evolution of populations (fractions of trajectories) for the ground state
(\( S_0 \)), \( n\pi^* \) and \( \pi\pi^* \) states. (b) Time evolution of the end-to-end distance (between hydrogen
atoms in para-positions of the phenyl rings) for the reactive trajectories.

Inspection of the lifetimes as tabulated in Tab. 1 indicates that the lifetime of the \( \pi\pi^* \)
states is almost five times larger for the isolated dimer than for the monomer, increasing from about 300 to close to 1500 fs. As a result of the excitonic coupling between $\pi\pi^*$ states, in the dimer the higher state of the Davyдов split pair is populated. The energy gap between this state and the $n\pi^*$ ones is larger than in the monomer and this may explain its slower decay. Interestingly, the long lifetime for the isolated dimer is considerably reduced, by a factor of three, for the “SAM” dimer, showing that the vdW constraint leads to a faster decay of the $\pi\pi^*$ states, to $n\pi^*$. We have verified that the torsion of the CN bonds (NNCC dihedral angles), while the trajectories evolve in the $\pi\pi^*$ states, is more free in the dimer than in the “SAM” (Fig. S6). The same is true, to a lesser extent, for the NN bond torsion (CNNC dihedral). This kind of geometrical relaxation increases the energy gap with the $n\pi^*$ states (see Fig. 1 and Tab. 5 of Ref. 6). In fact we find in the average larger energy gaps in the dimer than in the “SAM” (Fig. S7), which explains the difference in the $\pi\pi^*$ lifetime. The lifetime of the $n\pi^*$ states, in comparison to the monomer, is somewhat larger for the isolated dimer and greatly increased for the “SAM”, due to population of the $n\pi^*$ states from the ground state during all 5 ps in the case of undetermined trajectories. Note that the excited state lifetimes are not directly related to switching yields.

Finally, we compared the change in the end-to-end distance of the AB molecule (molecular length) upon the $\text{trans} \rightarrow \text{cis}$ isomerization. To do so we tracked the distance between hydrogen atoms in para-positions of the phenyl rings of AB, for reactive trajectories only (Fig. 4 (b)). We find that the $\text{cis}$ isomer length spans a broader range of distances in the case of the monomer and the free dimer than for the “SAM” dimer. In other words, the vdW constraint keeps the molecules in a more open form (larger end-to-end distance) after the $\text{trans} \rightarrow \text{cis}$ isomerization. As another consequence of the steric confinement in addition to altered excited state lifetimes and switching probabilities, therefore, also the geometry of the switched molecules differs: In the confined dimer, they stay in a $\text{trans}$-typical elongated form after switching, however, with a dihedral angle characteristic for the $\text{cis}$ form. In the unconstrained dimer, both characteristics (molecular length and dihedral)
change substantially.

In conclusion, we performed nonadiabatic molecular dynamics simulations for free and vdw-constrained ("SAM") AB dimers. We treated both dimer molecules using the AM1/FOMO-CI method, thus accounting for the change in electronic structure upon dimerization. Importantly, we found (i) a very similar $\text{trans} \rightarrow \text{cis}$ quantum yield (after $\pi\pi^*$ excitation) for the free dimer ($\Phi = 0.19 \pm 0.05$) in comparison to the monomeric reference ($\Phi = 0.21 \pm 0.05$), and (ii) pronounced decrease of the quantum yield for the “SAM” ($\Phi = 0.11 \pm 0.03$). We conclude that in the present model at least (which has both strong electronic coupling and large steric hindrance), steric effects are the main reason why switching is suppressed in densely packed monolayers of AB molecules on surfaces. We further found that the lifetimes of the excited states for the dimer models are increased in comparison to the monomer. The end-to-end distance of the cis isomer, formed after photoisomerization, is on average larger for the “SAM” model, suggesting that steric confinement can also lead to different product geometries.

Of course, the present models should be refined in the future. In particular, enlargement of the QM part, inclusion of motion for the MM environment, inclusion of the substrate and, finally, a systematic study of effects of the packing density are worthwhile directions to go.

**Acknowledgements**

This research was done in the framework of the IMPRS on Multiscale Bio-Systems. We thank Dr. G. Floß for most valuable discussions. We are grateful to Prof. W. Thiel for computational time for the DFT/MRCI calculations.

**Supporting Information**

Details on models and dynamical calculations; absorption spectra, spectral shift, and exciton splitting; CN and NN bond torsions during Brownian and photodynamics.
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(2) Valley, D. T.; Onstott, M.; Malyk, S.; Benderskii, A. V. Steric Hindrance of
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(4) Toniolo, A.; Ciminelli, C.; Persico, M.; Martínez, T. J. Simulation of the Photodynamics
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(7) Fabiano, E.; Groenhof, G.; Thiel, W. Approximate Switching Algorithms for Trajectory

(8) Weingart, O.; Lan, Z.; Koslowski, A.; Thiel, W. Chiral Pathways and Periodic Decay


4. Reprints


Supporting Information for:

“Dynamics of Azobenzene Dimer Photoisomerization: Electronic and Steric Effects”

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Details on models and dynamical calculations

The geometry of the trans-azobenzene (AB) monomer in the electronic ground state was optimized at the B3LYP/6-31G* level of theory using Gaussian 09 (Revision D.01). The minimum nature of the obtained structure was proven by vibrational frequency analysis, which yielded only real frequencies. The geometry of the monomer was found to be planar. This structure was used as a starting geometry for model (i) of the main text (monomer), but also for the dimer models (ii) (isolated dimer) and (iii) (“SAM” model).

The dimer model (ii) was constructed by applying a translation of 3.5 Å to all atoms of the optimized monomer in the direction perpendicular to the molecular plane. The “SAM” model (iii) was constructed by further translating AB monomers as shown in Fig. 1 (b–d) of the main text. Note that the simple translation was chosen for the dimer and “SAM” construction (instead of, e.g., optimization of the geometry with DFT plus a dispersion correction) to have the same intermolecular separation and molecular arrangement for the free dimer and the “SAM”, which can also be easily varied to study, e.g., packing density effects. For both the free and the vdW-constrained models, the four bottom atoms of the QM dimer, two carbons and two hydrogens, were frozen during the dynamics to keep two AB molecules together.

The potential energy surfaces (PESs), gradients and nonadiabatic couplings were calculated “on the fly” by means of semiempirical (reparameterized for the single AB molecule AM1) configuration interaction (CI), employing SCF molecular orbitals (MO) with floating occupation (FO) numbers (abbreviated as AM1/FOMO-CI) by using the development version of the MOPAC 2002 program. The active space (for all models) contained 22 electrons in 21 orbitals. In the CI, all single excitations within active space plus multiple excitations within complete active (sub)space (CAS) of 8 electrons in 6 orbitals were included. This method, denoted as AM1/FOMO-CI/(22,21)/(8,6), was used previously for the bisazobenzenes. Note that we did not use the added potential and state-specific corrections for the PESs, developed previously for the single AB molecule.
orbitals comprising the CAS are presented in Fig. S1. It is seen that the six frontier orbitals of the dimer correspond to the HOMO−1 (\(\pi\)), HOMO (\(n\)), and LUMO (\(\pi^*\)) of the monomer.

![Figure S1: Molecular orbitals comprising the complete active (sub)space (CAS).](image)

The vdW interactions for the “SAM” model were treated by means of the MM3-2000 force field\textsuperscript{S13,S14} with the help of the TINKER package.\textsuperscript{S15} The MM molecules were kept fixed during the simulation.

The first 15 singlet states (ground and 14 excited) were used for the surface hopping dynamics, for all models.

**Absorption spectra, spectral shift, and exciton splitting**

We calculated vertical absorption spectra of the *trans* monomer and the *trans–trans* dimer using various methods to judge on the performance of AM1/FOMO-CI approach used for the dynamics afterwards. Altogether 18 methods were used: AM1/FOMO-CI/(22,21)/(8,6); DFT/MRCI\textsuperscript{S16}/def2-SVP;\textsuperscript{S17,S18} TD-HF (see, *e.g.*, Refs. S19, S20)/6-31G*; TD-DFT (see, *e.g.*, Ref S21)/6-31G* with the following functionals: BHandHLYP (Gaussian 09 implementation, for “half-and-half” theory see ref. S22), M06-2X,\textsuperscript{S23} M06-
HF,\(^{24}\) CAM-B3LYP,\(^{25}\) LC-\(\omega\)-PBE,\(^{26}\) M11,\(^{27}\) \(\omega\)B97,\(^{28}\) \(\omega\)B97X,\(^{29}\) \(\omega\)B97X-D;\(^{29}\) CC2\(^{30}\) and ADC(2)\(^{31,32}\) with aug-cc-pVDZ basis set,\(^{33-35}\) as well as their spin-component scaled variants SCS and SOS.\(^{36}\) The TD-HF and TD-DFT calculations were done with Gaussian 09 (Revision D.01), the CC2 and ADC(2) calculations were performed with TURBOMOLE (Version 6.5).\(^{37}\) For the latter the resolution of the identity (RI)\(^{38,39}\) and the frozen core approximations were used. The auxiliary basis set for RI\(^{40}\) was also employed. DFT/MRCI calculations were done using TURBOMOLE (Version 6.3).\(^{41}\)

The vertical stick spectra were broadened with Gaussian functions:\(^{42}\)

\[
I(\lambda) = \sum_i f_i \exp \left( -\frac{1}{2\sigma^2} \left( \frac{1}{\lambda} - \frac{1}{\lambda_i} \right)^2 \right).
\]

Here, \(I\) is the absorbance (in arbitrary units), \(\lambda\) is the wavelength, \(\lambda_i\) and \(f_i\) are computed excitation wavelengths and oscillator strengths, respectively, \(\sigma\) is a broadening parameter (we chose (arbitrarily) \(\sigma = 1500 \text{ cm}^{-1}\)).

Excitation energies and oscillator strengths for the first 14 transitions for all the methods are tabulated in Tab. S1 (monomer) and Tab. S2 (dimer). The broadened spectra obtained with AM1/FOMO-CI, DFT/MRCI, TD-HF, TD-M11, CC2, and SCS-CC2 are presented in Fig. S2. In Fig. S2 the experimental wavelength, 301 nm (4.12 eV), is also shown. This wavelength corresponds to the maximal absorption of the \textit{trans}-AB monomer, recorded in gas phase.\(^{43}\)

From Fig. S2 it is seen that the semiempirical spectra are energetically close (in terms of a location of the \(\pi\pi^*\) absorption band) to the TD-HF ones, showing a blue shift with respect to other methods and to the available experimental gas-phase result.\(^{44}\) At the same time, the difference with modern range-separated density functionals (such as M11 or \(\omega\)B97) or the wave-function SCS-CC2 method is not very pronounced (~0.1–0.25 eV). Moreover, AM1/FOMO-CI shows the presence of doubly excited states, which are also found with DFT/MRCI. For example, on the AM1/FOMO-CI and DFT/MRCI levels the \(S_0 \rightarrow S_3\)
transition of the dimer has the double $n\pi^*$ character.

More specifically and returning to Tabs. S1 and S2 we note that for the monomer (Tab. S1) all the methods show that the $S_0 \rightarrow S_2 \ (\pi \rightarrow \pi^*)$ transition is the first bright transition, with oscillator strength ranging from 0.73 (SOS-CC2) to 0.91 (AM1/FOCI). The excitation energies for this transition are in the interval $3.79 \ (\text{DFT/MRCI}) - 4.59 \ (\text{M06-HF}) \ eV$, i.e., differing maximally by 0.8 eV.

For the dimer (Tab. S2), TD-HF and TD-DFT produce the 4th transition as the first bright transition, while with CC2 and ADC2 methods this first bright transition is the 6th one. AM1/FOMO-CI also shows the first bright transition to be the 6th one, whereas with DFT/MRCI this is the 9th transition. Excitation energies for the first bright state range from $3.72 \ (\text{DFT/MRCI})$ to $4.71 \ (\text{M06-HF}) \ eV$, i.e., differ maximally by 1 eV. The oscillator strength for this first bright transition of the dimer ranges from 0.97 (SOS-CC2) to 1.56 (DFT/MRCI). Here we should note that the original DFT/MRCI method$^{16}$ is not suitable for the description of the absorption of the dimeric systems.$^{34}$
Table S1: Excitation energies $\Delta E$ and oscillator strengths $f$ of the trans-azobenzene monomer

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Table S2: Excitation energies $\Delta E$ and oscillator strengths $f$ of the trans-azobenzene–trans-azobenzene dimer at the monomer separation of 3.5 Å.

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CAM-B3LYP | LCωPBE | M11 | ωB97 | ωB97X | ωB97X-D |
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CC2 | ADC(2) | SCS-CC2 | SCS-ADC(2) | SOS-CC2 | SOS-ADC(2) |
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Figure S2: Broadened and stick vertical absorption spectra of the monomer and the dimer calculated with various methods. Grey thick line represents experimentally detected gas-phase wavelength of maximal absorption, for the monomer. \cite{S43}
Next, we see that the dimerization causes small spectral shift ($\lesssim 0.2$ eV), mainly to the blue with exception of DFT/MRCI (see also Figs. S2 and S3), and the increase of the oscillator strength of the bright transition. This shift can be explained in terms of the molecular exciton theory, which predicts the splitting of the bright state in two states, the upper of which is allowed and the lower forbidden for a dimer composed of two identical monomers located side by side, as it is for our model — so-called exciton or Davydov splitting. The excitation energies of the split states in the dimer are $\Delta E_{\pm, \text{dimer}} = \Delta E_{\text{monomer}} \pm \frac{\Delta E_{\text{exciton}}}{2} + \Delta D$.\textsuperscript{S45, S46} Here $\Delta E_{\text{monomer}}$ is the excitation energy of the bright transition for the monomer, $\Delta E_{\text{exciton}}$ exciton splitting in the dimer, $\Delta D$ van der Waals correction. Usually $\Delta D < 0$, that leads to the red shift of the splitting origin relative to the monomer excitation energy.

We determined the exciton splitting from our first-principles calculations based on analysis of canonical and/or natural transition orbitals of the lowest transitions, up to the bright one.\textsuperscript{S42} The splitting turned out to be $\gtrsim 0.6$ eV (Fig. S3). The excitation energy differences corresponding to the exciton splitting of the bright transition are shown in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{exciton_splitting.png}
\caption{\label{fig:exciton_splitting} $\Delta E_{\text{exciton}} = \Delta E_{+, \text{dimer}} - \Delta E_{-, \text{dimer}}$ and $\Delta E_{\text{shift}} = \Delta E_{\text{dimer}} - \Delta E_{\text{monomer}}$ ($\Delta E_{\text{dimer}} = \Delta E_{+, \text{dimer}}$).}
\end{figure}
Tab. S3. It is also interesting to note that the found method dependence of the exciton splitting (Fig. S3) is quite moderate, however, it is more pronounced than for the tilted 4-nitroazobenzene dimer studied by us recently.\textsuperscript{S42}

Table S3: Excitation energy differences used to calculate the exciton splitting

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<th>Method</th>
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<tr>
<td>DFT/MRCI</td>
<td>$\Delta E_9 - \Delta E_4$</td>
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<td>TD-HF</td>
<td>$\Delta E_4 - \Delta E_3$</td>
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<tr>
<td>TD-DFT</td>
<td>$\Delta E_4 - \Delta E_3$</td>
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<tr>
<td>(SCS/SOS-)CC2, ADC(2)</td>
<td>$\Delta E_6 - \Delta E_3$</td>
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Finally, the absorption spectrum of the “SAM” model differs from the spectrum of the dimer, as it should be expected from the molecular exciton theory. We demonstrate this by using the TD-HF/6-31G* method calculating the spectrum of all twelve molecules of the “SAM” together (this approach can be refered to as the supermolecule approach). The result is shown in Fig. S4. In the monomer the bright transition at this level of theory is $S_0 \rightarrow S_2$. In the dimer, in agreement with the exciton theory, the bright transition is $S_0 \rightarrow S_4$, i.e., the first monomer excited state splits into two states in the dimer as well as the second (bright) monomer excited state does. In the “SAM” model the bright (the most intense) transition is $S_0 \rightarrow S_{24}$, that corresponds to the splitting of the second excited state of the monomer into 12 excited states of the “SAM” (and the splitting of the monomer first excited state into 12 states in the “SAM”). The bright transition in the “SAM” is blue-shifted by $\sim0.25$ eV in comparison to the dimer, the oscillator strength is $\sim3.8$ times larger.
Figure S4: Broadened and stick vertical absorption spectra of the monomer, the dimer, and the “SAM” model calculated with the TD-HF/6-31G* method. The bright transitions are labeled.

CN and NN bond torsions during Brownian and photodynamics

Brownian dynamics

The oscillator strength of the $n\pi^*$ transition ($S_0 \rightarrow S_1$) of trans-AB was shown to markedly depend on CN bond torsions of the phenyl rings and, to smaller extent, on the torsion of the NN bond. To explain the difference in the intensity of the $n\pi^*$ bands between the studied systems (see Fig. 2 (b) of the main text), we tracked the NNCC as well as CNNC dihedrals (see Fig. S5 for the definition of the angles) during the Brownian dynamics. The time-averaged values are presented in Tab. S4. From Tab. S4 it is seen that the molecules become on average more planar (bigger mean values of the dihedrals), meaning the smaller oscillator strength, when going from the monomer over the dimer to the “SAM”. This explains why we do not observe the enhancement of the absorption for the dimer in comparison to the monomer, as it would be expected from the exciton theory. Moreover, this explains the very weak absorption of the “SAM”. Also note that the standard deviations of the dihedrals decrease with model complexity.
Figure S5: Definition of the dihedral NNCC and CNNC angles. Fixed carbon atoms are shown in black, fixed hydrogen atoms in yellow. The geometry corresponds to the end of the Brownian trajectory for the isolated dimer.

Table S4: Time-averaged dihedral NNCC and CNNC angles (in degrees) for the Brownian trajectories

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<th>“SAM”</th>
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<td>171 ± 7</td>
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Photodynamics

Below we present the time evolution of the ensemble-averaged NNCC and CNNC dihedrals (Fig. S6) as well as the $n\pi^*-\pi\pi^*$ ($E_4 - E_3$) energy gap (Fig. S7) for the dimer and the “SAM”, while trajectories travel in any of the states of the $\pi\pi^*$ manifold. All trajectories (reactive, unreactive, and undetermined) were considered for this analysis. Note that, in general, the number of trajectories in the ensemble (used for averaging) depends on the time.
Figure S6: Time evolution of the ensemble-averaged NNCC and CNNC dihedrals, while trajectories are on any of the surfaces of the $\pi\pi^*$ manifold.

Figure S7: Time evolution of the ensemble-averaged $E_4 - E_3$ energy gap, while trajectories are on any of the surfaces of the $\pi\pi^*$ manifold.
References

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4. Reprints


4. Reprints


5. Discussion and Conclusions

The presented investigations address several aspects of widely-used molecular photoswitch azobenzene. In the first paper, we have estimated the reaction rate for the thermal back (cis $\rightarrow$ trans) isomerization of a set of AB-containing molecules upon electron attachment and withdrawal. In this paper, studying the thermal isomerization of azobenzenes in the solution containing gold nanoparticles, we have been guided by the hypothesis of an electron transfer between an AB derivative and a gold nanoparticle, which leads to formation of (i) an anion (electron attachment) or a cation (electron withdrawal) in the case of considered small azobenzenes, which are initially neutral, or (ii) a neutral (electron attachment) or a doubly positively charged cation (electron withdrawal) in the case of the used, originally cationic (in the reference state), surfactant.

Using hybrid DFT (namely, B3LYP), the calculated isomerization rates are enormously increased ($\sim 10^{12}$–$10^{15}$ times) upon the electron transfer, independently of its direction, i.e., from the molecule to the nanoparticle, or other way around. Since in our model we neglect an explicit treatment of gold nanoparticles, the explored problem reduces to the task about gas-phase isomerization of AB radicals with an added or removed electron. In this connection several previous works should be highlighted.

Neta and Levanon have measured transient absorption spectra of trans- and cis-AB solutions using spectrophotometric pulse radiolysis. They have observed that the spectra recorded after $\sim 1$ ms after the pulse are identical, suggesting that they correspond to a single structure. The authors have concluded that the radical detected upon reduction of AB is always trans$^-$, independent of the initial state (cis or trans), that can be achieved via very rapid cis$^-$ $\rightarrow$ trans$^-$ isomerization (proceeding at least on a submicrosecond time scale), when starting from the predominantly cis isomer solution.

Further, Laviron and Mugnier have used electrochemical methods to study the reduction of cis-AB. They have observed, in particular, no difference in polarograms for both isomers, and suggested the following rationalization of the experimental results: the one-electron reduction of the cis isomer ($cis^0 + e^- \rightarrow cis^-$) is followed by very fast isomerization of the formed cis anion to the trans anion ($cis^- \rightarrow trans^-$), which, in turn, reacts with a cis neutral through an electron-transfer path ($trans^- + cis^0 \rightarrow trans^0 + cis^-$), yielding the neutral trans isomer, and the cis anion radical.

The conclusion about very rapid isomerization of a cis-AB anion, based on the experimental findings in the late 1970s, is supported by quantum chemical computational investigations. Füchsel and co-workers have performed relaxed PES scans along the CNNC dihedral angle for a set of AB-containing molecules in neutral and anionic states. From these scans, in particular, the activation energy barriers for the cis $\rightarrow$ trans isomerization have been obtained and it has turned out that these barriers are 5–7 times (depending on the molecule) smaller upon electron attachment. We note that in ref. 19 the anion formation has been discussed in connection with the experiments on isomerization of azobenzenes with a scanning tunneling microscope (STM).
The lowering of the activation energy barriers in the anionic state has also been found by Chapman and Paci for another AB derivative. They have considered the potential rotation and inversion isomerization paths for the isolated molecule in gas phase as well as adsorbed in an upright conformation on a gold surface. For the adsorbed case the authors have also applied a static electric field, which is the case for an STM experiment. The barrier decrease upon electron attachment has been found to be more moderate on the surface. As in the previous study, the modeling has been motivated by the STM experiments, in particular those where an AB-containing molecule had been embedded in n-dodecanethiol SAM.

Recently, electron transfer has been proposed to be responsible for the observed, rapid thermal back isomerization of azobenzenes in the solution containing gold nanoparticles. Hallett-Tapley and co-workers have measured UV/Vis absorption spectra of small AB derivatives after addition pseudo-naked ~ 12 nm spherical gold nanoparticles to the solution pre-illuminated with UV light, i.e., containing mostly the molecules in the cis form. They have observed that the buildup of the trans isomer of the parent AB had been finished in 30 minutes, while in the control experiment, without gold nanoparticles, no significant changes in the absorption had been registered after this period. In this study the authors have suggested that upon interaction of AB with a gold nanoparticle an electron is transferred from the molecule to the particle, and the formed cis-AB cation radical isomerizes very fast to the trans form. Interestingly, cationic states of azobenzenes have been investigated with the aid of DFT in above mentioned theoretical works, and similarly to the anion case the reduction of activation barriers has been traced from the relaxed cationic PES scans.

A rapid cis → trans isomerization has also been reported for AB-containing sulfides confined in gold nanoparticle aggregates and for AB–oligoglycerol conjugates on cyclodextrin-coated gold nanoparticles. In ref. 34 the acceleration of the thermal back isomerization has been related with the weakening of the NN bond, without discussing the possible electron transfer mechanism. In ref. 36 apart from the electron-transfer mechanism the potential role of a plasmon resonance of gold nanoparticles is mentioned, which, in our opinion, may be ruled out, since the thermal isomerization is a process which can happen in the dark, where no optical illumination to excite plasmons is provided (except for the light source of a spectrophotometer).

Simoncelli and Aramendia have reported a 10\(^1\)–10\(^6\)-fold enhancement of the back isomerization for a set of azobenzenes in the presence of ~ 15 nm diameter gold nanoparticles. We note that a sub-nanomolar amount of gold nanoparticles has been enough to accelerate the cis → trans isomerization, showing that gold nanoparticles are truly catalysts for the thermal back isomerization.

Recently, the accelerated back isomerization of an AB-containing surfactant has been found in the solution of bare ~ 10 nm gold nanoparticles. Such a surfactant has been utilized previously for the studies of photoreversible DNA compaction.

Our work, presented in this dissertation (paper 142), complements the investigations outlined above. In contrast to previous approaches, considering specific paths along certain coordinates (either CNNC dihedral or CNN bond angles) we have optimized TSs for species with an added or removed electron. We have considered both directions of a charge transfer, since a priori it is difficult to exclude one of them. The simple
estimate of ion formation energies, utilizing the gas-phase electron affinity (for an anion) or ionization potential (for a cation), gold work function, and image charge interaction term suggests the easier formation of the cation than the anion in the vicinity of a gold surface.\textsuperscript{42}

Paper 1 (ref. 42) also provides the information about activation energy and activation Gibbs free energy of the thermal back isomerization for reference states of the studied AB-containing compounds, i.e., the neutral small azobenzenes and the cationic large surfactant. We list additional activation parameters in Tab. A.1. Specifically, we present there zero-point energy (ZPE) corrected activation energies, activation enthalpies and activation entropies. While the activation enthalpies are usually in good agreement with experiments, the activation entropies are found to be rather small and positive, in contrast to experiments. In fact, the activation entropies computed for the gas phase or within a polarizable continuum model (PCM) have been reported to largely deviate from experimentally determined values, measured for azobenzenes in solution.\textsuperscript{26,127}

Apart from the explicit solvent effect, the anharmonicity of molecular vibrations can play a role. Namely, thermodynamic properties (including the entropies) are typically calculated with the help of harmonic frequencies—this approximation may not be valid for low-frequency modes of large molecules. Thus, we have made an attempt to take account of the anharmonicity by introducing the calculation scheme described in appendix B.

Paper 2 (ref. 44) included in this dissertation considers the photophysics of azobenzenes and investigates the excited states of 4-nitroazobenzene, specifically upon dimerization and adsorption on a silicon surface. The excited states of the monomers of AB and its derivatives have been previously addressed with different methods, such as TD-DFT,\textsuperscript{128,129} CIS,\textsuperscript{128} ZINDO/S,\textsuperscript{128} CC2,\textsuperscript{18} SOPPA,\textsuperscript{130} ADC(2),\textsuperscript{131} ΔSCF,\textsuperscript{132} quantum Monte Carlo.\textsuperscript{133,134} The $S_0 \rightarrow S_1 \left( n \rightarrow \pi^* \right)$ transition of the trans isomer of AB, when computed at the optimized geometry, which is found to be planar in gas phase,\textsuperscript{18,135} has a zero oscillator strength. Vibrational motion, leading to the deviation from the equilibrium structure, renders the $S_0 \rightarrow S_1$ transition allowed, but weak in intensity.\textsuperscript{136} The $S_0 \rightarrow S_2 \left( \pi \rightarrow \pi^* \right)$ transition of the trans-AB is much more intense, and allowed at the equilibrium planar geometry. Substituents on the phenyl rings can result in additional specific excited states, e.g., with partial charge transfer involving the given substituent, as demonstrated in our paper for 4-nitroazobenzene.\textsuperscript{44} Such excited states can energetically settle between the already mentioned $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ states.\textsuperscript{44} Both $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions are allowed for the optimized cis-AB.\textsuperscript{18}

The excited states of the dimeric AB systems are less intensively studied. However, several reports can be found in literature. Here one can distinguish between non-covalently interacting, e.g., via vdW interactions, and covalently bound dimers or oligomers of azobenzenes. Utecht and co-workers have used TD-B3LYP to compute vertical excitation energies of non-covalently bound dimers and oligomers (in 1D and 2D arrangements) of an AB derivative, to study the exciton splitting in SAMs.\textsuperscript{39} The obtained spectra have been rationalized based on the simple molecular exciton theory.\textsuperscript{84,85} It has been observed that at small intermolecular distances, namely $< 4.5$ Å, the calculated absorption spectra do not match the expectations from the molecular exciton theory. Particularly, both, red- and blue-shifted transitions (relative to the
5. Discussion and Conclusions

bright transition of the monomeric unit) with sizable oscillator strengths have been obtained, whereas the simple exciton theory would predict always a blue shift for the H aggregates under study.

The absorption spectra of covalently bound dimers\textsuperscript{137,138} and trimers\textsuperscript{138} have also been reported, on different levels of theory. In ref. 137 TD-DFT (namely, TD-B3LYP) has been applied to bisazobenzenes, having three or four phenyl rings with connection of AB units through \( \text{para} \) position. For the \textit{trans–trans} species, a red shift with respect to the \textit{trans} monomer has been found with magnitude depending on the degree of conjugation. In ref. 138 also a red shift for the all-\textit{trans} dimeric and trimeric multiazobenzenes has been found when comparing to the \textit{trans} monomer, using the CC2 method. Notably, the authors have reported the splitting of about 0.6 eV for \( \pi \rightarrow \pi^* \) states (corresponding to the \( S_4 - S_3 \) energy difference) in the dimer (named BPAPA in that work), with the enhanced \( S_0 \rightarrow S_3 \) transition and the \( S_0 \rightarrow S_4 \) transition being almost dark.\textsuperscript{138}

In paper 2 (ref. 44) we have demonstrated, for the example of a 4-nitroazobenzene H-like dimer, that density functionals which include relatively low fraction of exact exchange, ca. \(< 50 \%\), lead to spurious charge-transfer excited states, or admixture of charge transfer to the local excitations, for the dimers of azobenzenes. This problem of certain density functionals (local, semilocal, global hybrids with small amount of exact exchange) has been shown and explained (by the self-interaction error) for other dimers and big molecules previously.\textsuperscript{139–145}

We have deduced the exciton splitting from first-principles calculations, identifying the nature of electronically excited states with the aid of the NTO analysis.\textsuperscript{44} This analysis, utilizing the singular value decomposition of an electronic single-particle transition density matrix, transforms the set of conventional molecular orbitals to the so-called “hole” and “particle” contributions, usually resulting in the reduction of dominant orbital pairs, describing the transition in question. As a side remark we note that the procedure similar to that described in ref. 98 has also been proposed in other works\textsuperscript{146,147} for the analysis of configuration interaction singles (CIS) wave functions.

The determined exciton splitting of about 0.3 eV has turned out to be substantially method-independent, provided that a suitable method is used (TD-HF, CC2, range-separated functionals, or global hybrids with relatively large fraction of exact exchange (ca. \( \geq 50 \% \))). This value for the exciton splitting has been calculated at the geometry obtained from dispersion-corrected DFT (B3LYP+D3\textsuperscript{148}) optimization of the dimer on a silicon nanocluster. This geometry is slightly tilted relative to the surface normal, and the corresponding distance between the centers of monomeric coordinates is about 3.6 Å. For the sandwich dimer obtained by translation of the optimized monomer in the direction perpendicular to the molecular plane the exciton splitting is more than two times greater and amounts to 0.65 eV (on the CC2/aug-cc-pVDZ level) at the same intermolecular separation (3.6 Å). For a bit smaller distance of 3.5 Å the exciton splitting increases further, to 0.76 eV (on the same, CC2/aug-cc-pVDZ, level). Thus, seemingly slight changes in molecular arrangement and separation result in a substantial change of the exciton splitting in the studied dimer.

The exciton splitting in the dimer can be related to the excitation transfer time between molecules, specifically, \( \tau = \frac{\hbar}{2\Delta E_{\text{exciton}}} \) (see, e.g., ref. 149) for a simple Rabi-type
model accounting only for two $\pi \to \pi^*$ monomeric states. Using the calculated splitting of $\sim 0.3$ eV (the lowest among those mentioned above), one obtains a transfer time of $\sim 7$ fs, that is much smaller than typically needed for isomerization. We stress, however, that this estimate is rather simple, and dynamical simulations accounting for multiple excited states are desired to answer the question of isomerization possibility in densely packed environments.$^{31,32,39,45,150}$ Moreover, we note that the exciton splittings calculated from vertical or adiabatic energy differences, relying inherently on the Born–Oppenheimer (fixed-nuclei) approximation, are several times larger than those experimentally determined for the case of weakly coupled hydrogen-bonded dimers, and are quenched due to vibronic coupling in such dimers.$^{151–155}$ Therefore, we can expect diminished splittings for the AB dimers, when accounting for vibronic couplings.

Remarkably, the shift in excitation energy of the bright $\pi \to \pi^*$ transition upon dimerization has been found to be very small, $\sim 0.05$ eV, in ref. 44 when using free dimers, which are in H-type orientation. The direction of the shift, either to the blue or to the red, depends on the method. The smallness of this shift points out the importance of the vdW correction, causing the red shift of the splitting origin relative to the monomeric excitation energy. Therefore, the elucidation of exciton splittings simply from spectral shifts is questionable.

Further, the grafting of azobenzenes directly to a silicon surface shifts absorption to the red, at least for the 4-nitroazobenzene system studied by us, which was covalently linked to a silicon nanocluster.$^{44}$ In the case of the considered adsorbed dimer, apart from the relatively small distance (of $\sim 3.6$ Å) between photochromic units, the covalent linkage is additionally realized between two molecules, by means of Si atoms of the cluster. The exciton splitting, similar to the one calculated for the free dimer, has been obtained for the dimer connected to the silicon nanocluster. Notably, this conclusion has been made based on the TD-HF and TD-DFT calculations; CC2 gives a different absorption picture of the adsorbed dimer (Fig. C.1, for 4-nitroazobenzene; cf. Fig. 6 of paper 2 (ref. 44)), deviating larger from expectations based on the molecular exciton theory. Two strong bright transitions arise here for the dimer on Si Penta, $S_0 \to S_4$ and $S_0 \to S_8$, bearing a certain contribution from a silicon cluster, and the $S_4 - S_8$ energy difference is about 0.24 eV, in comparison with the exciton splitting of $\sim 0.30$ eV obtained from TD-DFT. Moreover, the difference with the exciton splitting in the free dimer is somewhat pronounced (cf. 0.31 eV for the free dimer, on the CC2 level). The CC2 results are mostly resembled with the results obtained using another wave function-based, post-Hartree–Fock method, ADC(2)$^{156,157}$ (Fig. C.1).

The third paper (ref. 45), presented in this dissertation, deals with the nonadiabatic molecular dynamics (MD) of AB switching, particularly in the free dimer and the dimer embedded in the SAM-like environment of “classical” MM azobenzenes, elucidating the isomerization in densely packed SAMs. The experimental works on AB-containing SAMs report strong suppression of photoisomerization at high grafting densities of molecules on a surface.$^{31,32,38}$ The discussed factors responsible for this suppression are the steric hindrance and exciton coupling between neighboring molecules.$^{31}$ The latter is supposed to promote the ultrafast excitation transfer in a SAM. The models built and investigated with the aid of nonadiabatic MD in paper 3$^{45}$ and ref. 150 allow to address the potential reasons responsible for the hindered isomerization. Being
nonadiabatic, this approach is also free of possible overestimation of exciton coupling of Born–Oppenheimer-type quantum chemistry as discussed above.

Generally, there are two main approaches to investigate pathways of isomerization: (i) calculating and analyzing PESs and (ii) performing directly dynamical simulations. Pioneering theoretical PES calculations of AB employing CI have suggested that isomerization occurs via inversion upon $S_0 \rightarrow S_1$ excitation (as well as for the ground-state reaction), and rotation upon the $S_0 \rightarrow S_2$ excitation.\(^{27}\) This view has mostly been supported by CASSCF and multireference perturbation theory calculations, which note, though, that the rotational pathway upon the $S_0 \rightarrow S_1$ excitation cannot be excluded.\(^{158}\) In the subsequent work by the Orlandi group it has been concluded that isomerization initiated with excitation to $S_1$ occurs via rotation.\(^{29}\) Moreover, a doubly excited intermediate state has been found for the photoisomerization path upon excitation to the $S_2$ state.\(^{159}\) Very recent work\(^{25}\) on isomerization pathways of AB, explored by means of a CASSCF/CASPT2 approach, draws an extended, more complicated picture of the isomerization mechanism: Accordingly, after excitation of the trans isomer to the $S_2$ state the relaxation through a pedal-like non-rotated geometry to $S_1$ takes place, from where the molecule can relax either through rotated (CNNC dihedral $\sim 90^\circ$, more favored pathway) or planar (CNNC dihedral $\sim 180^\circ$, less favored pathway) geometries of the $S_1/S_0$ conical intersection seam to the ground state. Furthermore, an additional pathway of $S_2$ decay exists, implying the crossing with a doubly-excited singlet state at slightly rotated (CNNC dihedral $\sim 140^\circ$) geometry.

The photoisomerization dynamics of a monomer of AB and its various derivatives have been extensively modeled for more than ten years to date.\(^{11,23,24,101–114}\) In 2004 Persico, Granucci and co-workers reported the simulation of trans $\rightarrow$ cis and cis $\rightarrow$ trans isomerization dynamics upon the lowest $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations, employing a surface hopping scheme and “on the fly” calculations of PESs as well as electronic wave functions on a semiempirical level (AM1/FOMO-CI).\(^{11}\) It has been concluded that for all four cases the isomerization proceeds through the torsion around the NN bond. Apart from the mechanism of isomerization the modeling of dynamics allows one to determine quantum yields, by running multiple MD trajectories and counting successful events (those trajectories, which result in isomerization). In ref. 11 the quantum yields have been computed and found to be in satisfactory agreement with experiments. It has been obtained that the quantum yield for the cis $\rightarrow$ trans isomerization is larger than that for the trans $\rightarrow$ cis isomerization, and for both isomerization directions the quantum yield is larger upon the $n \rightarrow \pi^*$ excitation than the $\pi \rightarrow \pi^*$ one.

Subsequent simulations of AB isomerization dynamics performed by Marx and co-workers using the restricted open-shell Kohn–Sham (ROKS) approach to model the $S_1$ excited state have shown that the change in the central (CNNC) dihedral during isomerization occurs mostly due to motion of nitrogen atoms,\(^{24}\) resembling the pedal motion.\(^{24}\) The subsequent movement of phenyl rings completes the isomerization reaction.

The isomerization dynamics has also been modeled in solution,\(^{102,103,115}\) in the liquid state,\(^{23,24}\) and on surfaces.\(^{116,117}\) For the latter, vdW interactions with a surface lead to reduced quantum yields. Interestingly, a large decrease of the quantum yield has been found for a model of the covalently bound H-like dimer, where one of the molecules has
been treated on a MM level.\textsuperscript{79}

In our study,\textsuperscript{45} motivated by the challenge of AB isomerization in densely packed monolayers, we have treated two AB molecules on the QM level (AM1/FOMO-CI), and the rest of molecules (presenting in the “SAM” model) on the MM level (the MM3-2000 force field). Modeling of the isolated QM dimer has revealed that the quantum yield is very similar to the single molecule case. On contrary, the steric hindrance imposed by fixed perimeter molecules causes the pronounced reduction of the quantum yield. Moreover, we have demonstrated that the geometry of the formed \textit{cis} isomer differs substantially for free and vdW-constrained dimers, what highlights the steric hindrance effect. The isomerization mechanism observed in our investigation is complex and has a mixed behavior. It involves the increase in the bond NNC angles in the excited states with eventual rearrangement of the CNNC atoms to the \textit{cis} form.

Remarkably, the very recent simulations of Persico, Granucci, and co-workers, considering a single QM molecule of azobiphenyl in rather large movable MM SAM, manifest the isomerization suppression in densely packed SAMs of azobiphenyls on a gold surface, and demonstrate the importance of defects as nuclei for the isomerization reaction.\textsuperscript{150}

In conclusion, this dissertation contributes to the field of molecular photoswitches, more specifically, azobenzene-containing molecules. The ground-state calculations of minima and TS for azobenzenes with added/removed electrons demonstrate reduced activation barriers for the thermal \textit{cis} $\rightarrow$ \textit{trans} isomerization, which supports the hypothesis of a charge transfer as a key trigger for rapid back isomerization in the AB solutions containing gold nanoparticles. The estimate of “energy costs” needed for ion formation from neutral small azobenzenes in the vicinity of a gold surface indicates the more preferable cation formation over an anion. The activation parameters for reference (neutral for small \textit{para}-substituted azobenzenes and cationic for the surfactant) states are presented, and a scheme of anharmonic corrections to the activation entropy is proposed and realized for the parent AB molecule. We have found (appendix B) that the account of anharmonicity leads to the decrease of activation entropy.

Further, the electronically excited states of 4-nitroazobenzene and AB are thoroughly investigated, specifically for the case of molecular dimers and molecule–surface (4-nitroazobenzene–silicon nanocluster) composites. Natural transition orbital (NTO) analysis has allowed us to determine the nature of excited states and establish the split Davydov pairs in question, thereby providing the way to deduce exciton splitting magnitudes from first-principles calculations. The spectral shift upon dimerization is small (for the studied 4-nitroazobenzene dimer), and together with sizable exciton splitting points out the significance of van der Waals corrections in the exciton model. We have shown, via comparison of different excited-state methods, that large fraction of exact exchange or range-separation is required for DFT-based methods to describe absorption of the dimer properly. The determined exciton splitting is fairly method-independent, among the appropriate methods. The covalent grafting to silicon leads to a red shift of the low-lying bright states. At the TD-HF and TD-DFT (with suitable functionals) levels of theory the expectations from the exciton model are justified.

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to a large extent for the adsorbed dimer. However, post-Hartree–Fock, WFT-based methods (CC2, ADC(2)) considerably deviate from the anticipated scenario, indicating the complicated interplay between photoswitches and silicon.

Next, the results of direct photoisomerization simulations, employing the surface hopping nonadiabatic molecular dynamics, show that the quantum yield of switching for the isolated dimer (treated entirely quantum-mechanically) is similar to the one for the monomer. In contrast, the steric hindrance, imposed on the dimer via vdW interactions with the environment, causes a decrease of the quantum yield. In this way, the steric effects dominate over exciton coupling, for the examined models. In addition, the excited-state lifetimes are affected by both dimerization and the vdW constraint. Moreover, the \textit{cis} isomer geometries, which are the outcome of switching, are more open in the sterically confined case. This demonstrates the direct effect of confinement on structure of the reaction product.
Appendices

A. Activation parameters of the thermal cis $\rightarrow$ trans isomerization of azobenzenes

Table A.1. Activation parameters of the thermal cis $\rightarrow$ trans isomerization of azobenzenes

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\Delta\varepsilon$ (eV)</th>
<th>$\Delta(\varepsilon + \text{ZPE})$ (eV)</th>
<th>$\Delta H^a$ (eV)</th>
<th>$\Delta S^a$ (cal mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G^a$ (eV)</th>
<th>$k_{c\rightarrow t}^a$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB$^b$</td>
<td>1.10</td>
<td>1.04</td>
<td>1.05</td>
<td>4.726</td>
<td>0.99</td>
<td>$1.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>4-CH$_3$-AB$^b$</td>
<td>1.08</td>
<td>1.03</td>
<td>1.03</td>
<td>3.920</td>
<td>0.98</td>
<td>$1.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>4-OCH$_3$-AB$^b$</td>
<td>1.06</td>
<td>1.01</td>
<td>1.01</td>
<td>2.096</td>
<td>0.98</td>
<td>$1.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>4-NH$_2$-AB$^b$</td>
<td>1.04</td>
<td>0.98</td>
<td>0.98</td>
<td>1.819</td>
<td>0.96</td>
<td>$3.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>4-CF$_3$-AB$^b$</td>
<td>0.98</td>
<td>0.93</td>
<td>0.93</td>
<td>0.801</td>
<td>0.92</td>
<td>$1.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>4-NO$_2$-AB$^b$</td>
<td>0.83</td>
<td>0.80</td>
<td>0.79</td>
<td>0.052</td>
<td>0.79</td>
<td>$2.8 \times 10^{-1}$</td>
</tr>
<tr>
<td>AzoC$_6$$^c$</td>
<td>1.16</td>
<td>1.10</td>
<td>1.11</td>
<td>5.661</td>
<td>1.04</td>
<td>$1.6 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

$^a$ at $T = 298.15$ K  
$^b$ neutral  
$^c$ cation

In Tab. A.1 the following notations are used:

- $\varepsilon$: energy of a point on the ground-state PES
- ZPE: zero-point energy
- $H$: enthalpy
- $S$: entropy
- $G$: Gibbs free energy
- $k_{c\rightarrow t}$: cis $\rightarrow$ trans isomerization rate
- $T$: temperature
- $\Delta\cdot$: $\bullet$(TS) $-\bullet$(cis)

B. Anharmonic corrections to activation entropy of the thermal cis $\rightarrow$ trans isomerization of azobenzene

In the following, we present a scheme by which “diagonal” anharmonicities (without couplings between different modes) are considered for the computation of (activation) entropies for the isomerization of azobenzenes.

We consider a set of uncoupled 1D anharmonic oscillators upon Cartesian
displacements along normal modes:

\[ \mathbf{q}_i(f) = \mathbf{q}(0) + f \Delta \mathbf{q}_i, \quad i = 1, \ldots, 3\tilde{N} - 6, \]

where \( \mathbf{q}(0) \) is the minimum geometry (standard orientation from Gaussian 09 output), \( \{ \Delta \mathbf{q}_i \}_{i=1,\ldots,3\tilde{N}-6} \) are Cartesian displacements corresponding to normal modes (from Gaussian 09 frequency calculations, in Å, \( \| \Delta \mathbf{q}_i \| = \sqrt{(\Delta q_{i,x}, \Delta q_{i,y}, \Delta q_{i,z})} = 1 \) Å), \( \tilde{N} \) is the number of atoms in the molecule, \( f \) is a scalar scaling factor (dimensionless).

After calculation of the points of the 1D PESs (with the B3LYP/6-31G* method in our case) at different \( f \) values we use polynomials of the following forms:

\[ V_i(f) = a_i f^2 + b_i f^4 \text{ or } V_i(f) = a_i f^2 + b_i f^4 + c_i f^3 \]

(B.2)

Figure B.1. The polynomial fit of PES points along the lowest frequency mode (mode 1) of cis-AB.

Solving a 1D nuclear Schrödinger equation (1D SE):

\[ \left[ -\frac{\hbar^2}{2m_i} \frac{d^2}{df^2} + V_i(f) \right] \psi(f) = E_i \psi(f) \]  

(B.3)

with potential \( V_i(f) \) for mode \( i \) numerically we obtain a set of eigenvalues \( E_{i,n} \). These can be used to get a contribution to the vibrational entropy from mode \( i \) \( S_{i,vib} \), by
calculating corresponding partition function $Z_i$: \(^{161}\)

\[
S_{i,\text{ vib}} = R \left( \ln Z_i + T \frac{\partial \ln Z_i}{\partial T} \right) = R \left( \ln Z_i + \frac{T}{Z_i} \frac{\partial Z_i}{\partial T} \right) = R \left( \ln Z_i + \frac{\beta}{Z_i} \sum_{n=0}^{\infty} E_{i,n} \exp(-\beta E_{i,n}) \right). 
\]

(B.4)

The partition function is given as:

\[
Z_i = \sum_{n=0}^{\infty} \exp(-\beta E_{i,n}), \quad \beta = \frac{1}{k_B T}. 
\]

(B.5)

In practice the sum over $n$ goes to some finite value of $n$.

As a mass $m_i$ the mass for the corresponding normal mode from a Gaussian 09 frequency calculation is used. We can consider $f$ to be in Å whereas $\|\Delta q_i\| = 1$. Then, working in eV, we use $h$ in eV·s and transform $mf^2$ from amu·Å\(^2\) to eV·s\(^2\) to be employed for solving (B.3).

To numerically solve (B.3) we use the discrete variable representation (DVR) described in ref. 162. The DVR of the kinetic energy operator $\hat{T} = -\frac{\hbar^2}{2m_i} \frac{d^2}{df^2}$ has the following form:

\[
T_{jj'} = \frac{\hbar^2 \pi^2}{4m_i(2L)^2} \left[ \frac{2K^2 + 1}{3} \frac{1}{\sin^2\left(\frac{\pi j}{K}\right)} \right] \quad \text{for } j = j',
\]

\[
T_{jj'} = \frac{\hbar^2 \pi^2}{4m_i(2L)^2}(-1)^{j-j'} \left[ \frac{1}{\sin^2\left(\frac{\pi (j-j')}{2K}\right)} \frac{1}{\sin^2\left(\frac{\pi (j+j')}{2K}\right)} \right] \quad \text{for } j \neq j'.
\]

(B.6)

The grid \(\{f_j\}\) for the DVR is equally spaced:

\[
f_j = -L + \frac{2L}{K} j, \quad j = 1, \ldots, K - 1.
\]

(B.7)

We set $L = 10$ and $K = 2000$ in our calculations.

The results are summarized in Tab. B.1, where harmonic and anharmonic frequencies along with harmonic $S_{i,\text{ vib}}^{\text{h}}$ (from Gaussian 09 output) and anharmonic $S_{i,a}^{\text{vib}}$ entropies for the first 8 modes of the cis isomer (modes 1–8) and TS (modes 2–9) are collected. (In passing we note that fitting of PES points has been performed with gnuplot 4.6.) From Tab. B.1 one can see that anharmonic entropies are smaller than harmonic ones. Notably, the difference between $S_{i,a}^{\text{vib}}$ and $S_{i,h}^{\text{vib}}$ is especially large for the first (low frequency) modes (Fig. B.2).
Table B.1. Harmonic and anharmonic frequencies, contributions to vibrational entropy, and \( V_i(f) \) fits used for cis isomer and TS of azobenzene

<table>
<thead>
<tr>
<th>( i )</th>
<th>( \tilde{\nu}_{i,h} ) (cm(^{-1}))</th>
<th>( \tilde{\nu}_{i,a} ) (cm(^{-1}))</th>
<th>( S_{i,h}^{\text{vh}} ) (cal·mol(^{-1})·K(^{-1}))</th>
<th>( S_{i,a}^{\text{vh}} ) (cal·mol(^{-1})·K(^{-1}))</th>
<th>( V_i(f) ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>44.7377</td>
<td>66.5340</td>
<td>5.037</td>
<td>3.6745</td>
<td>0.0207104(f^2) + 0.0330322(f^4)</td>
</tr>
<tr>
<td>2</td>
<td>46.9247</td>
<td>68.4882</td>
<td>4.943</td>
<td>3.8154</td>
<td>0.031599(f^2) + 0.0198153(f^4) + 0.0038205(f^6)</td>
</tr>
<tr>
<td>3</td>
<td>69.9965</td>
<td>84.5800</td>
<td>4.153</td>
<td>3.5250</td>
<td>0.0503001(f^2) + 0.0249623(f^4) - 0.00457472(f^6)</td>
</tr>
<tr>
<td>4</td>
<td>158.2266</td>
<td>166.6526</td>
<td>2.571</td>
<td>2.4384</td>
<td>0.242451(f^2) + 0.0506146(f^4)</td>
</tr>
<tr>
<td>5</td>
<td>173.7629</td>
<td>179.8804</td>
<td>2.394</td>
<td>2.2955</td>
<td>0.3004(f^2) + 0.0997681(f^4) - 0.0794405(f^6)</td>
</tr>
<tr>
<td>6</td>
<td>274.2476</td>
<td>273.9429</td>
<td>1.569</td>
<td>1.5683</td>
<td>0.621841(f^2) + 0.0357044(f^4) - 0.00317366(f^6)</td>
</tr>
<tr>
<td>7</td>
<td>284.8410</td>
<td>288.7696</td>
<td>1.504</td>
<td>1.4780</td>
<td>0.926301(f^2) + 0.0916123(f^4)</td>
</tr>
<tr>
<td>8</td>
<td>412.8750</td>
<td>414.2553</td>
<td>0.917</td>
<td>0.9110</td>
<td>0.958345(f^2) + 0.0944081(f^4)</td>
</tr>
</tbody>
</table>

\(a\tilde{\nu}_{i,a} = \frac{E_{i,1} - E_{i,0}}{hc}\)

Figure B.2. The difference between harmonic \( S_{i,h}^{\text{vh}} \) (\( S_h \) in the plot) and anharmonic \( S_{i,a}^{\text{vh}} \) (\( S_a \) in the plot) entropies as a function of mode number.
The experimental value of the activation entropy $\Delta S = S(TS) - S(cis)$ of AB in hexane is $-12$ e.u. ($\text{cal mol}^{-1} \text{K}^{-1}$) ($-50.2 \text{ J mol}^{-1} \text{K}^{-1}$). The calculated value of $\Delta S$ in the gas phase is $+4.726 \text{ cal mol}^{-1} \text{K}^{-1}$ ($+19.774 \text{ J mol}^{-1} \text{K}^{-1}$) (B3LYP/6-31G*, Gaussian 09, harmonic approximation). Having the largest effect of anharmonicity on the first modes we correct $\Delta S$ as follows:

$$\Delta \tilde{S} = \Delta S_1 + \Delta S_2,$$

$$\Delta S_1 = \sum_{i=2}^{9} S_{vib,TS}^{vib,i} - \sum_{i=1}^{8} S_{vib,cis}^{vib,i},$$

$$\Delta S_2 = \Delta S - \left( \sum_{i=2}^{9} S_{i,h}^{vib,TS} - \sum_{i=1}^{8} S_{i,h}^{vib,cis} \right).$$

Using $\Delta S = 4.726 \text{ cal mol}^{-1} \text{K}^{-1}$ and the values of $S_{i,h}^{vib}$ and $S_{i,a}^{vib}$ from Tab. B.1 we get $\Delta \tilde{S} = 1.443 \text{ cal mol}^{-1} \text{K}^{-1}$ ($6.038 \text{ J mol}^{-1} \text{K}^{-1}$). Thus, we can conclude that the applied anharmonic corrections lead to a substantial decrease in activation entropy of the thermal $cis \to trans$ isomerization of AB.

Finally, the following remark is in place here. It might well be that the performed sampling of PES, utilizing Cartesian displacements, is not the best option. In general, the use of internal coordinates for construction of 1D potentials $\{V_i(f)\}$ should improve obtained results.164,165

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C. Absorption spectra of free and adsorbed on silicon 4-nitroazobenzene monomers and dimers from CC2 and ADC(2)

![Broadened vertical absorption spectra](image)

**Figure C.1.** Broadened vertical absorption spectra of the isolated 4-nitroazobenzene monomer (“monomer 0”) and dimer (“non-symmetric”) as well as the monomer on Penta and dimer on Penta models calculated at the CC2/aug-cc-pVDZ (left panel) and ADC(2)/aug-cc-pVDZ (right panel) levels of theory. Sticks show oscillator strengths. Broadening is identical to that of paper 2. The calculations have been performed with TURBOMOLE (Version 6.5).
Bibliography


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Publications authored by E. Titov

Publications composing this work


Other publications


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Erklärung

Hiermit versichere ich, dass die vorliegende Arbeit an keiner anderen Hochschule eingereicht sowie selbständig und ausschließlich mit den angegebenen Mitteln angefertigt worden ist.

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