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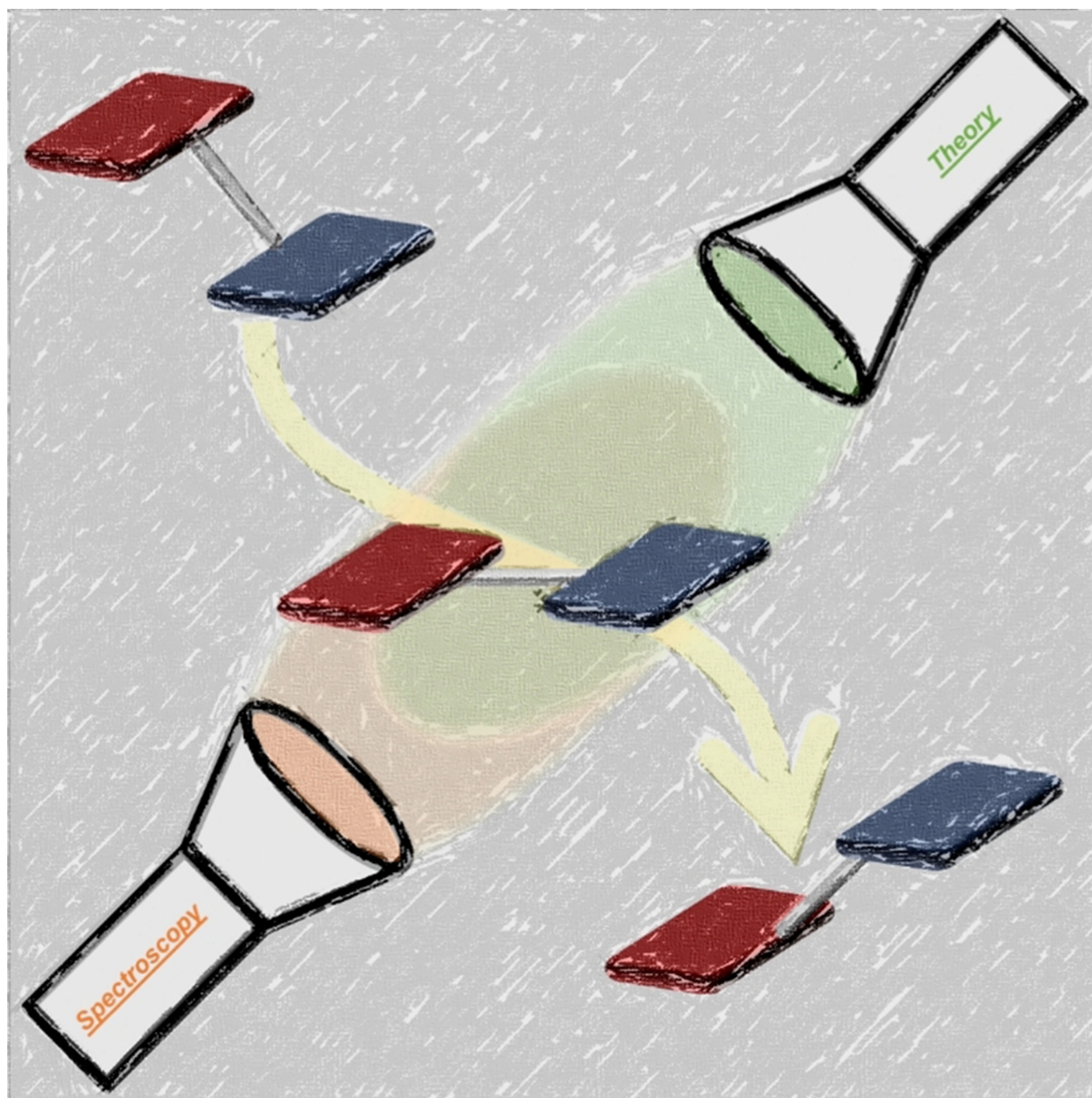
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# Light on the Structural Evolution of Photoresponsive Molecular Switches in Electronically Excited States

Saeed Amirjalayer\*<sup>[a]</sup> and Wybren Jan Buma\*<sup>[b]</sup>

**Abstract:** Stimuli-responsive materials are attracting extensive interest as they offer the opportunity to transform external inputs such as light into a functionality by control at the molecular level. As a result, a large number of molecular building units have been developed that enable switching between two or more states. Since the trajectory describing the transition between the various states defines the efficiency of the usually immobilized unit and the resulting functionality, it does not suffice to merely consider the initial and final states of the switching process. A key challenge is in fact to decipher at the atomic scale the actual motion that takes place after photoexcitation. Understanding and being able to manipulate this trajectory is crucial for an efficient implementation of photoactive molecular switches into functional materials, as well as to rationally develop novel tailor-made materials. In this Concept article, we highlight the potential to characterize in detail photoinitiated switching mechanisms by combining quantum chemical calculations with advanced laser spectroscopic techniques that probe the vibrational manifold of electronically excited states and its evolution.

## Introduction

The spatial and temporal control of molecular processes is essential to optimize elementary steps defining the functionality of materials for applications in for example, catalysis, medicine or molecular computing.<sup>[1]</sup> To design new functional materials with tunable properties, it is therefore highly desirable to be able to influence the structure, interactions and dynamics on the molecular level by external stimuli such as light, which can be employed to trigger selectively with a high space and time resolution. A key element in this regard are externally addressable and responsive molecular units that can be reversibly switched between various well-defined states differing in their chemical and/or physical properties. Triggering the interconversion between these states enables the user to influence the molecular environment by modifying intermolecular interactions.<sup>[2]</sup> Consequently, the switching of a single molecule can propagate over longer distances and result in a change of the

functionality of the whole system, effectively transmitting a response at the molecular level to the macroscopic world. A prototypical example from nature is the process of vision.<sup>[3]</sup> Here, the specific embedding of a photoactive unit in our eyes allows the incident light to initiate a cascade of processes leading to the function of vision by switching of this unit.<sup>[4]</sup>

Although a large number of biological processes are governed by molecular switching units, a direct implementation of these biological building units into artificial functional materials is not possible due to various limitations including synthesis and stability. Moreover, evolution in nature has been directed by considerations different from those normally aimed for in technological applications. Artificial responsive molecular systems that allow control over a macroscopic functionality thus require the development of new molecular switching units that are easily accessible and chemically robust, but still show a highly selective and efficient switching behavior.


However, in addition to the synthetic challenges to develop new photoactive molecular switching units, a detailed understanding of the operation mechanism in real time is necessary to rationally develop and optimize the photoactive unit (e.g., improvement of quantum yield). Furthermore, identifying the underlying trajectory of the molecular switching process after photoexcitation is essential to incorporate them into designated matrices, for example, in porous materials, on a surface, or in dynamic molecular environments. As highlighted by the process of vision, the embedding of the photoactive unit is one of the key elements to transfer the molecular switching property over large distances and to control the intended functionality on a macroscopic scale.<sup>[4]</sup>

One of the major challenges for following and understanding photoinitiated structural evolution is to identify the structural changes of the molecule that occur upon photoexcitation. For this, one intuitively tends to focus on identifying the structure of the molecule after that it has relaxed back to the electronic ground state. However, it should be realized that detection of ground-state conformers upon radiation that are different from the initial conformer only allows one to conclude that something has happened but not along which path. In particular, since both different structural coordinates and various electronic states can be involved upon light excitation, both theory and experiment are needed to obtain a complete picture.

From this point of view, vibrational spectroscopy provides a powerful tool to obtain unique fingerprints of a molecular species and its evolution by correlating measured vibrational spectra with corresponding quantum chemical calculations. At the same time, it allows one to capture time scales in the range of 100 fs to ns and beyond so that the full photoinitiated process including the excited-state dynamics of the molecular switch can be followed. Here, we report on our recent work on elucidating the excited states dynamics of photoactive molecular switches by combining studies of the vibrational manifold of electronically excited states with quantum chemical calculations. Both high-resolution gas-phase spectroscopy and time-resolved vibrational measurements in solution can be correlated with atomistic calculations providing a detailed picture of

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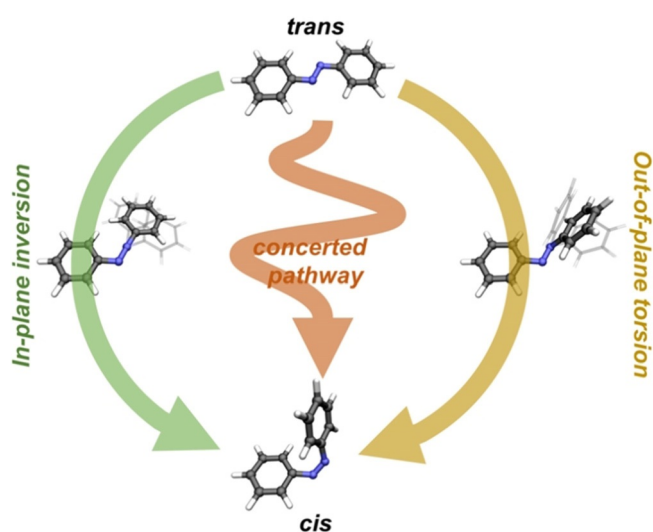


the molecular trajectory after excitation with light. Our goal is not to give a comprehensive overview of the literature but rather to highlight the potential (and necessity) of this approach, and thereby to stimulate more studies along this line.

## Forces Acting Directly after Photoexcitation of Azobenzene

Amongst the large number of molecular switches that have been developed over the years, azobenzene and its derivatives are one of the most employed building units to obtain photoresponsivity in functional materials. For instance, by embedding azobenzene derivatives in porous materials/zeolites the mobility of guest molecules can be controlled by light<sup>[5]</sup> or the interfacial properties can be changed by azobenzene-functionalized metal surfaces.<sup>[6]</sup> In all of these cases, isomerization of the N=N bond between the *trans* and *cis* states is at the core of the light-triggered phenomena. The two isomers differ significantly in their structural and physical properties (e.g., dipole moment and spatial extension) and are spectroscopically easily distinguishable. The detailed structural path followed by the molecule after photoexcitation, on the other hand, has until recently been subject of fierce discussions. The reason is that isomerization can in principle proceed along two pathways (or a mixture of these two) including a torsion around the N=N bond or an in-plane inversion about one of the nitrogen centers (Figure 1). Numerous experimental<sup>[7]</sup> and theoretical<sup>[8]</sup> studies on azobenzene and derivatives in different environments have been reported. However, although the theoretical studies provided a detailed picture of the dynamics a direct correlation with experimental results remained challenging leading to conflicting conclusions on the excited-state dynamics and the corresponding isomerization pathway.

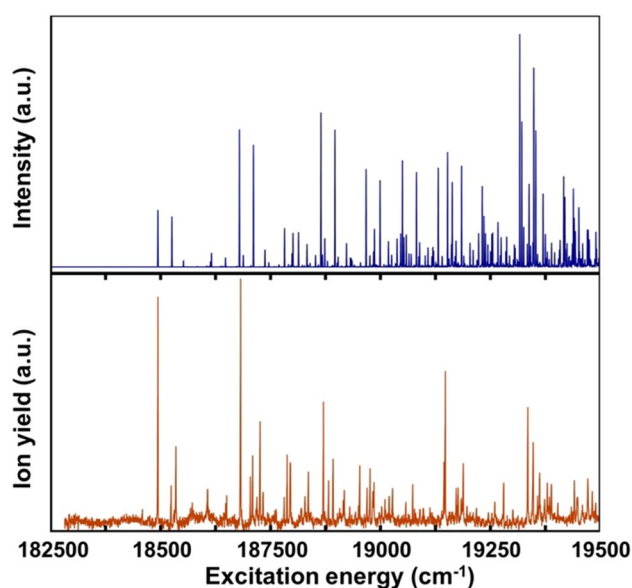
In particular, the question which forces act on the molecule after excitation was for a long time unanswered. Here, experimental studies focusing on the potential energy surfaces of



**Figure 1.** Potential pathways for the isomerization of *trans*-azobenzene to *cis*-azobenzene: inversion (green) or torsion (yellow) around the N=N centers or a concerted pathway (orange) involving both structural coordinates.

the relevant excited states under isolated molecule conditions are required.<sup>[9]</sup> Understanding these intrinsic excited-state dynamics of the azobenzene units are important for designing of corresponding light-responsive functional materials.

High-resolution gas-phase laser spectroscopic studies have recently provided answers to this question.<sup>[10]</sup> Operating in the frequency domain instead of the usually considered time domain afforded a direct insight into the vibrational manifold of the electronic excited states. Measurements under molecular beam conditions yielded excitation spectra with series of distinct but also complex spectral features that directly reflected the initial forces acting on *trans*-azobenzene after photoexcitation and the structural pathways resulting from these forces. However, to decipher and assign the observed bands, excited-state calculations simulating the spectra needed to be employed (Figure 2).



**Figure 2.** Experimental (lower trace) and predicted (upper trace) excitation spectrum of  $S_1 \leftarrow S_0$  transition of *trans*-azobenzene.

Combining these calculations with the measured spectra, it has become clear that excitation of the  $S_1(n\pi^*)$  state leads to activation of a symmetric in-plane bending mode associated with changes in the hybridization angles of the nitrogen atoms. The importance of this mode has been discussed before.<sup>[7h,j,8g,k,11]</sup> On the basis of this activity one would be tempted to conclude that in-plane inversion is the dominant structural relaxation path along which isomerization of *trans*-azobenzene takes place. However, excitation of the  $S_1(n\pi^*)$  state is dipole-forbidden and can only take place by vibronic coupling to other electronic states. Remarkably, the same studies found that such a coupling most effectively takes place if the CNNC torsional mode is excited. Thus, accessing the  $S_1(n\pi^*)$  state intrinsically activates motions directly related to the torsional isomerization pathway around the N=N bond. One therefore needs to conclude that both in-plane inversion as well as torsion are involved in the isomerization pathway of *trans*-azo-

benzene. Analyzing the experimental data in more detail shows that along this path an energy barrier of  $2 \text{ kcal mol}^{-1}$  has to be overcome in order to reach the conical intersection between the ground and excited state, in excellent agreement with theoretical predictions.<sup>[8d]</sup>

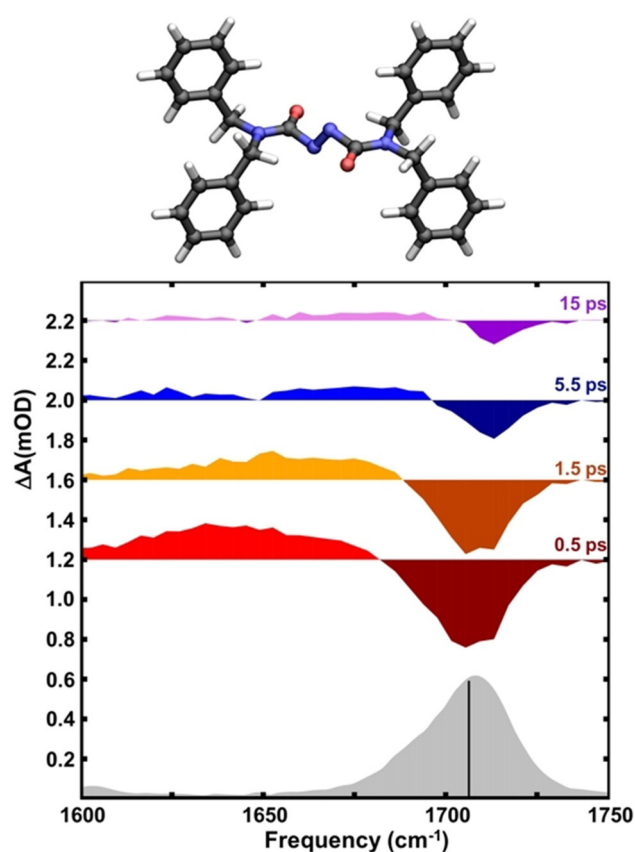
The conclusion on the involvement of not just a single structural coordinate is important as it provides a rational explanation for the often opposing conclusions that have been drawn in previous experimental studies. These studies considered, for example, how photoisomerization depends on solvent properties like polarity and viscosity, or how photoisomerization is influenced by substituents.<sup>[12]</sup> Under such conditions the actual contribution of the different pathways is likely to change from one case to another, and one can thus very well expect that in one type of experiment the torsional pathway dominates while under different conditions the inversion pathway takes over. It is only by studies on the isolated molecule that one can determine the intrinsic "basic" photoresponse which can then serve to find means for further tuning by external perturbations such as substituents and solvents. They also are the necessary starting point for successive investigations that focus on the influence of an embedding within different matrices. In addition, the direct correlation of the high-resolution data with calculated spectra, allows to benchmark theoretical methods.

### Volume-Conserving Motion of a Molecular Switch

To apply the externally tunable properties of molecular switches for spatial or temporal control in materials, embedding within generally confined spaces such as polymers or crystals is crucial. This condition imposes severe restrictions on the trajectories connecting the different states of the switch, and in fact calls for switches with only minimal volume changes during operation. Once again, a mere consideration of the conformers in the electronic ground state only gives evidence that a switching process has taken place, but does not elucidate the motions that lie at the basis of this transformation.

Recently, novel azodicarboxamide-based molecular systems have been developed.<sup>[13]</sup> The carbonyl groups provide in this case potential hydrogen binding sites while the central  $\text{N}=\text{N}$  bond can act as the photochromic unit. In contrast to aromatic azo-functionalized molecules such as azobenzene, the conjugation with the adjacent amide groups leads in these molecules to a nonplanar geometry in the ground state (Figure 3). Considering the orientation of the carbonyl groups, two different arrangements with respect to the central  $\text{N}=\text{N}$  bond are possible. These arrangements are equivalent in solution for the bare, symmetric molecule, but can become inequivalent if, for instance, chiral local environments are constructed by nonsymmetric substitution or hydrogen bonding, thus allowing to distinguish the two conformers.

The reaction coordinate interconverting the two structures mainly involves torsion around the  $\text{C}-\text{N}$  bond. Interestingly, the geometry of the transition state along this path is planar



**Figure 3.** Ball-and-stick model of the investigated  $N,N,N',N'$ -tetrabenzylazodicarboxamide molecular switch (top) and FTIR spectra in chloroform (gray, solvent corrected) and calculated stick spectra of the ground state conformer (black) together with UV-pump/IR-probe transient IR spectra of the molecular switch at the indicated time delays after 350 nm UV excitation (bottom).

with both carbonyl groups in opposite directions. Consideration of the relevant molecular orbitals makes one suspect that this geometry might actually well be a stable minimum on the potential energy surface of the lowest electronically excited state, which then would imply that a photoinduced switching motion with minimal changes in volume could be induced. Whether this is indeed the case, can only be determined by following the structural evolution in the electronically excited state. For the prototype chromophore the two conformers involved in the switching process cannot be distinguished spectroscopically in the electronic ground state. However, the carbonyl stretch mode is an excellent probe to follow the transition from the nonplanar to the planar geometry and therefore to elucidate the photodynamics of the azodicarboxamide-based molecular switch.

Time-resolved infrared spectroscopy (TRIR) in combination with density functional theory calculations indeed provides detailed insight into the light-triggered switching process.<sup>[14]</sup> Excited-state calculations, which accurately reproduce the measured UV/Vis spectra, reveal that upon UV irradiation initially the  $S_3$  electronic state is populated. Structural relaxation of the molecule in this state, however, does not lead to a stable structure. Instead, it is predicted that internal conversion to the  $S_1$

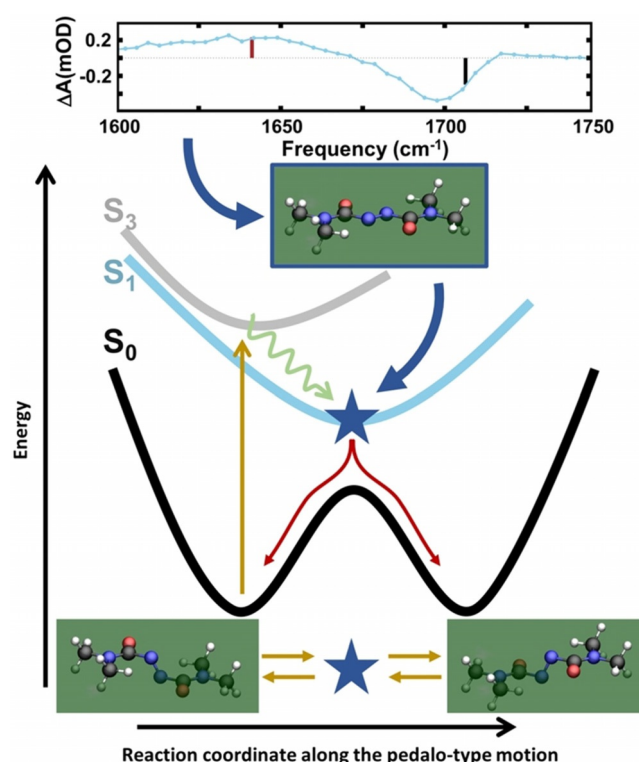
state takes place, and that in this state the molecule adopts a stable planar geometry. These theoretical predictions are in excellent agreement with the experimental observations (Figure 3). TRIR measurements reveal that excitation is accompanied by major changes in the carbonyl stretch frequency region. At the frequency of the ground-state C=O vibration ( $1708\text{ cm}^{-1}$ ) a bleach is observed in the transient spectra while simultaneously an induced absorption at  $1640\text{ cm}^{-1}$  is created. Both spectral features vanish on a time scale of 30 ps through a biexponential decay with decay times of 1.5 and 8.6 ps associated with decay of the  $S_1$  state and subsequent vibrational cooling in the ground state.

Comparison of the frequencies of the experimentally observed bands with theoretical calculations of vibrational spectra of the optimized structures for the nonplanar ground and the planar excited state species in  $S_1$  shows an excellent agreement (a shift by  $66\text{ cm}^{-1}$  from  $1715\text{ cm}^{-1}$  to  $1649\text{ cm}^{-1}$ ). Importantly, this large shift cannot be reproduced if the molecule would adopt a nonplanar structure in the excited state. The experiment thus shows that the photoinduced structural dynamics take the molecule to a stable planar conformer that coincides with the transition state along the C–N torsion pathway in the electronic ground state. As a result, the molecule undergoes a pedalo-type of switching motion that is largely volume-conserving (Figure 4).

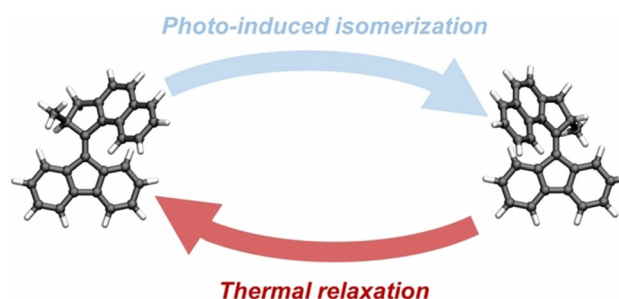
Once again, it should be emphasized that from a structural point of view the result of the pedalo-type of motion can also be reached by inversion at the two azo-nitrogen atoms or by a combination of torsion and inversion. Identification of the final photoproducts therefore does not shed light on the actual motional pathway followed in the excited-state manifold. It is only by this combination of experiment and theory that the full switching motion can be determined.

## Beyond Simple Molecular Switches: Operation Mechanism of a Molecular Motor

Although a molecular switch has two or more well-defined states, the molecular system in which it is incorporated has per definition no directionality with respect to the structural evolution. The molecular switch therefore does not allow work to be performed on the molecular level, which would open a further level of spatial and temporal control of molecular phenomena. This can be changed, however, by embedding the photoactive unit in an asymmetric and chiral environment in which case photoinduced isomerization can lead to unidirectional motion.<sup>[15]</sup> The overcrowded alkene-based molecular motors developed by Feringa and co-workers,<sup>[16]</sup> are prominent examples of how such a unidirectional molecular rotation can be realized. Key to the functioning of this class of molecular machines is a C=C bond that acts as the axis for rotation of the rotor part with respect to the stator part (Figure 5). The chiral center in the system induces a helicity that guides the unidirectional rotation by creating stable and metastable conformers along the rotation coordinate. The full cycle includes thermal and photoinduced steps, and it is clear that for the optimi-



**Figure 4.** Species-associated difference spectra of the first species extracted from the transient IR data (Figure 3), which can be assigned to the planar electronically excited-state species by comparing the measured spectra with the calculated spectra of the corresponding species (stick-spectra) (top). Based on this the full pathway of the photodynamics of the *N,N,N',N'*-tetra-benzylazodicarboxamide molecular switch describing a pedalo-type motion was derived (bottom).



**Figure 5.** Schematic representation of the unidirectional motion of the studied molecular motor. The operational cycle includes a photoinduced isomerization step and a thermal relaxation step. The corresponding ground-state conformers of the molecular motor are shown as ball-and-stick models (left: thermally stable; right: *meta*-stable structure).

zation of the latter steps a complete picture of the excited-state trajectory is needed.

The excited-state dynamics are, however, still subject of ongoing debate. So far, only a limited number of experimental<sup>[17]</sup> and theoretical<sup>[18]</sup> studies have been reported. Ultra-fast time-resolved fluorescence and absorption measurements have provided a first insight but lack the level of detail provided by vibrational spectroscopy.<sup>[17a-c]</sup> High-level theoretical studies, on the other hand, are hampered by the extended  $\pi$ -system and

the multi-reference character of the electronically excited states, although calculations on smaller model systems already indicate that the photodynamics involve several electronically excited states.<sup>[18d]</sup>

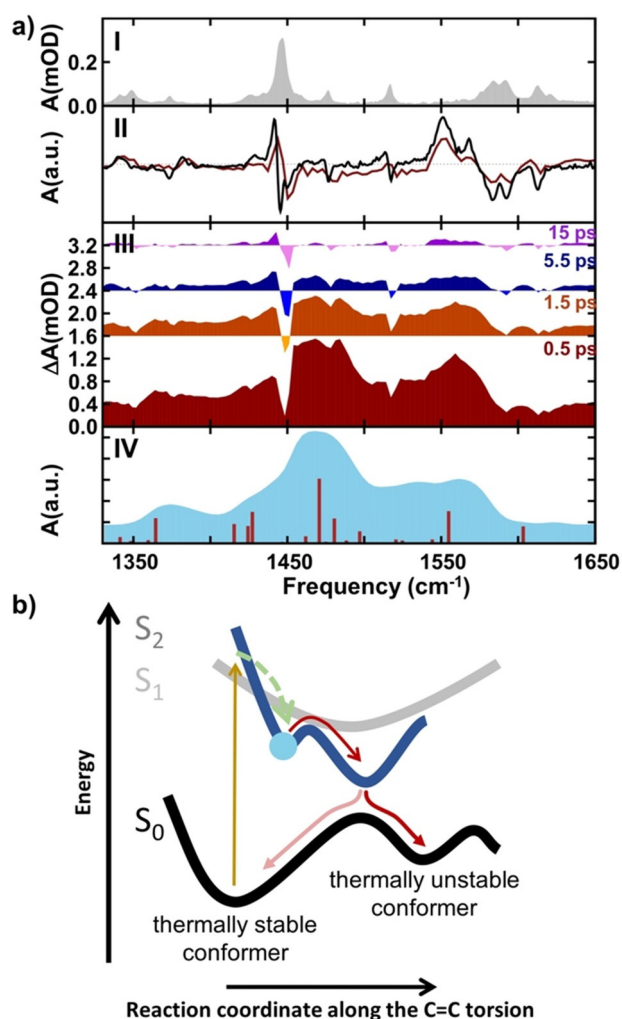
TRIR studies in combination with time-dependent density functional theory (TDDFT) calculations have enabled a detailed understanding of the fundamental aspects of the operation mechanism of these motors.<sup>[19]</sup> These studies lead to the conclusion that upon electronic excitation the “bright”  $S_2$  state is populated. During the subsequent geometry relaxation an ultrafast internal conversion process to the energetically almost degenerate “dark”  $S_1$  state occurs, presumably through a conical intersection. Such a transition is in good agreement with the reported ultrafast decay of the fluorescence signal<sup>[17b]</sup> and is supported by multireference studies on a smaller molecular motor system.<sup>[18d]</sup> Using the high structural sensitivity of vibrational spectroscopy, TRIR studies identify a stable excited-state species by deriving species associated spectra (SAS) from the measured transient spectra. Comparison of the pertinent SAS spectrum with the spectrum predicted for the motor optimized in the  $S_1$  state shows a very good agreement. After overcoming an energy barrier, this intermediate species then relaxes back to the ground state forming the final conformer of the photochemical step (Figure 6).

This work demonstrates that the photoinitiated rotation involves relaxation on the potential energy surfaces of several electronically excited states. It also shows for the first time that this relaxation does not occur barrierless but involves the stable minimum of a “dark” electronically excited state. This is important since it implies that the conical intersection between this “dark” electronically excited state and the ground state is a key player in determining the efficiency of the motor. To rationally tune the performance of photoinitiated unidirectional rotation thus involves a multicoupled-state optimization of nuclear motion.

## Conclusions

We have shown how a judicious combination of theoretical and experimental methods is able to reveal the key details of the electronic and structural dynamics of molecular switches. In particular, our examples underline the unique access to the photoinduced “reaction coordinate” offered by considering the evolution of the vibrational manifold. By directly correlating the experimental spectra with calculated data an atomistic picture of the photodynamics can be extracted. Importantly, the obtained insight goes beyond a mere verification as to whether switching between two (or more) states has happened, but allows one to determine the dominating structural motion and to identify intermediate states along the trajectory.

Considering the implementation of photoactive building units in responsive functional materials, such a level of understanding is crucial since the photoinitiated trajectory will be influenced—and in the worst case even completely blocked—by the confinement imposed by a matrix into which the unit needs to be incorporated. As a result, not only the efficiency of the switching process but also the overall performance of the



**Figure 6.** a) FTIR spectra of the thermally stable conformer (I), difference FTIR spectra of thermally stable and thermally unstable conformer (black) together with the species associated different spectra of final species extracted from the transient IR data (brown) (II); UV-pump/IR-probe transient IR spectra of the molecular switch at the indicated time delays after UV excitation (III); SAS of the first species extracted from the transient IR data (cyan) and the corresponding calculated stick spectra (red) (IV). b) Full pathway of the light-driven molecular motor; the dark-state species (Sp1) is indicated by the cyan circle.

material will be influenced. The presented concept enables to establish a strong platform to develop and implement molecular switches in the emerging field of stimuli-responsive nanomaterials.

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## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** excited-state dynamics · photoswitch · quantum chemical calculations · stimuli-responsive materials · time-resolved spectroscopy

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