Conserving Coherence and Storing Energy during Internal Conversion: Photoinduced Dynamics of cis- and trans-Azobenzene Radical Cations

Kristin Munkrup, Dmitri A. Romanov, Timothy Bohinski,
Anne B. Stephansen, Robert J. Levis, and Theis Ivan Sølling

J. Phys. Chem. A, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpca.7b09185 • Publication Date (Web): 23 Oct 2017

Downloaded from <http://pubs.acs.org> on October 29, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

**Conserving Coherence and Storing Energy during Internal Conversion: Photoinduced
Dynamics of *cis*- and *trans*-Azobenzene Radical Cations**

*Kristin Munkerup,^{†,§} Dmitri Romanov,^{‡,§§} Timothy Bohinski,^{‡, §§§} Anne B. Stephansen,^{‡‡}
Robert J. Levis^{‡, §§§} and Theis I. Sølling^{*, ‡}*

§KAUST Catalysis Center, Division of Physical Science & Engineering, 4700-King Abdullah
University of Science and Technology, 23955 Thuwal, Kingdom of Saudi Arabia.

[†]Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø,
Denmark

[‡]Center for Advanced Photonics Research, ^{§§}Department of Physics, and ^{§§§}Department of Chemistry,
Temple University, Philadelphia, Pennsylvania 19122, United States

^{‡‡}Fritz-Haber-Institut der Max-Planck-Society, Faradayweg 4-6, 14195 Berlin, Germany

Abstract:

Light harvesting via energy storage in azobenzene has been a key topic for decades, and the process of energy distribution over the molecular degrees of freedom following photoexcitation remains to be understood. Dynamics of a photoexcited system can exhibit high degrees of non-ergodicity when it is driven by just a few degrees of freedom. Typically, an internal conversion leads to the loss of such localization of dynamics, as the intramolecular energy becomes statistically redistributed over all molecular degrees of freedom. Here, we present a unique case where the excitation energy remains

localized even subsequent to internal conversion. Strong-field ionization is used to prepare *cis*- and *trans*-azobenzene radical cations on the D₁ surface with little excess energy, at the equilibrium neutral geometry. These D₁ ions are preferably formed because in this case D₁ and D₀ switch place in the presence of the strong laser field. The post-ionization dynamics is dictated by the potential energy landscape. The D₁ surface is steep downhill along the *cis/trans* isomerization coordinate and towards a common minimum shared by the two isomers in the region of D₁/D₀ conical intersection. Coherent *cis/trans* torsional motion along this coordinate is manifested in the ion transients by a cosine modulation. In this scenario, D₀ becomes populated with molecules that are energized mainly along the *cis-trans* isomerization coordinate, with the kinetic energy above the *cis-trans* inter-conversion barrier. These activated azobenzene molecules easily cycle back and forth along the D₀ surface, and give rise to several periods of modulated signal before coherence is lost. This persistent localization of the internal energy during internal conversion is provided by the steep downhill potential energy surface, small initial internal energy content, and a strong hole-lone pair interaction that drives the molecule along the *cis-trans* isomerization coordinate to facilitate the transition between the involved electronic states.

Introduction

Femtosecond time-resolved mass spectrometry (FTRMS) has brought about many discoveries pertaining to the electronic structure and initiated dynamics of polyatomic molecules, as well as to the understanding of (non)-ergodicity in chemical reactions.¹⁻⁷ Recently, this technique has been increasingly applied to studying the post-ionization dynamics of radical cations.⁸⁻¹⁷ A major challenge in these experiments stems from the fact that ionization via multiphoton absorption typically produces vibrationally hot ions.¹⁰ This results in extensive fragmentation, which makes it difficult to actually probe the dynamics of the intact parent ion.^{10, 18} A solution to this problem was found in employing strong-field adiabatic ionization by long-wavelength (IR) laser pulses, which was shown to create

vibrationally cold cations and thus effectively open up the possibility for controlling the fragmentation channels.^{12, 17, 18}

The interaction of *cis*- and *trans*-azobenzene with laser radiation in both the gas and liquid phases have been studied extensively with femtosecond spectroscopy,¹⁹⁻²² and it is well established that neutral azobenzene undergoes photoisomerization when excited to $S_1(n,\pi^*)$ or to one or more higher lying π^* excited states $S_{2/3/4}(\pi,\pi^*)$.²² Studies of the ionized species are however sparse. The current focus is on deciphering the processes that drive the internal conversion and subsequent dissociative processes in ions. In several molecular systems, the dynamics involved in the internal conversion processes exhibit a high degree of non-ergodicity, which is manifested in experiment as oscillating transient signals and/or non-statistical decay rates.⁴ Examples of such non-ergodicity are the internal conversion processes in ketones and amines that are driven by ring puckering and nitrogen inversion, respectively.^{5-7, 23} In these cases, the non-ergodicity arises because the potential energy landscape is steep downhill along specific degrees of freedom and the internal kinetic energy gained from the relaxation process is therefore highly localized in those coordinates. This energy localization decreases on a picosecond timescale, so that the localized dynamics is mainly observed in the early stages of the processes occurring on the initially accessed ionic potential surface.

The presence of several neighboring and rigid chromophores in azobenzene seems to be an excellent probe for the non-ergodic process that results from the interaction between chromophores. Ho et al. have investigated *trans*-azobenzene by femtosecond photoionization-photofragmentation spectroscopy, and an observed damped oscillation in the transients.²⁴ This oscillation was attributed to the rapidly dephasing vibrational motion of the phenyl-ring torsion and/or CNNC torsional coordinate on the *trans*-azobenzene radical cation ground-state surface D_0 . The mechanism of dissociation is similar to 1,3-dibromopropane where the interaction between the lone pairs on the two bromines drives internal

conversion and subsequent bond breakage upon photofragmentation.¹⁶ In another study of *trans*-azobenzene radical cations, photoelectron spectroscopy was used to show that the multiphoton ionization yields cations on both the ground cationic D_0 , and second or third cationic states D_2 , D_3 .²² Time-resolved photoionization studies employing a multiphoton ionization scheme also showed indications of a combination of neutral excited state dynamics and cationic dynamics.²⁴ These complications are avoided when using strong-field ionization. It is not possible to completely rule out that there is a contribution from multiphoton ionization as employed by Ho et al.²⁴ via accidental resonances but under the experimental conditions the Keldysh parameters show that the principal pathway is via tunnel ionization. Such a contribution would under our experimental conditions simply not exhibit a time dependence.

Herein we are reporting on both *trans*-azobenzene and *cis*-azobenzene dynamics using FTRMS to further elucidate the initial dynamics of azobenzene radical cations. By employing strong-field adiabatic ionization in the time-resolved investigation we avoid to blur the picture by neutral excited state dynamics. We focus on whether *cis*-azobenzene displays oscillations in the same fragment ion transients as *trans*-azobenzene and how the differences and similarities of the dynamics exhibited by the two isomers shed new light on the photoinduced processes. We investigate the potential energy surfaces of the electronic states that may be involved in the observed dynamics. We suspect that charged chromophores have the potential to drive the internal conversion in a much stronger manner than their neutral counterparts if the potential energy surface directs the dynamics towards an area where the charge is stabilized by interacting chromophores. A possible consequence of this could be preservation of coherence subsequent to internal conversion, in other words dynamics that remain localized even on a potential energy surface different from the one initially accessed – a phenomenon that has not previously

been observed, but can have significant implications to a broad spectrum of scientific disciplines such as photonics,²⁵ energy storage,²⁶ and novel materials.^{27, 28}

Experimental

i) Preparation of chemicals: Samples of *trans*-azobenzene were used as supplied from Sigma-Aldrich (98% purity). *Cis*-azobenzene was synthesized by dissolving *trans*-azobenzene in dichloromethane and irradiating the solution with 365 nm light for 24 hours yielding a mix of *cis*- and *trans*-azobenzene. After irradiation *cis*-azobenzene is separated from *trans*-azobenzene by either flash or dry column chromatography.²⁹

ii) Steady state and Femtosecond Time-resolved Mass Spectrometry: The setup at University of Copenhagen using multiphoton ionization is described in detail elsewhere.³⁰ The setup employs a femtosecond pulsed laser and is suitable for time-resolved experiments. However for the investigation reported here we have only used this setup in one-color/steady state mode. Briefly the setup consists of a continuous wave diode-pumped Nd:YAG laser that pumps a Tsunami oscillator producing 800 nm 70 fs laser pulses with a 80 MHz repetition rate. The laser is amplified by a regenerative amplifier (Spitfire, Spectra-Physics) delivering 100 fs full width half maximum (fwhm) laser pulses centered at 800 nm with an intensity of 1 mJ energy at 1 kHz repetition rate. The laser train is divided by a beam splitter, 50 % is sent through an optical parametric amplifier (OPA) (TOPAS-C, Light conversion) set to generate pulses centered at 286 nm and used for multiphoton ionization. The remaining 50% were not used in the current experiments. The 286 nm laser pulses were directed into the vacuum chamber and crossed with the molecular beam. The molecular beam was generated by continuous supersonic expansion of azobenzene seeded in helium into the differentially pumped vacuum chamber. The cations generated by intersecting the molecular beam with the laser pulses were subsequently accelerated and separated by time-of-flight, and detected by a stack of microchannel plates (MCPs).

The femtosecond time-resolved mass spectrometry setup at Temple University using strong-field adiabatic ionization has been described in detail elsewhere.^{13, 31} Both one-color and time-resolved mass spectroscopic investigations were conducted. In short, a Ti:Sapphire regenerative amplifier is divided by a 75/25 beam splitter where 75% of the output is used to pump the nonlinear-OPA thereby generating a tunable signal laser pulse in the IR regime with the wavelength λ ranging from 1150 nm to 1550 nm and an intensity I of the ionizing pump pulse of (40-55 $\mu\text{J}/\text{pulse}$, $1.08 - 2.44 \times 10^{14} \text{ W}/\text{cm}^2$). The remaining 25% of the Ti:Sapphire fundamental (800 nm) is used as the probe pulse (1-5 μJ) in the time-resolved experiments. Pulse durations were determined by fitting of the transients or by frequency resolved optical gating, and the pulse durations were 60-100 fs. The pump pulse is focused into the mass spectrometry chamber where it interacts with neutral gas molecules creating the corresponding radical cations. The dried samples were leaked into the mass spectrometry chamber, which had a base pressure of $1.3 \times 10^{-6} \text{ Pa}$ increasing to $4.8 \times 10^{-6} \text{ Pa}$ during leak of sample. The samples were heated to 37 °C to increase the rate of evaporation. Under the experimental conditions, the Keldysh parameter,

$$\gamma = \frac{2\pi}{\lambda e} \sqrt{\frac{E_{IP} m_e \epsilon_0 c^3}{I}}, \quad (1)$$

calculated for the azobenzene ionization energy $E_{IP} = 8.4 \text{ eV}$, with e being the elementary charge, m_e the electron mass, ϵ_0 the permittivity of vacuum, and c the speed of light, has the values from 0.28 to 0.47, i.e. within the tunneling regime.³² The calculated values only change slightly if ionization takes place to higher lying ionic states. In the case of D_1 with an ionization energy of approximately 10 eV (upper bound) the values would have to be multiplied by 1.09.

Calculations:

All *ab initio* calculations were performed with the Gaussian 09 program package.³³ The CAM-B3LYP³⁴ functional and 6-31+G(d) basis set was used to optimize geometries and perform relaxed scans. The optimized geometries were confirmed to be minima by frequency calculations (zero imaginary frequencies). Relaxed scans of CNNC dihedral angle were performed with the D₀ optimized radical cation structures as starting points. Each point in the scan was excited using Time-Dependent DFT in order to get the excited state potential energy surfaces. Molecular orbitals have been calculated with B3LYP/6-31+G(d) level of theory. The molecular orbitals for the D₁ excited states were calculated by identifying molecular orbitals active in the D₀-D₁ transition. In both isomers this transition corresponds to the SOMO-SOMO+1 transition. The Stark shift that is induced by the presence of the laser field was investigated with the FIELD keyword at the Franck-Condon geometries. Various fields up to 0.35 au were applied in the direction of the long axis of the molecule (through both phenyl groups). In addition to the UCAM-B3LYP/6-31G(d) calculations, calculations at the EOMCCSD/6-31G(d) and EOMCCSD/aug-cc-pvdz level were also attempted. The success was limited because of convergence problems at field strengths beyond 0.3 au but the observed trends were similar to the DFT results. At the CIS/aug-cc-pvdz level convergence could be achieved at field strengths up to 0.25 au.

The evolution of vibrational wavepackets on the ionic potential surfaces D₀ and D₁ was assessed using classical trajectories^{35, 36} of the packet center. The dependence of the potential surfaces on the CNNC angle, φ , was represented via the truncated Fourier series,

$$V_{D0}(\varphi) = \sum_{n=0}^N a_n \cos(n\varphi); \quad V_{D1}(\varphi) = \sum_{n=0}^N b_n \cos(n\varphi), \quad (2)$$

with N=7 being sufficient to fit the surfaces obtained from the *ab initio* calculations. The trajectory $\varphi(t)$ of the wavepacket center is determined by the classical equation of motion,

$$\frac{d\varphi}{dt} = \sqrt{\frac{2}{I}(V(\varphi(0)) - V(\varphi(t)))} \quad (3)$$

where $V(\varphi)$ is either $V_{D_0}(\varphi)$ or $V_{D_1}(\varphi)$ presented by Eq. (2), and I is the reduced moment of inertia for the torsional motion with respect to the CNNC angle. Neglecting possible small changes in the value of I when switching from D_0 surface to D_1 surface, this value was determined to be $I = 4.31798 \cdot 10^{-38}$ g cm² by utilizing a quadratic expansion of $V_{D_0}(\varphi)$ near its minimum at $\varphi_0 \approx 152^\circ$: $V_{D_0}(\varphi) \approx V_{D_0\min} + I\omega^2(\varphi - \varphi_0)^2/2$ with the known frequency ω of the torsional vibrations. Equation (3) was solved numerically using variable-step fourth and fifth order Runge-Kutta method as implemented in the ode45 integrator in MATLAB.

Results and discussion

The results from the time-resolved mass-spectrometric investigation yield new and surprising information about the dynamics of azobenzene on the cationic surface. The essential novelty of the current investigation rests on the fact that both *cis*- and *trans*-isomers of azobenzene have been assessed, in contrast to previous studies, which focused solely on the *trans*-isomer. Moreover, we focus on the actual ionization mechanisms as the present set of results represents the first set of tunnel ionization data for azobenzene. As will become apparent in this section, the observed complementarity of the ion transients of the two isomers essentially reveals the nature of the dynamics, and the mechanism of the characteristic photoinduced processes proposed here is different from previous investigations with the most important aspects of our interpretation being extracted from the new results on the *cis*-isomer. We present the first (to the best of our knowledge) example of preservation of coherence during and after the transition from one electronic state to another. This section is organized as follows: First, we address the

one-color and pump-probe mass spectrometry results (i); second, we present and discuss calculated potential energy surfaces on the basis of the experimental observations (ii); the different cationic states, the impact of a strong laser field on the relative energies, and the nature of the pump and probe processes are discussed subsequently (iii), before we present a unifying interpretation of all results available from studies of *trans*-azobenzene radical cations (iv). This unifying picture is finally scrutinized (and verified) in a dynamics simulation in (v).

i) *One-color and time-resolved mass spectrometry:*

Mass spectra obtained from strong-field ionization and multiphoton ionization of *cis*- and *trans*-azobenzene are shown in Figure 1. The mass spectra of *cis*- and *trans*-azobenzene show identical mass peaks and approximately the same relative intensity of the fragment ions with both multiphoton and strong-field ionization. A significant difference in the molecular ion signal when comparing tunnel ionization (Figure 1. a and c, large Keldysh parameter) and multiphoton ionization (Figure 1. b and d, smaller Keldysh parameter) is the higher molecular ion yield ($m/z = 182$) observed when strong-field ionization is applied. The fragment with $m/z = 77$, corresponding to the phenyl ion fragment, is abundant in all mass spectra thereby indicating that the C-N bond dissociation is prominent regardless of ionization method. C-N bond dissociation yields phenyl and the phenyldiazonium fragment ions ($m/z=105$) ion, and these two ions along with the molecular ion are particularly important when assessing the dynamics of ionized azobenzene. The structures and masses (in atomic units) of these ions are shown in Figure 2. The distribution of fragment ions with m/z below 77 is similar to the mass spectrum of benzene which implies that they arise from secondary decomposition of the phenyl ion and are therefore not directly relevant to the cationic dynamics of azobenzene.³⁷

Figure 1. Mass spectra of *trans*- (a, b) and *cis*-azobenzene (c, d) using strong-field ionization conditions (a, c, d) and multiphoton ionization conditions (b). The used wavelength and Keldysh parameter is given in the upper right corner for each individual mass spectrum.

Figure 2. Molecular and fragment ions that display radical cation dynamics in the FTRMS experiments.

Time-resolved mass spectrometry with strong-field ionization was conducted with pump wavelengths ranging from 1150 nm to 1550 nm for both *cis*- and *trans*-azobenzene. The transients associated with the molecular ion and the two important fragment ions are similar across the entire wavelength range. The same insensitivity of the dynamics towards different pump wavelengths is also observed when employing resonant/non-resonant multiphoton ionization with pump wavelengths 260-450 nm on *trans*-azobenzene.²⁴ Representative transients from the current investigation of the molecular ion (182 amu),

phenyldiazonium ion (105 amu), and the phenyl cation (77 amu) for *cis*- and *trans*-azobenzene are shown in Figure 3 (*trans*) and Figure 4 (*cis*). The ion transients of *cis*- and *trans*-azobenzene can be fitted to the convolution of a Gaussian instrument response function and a molecular response function consisting of an exponential function modulated by cosine and with a constant positive/negative off set. The resulting parameters are summarized in Table 1. The lifetime τ_1 of the molecular ion is slightly shorter for *cis*-azobenzene compared to *trans*-azobenzene. A similar observation is made for the oscillation periods in the case of *cis*-azobenzene, the oscillation period is shorter by approximately 220 fs compared to the fitted result for *trans*-azobenzene.

Importantly, all transients display oscillations with similar oscillation period within the error bars (albeit with different amplitudes). The oscillations in the *trans*-azobenzene molecular ion transient (Figure 3a) are phase-shifted by π with respect to the transients of the phenyldiazonium (Figure 3b) and phenyl ions (Figure 3c), which agrees with the observations made by Ho et al.,²⁴ though a different ionization method was used in that investigation. For the *cis*-azobenzene isomer, the signal to noise ratio (S/N) is generally lower compared to that for the *trans*-form. The lower S/N observed in the FTRMS experiments of *cis*-azobenzene is mainly due to the lower vapor pressure of this isomer as compared to the *trans*-form and to the possibility of thermal *cis-trans* isomerization favoring the *trans*-form.³⁸ However, oscillations are also observed in the molecular ion (Figure 4a) and phenyldiazonium ion transients (Figure 4b). For the phenyl ion (Figure 4c), the S/N was too low for clear oscillations to be observed. A π phase shift between the phenyldiazonium transient relative to the molecular ion transient is also observed for the *cis* isomer. Interestingly, all of the *cis*-azobenzene transients are also phase shifted by π compared to the respective *trans*-azobenzene transients. This observation is a central point for the overall interpretation of the dynamics as elaborated on and discussed in section 3.iv. A reasonable assumption is that the observed oscillatory signals are due to the same vibrational motion in

cis- and *trans*-azobenzene, with the most obvious candidate being the torsional motion spanned by the CNNC dihedral angle.

Figure 3. Representative *trans*-azobenzene ion transients including (a) the molecular ion (182 amu, top), (b) phenyldiazonium (105 amu, middle), and (c) the phenyl ion (77 amu, bottom) with $\lambda_{\text{pump}} = 1540$ nm and $\lambda_{\text{probe}} = 800$ nm. The blue circles are the data points, the dark red line represents the fit, and the blue lines show the fitted components.

Figure 4. Representative *cis*-azobenzene ion transients including (a) the molecular ion (182 amu, top), (b) phenyldiazonium (105 amu, middle), and (c) the phenyl ion (77 amu, bottom) with $\lambda_{\text{pump}} = 1480$ nm and $\lambda_{\text{probe}} = 800$ nm. The red circles are the data points, the dark red line represents the fit, and the blue lines show the fitted components.

Table 1. The table summarizes the lifetime (τ), the oscillation period (T), and the oscillation phase (Φ) obtained from the fits to the *cis*- and *trans*-azobenzene molecular ion transients (Figure 3 and 4).

Parameter	<i>cis</i> -azobenzene			<i>trans</i> -azobenzene		
	Parent ^{•+}	Phenyldiazonium	Phenyl ⁺	Parent ^{•+}	Phenyldiazonium	Phenyl ⁺
τ	0.85 ps	0.82 ps	0.80 ps	1.01 ps	1.17 ps	0.93 ps
T	0.86 ps	0.83 ps	1.00 ps	1.08 ps	1.07 ps	1.09 ps
Φ^a	0.44 (2.77)	5.84	5.84	0.00	3.29	3.33

^a Φ is given in radians.

1
2
3 **ii) Potential energy surfaces:**
4

5
6 The complementarity of the *cis*- and *trans*-azobenzene results strongly suggests that a common
7
8 coordinate is activated at initial times. We start the computational investigation of the resulting
9
10 dynamics with a survey of the potential energy landscape. Considering that *cis-trans* isomerization can
11
12 occur on the neutral excited state surface,¹⁹⁻²² the CNNC dihedral angle appears as an obvious reaction
13
14 coordinate to explore. It should be mentioned, that the ground state neutral *cis*- and *trans*-geometries
15
16 have CNNC dihedral angles fairly similar to the radical cationic ground state geometries while the main
17
18 difference between the S₀ and D₀ minima involves rotation of one phenyl moiety. This phenyl-rotation
19
20 has previously been implied to be responsible for the oscillations.²⁴ However, there is good reason to
21
22 suggest that a rotation of the phenyl groups is different for the *cis*- and *trans*-isomers, respectively.
23
24 Calculations indicate that the barriers for rotation differ by 7 kJ mol⁻¹ and the potential energy surfaces
25
26 for rotation are included as supporting information (Figure S1). Thus, we do not expect that the
27
28 involvement of such a motion should yield similar (out of phase) modulations of both isomers. Instead,
29
30 we consider the CNNC coordinate.
31
32
33
34
35
36
37
38

39 The relaxed scan of the CNNC angle performed on the *cis*-azobenzene radical cation ground state (D₀)
40
41 are shown as the orange points in Figure 5. The vertical excited state energies of D₁–D₂ were calculated
42
43 (CAM-B3LYP TD) from each point of the relaxed ground state surface in Figure 5. It is noted that the
44
45 experimental He I spectra give ionization values of 8.4, 8.75, 9.3 eV.^{39, 40} Thus, there may some
46
47 uncertainty associated with the TDDFT calculations but the qualitative appearance remains sound. The
48
49 data points marked with “x” have been excluded from the analysis as the DFT calculation is unable to
50
51 describe the electron density when the two lone pairs on the nitrogen atoms are perpendicular to each
52
53 other, that is, where a multi-configurational description is necessary. It can be seen from Figure 5 that
54
55
56
57
58
59
60

there is a shared minimum between the two isomers of azobenzene on the D_1 state in the CNNC scan coordinate. In contrast, D_0 exhibits a local maximum at this point indicating the likelihood of a conical intersection between D_1 and D_0 in this area of the potential energy landscape.

As will be elaborated and discussed in section 3.iv, the D_0 surface is not a likely starting point for initiating an oscillatory motion of the phenyl chromophores since there are no gradients on the potential energy surfaces towards neither a common minimum nor a *cis-trans* isomerization. In contrast, the D_1 surface appears as a much more likely candidate considering the steep slope downhill towards the same shared minimum/conical intersection point. The importance of a common minimum is discussed in section 3.iv, first we establish the initial population of the D_1 surface.

Figure 5. Relaxed scan (on the D_0 surface) along the CNNC dihedral angle in azobenzene starting from the *cis*-azobenzene S_0 geometry (with a CNNC dihedral of 10°), passing the *trans* S_0 minimum geometry (with a CNNC dihedral of 180°) calculated on the CAM-B3LYP/6-31+G(d) level of theory. Y-axis is the energy in eV relative to the minimum on the D_0 PES surface (orange). The data points marked with “x” show where the calculations have difficulties describing the energy appropriately (near CNNC angles of 90°). The D_1 (blue) and D_2 (green) surfaces represent the vertical excitations from the D_0 optimized geometries. The D_0 optimized *cis* and *trans* minimum energy geometries are shown below the

potential energy curves. The ground state neutral Franck-Condon regions are indicated by the blue shades.

iii) Strong-field ionization: The initially accessed state.

To understand the photoinduced dynamics of *cis/trans*-azobenzene it is of utmost importance to know what state is accessed initially in the pump process.. Our calculations show that D_1 correlates with the neutral ground state highest occupied molecular orbital (HOMO) and that D_0 correlates with HOMO-1 (Figure S2). Given that the electron removed by strong-field ionization originates from the HOMO of the neutral species, the cationic state reached in the pump process is most likely D_1 . Moreover, our calculations indicate that the D_1 and D_0 energies approach each other in the presence of a strong laser field (Figure S3). At the UCAM-B3LYP/6-31+G(d) level of theory there is a swap over in energy at a field of 0.35 au along the long x-axis of the molecule (see Figure S4), at the Franck-Condon geometry. The change along the y- and z-axis was found to be very small. At the CIS/aug-cc-pvdz level, convergence could only be reached at fields lower than 0.25 au, in which case the energy difference is already reduced to 0.7 eV. The energy turnover can be qualitatively understood in terms of the polarity difference between D_1 and D_0 . The electrostatic potential maps and their differences based on the UCAM/6-31+G(d) wave functions are shown in Figure 6. As seen, the charge is more widely spread over the molecule in D_1 state than it is in the D_0 case; this is even more evident in the difference plot where charge difference along the long axis of the molecule is evident. The result is that D_1 is stabilized to a higher degree by the laser field in that direction, and that the D_1/D_0 energy difference decreases as the field strength increases.

These findings are in agreement with the experimentally observed transients described in section 3.i, as they support the scenario in which the steeply sloped D_1 potential energy surface (section 3.ii) is initially occupied and is capable of driving the *cis-trans* isomerization, as opposed to D_0 surface where

there is a barrier to isomerization and thus no possibility of initiating coherent dynamics. The proposed initial excitation to D_1 contrasts the previous observations reported for *trans*-azobenzene.²⁴ We will therefore discuss the potential implication of the possibility of initially accessing D_0 as well, to clarify why this scenario should be ruled out.

Figure 6. Electrostatic potential maps, and the difference between them ($D_0 - D_1$) (UCAM-B3LYP/6-31+G(d)).

Strong-field adiabatic ionization (tunneling) and non-adiabatic (resonant/non-resonant multiphoton) ionization are generally different types of processes and may potentially create ions in different electronic and vibrational states. Furthermore, when resonant multiphoton ionization is used, the dynamics observed may both contain neutral excited state and cationic dynamics which can be hard to distinguish. *Trans*-azobenzene has previously been studied at several different pump intensities and

energies in the UV regime and the authors concluded that the observed processes changes gradually from involving neutral dynamics to actually probe the cationic surface in the higher end of the laser intensity spectrum.²⁴ To probe cationic dynamics, the previous study employed a non-resonant/resonant multiphoton ionization scheme where S_2 correlates with D_0 ; S_1 ionization, on the other hand, gives rise to ions in the D_1 state. In brief, the same overall dynamics were observed throughout the energy range with the same features as revealed by our data, but with a notable difference in the amplitudes of the oscillations and the prominence of the constant off set.

Considering the similarity between the multiple sets of experimental results recorded using a range of different ionization schemes and energies (especially ref. 24 and the current results), that are likely to involve different initial states, we propose that both D_0 and D_1 may be involved in most cases, but to varying degrees. Certainly, in this case we do propose that both are in play. While the observed oscillations result from an initial access of D_1 , D_0 mainly contributes to the constant off set as explained below. The result that the HOMO and D_1 SOMO are identical as shown in Figure S2 is consistent with the proposal that D_1 is the most probable initial state in the current experiments, however, it is noted that arguments based on first order perturbation matrix elements may be simple in the presence of strong laser fields. We further suggest that Ho et al.^{22, 24} access a combination of D_0 and D_1 . We do however note that the D_1 state was not evident in the photoelectron study by Stolow where the focus was on ionization via S_1 and S_2 .¹⁸ Excited cationic states have previously been shown to be involved in the photodynamics of radical cations of for instance halomethanes and CO_2 .⁴¹⁻⁴³

iv) Unifying picture of azobenzene radical cation dynamics:

The key feature of the unifying picture of the cation dynamics starting with either *cis*- or *trans*-isomer is that this system reveals a completely new aspect of internal conversion, namely coherence

preservation in transition from one state to another; this is enabled by the swap of the D_1/D_0 states, which is effected by the strong laser field associated with the tunnel ionization. Throughout this section, we will refer to the sketch in Figure 7, where the dynamics of the *cis* and *trans* isomers are denoted with red and blue arrows and numbers, respectively.

Figure 7. Schematics of photoinduced dynamics of *cis*- and *trans*-azobenzene on the D_1 and D_0 electronic surfaces. The red/blue arrows and wavepacket shapes denote the dynamics of the *cis*/*trans*-isomers, respectively. Both isomers relax along a steep potential energy surface (panel (i)) to reach a common minimum/conical intersection point where they internally convert to the D_0 surface (panel (ii)). The wavepacket motions proceed on the D_0 surface (panel (iii)) where the isomers cycle back and forth between the *cis*- and *trans*-minima. Every time an isomer visits the *trans*- D_0 minimum (the red wavepacket in panel (iii) and the blue wavepacket in panel (iv)), probe photon absorption is efficient and a high degree of fragmentation is observed, while probe photon absorption is less efficient in the *cis*-isomer region of the D_0 surface, where less fragmentation is observed and the result is a higher yield of the intact parent ion.

When *cis*- or *trans*-azobenzene molecule is ionized with a femtosecond pump pulse, a wavepacket emerges on the D_1 surface and moves in the direction of steepest decent path. On the D_1 potential energy surface there is a large gradient downhill towards the common minimum shared by the *cis*- and *trans*-isomers (i). Relaxation along this pathway will thus initiate the same torsional motion for both isomers. The torsional motion makes the molecules visit the region of the potential surface where D_1 and D_0 couple strongly to facilitate immediate internal conversion (ii); The *cis*- and *trans*-isomers reach the D_0 surface at the same region (near the local maximum/conical intersection), but the (D_1) *cis*-isomer has momentum towards the (D_0) *trans*-isomer whereas the (D_1) *trans*-isomer has momentum towards the (D_0) *cis*-isomer (iii).

The root cause of the out-of-phase oscillations in the parent versus the fragment transients is the same as that of the *trans*- versus the *cis*-isomer; it is anchored in the *cis/trans* torsional motion involving the phenyl groups. We have verified that the reason is absorption differences between the *cis*- and the *trans*- D_0 radical cations by calculations of the cross sections for probe photon absorption on the D_0 surface (Figures S5). The results show a smaller cross section in the geometry of the *cis* local minimum compared to the *trans*-minimum. Probing the *cis* D_0 minimum (less absorption) is therefore expected to result in less fragmentation than the *trans*- D_0 minimum. Thus, whenever the *cis*- D_0 is probed we expect more parent ion signal (less absorption) and correspondingly less fragment ion signal. In contrast, when *trans*- D_0 is probed we expect less parent ion signal (more absorption) and correspondingly more fragment ion signal.

A *cis* - *trans* cycling along the D_0 curve will thus give rise to a periodic modulation of the ion current with maximum amplitude at the (D_0) *cis*-parent signal and consequently minimum amplitude at the associated fragment ion transients. Conversely, for the (D_0) *trans*-parent signal the amplitude is at a minimum with the associated maximum amplitude of the fragment signals.

This theoretical picture agrees well with our experimental data described in Section 3.i. The key is that the initially D_1 -*trans* wavepacket becomes D_0 -*cis* wavepacket within a time interval much shorter than the oscillation period, and vice versa for the initially D_1 -*cis* wavepacket. At the start, the D_1 *trans*-wavepacket has momentum towards the *cis*-area of the CNNC angle coordinate, and it relaxes through the conical intersection and down to the D_0 surface where it will visit the low-absorbing *cis* D_0 minimum first, resulting in little fragmentation. Accordingly, the parent ion transient initially has a large amplitude, while the fragment transients have minimum amplitude (Figure 3). In contrast, the D_1 *cis*-wavepacket gains momentum towards the D_0 *trans*-area and will visit the D_0 *trans* geometry first, absorbing there the probe photon efficiently and thus undergoing fragmentation at the beginning of oscillations, as also observed in Figure 4.

On the D_0 potential energy surface the barrier for *cis-trans* interconversion is smaller than the internal kinetic energy deposited and localized specifically in the torsional motion. The azobenzene molecules can therefore easily cycle back and forth between the *cis*- and *trans*-isomers and consequently give rise to several periods of modulation of the ion signals. This interpretation also explains why the *cis* and *trans* transients are phase-shifted by π - relative to each other; it is simply a matter of one isomer starting its torsional motion out by giving rise to a maximum amplitude whereas the other isomer gives rise to minimum amplitude, and that the motion interconverting the two is the same regardless of the starting point. The identity of the system seems to indicate a potential energy surface with a high degree of symmetry and a commonly shared minimum.

The exponential decay of each transient corresponds to the timescale for intermolecular redistribution of the internal energy on the D_0 surface. Exactly as reported by Ho et al.²⁴ As the energy redistributes, the sum of absorption differences over the ensemble is averaged out by the statistical distribution on the available degrees of freedom. Thus, it is not possible to distinguish the yield of fragment ions from one

time step to another and the ion current becomes time independent. To put it another way, the part of the ion population that originally came from D_1 becomes equivalent to the ions that were formed on the D_0 surface in the first place, both of them giving rise to a constant offset signal.

The most striking aspect of this interpretation is that the coherent wavepacket is formed on one electronic surface (D_1) with the coherence being conserved subsequent to internal conversion (to D_0). While coherence both on ionic and neutral surfaces have been probed before, this is the first example of coherent dynamics that is not lost upon internal conversion. To the best of our knowledge, coherence has hitherto been considered to be lost in the internal conversion process where upon a statistical distribution of the internal energy takes over. We hypothesize that the steep potential energy surface of D_1 and the rigidity of the system makes this an extreme example of dynamics localization. Furthermore, the combination of a radical cation being produced with small excess internal energy by virtue of the strong-field ionization and the type of interaction (hole-lone pair) may drive the torsional motion more strongly than what is possible in the neutral counterparts.

v) Dynamic simulation of the proposed azobenzene radical cation dynamics:

To challenge the outlined scenario of the temporal evolution of the system between the pump and the probe pulses, and especially to verify the probe-pulse timing that leads to enhanced fragmentation the motion of the wavepacket on the D_0 and D_1 surfaces presented in Figure 5 was modelled, as discussed in the **Calculations** section.

Firstly, the cyclical motion of the wavepacket on the D_0 surface was considered, assuming the D_0 population was created by letting the D_1 wavepacket pass through the D_1/D_0 conical intersection with some loss of kinetic energy. The calculated period of this cyclic motion depends considerably on the remaining kinetic energy, and it matches the period of the observed oscillations in Figure 3 and 4, and reported in Table 1, that is, $T \sim 1.0$ ps, when this remaining kinetic energy is 0.36 eV. As the energy

differences between the maximum of $V_{D_0}(\varphi)$ and the Franck-Condon regions of $V_{D_1}(\varphi)$ are 1.92 eV for the *cis*-side and 1.41 for *trans*-side of the curves in Figure 5, we must assume that about 1 eV of energy is transformed into other degrees of freedom upon passing from D_1 to D_0 through the conical intersection. This fast rate of energy loss and the fact that it is greater for the initial *cis*- configuration corroborates with the subsequent considerable damping of the observed oscillations in Figure 3 and 4.

Secondly, we considered the wavepacket motion on the D_1 surface, from the moment of its emergence in the Frank-Condon region on either the *cis*- or the *trans*- side to its arrival in the conical intersection region. In the case of the *cis*-wavepacket, this initial motion over the steep downhill region of the potential energy curve takes 287 fs. The motion of initially D_1 *trans*-wavepacket is harder to ascertain. The DFT calculations predict that the D_1 potential energy curve becomes very flat on the *trans*-side, and that there may even be a shallow minimum at 180° (see Figure 5). In neutral azobenzene the existence of such minimum is of some controversy and has been referred to as the phantom state.^{44, 45} Thus, there is a risk that the D_1 potential energy surface might not be fully representative in the region around 180° . The single trajectory approach may be questionable here, and indeed the trajectory simulations estimate the D_1 propagation time in excess of 500 fs and highly dependent on the initiation point, which indicate that this case will require a higher-level approach. We also estimated the time it takes the initially-*cis* wavepacket that is injected on the D_0 surface with the kinetic energy of about 0.36 eV and moves to the right in Figure 5 to reach the region that is favorable for the probe-induced transitions to higher potential energy surfaces. This time interval was found to be 198 fs, and it adds up to the mentioned 287 fs of the motion on the D_1 surface to make for 485 fs between the moment of ionization and the first moment of effective probe-ion interaction, which is close to the observed phase shift of the observed fragmentation oscillations in Figure 4.

Conclusions

Radical cation dynamics of *cis*- and *trans*-azobenzene have been probed using time-resolved mass spectrometry with strong-field tunnel ionization. The radical cations were initially prepared on the D_1 surface and were found to undergo fast (~ 200 fs) internal conversion to the cationic ground state, D_0 . The dynamics of the internal conversion process was studied by tracing the pump-probe time evolution of the ion current of the molecular ion (m/z 182), the phenyldiazonium ion (m/z 105), and the phenyl ion (m/z 77). All these transients were fitted to an exponential function modulated by a cosine function on top of a constant offset, and in both cases the molecular ion transients were found to be phase shifted by π relative to the associated fragment ion transients. Furthermore and importantly, the transients in *cis*-azobenzene case were all π -shifted from the respective transients in *trans*-azobenzene case.

On the basis of the calculated potential energy surfaces and absorption cross sections, these experimental results were interpreted to show that internal conversion from D_1 to D_0 is driven by the CNNC *cis/trans* torsional coordinate. As the electronic energy is transferred to vibrational energy in the internal conversion process, the steep D_1 potential energy surface directs the dynamics and ensures that the energy is localized in the CNNC torsional motion. The dynamics remain localized even subsequent to internal conversion, and several cycles of *cis/trans* isomerization is observed on the cationic ground state.

To the best of our knowledge, this is the first example of conserved coherence subsequent to internal conversion. We suggest that the high degree of energy localization is due to the cations being produced with little excess internal kinetic energy (strong-field ionization), whereby the internal energy content is dictated by the shape of the potential energy surface which is steeply downhill in the CNNC coordinate.

Furthermore, the rigidity of the system and the strong interaction driving the torsional motion may contribute to maintaining the energy in this mode.

This investigation furthermore shows the benefits of investigating complementary isomers of the same molecule: The complementarity of the structures is reflected in the experimental results with the consequence that the dynamics is directly revealed by the data itself. In other words, in the current work we are less dependent on theoretical preconditions and do not have to “guess” what vibrational coordinates are responsible for the observed modulation, as it is directly apparent in the data when comparing the data sets for the complementary isomers.

Author Information

Corresponding Author

*Dr. Theis I. Sølling, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 , E-mail: theis@chem.ku.dk.

Acknowledgement

We gratefully acknowledge the generous support of the Villum foundation.

Supporting Information

Potential energy surface for phenyl rotation, Molecular orbitals, Field calculations, XYZ axes on azobenzene molecules, TDDFT oscillator strengths plot, TDDFT D₁-D₆ energy plot, xyz coordinates of optimized structures.

References

1. Zewail, A. H., Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond. *J. Phys. Chem. A* **2000**, *104*, 5660-5694.
2. Wan, C.; Fiebig, T.; Kelley, S. O.; Treadway, C. R.; Barton, J. K.; Zewail, A. H., Femtosecond Dynamics of DNA-Mediated Electron Transfer. *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 6014-6019.
3. Diau, E. W. G.; Herek, J. L.; Kim, Z. H.; Zewail, A. H., Femtosecond Activation of Reactions and the Concept of Nonergodic Molecules. *Science* **1998**, *279*, 847-851.
4. Sølling, T. I.; Kuhlman, T. S.; Stephansen, A. B.; Klein, L. B.; Møller, K. B., The Non-Ergodic Nature of Internal Conversion. *ChemPhysChem* **2014**, *15*, 249-259.
5. Kuhlman, T. S.; Sølling, T. I.; Møller, K. B., Coherent Motion Reveals Non-Ergodic Nature of Internal Conversion between Excited States. *ChemPhysChem* **2012**, *13*, 820-827.

6. Kuhlman, T. S.; Sauer, S. P. A.; Sølling, T. I.; Møller, K. B., Symmetry, Vibrational Energy Redistribution and Vibronic Coupling: The Internal Conversion Processes of Cycloketones. *J. Chem. Phys.* **2012**, *137*, 22A522.
7. Kuhlman, T. S.; Pittelkow, M.; Sølling, T. I.; Møller, K. B., Pulling the Levers of Photophysics: How Structure Controls the Rate of Energy Dissipation. *Angew. Chem. Int. Edit.* **2013**, *52*, 2247-2250.
8. Assmann, M.; Weinacht, T.; Matsika, S., Surface Hopping Investigation of the Relaxation Dynamics in Radical Cations. *J. Chem. Phys.* **2016**, *144*, 034301.
9. Assmann, M.; Koppel, H.; Matsika, S., Photoelectron Spectrum and Dynamics of the Uracil Cation. *J. Phys. Chem. A* **2015**, *119*, 866-875.
10. Bohinski, T.; Tibbetts, K. M.; Munkerup, K.; Tarazkar, M.; Romanov, D. A.; Matsika, S.; Levis, R. J., Radical Cation Spectroscopy of Substituted Alkyl Phenyl Ketones via Tunnel Ionization. *Chem. Phys.* **2014**, *442*, 81-85.
11. Tibbetts, K. M.; Bohinski, T.; Munkerup, K.; Tarazkar, M.; Levis, R., Controlling Dissociation of Alkyl Phenyl Ketone Radical Cations in the Strong-Field Regime through Hydroxyl Substitution Position. *J. Phys. Chem. A* **2014**, *118*, 8170-8176.
12. Bohinski, T.; Tibbetts, K. M.; Tarazkar, M.; Romanov, D. A.; Matsika, S.; Levis, R. J., Strong Field Adiabatic Ionization Prepares a Launch State for Coherent Control. *J. Phys. Chem. Lett.* **2014**, *5*, 4305-4309.
13. Bohinski, T.; Tibbetts, K. M.; Tarazkar, M.; Romanov, D.; Matsika, S.; Levis, R. J., Measurement of an Electronic Resonance in a Ground-State, Gas-Phase Acetophenone Cation via Strong-Field Mass Spectrometry. *J. Phys. Chem. Lett.* **2013**, *4*, 1587-1591.
14. Zhang, Y.; de La Harpe, K.; Beckstead, A. A.; Martinez-Fernandez, L.; Improta, R.; Kohler, B., Excited-State Dynamics of DNA Duplexes with Different H-Bonding Motifs. *J. Phys. Chem. Lett.* **2016**, *7*, 950-954.
15. Stephansen, A. B.; Larsen, M. A. B.; Klein, L. B.; Sølling, T. I., On the Photostability of the Disulfide Bond: An Electronic or a Structural Property? *Chem. Phys.* **2014**, *442*, 77-80.
16. Brogaard, R. Y.; Møller, K. B.; Sølling, T. I., Real-Time Probing of Structural Dynamics by Interaction between Chromophores. *J. Phys. Chem. A* **2011**, *115*, 12120-12125.
17. Konar, A.; Shu, Y.; Lozovoy, V. V.; Jackson, J. E.; Levine, B. G.; Dantus, M., Polyatomic Molecules under Intense Femtosecond Laser Irradiation. *J. Phys. Chem. A* **2014**, *118*, 11433-11450.
18. Lezius, M.; Blanchet, V.; Ivanov, M. Y.; Stolow, A., Polyatomic Molecules in Strong Laser Fields: Nonadiabatic Multielectron Dynamics. *J. Chem. Phys.* **2002**, *117*, 1575-1588.
19. Nagele, T.; Hoche, R.; Zinth, W.; Wachtveitl, J., Femtosecond Photoisomerization of Cis-Azobenzene. *Chem. Phys. Lett.* **1997**, *272*, 489-495.
20. Lednev, I. K.; Ye, T. Q.; Matousek, P.; Towrie, M.; Foggi, P.; Neuwahl, F. V. R.; Umaphathy, S.; Hester, R. E.; Moore, J. N., Femtosecond Time-Resolved UV-Visible Absorption Spectroscopy of Trans-Azobenzene: Dependence on Excitation Wavelength. *Chem. Phys. Lett.* **1998**, *290*, 68-74.
21. Chang, C. W.; Lu, Y. C.; Wang, T. T.; Diao, E. W. G., Photoisomerization Dynamics of Azobenzene in Solution with S-1 Excitation: A Femtosecond Fluorescence Anisotropy Study. *J. Am. Chem. Soc.* **2004**, *126*, 10109-10118.
22. Schultz, T.; Quenneville, J.; Levine, B.; Toniolo, A.; Martinez, T. J.; Lochbrunner, S.; Schmitt, M.; Shaffer, J. P.; Zgierski, M. Z.; Stolow, A., Mechanism and Dynamics of Azobenzene Photoisomerization. *J. Am. Chem. Soc.* **2003**, *125*, 8098-8099.
23. Klein, L. B.; Sølling, T. I., Internal Conversion Mediated by Specific Nuclear Motions: The Nitrogen Inversion in Amines. *Chem. Phys.* **2014**, *442*, 62-67.

24. Ho, J. W.; Chen, W. K.; Cheng, P. Y., Femtosecond Pump-Probe Photoionization-Photofragmentation Spectroscopy: Photoionization-Induced Twisting and Coherent Vibrational Motion of Azobenzene Cation. *J. Chem. Phys.* **2009**, *131*, 134308.
25. Ikeda, T.; Tsutsumi, O., Optical Switching and Image Storage by Means of Azobenzene Liquid-Crystal Films. *Science* **1995**, *268*, 1873-1875.
26. Kolpak, A. M.; Grossman, J. C., Azobenzene-Functionalized Carbon Nanotubes As High-Energy Density Solar Thermal Fuels. *Nano Lett.* **2011**, *11*, 3156-3162.
27. Browne, W. R.; Feringa, B. L., Making Molecular Machines Work. *Nat. Nanotechnol.* **2006**, *1*, 25-35.
28. Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M., Rapid and Reversible Shape Changes of Molecular Crystals on Photoirradiation. *Nature* **2007**, *446*, 778-781.
29. Janssen, J. F., Photoisomerization of Azobenzene - a TLC Experiment for Undergraduate Organic Laboratory. *J. Chem. Educ.* **1969**, *46*, 117-118.
30. Rusteika, N.; Moller, K. B.; Sølling, T. I., New Insights on the Photodynamics of Acetone Excited with 253-288 nm Femtosecond Pulses. *Chem. Phys. Lett.* **2008**, *461*, 193-197.
31. Bohinski, T.; Moore Tibbetts, K.; Tarazkar, M.; Romanov, D.; Matsika, S.; Levis, R., Measurement of Ionic Resonances in Alkyl Phenyl Ketone Cations via Infrared Strong Field Mass Spectrometry. *J. Phys. Chem. A* **2013**, *117*, 12374-12381.
32. Keldysh, L. V., Ionization in Field of a Strong Electromagnetic Wave. *Sov. Phys. JETP-USSR* **1965**, *20*, 1307-1314.
33. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A., et al., *Gaussian, Inc* **2009**, Wallingford CT.
34. Yanai, T.; Tew, D. P.; Handy, N. C., A New Hybrid Exchange-Correlation Functional using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51-57.
35. Rose, T. S.; Rosker, M. J.; Zewail, A. H., Femtosecond Real-Time Probing of Reactions. 4. The Reactions of Alkali-Halides. *J. Chem. Phys.* **1989**, *91*, 7415-7436.
36. Petersen, J.; Henriksen, N. E.; Møller, K. B., Validity of the Bersohn-Zewail Model beyond Justification. *Chem. Phys. Lett.* **2012**, *539*, 234-238.
37. Antonov, V. S.; Letokhov, V. S.; Shibanov, A. N., Photoionization Mass-Spectrometry of Benzene and Benzaldehyde Molecules with an Excimer KrF Laser. *Appl. Phys. A* **1980**, *22*, 293-297.
38. Schulze, F. W.; Petrick, H. J.; Cammenga, H. K.; Klinge, H., Thermodynamic Properties of Structural Analogs Benzo [C] Cinnoline, Trans-Azobenzene, and Cis-Azobenzene. *Z. Phys. Chem.* **1977**, *107*, 1-19.
39. Redchenko, V. V.; Egorova, T. I., Photoelectron Spectroscopy: Study of the Electronic Structure of Azobenzene and Several of its Derivatives. *J. Appl. Spectrosc.* **1978**, *29*, 858-860.
40. Petrachenko, N. E.; Vovna, V. I.; Furin, G. G., Photoelectron HeI Spectra of Fluorinated Azo- and Azoxy-Benzenes. *J. Fluorine Chem.* **1993**, *63*, 85-99.
41. Pisanty, E.; Ivanov, M., Momentum Transfers in Correlation-Assisted Tunneling. *Phys. Rev. A* **2014**, *89*, 043416.
42. Geißler, D.; Rozgonyi, T.; Gonzalez-Vazquez, J.; Gonzalez, L.; Nichols, S.; Weinacht, T., Creation of Multihole Molecular Wave Packets via Strong-Field Ionization. *Phys. Rev. A* **2010**, *82*, 011402.
43. Gonzalez-Vazquez, J.; Gonzalez, L.; Nichols, S. R.; Weinacht, T. C.; Rozgonyi, T., Exploring Wavepacket Dynamics behind Strong-Field Momentum-Dependent Photodissociation in CH₂BrI⁺. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14203-14216.

- 1
2
3 44. Saltiel, J., Perdeuteriostilbene. Role of Phantom States in Cis-Trans Photoisomerization of
4 Stilbenes. *J. Am. Chem. Soc.* **1967**, *89*, 1036-1037.
5
6 45. Conti, I.; Garavelli, M.; Orlandi, G., The Different Photoisomerization Efficiency of Azobenzene
7 in the Lowest $n \pi^*$ and $\pi \pi^*$ Singlets: The Role of a Phantom State. *J. Am. Chem. Soc.* **2008**, *130*,
8 5216-5230.
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

TOC Graphic