

Wave Packet Movements near the Conical Intersection between Two Excited Potential Surfaces May Create Observable Molecular Oscillations

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A femtosecond pump-probe experiment is performed on tetrakis(dimethylamino)ethylene. The evolution resulting from the $\pi-\pi^*$ excitation of the CC double bond corresponds to movement along a single adiabatic potential surface with deformation along several coordinates and passage near a conical intersection. Surprisingly, this movement excites the umbrella mode of the amino groups, resulting in a measurable oscillation regime.

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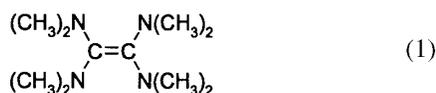
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Reaction dynamics aims to characterize the movements of the reagents towards the products traveling over one or several potential energy surfaces, in order to visualize the forces that drive these movements. Electronic relaxation in polyatomic molecules is particularly attractive in this respect since photoexcited molecules experience movements along downhill potential surfaces connecting different electronic configurations [1–5].

The connection between excited potential surfaces in polyatomic molecules results from avoided crossings and more effectively and more generally from conical intersections (CI). CI's are localized accidents on potential energy surfaces (PES) that are due to the exact degeneracy between two electronic states. Their dimensionality is low, $n - 2$, when the system has n degrees of freedom. The dimension of standard avoided crossings is $n - 1$.

The CI concept was introduced by Wigner [6]. It is recognized now as essential for describing the dynamics of electronically excited polyatomic molecules [2,7–11]. Particular attention has been given recently to ethylenic compounds through *ab initio* studies [12–15]. The potential gradients near CI's induce rapid downhill wave packet movements, which are multidimensional in essence. They drive the system from excited electronic configurations down to a lower one. In real-time pump-probe experiments, the passage through one or several CI's, since it forces movements on anharmonic surfaces, is expected to spread quickly the wave packet created by the pump laser and to dump irreversibly all movements over the coordinates that define the CI's.

We report here on the photodynamics of tetrakis(dimethylamino)ethylene (TDMAE), a fairly large polyatomic molecule of structural formula



Its central skeleton $\begin{array}{c} \text{N} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{N} \end{array}$ is approximately planar. The originality here is the following: the force field that appears in the vicinity of a conical intersection drives

the electronically excited molecule towards a lower energy configuration but strikingly, it impulses coherent observable oscillations within moieties of the molecule.

This observation is actually surprising given our former work on TDMAE showing a single damping time constant of 300 fs [4]. An ultrashort pulse at 266 nm excites the molecule in the Franck-Condon region of a state with dominant valence character (V) $(\pi)^1(\pi^*)^1$. The excited molecule is quasipolar in this region and is far from its equilibrium geometry. Hence, a twist about the CC bond follows, as well as a pyramidalization of one carbon atom of the CC bond. Both movements force the initial wave packet to pass near a conical intersection where the excited surface V exchanges its valence character with an upper surface Z, the Z surface having a dominant zwitterionic character $(\pi)^0(\pi^*)^2$ above the Franck-Condon region where the molecular skeleton is approximately planar. A similar situation has been described by *ab initio* calculations carrying on ethylene and stilbene molecules [13,15]. According to this picture, the wave packet moves on a single potential surface which changes character from V to Z in the CI region. This movement is pictured by the arrow in Fig. 1. As in Ref. [4], we say for convenience that the wave packet evolves from level V to level Z although this terminology is somehow misleading by suggesting that the system switches from one potential energy surface to another. This wave packet movement was monitored in our former work with a 800 nm probe as a single exponential decay of a 300 fs time constant. The system further decays from level Z in 120 ps to a lower charge transfer (CT) state, which fluoresces to ground state [4].

Aside from monotonic decays, the literature also reports wave packet recurrences corresponding to oscillations within the attractive region of an excited electronic state [16,17]. The simplest situation corresponds to an entrance channel excitation of the oscillations when the laser excitation drives directly the vibrational mode to be observed [18,19]. The damping of these oscillations is caused either by a population decay through an avoided

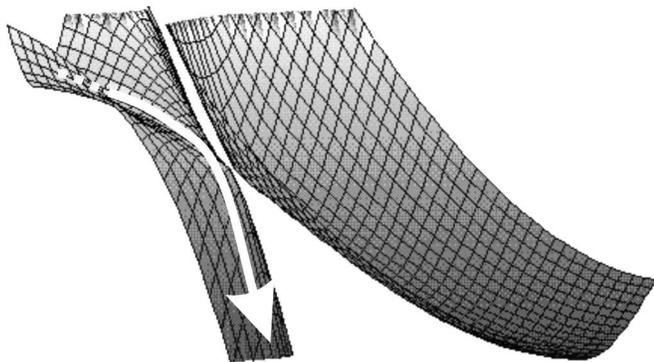


FIG. 1. Sketch showing the conical intersection between the V and Z molecular states of TDMAE. The white arrow pictures the wave packet movement out of the Franck-Condon as explained in the text.

crossing with a neighboring state that constitutes the exit channel of the photodissociation, or by a loss of coherence through anharmonic couplings. Coherent oscillations can also result from the photodissociation event itself, when a sudden impulse is imparted to a newly formed bond in the exit channel of the dissociation. This was called “exit channel coherences” by Bixon and Jortner [20] and has been encountered at first in the photodissociation of I-Hg-I, where the I_2 molecule is formed, stretched far away from its equilibrium position and oscillates subsequently [21]. Similarly, the polyatomic fragment Cr-(CO)₅ experiences large amplitude motions after ejection of CO from Cr-(CO)₆ [22]. Slightly different is the situation encountered when an I_2 molecule is photodissociated and then recombines on another potential energy curve after the I atoms have hit the repulsive wall of the cage defined by a substitution site in a rare gas matrix [23].

The present work reports real-time dynamics of the TDMAE molecule using a different pump-probe scheme than that used in Ref. [4]. The pump is again at 266 nm, thus initiating the same dynamics as before but now, the wavelength of the ionization probe is 400 nm instead of 800 nm. The present larger energy of the probe photons extends the time window for observing wave packet movements and allows the molecules to be probed beyond the CI region.

Ions of either mass 200 or 185 amu have been recorded using a time-of-flight (TOF) mass spectrometer (MS), as a function of the delay time between the pump and probe pulses. The former ions correspond to the parent mass in a one photon ionization of TDMAE by the probe laser at 400 nm. The latter ions correspond to the loss of a methyl group by hot TDMAE⁺ when neutral TDMAE is probed by ionization with two 400 nm photons. Of course, the relative importance of the one and two photon ionization processes can be varied by changing the energy per pulse of the probe laser. Probe pulse energies larger than 5 μJ are used to get measurable signals at mass 185 amu.

The results at mass 185 amu are shown as curves (a) in Fig. 2. Several features are striking:

(i) The ion signal starts rising at zero time delay, indicating that the 185 amu fragment can be formed as soon as the molecule has been excited.

(ii) Distinct oscillations are observed within a plateau. A Fourier transform of the signal is shown to the right of curves (a). It exhibits a distinct peak for an oscillation period of 250 fs that is substantially larger than the 140 fs of the cross correlation time width of the laser (excluding that the observed oscillations are due to coherences induced by the laser pulse).

The ion signal at mass 200 amu is shown as curves (b) in Fig. 2. Although less distinct, the same oscillation regime as in curves (a) is also visible.

Curve (c) in Fig. 2 shows the former result of Ref. [4] for the one 800 nm photon probe and the measurement of photoelectrons with ca. 0 eV energy. As recalled above, a single exponential decay is observed with a 300 fs time constant that was inferred to the passage from state V to state Z . This focuses the attention on the third striking point in curves (a):

(iii) The damping of the oscillations in curves (a) is conspicuously longer than the 300 fs decay of the initial V state.

The oscillations that appear both in curves (a) and (b) in Fig. 2 have a quite long period, 250 fs, corresponding to 133 cm⁻¹ in energy units. This energy is close to a group of frequencies found in Raman scattering of ground state TDMAE, namely, frequencies at 124 and 148 cm⁻¹ that were assigned to the umbrella mode of the amine groups [24]. Several other modes lie at slightly higher frequencies. Since electronic excitation to either the excited valence state or the zwitterionic state do not involve explicitly orbitals of the amine groups, similar frequencies are expected in excited TDMAE and the 250 fs oscillation period is assigned to the umbrella motion.

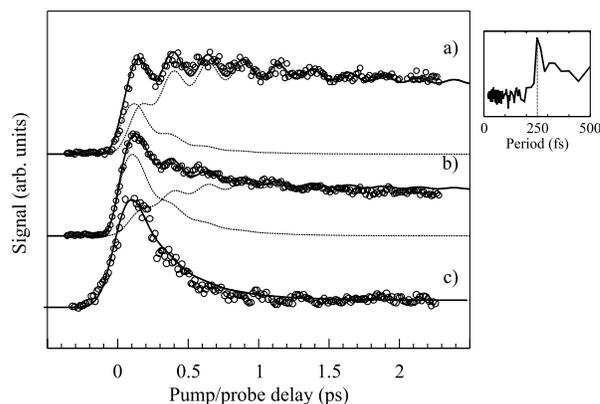


FIG. 2. Signals measured with the TOF-MS set at masses 185 amu [curves (a)] and 200 amu [curves (b)] as a function of the pump(266 nm)-probe(400 nm) delay. Curve (c) recalls a 0 eV photoelectron signal recorded using a different probe wavelength, 800 nm [4]. The solid lines passing through the experimental points are fits, as explained in the text. The right inset is a Fourier transform of curves (a).

The question now is to examine how coherent excitation of the umbrella mode is possible and why it can be detected. For convenience we answer the second question first. We thus assume for the moment that an oscillating wave packet has been created in the umbrella mode of TDMAE. Actually, this is not a sufficient condition for detecting an oscillating signal. The probe efficiency must also depend on the location of the wave packet along the molecular deformation. As we inferred in Ref. [4], the geometry of the relaxed TDMAE⁺ ion should involve at least a planar positive nitrogen atom while all the nitrogen atoms are pyramidal in the valence and zwitterionic configurations of neutral TDMAE. This provides the necessary difference between the neutral and ionic surfaces to make the ionization cross section sensitive to the umbrella motion, hence making the ion signal oscillate. The far more pronounced oscillations observed in Fig. 2 for the fragment at mass 185 [curves (a)] can likely be understood, given the greater spatial discrimination opened by the two photon excitation.

We come now to the question of exciting the umbrella motion in TDMAE. The pump laser excites the *V* states of TDMAE and creates a vibrational wave packet that is localized spatially at time zero. The latter starts moving subsequently with a time constant of $\tau_1 = 300$ fs [4] to reach the CI region where the *V* and *Z* PES exchange their character. This movement involves two coordinates, a twist about the central CC's and a pyramidalization of one central carbon atom. Both movements affect the position of the four N atoms, hence putting these atoms into movement at the same time. The terminal methyl groups, although they are far away from the distorted CC bond, are pulled or pushed in a coherent fashion by the moving N atoms, as if they were at the end of a shaken carpet. This is likely to result in excitation of the umbrella motion of the molecule.

Strikingly, the wave packet does not spread significantly before the umbrella mode is excited. Otherwise, it would be impossible that it could feed a subsequent oscillation regime with enough coherence for the oscillations to be observed. The real question is here and two opposite interpretations can be proposed.

One assumes that excitation of the umbrella mode is an early process occurring when the wave packet starts moving. In that case, the oscillation regime is characterized by an induction time τ_{ind} which must be small, compared to the time constant $\tau_1 = 300$ fs of the *V* to *Z* energy transfer. It is characterized fully by adding the vibrational period $T_{\text{osc}} = 250$ fs found from the Fourier transform of the experimental signal and a damping time constant τ_{coh} . The oscillation term is then given by

$$f_{\text{osc}}(t) = \left[1 - \exp\left(-\frac{t}{\tau_{\text{ind}}}\right) \right] \exp\left(-\frac{t}{\tau_{\text{coh}}}\right) \sin^2\left(\frac{\pi t}{T_{\text{osc}}}\right). \quad (2)$$

Since the molecular deformations that induce the *V* to *Z*

energy transfer in the CI region are those that have excited the umbrella vibration, the latter is likely to survive the change of configuration from *V* to *Z*. Hence it likely modulates both cross sections for detecting *V* and *Z*.

The second interpretation assumes that the umbrella motion is excited impulsively by the passage from *V* to *Z* in the CI region. This relies on the assumption that the potential energy surfaces *V* and *Z* are fairly flat outside the CI region and have steep slopes only in the the CI vicinity. With this interpretation, the wave packet is moving quite slowly at the beginning in regions that are not too anharmonic. Hence, it has not spread significantly when it reaches the steep potential slopes of the CI region. It is accelerated tremendously there for a short time. Large internal forces (or torques in the present case) appear that impulse deformations to the TDMAE molecule. The latter concerns nonsolely the two coordinates that define the CI but, as we have seen above, the umbrella deformation also. In that case, the oscillation regime is induced by a percussion at time $\tau_1 = 300$ fs. The full oscillation regime thus appears as the convolution between this percussion and a damped oscillating function $\sin^2\left(\frac{\pi t}{T_{\text{osc}}}\right) \exp\left(-\frac{t}{\tau_{\text{coh}}}\right)$. Since the umbrella motion is excited by the CI itself, the resulting vibration is likely to affect only the state that is populated by passage through the CI region, i.e., state *Z*.

Both these excitation mechanisms can be turned very simply into a model to fit the experimental results of Fig. 2. The three state model used in Ref. [5] is used for this purpose, however, with adjunctions to account for the oscillations in the measured signals. A set of two differential cross sections describes the decay from *V* (level 1) to *Z* (level 2) and subsequently from *Z* to CT (level 3). The population of levels 1 and 2 is given by

$$S_1(t \geq 0) = \exp\left(-\frac{t}{\tau_1}\right), \quad (3)$$

$$S_2(t \geq 0) = \frac{\tau_2}{\tau_1 - \tau_2} \left[\exp\left(-\frac{t}{\tau_1}\right) - \exp\left(-\frac{t}{\tau_2}\right) \right], \quad (4)$$

where the time constants $\tau_1 = 300$ fs and $\tau_2 = 120$ ps are those determined in Ref. [4]. The measured signal $S(t)$ corresponds to ionization of either level 1 or 2 with cross sections σ_1 and σ_2 that are modulated by the umbrella motion.

Only fits corresponding to the first excitation model proposed above are reported here. Both excitation models lead indeed to fits of similar quality, however, with a slight preference to the first model. According to this model, the umbrella oscillation affects the ionization of both levels 1 and 2 in the same way. Hence, the detected signal can be written

$$S(t \geq 0) = [\sigma_1 \cdot S_1(t) + \sigma_2 \cdot S_2(t)] \cdot [1 + \alpha \cdot f_{\text{osc}}(t)] \quad (5)$$

TABLE I. Parameters used to best fit curves (a) and curves (b) (numbers between parentheses) in Fig. 2. The values of τ_1 , τ_2 , and T_{osc} are not fitted. The two former are taken from Ref. [4] and the latter is taken from the inset of Fig. 2.

$\tau_1 = 300$ fs
$\tau_2 = 120$ ps
$T_{\text{osc}} = 250$ fs
$\tau_{\text{ind}} = 30$ fs
$\tau_{\text{coh}} \approx 1000$ fs
$\alpha = 1.5$ (0.65)
$\sigma_1 = 0.4 \cdot \sigma_2$ ($0.7 \cdot \sigma_2$)

using a multiplying factor to modulate both ionization cross sections σ_1 and σ_2 at the same time. $\frac{\alpha}{1+\alpha}$ is the maximum amplitude of modulation. The ratio $\frac{\sigma_1}{\sigma_2}$ appears as the detection ratio between levels V and Z. For a final comparison with the experimental results, $S(t)$ is convoluted by cross correlation time width of the lasers (140 fs FWHM). The free parameters to best fit the experimental data of Fig. 2 are τ_{ind} and τ_{coh} in Eqs. (2) and $\frac{\sigma_1}{\sigma_2}$ and α in Eq. (5). The best fit curves are shown as a solid line in Fig. 2 and the corresponding fit parameters are listed in Table I. The dotted curves in Fig. 2 are the contributions S_1 (only a transient) and S_2 (a transient followed by a plateau).

Note that in the fit of the zero energy electrons in the ionization at 800 nm [curve (c) in Fig. 2] the solid curve accounts for a small contribution, 5%, of the Z state.

The agreement between the model and the experiment is quite satisfactory given that the same set of parameters, τ_{osc} , τ_{ind} , and τ_{coh} , that describe the oscillation regime itself is able to reproduce all the experimental data of Fig. 2. Of course the other two parameters, which represent the detection cross section, must be adapted to each experiment.

In conclusion, coherent oscillations of 250 fs period and 1000 fs damping constant have been detected in the course of electronic relaxation of TDMAE from a laser excited $\pi-\pi^*$ excited valence state towards a zwitterionic state. A tentative explanation is the following: the oscillation regime is not created by the laser excitation directly but by the wave packet movement that ultimately brings the molecule from V to Z in the vicinity of a conical intersection where the two states are strongly coupled. In that sense, the situation is akin to that observed in the caging recoil recalled above [23]. We anticipate that this excitation mechanism of coherent oscillations in large polyatomic molecules should be quite

general and would appear as the onset of vibrational redistribution in polyatomic molecules.

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