Semiclassical treatment of the photofragmentation of azomethane

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Abstract

We have studied the photofragmentation of azomethane by classical trajectories plus surface hopping, run on ab initio potential energy surfaces. Transition probabilities are evaluated with the help of a general diabatization technique. The radiationless transition from \( S_1 \) to \( S_0 \) occurs within 0.5 ps and the fragmentation takes place almost exclusively in the ground state. About 2/3 of the trajectories lead to almost simultaneous breaking of both N–C bonds, while 1/3 go through formation of the CH\(_3\)NN\(^-\) radical; however, the latter breaks apart with a short delay of the order of 1 ps. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Azomethane is the prototypical open-chain azoalkane, a class of compounds which exhibits an interesting photochemistry [1]. In gas phase, the azoalkanes undergo photofragmentation, yielding N\(_2\) and two alkyl radicals. In condensed phases, dissociation is inhibited and trans–cis isomerization takes place instead. It is not clear which electronic states are involved in the photofragmentation: in particular, whether bond breaking occurs directly in the \( S_1 \) state; or in the ground state, following a fast internal conversion (IC); or in the triplet manifold, perhaps after intersystem crossing (ISC) \( S_1 \rightarrow T_2 \).

Another open question is whether the breaking of the two N–C bonds is synchronous or simply concerted (i.e. with a small time delay and no detectable intermediates) or sequential: in the latter case, the methyl diazenyl radical should be produced in the primary step to be further decomposed into CH\(_3\) and N\(_2\) in the secondary step. Only a synchronous fragmentation may yield perfectly equivalent translational, rotational and vibrational energy distributions in the two methyl radicals.

CARS spectroscopy of CH\(_3\) and N\(_2\) produced by photodissociation at 355 nm in the presence of He as buffer gas to insure rotational thermalization was carried out with nanosecond time resolution: the results were interpreted as implying stepwise dissociation, with a substantial time delay of about 5 ns between the appearance of the first (vibrationally hot) and of the second (cold) methyl radical [2,3].

The velocity distribution of the fragments was measured in molecular beam experiments, following photolysis at 351 nm: the observed vector correlation between the methyl velocities leads the authors to the conclusion that the methyl diazenyl radical, if formed, has a lifetime much shorter than its rotational period \( \approx 1 \) ps [4]. The fragmentation, however, is not symmetric: the second methyl radical is ejected with a much larger average kinetic energy than the first one.

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Recent measurements of translational, rotational and vibrational energy distributions of CH$_3$ following photodissociation at 333 nm, again in collisionless conditions, were analyzed by means of a barrier impulsive model of the bond breaking process: if one admits that only the second, fast CH$_3$ is detected in this experiment, the results are consistent with those obtained in molecular beams [5].

In view of the lack of experimental evidence as to which electronic states are implied in the photolysis of azomethane and of the contrasting interpretations concerning the temporal sequence of the C–N bond breakings, we have undertaken an extensive theoretical study of the azomethane photochemistry. This work presents a simulation of the photodissociation in vacuo, based on classical trajectories with surface hopping (TSH). Potential energy surfaces (PES) and couplings were obtained in the form of an effective hamiltonian in a quasi-diabatic basis, by means of a recently developed procedure [6]. In this preliminary work the methyl groups are contracted to single point masses, therefore their internal vibrational energy is neglected. The treatment of the full set of internal coordinates is under way. Also planned are simulations of the azomethane photochemistry in solution.

2. Quasi-diabatic states

The theoretical study of geometry relaxation and radiationless transitions following excitation requires knowledge of the PES and couplings of the relevant electronic states. A convenient solution of the problem consists of determining quasi-diabatic (QD) states [7,8]. The electronic hamiltonian matrix H in the QD basis {\ldots |\eta> \ldots} contains virtually all the information needed to run dynamical calculations. Its eigenvalues are the adiabatic potentials $U_i$; however, the $H_{ij}(Q)$ matrix elements are much easier to fit or interpolate, as functions of the $Q$s, than the eigenvalues $U_i(Q)$, especially in the presence of conical intersections. Moreover, the diabatic representation facilitates the determination of nonadiabatic transition probabilities: if the calculation is run directly in the QD basis, the couplings are simply the off-diagonal matrix elements of $\mathcal{H}$; if the adiabatic (AD) basis is adopted, the derivatives of $\mathcal{H}$ with respect to nuclear coordinates $Q$, combined with the eigenvectors, provide a simple approximation of the nonadiabatic couplings [6].

The photochemistry of azomethane involves several different reaction coordinates: breaking of either one or the other N–C bond, or both; torsion of the double bond; inversion at the N atoms. To produce a set of electronic states which are (quasi-)adiabatic under all of these geometrical transformations is not trivial and has required a substantial extension of our method based on diabatic templates. The new diabatization procedure and its application to the problem discussed here are described in Ref. [6]. Here a few essential points should be mentioned to clarify the nature of the QD states we have defined for the azomethane molecule.

We are interested in the $S_0$ and $S_1$ states: in view of the high efficiency of the IC process (see below), it is probably safe to leave the triplet states out of the dynamical treatment, although they were determined by ab initio calculations [6] along with the singlets and their spin–orbit couplings. $S_1$ is a $n \to \pi^*$ state of $^1\text{B}_u$ symmetry in the $C_{2v}$ point group (trans-azomethane) and $^1\text{B}_1$ in the $C_{2v}$ group (cis-azomethane). If the torsion about the double bond (CNNC dihedral angle) takes place by conserving the $C_2$ symmetry, we define the first QD state $|\eta_1>\rangle$ as $^1\text{A}$ and $|\eta_2>\rangle$ as $^1\text{B}$ (i.e. $S_0$ and $S_1$, respectively, at the two isomers equilibrium geometries). As long as a symmetry element (here the $C_2$ axis) exists, the QD and the AD states coincide. For small symmetry breaking displacements, the QD states are similar to $^1\text{A}$ and $^1\text{B}$ of the closest symmetric geometry.

When one of the N–C bonds is substantially elongated, we switch smoothly to another definition of the QD states, based on antisymmetriized products of fragment wavefunctions. The methyl radical is always in its $^2\text{A}_g$ state, while CH$_2$NN$^+$ has two low lying states, $^2\text{A}$ and $^2\text{X}$, which are associated with $|\eta_1>\rangle$ and $|\eta_2>\rangle$, respectively. Therefore, for all geometries with a symmetry plane (e.g. N–C bond elongation and/or nitrogen inversion, without torsion), the QD states are $^1\text{A}$ and $^1\text{X}$, and again coincide with the AD states. The simultaneous breaking of both N–C bonds has not been explicitly considered in our previous work [6], but the definition of QD states for these geometries may be seen as a trivial extension of the one-bond breaking case, with further dissocia-
tion of CH$_3$NN$^-$.

The $|\eta_1\rangle$ and $|\eta_2\rangle$ QD states correlate with the $1\Sigma_g^+$ ground state of the N$_2$ molecule and with its $\Delta_u$ state, respectively; the latter, however, plays no role in the photochemistry of azomethane, at least at the wavelengths considered here.

Details about the ab initio calculation and the fit of the $\hat{H}$ matrix elements as functions of the internal coordinates will be published elsewhere [9]. Briefly, we have run CIPSI-QDPT calculations [6,10–12], making use of the 6-31G* basis set [13] and of natural orbitals obtained from state average complete active space self-consistent field (CASSCF) calculations. As a preliminary step, we ran a set of geometry optimizations at the state specific CASSCF level with an active space of 6 electrons in 6 MOs, for CH$_3$; N$_2$; CH$_3$NN$^-$; cis, trans, twisted and semilinear CH$_3$NNCH$_2$, in the ground state and/or $S_1$, as appropriate. This allowed us to adjust the methyl internal coordinates, keeping them close to their optimal values while varying the CNNC skeleton geometry, i.e. the $R = R$(NN), $R_1 = R$(N$_i$C$_1$) and $R_2 = R$(N$_i$C$_2$) bond lengths, the $\theta_1 = \text{NNC}_i$ and $\theta_2 = \text{NNC}_2$ bond angles and the $\phi = \text{CNNC}$ dihedral angle. About 270 geometries were chosen for the ab initio calculations and the fit of the $H_i(Q)$ functions.

The fitting function for the diagonal elements is an 88 parameter sum of terms, mostly products of powers of $R_1$ and $R_2$, damped by exponentials of the kind $\exp(-KR)$, with trigonometric functions of $\theta_1$, $\theta_2$ and $\phi$. A similar but simpler expansion is adopted for $H_{ii}(Q)$. Restrictions are applied to the analytic forms of the three matrix elements, as dictated by the symmetry of the electronic states for all accessible geometries. A weighted least squares fit of the ab initio results yielded a standard deviation of 2.0 kcal/mol, with the largest errors and the lowest weights concentrated in the steep repulsive regions of the PES.

Figs. 1 and 2 are two views of the diabatic PES, i.e. the $H_{ii}$ functions. In Fig. 1 we consider the symmetric elongation of the N–C bonds ($R_1 = R_2$) and torsion ($\phi$). In Fig. 2 we have the single bond breaking ($R_1$) and torsion. In both cases, all other coordinates are kept fixed ($R = 2.25$, $R_2 = 2.50$ bohr, NNC = 130$^\circ$), in order to show the crossing seam between the two surfaces: in this sense, the two plots provide only qualitative information on the PES. In fact, when the $R$, $\theta_1$ and $\theta_2$ coordinates are optimized, even in the upper surface, no intersection can be found, save at short $R_1 = R_2$ and high energies. The crossing seam is found in the proximity of $\phi = 90^\circ$. Due to the symmetry, in Fig. 1 the adiabatic and diabatic surfaces coincide: along the crossing seam $S_0$ and $S_1$ they are actually degenerate. However, one of the two coordinates of Fig. 2, $R_1$, breaks the $C_2$ symmetry which makes the $S_0$–$S_1$ curve crossing allowed: therefore, only two points of conical intersection between the adiabatic surfaces exist in this plot, and they are marked with black dots. They lie on the short $R_1$ side of the valley which connects the cis and trans isomers in $S_1$. A geometry optimization with the constraint of $S_0$–$S_1$ degeneracy locates the lowest energy intersection point at 77.1 kcal/mol over the ground state trans-azomethane minimum (see Table 1). This is a bit higher than the twisted minimum in $S_1$ (71.1 kcal/mol) but substantially lower than the vertical excitation energy (89.7 kcal/mol) or the 333–355

![Fig. 1. Potential energy surfaces (in kcal/mol) of the first two singlet states of azomethane, for symmetric NC bond breaking, as functions of the CNNC dihedral angle ($\phi$/degrees) and of the NC bond length ($R_1 = R_2$). All other coordinates are fixed: $R = 2.25$ bohr, $\theta_1 = \theta_2 = 130^\circ$. The diabatic ($H_i$) and adiabatic ($U_i$) potentials coincide, because of symmetry.](image-url)
nm photon (80.5–86 kcal/mol), which makes the conical intersection quite accessible to the excited molecule. However, the diabatic surfaces do intersect along a crossing seam which extends to significantly lower energies. As a consequence, this region of strong nonadiabatic couplings is probably more important for the IC process than the conical intersection itself. One may conclude that the exact location of the minimum in the crossing seam between the adiabatic surfaces is of little consequence as to the photochemistry of azoalkanes.

The most important energy data concerning the fitted surfaces are given in Table 1 and compared with the results of Liu et al. [14]; in that work, more extensive basis sets were employed, but only in special cases were multi-reference methods for electron correlation applied. The two sets of results are in fair agreement. The main discrepancies concern the dissociation energies of azomethane to CH$_3$NN$^-$ + CH$_3$ and to N$_2$ + 2CH$_3$NN$^-$: both are probably underestimated in our treatment. No transition state (TS) is found by Liu et al. for the first NC bond breaking, but the energy required for this process is about the same in their and in the present treatment. However, their TS for simultaneous fragmentation is lower than ours and not quite symmetric. Also the minimum energy structure on the crossing seam is non-symmetric according to Liu et al. while we find it symmetric (C$_2$). As we shall see, the photofragmentation dynamics is largely independent of such details, mostly because of the large energy excess available to cross the barriers (20–30 kcal/mol).

### Table 1

Energies of relevant structures in the fitted potential surfaces, relative to trans-CH$_3$NNCH$_3$ (kcal/mol)

<table>
<thead>
<tr>
<th>Structure</th>
<th>This work</th>
<th>Ref. [14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-CH$_3$NNCH$_3$</td>
<td>11.7</td>
<td>–</td>
</tr>
<tr>
<td>TS for N inversion</td>
<td>59.4</td>
<td>–</td>
</tr>
<tr>
<td>TS for first NC bond breaking</td>
<td>54.5</td>
<td>57.4</td>
</tr>
<tr>
<td>CH$_3$NN$^-$ + CH$_3$</td>
<td>47.2</td>
<td>57.4</td>
</tr>
<tr>
<td>TS for NC bond breaking in CH$_3$NN$^-$</td>
<td>49.9</td>
<td>60.0</td>
</tr>
<tr>
<td>TS for symmetric NC bond breaking</td>
<td>59.2</td>
<td>53.2–58.0</td>
</tr>
<tr>
<td>N$_2$ + 2CH$_3$NN$^-$</td>
<td>19.2</td>
<td>33.0</td>
</tr>
<tr>
<td>vertical S$_1$</td>
<td>89.7</td>
<td>87.0</td>
</tr>
<tr>
<td>optimized S$_1$ (planar, trans)</td>
<td>76.8</td>
<td>–</td>
</tr>
<tr>
<td>optimized S$_1$ (twisted)</td>
<td>71.2</td>
<td>74.9</td>
</tr>
<tr>
<td>optimized crossing seam</td>
<td>77.1</td>
<td>70.5</td>
</tr>
</tbody>
</table>

3. Classical trajectories with surface hopping

We ran a batch of 2000 classical trajectories on the adiabatic potential energy surfaces, treating the azomethane molecule as a tetra-atomic system with the methyl groups replaced by equivalent point masses. The electronic Schrödinger equation:

$$i\hbar \frac{d}{dt}\langle \psi(t) \rangle = \hat{H}_{el}\langle \psi(t) \rangle$$

is solved by expansion of $|\psi(t)\rangle$ in the QD basis:

$$|\psi(t)\rangle = \sum_i d_i(t)|\eta_i\rangle$$

In this way, only the matrix $\hat{H}$ and its eigenvalues $U_i$ are needed for the simultaneous numerical integration of the trajectory and of the time-dependent electronic wavefunction. The eigenvectors of $\hat{H}$ constitute the transformation matrix from the diabatic to...
adiabatic representation; by applying the transformation to the \( d_i(t) \) coefficients, one obtains the adiabatic coefficients \( a_i(t) \) and the related probabilities \( |a_i(t)|^2 \). Electronic transitions (‘hops’) are governed by Tully’s ‘fewest switches’ algorithm \(^{15}\), according to the \( |a_i(t)|^2 \) functions. More details can be found in Ref. \(^{16}\).

The initial conditions were sampled by integrating Langevin’s equation in the ground state surface, until the time averages of the potential and kinetic energy were stable. This required a few ps with friction coefficients \( \gamma = 41 \times 10^{13} \text{s}^{-1} \). Then, every 20 fs, a trajectory was initiated by transition to \( S_1 \), without changing the nuclear coordinates and momenta and switching off both friction and white noise. The vertical excitation energy \( \Delta U = U_i - U_0 \) was recorded for further elaboration.

98.35\% of the trajectories ended with dissociation of both NC bonds \((R_1 \text{ and } R_2 > 10 \text{ bohr})\) within 10 ps. Before fragmentation, almost all trajectories undergo IC from \( S_1 \) to \( S_0 \); only in 1.6\% of cases is one NC bond broken on the \( S_1 \) surface. The IC process is fast \(< 400 \text{ fs} \), as shown by the surface hopping time histogram of Fig. 3. A plot of the CNNC dihedral angle \( \phi \) versus time for the first hopping of each trajectory (Fig. 4) shows that most nonadiabatic events take place with \( 70^\circ < \phi < 110^\circ \), within the first complete oscillation in the torsional potential; the oscillation period is about 200 fs. Two peaks in the histogram correspond to the first forward and backward passage through the strong interaction region. 65\% of the surface hoppings occurred at geometries where the \( S_0 \) and \( S_1 \) surfaces are separated by \( \Delta U > 5 \text{ kcal/mol} \) and 44\% with \( \Delta U > 10 \). These data show that, although transitions are obviously more probable when the energy gap is smaller, they do not occur exclusively in the close proximity of the crossing seam.

We have investigated the fragmentation mechanism, which may be stepwise:

\[
\text{CH}_3\text{NNCH}_3 \rightarrow \text{CH}_3\text{NN}^- + \text{CH}_3\text{.} \tag{3}
\]

\[
\text{CH}_2\text{NN}^- + \text{CH}_3 \rightarrow \text{N}_2 + 2\text{CH}_3\text{.} \tag{4}
\]

or involve simultaneous breaking of the two NC bonds:

\[
\text{CH}_3\text{NNCH}_3 \rightarrow \text{N}_2 + 2\text{CH}_3\text{.} \tag{5}
\]

The formation of \( \text{CH}_3\text{NN}^- \) along a trajectory is acknowledged when \( R_1 \) exceeds 8 bohr with \( R_2 < 4 \) bohr, or viceversa. With this definition, the fragmentation is stepwise in 36\% of the trajectories and almost simultaneous in 64\%. These percentages remain virtually unchanged (38\% vs. 62\%) when we select the trajectories according to the excitation energy \( \Delta U \), requiring that \( 80 < \Delta U < 88 \text{ kcal/mol} \): this range includes the photon energy for the experiments outlined in Section 1. Notice that the preference for simultaneous versus stepwise bond breaking is at variance with the relative height of the potential energy barriers see Table 1. In fact, the large excess of vibrational energy available in \( S_0 \) promotes a fast dissociation of both NC bonds and it is probably rather arbitrary to trace a boundary between the two mechanisms. Although \( \text{CH}_3\text{NN}^- \) can be formed as a reaction intermediate, it breaks apart in a short time. Fig. 3 shows histograms of the times needed to complete the three reaction steps (3–5) and also for the overall methyl radical production. The delay between primary and secondary \( \text{CH}_3 \) production, reactions (3) and (4), is barely detectable; moreover, reactions (3) and (5) occur with quite similar time distributions. We made a least squares
fit by exponential functions of the long time queue of these histograms, i.e. $t > 400$ fs for reactions (3) and (5), and $t > 600$ fs for reaction (4). The resulting lifetimes are 366, 403 and 377 fs, for reactions (3–5), respectively. Somewhat longer lifetimes (518, 529 and 548 fs) are obtained by selecting only the trajectories with vertical excitation energy between 80 and 88 kcal/mol.

4. Conclusions

Two main conclusions can be drawn from this preliminary study. First, the internal conversion in azomethane is efficient, because the $S_1$–$S_0$ crossing seam and the nearby region of strong nonadiabatic coupling are quite accessible. Therefore, the fragmentation takes place almost exclusively on the ground state PES. We cannot explicitly rule out a role of the triplet states in the reaction mechanism, but it seems unlikely that ISC may compete with such a fast IC. Future calculations including spin–orbit coupling will settle the question.

Second, both NC bonds are broken within a short time, of the order of 1 ps. The majority of trajectories show almost simultaneous bond breaking. Even when CH$_3$NN$^*$ is formed, its lifetime is so short that it could not be experimentally detected: moreover, it would be difficult, on the basis of detachment time alone, to distinguish between the primary and secondary ejected CH$_3$ radical. These results are consistent with a concerted mechanism, as deduced from molecular beam experiments [4], rather than with stepwise fragmentation [2,3].

Work is in progress to run simulations of azomethane photodissociation with an improved potential energy surface, including all internal coordinates. This will enable us to study the important
question of energy disposal, about which there are some interesting but uncomplete sets of experimental data. Preliminary results show that the inclusion of the methyl internal coordinates in the treatment slows down the fragmentation dynamics, without upsetting the present conclusions.

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