The ground and excited state potential energy surfaces of nitromethane related to its dissociation dynamics after excitation at 193 nm

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The relevant low-lying singlet and triplet potential energy surfaces in the photolysis of nitromethane have been studied by using the multistate extension of the multiconfigurational second-order perturbation theory in conjunction with large atomic natural orbital-type basis sets. The proposed mechanism for the photolytic decomposition of CH₃NO₂ provides a consistent and reinterpreted picture of the available experimental results. Two reaction paths are found in the photolysis of nitromethane after excitation at 193 nm: (1) Major Channel, CH₃NO₂(1A′) + hν(193 nm) → CH₃NO₂(2A″) IC → CH₃NO₂(2A′) → CH₃(1A₁) + NO₂(1²B₁) IC → CH₅(1A₁) + NO₂(1²A₁) → CH₃(1A₁) + NO + O(3Σ⁺) + αO(3P) + βO(1D). (2) Minor Channel, CH₃NO₂(1A′) + hν(193 nm) → CH₃NO₂(2A″) → CH₃(1A₁) + NO₂(1²A₂) → CH₅(1A₁) + NO(X²Π) + αO(3P) + βO(1D), being α and β fractional numbers. No ionic species are found in any dissociation path. Additionally, the respective low-lying Rydberg states of nitromethane and nitrogen dioxide have been studied too. © 2003 American Institute of Physics. [DOI: 10.1063/1.1600436]

I. INTRODUCTION

Nitro-containing compounds exhibit interesting physical and chemical properties, for example, they play a significant role in propellant ignition, combustion, and atmosphere pollution. Consequently, thermal and photochemical decomposition of such compounds have attracted considerable attention among many research groups. Nitromethane (CH₃NO₂) is the parent molecule of the nitroalkane family as well as a prototypical energetic material. Although it is an explosive substance, strong initiation is required to make it detonate, and moderate care is sufficient for safe handling of this volatile liquid. Its structural simplicity contrasts to the rich chemistry exhibited on both the ground and excited potential energy surfaces.

Thermally, two reaction channels are dominant [Eqs. (1) and (2)].

\[ \text{CH₃NO₂} \rightarrow \text{CH₃} + \text{NO}_2, \]  
\[ \text{CH₃NO₂} \rightarrow \text{CH₃ONO} \rightarrow \text{CH₃O} + \text{NO}. \]

Lee and co-workers demonstrated via infrared multiphoton dissociation (IRMPD) experiments that NO₂ and NO formation essentially occurs without translational energy release, which is in agreement with a fragmentation of a simple bond with no exit barrier. Previously, it had been suggested that a third reaction [Eq. (3)] was competing with methoxy radical formation [Eq. (2)]. However, the mentioned authors did not find any evidence of this third route in their IRMPD experiments.

\[ \text{CH₃NO₂} \rightarrow \text{CH₃ONO} \rightarrow \text{H}_2\text{CO} + \text{HNO}. \]

The understanding of the photodissociation dynamics of nitromethane is complicated by the large number of states involved in it. Its electronic absorption spectrum in the near ultraviolet consists of two bands: a strong band centered at 198 nm, and a much weaker band centered at around 270 nm. The strong band at 198 nm was assigned to a π → π* transition localized on the NO₂ moiety, and the weak band was assigned to an n → π* transition from a nonbonding electron of O. Electron impact spectra and photoelectron spectra provide more information about other excited states. Flicker et al. observed a feature with a maximum intensity at 3.8 eV energy loss in their electron impact spectra. This peak was assigned to a singlet–triplet transition, playing a central role in the gas phase photolysis of nitromethane. Other transitions ranging from ~4.00 to ~12.00 eV, either optically allowed or optically forbidden, were also observed in these electron impact spectra (see Table I).

The primary photolytic process following excitation of either of the two lowest optical transitions is the cleavage of the C–N bond [Eq. (4)].

\[ \text{CH₃NO₂} + hν \rightarrow \text{CH₃} + \text{NO}_2. \]

There is also evidence of minor competing channels [Eqs. (5) and (6)]

\[ \text{CH₃NO₂} + hν \rightarrow \text{CH₃O} + \text{HNO}, \]  
\[ \text{CH₃NO₂} + hν \rightarrow \text{CH₃NO} + \text{O}. \]

The decomposition following excitation via the long wave absorption leads to the production of vibrationally ex-
cited NO$_2$ in its electronic ground state ($^2A_1$) along with small quantities of it in an unidentified excited electronic state. It is not clear the formation of other reaction products such as OH radicals. While Zabarnick et al. detected a small yield of OH in the collision free photodissociation of CH$_3$NO$_2$ at 266 nm; Greenblatt et al. did not find any evidence of OH formation from photolysis of nitromethane at 282 nm.

Recently, Park et al. have studied the dynamics of oxygen atom formation [Eq. (6)] in the gas-phase photolysis of nitromethane at two ultraviolet (UV) laser wavelengths of 248 and 266 nm. They conclude from the analysis of product translational energy and fine-structure state population distribution of the O atoms that at both dissociation wavelengths the O atoms are produced mainly via an indirect predissociation mechanism, but at 248 nm there is an additional contribution from a direct predissociation mechanism. They are able to determine the absolute quantum yields for O($^3P$), $\phi(O) = 0.18$ at 248 nm and $\phi(O) = 0.13$ at 266 nm. The estimated value of NO$_2$ quantum yields amounts to $\phi$(NO$_2$) = 0.73 at 266 nm.

Excitation of nitromethane in the $\pi \rightarrow \pi^*$ transition gives Eq. (4) as the primary process. These authors propose the following dissociation pathways via photon absorption at 193 nm:

Major channel

\[
\text{CH}_3\text{NO}_2 + h\nu(193 \text{ nm}) \rightarrow \text{CH}_3 + \text{NO}_2 \left( 1^2B_2 \right) \rightarrow \text{CH}_3 + \text{NO}(X^2\Pi) + \text{O}^3P, (4a)
\]

Minor channel

\[
\text{CH}_3\text{NO}_2 + h\nu(193 \text{ nm}) \rightarrow \text{CH}_3 + \text{NO}_2 \left( 2^2B_2 \right) \rightarrow \text{CH}_3 + \text{NO}(A^2\Sigma^+) + \text{O}^3P. (4b)
\]

In addition, recent experiments on the photolytic decomposition of NO$_2$ at 193 nm yields O($^3P$) and O($^1D$) as reaction products [Eq. (7)] with a branching ratio $O(1^D)/[O(1^D) + O^3P] = 0.55 \pm 0.03$

\[
\text{NO}_2 \rightarrow \text{NO} + a\text{O}(^3P) + b\text{O}(^1D). (7)
\]

The experimental observations on the 193 nm photolysis of nitromethane are summarized by Moss et al. as follows: (i) The observed translational energy distributions of methyl radical are indicative of two dissociation pathways. (ii) The internal excitation energy of the methyl fragment is observed to be relative modest. (iii) The secondary dissociation products of the major channel [Eq. (4a), NO($X^2\Pi$) and O($^3P$)] have a distribution of internal and translational energy consistent with a dissociation on a repulsive surface. (iv) Electronically excited NO (A$^2\Sigma^+$) is found to be a secondary

### Table I. MS-CASPT2 energies of the vertical transitions of nitromethane.$^a$

<table>
<thead>
<tr>
<th>State</th>
<th>Configuration</th>
<th>$\omega^a$</th>
<th>MS-CASPT2</th>
<th>$\nu (eV)$</th>
<th>Expt. ($eV)^b$</th>
<th>$f^c$</th>
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<tr>
<td>G. S.</td>
<td></td>
<td>90</td>
<td>$-244.542 17$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 $^1A'$</td>
<td>$\sigma(CN) \rightarrow \pi^*(NO)$</td>
<td>79</td>
<td>$-244.382 23$</td>
<td>4.35</td>
<td>4.45</td>
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</tr>
<tr>
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<td>$\sigma(CN) \rightarrow 2\pi$</td>
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<tr>
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<td>$n\sigma \rightarrow 3\pi_p$</td>
<td>79</td>
<td>$-244.225 58$</td>
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<td>8.8$\pm0.1$</td>
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</tr>
<tr>
<td>5 $^1A'$</td>
<td>($n\sigma)^2 \rightarrow [\pi^*(NO)]^{1,2,3}$</td>
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<td>$-244.205 01$</td>
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<td>—</td>
<td>0.1806d$-04$</td>
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<td>6 $^1A'$</td>
<td>$n\pi \rightarrow 3\pi_p$</td>
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<td>$-244.201 96$</td>
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<td>9.43</td>
<td>0.7825d$-02$</td>
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<td>6.36</td>
<td>6.23</td>
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<tr>
<td>4 $^1A'$</td>
<td>$n\sigma \rightarrow 3\pi_p$</td>
<td>78</td>
<td>$-244.225 29$</td>
<td>8.62</td>
<td>8.8$\pm0.1$</td>
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<tr>
<td>5 $^1A'$</td>
<td>$n\pi \rightarrow 3\pi_p$</td>
<td>86</td>
<td>$-244.201 78$</td>
<td>9.26</td>
<td>9.43</td>
<td>…</td>
</tr>
<tr>
<td>1 $^1A''$</td>
<td>$n\pi \rightarrow \pi^*(NO)$</td>
<td>93</td>
<td>$-244.404 66$</td>
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<td>…</td>
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<tr>
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<td>3.81</td>
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<tr>
<td>5 $^1A''$</td>
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<td>80</td>
<td>$-244.216 72$</td>
<td>8.86</td>
<td>8.8$\pm0.1$</td>
<td>…</td>
</tr>
</tbody>
</table>

$^a$AN0-L basis sets, CAS (12e,12o). Applied imaginary level shift equal to 0.1.
$^b$Weight of the configuration (%).
$^c$Values from electron impact excitation experiments in Ref. 11. The estimated uncertainty in the transitions is $\pm0.05$ eV, unless otherwise indicated.
$^d$Oscillator strength in a.u.
product of the minor channel, Eq. (4b), a product that requires absorption of two 193 nm photons. (v) Relatively little translational energy is released in the second decomposition step of the minor channel, which is inconsistent with an impulsive dissociation.

The assignment of the major channel to the $^2B_1$ state of NO$_2$ was based on the fluorescence emission studies from the photolysis of nitromethane. However, it is worthy to note that the authors recognize this assignment only as tentative.

From the theoretical standpoint, most of the previous studies on the photolysis reactivity have dealt with its reactions on the ground state potential energy surface.\\textsuperscript{21–26} Determination of the structure and energy of the transition state involved in Eq. (2) has been the focus of interest and contention of many of these works.\\textsuperscript{21–25} Perhaps, up to date, the most complete work on the thermal unimolecular decomposition of nitromethane has been carried out by Hu et al., who have studied six of its thermal reactions including dissociation, isomerization, and elimination channels by using the density functional theory in conjunction with the G2MP2 approach.\\textsuperscript{30} The above mentioned work and our own results\\textsuperscript{25(a)} agree in that Eqs. (1) and (2) have similar energy barrier heights ($\approx$62 kcal/mol), being favored the dissociation channel for about 2 kcal/mol. Recently, Nguyen et al.\\textsuperscript{25(b)} have found that the energy of the isomerization channel is at least 6 kcal/mol above the CH$_3$+NO$_2$ asymptote. The second step both in Eqs. (2) and (3) is predicted to be about 40 kcal/mol.

To our knowledge only two articles dealing with the excited potential energy surfaces of nitromethane have been published.\\textsuperscript{27,28} Mijoule et al.\\textsuperscript{27} investigated the first excited singlet states at the SCF+Cl level. They obtained strongly predissociative potential surfaces for each of the studied excited states. Later, Roszak and Kaufman\\textsuperscript{28} studied at the multiple reference double-excitation configuration-interaction (MRDCl) level in conjunction with the Huzinaga/Dunning/Hay basis sets,\\textsuperscript{31} the low-lying excited singlet and triplet potential energy curves for the decomposition of nitromethane. In contrast to the former authors, assuming $C_z$ symmetry along the dissociation curves, they found that the only predissociative curve occurs at the first $A''$ singlet, while the two $A'$ singlets are bonding and the second $A''$ state is repulsive. Interestingly, these authors concluded that at the dissociation limit singlets $A'$ yield two radicals (ground state) and anion–cation (first excited state) fragments.

The present work explores computationally the potential energy surfaces (ground and excited states) related to yielding of NO$_2$ and NO from the precursor material (CH$_3$NO$_2$) at the complete active space self-consistent field (CASSCF) and multiconfigurational second-order perturbation theory (MS-CASPT2) levels of theory. This paper is structured in four sections: I. Introduction, in which the most relevant preceding works are summarized; II. Methods of Calculation, where the computational details are described; III. Results and Discussion, which deals with the vertical transitions of CH$_3$NO$_2$ and NO$_2$, respectively, as well as their dissociation paths; and IV. Summary of the results and conclusions obtained from them.

II. METHODS OF CALCULATION

Generally contracted basis sets of atomic natural orbital (ANO) type obtained from C,N(14s9p4d)/H(8s4p3d) primitive sets,\\textsuperscript{32} the so-called ANO-L basis sets, with the C,N[4s3p2d]/H[3s2p1d] contraction schemes were used in all of the geometry optimizations of the relevant species involved in the photolysis of nitromethane, which were performed at the CASSCF\\textsuperscript{33} level of theory as implemented in the MOLCAS 5.4 program.\\textsuperscript{34} Hereafter, CAS(2e,2o) means the active space built by distributing N electrons in M orbitals. The stationary points (minima and saddle points) were characterized by their CASSCF analytic harmonic vibrational frequencies computed by diagonalizing the mass-weighted Cartesian force constant matrix, i.e., the Hessian matrix, $H$.

In addition, the energies of all critical points have been recomputed with the multistate extension of the MS-CASPT2.\\textsuperscript{35} Therefore, the CASSCF wave functions were used as reference in the second-order perturbation treatment, keeping frozen the 1s electrons of the carbon and nitrogen atoms respectively, as determined in the CASSCF calculations. To minimize the contamination of the pertubated wave function by intruder states,\\textsuperscript{36} the technique of the imaginary level shift\\textsuperscript{37} has been introduced when necessary.

The transition dipole moments were computed according to the CAS state interaction procedure\\textsuperscript{38} in conjunction with the perturbatively modified CAS reference functions obtained as linear combinations of all the states involved in the MS-CASPT2 calculation.

The spin-orbit coupling constants, which are the matrix elements that represent the coupling between two states of different multiplicity,\\textsuperscript{39}

$$\langle H_{SO}\rangle_{M_sM'_{s},r}=\langle M_s\Psi(M_s)\vert H_{SO}\vert M'_s\Psi(M'_s)\rangle,$$

\hspace{1cm} $r=x,y,z$ \hspace{1cm} (8)

have been computed by using an effective one-electron Fock-type spin–orbit Hamiltonian, as suggested by Hess and co-workers,\\textsuperscript{39} and with the RASSI program as implemented in MOLCAS 5.4, $(M_s\Psi(M_s)$ is the wave function including the spin state and $M_s$ the component of one sublevel). To avoid the calculation of multicenter one- and two-electron integrals, the atomic mean field integrals have been used.\\textsuperscript{40} Spin–orbit coupling between configuration interaction (CI) eigenvectors of the effective Hamiltonian form a Hermitian matrix. Since the basis set is real and the spin–orbit coupling operator is complex, all spin–orbit couplings are off-diagonal. The diagonal elements are the CI energies without spin–orbit couplings. Diagonalizing this Hermitian matrix yields spin–orbit coupled (SOC) states.\\textsuperscript{41} To estimate the spin–orbit coupling interaction between two states of different multiplicity, we have used the root mean square defined by Eq. (9)

$$\text{SOC} = \left[ \sum_{M_s,M'_s} \langle H_{SO}\rangle_{M_sM'_s,x}^2 + \langle H_{SO}\rangle_{M_sM'_s,y}^2 + \langle H_{SO}\rangle_{M_sM'_s,z}^2 \right]^{1/2}.$$  

(9)
III. RESULTS AND DISCUSSION

A. Electronic structure of nitromethane and active space

Nitromethane has two important $C_s$ conformational isomers (staggered and eclipsed). Both geometries are practically isoenergetic. However, the staggered conformer is computationally more convenient. Therefore, in what follows the discussion will be based on the staggered structure. At the ground state geometry, the Hartree–Fock electronic configuration is

\[
\begin{align*}
1s_O & , 1s_O, 1s_N, 1s_C, & 2s_O, 2s_O, 2s_O, \\
\pi_{NO} & , \pi_{NO}, \sigma_{CN}, & \sigma_{CN}, \sigma_{NO}, \sigma_{NO}, \\
\pi_{NO} & , \sigma_{NO}, \sigma_{CH}, & \sigma_{CH}, \sigma_{CH}, \pi_{O}, \pi_{O},
\end{align*}
\]

which corresponds with the following assignment of the molecular orbitals:

\[
1s_O, 1s_O, 1s_N, 1s_C, 2s_O, 2s_O, 2s_O, \sigma_{NO}, \sigma_{CN}, \sigma_{NO}, \sigma_{NO}, \pi_{NO}, \pi_{NO}, \sigma_{CN}, \sigma_{CN}, \sigma_{NO}, \sigma_{NO}, \pi_{O}, \pi_{O},
\]

and where the subscripts indicate the dominant character of each orbital.

The selection of the active space is straightforward after the work of Blahous et al. on NO$_2$ radical ($C_{2v}$). In their study of the surface crossing of the $^2A_1$ and $^2B_2$ states of NO$_2$, they pointed out that in order to provide sufficient flexibility to the wave functions to describe properly both states, the CASSCF space must comprise 13 electrons in ten orbitals. By the way, this choice prevents for symmetry breaking of the wave function, a phenomenon which is prompt to occur at the SCF level when the O–N–O angle is substantially decreased and from which the CASSCF functions are not free. Therefore, as we shall be interested in NO$_2$ formation in different electronic states, and at different structural arrangements, the selected molecular orbitals of nitromethane for their inclusion in the active space were those arising from all the valence orbitals, with the exception of the 2$s$’s on oxygen and the three $\sigma$(CH$_3$) orbitals. The remaining 11 molecular orbitals and 14 electrons build the active space which is plotted in Fig. 1.

B. Vertical transitions of nitromethane

The most intense ultraviolet (UV) absorption band of nitromethane centered at 6.26 eV lies at a rather high-energy range, where involvement of Rydberg states could be of relevant importance. Consequently, an exploring of the excited state potential energy surfaces around the Franck–Condon region becomes demanding. In this section we shall document the results obtained on the vertical transitions of nitromethane. In order to take into account the electronic transitions to Rydberg states, the ANO basis sets have been supplemented with a $1s1p$ set of diffuse-type functions (contracted from eight primitives for each angular momentum type), which were built following the procedure described by Ross and co-workers. The additional functions were placed at the geometrical center of the NO$_2$ moiety, and were contracted from the CASSCF(1e,1o) calculation of the $1^2A'$ state of the radical anion. The optimized geometry [Fig. 2(a)] obtained with only valence orbitals included in the active space CASSCF(14e,11o) was used for both basis set optimization and computation of vertical transition.

The active space for the treatment of the Rydberg states of CH$_3$NO$_2$ contains 12 electrons distributed in 12 orbitals. Excepting the $2s_N$ orbital that has been excluded from it, the active space is composed for the same orbitals that will be used in the optimizations of valence state geometries plus one 3$s$-type orbital and one 3$p$-type orbital.
The MS-CASPT2 energies of the singlet and triplet transitions along with the oscillator strength magnitudes of the singlet excitations are collected in Table I. Regarding the vertical transitions of nitromethane related to its photolysis, the assignment of the transitions has been done on the basis of the MS-CASPT2 electronic configurations. Our results are coincident with those given by Flicker et al.11 (1) The peak of the electron impact spectrum at 3.8 eV corresponds to singlet–triplet transitions where two almost degenerate triplet states are involved; (2) all the valence triplet transitions occur in the 3.5–4.2 eV range of energy; (3) the most intense feature of the spectrum comes from the $1A' \rightarrow 2A''$ ($n\pi \rightarrow \pi^*$) transition; and (4) the Rydberg states appear above the 7.0 eV region.

C. Dissociation of nitromethane into CH$_3$+NO$_2$

Prior to the discussion of the reaction paths leading to C–N bond breaking of nitromethane, the stationary points on the ground and excited potential energy surfaces of nitromethane and nitrogen dioxide are presented (Figs. 2 and 3).

The electronic ground state for staggered nitromethane is $1A'$ [Fig. 2(a)]. Above this state the following excited states exist: (i) $1A''$ [Fig. 2(b)]; (ii) $1B'$ first order saddle point [Fig. 2(c)]; (iii) $2A''$ first order saddle point [Fig. 2(d)]; (iv) $1A'$ minimum [Fig. 2(e)]; (v) $2A'$ minimum [Fig. 2(f)]; and (vi) $2A''$ first order saddle point [Fig. 2(g)]. Table II collects the energetic of all these points as well as the vertical excitations obtained with a 14 electron 11 orbital active space.

The nitrogen dioxide radical located in the $\sigma(yz)$ plane with the $z$ axis being the $C_2$ symmetry axis, belongs to the $C_{2v}$ point group. In increasing energy order, the following valence stationary structures were localized: (i) $A_1$ minimum [Fig. 3(a)]; (ii) $B_2$ first order saddle point [Fig. 3(b)]; (iii) $B_1$ first order saddle point [Fig. 3(c), $D_{2h}$]; (iv) $A_2$ first order saddle point [Fig. 3(d)]; (v) $2A_2$ first order saddle point [Fig. 3(e)]; and (vi) $2B_2$ first order saddle point [Fig. 3(f)]. Interestingly, the computation of the analytical frequencies for the $B_2$ state yields it as a first order saddle point in agreement with the CI results of Jackels and Davidson,46 while the
CASSCF frequencies of Ref. 43 describe this geometry as a minimum. The energetic of these points as well as the vertical transition of the $^2A_1$ state are shown in Table III.

Figure 4 displays the $C_s$ dissociation potential energy curves for each electronic state of nitromethane leading to the emerging fragments NO$_2$ and CH$_3$. These curves have been obtained via interpolation between the stationary geometries of nitromethane [Figs. 2(a)–2(e)] and those corresponding to the isolated fragments (NO$_2$ [Figs. 3(a)–3(d)] and CH$_3$ [Fig. 3(g)]. Provided that the observed internal excitation energy of the methyl group (included the electronic excitation) is small,$^5$ the assumption that at the dissociation limit the electronic transitions take place only in the NO$_2$ fragment seems to be a rather reasonable hypothesis. Keeping this in mind, the correlation between the initial and final points of each interpolation is straightforward:

$$\text{[CH}_3\text{NO}_2 (1^1A', 3^1A') \rightarrow \text{NO}_2 (1^2B_2); \text{CH}_3\text{NO}_2 (1^1A'', 1^3A'')}$$

$\rightarrow \text{NO}_2 (1^2B_1); \text{CH}_3\text{NO}_2 (2^1A')$

$\rightarrow \text{NO}_2 (1^2B_1); \text{CH}_3\text{NO}_2 (2^1A'', 2^3A'')$

$\rightarrow \text{NO}_2 (1^2A_2)]$. 

Table II. MS-CASPT2 energies of the vertical transitions of nitromethane and critical points on the potential energy surfaces evaluated with a CASSCF(14e,11o) reference function.$^{ab}$

<table>
<thead>
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<th>Geometry</th>
<th>Configuration</th>
<th>$\Delta E$ (eV)</th>
<th>Geometry</th>
<th>Configuration</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m, $1^1A'$ [Fig. 2(a)]</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>vt, $2^1A'$</td>
<td>$\alpha$(CN)$\rightarrow\pi^+(\text{NO})$</td>
<td>4.31$^f$</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>vt, $1^1A'$</td>
<td>$\sigma$(NO)$\rightarrow\pi^+(\text{NO})$</td>
<td>3.97$^f$</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>vt, $2^1A^*$</td>
<td>$\pi^+(\text{NO})$</td>
<td>6.16$^f$</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>m, $1^3A''$ [Fig. 2(b)]</td>
<td>$\sigma$(NO)$\rightarrow\pi^+(\text{NO})$</td>
<td>2.65</td>
<td>sd1, $1^3A''$ [Fig. 2(j)]</td>
<td>$\sigma$(NO)$\rightarrow\pi^+(\text{NO})$</td>
<td>3.81</td>
</tr>
<tr>
<td>sd1, $1^3A''$ [Fig. 2(c)]</td>
<td>$\sigma$(NO)$\rightarrow\pi^+(\text{NO})$</td>
<td>2.80</td>
<td>sd2, $1^3A''$ [Fig. 2(k)]</td>
<td>$\sigma$(NO)$\rightarrow\pi^+(\text{NO})$</td>
<td>3.95</td>
</tr>
<tr>
<td>sd1, $2^3A''$ [Fig. 2(d)]</td>
<td>$\pi^+(\text{NO})$</td>
<td>2.94</td>
<td>sd1, $2^3A''$ [Fig. 2(l)]</td>
<td>$\pi^+(\text{NO})$</td>
<td>4.65</td>
</tr>
<tr>
<td>m, $1^3A'$ [Fig. 2(e)]</td>
<td>$\alpha$(CN)$\rightarrow\pi^+(\text{NO})$</td>
<td>3.29</td>
<td>sd2, $1^3A'$ [Fig. 2(m)]</td>
<td>$\alpha$(CN)$\rightarrow\pi^+(\text{NO})$</td>
<td>3.47</td>
</tr>
<tr>
<td>m, $2^3A'$ [Fig. 2(f)]</td>
<td>$\alpha$(CN)$\rightarrow\pi^+(\text{NO})$</td>
<td>3.58</td>
<td>sd1, $2^3A'$ [Fig. 2(n)]</td>
<td>$\alpha$(CN)$\rightarrow\pi^+(\text{NO})$</td>
<td>4.47</td>
</tr>
<tr>
<td>sd1, $2^3A'$ [Fig. 2(g)]</td>
<td>$\pi^+(\text{NO})$</td>
<td>5.02</td>
<td>sd2, $2^3A'$ [Fig. 2(o)]</td>
<td>$\pi^+(\text{NO})$</td>
<td>5.59</td>
</tr>
<tr>
<td>m, $2A'(C_i)$ [Fig. 2(h)]</td>
<td>$\sigma$(NO)$\rightarrow\pi^+(\text{NO})$</td>
<td>2.97</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Cl, $4A'(C_i)$ [Fig. 2(i)]</td>
<td>$\pi^+(\text{NO})$</td>
<td>4.87</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Dissociation $1^1A'$</td>
<td>NO$_2(1^2A_1)$</td>
<td>2.58</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Dissociation $1^1A''$</td>
<td>NO$_2(1^2B_2)$</td>
<td>3.81</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Dissociation $2^1A'$</td>
<td>NO$_2(1^2B_1)$</td>
<td>4.30</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Dissociation $2^1A''$</td>
<td>NO$_2(1^2A_2)$</td>
<td>4.80</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Dissociation $3^1A''$</td>
<td>NO$_2(2^2A_2)$</td>
<td>6.75</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Dissociation $3^1A'$</td>
<td>NO$_2(2^2B_2)$</td>
<td>7.41</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$ANO-1 basis sets, CAS(14e,11o).

$^b$Two roots are included in each multistate calculation.

$^c$Oscillator strength: $f (2^1A'') = 0.001; f (1^1A'') = 0.2 \times 10^{-6}; f (1^1A') = 0.0190$.

$^d$vt: vertical transition. m: minimum; sd1: first order saddle point; sd2: second order saddle point.
Additionally, the next restrictions have been imposed: (1) In all the interpolations, the end C–N distance is 4.5 Å. This choice is based on two criteria fulfilled in the ground state: (i) there is no significant gradient of energy at this distance; and (ii) the charges of the resulting fragments are already zero. (2) The geometry of CH₃ at the end of all the interpolations is always its optimized structure for the ground state obtained by performing a CASSCF calculation with only one orbital. (3) The final dihedral angle between the respective planes containing to the CH₃ and NO₂ radicals is 90°.

Except for the ground state, all of the other potential curves show an exit barrier for CH₃NO₂ decomposition. In fact, we were able to localize on this region of the 2₂N potential surface a first order saddle point [Fig. 2(g)] leading to dissociation of nitromethane into CH₃ and NO₂. Some of them are first order saddle points and the others second order saddle geometries (see Fig. 2 and Table II). Other features of all of the potential energy curves are that at the dissociation distance, the energy of the supermolecule is independent of the state multiplicity (singlet or triplet) and neutral fragments are formed.

In principle, after excitation of nitromethane in the \( n\pi \rightarrow \pi^* \) state, the four dissociation channels corresponding to the four minima of nitrogen dioxide [Figs. 3(a)–3(d)] are energetically accessible. A different question is what are the dynamically allowed channels. In our opinion, the nature of the starting structure on the 2₂N surface [\( S_1 \) state, Fig. 2(g)] plays a crucial role in this context. As it was pointed out in the preceding paragraphs, the only stationary geometry that we were able to localize on this region of the 2₂N potential surface was a first order saddle point [Fig. 2(g)]. The transition vector corresponding to the imaginary frequency should lead to a \( C_1 \) minimum. However, when we searched for this \( C_1 \) minimum, we arrived at a molecular arrangement where a degeneracy of two states (\( S_3 \) and \( S_2 \)) exists. This must correspond to a crossing [conical intersection (IC)] where an

### TABLE III. Energetic of the potential energy surfaces of nitrogen dioxide.

<table>
<thead>
<tr>
<th>State</th>
<th>Assignment</th>
<th>CAS-SCF</th>
<th>CASPT2</th>
<th>( \Delta E ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>( n\sigma_N )</td>
<td>-204.283 89</td>
<td>-204.716 39</td>
<td>0.90</td>
</tr>
<tr>
<td>( \nu_1 A_1 )</td>
<td>( \sigma_{SO} - n\sigma_N )</td>
<td>-203.994 15</td>
<td>-204.439 19</td>
<td>0.78</td>
</tr>
<tr>
<td>( \nu_2 A_1 )</td>
<td>( \pi_{SO} \pi_{n\sigma_N} )</td>
<td>-203.947 14</td>
<td>-204.393 06</td>
<td>0.88</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>( \sigma_{SO} \pi_{n\sigma_N} )</td>
<td>-204.165 39</td>
<td>-204.611 27</td>
<td>0.88</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>( \pi_{SO} - n\sigma_N )</td>
<td>-203.999 45</td>
<td>-204.431 05</td>
<td>0.89</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>( (n\sigma_N)^2 - \pi_{SO} \pi_{n\sigma_N} )</td>
<td>-203.919 49</td>
<td>-203.371 12</td>
<td>0.87</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>( \pi_{n\sigma_N} \pi_{n\sigma_N} )</td>
<td>-204.158 64</td>
<td>-204.580 96</td>
<td>0.90</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>( n\sigma_{SO} \pi_{n\sigma_N} )</td>
<td>-204.082 89</td>
<td>-204.526 30</td>
<td>0.89</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>( n\sigma_{SO} - n\sigma_N )</td>
<td>-204.023 99</td>
<td>-204.481 53</td>
<td>0.88</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>( n\sigma_{SO} \pi_{n\sigma_N} )</td>
<td>-204.163 20</td>
<td>-204.599 86</td>
<td>0.89</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>( n\sigma_{SO} - n\sigma_N )</td>
<td>-204.061 73</td>
<td>-204.510 67</td>
<td>0.88</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>( \pi_{SO} \pi_{n\sigma_N} )</td>
<td>-204.250 55</td>
<td>-204.671 27</td>
<td>0.90</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>( \pi_{n\sigma_N} \pi_{n\sigma_N} )</td>
<td>-204.225 18</td>
<td>-204.651 59</td>
<td>0.90</td>
</tr>
<tr>
<td>( A_3 )</td>
<td>( \pi_{n\sigma_N} \pi_{n\sigma_N} )</td>
<td>-204.223 66</td>
<td>-204.634 87</td>
<td>0.91</td>
</tr>
<tr>
<td>( 2A_1 )</td>
<td>( n\sigma_{SO} \pi_{n\sigma_N} )</td>
<td>-203.133 50</td>
<td>-204.561 76</td>
<td>0.89</td>
</tr>
<tr>
<td>( 2B_1 )</td>
<td>( n\sigma_{SO} - n\sigma_N )</td>
<td>-204.101 71</td>
<td>-204.538 87</td>
<td>0.88</td>
</tr>
</tbody>
</table>

\( ^a \)ANO-L basis sets, CAS(13e,10o).
\( ^b \)Weight of the reference function (%).
\( ^c \)Evaluated including only one root in the CASPT2 calculation.
\( ^d \)vt: vertical transition.

![FIG. 4. Potential energy curves of the valence states of nitromethane leading to its dissociation into CH₃ and NO₂.](image-url)
efficient $S_3 \rightarrow S_2$ radiationless transition occurs. Therefore, we propose the following dissociation mechanism:

**Major Channel**

$$\text{CH}_3\text{NO}_2 + h\nu (193 \text{ nm})$$

$$\rightarrow \text{CH}_3\text{NO}_2(2A'^1) \rightarrow \text{CH}_3\text{NO}_2(2A')$$

$$\rightarrow \text{CH}_3(1^2A'_1) + \text{NO}_2(1^2B_1).$$  \(10a\)

**Minor Channel**

$$\text{CH}_3\text{NO}_2 + h\nu (193 \text{ nm})$$

$$\rightarrow \text{CH}_3\text{NO}_2(2A'^1) \rightarrow \text{CH}_3(1^2A'_1) + \text{NO}_2(1^2A_2).$$  \(10b\)

These reaction pathways are in clear disagreement with those given by previous authors.\(^2\)\(^-\)\(^5\) However, we can rationalize our mechanism in the following manner. First, the NO\(_2\)(2\(^2B_2\)) state cannot be formed in the minor channel [Eq. (4b)] because it is not energetically accessible (Table II), but in the hypothetical case it were reachable, its formation implies a nonadiabatic surface crossing from the lower state ($S_3$) to the upper one ($S_4$), which is not probable. Second, the involvement of the NO\(_2\)(1\(^2B_2\)) state in the major channel [Eq. (4a)] was tentatively proposed on the basis of the emission spectrum and fluorescence lifetime of NO\(_2\) “formed” in the photolysis of nitromethane. But, in our opinion, this state cannot be responsible for such fluorescence emission. If the 1\(^2B_2\) would be formed, then it would lie in the domain of the potential surface where the lowest electronic state is precisely itself, from which fluorescence emission is impossible. Additionally, it is known that the 2\(^A_2\) state of NO\(_2\) is nonfluorescing. Therefore, the only state able to emit a photon is the 1\(^2B_1\) state.

**D. The secondary dissociation products: NO and O**

In this section, we present the potential energy curves for dissociation of NO\(_2\) leading to formation of oxygen atomic and nitric oxide (NO). Figure 5(a) shows the interpolation curve, which starting at the geometry of the 2\(^A_2\) minimum of NO\(_2\), ends at the decomposition products NO(1\(^2\)II) + O(1\(^D\)). The exit barrier is about 2 kcal/mol, the actual value will be smaller indeed, so that NO\(_2\) formed in the 2\(^A_2\) state will immediately dissociate. In the same figure is plotted the interpolation curve starting at the lowest quartet state

<table>
<thead>
<tr>
<th>State</th>
<th>Assignment</th>
<th>MS-CASPT2</th>
<th>$\Delta E (eV)$</th>
<th>$\omega^c$</th>
<th>$f^d$</th>
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<tr>
<td>$A_1$</td>
<td>$n\sigma_N$</td>
<td>-204.718 67</td>
<td>...</td>
<td>87</td>
<td>—</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$n\sigma_N - \pi^*_N$</td>
<td>-204.614 03</td>
<td>2.85</td>
<td>85</td>
<td>0.1223d - 02</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$n\sigma_N - \pi N$</td>
<td>-204.601 97</td>
<td>3.18</td>
<td>81</td>
<td>0.6301d - 02</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$n\pi_N - n\sigma_N$</td>
<td>-204.584 15</td>
<td>3.66</td>
<td>88</td>
<td>0.2233d - 14</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$\pi^*_N - n\sigma_N$</td>
<td>-204.527 83</td>
<td>5.19</td>
<td>77</td>
<td>0.2006d - 15</td>
</tr>
<tr>
<td>$B_3$</td>
<td>$n\pi^*_N - n\sigma_N$</td>
<td>-204.513 51</td>
<td>5.58</td>
<td>70</td>
<td>0.3084d - 02</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$n\pi^<em>_N - \pi^</em>_N$</td>
<td>-204.484 12</td>
<td>6.38</td>
<td>62</td>
<td>0.3708d - 15</td>
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<tr>
<td>$A_3$</td>
<td>$n\pi_N - 3s$</td>
<td>-204.452 40</td>
<td>7.25</td>
<td>72</td>
<td>0.1427d - 03</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$n\pi^<em>_N - \pi^</em>_N$</td>
<td>-204.438 02</td>
<td>7.64</td>
<td>40</td>
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<td>$\pi_N - n\sigma_N$</td>
<td>-204.435 21</td>
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<td>0.3639d - 01</td>
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<tr>
<td>$B_1$</td>
<td>$\pi_{3s} - n\sigma_N$</td>
<td>-204.433 81</td>
<td>7.75</td>
<td>63</td>
<td>0.8178d - 02</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$(n\sigma_N)^0 - \pi_{3s}, n\sigma_N$</td>
<td>-204.372 58</td>
<td>9.42</td>
<td>51</td>
<td>0.1727d - 02</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$n\pi_N - 3s$</td>
<td>-204.361 60</td>
<td>9.72</td>
<td>85</td>
<td>0.1459d - 13</td>
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<tr>
<td>$A_2$</td>
<td>$n\pi_N - 3s$</td>
<td>-204.348 83</td>
<td>10.06</td>
<td>83</td>
<td>0.4362d - 12</td>
</tr>
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</table>

\(^a\)ANO-L basis sets, CAS(13e,11o). Applied imaginary level shift equal to 0.1.\n
\(^b\)One 3\(^s\)-type Rydberg orbital included in the active space.\n
\(^c\)Weight of the reference function (%).\n
\(^d\)Oscillator strength in a.u.
which would yield NO(X(2Π)) + O(3P). Figure 5(b) represents the spin–orbit coupling constants, Eq. (9), between 2 2A" → 1 4A" and 2 2A" → 1 4A' states, respectively. The magnitude of spin–orbit coupling constant and low energy difference between 2 2A" and 1 4A' states do not exclude the 2 2A" → 1 4A' intersystem crossing process. However, we cannot establish the actual efficiency of this mechanism in the decomposition path.

On the other hand, if the 2 2A_2 state behaves as Fig. 4(a) suggests, its lifetime is not long enough to absorb a second photon. Therefore, the unique state available to do that is the 2 2B_1 state formed in the major channel. But this state can decay to the ground state: (i) via fluorescence emission or (ii) via a nonradiative transition (inset in Fig. 4). In fact, the only resonant energy level at 193 nm corresponds to the 1 2A_1 → 3 2A_2 excitation (Table IV). However, it is a forbidden transition by the selection rules as the oscillator strength shows (Table IV). In addition, Petsalakis et al. have studied at the MRDCI level the valence and Rydberg vertical transitions of several electronic states of NO_2 including those from the 1 2B_1 minimum. They found the same resonant level than ourselves, in contrast no resonant excitation of NO_2(1 2B_1) appeared at the 193 nm energy range. Consequently, provided that no resonant transition from both NO_2(1 2A_1) and NO_2(1 2B_2) exists, we propose the 1 2A_1 → 2 2A_2 excitation (Table IV) as the best candidate to be responsible for the 193 nm absorption of NO_2.

From the preceding discussion we propose the following secondary dissociation channels:

**Major Channel**

\[
\text{NO}_2(1 2B_1) \xrightarrow{\text{IC}} \text{NO}_2(1 2A_1) \\

\xrightarrow{-h\nu'} \text{h\nu} \\

\xrightarrow{193 \text{ nm}} \text{NO}(A^2Σ^+) + \alpha O(3P) + \beta O(1D),
\]

(10a)

**Minor Channel**

\[
\text{NO}_2(1 2A_2) \rightarrow \text{NO}(X 2Π) + \alpha O(3P) + \beta O(1D).
\]

(10b)

**IV. SUMMARY**

The ground and excited potential energy surfaces of nitromethane related to its photodissociation dynamics have been studied at the MS-CASPT2 level. From this study it is concluded that the two dissociation channels observed in the photolysis experiments after excitation at 193 nm are

**Major Channel**

\[
\text{CH}_3\text{NO}_2(1A') + h\nu(193 \text{ nm}) \rightarrow \text{CH}_3\text{NO}_2(2A'') \\

\xrightarrow{\text{IC}} \text{CH}_3\text{NO}_2(2A') \rightarrow \text{CH}_3(1A') + \text{NO}_2(1 2B_1) \\

\xrightarrow{-h\nu'} \text{h\nu} \rightarrow \text{CH}_3(1A') + \text{NO}(A^2Σ^+) + \alpha O(3P) + \beta O(1D).
\]

**Minor Channel**

\[
\text{CH}_3\text{NO}_2(1A') + h\nu(193 \text{ nm}) \\

\rightarrow \text{CH}_3\text{NO}_2(2A'') \\

\rightarrow \text{CH}_3(1A') + \text{NO}_2(1 2A_2) \\

\rightarrow \text{CH}_3(1A') + \text{NO}(X 2Π) + \alpha O(3P) + \beta O(1D).
\]

Additionally, the next conclusions are obtained about of the excited states surfaces: (1) The peak of the electron impact spectrum at 3.8 eV corresponds to singlet–triplet transitions where two almost degenerate triplet states are involved. (2) All the valence triplet transitions occur in the 3.5–4.2 eV range of energy. (3) The strongest feature of the absorption spectrum comes from the 1A' → 2A'' (nπ→π*) transition. (4) The Rydberg states appear above the 7.0 eV region.

**ACKNOWLEDGMENTS**

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Potential energy surfaces of nitromethane

31 K. Andersson et al., MOLCAS Version 5.4. (Lund University, Sweden, 2002).
33 Some states, that are not included in the CASSCF configuration but have energies within the range of the lowest CAS states, cause frequent problems with excited states calculations, since they often give large denominators and even, at particular geometries, singularities. By analogy to a similar phenomenon in multistate perturbation, they are called intruder states. L. Serrano-Andrés and N. Moriarty, in User’s Manual MOLCAS 5.4 (Lund University, Sweden, 2002), Part II.