Theoretical studies of spin-forbidden radiationless decay in polyatomic systems. II. Radiationless decay of a-N2O2
Kiet A. Nguyen, Mark S. Gordon, John A. Montgomery Jr., H. Harvey Michels, and David R. Yarkony

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Theoretical studies of spin-forbidden radiationless decay in polyatomic systems. II. Radiationless decay of $a$-N$_2$O$_2$

Kiet A. Nguyen and Mark S. Gordon

Iowa State University, Ames, Iowa 50011-3111

John A. Montgomery, Jr. and H. Harvey Michels

United Technologies Research Center, East Hartford, Connecticut 06108

David R. Yarkony

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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The stability with respect to spin-forbidden radiationless decay of the previously reported [J. Chem. Phys. 88, 7248 (1988)] asymmetric dimer of NO, N-N-O-O (a-N$_2$O$_2$) is considered. The spin-allowed decay channel a-N$_2$O$_2$($'A'$) $\rightarrow$ N$_2$O($X'\Sigma^+$) + O($'D'$) is endoergic. However, the spin-forbidden decay channel a-N$_2$O$_2$($'A'$) $\rightarrow$ N$_2$O($X'\Sigma^+$) + O($'P'$) is exoergic. Large scale multireference configuration interaction wave functions, approximately 300 000 – 1 400 000 configuration state functions, based on double zeta polarization and triplet zeta polarization bases are used to study this process. The minimum energy crossing of the ground singlet $'A'$ state and the lowest excited triplet $3'A''$ state was determined as was the interstate spin–orbit coupling. This electronic structure data was used in the context of a simple one-dimensional model to show that a-N$_2$O$_2$ is rapidly predissociated to N$_2$O($X'\Sigma^+$) and O($'P'$).

I. INTRODUCTION

Recently there has been considerable interest in the potential for developing energetic materials for use in high specific impulse fuels. One direction of investigation focuses on energetic species that are geometrically strained or nontraditionally bonded molecules. This has led recently to a number of interesting theoretical studies of "hypothetical" ring strained molecules including the oxygen ring systems O$_4$ and O$_5$ (Refs. 1–3) and the nitrogen ring systems N$_4$, N$_6$, and N$_8$ (Refs. 4–7). Candidate systems must exist at a local minimum on the ground state potential energy surface that is significantly endothermic with respect to a decomposition channel. The requisite situation is illustrated in Fig. 1. Here a barrier hinders, and endoergicity precludes, the energetic material $ABCD$ from decomposing into either of two spin-allowed channels. However, because the system is energetic, surface crossings with states of different spin multiplicity may provide alternative, lower energy, decay channels. This situation is not at all uncommon. Spin-forbidden decay is the principal decay channel for the metastable cation CH$_3$O$^+$ (Ref. 8) and appears to provide a low energy decay pathway for the potential energetic material, tetrahedral N$_4$ (Refs. 4–7).

Recently an asymmetric nitric oxide dimer N–N–O–O (see Fig. 2) has been suggested as a possible energetic material. This isomer of N$_2$O$_2$, denoted a-N$_2$O$_2$, has been estimated to be unstable by 102 (62) kcal/mol relative to N$_2$ + O$_2$ (NO + NO). At the equilibrium geometry of a-N$_2$O$_2$, the lowest excited triplet state is approximately 24 kcal/mol above the ground $'A'$ potential energy surface (see Sec. III). Thus spin-forbidden radiationless decay might not be considered a viable decay pathway. However, as suggested above, it was recently shown that in tetrahedral N$_4$, the barrier to spin-allowed decay (or isomerization) is approximately 60 kcal/mol, while a spin-forbidden channel with only half this barrier exists. Thus it is relevant to consider the possibility of spin-forbidden radiationless decay of a-N$_2$O$_2$.

To address this question, we will focus on the minimum energy point on the surface of intersection of the ground $'A'$ potential energy surface and the lowest triplet surface in the region of the equilibrium geometry of a-N$_2$O$_2$. In general, this point, referred to as the minimum energy crossing point, represents a key bottleneck along the minimum energy path and is frequently the transition state for this pathway. Thus the determination of this point provides the barrier for the decomposition pathway, or at least a lower bound if the true transition state lies elsewhere on the bound state surface; and (ii) can, particularly for a late or product channel minimum energy crossing point, establish the products of the radiationless decay process. Clearly then the determination of this point provides essential information concerning the mechanism and feasibility of spin-forbidden radiationless decay and is a logical starting point for any treatment of this process. In this work, it will be shown that spin-forbidden radiationless decay indeed provides a low energy decay pathway through the radiationless decomposition process a-N$_2$O$_2$($'A'$) $\rightarrow$ N$_2$O$_2$($3'A''$) $\rightarrow$ N$_2$O($X'\Sigma^+$) + O($'P'$).}

II. THEORETICAL APPROACH

In this section, the wave functions used to characterize, the $'A'$ ground state and the low-lying $3'A''$ state of
a-N₂O₂, the spin–orbit interactions that couple the 1A' and 3A" states, and the method used to determine the minimum energy crossing point, are considered. The simple model used to estimate the radiationless decay rate is dependent on the specific results of the electronic structure treatment and its development is deferred until Sec. III.

A. Electronic states

Preliminary electronic structure calculations served to show that the process of principal interest is that noted in the Introduction

\[ a\text{-N}_2\text{O}_2(1A') \rightarrow \text{N}_2\text{O}_2(3A'') \rightarrow \text{N}_2\text{O}(X 1\Sigma^+) + O(3P). \]  

(2.1)

From this perspective, the 1A' state of a-N₂O₂ can be viewed as arising from a dative bond formed from an oxygen lone pair on N₂O(X 1Σ⁺) and an empty oxygen 2p orbital on O(1D). As this dative bond is stretched and the corresponding O=O antibonding (σ*) orbital is stabilized, the excited triplet state (3A'') formed from an n→σ* excitation is stabilized. Thus (using C₆ symmetry), the 1A' state is dominated by the following electron configuration:

\[ 1a'^2 \cdot 11a'^2 12a'^2 13a'^1 12a''2 2a''2 3a'', \]  

(2.2)

while the 3A'' state is dominated by the electron configuration

\[ 1a'^2 \cdot 11a'^2 12a'^2 13a'^1 1a''2 2a''2 3a''. \]  

(2.3)

where the above noted n→σ* promotion corresponds to the 3a''→13a' promotion. The (12a',3a'') and (12a',13a',3a'') orbitals in the equilibrium and highly stretched geometries, respectively, are sketched in Fig. 3.

State-averaged multiconfiguration self consistent field (SA-MCSCF) 12-15/configuration interaction (CI) wave functions are used to describe these states. The SA-MCSCF wave functions are complete active space (CAS) 16-18 wave functions relative to the four electron three orbital active space (12a'–13a',3a''). The molecular orbitals obtained from the SA-MCSCF procedure are used to determine multireference single and double excitation CI (MR-CISD) wave functions relative to the CAS reference space in which the 1a'-4a' orbitals (the nitrogen and oxygen 1s orbitals) are kept doubly occupied and the four corresponding correlating orbitals in the virtual space, the four orbitals with largest orbital energies, are truncated. The use of wave functions based on SA-MCSCF orbitals is dictated by the need to treat the full microscopic Breit–Pauli spin–orbit operator 20,21 H₀, i.e., both the one electron spin–orbit and two electron spin-other-orbit contributions to H₀ are included.

Two basis sets were employed—a Huzinaga–Dunning double zeta polarization (DZP) basis 22 (9s5p1d|4s2p1d) on oxygen and nitrogen and a triple zeta polarization (TZP) basis (11s7p1d|6s3p1d) on nitrogen 23 and oxygen. 24,25 Using the DZP[TZP] bases, the 1A' and 3A'' states are described by configuration state function (CSF) 26 expansions of dimension 310, 058|921, 418 and 462, 165|1, 383, 013, respectively. The reliability of these descriptions (denoted MR-CISD/DZP and MR-CISD/TZP) will be addressed in Sec. III, where comparisons with a QCISD treatment 27-29 based on the DZP basis (denoted QCISD/DZP) will be provided.

B. Spin–orbit interactions

There are in principle three spin–orbit matrix elements connecting the nonrelativistic wave functions \( \Psi[1A'(0)] \) and \( \Psi[3A''(M)] \), Mᵣ=1,0,—1. However, in the C₆ point group, only two are unique. In particular, defining 30
TABLE I. Energies, spin–orbit interactions, and structures at minima obtained from MR-CISD wave functions.*

<table>
<thead>
<tr>
<th>Structure</th>
<th>MIN($1'A'$) (DZP)</th>
<th>MIN($1'A'$) (TZP)</th>
<th>MEX (DZP)</th>
<th>MEX (TZP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R(\text{N}^1-\text{N}^2)$</td>
<td>1.111 5</td>
<td>1.097 5</td>
<td>1.114 3</td>
<td>1.100 8</td>
</tr>
<tr>
<td>$R(\text{N}^2-\text{O}^1)$</td>
<td>1.241 5</td>
<td>1.232 4</td>
<td>1.229 2</td>
<td>1.219 0</td>
</tr>
<tr>
<td>$R(\text{O}^2-\text{O}^1)$</td>
<td>1.563 9</td>
<td>1.558 2</td>
<td>1.672 0</td>
<td>1.679 5</td>
</tr>
<tr>
<td>$\angle \text{N}^1\text{N}^2\text{O}^1$</td>
<td>179.26</td>
<td>178.49</td>
<td>180.52</td>
<td>180.63</td>
</tr>
<tr>
<td>$\angle \text{N}^2\text{O}^1\text{O}^2$</td>
<td>102.29</td>
<td>102.03</td>
<td>102.09</td>
<td>101.82</td>
</tr>
<tr>
<td>$E(1'A')$</td>
<td>$-258.981\text{,}267$</td>
<td>$-259.070\text{,}881$</td>
<td>$-258.978\text{,}869$</td>
<td>$-259.067\text{,}517$</td>
</tr>
<tr>
<td>$E(3'A''')$</td>
<td>$-258.943\text{,}461$</td>
<td>$-259.028\text{,}137$</td>
<td>$-258.978\text{,}868$</td>
<td>$-259.067\text{,}518$</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>23.72</td>
<td>26.82</td>
<td>1.51</td>
<td>2.11</td>
</tr>
<tr>
<td>$H_l'$</td>
<td>12.4</td>
<td>11.1</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>$H_l''$</td>
<td>71.1</td>
<td>73.6</td>
<td>76.7</td>
<td></td>
</tr>
</tbody>
</table>

*Distances in Ångstroms, angles in degrees, total energies in atomic units, $\Delta E=E(3'A''')-E(1'A')$ in kcal/mol and spin–orbit couplings $H_l'$ and $H_l''$ in cm$^{-1}$. For comparison, using the QCISD/DZP approach, MIN($1'A'$) corresponds to $R(\text{N}^1-\text{N}^2)=1.1331\text{ Å}$, $R(\text{N}^2-\text{O}^1)=1.2617\text{ Å}$, $R(\text{O}^2-\text{O}^1)=1.5475\text{ Å}$, $\angle \text{N}^1\text{N}^2\text{O}^1=179.40^\circ$, $\angle \text{N}^2\text{O}^1\text{O}^2=103.31^\circ$ with $E(1'A')=-259.075\text{,}422$, and $\Delta E=23.0\text{ kcal/mol.}$ At the equilibrium structure of $\text{N}_2\text{O}(X^1\Sigma^+)$ $R(\text{N}-\text{N})=1.128\text{ Å}$ and $R(\text{N}-\text{O})=1.184\text{ Å}$ from Ref. 36.

\[\Psi_{1A'}(1A')=\Psi_1^1(1A')(0),\]  
\[\Psi_{1A'}(3A'')=i\Psi_1^3(3A''(0)),\]  
\[\Psi_{2A'}(3A'')=i[\Psi_2^3(3A''(1))-\Psi_2^3(3A''(-1))]/\sqrt{2},\]  
\[\Psi_{1A'''}(3A'')=i[\Psi_1^3(3A''(1))+\Psi_1^3(3A''(-1))]/\sqrt{2},\]

we have

\[H_{l0}(\Psi_{1A'}(3A'')|H_{l0}|\Psi_{1A'}(1A'))\]  
\[H_{l0}(\Psi_{1A'}(3A'')|H_{l0}|\Psi_{1A'}(1A'))\]

while

\[\langle\Psi_{1A'''}(3A'')|H_{l0}|\Psi_{1A'}(1A')\rangle=0\]

by symmetry. The triplet wave functions are chosen to be purely imaginary valued, so that the spin–orbit matrix elements will be real valued.

C. Minimum energy crossing point

Key to the present treatment is the efficient location of the minimum energy crossing point. The methodology used to accomplish this has been described previously.\textsuperscript{7,9,21} Briefly, the minimum energy crossing point is obtained directly, i.e., without prior determination of either the potential energy surfaces or the surface of crossing points, as the solution of

\[\begin{bmatrix} W_{ij}(R,\lambda) & g_{ij}(R) \end{bmatrix} \begin{bmatrix} \delta R \cr \delta \lambda \end{bmatrix} = - \begin{bmatrix} g_{ij}(R) + \lambda g_{ij}^H(R) \cr \Delta E_{ij}(R) \end{bmatrix},\]

where $\delta R=R'-R$, $\delta \lambda=\lambda'-\lambda$, $\lambda$ is a Lagrange multiplier, $\Delta E_{ij}(R)=E_{ij}(R)-E_{ij}(R)$, the energy gradient $g_{ij}(R)=[\partial E_{ij}(R)]/\{\partial R\}$, the energy difference gradient $g_{ij}^H(R)=g_{ij}(R)-g_{ij}(R)=[\partial \Delta E_{ij}(R)]/(\partial \lambda)$, and $E_{ij}(R)$ also denoted $E[I]$ or $E[J](R)$ in Sec. III is the potential energy surface of the $I$th electronic state. The second derivative matrix $W_{ij}^H(R,\lambda)$ is given by

\[W_{ij}^H(R,\lambda)=\frac{\partial^2[E_{ij}(R)+\lambda \Delta E_{ij}(R)]}{\partial R_i \partial R_j},\]

and is determined using a forward difference of $g_{ij}^H+\lambda g_{ij}^H$, i.e.,

\[W_{ij}^H(R,\lambda)=[(g_{ij}^H(R)+\epsilon \Gamma^\alpha)+\lambda g_{ij}^H(R+\epsilon \Gamma^\alpha)]-[(g_{ij}^H(R)+\lambda g_{ij}^H(R))/\epsilon],\]

where $\Gamma^\alpha$ is a unit vector along the direction $R_i$. The energy gradients $g_{ij}^H(R)$ and energy difference gradients $g_{ij}^H(R)$ for the above discussed SA-MCSCF/CI wave functions are determined using analytic derivative techniques.\textsuperscript{31} It is important to observe that because analytic gradient techniques are used to evaluate the right hand side of Eq. (2.6), it is not necessary to limit the number of nuclear degrees of freedom considered in that equation. The character of the extrema in question will be determined from the eigenvalues of $W_{ij}^H(R,\lambda)$ restricted to the directions orthogonal to the energy difference gradient, the normal to the crossing surface.\textsuperscript{32}

III. RESULTS AND DISCUSSION

The key result of this study is the geometrical arrangement of the nuclei at the minimum energy crossing point in the vicinity of the equilibrium geometry of $a$-$\text{N}_2\text{O}_2$. This information is included in Table I which reports the equilibrium geometry of $a$-$\text{N}_2\text{O}_2$ on the $1A'$ potential energy surface, denoted MIN($1'A'$), and the molecular geometry at the minimum energy crossing point of the $1A'$ and $3A''$ potential energy surfaces, denoted MEX. Results for both the MR-CISD/DZP and MR-CISD/TZP treatments are reported. The molecular arrangement is expressed in terms of a set of five internal nuclear coordinates, denoted $R$, employing the molecular numbering given in Fig. 2. From
It is seen that the numerical procedure used to obtain the solution of Eq. (2.6) routinely yields energies that are degenerate to less than $2 \times 10^{-6}$ a.u. The DZP and TZP calculations used a common $W$ matrix constructed from the DZP based wave functions using Eq. (2.8). Analysis of this $W$ matrix showed that the extremum MEX is in fact a local minimum on the $1^{A'}-3^{A''}$ crossing surface. Table I (see footnote) also compares the $\text{MIN}(1^{A'})$ structure obtained from the MR-CISD/DZP wave functions with the QCISD/DZP result. Agreement is seen to be quite good, with the bond distances differing by less than 0.02 Å and bond angles by less than 1°.

From Table I, it is seen that the geometrical arrangements at $\text{MIN}(1^{A'})$ and MEX are quite similar. The principal difference is $R(\text{O}-\text{O}^2)$ which increases by 0.12 Å going from $\text{MIN}(1^{A'})$ to MEX. The energy at MEX relative to that at $1^{A'}$ (MIN) is $\Delta E[\text{MEX}]=1.51(2.11)$ kcal/mol and is in good agreement with the MCSCF value reported by Nguyen et al.\textsuperscript{10} $\Delta E[\text{MIN}(1^{A'})]=23.1$ kcal/mol, and the QCISD/DZP value of $\Delta E[\text{MIN}(1^{A'})]=23.0$ kcal/mol. The good agreement between the present MR-CISD/DZP results and those obtained from the QCISD/DZP approach which is based on orbitals optimized for individual states supports the viability of the present approach.

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The vertical excitation energy at $\text{MIN}(1^{A'})$ obtained at the MR-CISD/DZP (MR-CISD/TZP) level is $\Delta E[\text{MIN}(1^{A'})]=23.7$ (26.8) kcal/mol and is in good agreement with the MCSCF value reported by Nguyen et al.\textsuperscript{10} $\Delta E[\text{MIN}(1^{A'})]=23.1$ kcal/mol, and the QCISD/DZP value of $\Delta E[\text{MIN}(1^{A'})]=23.0$ kcal/mol. The principal difference is $R(\text{O}-\text{O}^2)$ which increases by 0.12 Å going from $\text{MIN}(1^{A'})$ to MEX. The energy at MEX relative to that at $1^{A'}$ (MIN) is $\Delta E[\text{MEX}]=1.51(2.11)$ kcal/mol and is in good agreement with the MCSCF value reported by Nguyen et al.\textsuperscript{10} $\Delta E[\text{MIN}(1^{A'})]=23.1$ kcal/mol, and the QCISD/DZP value of $\Delta E[\text{MIN}(1^{A'})]=23.0$ kcal/mol. The good agreement between the present MR-CISD/DZP results and those obtained from the QCISD/DZP approach which is based on orbitals optimized for individual states supports the viability of the present approach.

The simple relation between $\text{MIN}(1^{A'})$ and MEX served to motivate an alternative determination of an effective one dimensional potential energy curve based on a QCISD/DZP treatment, also reported in Fig. 4. In these calculations, $\Delta E[\text{MIN}(1^{A'})]$ achieved a maximum in this region, and the remainder of the geometrical parameters taken from the MEX structure. Note that the $3^{A''}$ potential energy curve decreases rapidly as $\delta(R)$ increases through MEX $[\Delta E[\text{MEX}]=0]$. This is consistent with the small value of $\Delta E[\text{MEX}]$ reported in Table I.

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with $706(652) \text{ cm}^{-1}$ obtained at the MR-CISD/DZP [second-order Møller–Plesset (MP2)] level for the normal mode of $a-N_2O_2$ identifiable as a largely O=O stretch. To account for this, lifetimes were computed using both the $^1A'$ potential energy curve in Fig. 4 and model potential energy curves with fundamental frequencies of 600–700 cm$^{-1}$. In each case, the lifetime of the lowest vibrational levels are on the order of picoseconds. Raising the $^2A'$ potential energy curve by 5 kcal/mol increased the lifetime of the lowest vibrational level by only a factor of 10. Thus although this type of estimate is likely to be a lower bound to the lifetime, it is clear that $a-N_2O_2$ will be unstable with respect to predissociation to $N_2O(X^2\Sigma^+)+O(3P)$.

**IV. SUMMARY AND CONCLUSIONS**

The asymmetric dimer of NO, $a-N_2O_2$, has previously been suggested as a potential energetic material. This work considered the stability of this system with respect to the exoergic but spin-forbidden radiationless decay process $a-N_2O_2(^1A')\rightarrow N_2O(^2\Sigma^+)+O(3P)$. Large scale multireference configuration interaction wave functions, comprised of approximately 300 000–1 400 000 configuration state functions, based on double zeta polarization and triplet zeta polarization bases were used to study this process. The minimum energy crossing of the ground singlet $^1A'$ and the lowest excited triplet $^3A'$ potential energy surfaces was determined as was the interstate spin–orbit coupling.

$a-N_2O_2$ is perhaps best described as O($^1D$) dative bound to N$_2$O(X$^2\Sigma^+$). A low-lying triplet state correlating with N$_2$O(X$^2\Sigma^+$)+O(3P) was found to intersect (at a geometrical arrangement labeled MEX) the $^1A'$ potential energy surface only 1.0–2.0 kcal/mol above the $a-N_2O_2$ equilibrium structure, denoted MIN($^1A'$). MIN($^1A'$) and MEX differ only in $R(O^1-O^3)$, which increases by 0.12 Å going from MIN($^1A'$) to MEX. The spin–orbit coupling $H_{SO}$ was found to be large in this region $H_{SO}$ $\sim$ 75 cm$^{-1}$. The structural similarity among MIN($^1A'$), MEX, and isolated $N_2O(X^2\Sigma^+)$ permits the spin-forbidden predissociation to be studied using a simple one-dimensional model. This model predicts that $a-N_2O_2$ will be rapidly (on the order of picoseconds) dissociated to N$_2$O(X$^2\Sigma^+$) and O(3P).

The question of spin-forbidden radiationless decay in energetic species appears to be a fairly general one. Previously the methodology used in this work has been used to show that spin-forbidden radiationless decay plays a potentially important role in the metastability of the ion CH$_2$O$^+$ and the proposed energetic material tetrahedral N$_4$.$^7$ Very recently, sophisticated theoretical methods have suggested the existence of additional metastable geometrical isomers of NO dimer$^{23,24}$ and a metastable dication of O$_4$ (Ref. 35) (isoelecronic with N$_2$O$_2$) has also been predicted. It will be important to learn whether spin-forbidden radiationless decay plays a significant role in limiting the lifetime of these species.

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