Intersystem Crossing and Nonadiabatic Product Channels in the Photodissociation of N\textsubscript{2}O\textsubscript{4} at 193 nm

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This paper presents velocity and angular distribution measurements of the products of N\textsubscript{2}O\textsubscript{4} photodissociated at 193 nm. The data show evidence for only N−N bond fission, with no significant branching to N−O bond fission or NO elimination products. The translational energy distribution of the N−N bond fission products is bimodal, indicating that at least two different NO\textsubscript{2} + NO\textsubscript{3} product channels contribute significantly to the observed products. Both product channels have an anisotropy parameter of $\beta = 1.7 \pm 0.2$. Using a Franck−Condon-like sudden analysis, we tentatively assign the two fragmentation channels observed as NO\textsubscript{2}($X^2\Pi\text{A}_1$) + NO\textsubscript{2}($1^1\Sigma\text{A}_2$) and NO\textsubscript{2}($X^2\Pi\text{A}_1$) + NO\textsubscript{2}($2^2\Sigma\text{B}_2$). To further characterize the system we present ab initio calculations (at the level of configuration interaction with single excitations) of the relevant excited states of N\textsubscript{2}O\textsubscript{4}. The data considered together with the calculations suggest a model for the product branching in which there is spin−orbit coupling in the Franck−Condon region between the excited state, which has mixed singlet $\pi\pi^*$ and $\pi\sigma^*$ character, and a state with $^1\pi\sigma^*$ character. Branching to the NO\textsubscript{2}($X^2\Pi\text{A}_1$) + NO\textsubscript{2}($2^2\Sigma\text{B}_2$) occurs from the singlet $\pi\pi^*$ state nonadiabatic dynamics. Finally, we note that the observed parallel photofragment anisotropy, unexpected for $\pi\pi^*$ electronic excitation of N\textsubscript{2}O\textsubscript{4}, likely results from vibronic coupling with a $\sigma\sigma^*$ electronic state.

I. Introduction

The photochemistry of the oxides of nitrogen is crucial to the atmosphere, given the role that these species play in the catalytic destruction of O and O\textsubscript{3} in the stratosphere and the troposphere. Whereas the principal species present in the atmosphere are NO, NO\textsubscript{2}, NO\textsubscript{3}, and N\textsubscript{2}O\textsubscript{5}, the photochemistry of related molecules, such as N\textsubscript{2}O\textsubscript{4}, is of direct interest to the atmospheric chemistry community as well. In particular, N\textsubscript{2}O\textsubscript{4} is formed by three-body recombination in the region around 193 nm. The data show evidence for only N−N bond fission, with no significant branching to N−O bond fission or NO elimination products. The translational energy distribution of the N−N bond fission products is bimodal, indicating that at least two different NO\textsubscript{2} + NO\textsubscript{3} product channels contribute significantly to the observed products. Both product channels have an anisotropy parameter of $\beta = 1.7 \pm 0.2$. Using a Franck−Condon-like sudden analysis, we tentatively assign the two fragmentation channels observed as NO\textsubscript{2}($X^2\Pi\text{A}_1$) + NO\textsubscript{2}($1^1\Sigma\text{A}_2$) and NO\textsubscript{2}($X^2\Pi\text{A}_1$) + NO\textsubscript{2}($2^2\Sigma\text{B}_2$). To further characterize the system we present ab initio calculations (at the level of configuration interaction with single excitations) of the relevant excited states of N\textsubscript{2}O\textsubscript{4}. The data considered together with the calculations suggest a model for the product branching in which there is spin−orbit coupling in the Franck−Condon region between the excited state, which has mixed singlet $\pi\pi^*$ and $\pi\sigma^*$ character, and a state with $^1\pi\sigma^*$ character. Branching to the NO\textsubscript{2}($X^2\Pi\text{A}_1$) + NO\textsubscript{2}($2^2\Sigma\text{B}_2$) occurs from the singlet $\pi\pi^*$ state nonadiabatic dynamics. Finally, we note that the observed parallel photofragment anisotropy, unexpected for $\pi\pi^*$ electronic excitation of N\textsubscript{2}O\textsubscript{4}, likely results from vibronic coupling with a $\sigma\sigma^*$ electronic state.
193 nm, they used results of theoretical calculations that underestimate the NO\(_2\) (2\(^2\)B\(_2\)) state energy. In contrast, the weak (12.69 kcal/mol\(^{12}\) N–N bond in N\(_2\)O\(_4\) means that the \(\pi\pi^*\) diabatic products, NO\(_2\)(X\(^2\)A\(_1\)) + NO(\(2^2\)B\(_2\)), are energetically accessible. Thus, this experiment on N\(_2\)O\(_4\) provides the opportunity to test whether the \(\pi\pi^*\) diabatic products will be found in the photodissociation when that channel is energetically available. It also allows us to assess the importance of spin–orbit coupling in accessing quartet products, as NO\(_2\)(1\(^2\)B\(_2\)) products were considered for the second observed R–N\(_2\)O\(_3\) channel in nitric acid.

Several groups have carried out investigations of the dissociation of N\(_2\)O\(_4\) excited at 193 nm. Kawasaki et al.\(^{13}\) performed photofragment translational spectroscopy experiments and observed emission from the photofragments. They determined that the photofragment recoil kinetic energy distribution at 193 nm is consistent with N–N bond fission forming two electronically excited momentum-matched NO\(_2\) fragments, where the product electronic states could be either 1\(^2\)B\(_2\) or 1\(^2\)B\(_1\). Although other fragmentation channels (such as N\(_2\)O\(_2\) + O + N\(_2\) and N\(_2\)O\(_4\) + NO + NO\(_3\)) are energetically accessible, Kawasaki and co-workers were not able to detect photofragment time-offlight signal for either NO\(^+\) or O\(^+\), so they could not assess the importance of these other channels. The lack of signal at NO\(^+\) and O\(^+\) is curious, since even the NO\(_2\) product should give daughter ion signal at these masses as a consequence of the electron bombardment used to ionize the photofragments. Geometric constraints preventing quantitative detection of slowly recoiling products also prevented analysis of NO\(_2\) resulting from processes partitioning less than \(\sim\)20 kJ/mol of energy into translation.

Sisk and co-workers\(^{14}\) photodissociated N\(_2\)O\(_4\) at 193 nm (as well as at 248 and 351 nm), observing emission from the NO\(_2\) photofragment. They combined their results with the product translational energy distributions determined by Kawasaki et al.\(^{13}\) and invoked molecular orbital considerations to assign the observed 193 nm dissociation products as NO\(_2\)(1\(^2\)B\(_2\)) + NO\(_2\)-(1\(^2\)B\(_2\)).

At this point it is important to note that the calculations of Mason,\(^{3}\) which were used by both Sisk et al.\(^{14}\) and Kawasaki et al.\(^{13}\) to aid in interpretation of their experimental results, were performed with the planar N\(_2\)O\(_4\) molecule positioned in the Cartesian coordinate system such that the \(x\) axis lay along the N–N bond, with the molecule lying in the \(xz\) plane. The coordinate system used by Sisk et al., Kawasaki et al., and most electronic structure theorists\(^{15–17}\) also has the molecule in the \(xz\) plane, but with the \(z\) axis along the N–N bond. We adopt the latter coordinate system in this work. The difference in axis systems means that vibrational modes, molecular orbitals, and electronic states may have different symmetry labels in the two systems, a fact for which neither Kawasaki et al. nor Sisk et al. accounted. Consequently, many of the arguments they make based on symmetry labels are in error. For example, Sisk and co-workers neglected to transform Mason’s label for the state excited at 193 nm; Mason labels the state B\(_{1u}\), which should be transformed to B\(_{2u}\) upon changing the coordinate system. This error means that the argument made by Sisk and co-workers invoking a curve crossing to a state that forms NO\(_2\)(1\(^2\)B\(_2\)) + NO\(_2\)(1\(^2\)B\(_2\)) products is also incorrect.

Similarly, the results of Mason\(^{3}\) indicate that the transition dipole connecting the N\(_2\)O\(_4\) ground state and the \(1^2\)B\(_{3u}\) state excited by 193 nm radiation lies along the \(z\) axis, meaning that the transition dipole moment lies in the plane of the molecule but perpendicular to the N–N bond. However, since the \(z\) axis lies along the N–N bond in the coordinate system used by Kawasaki and co-workers, that group took the theoretical results to mean that the transition dipole lies parallel to the N–N bond. Consequently, they missed the conflict between Mason’s theoretical prediction and their experimental results, which showed the transition dipole moment to be largely parallel to the N–N bond, with an anisotropy parameter, \(\beta\), of 1.2.

This photofragment translational spectroscopy study of the photodissociation of N\(_2\)O\(_4\) at 193 nm addresses the questions raised in the previous studies and attempts to evaluate the importance of electronically nonadiabatic effects in this system as compared to nitric acid and nitromethane. We present product translational energy distributions extracted from the data, as well as the photofragment angular distribution.

II. Experimental Section

These experiments measure the recoil velocity and angular distributions of photofragments from N\(_2\)O\(_4\) dissociated at 193 nm. We first collect photofragment spectra using unpolarized light, then polarize the laser beam and take spectra at several polarization angles to measure the angular distribution of the photofragments. The experiments use a crossed laser–molecular beam apparatus with a rotating molecular beam source and universal electron bombardment detector.\(^{8,19}\)

A 10% mixture of NO\(_2\)/N\(_2\)O\(_4\) in helium expands into the vacuum chamber through a 127 nm orifice, generating a continuous molecular beam. The pressure of the gas in the stagnation region behind the nozzle is approximately 300 Torr, yielding a mixture in which N\(_2\)O\(_4\) comprises 24% of the NO\(_2\)/N\(_2\)O\(_4\) at 293 K.\(^2\) Proper analysis of the time-of-flight data requires knowledge of the molecular beam velocity and velocity spread, measured by directing the molecular beam straight into the detector and inserting a chopper wheel into its path. This gave an average mean molecular beam velocity of 1110 m/s and a velocity spread (\(\Delta v/v\)) of 12.7% as given by the full width at half-maximum (fwhm) of the arrival time distribution.

For the first part of the experiment, we focus the unpolarized 193 nm output of a Lumonics PM-848 pulsed excimer laser (set to approximately 3 mJ/pulse) to a 2 mm \(\times\) 3 mm spot in the interaction region. With each laser pulse, products scatter from the interaction region with laboratory-frame velocities determined by the vector sum of the molecular beam velocity and the recoil velocity imparted during the dissociation. Some of the fragments scatter into the 1.5° acceptance angle of the detector, traveling a total of 44.4 cm to an electron bombardment ionizer that can produce both parent and daughter ions from the neutral photofragments. The electron energy used is 200 eV. The ions are mass-selected by a quadrupole mass filter and then, using a Daly detector in combination with a multichannel scaler, counted as a function of time after the excimer laser pulse.

We collected time-of-flight arrival spectra at several different fragment masses and source-detector angles. For \(m/e = 46\) (NO\(_2^+\)), we collected \(4 \times 10^6\) laser shots at a source-detector angle of 10° (at a rate of about 7020 counts of signal per second) and \(3 \times 10^6\) shots at 15°. We also collected TOF spectra at \(m/e = 30\) (NO\(_2^+\)) at an angle of 10° for \(2 \times 10^6\) shots, and \(m/e = 16\) (O\(^+\)) at 10° for \(7.5 \times 10^6\) laser shots at rates of 53000 and 11000 counts/second, respectively. Observation of higher masses could give clues to the relative contribution of (NO\(_2^+\))\(_n\) (\(n \geq 2\)) clusters to the total signal. Accordingly, we collected data at a source angle of 0° at \(m/e = 92\) (N\(_2\)O\(_4^+\)), \(m/e = 76\) (N\(_2\)O\(_3^+\)), \(m/e = 62\) (NO\(_2^+\)), and \(m/e = 60\) (N\(_2\)O\(_3^+\)). No significant signal was apparent; it appears that N\(_2\)O\(_4\) and other higher order
clusters are too unstable to withstand the 200 eV electron bombardment and so they all crack to lighter fragments in the ionizer. To assess the contribution from product channels other than NO$_2^+$ + NO$_2$, it is useful to compare the NO$_2^+$, NO$^+$, and O$^+$ spectra with those of NO$_3^+$ and N$_2$O$_3^+$. Accordingly, we looked for photofragment signal at the masses corresponding to these fragments; nothing was observable at either m/e = 62 after one million laser shots or at m/e = 76 after two million shots collected at a source-detector angle of 10$^\circ$.

The second part of the experiment measures the angular distribution of the m/e = 46 product. To do this, the unpolarized excimer laser light passes through a single-crystal quartz Pellin-Broca prism that separates it into two linearly polarized components. A half-wave retarder then rotates the horizontally polarized output of the prism to the desired angle. We collected a time-of-flight spectrum with the retarder set to each of six different angles; each spectrum yields one point on the angular distribution plot with a total of 4.5 × 10$^5$ laser shots collected at each angle. However, to eliminate the need to normalize for errors due to variation of molecular beam conditions or laser beam intensity, we did not follow a procedure in which all shots were collected for one angle before moving on to the next. Rather, we summed nine sets of TOF spectra in which data were obtained at each angle for 5 × 10$^4$ laser shots, varying with each set the order in which the angles were done.

We measure both the molecular beam source and laser polarization angles with respect to the detector axis, but in senses opposite to each other. For example, if a positive angle for the molecular beam source involves a clockwise rotation from the detector axis (clockwise or counterclockwise of course depends on the direction from which the apparatus is viewed), then positive angles of the laser polarization angle involve counterclockwise rotation from the detector axis.

### III. Results

Our data show that the only significant primary dissociation process is N–N bond fission, although some of the NO$_2$ products are formed with enough internal energy to undergo secondary dissociation. The N–N bond fission results in at least two different product channels, which are assigned in section IVA. The upper plot in Figure 1 shows the time-of-flight spectrum obtained for m/e = 46 (NO$_2^+$) at a source-detector angle of 10$^\circ$ with a room temperature molecular beam nozzle. Note that the spectrum is composed of two main peaks, one at relatively short arrival times and the other coming in at longer times. Retaking the spectrum with a nozzle temperature of approximately 35 °C (lower plot in Figure 1), we see that the slow peak arriving near 450 μs decreases significantly in intensity. Although the slightly higher nozzle temperature causes a corresponding increase in molecular beam velocity, the predicted change in the relative heights of the peaks in the TOF spectrum is calculated to be negligible if both peaks result from N$_2$O$_4$ photodissociation. However, at the elevated temperature, the slow peak is reduced in intensity by more than 40% relative to the fast one. Therefore, it must result from photolysis of higher-order clusters whose concentration is depleted more than that of N$_2$O$_4$ in the expansion at the higher nozzle temperature. Figure 2 shows the m/e = 46 (NO$_2^+$) TOF spectrum collected at 15$^\circ$. We determined a product translational energy distribution, P(E$_T$), for the NO$_2$ + NO$_2$ dissociation channel using a forward convolution fit to the data in Figures 1 and 2 (not fitting the signal shown to result from higher order clusters); the P(E$_T$) shown in Figure 3 gives the fits shown in Figures 1 and 2. To confirm that the signal results from NO$_2$ neutral photofragments formed by N–N bond fission, we took spectra for the NO$^+$ and O$^+$ daughter ions. There was no significant signal at NO$_3^+$ and N$_2$O$_3^+$ (see section II). Figure 4 gives the TOF spectra for m/e = 16 (O$^+$) and m/e = 30 (NO$^+$), with the arrival times corrected for the ion flight time through the quadrupole mass filter. (All the other spectra shown in this paper are raw data; no ion flight times have been subtracted.) Once this correction has been made, a direct comparison can be made of the shapes of the two spectra.

Any peaks appearing in the NO$^+$ or O$^+$ spectra that do not appear in the NO$_2^+$ spectrum would indicate either the existence of another N$_2$O$_4$ dissociation channel or contribution to the signal from dissociation of NO$_2$. However, although NO$_2$ is favored in the equilibrium between NO$_2$ and N$_2$O$_4$ under the conditions existing in the stagnation region behind our nozzle, the photodissociation of NO$_2$ clearly does not contribute significantly to our TOF spectra. There are no peaks in the NO$^+$ and O$^+$ spectra that do not appear in the NO$_2^+$ spectrum; the peaks...
Thus, the dissociation of N$_2$O$_4$ near 200
the upper part of Figures 1 and 2 show a fast peak arriving
and, to a larger extent, the O
spectra also mean that the only significant primary channel in
the NO$_2$ primary product (see text for details).

Figure 3. Product translational energy distribution, P(E$_T$), used to fit
the data shown in Figures 1 and 2. The accuracy in determining recoil
energies is roughly 2 kcal/mol.

Although the signal-to-noise ratio is limited, the spectra in
the former spectra are centered at the same arrival time as
the corresponding peaks in the latter spectrum, which cannot
come from the continuous NO$_2$/N$_2$O$_4$ expansion. The lack of
contribution from NO$_2$ photodissociation is not surprising since
the absorption coefficient of N$_2$O$_4$ at 193 nm is well over 2
orders of magnitude greater than that of NO$_2$. The absence of
photofragment signal at NO$_2^+$ and N$_2$O$_4^+$, combined with the
essentially similar appearances of the O$^+$, NO$^+$, and NO$_2^+$
spectra also mean that the only significant primary channel in
the dissociation of N$_2$O$_4$ excited at 193 nm is N$_2$O$_4$ → NO$_2$ + NO$_3$.

Although the signal-to-noise ratio is limited, the spectra in
the upper part of Figures 1 and 2 show a fast peak arriving
near 200 μs with a shoulder at ~20–40 μs longer arrival times.
Thus, the dissociation of N$_2$O$_4$ → NO$_2$ + NO$_2$ evidences a bimodal recoil kinetic energy distribution (shown in Figure 3),
suggesting that the dissociation proceeds via at least two distinct product channels. The fast peaks in the NO$_2^+$ and O$^+$ spectra at 10°
are centered at the same arrival times as the corresponding peak in the NO$_2^+$ spectrum (after correction for the mass-
dependent ion flight time through the quadrupole mass filter),
indicating that they result from the same primary photodissociation
process. However, closer inspection reveals that the NO$_2^+$
and, to a larger extent, the O$^+$ TOF spectra are broader than
the NO$_2^+$ spectrum in the top part of Figure 1. If the primary
NO$_2$ products were all arriving intact at the ionizer and the
lower-mass fragments were simply formed by cracking in the
ionizer, the peaks in the measured TOF spectra for all masses
should have exactly the same widths and shapes. The fact that
they do not indicates that some of the NO$_2$ products underwent
secondary unimolecular dissociation, yielding O and NO fragments
with a broader range of laboratory velocities than the
NO$_2$ as a result of the additional recoil energy imparted in the
secondary dissociation. By conservation of momentum, the O
atom will emerge from the NO$_2$ dissociation with larger velocity
than the NO, so comparison of the O$^+$ and NO$_2^+$ TOF spectra
in Figure 4 is useful to show the presence of the secondary
dissociation. Note that the broadening is very slight, as expected
if the secondary dissociation of NO$_2$ products to NO + O
releases little energy to product recoil. Furthermore, the NO$_2^+$
spectrum does not show the shoulder that the NO$_2^+$ spectrum
does because the slight recoil of NO from O contributes to the
NO$_2$ spectrum, thus smearing the time-of-arrival distribution.

It is well known that the angular distribution of products from
a dissociation can be described in the center-of-mass frame by the
classical electric dipole expression

$$I(\theta_{cm}) = \frac{1}{4\pi}[1 + \beta P_2(\cos\theta_{cm})]$$

where $\theta_{cm}$ is the angle between the photofragment recoil
direction in the center-of-mass reference frame and the electric
vector of the linearly polarized light. In the limit of prompt,
axial photofragment recoil, the anisotropy parameter, $\beta$, is given by

$$\beta = 2P_2(\cos\alpha)$$

where $\alpha$ is the angle between the transition dipole moment for
the absorption and the breaking bond. $\beta$ varies from a value of
$-1$ when the transition dipole moment is perpendicular to the
breaking bond (called a “perpendicular” distribution) to 2 when
the transition dipole is parallel to the bond (a “parallel”
distribution).

Before the expression in Equation 1 can be used to describe
the angular distributions obtained in our experiment, it must be
converted into the laboratory frame, taking into account the
molecular beam velocity distribution, source-detector angle, and
the P(E$_T$) obtained in the experiment performed with unpolarized
light. Figure 5 shows the experimentally measured angular
distribution of the NO$_2$ photofragments along with curves
simulated using several different values of $\beta$ in the procedure
described above. The individual data points on the plot were
obtained by finding the area under the fast peak (using limits of 140–250 μs) in the m/e = 46 TOF spectra collected with the laser set to the specified polarization angles. By comparing the experimental points with the simulated curves, we see that the laser set to the specified polarization angles. By comparing among those internal modes. Nevertheless, using known NO2 of energy partitioned into the fragments’ internal modes. However, we cannot determine how the energy is distributed to consider not the maximum available energy for product channel and the most probable translational energy for each channel using a Franck–Condon-like sudden analysis. Calculating the maximum amount of energy available for partitioning into translation simply requires values of $T_0$, the energy required to excite from the zero-point level of the ground electronic state of NO2 to the zero-point level of an electronically excited state. $T_0$ excitation energies for various NO2 electronic states and the corresponding “maximum available” translational energies ($E_{T,\text{max}}$) for those states produced in coincidence with NO2(2$^2$A1) are given in Table 1. It is more instructive, however, to consider not the maximum available energy for product translation but rather the most probable kinetic energy release for each product channel. We assume that the most probable vibrational excitation in the ground or electronically excited product is the one that results when the nascent NO2 molecule is formed with the geometry it had in ground-state N2O4. In other words, the energy of the NO2 product is determined by vertical excitation to the NO2 electronic state at the geometry the group had in the intact N2O4 molecule. Thus, to arrive at a prediction for the most probable translational energy for each possible product channel, we use literature values of the energies of the various NO2 electronic states at the geometry of the NO2 groups in N2O4. Since this geometry is almost exactly the same as the equilibrium geometry of NO2(2$^2$A1) ($r_{NO} = 1.195$ Å and ONO angle = 133.7°) for NO2;26 $r_{NO} = 1.19$ Å and ONO angle = 135.4° for N2O5),27 we can just use the vertical excitation energies of NO2. These energies are also given in Table 1, and the “most probable” translational energies calculated with them are designated as $E_{T,\text{mp}}$. (Reference 24 provides a value for vertical excitation to a quartet state. Due to resolution limitations, IV. Discussion

A. Assigning NO2 + NO4 Product Channels. With the measured product translational energy distribution of the NO2 + NO2 photofragments and the N–N bond dissociation energy, we can use conservation of energy to determine the total amount of energy partitioned into the fragments’ internal modes. However, we cannot determine how the energy is distributed among those internal modes. Nevertheless, using known NO2 excited-state energies along with the O2N–NO2 bond dissociation energy ($D_0 = 12.69$ kcal/mol),12 we can calculate both the maximum energy available for partitioning into translation for each product channel and the most probable translational energy for each channel using a Franck–Condon-like sudden analysis. Calculating the maximum amount of energy available for partitioning into translation simply requires values of $T_0$, the energy required to excite from the zero-point level of the ground electronic state of NO2 to the zero-point level of an electronically excited state. $T_0$ excitation energies for various NO2 electronic states and the corresponding “maximum available” translational energies ($E_{T,\text{max}}$) for those states produced in coincidence with NO2(2$^2$A1) are given in Table 1. It is more instructive, however, to consider not the maximum available energy for product translation but rather the most probable kinetic energy release for each product channel. We assume that the most probable vibrational excitation in the ground or electronically excited product is the one that results when the nascent NO2 molecule is formed with the geometry it had in ground-state N2O4. In other words, the energy of the NO2 product is determined by vertical excitation to the NO2 electronic state at the geometry the group had in the intact N2O4 molecule. Thus, to arrive at a prediction for the most probable translational energy for each possible product channel, we use literature values of the energies of the various NO2 electronic states at the geometry of the NO2 groups in N2O4. Since this geometry is almost exactly the same as the equilibrium geometry of NO2(2$^2$A1) ($r_{NO} = 1.195$ Å and ONO angle = 133.7°) for NO2;26 $r_{NO} = 1.19$ Å and ONO angle = 135.4° for N2O5),27 we can just use the vertical excitation energies of NO2. These energies are also given in Table 1, and the “most probable” translational energies calculated with them are designated as $E_{T,\text{mp}}$. (Reference 24 provides a value for vertical excitation to a quartet state. Due to resolution limitations, TABLE 1: Experimentally Determined Excitation Energy and Energy Available for Translation for Various Combinations of NO2 Products

<table>
<thead>
<tr>
<th>products</th>
<th>$T_0$ (eV)</th>
<th>$E_{T,\text{max}}$ (kcal/mol)</th>
<th>$E_{\text{vertical}}$ (eV)</th>
<th>$E_{T,\text{mp}}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^2A_1 + 1^2B_1$</td>
<td>1.207a</td>
<td>107.4</td>
<td>2.95</td>
<td>67.20</td>
</tr>
<tr>
<td>$X^2A_1 + 1^2B_1$</td>
<td>1.83b</td>
<td>93.02</td>
<td>2.84</td>
<td>69.73</td>
</tr>
<tr>
<td>$X^2A_1 + 1^2B_1 + 1^2A_2$</td>
<td>unknown</td>
<td>4.49</td>
<td>31.68</td>
<td></td>
</tr>
<tr>
<td>$X^2A_1 + 2^2B_2$</td>
<td>4.98c,d</td>
<td>20.38</td>
<td>5.22</td>
<td>14.85</td>
</tr>
<tr>
<td>$1^2B_1 + 1^2B_2$</td>
<td>2.414</td>
<td>79.55</td>
<td>5.90</td>
<td>insufficient energy</td>
</tr>
</tbody>
</table>

* Reference 20. * Reference 21. * Reference 22. * Reference 23. * Reference 24. (The data provide a value for vertical excitation to a quartet state. Due to resolution limitations, Rianda and co-workers were unable to distinguish between $^4B_2$ and $^4A_2$, which are predicted to be similar in energy.) * Results of reference 23 as interpreted by reference 25.

Rianda and co-workers were unable to distinguish between $^4B_2$ and $^4A_2$, which are predicted to be similar in energy. Ab initio multireference configuration interaction calculations on the vertical and minimum-to-minimum excitation energies of the doublet and quartet states are presently underway.28 This Franck–Condon-like method of course predicts that NO2(2$^2$A1) is formed withno vibrational energy, since the change between the geometry of the NO2 group in ground-state N2O4 and that of free NO2(2$^2$A1) is negligible. However, nascent NO2 formed in the $^1B_2$ state, for example, is most likely to have vibrational energy considerably in excess of that of the zero-point of the excited electronic state.

Figure 6 shows the $P(E_T)$ shown in Figure 3. The slow and fast distributions peak at 19.50 and 34.62 ± 2 kcal/mol, respectively. When scaled as plotted by the relative probability coefficients for each channel, 34% and 66%, respectively, they give the $P(E_T)$ shown in Figure 3. Arrows indicate maximum available and most probable energies for selected possible combinations of product electronic states, as discussed in the text. Exact values for these energies are given in Table 1.
cannot compete with fast dissociation processes on a singlet release peaks at about 34 kcal/mol. Clearly, we need to triplet excited states of N2O4 at the level of configuration al.


and the previously published singlet N2O4 potential surfaces of basis set using interaction with single excitations (CIS) and a 6-311 basis set frozen at their N2O4 equilibrium positions. 27 For reasons of clarity, we plot only singlet states of B

amounts would be detectable in the previous studies by Sisk et al. 14 and Kawasaki et al. 13 We note that the kinetic energy distribution determined for the NO2 + NO2 product channel by Kawasaki and co-workers is quite different from ours. Their distribution peaks near 10 kcal/mol and decreases to half of the maximum value at about 35 kcal/mol of total translational energy. It seems likely that the photofragments detected in their TOF spectra included contributions from the dissociation of higher-order clusters in their pulsed-beam expansion.

B. Examining Candidates for an Intersystem Crossing Process Yielding NO2(X2A1) + NO2(1B2/1A1). Production of NO2(X2A1) + NO2(1B2/1A1) following excitation of a singlet N2O4 state is a spin-forbidden process. Little is known about spin–orbit coupling in N2O4. However, if there exists a triplet state of the proper symmetry and with energy similar to that of the initially excited singlet state at the Franck–Condon geometry, the coupling between the two states may be sufficient to cause significant transfer of population from the singlet to the triplet state. Note, however, that the intersystem crossing must happen on a time scale shorter than the rotational period of the molecule at about 50 K, since our measured anisotropy parameter is β = 1.7 ± 0.2. Although it is a common assumption that dissociation processes requiring intersystem crossing on a short time scale can be neglected, that assumption cannot hold true in N2O4 if we have correctly assigned as NO2(X) + NO2(1B2/1A1) the product channel whose kinetic energy release peaks at about 34 kcal/mol. Clearly, we need to reexamine the common assumption that intersystem crossing cannot compete with fast dissociation processes on a singlet state; the case of N2O4 is not the first example of this phenomenon. 30,31

To assess whether there exists a good candidate triplet state for an intersystem crossing product channel, we calculated the triplet excited states of N2O4 at the level of configuration interaction with single excitations (CIS) and a 6-311+g(d,p) basis set using Gaussian 94. 32 Previous calculations performed in this laboratory for the singlet state used the same basis set and level of theory. 6 Figure 7 shows cuts through both the triplet and the previously published singlet N2O4 potential surfaces of B synchronously vs the N–N bond length, keeping all other parameters frozen at their N2O4 equilibrium positions. 32 For reasons of clarity, we plot only singlet states of B synchronously and the two triplet states crossing the 1B3u state in the Franck–Condon region, although there are multiple lower and higher lying states of other symmetries. Figure 7 also shows the electronic states of the NO2 products to which the pictured surfaces correlate adiabatically in D2h geometry (multiple conical intersections change the adiabatic correlations at geometries of lower symmetry). The results of these calculations indicate that the 2B3u and 2A1u states cross the initially excited 1B3u state very close to the Franck–Condon region (gas-phase electron diffraction experiments give values of 1.75–1.782 Å for the N2O4 equilibrium bond length26,27,33), so one would expect one or the other to play a role in a fast intersystem crossing process. Our preliminary spin–orbit coupling calculations, done with the January 2000 version of GAMESS 34 using single excitations from a CISP ground state wavefunction [6-311g+(s,*) basis], indicate that the 2A1u state has significant coupling (109 cm−1) to the 1B3u state in the Franck–Condon region. Significant spin–orbit coupling to the 2A1u state, but not the 2B3u state, is consistent with the usual expectations outlined by McGlynn. 35

The electronic character of this triplet state (the 2A1u) in the crossing region is primarily πσ*. The 1B3u state has just over 50% nσ* character and 40% ππ* character (combining the contributions of in-phase and out-of-phase configurations) at the crossing point. The 2A1u state adiabatically correlates to NO2 (X2A1) + NO2 (1A1) in D2h geometry, since it evolves from 1ππ* near the crossing with the singlet state to 3nπ* at the product asymptote.

The results thus far suggest a possible mechanism for the branching to the observed product channels. In a diabatic picture, one can view the 1B3u state electronic wavefunction at the point of the crossing with the triplet state as a linear combination of the nσ* and 1ππ* diabats (which are coupled off-diagonal potential coupling). If the nσ* and ππ* diabats are strongly coupled, the portion of the molecular wavefunction with nσ* character may preferentially undergo intersystem crossing to the 1ππ* diabat and go on to yield the NO2(X) + NO2(1A1) products, while the part of the wavefunction with 1ππ* character results in NO2(X) + NO2(2B2) ππ* diabatic products observed. This mechanism is purely speculative at this point and requires further investigation. The relative probability weightings required to obtain a good fit to the data using the two P(E) shown in Figure 6 are 34% and 66% for the slow and fast distributions, respectively. This result is in general agreement with our model, which predicts 40% and just over 50% for the slow and fast distributions, respectively, if the nσ* configuration contribution to the wave function at the point of crossing results in NO2(X) + NO2(1A1) and the ππ* contribution results in NO2(X) + NO2(2B2). More detailed calculations are necessary to assess accurately the importance of spin–orbit coupling in this system and to obtain the necessary input for a full dynamical calculation including spin–orbit coupling to the triplet surfaces.

The mechanism described above for the competition between the nσ* NO2(X) + NO2(1A1) channel requiring intersystem crossing and the NO2(X) + NO2(2B2) diabatic singlet channel for the ππ* configuration invites further examination of this group’s previous results on nitric acid. 7 Similar to the case of N2O4, Myers et al. detected two HO–NO2 bond fission channels. Using the same Franck–Condon-like sudden analysis used here, they assigned the one partitioning larger amounts of energy into translation, and hence less energy into internal modes, to the adiabatic channel analogous to the NO2(X) + NO2(1B2) pathway not observed in N2O4. In nitric acid, the 2A1’ state excited at 193 nm is nearly pure ππ* in character;
adiabatic traversal of the $\pi\pi^*$ or $\sigma\pi^*$ avoided crossing near the Franck–Condon region yields adiabatic OH(X) + NO$_2$(1B$_2$) products. The second, nonadiabatic HO–NO$_2$ bond fission channel in nitric acid was not definitively assigned. The diabatic $\pi\pi^*$, products, OH(X) + NO$_2$(2B$_2$), are not energetically accessible upon excitation with 193 nm radiation, so Butler and co-workers$^{2,20}$ speculated that this second observed product channel might be OH(X) + NO$_2$(1B$_3$). Thus, we were surprised when N$_2$O$_4$ dissociation did not result in any singlet-surface adiabatic products, since there is already strong mixing of $\pi\pi^*$ and $\sigma\pi^*$ character in the Franck–Condon region, making the NO$_2$(X) + NO$_2$(1B$_2$) channel more electronically accessible.$^{36}$ (Recall that the $\sigma\pi^*$ state correlates diabatically to NO$_2$–(X) + NO$_2$(1B$_2$)). The only reasonable explanation for the lack of adiabatic products is that a repulsive triplet state in N$_2$O$_4$ lies very near the Franck–Condon region, so in a diabatic picture the flux on the $\pi\sigma^*$ diabat moves via spin–orbit coupling to the triplet state, resulting in NO$_2$(X) + NO$_2$(1B$_2$) asymptote. The remaining flux on the $\pi\pi^*$ diabat can evolve to the NO$_2$(X) + NO$_2$(2B$_2$) asymptote, the $\pi\pi^*$ diabatic channel that is energetically allowed in N$_2$O$_4$ but not in nitric acid.

C. Anomalous Photofragment Angular Distribution. The measured angular distribution of the NO$_2$ product channel has an anisotropy parameter $\beta = 1 \pm 0.2$. This result indicates that the transition dipole for the absorption at 193 nm is nearly parallel to the N–N bond in N$_2$O$_4$. Previous work by Kawasaki et al.$^{13}$ also reported a parallel anisotropy parameter; their measured value was $\beta = 1.2$, but their data probably included some contribution from higher-order clusters, which would be expected to decrease the anisotropy of the measured distribution. As discussed in the Introduction, the calculations of Mason$^1$ predict a transition dipole moment lying in the plane of the molecule but perpendicular to the N–N bond. Because of the different coordinate systems used, Kawasaki et al. misinterpreted this result.$^{13}$ Consequently, they missed the discrepancy between their results, which showed the angular distribution to be parallel to the N–N bond, and Mason’s theoretical results.

Closer examination of the excited electronic configurations of N$_2$O$_4$ reveals a possible explanation for the conflicting theoretical and experimental results for the direction of the transition dipole moment. Although the 1B$_3$ state is of pure $\pi\pi^*$ electronic character in D$_h$ symmetry, at the nonsymmetric geometries occurring as a result of zero-point motion the excited state may include contributions from other electronic configurations with parallel transition moments. In this case, an overall transition moment could result that is intermediate between pure parallel and pure perpendicular. The CIS calculations of singlet excited states previously performed in this laboratory$^6$ using Gaussian 94 give a 1B$_3$ state with a vertical excitation energy near 8 eV and a very large oscillator strength, 1.0257. The transition dipole moment connecting this state with the ground electronic state (1$\text{A}_g$) lies parallel to the N–N bond. The 1B$_3$ state’s $\pi\pi^*$/h$\sigma^*$ electronic configuration can mix with the parallel $\sigma\sigma^*$ configuration (1B$_1$ in D$_h$ symmetry) at geometries including the zero-point motion of N$_2$O$_4$’s $v_5$ out-of-phase antisymmetric stretch mode,$^{37}$ which is of $h_2$ symmetry in our coordinate system. At these geometries, the molecular symmetry is C$_2v$, and the 1B$_1$ and 1B$_3$ states both become 1B$_a$. The lower adiabat in this 1B$_a$ pair retains the primarily $\pi\pi^*$/$\sigma\pi^*$ electronic configuration that characterizes the D$_h$ symmetry 1B$_3$ state, but a small amount of $\sigma\sigma^*$ character is mixed in. Although the $\sigma\sigma^*$ contribution to the electronic wavefunction is so small that it is likely unimportant when considering the influence of electronic character on product channels, the oscillator strength associated with the $\sigma\sigma^*$ contribution to the transition moment is very large. As a result, the transition dipole moment rotates to be nearly parallel to the N–N bond, as observed experimentally. Although crude calculations performed using Gaussian support it, this explanation awaits confirmation with better electronic structure calculations. CIS calculations such as those performed here can have vertical excitation energies in error by 1 eV or more, so the energies calculated for the 1B$_3$ and 1B$_1$ states are subject to that error. Current emission spectroscopy results,$^6$ however, also support such a vibronic coupling mechanism, since emission spectra from N$_2$O$_4$ excited near 200 nm show progressions in $v_3$, the torsional mode, and $v_5$, the out-of-phase antisymmetric stretch,$^{37}$ which result from vibronic coupling of the 1B$_3$ state to a 1B$_1$ state, presumably the same one indicated here.

V. Conclusions

Photofragment translational spectroscopy experiments on the 193 nm photodissociation of N$_2$O$_4$ show evidence of two primary N–N bond fission channels, but no significant branching to other bond fission or elimination products. The product translational energy distribution P(E$_T$) determined from the data for N–N bond fission is bimodal; we tentatively assign the two dominant bond fission channels to NO$_2$(X$^2A_1$) + NO$_2$(1B$_2$)/1B$_2$ and NO$_2$(X$^2A_1$) + NO$_2$(2B$_2$). Since the initially excited 1B$_3$ state of N$_2$O$_4$ correlates diabatically in D$_h$ symmetry to NO$_2$(X$^2A_1$) + NO$_2$(1B$_2$), branching to both observed product channels requires transitions to other potential surfaces. Formation of NO$_2$(X$^2A_1$) + NO$_2$(1B$_2$)/1B$_2$ products requires intersystem crossing, and NO$_2$(X$^2A_1$) + NO$_2$(2B$_2$) are the diabatic products of the $\pi\pi^*$ electronic configuration.

Previous workers$^{13,14}$ had detected formation of NO$_2$(1B$_1$) or NO$_2$(1B$_2$) by examining emission from the products of the N$_2$O$_4$ dissociation. Although this channel is not assigned to either of the dominant product channels in our work, a relatively small fraction of the N$_2$O$_4$ molecules could dissociate to give these products. A small contribution may not be discernible as a major peak in our TOF spectra, but because these species fluoresce readily, they would show up clearly in an emission experiment.

Measurement of the angular distribution of the NO$_2$ products yielded a value for the anisotropy parameter, $\beta$, of 1.7 $\pm$ 0.2. Calculations by Mason$^1$ predicted a perpendicular transition dipole leading to the 1B$_3$ state believed to be excited upon irradiation by light at 193 nm. The disagreement between theory and experiment can be resolved by recognizing that a state with large oscillator strength and 1B$_1$ symmetry (as labeled for N$_2$O$_4$ in D$_h$ symmetry) can mix with the 1B$_3$ state upon inclusion of the zero-point motion of the out-of-phase antisymmetric stretch ($v_5$). Inclusion of this vibrational motion decreases the symmetry of the N$_2$O$_4$ to C$_2v$ and allows the two states to couple, giving a transition dipole moment that lies nearly parallel to the N–N bond.

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References and Notes

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