Emission spectroscopy of photodissociating $\text{N}_2\text{O}_4$ excited near 200 nm to the $\pi_{nb,O} \pi_{\text{NO}_2}^*/n\sigma_{\text{N–N}}^*$ avoided crossing

The James Franck Institute and Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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These experiments and complementary electronic structure calculations seek to probe the early dissociation dynamics of $\text{N}_2\text{O}_4$ excited in the strong 186 nm ultraviolet absorption band. Laser photons of 199.7, 203, and 205 nm are used to dissociate $\text{N}_2\text{O}_4$ molecules expanded in a free jet. The emission from the dissociating molecules is dispersed in a spectrometer and collected with an optical multichannel analyzer (OMA). We observe a strong progression in $v_3$, the N–N stretching mode, consistent with electronic structure calculations and a previous observation of N–N bond fission leading to NO$_2$ photoproducts in this band. We also observe emission to combination bands in $v_4$, the torsion, and $v_5$, the out-of-plane antisymmetric NO$_2$ stretch, which we attribute to vibronic coupling to a $\sigma\pi^*$ excited state configuration. Analysis of our data allows for an assignment of the torsional frequency of NO$_2$. Around 200 nm nitric acid, nitromethane, and N$_2$O$_4$ all exhibit a similar absorption to an adiabatic surface that changes electronic character from $\pi_{nb,O} \pi_{\text{NO}_2}^*$ at short O$_2$N–R (R=CH$_3$, OH, NO$_2$) internuclear distances to $n\sigma^*$ at extended internuclear distances. We compare our present emission spectra of N$_2$O$_4$ with previous emission experiments on nitromethane to understand how the character of the Franck–Condon region of the excited states in these two molecules differ. © 1999 American Institute of Physics.

I. INTRODUCTION

Molecules with NO$_2$ functional groups and molecules well described as covalently bonded clusters$^1$ play a key role in atmospheric chemistry, yet much of their photochemistry and photophysics is still poorly understood. In this work we seek to compare and contrast the early photofragmentation dynamics of the NO$_2$ dimer, N$_2$O$_4$, upon excitation in the strong 186 nm ultraviolet absorption band with those of nitric acid and nitromethane excited in the analogous $\pi_{nb,O} \pi_{\text{NO}_2}^*$ absorption band$^2$ characteristic of molecules with NO$_2$ functional groups. Of particular interest in this study are (1) how torsional motion and antisymmetric stretching are coupled in the early dissociation dynamics and (2) how Franck–Condon access to the excited electronic state from a ground state with an unusually long equilibrium N–N bond length could probe the region of avoided crossing of the $\pi_{nb,O} \pi_{\text{NO}_2}^*$ and $n\sigma^*$ electronic configurations along the N–N bond fission excited-state reaction coordinate.

The structure of N$_2$O$_4$ has been studied by x-ray diffraction,$^3$–$^5$ neutron diffraction in the crystal,$^6$ and gas-phase electron diffraction.$^7$–$^9$ The lowest-energy structure of this molecule has $D_{2h}$ symmetry with an exceptionally long NN bond, 1.75–1.782 Å. Additionally, the NO bond, 1.190 Å, and the ONO bond angle, 135.4°, are little changed from the values in ground state NO$_2$, 1.199 Å and 133.7°, respectively.$^9$ Theoretical studies have attempted to explain the unusual features of N$_2$O$_4$: the long N–N bond and the planar conformation.$^7$–$^{10}$–$^{15}$ The calculation of an accurate value for the N–N bond length has proven difficult; only recently, by considering the effect of electron correlation, have theoretical bond lengths become consistent with the experiment.$^{15}$–$^{20}$

Before discussing the electronic character of N$_2$O$_4$ excited in the 186 nm absorption band and the interpretation of the few experiments probing the resulting dissociation dynamics, we note that the symmetry labels of the relevant molecular orbitals and the symmetry label given to the excited state accessed depend on the coordinate system chosen for the N$_2$O$_4$ molecule. Unfortunately, no single convention for the choice of coordinate axes has been uniformly adopted, and this had led to considerable confusion when experimentalists studying the photofragmentation channels$^{21,22}$ have compared their results to the only available excited state electronic structure calculations, those of Mason.$^{23}$ The top frame in Fig. 1 depicts the convention for coordinate axes most commonly used by experimentalists$^{21,22}$ and most electronic structure theorists,$^{13}$–$^{15,24}$ with the planar molecule in the XZ plane and the Z axis directed along the N–N bond. The next frame down in Fig. 1 shows the coordinate system adopted in the calculations of the excited states of N$_2$O$_4$ by Mason,$^{23}$ with the molecule in the XZ plane but the X axis directed along the N–N bond. Thus, the symmetry of the excited state accessed at 186 nm is given as $1^1B_{1u}$ in the work of Mason (with a transition dipole oriented in her Z axis direction, in the molecular plane but perpendicular to the N–N bond), but when that label is transformed into the coordinate system used by other elec-

$^{4}$Electronic mail: 1-butler@uchicago.edu

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tronic structure theorists and experimentalists it should be redesignated as the $1^1B_{3u}$ state. Neither Kawasaki and co-workers\textsuperscript{21} nor Johnston and co-workers\textsuperscript{25} noticed that Mason\textsuperscript{24} used a different coordinate system than they, so the interpretation of their experimental results with respect to Mason’s work is in error. In this paper, we adopt the most common coordinate system (Fig. 1, top) used for the electronic configuration of N$_2$O$_4$, with the molecule in the XZ plane and the Z axis along the N–N bond, and where necessary transform the work of Mason to this coordinate system. We also use the nearly universally adopted coordinate system for the NO$_2$ product, with the molecule in the YZ plane and the Z axis along the C$_2$ axis [Fig. 1(c)].

The electronic configuration of N$_2$O$_4$ in the ground state (with the coordinate system as depicted in the top of Fig. 1) is\textsuperscript{23}

$$$(4b_{3u})^2(4b_{2g})^2(1b_{1g})^2(1a_u)^2(6a_u)^2(2b_{2u})^0(6b_{1u})^0 \times (2b_{3g})^0,$$$

where we also show the lowest unoccupied orbitals in the energetic order determined by von Niessen \textit{et al.}\textsuperscript{24} The absorption spectrum of N$_2$O$_4$ has been previously studied between 240 and 500 nm\textsuperscript{26} and between 185 and 390 nm.\textsuperscript{27} The spectrum of Bass \textit{et al.}\textsuperscript{27} shows a strong broad absorption, indicative of a dissociative transition, peaking between 185 and 190 nm and extending to 230 nm. CNDO/S electronic structure calculations of Mason\textsuperscript{23} suggest that the excited state reached is of $1^1B_{3u}$ symmetry [Mason’s $1^1B_{1u}$ label is for a nonstandard coordinate system, Fig. 1(b)] and is best described as a configuration-interaction mixture of two dominant electronic configurations, one in which an electron is promoted from the $\pi$ nonbonding oxygen molecular orbital to the $\pi^*$ orbital (a delocalized version of the transition resulting in the strong 190 nm absorption in nitromethane and nitric acid) and the other contributing configuration corresponding to promotion of an electron from a nonbonding in-plane molecular orbital localized on the O atoms to an orbital that has $\sigma^*$ character with respect to the N–N bond. Thus, in the most commonly used coordinate system, the $1^1B_{3u}$ excited state (Mason’s $1^1B_{1u}$) accessed in the 186 nm absorption band is an admixture of two electronic configurations in the Franck–Condon region,

$$$
(4b_{3u})^2(4b_{2g})^2(1b_{1g})^2(1a_u)^2(6a_u)^2(2b_{2u})^0(6b_{1u})^0 \times (2b_{3g})^0, \quad \text{the } \pi_{nb,O}(1b_{1g}) \rightarrow \pi^*(2b_{2g}) \text{ configuration, and}$$$

$$$(4b_{3u})^2(4b_{2g})^2(1b_{1g})^2(1a_u)^2(6a_u)^2(2b_{2u})^0 \times (6b_{1u})^1(2b_{3g})^0, \quad \text{the } n_O(4b_{2g}) \rightarrow \sigma^*(6b_{1u}) \text{ configuration, with the transition moment directed perpendicular to the N–N axis and in the molecular plane. [Kawasaki \textit{et al.}\textsuperscript{21} and Sisk \textit{et al.}\textsuperscript{22} mistakenly described Mason’s assignment as } \sigma(6a_u) \rightarrow \sigma^*(6b_{1u}) \text{ because they did not realize that Mason was using a different coordinate system than most other workers.]}
$$$
The photodissociation of N$_2$O$_4$ has been investigated previously in both the 186 nm absorption band\textsuperscript{21,22} and in the lower-energy absorption bands.\textsuperscript{28,29} There is evidence for a competition between N–N fission and N–O fission upon excitation at 280 and 265 nm in the lower absorption bands.\textsuperscript{25,28,29} We review only the photofragmentation results upon excitation in the 186 nm absorption band since they are most relevant to our emission spectroscopy studies, performed at excitation wavelengths near 200 nm.

Kawasaki \textit{et al.}\textsuperscript{21} observed the time-of-flight spectrum of photofragments from N$_2$O$_4$ dissociated at 193 and 248 nm. They detected the signal from neutral photofragments, which gave NO$_2^+$ upon electron bombardment ionization, but were not able to observe a signal at NO$^+$ or O$^+$. This limitation prevented them from probing a potential N$_2$O$_3$+O product channel. Slow photofragments were obscured by a laser-independent but time-dependent background, presumably from the pulsed beam source. Four direct dissociation channels were considered in these studies:

$$$
\begin{align*}
\text{(1)} & \quad \text{N}_2\text{O}_4 + h\nu \rightarrow \text{NO}_2 + \text{NO}_2, \\
\text{(2)} & \quad \text{N}_2\text{O}_4 \rightarrow \text{N}_2\text{O}_3 + \text{O}, \\
\text{(3)} & \quad \text{N}_2\text{O}_4 \rightarrow \text{NO}_3 + \text{NO}, \\
\text{(4)} & \quad \text{N}_2\text{O}_4 \rightarrow \text{NO}_2 + \text{NO} + \text{O}.
\end{align*}$$$

Based on the available energy after dissociation and the observed translational energy distributions of the photofragments, only (1) and (3) could result in the fastest observed signal at NO$_2^+$ at either 193 or 248 nm. Since no NO$^+$ was
detected, Kawasaki et al. \(^{21}\) concluded that (1) is the primary channel at both wavelengths. (This is a problematic argument because a vibrationally or electronically excited \(NO_2\) product is known\(^{30-32}\) to also produce \(NO^+\) daughter ions, and because energetic considerations only precluded the other channels for the fastest products. One cannot conclude that some of the slower signals at \(NO_2^+\) do not result from the other channels; the lack of data at any other ion precludes any further analysis.) Kawasaki et al. note that the maximum energy released to product translation at 193 nm is consistent with the formation of \(NO_2\) molecules in either the \(\tilde{A}^2B_1\) or \(\tilde{B}^2B_1\) states. However, based on fluorescence measurements they believe the \(\tilde{B}^2B_1\) is largely formed from the photolysis at 193 nm. Finally, the 193 nm photodissociation resulted in a parallel photofragment angular distribution, \(\beta = 1.2\). This is particularly surprising since the electronic structure calculation of Mason\(^{25}\) indicated the absorption at 193 nm is carried by a transition moment perpendicular to the \(N-N\) bond, similar to that for nitromethane\(^{33}\) and nitric acid,\(^{31,32}\) but Kawasaki’s paper misses the discrepancy because of the confusion over the symmetry label of the excited state in the different coordinate systems used by the two groups.

Sisk et al.\(^{22}\) later studied the fluorescence of \(NO_2^+\) from the photodissociation of \(N_2O_4\) at 193, 248, and 351 nm. By coanalyzing their photolysis-induced fluorescence data with the time-of-flight data of Kawasaki et al., they determine that photolysis at 193 nm leads to two \(NO_2^+\) fragments in the \(\tilde{A}^2B_2\) state. [They note that the assignment of the product channel is more uncertain than at 351 nm, where they assign the product channel to be \(NO_2(\tilde{A}^2A_1) + NO_2^+(\tilde{B}^2B_1)\), where the \(NO_2^+(\tilde{B}^2B_1)\) is vibrationally excited.] Sisk et al.\(^{22}\) mistakenly refer to the 186 nm electronic transition calculated by Mason as \(\sigma(6a_o) \rightarrow \sigma^*(6b_1\alpha)\), missing the change in the coordinate system described above, so their subsequent discussion of a possible electronic curve crossing in the dynamics is in error.

In this paper we report the dispersed emission from photodissociating \(N_2O_4\) at several wavelengths near 200 nm. The emission spectra evidence activity in the \(N-N\) stretch and in progressions in antisymmetric stretching modes in combination with torsion. The spectra presented here allow us to correct the literature value of the ground state torsional mode frequency and, when combined with other workers’ results, give a gas phase frequency for \(\nu_6\), the out-of-phase \(NO_2\) rocking mode. We also report complementary CIS \(ab\) \(initio\) electronic structure calculations of some of the relevant excited states of \(N_2O_4\). In the discussion we attempt to elucidate the origin of the early part of the dissociation dynamics revealed in the emission spectra and we speculate how it may influence the branching to different final product channels.

II. EXPERIMENT

The instrumentation used in these experiments has been discussed previously,\(^{34,35}\) so we give only a brief description here. The laser light used was generated either by anti-Stokes Raman shifting 266 nm light in \(H_2\) or by tripling the output of a Nd:YAG-pumped dye laser. The 532 nm output of a Quantel YG580-C series Nd:YAG laser operating at 20 Hz pumps a Lambda Physik FL3002E dye laser with an intra-cavity etalon to reduce the bandwidth of the dye laser to 0.05 cm\(^{-1}\). Rhodamine 640 dye was used to generate light between 609 and 615 nm. The output of the dye laser was frequency doubled in a KDP crystal (Lambda Physik FL 30), giving between 7 and 9 mJ per pulse. The 300 and 600 nm beams were frequency summed in a BBO crystal (Inrad 561-044). A Pellin–Broca prism then separated the colinear 200, 300, and 600 nm photons.

The 199.7 nm light was generated by Raman shifting the 266 nm output of an injection-seeded Nd:YAG laser (Continuum PowerLight 9020) in \(H_2\). A 50 cm focal length plano-convex lens was used to focus the \(\sim 200\) mJ/pulse 266 nm light into the Raman cell. This cell, a 70 cm long stainless steel tube fitted with 3/8 in. thick Suprasil windows at either end, is filled with \(H_2\) to pressure of 50 psig. The divergent output of the Raman cell contained colinear Stokes and anti-Stokes shifted light as well as the 266 nm fundamental; this light was recollimated with a 16 in. focal length plano-convex lens whose position was optimized for the 199.7 or 218 nm light. The light to be used in the experiments was separated from the other wavelengths using a Pellin–Broca prism and finally focused with a 16 in. focal length lens so the light would overlap well with the free jet expansion.

The \(NO_2/N_2O_4\) was introduced into the vacuum chamber as a free jet expansion from an IOTA ONE pulsed valve (General Valve Corp) with an open time of 200–260 \(\mu\)s for each gas pulse. The excitation light interacted with the free jet expansion about 1.0 cm from the pulsed nozzle orifice. Neat \(NO_2\) (Matheson 99.5\%) was used for most experiments, but some were performed with 10 % \(NO_2\) in \(He\) (Matheson) to confirm that the observed spectra were from \(N_2O_4\) and not higher-order clusters. The backing pressure of the gas was varied between 150 and 800 Torr to control the amount of \(NO_2\) in the expansion and provide further evidence against emission from this species.

Light scattered at 90° to the incident laser propagation direction was collected with a 4 inch focal length lens and focused with a 10 inch focal length lens onto the entrance slit of a spectrometer (Acton SpectraPro 275), which dispersed the light using a 2400 gr/mm holographic grating (Milton-Roy). The dispersed light was then imaged onto an optical multichannel analyzer, OMA. (EG&G PARC 1456B-990-HQ) equipped with a blue-enhanced intensifier and 990 active pixels. Spectral resolution is limited by the spectrometer length and grating and is about 25 cm\(^{-1}\), using a 2400 gr/mm grating. The linear dispersion in the spectra here were calibrated using the laser line and the known Hg line at 230.2065 nm.

III. THEORETICAL METHOD

\(Ab\) \(initio\) electronic structure calculations were performed using the GAUSSIAN 94\(^{36}\) program package to characterize the excited state accessed in the experiments and help understand the emission spectra. The vertical excited-state calculations were based on ground state equilibrium geometries obtained from gas phase electron diffraction studies.\(^8\) A configuration interaction with single excitation (CIS) cal-
calculations using a 6-311 + G(d,p) basis set generated the oscillator strengths, orbital symmetries, and vertical excitation energies presented here. Symmetry and bonding character of the orbitals contributing to the excitation were classified using the linear combinations of atomic orbitals output by the Gaussian program.

Potential energy curves depicted in the paper were generated by repeating the vertical excitation calculation at incremental bond separations or angles. At each geometry, the program computes the ground state energy at the MP2 level of theory.

IV. RESULTS

A. Eliminating the contribution of NO$_2$ and higher order clusters of N$_2$O$_4$

The absorption cross section of NO$_2$ is about two orders of magnitude smaller than that of N$_2$O$_4$ around 200 nm. Thus, we expect the contribution of NO$_2$ to our emission spectra to be much less than the contribution from N$_2$O$_4$. Furthermore, the features in the emission spectra collected in this wavelength region are very easily assigned to either individual N$_2$O$_4$ normal modes or combinations of them, while an assignment to the modes of NO$_2$ proved impossible. We checked for the contribution of higher-order (NO$_2$)$_n$ ($n \geq 3$) clusters in the observed emission spectra by minimizing the number of higher-order clusters in the expansion. Sisk et al. observed that higher-order clusters could be minimized by using 10% NO$_2$ seeded in He. Figure 2 presents the emission spectrum at 203 nm using 10% NO$_2$ in He, and Fig. 4 shows the emission spectrum at 203 nm using neat NO$_2$. The qualitative features of these two spectra are the same. Both spectra show a progression assigned as the N–N stretch and a series of combination bands involving the out-of-phase antisymmetric stretch and torsion assignments will be discussed in the following section. Thus, the identical features in the 203 nm spectrum taken using neat NO$_2$ are due to N$_2$O$_4$. Hence, all later spectra were collected using neat NO$_2$, which we found to give a better signal-to-noise ratio.

FIG. 2. Emission spectrum of N$_2$O$_4$ formed in a 10% NO$_2$ in He expansion with excitation at 203 nm. Peaks are labeled as the final vibrational eigenstates, assuming the molecule was in the lowest vibrational eigenstate before excitation (for hot bands the assignment corresponds to the change in vibrational quanta in the final state). Labels are 3: n vibrational quanta in the N–N stretch normal mode, $\nu_1$; 4: n vibrational quanta in the torsional normal mode, $\nu_4$; 5: n vibrational quanta in the out-of-phase antisymmetric stretch normal mode, $\nu_5$. Starred features are fluorescence from the NO $\gamma$ band (see the discussion in Sec. IV E). The features in this spectrum are due to N$_2$O$_4$ (see the discussion in Sec. IV A).

FIG. 3. Emission spectrum of N$_2$O$_4$ formed in a neat NO$_2$ expansion with excitation at 199.7 nm. Labels are the same as in Fig. 2.

FIG. 4. Emission spectrum of N$_2$O$_4$ formed in a neat NO$_2$ expansion with excitation at 203 nm. The top spectrum was taken with 600 Torr backing pressure. Labels are as in Fig. 2. The similarity of this spectrum to that in Fig. 2 indicates that the features are due to N$_2$O$_4$. The bottom spectrum was taken with 750 Torr backing pressure. The reduction in intensity of the $\nu_5$ + $\nu_4$ combination bands with highest torsional motion indicates these result from molecules with a thermal population in higher torsional levels of the ground electronic state (see the discussion in Sec. IV B).
B. Emission features at 199.7, 203, and 205 nm

The emission spectra of N$_2$O$_4$ collected with laser excitation at 199.7, 203, and 205 nm are presented in Figs. 3–5, respectively. The emission spectra of N$_2$O$_4$ all share several interesting features. All of the spectra show a progression with the first peak near 260 cm$^{-1}$ and the spacing between subsequent peaks of about 255 cm$^{-1}$. Since Dyer and Hendra assigned the frequency of $\nu_3$, the N–N stretch, as 254 cm$^{-1}$, this progression is easily assigned as a progression in $\nu_5$, the N–N stretch. The 199.7 nm spectrum shows a long progression in the N–N stretching motion, with resolved peaks extending to ten quanta in $\nu_3$. The $3_7$ (when referring to the change in the number of vibrational quanta in a given normal mode, we use this notation throughout, where $3_7$ refers to an additional seven vibrational quanta in $\nu_5$ after photon absorption and emission) peak comes at slightly larger shifts than the fundamental of $\nu_5$, the out-of-phase antisymmetric stretch, and is not labeled in the spectrum.

A second progression appears in these spectra, starting at about 1725 cm$^{-1}$. The vibrational frequency of $\nu_5$, the out-of-phase antisymmetric stretch, is 1712 cm$^{-1}$. The only other mode near 1725 cm$^{-1}$ is the in-phase antisymmetric stretch, $\nu_9$, which occurs around 1735 cm$^{-1}$ but it is disallowed by selection rules. Thus, the fundamental peak in this progression is assigned as $\nu_5$. We discuss how emission into odd quanta of $\nu_5$ may be vibronically allowed later in this section.

The next peaks in this progression are spaced by a frequency of about 135 cm$^{-1}$. This corresponds closely to our value for $2\nu_4$ (see the discussion in Sec. IV D). The next peak is thus assigned as $5_1+4_2$. The peak near 3570 cm$^{-1}$ is assigned as $5_2+4_2$. Assuming the torsional frequency increases with excitation of $\nu_3$ (which we observe in the case of $5_1+4_2$), then this value is about 15 cm$^{-1}$ lower than expected. The next peak is again about 135 cm$^{-1}$ away and is assigned as $5_2+4_3$. The final peaks in the spectrum appear at 5400 and 5530 cm$^{-1}$ and are assigned as $5_3+4_4$ and $5_3+4_6$, respectively.

Figure 4 presents the emission spectra taken at 203 nm under two different expansion conditions. The peaks are assigned similarly to those in the 199.7 nm. The spectra again show a progression in the N–N stretch, $\nu_3$. Again, out-of-phase antisymmetric stretch and the torsion are present in combination bands. In the top spectrum in Fig. 4, the combination bands appear as a series of “quartets.” We note that the spacing decreases between the peaks in the series $5_1$, $5_1+4_2$, $5_1+4_4$, and $5_1+4_6$. This is likely due to the anharmonicity of the oscillator though the resolution of the detector limits this analysis. We repeated the 203 nm spectrum using neat NO$_2$ at higher backing pressures around 750–800 Torr, shown in Fig. 4, bottom spectrum. The combination bands of $\nu_5$ and $\nu_4$ in this spectrum (Fig. 4 bottom) appeared as a series of “triplets” corresponding to the first three peaks from the “quartets” in Fig. 4 (top) spectrum. The final peak in the combination bands is evident, though much reduced in intensity. The increase in backing pressure should favor additional cooling of molecular rotation, and to a lesser extent, vibrations. The changes in the spectra under these different experimental conditions may result from a decrease in the contribution of hot bands to the spectrum taken at the higher backing pressure. If a low-energy motion such as $\nu_4$ is present in the molecule, then a significant vibrationally excited population exists at 298 K. Thus, if a molecule in the $4_1$ vibrational state is excited with a photon and shows emission intensity in the band labeled $5_2+4_6$, then the actual vibrational state of the molecule after emission is $5_2+4_7$. We explicitly indicate bands with a contribution from hot bands in our 203 nm spectrum with the notation $5_n+4_m/h\nu$, but we do not indicate these in the other figures in the paper.

It is interesting to consider how we can see emission into bands with odd quanta in $\nu_5$. To understand the origin of emission intensity into odd quanta in an antisymmetric mode, nominally an electric–dipole forbidden in emission spectroscopy, we consider the emission in a time-independent formalism in which the intensity is proportional to the square of $\alpha_f(\omega_I)$,

$$\alpha_f(\omega_I) = \sum_n \frac{\langle f|\mu_{cm}^*e_S^I|h\rangle\langle n|\mu_{ab}e_f|i\rangle}{E_f + \hbar \omega_I - E_n - i\hbar \Gamma}.$$  

(5)

The subscript $I$ stands for incident and $S$ stands for scattered, and $\Gamma$ is a lifetime factor. We consider only the second term, responsible for emission, making the assumption that all molecules emit from the same excited electronic state. The intermediate state, $|n\rangle$, and the final state, $|f\rangle$, can be expressed as a product of rotational, vibrational, and electronic states. Assuming that the rotational part can be factored out (neglecting Coriolis coupling) the intermediate and final states become

$$|n\rangle = |(ve)_n\rangle,$$

$$|f\rangle = |(ve)_f\rangle.$$  

(6)

(7)

Finally, we assume that the initial $1^1B_{3u} \rightarrow \bar{X}^1A_g$ excitation is from the $a_g$ ground vibrational level in the ground electronic state, so the operative transition moment $\mu_{ab}$ is $b_{3u}$ as in Fig. 1(a)] and the intermediate, $|n\rangle$, vibrational symmetry
is then \( a_g \). Then emission to a \( b_2g \) vibrational state (\( \nu_5 \)) of an \( A_g \) electronic state from an \( a_g \) vibrational level of the \( B_{3u} \) state requires a dipole moment to have the symmetry of the product \( b_2g \otimes A_g \otimes a_g \otimes B_{3u} = b_{1u} \) (note that we are assuming the electronic coordinate system [Fig. 1(a)] and use the vibrational symmetry of \( \nu_5 \) in this coordinate system). Thus, the term for emission becomes

\[
\langle b_{2g} A_g | b_{1u} | a_g B_{3u} \rangle.
\]

(8)

According to Table II, the ninth excited state has \( B_{1u} \) symmetry and a very large oscillator strength. This state seems a likely candidate for the intensity borrowing\(^{46} \) required for vibronically allowed emission into these antisymmetric vibrational modes.

Finally, we investigated the dependence of the emission intensity on the polarization of the 203 nm excitation laser. This technique has proven useful in the identification of emission features resulting from a state with a transition dipole oriented perpendicular to that for absorption.\(^{33,41} \) Using 600 Torr of neat NO\(_2\) (conditions known to give “quartets” in the antisymmetric stretch/torsion progression), we found that the second peak in each quartet (assigned as \( 5_a + 4_{2n} : n = 1,2,3 \)) was reduced in intensity when the incident laser light was polarized parallel to the plane defined by the detector and the direction of propagation of the laser beam. These peaks in the quartets must then result from two different transitions from the excited state, one with a transition dipole oriented perpendicular to that for absorption and one oriented the same as for absorption. However, we have been unable to find another assignment of these peaks. Emission by a vibronic mechanism requires the polarization of the emitted photon to be directed along the N–N bond [since \( b_{1u} \) transforms as the Z axis in the electronic coordinate system; Fig. 1(a)]. Thus, the intensity of the combination bands should depend upon the polarization studied. However, if the emission occurs slowly (on the time scale of molecular rotations) then the intensity dependence on polarization will be reduced.

Figure 5 shows the emission spectrum of N\(_2\)O\(_4\) excited at 205 nm. Again, we observe a feature in this spectrum at ca. 255 cm\(^{-1}\) assigned as 3\(_1\). A progression in \( \nu_3 \), the N–N stretch, appears with a spacing of 255 cm\(^{-1}\) and extends to four quanta. A progression in combination bands of the out-of-phase antisymmetric stretch with even quanta of torsion also appears. The combination bands appear as a series of “doubles” spaced by about 140 cm\(^{-1}\) or 4\(_2\) (the peaks are assigned as discussed and not discussed in detail here). Finally, a relatively weak line appears at 128 cm\(^{-1}\), which we again assign as the torsion.

### C. Gas phase assignments for the torsional frequency, \( \nu_4 \), and out-of-phase NO\(_2\) rock, \( \nu_6 \)

The first feature in the 203 nm spectrum is shifted from the laser line by 128 cm\(^{-1}\). The only vibration with a frequency under 250 cm\(^{-1}\) is the torsion,\(^{38} \) and while a single quantum in the torsional mode is symmetry disallowed for both Raman and IR spectroscopy, even quanta of any motion are symmetry allowed. The only other possibility is that this peak is due to an impurity with a vibrational frequency near 64 cm\(^{-1}\), in addition to a mode around 1725 cm\(^{-1}\) (since we observe a mode near 130 cm\(^{-1}\) coupled with a motion near 1700 cm\(^{-1}\)). The molecule O\(_2\)NNO has a torsional frequency at 63 cm\(^{-1}\) but does not have a mode around 1725 cm\(^{-1}.\)\(^{38} \) The antisymmetric NO dimer, ONON, has vibrational frequencies of 116 and 1690 cm\(^{-1}.\)\(^{42} \) However, this molecule was observed in the presence of strong Lewis bases at 77 K and is unlikely to occur in our free jet. Thus, we assign this feature as 4\(_2\). This is the first observation of the torsional motion in N\(_2\)O\(_4\) not in combination with any other band; the previous assignment of the ground state torsional frequency was obtained from a combination band with \( \nu_6.\)\(^{43,44} \) Both groups observed combination bands assigned as \( (\nu_6 + \nu_4) + n' \nu_4 - n'' \nu_4 \) (\( \nu_6 \) is the out-of-phase NO\(_2\) rock, \( \nu_4 \) is the torsional frequency with the \( \nu_6 \) vibration singly excited, and \( \nu_4 \) refers to the torsional frequency with \( \nu_6 \) in the ground vibrational state). The vibrational frequencies were then fit to potentials modeling the torsion with \( \nu_6 \) in its ground and first excited state. Both groups assumed the value of \( \nu_6 \) to be 480 cm\(^{-1}\) (a value taken from a combination of liquid and vapor phase data).\(^{43,44} \) However, with our more direct observation of \( \nu_4 \), the value of the torsional frequency should be revised to 64 cm\(^{-1}\). Using our value of the torsional frequency and the frequencies of the first two peaks in the work of Bibart and Ewing,\(^{43} \) we can derive a value for \( \nu_6 \). The difference between the value for \( \nu_6 + \nu_4 = 554.3 \) cm\(^{-1}\) and \( (\nu_6 + \nu_4) + \nu_4' - \nu_4'' = 547.7 \) cm\(^{-1}\) gives \( \nu_4' - \nu_4'' = -6.6 \) cm\(^{-1}\). Combining our value for the ground state torsional frequency with the difference \( \nu_4' - \nu_4'' \) gives a value for the torsional frequency with \( \nu_6 \) singly excited of about 57 cm\(^{-1}\). Combining this result with \( \nu_6 + \nu_4 = 554.3 \) cm\(^{-1}\) gives a gas phase value of \( \nu_6 \) as 497 cm\(^{-1}\), in close agreement with the value obtained using Ne matrices.\(^{43} \)

### D. Assignment of NO fluorescence

The spectra taken at 199.7, 203, and 205 nm all exhibit two broad peaks that we attribute to NO (\( \tilde{A} \)) fluorescence. The wave number, \( \tilde{\nu}_{\text{abs}} \), of the excitation energy and position of the maximum, \( \tilde{\nu}_{\text{abs}} - \tilde{\nu}_{\text{emit}} \), for these peaks in the spectra are given in Table I. Table I also presents the \( \tilde{\nu}_{11}(0 - 0) \) and \( (1 - 0) \) band head positions for fluorescence of NO from the \( \tilde{\gamma} \) band, \( (\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi)\).\(^{46} \) The energy of the maximum for the two broad features corresponds quite well with the energy of the band heads. Thus, we assign the feature around 44 230 cm\(^{-1}\) in these spectra to the \( (0 - 0) \) transition of the \( \gamma \) band of NO and the feature around 46 600 cm\(^{-1}\) to the

<table>
<thead>
<tr>
<th>( \nu' - \nu'' )</th>
<th>Literature NO band heads(^a)</th>
<th>( \tilde{\nu}_{\text{abs}} ) (cm(^{-1}))</th>
<th>( \tilde{\nu}<em>{\text{abs}} - \tilde{\nu}</em>{\text{emit}} ) (cm(^{-1}))</th>
<th>Emitted photon energy(^b) ( \tilde{\nu}_{\text{emit}} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0</td>
<td>44 197.48</td>
<td>50 075</td>
<td>5835</td>
<td>44 240</td>
</tr>
<tr>
<td>1-0</td>
<td>46 539.36</td>
<td>50 075</td>
<td>3430</td>
<td>46 645</td>
</tr>
<tr>
<td>1-0</td>
<td>46 539.36</td>
<td>49 247</td>
<td>2665</td>
<td>46 582</td>
</tr>
</tbody>
</table>

\(^a\)Values are for the \( \tilde{Q} \) state from J. Danielak, U. Domin, R. Kepa, M. Rytel, and M. Zachwieja, J. Mol. Spectrosc. 181, 394 (1997).

\(^b\)Determined from our spectra.
(1 − 0) transition of the γ band of NO. Though the peak positions are in fair agreement with the Q_{11} branch of each fluorescence band, our resolution is too low to make a definitive assignment.

The A state of NO from which we see fluorescence may result from secondary photodissociation of the nascent NO_2 product if it absorbs another photon, or by unimolecular dissociation of the NO_2 photofragment to give NO(\bar{X}) + O, with the NO(\bar{X}) then fluorescing after absorption of a second photon. We judge the former to be more likely since the energy of the NO(\bar{X}) fluorescence is roughly independent of excitation energy.

### E. Computational results

Table II gives the vertical excitation energy and symmetries for the excited states calculated using the CIS methods. Each state in this calculation, which includes configuration interaction, can contain contributions from one or more electronic configurations of one-electron excitations from the reference configuration (ground state). The CIS expansion for the bright state accessed in the transition near 200 nm (1^1B_{2u}) is shown in Table II and the relevant orbitals are depicted in Fig. 6, as visualized using the program SPARTAN.\(^47\) Figures 6(a) and 6(c) are the in- and out-of-phase linear combinations of the same orbitals. Figure 6(a) corresponds to the dominant π\pi^* configuration in the excitation and contributes a bonding character to the N−N bond. Figure 6(b) shows the orbitals contributing to the nσ^*_{N-N} electronic character of the excited state. This configuration contributes antibonding character to the N−N bond. The symmetry labels are based on the coordinate convention in Fig. 1(a). When the results of Mason\(^23\) are translated to this coordinate convention, they are in qualitative agreement with the orbitals presented here. The calculated vertical energy of the 1^1B_{2u} \rightarrow 1^1A_{g} excitation is greater than 6.67 eV (the 186 nm peak in the absorption spectrum); however, CIS can overestimate the excitation energy by as much as 1−2 eV.\(^48\)

In both nitric acid and nitromethane, a broad absorption is present in the neighborhood of 200 nm. This transition has been previously assigned as π_{n b}π^*, localized on the NO_2 moiety.\(^2\) The 186 nm transition in N_2O_4 is similar in character, although the excitation is delocalized onto both NO_2 groups. However, in N_2O_4 at the ground state equilibrium geometry, the transition shows a considerable nσ^* character. When the N−N bond length is contracted to 1.3 Å, nearer the equilibrium bond lengths for nitromethane and nitric acid, the character of the 1^1B_{3u} state is π_{n b}π^*, analogous to both nitric acid and nitromethane.

Figure 7 shows a cut along the 1^1B_{3u} excited state (the state accessed in the 186 nm band) versus N−N bond length. Three higher B_{3u} states, the lowest of which forms an avoided crossing with the 1^1B_{3u} state, are also depicted in Fig. 7. The avoided crossing at the equilibrium geometry results from a configuration interaction of three one-electron excitations. The dominant one-electron excitations, π_{n b}Oπ^*_{NO_2}, and nσ^*, are shown in Figs. 6(a) and 6(b). The

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**TABLE II. Vertical excitation energies for N_2O_4.**

<table>
<thead>
<tr>
<th>Excited state</th>
<th>Electronic character</th>
<th>Excitation energy (eV)</th>
<th>Oscillator strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>1^1B_{2u}</td>
<td></td>
<td>4.6</td>
<td>0.0</td>
</tr>
<tr>
<td>1^1A_{u}</td>
<td></td>
<td>5.3</td>
<td>0.0</td>
</tr>
<tr>
<td>1^1B_{1g}</td>
<td></td>
<td>5.7</td>
<td>0.0</td>
</tr>
<tr>
<td>1^1B_{3g}</td>
<td></td>
<td>6.2</td>
<td>0.0</td>
</tr>
<tr>
<td>1^1B_{3u}</td>
<td>π_{n b,o}π^<em>_{NO_2}/nσ^</em>_{N-N}</td>
<td>6.9</td>
<td>0.1474</td>
</tr>
<tr>
<td>1^3B_{2g}</td>
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<td>7.2</td>
<td>0.0</td>
</tr>
<tr>
<td>2^1B_{1g}</td>
<td></td>
<td>7.3</td>
<td>0.0</td>
</tr>
<tr>
<td>2^1A_{u}</td>
<td></td>
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<td>0.0</td>
</tr>
<tr>
<td>1^1B_{1s}</td>
<td>σσ^*</td>
<td>8.1</td>
<td>1.0257</td>
</tr>
<tr>
<td>2^1B_{3u}</td>
<td></td>
<td>9.3</td>
<td>0.5149</td>
</tr>
</tbody>
</table>

---

**FIG. 6.** Orbitals involved in the excitation at 200 nm. (a) Dominant π_{n b,o}π^*_{NO_2} electronic configuration leading to an additional N−N bonding character. (b) nσ^* electronic configuration leading to an antibonding N−N character. (c) Minor π_{n b}π^*_{NO_2} electronic configuration leading to an antibonding N−N character.

**FIG. 7.** Excited state potential energy surface for the 1^1B_{3u} excited states of N_2O_4 vs N−N bond length. The 1^1B_{3u} is the surface accessed in the transition near 200 nm. The vertical arrow is drawn at the ground state equilibrium geometry to show the Franck–Condon region of the excited state. Note: CIS energies typically overestimate the excitation by 1–2 eV.
third configuration has a much smaller coefficient in the expansion and is depicted in Fig. 6. Figure 8 shows the adiabatic correlation diagram for N₂O₄ in D₂h symmetry going to two NO₂ molecules. N₂O₄ D₂h symmetry labels are for N₂O₄ in the XZ plane with the Z axis along the N–N bond [Fig. 1(a)], the “standard” N₂O₄ coordinates, while the NO₂ product symmetry labels are for the fragments in the YZ plane [Fig. 1(c)]. The solid line indicates the correlation for the excited state accessed at 200 nm. The relative energies of the NO₂ states are taken using the vertical excitation energies from MRSDCI calculations from Ref. 49 using the ground state NO₂ geometry \( \angle \text{ONO}=134^\circ \) and N–O = 1.193 Å.

V. DISCUSSION

Emission spectra of N₂O₄ in the region around 200 nm all show a strong progression in \( n_3 \), the N–N bond stretch. The potential energy surface for the \( 1^1B_{3u} \) state accessed in this transition is repulsive along the N–N bond coordinate, as shown in Fig. 7. The CIS calculations indicate that as the N–N bond stretches, only the \( 1^1B_{3u} \) excited state has appreciable oscillator strength if one restricts the molecule to D₂h symmetry. Thus, the only dynamics yielding a pure progression in \( n_3 \) is simple: when the molecule is initially prepared on the \( 1^1B_{3u} \) adiabat, it feels the repulsive potential and dissociates, giving two NO₂ molecules. A small fraction of the molecules emit light and return to the ground state instead of dissociating, yielding the observed progression.

Previous workers 21,22 have observed NO₂ photoproduction s tentatively assigned as either the \( 1^1B_2 \) or the \( 1^2B_1 \) state. As previously discussed, CIS calculations 36 performed at the experimental ground state geometry show the excited state accessed in this transition has \( B_{1u} \) symmetry using the standard coordinate convention [Fig. 1(a)]. This transition has two dominant contributions: one from an \( n\sigma^* \) electronic configuration and the other from a \( \pi\pi^* \) electronic configuration, consistent with the calculations of Mason. 23 The \( 1^1B_{3u} \) potential energy surface correlates adiabatically in D₂h symmetry to NO₂(\( \tilde{X}^2A_1 \)) + NO₂(\( 1^2B_2 \)) but, as in nitric acid 32 photolysis, the dominant product channel may not be the
adiabatic channel. We are presently pursuing photofragment velocity and angular distribution experiments to determine the dissociation products.

The spectra also evidence strong combination bands involving torsional and antisymmetric stretching. In the results described in Sec. IV B, we noted that emission to bands with odd quanta in \( \nu_5 \) may be vibronically allowed by coupling to a higher electronic state with \( B_{1u} \) symmetry. We noted a likely candidate upon examination of the vertical excitation energies presented in Table II. The \( 1^1B_{1u} \) state, of \( \sigma\sigma^* \) electronic character, has a very strong oscillator strength, making it a likely candidate for this vibronic coupling. Furthermore, both the \( 1^1B_{3u} \) and the \( 1^1B_{1u} \) states reduce to \( B_u \) symmetry as the molecular framework is displaced along the \( \nu_5 \) mode, so the lower state may include a small admixture of \( \sigma\sigma^* \) character at these geometries. This vibronic coupling with the \( 1^1B_{1u} \) state makes the \( \nu_5 \) mode active in the emission spectrum. To understand why our emission spectra show \( \nu_5 \) in combination with the torsional mode, \( \nu_3 \), we calculated the excited state potential energy surfaces along the torsional angle. The \( 1^1B_{1u} \) state we believe to be involved in the vibronic coupling mechanism has a minimum in the potential energy surface at \( \phi = 90^\circ \) (see Fig. 10). Thus, at nonsymmetric geometries the coupling of the \( 1^1B_{1u} \) state with the \( 1^1B_{3u} \) state gives the molecules on the lower state some force along the torsional coordinate, leading to emission into \( \nu_3 \) in combination with \( \nu_5 \).

Nitric acid and nitromethane each have an absorption band around 200 nm with \( \pi_{nb,O} \pi^*_{NO_2} \) electronic character localized on the NO$_2$ group. Both nitric acid and nitromethane dissociate into R+NO$_2$(R=OH,CH$_3$) through two channels; the first forms NO$_2$(\( 1^2B_2 \)) and the second channel has not been definitively assigned.\(^{32,33}\) The adiabatic surface accessed in both nitric acid and nitromethane changes electronic character from \( \pi_{nb,O} \pi^*_{NO_2} \) to \( n\sigma^* \) at an avoided crossing beyond the Franck–Condon region.\(^{30,32,33}\) As in NO$_2$, confined to \( D_{zh} \) symmetry, the adiabatic surface accessed by nitric acid and nitromethane near 200 nm leads to NO$_2$(\( 1^2B_2 \)). The Franck–Condon region of NO$_2$ has mixed \( \pi_{nb,O} \pi^*_{NO_2} \) to \( n\sigma^* \) electronic character on the bright state. Thus, the emission spectra for NO$_2$ are sensitive to the dynamics at this avoided crossing. Previous studies on the emission spectra of nitromethane obtained at 200 and 218 nm excitation show strong progressions in the NO$_2$ symmetric stretch and much weaker combination bands of the NO$_2$ symmetric stretch and C–N stretch.\(^{33,35}\) The emission spectra collected in solution-phase experiments showed weak features assigned as NO$_2$ antisymmetric stretch and features due to NO$_2$ bending motion.\(^{52}\) The prominence of the progression in the NO$_2$ symmetric stretch is not surprising because the initial transition is to an electronic state nominally \( \pi_{nb,O} \pi_{NO_2} \) in character.\(^{41,52}\) Since the final products of the photodissociation are CH$_3$+NO$_2$, the excited molecule must eventually reach an electronic configuration repulsive along the C–N bond coordinate. The weak combination bands involving C–N stretch and NO$_2$ symmetric stretch are possible evidence for this change in electronic character, but in N$_2$O$_4$ the pure N–N stretch progression is much stronger, reflecting that N$_2$O$_4$ has considerable \( n\sigma^* \) character in the Franck–Condon region.

VI. CONCLUSIONS

We reassign the torsional frequency as 64 cm$^{-1}$ and, using the data of previous workers,\(^{33,44}\) find a value for \( \nu_6 \) of 497 cm$^{-1}$, consistent with the value found in Ne matrices.\(^{45}\) We observe combination bands involving \( \nu_4 \) and \( \nu_5 \). The fundamental and second overtone appear to arise from vibronic coupling with a nearby state of \( 1^1B_{1u} \) electronic character.

We have investigated the emission spectroscopy of N$_2$O$_4$ at three wavelengths near 200 nm, where the excitation is to the \( 1^1B_{3u} \) surface. Computational results indicate this surface is repulsive along the N–N bond coordinate. Our emission spectra taken near 200 nm all show that the early time dynamics involve a change in the length of the N–N bond, leading to emission into higher overtones of \( \nu_5 \), the N–N stretch. The adiabatic excited states accessed near 200 nm in N$_2$O$_4$ nitric acid, and nitromethane all change from \( \pi_{nb,O} \pi^*_{NO_2} \) at short O$_2$N–R (R=NO$_2$,OH,CH$_3$) bond lengths to \( n\sigma^* \) at extended bond lengths. The exceptionally long N–N bond length of N$_2$O$_4$ makes the dissociation particularly sensitive to the dynamics near the avoided crossing on the potential energy surface. Thus, the emission spectra of this molecule show strong activity in the N–N stretch normal mode, whereas the emission spectrum of nitromethane near 200 nm shows only weak features involving the C–N stretch. The emission spectrum also shows combination bands in \( \nu_4 \) and \( \nu_5 \), tentatively assigned to vibronic coupling with the \( 1^1B_{1u} \) excited state.

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\(^{10}\) E. A. Coulson and J. Duschies, Bull. Cl. Sci., Acad. R. Belg. 43, 522 (1957).