# The kinetic and internal energy of NO from the photodissociation of nitrobenzene

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Laser induced fluorescence probing of the nitric oxide fragment determines the distribution of rotational and vibrational energies of NO produced in the 226 and 280 nm photolysis of nitrobenzene. Combining these results with kinetic energy measurements using vacuum ultraviolet photoionization to detect the fragment gives a detailed view of the energy release in the photolysis. Boltzmann distributions describe the rotational state populations at both photolysis wavelengths. The rotational temperature of NO from the 226 nm photolysis is  $(3700\pm350)$  K, corresponding to an average rotational energy of  $(0.32\pm0.03)$  eV, and that of NO from the 280 nm photolysis is  $(2400\pm200)$  K, corresponding to an average rotational energy of  $(0.20\pm0.03)$  eV. We observe no vibrationally excited NO and place an upper limit of 10% on the fraction of nitric oxide produced in any one vibrationally excited state. Two different limiting models, impulsive energy release and statistical energy redistribution, both correctly predict much more rotational than vibrational excitation, but neither completely describes the observed internal and kinetic energies. The impulsive model finds more NO rotational and translational energy, but much less phenoxy fragment internal energy than we observe. The statistical model does better for the NO rotation and phenoxy fragment internal energy, but underestimates the translational energy substantially. A combination of these two types of behavior provides a physical picture that qualitatively explains our observations. It is likely that statistical energy redistribution occurs during the approach to the transition state for isomerization of nitrobenzene to phenyl nitrite and impulsive energy release dominates during the subsequent rupture of the CO-NO bond.

## I. INTRODUCTION

Several different products are energetically accessible in the photodissociation of nitrobenzene  $(C_6H_5NO_2)$ , a prototypical molecule for combustion and decomposition of energetic materials. In an early study using a discharge lamp for photolysis, Schuler and Woeldike observed emission from nitrogen dioxide  $(NO_2)$  (Ref. 1) with phenyl radical  $(C_6H_5)$  being the likely coproduct. Hastings and Matsen<sup>2</sup> found solid nitrosobenzene ( $C_6H_5NO$ ) after irradiation of a nitrobenzene sample. Later Porter and Ward<sup>3</sup> reported detection of cyclopentadiene  $(C_5H_5)$  in the flash photolysis of nitrobenzene, speculating about elimination of a CNO<sub>2</sub> moiety from its ring. Very recently, Marshall et al.<sup>4</sup> performed a study on nitrobenzene using resonance enhanced multiphoton ionization (REMPI) to detect a variety of products, essentially a number of  $C_n H_m$  (n = 1-6, m=0-5) fragments as well as NO. They suggest that the initial fragmentation process for the parent nitrobenzene forms phenyl radical and nitrogen dioxide. In a recent study, we used vacuum ultraviolet (VUV) photoionization mass spectrometry to observe three dissociation pathways in the photolysis of nitrobenzene at wavelengths between 220 and 280 nm,<sup>5</sup>

 $C_{6}H_{5}NO_{2} + h\nu \rightarrow C_{6}H_{5} + NO_{2},$   $C_{6}H_{5}NO_{2} + h\nu \rightarrow C_{6}H_{5}NO + O,$  $C_{6}H_{5}NO_{2} + h\nu \rightarrow C_{6}H_{5}O + NO,$ 

where the species in bold-faced type are the ones that we have observed as the corresponding ion. (Production of NO by a triple dissociation  $C_6H_5NO_2 \rightarrow C_5H_5 + CO + NO$  is also energetically possible, and we cannot distinguish the two experimentally. Because we expect a significant barrier to removing the carbon atom from the ring in the neutral decomposition, we treat the production of NO as the process  $C_6H_5NO_2 \rightarrow C_6H_5O + NO$ .)

The approach we used identifies the products and provides an estimate of the energy released into translation from the shape of the arrival time distribution of the ions of a particular mass in a time-of-flight mass spectrometer. The relative amounts of NO2 and NO produced depend on the photolysis wavelength, varying from a 30% excess of NO<sub>2</sub> at 280 nm to a sixfold excess at 222 nm.<sup>5</sup> Our measurements suggest that many nitrobenzene molecules first isomerize to phenyl nitrite C<sub>6</sub>H<sub>5</sub>ONO and subsequently decompose by breaking the C-ONO bond to release NO<sub>2</sub>, or the O-NO bond to produce NO, or the ON-O bond to form O. We can obtain a more detailed picture of the channel producing NO by determining the internal energy of the NO fragment using laser induced fluorescence (LIF).<sup>6-8</sup> Here we describe experiments that directly measure the rotational and vibrational state distributions of

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NO from the photolysis of nitrobenzene at 226 and 280 nm. Photolysis at these two wavelengths to produce phenoxy radical ( $C_6H_5O$ ) and NO provides energies of  $E_{avl}$  = 4.7 and 3.7 eV, respectively, for distribution into relative translation and internal degrees of freedom of the products. Our measurements of the internal energy content of the NO fragment in combination with our previous data on kinetic energy release<sup>5</sup> paint a detailed picture of energy disposal in the photodissociation of nitrobenzene to produce NO.

## **II. EXPERIMENTAL APPROACH**

We use a modified version of the source chamber of our molecular beam VUV-photoionization apparatus<sup>9</sup> for photolysis of nitrobenzene and detection of NO by LIF using the  $A^{2}\Sigma^{+} \leftarrow X^{2}\Pi$  transition. A pulsed expansion of nitrobenzene seeded in helium enters the interaction region located directly below fluorescence collection optics, and ultraviolet (UV) photolysis light from a pulsed laser intersects the expansion at a right angle. For the 226 nm photolysis experiments, the photolysis laser also serves as the tunable probe laser, providing a pulse energy of about 100  $\mu$ J. In the 280 nm photolysis experiments, a separate photolysis beam propagates in the opposite direction to the tunable 226 nm probe beam. A pulsed Nd:YAG laser/dyelaser system (Quanta-Ray DCR-2A/PDL-2/WEX-1) generates the 226 nm light for both photolysis and LIF detection. For the 280 nm photolysis studies, frequency doubled light from a second Nd:YAG/dye laser with a pulse energy of 6 mJ photolyzes nitrobenzene, and the 226 nm light probes the rotational state population of the NO fragment after a 300 ns delay. Because the 226 nm probe laser light can also photolyze nitrobenzene, we reduce its energy to about 50  $\mu$ J, so that the probe laser alone produces no fluorescence, ensuring that all of the signal comes from NO formed in the 280 nm photolysis. This reduction in the 226 nm pulse energy decreases the signal to noise ratio substantially. A 2:1 reducing telescope images the fluorescence onto a photomultiplier tube (EMI 9635 QB), and a boxcar integrator (Stanford Research Systems Gated Integrator, model SR250) captures the signal and transfers it to a laboratory computer.

The pulsed expansion is very similar to the one used to form the molecular beam in our earlier studies.<sup>5</sup> A heated sample holder and heated pulsed nozzle generate the expansion. Heating the sample holder to a temperature of 100 °C and using a backing pressure of 295 Torr of helium forms a pulsed expansion containing 6.3% nitrobenzene. The pulsed nozzle is 2.0 cm from the interaction region, corresponding to approximately 20 nozzle diameters, which is sufficient for extensive cooling of the nitrobenzene in the expansion. Analysis of the LIF excitation spectrum of nitric oxide seeded in helium under these conditions shows that the center of the pulsed expansion has a rotational temperature of approximately 15 K.<sup>10</sup>



FIG. 1. Laser induced excitation spectra of NO in (a) a room temperature sample; (b) from the 280 nm photolysis of  $C_6H_5NO_2$ ; and (c) from the 226 nm photolysis of  $C_6H_5NO_2$ . The expanded portion shows the measurement along with a simulation for Boltzmann distribution of rotational states at a temperature of 3700 K.

#### **III. RESULTS**

We extract the rotational state populations from the  $A^{2}\Sigma^{+}(v'=0)$ excitation spectrum of the LIF  $-X^2\Pi(v''=0)$  transition in NO. Figure 1 shows spectra of NO in a room temperature sample [Fig. 1(a)], from the 280 nm photolysis of  $C_6H_5NO_2$  [Fig. 1(b)], and from the 226 nm photolysis of  $C_6H_5NO_2$  [Fig. 1(c)]. The figure shows an expanded portion of the spectrum for the 226 nm photolysis products along with a simulation<sup>11,12</sup> for a rotational distribution at 3700 K. As the expanded spectrum illustrates, we can observe the relative intensities  $I(J' \leftarrow J'')$ of many P, Q, and R transitions directly, and we extract relative populations N(J'') from them using the Hönl-London factor  $S(J' \leftarrow J'')$  (Ref. 13) that relates the two  $I(J' \leftarrow J'') = S(J' \leftarrow J'')N(J'')$ . If the rotational state populations follow a Boltzmann distribution, a semilog plot of the relative state populations N(J'') vs J''(J''+1) has a slope of -B''/kT, where B'' is the rotational constant and T is the temperature. Figure 2 shows representative plots for different rotational branches in the spectrum of NO from the photolysis. For the 226 nm photolysis [Fig. 2(a)], several branches give linear plots with a range of rotational temperatures from 3300 to 4100 K and an average rotational temperature of  $(3700 \pm 350)$  K, corresponding to a rotational energy of  $(0.32 \pm 0.03)$  eV for NO formed in the 226 nm photolysis. The simulation in Fig. 1 shows that a Boltzmann distribution with this temperature reproduces the spectrum well. A similar analysis for the 280 nm photolysis [Fig. 2(b)] gives temperatures in the range of 1900– 2700 K for different branches and an average temperature of  $(2400 \pm 300)$  K, corresponding to a rotational energy of  $(0.20 \pm 0.03)$  eV.

Photolysis of nitrobenzene at either 226 or 280 nm produces fewer than 8% of the NO fragments in any one



FIG. 2. Semilog plots of the ratio of the relative population to the Hönl-London factor vs J(J+1) for (a) 226 nm photolysis of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> and (b) 280 nm photolysis. These Boltzmann plots have a slope of -B/kT from which we extract an effective rotational temperature. The lines are for different rotational branches in the excitation spectra and give average rotational temperatures of  $(3700 \pm 350)$  and  $(2400 \pm 300)$  K for the 226 and 280 nm photolyses, respectively.

vibrationally excited state. We observe no LIF excitation signal on  $\Delta v = 0$  transitions from either NO(v'' = 1) or NO(v''=2), even though the signal to noise ratio of the  $0 \leftarrow 0$  transition is about 20:1. Since the Franck-Condon factors for  $\Delta v = 0$  transitions from v'' = 1 and 2 are about 60% and 45%, respectively, of that for v''=0, <sup>14,15</sup> each of these states must contain less than 8% of the population. We also observe only NO(v''=0) products from the 280 nm photolysis, where the lower signal to noise ratio of 10:1 due to the lower probe pulse intensity places a limit of 15% on the fraction of the NO molecules that could be in v'' = 1or 2. These are very conservative limits on the fraction of molecules that are vibrationally excited and, in any event, these amounts of vibrational excitation correspond to only a small fraction of the available energy. For example, having 10% of the NO molecules in v=1 corresponds to a vibrational energy of only  $E_n(NO) = 190 \text{ cm}^{-1} = 0.024 \text{ eV}$  $(\omega_e = 1904.405 \text{ cm}^{-1})$  (Ref. 12) compared to the available energy of 3.7-4.7 eV.

#### IV. MODELS OF ENERGY DISPOSAL

Our previous measurements of the recoil energy of the fragments along with the determination of the rotational and vibrational energy content described here allow us to infer the internal energy of the undetected phenoxy fragment. Table I summarizes the energy in relative translation, rotation, and vibration of NO, and internal excitation of the phenoxy radical that we obtain by combining our

TABLE I. Observed and calculated energies (in electron volts) for the impulsive and the statistical models of energy release.

| · ·                   | Observed $\lambda = 226 \text{ nm}$ | Impulsive<br>model<br>E <sub>avl</sub> =4.7 eV | Statistical model |
|-----------------------|-------------------------------------|--|-------------------|
| $E_r(NO)$             | $0.32 \pm 0.03$                     | 1.2  | 0.20              |
| $E_{\nu}(NO)$         | < 0.1                               | 0.14   | 0.10              |
| $E_t$                 | $1.1 \pm 0.2$                       | 1.6  | 0.30              |
| $E_{\rm int}(\Phi O)$ | $3.3 \pm 0.2$                       | 1.8  | 4.1               |
|                       | $\lambda = 280 \text{ nm}$          | $E_{\rm avl}$ =3.7 eV                          | 1                 |
| $E_r(NO)$             | $0.20 \pm 0.03$                     | 0.92   | 0.16              |
| $E_{v}(NO)$           | < 0.1                               | 0.11   | 0.07              |
| E <sub>t</sub>        | $0.56 \pm 0.12$                     | 1.2  | 0.25              |
| $E_{\rm int}(\Phi O)$ | $2.9 \pm 0.2$                       | 1.5  | 3.2               |

previous recoil energy measurements with our internal energy measurements for NO. For the 226 nm photolysis  $(E_{avl}=4.7 \text{ eV})$ , we find  $E_v < 0.1 \text{ eV}$  in vibration,  $E_r=0.32$ eV in rotation, and  $E_t=1.1 \text{ eV}$  in relative translation,<sup>5</sup> leaving 3.3 eV for internal excitation of the phenoxy fragment. For the 280 nm photolysis  $(E_{avl}=3.7 \text{ eV})$ , we also find  $E_v < 0.1 \text{ eV}$ ,  $E_r=0.20 \text{ eV}$ , and  $E_t=0.56 \text{ eV}$ ,<sup>5</sup> leaving 2.9 eV in the phenoxy fragment. These results allow us to compare the observed energy disposal in the NO producing channel of nitrobenzene with the predictions of two limiting cases, impulsive or statistical energy release. In applying both of these models, we assume that nitrobenzene first isomerizes to phenyl nitrite and subsequently decomposes into a NO molecule and a phenoxy radical.<sup>5</sup>

## A. Impulsive model

We use the soft radical model of Tuck<sup>16</sup> to calculate the impulsive energy release in nitrobenzene. In this model, excitation of a molecule creates a repulsive potential between two atoms  $\gamma$  and  $\delta$ , breaking the bond between them and releasing the available energy into relative translation of those two atoms. Collisions of the recoiling atoms with the other atoms in the fragment to which they are bound convert the initial translational energy of the atoms into internal energy and relative translation of the fragments. Applying conservation of momentum to each of the fragments gives their relative kinetic energy as

$$E_t = \frac{\mu_{\gamma\delta}}{\mu_{\rm frag}} E_{\rm avl}, \qquad (1)$$

where  $\mu_{\text{frag}}$  is the reduced mass of the fragment pair and  $\mu_{\gamma\delta}$  is the reduced mass of atoms  $\gamma$  and  $\delta$ . Table I collects the predictions of this impulsive model for both the 226 and 280 nm photolysis of nitrobenzene to produce phenoxy and NO. The model predicts that 33% of the available energy appears as relative kinetic energy of the products. For the 226 nm photolysis, the prediction of 1.6 eV for the total kinetic energy release is reasonably close to the observed total kinetic energy of  $(1.1\pm0.2)$  eV at this photolysis wavelength.<sup>10</sup> However, the prediction of 1.2 eV of total kinetic energy for the 280 nm dissociation disagrees with the experimental result of  $(0.56\pm0.12)$  eV of total



FIG. 3. Calculated equilibrium structure of the phenyl nitrite  $(C_6H_5ONO)$  intermediate formed in the decomposition of nitrobenzene. The structure comes from a Gaussian 92 calculation at the MP2/6-31G\* level.

kinetic energy of the phenoxy and nitric oxide fragments.<sup>10</sup> The soft radical model predicts rotational energies by determining the angular momenta  $J_{\gamma}$  and  $J_{\delta}$  of rotation of each fragment about its center of mass generated by the recoiling atoms. Conservation of the angular momentum gives the rotational energy

$$E_{r}^{\text{frag }\delta} = \frac{J_{\delta}^{2}}{2I_{\text{frag }\delta}} = \frac{m_{\delta}m_{\gamma}}{m_{\delta} + m_{\gamma}} \frac{r_{\delta}^{2} \sin^{2} \chi_{\text{frag }\delta}}{I_{\text{frag }\delta}} E_{\text{avl}}, \qquad (2)$$

where  $J_{\delta}$  is the angular momentum of the fragment containing atom  $\delta$ ,  $I_{\delta}$  is its moment of inertia,  $r_{\delta}$  is the distance of atom  $\delta$  to the center of mass of the fragment, and  $\chi_{\text{frag }\delta}$ is the angle between the bond to be broken and a line from the center of mass of the fragment to the atom  $\delta$ . An analogous expression gives the rotational energy of the fragment containing atom  $\gamma$ .

There are no experimental measurements or theoretical calculations of the geometry of phenyl nitrite, but we expect the geometry of the CONO group in phenyl nitrite to be similar to that in other nitrites. For example, Tuck<sup>16</sup> uses tetrahedral angles for C-O-N-O bonds in ethyl nitrite, and in methyl nitrite these angles are about 114.5°.<sup>17-19</sup> We have performed an *ab initio* calculation at the second-order Møller-Plesset (MP2)/6-31G\* level using the Gaussian 92 package to obtain the equilibrium geometry shown in Fig. 3.<sup>20</sup> The angles for the O-O-N bond (109.9°) and the O-N-O bond (109.8°) are indeed very nearly tetrahedral, and we use the value of 109.4° in our calculations. The impulsive model predicts that 25% of the available energy should appear as rotation of the NO fragment and 14% should appear in rotation of the phenoxy radical. These fractions correspond to rotational energy in NO of 1.2 eV for the 226 nm photolysis and 0.92 eV for the 280 nm photolysis, both of which substantially exceed our measurements of 0.32 and 0.20 eV, respectively. The balance of the energy not appearing in rotation or translation becomes vibrational energy of NO and of the phenoxy fragment. The impulsive model predicts that only 3% of the available energy becomes vibrational energy of NO with

#### **B. Statistical model**

The statistical model we use to predict translational, rotational, and vibrational energies assumes that all possible combinations of product states that conserve energy are equally probable. This approach, which ignores any angular momentum constraints, is equivalent to the simplest calculation of the prior distributions in the information theory analysis of energy disposal by Levine and Bernstein.<sup>21</sup> The probability of depositing a given amount of energy into any degree of freedom is proportional to the number of product states available that conserve energy. For an available energy  $E_{avl}$ , the probability of the fragments having a total kinetic energy  $E_{t'}P(E_{t'}E_{avl})dE_{t'}$  is the ratio of the density of states for fragments with that kinetic energy to the total density of states

$$P(E_{t'}E_{avl})dE_{t}$$

$$=\frac{\rho(E_{t'}E_{avl})}{\rho(E_{avl})}$$

$$=\frac{dE_{t}\rho_{t}(E_{t})\int_{0}^{E_{avl}-E_{t}}\rho_{1}(\epsilon)\rho_{2}(E_{avl}-E_{t}-\epsilon)d\epsilon}{\int_{0}^{E_{avl}}\rho_{t}(E_{t})\int_{0}^{E_{avl}-E_{t}}\rho_{1}(\epsilon)\rho_{2}(E_{avl}-E_{t}-\epsilon)d\epsilon dE_{t}},$$
(3)

where  $\rho_1(\epsilon)$  is the rovibronic density of states for fragment 1 with internal energy  $\epsilon$ , and  $\rho_2(E_{av}-E_t-\epsilon)$  is the rovibronic density of states for fragment 2 with internal energy  $E_{av} - E_t - \epsilon$ . The translational density of states  $\rho_t(E_t)$  is proportional to  $E_t^{1/2,21}$  Although the rovibronic density of states can be calculated by several methods, we use the simple Whitten and Rabinovitch expression.<sup>22,23</sup> We have a complete set of neither the experimental nor theoretical frequencies of the phenoxy radical, even though there are several calculations of the equilibrium geometry.<sup>24,25</sup> Because the experimental frequencies that are available for the phenoxy radical are similar to those of phenol, except for the C-O stretching mode, we use the values for the phenol molecule given by Bist et al.,<sup>26</sup> omitting the O-H stretching and C-O-H bending modes, as shown in Table II. Since the C-O stretch has a fairly high frequency, its difference between phenol (1261  $\text{cm}^{-1}$ ) and phenoxy

TABLE II. Vibrational frequencies<sup>a</sup> for the phenoxy radical  $(cm^{-1})$  used in the statistical calculations.

| 3087                     | 3063 | 3027 | 1603 | 1501 |
|--------------------------|------|------|------|------|
| 1261(1505 <sup>b</sup> ) | 1168 | 1025 | 999  | 823  |
| 526                      | 3070 | 3049 | 1610 | 1472 |
| 1343                     | 1277 | 1150 | 1070 | 619  |
| . 403                    | 995  | 817  | 408  | 973  |
| 881                      | 751  | 686  | 503  | 244  |

<sup>a</sup>Reference 26.

<sup>b</sup>Reference 27.

 $(1505 \text{ cm}^{-1})$  changes the model energies in Table I by less than 0.1%. We calculate the average recoil energy as

$$\langle E_t \rangle = \int_0^{E_{\text{avl}}} E_t P(E_t, E_{\text{avl}}) dE_t.$$
(4)

Table I summarizes the kinetic energies predicted by this statistical model for the 226 and 280 nm photolysis of nitrobenzene. For both photolysis wavelengths, the statistical model predicts much smaller amounts of kinetic energy than we observe. It finds a total kinetic energy release of 0.30 eV in the 226 nm photolysis compared to our observation of  $(1.1\pm0.2)$  eV. Similarly, the predicted value for the 280 nm photolysis 0.25 eV is much less than the  $(0.56\pm0.12)$  eV we observe.<sup>10</sup> The statistical probability of creating NO(v=0) fragments with a rotational quantum number J, corresponding to a rotational energy  $E_r = BJ(J + 1)$ , is

$$P[J(v=0), E_{avl}] = \frac{(2J+1)\int_{\epsilon=0}^{E_{avl}-E_r} \rho_{rv}(\epsilon) \rho_t(E_{avl}-E_r-\epsilon)d\epsilon}{\sum_{J=0}^{J_{max}} (2J+1)\int_{\epsilon=0}^{E_{avl}-E_r} \rho_{rv}(\epsilon) \rho_t(E_{avl}-E_r-\epsilon)d\epsilon},$$
(5)

where 
$$(2J+1)$$
 is the sum of the rotational states of NO for  
a given J,  $\rho_t(E_{avl}-E_r-\epsilon)$  is the translational density of  
states for the fragment pair, and  $\rho_{rv}(\epsilon)$  is the rovibronic  
density of states for the phenoxy fragment calculated using  
the Whitten and Rabinovitch expression.<sup>22,23</sup> The average  
rotational energy for this distribution of rotational states is

$$\langle E_r^{v=0} \rangle = \sum_{J=0}^{J_{\text{max}}} BJ(J+1)P[J(v=0), E_{\text{avl}}],$$
 (6)

where  $B = 1.6956 \text{ cm}^{-1}$  is the rotational constant of NO.<sup>12</sup> The predicted rotational energies, 0.20 eV for the 226 nm photolysis and 0.16 eV for the 280 nm photolysis, agree fairly well with our measurements of  $(0.32\pm0.03)$  and  $(0.20\pm0.03)$  eV, respectively, for the two wavelengths. The calculated and measured distributions of rotational state populations also have qualitatively similar shapes.<sup>10</sup>

A very similar approach gives the amount of vibrational energy in the NO fragment for the statistical model and shows that it consistently predicts more vibrational excitation of NO than we observe, but by amounts that are on the order of the upper limits we have determined. The probability of NO being in a particular vibrational state v is

$$P(E_v, E_{avl}) = \frac{\sum_{J=0}^{J_{max}} (2J+1) \int_{\epsilon=0}^{E_{avl}-E_v} \rho_{rv}(\epsilon) \rho_t(E_{avl}-E_v-E_r-\epsilon) d\epsilon}{\sum_{v=0}^{v_{max}} \sum_{J=0}^{J_{max}} (2J+1) \int_{\epsilon=0}^{E_{avl}-E_v-E_r} \rho_{rv}(\epsilon) \rho_t(E_{avl}-E_r-\epsilon) d\epsilon},$$
(7)

where  $E_v$  is the vibrational energy of NO in state v,  $v_{max}$  is the maximum vibrational level with less energy than  $E_{avl}$ and  $J_{max}$  is the maximum rotational level with less energy than  $E_{avl} - E_v$ . This model predicts a vibrational distribution of NO for the 226 nm photolysis having 69% of the population in v=0, 22% in v=1, and 7% in v=2, corresponding to an average vibrational energy of 0.09 eV for the NO fragment. The calculated population in v=1 substantially exceeds our experimental upper limit of 8%. The predicted NO distribution for the 280 nm photolysis is 76% in v=0, 19% in v=1, and 4% in v=2, corresponding to an average vibrational energy of 0.06 eV and having a population in v=1 that is comparable to our experimental upper limit.

## **V. DISCUSSION**

Both the impulsive and statistical models of energy disposal fail to describe the photodissociation of nitrobenzene completely, as Table I shows. The impulsive model places too much energy in NO rotation and relative translation and too little in internal excitation of the phenoxy fragment. The statistical model, on the other hand, places too little energy in translation, but does better with the other degrees of freedom. As described above, our simplest picture of the progress of nitrobenzene decomposition is that the excited state isomerizes to phenyl nitrite, which produces NO by cleaving the  $C_6H_5O$ –NO bond. This model explains our observation of the three products NO, O, and NO<sub>2</sub>, and their variation with wavelength,<sup>5</sup> and also agrees with results on the infrared multiphoton initiated decomposition of CH<sub>3</sub>NO<sub>2</sub>.<sup>28</sup> Thus we use the phenyl nitrite geometry in our impulsive energy release calculations. An impulsive energy release model seems to describe the photolysis of methyl,<sup>29,30</sup> ethyl,<sup>16</sup> and *t*-butyl<sup>30</sup> nitrite fairly well. Methyl nitrite, for example, produces NO with a Gaussian distribution of population having a maximum near J=32.<sup>31–34</sup>

Our impulsive model calculations also predict large amounts of rotational excitation in the decomposition of nitrobenzene through the phenyl nitrite intermediate, in disagreement with our measurements that find roughly a factor of 4 less rotational energy than the impulsive model predicts (Table I). One possible source of the difference in the measurement and calculation is the equilibrium geometry we use for the phenyl nitrite since the rotational energy release depends strongly on the O–N–O bond angle  $\gamma$ , as Eq. (2) shows. In nitrobenzene,<sup>35</sup> the angle is 124° compared to 134° in free NO<sub>2</sub> (Ref. 36) and 109° in the nitrite. The angle could open in the transition state for the isomerization to phenyl nitrite, but it must be about 150° to reproduce our observed NO product rotational energy content. Assuming this geometry, however, leads to a new disagreement with the measurements. Because the energy no longer appearing in rotation becomes vibration, this geometry predicts substantial vibrational excitation of NO (1.0 eV in the 226 nm photolysis), contrary to our LIF

measurements. The form of the rotational energy distributions for impulsive energy release also disagrees with our observation of a roughly Boltzmann distribution of NO internal energy. Impulsive energy release should produce Gaussian distributions with a maximum at large J, such as observed in methyl and *t*-butyl nitrite.<sup>31-34</sup>

A solely impulsive model of the decomposition of nitrobenzene to produce NO fails in describing the rotations of the NO product, the relative translational energy, and the internal energy of the phenoxy fragment, although it correctly predicts small amounts of vibrationally excited NO. This failure suggests that a statistical model, which deposits more energy in the phenoxy fragment because of its large number of vibrations and, hence, puts a smaller amount of energy in product rotations, might be appropriate. However, the comparisons in Table I show that the statistical model, while describing rotations better, places slightly too much energy in the phenoxy fragment and underestimates the amount of energy in translations by at least a factor of 2. While adjusting the density of states in the statistical model could alter this energy distribution, we cannot justify detailed adjustments in this approximate, limiting model.

The pattern of energy release and the likely role that isomerization plays in the decomposition hint at a hybrid mechanism that seems physically plausible. A relatively slow isomerization, which is a distinct possibility if it occurs on the ground electronic state surface after internal conversion, could distribute the available energy statistically at the transition state to isomerization, but impulsive dynamics could determine the release of the energy stored as potential energy at the transition state. Because the mechanism distributes less than the total energy statistically, less appears as internal excitation of the phenoxy radical. The remaining energy, stored as potential energy at the transition state, appears mostly in translation in the impulsive energy release as the system moves from the top of the barrier to products. Although this simple physical picture omits possible exit channel interactions, it should produce intermediate values of internal and translational energy that more nearly agree with the measurements.

#### **VI. SUMMARY**

The photolysis of nitrobenzene at 226 and 280 nm produces NO and phenoxy radicals in one of its decomposition channels. Previous measurements using vacuum ultraviolet photoionization and time-of-flight mass spectrometry have shown that about 15% to 25% of the available energy appears in relative translation.<sup>5</sup> Using laser induced fluorescence detection, we have determined the internal energy content of the NO product molecules. They are rotationally excited, containing about 5%-7% of the available energy in rotational degrees of freedom. We detect no vibrationally excited NO, and our conservative upper limit has less than 3% of the available energy appearing in NO vibration. Thus, the available energy becomes primarily relative translation, rotation of NO, and internal excitation of the phenoxy radical fragment. Impulsive and statistical models of energy release both predict little vibrational excitation, in qualitative agreement with our measurements, but the impulsive model predicts far too much NO rotation, while the statistical model predicts too little translational excitation. A more realistic picture would combine statistical energy redistribution up to a transition state followed by impulsive release of energy as the system descends from the top of the barrier. A comparison of the calculations and experiment certainly suggests that producing the observed internal energy content of the phenoxy radical requires some modification of the simple impulsive model, which predicts too little, and the statistical model, which predicts too much.

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