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The Doppler spectra of $O(^{1}D)$ from the photodissociation of O_{2} , NO_{2} , and $N_{2}O_{2}$

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The Doppler profiles of the O(¹D) products from the photodissociation of O₂ at 157.6 nm and NO₂ and N₂O at 205.47 nm are detected by a resonance enhanced multiphoton ionization technique. The translation energy and angular distributions are deduced for the O(¹D) atoms. Present results indicate that (a) O₂ ($B^{3}\Sigma_{u}^{-}$) has a short dissociative lifetime when irradiated at 157.6 nm, (b) NO(²Π) photofragment from NO₂ at 205.47 nm is mostly vibrationally excited, and (c) most of the available energy is released as kinetic energy when N₂O is photodissociated at 205.47 nm.

INTRODUCTION

The electronic energy of the oxygen atom in the $O({}^{1}D)$ level is 1.967 eV above the ground state $O({}^{3}P_{2})$. Since the transition to the ground state is forbidden by electric dipole and spin selection rules, the $O({}^{1}D)$ atom can react with H_{2} , O_{2} , $N_{2}O$, hydrocarbons, etc., during its radiative lifetime of 147 s.¹ Although the direct detection of $O({}^{1}D)$ has been made only recently, it has been known for some time that $O({}^{1}D)$ is produced in the photolyses of O_{2} , $N_{2}O$, NO_{2} , O_{3} , and CO_{2} . Because of the important role of $O({}^{1}D)$ in hot atom chemistry and the fact that photodissociation is a good source of hot atoms, an observation of the translational energy release of $O({}^{1}D)$ photoproduct is important to analysis of experimental results for reactions that use $O({}^{1}D)$ as a reactant as well as to understanding of the photodissociation dynamics involved.

Because the absorption probability is greatest when the transition dipole moment of a molecule is parallel to the electric vector of the dissociating light, a photofragment is not randomly directed with respect to the photolysis light beam. Thus, if the lifetime of the excited molecule is less than its period of rotation, the photofragments show a corresponding anisotropy. The Doppler shape of a resonant line in an atomic photofragment contains information about this anisotropy as well as the translational energy released in a photodissociation.

Resonance-enhanced multiphoton ionization (REMPI) is a very sensitive technique for the gas-phase detection of atoms. With a time-of-flight detection scheme, the created ions can be mass selected and collected with near unit efficiency. Recently, Pratt *et al.*² have reported a REMPI detection of O(${}^{1}D$) for the first time, using the two-photon resonances of the $3p' {}^{1}P_{1} - {}^{1}D_{2}$ and $3p' {}^{1}F_{3} - {}^{1}D_{2}$ transitions at 205.47 and 203.82 nm, respectively. They discussed the autoionization processes in the $3p' {}^{1}P_{1}$ and

 $3p' {}^{1}F_{3}$ levels of O atom. Because a resonant process is used, the velocity distribution of the atoms along the direction of the probe laser can be obtained from Doppler profile measurements. In this work, we report on the REMPI observation of nascent O(${}^{1}D$) atoms produced from the photolysis of O₂ at 157.6 nm, and NO₂ and N₂O at 205.47 nm. From the results of the Doppler profile measurements, the dynamics of their photodissociation processes is discussed.

EXPERIMENT

205.47 nm laser light $(0.08 \text{ cm}^{-1} \text{ resolution})$ was focused into the center of a chamber, both to dissociate approximately 10^{-4} Torr of NO₂ or N₂O supplied by an effusive beam and to ionize the O(¹D) photoproduct by REMPI via the autoionizing O(3p' ¹P₁) state. For O₂ photodissociation, the 157.6 nm F₂ laser light was aligned collinearly with the probe laser light used to dissociate O₂ molecules. A repeller plate (150 mm diam) was charged to 800 V to force the oxygen atom ions into a Tenex Channel Multiplier detector through a hole of 10 mm diam. The resulting ion pulse was amplified, averaged with a gated integrator, and collected as a function of probe laser frequency.³

0.1 to 0.2 mJ of 205.47 nm light was formed from 15–20 mJ of 616.42 nm excimer-pumped dye laser light by a technique similar to that of Pratt and co-workers.² We used a KDP crystal to generate 308.21 nm light. Before the resulting mixture of 616.42 nm and 308.21 nm light could be passed through a BBO crystal for sum frequency generation, the polarization of the two beams had to be aligned with each other. To do this we did not separate the 616.42 nm light from uv light. UV and VIS light were just mixed in the BBO crystal because the output from the dye laser was depolarized to some extent. The polarization of the two beams were thus aligned.

RESULTS AND DISCUSSION

To interpret the Doppler spectra of $O({}^{1}D)$, we first note that the distribution of velocity vector v of the $O({}^{1}D)$ atoms produced is given by⁴

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$$f_i(\bar{v}) = \frac{\delta(|\hat{v}| - v_i)}{4\pi v_i^2} \left[1 + \beta_i P_2\left(\frac{\widehat{E} \cdot \hat{v}}{|\widehat{E}||\hat{v}|}\right) \right]. \tag{1}$$

Here v_i is the speed of the the oxygen atom as determined by conservation of energy, β_i is the anisotropy parameter for the photodissociation to the O(¹D) state, \tilde{E} is the polarization vector of the pump laser, and $P_2(x)$ is the second Legendre polynomial, $(3/2)x^2 - 1/2$. The subscript *i* denotes the dissociation channel in which O(¹D) and the complementary fragment in the *i*th internal state are generated. For the collinear geometry of the dissociation and probe laser light, this leads to a normalized Doppler profile $g_i(v)$ of the following form:⁵

$$g_{i}(\nu) = \frac{1}{2\nu_{i}\nu_{0}} \left\{ 1 - \frac{\beta_{i}}{2} P_{2} \left[\frac{(\nu - \nu_{0})c}{\nu_{i}\nu_{0}} \right] \right\} \times \Theta \left(1 - \frac{|\nu - \nu_{0}|c}{\nu_{i}\nu_{0}} \right).$$
(2)

Here v_0 is the resonant frequency of the MPI process, $\Theta(x) = 0$ for x < 0, and $\Theta(x) = 1$ for x > 0.

The velocity distribution of the $O({}^{1}D)$ atoms produced is given by

$$F(\hat{v}) = \sum a_i f_i(\hat{v}). \tag{3}$$

Here a_i is a branching ratio of the dissociation channel. For the geometry of our experiment, this leads to a normalized Doppler profile I(v) of the following form:

$$I(v) = \sum a_i g_i(v). \tag{4}$$

This profile is a weighted sum of channels which each depend on both β_i and the translation energy for a photodissociation to the complementary photoproduct in the *i*th rovibronic state.

A. Photodissociation of oxygen molecules at 157.6 nm

The Doppler profile of the $O({}^{1}D)$ atoms produced from the photodissociation of O_{2} at 157.6 nm is shown in Fig. 1.



FIG. 1. Two-photon Doppler spectrum of $O({}^{1}D)$ atom produced from the photodissociation of O_2 at 157.6 nm. The two smooth solid lines are the expected Doppler profiles with $\beta = 2$ and 1, when 0.79 eV of the available energy is released to translation. This is convoluted with the Gaussian line shape of our uv laser and the thermal energy (total 0.10 cm⁻¹ FWHM). The horizontal axis is the uv detuning of the probe laser in cm⁻¹, while the vertical axis is the relative REMPI signal intensity of $O({}^{1}D)$.

The solid smooth curves are calculated ones with assumption that (a) $\beta = 2$ or 1 and (b) a dissociation channel of $O(^{1}D) + O(^{3}P)$, using Eq. (2) and

 $O_2 \rightarrow O(^3P) + O(^1D) \quad \Delta H = 7.08 \text{ eV}.$

For the photodissociation of O_2 to $O({}^1D) + O({}^3P_j)$, one channel averaged for j = 0, 1, and 2 is calculated since the energy separations in $O({}^3P_j)$ are quite small compared with our energy resolution. Figure 1 shows that the calculated Doppler profile with $\beta = 2$ fits the experimental one well. Since the anisotropy parameter β is as large as 2, the dissociation lifetime is quite short compared with a period of molecular rotation at room temperature and the optical transition is parallel to the molecular axis.⁴

A broad vuv absorption of O₂ peaks at 144 nm and extends from 135 to 200 nm. This absorption, called the Schumann-Runge band, is assigned to the $B^{3}\Sigma_{u}^{-}-X^{3}\Sigma_{g}^{-}$ transition. The $B^{3}\Sigma_{\mu}$ state is bound and correlates into $O(^{3}P) + O(^{1}D)$ atomic states. The thermoenergetic threshold for the dissociation channels to $O({}^{3}P) + O({}^{1}D)$ corresponds to the absorption wavelength of 175 nm. The results of this experiment are consistent with the conclusion which was derived from the Doppler profile of $O({}^{3}P)$ and emission measurements of $O(^{1}D)$ fragments from O_{2} at 157.6 nm^{3,6}: i.e., photodissociation of O₂ at 157.6 nm leads predominantly to the products $O(^{1}D) + O(^{3}P)$ and that the transition is parallel in nature. These results at 157.6 nm are in agreement with those at 147 nm reported by Stone et al.⁷ From the time-of-flight measurements of O atoms in the photodissociation of O_2 at 147 nm, they concluded that the dominant dissociation process is to $O(^{1}D) + O(^{3}P)$ and the angular distribution is attributable to a parallel transition.⁷ The ${}^{3}\Pi_{\mu} - X {}^{3}\Sigma_{e}^{-}$ transition can be ruled out because the ${}^{3}\Pi_{\mu}$ state correlates adiabatically to two $O({}^{3}P)$ atoms and also the Franck-Condon factor for the transition of 157 nm is extremely small.⁸ The 157.6 nm photon excites O₂ molecules at the repulsive limb of the $B^{3}\Sigma_{\mu}^{-}$ state but not at that of the ${}^{3}\Pi_{u}$ state, since the ${}^{3}\Pi_{u} - X {}^{3}\Sigma_{g}^{-}$ transition is perpendicular $(\beta = -1)$ and our result shows $\beta = 2$.

B. Photodissociation of nitrogen dioxide at 205.47 nm

Figure 2 shows the Doppler profile of the $O({}^{1}D)$ atoms produced from the one-color dissociation of NO₂ at 205.47 nm. At this wavelength one reaction pathway yields NO($X^{2}\Pi$) and O(${}^{1}D$):

$$NO_2 \rightarrow NO(X^2\Pi) + O(^1D) \quad \Delta H = 5.08 \text{ eV}.$$

Since the photon energy of 205.47 nm is 6.03 eV and the internal energy of NO₂ is 0.038 eV at room temperature, the excess energy should be 0.99 eV and the maximum vibrational level of NO is four. If we take the second moment of the Doppler profile of Fig. 2 for $O(^{1}D)$, we find that

$$\frac{3}{2}m_0c^2 \int_{-\infty}^{\infty} \left[(v - v_0)/v_0 \right]^2 P(v) dv$$
$$= \sum_i \frac{(1 - \beta_i/5)}{2} a_i m_0 v_i^2, \tag{5}$$

where β_i is an anisotropic parameter and a_i is a branching



FIG. 2. Two-photon Doppler spectrum of $O({}^{1}D)$ atoms produced from the photodissociation of NO₂ at 205.47 nm. The horizontal axis gives the uv detuning. The smooth solid lines are the expected Doppler profiles for $\beta = 1.3$ and for NO($X^{2}\Pi$, v = 3 or 2) + O(${}^{1}D$). The rotational temperature of NO is assumed to be T = 900 K.

ratio for the dissociation channel which produces NO in the *i*th rovibrational state, and P(v) is the normalized Doppler spectrum. Calculating the second moment of this spectrum, the left hand side of Eq. (5) was found to be 0.084 eV and the value of the translational energy released to the O(¹D) photofragments was between 0.070 eV ($\beta = -1$) and 0.14 eV ($\beta = 2$). Hence the total translational energies are 0.11 eV ($\beta = -1$) and 0.21 eV ($\beta = 2$). Those values are only 11% to 21% of the available energy and the residual energy is released to the rotational and vibrational energy in the NO fragment.

Since the total angular momentum in the system must be conserved, the relationships among the orbital angular momentum of the fragments, L', and the rotational angular momenta of the parent molecule J_{NO_2} and of the molecular fragment, j_{NO} , are expressed as follows:

$$L' \equiv \mu v b = |\hat{J}_{NO_2} - \hat{j}_{NO}|,$$
 (6)

where μ is the reduced mass of the system, v is relative speed between the two fragments, and b is the impact parameter.⁹ In the photodissociation of NO_2 at 205.47 nm the rotational excitation in the NO fragment should be small, since only a small amount of energy is released into the translational degree of freedom; i.e., the relative speed v is small and the torque for the rotation is small. For a bent geometry during the dissociation and neglecting $J_{\rm NO_2}$, even if we put the value of the impact parameter to be 2.4 Å, which is twice as large as the N-O bond length of NO₂ in the ground state, and take the upper limit of the center of mass velocity $v = (2E_t/\mu)^{1/2}$, the maximum rotational energy as determined by Eq. (6) is found to be 0.038 eV. Therefore in the photodissociation of NO₂ at 205.47 nm, $80 \pm 5\%$ of the available energy (0.74– 0.84 eV) must go into the vibrational energy of the NO fragment. This means that the NO fragments are excited to around v = 3 ($E_{vib} = 0.69 \text{ eV}$). For a linear NO₂ and putting L' = 0 in Eq. (6), then the averaged rotational energy is calculated to be 0.10 eV, which also leaves enough vibrational energy to populate NO (v = 3).

Several studies have been performed on the internal

state distribution of the nascent NO fragments from the photodissociation of NO₂ at uv.¹⁰⁻¹² Bigio *et al.*¹⁰ reported in their NO₂ photodissociation at 220–226 nm that the v = 2level of NO was more populated than the v = 0 or 1 level and that the rotational distribution is approximated by temperatures of $T_r = 360-1600$ K.

Slanger et al.¹¹ studied the nascent NO vibrational distribution with laser-induced fluorescence detection for the photodissociation of NO₂ at 248.5 nm which is slightly longer than the threshold wavelength of 243.9 nm for $NO + O(^{1}D)$ process. They found that the population was strongly inverted in v = 6-8 for the nascent NO when the thermodynamic limit is v = 8 for the NO + O(³P) process. Our results suggest that the NO fragments from the $NO + O(^{1}D)$ photodissociation process at 205.47 nm is populated most probably at v = 3, where the thermodynamical limit is v = 4. The reasonable explanation for the high vibrational excitation is that a significant change in bond length occurs between the NO₂ ground state and the optically excited state, which was proposed for the NO + O(${}^{3}P$) process at longer wavelengths by Slanger et al.¹¹ and Zacharias et al.¹² Actually, the N–O bond length in the 2 $^{2}B_{2}$ state is 1.314 Å, while that in the ground state is 1.19 Å. A well analyzed transition in NO2 located around 205.47 nm is the $2^{2}B_{2}-\tilde{X}^{2}A_{1}$ transition, which shows discrete rotational structure near its origin at 249.1 nm but becomes completely diffuse below 245.9 nm due to predissociation. In this transition NO₂ is placed at a highly excited position on the potential surface and then transverse on the steep wall to the exit dissociation channel. This results in little translational energy between the NO and $O(^{1}D)$ fragments and large vibrational excitation in the NO fragment.

According to Kinugawa et al.,¹³ the β value for NO($X^2\Pi$, v = 0) is 1.6 \pm 0.15 and the rotational temperature is 800 ± 100 K by measurement of the imaging of the NO photofragments for the primary process of $NO(X^2\Pi, v = 0) + O(^1D)$ at 226.9 nm. This is reasonable since the 2 ${}^{2}B_{2} - \tilde{X} {}^{2}A_{1}$ transition moment lies along the direction of the oxygen-oxygen axis. When the structure of the ground state of NO₂ ($\angle ONO = 134^\circ$) is retained in the excited state and oxygen recoils from the N atom, the anisotropy parameter β_0 is calculated to be 1.54.¹⁴ However, when the translational energy of the $O(^{1}D)$ photofragments is small, the value of β_0 is lowered because the tangential velocity of the fragments during molecular rotation is not negligible compared to the axial velocity of recoil. The relationship between the β value and the relative velocity of the fragments in the NO₂ photodissociation was discussed by Busch and Wilson.¹⁴ According to them, the observed anisotropy parameter β is approximately represented by β_0 $\times P_2$ (cos α), where α is the tipping angle. First, we assume that $\beta = 1.54$ and hence the translational energy of O(¹D) is calculated to be 0.12 eV from Eq. (5). This translational energy corresponds to $\alpha = 18^{\circ}$ and hence the β value is reduced to 86% of that of the high energy limit. This gives $\beta = 1.32$. The translational energy of 0.12 eV for O(¹D) is in agreement with the value calculated thermoenergetically for the process of NO(v = 3, $T_R = 900$ K) + O(¹D). The smooth solid curve in Fig. 2 is a simulated one with the translational energy of 0.12 eV and the anisotropy parameter β of 1.3, which well fits to the obtained Doppler spectrum. For comparison purpose, a simulated curve for NO(v = 2) is also shown in Fig. 2.

C. Photodissociation of nitrous oxide at 205.47 nm

UV photodissociation of N₂O is induced by a pulsed dye laser tuned to the REMPI transition for O(^{1}D) at 205.47 nm. A single laser pulse serves as both a photodissociation source and a probe. The Doppler profile of the O(^{1}D) atoms produced from this one-color dissociation is shown in Fig. 3. The photodissociation process is as follows:

$$N_2 O \rightarrow N_2 + O(^iD) \quad \Delta H = 3.64 \text{ eV}.$$

We attempted without success to observe $O({}^{3}P)$ from the photodissociation of N₂O in a two-color experiment utilizing 193.5 nm excimer laser light to photodissociate the N₂O molecule and 226 nm light to ionize the $O({}^{3}P)$ by a resonant enhanced multiphoton ionization technique. To align our lasers, we observed strong signal of $O({}^{3}P)$ atoms produced from the photodissociation of O₂ at 193.5 nm. The fact that we could not observe $O({}^{3}P)$ atoms from the photodissociation of N₂O is consistent with previous observations that excited oxygen atoms are produced almost exclusively from the photodissociation of N₂O in this wavelength region.^{15,16}

The quantity of the second moment of the Doppler profile of Fig. 3 defined by the left hand side of Eq. (5) was found to be 0.89 ± 0.03 eV. Since the photon energy of 205.47 nm is 6.03 eV, and the internal energy of N₂O is 0.03 eV at room temperature, the excess energy of 2.42 eV is distributed to the kinetic energy and the internal energy of N₂ fragment for the O(¹D) channel. When we substitute the minimum value of β_i ($\beta = -1$) and the maximum value of β_i ($\beta = 2$) for all β_i on the right-hand side of Eq. (5), we find a lower and upper limit of 0.74 ± 0.03 eV and 1.48 ± 0.05 eV, respectively, for the average O(¹D) atom translational energy in the laboratory frame. Thus we can conclude that between 1.16 ± 0.05 eV for $\beta = -1$, and 2.32 ± 0.08 eV for $\beta = 2$ of the available 2.42 eV in the photo dissociation of N_2O at 205.47 nm is released to kinetic energy.

 N_2O has a weak absorption band in a region stretching from 160 to 250 nm that peaks at 181 nm with a value of roughly 4 atm⁻¹ cm^{-1,17} The ground state of N₂O is linear and its electronic wave function has the assignment $\tilde{X}^{1}\Sigma^{+}$. A detailed calculation of the electronic spectrum of the N₂O molecule has been done by Hopper.¹⁸ His estimate of the vertical transition energy of the lowest lying $\tilde{a}^{3}\Sigma^{+}$ state is 6.5 eV above the ground state; close to the photon energy of our laser. However, it is unlikely that the $\tilde{a}^{3}\Sigma^{+}$ state is responsible for the photodissociation, because it is difficult to explain the almost exclusive production of $O(^{1}D)$ that has been observed as the atomic N₂ O photoproduct. If the dissociation were to occur from a triplet state, the O atom fragments should be in the ${}^{3}P$ state due to a spin conservation rule. Preston and Barr¹⁵ confirmed that the production of $O(^{1}D)$ atom is indeed the major channel for the photodissociation of N₂O in this wavelength region. More recently Zhu and Gordon¹⁶ determined from real time measurements that $O(^{1}D)$ is produced almost exclusively from the photodissociation of N₂O at 193 nm. We observed no REMPI signals of $O({}^{3}P)$ from the photodissociation of N₂O at 226 or 193 nm.

The lowest lying vertical singlet-singlet transitions from the linear ground state of N₂O are to the $\tilde{A}^{1}\Sigma^{-}$ and $\tilde{B}^{1}\Delta_{s}$ states. Hopper¹⁸ found that the energy of these vertical transitions are 7.6 and 7.7 eV, respectively, so at first glance it seems inappropriate to think of a dissociation along these states. However, when the molecule is slightly bent to an angle of 130° as shown in Fig. 4, the excitation energy is reduced to 3.8 \pm 0.5 eV.¹⁹ Thus when the ground state of the molecule is bent, the $\widetilde{A}^{1}\Sigma^{-}$ and $\widetilde{B}^{1}\Delta_{s}$ evolve into states which provide allowed singlet-singlet $A' \leftrightarrow A''$ and $A' \leftrightarrow A'$ transitions by which the N₂ O molecule can dissociate. If this model is correct, one would expect that N₂O which is vibrationally excited should absorb much more strongly than the ground state N₂O because increased nuclear motion creates a much higher probability for a bent configuration to occur. This is supported by N_2O absorption studies by Selwyn et

FIG. 3. Two-photon Doppler spectrum of $O({}^{1}D)$ atom produced from the photodissociation of N₂O at 205.47 nm. The smooth solid (broken) line is the profile for $\beta = 2$ (or 1) and the available energy released to translation is 2.32 eV (or 1.74 eV). The smooth dotted line is for $\beta = -1$ and 1.16 eV.

J. Chem. Phys., Vol. 95, No. 9, 1 November 1991



FIG. 4. Electronic potential energy curves of the N_2O molecule as a function of bond angle at fixed bond lengths. Adopted from Ref. 18.

al.¹⁹ and Merienne et al.¹⁸ which show that the absorption of N₂O above 200 nm has a strong temperature dependence. At 205.47 nm, one can use the data of Merienne et al.²⁰ to find the N₂O cross section at 296, 240, and 220 K to be 17.6, 13.1, and 11.9 in units of 10^{-21} cm². If we assume that this temperature dependence is due to the fact that dissociation may occur from either the vibrational ground state of N₂O or from an N₂O molecule with 1 quantum (0.0729 eV) of bending vibration,²¹ then we can conclude that at 205.47 nm the first vibrational state of N₂O absorbs 25 times more efficiently than the ground state and in our room temperature experiment 60% of the O(¹D) observed is produced from a vibrationally excited molecule.

According to Hopper's work,¹⁸ the two states of linear N2O that evolve into energetically accessible allowed transitions when the molecule is bent are the $\widetilde{A}^{1}\Sigma^{-}$ and $\widetilde{B}^{1}\Delta_{c}$. states. If the transition is via the $\tilde{A}^{1}\Sigma^{-}$ state the transition is a ${}^{1}A' \leftrightarrow {}^{1}A''$ transition and as such the dipole moment must be perpendicular to the plane of the bent N_2O molecule.²³ If this is the case, we expect a perpendicular transition with $\beta = -1$ for all possible product N₂ states and the translational energy of 1.16 ± 0.05 eV from Eq. (5). However, as shown by a smooth broken line in Fig. 3, it is difficult to simulate our spectra with the values of $\beta = -1$ and 1.16 eV. If we assume the photodissociation is along the $\tilde{B}^{1}\Delta_{s}$ state, then the transition is ${}^{1}A' \leftrightarrow {}^{1}A'$ and the dipole moment must be in the plane of the molecule. Since it is clear from the experimental data that the angular distribution of $O(^{1}D)$ is peaked along the dissociation polarization direction, it is not unreasonable that the dipole moment is aligned nearly along the axis of the NO bond. This implies a positive value for β . Winter²² predicted that the $\tilde{B}^{1}\Delta_{s}$ state is responsible for this transition. Our experimental results of the Doppler profile measurement support his prediction.

To estimate the energy released to the oxygen molecule, we remind ourselves that the N₂ ground state bond distance $(1.097 \text{ A})^{21}$ and the N-N bond distance in N₂O (1.128 A)²³ have similar values. Because of this it is likely that after the N₂O molecule is excited, the N-N nuclear distance will be close to a potential minimum. The Franck-Condon principle suggests that the N2 vibrational excitation should be as small as 0.06 eV for the small difference of the N-N bond distances between N_2 and N_2O . If this is the case, then the available 2.42 eV of energy is released into the translational energy of the photofragment. If we assume $\beta = 2$, then the translational energy is 2.32 + 0.08 eV from Eq. (5). This implies that the dipole moment is along the axis of the NO bond and the rotational excitation is negligible. The smooth broken line in Fig. 3 shows the Doppler spectrum expected if the N₂O molecule releases 2.32 eV into translation and $\beta = 2$. The profile calculated is in good agreement with that obtained experimentally. The qualitative agreement of this simple model with experiment provides strong evidence that a transition to the $\tilde{B}^{1}\Delta_{s}(A')$ state is responsible for the photodissociation of N₂O at 205.47 nm as predicted by Winter.²² The influence of rovibronically allowed transitions in molecules is by no means unique to the photodissociation of N₂O. In fact, it is most likely a general phenomenon in polyatomic molecules which exhibit a symmetry that can be broken by nuclear motion. In a recent paper by Person et al.,²⁴ the effect of the rovibronic coupling from C_{3v} to C_s symmetries in CF₃I was studied by a temperature dependence of the $I({}^{2}P_{i})$ branching ratio from CF₃ I photodissociation at 248 nm.

SUMMARY

(a) O(¹*D*) from O₂ at 157.6 nm has $\beta = 2$.

(b) $O({}^{1}D)$ from NO₂ at 205.47 nm has a β value of 1.3 and translational energy distribution that peaks at 0.12 eV. The complementary NO photofragment is rovibrationally excited at the averaged vibrational level of three.

(c) O(¹D) from N₂O at 205.47 nm has $\beta = 2$ and translational energy of 2.32 \pm 0.08 eV. Most of the excess energy goes into translational motion.

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