Photodissociation of the NO dimer: rotational energy distribution and alignment of the NO($B^2\Pi$) fragments

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We have determined the rotational distribution and the rotational alignment $A_{\delta}^{(2)}$ of the photofragment NO(B ²Π; $\nu=0$) produced on the photodissociation of the NO dimer at 193 nm. The rotational spectrum observed can be reproduced under the assumption of a bimodal distribution with dual rotational temperatures, 400 and 1400 K. This Boltzmann-like distribution indicates the occurrence of energy randomization among the low-frequency van der Waals modes, in spite of the dissociation along the repulsive energy surface. The observed negative value of the rotational alignment $A_{\delta}^{(2)}$, around -0.1, implies that the NO dimer preferentially dissociates via a planar geometry. The excitation of the out-of-plane motion due to the energy randomization may offer an explanation for the deviation of $A_{\delta}^{(2)}$ from the limiting value -0.4 (complete planarity).

1. Introduction

The chemistry of van der Waals molecules has been developed in this decade and the various features appearing in the dissociation of van der Waals bondings have been one of the main subjects of recent research [1]. A number of studies on the rate of the vibrational predissociation have been reported [2], and even the vibrational-mode dependence of the dissociation rate has been studied using both the picosecond technique [3] and high-resolution spectroscopy [4]. However, very little information is available and the photodissociation dynamics of these molecules in terms of product-state distributions [5,6] and the vector correlations [7]. The vector correlations offer reliable information to clarify the stereochemical aspects of the dissociation dynamics [8,9]. For example, the v-J correlation in the photodissociation of H_2O_2 showed that the two OH fragments recoil while rotating like a cart-wheel owing to the excitation of the torsional motion [10]. The measurement of the vector correlations in the dissociation of van der Waals molecules, which possess floppy or large-amplitude motions, may reveal novel features of the photodissociation dynamics.

In the present investigation, we applied this technique to the photodissociation of a van der Waals molecule, $(NO)_2$. The NO dimer has cis planar geometry [11] and the dissociation energy is estimated to be 560–710 cm⁻¹ in the ground state [7,12]. The two different paths were found to exist in the photodissociation at 193 nm [13],

$$(NO)_2 + h\nu \rightarrow NO(A^2\Sigma^+) + NO(X^2\Pi), \qquad (1)$$

$$\rightarrow \text{NO}(B^2\Pi) + \text{NO}(X^2\Pi) . \tag{2}$$

Previously, we measured the emission spectra of the photofragments NO(A ${}^{2}\Sigma^{+}$) and NO(B ${}^{2}\Pi$) between 200 and 300 nm and determined the vibrational and rotational distributions. The vibrational

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distribution of the NO(B) fragments was found to be partly inverted [13]. In this spectral region, however, A-X vibrational bands were predominantly observed and, hence, the rotational distributions of the NO(B) fragments were estimated only approximately.

In this study, the emission spectrum was measured at wavelengths longer than 300 nm where the B-X (0-8) transition was almost free from other bands and, consequently, the rotational distribution of the v=0 state was determined unambiguously. From the polarization of the emission observed for this transition, the rotational alignment $A_0^{(2)}$ was also determined. Based on the rotational distribution and the rotational alignment $A_0^{(2)}$, we discuss the photodissociation mechanism of the dissociation path (2).

2. Experimental

The experimental apparatus used in the present study is schematically shown in fig. 1. The NO dimer was produced by expanding a 15% NO/He (NO: Nippon Sanso 99.99%, He: Teisan 99.99995%) mixture from a pulsed nozzle with a 400 μ m orifice. The stagnation pressure was about 1.7 atm. The 193 nm light from an ArF excimer laser (Lambda Physik EMG 53 MSC) was used for the photolysis. The pulse energy was about 30 mJ. The laser beam passed through a lens (f=500 mm) and was introduced into a vacuum chamber while being off-focused at the photolysis region. The nozzle orifice and the laser light were kept 12 mm apart to attain the collisionless condition in a free jet.

The chemiluminescence from the photofragment was collected by a lens system from the direction perpendicular to the laser beam, dispersed by a 25 cm monochromator (Nikon P-250) and detected with a photomultiplier tube (Hamamatsu R928). The resolution of the monochromator was set at 0.09 nm in the measurement of the photofragment rotational spectrum. The rotational lines were only partially separated at this resolution. The emission signal was processed by a boxcar integrator and an A/ D converter and stored in a microcomputer. The intensity of the laser was also monitored by a photodiode and used to normalize the emission signal.

For the polarization measurements, the unpolarized light from the ArF excimer laser was passed through a pile of ten Suprasil plates set at the Brewster angle in order to obtain linearly polarized light. The degree of polarization was about 95%. The direction of the electric vector E, which defined the Zaxis of the laboratory frame, was set perpendicular to the direction of the observation. To measure the polarization of the emission, we placed a sheet of polarizer (Polaroid HNP'B) in front of the monochromator. The direction of the polarization vector \boldsymbol{s}_{d} could be changed by rotating the polarizer. We also inserted a depolarizer (Sigumakouki) between the polarizer and the monochromator slit to eliminate the effect of polarization dependence of the monochromator sensitivity. The depolarizer axis was rotated exactly in accordance with the polarizer axis \boldsymbol{e}_{d} so that the completely depolarized light entered into



Fig. 1. Schematic diagram of the experimental apparatus used in the polarization measurement. The Z-axis is parallel to the electric vector of the ArF excimer laser light. L_n : lens; S_n : Suprasil plate set at the Brewster angle; I: iris; P: polarizer; D: depolarizer; M: mono-chromator; PM: photomultiplier tube; N: pulsed nozzle.

the monochromator. For this measurement, the slit width of the monochromator was broadened a little in order to earn the signal intensity weakened by the polarizer.

We performed several sets of experiments with two electric vectors being parallel $(E || \mathbf{e}_d)$ and perpendicular $(E \perp \mathbf{e}_d)$ alternatively at various fixed wavelengths. The pair of intensities I_{\parallel} and I_{\perp} were obtained each time by integrating the emission signals during 2400 laser shots. This process was repeated several times and finally I_{\parallel} and I_{\perp} were determined by averaging. Using these signal intensities, we calculated the anisotropy of the polarization R and deduced the rotational alignment $A_0^{(2)}$ by the standard method [14].

3. Results and discussion

3.1. The rotational distribution

Fig. 2a shows the emission spectrum of the NO(B-X) 0-8 band, which consists of four main rotational branches. In this region, no other vibrational bands were observed except for the band-head region near 320 nm where the tail of the NO(B-X) 2-9 band overlaps. The figure clearly shows that this spectrum has a high J component, which we were not able to observe at the shorter wavelength because of the strong NO(A-X) transitions.

Fig. 2b represents the spectrum of the same region simulated under the assumption of the dual rotational temperatures, 400 and 1400 K, with the population ratio of 1:2. In order to calculate the energy levels of the B²II and X²II states and also the Hönl-London factors, we utilized the molecular constants together with the formula given by Hill and Van Vleck [15,16]. These two spectra show good agreement. The possible error in the rotational temperature was ± 100 K in both components.

The available energy, E_{avl} , for the products NO(B) + NO(X) in the photodissociation at 193 nm can be expressed as

$$E_{\rm avt} = h\nu(193\,\rm{nm}) - D_0 - T_0(\rm{NO}(B)), \qquad (3)$$

where D_0 is the dissociation energy of (NO)₂ in the ground state and $T_0(NO(B))$ represents the electronic energy of the B² Π state measured from the



Fig. 2. (a) The emission spectrum of NO(B-X) 0-8 band observed in the photodissociation of $(NO)_2$ at 193 nm. The asterisks (*) indicate the peaks at which the polarization of the emission was measured. (b) The simulated NO B-X emission spectrum under the assumption of a bimodal distribution with dual rotational temperatures, 400 and 1400 K, with the population ratio 1:2.

ground state. From the available experimental data, E_{avl} was evaluated to be about 5700 cm⁻¹. Using this amount of available energy, we calculated the rotational distribution on the basis of the phase-space theory (PST) [17]. The resulting distribution can be approximately expressed as a Boltzmann distribution with the rotational temperature of 1800 K. This distribution is similar to that observed, which probably indicates that energy randomization occurs during the dissociation. However, the fact that the vibrational distribution is partly inverted [13] and the rotational distribution has two components means that some restrictions on the statistical energy flow are also operative in the dissociation process.

3.2. The rotational alignment

By using a set of emission intensities, I_{\parallel} and I_{\perp} , observed at a given wavelength, we determined the anisotropy R on the basis of the relation

$$R = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \,. \tag{4}$$

Generally, the relations between the alignment $A_0^{(2)}$ and the emission intensity of each rotational transition are given as [14]

$$I_{\parallel}(J') = \frac{1}{3}I_{0}(J') \times [1 + g(J')h(J', J'')A_{0}^{(2)}(J')], \qquad (5)$$

$$I_{\perp}(J') = \frac{1}{3}I_0(J') \times \left[1 - \frac{1}{2}g(J')h(J', J'')A_0^{(2)}(J')\right],$$
(6)

where h(J', J'') is a geometrical factor and g(J') corrects the hyperfine depolarizing effect by the nuclear spin *I*, which at low *J'* has an important influence. $I_0(J')$ is expressed as

$$I_0(J') = S(J', J'') P(J') f(\lambda) , \qquad (7)$$

where S(J', J'') stands for the Hönl-London factors, and P(J') is the population at the rotational level J' in NO(B) and considered to be identical to the result of the simulation. The slit function of the monochromator $f(\lambda)$ is assumed to be Gaussian with a fwhm of 0.12 nm.

Since the emission intensity obtained in the present study includes several rotational transitions because of the low dispersion of our monochromator, the denominator and the numerator of eq. (4) can be written as

$$I_{\parallel} + 2I_{\perp} = \sum I_{\parallel}(J') + 2\sum I_{\perp}(J') = \sum I_{0}(J'), \quad (8)$$

$$I_{\parallel} - I_{\perp} = \sum \frac{1}{2} g(J') h(J', J'') A_0^{(2)}(J') I_0(J') .$$
 (9)

The summation is carried out over J' terms included in a given peak of the emission. If $A_0^{(2)}(J')$ is constant, independent of J' within a narrow range of J', and takes the same value for both spin-orbit states ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$, $A_0^{(2)}$ can be replaced by an average value as

$$I_{\parallel} - I_{\perp} = \frac{1}{2} \bar{A}_{0}^{(2)} \sum g(J') h(J', J'') I_{0}(J') . \qquad (10)$$

Using the above relations, we can rewrite R as

$$R = \frac{\bar{A}_0^{(2)} \sum g(J') h(J', J'') I_0(J')}{2 \sum I_0(J')}.$$
 (11)

We utilized this formula to determine the rotational alignment $\bar{A}_0^{(2)}$. The alignment thus obtained is the average among several rotational levels observed, and the actual value for each J' level may be different from each other. Nevertheless, we assume that the values are the same for these several J' levels, which seems to be correct because the alignments $\bar{A}_0^{(2)}$ of a given J' determined at different wavelengths coincide within one-half of the standard deviation. Thus, the average of these $\bar{A}_0^{(2)}$ values is adopted as the actual $\overline{A}_0^{(2)}$ of a given J' level. Fig. 3 shows the alignment $\bar{A}_0^{(2)}$ of the NO(B; v' = 0) photofragments as a function of rotational angular momentum J'. The error bars represent the standard deviation as a result of several measurements. For all J', the alignment $\bar{A}_0^{(2)}$ is negative and shows weak J' dependence, which seems to justify the above assumption. At low J' the value is bout -0.05, whereas at high J' it reaches -0.15. These values are much smaller in magnitude than the limiting value for the perpendicular case, i.e. -0.4.

3.3. The photodissociation mechanism

The NO dimer has C_{2v} symmetry [11]. The excitation at 193 nm corresponds to $a_1 \rightarrow b_2$ promotion in molecular orbital description. As a result, the transition dipole moment μ_{abs} is parallel to the N-N van der Waals bond. The value of the alignment $A_0^{(2)}$ then indicates that the rotational angular momentum vector J is roughly perpendicular to μ_{abs} , or to the molecular plane in the case of the planar NO dimer. This implies that the coplanar photodissociation occurs preferentially; as the N-N van der Waals bond is breaking, two NO photofragments recoil while rotating in the plane of the parent molecule. However, the alignment deviates to a considerable extent from the limiting value. The reason for this will be discussed in the following:

First, when the photo-excited parent molecule rotates before the dissociation, the correlation between J and the Z-axis of the laboratory frame reduces, resulting in the deviation of the rotational alignment from the limiting value, -0.4. In the case of a pro-



Fig. 3. The rotational alignment $\bar{A}_{\delta}^{(2)}$ of the NO(B ${}^{2}\Pi, \nu'=0$) photofragment as a function of rotational quantum number J'. Error bars represent the standard deviation.

late-top molecule having an in-plane transition dipole vector along the figure axis, the value of the alignment converges to -0.1 in the limit of the infinite dissociative lifetime [18]. Although (NO)₂ is a nearly prolate-top molecule, the alignment in the present study is even larger than -0.1 at low J. Since the absorption spectrum of (NO)₂ is reported to be much broader and structureless [12], it is not plausible that (NO)₂ has a long dissociative lifetime in the electronic excited state. Therefore, the rotation during the lifetime of the excited state cannot be sufficient to explain the reduction in the alignment $A_0^{(2)}$.

Secondly, it is possible for the out-of-plane motion (ν_6) to play an important role in the dissociation process. In the ground state, this vibrational mode has the lowest frequency, 88.2 cm⁻¹, among all six vibrational modes [19]. This motion can cause angular momentum parallel to the N-N van der Waals bond. If this couples with the coplanar dissociation process, the distribution of the rotational angular momentum vector of the photofragment will tilt from the direction perpendicular to the molecular plane. In the jet condition, however, the vibrational excitation in the ground state might hardly occur, although we have no quantitative information about it. Therefore, the contribution of the original out-of-plane motion does not give a sufficient explanation.

The third possibility is concerned with the poten-

tial energy surface of the excited state. Although it is repulsive in the direction of the N-N stretching vibration, the surface may be very flat or rather have a shallow double minimum in the direction of the out-of-plane vibration. That is, the electronically excited NO dimer is not necessarily planar. In that case, the out-of-plane motion is enhanced in the course of the dissociation along the repulsive potential surface. As a result, the value of the alignment $A_0^{(2)}$ could deviate from the perpendicular limit as shown in fig. 4. At the same time, the excess energy may be distributed among various low-frequency van der Waals modes, which causes the quasi-statistical fast energy randomization among the degrees of freedom except for the N-O stretching modes. This fact may partially explain the reason for the Boltzmann-like rotational energy distribution.

Based on the above mechanism, we can also ex-



Fig. 4. Schematic representation in the photodissociation process of $(NO)_2$. The excitation of the out-of-plane motion produces the angular momentum parallel to the N–N van der Waals bond. This causes the rotational angular momentum of the photofragment to tilt from the direction perpendicular to the molecular plane.

plain the J-dependence of the alignment $A_{\lambda}^{(2)}$. At high J, the main part of the torque is produced by the N-N bond cleavage along the steep repulsive potential energy surface and, hence, J tends to be perpendicular to the molecular plane. On the other hand, at low J, the contribution from the out-of-plane vibration becomes relatively large and causes J to tilt towards the molecular plane, that is, it reduces the alignment $A_{\delta}^{(2)}$ from the perpendicular limit. Futhermore, the J-dependence of the alignment could also be interpreted from the dependence of the lifetime on J. Since the repulsive force acting on the N-Nbond creates both the rotational and translational motion, the photofragments with larger J must recoil at higher speed as well. In other words, the photofragment with larger J has a shorter lifetime and, hence, the alignment is less reduced. The observed trend in the J-dependence of the alignment is in accordance with these considerations.

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