REACTION BETWEEN ELECTRONICALLY EXCITED SPECIES: O(¹D₂)+NO^{*}₂→NO(A)+O₂

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The high-intensity laser permits the study of reactions between electronically excited species. The laser irradiation of NO_2 generated NO_2^* by one-photon excitation and $O(^{1}D)$ by two-photon dissociation. These two species react with each other, producing electronically excited NO(A). The product energy distribution was nearly statistical, indicating the possible presence of a long-lived collision complex.

1. Introduction

The reactions between electronically excited species are usually difficult to study in the laboratory because of the short lifetime due to quenching and hence the small stationary concentration under the usual experimental conditions. However, such reactions must play important roles in strong laser fields where the high photon density sometimes favors the population of electronically excited species over ground-state molecules. In the liquid phase, the reactions between electronically excited species such as triplet-triplet annihilation have been reported [1]. We can expect that reactions between electronically excited species may reveal a new feature of chemical kinetics.

In the present investigation the reaction between two electronically excited species, $O(^{1}D)$ and NO_{2}^{*} , was studied. Both species are known to be constituents of the stratosphere, though the importance of the reaction has not yet been assessed. The laser excitation of NO_{2} easily produces electronically excited NO_{2}^{*} in high concentration. Further increase of the laser intensity enables NO_{2}^{*} to absorb one more photon and to dissociate into $O(^{1}D) + NO(X)$. Thus, the reaction between NO_{2}^{*} and $O(^{1}D)$ can have a good chance to occur.

Concerning the multiphoton photolysis of NO₂, Bigio et al. [2] studied the vibrational distribution of NO(X) produced by the two-photon dissociation of NO₂ at 450 nm. They found that the vibrational

indicates on the basis of energy balance that the counterproduct must be the $O(^{1}D)$ atom with 190 kJ/mol electronic energy. Recently, Shibuya et al. [3] observed the formation of highly vibrationally excited $O_2(X)$ during the multiphoton photolysis of NO₂ and attributed this to the reaction between NO₂ and $O(^{1}D)$ generated by the three-photon dissociation of NO_2 . On the other hand, Jusinski et al. [4] claimed that the reaction between $O(^{1}S)$ and NO_{2} must be responsible for the production of highly vibrationally excited O_2 . They proposed that $O(^1S)$ is formed by the four-photon photolysis of NO₂. During the study of $O(^{1}D)$ reaction using NO₂ photolysis, we observed the y band emission from electronically excited NO(A). From the evidence given below, it is concluded that the emission originates from the reaction between two electronically excited species, $O(^{1}D)$ and NO_{2}^{*} . The product energy distribution and its mechanistic implication is also presented in this Letter.

levels higher than v'' = 2 are not populated. This fact

2. Experimental

The photolysis was carried out in a conventional reaction cell containing 2 Torr of NO₂. In some experiments, NO₂ was made to flow slowly so as to avoid the accumulation of the reaction product. A dye laser (Molectron DL14P) pumped by an exci-

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mer laser (Lambda Physik EMG 50) provided a laser beam of about 1 mJ, which was further focused into the center of the photolysis cell with a quartz lens of 150 mm focal length. The electronically excited NO(A) was monitored by the γ band emission. The emission was dispersed by using a 25 cm monochromator (Nikon P-250) and detected by a solarblind photomultiplier (Hamamatsu R166). The signal was fed into a home-made boxcar integrator and stored on a disk through a microcomputer. The vibrational distribution of NO(A) was evaluated by simulating the observed spectrum using the reported Franck-Condon factors [5].

3. Results and discussion

3.1. The formation of NO(A)

Fig. 1 shows the LIF spectrum of NO₂ taken by monitoring the emission between 230 and 310 nm (Corning filter 7-54+R166 photomultiplier response). The sharp structure is due to the two-photon resonance excitation of the ground-state NO(X, v'' = 1), which is formed by the photolysis of NO₂ or the reaction O(¹D, ³P)+NO₂. The peaks observed above 478 nm cannot be assigned at present ^{#1}. In addition to these sharp peaks, a broad background is observed even at the off-resonance

*1 Matsumi et al. [6] found the one-photon LIF of O₂ B-X (2-23) in this region. However, the unassigned peaks observed in the present experiment do not coincide with them.



Fig. 1. The excitation spectrum of NO_2 . Only the ultraviolet emission (230–310 nm) was monitored. The presence of broad background emission in addition to the sharp resonant peaks should be noted.



Fig. 2. The dispersed fluorescence spectrum of NO₂ excited at 475 nm. The spectral resolution is 3.0 nm. This emission is assigned as the NO γ band (A² Σ ⁺-X² Π).

wavelength. This broad background decreases towards longer wavelength.

Fig. 2 shows the emission spectrum obtained upon excitation of 2 Torr NO₂ at 475 nm. This wavelength does not coincide with any resonance lines of NO nor any unassigned peaks; purely background emission was dispersed in order to elucidate the nature of the emission. The spectrum observed was unambiguously assigned as the γ band emission from the electronically excited NO in the A ${}^{2}\Sigma^{+}$ state.

A detailed look in the short-wavelength region (fig. 5) reveals that the 3-0 transition is clearly present though faint. This indicates that the process producing NO(A) should have its threshold around the energy of the NO(A, v'=3) level.

3.2. The origin of the NO(A) emission

The one-photon photolysis of NO₂ below 144.8 nm can cause the decomposition into O(³P) + NO(A) on energetic grounds and actually the emission from NO(A) was observed [7]. The three- and four-photon thresholds for this path correspond to 434.4 and 579.2 nm, respectively. If the direct multiphoton photolysis is responsible for the formation of NO(A), the photolysis at 475 nm would supply 15000 cm⁻¹ excess energy, resulting in the formation of NO(A) with vibrational quanta up to v' = 6. Since the present experiment gave no indication of the presence of such a highly vibrationally excited NO(A), one can exclude the possibility of the direct formation of NO(A).

The second possibility is the chemical reaction, $O(^{1}D) + NO_{2}$. The photolysis of NO₂ at 475 nm can yield the $O(^{1}D) + NO_{2}$. The photolysis of NO₂ at 475 nm can yield the $O(^{1}D)$ atom at the two- or threephoton level. Shibuya et al. [3] actually observed the reaction of NO₂ with $O(^{1}D)$ and suggested that the $O(^{1}D)$ atom was generated by the three-photon dissociation of NO₂ under high-pressure (above a few Torr) conditions. However, this reaction cannot provide electronically excited NO(A); additional energy of 12200 cm⁻¹ is necessary to reach the energy level NO(A, v' = 0) + O₂(X, v'' = 0).

The third possibility is the reaction between $O(^{1}S)$ and NO_{2} . From the heat of formations at 0 K for relevant chemical species, the exothermicity of the following reaction can be evaluated:

$$O(^{1}S) + NO_{2} \rightarrow O_{2} + NO(A) ,$$

$$\Delta H_0 = -68.46 \text{ kJ/mol} . \tag{1}$$

The exothermicity of reaction (1) falls 1200 cm^{-1} short of the production of NO(A, v' = 3). Therefore, the maximum allowed vibrational level for NO(A) must be v' = 2 even if the internal energy of NO₂ at room temperature is taken into account.

Finally, the reaction between $O({}^{1}D)$ and electronically excited NO^{*}₂ must be considered. In this case, the energetics depends on the amount of energy possessed by the excited NO^{*}₂. When NO₂ is excited at 475 nm, the excess energy liberated by the reaction is:

$$O(^{1}D) + NO_{2}^{*} \rightarrow O_{2} + NO(A)$$
,

 $\Delta H_0 = -105.88 \text{ kJ/mol.}$ (2)

This exothermicity can produce the vibrationally excited NO(A) up to v' = 3 and the result observed is in good agreement with the expectation.

3.3. The pressure dependence of the NO(A) emission

Fig. 3 shows the NO₂ pressure dependence of the γ band emission intensity. The photolysis wavelength was fixed at 475 nm. The absorption by NO₂ at this wavelength along the reaction cell deduced the





Fig. 3. The dependence of the emission intensity on the NO_2 pressure. The excitation wavelength was fixed at 475 nm. The second-order dependence indicates the contribution of two NO_2

molecules to the process of NO(A) formation.

intensity of the photolysis light at the center of the cell. This reduction was corrected by using the absorption coefficient at 475 nm [8]. An additional correction was carried out for the quenching of the emitting state NO(A) by NO₂ using the reported quenching rate constant, 3.7×10^{-10} cm³ molecule⁻¹ s⁻¹ [9]. Fig. 3 thus obtained demonstrates that the dependence can be expressed in the form

$$I_{\rm emission} = C[NO_2]^{2.0 \pm 0.05}$$

The expression indicates that two NO_2 molecules must be involved in the NO(A) emission as expected from the proposed mechanism; one for the photolytic production of electronically excited oxygen atoms and the other NO_2 as one of the reactants.

3.4. The threshold for NO(A) production

Fig. 4 displays the decrease of the background NO(A) emission toward longer wavelength. The spectrum was taken with low laser powers because



Fig. 4. The excitation spectrum of NO₂. The laser intensity was much attenuated so as to suppress the contribution from the resonant excitation. The threshold observed around 490 nm is in good agreement with the two-photon threshold (488 nm) for yielding the O(1 D).

the ratio of the resonance emission to the background decreases with decreasing laser intensity. The background emission almost vanishes at around 490 nm. This is partly due to the decrease of the NO_2 absorption but mainly to the inefficiency of the photolysis in producing $O(^1D)$ or $O(^1S)$.

The endothermicity of the dissociation of NO₂ into $O({}^{1}S) + NO(X)$ at 0 K is 704.8 kJ/mol and hence the three-photon threshold for producing $O({}^{1}S)$ is 509.2 nm. On the other hand, the dissociation into $O({}^{1}D) + NO(X)$ requires 490.4 kJ/mol, which could be supplied by the two photons of 487.8 nm or shorter. The observed threshold of 490 nm is in good agreement with that of the $O({}^{1}D)$ scheme. The minor discrepancy may be rationalized by taking account of the thermal energy possessed by NO₂ at room temperature.

3.5. Quenching of the emission by N_2

Since molecular nitrogen quenches the $O({}^{1}D)$ atom very efficiently while it hardly gives any effect on the $O({}^{1}S)$ atom, the addition of N₂ into the system enables us to tell which species is responsible for the observed emission. Experimentally, the addition of N_2 sharply decreases the emission intensity, indicating that NO(A) is most likely generated by the reaction of O(¹D) with NO^{*}₂. The Stern-Volmer plot for the N₂ addition did not obey a linear relation but showed a 1.4th power dependence. This implies that the N₂ molecule not only quenches the O(¹D) atom but also partly deactivates the electronically excited NO^{*}₂ during the up-pumping process.

3.6. The vibrational distribution in NO(A)

In order to derive the initial vibrational distribution of NO(A), the emission in the 190–230 nm region was examined in detail. Since the presence of 2 Torr NO₂ in our experiment could cause the vibrational relaxation, its effect should be estimated. Although the rate constant for the vibrational deactivation of NO(A) by NO₂ has not been reported, it must be of the order of 10^{-11} cm³ molecule⁻¹ s⁻¹ on the basis of the rate constant for NO(X), 1.6×10^{-11} cm³ molecule⁻¹ s⁻¹ [10]. In this case, the vibrational relaxation of nascent NO(A) during the lifetime of the NO(A) state (200 ns) cannot be significant at the NO₂ pressure of 2 Torr. Fig. 5 represents the observed emission spectrum together with



Fig. 5. The dispersed fluorescence spectrum of NO(A) emission (475 nm excitation). The spectral resolution is 3.0 nm. (a) The observed spectrum. (b) The simulated spectrum using the detection sensitivity and the vibrational distribution given in the text.

the best-fit simulation. The rotational temperature of each vibrational level was assumed to obey the statistical calculation. The best fit to the observed emission was attained for the vibrational distribution, 1.0:0.24:0.06:0.02 for v' = 0-3. These figures show fair agreement with the result of the simple statistical calculation (the phase-space theory of Light [11]) which gave the distribution, 1.0:0.39:0.11:0.01 for v' = 0-3.

The vibrational distribution generally reflects the lifetime of the collisional state. If the collision complex $O-NO_2$ has a long lifetime, sufficient for energy randomization within the adduct, then the statistical vibrational distribution should be observed. In this

sense, the derived vibrational distribution suggests a fairly long lifetime of the collision complex, NO³.

3.7. Symmetry considerations on the reaction path

In order to infer the detailed reaction path for

$$O(^{1}D) + NO_{2}(1^{2}B_{2,1})$$

$$\rightarrow NO(A^{2}\Sigma^{+}) + O_{2}(X^{3}\Sigma_{g}^{-}),$$

the symmetry correlation between reactants and products was examined with the aid of the Wigner -Witmer procedure [12]. It was found that $O(^{1}D) + NO_{2}(1^{2}B_{2})$ can correlate with $NO(A) + O_{2}(X)$ only when the O atom approaches NO_{2} within the plane of NO_{2} while conserving C_s symmetry. No such reaction occurs if the O atom attacks NO_{2} along any paths on the symmetry plane bisecting NO_{2} . Therefore, the reaction proceeds most probably via a planar adduct NO_{3}^{*} with a long lifetime.

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