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Crossed-beam study of the reaction of van der Waals molecule $H+(NO)_2$

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Chemiluminescent reaction $H + (NO)_2 \rightarrow HNO^* + NO$ was studied under single collision condition. The built-in third body much enhanced the formation of $HNO^*(A\ ^1A\ '')$ in bimolecular relatively large population in bending vibration (v_3) as compared with the HNO^* produced from the termolecular recombination, $H + NO + M$. This apparent excitation in bending mode can be attributed to the smaller internal energy of HNO^* produced in $H + (NO)_2$ reaction. Higher rotational states of the (001) vibration, if formed in $H + NO + M$ reaction, most probably suffer rapid losses to $X\ ^1A\ '$ state by internal conversion. The lower energy content of HNO^* formed in $H + (NO)_2$ reaction suppresses this internal conversion and hence the relative population of the (001) state becomes large. The reaction probability was also measured as a function of collision energy and the result indicates the absence of the reaction barrier.

INTRODUCTION

The recombination reaction

$$H + NO \rightarrow HNO^* \qquad (1)$$

has been widely studied under multiple collision conditions[1-6] and chemilumicescence of $HNO(A\ ^1A\ '')$ has been measured for various third bodies. Several theoretical studies were also carried out to determine the potential energy surfaces of the lowest three electronic states, $X\ ^1A\ ',A\ ^1A\ ''$, and $a\ ^3A\ ''$.[7-12] According to these studies, the ground state fragments H and NO cannot correlate with the A state except via a potential barrier; several values are proposed for the height of this barrier. The presence of such a barrier must significantly lower the probability of reaction (1) to occur. The vibrational level structure of the A state also suggests the presence of potential barrier. That is, the vibrational levels of the A state was found to continue above the predissociation limit. Because of this barrier, the indirect reaction path for forming the A state has been proposed instead of the direct barrier crossing.

Clyne and Thrush[1] measured the rate constant of reaction (1) at several temperatures and noticed negative temperature dependence of the rate constant. They concluded that the reaction proceeds without energy barrier and proposed the indirect mechanism in which the intersystem crossing occurs at short internuclear distance from initially formed $a\ ^3A\ ''$ state to $A\ ^1A\ ''$ state.

Another important information about the interaction among the three lowest lying states of HNO was given by the study of the reverse process, the predissociation of $HNO(A)$. Dixon and co-workers[13] studied the predissociation of HNO molecule by using laser induced fluorescence and observed that the breaking-off energy is a function of J' but not of K' or the vibrational quantum number. They concluded that the internal conversion from the A state to X state plays the key role in the predissociation and the crossing occurs at linear structure in which the A and X states become degenerate.

In order to analyze the detailed mechanism of the termolecular recombination reaction, the control of the third-body collision is very important, because the third-body can play a key role not only for stablizing the nascent HNO (a or X state) but also for surface crossing. Single collision of the third body could not be assured for the experiments using the traditional flow condition. In contrast, the built-in third body technique, using reactants weakly bonded with third-body molecule provides a unique opportunity to study the role of third body under single collision condition. In the previous paper[14] we applied this method to $O + (NO)_2$ reaction and demonstrated its potential power for the study of termolecular reactions.

In this paper, we wish to report the experimental study of the reaction

$$H + (NO)_2 \rightarrow HNO^* + NO, \qquad (2)$$

by using crossed molecular beams. Chemiluminescence of $HNO(A)$ was measured and the vibrational distribution of HNO from reaction (2) was compared with that of HNO from the third-body reaction. The reaction probability was also measured as a function of collision energy.

EXPERIMENTAL

Experiments were carried out by use of a crossed molecular beam apparatus whose detail was described in the previous paper.[14] The beam of the NO dimer was formed by supersonic expansion of a gas mixture of about 10% NO in He through a nozzle of 0.03 mm diameter. This beam was collimated by a conical skimmer of 0.94 mm diameter. The concentration of the NO dimer was monitored with a quadrupole mass spectrometer which was located downstream of the beam. Hydrogen atom flow was issued effusively from a Teflon nozzle of 1.0 mm diameter, and collimated by a skimmer of 1.0 mm diameter. Both beams were crossed with each other at right angles. Whole system was differentially pumped and typical pressure of the reaction chamber during the experiments was less than 5×10^{-5} Torr.
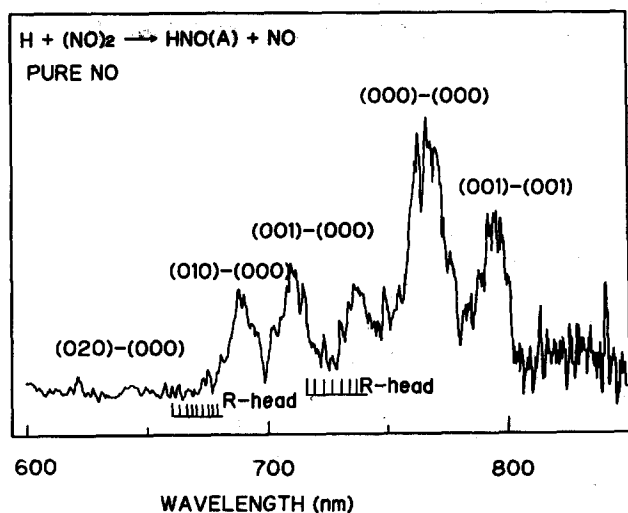
FIG. 1. Chemiluminescence spectrum of HNO produced from reaction H + (NO)₂. Intensity of emission was corrected by sensitivities of monochromator, lens system, and photomultiplier. Assignments of vibronic bands are also shown.

The emission from the crossing region was collected with a lens-optical fiber system, dispersed by a monochromator (NIKON P-250) and detected by a photomultiplier tube (HAMAMATSU R-649). The sensitivity of the detection system (lens, fiber, monochromator and photomultiplier) was calibrated as a function of wavelength by use of a standard lamp.
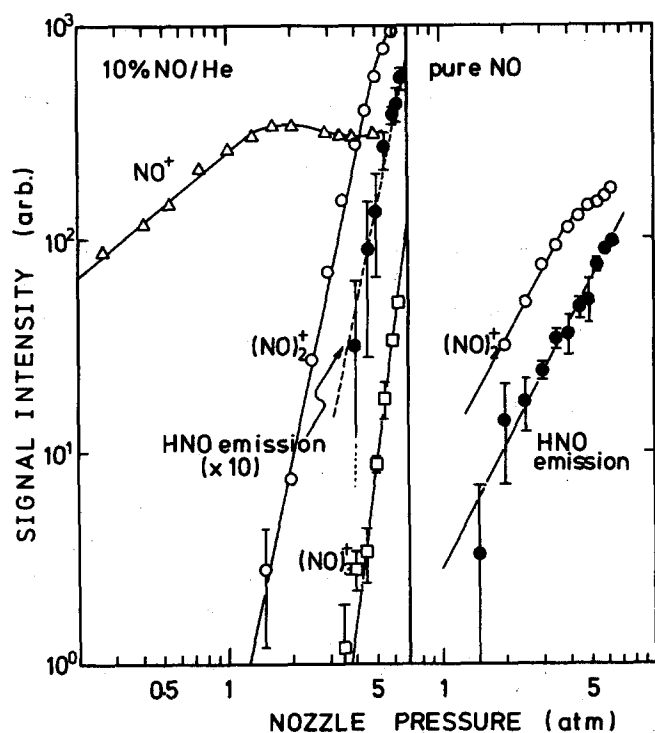

FIG. 2. Nozzle pressure dependence of HNO chemiluminescence intensity. Ion intensities of NO⁺, (NO)₂⁺, and (NO)₃⁺ are also shown as functions of nozzle pressure. (a) Mixture of 10% NO in He was used for source of NO dimer. (b) Pure NO was used.

Sample gases, He(99.998%), NO(99.9%), and H₂ (99.9999%), were purchased from Japan Oxygen Co. and used without further purification. Various gas mixtures were prepared prior to the experiments.

RESULTS AND DISCUSSION

Origin of the chemiluminescence of HNO(A $^1A''$)

Figure 1 shows the spectrum of the emission observed at the crossing region. Each peak of this spectrum can be assigned as the vibronic band of A $^1A''$–X $^1A'$ transition of HNO. In order to identify the source reaction to form HNO(A), the intensity of the chemiluminescence was measured as a function of the nozzle pressure. In this measurement, total emission was collected without the monochromator.

Figure 2 shows the results, together with the pressure dependence of the intensities of NO⁺, (NO)₂⁺, and (NO)₃⁺ measured by the mass spectrometer. Figure 2(b) shows similar pressure dependence for supersonic expansion of pure NO gas instead of NO/He mixtures. In the latter figure, only (NO)₂⁺ intensity is shown for comparison; the intensity of (NO)₃⁺ was negligibly small. Obviously, in both gas samples, the HNO(A) emission increases in close parallel with the (NO)₂⁺ signal as the nozzle pressure increases.

Generally speaking, the intensity of the cluster ion is not necessarily parallel with the concentration of the cluster, since the electron impact often produces fragment ions from higher clusters. However, concerning the NO dimer, this parallelism was known to be fairly good when the low energy electron impact (20 eV) was used.[14] Therefore, we concluded that the chemiluminescence of HNO is surely produced from the reaction (2),

$$H + (NO)_2 \rightarrow HNO(A\ ^1A'') + NO.$$

Chemiluminescence spectrum and vibrational distribution

Chemiluminescence spectrum shown in Fig. 1 is corrected for the sensitivity of the detection system. The relative sensitivity of the system was measured by use of a standard lamp. Four dominant bands can be seen in this spectrum and the assignment is also given in the figure. For the assignment, vibrational constants tabulated by Jacox[15] were used for the ground state and the values determined by Bancroft et al.[16] and Dalby[17] were adopted for the A state. The vibrational frequencies are 2854 and 2684 cm⁻¹ for ν_1 NH stretching, 1421 and 1565 for ν_2 NO stretching, and 981 and 1501 for ν_3 bending vibrations, in the A and X states, respectively. The dissociation energy, 16450 cm⁻¹, determined by Dixon et al.[13] was used for the calculation.

There are some differences in the intensities of vibrational band between the spectrum of this work and that observed in the termolecular reaction.[3] Although it is not clear that the HNO spectrum reported for the termolecular reaction was calibrated by the sensitivities of detection system, the comparison between relative intensities of two adjacent bands is not unreasonable.

One marked difference can be seen in the relative intensities of the (001)–(000) and (010)–(000) bands. In the

case of the H + (NO)$_2$ reaction, the former band has greater intensity than the latter. The (001)–(001) band also has relatively high intensity and hence the (001) vibrational level must be much populated. Similar features were reported in an early crossed beam study by Ibaraki et al.[18] Since the beam was issued from a cooled nozzle, the NO dimer probably played a dominant role. Therefore, the above trend, i.e., large population in the HNO bending mode, seems to be characteristic of the reaction of the NO dimer. On the other hand, in the termolecular reaction H + NO + M, the (010)–(000) band has higher intensity than the (001)–(000) band. In addition, the K' rotational levels up to the threshold energy are clearly seen for the (000) and (010) vibrational states.

There may be two possible explanations for the difference in the population of the bending mode. The first possibility is the occurrence of two different pathways for reactions (1) and (2), respectively. In the case of H + NO + M reaction, H atom most probably approaches the unpaired p orbital of NO to form the A' state in the initial stage. In contrast, this p orbital is not available in the case of H + (NO)$_2$ reaction because the van der Waals bonding between two NO molecules already utilizes the p orbitals. Therefore, H atom may approach the N atom perpendicularly to the NO dimer molecular plane, and consequently form the A'' state directly. Although the direct formation of the A'' state needs barrier crossing as mentioned in introduction, the reported height of the barrier depends on the calculation and could be as low as a few kcal/mol.[9] In such a case, a new channel may be opened for the dimer reaction with the help of collision energy. There is few information, however, about the feature of the potential energy surface to explain the excitation of the bending mode.

Second, these trends can be explained in terms of the difference in internal energy of HNO(A) produced by these two processes. In the case of termolecular recombination where the stabilizing collision with a third body removes only a small portion of the excess energy, the energy content of HNO(A) is rather high, very close to the dissociation threshold. This must cause the loss of the (001) state owing to the internal conversion or intersystem crossing. On the other hand, in H + (NO)$_2$ reaction, a built-in third body (NO molecule in the present case) closely couples with HNO* molecule during the reaction and hence a rather large portion of the excess energy must be removed. Further, the binding energy of (NO)$_2$ must be always taken away from the system, since this amount of translational energy is requisite for the NO molecule to depart from HNO*. The resulting low energy content of HNO* most probably suppresses the curve crossing from $^1A''$ to $^1A'$ or $^3A''$ state. Thus, the relative population of the (001) state increases in the H + (NO)$_2$ reaction.

High intensity of (001)–(000) band was also observed by Ishiwata et al.[4,5] in the chemiluminescence of HNO ($A\,^1A''$) formed by the two step energy transfer from O$_2$ ($^1\Delta_g$). In their system, electronically excited HNO is first produced in $^3A''$ state and, after vibrational relaxation within the $^3A''$ state, the second energy transfer from O$_2(^1\Delta_g)$ forms HNO* of low internal energy. The resemblance of the

emission spectrum between this reaction and H + (NO)$_2$ reaction supports the interpretation that the population of the (001) state is rapidly lost only when generated in high rotational state.

The rapid curve crossing from the higher rotational state of the (001) level is supported from the different point of view. Dixon and co-workers[13] studied the predissociation of HNO by laser induced fluorescence. They proposed the following predissociation mechanism. The predissociation occurs via a curve crossing from A to X states. Since the bent $A(^1A'')$ and $X(^1A')$ states converge to $^1\Sigma$ state at a linear configuration, the bending vibration which helps the molecule to form linear structure must accelerate the internal conversion. Further, at this vibrational level, the electro-Coriolis coupling favors the internal conversion from higher rotational levels. This mechanism provides an important insight into the depopulation of the (001) level, especially in its higher rotational states. The fluorescence lifetime measurement of HNO($A\,^1A''$) also shows that the excitation of bending vibration enhances the A–X internal conversion rate.[19]

The above explanation, i.e., the higher the energy content, the faster the rate of predissociation, is consistent with the crossed beam study by Yoshimura et al.[20] They detected the chemiluminescence of HNO(A) formed from the two-body recombination reaction under single collision condition. Their spectrum was characterized by the quite weak intensities of the (001)–(000) and (010)–(000) bands. In their condition, no energy stabilizing collision occurs, hence most of the vibrationally excited states of HNO(A) dissociates back to H + NO within the radiative lifetime.

The lack of (020)–(000) band, one of the characteristic feature of the reaction (2), can be explained from the energetic consideration. The bond energy of the NO dimer was recently determined to be 800 cm^{-1},[21] and the reaction of the NO dimer is less energetic by this amount of energy than the reaction of NO. Of course, we must take account of the collision energy, i.e., 283 cm^{-1} for the case of pure NO expansion. The available energy is still not enough to excite the product HNO* to the (020) state.

Translational energy dependence of the reaction probability

As we discussed in the previous section, the X state occurs as the intermediate in the reaction (2). However, if the reaction (2) produces the A state directly, the energy barrier

TABLE I. Velocities of (NO)$_2$ and collision energies are listed for various sources of (NO)$_2$.

	$V_{(NO)_2}$	$E_{collision}$
3.7%NO/H$_2$	2.4×10^5 cm/s	5.9 kJ/mol
3.6%NO/He	1.7×10^5	4.5
10%NO/He	1.5×10^5	4.2
Pure NO	8.0×10^4	3.4
10%NO/Ar	2.4×10^4	3.1
$V_H = 2.5 \times 10^5$ cm/s		
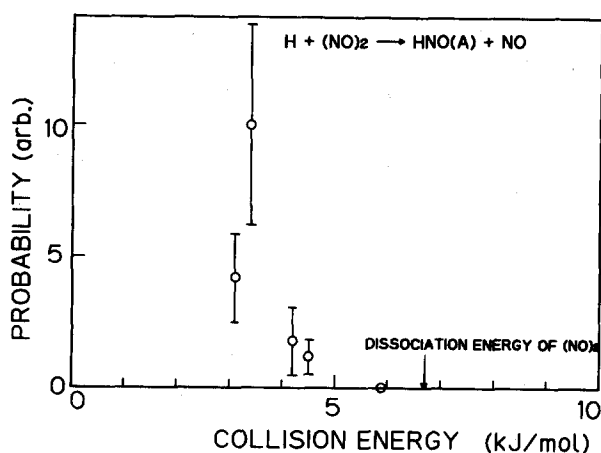
FIG. 3. Reaction probability is plotted as a function of collision energy.

as the NO dimer, the value of the lowest collision energy may suffer from the effect of the reaction H + NOAr and hence should be used only for rough comparison. Apparently, the reaction probability decreases with the increase of the collision energy at most of the energy measured. Only at the lowest energy range the probability seems to increase with the collision energy. The observed decrease of the reaction probability is true, though the collision energy has a rather large uncertainty because of the wide velocity spread in the H atomic beam. This trend is completely in accord with the previous study by Clyne and Thrush. They observed the negative temperature dependence of the recombination rate. The negative collision energy dependence is consistent with the explanation that the $X\,^1A\,'$ state, which correlates with the H + NO reactants without energy barrier, is initially formed.

plays an important role and the reaction probability is expected to increase with the increase of the collision energy. The reaction probability was measured as a function of the collision energy. The collision energy was changed by changing the velocity of (NO)₂. Since thermal H atomic source was used, the velocity distribution of H atom was rather broad. The collision energies for the used mixtures are summarized in Table 1. However, it must be noted that the width of the energy distribution is fairly large.

The reaction probability at each collision energy was determined by use of the same procedure as the previous paper.[14] Briefly, the probability was given by the relation,

$$p = n_{HNO*}/[n_H \cdot n_{(NO)_2} \cdot v_{rel}],$$

where n_{HNO*}, n_H, and $n_{(NO)_2}$ are densities at the crossing region of HNO*, H, and (NO)₂, respectively. The density of HNO* was determined by the intensity of the chemiluminescence of HNO. The density of (NO)₂ was determined by the mass spectrometer and converted to the value at the crossing region by some correction. The relative velocity v_{rel} was determined by the time-of-flight(TOF) measurement of (NO)₂ and the most probable velocity of the thermal H atom.

The results were shown in Fig. 3. Since the supersonic beam of the NO/Ar mixture generates NOAr cluster as well

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