THE INTERNAL ENERGY DISTRIBUTION OF HNO ($\tilde{A}\,^2A''$) FORMED IN THE REACTION OF H + NO

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The chemiluminescence in the reactions of H + NO and D + NO were observed using the crossed diverging-beam method. In either case of HNO or DNO the electronically excited state ($\tilde{A}\,^1A''$) is preferentially populated in the (000) vibrational state. As for the rotational distribution of the (000) vibrational state, the spectral simulation on the present data indicated a room-temperature distribution.

1. Introduction

In the radiative recombination reactions [1–3], the reaction of nitric oxide with hydrogen atom has been one of a few examples which exhibits an electronic emission spectrum with structure, and the assignment of which has been well established [4,5].

Although conventional flow methods have been used to examine the reaction mechanism of the formation of the electronically excited HNO molecule [6,7], direct observation of the primary reactions between the hydrogen atom and nitric oxide is difficult, since the internal energy distribution of HNO may be destroyed by collisional relaxation and also by subsequent secondary reactions [6]. Clearly, it seems to be an advantage to introduce the molecular beam technique into the observation of the initial energy distributions in the chemiluminescent reaction.

We observed HNO chemiluminescence using crossed diverging beams to exclude effects of multicollisional processes and secondary reactions. In both reactions of H + NO and D + NO, most of the electronically excited products ($\tilde{A}\,^1A''$) were found to be formed in the (000) vibrational ground state while the conventional flow methods have given reaction products in the vibrationally excited states. And the initial rotational distributions of the (000) vibrational state were found to be room-temperature distributions.

2. Experimental

Basically, the apparatus used in the present study was similar to that described previously [8]. Some improvements were given on two points. The pumping speed of the reaction chamber was increased with two 6 inch diffusion pumps to allow the introduction of a large amount of reactant gases. Second, a photomultiplier (Hamamatsu R-943-02) of high quantum efficiency in the wavelength region of 300–900 nm was used for photon counting.

The hydrogen atom is produced by microwave discharge of wet hydrogen [9] and was introduced into the reaction chamber through a teflon nozzle (1.5 mm inner diameter) and collimated with a pick-up aperture (2.0 mm inner diameter) to form the atom beam. Trace amounts of water in hydrogen were confirmed to merely increase the efficiency of hydrogen atom generation in the microwave discharge by gas-phase ESR detection. Nitric oxide is effused from the multichannel nozzle and crosses the hydrogen atom beam at right angles.

The background pressure of the chamber was 1×10^{-6} Torr (1 Torr = 133 Pa) in the absence of the beams and the operating pressure was in the range of a few submilliTorr. It was reported that the material of the reactors strongly influences the gas-phase recombination reactions on the walls [10]. To avoid any wall effects, the wall of the chamber was coated

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with teflon resin. No significant wall effects on the chemiluminescence were observed in the present experiment.

The chemiluminescence of HNO was detected by photon counting. The photon counting system and the monochromator scanning were controlled by a microcomputer. The chemiluminescence was counted for 10 s at each step of 1 nm in the wavelength region from 650 to 900 nm. The scanning was repeated up to thirteen times and the spectrum obtained in each run was accumulated to improve the signal to noise ratio.

To observe the total emission, a glass filter (V-R63) was used in place of the monochromator.

Nitric oxide (99 vol% purity), hydrogen (99.9995 vol% purity), and deuterium (99.5 vol% purity) were purchased from Takachiho Shōji Co. Ltd. and used without further purification.

3. Results and discussion

Fig. 1 shows the chemiluminescent spectrum of HNO at flow rates of 15.0 μmol/s for hydrogen and 1.9 μmol/s for nitric oxide, respectively. Direct measurement of the effective beam intensities in the crossing region was difficult. About one tenth of the flow of reagent gas is estimated to enter the crossing region [11] and the flow rate is presented hereafter instead of the effective beam intensity. The spectrum is assigned to the transition from the first excited state $\tilde{A}\,^1A''$ to the ground state $\tilde{X}\,^1A'$. This spectrum was obtained by the accumulation of thirteen runs. The emissive rate constant of the reaction $H + NO \rightarrow HNO(^1A'')$ at low flow rates in fig. 1 was estimated to be $\approx 10^{-17}$ cm^3 molecule^{-1} s^{-1} (cross section of $\approx 10^{-8}$ nm^2) under the typical experimental conditions that the densities of NO and H at the intersection of the beams are 10^{13} and 10^{11} molecule cm^{-3}, respectively, and the relative velocity of reactants is as thermal. The intensity of the (000)–(000) vibrational band was larger than that of the other bands, such as the (010)–(000) and (001)–(000) bands, by a factor of three. Especially in the case of DNO chemiluminescence, most of the emission is concentrated at the (000) vibrationally ground state of $^1A''$ (fig. 2). As for the total emission, the DNO chemiluminescence was found to be about three times stronger than the HNO chemiluminescence.

When the flow rate of nitric oxide is increased to $\approx$50 μmol/s, which is 25 times greater than the flow rate in fig. 1, the vibrationally excited bands of the HNO chemiluminescence, such as (010)–(000), (001)–(000), and (001)–(001), become dominant as shown in fig. 3A. The normal beam condition is no longer held in this case, where the background pressure is raised by an order of magnitude in pressure. Thus one can expect that other reaction processes in which the NO molecule is involved to form the vibrationally excited products, become dominant under such a high pressure of nitric oxide.

In the crossed diverging beam, the HNO emission should be limited within a volume of $\approx$1 cm^3 owing to its radiative lifetime of $\approx$25 μs [12] and the emission in the intersection of both beams is selectively

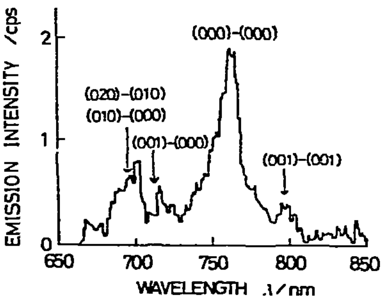

Fig. 1. Emission spectrum of HNO with the spectral resolution of 3 nm. Flow rates of H (H_2) and NO are 15.0 μmol/s and 1.9 μmol/s, respectively.

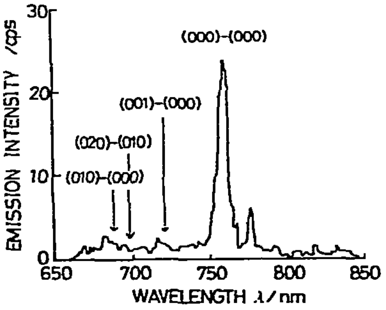

Fig. 2. Emission spectrum of DNO with the spectral resolution of 3 nm. Flow rates of D (D_2) and NO are 20.5 μmol/s and 1.9 μmol/s, respectively. The sharp peak at 775 nm is due to the stray light from the discharge of wet deuterium.

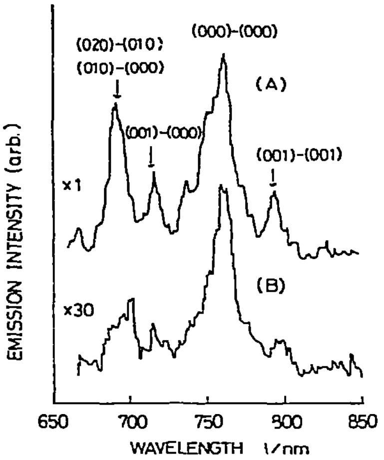

Fig. 3. (A) Emission spectrum of HNO with the spectral resolution of 3 nm. Flow rates of H (H_2) and NO are 15.0 μmol/s and 50 μmol/s, respectively. (B) The spectrum shown in fig. 1.

collected by a concave mirror. In this manner, there is no possibility to observe any emission of HNO due to recombination reactions involving the walls of the reaction chamber.

Wren and Menzinger [3] have proposed a three-body process with a collisional stabilization as the major mode of BaX_2 formation in the Ba + X_2 (Cl_2, Br_2, I_2) → BaX_2 radiative recombination even at microTorr pressures. In the alkaline earth metal plus Cl_2 system, the reactions take place via an ionic potential surface with long-range interaction to form a collision complex. The collisional stabilization right after complex formation can be a dominant process due to the bulkiness of the reaction complex. In the radiative reaction of H with NO, it is unlikely that the reaction proceeds via an ionic process, and the formation of an ionic collision complex with a large cross section becomes less important as compared with the $BaCl_2$ radiative systems. As for the radiative lifetime, 25 μs of HNO is significantly shorter than the radiative lifetime of $BaCl_2$. Thus the collisional stabilization process in the low-pressure region is less likely to occur in the H + NO reaction. Besides it is difficult to explain the change in spectral pattern in fig. 3 solely in terms of changes in the three-body radiative mechanisms, although the three-body processes for collisional stabilization of a collision complex cannot be ruled out in the present pressure region.

It is necessary to evaluate the extent of vibrational energy transfer between HNO($^1A''$) and other molecules, such as H_2, H_2O and D_2O in the crossing region of both beams. Assuming a cross section of 10^{-2} nm^2 for resonant energy transfer between like molecules as mentioned above [13], the probability of vibrational relaxation of HNO($^1A''$) was estimated to be ≈0.01 during its radiative lifetime under the experimental conditions mentioned before according to the procedure of Lubman et al. [14]. On the basis of this estimation, the HNO($^1A''$) molecule could be shown to be free from vibrational energy relaxation.

The dependence of the emission intensity of the (000)–(000) vibrational band on the flow rate of NO is presented in fig. 4 in the range of flow rates 0.08–35.0 μmol/s. The plot in fig. 4 clearly shows the linear relationship between the HNO($^1A''$) concentration and the flow rate of NO.

When the flow rate of NO is increased over 50 μmol/s, the emission intensity tends to turn into a second-order dependence on the flow rate of NO. This indicates that more than one NO molecule is included in the formation of HNO($^1A''$). Clyne and Thrush [6] have shown a linear dependence of emission intensity of HNO($^1A''$) on the flow rate of NO in the presence of a foreign gas at the fairly high pressure of 1–2 Torr, and have concluded that the foreign gas is involved both in the formation and quenching of excited HNO. In the present study, however, neither NO nor an other bath gas probably acts as a foreign gas at the low flow rate of NO of 2 μmol/s.

Spectral simulation was carried out as a tentative

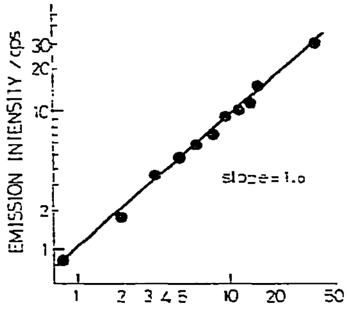

Fig. 4. Dependence of HNO emission intensity (762 nm) on the flow rate of NO, where the flow rate of hydrogen is held constant at 15.0 μmol/s.

way to discuss the rotational distributions in the (000)–(000) vibrational band of HNO and DNO. A reported value of 16450 cm^{-1} [15] for the predissociation limit was taken and a Boltzmann-type distribution as a prior distribution for rotation was assumed. The "rotational temperature" was used merely as a parameter for the rotational distribution. The radiation frequencies and the rotational term values were derived from the spectroscopic constants of Bancroft et al. [5].

In the case of DNO chemiluminescence, most of the emission comes from the (000)–(000) band. Therefore it is convenient to simulate the (000)–(000) band of DNO to make accurate determination of the rotational distribution of the reaction product. Fig. 5 shows the simulation of the (000)–(000) band of DNO for two different rotational temperatures. The best fit was obtained with a rotational temperature of 300 ± 100 K which corresponds to maximum population at the ninth rotational level. Similarly, a rotational temperature of ≈300 K was also obtained for HNO.

A HNO molecule was estimated to experience collisions for rotational energy transfer to other molecules in the beam merely 1–2 times during its radiative lifetime with a collisional cross section for rotation of 3 nm^2 allowing a $\Delta J_{HNO} = \pm 1$ transition [16]. Thus, the initial distribution in the rotation of HNO could almost be preserved under the present experimental conditions.

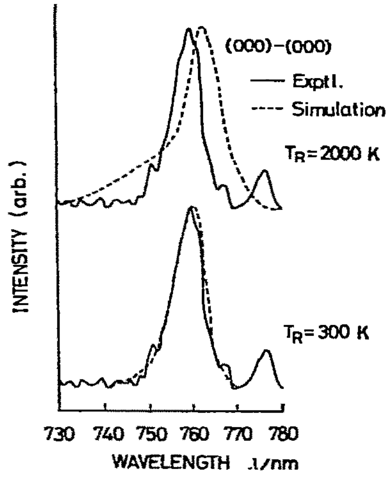

Fig. 5. Spectral simulations of the (000)–(000) band of DNO at the rotational temperatures of 300 and 2000 K, respectively.

The rotational distribution thus obtained could be supported by the conservation of total angular momentum. In the present recombination process, the following relation holds:

$$|J_{NO}| - |L| < |J_{HNO}| < |J_{NO}| + |L|.$$

At 300 K in the H + NO system, the contribution of L is small due to light-atom collisions, and

$$4\hbar < |J_{HNO}| < 12\hbar ,$$

where L is the orbital angular momentum between H and NO, and J is the internal angular momentum of the molecule. This result is consistent with the angular momentum of $9\hbar$ which is estimated by the spectrum simulation.

Most of the emission concentrates at the (000) vibrational state of $^1A''$ with the rotational levels centered at $J = 9$. These levels are lower than the predissociation limit of 16450 cm^{-1} by ≈3000 cm^{-1}. The energy release of 3000 cm^{-1} from HNO($\tilde{A}$) by collision may be difficult during its radiative lifetime of 25 μs in the crossing region of beams owing to the estimation stated above.

References

[1] K.H. Becker, W. Groth and D. Thran, Chem. Phys. Letters 15 (1972) 215.
[2] C.D. Jonah and R.N. Zare, Chem. Phys. Letters 9 (1971) 65;
C.D. Jonah, R.N. Zare and Ch. Ottinger, J. Chem. Phys. 56 (1972) 263.
[3] D.J. Wren and M. Menzinger, Chem. Phys. Letters 27 (1974) 572.
[4] M.J.Y. Clement and D.A. Ramsay, Can. J. Phys. 39 (1961) 205.
[5] J.L. Bancroft, J.M. Hollas and D.A. Ramsay, Can. J. Phys. 40 (1962) 322.
[6] M.A.A. Clyne and B.A. Thrush, Discussions Faraday Soc. 33 (1962) 139;
D.B. Hartley and B.A. Thrush, Proc. Roy. Soc. A297 (1967) 520.
[7] T. Ishiwata, I. Tanaka and H. Akimoto, J. Phys. Chem. 82 (1978) 1336.
[8] T. Kasai, T. Masui, H. Nakane, I. Hanazaki and K. Kuwata, Chem. Phys. Letters 56 (1978) 84.
[9] T. Kasai, Y. Hosokawa and K. Kuwata, to be published.

[10] N. Washida, H. Akimoto and M. Okuda, J. Phys. Chem. 82 (1978) 2293.
[11] J.A. Giordmaine and T.C. Wang, J. Appl. Phys. 31 (1960) 463.
[12] K. Obi, Y. Matsumi, Y. Takeda, S. Mayama, H. Watanabe and S. Tsuchiya, Chem. Phys. Letters 95 (1983) 520.
[13] G. Hancock and I.W.M. Smith, Appl. Opt. 10 (1971) 1827.
[14] D.M. Lubman, C.T. Rettner and R.N. Zare, J. Phys. Chem. 86 (1982) 1129.
[15] R.N. Dixon, K.B. Jones, M. Noble and S. Carter, Mol. Phys. 42 (1981) 455.
[16] M.L. Unland and W.H. Flygare, J. Chem. Phys. 45 (1966) 2421.