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Radiative Lifetime Measurements of $N_2(C^3\Pi_u)$, $NH(A^3\Pi)$ and $NH(c^1\Pi)$

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The radiative lifetimes of $N_2(C^3\Pi_u)$, $NH(A^3\Pi)$, and $NH(c^1\Pi)$ states were measured by the use of the time-sampling technique. The excited molecules were produced by the electron bombardment of N_2 and NH_3 gas. The lifetimes obtained in this experiment for $N_2(C^3\pi\Pi)$, $NH(A^3\Pi)$, and $NH(c^1\Pi)$ were $(4.8\pm0.3)\times10^{-8}$ sec, $(4.1\pm0.2)\times10^{-7}$ sec, and $(4.3\pm0.2)\times10^{-7}$ sec respectively. The oscillator strengths of the respective transitions were also calculated.

The radiative lifetimes of several unstable chemical species, such as ions or free radicals, have been measured by several investigators.[1-4] Knowledge of lifetimes is very important in the field of astrophysics and spectroscopy. Particularly, oscillator strengths and dipole transition probabilities can be obtained from the lifetimes provided that the theoretical or experimental Franck-Condon factors are known.

We wish to report here on one radiative-lifetime measurements of $N_2(C^3\Pi_u)$, $NH(A^3\Pi)$, and $NH(c^1\Pi)$. These excited molecules are produced by electron impact below 200 eV, and the lifetimes are obtained by determining the fluorescence decay directly. Lifetime measurements of the $N_2(C^3\Pi_u)$ level have been performed previously,[1,2,5,6] but there have been different interpretations of the collision quenching and cascading effect. In this paper, new evidence will be reported. In the case of NH, Bennet and Dalby[7] measured $NH(A^3\Pi)$, and Fink and Welge[2] measured $NH(A^3\Pi)$ and $NH(c^1\Pi)$, using the phase shift method. We studied these lifetimes in more detail and obtained slightly different results.

The approximate absorption oscillator strengths of the $(C^3\Pi_u-B^3\Pi_g)$ system of N_2 and the $(A^3\Pi-X^3\Sigma)$ system and the $(c^1\Pi-a^1\Delta)$ system of NH were calculated on the assumption that the electronic dipole strengths are constant for each v''-progression.

Experimental

The excited molecules are formed by the bombardment of pulsed low-energy electrons (15—200 eV) at a repetition rate of 5 Hz. The emitted light from excited molecules is dispersed with a small Nippon-Jarrel Ash grating monochromator and detected by a photomultiplier. The photomultiplier (EMI 6256S, 9514S) detects light only during the pulsed period. The gate pulse is fed into the alternate dynodes of the photomultiplier through the load resistance. The potentials of the alternate dynodes are the same as those of the adjacent dynodes during the closed-gate period. This pulse is phased slowly by means of a variable-delay network. Then, the emitted light intensity is recorded as a function of the time on a recorder. This method is called the time-sampling technique. The time-resolution used in this experiment was about 10 nsec. The details of the apparatus will be published elsewhere.[8]

Results and Disussion

Lifetime Measurement of $N_2(C^3\Pi_u)$. When N_2 gas at a pressure of 1 μ is bombarded with electrons below 200 eV, the emission of the $(C^3\Pi_u-B^3\Pi_g)$ system of N_2 appears very readily. The peak at 3371 Å is the (0,0) band. The peaks at 3577 Å and 3805 Å are the (0,1) band and the (0,2) band respectively. The radiative lifetime was measured

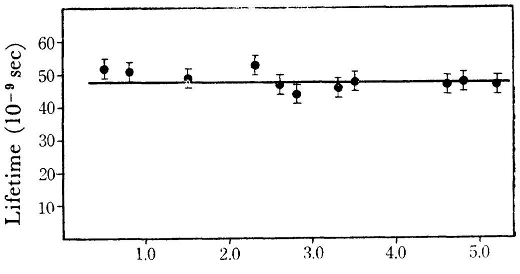

Fig. 1. The dependence of radiative lifetime of N_2 $(C^3\Pi_u)$ level upon gas pressure.

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[1] R. G. Bennet and F. W. Dalby, *J. Chem. Phys.*, **31**, 434 (1959); **32**, 1111 (1960); **33**, 179 (1960); **36** 399 (1962); **40**, 1414 (1964).

[2] E. H. Fink and K. H. Welge, *Z. Naturforsch.*, **19a**, 1193 (1964); *J. Chem. Phys.*, **46**, 4315 (1967).

[3] M. Jeunehomme and A. B. F. Duncan, *J. Chem. Phys.*, **41**, 1962 (1964); M. Jeunehomme and R. P. Schwenker, *ibid.*, **42**, 2406 (1965).

[4] G. M. Lawrence, *J. Quant. Spectrosc. Radiat. Transfer*, **5**, 359 (1965).

[5] M. Jeunehomme, *J. Chem. Phys.*, **44**, 2672 (1966).

[6] J. E. Hesser, *ibid.*, **48**, 2518 (1968).

[7] R. G. Bennet and F. W. Dalby, *ibid.*, **32**, 1716 (1960).

[8] T. Sawada and H. Kamada, This Bulletin, **43**, 325 (1970).

for the (0,0) band of N_2 by the use of a 0.5 m grating monochromator (about 15 Å bandwidth) in order to separate the other emission bands. τ was measured as a function of the gas pressure in order to investigate the collision quenching effect. This is shown in Fig. 1. No such strong dependence of τ upon the pressure was observed in the region below 5 μ. Fink and Welge[2] reported a slow decrease in τ with a decrease in the gas pressure. This dependence was in the wrong direction to be explained by collision quenching, and so they spoke of the possibility of some chemical reactions. However, Jeunehomme[5] indicated a marked increase in τ at pressures lower than 70 μ. He explained this dependence on the basis of the presence of a recombination process between slow electrons and molecular ions. Our results indicate that both possibilities, that of chemical reactions and that of the presence of a recombination process, can be ruled out at pressures below 5 μ.

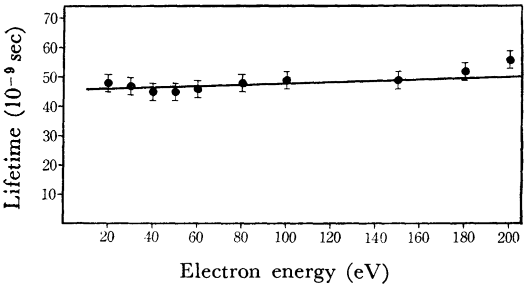

Fig. 2. The dependence of radiative lifetime of $N_2(C^3\Pi_u)$ level upon electron energy.

Figure 2 shows the energy dependence of τ. There appears a slight decrease with a diminishing in the electron energy. This indicates the existence of some cascading states. Similar tendencies have been reported by Bennet and Dalby[1] and by Fink and Welge.[2] However, their results show a more marked decrease in τ than do ours. In order to check the cascading effect in detail, the width of the excitation electron-pulse was varied within a wide range (0.02 μsec—0.3 μsec) at a constant electron energy. If there are some long-lived cascading states, the measured lifetime should be affected by the excitation electron-pulse duration. Thus, if the lifetimes of the initial states in the cascades are different from that of the $N_2(C^3\pi\Pi)$ state, the relative excitation of these states may depend upon the electron pulse duration. The radiative lifetime decreased slightly (17% from 0.02 μsec to 0.3 μsec) when the electron-pulse duration was shortened. These results indicate strongly the presence of some long-lived cascading states. Extrapolating to the excitation threshold and zero pulse duration, we obtained:

$$(4.8\pm0.3)\times10^{-8}\ \text{sec}$$

as the radiative lifetime of the $N_2(C^3\Pi_u)$ level. Our result agrees very well with Jeunehomme's extrapolated value, $(4.9\pm0.5)\times10^{-8}$ sec.

Lifetime Measurement of NH($A^3\Pi$) and NH($c^1\Pi$). When NH_3 is bombarded Eith 100 eV electrons, the ($A^3\Pi$-$X^3\Sigma$)system and the ($c^1\Pi$-$a^1\Delta$) system of NH appear within the wavelength region of 3240—3400 Å. Th emission spectrum is shown in Fig. 3. The peak at 3360 Å is the (0,0) band of the NH($A^3\Pi$–$X^3\Sigma$) system, while the wide-spread emission from 3240 Å to 3400 Å is the (0,0) band of the NH($c^1\Pi$–$a^1\Delta$) system.

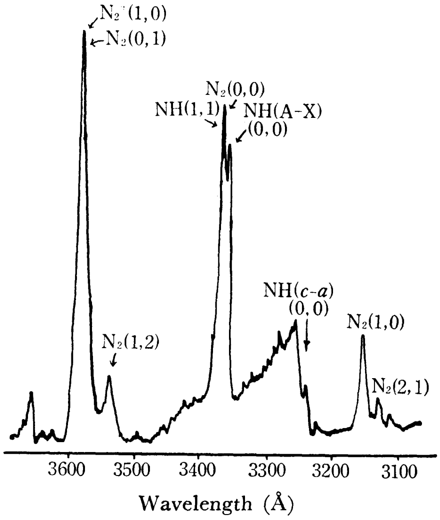

Fig. 3. The emission spectrum obtained when NH_3 gas was bombarded with 100 V electrons at a gas pressure of 0.5 μ.

The apparent lifetime of the NH($A^3\Pi$) level was measured as a function of the electron energy in order to investigate the cascading effect and the trapped resonance radiation. The (0,0) band of the N_2(C–B) system appears near the (0,0) band of the NH(A–X) system. Therefore, the grating monochromator (10 Å bandwidth) was used to separate the interfering bands.

The bands at 3370 Å consist of the (1,1) band of the NH(A–X) system and the (0,0) band of the N_2(C–B) system, as is shown in Fig. 3. The energy dependence of τ at a constant wavelength of 3365 Å is shown in Fig. 4 (b), and at one of 3358 Å, in Fig. 4 (a). In Fig. 4 (a), the lifetime is constant within the range from 60 V to 200 V, but τ decreases with a diminishing in the electron energy at 3365 Å. This effect can be explained as the mixing effect of the N_2 (0,0) band rather than the cascading from the higher electronic states. The time-resolved spectrum within the wavelength region from 3000 to 3600 Å at a fixed delay-time of 0.1 μsec after the cut-off of the excitation electrons[9] showed that the (0,0) band of the N_2(C–B)

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[9] T. Sawada and H. Kamada, unpublished data.

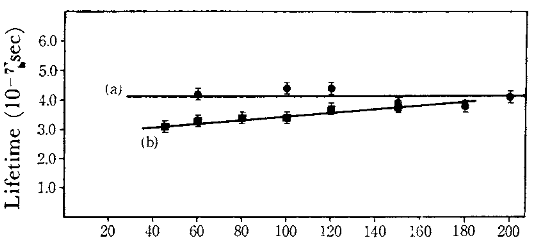

Fig. 4. The dependence of radiative lifetime of $NH(A^3\Pi)$ level upon electron energy.
The fixed wavelength, (a) 3358 Å, (b) 3365 Å

system is superimposed upon the (1,1) band of NH with an intensity of about 55% at an energy of 200 eV. It can be assumed that the effect of the interfering band is considerably eliminated in the lifetime measurement at 3358 Å. No significant pressure-dependence was observed in the range from 1 μ to 5 μ. A lifetime of

$$(4.1\pm0.2)\times10^{-7}\text{ sec}$$

was obtained. This value agrees within the limits of experimental error with that of Fink and Welge,$^{2)}$ $(4.6\pm0.8)\times10^{-7}$ sec, measured by the phase shift method. Bennet and Dalby$^{1)}$ obtained $(4.25\pm0.6)\times10^{-7}$ sec using an interference filter with a 100 Å bandwidth. Figure 5 shows the emission decay of the $NH(A^3\Pi)$ level plotted on the semilogarithmic graph.

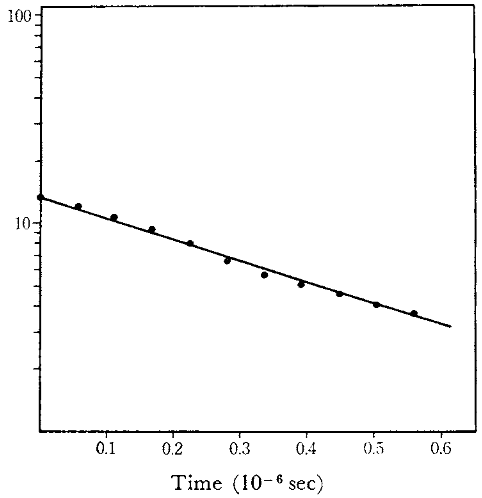

Fig. 5. Semilogarithmic plot of the emission decay associated with the $(A\text{-}X)$ system of NH.

The radiative lifetime of the $NH(c^1\Pi)$ level was measured at a fixed wavelength of 3240 Å. The energy dependence of τ within the range from 45 eV to 150 eV was investigated. However, no significant effect was observed. Consequently, the possibility of the cascading effect from the higher electronic states should be investigated in detail. The $NH(d^1\sum)$ level can be allowed to combine with the $NH(c^1\Pi)$ level,$^{10)}$ but it can be assumed that the cascading from the level is negligibly small. No variation in τ with the gas pressure was observed within the range of our experiment, from 1 μ to 5 μ. A lifetime of

$$(4.3\pm0.2)\times10^{-7}\text{ sec}$$

was obtained. This value agrees with Fink and Welge's value $(4.3\pm0.4)\times10^{-7}$ sec. The exponential decay of the $NH(c^1\Pi)$ level is plotted in Fig. 6.

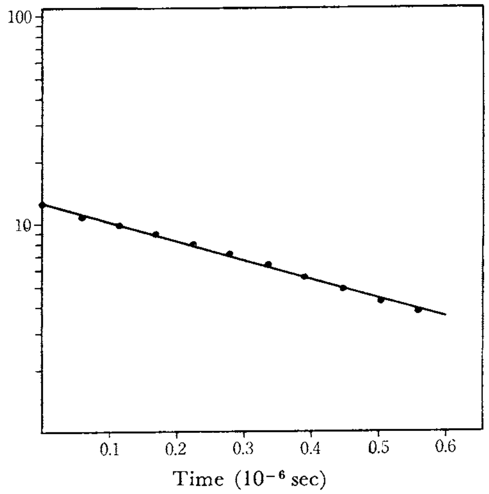

Fig. 6. Semilogarithmic plot of the emission decay associated with the $(c\text{-}a)$ system of NH.

Oscillator Strength. The radiative lifetime, $\tau_{v'}$, of the upper vibrational level in an electronic transition can be expressed by summing over the fine structure due to rotational and electron spin;

$$1/\tau_{v'}=A_{v'}=\sum_{v''}A_{v'v''}$$

where $A_{v'v''}$ is the Einstein coefficient. On the assumption that the mean-square electronic transition moment, $R_e^2(v')$, is constant for all v''-progressions, approximate absorption oscillator strengths can be obtained from this equation:

$$f_{v'v''}=1.51\cdot(G'/G'')\cdot q_{v'v''}\cdot\lambda^2_{v'v''}/\tau_{v'}$$

where G'/G'' is the ratio of the upper electronic statistical weight to the lower, as defined by Mulliken,$^{11)}$ where $q_{v'v''}$ is the Franck-Condon factor, and where $\lambda_{v'v''}$ is the wavelength in cm.

In calculating oscillator strengths, it is necessary to use the theoretical calculations of the Franck-Condon factors. The oscillator strengths for the (0,0) band of the$(C^3\Pi_u\text{-}B^3\Pi_g)$ system of N_2 is evaluated by use of the q_{00} value of Nicholls as:

$$f_{00}=(1.6\pm0.1)\times10^{-2}.$$

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10) R. W. B. Pearce and A. G. Gaydon, "The Identification of Molecular Spectra," Chapman & Hall Ltd., London (1950).

11) R. S. Mulliken, *J. Chem. Phys.*, **7**, 14 (1939).

The wavelength used here is 3371 Å. G'/G'' is equal to one.

Similar calculations were carried out for the (0,0) band of the NH($A^3\Pi$–$X^3\Sigma$) and the (0,0) band of the NH($c^1\Pi$–$a^1\Delta$). However, no theoretical calculations of the Franck-Condon factors for the above electronic transitions have been reported. Hence, f_{00}/q_{00} was calculated instead of f_{00}. Thus, for the (0,0) band of NH($A^3\Pi$–$X^3\Sigma$) we obtained:

$$f_{00}/q_{00} = (8.3\pm0.4)\times10^{-3}$$

and for the (0,0) band of NH($c^1\Pi$–$a^1\Delta$) we obtained:

$$f_{00}/q_{00} = (3.9\pm0.2)\times10^{-3}$$

where the wavelengths were 3360 Å and 3350 Å. It may be assumed that the Franck-Condon factors for the (0,0) bands of NH(A–X) and NH(c–a) are almost equal to one.

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[12] R. W. Nicholls, *J. Res. Nat. Bur. Stand., A*, **65**, 451 (1961).