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Radiative Lifetimes of $NH_2(^2A_1)$ Produced by Photodissociation of NH_3 on Irradiation with Vacuum Ultraviolet Light

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$NH_2(\tilde{A}^2A_1)$ was produced by photolysis of NH_3 on irradiation with vacuum ultraviolet light. The zero pressure lifetimes were evaluated to be *ca.* 15 μs from the phase lag of the emission excited by modulated Xe and Kr resonance lamps. The quenching rate coefficient of $NH_2(^2A_1)$ for NH_3 was determined to be *ca.* $(1.6\pm0.3)\times10^{-10}$ cm^3/molecule·s.

Emission from $NH_2{}^*$ (* denotes $^2A_1$) in the visible region was observed from various sources in discharges and flames.[1] Steady state fluorescence was measured following the production of the excited state radical by photodissociation of NH_3 on irradiation with vacuum ultraviolet light from a hydrogen discharge lamp.[2] Rare gas resonance lamps have been rarely used as an exciting light source.

The radiative lifetimes and the quenching rate of the fluorescence for NH_3 was studied by Lenzi *et al.*[3] by a static method. No absolute values could be determined. Only the product value $\tau_0 k_q$ could be obtained, where τ_0 is the zero pressure lifetime and k_q the quenching rate coefficient for NH_3. Halpern *et al.*[4] observed the time resolved fluorescence from $NH_2{}^*$ following the excitation of the radical in its ground state by means of a pulsed tunable dye laser, and measured zero pressure lifetimes and collisional de-excitation rate constants for several rovibronic levels of $NH_2{}^*$. The calculated values of $\tau_0 k_q$ from their data disagreed with the values in the UV photolysis experiment.[3]

This work was undertaken with the object of measuring τ_0 and k_q, separately, for $NH_2{}^*$ produced in the UV photolysis by using modulated resonance lamps. Through this work deals only with the lifetime measurement of $NH_2{}^*$, it has a wide applicability. Recently, the pulse method seems to be much more popular than the modulation method for measuring emission lifetimes. This seems to be mainly due to the usefulness of pulsed lasers with a very short pulse width. It is not easy to find a good pulsed light source in the vacuum UV region. Thus the method using modulated resonance lamps and digital lock-in detection of feeble emission light should be utilized for the lifetime measurement of various excited species produced by vacuum UV photolysis.

Experimental

The apparatus is shown in Fig. 1. The fluorescence cell with several appropriate light horns is made of glass, the outside being blackened; the total volume is *ca.* 600 cm^3.

The sample gas, NH_3, is illuminated with light from a 2450 MHz microwave discharge lamp inserted directly into the fluorescence cell. The Xe (CaF_2 window) and Kr(LiF window) lamps were of the type described by Loewenstein *et al.*[5] The microwave power was modulated by a circuit similar to that described by Phillips.[6] The light from the discharge lamp could be modulated as nearly a sine-wave form, judging from its oscilloscope trace. Observation was restricted to the UV-visible light from the lamp.

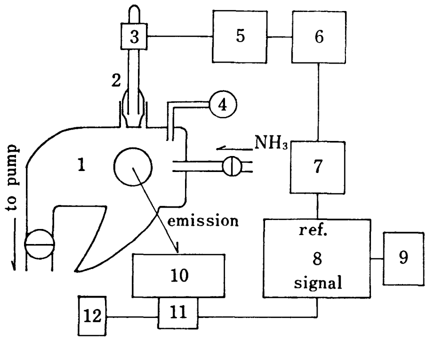

Fig. 1. Reaction apparatus.
1: Fluorescence cell, 2: vuv resonance lamp, 3: microwave cavity, 4: oil manometer, 5: microwave generator, 6: modulation circuit, 7: sine wave generator, 8: photon-counter with a synchronous sampler, 9: chart recorder, 10: monochromator, 11: photomultiplier, 12: high voltage power supply.

Emission from $NH_2{}^*$ was observed at right angles to the exciting beam with a *f*/4.5 monochromator (Nikon P-250). The emission light was then converted into electron pulses by H.T.V. R464 and/or R456 photomultipliers and fed to a Brookdeal 5 Cl photon counter. For lifetime measurements, the reference signal in each cycle from the modulation circuit was fed to the synchronous sampler 5C21. The data of "*A*"−"*B*" were recorded, where "*A*" is the photon count number during a small sampling interval lagging from the reference signal by an arbitrary degree ϕ and "*B*" is that by $\phi+180$ degree. The percent duty, 2×(sampling interval)/(time for one cycle), was set to be 5%.

Ammonia (Matheson Co., 99.99%) was purified by freeze-thaw cycles. The pressure of NH_3 in the cell was measured with an oil manometer.

Results and Discussion

When NH_3 was irradiated by a Xe lamp with a CaF_2 window (147 nm), a weak emission was observed in the range 380—650 nm. The cut-off wavelength at the longer wavelength side could not be determined accurately because of the poorer response of the detector system at longer wavelengths. The Xe lamp with a LiF window (147, 129.6 nm) and a Kr lamp (123.6 nm) eventually gave the same emission besides a much stronger NH (c→a) emission at 327 nm. Because of the weakness of emission, it could only be detected under relatively poor resolution of the monochromator (a band path width above 1.2 nm was adopted) and we could not determine whether the emission was of continuous or many-line type. However, it was evident

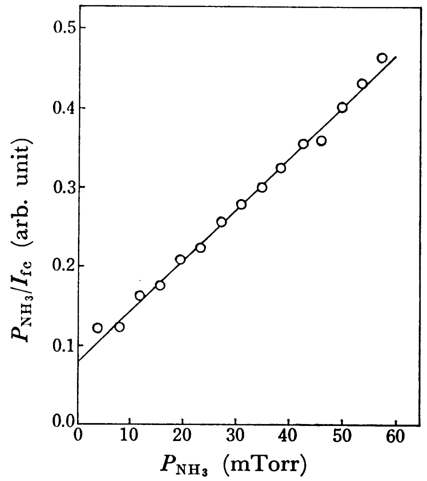

Fig. 2. A typical relationship between P_{NH_3}/I_{fc} and P_{NH_3}.
Excitation by Xe lamp, observation at 520±6 nm. $k_q/k_B = (2.6\pm0.4)\times10^{-15}$ cm³/molecule is obtained.

from its behavior and the quenching experiments that the emission was from the electronically excited NH_2. Becker and Welge[7] failed to observe this emission with similar resonance lamps. This might be due to the fact that the emission lines were buried in the background under their relatively higher resolution, as suggested by Okabe and Lenzi.[2]

A typical plot is given in Fig. 2 which shows the quenching of NH_2^* due to NH_3. The data for the quenching was treated according to the usual mechanism.

$$NH_3 + h\nu \longrightarrow NH_2^* + H$$
$$NH_2^* \longrightarrow NH_2(X) + \text{fluorescence} \quad k_B = \tau_0^{-1}$$
$$NH_2^* + NH_3 \longrightarrow NH_2(X) + NH_3 \quad k_q$$

The fluorescence intensity, I_{fc}, is related to NH_3 pressure, P_{NH_3}, by the equation

$$P_{NH_3}/I_{fc} \propto k_B + k_q P_{NH_3}. \quad (1)$$

Under higher NH_3 pressures, the effect of NH_3 pressure on the light absorption should be considered. Necessary corrections were made on the basis of the geometry of the cell and the extinction coefficient of NH_3 against the exciting lines.[8] The maximum correction was *ca.* 4%.

Table 1. The ratio k_q/k_B

Exciting light (nm)	Observation wavelength (nm)	k_q/k_B (10^{-15} cm³/ molecule)	Lit
151.8	≥350	2.9±0.5	3
147 (Xe)	400±6[a]	2.4±0.5	this work
	440±6	2.3±0.4	this work
	520±6	2.6±0.4	this work
	560±6	3.0±0.4	this work
139.7	≥350	2.2±0.3	3
125.3	≥350	3.0±0.3	3
123.6 (Kr)	460±9	3.1±0.4	this work
	530±9	2.9±0.4	this work

a) Band path width.

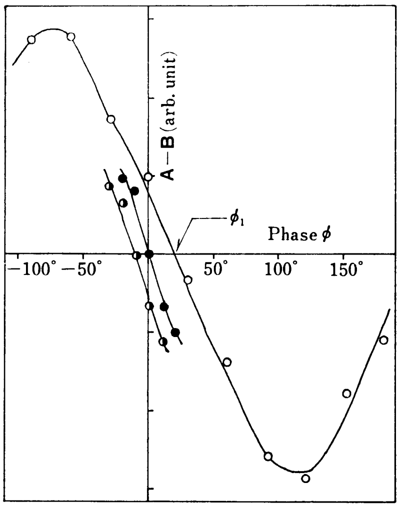

Fig. 3. The data of "*A*"−"*B*" at various phases in a modulation experiment.
Excitation by modulated Kr lamp (50 kHz), observation at 520±12 nm. P_{NH_3}=450 mTorr (○), 110 mTorr (●), 50 mTorr (◑). As for ϕ_1, see text.

The fluorescence was observed at several wavelengths. k_p/k_B were evaluated from similar plots to those in Fig. 2 and are given in Table 1. The values are almost independent of the observation wavelength, though allowance should be made for the fact that the fluorescence was observed under relatively low resolution. These values seem to be in good agreement with those of Lenzi *et al.*[3]

Direct lifetime measurements were carried out by means of a modulation technique. The exciting light was modulated as $I_0 = \bar{I}_0 + \tilde{I}_0 \sin(2\pi f t)$, where $\bar{I}_0$ is the d.c. part and $\tilde{I}_0$ is the amplitude of the a.c. part. The possible phase lag of the fluorescence is related to the kinetic process by the equation

$$\theta = \tan^{-1}[2\pi f (k_B + k_q P_{NH_3})^{-1}]. \quad (2)$$

The value "*A*"−"*B*" could be measured against any desired phase of degree ϕ (Fig. 3). If we find the degree ϕ_1 at which "*A*"−"*B*" is zero, ϕ_1 is equal to $\theta+\phi_0$, where ϕ_0 is the common, though unknown, phase lag of the exciting light from the reference signal of the modulation circuit. ϕ_0 was not measured directly. However, it was so selected that it might give the best linearity as indicated in Eq. 2 between $\theta(=\phi_1-\phi_0)$ and P_{NH_3} at various NH_3 pressures.

The experiments were carried out with several modulation frequencies. Figures 4 and 5 show the results in the case of Xe and Kr lamp excitation, respectively. Because of the weakness of emission, the slightly different wave form of the a.c. part of the exciting light from a precise sine wave, and the relatively large duty factor in measuring "*A*"−"*B*", the precision in the measurements of the phase lag was only within ±5 degree. The data do not lie exactly on the straight line, the error limit at the zero pressure limit not being small. In order to confirm the reliability of this technique, measurement was made of the zero pressure lifetime of the c state of NH produced by the Kr lamp excitation. The lifetime of 530 ns ($k_B = 1.9\times10^6$/s) was

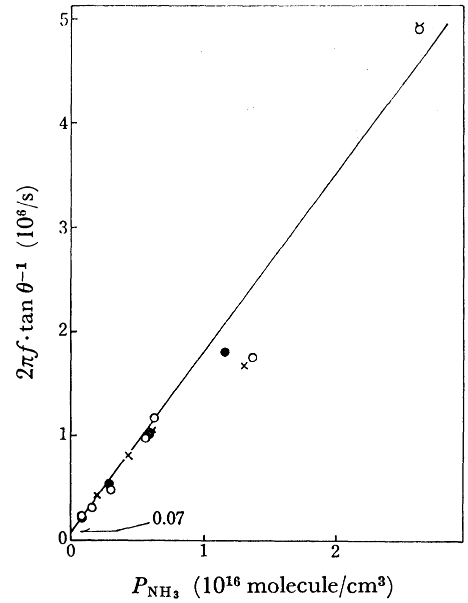

Fig. 4. Emission lifetimes of NH_2^* produced by modulated Xe lamp at various pressures of NH_3. Excitation by Xe lamp, observation at 530±12 nm. Modulation frequency, 54.3 kHz (○), 87.7 kHz (●), 96.2 kHz (×). $k_B=(0.7\pm0.3)\times10^5$/s, $k_q=(1.7\pm0.3)\times10^{-10}$ cm^3/molecule·s are obtained.

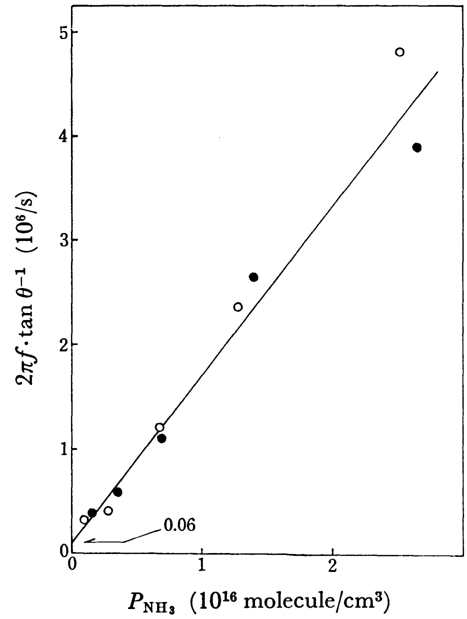

Fig. 5. Emission lifetimes of NH_2^* produced by modulated Kr lamp at various pressures of NH_3. Excitation by Kr lamp, observation at 520±12 nm. Modulation frequency, 54.1 kHz (●), 87.7 kHz (○). $k_B=(0.6\pm0.3)\times10^5$/s, $k_q=(1.6\pm0.3)\times10^{-10}$ cm^3/molecule·s are obtained.

obtained by the same procedure (Fig. 6). The result agrees with the reported value 480±90 ns.[9]

The zero pressure lifetime 14 μs [$k_B=(0.7\pm0.3)\times10^5$ /s] for Xe lamp and 16 μs [$k_B=(0.6\pm0.3)\times10^5$/s] for Kr lamp excitation are near the lifetime 10 μs for the (0,9,0) state obtained by laser light excitation.[4]

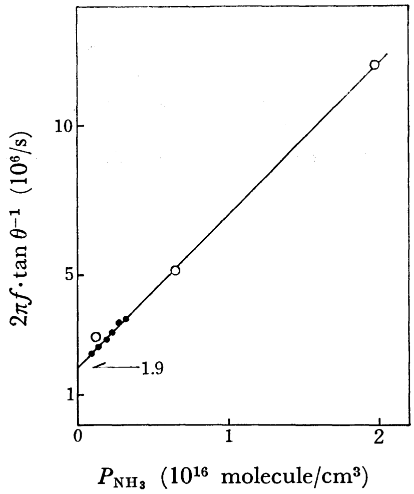

Fig. 6. Emission lifetimes of NH (c) produced by Kr lamp at various pressures of NH_3.
○: $2\pi f\cdot\tan\theta^{-1}$ *vs.* P_{NH_3}, excitation by modulated Kr lamp, observation at 327±3 nm, modulation frequency, 87.7 kHz.
●: P_{NH_3}/I_{fc} *vs.* P_{NH_3}, obtained by steady illumination of Kr lamp, observation at 327±3 nm. In this case, the unknown k_B value (for NH) is assumed to be 1.9×10^6/s in order to plot the value of P_{NH_3}/I_{fc} in the same scale as the data of $2\pi f\cdot\tan\theta^{-1}$.

The k_q values were $(1.7\pm0.3)\times10^{-10}$ (Xe lamp) and $(1.6\pm0.3)\times10^{-10}$ cm^3/molecule·s (Kr lamp). The product values $\tau_0 k_q$ of 2.4×10^{-15} (Xe lamp) and 2.7×10^{-15} cm^3/molecule are in good agreement with the values given in Table 1.

The k_q values are much smaller than the value 10×10^{-10} cm^3/molecule·s for the (0,9,0) state. Thus the discrepancy between the $\tau_0 k_q$ value given by Halpern *et al.*[4] and by Lenzi *et al.*[3] seems to be mainly due to the large difference in the k_q value. The present values as well as those of Lenzi *et al.*[3] are the average of the quenching coefficients for various different vibronic levels of NH_2^* produced by the dissociation of NH_3. Fluorescence under low resolution was observed. It should thus consist of the primary emission from the excited NH_2^* before any relaxation plus a secondary emission from the relaxed but still electronically excited NH_2. The relatively small k_q values in our case as compared with those of Halpern *et al.*[4] indicates an appreciably efficient vibrational relaxation within the upper electronic state of NH_2 against electronic relaxation to the ground state NH_2.

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