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The Quenching of the Cadmium Resonance Radiation at 326.1 nm by Ammonia and the Emission from the Complex between Excited Cadmium Atoms and Ammonia in the Presence of Argon

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The pressure dependences of the emission intensities at 326.1 and 432 nm in the cadmium-photosensitized reaction of ammonia have been measured. In order to interpret the nonlinear Stern-Volmer plots for the quenching of the 326.1 nm resonance line, the following reactions have to be taken into account in the reaction scheme: $Cd^*+NH_3 \rightleftarrows CdNH_3{}^*{}_v$, $CdNH_3{}^*{}_v+M \rightarrow CdNH_3{}^*+M$. The pressure dependence of the emission from the $CdNH_3{}^*$ complex (at 432 nm) was also well explained in terms of a reaction scheme involving the above reactions.

It is well known that excited mercury atoms form complexes with some molecules (NH_3, H_2O, *etc.*) and that these complexes fluoresce.[1—3] Since the electronic character of cadmium atoms is similar to that of mercury atoms except for the amount of energy involved, the complexes of excited cadmium atoms with some molecules are expected to fluoresce. Recently, two groups, including one in our laboratory,[4,5] have reported a cadmium-photosensitized emission of ammonia at the wavelength of 432 nm; this emission has been attributed to that from the complex between excited cadmium atoms and ammonia. In a short communication,[4] Morten *et al.* assigned the emitting complex to that formed between $Cd(^3P_0)$ atoms and ammonia, by analogy with the Hg–NH_3 system.

As was mentioned in a previous paper,[6] the absorption intensity at 326.1 nm ($5^3P_1 \leftarrow 5^1S_0$) is dependent upon the pressure of foreign gases through the pressure broadening of the absorption line. In a previous study[5] of the cadmium-photosensitized luminescence of ammonia, however, this effect was not taken into account. The present paper will report the results of a study of the cadmium-photosensitized luminescence and of the quenching for the 326.1 nm resonance line under the conditions of the ammonia being diluted with argon and the total pressure being kept constant in order to minimize the effect of the pressure broadening. These results will reveal a somewhat detailed mechanism of the complex-formation between the excited cadmium atoms and ammonia.

Experimental

The apparatus and procedure were almost the same as those previous described.[5] The reaction cell and the cadmium resonance lamp were kept in an electric furnace at 220±1 °C. The vapor pressure of cadmium at 220 °C is 1.04×10^{-3} Torr. The lamp was operated by an alternating current (50 Hz).[6]

The cadmium metal used was high-purity cadmium (99.9999%) manufactured by the Osaka Asahi Metal Co. Pure-grade ammonia (Takachiho Shoji Co.) was used after degassing at the temperature of liquid nitrogen. Pure-grade argon purchased from the Takachiho Shoji Co. was used after repeated adsorption and desorption on a molecular sieve at the temperature of liquid nitrogen.

Results

When the empty cell was illuminated by means of the cadmium lamp, line spectra were observed at 326, 340, 347, 361, 468, 480, and 509 nm. In the presence of the cadmium vapor in the cell at 220 °C, the intensity of the 326.1-nm emission increased, but those of the other lines remained unchanged. When argon was added, the intensity of the 326.1-nm emission increased with the increase in the pressure, as is shown in Fig. 1. This increase has been attributed to the increase in the absorption of the exciting light on the basis of the pressure broadening of the absorption line.[6]

When an ammonia–argon mixture was added, the intensity of the emission at 326.1 nm decreased with the increase in the partial pressure of ammonia, while the total pressure was kept constant, and a new band emission was observed at 432 nm. The position and the profile of the new band emission at 432 nm were independent both of the total pressure examined and of the pressure ratio of ammonia to argon, while the intensity changed with the increase in the partial pressure of ammonia, as is shown in Fig. 2. As the intensity of the 432-nm emission decreased with the increase in the irradiation time, the emission intensities shown in Fig. 2 were obtained by extrapolation to zero irradiation time.

The Stern-Volmer plots for the quenching of the 326.1-nm resonance line are shown in Fig. 3, where $I^0_{326.1}$ and $I_{326.1}$ are the emission intensities at 326.1 nm in the absence and in the presence of ammonia

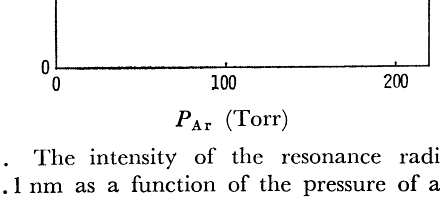

Fig. 1. The intensity of the resonance radiation at 326.1 nm as a function of the pressure of argon.

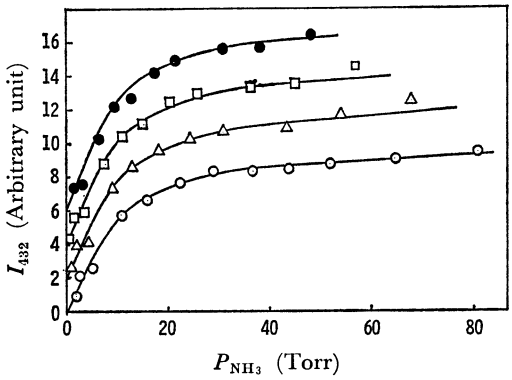

Fig. 2. The emission intensity at 432 nm as a function of the partial pressure of ammonia. The total pressures are 208 (○), 175 (△), 147 (□), and 123 (●) in Torr. Solid lines show the values calculated according to Eq. (2). The plots are displaced upwards by 2 units of I_{432} for clarity in the above order of the total pressure.

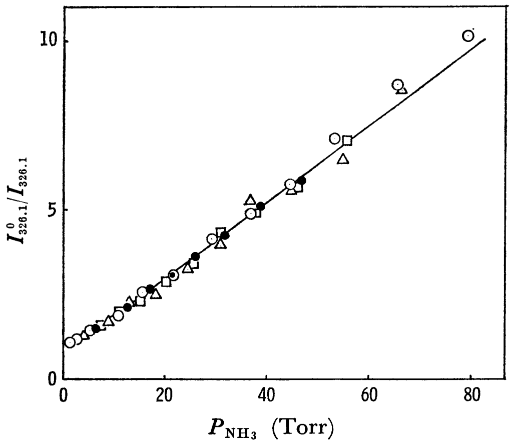

Fig. 3. Stern-Volmer plots for the quenching of the resonance radiation at 326.1 nm by ammonia diluted with argon. The total pressures are 208 (○), 175 (△), 147 (□), and 123 (●) in Torr. Solid line shows the values calculated according to Eq. (1).

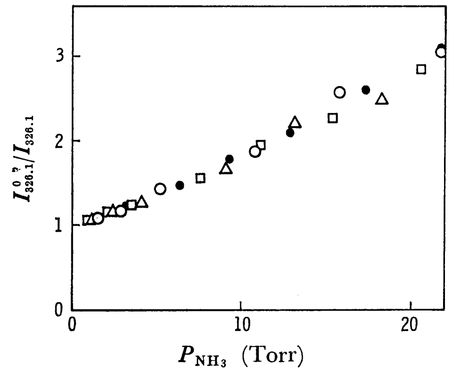

Fig. 4. Stern-Volmer plots in the low pressure region. The total pressures are 208 (○), 175 (△), 147 (□), and 123 (●) in Torr.

respectively. On the assumption that 100 Torr carbon dioxide quenches the Cd($^3P_1$) atoms completely,[6] the scattered light intensity at 326.1 nm was estimated to be less than 0.2% of $I^0_{326.1}$; hereafter, it was neglected. The emission intensity at 326.1 nm hardly changed with the irradiation time. As is shown in Fig. 3, the plots obtained at various total pressures lie on one curve, and no total pressure dependence can be seen. The intercept of the Stern-Volmer plots at zero pressure of ammonia obtained in the previous paper[5] was less than unity, but that in Fig. 3 was equal to unity. This discrepancy can be attributed to the neglect of the effect of the pressure broadening in the previous study. The plots obtained with ammonia were previously regarded as lying on a straight line; however, the plots shown in Fig. 3 deviate from a straight line, especially in the low-pressure region. The deviation is observed more clearly in Fig. 4. This finding forced us to modify the reaction scheme previously proposed.[5]

Discussion

The energy difference between the 5^3P_1 and 5^3P_0 states of cadmium atoms is only 1.6 kcal/mol. In the presence of foreign gases, for example, 5 Torr of Ar or 0.1 Torr of ammonia,[7] the equilibrium between the two electronic states is readily established. Consequently, we cannot discriminate the reactions of two states. Morten *et al.* used the phase-shift technique to observe the emission at 432 nm and said that the emitting species is produced by the reaction between the 5^3P_0 state of cadmium atoms and ammonia; however, if the equilibration reaction between 5^3P_1 and 5^3P_0 states is very fast, their assignment is not necessarily unique. In the following treatment, therefore, we will consider both Cd($^3P_1$) and Cd($^3P_0$) as precursors of the emitting species and will use the symbol Cd* to express either Cd($^3P_1$) or Cd($^3P_0$).

Quenching of the 326.1-nm Resonance Line. As was mentioned in the "Results" section, the Stern-Volmer plots for the quenching of the 326.1-nm resonance line by ammonia do not lie on a straight line. In order to explain such Stern-Volmer plots, the following reaction mechanism was considered:

$\mathrm{Cd} + h\nu \longrightarrow \mathrm{Cd}(^3P_1)$	I_a
$\mathrm{Cd}(^3P_1) \longrightarrow \mathrm{Cd} + h\nu$	k_0
$\mathrm{Cd}(^3P_1) + \mathrm{M} \rightleftharpoons \mathrm{Cd}(^3P_0) + \mathrm{M}$	k_1, k_{-1}
$\mathrm{Cd}(^3P_1) + \mathrm{NH_3} \longrightarrow \text{products}$	k_2
$\mathrm{Cd}(^3P_0) + \mathrm{NH_3} \longrightarrow \text{products}$	k_3
$\mathrm{Cd^*} + \mathrm{NH_3} \rightleftharpoons \mathrm{CdNH_3{}^*{}_v}$	k_4, k_{-4}
$\mathrm{CdNH_3{}^*{}_v} + \mathrm{NH_3} \longrightarrow \mathrm{CdNH_3{}^*} + \mathrm{NH_3}$	k_5
$\mathrm{CdNH_3{}^*{}_v} + \mathrm{Ar} \longrightarrow \mathrm{CdNH_3{}^*} + \mathrm{Ar}$	k_5'
$\mathrm{CdNH_3{}^*} \longrightarrow \mathrm{Cd} + \mathrm{NH_3} + h\nu'$	k_6
$\mathrm{CdNH_3{}^*} + \mathrm{NH_3} \longrightarrow \mathrm{Cd} + 2\mathrm{NH_3}$	k_7
$\mathrm{CdNH_3{}^*} + \mathrm{Ar} \longrightarrow \mathrm{Cd} + \mathrm{NH_3} + \mathrm{Ar}$	k_7'

Here, M stands for Ar or NH_3. $CdNH_3{}^*{}_v$ and $CdNH_3{}^*$ represent, respectively, an unstabilized and a stabilized complex between the triplet cadmium and ammonia. In this mechanism, it is assumed that the unstabilized complex does not fluoresce, because the profile of the emission band is independent of the pressures of ammonia and argon.

A steady-state treatment on the assumptions that the equilibration reaction between the 5^3P_1 and 5^3P_0 states is very fast and that either the $^3P_1$ or the $^3P_0$ state is the precursor of the emitting species gives the following relation:

$$\frac{I^0_{326.1}}{I_{326.1}} = 1 + a[\mathrm{NH_3}] + \frac{b[\mathrm{NH_3}]}{1+\dfrac{1}{c+d[\mathrm{NH_3}]}} \tag{1}$$

Here, $I^0_{326.0}$ and $I_{326.1}$ are the emission intensities at 326.1 nm in the absence and in the presence of ammonia respectively. a, b, c, and d are constants depending only on the total pressure. When Cd*= Cd($^3P_1$), then

$$a = \frac{1}{k_0}\left(k_2+\frac{k_1}{k_{-1}}k_3\right),\quad b = \frac{k_4}{k_0},\quad c = \frac{k_5'}{k_{-4}}[\mathrm{M}],$$

and

$$d = \frac{k_5-k_5'}{k_{-4}}$$

In the case of Cd*=Cd($^3P_0$), a, c, and d are expressed in the same manner as above, while

$$b = \frac{k_1}{k_{-1}}\frac{k_4}{k_0}.$$

At the temperature of 220 °C, the equilibrium constant between $^3P_1$ and $^3P_0$ states is 1.68 $(=1/3\exp(1.6/RT)=K=k_1/k_{-1})$.

According to Eq. (1), the $I^0_{326.1}/I_{326.1}$ ratio should have a linear dependence on the pressure of ammonia in the high-pressure region and a second-order dependence in the low-pressure region. These tendencies agree with the observations. By applying Eq. (1) to the observed values, the constants, a, b, c, and d, could be obtained by trial and error. The results are summarized in Table 1. The solid line in Fig. 3 was drawn by introducing these values into Eq. (1). The c term is so small that the $I^0_{326.1}/I_{326.1}$ ratios calculated are scarcely dependent at all on the total pressure.

TABLE 1. THE CONSTANTS INVOLVED IN Eq. (1)

$a = 0.010 \pm 0.002$	Torr^{-1}
$b = 0.103 \pm 0.002$	Torr^{-1}
$c/[\mathrm{M}] = 0.0024$	Torr^{-1}
$d = 0.30$	Torr^{-1}

The Pressure Dependence of the Emission at 432 nm. The steady-state treatment of the above mechanism gives the following relation for the intensity of the emission at 432 nm:

$$\frac{I_{326.1}[\mathrm{NH_3}]}{I_e} = (e+f[\mathrm{NH_3}])\left(1+\frac{g}{h+[\mathrm{NH_3}]}\right) \tag{2}$$

Here, I_e represents the total emission intensity arising from the stabilized complex. Since the emission profile was the same at all pressures and compositions examined, the observed emission intensity at 432 nm (I_{432}) should be proportional to the total emission intensity; *i.e.*, $I_e=\alpha I_{432}$. The proportional factor, α, depends on the geometry of the apparatus, the slit width, and the sensitivity of the photomultiplier used. e, f, g, and h are constants depending only on the total pressure; when Cd*=Cd($^3P_1$),

$$e = \frac{k_0}{k_4} + \frac{k_0}{k_4}\frac{k_7'}{k_6}[\mathrm{M}],\qquad f = \frac{k_0}{k_4}\frac{k_7-k_7'}{k_6},$$

$$g = \frac{k_{-4}}{k_5-k_5'},\qquad \text{and}\qquad h = \frac{k_5'}{k_5-k_5'}[\mathrm{M}].$$

In the case of Cd*=Cd($^3P_0$), k_4 should be replaced by $(k_1/k_{-1})k_4$. These constants have been evaluated by the method given in the Appendix and are listed in Table 2. The solid lines in Fig. 2 were drawn by substituting the values in Table 2 into Eq. (2). The agreement between the calculated values and the observed ones is good at all the pressures examined.

TABLE 2. THE CONSTANTS INVOLVED IN Eq. (2)

[M] (Torr)	αe (Torr)	αf	g (Torr)	$h/[\mathrm{M}]$
208	2.17	0	3.20	0.0072
175	1.99	0	3.23	0.0072
147	1.87	0	2.78	0.0072
123	1.74	0	2.52	0.0072

The lifetime (τ_0) of Cd($^3P_1$) has been reported to be 2.39×10^{-6} s.[8] As was mentioned in a previous paper,[6] the effective lifetime is independent of the pressure of foreign gases in the range we are studying. Therefore, k_0 may be set equal to $1/\tau_0$. On the other hand, several ratios of the rate constants can be evaluated from the relationships between the constants, a, b, c, d, e, f, g, and h, and the total pressure ([M]). The results are summarized in Table 3. A comparison of k_4 with $(k_2+1.68\,k_3)$ indicates that the cross section for the quenching of the excited cadmium atoms through the formation of the complex is about 10 times that for the quenching through other processes, such as the abstraction of the hydrogen atom. The half-quenching pressure of ammonia is calculated to be 12.6 Torr. This value is less than a half that reported previously (29.8 Torr).[5] The latter value, however, was obtained while paying no attention to the pressure broadening of the absorption line. Therefore, the value obtained here should be more reliable.

TABLE 3. SEVERAL RATE CONSTANTS AND RATIOS BETWEEN THE RATE CONSTANTS

$k_2 + 1.68\,k_3 = (2.1\pm0.4)\times10^{-13}$ cm^3 molecule^{-1} s^{-1}
k_4 (or $1.68\,k_4$) $= (2.2\pm0.4)\times10^{-12}$ cm^3 molecule^{-1} s^{-1}
$k_5/k_{-4} = 0.336\pm0.012$ Torr^{-1}
$k_5/k_5' = 139$
$k_7/k_6 = (4.9\pm0.2)\times10^{-3}$ Torr^{-1}
$k_7/k_7' = 1$

On the basis of the data obtained by using a flash technique, Callear and McGurk[3] proposed two types of the formation of the emitting complex in the system of Hg and NH_3:

$$\mathrm{Hg^* + NH_3 \longrightarrow HgNH_3^*} \qquad k_b$$

$$\mathrm{Hg^* + NH_3 + M \longrightarrow HgNH_3^* + M} \qquad k_t$$

The lifetime of Hg*, therefore, was expressed as follows:

$$\tau^{-1} = \tau_M^{-1} + k_b[\mathrm{NH_3}] + k_t[\mathrm{NH_3}][\mathrm{M}]$$

where τ_M is the lifetime of Hg* in the absence of foreign gases. Morten *et al.*[4] assumed a similar mechanism for the formation of the emitting cadmium complex and estimated that $k_b=(1.7\pm0.3)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} at 560 K. In our treatment, the lifetime of Cd($^3P_1$) may be expressed in this form:

$$\tau^{-1} = \tau_M^{-1}\left(1+a[NH_3]+\frac{b[NH_3]}{1+\dfrac{1}{c+d[NH_3]}}\right)$$

As is shown in Table 1, we obtained d=0.3 Torr^{-1}. The experiment of Morten *et al.* was carried out at more than a few Torr of NH_3. Therefore, the k_b value obtained by Morten *et al.* may be compared with the value of $(a+b)/\tau_M$. The calculated value is 2.4×10^{-12} cm^3 molecule^{-1} s^{-1} at 493 K. It may be said that these two values are in good agreement.

By assuming the cross section of 9 Å^2 for Reaction (5), which corresponds to $k_5=2.36\times10^{-10}$ cm^3 molecule^{-1} s^{-1} at 220 °C, the lifetime of the unstabilized complex was calculated to be 7.4×10^{-8} s. This is the shortest possible lifetime of the unstabilized complex. Therefore, if other molecules which are more complex than ammonia can form emitting species, and if the back reaction is not important, we shall not be able to observe the second order pressure dependence of the Stern-Volmer plots in the low-pressure region, as was observed in the present case of ammonia.

The ratio of $k_5'/k_5=0.0072$ shows that the stabilization of the unstabilized complex by ammonia is about 140 times as efficient as that by argon. On the other hand, $k_7'/k_7=1$ suggests that the efficiency of the deactivation of the stabilized complex is almost the same for both quenchers. Morten *et al.* estimated the lifetime of the emitting complex to be $(4.9\pm0.2)\times10^{-7}$ s. This suggests that Reactions (7) and (7′) are extremely inefficient.

Appendix

At the pressure of ammonia high enough for $1+\dfrac{g}{h+[NH_3]}\approx1$, Eq. (2) can be reduced to this form:

$$\frac{I_{326.1}[NH_3]}{I_{432}} = \alpha e + \alpha f[NH_3] \qquad (3)$$

The left-hand side of Eq. (3) is plotted against the pressure of ammonia, and the constants, αe and αf, are evaluated from the intercept and the slope of the straight line obtained in the high-pressure region.

Equation (2) can be rewritten as follows:

$$\frac{I_{326.1}[NH_3]}{I_{432}}\frac{1}{\alpha(e+f[NH_3])} = 1+\frac{g}{h+[NH_3]} \qquad (4)$$

The left-hand side of Eq. (4) can be calculated by using the values of αe and αf obtained above. The g and h constants are determined by using the method of curve-matching. Then, according to Eq. (2), the αe and αf constants can be determined in turn by using the values of g and h just obtained. These constants should be equal to the values obtained above. We, therefore, used the circulating procedure until a self-consistent set of constants was obtained. The final values are listed in Table 2.

References

1) S. Penzes, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **45**, 2322 (1966); H. E. Gunning, S. Penzes, H. S. Sandhu, and O. P. Strausz, *J. Amer. Chem. Soc.*, **91**, 7684 (1969).

2) C. G. Freeman, M. J. McEvan, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.*, **5**, 555 (1970); **6**, 482 (1970); **8**, 226 (1971); **9**, 578 (1971); *Trans. Faraday Soc.*, **66**, 2974 (1970); **67**, 2004, 2565 (1971); R. H. Newman, C. G. Freeman, M. J. McEvan, R. F. C. Claridge, and L. F. Phillips, *ibid.*, **66**, 2827 (1970); **67**, 1360 (1971).

3) A. B. Callear and J. McGurk, *Chem. Phys. Lett.*, **7**, 491 (1970); J. Koskikallio, A. B. Callear, and J. H. Conner, *ibid.*, **8**, 467 (1971); A. B. Callear and J. H. Conner, *ibid.*, **13**, 245 (1972).

4) P. D. Morten, C. G. Freeman, M. J. McEvan, R. F. C. Claridge, and L. F. Phillips, *ibid.*, **16**, 148 (1972).

5) S. Tsunashima, T. Toyono, and S. Sato, This Bulletin, **46**, 2654 (1973).

6) S. Yamamoto, M. Takaoka, S. Tsunashima, and S. Sato, *ibid.*, **48**, 130 (1975).

7) M. Takaoka, S. Yamamoto, S. Tsunashima, and S. Sato, *Chem. Lett.*, **1974**, 343.

8) F. W. Byron, Jr., M. N. McDermott, and R. Novick, *Phys. Rev.*, **134**, A615 (1964).