Phase-shift Studies of Cadmium-photosensitized Luminescence of Ammonia and Some Aliphatic Amines

Hironobu UMEMOTO,* Shigeru TSUNASHIMA, and Shin SATO

Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

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A phase-shift method was used to study the cadmium-photosensitized luminescence of ammonia and some aliphatic amines. The phase angles between the resonance fluorescence at 326.1 nm and the luminescence from the excited complexes have been measured at various modulation frequencies (10—99 kHz). The results could not be explained by means of the reaction mechanism proposed by analogy with the mercury-photosensitized luminescence of ammonia. In order to obtain a consistency, the equilibrium between the unstabilized and stabilized complexes: $CdNH_3^{\dagger}+NH_3 \rightleftarrows CdNH_3^{*}+NH_3$, had to be taken into account. The reverse reaction was not necessary to explain the results of the mercury-photosensitized luminescence of ammonia. This discrepancy may be ascribed to the difference in the energy gap between the $^3P_1$ and $^3P_0$ states of mercury and cadmium.

In the cadmium(5^3P_1)-photosensitized reactions of ammonia and some other electron-donor molecules, such as water and amines, broad, diffuse emission bands can be observed in the visible light region, while in the cases of mercury(6^3P_1)-photosensitization, similar emission bands are observed in the ultraviolet region.

To the studies of mercury-photosensitized luminescence, flash methods and modulation techniques have been applied by several groups.[1-6] The mercury–ammonia system has been especially well studied because of the high quantum yield of the luminescence. It is now well established that the sensitized luminescence arises from a charge-transfer complex formed between an ammonia molecule and an excited mercury atom, and that an Hg($^3P_0$) atom plays a significant role in the formation of this complex. The lifetime of the $HgNH_3^*$ complex has been measured by several groups.[1-6]

As for cadmium-photosensitized luminescence, however, there is only one example of such a measurement.[7] In the last several years, we have studied this cadmium-photosensitized luminescence by using a method of stationary excitation at 326.1 nm.[8-10] We have measured the steady-state intensities of the resonance fluorescence at 326.1 nm and of the sensitized luminescence as a function of the pressure of foreign gases. The quantum yield of the luminescence for ammonia was larger than those for other substrates.[9-10] In the photosensitization of ammonia, the ratio of the resonance fluorescence at 326.1 nm in the absence of ammonia to that in the presence of ammonia increased nonlinearly with an increase in the ammonia pressure in the low-pressure region, although it increased linearly in the high-pressure region.[8] In order to explain this nonlinearity, we considered the formation of an unstabilized complex which is in equilibrium with the excited cadmium atom and ammonia and which is stabilized by collisions with third bodies.

In the present study, in order to investigate the mechanism of the luminescence, we applied a phase-shift method to the cadmium–ammonia and cadmium–aliphatic amine systems.

Experimental

The experimental system was similar to that described previously for the study of the mercury-photosensitized luminescence,[6] except that the reaction vessel was kept in an electric furnace at 525±1 K. The vapor pressure of the cadmium in the cell was kept constant, 4.0×10^{-3} Torr (1 Torr≃133.3 Pa),[11] by maintaining the temperature of the cadmium reservoir at 519±1 K. The exciting resonance lamp was a home-made microwave-powered one containing about 10 Torr of helium as a carrier gas. This cadmium lamp was made of Pyrex glass, which cut off another resonance line at 228.8 nm. The emitting part of the lamp was covered with another Pyrex glass tube, and the intervening space was evacuated to prevent cadmium metal from depositing on the wall of the lamp. The reaction vessel was made of quartz.

The emission from the reaction system was focused by means of a quartz lens and detected with a 1P28 photomultiplier (Hamamatsu TV) in conjunction with a Shimadzu QV-50 monochromator. The phase angles of the photomultiplier signals relative to the internal reference signal of a lock-in amplifier (NF Circuit Design Block Co., LI-573) were measured. The pressures of the gases were measured with a Wallace & Tiernan model 61-050 pressure gauge.

The cadmium used was a high-purity sample (99.9999%) manufactured by the Osaka Asahi Metal Co. Pure-grade ammonia (Takachiho Shoji Co.) was used after being degassed at the temperature of liquid nitrogen. Pure-grade methylamine and dimethylamine (Takachiho Shoji Co.) were used after repeated trap-to-trap distillation. An aqueous solution of trimethylamine (Tokyo Kasei Co.) was used after repeated trap-to-trap distillation and drying with calcium hydride and with an alloy of sodium and potassium.

Results

In the cadmium–ammonia system, the phase difference between the resonance fluorescence at 326.1 nm and the sensitized emission from the excited complex at 432 nm decreased with the increase in the pressure of ammonia, as is shown in Fig. 1. It is well known that, in the case of a pseudo-first order reaction, the phase shift, ϕ, is related to the lifetime of the excited species, τ, by means of the following equation:

$$\frac{\tan\phi}{\omega}=\tau,$$

where ω is the angular frequency of modulation.[12] In the present case, although this value of $\tan\phi/\omega$ was independent of the frequency, it depended on the ammonia pressure and had a linear relation with the reciprocal of the pressure in the range of 15—200 Torr, as is shown in Fig. 2. The phase angle of the

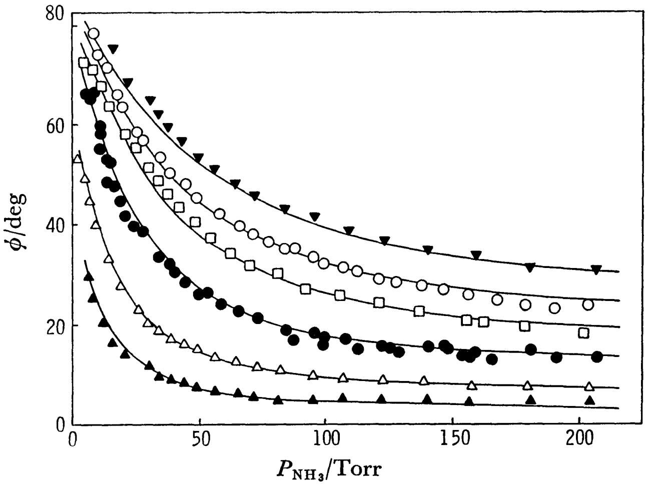

Fig. 1. Phase difference between the resonance fluorescence at 326.1 nm and the luminescence from $CdNH_3^*$ at 432 nm as a function of NH_3 pressure.
▲: 10 kHz, △: 20 kHz, ●: 40 kHz, □: 60 kHz, ○: 78 kHz, ▼: 99 kHz.
Solid lines show the values calculated according to Eq. 12.

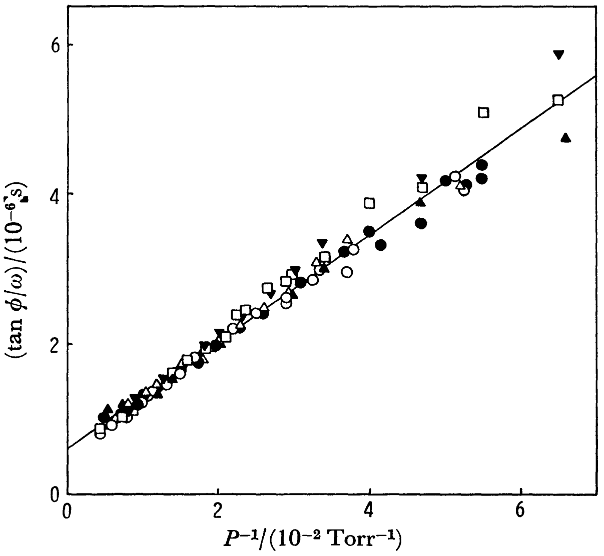

Fig. 2. Values of $\tan \phi/\omega$ as a function of the reciprocal of the NH_3 pressure.
▲: 10 kHz, △: 20 kHz, ●: 40 kHz, □: 60 kHz, ○: 78 kHz, ▼: 99 kHz.

sensitized emission was independent of the wavelength of the emission band of the complex. Similar results could also be obtained in the cases of methylamine, dimethylamine, and trimethylamine, which are illustrated in Figs. 3—5 and 6. The phase angle did not change when a UVD-25 filter, which removes visible light, was inserted between the exciting lamp and the cell. The intensity of the background scattered light at 326.1 nm was measured on the assumption that 100 Torr of hydrogen can quench the triplet cadmium completely;[13] it was estimated to be 0.2% of the emission intensity at 326.1 nm in the absence of quenching gases.

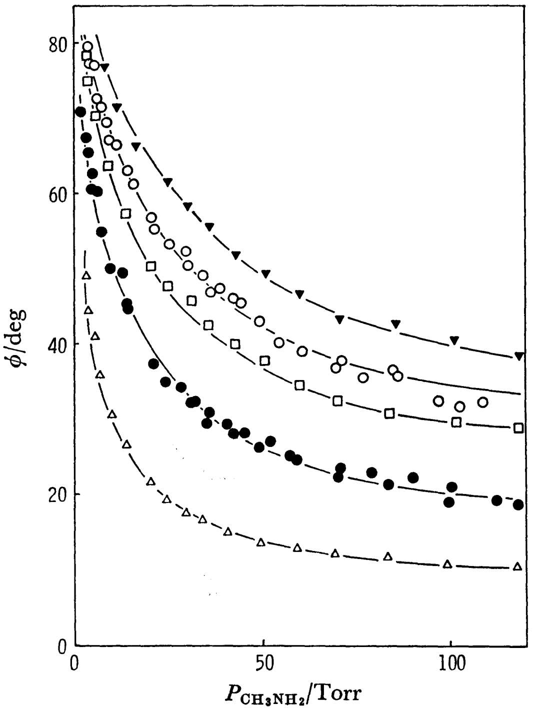

Fig. 3. Phase difference between the resonance fluorescence at 326.1 nm and the luminescence from $CdCH_3NH_2^*$ at 449 nm as a function of CH_3NH_2 pressure.
△: 20 kHz, ●: 40 kHz, □: 60 kHz, ○: 78 kHz, ▼: 99 kHz.

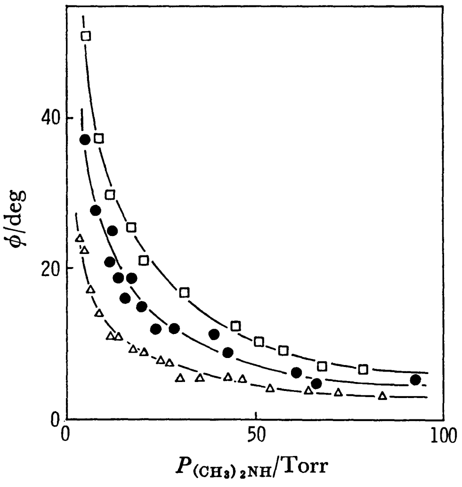

Fig. 4. Phase difference between the resonance fluorescence at 326.1 nm and the luminescence from $Cd(CH_3)_2NH^*$ at 450 nm as a function of $(CH_3)_2NH$ pressure.
△: 20 kHz, ●: 40 kHz, □: 60 kHz.

Discussion

In a recent phase-shift study of the reaction of ammonia with triplet mercury, we found that the phase angle between the resonance fluorescence at 253.7 nm and the luminescence from the excited complex varies with the wavelength of the emission band of the complex.[6] This finding suggests that there are at

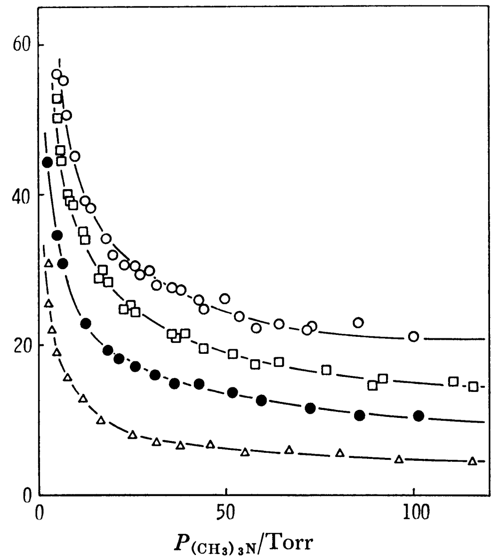

Fig. 5. Phase difference between the resonance fluorescence at 326.1 nm and the luminescence from $Cd(CH_3)_3N^*$ at 435 nm as a function of $(CH_3)_3N$ pressure.
△: 20 kHz, ●: 40 kHz, □: 60 kHz, ○: 78 kHz.

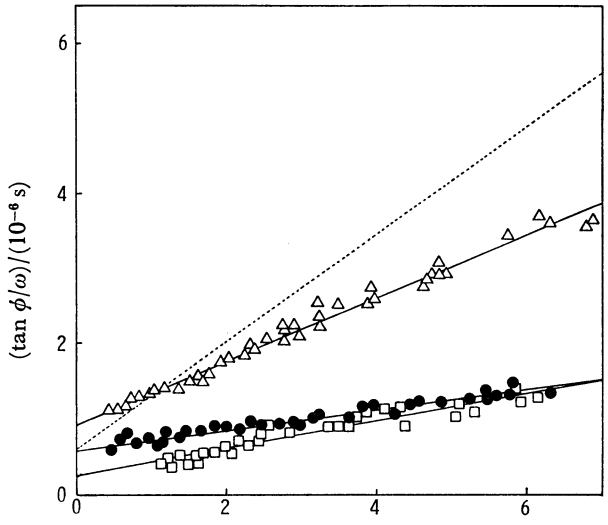

Fig. 6. Values of $\tan\phi/\omega$ as function of the reciprocal of the pressure.
△: CH_3NH_2, □: $(CH_3)_2NH$, ●: $(CH_3)_3N$.
The broken line shows the value for NH_3.

least two kinds of emitting species in this system. On the other hand, in the cadmium–ammonia system, the phase angle of the sensitized luminescence was found to be independent of the wavelength. In other words, the presence of an unstabilized complex could not be confirmed by the present measurements. However, as has been mentioned above, we have found nonlinearity in the Stern-Volmer plots for the quenching of the 326.1 nm resonance line.[8] This nonlinearity cannot be explained without assuming the presence of an unstabilized complex as a precursor of an emitting complex. Accordingly, at first, the following reaction mechanism, which is similar to the one proposed for the mercury–ammonia system, was considered:

$$Cd + h\nu \rightarrow Cd_1^*, \tag{1}$$
$$Cd_1^* \rightarrow Cd + h\nu, \tag{2}$$
$$Cd_1^* + NH_3 \rightarrow \text{Products}, \tag{3}$$
$$Cd_1^* + NH_3 \rightleftarrows CdNH_3^\dagger, \tag{4}$$
$$CdNH_3^\dagger \rightleftarrows Cd_0^* + NH_3, \tag{5}$$
$$CdNH_3^\dagger + NH_3 \rightarrow CdNH_3^* + NH_3, \tag{6}$$
$$CdNH_3^* \rightarrow Cd + NH_3 + h\nu'. \tag{7}$$

Here, Cd, Cd_1^*, and Cd_0^* stand for Cd atoms in the 5^1S_0, 5^3P_1, and 5^3P_0 states respectively, and $CdNH_3^\dagger$ and $CdNH_3^*$ stand for unstabilized and stabilized complexes. Since the energy difference between the $^3P_1$ and $^3P_0$ states is only 6.5 kJ/mol, the reverse reaction of Reaction 4, which was not considered in the mercury–ammonia system, was added. However, in consequence, we failed to explain the present experimental results in terms of this reaction mechanism. According to the above reaction scheme, the measured phase shift, ϕ, can be separated into two parts, the one associated with the finite rate of the removal of $Cd(^3P_0)$ and $CdNH_3^\dagger$ by Reactions 4—6, and the other, with the finite rate of Reaction 7. At limiting high pressures of ammonia, the former part of the phase delay can be ignored compared with the latter one, and the limiting value of $\tan\phi/\omega$ at high pressures, $\tan\phi_\infty/\omega$, becomes equal to the reciprocal of the emitting rate, which is identical to the lifetime of the complex. It should be noted that the rates for Reactions 1—3 make no contribution to the phase difference between the resonance fluorescence (Reaction 2) and the sensitized luminescence (Reaction 7). Once the value of ϕ_∞ has been estimated from the intercept of the linear relationship in Fig. 2, we can obtain the phase delay due to Reactions 4—6 in the low-pressure region by subtracting ϕ_∞ from ϕ. It can easily be verified that this value of $(\phi_\infty - \phi)$ corresponds to the phase difference between the a.c. component of the concentration of the unstabilized complex and that of Cd $(^3P_1)$. Figure 7 shows the the value of $\omega/\tan(\phi-\phi_\infty)$ increases linearly with the ammonia pressure. The fault of the above mechanism, Reactions 1—7, is that

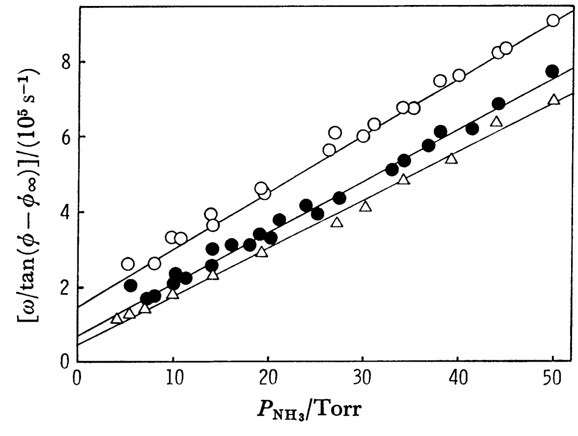

Fig. 7. Values of $\omega/\tan(\phi-\phi_\infty)$ as a function of NH_3 pressure.
△: 20 kHz, ●: 40 kHz, ○: 78 kHz.
Values for other modulation frequencies also showed similar pressure dependence.

the linear relation cannot be derived

Morten *et al.* also have presented a reaction mechanism for this system by analogy with the mercury–ammonia system; in this reaction mechanism a termolecular reaction is assumed in the formation of the complex.[7] However, the linear relationship shown in Fig. 7 cannot be interpreted in terms of their mechanism, either.

On the other hand, the following rather simple mechanism, in which only one intermediate complex is assumed, can explain the linear relations shown in Figs. 2 and 7:

$$\mathrm{Cd} + h\nu \rightarrow \mathrm{Cd_1}^*, \tag{1}$$

$$\mathrm{Cd_1}^* \rightarrow \mathrm{Cd} + h\nu, \tag{2}$$

$$\mathrm{Cd_1}^* + \mathrm{NH_3} \rightarrow \text{Products}, \tag{3}$$

$$\mathrm{Cd_1}^* + \mathrm{NH_3} \rightleftarrows \mathrm{CdNH_3}^*, \tag{8}$$

$$\mathrm{CdNH_3}^* \rightleftarrows \mathrm{Cd_0}^* + \mathrm{NH_3}, \tag{9}$$

$$\mathrm{CdNH_3}^* \rightarrow \mathrm{Cd} + \mathrm{NH_3} + h\nu'. \tag{7}$$

As will be shown in the Appendix, the phase difference between Reactions 2 and 7 is given by

$$\frac{\tan\phi}{\omega} = \frac{\omega^2 + k_{-9}^2[\mathrm{A}]^2 + k_9 k_{-9}[\mathrm{A}]}{(k_9+k_7+k_{-8})\omega^2 + (k_7+k_{-8})k_{-9}^2[\mathrm{A}]^2}, \tag{10}$$

where the rate coefficient for Reaction j is denoted by k_j, and the reverse reaction, by k_{-j}. The ammonia pressure is represented by [A]. If the following inequality is valid under the conditions that $\omega/2\pi < 99$ kHz and $[\mathrm{A}] > 15$ Torr:

$$(k_7+k_{-8})k_{-9}^2[\mathrm{A}]^2 \gg (k_9+k_7+k_{-8})\omega^2,$$

then Eq. 10 can be simplified as follows:

$$\frac{\tan\phi}{\omega} \simeq \frac{1}{k_7+k_{-8}} + \frac{k_9}{(k_7+k_{-8})k_{-9}} \frac{1}{[\mathrm{A}]}. \tag{11}$$

Equation 11 corresponds to the linear plots in Fig. 2. The linear relation between $\omega/\tan(\phi-\phi_\infty)$ and [A] shown in Fig. 7 can also be derived under appropriate conditions such as

$$\omega^4 + \omega^2\{k_{-9}^2[\mathrm{A}]^2 + (k_7+k_{-8})(k_7+k_{-8}+k_9)\}$$
$$\ll \omega^2 k_9 k_{-9}[\mathrm{A}] + (k_7+k_{-8})^2 k_{-9}^2[\mathrm{A}]^2$$

and

$$\omega^2 \ll k_{-9}[\mathrm{A}](k_7+k_{-8}).$$

However, the value of $(\phi-\phi_\infty)$ as well as the value of $\tan\phi_\infty/\omega$ in this mechanism loses its simple physical meaning because of the presence of decay processes of the complex back into its initial components. Even though this scheme is consistent with the linear relations shown in Figs. 2 and 7, the nonlinearity in the Stern-Volmer plots for the quenching of the resonance line cannot be derived.

In order to overcome this discrepancy, we tried to combine these two reaction mechanisms. This was done by including the reverse reaction of Reaction 6 in the first mechanism, Reactions 1—7. Provided that the decay rate of the stabilized complex, $\mathrm{CdNH_3}^*$, is much larger than the angular frequency of the modulation, ω, the phase difference between the concentrations of $\mathrm{CdNH_3}^*$ and $\mathrm{CdNH_3}^\dagger$ can be neglected and an equation similar to Eq. 11 can be obtained for the representation of $\tan\phi/\omega$. The exact expression of $\tan\phi/\omega$, according to the modified mechanism, is given by

$$\frac{\tan\phi}{\omega} = \frac{(k_{-4}+k_5+k_6[\mathrm{A}]+k_{-6}[\mathrm{A}]+k_7)\omega^2 + (k_{-4}+k_6[\mathrm{A}]+k_{-6}[\mathrm{A}]+k_7)k_{-5}^2[\mathrm{A}]^2 + (k_{-6}[\mathrm{A}]+k_7)k_5k_{-5}[\mathrm{A}]}{-\omega^4 + \omega^2\{k_{-4}k_7 + k_5k_7 + (k_{-4}k_{-6}+k_5k_{-6}+k_6k_7-k_5k_{-5})[\mathrm{A}] - k_{-5}^2[\mathrm{A}]^2\} + \{k_{-4}k_7 + (k_{-4}k_{-6}+k_6k_7)[\mathrm{A}]\}k_{-5}^2[\mathrm{A}]^2}. \tag{12}$$

If the following inequalities can be assumed

$$k_{-6}[\mathrm{A}] \gg k_7,\ \frac{\omega^2}{k_{-4}},\ \frac{k_5\omega^2}{k_{-4}k_{-5}[\mathrm{A}]}, \tag{13}$$

$$k_{-5}^2[\mathrm{A}]^2 \gg \frac{k_5\omega^2}{k_{-4}},\ \left\{1+\frac{k_5}{k_{-4}+(k_6+k_{-6})[\mathrm{A}]}\right\}\omega^2, \tag{14}$$

Eq. 12 can be approximated by the following equation:

$$\frac{\tan\phi}{\omega} \simeq \frac{k_6+k_{-6}}{k_{-4}k_{-6}+k_6k_7} + \frac{k_{-4}k_{-5}+k_5k_{-6}}{(k_{-4}k_{-6}+k_6k_7)k_{-5}} \frac{1}{[\mathrm{A}]}. \tag{15}$$

The validity of Eqs. 13 and 14 will be checked in the Appendix. The intercept and the slope of the relationship shown in Fig. 2 correspond to the first and the second terms of the right-hand side of Eq. 15 respectively. The intercepts and the slopes in Fig. 6 also give the relations among the rate constants in the cases of the cadmium–aliphatic amine systems, which are summarized in Table 1.

TABLE 1. RELATIONS AMONG THE RATE CONSTANTS DEDUCED FROM Eq. 15

	$\dfrac{k_{-4}k_{-5}+k_5k_{-6}}{k_{-5}(k_{-4}k_{-6}+k_6k_7)}/10^{-5}$ s Torr	$\dfrac{k_6+k_{-6}}{k_{-4}k_{-6}+k_6k_7}/10^{-7}$ s
$\mathrm{NH_3}$	7.1±0.1	6.0±0.3
$\mathrm{CH_3NH_2}$	4.2±0.1	9.6±0.2
$\mathrm{(CH_3)_2NH}$	1.8±0.2	2.9±0.8
$\mathrm{(CH_3)_3N}$	1.4±0.1	5.7±0.2

It should be noted that, although the reaction mechanism proposed in this paper is a little different from that we presented in previous papers, where the reverse reaction of Reaction 6 is not considered,[8–9] this difference has no essential influence on the steady-state treatment. Tiny change in the meaning of the parameters has to be taken into account.

Because of the presence of the reverse reaction of Reaction 6, we could not determine the radiative lifetime of the complex, $\mathrm{CdNH_3}^*$. The determination of the lifetime would be very difficult, even if the phase angle of the $\mathrm{Cd}(^3\mathrm{P}_0)$ absorption could be measured. In the mercury-photosensitized luminescence of ammonia, the radiative lifetime of $\mathrm{HgNH_3}^*$ could be precisely determined to be (1.4±0.1) μs.[6] The difficulty in determining the radiative lifetime of $\mathrm{CdNH_3}^*$ obviously results from the small energy difference between the $\mathrm{Cd}(^3\mathrm{P}_1)$ and $\mathrm{Cd}(^3\mathrm{P}_0)$ states.

Appendix

Derivation of Eq. 10. When the initial intensity of the resonance radiation from the lamp is modulated with the angular frequency, ω, the concentration of the excited species oscillates with the same frequency. In the cases of Reactions 1—3 and 7—9, the concentration may be written as follows:

$$[\mathrm{Cd}_1{}^*] = \bar{a} + \tilde{a}\mathrm{e}^{\mathrm{i}\omega t},$$
$$[\mathrm{Cd}_0{}^* = \bar{b} + \tilde{b}\mathrm{e}^{\mathrm{i}(\omega t-\theta)},$$
$$[\mathrm{CdNH}_3{}^*] = \bar{c} + \tilde{c}\mathrm{e}^{\mathrm{i}(\omega t-\phi)}.$$

Here, the d.c. and a.c. components of the concentration are respectively expressed by the first and the second terms of the right-hand sides. The phase angles of $[\mathrm{Cd}_0{}^*]$ and $[\mathrm{CdNH}_3{}^*]$ are denoted by θ and ϕ. On the basis of Reactions 1—3 and 7—9, the following differential equations can be obtained:

$$\frac{\mathrm{d}[\mathrm{Cd}_0{}^*]}{\mathrm{d}t} = \mathrm{i}\omega\tilde{b}\mathrm{e}^{\mathrm{i}(\omega t-\theta)}$$
$$= k_9(\bar{c}+\tilde{c}\mathrm{e}^{\mathrm{i}(\omega t-\phi)}) - k_{-9}[\mathrm{A}](\bar{b}+\tilde{b}\mathrm{e}^{\mathrm{i}(\omega t-\theta)}),$$
$$\frac{\mathrm{d}[\mathrm{CdNH}_3{}^*]}{\mathrm{d}t} = \mathrm{i}\omega\tilde{c}\mathrm{e}^{\mathrm{i}(\omega t-\phi)}$$
$$= k_8[\mathrm{A}](\bar{a}+\tilde{a}\mathrm{e}^{\mathrm{i}\omega t}) + k_{-9}[\mathrm{A}](\bar{b}+\tilde{b}\mathrm{e}^{\mathrm{i}(\omega t-\theta)})$$
$$- (k_9+k_7+k_{-8})(\bar{c}+\tilde{c}\mathrm{e}^{\mathrm{i}(\omega t-\phi)}).$$

Separating the time-dependent parts, we obtain

$$(\mathrm{i}\omega+k_{-9}[\mathrm{A}])\tilde{b}\mathrm{e}^{-\mathrm{i}\theta} - k_9\tilde{c}\mathrm{e}^{-\mathrm{i}\phi} = 0,$$
$$-k_{-9}[\mathrm{A}]\tilde{b}\mathrm{e}^{-\mathrm{i}\theta} + (\mathrm{i}\omega+k_9+k_7+k_{-8})\tilde{c}\mathrm{e}^{-\mathrm{i}\phi} = k_8[\mathrm{A}]\tilde{a}.$$

Equation 10 can easily be derived from these simultaneous equations. Equation 12 can also be obtained in a similar manner.

Validity of Eqs. 13 and 14. In order to explain theoretically the observed pressure dependence of the phase angle, ϕ, in Fig. 1, we tried to find a set of parameters according to the reaction mechanism proposed. The following values are some examples: $k_{-4}=5.5\times10^6\ \mathrm{s}^{-1}$, $k_5=3.8\times10^8\ \mathrm{s}^{-1}$, $k_{-5}=9.1\times10^5\ \mathrm{s}^{-1}\ \mathrm{Torr}^{-1}$, $k_6=2.2\times10^7\ \mathrm{s}^{-1}\ \mathrm{Torr}^{-1}$, $k_{-6}=8.6\times10^6\ \mathrm{s}^{-1}\ \mathrm{Torr}^{-1}$, and $k_7=1.7\times10^5\ \mathrm{s}^{-1}$. The solid lines in Fig. 1 were drawn according to Eq. 12 by using these values. From these values, the validity of Eqs. 13 and 14 can easily be derived. Since the observable value is only the phase difference between the two kinds of emission, the resonance fluorescence at 326.1 nm and the luminescence from the excited complex, we cannot verify that the above set of parameters is unique.

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