The Cd 5 $^3P_0$ State in the Cadmium-photosensitized Reaction and the Quenching of the Resonance Radiation at 326.1 nm by Nitrogen, Carbon Monoxide, and Carbon Dioxide

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(Received July 8, 1974)

The emission of the resonance line at 326.1 nm (5 $^3P_1 \rightarrow 5\ ^1S_0$) and the absorptions of Cd($^3P_0$) at 340.4 nm (5 $^3D_1 \leftarrow 5\ ^3P_0$) and of Cd($^3P_1$) at 346.6 nm (5 $^3D_2 \leftarrow 5\ ^3P_1$) have been measured as functions of the pressure of foreign gases at 250 °C. At the pressures higher than 1 Torr of any rare gas, an equilibrium was established between 5 $^3P_1$ and 5 $^3P_0$ states. The efficiency of nitrogen in producing the 5 $^3P_0$ state from the 5 $^3P_1$ state was found to be more than 10^3 times those of rare gases. The quenching efficiencies of nitrogen, carbon monoxide, and carbon dioxide for the resonance radiation at 326.1 nm were also measured by using argon as the diluent gas. The half-quenching pressures obtained were 73 ± 3, 0.47 ± 0.01, and 0.096 ± 0.003 Torr for nitrogen, carbon monoxide, and carbon dioxide respectively.

The energy state, 5 $^3P_0$, of cadmium is 86.1 kcal mol^{-1} above the ground state, Cd 5 $^1S_0$, and 1.6 kcal mol^{-1} below the Cd 5 $^3P_1$ state. Recently, Breckenridge and Callear observed the formation of the Cd($^3P_0$) state in the system of cadmium vapor and methane illuminated by the resonance line at 228.8 nm (5 $^1P_1 \rightarrow 5\ ^1S_0$).$^{1)}$ In the 326.1 nm cadmium-photosensitized reactions, however, the participation of the 5 $^3P_0$ state has not yet been ascertained, although, by analogy with the Hg–NH$_3$ system, Morten *et al.* assumed the 5 $^3P_0$ state as the precursor of the emitting species in the cadmium-photosensitized emission of ammonia.$^{2)}$ On the other hand, the 6 $^3P_0$ state of mercury atoms was studied by several groups,$^{3-7)}$ and now it is well established that the Hg 6 $^3P_0$ state plays an important role in the mercury photosensitization.

In a previous short communication,$^{8)}$ we reported that the 5 $^3P_0$ state of cadmium atoms produced in the cadmium-photosensitized reactions in argon, nitrogen, and ammonia can be observed by the absorptions at the wavelengths of 340.4 nm (5 $^3D_1 \leftarrow 5\ ^3P_0$) and 467.8 nm (6 $^3S_1 \leftarrow 5\ ^3P_0$).

The present paper will report the details of the absorption measurement of Cd($^3P_0$) and Cd($^3P_1$) as well as the quenching of the resonance radiation at 326.1 nm (5 $^3P_1 \rightarrow 5\ ^1S_0$) by nitrogen, carbon monoxide, and carbon dioxide.

Experimental

The apparatus used in the present experiment was previously outlined.$^{8)}$ The reaction cell was a quartz tube, 2 cm in diameter and 30 cm long, with two flat planes. The exciting resonance lamp was a home-made, U-shaped cadmium lamp made of Pyrex, while the light source for the measurement of the absorption was made of quartz. Both lamps were kept in electric furnaces at 250±1 °C and operated by an alternating current (50 Hz). The intensity from the lamp, therefore, changes with the frequency of 100 Hz. However, since the lifetimes of Cd($^3P_1$) and Cd($^3P_0$) are known to be very short compared with the period of the change in the light intensity,$^{9)}$ the light intensities observed in the present experiment are regarded as the averages over the period. The vapor pressure of cadmium in the cell was kept constant (3.2×10^{-3} Torr) by maintaining the temperature of the cadmium storage at 240±1 °C in all the photosensitized reactions. The light intensity from the cell was measured by means of a combination of a monochromator (Shimadzu photoelectric spectrophotometer, model QV-50), a 1P28 photomultiplier, and a Ritsu photometer, type 101A, and was recorded by means of a Yokogawa Laboratory recorder, type 3043. The slit of the monochromator was properly opened, so that the observed intensity was one integrated over the spectral line profiles at 326.1, 340.4, and 346.6 nm. The pressure of the gases was measured by a W & T model 62–075 pressure gauge supplied by the Nagano Keiki Co.

The cadmium metal used was high-purity cadmium (99.9999%) manufactured by the Osaka Asahi Metal Co. Pure-grade rare gases (He, Ne, Ar, Kr, and Xe) purchased from the Takachiho Shoji Co. were used after repeated adsorption and desorption on a molecular sieve at the temperature of liquid nitrogen. Pure-grade N$_2$, CO, and CO$_2$ were used after they had been treated as previously described.$^{10)}$

Since the absorption of the 326.1 nm resonance line with the cadmium vapor at 3.2×10^{-3} Torr is small (the *f*-value of the Cd 326.1 nm line is 0.002,$^{9)}$ nearly 1/20 of that of the Hg 253.7 nm line), 30% of the absorption occurs in a path length of 1 cm. Therefore, the formation of the Cd($^3P_1$) state in the cell is almost uniform.

Results

Pressure Dependence of the Emission Intensity at 326.1 nm. When the cell containing cadmium vapor was illuminated by means of the exciting lamp, the emission was observed at 326.1 nm. Upon the addition of rare gases, the intensity of the emission increased with the increase in the pressure, as is shown in Fig. 1. Rare gases other than Ne showed almost the same pressure dependence of the intensity. The deviation observed in the case of Ne is probably due to the impurity, which could not be removed by the method described above. When N$_2$ was added, the intensity increased slightly up to a few Torr and then gradually decreased with the increase in pressure. In the case of CO and CO$_2$, the intensity decreased rapidly, even in the low-pressure region. The efficiencies of CO and CO$_2$ in quenching the resonance radiation must be considerably larger than that of N$_2$.

The Absorption of the 346.6 nm Spectral Line by Cd($^3P_1$).

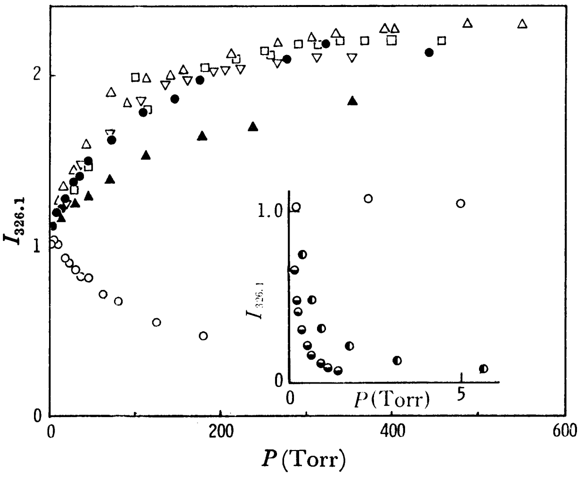

Fig. 1. The intensity of the resonance radiation at 326.1 nm as a function of the pressure of the foreign gas. △: He, ▲: Ne, ●: Ar, □: Kr, ▽: Xe, ○: N_2, ◐: CO, ◒: CO_2.

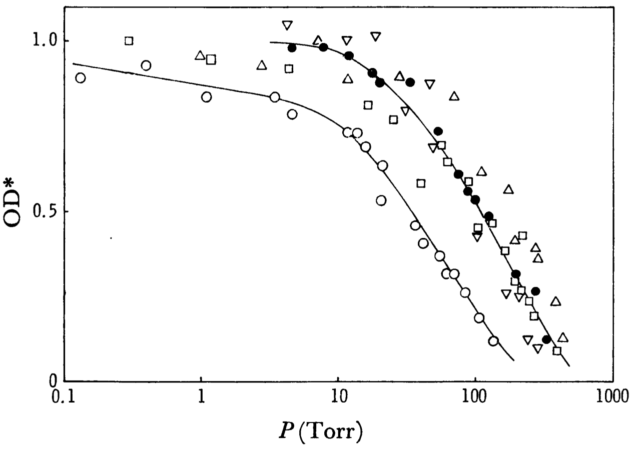

Fig. 2. The relative optical density of Cd($^3P_1$) atoms at 346.6 nm as a function of the pressure of the foreign gas. △: He, ●: Ar, □: Kr, ▽: Xe, ○: N_2.

Figure 2 shows the pressure dependence of the relative optical density at 346.6 nm. For all the gases used, the optical density was constant in the low-pressure region and decreased gradually with the increase in the pressure. The curves for rare gases are in agreement with each other within the limits of experimental error. In the case of N_2, the optical density began to decrease at lower pressures.

The Absorption of the 340.4 nm Spectral Line by Cd($^3P_0$). Figure 3 shows the relative optical density at 340.4 nm as a function of the pressure. All the curves have maxima. Obviously, the efficiency in producing the Cd($^3P_0$) state increases in the order: He<Ar~Kr<Xe<N_2. The pressure dependences of the decrease in optical density in the high-pressure region agree approximately with each other for all the rare gases. In nitrogen, the optical density began to decrease at a pressure lower than that in rare gases. This is similar to the tendency observed in the absorption of the 346.6 nm spectral line by Cd($^3P_1$).

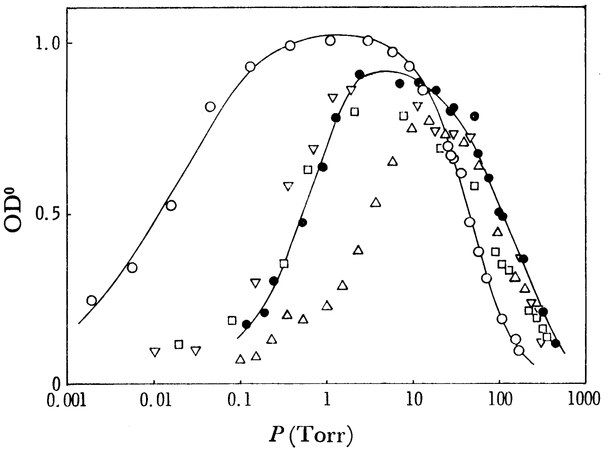

Fig. 3. The relative optical density of Cd($^3P_0$) atoms at 340.4 nm as a function of the pressure of the foreign gas. △: He, ●: Ar, □: Kr, ▽: Xe, ○: N_2.

The absorption of the 467.8 nm spectral line by Cd($^3P_0$) was also measured, although the data are not shown here. The pressure dependence of the relative optical density was almost the same as that obtained with the absorption of the 340.4 nm line.[8] The optical density at 467.8 nm was much smaller than that at 340.4 nm.

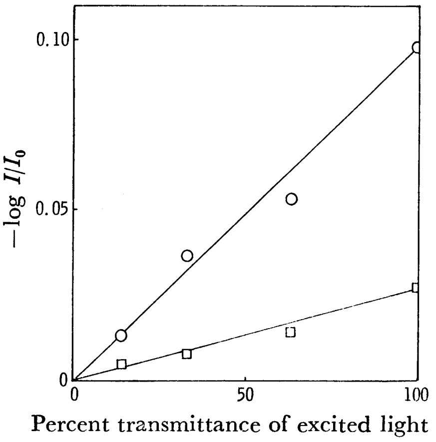

Fig. 4. The optical densities at 340.4 nm (P_{Ar}=18 Torr) (○) and at 346.6 nm (P_{Ar}=25 Torr) (□) as functions of the intensity of the exciting light.

The Lambert-Beer Law. In atomic absorption spectroscopy, it should be checked whether the Lambert-Beer law can be applied or not. In order to investigate this point in the present experiment, we measured the absorptions at 340.4 and 346.6 nm as functions of the intensity of the exciting lamp. The intensity was changed by inserting a screen between the cell and the exciting lamp. The results are shown in Fig. 4. Plots of the optical densities *vs.* the light intensity, to which the concentration of excited atoms should be proportional, give straight lines which pass through the point of origin. These results show that the Lambert-Beer law holds in the present measurements.

$$-\log (I/I_0)_{346.6} = \mathrm{OD}^* = \varepsilon^* l[\mathrm{Cd}^*] \qquad \text{(I)}$$

$$-\log (I/I_0)_{340.4} = \mathrm{OD}^0 = \varepsilon^0 l[\mathrm{Cd}^0] \qquad \text{(II)}$$

where, ε^* and ε^0 are the apparent extinction coefficients of the Cd($^3P_1$) and Cd($^3P_0$) atoms for the absorption of the spectral lines at 346.6 and 340.4 nm from the light source for the absorption measurement and where l is the length of the cell.

Pressure Dependence of the Apparent Extinction Coefficient. Both the emission intensity at 326.1 nm and the optical density of the absorption at 346.6 nm are measures of the concentration of Cd($^3P_1$) atoms. As was shown above, the optical density at 346.6 nm can be correlated to the concentration of Cd($^3P_1$) atoms by Eq. (I). On the other hand, this concentration should be correlated to the emission intensity at 326.1 nm by the following equation:

$$I_{326.1} = \tau^{-1}[\mathrm{Cd}^*] \qquad \text{(III)}$$

where τ is the effective lifetime of the Cd($^3P_1$) atoms. As is shown in Fig. 2, the optical density of the Cd($^3P_1$) atoms decreases at pressures higher than 10 Torr, while, as is shown in Fig. 1, the emission intensity at 326.1 nm does not decrease in this pressure region. This apparent discrepancy must be due to the different pressure dependences of ε^* and τ^{-1}.

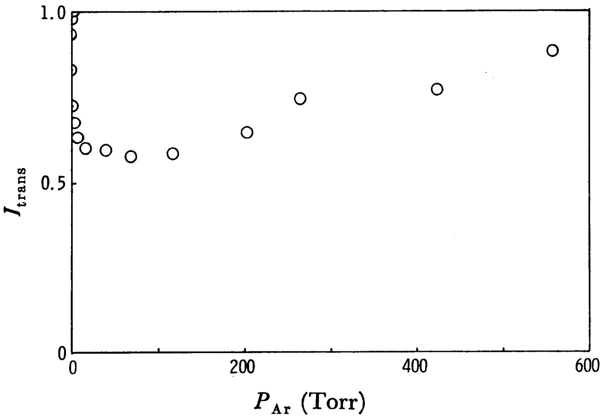

Fig. 5. The intensity of the transmitted light at 326.1 nm as a function of the pressure of argon. The vapor pressure of cadmium is 1.0×10^{-4} Torr (180 °C).

In order to examine the pressure dependence of the apparent extinction coefficient, we measured the intensity of the transmitted light at 326.1 nm from the light source for the absorption measurements at various pressures of argon, while keeping the cadmium vapor pressure constant, 10^{-4} Torr. The results are shown in Fig. 5. Obviously, the intensity of the transmitted light at 326.1 nm decreased initially with the increase in the argon pressure and then gradually increased with the further increase in pressure. The significance of this experiment will be discussed later.

In practice, we wanted to measure the pressure dependence of ε^* and ε^0. However, we could not do so because we have no proper method of producing constant concentrations of Cd* and Cd^0 by changing the argon pressure.

As will be shown later on the basis of the kinetic analysis, τ is estimated to be independent of the examined pressures of rare gases. Consequently, it may be concluded that the apparent discrepancy described above is due to the pressure dependence of the apparent extinction coefficient, ε^*.

Quenching of the Resonance Radiation at 326.1 nm by N_2, CO, and CO_2. As was mentioned above, the absorption intensity at 326.1 nm is dependent upon the pressure of foreign gases. Therefore, the curves obtained with N_2, CO, and CO_2 in Fig. 1 cannot be pure quenching curves for the Cd($^3P_1$) atoms. In order to minimize the effect of the pressure broadening, quenching gases were diluted with argon and the total pressure was kept constant. The experimental data thus obtained are listed in Table 1, from which we can estimate the quenching efficiencies of N_2, CO, and CO_2 quantitatively.

TABLE 1. THE INTENSITY OF THE RESONANCE RADIATION AS A FUNCTION OF THE PRESSURE OF N_2, CO OR CO_2. THE TOTAL PRESSURE IS CONTROLLED BY ADDING ARGON

Nitrogen

Total pressure (Torr)							
210		140		94		63	
N_2	I	N_2	I	N_2	I	N_2	I
0	2.05	0	1.88	0	1.73	0	1.58
2.7	1.99	3.5	1.76	2.3	1.71	1.5	1.53
5.2	1.92	6.9	1.65	4.6	1.62	3.1	1.45
10.4	1.92	10.4	1.61	6.9	1.61	4.6	1.45
15.6	1.69	17.4	1.46	11.6	1.53	7.7	1.39
26.0	1.50	26.1	1.38	17.4	1.43	15.6	1.30
39.2	1.35	34.9	1.24	23.4	1.32	23.1	1.27
52.5	1.19	51.7	1.10	34.7	1.21	32.0	1.15
77.8	1.09	71.4	1.01	48.0	1.16	39.5	1.10
106.9	0.87	88.3	0.90	59.2	1.06	46.9	1.00
131.9	0.80	104.8	0.81	70.4	0.97		
156.4	0.70						

Carbon monoxide

Total pressure (Torr)					
80		48		28.5	
CO	I	CO	I	CO	I
0	1.67	0	1.50	0	1.37
0.10	1.29	0.062	1.26	0.073	1.15
0.20	1.20	0.12	1.15	0.10	1.04
0.29	1.07	0.17	1.08	0.20	0.90
0.55	0.82	0.33	0.90	0.39	0.75
1.10	0.53	0.66	0.67	0.55	0.63
1.54	0.46	0.91	0.50	0.94	0.45
2.66	0.26	1.58	0.35		

Carbon dioxide

Total pressure (Torr)					
80		48		28.5	
CO_2	I	CO_2	I	CO_2	I
0	1.67	0	1.50	0	1.37
0.008	1.47	0.005	1.44	0.012	1.18
0.033	1.16	0.020	1.24	0.049	0.91
0.14	0.71	0.083	0.84	0.082	0.68
0.23	0.44	0.14	0.50	0.21	0.48
0.59	0.27	0.35	0.37	0.35	0.30
0.98	0.15	0.58	0.22		

Discussion

The Pressure Broadening of the Absorption Line. As Fig. 5 shows, the intensity of the transmitted light at 326.1 nm decreased with the increase in argon pressure up to 100 Torr. This is probably due to the pressure broadening of the absorption line of the cadmium atoms in the ground state. This reasoning is also applicable to the increase in the emission at 326.1 nm with the increase in the pressure of rare gases, which is shown in Fig. 1. However, the increase in the emission intensity with the increase in the pressure is much slower than the decrease in the transmitted light shown in Fig. 5. This is probably because the spectral line from the exciting lamp is much broader than that from the light source for the absorption measurement.

Upon the further increase in argon pressure over 100 Torr, the absorption line of the cadmium atoms in the ground state will be broadened more than the spectral line from the light source. Consequently, the apparent extinction coefficient will be reduced. This explanation matches the observed increase in the intensity of the transmitted light at 326.1 nm shown in Fig. 5. On the other hand, the emission intensity, which is shown in Fig. 1, does not suffer from such an effect at the pressures examined, because the spectral line from the exciting lamp is much broader than that from the light source for the absorption measurements.

In Figs. 2 and 3, we show the pressure dependences of the absorption of Cd($^3P_1$) and Cd($^3P_0$) atoms. The decrease in the optical densities at the higher pressures of rare gases may be explained by the reasoning presented above. That is, the quenching efficiency of rare gases is negligibly small and the decrease in the optical densities over 10 Torr of rare gases is due to the decrease in the apparent extinction coefficients, ε^* and ε^0. In the case of N_2, however, both the pressure broadening of the absorption line and the quenching of the excited atoms have to be considered.

Formation and Quenching of Cd($^3P_0$) Atoms. In order to make a kinetic analysis of the steady-state processes occurring in a cell under a constant illumination, the following reactions are considered:

$$\begin{array}{lll}
(1) & \mathrm{Cd}(^1\mathrm{S}_0) + h\nu(326.1) \longrightarrow \mathrm{Cd}^*(^3\mathrm{P}_1) & I_\mathrm{a} \\
(2) & \mathrm{Cd}^* \longrightarrow \mathrm{Cd} + h\nu & k_0 \\
(3) & \mathrm{Cd}^* + \mathrm{M} \longrightarrow \mathrm{Cd} + \mathrm{M} & k_1 \\
(4) & \mathrm{Cd}^* + \mathrm{M} \longrightarrow \mathrm{Cd}^0(^3\mathrm{P}_0) + \mathrm{M} & k_2 \\
(5) & \mathrm{Cd}^0 \longrightarrow \mathrm{Cd}\ (\text{on wall}) & k_3 \\
(6) & \mathrm{Cd}^0 + \mathrm{M} \longrightarrow \mathrm{Cd} + \mathrm{M} & k_4 \\
(7) & \mathrm{Cd}^0 + \mathrm{M} \longrightarrow \mathrm{Cd}^* + \mathrm{M} & k_5
\end{array}$$

where M stands for rare gases, N_2, CO, or CO_2. If Cd is replaced by Hg, this reaction mechanism is the same as that proposed by Kimbell and LeRoy[3] for the case of the Hg–N_2 system except for the emission from the $^3P_0$ state. Such an emission could not be observed in the present system. Reaction (5) is a diffusion-controlled reaction, and its rate may be expressed as $k_3[\mathrm{Cd}^0]/[\mathrm{M}]$. Therefore, the steady-state-treatment of Reactions (1)—(7) gives the following relation:

$$\frac{I_\mathrm{a}}{[\mathrm{Cd}^0]} = \frac{A}{[\mathrm{M}]^2} + \frac{B}{[\mathrm{M}]} + C + D[\mathrm{M}] \qquad \text{(IV)}$$

where A, B, C, and D are constants depending on the foreign gas. For rare gases, we can ignore Reactions (3) and (6), as has been discussed in the previous section. Therefore,

$$A = k_0k_3/k_2,\ B = k_3,\ C = k_0k_5/k_2 \text{ and } D = 0,$$

while, for nitrogen,

$$A = k_0k_3'/k_2',\ B = k_3'(k_1'+k_2')/k_2',$$
$$C = k_0(k_4'+k_5')/k_2' \text{ and } D = (k_1'k_4'+k_2'k_4'+k_1'k_5')/k_2'.$$

where the prime indicates the value in nitrogen. By using Eq. (II), the left-hand side of Eq. (IV) can be expressed as follows:

$$\frac{I_\mathrm{a}}{[\mathrm{Cd}^0]} = \frac{I_\mathrm{a}}{\mathrm{OD}^0}\varepsilon^0 l \qquad \text{(V)}$$

Since the pressure dependence of the apparent value of ε^0 can be estimated from Fig. 3, as has been discussed in the previous section, we can calculate the relative values of A, B, C, and D by the method given in the Appendix. The results are tabulated in Table 2. This procedure is the same as that used by Kimbell and LeRoy for the analysis of the Hg($^3P_0$) atoms.[3] The solid lines in Fig. 6 were drawn by substituting the values in Table 2 into Eq. (IV).

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

Gas	A (Torr^2 s^{-1})	B (Torr s^{-1})	C (s^{-1})	D (Torr^{-1} s^{-1})
He	0.030	4.00	0.98	0
Ar	0.015	0.58	0.98	0
Kr	0.015	0.58	0.98	0
Xe	0.005	0.33	0.98	0
N_2	8×10^{-6}	0.008	1.03	0.033

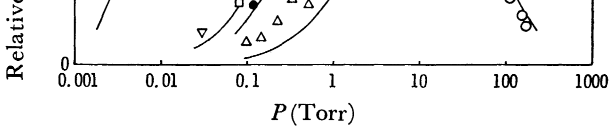

Fig. 6. The relative concentration of Cd($^3P_0$) atoms as a function of the pressure of the foreign gas. —: He, ●: Ar, □: Kr, ▽: Xe, ○: N_2. Solid lines were obtained by substituting the values in Table 2 into Eq. (IV).

From the values of A, it is found that the values of k_2 (or k_2') increase in the order: He<Ar~Kr<Xe≪N_2. This order corresponds to the efficiency of the formation of Cd($^3P_0$) atoms. A comparison suggests that the efficiency of N_2 in producing Cd($^3P_0$) is more than 10^3 times those of rare gases. The value of B for rare

gases is equal to k_3, which is directly proportional to the diffusion coefficient of $Cd(^3P_0)$ atoms in rare gases. The order of the k_3 values with respect to the kind of rare gases seems to be reasonable, because the diffusion coefficient in a lighter gas may be larger than that in a heavier gas. The values of C for all the gases examined are approximately equal. This constancy should hold for rare gases, because $C=k_0k_5/k_2$ and the ratio of k_5/k_2 should be equal to the equilibrium constant between $[Cd^0]$ and $[Cd^*]$. In the case of nitrogen, this equilibrium constant should be expressed by k_5'/k_2'. The constancy of C, therefore, suggests that k_4' is much smaller than k_5'.

The equilibrium between $[Cd^0]$ and $[Cd^*]$ at 250 °C can be calculated as follows:

$$[Cd^0]/[Cd^*] = \frac{1}{3}\exp(1.6/RT) = 1.54$$

The ratio of the optical densities of Cd^0 and Cd^* atoms is 2.5 ± 0.4 at pressures higher than 10 Torr. The difference in number is due to the difference in extinction coefficient. Below 10 Torr, Reaction (5) seems to play a part in the reaction mechanism.

Quenching of the Resonance Radiation by N_2, CO, and CO_2. When only argon is present in the cell, Reactions (3) and (6) may be ignored; if the pressure is higher than 10 Torr, Reaction (5) may also be ignored. Therefore, the following equation should hold in the steady state:

$$I^{Ar}_{326.1} = k_0[Cd^*] = I_a \tag{V}$$

Here, $I^{Ar}_{326.1}$ is the intensity of the emission at 326.1 nm. When nitrogen is a substrate, the steady-state-treatment gives the following relation:

$$I^{N_2}_{326.1} = \frac{I_a}{1+\left\{\frac{k_1'}{k_0}+\frac{k_2'k_4'}{k_0(k_4'+k_5')}\right\}[N_2]} \tag{VI}$$

By substituting Eq. (V) into Eq. (VI) and by using the $k_5' \gg k_4'$ relation, we can obtain the following equation:

$$\frac{I^{Ar}_{326.1}}{I^{N_2}_{326.1}} = 1 + \frac{1}{k_0}\left(k_1'+\frac{k_2'k_4'}{k_5'}\right)[N_2] \tag{VII}$$

This equation can be used to compare the emission intensity at the same pressures of Ar and N_2.

Similarly, the following equations can be obtained for the absorptions at 346.6 and 340.4 nm:

$$\frac{OD^{*Ar}}{OD^{*N_2}} = 1 + \frac{1}{k_0}\left(k_1'+\frac{k_2'k_4'}{k_5'}\right)[N_2] \tag{VIII}$$

$$\frac{OD^{0Ar}}{OD^{0N_2}} = 1 + \frac{1}{k_0}\left(k_1'+\frac{k_2'k_4'}{k_5'}\right)[N_2] \tag{IX}$$

Here, the superscripts Ar and N_2 designate that these values were obtained in Ar and N_2 respectively.

Figure 7 shows the experimental plots for Eqs. (VII), (VIII), and (IX). The straight line obtained shows the validity of the three equations. The half-quenching pressure, which corresponds to the reciprocal of the slope, was calculated to be about 60 Torr.

When a quenching gas is diluted with argon and the total pressure is kept constant, the following Stern-Volmer expression can be obtained:

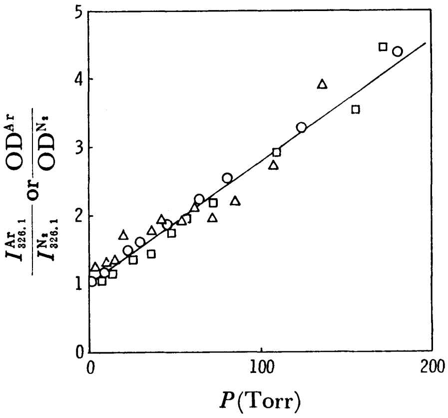

Fig. 7. Experimental plots for Eq. (VII) (○), Eq. (VIII) (△) and Eq. (IX) (□).

$$\frac{I^0_{326.1}}{I_{326.1}} = 1 + \frac{k_1'}{k_0}[N_2] + \frac{k_4'[N_2]}{k_0}\,\frac{k_2[Ar]+k_2'[N_2]}{k_4'[N_2]+k_5[Ar]+k_5'[N_2]} \tag{X}$$

Here, $I^0_{326.1}$ and $I_{326.1}$ are the emission intensities at 326.1 nm in the absence and in the presence of a quencher, N_2. Since $k_5' \gg k_4'$ and $k_2'/k_5' = k_2/k_5$, Eq. (X) can be reduced to the form:

$$\frac{I^0_{326.1}}{I_{326.1}} = 1 + \frac{1}{k_0}\left(k_1'+\frac{k_2'k_4'}{k_5'}\right)[N_2] \tag{XI}$$

The right-hand side of this equation is exactly the same as those of Eqs. (VII), (VIII), and (IX). The experimental plots obtained with N_2 at various total pressures are shown in Fig. 8, together with the plots obtained by using CO and CO_2 as the quencher. All the plots for each quencher lie on each straight line, and no dependence on the total pressure can be seen. This result strongly suggests that k_0 is independent of the pressure in the range examined. In other words, the lifetime of the $Cd(^3P_1)$ atoms, τ, is independent of the pressure of the foreign gas in the pressure range examined.

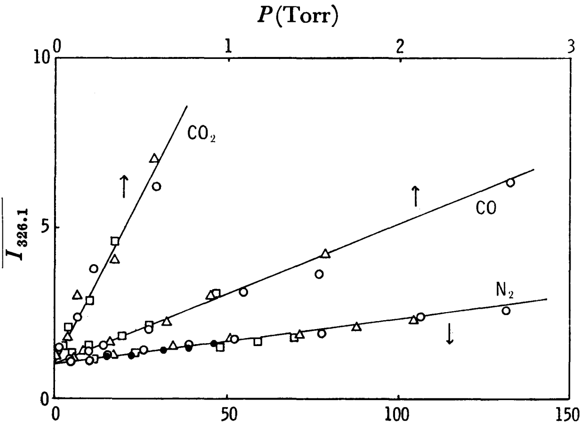

Fig. 8. Stern-Volmer plots for the quenching of the resonance radiation at 326.1 nm by N_2, CO and CO_2. The quenching gas is diluted with argon. For N_2, the total pressures are 210 (○), 140 (△), 94 (□), and 63 (●) in Torr. For CO and CO_2, the total pressures are 80 (○), 48 (△), and 28.5 (□) in Torr.

Table 3. Half-quenching pressures for the resonance radiation at 326.1 nm (Torr)

Quencher	This work	Ref. 10
N_2	73 ± 3	220 ± 3
CO	0.47 ± 0.01	0.34 ± 0.09
CO_2	0.096 ± 0.003	0.06 ± 0.03

Table 3 summarizes the half-quenching pressures calculated from the linear plots in Fig. 8. The value obtained for nitrogen is in fair agreement with that obtained from the plots in Fig. 7. The small discrepancy may be due to the complete neglect of k_4' in relation to k_5' in Eqs. (VII), (VIII), and (IX). The third column in Table 3 shows the half-quenching pressures reported in the previous paper.[10] These values were obtained by paying no attention to the pressure broadening of the absorption lines. Therefore, the values obtained in the present paper should be more reliable.

The authors are indebted to Dr. Soji Tsuchiya of the University of Tokyo for his valuable discussions.

Appendix

By substituting Eq. (V) into Eq. (IV), we can obtain the following equation:

$$\frac{I_a}{OD^0}\varepsilon^0 l = \frac{A}{[M]^2} + \frac{B}{[M]} + C + D[M] \qquad \text{(XII)}$$

The A, B, C, and D constants can be obtained by examining the relationship between $I_a\varepsilon^0/OD^0$ and [M] in the low-, medium-, and high pressure regions. When the pressure of the foreign gas is low, the last term on the right-hand side of Eq. (XII) can be ignored. For this pressure region, the following equation can be obtained:

$$\frac{I_a}{OD^0}\varepsilon^0 l[M]^2 = A + B[M] + C[M]^2 \qquad \text{(XIII)}$$

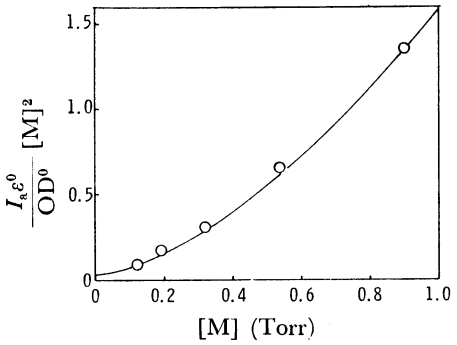

Fig. 9. $I_a\varepsilon^0[M]^2/OD^0$ in arbitrary unit as a function of argon pressure in the low pressure range.

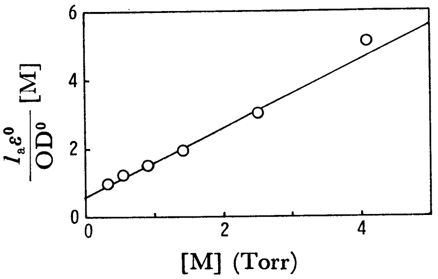

Fig. 10. $I_a\varepsilon^0[M]/OD^0$ in arbitrary unit as a function of argon pressure in the medium pressure range.

In Fig. 9, the relative value of $I_a\varepsilon^0[M]^2/OD^0$ for argon is plotted against [M] for the pressures below 1 Torr. From the curve, the relative values of A, B, and C were obtained. In Fig. 10 the relative value of $I_a\varepsilon^0[M]/OD^0$ for argon is plotted against [M] for the pressure region from 0.4 to 5.0 Torr. A linear relationship was thus obtained. This shows that the first and last terms on the right-hand side of Eq. (XII) can be ignored in this pressure region. From the intercept and the slope of the straight line in Fig. 10, the relative values of B and C can be obtained. These values were found to agree with the values obtained above. Similar treatments were carried out in order to determine the constants, A, B, and C for other foreign gases. The D constant for N_2 was obtained by taking the simple average of the quantity:

$$\{(I_a\varepsilon^0)/OD^0 - (A/[N_2]^2 + B/[N_2] + C)\}/[N_2]$$

in the pressure region from 5 to 200 Torr.

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