Quenching of Excited Zinc(^3P_J) and Zinc($^1P_1$) Atoms by Several Gases

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The intensities of the 307.6 nm and 213.9 nm resonance lines of zinc were measured at different pressures of several gases, and the quenching rate constants were determined on the basis of the Stern-Volmer plots. The quenching cross-sections obtained here were compared with those for mercury and cadmium. The simple charge-transfer curve-crossing theory proposed by Breckenridge and Renlund for the quenching of excited cadmium and mercury atoms by N_2, CO, CO_2, and so on was found to be useful for the quenching of excited zinc atoms, as well. Isotope effects on the quenching of Zn(^3P_J) and Zn($^1P_1$) by H_2 and D_2 were also discussed.

Recently, Breckenridge *et al.* have measured the quenching cross-sections of excited cadmium (^3P_J) and cadmium ($^1P_1$) atoms by several gases.[1] They have compared their values with those for the quenching of mercury ($^3P_1$ and $^3P_0$) atoms and other excited atoms, and have discussed several possible exit channels for the quenching of excited metal atoms.

In spite of several comprehensive studies of the quenching and chemical reactivity of excited mercury[2-4] and cadmium[5] atoms, there have been almost no studies of the excited states of zinc (valence isoelectronic atom with cadmium and mercury). Since the excitation energy of Zn($^3P_1$) lies between those of Cd($^3P_1$) and Hg($^3P_1$), we expected that a comparison of the reactions photosensitized by these three atoms would give further information about the detailed mechanism of the reactions.

In a previous short communication,[6] we reported the quenching cross sections of Zn(^3P_J) by H_2, D_2, and CH_4. The present paper will report the details of the quenching of Zn(^3P_J) and Zn($^1P_1$).

Experimental

The apparatus was the same as that previously described.[6] The reaction cell and the zinc lamp made of quartz were kept in a furnace at 305±2 °C. Two resonance lines (213.9 and 307.6 nm) are emitted from the lamp. These lines give rise to Zn($^1P_1$) and Zn($^3P_1$) atoms respectively. In the measurement of the quenching rate of the Zn(^3P_J) atoms, the 213.9 nm resonance line was filtered out by inserting a Pyrex plate between the cell and the lamp. The light intensities from the cell were measured by means of a Hitachi spectrophotometer, Model 139. The pressure of the gases was measured by means of a W & T model 62-075 pressure gauge (Nagano Keiki Co). The low pressures of the quenching gases were measured using calibrated expansion volumes.

The zinc metal used was high-purity zinc (99.9999%) manufactured by the Osaka Asahi Metal Co. Research-grade H_2(99.999%), D_2(99.5%), CH_4(99.95%), N_2(99.999%), CO(99.8%), and CO_2(99.99%) purchased from the Takachiho Shoji Co., were used without further purification. Pure-grade NH_3 (Takachiho Shoji Co. 99.5%) was freeze-pumped several times. Pure-grade Ar (Daido Sanso Co. 99.999%) was used without further purification.

Results

Pressure Dependence of the Emission Intensities at 213.9 and 307.6 nm. When a cell containing zinc vapor was illuminated by means of the exciting lamp, two resonance lines were observed, at 213.9 and 307.6 nm. The 213.9 nm resonance line disappeared when a Pyrex plate was inserted between the cell and the lamp. Upon the addition of argon, the intensities of the lines increased with the increase of the pressure, as is shown in Fig. 1.

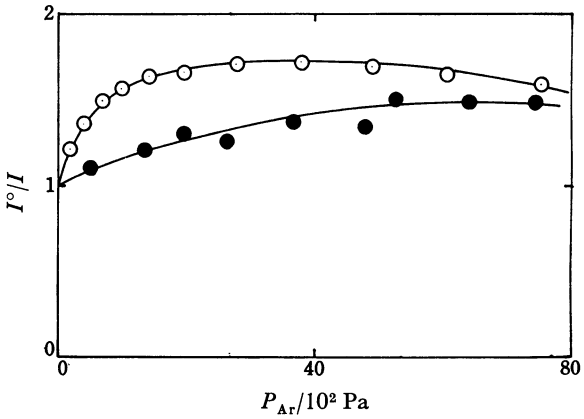

Fig. 1. Intensities of resonance lines at 213.9 (○) and 307.6 nm (●) as functions of argon pressures.

A similar increase of the intensity of the 326.1 nm resonance line of cadmium was previously observed; it was attributed to the increase in the light intensity absorbed by cadmium atoms because of the pressure broadening of the absorption line.[7] In order to minimize the pressure dependence of the absorption of the resonance line, quenchers were diluted with a large

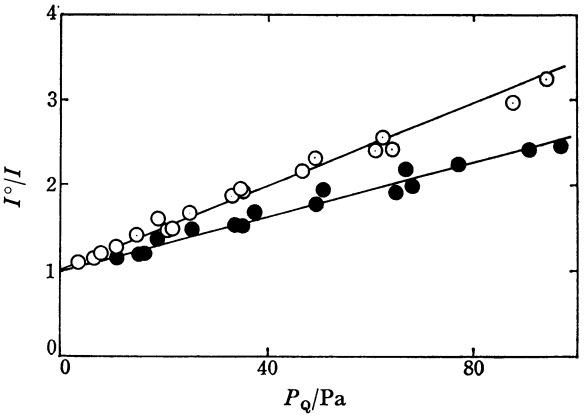

Fig. 2. Stern-Volmer plots for quenching of resonance line at 213.9 nm by H_2 (●) and D_2 (○). The total pressure is 4000 Pa.

amount of argon and the total pressure in the reaction cell was kept constant (4000 and 1300 Pa in the cases of the measurements at 213.9 and 307.6 nm respectively).

When quencher-argon mixtures were added, the intensities of the resonance lines decreased with the increase in the partial pressure of the quenchers. Representative Stern-Volmer plots for the quenching of the 213.9 and 307.6 nm resonance lines by several quenchers are shown in Figs. 2 and 3, where I° and I

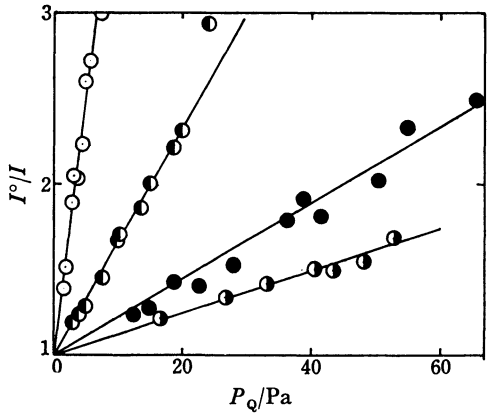

Fig. 3. Stern-Volmer plots for quenching of resonance line at 307.6 nm by CO_2 (○), CO (◐), N_2 (●), and CH_4 (◑). The total pressure is 1300 Pa.

are the intensities of the resonance lines in the absence and in the presence of quenchers respectively. All of the plots form straight lines, the intercepts of which are unity. Similar plots were obtained for other quenchers.

Quenching of the 307.6 nm Resonance Line. By analogy with the mechanism presented for the quenching of $Cd(^3P_J)$,[1a] the quenching of $Zn(^3P_J)$ can be discussed in terms of the following reactions:

$$Zn(^1S_0) + h\nu(307.6) \longrightarrow Zn(^3P_1) \quad I_a$$
$$Zn(^3P_1) \longrightarrow Zn(^1S_0) + h\nu(307.6) \quad k_0$$
$$Zn(^3P_1) + M \rightleftarrows Zn(^3P_0) + M \quad k_1, k_{-1}$$
$$Zn(^3P_1) + M \rightleftarrows Zn(^3P_2) + M \quad k_2, k_{-2}$$
$$Zn(^3P_0) + Q \longrightarrow \text{quenching} \quad k_3$$
$$Zn(^3P_1) + Q \longrightarrow \text{quenching} \quad k_4$$
$$Zn(^3P_2) + Q \longrightarrow \text{quenching} \quad k_5$$

Here, M denotes Ar and/or quenchers. As the energy differences between $Zn(^3P_0)$ and $Zn(^3P_1)$, and between $Zn(^3P_1)$ and $Zn(^3P_2)$ are very small (2.30 and 4.73 kJ/mol), equilibria must be attained fairly rapidly among these three states. By assuming the steady-state for $Zn(^3P_0)$, $Zn(^3P_1)$, and $Zn(^3P_2)$, the following equation can be derived:

$$\frac{[Zn(^3P_1)]_{Q=0}}{[Zn(^3P_1)]} = 1 + \frac{1}{k_0}\left(\frac{k_1}{k_{-1}}k_3 + k_4 + \frac{k_2}{k_{-2}}k_5\right)[Q] \quad (1)$$

As $I^\circ_{307.6} = k_0[Zn(^3P_1)]_{Q=0}$ and $I_{307.6} = k_0[Zn(^3P_1)]$, the above equation becomes:

$$\frac{I^\circ_{307.6}}{I_{307.6}} = 1 + \frac{1}{k_0}\left(\frac{k_1}{k_{-1}}k_3 + k_4 + \frac{k_2}{k_{-2}}k_5\right)[Q] \quad (2)$$

The linear Stern-Volmer plots in Fig. 3 are accounted for by Eq. 2. As the *f*-value of the zinc 307.6 nm line is about one-tenth of that of the cadmium 326.1 nm line,[8] the absorption of the 307.6 nm line by the zinc vapor at 0.36 Pa (305 °C) seems to be too small to cause any significant radiation trapping. If the lengthening of the effective radiation lifetime of $Zn(^3P_1)$ caused by radiation imprisonment is not negligible for the vapor pressure of zinc at 305 °C, the effective lifetime must be dependent on the total pressure. In Fig. 4, the values of $I^\circ_{307.6}/I_{307.6}$ obtained for H_2 and N_2

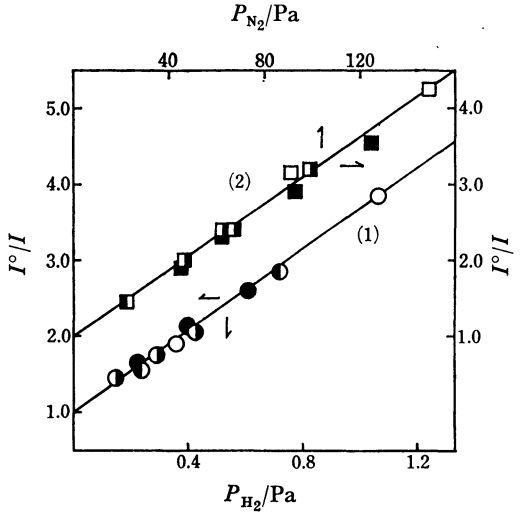

Fig. 4. Stern-Volmer plots for quenching of resonance line at 307.6 nm by H_2 and N_2.
1) H_2; total pressure are 7200 (○), 4900 (◐), 1300 (●), and 1000 (◑) in Pa. 2) N_2; 7200 (□), 4900 (◧), 1300 (□), and 1000 (◨).

at various total pressures are plotted as functions of the partial pressures of the quenchers. The points for each quencher lie on a straight line, and no dependence on the total pressure can be seen. This strongly suggests that the radiative lifetime of the $Zn(^3P_1)$ atoms in this system is independent of the pressure of the foreign gas. Therefore, k_0 can be taken as the reciprocal of the natural lifetime of $Zn(^3P_1)$ ($\tau = 2.0 \times 10^{-5}$ s[9]).

From the slopes of the straight lines in Fig. 3, the composite rate constants of the quenching, $(k_1/k_{-1})k_3 + k_4 + (k_2/k_{-2})k_5$, are estimated. Since the three triplet states are in equilibrium, $k_1/k_{-1} = (1/3)\exp(2300/RT)$ and $k_2/k_{-2} = (5/3)\exp(-4730/RT)$, and at 305 °C k_1/k_{-1} and k_2/k_{-2} are 0.54 and 0.62 respectively. The quenching rate constants, $k_q (= 0.54k_3 + k_4 + 0.62k_5)$, are listed in Table 1. The corresponding quenching cross-sections

Table 1. Quenching of $Zn(^3P_J)$ by various gases

Gas	$10^{11}k_q$ / cm^3 molecule^{-1} s^{-1}	$10^{16}\sigma_q^2$ / cm^2
H_2	106.6±7.2	13.6±0.9
D_2	64.1±4.5	11.3±0.8
N_2	0.92±0.01	0.37±0.01
CO	2.58±0.18	1.04±0.07
CO_2	9.44±0.75	4.41±0.35
NH_3	9.54±0.93	3.20±0.31
CH_4	0.50±0.01	0.16±0.01

for equilibrated $Zn(^3P_{0,1,2})$ are calculated using the simple collision theory expression:

$$\sigma_q^2 = k_q\left(8\pi RT\frac{M_{Zn}+M_Q}{M_{Zn}M_Q}\right)^{-1/2} \quad (3)$$

where M_{Zn} and M_Q are the atomic and molecular weights of zinc and the quenchers respectively. The cross-sections are also listed in Table 1.

Quenching of the 213.9 nm Resonance Line. The quenching of $Zn(^1P_1)$ can be discussed in terms of the following reactions:

$$Zn(^1S_0) + h\nu(213.9) \longrightarrow Zn(^1P_1)$$
$$Zn(^1P_1) \longrightarrow Zn(^1S_0) + h\nu(213.9) \qquad k_r$$
$$Zn(^1P_1) + Q \longrightarrow \text{quenching} \qquad k_Q$$

The steady-state treatment gives the following relation:

$$\frac{I^\circ_{213.9}}{I_{213.9}} = 1 + \frac{k_Q}{k_r}[Q] \quad (4)$$

Here, $I^\circ_{213.9}$ and $I_{213.9}$ are the emission intensities at 213.9 nm in the absence and in the presence of quenchers respectively. From the slopes of the straight lines in Fig. 2, the values of k_Q/k_r can be obtained; they are listed in Table 2. k_r is the effective rate constant for the escape of 213.9 nm fluorescent photons from the reaction vessel. Contrary to the case of the 307.6 nm resonance line, k_r must be significantly different from the limiting rate of natural radiative decay at a very low vapor concentration, because radiation imprisonment can not be neglected because of the large absorption coefficient. Therefore, it is difficult to estimate the absolute k_Q values. Since the quenchers are diluted with a large amount of argon, it can be assumed that k_r is independent of the pressures of the quenchers and of the kind of quencher. The relative values of k_Q and relative quenching cross-sections are listed in Table 2.

TABLE 2. QUENCHING OF $Zn(^1P_1)$ BY VARIOUS GASES

Gas	$\frac{10^2 k_Q/k_r}{Pa^{-1}}$	k_Q(rel)	σ_Q^2 (rel)
H_2	2.42±0.02	1.00	1.00
D_2	1.56±0.01	0.64	0.90
N_2	0.83±0.01	0.34	1.08
CO	1.04±0.02	0.40	1.28
CO_2	1.10±0.01	0.46	1.70
NH_3	1.88±0.02	0.78	2.06
CH_4	1.37±0.01	0.56	1.44

Discussion

Breckenridge *et al.* discussed several factors which govern the quenching efficiencies of $Cd(^1P_1)$ and $Cd(^3P_J)$ by several gases.[1] They found that there is a correlation of the cross-sections for the quenching of excited metal atoms with a parameter, Δ, the energy difference between Me^*+Q and $Me^+ + Q^-$ at an infinite Me—Q distance, which is itself given by:

$$\Delta = I_p(Me^*) - E_a(Q)$$

They described[1b] that, in general, the cross-section increases with a decrease in Δ for the quenching of $Cd(^1P_1)$, $Cd(^3P_J)$, $Hg(^3P_0)$, and $Hg(^3P_1)$ by N_2, CO, CO_2, and so on, and that the charge-transfer curve-crossing theory is useful in explaining the magnitudes of the quenching cross-sections.

In Table 3, a comparison of the quenching cross-sections of $Zn(^3P_J)$, $Cd(^3P_J)$, $Hg(^3P_0)$, and $Hg(^3P_1)$ is shown. In this table, the values of Δ are also included. For mercury, the cross-section for the quenching processes, $^3P_1 \rightarrow {}^1S_0$ and $^3P_0 \rightarrow {}^1S_0$, have been determined separately.[4] However, for cadmium and zinc, only the composite cross-sections for the quenching of the ^3P_J states can be determined, for the equilibration reactions among these states are very rapid.

The quenching cross-sections of $Zn(^3P_J)$ by CH_4, N_2, CO, and CO_2 increase in this order. This order is almost the same as those for $Cd(^3P_J)$ and $Hg(^3P_1)$; it is also consistent with the order of the decrease in Δ. In the cases of $Cd(^3P_J)$ and $Hg(^3P_1)$, these orders have been successfully explained in terms of the charge-transfer curve-crossing mechanism.[1b] Therefore, it is reasonable to consider that the same mechanism may be valid for $Zn(^3P_J)$.

For a single quencher, the correlation between the cross-sections and Δ is not simple. For CO_2, the cross-sections increase with a decrease in Δ, but for the other quenchers they do not do so. Since the difference in Δ between the quenchers is comparatively large, the order of the quenching cross-sections for an excited atoms must be determined by only the magnitudes of Δ. However, since the difference in Δ between the metal

TABLE 3. COMPARISON OF QUENCHING CROSS-SECTIONS OF VARIOUS EXCITED METAL ATOMS

Gas	$Zn(^3P_j)$[a]		$Cd(^3P_j)$[a,b]		$Hg(^3P_0)$[c]		$Hg(^3P_1)$[c]	
	$\frac{10^{16}\sigma_q^2}{cm^2}$	$\frac{\Delta}{kJ}$	$\frac{10^{16}\sigma_q^2}{cm^2}$	$\frac{\Delta}{kJ}$	$\frac{10^{16}\sigma_q^2}{cm^2}$	$\frac{\Delta}{kJ}$	$\frac{10^{16}\sigma_q^2}{cm^2}$	$\frac{\Delta}{kJ}$
H_2	13.6	519	3.9		2.1		7.8	
D_2	11.3		2.0		2.9		7.2	
N_2	0.37	703	0.0076	686	2×10^{-4}	741	0.03	720
CO	1.04	644	1.7	628	0.69	682	3.0	661
CO_2	4.41	577	12.0	561	0.032	615	3.2	594
NH_3	3.20		0.044		0.016		2.75	
CH_4	0.16	812	0.0012	795	1.4×10^{-4}	849	0.07	828

a) The cross-sections are actually sums of population weighted cross-sections for equilibrated $Zn(^3P_{0,1,2})$ and $Cd(^3P_{0,1})$: $\sigma_q^2(Zn)=0.54\sigma_0^2+\sigma_1^2+0.62\sigma_2^2$; $\sigma_q^2(Cd)=1.37\sigma_0^2+\sigma_1^2$. b) Ref. 1. c) Ref. 4.

atoms is small, the order can not be determined by only the magnitudes of Δ; such other factors as the polarizability of the Me^+-Q^- complex must also be taken into account, as has been mentioned by Breckenridge and Renlund.[1b]

One major channel in the quenching of $Cd(^3P_J)$ and $Hg(^3P_{0,1})$ by NH_3 has been shown to involve the formation of Cd–NH_3* and Hg–NH_3* exciplexes, and the emission from these exciplexes has been observed.[10,11] In the $Zn(^3P_J)$–NH_3 system, however, the exciplex emission could not be observed. One of the following reasons may be responsible for this; (a) the exciplex does not form; or (b) even if the exciplex forms, it is completely quenched before emission, or (c) the exciplex emission is too weak to be observed by our detector. By analogy with the Cd–NH_3 and Hg–NH_3 systems, it does not seem reasonable to consider reason (a) and/or (b) to be responsible for the lack of luminescence in the Zn–NH_3 system.

If the quenching of $Zn(^3P_J)$ by ammonia occurs exclusively through the formation of the exciplex in a manner similar to that of $Cd(^3P_J)$, the emission intensity from the exciplex can be expressed as follows;

$$I_e = I^\circ[k_e/(k_e+k_n[Ar])] \quad (5)$$

where I° is the intensity of the resonance line and where k_e and k_n are the rate constants for the following reactions:

$$Zn\text{–}NH_3^* \longrightarrow Zn + NH_3 + h\nu_e \qquad k_e$$

$$Zn\text{–}NH_3^* + Ar \longrightarrow Zn + NH_3 + Ar \qquad k_n$$

In order to consider the emission intensity of the Zn–NH_3* exciplex by comparing the intensity with that for the Cd–NH_3* exciplex, we measured the cadmium-photosensitized luminescence of ammonia using our apparatus; we could thus observed an emission band consistent with that shown in the literature.[10] It was proved that, by our apparatus, we can not observe an emission whose intensity is smaller by a factor of 500 than that from the Cd–NH_3* exciplex. (The light intensity which can be detected by our spectrophotometer with the maximum sensitivity was estimated by means of potassium ferrioxalate actinometry to be about 5×10^{-14} Einsteins s^{-1} cm^{-2} at 400 nm at the incidence slit.) The intensity ratio of the resonance line of zinc to that of cadmium, corrected for the sensitivity of the spectrophotometer at 307.6 and 326.1 nm, was about 1/100 (the intensity of the zinc lamp was about 1/3 of that of the cadmium lamp; the other factor must be based on the difference in the absorption coefficients). Therefore, if the value of $k_e/(k_e+k_n[Ar])$ in the Zn–NH_3 system is smaller by a factor of 5 than that for the Cd–NH_3 system (0.67 for an argon pressure of 13300 Pa[10]), the emission from the Zn–NH_3* exciplex can not be detected by our apparatus. This seems the most reasonable explanation for our failure to observe the exciplex emission in the zinc-photosensitized reaction of ammonia.

In Table 4, the relative quenching cross-sections of $Zn(^1P_1)$ and the values of Δ are shown. For comparison, these values for $Cd(^1P_1)$ are also included. The quenching cross-sections of $Zn(^1P_1)$ and $Cd(^1P_1)$ by N_2, CO, and CO_2 again increase with a decrease in Δ. Thus,

Table 4. Comparison of relative quenching cross-sections of $Zn(^1P_1)$ and $Cd(^1P_1)$

Gas	$Zn(^1P_1)$		$Cd(^1P_1)$[a]	
	σ_Q^2 (rel)	$\frac{\Delta}{kJ}$	σ_Q^2 (rel)	$\frac{\Delta}{kJ}$
H_2	1.00		1.00	
D_2	0.90		1.25	
N_2	1.08	531	2.17	527
CO	1.28	473	2.33	469
CO_2	1.70	406	3.58	402
NH_3	2.06		2.00	
CH_4	1.44	640		

a) Ref. 1.

by analogy with the case of $Zn(^3P_J)$, it is reasonable to consider that the charge-transfer mechanism may be valid for $Zn(^1P_1)$.

As is shown in Table 3, $Zn(^3P_J)$ is quenched efficiently by the isotopic hydrogens. The difference between the quenching cross-sections of $Hg(^3P_0)$ and $Hg(^3P_1)$ by hydrogen has been explained simply by the difference in the energy content.[4] If the cross-sections are of a comparable magnitude for the quenching of the ^3P_J states of zinc and for those of cadmium by hydrogen, the cross-sections for $Hg(^3P_1)$ should be compared with half those for $Zn(^3P_J)$ and $Cd(^3P_J)$.[6] It can be said that the cross-sections of $Cd(^3P_1)$, $Zn(^3P_1)$, and $Hg(^3P_1)$ increase in this order; this order is consistent with the order of the excitation energy of metal atoms.

In a previous letter,[6] we discussed the isotope effects on the quenching of $Zn(^3P_1)$, $Cd(^3P_1)$, and $Hg(^3P_1)$ by hydrogen in terms of the following processes:

$$Me^* + Q \underset{k_b}{\overset{k_a}{\rightleftharpoons}} (Me-Q)^* \begin{cases} \xrightarrow{k_c} \text{decomposition of Q} \\ \xrightarrow{k_d} \text{vibrational excitation of Q} \end{cases}$$

Here, $(Me-Q)^*$ denotes a short-lived intermediate. The quenching rate constant, k, becomes:

$$k = k_a\frac{k_c+k_d}{k_b+k_c+k_d} \quad (6)$$

For the quenching of $Hg(^3P_1)$ by H_2 and D_2, it was pointed out that k is nearly equal to k_a, since $k_c \gg k_b$ and $k_c \gg k_d$, for the energy content of the complex is large enough to decompose H_2 and D_2; therefore, it does not show a large isotope effect.[4,12] On the other hand, in the cases of $Zn(^3P_1)$ and $Cd(^3P_1)$ the excitation energies are smaller than the bond energies of H–H and D–D, and perhaps k_c is not large enough for us to neglect k_b and k_d; therefore, the overall quenching-rate constants probably depend on the values of k_c+k_d. (1) If $k_c \gg k_d$, the quenching rate depends on the rates of the decomposition of H_2 and D_2, and the isotope effect based on the difference in the zero-point energies of H_2 and D_2 should be observed. (2) If $k_c \approx k_d$ or $k_c < k_d$, no conclusive explanation for the isotope effects can be deduced, since we have no information about the isotope effects on k_d. In this case, the observed isotope effects might indicate that $k_d(D_2) \approx k_d(H_2)$ or $k_d(D_2) < k_d(H_2)$. Actually, the quenching cross-sections of $Cd(^3P_1)$, $Zn(^3P_1)$, and $Hg(^3P_1)$ increase in this order,

while the isotope effects decrease in this order.

Recently, Breckenridge and Renlund measured the quenching cross-sections of $Cd(^3P_J)$ and $Cd(^1P_1)$ by means of isotopic hydrogens and compared these cross-sections with those of other excited metal atoms.[1c] They pointed out that the adiabatic pathways from Me^*+H_2 to MeH+H provide a reasonable explanation of the quenching of excited zinc, cadmium, and mercury atoms by hydrogen. In Table 5 the ratios of the quenching cross-sections of H_2 and D_2 for $Zn(^1P_1)$, $Zn(^3P_J)$, $Cd(^1P_1)$, $Cd(^3P_J)$, and $Hg(^3P_1)$ are shown.

TABLE 5. ISOTOPE EFFECT ON QUENCHING CROSS-SECTIONS

Reaction	$\frac{\Delta H}{\text{kJ mol}^{-1}}$	$\sigma_q^2[H_2]/\sigma_q^2[D_2]$
$Zn(^1P_1)+H_2\rightarrow ZnH+H$	−209	
$+D_2\rightarrow ZnD+D$	−204	1.11
$Zn(^3P_J)+H_2\rightarrow ZnH+H$	−39	
$+D_2\rightarrow ZnD+D$	−33	1.20
$Cd(^1P_1)+H_2\rightarrow CdH+H$	−158	
$+D_2\rightarrow CdD+D$	−151	0.80
$Cd(^3P_J)+H_2\rightarrow CdH+H$	0	
$+D_2\rightarrow CdD+D$	5	1.95
$Hg(^3P_0)+H_2\rightarrow HgH+H$	−53	
$+D_2\rightarrow HgD+D$	−47	0.72
$Hg(^3P_1)+H_2\rightarrow HgH+H$	−74	
$+D_2\rightarrow HgD+D$	−68	1.08

In Table 5 are also shown the ΔH values for the processes:

$$Me^* + H_2(D_2) \longrightarrow MeH(D) + H(D)$$

where Me^* is the $^1P_1$ state for $Zn(^1P_1)$ and $Cd(^1P_1)$ and is the $^3P_1$ state for $Zn(^3P_J)$, $Cd(^3P_J)$, and $Hg(^3P_1)$. For $Cd(^1P_1)$, $Zn(^3P_1)$, and $Hg(^3P_1)$, the $Me^*+H_2(D_2)\rightarrow MeH(D)+H(D)$ processes are both exothermic; therefore, the quenching cross-sections show very little isotope effect. However, in the case of $Cd(^3P_1)$, the $Cd^*+H_2\rightarrow CdH+H$ reaction is thermoneutral, while the $Cd^*+D_2\rightarrow CdD+D$ reaction is slightly endothermic. Therefore, for $Cd(^3P_1)$ a little larger isotope effect is observed. This explanation corresponds to the more detailed one for Case (2) of our explanation.

As is shown in Table 5, for $Zn(^1P_1)$ the reactions are largely exothermic and the isotope effect is very little. These findings are consistent with the above explanation of Breckenridge.

References

1) a) W. H. Breckenridge, T. W. Broadbent, and D. S. Moore, *J. Phys. Chem.*, **79**, 1233 (1975); b) W. H. Breckenridge and A. M. Renlund, *ibid.*, **82**, 1474 (1978); c) W. H. Breckenridge and A. M. Renlund, *ibid.*, **82**, 1484 (1978); d) W. H. Breckenridge and A. M. Renlund, *ibid.*, **83**, 303 (1979).

2) R. J. Cvetanovic, *Prog. React. Kinet.*, **2**, 39 (1964).

3) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y. (1966).

4) H. Horiguchi and S. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **47**, 2768 (1974).

5) For example, S. Tsunashima, S. Satho, and S. Sato, *Bull. Chem. Soc. Jpn.*, **42**, 329 (1966); S. Yamamoto, S. Tsunashima, and S. Sato, *ibid.*, **48**, 1172 (1975).

6) S. Yamamoto, T. Takei, N. Nishimura, and S. Hasegawa, *Chem. Lett.*, **1976**, 1413.

7) S. Yamamoto, M. Takaoka, S. Tsunashima, and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 130 (1975).

8) A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, Cambridge (1961).

9) F. W. Byron, M. N. McDermott, R. Novick, B. W. Perry, and E. Saloman. *Phys. Rev. A*, **134**, 47 (1964).

10) S. Tsunashima, T. Toyono, and S. Sato, *Bull. Chem. Soc. Jpn.*, **46**, 2654 (1973); S. Yamamoto, S. Tsunashima, and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 1172 (1975).

11) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. E. Phillips, *Chem. Phys. Lett.*, **5**, 555 (1970); J. Koskikallio, A. B. Callear, and J. H. Connor, *Chem. Phys. Lett.*, **8**, 467 (1971).

12) Kang Yang, *J. Am. Chem. Soc.*, **87**, 5294 (1965).