Deactivation of Cd(5^3P_J) by H_2 and D_2: Branching Ratios for the Production of CdH and CdD

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The deactivation processes of Cd(5^3P_1) and Cd(5^3P_0) by H_2 and D_2 were examined by employing a laser excitation-depletion technique. The concentration of the ground-state Cd(5^1S_0) atoms was measured in both the presence and absence of an intense saturable pump laser beam. In the presence of a pump laser, the concentration decreased in accordance with the production of CdH(CdD). From this decrease, the branching ratios for the production of CdH(CdD) could be determined. The depletion was unaffected when N_2 was added. This suggests that the branching ratios are the same for Cd(5^3P_1) and Cd(5^3P_0), although the production of CdH(CdD) is endothermic for Cd(5^3P_0). The branching ratios were 0.81±0.04 for H_2 and 0.76±0.06 for D_2. The efficient production of CdH(CdD) from not only Cd(5^3P_1), but also Cd(5^3P_0), can be accounted for by correlational considerations.

The production of CdH in the Cd(5^3P_1)-photosensitized reaction of H_2 has been recognized since the 1930's.[1] However, the absolute yield has not been measured. It has been believed that the quantum yield for the production of CdH in the quenching of Cd(5^3P_J) is near unity on the basis of indirect experimental results.[2]

The deactivation processes of excited triplet Cd by hydrogen and its isotopic variants have been studies by several groups.[2—10] The cross sections for the quenching of both Cd(5^3P_1) and Cd(5^3P_0) are slightly smaller than the gas kinetic one. This suggests the presence of small activation barriers. There are three possible exit channels: intramultiplet mixing among the ^3P_J sublevels, production of CdH(CdD), and an E-to-V energy transfer to produce Cd(5^1S_0). Although detailed rate constants for the intramultiplet mixing have been reported,[3,8,10] the branching ratios of the chemical quenching channel to the physical channel have not been measured.

In the quenching of Cd(5^3P_1) by H_2, the production of two H atoms is energetically inaccessible. This is in contrast to the case of the quenching of Hg(6^3P_1). The electronic energy of Hg(6^3P_1) exceeds the dissociation energy of H_2, and the production of vibrationally excited H_2 has been considered to be less likely.[11] On the other hand, for Cd(5^3P_1), the production of Cd(5^1S_0) and vibrationally excited H_2 can be one of the main exit channels, because this process is symmetrically allowed if the spin-orbit interaction is taken into account.[12] The production of CdH and H is also energetically and symmetrically allowed, and can be another main exit channel. Although Cd(5^3P_0) can be efficiently quenched, it is difficult to predict which is the main exit channel. There is no adiabatic route for physical quenching, unless rotation-electronic coupling is taken into account.[13] The adiabatic production of CdH and H is possible, but is endothermic by 6.5 kJ mol^{-1}.

In the determination of such branching ratios in the quenching of excited atoms, Mitchell et al. have shown that it is useful to measure the depletion of ground-state atoms after the irradiation of a saturable pump laser pulse.[14] They determined the branching ratio in the quenching of excited Ga atoms. In the present work, this technique was applied to the determination of the branching ratios for the production of CdH(CdD) from triplet state Cd, Cd(5^3P_1) and Cd(5^3P_0), and H_2(D_2).

Experimental

Ground-state Cd atoms were excited to the 5^3P_1 state by an intense pump laser at 326.1 nm. The pump laser was sufficiently intense to equilibrate Cd(5^1S_0) and Cd(5^3P_1). Although radiative decay and physical quenching processes regenerate Cd(5^1S_0), the concentration of Cd(5^1S_0) should decrease in accordance along with the production of CdH(CdD). The absolute yield for the production of CdH(CdD) can then be determined by measuring this decrease.

A mixture of Cd and the quencher gas in a quartz vessel, 4 cm in diameter and 5 cm in length, was kept in a furnace maintained at 460 K. Vaporized Cd atoms in the vessel were excited to the 5^3P_1 state by using a dye laser (Quanta-Ray, PDL-3) pumped by the second harmonic of a Q-switched Nd : YAG laser (Quanta-Ray, GCR-150). The pulse width of the laser was around 5 ns, and the quenching and relaxation of Cd(5^3P_1) were minor during the duration of the laser pulse. Then, when the laser was sufficiently intense, equilibration between Cd(5^1S_0) and Cd(5^3P_1) could be attained. When the pulse energy of the pump laser was around 4 mJ, the variation in the resonance fluorescence intensity against the laser power was minor.

It is desired that the quenching process be dominant over the radiative-decay process. Thus, the H_2 and D_2 pressures were chosen to be 65 and 200 Pa, respectively. Typically, 4 μs after the pump laser pulse, the concentration of Cd(5^1S_0) was probed by laser-induced fluorescence at 326.1 nm. Within 4 μs, Cd(5^3P_1) concentration decreased to less than 0.1% of the initial value. Radiation imprisonment can almost be ignored at 460 K. $Cd(5^3P_0)$ should also decay within 4 μs. The lifetime of CdH(CdD) is on the order of 100 μs, and the decay during 4 μs can be ignored.[15] The probe laser (Lambda Physik, LPD3000E) was pumped by a XeF excimer laser (Lambda Physik, LPX105i). The pulse energy of the probe laser was kept below 5 μJ. Both dye lasers were operated with DCM, and the outputs were doubled in frequency by a KDP or a BBO crystal. The delay time between the pump and probe lasers was controlled with a delay/pulse generator (Stanford Research Systems, DG535). $Cd(5^3P_1)$ fluorescence was detected with a photomultiplier tube (Hamamatsu, R212) through a monochromator (Nikon, P250). The photomultiplier signals were processed with a digital oscilloscope (LeCroy, 9450A) and a computer (NEC, PC9801).

The quencher gas, H_2 or D_2, was mixed with 2.6 kPa of He or N_2. N_2 was added to equilibrate $Cd(5^3P_1)$ and $Cd(5^3P_0)$, while He was added to minimize the effect of diffusion. He is known to be inefficient in the intramultiplet mixing or quenching of triplet Cd. In the presence of 2.6 kPa of N_2, the intramultiplet mixing rates are 10 times larger than the quenching rates by $H_2(D_2)$. The production of $Cd(5^3P_0)$ must be much accelerated in the presence of N_2. Then, the measured ratio should be the weighted average of those for $Cd(5^3P_1)$ and $Cd(5^3P_0)$. The rate constants for the intramultiplet mixing by H_2 and D_2 are comparable to their quenching rate constants, and equilibration between $Cd(5^3P_1)$ and $Cd(5^3P_0)$ cannot be expected in the absence of N_2. The gas pressures were measured with capacitance manometers (MKS Baratron, 122AA).

In order to minimize the effect of diffusion, the diameter of the pump laser beam was kept larger than the probe one (3 mm vs. 1 mm). The probe laser beam was aligned collinearly with the pump laser beam, and was totally embedded in it. In vacuum, Cd atoms may diffuse 1.2 mm in 4 μs. This is not small compared to the diameter of the pump laser beam. However, according to Baczyński et al., the diffusion rate in the presence of 2.6 kPa of N_2 is 3 orders of magnitude smaller than that in vacuum.[16] Then, the diffusional effect should completely be ignored in the present system.

The decay profiles of the resonance fluorescence at 326.1 nm were measured separately under the same conditions with the same apparatus. Only the XeF laser pumped dye laser was used in this case.

Cd was the product of Wako pure Chemical (99.999%). H_2 (Nihon Sanso, 99.99%), D_2 (Sumitomo Seika, isotopic purity 99.5%), He (Teisan, 99.995%), N_2 (Teisan, 99.999%), and CO_2 (Nihon Sanso, 99.99%) were used without further purification. CO_2 was used to check the procedure of the present study.

Results

Figure 1 shows the temporal profiles of the LIF signal of $Cd(5^1S_0)$ in both the presence and in the absence of intense pump laser pulses. 65 Pa of H_2 was added as a quencher gas, while 2.6 kPa of He was added as a buffer gas. The delay time between the pump and probe laser pulses was 4 μs. A very intense signal due to the pump laser is overscaled in the oscillogram, and is not shown, except for the tail. In Fig. 2, similar profiles obtained in the presence of 65 Pa of H_2 and 2.6 kPa of N_2 are illustrated. In both cases, the signal intensity in the presence of the pump laser is weaker than that in the absence of the pump laser. This decrease corresponds to a decrease in the concentration of $Cd(5^1S_0)$, and, consequently, to the production of CdH. Similar results were obtained in the D_2 systems. The measured ratios of the time-integrated intensities are summarized in Table 1. The error limits are one-standard deviations. These ratios were independent of the pulse energy of the pump laser between 3 and 5 mJ, or the pump-probe interpulse delay between 3 and 5 μs.

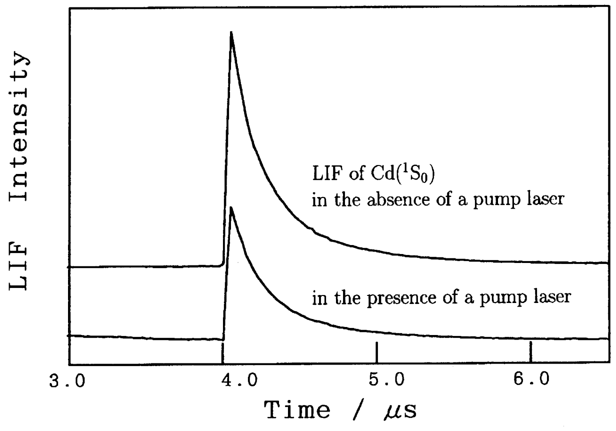

Fig. 1. Temporal profiles of the LIF signal of $Cd(5^1S_0)$ in the presence and in the absence of intense pump laser pulses. H_2 and He pressures were 65 Pa and 2.6 kPa, respectively. The delay time between the pump and the probe laser pulses was 4 μs.

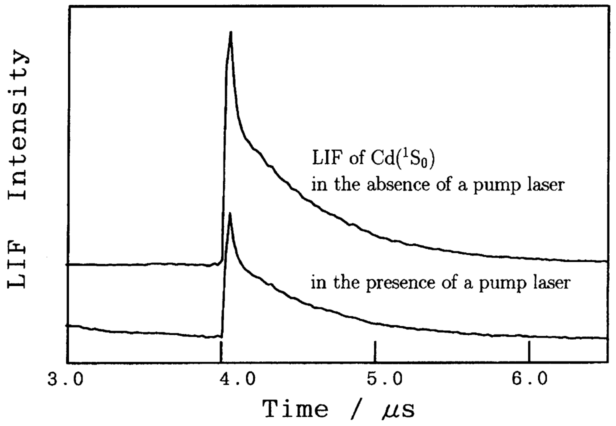

Fig. 2. Temporal profiles of the LIF signal of $Cd(5^1S_0)$ in the presence and in the absence of intense pump laser pulses. H_2 and N_2 pressures were 65 Pa and 2.6 kPa, respectively. The delay time between the pump and the probe laser pulses was 4 μs.

The ratios were almost 1 : 0.5 in every case. Before analyzing the data quantitatively, let us examine the results just qualitatively. 75% of the ground-state Cd atoms were excited to the $^3P_1$ state by the pump laser. Under steady-state con-

Table 1. Population Ratio of Ground-State Cd Atoms in the Presence and in the Absence of Intense Pump Laser Pulses

H_2/He	0.49 ± 0.03
H_2/N_2	0.46 ± 0.03
D_2/He	0.51 ± 0.04
D_2/N_2	0.50 ± 0.05

ditions, 65 Pa of H_2 quenches triplet Cd around 90%.[3] 10% of Cd(5^3P_1) decays radiatively and regenerates Cd(5^1S_0). If we assume that the production yield of CdH is 80%, the final population ratio of Cd(5^1S_0) in the presence and in the absence of pump laser should be 0.46, which roughly reproduce the present experimental result. Of course, this procedure is too crude. A steady-state cannot be assumed in the present system. Intramultiplet mixing has also to be taken into account. For a quantitative analysis, we employed a computer-simulation technique in which the rate equations were solved numerically.

In order to simulate the present system, we assumed the following reaction scheme:

$$\mathrm{Cd}(5^1S_0)+h\nu \rightarrow \mathrm{Cd}(5^3P_1), \tag{1}$$

$$\mathrm{Cd}(5^3P_1) \rightarrow \mathrm{Cd}(5^1S_0)+h\nu, \tag{2}$$

$$\mathrm{Cd}(5^3P_1)+\mathrm{H_2} \rightarrow \mathrm{Cd}(5^3P_0)+\mathrm{H_2}, \tag{3}$$

$$\mathrm{Cd}(5^3P_1)+\mathrm{H_2} \rightarrow \mathrm{CdH}+\mathrm{H}, \tag{4}$$

$$\mathrm{Cd}(5^3P_1)+\mathrm{H_2} \rightarrow \mathrm{Cd}(5^1S_0)+\mathrm{H_2}, \tag{5}$$

$$\mathrm{Cd}(5^3P_0)+\mathrm{H_2} \rightarrow \mathrm{Cd}(5^3P_1)+\mathrm{H_2}, \tag{6}$$

$$\mathrm{Cd}(5^3P_0)+\mathrm{H_2} \rightarrow \mathrm{CdH}+\mathrm{H}, \tag{7}$$

$$\mathrm{Cd}(5^3P_0)+\mathrm{H_2} \rightarrow \mathrm{Cd}(5^1S_0)+\mathrm{H_2}, \tag{8}$$

$$\mathrm{Cd}(5^3P_1)+\mathrm{N_2} \rightarrow \mathrm{Cd}(5^3P_0)+\mathrm{N_2}, \tag{9}$$

$$\mathrm{Cd}(5^3P_1)+\mathrm{N_2} \rightarrow \mathrm{Cd}(5^1S_0)+\mathrm{N_2}, \tag{10}$$

$$\mathrm{Cd}(5^3P_0)+\mathrm{N_2} \rightarrow \mathrm{Cd}(5^3P_1)+\mathrm{N_2}, \tag{11}$$

$$\mathrm{Cd}(5^3P_0)+\mathrm{N_2} \rightarrow \mathrm{Cd}(5^1S_0)+\mathrm{N_2}. \tag{12}$$

Figure 3 shows the temporal profiles of the resonance fluorescence from Cd(5^3P_1) in the H_2/He system. The dotted lines show the results of simulation. The rate constants determined in a phase-shift measurement at 458 K were employed in the simulation.[3] The agreement is excellent. It should be noted that the temporal profiles are independent of the branching ratios for processes (4) and (5) and processes (7) and (8), which were not determined in previous studies.

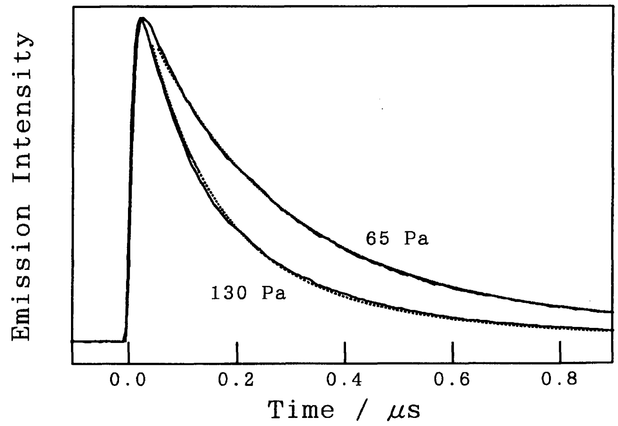

Fig. 3. Temporal profiles of the Cd(5^3P_1) emission followed by a pulsed excitation measured in the H_2/He system. The dotted lines show the results of simulation.

Similar good agreements were obtained in other systems: H_2/N_2, D_2/He, and D_2/N_2. These agreements support the validity of the present simulation procedure as well as the rate constants obtained in previous measurements.

As Table 1 shows, there was no change in the population ratios when He was replaced by N_2. This suggests that the production yields of CdH(CdD) from Cd(5^3P_1) and Cd(5^3P_0) are the same. Then, the number of the unknown parameter becomes just one, and it is possible to determine the production yields uniquely by comparing the measured population ratios of Cd(5^1S_0) listed in Table 1 with the simulation results. The yields were determined to be 0.81 ± 0.04 for the H_2 system and 0.76 ± 0.06 for the D_2 system. Combining with the results of the overall quenching rate measurement, the detailed rate constants can be obtained. The results are summarized in Table 2 in the forms of cross sections. The cross section is defined by $k(\pi\mu/8RT)^{1/2}$, where k is the rate constant, T is the absolute temperature, and μ is the reduced mass. The results for the intramultiplet mixing and quenching of Cd(5^3P_2) are also included.[5]

We also tried similar measurements by using CO_2 as a quencher. In this case, there are no energetically possible

Table 2. Cross Sections for the Quenching and Intramultiplet Mixing of Cd(5^3P_J) by H_2 and D_2 in units of 10^{-16} cm^2.

			H_2	D_2
Cd(5^3P_1)+H_2(D_2)	→	Cd(5^3P_0)+H_2(D_2)	7.7 ± 2.5	11.2 ± 4.2
	→	Cd(5^1S_0)+H_2(D_2)	1.3 ± 0.2	0.6 ± 0.2
	→	CdH(CdD)+H(D)	5.3 ± 1.0	1.9 ± 0.7
Cd(5^3P_0)+H_2(D_2)	→	Cd(5^3P_1)+H_2(D_2)	3.9 ± 1.4	5.7 ± 2.3
	→	Cd(5^1S_0)+H_2(D_2)	0.9 ± 0.2	0.6 ± 0.2
	→	CdH(CdD)+H(D)	4.0 ± 0.7	1.8 ± 0.5
Cd(5^3P_2)+H_2(D_2)[a]	→	Cd(5^3P_1)+H_2(D_2)	6.3 ± 0.3	4.4 ± 0.3
	→	Cd(5^3P_0)+H_2(D_2)	1.0 ± 0.1	0.9 ± 0.2
	→	CdH(CdD)+H(D) and Cd(5^1S_0)+H_2(D_2)	2.5 ± 0.8	1.6 ± 0.7

a) Ref. 5, obtained at 630 K.

chemical reaction channels. Cd(5^1S_0) showed no depletion by the irradiation of a pump laser pulse, as expected.

Discussion

In the classical work by Breckenridge and Callear, CdH(CdD) was monitored by the absorption of the (0,0) band of the D–X transition. They found that the relative yield of CdH(CdD) is unaffected by the addition of N_2. In other words, CdH(CdD) is produced both from Cd(5^3P_1) and Cd(5^3P_0) with the same efficiency. Equilibration between Cd(5^3P_1) and Cd(5^3P_0) in the absence of N_2 is not expected in their system, because Cd(5^3P_J) was mainly produced by the intersystem crossing from Cd(5^1P_1). The direct production of Cd(5^3P_0) from Cd(5^1P_1) by H_2(D_2) is inefficient.[17] The next point is that the production yield of CdH from H_2 is the same as that of CdD from D_2. They measured the CdH/CdD production ratio in a system of an equimolar H_2+D_2 mixture, and found that the ratio is nearly the same as that of the rate constants for the quenching by H_2 and D_2, k_{H_2}/k_{D_2}. Then, their results on the relative yields of CdH and CdD are completely consistent with the present results.

It is now well established that the reactions of excited group-12 metal atoms with hydrogen molecules proceed by an insertive mechanism.[7,12,18—21] A bent complex of the C_{2v} geometry is produced at the first step. In the quenching of triplet Cd, the complex must be $^3B_2$ symmetry because this state is the most stable.[21] If spin–orbit coupling is included the $^3B_2$ state splits into A_1, A_2, and B_1 states. Among them, the A_2 state correlates to Cd(5^3P_0)+H_2, while other two states correlate to Cd(5^3P_1)+H_2. A correlation diagram is shown in Fig. 4. Since the Cd(5^1S_0)+H_2 system belongs to the A_1 symmetry, and this state is highly repulsive, the A_1 states correlating to Cd(5^3P_1)+H_2 and Cd(5^1S_0)+H_2 may mix in the energetically accessible region. On the other hand, there is no adiabatic route to produce Cd(5^1S_0)+H_2 for Cd(5^3P_0). The adiabatic production of CdH+H is possible both for the Cd(5^3P_1) and Cd(5^3P_0) systems through a C_s geometry. The same discussion is possible for the Cd/D_2 system.

It is easy to explain the large efficiency for the production of CdH from Cd(5^3P_0), although this process is slightly endothermic. This is the only adiabatic exit channel. It is rather difficult to explain the minor production of Cd(5^1S_0)+H_2 from Cd(5^3P_0). This process may be attributed to the interaction between electronic and rotational motions.[13]

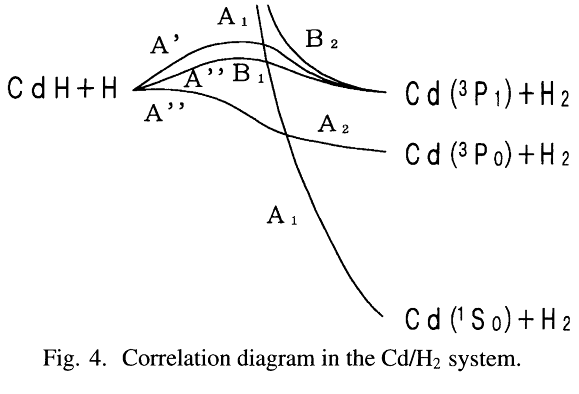

Fig. 4. Correlation diagram in the Cd/H_2 system.

The physical quenching process of Cd(5^3P_1) through the B_1 state is symmetrically forbidden. On the other hand, both the Cd(5^1S_0) and CdH routes are possible for the A_1 state. If B_1 and A_1 complexes are formed with the same probability, and 50% of the A_1 complex decompose to CdH+H, the branching ratio for the production of CdH shall be 0.75. This roughly reproduces the present experimental result.

It should be noted here that there is no adiabatic route to produce CdH from Cd(5^3P_2). It has been shown experimentally that the production of CdH cannot be a major process for Cd(5^3P_2).[5] The production yield of CdH is less than 25% and consistent with the present symmetrical consideration. Inefficient production of HgH from the $^3P_2$ state of Hg compared to those from the $^3P_1$ and $^3P_0$ states has also been demonstrated by Bras et al.[22]

Breckenridge et al. have proposed a late transition-state model in the quenching of Cd(5^3P_1) by isotopic hydrogens.[7] They found that the nascent rotational state distributions of CdH produced in the reaction of Cd(5^3P_1) with H_2 and that produced in the reaction of Cd(5^3P_1) with HD are the same. Similar results were obtained for the distributions of CdD. In order to explain this, they postulated that there are potential barriers and the available energies are the same for the Cd(5^3P_1)+H_2→CdH+H and Cd(5^3P_1)+HD→CdH+D reactions, although the zero-point energies are fairly different. It was shown that the potential barrier for the Cd(5^3P_1)+H_2 reaction is 6.3 kJ mol^{-1}, while that for the Cd(5^3P_1)+HD reaction is 9.7 kJ mol^{-1}. The barrier height for the Cd(5^3P_1)+H_2 reaction is almost the same as the energy difference between Cd(5^3P_1) and Cd(5^3P_0), 6.5 kJ mol^{-1}. Since the production of CdH+H from Cd(5^3P_1)+H_2 is thermoneutral, 6.5 kJ mol^{-1} corresponds to the endothermicity to produce CdH+H from Cd(5^3P_0)+H_2. The potential barrier for the Cd(5^3P_1)+D_2 reaction was estimated to be 11.4 kJ mol^{-1}. This value is also nearly equal to the endothermicity to produce CdD+D from Cd(5^3P_0)+D_2, 11.5 kJ mol^{-1}. As Table 2 shows, the cross sections for the production of CdH(CdD) from Cd(5^3P_1) agree with those for Cd(5^3P_0) within the error limits. It can be concluded that there are no activation barriers other than the endothermicity for the reactions of Cd(5^3P_0) with H_2(D_2) as far as we assume the same preexponential factors for the reactions of Cd(5^3P_1) and Cd(5^3P_0). In other words, there are activation barriers on the A_1 and B_1 surfaces, but there is no such a barrier on the A_2 surface except for the endothermicity.

Further information concerning the potential surfaces shall be obtained by measuring the nascent rotational state distributions of CdH(CdD) produced in the reactions of Cd(5^3P_0). Direct laser excitation of the ground-state Hg to the $^3P_0$ state has been reported by Bras et al.[22] However, a similar direct optical excitation to produce Cd(5^3P_0) must be hard because of the low natural abundance of odd isotopes as well as the low spin-orbit interaction. It seems rather realistic to carry out experiments employing a beam technique combined with electron bombardment. Selective production of the *J* state has been succeeded in the Ca system.[23]

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