

Photodissociation of Cadmium Diiodide

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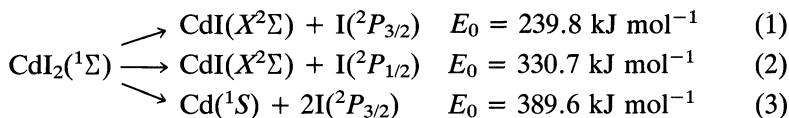
Photodissociation of cadmium diiodide was studied. The nascent vibrational distribution of $\text{CdI}(X^2\Sigma)$ on the photodissociation of CdI_2 at 308 nm was determined by the laser-induced fluorescence (LIF) technique. The temporal variation in the density of $\text{CdI}(X^2\Sigma)$ radicals was monitored and it was shown that second-order recombination reactions were important under our experimental conditions. Both the ground and the highly excited states of cadmium atoms were generated on photodissociation of CdI_2 . The multiphoton absorption process for the production of highly excited Cd atoms is discussed.

KEY WORDS: Photodissociation of cadmium diiodide; LIF; second order reactions; MP absorptions; excited state Cd atoms.

INTRODUCTION

The photodissociation of many of the triatomic group IIB metal halides continues to attract attention because it provides an efficient method for pumping of laser transitions in atomic and molecular species^{1–5}. Concerning cadmium halides, lasing has been reported for $\text{CdI}(B^2\Sigma^+)$ and $\text{Cd}(5^1D_2)$ and 6^3S_1 by excimer laser photodissociation of CdI_2 molecules. Dissociative excitation of mercury dihalide molecules in a fast transverse discharge^{6,7} and relativistic electron beam irradiation of gas mixture were also attempted^{8–10}. The first two pumping methods have an advantage over the third in that they involve a cyclic production scheme for the excited species, i.e. the MX_2 molecules are regenerated efficiently after lasing.

In the present paper, the photodissociation of a linear metal halide, CdI_2 , with a 308-nm XeCl laser or a 337-nm N_2 laser is studied in order to know the primary process and the reaction dynamics of the photodissociation. Possible dissociation processes with the one-photon energy are given as¹¹:



If the dissociation follows Eqn (1), $\text{CdI}(X^2\Sigma)$ produced must be excited to high vibrational levels. In the present paper, a spectroscopic study on $\text{CdI } C-X, D-X$ transitions, a kinetic study on CdI disappearance, and observation of atomic lines of Cd metal by multiphoton dissociation of CdI_2 are presented.

EXPERIMENTAL

The optical cells used in these experiments were made of quartz, 40 mm in length, 25 mm in diameter, and had a sidearm. After several milligrams of CdI_2 (Wako) were introduced into each cell, it was evacuated to <1 mTorr and sealed under vacuum. The cell was placed in an oven, and chromel–alumel thermocouples were used to monitor the temperature of the oven and the separately heated sidearm. The vapor pressure of the metal halide in the cell was estimated from the temperature of the sidearm, which was lower than that of the oven.

The experimental setup for the measurement of the laser-induced fluorescence (LIF) spectrum is given in Figure 1. A pulsed XeCl laser (Lambda Physik EMG 103MSC, ~ 100 mJ/pulse) was used as a photolysis source and as a pump laser of a dye laser (Lambda Physik LF2002) at the same time. After a delay of 10 ns, the $\text{CdI}(X^2\Sigma)$ radical produced was excited by the dye laser. The laser-induced fluorescence was detected by a photomultiplier (Hamamatsu 1P28) through a 25-cm monochromator (Nikon P-250 or G-250). The signal was fed to a Boxcar integrator (PAR 162/164) through a preamplifier (PAR 115) and was recorded by a strip chart recorder.

In the measurement of the temporal variation in the density of $\text{CdI}(X^2\Sigma)$ radicals, a homemade N_2 laser (~ 1 mJ/pulse) was used to

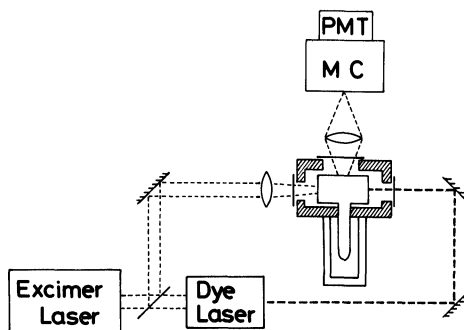


Figure 1 Experimental setup for the measurement of the LIF spectra. About 30 percent of the output of the 308-nm XeCl laser was used to dissociate CdI_2 , and the rest was used to pump the dye laser.

dissociate CdI_2 . An XeCl laser-pumped dye laser (0.1 mJ/pulse) was timed to probe the sample at selected delay times following the dissociation pulse. Intensity measurements of LIF from $\text{CdI}(C^2\Pi_{1/2}, \nu' = 0 \rightarrow X^2\Sigma, \nu'' = 0 \text{ or } 1)$ band gave a measure of the instantaneous density of CdI ground-state radicals.

The formation and decay of Cd atoms generated in its ground state in the 308-nm laser photolysis of CdI_2 were monitored by absorption using a cadmium hollow-cathode lamp. The light of the cadmium lamp was defocused to cover the whole photolysis cell in order for Cd atoms not to diffuse out of the viewing region. The laser light was also defocused and the output from a photomultiplier was digitized by a transient recorder. Typically, 1000 separate laser-initiated photolysis runs were accumulated in a signal averager.

The emission from the electronically excited Cd atoms was measured by the monochromator and a photomultiplier (Hamamatsu R928).

RESULTS AND DISCUSSION

LIF studies of CdI radical

Potential curves of CdI radical

Figures 2(a) and (b) show the LIF emission spectra from the $\nu' = 0$ states of the $C^2\Pi_{1/2}$ and $D^2\Pi_{3/2}$ states, respectively. From the relative intensity we can obtain the Franck-Condon factors as tabulated in

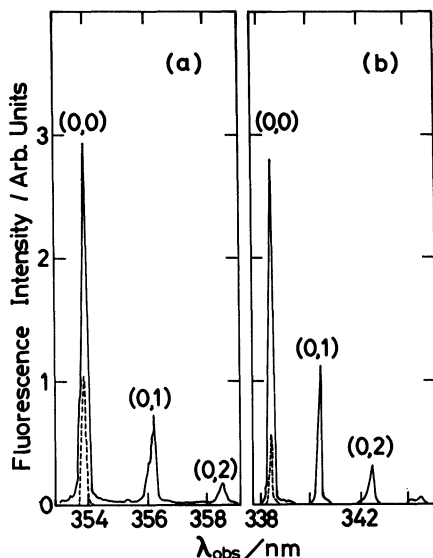


Figure 2 LIF spectra of CdI radical. (a) $\lambda_{\text{ex}} = 354.03 \text{ nm}$ ($C^2\Pi_{1/2} \leftarrow X^2\Sigma (0, 0)$ band). (b) $\lambda_{\text{ex}} = 338.40 \text{ nm}$ ($D^2\Pi_{3/2} \leftarrow X^2\Sigma (0, 0)$ band). Broken lines are with the photolysis laser off.

Table I. Since the Franck–Condon factors are sensitive to the relative location of two potential curves, we have calculated the Franck–Condon factors with the value of $\Delta r_e = r'_e - r''_e$, the deviation of the equilibrium internuclear distance of each $^2\Pi$ state from that of the ground state, as a parameter, and compared them with the experimental values. The potential curves of the ground, C , and D states were approximated by Morse functions. The values of ω_e and $\omega_e x_e$ for these three states of the CdI radical are given by Huber and Herzberg¹².

Table I Franck–Condon factors of CdI $C^2\Pi_{1/2} - X^2\Sigma$ and $D^2\Pi_{3/2} - X^2\Sigma$ transitions.

	$C-X$		$D-X$	
	Observed	Calculated ($\Delta r_e = -0.051 \text{ \AA}$)	Observed	Calculated ($\Delta r_e = -0.055 \text{ \AA}$)
(0, 0)	0.65 ± 0.02	0.66	0.61 ± 0.01	0.60
(0, 1)	0.26 ± 0.02	0.26	0.29 ± 0.02	0.29
(0, 2)	0.08 ± 0.01	0.07	0.08 ± 0.01	0.08

We found that the observed values of Franck–Condon factors were consistent with the calculated ones for $\Delta r_e = -0.051 \text{ \AA}$ for $C \leftarrow X$ transition, and for $\Delta r_e = -0.055 \text{ \AA}$ for $D \leftarrow X$ transition. These calculated values are also tabulated in Table I.

Since no band of the CdI radical has been thoroughly analyzed, r_e values of any states have not been known. The B states of the group IIB metal–halide diatomic molecules were ionic in character. In the case of $^{200}\text{Hg}^{127}\text{I}$ radical, r_e values are 2.18 \AA and 3.30 \AA for the X and B states, respectively¹³. Therefore, r_e of the B state of the CdI radical must be larger than that of the ground state. Contrary to the B state, r_e values of both the $^2\Pi$ excited covalent states, $C^2\Pi_{1/2}$ and $D^2\Pi_{3/2}$, of the CdI radical are shorter than that of the ground state, because the absorption bands in $C \leftarrow X$ and $D \leftarrow X$ transitions are degraded towards the violet¹⁴. Our results of the Franck–Condon factors show that r_e varies little among the X , C , and D states.

Vibrational population of the CdI($X^2\Sigma$) radicals photodissociated by an XeCl laser

Figure 3 shows the LIF excitation spectrum for the $D \leftarrow X$ transition of CdI radical obtained by observing the fluorescence of the $D \rightarrow X$

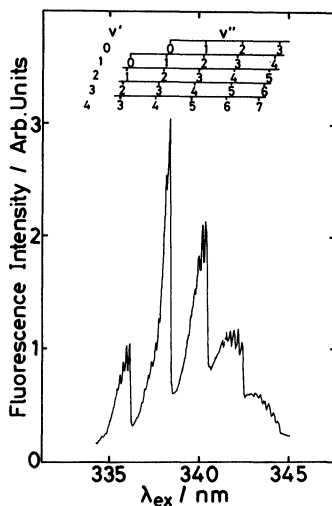


Figure 3 LIF excitation spectra for the $D \leftarrow X$ transition of CdI radical generated by photodissociation with 308-nm XeCl laser. $\lambda_{\text{obs}} = 338.4 \text{ nm}$. Resolution of the monochromator is $\sim 5 \text{ nm}$.

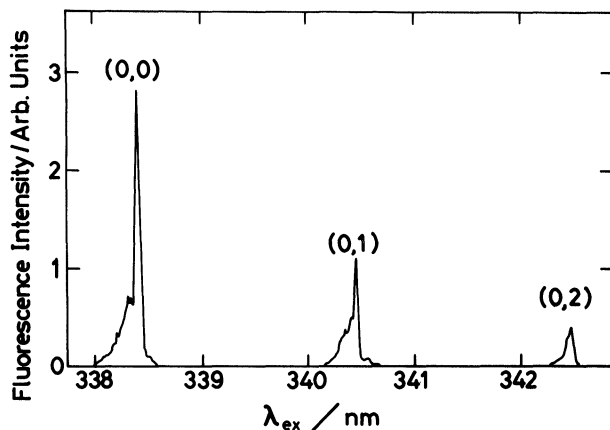


Figure 4 LIF excitation spectra for the $D \leftarrow X$ transition of the CdI radical. $\lambda_{\text{obs}} = 338.4 \text{ nm}$ ($D^2\Pi_{3/2} \rightarrow X^2\Sigma$ (0, 0) band).

transition with a broad resolution of the monochromator. This spectrum shows that several vibrational states are excited in the ground-state of CdI radical.

Figure 4 shows the LIF excitation spectra for the $D \leftarrow X$ transition obtained by observing the $D \rightarrow X$ (0, 0) emission. From the relative intensity of each band in this spectrum and the Franck–Condon factors obtained above, the ratios of the vibrational population of the CdI ground state produced by photodissociation of CdI₂ with a 308-nm XeCl laser were determined to be 1.00:0.85:0.80 for $\nu'' = 0, 1, 2$ levels, respectively.

We could determine the vibrational population for only the lowest three vibrational levels because the bands associated with higher vibrational levels are very much congested. Kawasaki *et al.*¹⁵ concluded that about half of the available energy was distributed as vibrational energy of CdI radicals in the photodissociation with 300-nm laser radiation, based on the results of a photofragment time-of-flight (TOF) experiment. Therefore, higher vibrational levels ($\nu \geq 3$) are expected to be occupied to a significant extent in our experimental conditions. Isotopically pure CdI₂ molecule should be used in order to obtain the vibrational population for the vibrational levels with larger quantum numbers in order to avoid the spectral congestion.

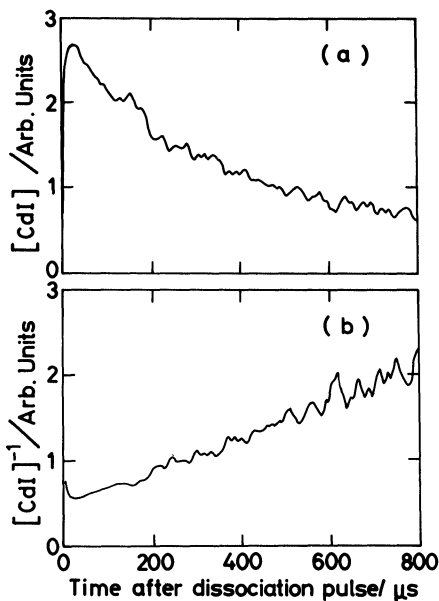
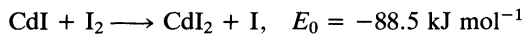


Figure 5 (a) An example of the temporal variation of the density of CdI($X^2\Sigma$) radicals following the dissociation of CdI₂ with a 337-nm N₂ laser. $\lambda_{\text{ex}} = 356.25$ nm ($C \leftarrow X(0, 1)$ band). $\lambda_{\text{obs}} = 354.03$ nm ($C \rightarrow X(0, 0)$ band). (b) The reciprocal plot of (a).

Temporal behavior of CdI($X^2\Sigma$) radicals

The temporal decay of CdI radical density was monitored as a function of time after the dissociation pulse. A nitrogen laser was used as a photolysis light source, and an XeCl laser-pumped dye laser was used as an LIF probe laser. Figure 5(a) shows an example of the temporal variation of the density of CdI($X^2\Sigma$, $v'' = 1$) radicals following dissociation of CdI₂. Monotonic decrease was observed even at 1.5 ns after the photolysis laser pulse.

The concentration of CdI($X^2\Sigma$) radical decayed after the very fast increase at the beginning. The decay curves were not exponential. From the reciprocal plot of the relative CdI($X^2\Sigma$) radical concentration versus time as shown in Figure 5(b), it turned out that the concentration decay of the CdI($X^2\Sigma$) radical was dominated by the second-order kinetics in our experimental conditions. This indicates that the bimolecular reaction:¹⁶

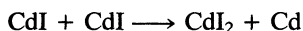


is not important for the regeneration of CdI_2 . This is in contrast with the case of HgBr_2 , in which Erlandson and Cool¹⁷ reported that the fast bimolecular reaction:

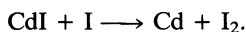


was responsible for the observed rapid and efficient regeneration of HgBr_2 in cyclic operation of the repetitively pulsed HgBr laser.

Since the observed second-order rate constant was independent of the cell pressure in the range of 0.2–1 Torr, three-body recombination reactions can be eliminated. Possible process for the decay of CdI is the radical–radical disproportionation reaction:



or the abstraction reaction by the iodine atom generated,

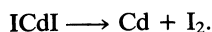


Formation of cadmium atoms in the ground and excited states

The energy levels of the cadmium atoms are shown in Figure 6. The ground state of Cd ($5s^2^1S$) can be generated in the one-photon dissociation process [Eqn (3)] at $\lambda \leq 307 \text{ nm}$, while the electronically excited states may be formed in the multiphoton dissociation of CdI_2 by focusing the photolysis laser light.

Formation and decay of $\text{Cd}(5s^2^1S)$

Since the thermodynamic threshold is 307 nm for the production of Cd atoms *via* the process in Eqn (3), the production of Cd atoms observed at 308 nm must have occurred from the hot parent molecules. The 337.1-nm irradiation gave quite a small Cd signal, i.e. the contribution of the following primary process is negligibly small, although it is thermodynamically possible at this wavelength. This is quite reasonable if the direct dissociation occurs from the linear structure of the parent CdI_2 :



An example of the observed signals in the 308-nm irradiation is shown in Figure 7. This signal was taken at the probe wavelength 326.1 nm which corresponds to the $5s^2^1S \rightarrow 5s5p^3P$ transitions. The

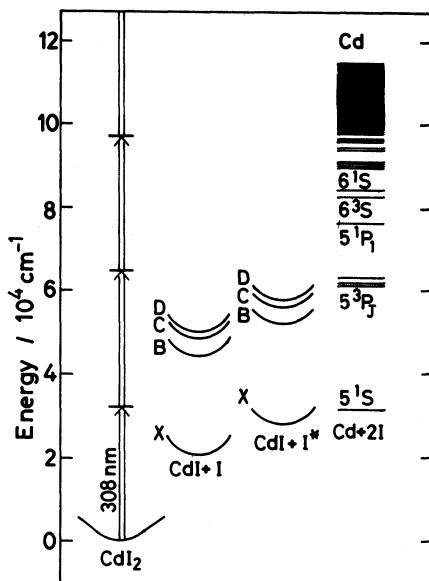


Figure 6 Energy level diagram for CdI₂, CdI, and Cd. I* refers to I(²P_{1/2}).

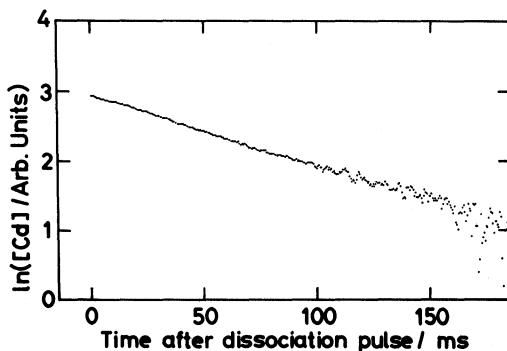


Figure 7 An example of the temporal variation of the density of Cd(5¹S) atoms following the dissociation of CdI₂ with a 308-nm XeCl laser. $\lambda_{\text{obs}} = 326.1$ nm.

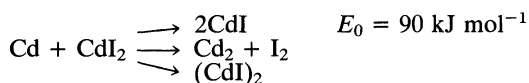
immediate rise of Cd signals after a laser pulse was observed within the time resolution (~ 100 ns) of our instruments. This rise rate does not correspond to the decay rate of CdI radicals shown in Figure 5. This result suggests that the Cd atoms are directly formed in the one-photon primary process in Eqn (3), but not by the disproportionation reaction

Table II First-order decay rates of Cd(5^1S) at various pressures of CdI₂.

$P_{\text{CdI}_2}(\text{Torr})^a$	$k(\text{s}^{-1})$
0.46	15.0
0.60	18.0
0.77	21.3
1.05	28.0

^a Pressures are estimated from the reservoir temperatures.

of CdI radicals. The first-order decay rates obtained at four pressures of CdI₂ were tabulated in Table II. Decay rates increased with the CdI₂ pressure. Then, the diffusion of Cd atoms out of the viewing zone was not significant in the experimental conditions. Three decay modes of Cd atoms are to be considered:



Among these three, the formation of CdI radicals can be eliminated because (a) it has the large heat of reaction and (b) at 1.5 ms after the photolysis laser pulse, no increase was observed in the LIF signal of CdI($X^1\Sigma$). Since the cadmium dimer is considered to be unstable in analogy to Zn₂¹⁸ the Cd₂ formation mechanism is also eliminated. Although there has been no report on CdI dimers the last process is the most plausible one. The formation of alkali halide dimers has been reported¹⁹.

Formation of electronically excited Cd atoms

When the photolysis laser (308 nm) was softly focused by a lens of $f = 100$ mm, the formation of Cd($5s5p^3P_J$) was observed by means of the LIF method at 467.9 nm, 480.1 nm, and 508.7 nm (Figure 8). The probe laser intensity was so strong that the saturation occurred in the pumping process from the lower 3P_J states to the higher $5s6s^3S$ state. The populations of the $J = 2, 1,$ and 0 levels were determined by the monochromatized emission intensity. The initial distribution of the J states of Cd(3P_J) determined here was almost equal for $J = 2, 1,$ and 0 . This distribution does not fit a Boltzmann distribution at any temperature. The nascent distribution is non-statistical.

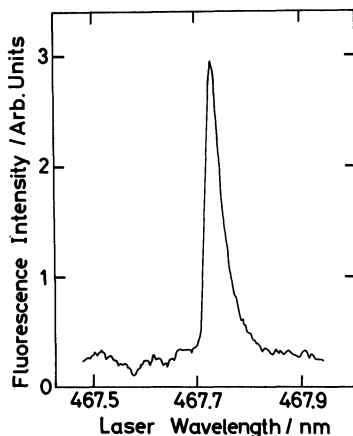


Figure 8 An example of laser-induced fluorescence spectrum of $\text{Cd}(5^3P_0)$ following the dissociation of CdI_2 with a 308-nm XeCl laser. $\lambda_{\text{obs}} = 480$ nm.

When the photolysis laser (308 nm or 337.1 nm) was hard focused by a lens of $f = 30$ mm, the higher electronically excited cadmium atoms Cd^* were generated as shown in the emission spectra of Figure 9. When the laser wavelength was 337.1 nm, resonant with the transition of $\text{CdI}(D-X)$, not only the atomic emission but also the $C-X$ and $B-X$ emissions of CdI were observed as shown in Figure 10. In this case, the formation mechanism of Cd^* is either the three-photon absorption of the parent molecules, or the two-photon absorption of the CdI fragments generated in the first one-photon process. However, in the 308-nm irradiation, the emission of the CdI^* radicals was quite weak. The three-photon absorption of the parent molecule is obvious at this wavelength resulting in the formation of Cd^* atoms (see Figure 6):



In order to test the formation of some specific electronic states of Cd^* in multiphoton absorption of CdI_2 molecules, the 308 nm laser intensity was changed by a factor of 20. The relative emission intensity ratio of $\text{Cd}(6^3D_2)$ or $\text{Cd}(5^3D_2)$ to $\text{Cd}(7^3S_1)$ was constant. These states can be generated by the three-photon absorption. Once the parent molecule absorbs enough photon energy, the energetically possible processes seem to occur without any selectivity in the formation of the Cd^* atoms.

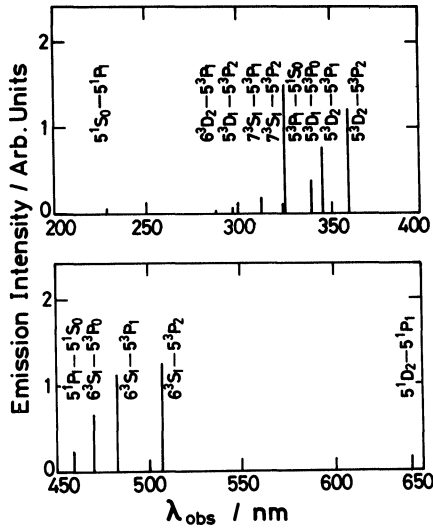


Figure 9 Emission spectra of the cadmium atom produced by the photodissociation of CdI_2 with a 308-nm XeCl laser.

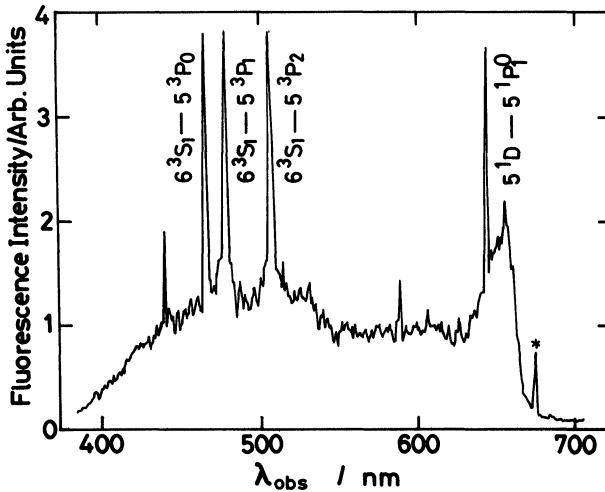


Figure 10 Emission spectra of the cadmium atom produced by the photodissociation of CdI_2 with a 337.1-nm N_2 laser. The peak marked by * indicates the scattered laser light.

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