

Predissociation and pooling effects in the laser-induced fluorescence spectrum of the HgZn excimer

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During a pump-and-probe spectroscopic study of the HgZn excimer, it was found that probing the Hg-Zn vapor cell with laser light in the 4200–4500-Å range resulted in the intense emission of Hg 4916-Å atomic fluorescence arising from the $8^1S_0 \rightarrow 6^1P_1$ transition. This observation is ascribed to the predissociation of the HgZn $F1$ state through a curve crossing with the repulsive $D0^-$ state, followed by pooling collisions of the resulting Hg 6^3P atoms, leading to the population of the 8^1S_0 state. This interpretation is corroborated by the results of spectroscopic and time-evolution experiments.

I. INTRODUCTION

We have recently reported the results of an investigation in which we studied laser-induced fluorescence (LIF) spectra and excitation spectra associated with the $E1$ (Hg $6^1S + \text{Zn } 4^1P$) and $F1$ (Hg $6^1S + \text{Zn } 5^3S$) states.¹ We used the pump-and-probe method in our experiments and showed that, when using probe-laser radiation in the spectral range 4200–4500 Å, low-lying vibrational levels of the $E1$ and $F1$ states became excited simultaneously. The $E1$ state which was populated by transitions from the $A0^+$ and $A0^-$ states, was found to decay solely by bound-free transitions to the repulsive $X0^+$ ground state. The $F1$ state was excited by transitions from the $A0^+$ state and decayed both to the $X0^+$ state and by resonance bound-bound transitions to the $A0^+$ state, giving rise to a fluorescence spectrum with vibrational structure. The excitation spectrum, recorded by monitoring LIF in the 2230–2260-Å region, consisted of three overlapping band systems arising from $E1 \leftarrow A0^+$, $E1 \leftarrow A0^-$, and $F1 \leftarrow A0^+$ transitions.¹ We now report a previously unobserved emission of an intense single LIF component at 4916 Å, superimposed on the wing of the 4750-Å continuum fluorescence,² which appeared when the probe laser was tuned to a wavelength corresponding to any vibrational peak in the $F1 \leftarrow A0^+$ excitation spectrum. The 4916-Å emission was identified as arising from the $8^1S_0 \rightarrow 6^1P_1$ transition in atomic mercury, and its presence was ascribed to the predissociation of the $F1$ state caused by a curve crossing. To verify this interpretation, a series of experiments was carried out, as described below.

II. EXPERIMENTAL DETAILS

The apparatus, experimental procedure, and the preparation of the HgZn vapor cell have been described elsewhere.^{1,3} The Hg-Zn vapor mixture (approximately 2.2-atm Hg and 1-torr Zn) contained in a quartz cell was irradiated with 3075.9-Å pump-laser pulses corresponding to the Zn $4^3P_1 \leftarrow 4^1S_0$ atomic transition. The

3075.9-Å radiation was produced by pumping a two-stage dye laser with the second harmonic of a Nd:YAG laser (where YAG denotes yttrium aluminum garnet) and then frequency doubling its 6151.8-Å output using a potassium dihydrogen phosphate (KDP) crystal. This caused the formation of HgZn in the $A1$, $A0^-$, and $A0^+$ metastable states.^{1–3} The probing radiation was generated with a tunable probe laser whose pulses were appropriately delayed relative to the pump pulses. The probe laser was a two-stage N₂ laser-pumped dye laser. The resulting fluorescence, emitted at right angles to the laser beams, was dispersed by an I.S.A. HR-320 monochromator fitted with a 1800-line/mm grating, and detected with an RCA 31034A photomultiplier. The output signals from the photomultiplier were registered with a 1024-channel Biomation Model 6500 transient digitizer whose highest time resolution was 2 ns/channel, and stored in a Commodore PET microcomputer which carried out signal averaging. Both the monochromator and the probe laser could be scanned by computer-controlled stepper motors in constant wavelength increments. The probe-laser wavelengths were measured with a precision of ± 1 Å using a Fizeau wavelength meter.⁴

The experiment was carried out in two mutually complementary stages. In the first stage, the probe laser was set at a particular wavelength while the fluorescence spectrum was scanned with the monochromator. The second stage involved probe-laser scans at a fixed monochromator wavelength setting. During both stages, ten fluorescence pulses were digitized, time integrated and accumulated in the computer memory corresponding to the wavelength setting of the monochromator (or the probe laser). The computer then advanced the monochromator (or the probe laser) wavelength by 1 Å and the procedure was repeated until the end of the wavelength scan. The scan was then repeated until a satisfactory signal-to-noise ratio was achieved.

III. RESULTS AND DISCUSSION

Figure 1 shows a trace of the excitation spectrum, obtained by scanning the probe laser in the 4200–4500-Å re-

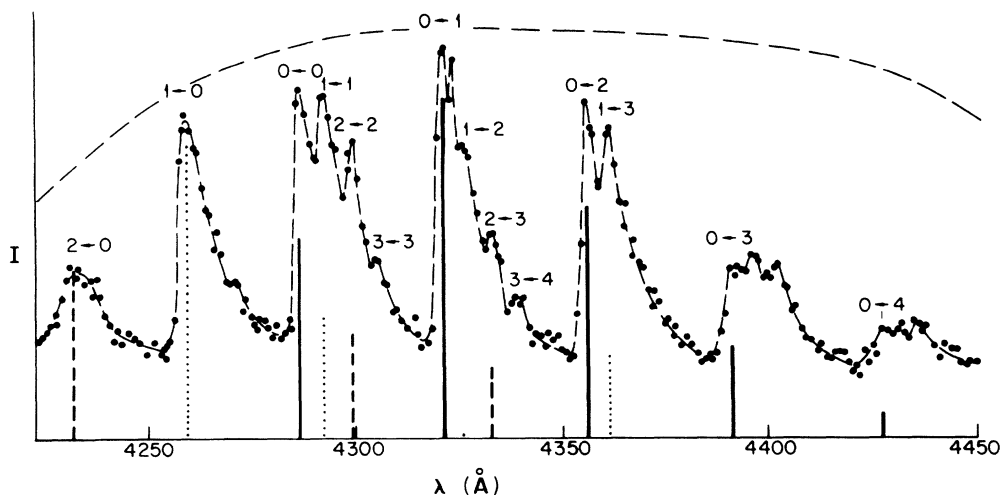
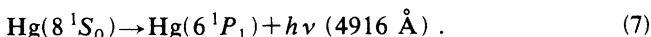
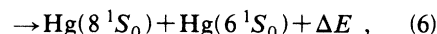
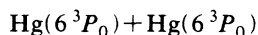
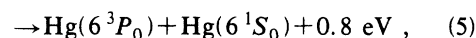
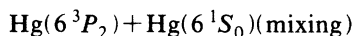
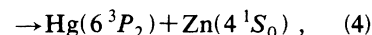
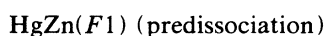
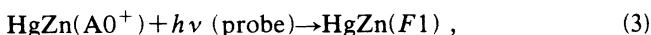
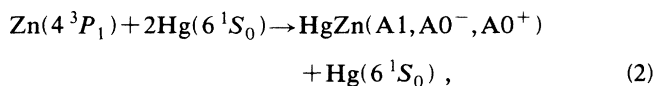
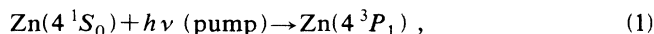


FIG. 1. The $F1 \leftarrow A0^+$ excitation spectrum, showing $v' \leftarrow v''$ assignments. The spectrum was monitored at 4916 Å. The vertical bars represent the relative intensities of the v'' progressions in the computer-simulated spectrum. Solid line, $0 \leftarrow v''$; dotted line, $1 \leftarrow v''$; dashed line, $2 \leftarrow v''$.

gion and monitoring the Hg fluorescence signal at 4916 Å. On comparison between it and Figs. 9–12 of Ref. 1, we concluded that it corresponded to the $F1 \leftarrow A0^+$ excitation spectrum. To verify this interpretation we calculated the intensities of the various components using the previously described computer-simulation procedure.⁵ The LIF spectrum produced when the probe laser was tuned to any peak in the excitation spectrum and the monochromator was scanned in the 4800–5000-Å region, consisted of only the Hg 4916-Å emission line superimposed on the extended tail of the persistent blue fluorescence band at 4750 Å, which was excited by the pump pulses. No other atomic emissions were detected by scanning the monochromator in the spectral region 2300–7000 Å, consistent with our previous observations.¹

We suggest that the Hg 4916-Å radiation emitted in the $\text{Hg } 8^1S_0 \rightarrow 6^1P_1$ decay was due to the predissociation of the $F1$ HgZn molecules, followed by collisional mixing and pooling among $\text{Hg } 6^3P_{0,1,2}$ atoms. The predissociation occurred through the curve crossing between the $F1$ state and the repulsive $D0^-$ state and produced metastable $\text{Hg } 6^3P_2$ atoms. Because of efficient collisional mixing and the strong imprisonment of the $\text{Hg } 2537\text{-}\text{Å}$ ($6^3P_1 \rightarrow 6^1S_0$) resonance radiation, the 6^3P_0 state became highly populated; its effective lifetime was limited by the decay time of the imprisoned resonance radiation, by collisions producing excited Hg_2 and HgZn molecules and by the pooling collisions of 6^3P_0 atoms, which resulted in the population of the $\text{Hg } 8^1S_0$ state and the emission of the 4916-Å radiation accompanying the $8^1S_0 \rightarrow 6^1P_1$ decay. The processes are illustrated in Fig. 2 and the mechanism may be summarized as follows.



The signal-to-noise ratio in Fig. 1 is very high and comparable to the other HgZn excitation and fluorescence spectra, suggesting that the mechanism by which the $\text{Hg } 8^1S_0$ state was populated must have been quite efficient. Further evidence for the mechanism involving the predissociation and pooling processes was provided by comparing the time evolution of the 4750-Å fluorescence band, emitted in the decay of the $A1$ and $A0^+$ reservoir states to the $X0^+$ ground state, with the variation of the 4916-Å LIF intensity in relation to the pump-probe delay. The comparison, shown in Fig. 3, showed identical rise and decay times which confirmed that the lower state involved in the probe-laser absorption was a reservoir state correlated with the $\text{Hg}(^1S) + \text{Zn}(^3P)$ atomic states. The possibility of pooling collisions between $\text{Zn } 4^3P$ and $\text{Hg } 6^3P_0$ atoms was also ruled out because of the large energy defect and also, because the density of $\text{Zn } 4^3P$ atoms was quite low at 450 ns after the pump-laser pulse.²

There have been several reports of pooling collisions involving $\text{Hg } 6^3P$ atoms.^{6–8} Bochkova, Gamarts, and Tolmachev⁶ observed several Hg atomic lines in the afterglow of a pulsed low-pressure discharge in a Hg-He mixture. They claimed that the 4916-Å line was due to $6^3P_0 - 6^3P_0$ pooling collisions. Fogel and Tolmachev⁶ used the same technique and claimed that $6^3P_2 - 6^3P_0$ collisions played the dominant role in producing the 4916-Å

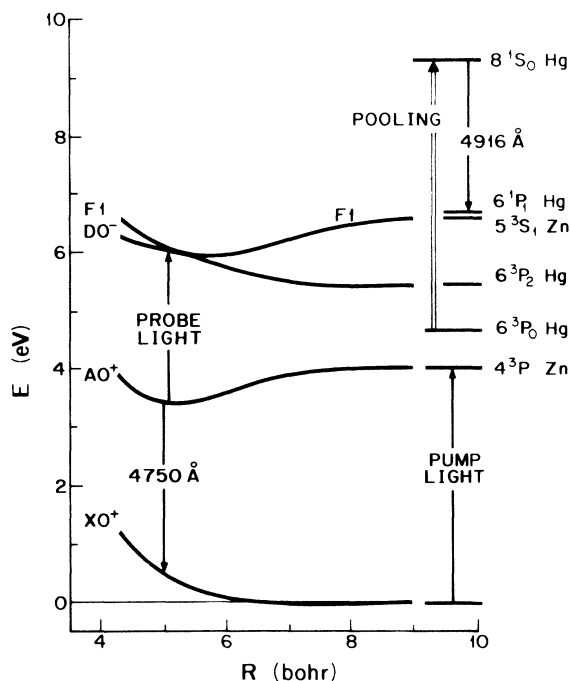


FIG. 2. A partial PE diagram showing predissociation and pooling resulting in 4916-Å emission.

line. Recently Majetich, Boczar, and Wiesenfeld⁸ observed a large number of atomic lines following excitation of Hg at low pressure, mixed with Ar or N₂, by a pulse of 2537-Å resonance radiation which directly populated the 6³P₁ state. They implied that the 4916-Å line was due to pooling collisions involving at least one 6³P₁ atom. Our results do not allow us to specify which 6³P_J states are involved in the pooling process, although we have reasons to believe that it is due to the collision of two 6³P₀ atoms. That in our experiment the partial pressure

of mercury is approximately 2.2 atm, compared with vapor pressures of a few millitorr in the other pooling collision studies, constitutes a major difference in experimental conditions. The much higher pressure in our case leads to a rapid thermalization among the 6³P_J states, with the resulting 6³P₀ population being 20 times the 6³P₁ population and 400 times the 6³P₂ population. The closest energy resonance for the collision of two Hg 6³P₀ atoms is the production of a ground-state 6¹S₀ atom and an 8¹S₀ atom, the upper state for the 4916-Å line. Our failure to observe other atomic lines supports this view.

We also found that the time evolution of the 4916-Å line followed that of the probe-laser pulse which had a decay time of approximately 5 ns. This decay time is much shorter than the radiative lifetime of the 8¹S₀ state, which is 63 ns.⁹ We measured the effective lifetime of the 8¹S₀ state under our experimental conditions by directly populating it by two-photon absorption from one laser pulse of wavelength 2687.2 Å and found the time evolution to be also similar to that of the exciting pulse, confirming that the short effective lifetime was due to collisional effects at the high operating pressure.

The excitation spectrum shown in Fig. 1 includes more vibrational components than are shown in Fig. 9 of Ref. 1. This is because several F1 vibrational levels can participate in the curve crossing and predissociation giving rise to the 4916-Å emission, while the excitation spectrum recorded by monitoring the structured-continuum uv fluorescence from the molecule favored particular vibrational levels of the F1 state. As confirmed by the modeling calculation, the relative intensities of the components in Fig. 1 are determined by the Franck-Condon (FC) factors and by the thermal distribution over the vibrational levels of the A0⁺ state.

The vibrational constants of the A0⁺ and F1 states were calculated by substituting the frequencies and frequency separations of the F1←A0⁺ band system into the standard term equation and were found to be identical with those reported previously.¹

IV. CONCLUSIONS

An intense Hg 4916-Å fluorescence emission was observed when the HgZn excimer was probed with laser radiation in the 4200–4500-Å region. This is interpreted as due to the predissociation of HgZn in the F1 state by a curve crossing with the repulsive DO⁻ state, followed by collisional mixing and pooling collisions between Hg 6³P₀ atoms. The atomic fluorescence was used to monitor the F1←A0⁺ excitation spectrum and confirmed our previous analysis of it.¹ The results of this experiment, taken in conjunction with the PE curves, corroborated the assignment of the F1 state as that which underwent radiative decays to the XO⁺ and A0⁺ states¹ and predissociation through a curve crossing.

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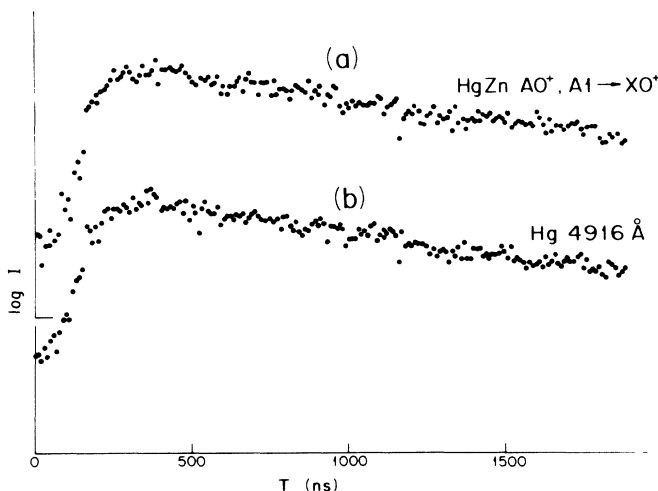


FIG. 3. Time evolution of the fluorescence. (a) Buildup and decay of the 4750-Å band excited with pump pulses only. (b) Intensity of the Hg 4916-Å atomic line plotted against the delay between pump and probe laser pulses.

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