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Laser-induced fluorescence spectroscopy of the Hg_3 excimer

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We report what we believe to be the first observation of a laser-induced fluorescence band, excited by absorption from a low-lying state of the Hg_3 excimer using a "pump-and-probe" method. A study of the fluorescence intensity as a function of the time separation between the "pump" and "probe" laser pulses provides clear evidence for the presence of both Hg_3 and Hg_2 molecules in the laser-excited mercury vapor. The fluorescence may be due to trimer emission or to dimer emission following dissociation of a trimer state.

Although the existence of molecular mercury emission bands at 3350 and 4850 Å has been known for over 50 years, they have, until recently, been attributed to the Hg_2 dimer,[1] particularly since their persistence times at low Hg-vapor densities were found to be identical and equal to about 50 ms.[2] More recent experiments, employing laser spectroscopy[3] and flash photolysis,[4] as well as theoretical calculations,[5,6] led to the conclusion that the 4850-Å continuum could not be emitted by Hg_2 and that it must be due to the radiative decay of a low-lying state of Hg_3. This has been assigned as an $A\,0_u^{\pm}$ state by Callear and Lai,[4] who also designate it as the lower state of a series of unstructured absorption bands ranging from 2900 to 4650 Å. We will use their assignment, although no other evidence is available to support it. There have been no reports of fluorescence from excited Hg_3 other than the 4850 Å, and Callear and Lai were not able to suggest any assignments for the other Hg_3 levels. The most recently observed laser-induced fluorescence (LIF) spectra of mercury excimers arise exclusively from various excited states of Hg_2.[7–9] In this communication, we present the first evidence of fluorescence emitted from a more highly excited state of Hg_3 which was populated by absorption from the Hg_3 $A\,0_u^{\pm}$ state using "pump and probe" techniques. Figure 1 shows a partial energy-level diagram for Hg_2 based on the calculations of Baylis[10] and Mies *et al.*,[5] and on our experimental results.[8,9] The energy level corresponding to the lowest Hg_3 state shown in the figure conforms to the data of Drullinger *et al.*[3]

The arrangement of the apparatus has been described elsewhere.[8,9] Mercury vapor, at a density of 5×10^{17} cm^{-3} and contained in a quartz cell, was irradiated with 2660-Å pulses from the fourth harmonic of a Nd yttrium-aluminum-garnet (YAG) laser, resulting in a population of Hg_2 $A\,0_g^{\pm}$ molecules. After a delay which was variable from 50 ns to 50 μs, pulses from a N_2 laser-pumped dye laser, directed collinearly with the Nd:YAG pulses, were used to probe the $A\,0_g^{\pm}$ molecules as well as the collisionally produced Hg_3 molecules. The resulting LIF spectrum was observed at right angles to the laser beams, resolved with a monochromator and detected with an EMI 9816QB photomultiplier. A Biomation model 6500 transient digitizer, controlled by a PET microcomputer, together constituted a signal integrating and/or averaging data acquisition system.

The experiment consisted of three separate parts. Firstly, monochromator scans of the time-integrated fluorescence were made with various pump-probe delays. Secondly, the intensity of the time-integrated fluorescence detected at a particular monochromator setting was measured as a continuous function of pump-probe delay. Finally, time-resolved fluorescence measurements were made at various monochromator settings, both with and without probe laser pulses. The monochromator and probe laser could be scanned in constant wavelength increments which were multiples of $\frac{1}{2}$ and $\frac{1}{28}$ Å, respectively. The pump-probe delay was produced by a computer controlled delay generator and could be programmed to values ranging from 50 ns to 1.8 ms in steps of 5.0 ns.

The Hg_3 $A\,0_u^{\pm}$ state is produced through collisional processes which involve the initial formation of Hg_2 in the $D\,1_u$ state by photoassociation of a ground-state atom pair. The $D\,1_u$ excimers collisionally relax to the $A\,0_g^{\pm}$ metastable states which participate in the formation of

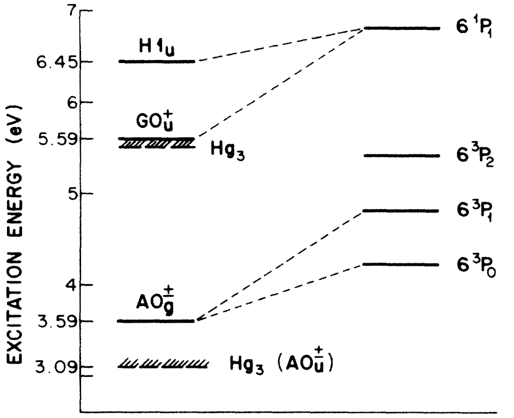

FIG. 1. Energy-level diagram showing the pertinent Hg_2 and Hg states. The locations of the Hg_3 ($A\,0_u^{\pm}$) state (Ref. 3) and of the higher Hg_3 states as suggested by the results of this experiment are also indicated.

Hg_3 excimers through three-body collisions involving two ground-state mercury atoms.[3,11] The trimer population time dependence is a function of the density and collision rate,[11] and its radiative decay gives rise to the 4850-Å band. The tunable probe laser may then be used to excite either the dimers or trimers to a higher state whose decay produces a spectrum characteristic of the two states involved in the fluorescence transition.

Figure 2 shows scans of the time-integrated LIF spectrum obtained at three different delay times of the probe pulse and with the probe wavelength set to 4335 Å. The peak near 1996 Å is due to the $H1_u \rightarrow X0_g^+$ emission from Hg_2,[9] and its intensity remains constant within a factor of 2 for pump-probe delays in the range 0–8 μs. However, the intensity of the broad LIF band centered near 2170 Å increases significantly with the probe pulse delay. Since the time-integrated intensity of an LIF band is proportional to the population density of the state absorbing the probe laser pulse, the different time behavior clearly shows that it is not the Hg_2 $A\,0_g^\pm$ states which are the absorbing species leading to the 2170 Å emission.

In order to identify the states associated with the 2170-Å band, the two additional experiments were carried out and their results are presented together in Fig. 3. The intensities of the 4850- and 3350-Å bands were measured as a function of time following the pump laser pulse and without using the probe laser. These data are shown in Figs. 3(a) and 3(b) and represent the time dependence of the Hg_3 $A\,0_u^\pm$ and Hg_2 $A\,0_g^\pm$ populations, respectively. In the final experiment, the LIF intensities of two bands were scanned in relation to the time delay between the pump and probe laser pulses. Figure 3(c) shows such a scan with the probe laser set at 4200 Å to excite the $A\,0_g^\pm \rightarrow J\,1_u$ transition[12] while detecting the LIF band at 5130 Å, arising from the $J\,1_u \rightarrow E2_g$ decay. The results of a similar scan of the 2170-Å band are shown in Fig. 3(d). The probe laser was set at 4650 Å in order to reduce fluorescence from dimer bands.[4,8,12] However, similar scans could be obtained with probe laser wavelengths between 4350 and 5150 Å. The similarities between Figs. 3(a) and 3(d) and between 3(b) and 3(c) are immediately obvious. They confirm that the Hg_2 $D1_u$ state, which emits the 3350-Å band is in equilibrium with the Hg_2 $A\,0_g^\pm$ states. They also show clearly that the initial absorbing state of the 2170-Å LIF band is either the Hg_3 $A\,0_u^\pm$ state or one in collisional equilibrium with it. The population of this state initially increases at a rate characterized by its own collisional and radiative decay time.[11] At times later than those shown in Fig. 3, all four curves decay at a common rate, which is the collisional decay rate of the Hg_2 $A\,0_g^\pm$ metastable reservoir.

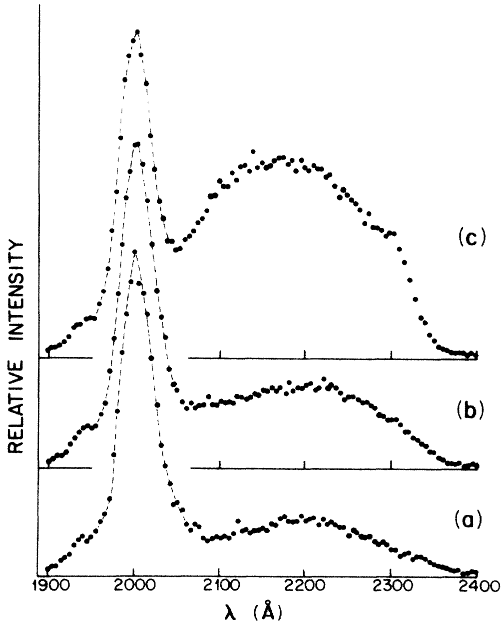

FIG. 2. 2170-Å LIF band of Hg_3 recorded at various pump-probe pulse delay times: (a) 150 ns; (b) 500 ns; (c) 9 μs. All intensities have been normalized to that of the 1996-Å peak due to $H1_u \rightarrow X0_g^+$ emission from Hg_2.

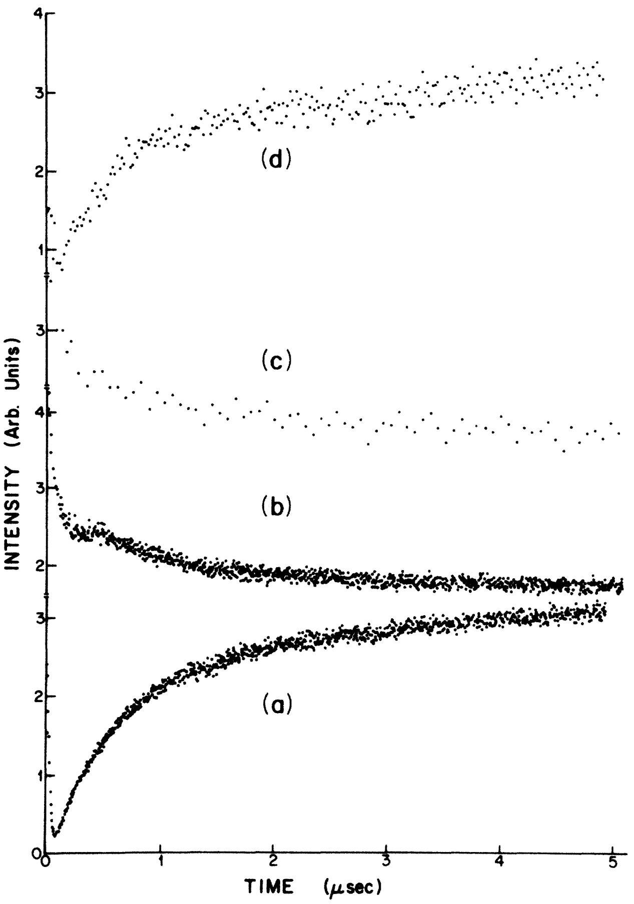

FIG. 3. (a) and (b) show time evolutions of the 4850-Å Hg_3 band and 3350-Å Hg_2 band, respectively, excited by pulses of pump-laser radiation. (c) and (d) show the LIF intensities of the 5130-Å Hg_2 band and 2170-Å Hg_3 band, respectively, in relation to the pump-probe delay.

While the results of our investigation clearly show that a Hg_3 state is the absorbing species giving rise to an absorption continuum which ranges from below 4150 to 5100 Å, the designation of the upper state of the strong 2170-Å fluorescence bands is uncertain. The fluorescence decay time of the 2170-Å band is less than 3 ns since it follows the probe pulse time dependence. This result is consistent with a strongly allowed radiative transition or with significant collisional quenching of the excited Hg_3 state. It is also likely that the terminal state for such a transition dissociates into three ground-state Hg atoms as is the case with the 4850-Å band. Alternatively, the excited trimer might rapidly dissociate to a free atom and a Hg_2 $G0_u^{\pm}$ molecule which emits in the same spectral region and has a short lifetime.[8] Since the dissociation could populate several vibrational states of the dimer, the Condon diffraction patterns would be averaged out to give the observed unstructured continuum. At present, we are unable to decide between these two possibilities.

The experiments described here show clearly the existence of an absorption band in the spectral region from 4150 to 5100 Å, arising from an excited Hg_3 molecule. If this state is located at 3.09 eV, the upper Hg_3 state must lie in the vicinity of 5.50—5.60 eV. Two possible sources for the resulting uv fluorescence are suggested, but a definitive answer must await further experimental and theoretical work.

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