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Laser induced fluorescence (LIF) of Hg_2 and Hg_3 via dissociation of $HgBr_2$ at 157 nm

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Abstract. Laser induced fluorescence of the mercury clusters Hg_2 and Hg_3 in the spectral range between 300 nm to 510 nm has been obtained from the dissociation of $HgBr_2$ at 7.88 eV (157.5 nm) with an F_2 molecular laser, together with fluorescence from mercury atomic transitions from highly excited states. The excitation process involves two photon absorption which dissociates the molecule at 15.76 eV total photon energy with the subsequent formation of the metallic clusters.

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1. Introduction

The photodissociation of $HgBr_2$ at 157.5 nm using an F_2 molecular laser is an efficient method for producing the mercury clusters Hg_2 and Hg_3 in their excited states [1]. Despite the fact that the photodissociation of mercury halides by an ArF excimer laser at 193 nm (and at other excimer and dye lasers wavelengths) has been extensively studied [2–7] there are no reports on any metallic cluster formation in this wavelength. The use of an F_2 molecular laser at 157.5 nm can induce the $1\,{}^1\Sigma_g^+ \rightarrow 2\,{}^1\Sigma_u^+$ transition of $HgBr_2$ at 7.88 eV, Fig. 1.

The $2\,{}^1\Sigma_u^+$ state correlates with the $D({}^2\Pi_{3/2})$ and $C({}^2\Pi_{1/2})$ states of HgBr with the subsequent break up

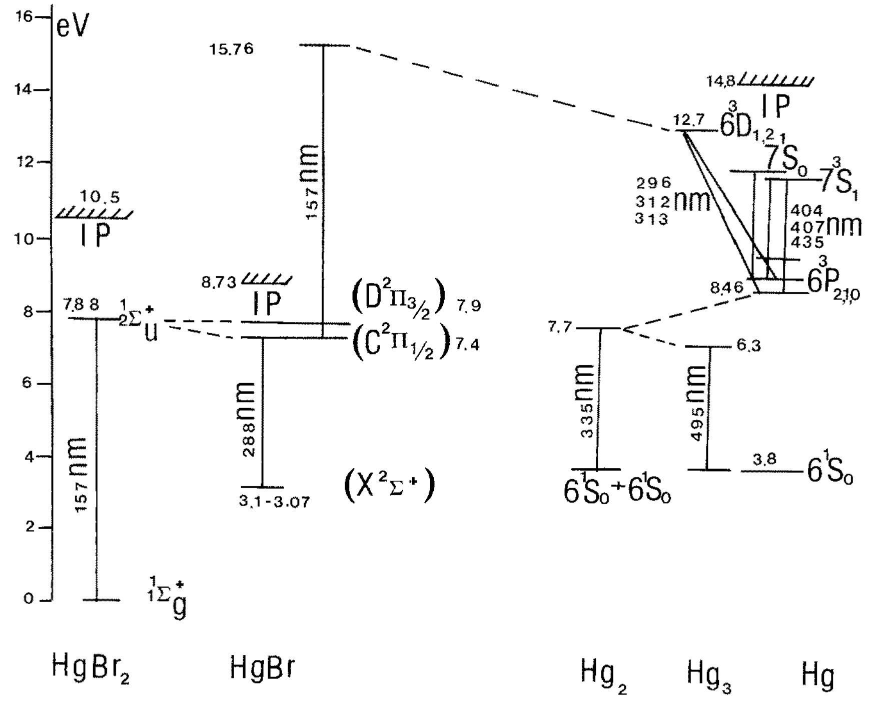

Fig. 1. Energy diagram of the one and two photon excitation processes, numbers indicate energies from the $1\,{}^1\Sigma_g^+$ state of $HgBr_2$ in eV

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to HgBr and Br. From there the nascent diatomic with the absorption of a second photon at 157.5 nm and a new break up populates the 6^3P manifold of the atomic mercury states. Mercury atoms in the 6^3P_0 metastable state after undergoing a collision with a ground state mercury atom can form a diatomic cluster which in a subsequent collision with another ground state atom can create a triatomic cluster in its excited state.

In this paper the LIF spectra of these clusters in the spectral range 300 to 500 nm have been recorded together with the $C \rightarrow X$ transition of HgBr. The total available energy of 15.76 eV from the absorption of two photons can populate the highly excited states of mercury through the correlation of these states with the ionic states of $HgBr^+$ [8] at 15.76 eV. The transitions from the triplet D states of mercury at 313.1 nm ($6\,^3D_1 \rightarrow 6\,^3P_1$), 312.5 nm ($6\,^3D_2 \rightarrow 6\,^3P_1$), and 296.7 ($6\,^3D_1 \rightarrow 6\,^3P_0$), have been observed along side with transitions from the lower states at 404.6 nm ($7\,^3S_1 \rightarrow 6\,^3P_0$), 407.7 nm ($7\,^1S_0 \rightarrow 6\,^3P_1$) and 435.8 nm ($7\,^3S_1 \rightarrow 6\,^3P_1$). Two new progressions of spectral lines around 357 nm and 380 nm have been recorded. These lines are probably transitions from the highly excited states of Hg_2 to the lower ones.

2. Experimental

The experimental apparatus has been described elsewhere [1] and it consisted of a pulsed discharge molecular fluorine laser at 157.5 nm [8], a heat pipe oven and the detection system. The VUV radiation from the F_2 laser was directed into the heat pipe oven through stainless steel vacuum lines which contained a few mgrs of $HgBr_2$. The temperature could be controlled between 30 °C and 300 °C. Despite the fact that the oven was not operated in the "heat pipe mode" the presence of the 20 cm long stainless steel mesh was found to reduce contamination of the mercury halide vapor on the windows even without the use of a buffer gas. The fluorescent signal was matched to a 0.2 m monochromator (Acton VM 502) both along the axis of excitation and at right angles with it. The signal was detected with an EMI 9829 photomultiplier and a 7401 Tektronix fast oscilloscope.

3. Results and discussion

The electronic structure of $HgBr_2$ and HgBr and the excitation mechanisms have been analysed both theoretically [9, 10] and experimentally [11, 12]. There are three allowed dipole transitions between the low lying electronic states of $HgBr_2$, $1\,^1\Pi_u$, $1\,^1\Sigma_u^+$, $2\,^1\Sigma_u^+$ and its ground state $1\,^1\Sigma_g^+$. The absorption of a VUV photon at 157.5 nm excites the transition $1\,^1\Sigma_g^+ \rightarrow 2\,^1\Sigma_u^+$ according to the process.

$$HgBr_2(1\,^1\Sigma_g^+) + h\nu(7.88\text{ eV}) \rightarrow HgBr_2(2\,^1\Sigma_u^+). \quad (1)$$

The $2\,^1\Sigma_u^+$ state of $HgBr_2$ at 7.88 eV correlates with the $C(^2\Pi_{1/2})$ and $D(^2\Pi_{3/2})$ states of HgBr and the ^2P state of Br.

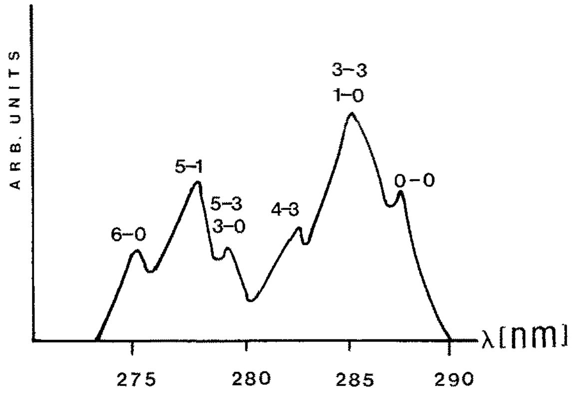

Fig. 2. $C-X$ transition spectra of HgBr with $v-v'$ assignement following excitation of $HgBr_2$ by one photon absorption at 157.5 nm to the excited state $2\,^1\Sigma_u^+$ and subsequent dissociation to HgBr and Br fragments

$$\begin{aligned} &HgBr_2(2\,^1\Sigma_u^+) \rightarrow HgBr_2(^2\Pi_{1/2}) + Br(^2P) \\ &HgBr_2(2\,^1\Sigma_u^+) \rightarrow HgBr_2(^2\Pi_{3/2}) + Br(^2P) \quad (2) \end{aligned}$$

The small energy gap between the D state and the available energy from one photon at 157.5 nm can be bridged thermally at high temperatures.

Therefore a fraction of the population is transferred to the D state [13] and the remaining part to the C state of HgBr. From the C and D states the molecules can either radiate to the X state or can absorb a second 157.5 nm photon and photoionize the HgBr molecule. The $C \rightarrow X$ transition at 285 nm (Fig. 2) is the strongest transition in the spectrum while the $D \rightarrow X$ transition at 265 nm is ~10 times weaker. The overall absorption cross section at 157.5 nm has been found to be $(4.5 \pm 2.6) \times 10^{-16}\text{ cm}^2$ [1] in the temperature range between 40 °C to 90 °C. This value is considerably higher than the value of the absorption cross section at 193 nm which has been found to be $3.8 \times 10^{-17}\text{ cm}^2$ [14]. However, the theoretical calculations of Wadt [9] predict that the absorption cross section between the $1\,^1\Sigma_g^+$ and $2\,^1\Sigma_u^+$ states at 157 nm should be smaller than the absorption cross section between the $1\,^1\Sigma_g^+$ and $1\,^1\Sigma_u^+$ states at 193 nm by a factor of 35. The above discrepancy between the experimental and theoretical values indicates that other loss mechanisms than the absorption between the $1\,^1\Sigma_g^+$ and $2\,^1\Sigma_u^+$ states should play the major part in the annihilation of VUV photons by the $HgBr_2$ molecules. These absorption mechanisms are one step ionization of HgBr from the C and D states and two step ionization of $HgBr_2$ from its ground state. The C and D states of HgBr at 7.88 eV correlate with the $6\,^3P_{0,1}$ metastable states of Hg either via one photon absorption and subsequent deexcitation to the $6\,^3P_{0,1}$ states:

$$\begin{aligned} &HgBr(^2\Pi_{1/2}, {}^2\Pi_{3/2}) + h\nu(7.88\text{ eV}) \rightarrow HgBr^+(15.76\text{ eV}) \\ &HgBr^+(15.76\text{ eV}) \rightarrow Hg(6D, 7S) + Br(^2P) \\ &Hg(6D, 7S) \rightarrow Hg(6P) + h\nu \quad (3) \end{aligned}$$

or through thermal dissociation according to

$$HgBr(^2\Pi_{3/2}, {}^2\Pi_{1/2}) + kT \rightarrow Hg(^3P_0, {}^3P_1) + Br(^2P). \quad (4)$$

The energy gap between the $^2\Pi_{3/2}$ state of HgBr and the Hg ($6\,^3P_0$) state of mercury is between 0.58 and 0.53 eV [15, 16] therefore at 300 °C less than ~0.1% of the population of the diatomic is thermally dissociating to the $\mathrm{Hg}(6\,^3P_0)+\mathrm{Br}(^2P)$ atoms. The observed emissions at 404.6, 435.8, 407.8, 312, 313, 296, 365, 366 and 254 nm are from the allowed dipole transitions from the $7S$, $6D$ and $6P$ states of mercury

$$
\begin{aligned}
&\mathrm{Hg}(7\,^1S_0)\rightarrow \mathrm{Hg}(6\,^3P_1)+h\nu(407.8\ \mathrm{nm})\\
&\mathrm{Hg}(7\,^3S_1)\rightarrow \mathrm{Hg}(6\,^3P_1)+h\nu(435.8\ \mathrm{nm})\\
&\mathrm{Hg}(7\,^3S_1)\rightarrow \mathrm{Hg}(6\,^3P_0)+h\nu(404.6\ \mathrm{nm})\\
&\mathrm{Hg}(6\,^3D_2)\rightarrow \mathrm{Hg}(6\,^3P_2)+h\nu(365.5\ \mathrm{nm})\\
&\mathrm{Hg}(6\,^1D_2)\rightarrow \mathrm{Hg}(6\,^3P_2)+h\nu(366.3\ \mathrm{nm})\\
&\mathrm{Hg}(6\,^3D_2)\rightarrow \mathrm{Hg}(6\,^3P_1)+h\nu(312.6\ \mathrm{nm})\\
&\mathrm{Hg}(6\,^3D_1)\rightarrow \mathrm{Hg}(6\,^3P_1)+h\nu(313.1\ \mathrm{nm})\\
&\mathrm{Hg}(6\,^3P_1)\rightarrow \mathrm{Hg}(6\,^1S_0)+h\nu(253.6\ \mathrm{nm})\\
&\mathrm{Hg}(6\,^3D_1)\rightarrow \mathrm{Hg}(6\,^3P_0)+h\nu(296\ \mathrm{nm}) \qquad (5)
\end{aligned}
$$

The kinetic processes associated with the formation of the Hg_2 ($AO_g^{\pm}$) from the $6\,^3P_{0,1}$ and $6\,^1S_0$ states have been studied in detail previously [17] and the spectroscopy of the Hg_2 molecule has been given by the excellent work of Niefer et al. [18], Callear et al. [19] and Drullinger et al. [20]. A collision between a metastable mercury atom $6\,^3P_0$ and a ground state atom $6\,^1S_0$ can create the mercury dimer Hg_2 in its excited states AO_g^- while a collision between a $6\,^3P_1$ mercury atom and a $6\,^1S_0$ ground state atom can form a mercury dimer either in the AO_g^+ state or in the $D1_u$ state depending on the thermal energy available. The $AO_g^{\pm}$ states which lie 2800 cm^{-1} below the optically active $D1_u$ state can either act as an energy reservoir for the formation of the Hg_3 cluster or can thermally populate the $D1_u$ state of Hg_2 which gives the 335 nm band through deexcitation to the dissociative ground state.

$$
\begin{aligned}
&\mathrm{Hg}(6\,^3P_0)+\mathrm{Hg}(6\,^1S_0) &&\rightarrow \mathrm{Hg}_2(AO_g^-)\\
&\mathrm{Hg}(6\,^3P_1)+\mathrm{Hg}(6\,^1S_0) &&\rightarrow \mathrm{Hg}_2(AO_g^+)\\
& &&\rightarrow \mathrm{Hg}_2(D1_u)\\
&\mathrm{Hg}(AO_g^{\pm})+kT(0.34\ \mathrm{eV})\rightarrow \mathrm{Hg}_2(D1_u)\\
&\mathrm{Hg}(D1_u)\rightarrow 2\mathrm{Hg}(6\,^1S_0) &&+h\nu(335\ \mathrm{nm}).
\end{aligned}
$$

The spectral lines detected in the region of 410–426 nm (Fig. 3a) originate from the deexcitation of the Hg_2 ($P1_u$) Rydberg state to the AO_g^+ state [18].

The Hg_2 ($P1_u$) state is created through a collision between a Hg ($7\,^3S_1$) atom with a ground state atom $\mathrm{Hg}(6\,^1S_0)$

$$
\begin{aligned}
&\mathrm{Hg}(7\,^3S_1)+\mathrm{Hg}(6\,^1S_0)\rightarrow \mathrm{Hg}_2(P1_u)\\
&\mathrm{Hg}_2(P1_u)\rightarrow \mathrm{Hg}_2(AO_g^+)+h\nu(410\text{–}426\ \mathrm{nm})
\end{aligned}
$$

This deexcitation channel is another pathway of populating the reservoir $AO_g^{\pm}$ states.

The LIF spectrum between 300 nm to 400 nm is shown in Fig. 3b. The 335 nm band is much narrower than the one previously reported from electric discharges [26]. The transition from the $6\,^3D_{1,2}$ manifold to the $6\,^3P_1$ state is located at 313 nm. Transitions from the same $6\,^3D_{1,2,3}$ manifold to the $6\,^3P_2$ state were recorded as well. Two new progressions of lines at 349 nm, 353 nm and 357 nm and at 371 nm, 375 nm and 380 nm had been observed. The first manifold has been observed previously in HgBr discharges and it was attributed to the presence of N_2. However, our spectra have been recorded alongside and sideways to the laser beam and the presence of N_2 should be excluded from our laser system.

The intensity of these spectral lines varies with temperature (they are very intense above 250 °C) and their temporal behavior suggests that they are transitions from excited states of the Hg_2 cluster which has been formed by the highly excited states to Hg without attempting any assignments. The dependence of the intensity of mercury lines at 404.6 nm and 366 nm with temperature alongside with rate of formation arguments suggest that these lines might originate from emissions from the highly excited states of Hg_2, eg. ($\mathrm{Hg}(7\,^1D_2)$ $+\mathrm{Hg}(6\,^1S_0)$) to lower ones. As far as the progression of lines around 380 nm is concerned, there is a dependence between the intensity of these lines and the intensity of mercury lines at 365 nm which originate from the $6\,^3D$ manifold. The remaining part of the spectrum between 385 and 400 nm consists of a series of lines. The temporal evolution of these spectral lines, (Fig. 4) suggests that they originate from transitions from the excitated states of the mercury triatomic Hg_3. Similar long lived states have been observed previously [1] around 446 nm and have been attributed to the complex potential surfaces of the Hg_3. The lifetime of the excited states of the Hg_2 cluster is believed to be short [21] and the long decay rates which have been observed previously are attributed rather to rates of formation of the clusters in their excited states. This argument is also supported by the temporal evolution of the 335 nm band (Fig. 4). Therefore, considering that our rates of formation are small the long lifetimes could be attributed to Hg_3 clusters because of the complicated structure of their potential surfaces. The strong perturbations which are present in the Hg_3 molecule alongside with tunneling effects could be the source of the long decay rates. The broad continuum in the blue-green region of the spectrum taken in mercury vapour column with maximum at 495 nm has been assigned to the emission from the Hg_3 molecules [20]. The same band has been observed previously [1] by laser induced fluorescence. Niefer et al. [18] using selective excitation in mercury vapor had assigned the observed absorption between 415 and 510 nm to the presence of the mercury cluster Hg_3. The sideways fluorescence of the 495 nm band between 480 nm and 510 nm indicates some vibrational structure with maximum at 494 nm (Fig. 5). The formation of Hg_3 originates from the collision of an Hg_2 molecule in its first excited state with a Hg atom in its ground state since the band is observed even without the use of a buffer gas.

$$
\begin{aligned}
&\mathrm{Hg}_2(AO_g^{\pm})+\mathrm{Hg}(6\,^1S_0)\rightarrow \mathrm{Hg}_3^*(AO_u^{\pm})\rightarrow \mathrm{Hg}_3(XO_g^{\pm})\\
&\qquad\rightarrow 3\mathrm{Hg}+h\nu(495\ \mathrm{nm\ band}). \qquad (6)
\end{aligned}
$$

The emitted radiation at 495 nm is highly directional and concentrated. Its superfluorescence nature [22] was

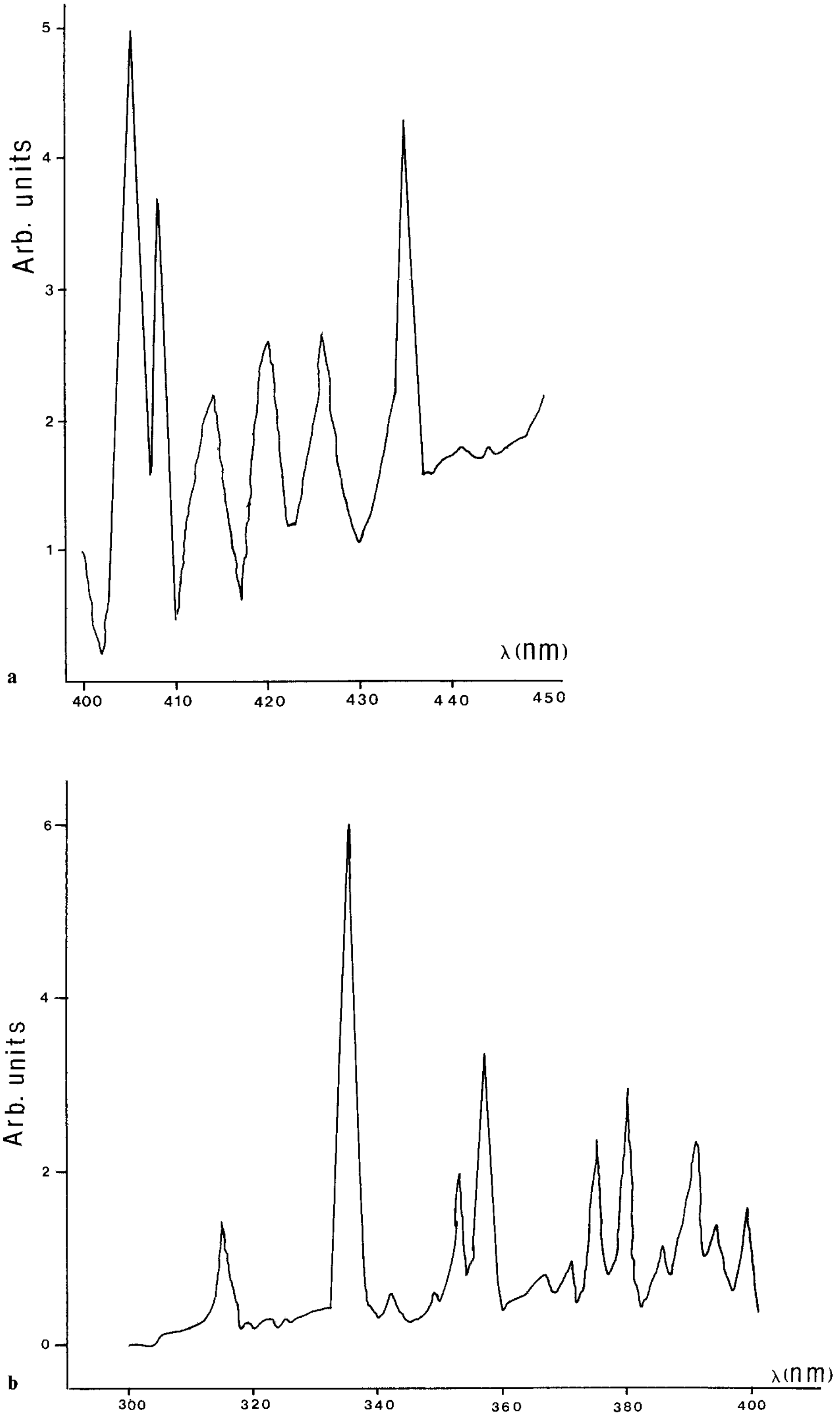

Fig. 3. a LIF spectra between 400 to 430 nm. **b** LIF spectra between 300 to 400 nm

manifested with the appearance of blue-green spots on a screen even 50 cm away from the fluorescence cell. Similar kind of blue-green spots have been observed by Shingenari et al. [23] at 404 and 407 nm during the photodissociation of $HgBr_2$ at 193 nm. The appearance of the spots suggests that at 495 nm the gain exceeds the absorption for this excitation scheme. The blue-green spots do not appear on a regular base, a fact which indicates that thermal gradients inside the heat pipe oven [24] might cause strong refractive index variations. From the intensity of the recorded signal we estimate that under the above experimental conditions the small signal gain at 495 nm, at 150 °C, is 0.004 cm^{-1}. This value is considerably higher than the one given by Ko-

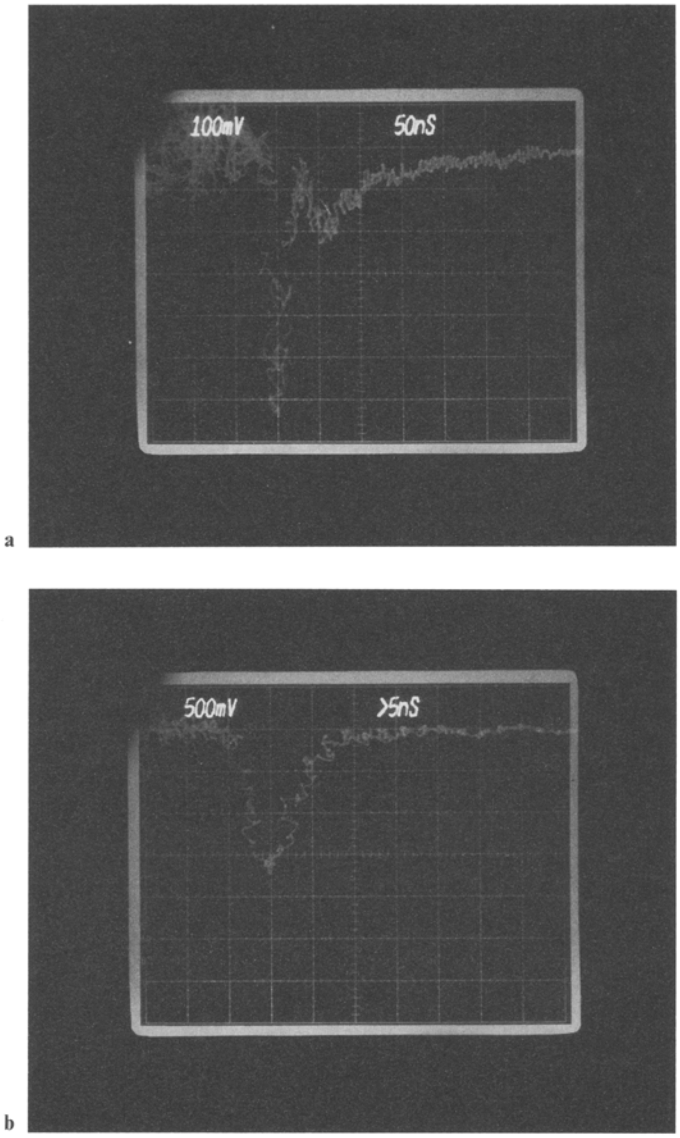

Fig. 4. **a** Temporal evolution of the fluorescence band at 385 nm the long decay rates are attributed to the Hg_3 cluster. **b** Temporal evolution of the 335 nm band indicated a short fluorescence lifetime

mine and Byer in a mercury vapor column [25]. However, the fluorescence spectra under these conditions differ significantly from ours. The cut-off frequency in a mercury discharge column was at 600 nm [26]. We believe that for excitation schemes which involve electrical discharges or selective excitation of mercury atomic levels at high temperatures the extension of the band towards the red is due to the formation of mercury clusters Hg_n ($n > 3$).

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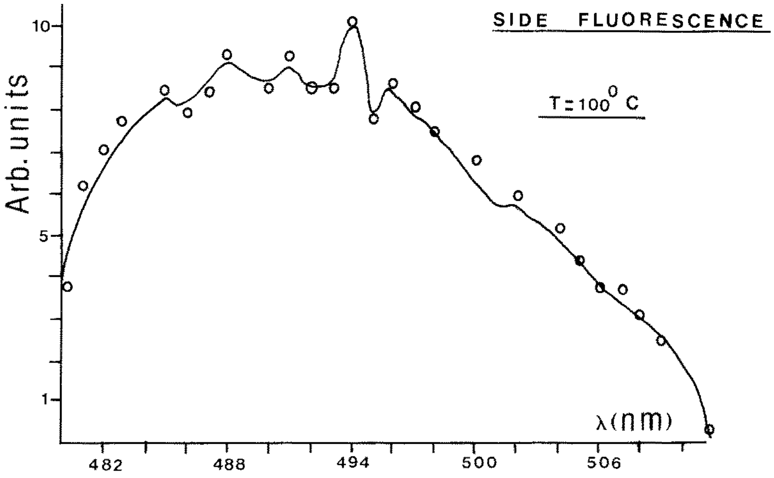

Fig. 5. LIF spectrum of the 495 band of Hg_3 with maximum at 494 nm

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