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 $^{1}\Sigma^+ \rightarrow 2^{1}\Sigma^+$ transition of HgBr$_2$ at 7.88 eV, Fig. 1.

The $^{2}\Sigma^+$ state correlates with the $D(2\Pi_{3/2})$ and $C(2\Pi_{1/2})$ states of HgBr with the subsequent break up
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 ($6^3D_1 \rightarrow 6^3P_0$, 312.5 nm ($6^3D_2 \rightarrow 6^3P_1$), and 296.7 ($6^3D_3 \rightarrow 6^3P_0$), 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 ($7^3S_0 \rightarrow 6^3P_1$) and 435.8 nm ($7^3S_1 \rightarrow 6^3P_0$). 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$_3$ 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 mgs 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$_2$, $1^3\Pi_u$, $1^3\Sigma_u^+$, $2^1\Sigma_u^+$ and its ground state $1^1\Pi^+$. The absorption of a VUV photon at 157.5 nm excites the transition $1^1\Sigma_u^+ \rightarrow 2^1\Sigma_u^+$ according to the process.

$$\text{HgBr}_2(1^1\Sigma_u^+) + h\nu(7.88 \text{ eV}) \rightarrow \text{HgBr}_2(2^1\Sigma_u^+) \quad (1)$$

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 $2^3P$ state of Br.

$$\text{HgBr}_2(2^1\Sigma_u^+) + h\nu(7.88 \text{ eV}) \rightarrow \text{HgBr}_2(2^1\Sigma_u^+) \quad (1)$$

$$\text{HgBr}_2(2^1\Sigma_u^+) \rightarrow \text{HgBr}(2^1\Pi_{1/2}) + \text{Br}(2^3P)$$

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

Fig. 2. $C \rightarrow X$ transition spectra of HgBr with $v \rightarrow v'$ assignment 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.

$$\text{HgBr}_2(2^1\Sigma_u^+) \rightarrow \text{HgBr}_2(2^1\Pi_{3/2}) + \text{Br}(2^3P)$$

$$\text{HgBr}_2(2^1\Sigma_u^+) \rightarrow \text{HgBr}_2(2^1\Pi_{3/2}) + \text{Br}(2^3P) \quad (2)$$

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 $(4.5 \pm 2.6) \times 10^{-18} \text{ cm}^2$ [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 $1^1\Sigma_u^+$ and $2^1\Sigma_u^+$ states at 157 nm should be smaller than the absorption cross section between the $1^1\Sigma_u^+$ 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 $1^1\Sigma_u^+$ 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:

$$\text{HgBr}(2^1\Pi_{1/2}, 2^1\Pi_{3/2}) + h\nu(7.88 \text{ eV}) \rightarrow \text{HgBr}^+(15.76 \text{ eV}) \quad (3)$$

$$\text{HgBr}^+(15.76 \text{ eV}) \rightarrow \text{Hg}(6^3D, 7S) + \text{Br}(2^3P)$$

$$\text{Hg}(6^3D, 7S) \rightarrow \text{Hg}(6P) + h\nu \quad (3)$$

or through thermal dissociation according to

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