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SATELLITE BANDS OF THE InHg EXCIMER

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We measured the spectrum of the InHg high-pressure discharge and observed several InHg satellites and molecular bands. Satellite bands around indium resonance lines at 451 and 410 nm are interpreted by a potential energy diagram based on TlHg ab initio calculations modified to match the position of the observed InHg satellite bands.

1. Introduction

Satellite bands around indium resonance lines in the violet spectral region have been reported in numerous papers[1,2,3]. However, we could not find any interpretation of their origin except the general ones. Unfortunately, there are no theoretical calculations of the relevant potential curves and the corresponding transition dipole moments for InHg excimer system. There are several sources of useful information for the interpretation of the satellite bands origin. First, there is a possibility to study the schematic trends in the spectral appearance of the related satellite bands in other analogous systems, like TlHg, InZn or InCd for example[3−11]. Second, the ab initio calculations for the TlHg excimer[12] with slight modifications could be successfully applied for the explanation of the TlHg satellite bands. If we assume a general similarity between TlHg and InHg excimers, we may offer a qualitative explanation of the InHg satellite bands, which could be verified later by appropriate theoretical calculations and subsequent experimental studies using laser induced fluorescence.

2. *Experiment*

Experimental arrangement is shown in Fig. 1. We investigated four InI-Hg-Ar lamps with different concentrations of InI and Hg. Quartz burner was 4 cm long with inner diameter of 1.8 cm. The lamp was equipped with standard inductive ballast and ignition device. The light from the lamp was spectrally resolved with the monochromator (Jobin Yvon) and detected by a photomultiplier EMI 9558 QB. Signal was processed by BOX-CAR averager in current reversal[17)] and current maximum mode, and recorded by strip chart recorder. The radiation of the indium lamps in the region from 300 to 400 nm is rapidly falling to zero value because of the absorption of ultraviolet light in the glass of lamp bulb.

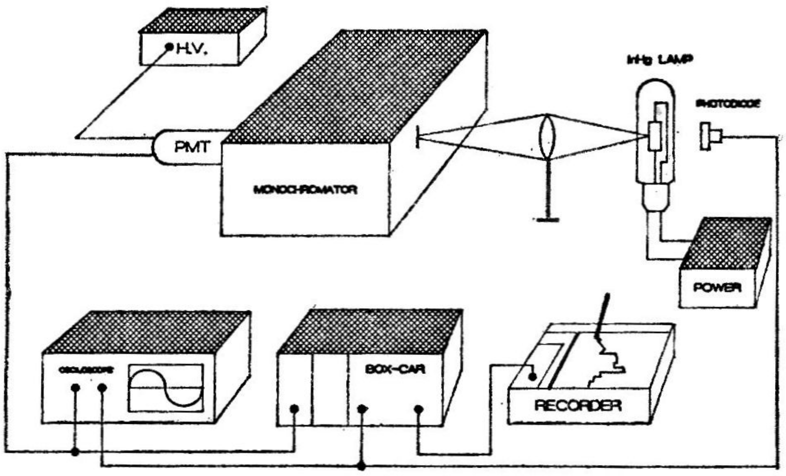

Fig. 1. Experimental arrangement.

3. *Results*

In Figs. 2 and 3 we present the emission profiles of two strongest resonance lines at 451.1 and 410.2 nm. Their line centres are completely reabsorbed at the cooler regions close to the quartz wall of the burner. The red wing is broadened by the presence of mercury and we may readily observe two satellite bands (shoulders) on the red wing of 451.1 nm line and one satellite band on the red wing of 410.2 nm line[1)]. In the near-blue wing we cannot discern any InHg, In_2, or InAr satellite band[2,13,14,15)] but there is a broad satellite band at 446.7 nm, which we tentatively ascribe to InHg excimer. The analogous InHg satellite in the far blue wavelenght wing of 410.2 nm line is located at 405.5 nm[11)]. Both bands could be much better seen in Fig. 4 where the enhanced emission spectrum from the whole spectral region from 380 nm is shown. In addition to this at even shorter wavelength there is another band at 391.8 nm. The analogous band in the blue wing of 451.1 nm line

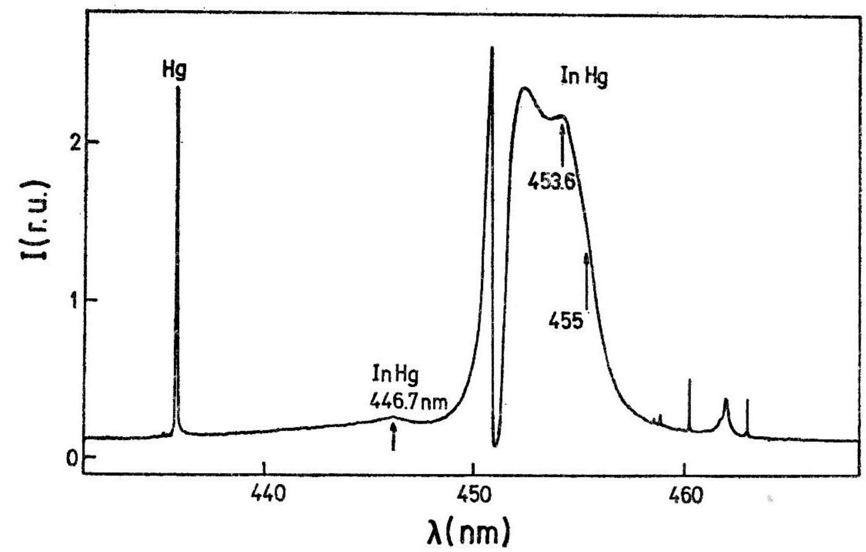

Fig. 2. The region of In *resonance line at 451.1* nm, *with three satellites at 453.6, 455 and 446.7* nm.

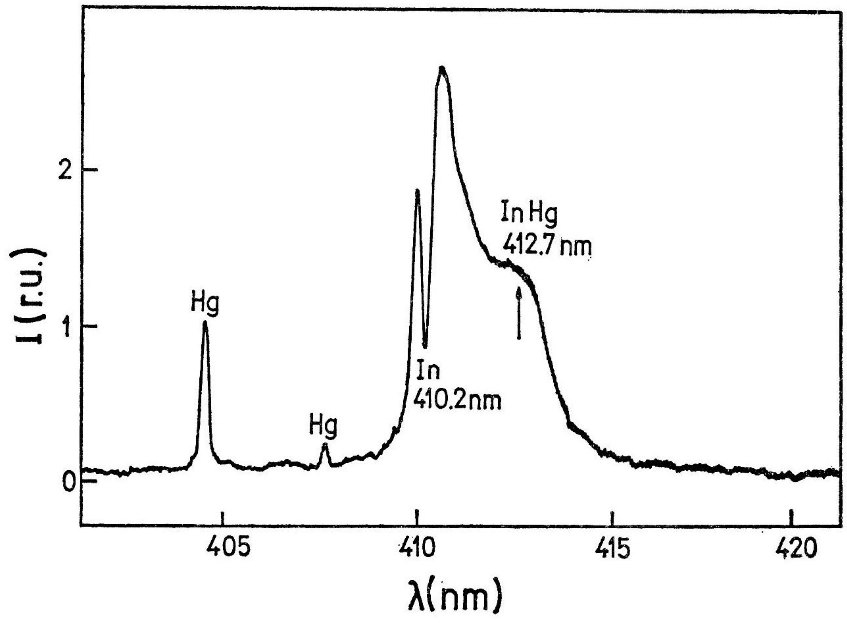

Fig. 3. The region of In *resonance line at 401.2* nm, *where we can observe satellite band at 412.6* nm.

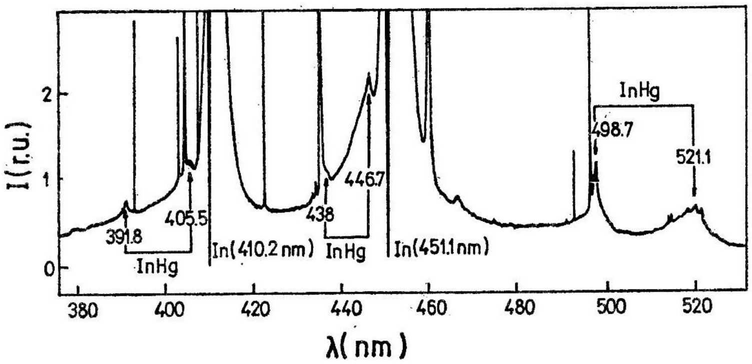

Fig. 4. The spectrum of InI-Hg-Ar *discharge lamp in the spectral region from 380 to 530* nm, *recorded in current reversal mode.*

can be observed as a weak diffuse band just below the Hg emission line at 438 nm. The positions of all these satellite bands are given in Table 1.

TABLE 1.

Line	Blue wing	ΔE (cm^{-1})	Red wing	ΔE (cm^{-1})
410.2 nm	391.8 nm	1145	412.6 nm	141
	405.5 nm	282	498.7 nm	4326
451.1 nm	438.0 nm	663	453.7 nm	122
	446.7 nm	218	455.0 nm	190
			521.1 nm	2977

InHg *satellite bands near the indium resonance lines and the energy separations to the correspondent line.*

The InHg molecular bands of bound-bound and bound-free transition nature are readily seen in Fig. 4 with their peaks at 498.7 nm and 521.1 nm[1,16].

4. Discussion

Figure 5 shows the ab initio potential energy curves for TlHg excimer calculated by Calvert-Celestino and Emler[12]. Indium and thallium atoms are both placed in the IIIA group of periodic table and posses the same outer electronic shell, containing two s and one p electron. Accordingly, we can expect that InHg potential energy diagram looks alike to the ab initio TlHg potential energy curves. We constructed the qualitative model for InHg potential energies by scaling TlHg potential curves, considering appropriate asymptotes in which InHg potentials ex-dissociate, a spin orbit splitting for indium in ground state of 2212.56 cm^{-1} and the experimental positions of InHg satellites.This qualitative picture of the InHg excimer potentials is given in Fig. 6, together with the lowest atomic energy levels of indium and mercury.

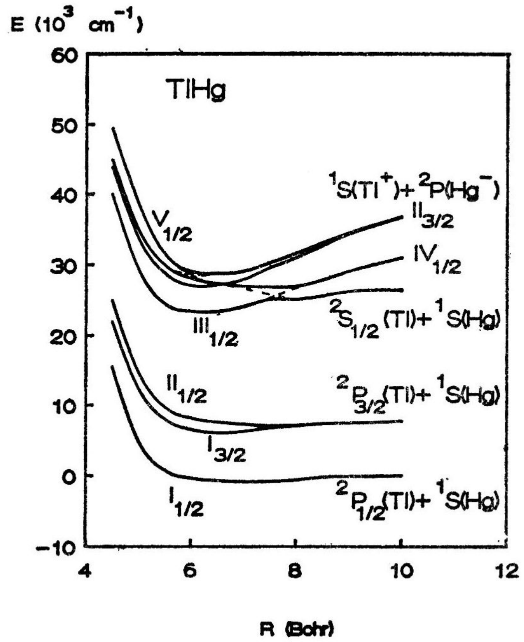

Fig. 5. The ab initio potential energy curves for TlHg *excimer calculated by Calvert-Celestino and Emler (Ref. 12).*

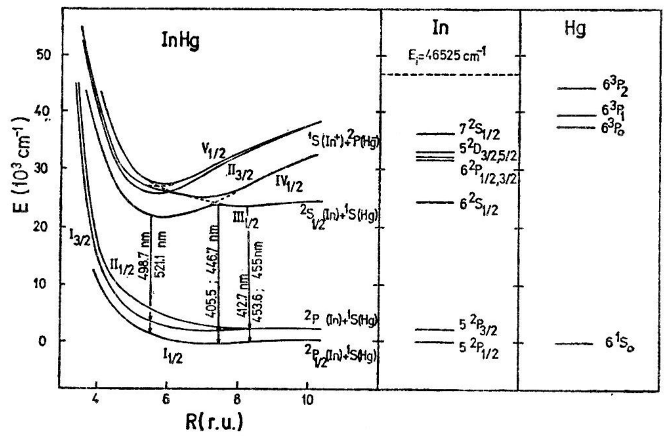

Fig. 6. Qualitative picture of the potential energy curves for InHg *excimer, together with the atomic energy levels of* In *and* Hg.

The depths of potential wells of the potential curves from $^1S_0(In^+) + ^2P_{1/2,3/2}(Hg)$ asymptotic level is taken to be the same as in the TlHg case. According to notation from Ref. 12, the ground $1^2\Pi_{1/2}$, $1^2\Pi_{3/2}$ and $1^2\Sigma_{1/2}$ states are marked $I_{1/2}$ and

$I_{3/2}$, respectively, the first excited $2^2\Sigma_{1/2}$ state is marked as $III_{1/2}$ and ionic $3^2\Sigma_{1/2}$, $2^2\Pi_{1/2}$ and $2^2\Pi_{3/2}$ states like $IV_{1/2}$, $V_{1/2}$ and $II_{3/2}$, respectively. The separation between $I_{1/2}$ and $I_{3/2}$ ground states we make equal to the asymptotic spin-orbit separation for the internuclear distances larger than 6 Bohr radii and only a little bit smaller then asymptotic value for the internuclear distances between 4.5 and 6 Bohr radii. According to this we may conclude that the number of satellite bands around both indium resonance lines will be the same, because those satellite bands origin from the same excited states, $III_{1/2}$ or $IV_{1/2}$, and the shapes of the relevant difference potentials, $III_{1/2}$-$I_{1/2}$ and $III_{1/2}$-$I_{3/2}$, are almost equal and separated by approximately 2000 cm^{-1} (see Fig. 7).

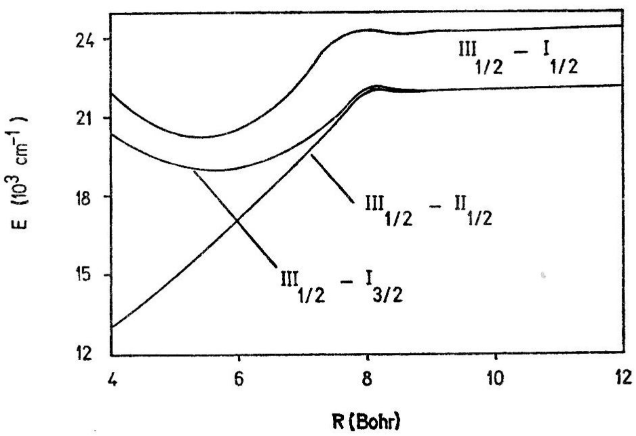

Fig. 7. The sketch of the difference potentials for the $III_{1/2}$-$I_{1/2}$, $III_{1/2}$-$I_{3/2}$ and $III_{1/2}$-$II_{1/2}$, transitions.

The red wings of both indium resonance lines are broadened in the interaction with the mercury atoms, what implies that the $III_{1/2}$-$II_{1/2}$, $III_{1/2}$-$II_{3/2}$ and $III_{1/2}$-$I_{1/2}$ transitions in InHg molecule have attractive difference potential energy curves on the large internuclear distances. From the analogy with the TlHg molecule, we can conclude that the $I_{1/2}$, $I_{3/2}$, $II_{1/2}$ and $III_{1/2}$ states are repulsive at the small and intermediate internuclear distances. The attraction at the large internuclear distances comes from the van der Waals interaction. The ratios between C_6 constants of van der Waals interaction[18] for the ground states are $C_6(I_{3/2}) : C_6(I_{1/2}) : C_6(II_{3/2}) = 1 : 4/3 : 5/3$ and, accordingly, the corresponding difference potentials between the $III_{1/2}$ state and above mentioned ground states have minima at different interatomic separations, with different well depths. Such shallow minima are giving the satellite bands appearing on the near red wings of the indium resonance lines. On the red wing of the indium $6^2S_{1/2}$-$5^2P_{1/2}$ resonance line we observed one satellite at 412.7 nm. This gives the depth of the van der Waals minimum in the $III_{1/2}$-$II_{1/2}$ difference potential of 141 cm^{-1}. On the red wing of indium $6^2S_{1/2}$-$5^2P_{1/2}$ resonance line we observed two satellites. The satellite at 453.6 nm may stem from the $III_{1/2}$-$I_{1/2}$ transition and the corresponding depth of the van der Waals minimum is 122 cm^{-1}. The second satellite at 455 nm possibly comes from the van der Waals minimum of the $III_{1/2}$-$I_{3/2}$ difference potential and the corresponding well depth is 190 cm^{-1}.

After the van der Waals minima, at internuclear separations of about 8 Bohr radii, the difference potentials become repulsive. However, in this region the repulsive covalent $^2\Sigma_{1/2}$ potential from the $6^2S_{1/2}$(In)+6^1S_0(Hg) asymptote makes avoided crossing with strongly attractive ionic $^2\Sigma^+_{1/2}$ potential from the $^1S(In^+) +^2 P(Hg^-)$ asymptote. Therefore, the $III_{1/2}$ potential bends down and forms the maximum in the region of avoided crossing. Accordingly, the satellite bands with peaks at 405.5 nm and 446.7 nm may stem from those maxima in the $III_{1/2}$-$I_{1/2}$ and $III_{1/2}$-$I_{3/2}$, $II_{3/2}$ difference potentials, respectively. The separations of near blue satellites from corresponding resonance line are 282 cm^{-1} and 218 cm^{-1}, what give the estimation for the position of difference potential maximum to the $6^2S_{1/2}$ (In)+6^1S (Hg) asymptote. The separation between those two satellites is 2238 cm^{-1}. This is close to the asymptotic spin-orbit splitting in the ground state. There may be two explanations for not observing the satellite from the $III_{1/2}$-$II_{1/2}$ transition. First is that the maximum in the $III_{1/2}$-$II_{1/2}$ difference potential gives the satellite band peaking too close to the center of the resonance line at 451.1 nm to be clearly resolved. The second is that the relevant two satellite bands overlap.

When the internuclear separation is further decreasing, the $III_{1/2}$ potential exhibits the deep minimum. We propose that the molecular bands in the green spectral region at 498.7 nm and 521.1 nm originate from the minima in the $III_{1/2}$-$I_{1/2}$ and $III_{1/2}$-$I_{3/2}$ difference potentials, respectively. From the analogy with the TlHg potentials we note that, at internuclear separations where the transition is taking place, the $I_{1/2}$ and $I_{3/2}$ states are mostly parallel and the $II_{1/2}$ state is more repulsive. Therefore, the $III_{1/2}$-$II_{1/2}$ state probably has no extreme (see the sketch of the relevant difference potentials in Fig. (7) and the third band does not appear in the spectrum. The green InHg excimer bands are in correspondence with the bands at 459 nm and 655 nm in the spectrum of TlHg[4)].

We observed two additional bands on the blue wings of indium resonance lines at 391.8 nm and 438 nm. Those bands were not observed in the LiF experiment[11)] when the In $6^2S_{1/2}$ state was excited, what gave all the InHg satellites and molecular bands connected with the $III_{1/2}$ upper state. We believe that the bands at 391.8 nm and 438 nm stem from the $IV_{1/2}$ or some other upper state.

The InCd and InZn bands observed in the laser induced fluorescence experiments[11)] look very much like the present InHg spectra. Therefore, the analogous potential curves for InZn and InCd excimers will probably be similar to the presently suggested InHg potentials.

The ionic $^1S(In^+) + 2P(Hg^-)$ asymptotic level lie higher than the 5^2D, 6^2P and 7^2S levels of In atom and there is a possibility that the repulsive potentials from those asymptotic levels make some additional avoided crossings. According to this we can expect to see interesting satellite structures in the ultraviolet spectral region. In the region of the In $5^2D_{3/2,5/2}$-$5^2P_{1/2,3/2}$ and $7^2S_{1/2}$-$5^2P_{1/2,3/2}$ resonance lines we already found several satellite structures, which could be attributed to InHg interaction, but it is hardly possible to say anything about the origin of those structures in advance, without any ab initio calculations of those states.

5. *Conclusion*

In presented spectra from the Inl-Hg-Ar high-pressure discharge lamp we observed all InHg satellite bands reported in the published literature and a few new bands in the blue wings of the indium resonance lines. We also attempted to make the interpretation of the observed spectra, using ab initio potential curves for TlHg and the specific data which characterize the InHg system. The main feature that could explain observed spectrum, which shows analogous structures as the TlHg spectrum, is the fact that the repulsive $\mathrm{III}_{1/2}$ potential from the first excited $6^2\mathrm{S}_{1/2}$ (In)+6^1S (Hg) asymptotic level makes the avoided crossing with the attractive $\mathrm{IV}_{1/2}$ potential from the ionic state coming from $^1\mathrm{S}(\mathrm{In}^+) +^2\mathrm{P}(\mathrm{Hg}^-)$ asymptotic level. This may explain the appearance of satellites and diffuse bands on the blue wings of indium resonance lines. The satellites on the red wings of resonance lines may have the origin from the van der Waals minimum of the $\mathrm{III}_{1/2}$-$\mathrm{I}_{1/2}$, $\mathrm{I}_{3/2}$, $\mathrm{II}_{1/2}$ difference potentials. From the work of S. Chilukuri we learned that spectra of InCd and InZn look similar as presented spectrum of InHg. From those facts we can conclude that the potential curves for those systems also look similar, but without ab initio calculations of the relevant potential curves one cannot make any further progress in the explanation of the InHg, InCd and InZn excimer structures.

In future experiments we intend to make laser induced fluorescence experiments in indium-zinc vapour mixture produced in the heat-pipe oven, excited by pulsed XeCl excimer laser pumped dye laser adjusted to the region around the In resonance line at 410.2 nm. In such arrangement we intend to measure the lifetimes of atomic lines, molecular bands and satellites appearing in the visible and ultraviolet spectrum.

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SATELITSKE VRPCE InHg EKSIMERA

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Mjerili smo spektar InHg visokotlačnog izboja i opazili nekoliko InHg satelita i molekulskih vrpci. Satelitske vrpce oko indijevih rezonantnih linija na 451 nm i 410 nm interpretirane su potencijalnim krivuljama dobivenim iz TlHg ab initio potencijalnih krivulja skaliranjem i prilagođavanjem opaženom InHg spektru.