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SATELLITE BANDS IN THE QUASI-STATIC WINGS OF Tl AND In RESONANCE LINES BROADENED BY Hg

VIŠNJA HENČ–BARTOLIĆ* and GORAN PICHLER

Institute of Physics of the University, P.O.Box 304, 10000 Zagreb, Croatia
**Faculty of Electrical Engineering and Computing, P.O.Box 170, 10000 Zagreb, Croatia*

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Using a high pressure metal–halide discharge lamps, we have measured the spectral positions of the satellite bands in the wings of Tl 535.1 nm and 377.6 nm, and In 451.1 nm and 410.2 nm resonance lines. The satellite bands in the red wings are attributed to the TlHg or InHg excimers, and those appearing in the near blue wings to the Tl_2, and In_2 molecules. Using the Abel inversion procedure, we obtained the relevant spatial temperature and spectral intensities distributions, from which we have concluded that the red satellite bands are due to the bound portion of the TlHg or InHg excited potentials.

1. *Introduction*

Satellite bands in the neighbourhood of the resonance lines usually stem from the extrema in the relevant difference potential curves. Such spectral features are of great help when calculated potential curves are tested by the observed continuous line wing spectrum [1]. Since ab initio calculations are less accurate at long range internuclear separations, it seems that the search for the satellite bands would be useful in testing the quality of potential energy calculations. In this paper we present our search for the satellite bands in the quasi-static wings of the thallium and indium resonance lines emitted from the plasma in the burner of the high pressure metal–halide lamps. We interpret the observed near-wing blue satellite bands in terms of resonance interaction of Tl-Tl or In-In atoms. The red wing satellite bands are attributed to Tl-Hg [2] or In-Hg [3] pair interaction.

We performed Abel inversion of the spectral intensity data in order to determine temperature distribution within the plasma inside the quartz burner. Abel inversion was used to plot the red satellite band peak intensity distribution within the discharge plasma. The results of the measurements show that the red TlHg and red InHg satellite bands are formed by the spectral transitions from the bound excited potential curves.

2. Experimental details

The experimental setup used for the measurement is shown in Fig. 1. The light source is a commercial high-pressure InI-TlI–NaI-Hg lamp. The data on filling of the quartz burner are listed in Table 1. The internal diameter of the burner is 17.2 mm and the distance between the electrodes is 40 mm. The electric discharge was supplied by 50 Hz alternating voltage of 195 V with a ballast inductance connected in series. The voltage and current data are also listed in Table 1. The light from a part of the vertically operated discharge plasma was focused onto the entrance slit of the grating monochromator (SPM-2, grating 1200 grooves/mm, focal length of parabolic mirror 400 mm, slit height 20 mm, resolution 0.1 nm – Carl Zeiss, Jena).

TABLE 1.
Data on the discharge tube filling and electric characteristics.

Thallium iodide	1.6 mg
Indium iodide	0.5 mg
Sodium iodide	21.1 mg
Mercury	52.0 mg
Argon pressure at filling	25 mbar
Tube voltage	195 rms V
Discharge current	3 rms A

In order to perform Abel inversion, this focusing lens was laterally moved by means of the translator stage with a motor drive to obtain $I(x) \rightarrow I(R)$ conversion. We assured by visual observation the cylindrical symmetry of the light source. This type of lateral movement, although simple, introduces an additional small error in the Abel inversion procedure. In front of the entrance slit, a mask with 10 or 14 holes was mounted in order to allow observation of different plasma column segments, extending from the lower to the upper electrode. The number of holes was sufficient to observe lateral intensities of the relevant spectral lines along the plasma axis, which allowed to determine the temperature distribution. At the exit slit, spectrally resolved light was detected by a sensitive photomultiplier (EMI 9524 B) and, after an appropriate amplification, recorded by the strip-chart recorder. The spectral response was determined by using a standard tungsten strip lamp [4].

Fig. 1. The experimental setup.

3. Results

Typical emission spectra of the resonance lines of Tl at 377.6 nm and 535.1 nm, and of In at 410.2 nm and 451.1 nm are shown in Fig. 2, where molecular structures in the extended wings are readily visible. The data correspond to the centre of the plasma segment at 6 mm above the lower electrode ($x = 0$ mm, $y = 6$ mm). The line centres of all resonance lines are self-reversed, but the extended red wings clearly exhibit a few satellite bands. Figure 3 presents the plot of logarithm of the line wing intensity against the logarithm of the wavelength separation from the line centre. This type of presentation helps to find the analytical expression for the line wings. In case of a satellite band in the line wing, a steep exponential fall–off beyond the peak of the satellite band indicates classically forbidden region [5]. Table 2 shows the wavelengths of the observed satellite band peaks of Tl and In resonance lines. These satellite bands have been previously observed by several authors (see e.g. Refs. 6–9), but no detailed explanation of their origin in terms of the relevant difference potential curves was presented. It should be noted that the exact position of the red satellite band peaks differ slightly when comparing different references. This is due to the spectrally extended shape of the red satellite bands, which can slightly change when using different discharge lamps.

The temperature distribution of the arc plasma was estimated by means of the relative intensity measurements with two mercury spectral lines. The Hg lines at 576.9 nm and 546 nm were taken for this simple temperature determination. Abel inversion procedure for both mercury spectral lines was performed in order to obtain the radial distribution of their intensities. From the ratio of radial intensities of mercury lines, we determined the radial temperature distribution for 14 sections at different heights of the arc plasma. Figure 4a shows temperature profile of the discharge between the electrodes for three radial positions.

Fig. 2. The profiles of Tl 377.6 nm *and* 535.1 nm *and* In 410.2 nm *and* 451.1 nm *resonance lines, at* 6 mm *above the lower electrode.*

Fig. 3. Logarithm of the thallium and indium resonance line intensities against the logarithm of the wavelength separations from the corresponding line centres (at 6 mm *above the lower electrode).*

In Fig. 4b, 4c we plotted the relative intensity distribution of the TlHg 538.7 nm red satellite band and InHg 413.4 nm red satellite band along the height of the arc plasma for several radial positions. For these intensity distributions, we performed the usual Abel inversion procedure for the satellite band peaks. The comparison of the temperature profiles in Fig. 4a and satellite intensity profiles in Fig. 4b, 4c clearly indicates that the observed red satellite bands of TlHg and InHg reach larger values at corresponding lower temperatures, suggesting that we are dealing with the bound upper electronic state responsible for the formation of the satellite band both in TlHg and InHg cases. Since Pfaff and Stock [6] obtained almost the same temperature dependence of the 538.7 nm and the 380.5 nm satellite bands of TlHg excimer, we concluded that in our case the same should apply for the red satellite of 377.6 nm or 535.1 nm lines of Tl, and 410.2 nm or 451.1 nm lines of In resonance lines.

Another interesting feature is that the maximum intensity values of the Tl satellite band is closer to the lower electrode than in the case of the corresponding In satellite bands. We believe that this fact is due to almost two times larger atomic mass of thallium atoms as compared to indium atoms.

Fig. 4. a) The temperature distribution along the arc axis $x = 0$ mm *(R0) and at a distance of* $x = 4$ mm *(R4) and* $x = 8$ mm *(R8) from the axis. b) Distribution of the* Tl *red satellite band peak intensity at* 538.7 nm *along the axis* $x = 0$ mm *and at* $x = 4$ mm *(R4) from the axis. c) Distribution of the red satellite band intensity peak at* 413.4 nm *along the axis* $x = 0$ mm *and at* $x = 6$ mm *(R6) and at* $x = 8$ mm *(R8) from the axis of the discharge in the region between lower (LE) and upper (UE) electrodes.*

4. Discussion

4.1. Red satellite bands

It is interesting to note that both In 451.1 nm and Tl 535.1 nm lines have two red satellite bands (see Table 2). This clearly indicates that a very similar energy diagram for TlHg and InHg excimers could describe the observed structures. The weaker resonance lines of In at 410.2 nm and Tl at 377.6 nm have one satellite band in the form of a shoulder. It should be pointed out that the energy separation between the analogous satellite bands of the stronger and weaker spectral lines of Tl(In) is almost equal.

As stated by Celestino and Ermler [2], the potential curve $\mathrm{III}_{1/2}$ from the Tl(7S)+Hg(^{1}S) asymptote should be repulsive all the way towards the smaller internuclear distances. However, at about 8 Bohr radius a_0, instead of crossing according to Ref. 2, there must be an avoided crossing with $\mathrm{IV}_{1/2}$ attractive potential curve, from the Tl(6P)+Hg($^3\mathrm{P}_0$) metastable, as it is shown in Fig. 5. After this first avoided crossing, $\mathrm{IV}_{1/2}$ potential curve has another avoided crossing with $\mathrm{V}_{1/2}$

potential curve at about $6a_0$. Due to the non–adiabatic effect in the region of the avoided crossings from all these potential curves we may expect strong radiative transitions to three lowest potential curves (see arrows at $6a_0$ and $8a_0$ in Fig. 5).

Fig. 5. Qualitative picture of the potential energy curves for TlHg *based on the ab initio calculations in Ref. 2, showing spectral transitions from the potential curves at two avoided crossings.*

In addition to this, a peculiar shape of the resulting difference potential curves, especially from the avoided crossing at $8a_0$, may be responsible for the formation of two red satellite bands of both In 451.1 nm and Tl 535.1 nm resonance lines. These satellite bands may arise from the extrema in $\mathrm{III}_{1/2}$-$\mathrm{I}_{3/2}$ and $\mathrm{III}_{1/2}$-$\mathrm{II}_{1/2}$ difference potential curves. Tl 377.6 nm and In 410.2 nm resonance lines possess just one red satellite since there is just one difference potential curve $\mathrm{III}_{1/2}$-$\mathrm{I}_{1/2}$ whose extremum may produce one red satellite band. It would be very difficult to quantitatively predict the exact shape of these difference potential curves at present level of our knowledge. Our main intention is to suggest a possible qualitative explanation, which should be tested by subsequent theoretical calculations and detailed experiments. Preliminary experimental results by Chilukuri [10] with laser induced fluorescence of InHg, InCd and InZn confirm the existence of two distinct red satellite bands of the 451.1 nm resonance spectral line, which is an additional support to our measurements, and will certainly be of great importance for the future development in this interesting field.

TABLE 2.
Blue and red satellite bands of the Tl *and* In *resonance lines. The second red satellite band of* In 451.1 nm *line has been observed only by using a box–car averager at current reversal instants when the molecular effects are most prominent.*

Element	Spectral line	Red satellite bands		Blue satellite bands	
	λ/nm	λ/nm	$\Delta\lambda$/nm	λ/nm	$\Delta\lambda$/nm
Tl	377.6	380.5	2.9	377.1	0.5
In	410.2	413.3	3.2	409.8	0.4
Tl	535.1	538.7 539.5	3.7 4.5	534.6	0.6
In	451.1	453.3 454.1	2.2 4.0	450.7	0.4

4.2. Blue satellite bands

The origin of the blue satellite bands could be explained by means of the model elaborated in the paper by Pichler and Carlsten [11]. Although they gave the direct interpretation only for the blue satellite at 377.1 nm of the 377.6 nm Tl resonance line, the same explanation could be used in the case of the blue satellite band of Tl resonance line at 535 nm. Of course, the blue satellite band in the case of analogous resonance lines of indium at 410.2 nm and 451.1 nm could be described by the same model. At large interatomic separations between Tl($7S_{1/2}$) and Tl($6P_{1/2,3/2}$) atoms, there exists a strong resonance interaction of the C_3/R^3 form, where + and – sign denotes repulsive and attractive potential curves, respectively. All potential curves stemming from the resonance interaction will be strongly influenced by the relatively strong attractive van der Waals interaction described by the $-C_6/R^6$ interaction law. Thus two of the repulsive potential curves at long range region are at smaller internuclear distances bent down and form two maxima. Only the highest maximum could be observed in the form of a blue satellite band. In the present report, our intention is not to analyse the blue part of the resonance line wings in terms of the resonance interaction C_3 and van der Waals C_6 interaction constants, due to the complex nature of the emission process involving Tl*+Tl or In*+In pairs, as described in Ref. 11. More quantitative approach and detailed analysis would be justified in the case of better defined experimental conditions what we plan in our future investigations.

5. *Conclusion*

The positions of the blue and red satellite bands of Tl and In resonance lines from the s → p transitions have been measured. Blue satellite bands were interpreted as stemming from the long range Tl_2 and In_2 dimers. The red satellite bands were attributed to TlHg and InHg excimers. From the temperature dependence of the red satellite bands (Abel inversion procedure of Ref. 12) we have concluded that the relevant upper potential curve $III_{1/2}$ of TlHg and InHg excimer, is bound in the region of about $8a_0$, where the red satellite bands are formed. This means that the $III_{1/2}$ potential curve has not a barrier at about $8a_0$ as is shown in Fig. 5. Detailed spectral simulations of the red satellite bands will be possible after new and more accurate ab initio calculations of the relevant TlHg and InHg potential curves become available.

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SATELITSKE VRPCE U KVAZISTATIČKIM KRILIMA Tl I In REZONANTNIM LINIJAMA PROŠIRENIH POMOĆU Hg

Upotrebivši visokotlačne metal–halogene izbojne svjetiljke, izmjerili smo spektralne položaje satelitskih vrpca rezonantnih linija Tl 535.1 nm i 377.6 nm, te In 451.1 nm i 410.2 nm. Satelitske vrpce u crvenim krilima pripadaju TlHg ili InHg ekscimerima, a one koje se pojavljuju u plavim krilima pripadaju Tl_2 i In_2 molekulama. Koristeći postupak Abelove inverzije zaključujemo da crvene satelitske vrpce pripadaju vezanom dijelu TlHg ili InHg pobuđenih potencijalnih krivulja.