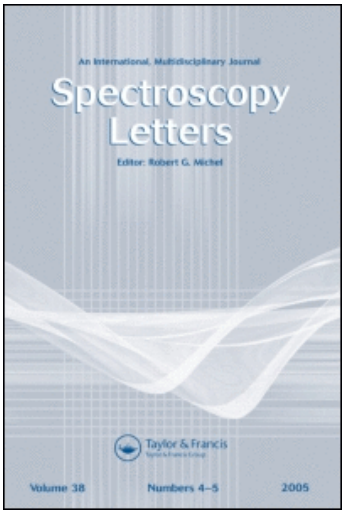

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Emission Cross-Sections of HgI Radicals and Hg Atoms

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EMISSION CROSS–SECTIONS OF HgI RADICALS AND Hg ATOMS

Key words: Mercury halide lasers, emission cross–section, HgI–radicals, Hg–atoms

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ABSTRACT

Emission bands of the (B–X) system of HgI–radicals and mercury atomic lines during transitions from various excited levels to lower levels have been observed due to collisions of N^+ and N_2^+ ions and HgI_2 molecules. By using the integrated intensity of these emissions, HgI_2 vapor density and the charge particle density, emission cross–sections have been measured at different laboratory kinetic energies of the projectile ions.

INTRODUCTION AND BACKGROUND

Laser action has been observed on the ($B\ ^2\Sigma - X\ ^2\Sigma$) transition of the HgX–radicals (X = Cl, Br, I) [1,2] in a discharge pumped mercury halide vapors. The laser power has been observed to increase substantially in the presence of N_2 gas in the discharge medium [2]. This enhancement was attributed to be due to the presence of

metastable $N_2(A)$ in the laser medium. In a mixture of N_2, HgX_2 (X = Cl, Br, I) and energetic electrons, a large number of ionized species such as N_2^+, N^+, HgX_2^+, HgX^+, and Hg^+, etc., are expected to be produced, in addition to the metastable state species such as $N_2(A)$ molecules and Hg ($^{1,3}P$) atoms, etc. The reaction rate constants for the formation of HgX ($B\ ^2\Sigma$)–radicals during the reaction of $N_2(A)$ and HgX_2 molecules have been measured by Setser and co–workers [3]. However, no such measurements are known involving the ionized species mentioned above and the HgX_2 molecules. We started a research program in our laboratory to measure the emission cross–sections of the excited state species produced due to the collisions involving HgX_2 vapors and these ions different laboratory kinetic energies. In a recent paper [4], we reported our results on the chemiluminescence studies involving collisions of N^+ and N_2^+ ions and HgX_2 (X=Cl, Br, I) molecules. Emission cross–sections of some of the excited state species observed during these collisions were reported and a mechanism responsible for the production of the excited states was proposed. However, we were unable to measure accurately the emission cross–sections of the ($B\ ^2\Sigma - X\ ^2\Sigma$) band system of the HgI–radicals and mercury atomic lines at low kinetic energies of the projectile ions. This was mainly due to the difficulties associated with the coating of the window used to observe emitted photons during the ion–molecule reactions inside the collision cell. These difficulties have now been overcome by modifying the vapor generator and the collision cell design so that they can be heated independently. In this letter, we wish to report our results on the emission cross–sections of the strongest bands of the (B–X) system of HgI–radicals and the mercury atomic lines in the laboratory kinetic range 50–900 eV.

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental procedures used to collect data in the present study were similar to those reported earlier [4]. Briefly, the N^+ and N_2^+ ions were produced in a low voltage DC discharge through N_2 gas, mass selected by a Wien velocity filter, passed through the collision cell containing the HgI_2 vapor, collected on a Faraday cup and measured by an

electrometer. The emitted photons due to the ion–molecule reactions inside the collision cell were dispersed by a 0.2m scanning monochromator, detected by a cooled PMT, displayed on a multi channel analyzer and plotted on a digital plotter. In all the studies reported here, the collision cell was always kept at a slightly higher temperature (20 • 5°C) than the vapor generator and no vapor deposition was observed on the window used to observe the emitted photons. With this arrangement, we were able to detect emitted photons at a kinetic energy as low as 50 eV of the projectile ions, which was not possible before [4].

The emission cross–sections of the emitted species, i.e., HgI–radicals and Hg–atoms, were obtained by integrating the intensity of the most intense bands due to the transition ($B\ ^2\Sigma,\ v' = 1 \rightarrow X\ ^2\Sigma,\ v'' = 18,19$, band width $\Delta\lambda = 2$ nm) and the mercury atomic lines from the excited states Hg ($7\ ^3S_1$) and Hg ($6\ ^3D_{3,2}$) terminating to the lower levels of Hg ($6\ ^3P_{0,1,2}$) according to the selection rule $\Delta J = 0, \pm 1$. These intensities were corrected for the detection efficiency of the optical systems and substituted in the expression $\sigma = I_s / I_p\ n\ L$ to determine the cross–sections at different kinetic energies of the charged particles. Here I_p is the number of charged particles involved in the reaction, n is the number density of the HgI_2 molecules and L is the interaction length of the charged particles and the HgI_2 vapors inside the collision cell. The HgI_2 vapor density was calculated by using the thermochemical data reported by Kubaschewski et al [5]. These cross–sections are reported in Tables I and II and plotted in Figures 1 – 3. The accuracy of these cross–sections is expected to be in the range of 20 – 30% and it is mainly because of the uncertainty in the calibration of the optical system and determination of the HgI_2 vapor density, as explained earlier [4]. It is to be noted here that the metastable nitrogen ions may be present in the ion beam but their concentration is expected to be very small under our experimental conditions, as it has been demonstrated by Ottinger and Simons [6] in an identical experimental set–up as ours. Therefore, their effects on the measured cross–sections of the atomic and molecular species should be regarded insignificant. It is also to be noted that due to the presence of metastable Hg–atoms, i.e., $Hg(^3P_0)$ and $Hg(^3P_2)$, the radiation corresponding to the transitions terminating to these levels may be trapped, if the optical thickness is significant. However, based on the oscillator strength [7]

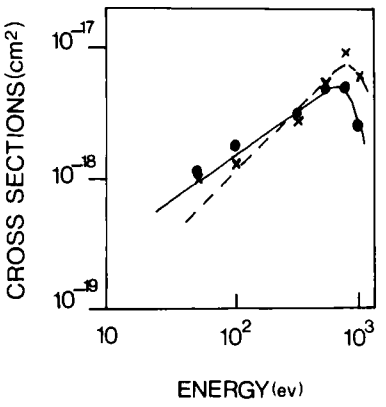

Fig. 1. Measured emission cross–sections of the (B–X) band system of the HgI–radicals during collisions of HgI_2 (T=150 ±5°C) and N^+ and N_2^+ ions at different laboratory kinetic energies.
✘ = $N^+ + HgI_2$, ● = $N_2^+ + HgI_2$.

TABLE I: Emission cross sections of the B–state formation of HgI radicals produced during collisions of HgI_2 and N^+ or N_2^+ ions at different laboratory kinetic energies.

Kinetic Energy (eV)	Cross–section (10^{-18} cm^2)	
	$N^+ + HgI_2$	$N_2^+ + HgI_2$
900	6.35	2.52
700	9.30	5.10
500	5.20	6.30
300	2.80	3.10
100	1.30	1.89
50	1.00	1.10

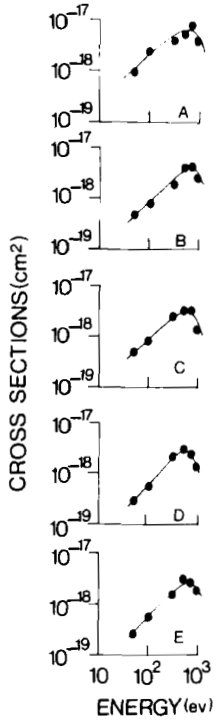

Fig. 2. Measured emission cross–sections of the strongest mercury atomic lines due to N^+ and HgI_2 collisions (T=150 ±5°C) at different laboratory kinetic energies. The notations A, B, C, D, and E have the same meaning as in Table II.

of the transitions involved, the number density of the metastable Hg–atoms ($\simeq 10^8$–10^{10} atoms/cm^3) present in our collision cell and the distance between the ion–molecule reaction zone and viewing window (L$\simeq$ 1 mm), the optical thickness responsible for trapping of the visible radiation(s), is expected to be very small and therefore, self–absorption of these emissions is expected to be insignificant. The measured emission cross–sections based on the total emission intensity should be regarded accurate within the experimental error mentioned above.

TABLE II: Emission cross–sections of the mercury atomic lines observed during collisions of HgI_2 molecules and N^+ or N_2^+ ions at different laboratory kinetic energies.

Kinetic Energy (eV)	Cross–section (10^{-18} cm^2)				
	A	B	C	D	E
900	0.90	0.57	0.20	0.24	0.45[a]
	4.00	2.50	1.30	1.40	1.80
700	3.50	1.20	0.76	0.79	1.60
	8.00	4.10	3.20	2.40	2.50
500	4.60	1.90	0.77	0.73	1.40
	5.30	3.96	3.10	2.96	3.30
300	4.70	1.38	0.51	0.47	0.88
	3.74	1.73	2.40	2.10	1.50
100	3.60	1.00	0.42	0.34	0.54
	2.40	0.79	0.78	0.59	0.54
50	1.00	0.30	0.18	0.16	0.20
	0.90	0.48	0.50	0.30	0.26

[a]The upper and lower entries are due to $N_2^+ + HgI_2$ and $N^+ + HgI_2$ collisions, respectively.

A= Hg ($7\,^3S_1 - 6\,^3P_2$), B= Hg ($7\,^3S_1 - 6\,^3P_1$), C= Hg ($7\,^3S_1 - 6\,^3P_0$), D= Hg ($6\,^3D_3 - 6\,^3P_2$), E = Hg ($6\,^3D_2 - 6\,^3P_1$).

In conclusion, we have measured the emission cross–sections of the (B–X) bands of the HgI–radicals and mercury atomic lines in the laboratory kinetic range 50–900 eV. These data along with our previously reported data on the collisions involving N^+ and N_2^+ ions and $HgCl_2$ and $HgBr_2$ may be helpful in developing a theoretical model to better understand the kinetics of the discharge pumped mercury halide lasers.

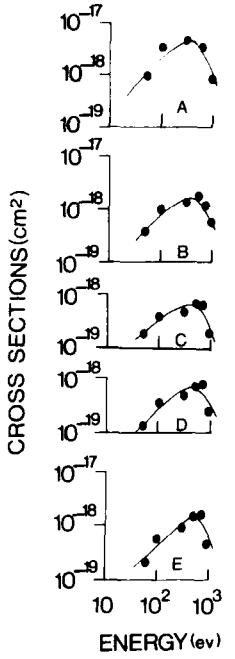

Fig. 3. Measured emission cross–sections of the strongest mercury atomic lines due to N_2^+ and HgI_2 collisions (T=150 • 5°C) at different laboratory kinetic energies. The notations A, B, C, D, and E have the same meaning as in Table II.

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