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Ion-molecule reactions with reference to HgCl (B-X) emission

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1. Introduction.

Laser action involving low vibrational levels of electronically excited state B$^2 \Sigma$ and high vibrational levels of ground state X$^2 \Sigma$ of HgCl radical has been observed in the past [1-10] either by optical or electrical discharge pumping of HgCl$_2$ vapor. The efficiency of this laser has been observed to increase significantly in the presence of N$_2$ gas in the discharge medium [3]. The reaction of discharge produced metastables N$_2$(A) with HgCl$_2$ molecules leading to HgCl(B-state) formation is endothermic by about 0.05 eV and no emission has been observed from the B$\rightarrow$X transition of HgCl[11]. Thus the enhancement of HgCl(B-X) emission cannot be explained on the basis of energy transfer phenomenon alone. In a discharge medium containing electrons, HgCl$_2$ vapor and N$_2$ gas, a variety of processes such as excitation, ionization, dissociation, energy transfer, etc. may take place leading to the formation of HgCl$^+_2$, HgCl$^+$, Hg$^+$, N$_2^+$, N$^+$, etc. besides HgCl(B-state) and N$_2$(A) formation during collisions of electrons, HgCl$_2$ and N$_2$ molecules. The ionization efficiency of N$_2$(A) and other highly excited states of N$_2$ present in the discharge medium, if any, is higher than that of the ground state N$_2$ [12, 13]. Thus collisions of electrons with N$_2$(A) in the discharge medium may lead to the formation of a large number of N$_2^+$ and N$^+$ ions. These ions collide with HgCl$_2$ molecules in the discharge medium and may play an important role in controlling HgCl(B-state) formation at different kinetic energies of the projectile ions. This paper reports measured excitation cross-sections of the most intense band of HgCl(B-X) system at 558 nm corresponding to (v' = 0$\rightarrow$X$^2 \Sigma$, v'' = 22) transition during collisions of HgCl$_2$ with N$_2^+$ /N$^+$ ions at different kinetic energies of the projectiles ions. This information may be useful in theoretical modelling and proper understanding of the discharge kinetics of HgCl(B$\rightarrow$X) laser.

2. Experimental details.

The schematic diagram of the experimental setup used in the present study is shown in figure 1. The ions were produced in a low voltage d.c. discharge by flowing N$_2$ gas through it, extracted from a small hole in the anode and then accelerated to an energy of about 1 keV before entering into a high resolution Wien velocity filter (Resolution : $M/\Delta M = 400$).
The desired mass-selected $N^+$ or $N_2^+$ ions were decelerated by a set of electrostatic lenses directed into a collision cell containing HgCl$_2$ vapor and collected on a Faraday cup connected to an electrometer. The $N^+$ or $N_2^+$ ion currents ranged from 1 $\mu$A to 1 nA depending upon the energies of these ions. The HgCl$_2$ vapor was generated by heating HgCl$_2$ salt kept in a container and located underneath collision cell. The collision cell and the vapor container were both made of copper. The temperature of HgCl$_2$ vapor was measured by a calibrated thermocouple and displayed on a digital thermometer. The collision cell had a slot (2 cm x 2 mm) parallel to the ion beam for monitoring the emitted photons due to ion-molecule reactions inside the collision cell. The Wein velocity filter, collision cell, vapor generator and Faraday cup were all housed in a stainless steel chamber which was pumped down to a pressure of $10^{-7}$ torr. The emitted photons from the collision cell were dispersed by a 0.2 m scanning monochromator having 4 nm/mm dispersion with 20 $\AA$ resolution at 500 nm slit width (Mc-Pherson model 275 monochromator and model 789 scanner) and detected by a cooled (-25 °C) photomultiplier tube (PMT) (EMI GenCom model 9865 QB/5). The output of the PMT was amplified and displayed on a photon counter (EMI GenCom model AD-100 amplifier and C-10 photon counter). The signal from the photon counter was sent to a multichannel analyzer (MCA) (Norland Corp. model 5608) for storing and plotting data.

Fig. 1. — Schematic diagram of the experimental setup used in the present study.

3. Results and discussion.

During collisions of $N^+$ or $N_2^+$ ions with HgCl$_2$ molecules, emission spectrum of the B $\rightarrow$ X transition of HgCl radical and atomic mercury lines at 546, 435.8, 404.6, 365 and 312.6 nm due to transitions $\text{Hg}(7\,^3\text{S}_1 \rightarrow 6\,^3\text{P}_0,1,2)$ and $\text{Hg}(6\,^3\text{D}_{1,2,3} \rightarrow 6\,^3\text{P}_0,1,2)$ according to the electric dipole selection rule $\Delta J = 0, \pm 1$ were observed at different kinetic energies of the projectile ions. At kinetic energies below 100 eV, no atomic or molecular emission was observed. The intensity of the HgCl(B-X) emission bands were observed to be slightly higher with $N^+$ than with $N_2^+$ ions under identical experimental conditions during collision with HgCl$_2$ molecules. Figure 2 shows the emission spectra observed at 700 eV during collisions of $N^+$ and $N_2^+$ ions with HgCl$_2$ vapor at a vapor pressure of about 0.1 torr.

3.1 COLLISION-INDUCED DISSOCIATIVE CHARGE TRANSFER PROCESSES:

$$N^+ / N_2^+ + \text{HgCl}_2 \rightarrow \text{HgCl}^+_2 + N/N_2 + \Delta E (3.03/4.08 \text{ eV}) \quad (1)$$

$$N^+ / N_2^+ + \text{HgCl}_2 \rightarrow \text{HgCl}^+_2 + \text{Cl} + N/N_2 + \Delta E (-1.03/0.02 \text{ eV}) \quad (2)$$

Based on these observations and those of Johnsen and Biondi [15], the following set of reactions may be proposed to explain the observation of HgCl(B-X) emissions bands and atomic mercury lines in the present studies.

![Emission spectra of HgCl(B-X) band system and atomic mercury lines observed during collisions of HgCl$_2$ with N$^+$ /N$_2^+$ ions at 700 eV (laboratory).](image-url)
N⁺ /N₂⁺ + HgCl₂ → Hg⁺ + Cl₂ + N/ N₂ + 
+ ΔE (1.57/2.62 eV) \hspace{1cm} (3)

N⁺ /N₂⁺ + HgCl₂ → HgCl + Cl⁺ + N/ N₂ + 
+ ΔE (1.93/ -0.88 eV) \hspace{1cm} (4)

N⁺ /N₂⁺ + HgCl₂ → Hg + Cl₂⁺ + N/ N₂ + 
+ ΔE (0.51/1.56 eV). \hspace{1cm} (5)

### 3.2 Collision-Induced Dissociative Excitation Processes:

\[ N⁺ /N₂⁺ + HgCl₂ → HgCl₂ (b¹⁺, Σ⁺) + \]
+ N⁺ /N₂⁺ + ΔE (6.88 eV) \hspace{1cm} (6)

\[ N⁺ /N₂⁺ + HgCl → HgCl₂ (B²Σ⁺) + \]
+ Cl + N⁺ /N₂⁺ + ΔE (6.42 eV) \hspace{1cm} (7)

\[ N⁺ /N₂⁺ + HgCl → Hg⁺ + Cl₂ + N⁺ /N₂⁺ + \]
+ ΔE (7.44 eV) \hspace{1cm} (8)

\[ N⁺ /N₂⁺ + HgCl → HgCl₂ (B²Σ⁺) + N⁺ /N₂⁺ + \]
+ ΔE (2.89 eV) \hspace{1cm} (9)

\[ N⁺ /N₂⁺ + HgCl → Hg⁺ + Cl + N⁺ /N₂⁺ + \]
+ ΔE (5.91 eV). \hspace{1cm} (10)

### 3.3 Radiative Decay Processes:

\[ HgCl₂ (b¹⁺, Σ⁺) → HgCl₂ (B²Σ⁺) + Cl \hspace{1cm} (11) \]

\[ HgCl₂ (B²Σ⁺) → HgCl₂ (X²Σ⁺) + hν \hspace{1cm} (12) \]

\[ Hg⁺ → Hg + hν \hspace{1cm} (13) \]

where HgCl₂, HgCl⁺, Hg⁺, Cl⁺, Cl₂⁻ are ground state ionized species; HgCl₂ (b¹⁺, Σ⁺), HgCl₂ (B²Σ⁺) and Hg⁺ (6P states) are electronically excited state species; HgCl₂ (X²Σ⁺) and Hg⁺ are ground state species; and ΔE represents the exothermicity (ΔE > 0) or endothermicity (ΔE < 0) of the reactions. These ΔE values were calculated by using the ground-state ionization potentials of N (14.53 eV), N₂ (15.58 eV), HgCl₂ (11.50 eV), HgCl (12.06 eV), Hg (10.44 eV), Cl₂ (11.50 eV), Cl (12.96 eV); and ground state dissociation energies of HgCl₂ → HgCl + Cl (3.50 eV), HgCl₂ → Hg + Cl₂ (2.52 eV) and HgCl → Hg + Cl (1.04 eV) [16-18].

Johnsen and Biondi [15] have observed HgBr⁺, HgBr⁺ and Hg⁺ with HgBr⁺ and Hg⁺ being the dominant species but there was no indication of Br⁺ and Br⁺ formation during collisions involving N₂⁺ and N₂⁺ ions with HgCl₂ molecules. However, the ionic end products of these reactions are expected to be identical with those observed during collisions of N⁺ with HgBr₂ molecules [15] with no formation of Cl⁺ and Cl₂⁻ ions. In the absence of Cl⁺ and Cl₂⁻ ions, the processes (4) and (5) may be ignored. To explain the emission spectrum of HgCl(B-X) band system and atomic mercury transitions, processes analogous to the collision-induced dissociative charge transfer, i.e., collision-induced dissociative excitation processes such as (9) and (10) may be considered. Because of the low dissociation energies of the ground-state species, collision-induced dissociative processes such as HgCl₂ → HgCl + Cl or HgCl₂ → Hg + Cl₂ or HgCl → Hg + Cl may occur before the excitation processes during collisions of N⁺ /N₂⁺ ions with HgCl₂ molecules. The electronic excitation of HgCl(B²Σ⁺) and Hg⁺ is most likely due to the conversion of kinetic energy of the projectile species into the internal energy of the target species. Such a conversion of kinetic energy into the internal energy of the product species has been observed in many other ion-molecule reactions [19]. On account of low resolution of our monochromator, it was not possible to resolve and identify each band head of the (B-X) transition in the wavelength range of 570-300 nm. However, the most intense band head of the HgCl(B-X) transition at 558 nm corresponding to \( v' = 0 \rightarrow v'' = 22 \) transition was observed in all the scans along with intense atomic mercury lines at various kinetic energies of projectile ions. By using integrated intensities of the most intense band head of HgCl(B²Σ⁺, v' = 0 → X²Σ⁺, v'' = 22) transition at 558 nm, emission cross-sections have been measured in the present studies at different kinetic energies of N⁺ and N₂⁺ ions (See Tab. I). These cross-sections were calculated by the expressions [20]:

\[ σ = I_v / (I_p \cdot n \cdot L) \]

where \( σ \) is the cross-section in \( \text{cm}² \); \( I_v, I_p, n, \) and \( L \) are emitted photons/s, ion current in ion/s, number density of HgCl₂ molecules.

<table>
<thead>
<tr>
<th>Kinetic energy (eV)</th>
<th>N⁺ + HgCl₂ Cross-section ( \times 10^{-18} \text{ cm}² )</th>
<th>N₂⁺ + HgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>1.24</td>
<td>0.85</td>
</tr>
<tr>
<td>900</td>
<td>2.81</td>
<td>1.90</td>
</tr>
<tr>
<td>700</td>
<td>4.57</td>
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<tr>
<td>500</td>
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<td>2.93</td>
</tr>
<tr>
<td>300</td>
<td>1.77</td>
<td>0.96</td>
</tr>
<tr>
<td>100</td>
<td>0.63</td>
<td>0.37</td>
</tr>
</tbody>
</table>
at a particular temperature in molecules/cm$^3$ \cite{21}, and the interaction length (2 cms) of the ion beam with HgCl$_2$ vapor, respectively. The accuracy of these measured cross-sections depends upon the accuracy of measurement of $I$, and $n$. The optical system was calibrated using calibrated lamps traceable to NBS in the wavelength range of 300-800 nm and rechecked by measuring cross-sections of hydrogen lines observed in charge transfer reactions involving He$^+$ and H$_2$ gas at different laboratory kinetic energies. These cross-sections were found to be about 20\% higher than those measured by Isler and Nathan \cite{22}. Thus, measured emission cross-sections of HgCl($B^2 \Sigma^+$) formation should be accurate to within 20-30\%.

4. Conclusion.

Ion-molecule reactions have been studied involving collisions of N$^+$/N$_2^+$ ions with HgCl$_2$ molecules and measured emission cross-sections of the most intense band of the HgCl(B-X) transition at 558 nm at different kinetic energies of the projectile ions. In the present studies collision-induced dissociative excitation processes seem to be the dominant mechanism in producing HgCl(B-X) emission.

Acknowledgments.

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References