Radiative lifetimes of trapped molecular ions: HCl$^+$ and HBr$^+$

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Excitation spectra in the A $^1\Sigma^+$ $\rightarrow$ X $^2\Pi$ system of HCl$^+(0,0)$ and HBr$^+(1,0)$ as well as radiative lifetimes of selectively excited rotational levels in the A $^1\Sigma^+$ electronic states have been measured in a RF ion trap using laser induced fluorescence and time-resolved single-photon counting techniques. Coherent ultraviolet radiation was generated by frequency mixing of a Nd:YAG/dye laser system. For HBr$^+$ the lifetimes of four rotational levels adjacent to the $\nu' = 1$ predissociation limit at $J' = 25/2$ were measured. No statistically significant variation with J was found. The average of these four values (3.89 $\pm$ 0.15 $\mu$s) is therefore reported as the effective lifetime of the $\nu' = 1$ level of A $^1\Sigma^+$ HBr$^+$. For HCl$^+$ the lifetime measurements likewise indicate no strong variation with J. The average lifetime of the $\nu' = 0$ level of the A $^1\Sigma^+$ state of HCl$^+$ is 3.4 $\pm$ 0.4 $\mu$s. Measurements of radiative lifetimes of molecular ions by the RF ion trap technique eliminates the determinate error that results from drift of ions out of the detection volume in conventional experiments.

INTRODUCTION

The experimental determination of radiative lifetimes of excited molecular electronic states is a difficult endeavor, subject to a variety of potentially serious systematic errors. This is particularly the case for long-lived ($\tau \approx 100$ ns) states of charged molecules, because space charge repulsions cause ions to accelerate rapidly out of the sampling volume in conventional lifetime experiments. Consequently, measured radiative lifetimes of such molecular ion states are likely to be too short unless proper care has been taken to account for this effect, as well as the more obvious problems with spectral blending, cascading, and collisional quenching. The seriousness of these effects is exemplified by the large variations in lifetimes for $\nu' = 0$ of the A $^1\Pi$ state of CH$^+$ ($\tau \approx 70$ ns $\leq \tau \leq 630$ ns) determined in several different types of experiments, none of which agree with the theoretical value of 800 ns. Mahan and co-workers$^4$ have described the use of laser induced fluorescence spectroscopy to measure electronic spectra and radiative lifetimes of molecular ions confined in a radio frequency trap. The electrodynamic confinement of ions coupled with state-selective excitation inherent in this technique overcomes the problems that plague lifetime determinations by more conventional (e.g., time-resolved electron impact) methods. For example, their recent determination of the average lifetime of $\nu' = 0$ of the A $^1\Pi$ state of CH$^+$ discussed above yielded the value 815 $\pm$ 25 ns,$^4$ in excellent agreement with the theoretical result.$^2$ In this paper we report the measurement of rotational-state resolved radiative lifetimes for the lowest excited states (A $^2\Sigma^+$) of HCl$^+$ and HBr$^+$ with the ion trap technique, using UV laser sources.

The A $^2\Sigma^+$ $\rightarrow$ X $^2\Pi$ systems of HCl$^+$ and HBr$^+$ have been studied by emission spectroscopy for many years. Norling,$^3$ Barrow and Caunt,$^4$ and Haugh and Bayes$^5$ have done extensive work on HBr$^+$, while Brice and Jenkins,$^6$ Kulp,$^7$ Norling,$^8$ Marsigny and Ferran,$^9$ and Sheasley and Mathews$^{10}$ have carried out definitive studies of HCl$^+$ and its isotopic variants, with subsequent detailed analyses and interpretations by Saenger et al.$^{11}$ Brown and Watson,$^{12}$ and Brown et al.$^{13}$ In these emission experiments it was revealed that the A $^2\Sigma^+$ state of HBr$^+$ is predissociated by a bound state correlating to the ground state products H($^2$S) and Br($^4$P$^o$), with the dissociation limit about 2180 cm$^{-1}$ above $\nu' = 0$ in the A state$^{11}$; similarly, HCl$^+$ is probably predissociated by such a quartet state, crossing near $\nu' = 8$ in the A state.$^{11,12}$ The only measurements of radiative lifetimes of excited states of these ions have been done by Mohlmann, Bhutan, and De Heer$^{14}$ (HCl$^+$) and by Mohlmann and De Heer$^{15}$ (HBr$^+$), using electron impact ionization and delayed coincidence counting techniques to sample incompletely resolved vibronic bands involving $\nu' = 0$--6 (HCl$^+$) and $\nu' = 0$, 1 (HBr$^+$) of the A $^2\Sigma^+$ states. They obtained the results listed in Table I. In these experiments, attempts were made to minimize the systematic errors from space charge and collisional effects by extrapolating the electron beam current and pressure dependences of the lifetimes. Nevertheless, the long (several $\mu$s) lifetimes measured could still contain residual systematic errors, especially for the case of $\nu' = 1$ A $^2\Sigma^+$

<table>
<thead>
<tr>
<th>$\nu'$</th>
<th>a</th>
<th>b</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>4.5 $\pm$ 0.4</td>
<td>2.58 $\pm$ 0.2</td>
</tr>
<tr>
<td>1</td>
<td>4.0 $\pm$ 0.4</td>
<td>2.30 $\pm$ 0.2</td>
</tr>
<tr>
<td>2</td>
<td>2.23 $\pm$ 0.3</td>
<td>2.06 $\pm$ 0.2</td>
</tr>
<tr>
<td>3</td>
<td>1.94 $\pm$ 0.2</td>
<td>1.90 $\pm$ 0.2</td>
</tr>
<tr>
<td>4</td>
<td>1.85 $\pm$ 0.2</td>
<td>1.85 $\pm$ 0.2</td>
</tr>
</tbody>
</table>

Results of Mohlmann and De Heer (Ref. 17) on the HBr$^+$ A $^2\Pi$ state for $\nu' = 0$, 1.

Results of Mohlmann, Bhutan, and De Heer (Ref. 16) on the HCl$^+$ A $^2\Sigma^+$ state for $\nu' = 0$--6.

TABLE I. Radiative lifetimes (in $\mu$s) of the HBr$^+$ and HCl$^+$ A $^2\Sigma^+$ state measured in previous work.

HBr*, where the effect of the predissociation might be to induce a considerable rotational state dependence in the lifetime as well as an overall reduction in the measured average.

In this work we have attempted to determine if indeed there exists a rotational variation in the radiative lifetime of \( v' = 1 \) states of \( A^2 \Sigma^+ \) HBr*. Since the galactic abundance of chlorine is sufficient to warrant consideration of the effects of chlorine chemistry on the dynamics of interstellar clouds, we have carried out similar rotational-state resolved lifetime measurements for \( v' = 0 \) of the \( A^2 \Sigma^+ \) state of HCl* in order to provide an accurate oscillator strength for the \( (0,0) A-X \) transition, which will hopefully be used by astronomers to search for HCl* in diffuse interstellar sources.

**EXPERIMENTAL**

Details of the mass-selective RF ion trap apparatus used in this study have been described previously. We have incorporated a Quanta-Ray YAG-pumped dye laser and wavelength extender system rented from the San Francisco Laser Center into the system to provide the high intensity pulsed ultraviolet radiation required to stimulate the fluorescence from HCl* and HBr*. The ions are created by a 2-5 ms, 10 \( \mu \)A electron pulse impinging on HCl or HBr (Matheson Purity) maintained at \( 10^{-6}-10^{-5} \) Torr inside the three-dimensional trap, operated with 1-5 amu mass resolution. After a delay period of 0.1-1.0 ms, which allows electron impact excited fluorescence to decay and the trapping to stabilize, a 10 ns UV pulse from the laser system passes through the center of the trap and excites the appropriate molecular ion resonance. The total fluorescence intensity is collected at right angles from the trap and, after an appropriate delay period with respect to the laser pulse, is processed with photon counting electronics. The mass-selected ions are then pulsed out of the trap and measured with a particle counter, and the cycle is repeated. To obtain a typical spectral scan fluorescence from \( \sim 500 \) such cycles is accumulated at each 0.1 \( \AA \) wavelength increment. This signal can be normalized to both the total laser intensity and the total density of ions in the trap. In order to measure radiative lifetimes, the laser wavelength is fixed at a given transition and the total fluorescence is monitored with a transient digitizer. The entire experiment is controlled by a PDP 8 computer system. A schematic of the apparatus is presented in Fig. 1.

Laser induced fluorescence spectra were measured for the \((1,0)\) band of the \( A^2 \Sigma^+ - X^2 \Pi \) system of HBr* near 330 nm. In this region, UV radiation of \( \sim 5 \) mJ per pulse was generated by frequency doubling the dye laser output (DCM). Laser scatter was minimized by using a bandpass filter (\( \lambda_{\text{center}} = 385 \) nm, FWHM 100 nm). Figure 2 shows a representative portion of the \( A-X \) system of HBr* with \( \Omega = 3/2 \) in the ground state. The sudden cutoff in the \( R \) branch (indicated by the arrow) at \( J = 25/2 \) is due to predissociation by the \( ^4 \Pi \) state. Radiative lifetime measurements were made for the four rotational levels near the dissociation, as summarized in Table II. Typically 5000 shots were averaged to produce a radiative decay curve with an acceptable statistical scatter.

In Fig. 3 the LIF spectrum of the \((0,0)\) band of the \( A^2 \Sigma^+ - X^2 \Pi_{1/2} \) system of HCl* near 350 nm is shown. The UV radiation was generated by sum frequency mixing of the dye laser output (C500) with the YAG 1.06 \( \mu \)m fundamental. Radiative lifetime measurements were
RESULTS AND DISCUSSION

According to the analysis of Haugh and Bayes, the 'l' state predissociating the $A^3\Sigma^+$ state of HBr$^+$ is bound and crosses the $A^3\Sigma^+$ potential curve at a point below its dissociation limit. In such cases the predissociation has an extremely rapid onset with maximum probability at the dissociation limit of the perturbing state. If this were indeed the case one would expect for hydrides like HCl$^+$ or HBr$^+$ to observe little variation in the radiative lifetime with rotational state as the predissociation limit ($\nu'=1$, $J=25/2$) is approached. The Haugh and Bayes result is substantiated by our state-resolved measurements. As Table II demonstrates, there is no statistically significant variation in the lifetimes of the four rotational levels adjacent to the $\nu'=1$ predissociation limit at $J=25/2$. We therefore report the average of these four values as the effective lifetime of the $\nu'=1$ level of $A^3\Sigma^+$, HBr$^+$ as $3.89 \pm 0.15 \mu s$.

While no predissociation has been directly measured in the lower vibrational levels of the corresponding $A^3\Sigma^+$ state of HCl$^+$, only states up to $\nu'=8$ have been excited in the photoelectron spectrum of HCl, and those with $\nu'=5$ show a marked reduction in intensity in the corresponding peaks in the photoelectron spectrum. Mohlmann, Bhutani, and de Heer$^{18}$ suggest that this is merely a result of small Franck–Condon factors, and not of a predissociation. We again expect only a very slight $J$ variation in the measured radiative lifetime of the $A^3\Sigma^+$ state, resulting from the centrifugal stretching of the HCl$^+$ bond and from the dependence of transition moment on the $R$ centroid. This conclusion is likewise substantiated by our measurements. We report the average lifetime of the $\nu'=0$ level of the $A^3\Sigma^+$ state of HCl$^+$ as $3.4 \pm 0.4 \mu s$.

The averages of our rotational state-resolved measurements are compared with the results of the low resolution measurements of Mohlmann, Bhutani, and de Heer$^{16}$ and Mohlmann and de Heer$^{17}$ in Table I for HCl$^+$ and HBr$^+$, respectively. Clearly the agreement of our results and theirs is excellent for HBr$^+$, but for
TABLE II. Radiative lifetimes of four rotational levels of the \( A^2\Sigma^+ \) state \((v' = 1)\) of HBr\(^+\) determined in the present study.

<table>
<thead>
<tr>
<th>( J )</th>
<th>( \tau, \mu s )</th>
</tr>
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<tbody>
<tr>
<td>( P_1 )</td>
<td>17/2</td>
</tr>
<tr>
<td>( Q_1 )</td>
<td>19/2</td>
</tr>
<tr>
<td>( Q_1 )</td>
<td>21/2</td>
</tr>
<tr>
<td>( Q_1 )</td>
<td>23/2</td>
</tr>
</tbody>
</table>

TABLE III. Radiative lifetimes of five rotational levels of the \( A^2\Sigma^+ \) state \((v' = 0)\) of HCl\(^+\) determined in the present study.

<table>
<thead>
<tr>
<th>( J )</th>
<th>( \tau, \mu s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1 )</td>
<td>9/2</td>
</tr>
<tr>
<td>( Q_2 )</td>
<td>7/2</td>
</tr>
<tr>
<td>( R_2 )</td>
<td>11/2</td>
</tr>
<tr>
<td>( R_2 )</td>
<td>3/2</td>
</tr>
<tr>
<td>( R_2 )</td>
<td>13/2</td>
</tr>
</tbody>
</table>

HCl\(^+\) we obtain a significantly longer lifetime (24%). In their experiments lifetimes were obtained by measuring the time dependence of fluorescence excited by pulsed electron impact ionization. The effects of space charge repulsion were empirically compensated for by measurement of the current dependence of the lifetime and extrapolation to zero; collisional quenching effects were similarly accounted for by extrapolating from the measured pressure dependence. Apparently, this procedure works reasonably well in several cases (CO\(^+\), H\(_2\)S\(^+\), HBr\(^+\),\(^\text{18}\)) but not for HCl\(^+\). One should note that a velocity of \(5 \times 10^6\) cm/s, as one might expect for an ion accelerated by a space charge, will exhibit a loss rate from a 1 cm\(^3\) volume corresponding to a lifetime of 2.0 \(\mu\)s. In the ion trap method excited ions cannot leave the detection volume during their lifetimes, and such problems are of no concern. In the case of HCl\(^+\), the thermal (300 K) velocity of the ion, which would not be compensated for by extrapolation of the electron beam current dependence, corresponds to a 20 \(\mu\)s decay time from a 1 cm\(^3\) volume. The inclusion of this thermal effect in the total lifetime nearly exactly could account for the shorter radiative lifetime observed by Mohlmann, Bhatani, and de Heer.\(^\text{18}\)

Finally, we present the value for the oscillator strength for the \((0,0)\) band of the \( A^2\Sigma^+ \rightarrow X^2\Pi \) system of HCl\(^+\) calculated with our lifetime as 1.08 (± 0.13) \(\times 10^{-4}\). It has been suggested that HCl\(^+\), formed by the exothermic reaction Cl\(^+\) + H\(_2\) = HCl\(^+\) + H, is important in the radiative cooling of diffuse interstellar clouds.\(^\text{18}\) As yet, no chlorine-containing molecule has been detected in interstellar sources. It is hoped that the more reliable value presented here for the A-X oscillator strength will be of use to astronomers in measurements of HCl\(^+\). Given the current interest in halocarbons in the upper atmosphere, this oscillator strength may be likewise useful for deducing accurate number densities of this ion from optical measurements of the atmosphere.

ACKNOWLEDGMENTS

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