

HALF-COLLISION DYNAMICS IN THE PENNING IONIZATION OF HBr

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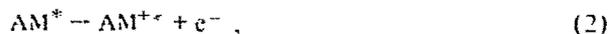
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The ionization of HBr by metastable helium and neon to give $\text{HBr}^+(\text{A } ^2\Sigma^+)$ was studied in crossed molecular beams, by measuring the $\text{A } ^2\Sigma^+ \rightarrow \text{X } ^2\Pi_{3/2, 1/2}$ emission spectrum. Vibrational distributions of $\text{HBr}^+(\text{A})$ were calculated from the spectrum, and compared with those determined by Penning ionization electron spectroscopy. With $\text{Ne}^* + \text{HBr}$ the final-state interaction [$\text{NeHBr}^+(\text{A}) \rightarrow \text{Ne} + \text{HBr}^+(\text{A})$] results in vibrational relaxation of $\text{HBr}^+(\text{A})$, which is accompanied by rotational excitation, indicating that formation of $\text{HBr}^+(\text{A})$ occurs predominantly by a close-range repulsive interaction with Ne^* at the hydrogen end of the molecule.

1. Introduction

When metastable rare-gas atoms (A^*) collide with molecules (M), several reaction channels are possible. If the A^* electronic excitation energy is greater than the M ionization potential, Penning ionization (PI) is usually the dominant process at thermal collision energies. The PI process may be regarded as the formation of an electronically excited collision complex which autoionizes by a Franck-Condon (FC) type of vertical electronic transition, producing a free electron and a positively charged AM^+ ion^{†1}.

Usually the AM^+ is formed in an unstable state, and dissociates into a rare-gas atom and a molecular ion. If sufficient energy is available, excited states of the ion are also formed, usually giving fluorescence. Schematically this can be written as:



Two spectroscopic techniques have been used to

^{†1} For discussion of the theory of PI the reader is referred to ref. [1].

study the Penning process. A large amount of information has been obtained using Penning ionization electron spectroscopy (PIES) which measures the kinetic energy of the electrons emitted from the collision complex (step (2)). The other technique which provides additional information is Penning ionization optical spectroscopy (PIOS). PIOS measures the photons emitted from the excited positive ions (step (4)). Since the electrons are emitted from the collision complex, whereas spontaneous emission from the excited ion occurs after separation of the collision complex into products, these techniques reveal two different but complementary aspects of the ionization process. Therefore, examination of the same reaction by PIES and PIOS provides a unique opportunity to compare the vibrational distribution produced in the reaction complex with that of the separated products. In some cases the influence of the ground-state rare-gas atom may cause the vibrational distributions found in PIOS to be significantly different from those determined from PIES. Such differences can be interpreted in terms of the "half-collision" leading from the reaction complex to products (step (3)).

The first PIOS study from this laboratory [2] reported results on the reaction $\text{Ne}^* + \text{HCl} \rightarrow \text{Ne} + \text{HCl}^+(\text{A } ^2\Sigma^+) + \text{e}^-$. The $\text{HCl}^+(\text{A})$ vibrational-state distribution was studied as a function of reactant collision energy, and found to be determined primarily by FC factors and by the endoergicity of the $\nu' = 2$

level. Recently we reported a PIOS study of $\text{He}^* + \text{HCl}$ ionization [3], in which it was found that the $\text{HCl}^+(\text{A})$ state vibrational distribution is essentially FC, in agreement with the PIES data [4–7]. This agreement showed that for this case the half-collision does not change the initial vibrational distribution formed in the reaction complex. In the present work we have conducted crossed-beam PIOS studies of the systems $\text{He}^* + \text{HBr}$ and $\text{Ne}^* + \text{HBr}$. The 1/0 vibrational branching ratio for $\text{HBr}^+(\text{A } ^2\Sigma^+)$ produced by collision with He^* is not FC, but is essentially the same as that found in PIES [5–7], again showing that the half-collision as the products separate has little effect on the final-state distribution. However, the 1/0 branching ratio of $\text{HBr}^+(\text{A})$ formed by reaction with Ne^* is found to be much lower than that obtained from PIES results [6], showing that with this system the half-collision (step (3)) results in a large change in the final $\text{HBr}^+(\text{A})$ vibrational distribution.

2. Experimental

The crossed molecular beam machine used in the present work was a slightly modified version of an apparatus that has been previously described [2,8]. A rare-gas supersonic nozzle beam emerged from the source chamber into the interaction chamber where it passed through a cold cathode discharge, forming the rare-gas metastables. The metastable beam was then passed through a pair of charged sweeper plates to remove any ions and high Rydberg states that may have been formed in the discharge. The beam then passed through the crossed-beam interaction region, and into a separate detector chamber, where it was detected by electron emission from a gold-plated surface. The nozzle source was capable of operating at temperatures ranging from 80 to 1000 K.

Determination of the metastable velocity distributions was done using standard time-of-flight techniques. Under typical operating conditions of 1000 Torr backing pressure, the intensity of the metastable beam was of the order of 10^{13} metastables/sr s. The cold cathode discharge excitation source produces both $\text{He}(2^1\text{S})$ and $\text{He}(2^3\text{S})$ metastable states. By use of an optical pumping technique, a room-temperature He beam from this type of source was previously found to consist of more than 90% $\text{He}(2^1\text{S})$ [9]. The

ratio of $\text{Ne}(3^3\text{P}_2)$ to $\text{Ne}(3^3\text{P}_0)$ from this source, which has electron energies in the keV range, is not known. The statistical ratio of 5 has been found using electron bombardment in the 80–160 eV energy range [10]. The metastable nozzle beam was crossed by an effusive HBr beam from a multichannel capillary array source at 300 K. Light emission from the interaction zone was viewed perpendicular to the plane of the two beams, and was focused by a quartz lens onto the entrance slit of a McPherson 0.3 m $f/5.3$ scanning monochromator. The light was detected by a cooled (250 K) EMI 9750 photomultiplier tube using photon counting techniques. The monochromator was stepped through the spectrum under computer control, collecting data at each wavelength for a preset time.

One to two hours were required to obtain a typical spectrum with a step size of 1.0 nm and resolution of 1.5 nm. In order to correct for long-term drifts in beam intensities, a second phototube was used to monitor the total light emission. The response function of the optical system was determined over the 200–400 nm spectral range using a standard deuterium lamp. Spectral scans were repeated 5–10 times to check reproducibility and were later summed to improve the signal-to-noise ratio. To test for possible secondary collision effects, the HBr backing pressure was varied between 2 and 10 Torr, giving background pressures of 2×10^{-5} to 1×10^{-4} Torr, and no resulting change in the emission spectrum with He^* was observed.

3. Results and discussion

A portion of the $\text{HBr}^+(\text{A } ^2\Sigma^+ \rightarrow \text{X } ^2\Pi_{3/2, 1/2})$ emission spectrum from ionization by Ne^* is shown in fig. 1. $\text{HBr}^+(\text{A})$ predissociates for ($v' = 1, J' > 12$), and therefore only $v' = 1, 0$ are observed in emission [11, 12]. The $^2\Pi_{3/2} - ^2\Pi_{1/2}$ splitting is 0.30 eV [13], giving sets of widely spaced doublets.

The relative cross sections $\sigma_{v'}$ for formation of $\text{HBr}^+(\text{A}, v')$ by Penning ionization (steps (1)–(3)) can be calculated from the $\text{HBr}^+(\text{A}, v') \rightarrow \text{HBr}^+(\text{X}, v'')$ emission spectrum (step (4)) using the expression

$$\sigma_{v'} = KI_{v', v''} / \tau_{v'} q_{v', v''} v_{v'}^3 R_{v', v''}^2 \quad (5)$$

where K is a constant, $I_{v', v''}$ is the band intensity (cor-

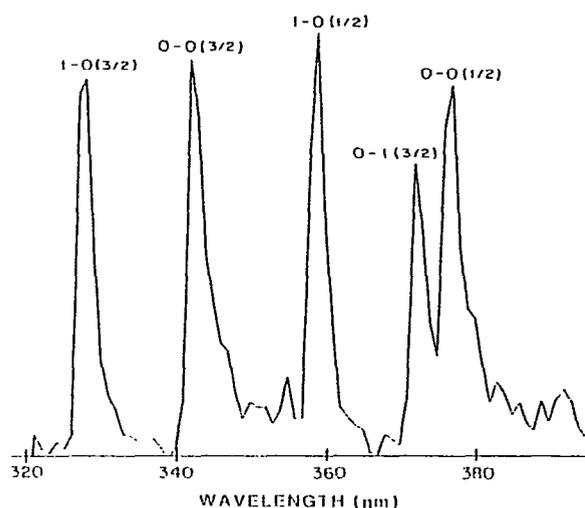


Fig. 1. $\text{HBr}^+(\text{A } 2^2\Sigma^+(v') \rightarrow \text{X } 2^2\Pi_{3/2, 2, 1/2}(v''))$ emission spectrum (corrected for optical system response) from the Penning ionization reaction $\text{Ne}^* + \text{HBr} \rightarrow \text{Ne} + \text{HBr}^+(\text{A}) + e^-$. Peaks are specified by the $v' - v''$ transitions.

rected for optical system response and predissociation). $\tau_{v'}$ is the lifetime of v' , $q_{v'v''}$ is the FC factor, $\nu_{v'v''}$ is the transition frequency, and $R_{v'v''}$ is the average electronic transition moment. For the spectra in this work (e.g. fig. 1) the ($v' = 1, J' > 12$) lines begin at wavelengths well above the wavelengths of the peak maximums, and predissociation did not significantly affect the peak heights at the maximums. The peak heights were therefore used to obtain the relative $I_{v'v''}$. Because of the overlap of the $\Pi_{3/2}(0-1)$

and $\Pi_{1/2}(0-0)$ peaks, only the $\Pi_{3/2}(0-0)$ and $(1-0)$ peaks were used to obtain the $v' 1/0$ branching ratio. Möhlmann and de Heer [14] measured the lifetimes $\tau_0 = 4.5 \mu\text{s}$ and $\tau_1 = 4.0 \mu\text{s}$, using $\text{HBr}^+(\text{A})$ with a rotational temperature of $\approx 300 \text{ K}$. At this temperature only $\approx 1\%$ of the ions have $J' > 12$, so the smaller $v' = 1$ lifetime is not a predissociation effect. Predissociation would not affect the $v' = 1$ radiative lifetime in any case, since the break-off in emission intensity for $J' > 12$ is sharp, showing that predissociation is much faster than emission. In a study of the variation of $R_{v'v''}$, Haugh found that $R_{00} \approx R_{10}$ [15]. Using this result and Haugh's FC factors, the σ_1/σ_0 branching ratios calculated from eq. (5) are 0.675 for $\text{He}^* + \text{HBr}$ and 0.750 for $\text{Ne}^* + \text{HBr}$, with both beams at 300 K giving an average collision energy of $\approx 60 \text{ meV}$. When the metastable beam source was raised to 750 K (giving average collision energies of $\approx 110 \text{ meV}$ for $\text{He}^* + \text{HBr}$ and 150 meV for $\text{Ne}^* + \text{HBr}$) the σ_1/σ_0 ratio remained essentially constant with $\text{He}^* + \text{HBr}$, and increased $\approx 13\%$ with $\text{Ne}^* + \text{HBr}$. The average collision energies were calculated using He^* and Ne^* velocities measured by time-of-flight, and the average HBr thermal velocity at 300 K.

Table 1 compares the relative vibrational populations obtained in this work with those from photoelectron spectroscopy (PES) and PIES. PES and PIES vibrational populations can be expected to be similar only when there is very little perturbation of the HX molecular potential by the approaching metastable. Therefore comparison of PES and PIES results reveals some of the dynamics of the first half of the collision. On the other hand, the PIES results give the $\text{HBr}^+(\text{A})$

Table 1
Relative vibrational populations of $\text{HBr}^+(\text{A } 2^2\Sigma^+)$

Method	Vibrational state relative populations				
	0	1	2	3	4
PES, 500 Å (a)	49	94	100	83	42
He(2^3S_1) PIES (b)	100	78	61	44	29
He(2^1S_0) PIES, this work	100	68			
He(2^3S_1) PIES, flowing afterglow (c)	100	5			
Ne(3^3P_1) PIES (b)	63	95	100	72	45
Ne(3^3P_1) PIES, this work	100	75			

(a) Ref. [7]. (b) Refs. [5,6]. (c) Ref. [16].

vibrational populations after the collision partners have separated again. Therefore, comparison of PIES and PIOS populations reveals some of the dynamics of the second half of the collisions.

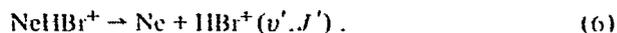
In comparing the PES, PIES, and PIOS results, the major questions are whether the PIES and PIOS populations are the same as the PES populations, and whether or not they differ significantly from each other. We first consider the $\text{He}^* + \text{HBr}$ case. The $\text{HBr}^+(\text{A})$ PIES distribution is strongly shifted toward lower v' compared to the PES distribution. This shift is more pronounced than in the HCl case [4–7], indicating a stronger perturbation of HBr and/or a greater sensitivity of the HBr FC factors to changes in the HBr potentials. As with HCl [3], the PIOS vibrational distribution of $\text{HBr}^+(\text{A})$ is nearly the same under molecular-beam single-collision conditions as the PIES distribution indicating that final-state interactions have little effect on the vibrational distribution. This is consistent with other data indicating a long-range process: the cross section for ionization of HBr by $\text{He}(^1\text{S})$ is 180 \AA^2 at 300 K [17], and the σ_1/σ_0 ratio in the present work was found to be essentially the same at a collision energy of 110 meV as at 60 meV.

It was found previously that the $\text{HCl}^+(\text{A})$ vibrational population from $\text{He}^* + \text{HCl}$ in flowing afterglows [16] disagrees with those found in molecular-beam PIES [4] and PIOS [3] experiments. The most likely explanation [3] for this discrepancy appears to be that at the pressures of 1 Torr or more used in flowing-afterglow experiments there may be quenching processes that preferentially depopulate the higher v' levels, or secondary reactions which preferentially produce $v' = 0$. The same situation is found here for $\text{He}^* + \text{HBr}$ (table 1), with the discrepancy between the flowing-afterglow data and the molecular-beam data even greater than in the $\text{He}^* + \text{HCl}$ case.

As can be seen from table 1, the $\text{Ne}^* + \text{HBr}$ case is quite different from $\text{He}^* + \text{HBr}$. With Ne^*/HBr the $\text{HBr}^+(\text{A})$ v' distribution found in PIES is similar to the PES distribution, indicating that the perturbation of HBr in the incoming half-collision is weak. However the PIOS distribution is strongly shifted toward lower v' , showing that the vibrational distribution is relaxed by the product half-collision. This is accompanied by rotational excitation. By comparing the relative integrated band intensities with the relative peak heights, the fraction of $\text{HBr}^+(\text{A}, v' = 1)$ with

$J' > 12$ (i.e. the fraction of $v' = 1$ which was predissociated) can be calculated. With 300 K beams, giving an average collision energy of 60 meV, this analysis gave $\approx 10\%$ with $J > 12$ from ionization by He^* and 23% from ionization by Ne^* . These percentages correspond to rotational temperatures of 600 and 900 K, and average rotational energies of 52 and 78 meV, respectively. For comparison, ΔE for the $v' 1 \rightarrow 0$ transition is -174 meV.

We now describe a model which qualitatively accounts for the principal observations in this work. The changes in both the vibrational and rotational distributions discussed above indicate a strong interaction between Ne and $\text{HBr}^+(\text{A})$ following electron ejection.



One reason for this and for the difference in the behavior of Ne^*/HBr versus He^*/HBr and He^*/HCl can be found by comparing the PIES peak shifts for the three cases. The only study of all three systems using the same instrument was that by Čermák [6], who found a peak shift of +15 meV for $\text{HBr}^+(\text{A})$ from Ne^*/HBr , -30 meV for $\text{HBr}^+(\text{A})$ from $\text{He}(^2^3\text{S})/\text{HBr}$, -15 meV for $\text{HCl}^+(\text{A})$ from $\text{He}(^2^3\text{S})/\text{HCl}$, and -50 meV for $\text{HCl}^+(\text{A})$ from $\text{He}(^2^1\text{S})/\text{HCl}$. Others [7,18] have also obtained negative shifts for Penning ionization by $\text{He}(^2^3\text{S})$ to give $\text{HBr}^+(\text{A})$ and $\text{HCl}^+(\text{A})$. The peak shifts depend on both the $\text{A}^* + \text{RX}$ and $\text{A} + \text{RX}^+$ potentials, but generally a negative shift indicates an ionization process which takes place in the attractive region of the $\text{A}^* + \text{RX}$ potential, whereas a positive shift indicates ionization occurring primarily in the repulsive region of the $\text{A}^* + \text{RX}$ potential. Therefore the indication is that $\text{Ne}^* + \text{HBr}$ undergoes PI at short range. This results in a short-range $\text{Ne} + \text{HBr}^+(\text{A})$ interaction, which favors vibrational relaxation and rotational excitation during the outgoing half-collision. However, such a repulsive interaction would be expected to be effective only if it occurs at the H end of the $\text{HBr}^+(\text{A})$ ion. Consideration of the HBr molecular orbitals indicates that this should be the preferred geometry for Penning ionization of HBr to give $\text{HBr}^+(\text{A})$. In Penning ionization the electron ejection is caused by a two-electron Auger mechanism which results from overlap of the A^* orbitals with the M orbitals. A given electronic state of the M^+ ion is produced by removal of an electron from the corresponding molecular orbital,

Thus the collisional orientation dependence of Penning ionization is expected to be correlated with the molecular-orbital geometry. In the present case, the formation of $\text{HBr}^+(\text{X}^2\text{II})$ requires the removal of an electron from the lone-pair 2π orbital, which should be favoured for collisions at the bromine end of the molecule. Formation of $\text{HBr}^+(\text{A})$ requires the removal of an electron from the bonding 5σ orbital, which should be favored for collisions at the hydrogen end of the molecule.

A strong $\text{Ne}-\text{HBr}^+(\text{A})$ interaction is also favored by the fact that in the vertical electronic transition $\text{HBr}(\text{X}) \rightarrow \text{HBr}^+(\text{A}) + e^-$, the $\text{HBr}^+(\text{A})$ is formed in a compressed phase of its vibrational motion. This is because the $\text{HBr}(\text{X})$ equilibrium internuclear distance is 1.448 Å and the $\text{HBr}^+(\text{A})$ equilibrium internuclear distance is 1.684 Å [19]. The $\text{HBr}^+(\text{A})$ expands rapidly with respect to the $\text{Ne}-\text{HBr}^+(\text{A})$ motion, and if this occurs when the Ne atom is in close proximity (i.e. close to the turning point of its trajectory), it can be expected to enhance the translational-rovibrational coupling and energy transfer following electron emission.

In conclusion, this work has demonstrated that crossed-beam PIOS studies, when used in conjunction with PIES results, can be a very informative method for studying the dynamics of the Penning process and post-Penning processes. The three systems studied in this work and the previous work [3] correspond to three different cases. In the $\text{He}^* + \text{HCl}$ case, the collisional perturbation of the HCl vibrational distribution in both the incoming and outgoing half-collisions is small. With $\text{He}^* + \text{HBr}$ there is a strong perturbation of the HBr vibrational distribution in the incoming half-collision, but not in the outgoing half-collision. With $\text{Ne}^* + \text{HBr}$ the reverse is true, i.e. a weak perturbation in the entrance channel and a strong perturbation in the exit channel.

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