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The $\text{HCl}+(\text{A}^2\Sigma^+-\text{X}^2\Pi)$ and $\text{HBr}+(\text{A}^2\Sigma^+-\text{X}^2\Pi)$ emissions produced by the $\text{He}(2^3\text{S})$, $\text{Ne}(3^3\text{P}_{0,2})-\text{HCl}$, HBr penning ionization in low-pressure flowing afterglows

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THE $\text{HCl}^+(\text{A}^2\Sigma^+-\text{X}^2\Pi)$ AND $\text{HBr}^+(\text{A}^2\Sigma^+-\text{X}^2\Pi)$ EMISSIONS PRODUCED BY THE $\text{He}(2^3\text{S})$, $\text{Ne}(^3\text{P}_{0,2})$ –HCl, HBr PENNING IONIZATION IN LOW-PRESSURE FLOWING AFTERGLOWS

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Penning ionization of HCl and HBr by $\text{He}(2^3\text{S})$ and $\text{Ne}(^3\text{P}_{0,2})$ metastable atoms leading to $\text{HCl}^+(\text{A}^2\Sigma^+)$ and $\text{HBr}^+(\text{A}^2\Sigma^+)$ has been investigated spectroscopically in low-pressure He and Ne afterglows. The vibrational and rotational distributions of $\text{HCl}^+(\text{A})$ from the $\text{Ne}(^3\text{P}_{0,2})$ –HCl system were invariant over the Ne bath pressure range of 25–800 mTorr. The vibrational distribution was shifted toward lower vibrational levels compared to the Franck–Condon distribution with rotational temperatures of 900, 550, and 350 K for $v' = 0$ –2, respectively. This is explained as a consequence of a short-range final state interaction in the $\text{NeHCl}^+(\text{A}) \rightarrow \text{Ne} + \text{HCl}^+(\text{A})$ process. A significant vibrational relaxation of $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ by collisions with buffer gas atoms has been found for the $\text{He}(2^3\text{S})$ –HCl, HBr and $\text{Ne}(^3\text{P}_{0,2})$ –HBr systems. On the basis of this fact, a discrepancy in the observed vibrational distributions in flowing afterglow and crossed beam experiments is attributed to preferential quenching of the higher vibrational levels by collisions with rare gas atoms in the former high-pressure experiment. In contrast to the significant vibrational relaxation, the produced rotational distributions (350–750 K) of $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ were independent of the rare gas pressure.

1. Introduction

There has been a continuous interest in Penning ionization of HCl and HBr since Richardson and Setser [1] found non-Franck–Condon (FC) vibrational populations in the $\text{A}^2\Sigma^+$ states of HCl^+ and HBr^+ . The processes were studied in a flowing afterglow (FA) using $\text{He}(2^3\text{S})$ Penning ionization optical spectroscopy (PIOS). The observed $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ vibrational distributions had a maximum at $v' = 0$ and decreased rapidly with increasing v' , while the most favorable FC factor for ionization is to the $v' = 1$ level of $\text{HCl}^+(\text{A})$ and the $v' = 2$ level of $\text{HBr}^+(\text{A})$. Because the vibrational distributions in $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ were essentially independent of the

He bath pressure between 0.5 and 4 Torr, they ruled out the possibility of vibrational relaxation by collisions with He atoms during the radiative lifetimes: 1.85–3.82 μs for $\text{HCl}^+(\text{A})$ [2,3] and 3.8–4.5 μs for $\text{HBr}^+(\text{A})$ [3,4]. Richardson and Setser [1] interpreted the significant deviations from the FC distributions due to a resonant excitation transfer process via an avoided surface crossing between the incoming Penning potential and a repulsive Rydberg potential. The possibility of such an excitation transfer process followed by autoionization to low v' levels has been ruled out by Hotop et al. [5] on the basis of a comparative study by Penning ionization electron spectroscopy (PIES) and photoelectron spectroscopy (PES).

Recently, Martin and co-workers [6–8] carried out a series of PIOS studies of the $\text{He}(2^1\text{S})$, $\text{Ne}(^3\text{P}_{0,2})$ –HCl, HBr systems under single collision conditions by using a crossed beam (CB)

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technique. They found essentially FC distributions of $\text{HCl}^+(\text{A})$ for the $\text{He}(2^1\text{S})\text{--HCl}$ and $\text{Ne}(^3\text{P}_{0,2})\text{--HCl}$ systems in agreement with the PIES studies [5,9–12], though the vibrational distribution in the latter system was dependent on the collisional energy. The strong enhancement of $v' = 0$ in $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ observed in the $\text{He}(2^3\text{S})$ FA experiments was attributed to either quenching processes that preferentially depopulate higher v' levels or to the occurrence of secondary reactions which preferentially produce $v' = 0$. In contrast, $\text{HBr}^+(\text{A})$ vibrational distributions for $\text{He}(2^1\text{S})$, $\text{Ne}(^3\text{P}_{0,2})\text{--HBr}$ were found not to follow the predicted FC factors. By combining the PIOS results with the reported PIES ones [9,10], the non-FC $\text{HBr}^+(\text{A})$ distribution for the $\text{He}(2^1\text{S})\text{--HBr}$ reaction was explained by a strong $\text{He}^*\text{--HBr}(\text{X})$ interaction in the incoming half-collisions, while that for the $\text{Ne}(^3\text{P}_{0,2})\text{--HBr}$ system by a strong $\text{Ne--HCl}^+(\text{A})$ interaction in the outgoing half-collisions.

In a more recent FA PIOS study of the $\text{He}(2^3\text{S})$, $\text{Ne}(^3\text{P}_{0,2})\text{--HCl}$ reactions, Yenchu [13] found no bath gas pressure dependence over the range of 0.1–2.5 Torr in either system. The observed $\text{HCl}^+(\text{A})$ vibrational distribution for the $\text{He}(2^3\text{S})\text{--HCl}$ ionization agreed with the earlier work of Richardson and Setser [1], while that for $\text{Ne}(^3\text{P}_{0,2})\text{--HCl}$ was FC like. Yenchu concluded that the non-FC vibrational distribution for the $\text{He}(2^3\text{S})\text{--HCl}$ ionization is an inherent feature of the He^* FA system and that the $\text{HCl}^+(\text{A--X})$ emission results from the combined effects of two active species: $\text{He}(2^3\text{S})$ and another species. He predicted the other active species to be probably thermal He^+ ions by reference with the fast ion-beam study between He^+ and HCl , where $v' = 0$ was preferentially produced [14].

We have recently used a new type of FA apparatus fitted with a very fast pumping system and a microwave discharge source, which operates at rare gas pressures below 0.1 Torr [15]. Here a PIOS study of the $\text{He}(2^3\text{S})$, $\text{Ne}(^3\text{P}_{0,2})\text{--HCl}$, HBr systems using this apparatus is presented. The object of the present work is (i) to determine initial vibrational and rotational distributions of $\text{HCl}^+(\text{A})$ from the $\text{Ne}(^3\text{P}_{0,2})\text{--HCl}$ ionization in the FA system for which no evidence of collisional

relaxation of $\text{HCl}^+(\text{A})$ by Ne atoms is found and (ii) to clarify the origin of the significant discrepancy in the PIOS data between the FA and CB experiments by using lower rare gas pressures than previously [1,13].

2. Experimental

The PIOS study of HCl and HBr has been carried out using both the low-pressure FA apparatus in Basel [15] and the higher-pressure FA apparatus in Kasuga [16]. In the former apparatus, the flow system was evacuated by a 30 000 ℓ/min Roots booster pump. Active species of He or Ne were generated by a fast rare gas flow through a 2450 MHz microwave discharge. Ionic active species were prevented from entering the reaction zone by application of an electrostatic potential to a pair of ion collector grids placed at the exit of the discharge tube. A sample gas was admixed into the discharge flow through concentric nozzles. The rare gas pressure in the reaction zone ranged from 0.04 to 1.0 Torr for He and from 0.018 to 0.1 Torr for Ne, while the sample gas pressure was about 1 mTorr. The reaction flame was observed through a quartz window using an $f/2$ 0.25 m monochromator. The relative intensity response was calibrated by the known intensity distributions in the v'' progressions of the $\text{N}_2(\text{C--B})$, $\text{N}_2^+(\text{B--X})$, $\text{HCl}^+(\text{A--X})$, $\text{HBr}^+(\text{A--X})$ and $\text{CO}^+(\text{A--X})$ emission systems.

The FA apparatus in Kasuga was essentially identical to the Basel apparatus, except for the pumping system (10 000 ℓ/min) and the optical detection system ($f/8.6$ 1 m monochromator). The rare gas pressure was 0.2–1.0 Torr for He and 0.2–0.8 Torr for Ne. The relative sensitivity of the detection system was calibrated by a halogen lamp.

3. Results and discussion

3.1. $\text{He}(2^3\text{S})\text{--HCl}$ system

Fig. 1 shows the emission spectra of $\text{HCl}^+(\text{A--X})$ obtained from the $\text{He}(2^3\text{S})\text{--HCl}$ reaction at three different He gas pressures. The vibra-

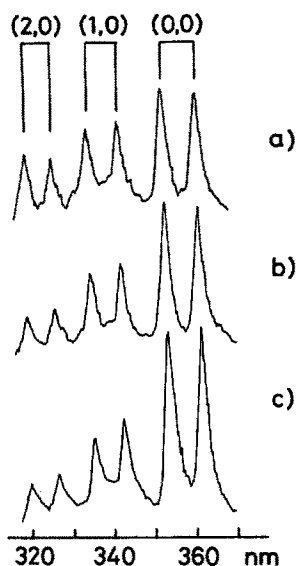


Fig. 1. $\text{HCl}^+(\text{A}^2\Sigma^+-\text{X}^2\Pi)$ emission produced from the $\text{He}(2^3\text{S})$ -HCl Penning ionization at He bath pressures of (a) 0.05, (b) 0.1 and (c) 1.0 Torr. The spectra were obtained with the Basel apparatus.

tional intensity distribution of $\text{HCl}^+(\text{A}-\text{X})$ at 1.0 Torr is similar to that reported by Richardson and Setser [1]. However, it should be noted that the relative band intensities originating from $v' = 1$ and 2 to that from $v' = 0$ increase with decreasing He gas pressure.

The relative vibrational population $N_{v'}$ was determined from the relation

$$N_{v'} \propto I_{v'v''}/q_{v'v''}v_{v'v''}^3 R_e^2(\bar{r}_{v'v''}), \quad (1)$$

where $I_{v'v''}$ is the relative emission intensity observed at the frequency $\nu_{v'v''}$ and $q_{v'v''}$ is RKR Franck-Condon factor calculated by Coxon^{*}. $R_e(\bar{r})$ is the electronic transition moment calculated from the empirical expression $R_e^2(\bar{r}) = C \exp(-2.53\bar{r})$ [18], where \bar{r} is the r -centroid given by Haugh et al. [19] and C is a constant. Since the radiative lifetimes of $\text{HCl}^+(\text{A}; v' = 0(2.58-3.82 \mu\text{s}), v' = 1(2.30 \mu\text{s}))$ [2,3] are shorter than the residence time of these cations in the reaction zone (about 30 μs), estimated from the measurement of linear flow velocity [20], the rela-

* RKR FC factors of $\text{HCl}^+(\text{A}-\text{X})$ calculated by Coxon were obtained from ref. [17].

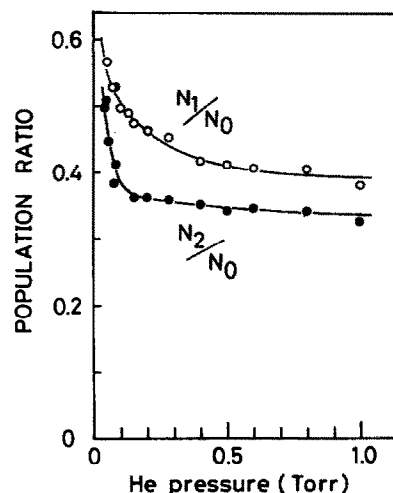


Fig. 2. Dependence of the relative vibrational populations of the $\text{HCl}^+(\text{A})$ state produced from the $\text{He}(2^3\text{S})$ -HCl Penning ionization on the He bath pressure.

tive vibrational populations were not corrected for the variation of $\tau_{v'}$.

In fig. 2 is presented the dependence of the N_1/N_0 and N_2/N_0 ratios on the He gas pressure in the range 0.04–1.0 Torr. Since the variation of the electronic transition moment with \bar{r} was taken into account in this evaluation, the observed N_1/N_0 and N_2/N_0 ratios at 1.0 Torr are smaller than those reported by Richardson and Setser [1] obtained assuming $R_e(\bar{r}) = \text{const}$. The N_1/N_0 and N_2/N_0 ratios increase slowly with decreasing He gas pressure until about 0.2 Torr and rise rapidly below. On the basis of this fact, the significant enhancement of $\text{HCl}^+(\text{A}; v' = 0)$ observed in the FA experiments is attributable to vibrational relaxation by collision with He atoms, which dominantly takes place below He pressure of about 0.2 Torr. This conclusion is inconsistent with the interpretation of Yenchu [13], who attributed it to a contribution of the $\text{He}^+ + \text{HCl}$ charge-transfer (CT) reaction. The absence of He^+ ions at He gas pressures < 0.1 Torr in the Basel FA apparatus and < 0.6 Torr in the Kasuga FA apparatus, has been confirmed by monitoring the $\text{N}_2^+(\text{B}-\text{X})$ emission from $\text{He}^+ + \text{N}_2$ [21,22] and the $\text{CS}^+(\text{B}-\text{A})$ emission from $\text{He}^+ + \text{CS}_2$ [23]. The contribution of the He^+ , $\text{He}_2^+ + \text{HCl}$ CT reactions to the observed $\text{HCl}^+(\text{A})$ emission at the higher He pres-

tures where He^+ and He_2^+ were present was examined by trapping ionic active species. Although the $\text{HCl}^+(\text{A-X})$ emission intensity was reduced by 5% at most by the ion trapping, the relative vibrational distribution was essentially invariant. It can therefore be concluded that the $\text{He}^+ + \text{HCl}$ CT reaction makes no contribution to the preferential population of $\text{HCl}^+(\text{A}: v' = 0)$ in the He afterglow reaction of HCl. The slow rates of the He^+ , $\text{He}_2^+ + \text{HCl}$ CT reactions leading to $\text{HCl}^+(\text{A}: v' = 0)$ are consistent with the prediction from the energy-resonance requirement, which is an important factor in low-energy CT reactions of He^+ and He_2^+ with small molecules [24,25]: the energy defect (ΔE) being 8.3 eV for $\text{He}^+ + \text{HCl}$ and 2.1–4.1 eV for $\text{He}_2^+ + \text{HCl}$.

Richardson and Setser [1] reported that the rotational distribution of $\text{HCl}^+(\text{A}: v' = 0)$ for the $\text{He}(2^3\text{S})\text{-HCl}$ reaction in the FA appeared to have a thermal rotational envelope. On the other hand, de Vries et al. [7] have recently found in their CB PIOS study that the rotational temperatures of $\text{HCl}^+(\text{A})$ produced in the $\text{He}(2^1\text{S})\text{-HCl}$ system varied from 600 K for $v' = 0$ to 300 K for

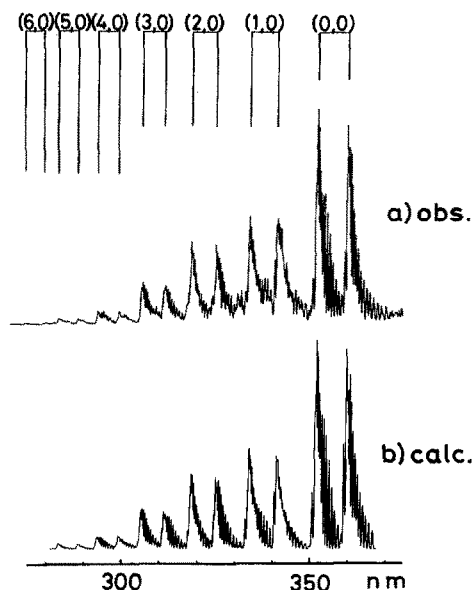


Fig. 3. (a) Observed and (b) simulated spectra of the $\text{HCl}^+(\text{A-X})$ emission produced from the $\text{He}(2^3\text{S})\text{-HCl}$ Penning ionization at a He bath pressure of 0.2 Torr. The spectrum was obtained with the Kasuga apparatus.

$v' = 3$. In fig. 3 is compared a typical emission spectrum of $\text{HCl}^+(\text{A-X})$ measured under better optical resolution with a simulation spectrum obtained assuming a single Boltzmann rotational distribution for each vibronic band. The spectrum was simulated by using the molecular constants given by Huber and Herzberg [26], with RKR FC factors of $\text{HCl}^+(\text{A-X})$ calculated by Coxon [17]. The observed rotational distribution was independent of the He bath gas pressure over the range of 0.04–1.0 Torr, indicating that the rotational relaxation by collisions with He atoms is insignificant. The best fit was obtained with effective rotational temperatures of 550 ± 50 , 600 ± 50 , 550 ± 50 , 600 ± 50 , 750 ± 50 , and 350 ± 50 K, for $v' = 0\text{--}5$, respectively. This finding shows that the $\text{HCl}^+(\text{A})$ ions are more rotationally excited than predicted by Richardson and Setser [1] and no systematic variation of the rotational temperature with v' is apparent.

3.2. $\text{Ne}(^3\text{P}_{0,2})\text{-HCl}$ system

In contrast to the $\text{He}(2^3\text{S})\text{-HCl}$ system, the relative vibrational distribution of $\text{HCl}^+(\text{A})$ from the $\text{Ne}(^3\text{P}_{0,2})\text{-HCl}$ reaction was essentially independent of the Ne pressure over the range 0.025–0.8 Torr as shown in fig. 4. This observation is consistent with the FA PIOS study of

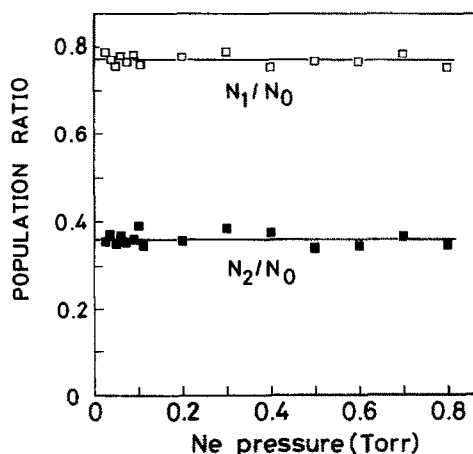


Fig. 4. Dependence of the relative vibrational populations of the $\text{HCl}^+(\text{A})$ state produced from the $\text{Ne}(^3\text{P}_{0,2})\text{-HCl}$ Penning ionization on the Ne bath pressure.

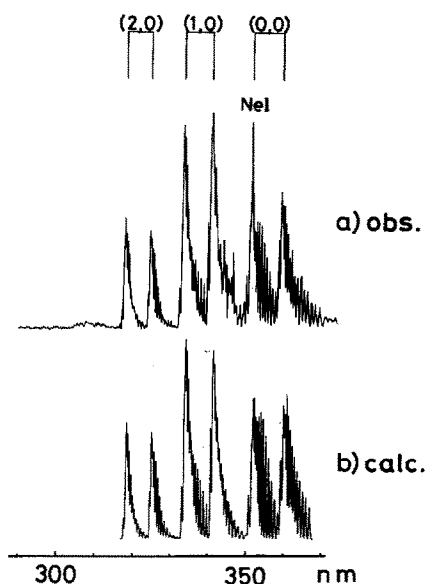


Fig. 5. (a) Observed and (b) simulated spectra of the $\text{HCl}^+(\text{A-X})$ emission produced from the $\text{Ne}(^3\text{P}_{0,2})\text{-HCl}$ Penning ionization at a Ne bath pressure of 0.3 Torr. The spectrum was obtained with the Kasuga apparatus.

Yenchu at the higher Ne pressures of 0.1–2.5 Torr [13]. The rotational distribution was also insensitive to the Ne pressure. As an example, fig. 5a shows the emission spectrum of $\text{HCl}^+(\text{A-X})$ obtained from the $\text{Ne}(^3\text{P}_{0,2})\text{-HCl}$ system at a Ne pressure of 0.3 Torr, where the $v' = 0\text{--}2$ bands are identified. The absence of the $\text{HCl}^+(\text{A-X})$ emission from $v' \geq 3$ follows from the energetics. Whereas the $v' = 0\text{--}2$ levels can be produced by $\text{Ne}(^3\text{P}_0)$ with an energy of 16.716 eV, the formation of $v' = 2$ by $\text{Ne}(^3\text{P}_2)$ with an energy of 16.619 eV is endoergic by 24 meV at 300 K [5]. The relevant features of the present FA spectrum at 300 K (39 meV) in comparison with the CB spectrum of Snyder et al. [6], taken at a higher collision energy (cf. fig. 3 in ref. [6]), are the broadening of the $(0, v'')$ bands due to rotational excitation and the weakness of the $(1, 0)$ and $(2, 0)$ bands relative to the $(0, 0)$ band.

The relative vibrational and rotational distributions of $\text{HCl}^+(\text{A})$ for $v' = 0\text{--}2$ were determined by computer simulation as shown in fig. 5b. The

Table 1

Relative vibrational populations and rotational temperatures of $\text{HCl}^+(\text{A}^2\Sigma^+)$ produced by the $\text{Ne}^* + \text{HCl}$ Penning ionization, and a comparison with other measurements

Method		Vibrational population			Ref.
		N_0	N_1	N_2	
FA PIOS ^{a)}	$\text{Ne}(^3\text{P}_{0,2})$	100 ± 3	77 ± 3	36 ± 3	this work
FA PIOS ^{a)}	$\text{Ne}(^3\text{P}_{0,2})$	$72 (100)^b$	$100 (88)$	$66 (66)$	[13]
CB PIOS ^{c)}	$\text{Ne}(^3\text{P}_{0,2})$	83	100	32	[27]
CB PIOS ^{d)}	$\text{Ne}(^3\text{P}_{0,2})$	56	100	59	[27]
PIES ^{e)}	$\text{Ne}(^3\text{P}_2)$	62	100		^{f)}
PIES ^{e)}	$\text{Ne}(^3\text{P}_0)$	62	100	92	^{g)}
POS ^{h)}	HeI	73	97	100	[28]
POS	HeI	56.9	80.0	100	[18]
POS	NeI	68.1	93.5	100	[18]
PES ^{h)}	HeI	57	100	98	[5,29,30]
FC factors ⁱ⁾		63	100	94	[5,6,31]
rotational temperature (K)					
FA PIOS ^{a)}	$\text{Ne}(^3\text{P}_{0,2})$	900 ± 50	550 ± 50	350 ± 50	this work

^{a)} Flowing afterglow Penning ionization optical spectroscopy, relative collision energy of 39 meV.

^{b)} Values in parentheses are vibrational population calculated from Yenchu's data [13] (see text).

^{c)} Crossed beam–Penning ionization optical spectroscopy, relative collision energy of 48 meV.

^{d)} Relative collision energy of 110 meV.

^{e)} Penning ionization electron spectroscopy, relative collision energy of 55 meV.

^{f)} J. Ganz and H. Hotop, unpublished results quoted in ref. [13].

^{g)} Photoionization optical spectroscopy.

^{h)} Photoelectron spectroscopy.

ⁱ⁾ Relative Franck–Condon factors.

results are given in table 1 along with previous measurements and FC factors for the ionization. The present PIOS data show that populations of lower vibrational levels are strongly enhanced with respect to the FC factors for ionization, and the rotational temperature decreases rapidly with increasing v' from 900 to 350 K. The observation of non-FC distribution is inconsistent with the FA results of Yenchu [13], who has obtained a FC-like distribution. However, this discrepancy is removed by taking account of the fact that measured transmission-corrected, band-integrated photon count rates for $\text{HCl}^+(\text{A}: v'-X: v''=0)$ are incorrectly indicated as vibrational populations in his review [32]. When the vibrational distribution was calculated from his data by using the same procedure as that employed here, a non-FC distribution was also obtained as shown in parentheses in table 1.

Snyder et al. [6] have measured the dependence of the $\text{HCl}^+(\text{A})$ vibrational distribution in the $\text{Ne}(^3\text{P}_{0,2})\text{-HCl}$ reaction in the collision energy range 48–110 meV and found that the N_1/N_0 ratio appears to be approaching the FC ratio at the lowest collision energy, but rises well above

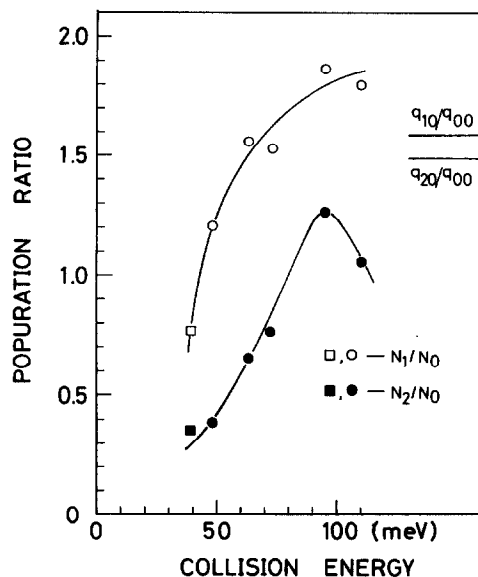


Fig. 6. Dependence of the relative vibrational populations of the $\text{HCl}^+(\text{A-X})$ emission produced from the $\text{Ne}(^3\text{P}_{0,2})\text{-HCl}$ Penning ionization on the collision energy. (\square, \bullet): this work, (\circ, \bullet): ref. [27].

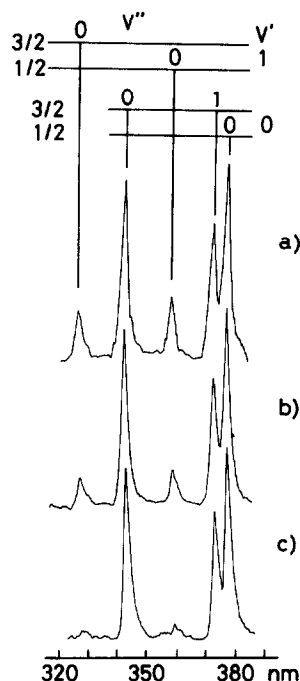
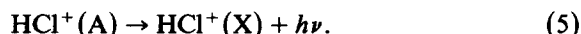
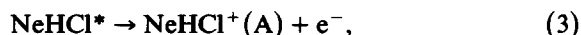
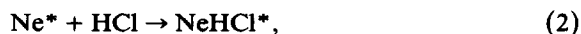


Fig. 7. $\text{HBr}^+(\text{A}^2\Sigma^+-\text{X}^2\Pi)$ emission produced from the $\text{He}(2^3\text{S})\text{-HBr}$ Penning ionization at He bath pressures of (a) 0.05, (b) 0.1 and (c) 1.0 Torr. The spectra were obtained with the Basel apparatus.

the FC ratio at higher energies. However, according to their revised data [27], the N_1/N_0 ratio at low energies is smaller than the FC ratio, but still rises above it at high energies, though not as much. The present data at 39 meV are compared with the revised CB data in fig. 6. Fig. 6 includes the FC ratios [5,6,31]. A smooth extrapolation of the CB data for the N_1/N_0 ratio to lower collision energy fits well the present FA result.

The $\text{Ne}(^3\text{P}_{0,2})\text{-HCl}$ Penning ionization leading to $\text{HCl}^+(\text{A})$ is supposed to proceed through the following processes:



The non-FC vibrational distribution, accompanied by a significant rotational excitation, reveals that the target HCl molecules are perturbed by an

interaction with the $\text{Ne}(^3\text{P}_{0,2})$ atoms either in the incoming half collision (process (3)) or in the outgoing one (process (4)). Since the PIES spectrum of $\text{Ne}(^3\text{P}_{0,2})$ –HCl has not been measured at thermal energy, it is difficult to evaluate directly the relative importance of the two processes. However, the total quenching cross section of HCl by $\text{Ne}(^3\text{P}_{0,2})$ is relatively small (24 \AA^2) [33] as in the case for the $\text{Ne}(^3\text{P}_{0,2})$ –HBr system [8] and the Penning ionization branching ratio leading to HCl^+ is 0.52 ± 0.10 [34]. By analogy with the $\text{Ne}(^3\text{P}_{0,2})$ –HBr system, it is reasonable to assume that a short-range Ne – $\text{HCl}^+(\text{A})$ repulsive interaction in the outgoing half-collision is more important. The short-range Ne – $\text{HCl}^+(\text{A})$ interaction enhances the translation–rovibronic coupling resulting in vibrational relaxation and rotational excitation of low vibrational levels during the traverse of the outgoing channel. Such a final state interaction becomes less efficient at higher energies with decreasing interaction time, providing a FC-like vibrational distribution without rotational excitation.

In view of the present observations and the CB studies [6–8], the $\text{He}(2^1\text{S})$ –HCl, HBr Penning ionization seems to take place at a long-range attractive part of the interaction potential, while the $\text{Ne}(^3\text{P}_{0,2})$ –HCl, HBr one occurs at a short-range repulsive part of it at low energies. From a comparative PIES and PES studies on a number of molecules, Čermák and Yenchu [35] and Ohno et al. [36] suggested that the probability of Penning ionization depends on the spatial electron distribution of an individual molecular orbital and on the degree of its overlap with the unfilled hole–shell orbital of metastable atoms (i.e. $1s$ shell for He^* and $2p$ shell for Ne^*). The $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ ions are produced by a loss of the $3p\sigma$ and $4p\sigma$ electrons from the neutral molecules, respectively. A long-range interaction for the $\text{He}(2^1\text{S})$ –HCl, HBr systems may be due to a larger overlap of the bonding $3p\sigma$ or $4p\sigma$ orbital with the centrosymmetric s -electron cloud compared with the directionally concentrated p -electron cloud.

As to the N_2/N_0 ratio of $\text{HCl}^+(\text{A})$ for the $\text{Ne}(^3\text{P}_{0,2})$ –HCl reaction, Snyder et al. [6] originally found that it rapidly increases with increasing collisional energy, and rises above the FC ratio

at higher energies by about 30%. However, their revised data [27] demonstrate that the N_2/N_0 ratio does not reach the FC ratio at higher energies as shown in fig. 6. The rapid increase in the N_2/N_0 ratio with increasing energy was attributed primarily to the increasing excitation function of $v' = 2$ above the 25 meV threshold for the $\text{Ne}(^3\text{P}_2)$ metastable atoms, the relative concentration of which was estimated to be close to the statistical ratio of 5 under electron-impact excitation at 80–160 eV. Provided that the excitation function falls off at 25 meV, it is expected that the Penning ionization cross section of the $\text{Ne}(^3\text{P}_0)$ –HCl system to give $v' = 2$ is small or that the $\text{Ne}(^3\text{P}_2)/\text{Ne}(^3\text{P}_0)$ ratio is much larger than the statistical ratio. Our N_2/N_0 value at 39 meV is comparable with that of Snyder et al. [6] determined at the lowest energy of 48 meV. Although we did not measure the ratio of the two spin–orbit states, the $\text{Ne}(^3\text{P}_2)/\text{Ne}(^3\text{P}_0)$ ratio is probably larger than the statistical value because of a faster decay of $\text{Ne}(^3\text{P}_0)$ than $\text{Ne}(^3\text{P}_2)$ in the discharge flow [37]. The ratio may be close to 8 as observed by Brom et al. [33] in a similar discharge flow system. The lack of bath gas pressure dependence of the N_2/N_0 value indicates that the $\text{Ne}(^3\text{P}_2)/\text{Ne}(^3\text{P}_0)$ ratio is not significantly different over the Ne pressure range of 0.025–0.8 Torr. Since the N_2/N_0 ratio must depend on the $\text{Ne}(^3\text{P}_2)/\text{Ne}(^3\text{P}_0)$ ratio, a detailed comparison of our FA data at 39 meV with the CB data at higher energies is difficult. However, a reasonable agreement of our N_2/N_0 ratio with the CB value at 48 meV shows that the contribution of $\text{Ne}(^3\text{P}_0)$ metastables is relatively small in both experiments. Although Snyder et al. [6] attributed the large deviation of the N_2/N_0 value from the FC ratio at low energies to the endoergicity of the reaction giving $v' = 2$, a similar tendency of the excitation functions for the N_1/N_0 and N_2/N_0 ratios indicates that the final state interaction may be also important for the non-FC N_2/N_0 ratio at thermal energy.

3.3. $\text{He}(2^3\text{S})$, $\text{Ne}(^3\text{P}_{0,2})$ –HBr systems

When the emission spectrum of $\text{HBr}^+(\text{A-X})$ from the $\text{He}(2^3\text{S})$ –HBr system was measured at various He bath gas pressures, a significant change

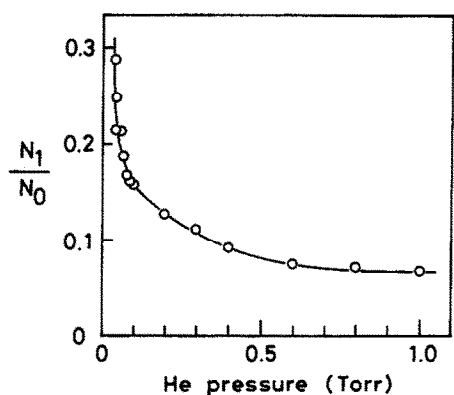


Fig. 8. Dependence of the N_1/N_0 ratio of the $\text{HBr}^+(\text{A-X})$ emission produced from the $\text{He}(2^3\text{S})$ -HBr Penning ionization on the He bath pressure.

in the relative intensity was found between the $(0, v'')$ and $(1, 0)$ bands as shown in fig. 7. The relative vibrational population, N_1/N_0 , has been estimated by the analytical method described previously [38]. Fig. 8 shows the N_1/N_0 ratio as a function of He gas pressure over the range of 0.04–1.0 Torr. The N_1/N_0 ratio rapidly increases below about 0.1 Torr. The variation of the N_1/N_0 ratio at a low He pressure is so drastic that the nascent vibrational distribution cannot be estimated by extrapolating the data to zero He pressure. Tyndall et al. [8] explained the discrepancy of the $\text{HBr}^+(\text{A})$ vibrational population between their CB result and the FA result of Richardson and Setser [1] to either quenching processes or to secondary reactions which preferentially populate $v' = 0$. The present result leads us to conclude that the former process is dominant.

The rotational temperatures of $v' = 0$ and 1 for $\text{HBr}^+(\text{A})$ from the $\text{He}(2^3\text{S})$ -HBr reaction, which were insensitive to the He bath pressure, were estimated to be 400 ± 50 and 350 ± 50 K, respectively, by comparing the calculated spectrum with the observed one (fig. 9). The observed rotational temperature for $v' = 0$ is slightly higher than 300 K as deduced by Richardson and Setser [1], while that for $v' = 1$ is lower than the $\text{He}(2^1\text{S})$ -CB result of 600 K at 60 meV [8].

In contrast to the $\text{Ne}(^3\text{P}_{0,2})$ -HCl system, the N_1/N_0 ratio of the $\text{Ne}(^3\text{P}_{0,2})$ -HBr system increased from 0.043 to 0.51 with decreasing the Ne

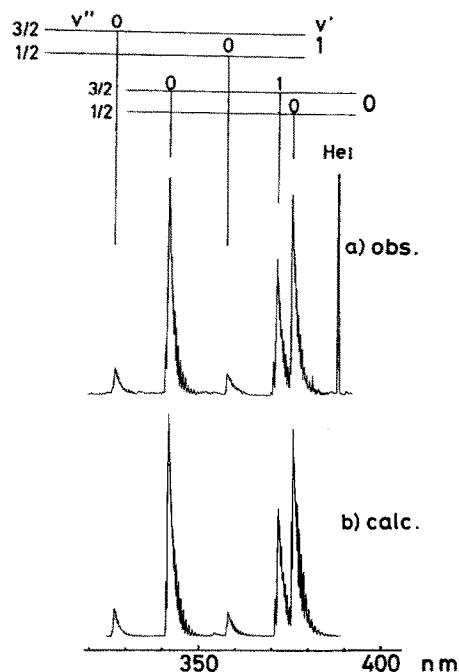


Fig. 9. (a) Observed and (b) simulated spectra of the $\text{HBr}^+(\text{A-X})$ emission produced from the $\text{He}(2^3\text{S})$ -HBr Penning ionization at a He bath pressure of 0.2 Torr. The spectrum was obtained with the Kasuga apparatus.

pressure from 400 to 18 mTorr. On the other hand, the rotational distributions for $v' = 0$ and 1 were essentially invariant under the same pressure range. The spectral simulation yielded the rotational temperatures of 500 ± 50 K for $v' = 0$ and 400 ± 50 K for $v' = 1$. The observed rotational temperature for $v' = 1$ is lower than the CB result of 900 K at 60 meV [8].

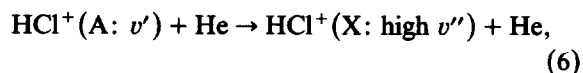
3.4. Vibrational relaxation of $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$

The present work demonstrates that the discrepancy of the PIOS vibrational distributions of $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ in the He^* -HCl, HBr systems between CB and FA experiments are attributable to fast collisional quenching processes by buffer rare gas atoms, which are significant below the rare gas pressure of about 0.2 Torr. Another important finding is that the quenching rate strongly depends on the reaction system. The depopulation rates for vibrationally excited states

relative to that for the vibrational ground state are large for the $\text{HCl}^+(\text{A})/\text{He}$, $\text{HBr}^+(\text{A})/\text{He}$, and $\text{HBr}^+(\text{A})/\text{Ne}$ systems relative to the $\text{HCl}^+(\text{A})/\text{Ne}$ and $\text{HBr}^+(\text{A})/\text{Ar}$ systems; no significant vibrational relaxation of $\text{HBr}^+(\text{A})$ by collisions with Ar atoms has been observed in the study of the Ar^+-HBr CT reaction [38]. The facts that the vibrational deactivation takes place significantly at a rare gas pressure of about 0.1 Torr for $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ in the He buffer, and the absence of vibrational relaxation at about 1 Torr for $\text{HCl}^+(\text{A})$ in the Ne buffer and for $\text{HBr}^+(\text{A})$ in the Ar buffer, suggest that the relaxation rates for the former cases are of the same order or larger than as gas kinetic collisions, while for the latter cases they are smaller by at least two orders of magnitude.

A similar vibrational relaxation by collisions with rare gas atoms in the discharge flow has been found for the $\text{CO}^+(\text{A})/\text{He}$, $\text{N}_2^+(\text{A})/\text{He}$, and $\text{CN}(\text{A})/\text{Ar}$ systems [39–42]. It was found that vibrationally excited levels relax via intermediate, highly excited, vibrational levels of the ground $\text{X}^2\Sigma_g^+$ state by collision induced energy-transfer processes based on laser-induced fluorescence studies. The potential energy curves of $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ overlap with the ground ionic states as in the cases of the A and X states of CO^+ , N_2^+ , and CN. However, the overlapping is less significant, because the emitting $\text{HCl}^+(\text{A}: v' = 0-6)$ and $\text{HBr}^+(\text{A}: v' = 0, 1)$ levels are located close to the dissociation limit of the X states [18,43]. Therefore, the dominant quenching pathways of $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$ may be different. Actually, there are some critical differences in the quenching processes between the hydrogen halide cations and $\text{CO}^+(\text{A})$, $\text{N}_2^+(\text{A})$, and $\text{CN}(\text{A})$. Firstly, in the latter cases, rotational relaxation by collisions with rare gas atoms is so fast that only thermal distributions can be obtained under similar experimental conditions; the slow rotational relaxation of the hydrogen halide cations is probably due to the larger rotational energy intervals of $\text{HCl}^+(\text{A}: B_e = 7.51 \text{ cm}^{-1})$ and $\text{HBr}^+(\text{A}: B_e = 5.97 \text{ cm}^{-1})$ than those of $\text{CO}^+(\text{A}: B_e = 1.59 \text{ cm}^{-1})$, $\text{N}_2^+(\text{A}: B_e = 1.74 \text{ cm}^{-1})$, and $\text{CN}(\text{A}: B_e =$

$1.72 \text{ cm}^{-1})$ [26]. Secondly, it seems that the vibrational relaxation rates of $\text{CO}^+(\text{A})$, $\text{N}_2^+(\text{A})$, and $\text{CN}(\text{A})$ are insensitive to the buffer rare gas in comparison with $\text{HCl}^+(\text{A})$ and $\text{HBr}^+(\text{A})$. These observations lead us to predict that an important relaxation process is not the collisional relaxation from upper emitting vibrational levels to lower ones but collisional transfer from emitting vibrational levels to non-emitting levels such as the process



or to non-emitting species such as the process



If rate constants of these quenching processes increase with increasing v' and they are nearly constant within rotational levels of a vibrational level, the present specific relaxation processes are explainable. In a recent FA mass spectroscopic study on the $\text{He}(2^3\text{S})-\text{HCl}$ system [33], HeH^+ ions have not been observed, although Hotop et al. [5] had detected a small amount of HeH^+ ions ($\text{HCl}^+ : \text{HeH}^+ \approx 100:4$) in a low-pressure beam experiment. Therefore, the possibility of existence of fast quenching processes of HeH^+ ions in FA experiments is not ruled out. In order to clarify special relaxation dynamics of hydrogen halide cations by collisions with rare gas atoms, further investigations such as time resolved laser-induced fluorescence measurements are required.

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