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Branching and rate coefficients of the $HBr^+ + HBr$ reaction through the isotope-resolved REMPI technique

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Abstract

The charge-, atom- and proton-transfer channels of the $HBr^+ + HBr$ reaction have been studied at low temperature in an HBr + Ar free jet. Exploring ordinary HBr gas with the natural $H^{79}Br + H^{81}Br$ (1:1) isotope abundance, the $H^{79}Br^+$ and $H^{81}Br^+$ ions in specific spin-orbit and vibrational states were prepared by resonance multiphoton ionisation in an isotope-selective manner that gave the opportunity to analyse reaction branching ratios and mechanisms.

Keywords: Isotope-selective ionisation; Mass spectrometry; Ion-molecule reaction; Reaction branching; Rate coefficient

1. Introduction

In this communication we demonstrate a new opportunity of mass spectrometry (MS) in combination with Br isotope-selected resonance-enhanced multiphoton ionisation (REMPI) for the study of branching and separate channel kinetics. The technique has been applied to study the ion-molecule reaction $HBr^+ + HBr'$ including charge transfer (CT, that yields the same products $\rightarrow HBr + HBr'^+$), H-atom transfer ($HT \rightarrow H_2Br^+ + Br'$) and proton transfer ($PT \rightarrow Br + H_2Br'^+$) channels. Some of these channels were studied previously under thermal conditions ($T \approx 300\,K$) [1–3] and in a free jet flow ($T \approx 10\,K$) [4–6]. Xie and Zare [1] investigated the state-selected CT reaction DBr^+ ($^2\Pi_i$, v^+) + HBr → $HBr^+ + DBr$ and found the rate coefficient $k_{CT} = 4.1$, 1.4, 3.8, 2.3 [$\times 10^{-10}\,cm^3/s$] for the ($i = 3/2$, $v^+ = 0$), (3/2, 1), (1/2, 0), (1/2, 1) ionic states. The rate coefficients of CT and PT channels of the reaction $HBr^+ + DBr$ were measured by Viggiano et al. [2] in a flowing afterglow as $k_{CT} = 2.5$ and $k_{PT} = 2.8$ [$\times 10^{-10}\,cm^3/s$], respectively. Two experimental techniques were explored by Green et al. [3] to study the reaction of HBr^+ ions with HBr and DBr. Preparing the reagent ion by REMPI and monitoring the disappearance of this ion by laser-induced fluorescence (LIF) gave the combined rate coefficient for the PT and HT processes $k_{PT+HT}\{HBr^+ + HBr\} = 6.7 \times 10^{-10}\,cm^3/s$. At the same time, their selected ion flow tube study of the $HBr^+ + HBr(DBr)$ reactions led to total reaction rate coefficients of 6.9 and 5.8 [$\times 10^{-10}\,cm^3/s$] for HBr and DBr, respectively, and was found to have branching percentages of 46(50), 32(28) and 21(21)% for the individual CT, PT, and H(D)T channels. Combination of REMPI and mass spectrometry in a free jet flow gave the low temperature rate coefficients [4–6]: $k_{PT+HT}\{HBr^+ + HBr\} = k_{D+T+DT}\{DBr^+ + DBr\} = 1.3 \times 10^{-9}\,cm^3/s$; $k_{PT+DT}\{HBr^+ + DBr\} = k_{D+T+HT}\{DBr^+ + HBr\} = 1.7 \times 10^{-9}\,cm^3/s$; $k_{CT}\{HBr^+ + DBr\} = k_{CT}\{DBr^+ + HBr\} = 0.6 \times 10^{-9}\,cm^3/s$.

Presently, we report a new isotope selective opportunity of the combined REMPI–MS technique for the study of the separate CT, PT and HT channels of the $HBr^+ + HBr$ reaction using an ordinary (natural, ≈1:1) isotope mixture of $H^{79}Br$ and $H^{81}Br$. Isotope-selected REMPI of $H^{79}Br$ and $H^{81}Br$ was used to study the CT kinetics (with similar reactants and

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products, HBr and HBr^+) as well as to separate the PT and HT channels producing the same H_2Br^+ ions.

2. Experimental

Branching of the $HBr^+ + HBr$ reaction was studied via collisions in a free jet flow reactor [7] using (2 + 1) REMPI to prepare a specific spin-orbit and vibrational state of the HBr^+ ($^2\Pi_i$, v^+) ions and employing time-of-flight mass-spectrometry for analysis of ionic products. A pulsed axisymmetric nozzle (general valve) with orifice diameter of 0.4 mm was used as a source of the Ar + HBr(<2%) free jet with the stagnation temperature $T_0 = 295$ K and the stagnation pressure in the range from 60 to 500 Torr. The REMPI laser beam was focused onto the jet axis at a distance, z_i, from the nozzle. The laser radiation in the range of interest, $\lambda = 250$–270 nm ($\Delta\lambda \sim 0.01$ nm), was produced from the frequency doubled (BBO) output of a Nd/YAG pumped dye laser (Coumarin 503 or 522). Ions were allowed to collide with other particles in the field free flow until at some distance, z_f, where they were extracted via a pulsed field (nominally 50 V/cm) into the time-of-flight mass spectrometer. Typical experimental values were $z_i = 10$ mm and $z_f = 30$ mm.

The reaction, HBr^+ ($^2\Pi_i$, v^+) + HBr, was studied for individual spin-orbit ($i = 1/2$, 3/2) and vibrational ($v^+ = 0$, 1) states. The $H^{79}Br^+$ ($^2\Pi_i$, v^+) and $H^{81}Br^+$ ($^2\Pi_i$, v^+) ions were prepared by (2 + 1) REMPI through the $f^3\Delta_2$ ($v = 0$), $f^3\Delta_2$ ($v = 1$), $F^1\Delta_2$ ($v = 0$) and $F^1\Delta_2$ ($v = 1$) Rydberg intermediates. According to REMPI-LIF and REMPI-PES studies of Xie and Zare [1], (2 + 1) REMPI through these states produces the HBr^+($^2\Pi_i$, v^+) ions almost exclusively (more than 98%) in a single spin-orbit and vibrational state, namely, ($i = 3/2$, $v^+ = 0$), ($i = 3/2$, $v^+ = 1$), ($i = 1/2$, $v^+ = 0$), and ($i = 1/2$, $v^+ = 1$), respectively. Unfortunately, a spectral resolution of our equipment (nominally 0.3 cm^{-1}) combined with the linewidth of the 2-photon transitions at the necessary laser power permitted the isotope-selective ionisation in HBr^+ ($^2\Pi_{3/2}$, $v^+ = 1$) and HBr^+ ($^2\Pi_{1/2}$, $v^+ = 1$) states only. This capability owes itself to the dependence of the transition frequency on ($v^+ + 1/2$) times the difference of the isotopic vibrational frequency in the 2-photon resonant state, minus that difference in the ground state. As it can be seen from Fig. 1, the resolution is not complete, but it is sufficient to produce a well-defined distribution of ion isotopomer and allowing for product branching analysis. The difference between the ionisation wavelength for $H^{79}Br^+$ ($v^+ = 0$) and $H^{81}Br^+$ ($v^+ = 0$) is sufficiently smaller (about three times) as to render their REMPI line shapes unresolved.

3. Isotope-selected kinetics in a free jet

After ionisation the ions move along the flow and react with species seeded within the flow. Let k_{ij}^m be the rate coefficient of an ion-molecule reaction between an ion I_i^+ and a molecule M resulting in a new ion I_j^+. Using an absolute number density of specific ions n_j^+ and neutrals n_j, an absolute number density of all ions $n^+ = \sum_j n_j^+$ and neutrals $n = \sum_j n_j$, a relative density of ions $N_j^+ = n_j^+/n^+$ and neutrals $N_j = n_j/n$; $\sum_j N_j^+ = \sum_j N_j = 1$, the initial set of differential kinetic equations for absolute densities of different species in a free jet

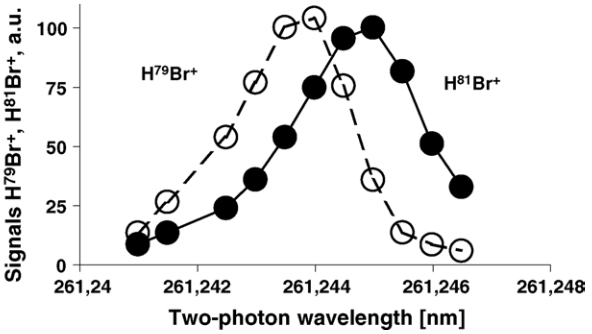

Fig. 1. Separation of REMPI signals of the $H^{79}Br^+$ and $H^{81}Br^+$ isotopes under ionisation through the $f^3\Delta_2$ ($v = 1$) Rydberg state using the $R(1)$ line.

$$\frac{\mathrm{d}n_j^+}{\mathrm{d}t} = \sum\nolimits_{i,m}(k_{jm}^i n_i^+ n_m - k_{ji}^m n_j^+ n_m) - n_j^+ f(t) \tag{1}$$

(where the last term describes temporal expansion in the free jet) can be transformed to the set for relative values along the free jet axis z

$$\frac{\mathrm{d}N_j^+}{\mathrm{d}z} = \left(\frac{n}{u}\right)\sum\nolimits_{i,m}(k_{ij}^m N_i^+ N_m - k_{ji}^m N_j^+ N_m) \tag{2}$$

Here the flow velocity u is approximately constant, determined largely by the buffer gas, since the reaction region is in the hypersonic part of the flow [8] and we have ignored the possibility of velocity slip and assume a constant u common to all species.

After the $H^{79}Br^+$ and $H^{81}Br^+$ionization, the following reactions are possible in the flow:

$$H^{79}Br^+ + H^{79}Br \rightarrow H^{79}Br + H^{79}Br^+ \tag{3a}$$

$$H^{79}Br^+ + H^{79}Br \rightarrow {}^{79}Br + H_2{}^{79}Br^+ \tag{3b}$$

$$H^{79}Br^+ + H^{79}Br \rightarrow {}^{79}Br + H_2{}^{79}Br^+ \tag{3c}$$

$$H^{79}Br^+ + H^{81}Br \rightarrow H^{79}Br + H^{81}Br^+ \tag{4a}$$

$$H^{79}Br^+ + H^{81}Br \rightarrow {}^{81}Br + H_2{}^{79}Br^+ \tag{4b}$$

$$H^{79}Br^+ + H^{81}Br \rightarrow {}^{79}Br + H_2{}^{81}Br^+ \tag{4c}$$

$$H^{81}Br^+ + H^{79}Br \rightarrow H^{81}Br + H^{79}Br^+ \tag{5a}$$

$$H^{81}Br^+ + H^{79}Br \rightarrow {}^{79}Br + H_2{}^{81}Br^+ \tag{5b}$$

$$H^{81}Br^+ + H^{79}Br \rightarrow {}^{81}Br + H_2{}^{79}Br^+ \tag{5c}$$

$$H^{81}Br^+ + H^{81}Br \rightarrow H^{81}Br + H^{81}Br^+ \tag{6a}$$

$$H^{81}Br^{+} + H^{81}Br \rightarrow {}^{81}Br + H_2{}^{81}Br^{+} \quad (6b)$$

$$H^{81}Br^{+} + H^{81}Br \rightarrow {}^{81}Br + H_2{}^{81}Br^{+} \quad (6c)$$

accounting for CT (a), HT (b) and PT (c) reactions. It should be noted that we are not able to investigate all of these twelve reactions separately. Even on first view, one can see that the reactions (3a) and (6a), are not discernible using mass spectrometry having the same reactant and product masses. In addition, there are two pairs of the reactions, (3b, 3c) and (6b, 6c), which are fully identical regarding reactants and products. Moreover, considering kinetics of the $H^{79}Br^+$, $H^{81}Br^+$, $H_2{}^{79}Br^+$, $H_2{}^{81}Br^+$ ions, one finds that the rate coefficients of the H-atom transfer reactions (3b, 4b, 5b, 6b) appear in the equations only as weighted sums, where the weights are presented by fractions of the neutrals, $H^{79}Br$ and $H^{81}Br$. Thus, an experiment under variation of these fractions or using isotopically pure gas is needed to study the individual rate coefficients of the HT process. As we use only a natural abundance (≈1:1) of the isotopes, we are not able to measure them separately. So, we can hope to define only five independent rate coefficients of the reactions (3–6). However, even with only five independent rates, expressions for the measured fraction of the $H^{79}Br^+$, $H^{81}Br^+$, $H_2{}^{79}Br^+$, $H_2{}^{81}Br^+$ ions remain too complicated for direct derivation of the rate coefficients from the experimental data. Let us suppose initially that there are only three different rate coefficients: k_a, k_b, k_c which are the same for all of the sets (3–6).

We now consider kinetics of all the ions along the free jet axis z, using the symbols of Eq. (1): $N_{80}{}^{+} = [H^{79}Br^{+}]/n^{+}$; $N_{82}{}^{+} = [H^{81}Br^{+}]/n^{+}$; $N_{81}{}^{+} = [H_2{}^{79}Br^{+}]/n^{+}$; $N_{83}{}^{+} = [H_2{}^{79}Br^{+}]/n^{+}$; $n^{+} = [H^{79}Br^{+}] + [H^{81}Br^{+}] + [H_2{}^{79}Br^{+}] + [H_2{}^{81}Br^{+}]$; $N_{80} = [H^{79}Br]/n$; $N_{82} = [H^{81}Br]/n$; $n = [H^{79}Br] + [H^{81}Br]$. Note, that $N_{80}{}^{+}(z_i)$ and $N_{82}{}^{+}(z_i)$ are the fraction of the ions initially ionised by REMPI, $N_{81}{}^{+}(z_i) = 0$, $N_{83}{}^{+}(z_i) = 0$; $N_{80} = N_{82} = 0.5$ is the natural fraction of the HBr isotopes conserved everywhere in the flow; and $N_{80}{}^{+}(z_f)$, $N_{81}{}^{+}(z_f)$, $N_{82}{}^{+}(z_f)$, $N_{83}{}^{+}(z_f)$ are equal to the signals of the corresponding masses measured at the point of detection, z_f. With these symbols, different rate expressions for the $H^{79}Br^+$, $H^{81}Br^+$, $H_2{}^{79}Br^+$ and $H_2{}^{81}Br^+$ ions along a free jet are given as:

$$\frac{dN_{80}^{+}}{dz} = \left(\frac{n}{u}\right)[-(k_b + k_c)N_{80}^{+} + k_a(N_{82}^{+}N_{80} - N_{80}^{+}N_{82})] \quad (7)$$

$$\frac{dN_{82}^{+}}{dz} = \left(\frac{n}{u}\right)[-(k_b + k_c)N_{82}^{+} + k_a(N_{80}^{+}N_{82} - N_{82}^{+}N_{80})] \quad (8)$$

$$\frac{dN_{81}^{+}}{dz} = \left(\frac{n}{u}\right)[k_b N_{80}^{+} + k_c(N_{80}^{+} + N_{82}^{+})N_{80})] \quad (9)$$

$$\frac{dN_{83}^{+}}{dz} = \left(\frac{n}{u}\right)[k_b N_{82}^{+} + k_c(N_{80}^{+} + N_{82}^{+})N_{82})] \quad (10)$$

4. Results and discussion

4.1. Rate coefficients of HBr$^+$ disappearance

The sum of Eqs. (7) and (8) leads to an equation for evolution of the HBr$^+$ ions

$$\frac{d(N_{80}^{+} + N_{82}^{+})}{dz} = \left(\frac{n}{u}\right)[-(k_b + k_c)(N_{80}^{+} + N_{82}^{+})] \quad (11)$$

that can be integrated between z_i and z_f giving an expression

$$(N_{80}^{+} + N_{82}^{+})_f = \exp[-(k_b + k_c)\zeta] \quad (12)$$

for determination of the rate coefficient, $(k_b + k_c)$. Here $\zeta = n_0 (aD)^2 (1/z_i - 1/z_f)/u$ is the reaction time integrated number density which is related to the number of collisions experienced between the ionisation and detection point in the jet, n_0 is the stagnation number density of HBr molecules, D is the nozzle diameter, u is the flow velocity, and a is the hemispherical expansion scale length ($n = n_0 a^2 D^2/z^2$) [8] that is equal to 0.401 and 0.298 for monatomic and diatomic gases, respectively, assuming their corresponding heat capacities ratios are 5/3 and 7/5. A plot of experimental data according to Eq. (12) is shown in Fig. 2. The sum of the H-atom transfer and proton transfer rate coefficients, $(k_b + k_c)$, have been determined for the individual internal states of the $HBr^+(^2\Pi_i, v^+)$ ions as 1.3, 1.1, 1.2 and 1.1 [10^{-9} cm^3/s, ±14%] for ($i = 3/2$, $v^+ = 0$), (3/2, 0), (3/2, 0) and (3/2, 0), respectively, which is in perfect agreement with our earlier measurements [4,6] and is greater than a factor 2 compare to room temperature experiments of Green et al. [3]. Explanation of this negative temperature dependence was described in [5,6] based on the attractive ion-dipole interaction potential. The absolute magnitudes of the total rate coefficients clearly indicate the efficiency of the total reaction, suggesting that nonreactive inelastic collisions are not important in this reaction system.

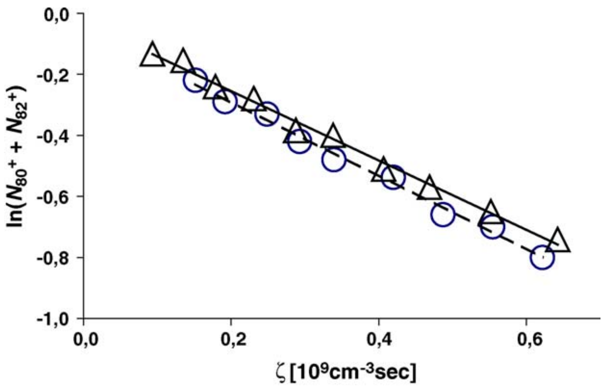

Fig. 2. Relative fraction of reactant ions, $H^{79}Br^+$ and $H^{81}Br^+$, at the detection point, z_f, vs. the integrated number density $\zeta = n_0 (aD)^2 (1/z_i - 1/z_f)/u$ for definition of the $(k_b + k_c)$ rate coefficient [see Eq. (12)]. Fraction of light ($H^{79}Br^+$) ions produced in the ionisation point, z_i, by REMPI via the $F^1\Delta$ ($v = 1$) state was 71% (circles) and 22% (triangles).

4.2. Rate coefficients for the charge transfer channel

As z_f is an arbitrary point of the flow, Eq. (12) with the substitution $z_f \to z$ presents the relative fraction of the HBr$^+$ ions at any point z. Then, using Eq. (12) we can integrate Eq. (7) arriving at the expression for the H^{79}Br$^+$ ion fraction at any final point z_f

$$N_{80}^{+}(z_f) = \exp[-(k_b + k_c)\zeta]\{N_{80} + [N_{80}^{+}(z_i) - N_{80}]\exp(-k_a\zeta)\} \tag{13}$$

Integration of Eq. (8) in the same manner gives for H^{81}Br$^+$

$$N_{82}^{+}(z_f) = \exp[-(k_b + k_c)\zeta]\{N_{82} + [N_{82}^{+}(z_i) - N_{82}]\exp(-k_a\zeta)\} \tag{14}$$

After subtraction of Eq. (14) from Eq. (13) and using Eq. (12) we can get

$$\left[\frac{(N_{80}^{+} - N_{82}^{+})}{(N_{80}^{+} + N_{82}^{+})}\right]_f = [2N_{80}^{+}(z_i) - 1]\exp(-k_a\zeta) \tag{15}$$

where we used $N_{80}{}^{+}(z_i) + N_{82}{}^{+}(z_i) = 1$ and $N_{80} = N_{82} = 0.5$ in our experiments. Eq. (15) was explored to determine the rate coefficient k_a as well as the initial fraction of the H^{79}Br$^+$ and H^{81}Br$^+$ ions under ionisation. An example of these data is presented in Fig. 3. As it was mentioned in Section 3, we were able to measure the rate coefficients of the charge transfer reaction only for vibrationally excited ions HBr$^+$ ($^2\Pi_{3/2}$, $v^+ = 1$) and HBr$^+$ ($^2\Pi_{1/2}$, $v^+ = 1$). In both cases we used three slightly different ionisation wavelengths producing different initial ratio between the H^{79}Br$^+$ and H^{81}Br$^+$ isotopes: roughly, in the ratios 1:2, 1:1 and 2:1. The rate coefficients of the charge transfer reactions, k_a, were measured as 6×10^{-10} (±20%) cm^3/s in all experiments independent of spin-orbit states of ionic reactants or mass of the laser selected ion. Such independence on bromine isotopic mass is expected, even at these low collision energies for a variety of reasons. First, the isotope selected ions are prepared with one quanta of vibrational energy, presumably available to overcome any small barriers. Secondly, the very slight endothermicity of Reaction 4a owing to zero point energy differences is insignificant ($\Delta E \le 25$ mK). While that for the H^{79}Br$^+$ ($v^+ = 1$) ion adiabatically undergoing change transfer to yield H^{79}Br ($v = 1$) would be approximately 150 K endothermic (and therefore very slow in these low temperature jet conditions) the reaction can occur essentially thermoneutrally to yield H^{81}Br$^+$ ($v^+ = 1$) with transfer of a vibrational quanta or to produce H^{79}Br$^+$ ($v^+ = 0$) + H^{81}Br$^+$ ($v^+ = 0$) in a highly exothermic reaction ($\Delta E \approx -1700$ K). Evidently, the role of the vibrational excitation in the charge transfer leads to identical CT rates to be observed independent of the isotope selection in these experiments. Measurements of charge transfer rates for the same and related ion-molecule pairs at 300 K give k_{CT} [$\times 10^{-10}$ cm^3/s] = 2.5 [2] and 2.9 [3] (for HBr$^+$/DBr); 3.2 [3] (for HBr$^+$/HBr); and 4.1 (3/2,0), 1.4 (3/2,1), 3.8 (1/2,0), 2.3 (1/2,1) for DBr$^+$ (i, v^+)/HBr [1]. It should be noted that deuterium substitution effects reaction energy much more significantly due to zero point vibrational energy effects.

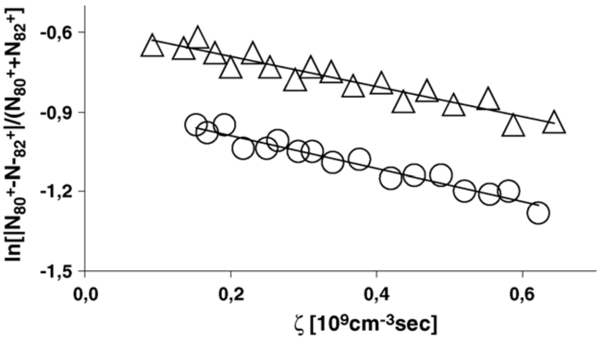

Fig. 3. Determination of the charge transfer rate coefficients, k_a, and initial fraction of the H^{79}Br$^+$ and H^{81}Br$^+$ ions [see Eq. (15)]. Two sets of the data correspond to the case of $N_{80}{}^{+}(z_i) > N_{82}{}^{+}(z_i)$—(circles) and $N_{80}{}^{+}(z_i) < N_{82}{}^{+}(z_i)$—(triangles).

4.3. Rate coefficients of the proton and H-atom transfer channels

Now, using [$N_{80}{}^{+}(z) + N_{82}{}^{+}(z)$], $N_{80}{}^{+}(z)$ and $N_{82}{}^{+}(z)$ as described by Eqs. (12)–(14), respectively, with substitution of $z_f \to z$, we can integrate Eqs. (9) and (10) to arrive at equations for the kinetics of the H$_2$^{79}Br$^+$ and H$_2$^{81}Br$^+$ ions

$$N_{81}^{+}(z_f) = N_{80}\{1 - \exp[-(k_b + k_c)\zeta]\} + \frac{k_b[N_{80}^{+}(z_i) - N_{80}]\{1 - \exp[-(k_a + k_b + k_c)\zeta]\}}{(k_a + k_b + k_c)} \tag{16}$$

$$N_{83}^{+}(z_f) = N_{82}\{1 - \exp[-(k_b + k_c)\zeta]\} + \frac{k_b[N_{82}^{+}(z_i) - N_{82}]\{1 - \exp[-(k_a + k_b + k_c)\zeta]\}}{(k_a + k_b + k_c)} \tag{17}$$

From Eqs. (16) or (17), using Eqs. (12) and (15) we can obtain the expression

$$\frac{k_b}{(k_a + k_b + k_c)} = \frac{[N_{82}N_{81}^{+}(z_f) - N_{80}N_{83}^{+}(z_f)]}{\{N_{80}^{+}(z_i) - N_{80}^{+}(z_f) - N_{80}[N_{81}^{+}(z_f) + N_{83}^{+}(z_f)]\}} \tag{18}$$

that along with Eqs. (12) and (15) allows definition of all the rate coefficients k_a, k_b, and k_c by mass spectrometry using the signals of mass 80 ($N_{80}{}^{+}$), 81 ($N_{81}{}^{+}$), 82 ($N_{82}{}^{+}$), 83 ($N_{83}{}^{+}$) a.m.u. Table 1 presents the values of the initial fraction of H^{79}Br$^+$ ions, $N_{80}{}^{+}(z_i)$, and combinations of the rate coefficients, $(k_b + k_c)$, k_a, [$k_b/(k_a + k_b + k_c)$] primarily determined via Eqs. (12), (15) and (18) as well as the individually determined rate coefficients, k_b and k_c. Within our accuracy, the rate coefficients appear to be independent of the spin-orbit state of the ions. The negative temperature dependence of

Table 1
Rate coefficients of the reaction $HBr^+ + HBr$ channels [10^{-9} cm^3/s]

State of ion[a]	$N_{80}{}^+(z_i)$[b]	$k_b + k_c$ [b]	k_a[b]	$k_b/(k_a + k_b + k_c)$[b]	k_b[c]	k_c[c]	k_{5a}/k_{4a}[b]
$^2\Pi_{3/2}, v^+ = 0$	0.63	1.3		Not measured			1.13
Green et al. [3]	($T \approx 300$K)[d]	(0.37)	(0.32)	(0.21)	(0.15)	(0.22)	
$^2\Pi_{3/2}, v^+ = 1$	0.33,0.57,0.72	1.1	0.6	0.15	0.26	0.84	1.09
$^2\Pi_{1/2}, v^+ = 0$	0.51	1.2		Not measured			1.17
$^2\Pi_{1/2}, v^+ = 1$	0.22,0.49,0.71	1.1	0.6	0.11	0.19	0.91	1.09
Accuracy	±0.02	±14%	±20%	±24%	±30%	±30%	±0.04

[a] Ionised via $f^3\Delta_2$ ($v = 0$), $f^3\Delta_2$ ($v = 1$), $F^1\Delta_2$ ($v = 0$), $F^1\Delta_2$ ($v = 1$) intermediate states.

[b] Values, directly observed via Eqs. (12), (15), (18) and (19).

[c] Derived values.

[d] Room temperature data of Green et al. [3] measured by the selective ion tube technique (using the combined REMPI-LIF technique they found $k_{HT+PT} = 6.9 \times 10^{-10}$ cm^3/s).

the rate coefficients observed by comparison with the data of Green et al. [3] has been mentioned in Section 4.1 and its possible source discussed in [5,6]. Thus, we only add some notes about branching. The total rate coefficient increases as much as 2.5 times upon cooling from room temperature ($k_{tot}\{300\,K\} = 6.9 \times 10^{-10}$ cm^3/s [3]) to temperatures well below 300 K realised in a free jet, $k_{tot} = 1.7 \times 10^{-9}$ cm^3/s, (estimated translational and rotational temperatures here are $T_t \approx 10$ K and $T_R \approx 80$ K [4,6]). The rate coefficients of the CT, HT and PT channels increase also, but not proportionally: as factors 2, 1.7 and 3.8, respectively for these channels. It is unlikely that these behaviours are defined by reaction thermodynamics, because both PT and HT processes are highly exothermic (10 kcal/mole) and the energetics of the CT process have been discussed in the context of vibrational excitation. A more reasonable explanation comes from the assumption of different branching for the specific channels owing to different dependencies on long-range direct and long-lived complex forming processes and their relative effectiveness on translational and rotational motion. Green et al. [3] estimated the role of the complex forming mechanism as 28% at $T = 300$ K, and it is suggested that the role of that mechanism increases at low temperatures. Thus, we can conclude that the reaction branching is significantly different for these two mechanisms shifting toward more efficiency of the proton transfer channel under complex formation.

4.4. *Isotopic sensitivity of the CT, HT and PT rate coefficients*

In general, one can derive expressions for the specific fractions of the ions through the rate coefficients k_{ia}, k_{ib}, k_{ic} which are individual to the isotopically specific reactions described by Eqs. (3)–(6). These are of course more complicated than Eqs. (12)–(14), (16), (17) used above, consisting of 6–8 exponential terms, and we avoid reproduction of them all here. As our experimental procedure allows determination of only 5 (of 12) independent rate coefficients (see Section 3), we can attempt to find two more rate coefficients in addition to the ones discussed earlier. The charge transfer reactions Eqs. (3a) and (6a) remain invisible to our technique as they have the same products as reactants and hence their rate coefficients do not influence observed kinetics (other than through possible energy transfer processes). Thus, we can hope to measure only two of the charge transfer rate coefficients, k_{4a} and k_{5a}.

As was also established in Section 3, in the context of our technique we are not able to distinguish individual rate coefficients for the H-atom transfer reactions (3b–6b). So, the fifth independent individual rate coefficient that we could attempt to isolate must be PT. Here we have assumed that the bulk of the ion-molecule interaction depends mostly on the nature of molecule through its natural and induced dipole moment, but not on the long range nature of the ion (with the exception of the subtle differences involved in bromine isotopic substitution). On making this assumption we consider also that the nature of the reaction surfaces and nonadiabatic crossings active in these reactions are insignificantly effected by changes in the Br mass.

Thus, there are five independent rate coefficients: $k_{4a} = k_{6a}$, $k_{5a} = k_{3a}$, $k_{3b} = k_{4b} = k_{5b} = k_{6b}$, $k_{4c} = k_{6c}$, $k_{5c} = k_{3a}$, which we choose to determine experimentally. The difference between individual rate coefficients of the proton transfer reactions, k_{4c} and k_{5c}, appears to be within the experimental error, that is 5% for the ratio k_{4c}/k_{5c}. Considering $k_{4c} = k_{5c}$, integration of Eq. (7) leads to a new expression for the fraction of the $H^{79}Br^+$ ions at the point of detection

$$\frac{N_{80}^{+}(z_f)}{N_{80}^{+}(z_f) + N_{82}^{+}(z_f)} = N_{80}^{+}(z_i)\exp[-(k_1 + k_2)\zeta] + \frac{k_1}{k_1 + k_2}\{1 - \exp[-(k_1 + k_2)\zeta]\} \tag{19}$$

where $k_1 = k_{5a} N_{80}$ and $k_2 = k_{4a} N_{82}$. Taking into account that $N_{80} = N_{82} = 0.5$ reflecting the natural abundance of the $H^{79}Br$ and $H^{80}Br$ isotopes, Eq. (19) has been explored to define $k_{5a}/(k_{5a} + k_{4a}) = k_1/(k_1 + k_2)$, using an ordinary linear regression procedure between the fraction of light isotope ions at the point of detection (left hand side of Eq. (19)) measured experimentally and the exponential term. But for more clarity in presentation, Fig. 4 shows the fraction of light ions as a function of the collision number ζ, both measured (symbols) and simulated by Eq. (19) (lines). The results demonstrate a slight, but systematic shift of ionic fractions toward domina-

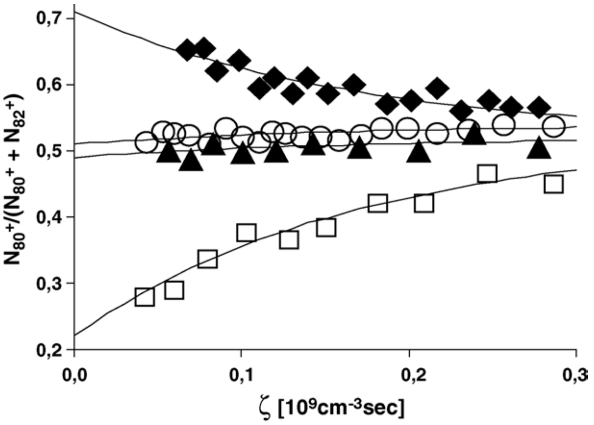

Fig. 4. Final fraction of light isotope of the HBr^+ ions at the detection point as a function of the integrated number density ζ (see caption of Fig. 2) under initial ionisation of the $H^{79}Br^+$ ($^2\Pi_{1/2}$, $v^+ = 1$) and $H^{81}Br^+$ ($^2\Pi_{1/2}$, $v^+ = 1$) ions in the proportions 71/29 (rhombs), 49/51 (triangles), 22/78 (squares) and of the $H^{79}Br^+$ ($^2\Pi_{1/2}$, $v^+ = 0$) and $H^{81}Br^+$ ($^2\Pi_{1/2}$, $v^+ = 0$) ions in the proportion 51/49 (circles). Lines represent a simulation of Eq. (19) with the rate coefficients from Table 1.

tion of light ions, $H^{79}Br^+$, which may mean slight increase of k_{5a} compared to k_{4a}. In spite of the low difference, a tendency of $N_{80}{}^+$ to exceed $N_{82}{}^+$ is clearly seen and a slight preference of the charge transfer to the $H^{79}Br$ molecule, Eq. (5a), compared to the reverse reaction (4a) is supported by statistical criteria within the 95% reliability level. Data on the ratios k_{5a}/k_{4a} measured under various experimental conditions are listed in the last column of Table 1. Note that a slight preference in the direction of the CT reaction towards lighter ion production was also observed by Green et al. [3] for the reactions $HBr^+ + (D^{79}Br, D^{81}Br) \rightarrow HBr + (D^{79}Br^+, D^{81}Br^+)$. Since it is not clear dynamically why these trends should present themselves when reaction energies are very small relative to kT, we might propose this effect occurs at the exit branch of the reactions going through the long-living collisional complexes.

5. Conclusions

The low temperature state-selective ion-molecule reaction $HBr^+ + HBr$ was studied in an $Ar + HBr(<2\%)$ free jet. The HBr^+ ($^2\Pi_i$, v^+) ions in a single spin-orbit and vibrational state ($i = 1/2$, $3/2$; $v^+ = 0, 1$) were prepared by (2 + 1) REMPI and ionic reaction products within the jet were monitored by TOF MS. The isotope-selective scheme of REMPI allowed variation of the initial fraction of $H^{79}Br^+$ ($^2\Pi_i$, v^+) and $H^{81}Br^+$ ($^2\Pi_i$, v^+) ions and through this, the investigation of the reaction branching. This allowed determination of the rate coefficients for the charge transfer, H-atom transfer and proton transfer channels. Thus, the explored technique may be considered as an alternative to the use of expensive enriched single-isotope gases. Analysis of kinetics in the free jet leads to simple expressions between final isotope fractions of the ions and rate coefficients for the reaction channels. Using these, the following rate coefficients were measured: two of four rates of the charge transfer reactions presented by Eqs. (4a) and (5a); one universal rate coefficient for all H-atom transfer reactions Eqs. (3b)–(6b), because the individual ones, k_{ib}, were not distinguishable under the use of the natural (≈ 1:1) abundance of the $H^{79}Br$ and $H^{81}Br$ neutrals; and two of four rate coefficients of the proton transfer reaction (with the other two being shadowed by other processes). No statistically valid difference between the individual PT rate coefficients was observed. The individual CT rate coefficients demonstrated a slight (about 10%) preference of the light ion production, Eq. (5a), compared to the reverse reaction, Eq. (4a), and the effect was some stronger for the lowest vibrational state of the ions compared to the $v^+ = 1$ level. The measured rate coefficient ($k_{HT} + k_{PT}$) of disappearance of the HBr^+ ions is in a good agreement with the results of preceding works in a free jet [4] and the total reaction rate is higher by a factor 2.5 compared to room temperature results [3]. As for the temperature effect on branching of the reaction, the CT rate coefficient changes similar to the total rate (factor 2). The HT and PT rate coefficients also increase when temperature decreases (as much as factors of 1.7 and 3.8, respectively). The enhancement of PT over HT channel may be caused by vibrational excitation of ions in our experiments. Another point, which may be important independently or in combination with vibrational excitation, is that the complex forming mechanisms may become more important at low temperatures even when internally excited ions are involved.

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References

[1] J. Xie, R.N. Zare, J. Chem. Phys. 96 (1992) 4293.
[2] A.A. Viggiano, R.A. Morris, J.F. Poulson, (unpublished data referenced in [1]).
[3] R.J. Green, J. Xie, R.N. Zare, A.A. Viggiano, R.A. Morris, Chem. Phys. Lett. 277 (1997) 1.
[4] A.E. Belikov, C. Mullen, M.A. Smith, J. Chem. Phys. 114 (2001) 6625.
[5] A.E. Belikov, M.A. Smith, Chem. Phys. Lett. 358 (2002) 57.
[6] A.E. Belikov, M.A. Smith, J. Phys. Chem. A 108 (2004) 3447.
[7] M.A. Smith, M. Hawley, in: N.G. Adams, L.M. Babcock (Eds.), Advances in Gas Phase Ion Chemistry, JAI Press, Greenwich, 1992, p. 167.
[8] H. Ashkenas, F. Sherman, in: Rarefied Gas Dynamics, Proceedings of fourth International Symposium, vol. 2 Academic Press, New York, 1966, p. 84.