Rotational Cooling of HD^+ Molecular Ions by Superelastic Collisions with Electrons

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Merging an HD^+ beam with velocity matched electrons in a heavy ion storage ring we observed rapid cooling of the rotational excitations of the HD^+ ions by superelastic collisions (SEC) with the electrons. The cooling process is well described using theoretical SEC rate coefficients obtained by combining the molecular R-matrix approach with the adiabatic nuclei rotation approximation. We verify the $\Delta J = -2$ SEC rate coefficients, which are predicted to be dominant as opposed to the $\Delta J = -1$ rates and to amount to $(1\text{–}2) \times 10^{-6}$ cm^3 s^{-1} for initial angular momentum states with $J \leq 7$, to within 30%.

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In dilute ionized media the interaction of molecular ions with the surrounding electrons is of key importance to understand the physical and chemical properties of these systems. At low temperatures, such as prevailing in a number of astrophysical environments, the two main processes to be considered are dissociative recombination (DR) and inelastic collisions (IEC). Of these DR has been studied in great detail in the last two decades, and a deep theoretical insight into the mediating processes has been gained [1]. On the other hand only few experimental studies have been performed so far dealing with IEC processes of low energetic electrons. In fact we are only aware of one *quantitative* measurement, performed by Krohn *et al.* [2] at the TSR storage ring, in which absolute rate coefficients for *vibrational* deexcitations of H_2^+ ions by superelastic collisions (SEC) with meV electrons were deduced. Surprisingly, theoretical treatments of the vibrational SEC process in H_2^+, which were either based on the R-matrix method [3] or the multichannel quantum-defect theory (MQDT) approach [4], resulted in SEC coefficients which are an order of magnitude lower than the measured values.

Both experiment as well as theory so far neglected the role of the rotational degree of freedom of H_2^+ in the SEC process, the experiment by averaging over the (time dependent) population of rotational states of the molecular ion, the theory by neglecting the rotational structure and couplings. Recently, however, evidence for a rotational quantum number dependence of the vibrational SEC rates in H_2^+ has been obtained [5], and first calculations of vibrational SEC cross sections for H_2^+ have been performed within MQDT [6] including rotational couplings, which approach the measured SEC rate coefficients already much more closely. The present experiment was designed to investigate SEC between rotational states built on the vibrational ground state of HD^+ in order to elucidate the role of rotational angular momenta in the SEC process and to provide an experimental basis for a more detailed comparison with ongoing theoretical developments [6–8]. Although rotational cooling by SEC in storage ring experiments has been conjectured before (see, e.g., [9]), this is the first quantitative measurement of *rotational* SEC rates for a molecular ion.

The experiment uses the DR process to probe the time evolution of the population $P_J(t)$ of the molecular rotational states J when merging rotationally hot $HD^+(v, J)$ ions circulating in a storage ring with cold electrons of the same velocity as the ions. Since HD^+ is known to relax to the $v = 0$ ground state within a few 100 ms [10] and the relative ion-electron energies E are smaller than the energy difference between two adjacent vibrational and rotational states, the only inelastic collisions which can take place thereafter are rotational SECs, i.e.,

$$HD^+(0, J) + e^-(E = 0) \rightarrow HD^+(0, J') + e^-(E' > 0), \quad (1)$$

with $J' < J$. The resulting time evolution of $P_J(t)$ is monitored observing the kinetic energy release $E_k(J)$ carried by the two DR fragments applying fragment imaging [11]. Since the only channel accessed by DR is

$$HD^+(0, J) + e^-(E = 0) \rightarrow H(nl) + D(ml') + E_k(J), \quad (2)$$

with $(n, m) = (1, 2)$ or $(2,1)$, $E_k(J)$ is given by $E_k(J) = E_0 + BJ(J + 1)$, where $E_0 = 0.726$ eV denotes the energy difference between the ionic ground state and dissociation channel and $B = 2.72$ meV is the rotational constant of HD^+ [12]; thus $E_k(J)$ is a unique function of J.

The experiment was carried out at the heavy ion storage ring (TSR) located at the Max Planck Institute for Nuclear Physics. HD^+ ions were created in a discharge ion source, accelerated to 1.44 MeV, injected into the storage ring within 30 μs, and stored for typically 10–20 s before

they were kicked out of the ring and a new injection took place. On every turn in the ring (circumference $C = 55.4$ m) the stored ions were merged with a velocity matched electron beam, which was supplied by the electron target station (ETS [13]) located in one of the straight sections of the TSR. The electrons were extracted from a thermionic cathode and expanded to form a 1.0 cm diameter beam with an energy distribution characterized by $kT_{\parallel} \approx 45$ μeV parallel and $kT_{\perp} \approx 2.8$ meV transversal to the beam direction in the comoving reference frame. The effective length of the electron target is $l_e = 1.22$ m. Three different electron densities $n_e = (0.28, 1.00,$ and $1.45) \times 10^7$ cm^{-3} were applied, which we will refer to as "low," "medium," and "high," respectively. The electrons were used for phase space cooling of the HD^+ ions, leading to an ion beam of <2 mm diameter and <25 μrad divergence within 0.5–1 s, and as the target for electron-ion collisions.

The two neutral fragments caused by DR of HD^+ were recorded downstream of the ETS by a high resolution imaging system [14]. This system is located at a distance of $\bar{s} = 12.24$ m from the center of the ETS and consists of an 80 mm diameter multichannel-plate detector, which is attached to a phosphor screen viewed by a CCD camera. The kinetic energy released in a dissociation event is translated into inter fragment distance upon reaching the imaging system, where the projected (transverse) distance D between the two neutral fragments was determined event by event with an accuracy of $\pm 0.3\%$. A 25 cm^2 energy sensitive Si detector could be temporarily placed about 1 m in front of the imaging detector to measure the total DR rate.

Projected distance distributions $F(D, t)$ and total DR rate coefficients $\alpha_{\mathrm{DR}}(t)$ were measured at $E = 0$ as a function of storage time t. Examples of (normalized) projected distance distributions (PDD) measured at "medium" electron density are shown in Fig. 1 for $D \geq 17$ mm, where these distributions are most sensitive to the rotational states populated. The total DR rate coefficient $\alpha_{\mathrm{DR}}(t)$ observed at "medium" electron density is displayed in Fig. 2. Here the absolute scale was normalized to the steady state value of 4.0×10^{-8} cm^3/s, estimated for the present electron temperatures using the data collected in Ref. [15]; the absolute normalization is believed to be accurate to about 20%.

At matched electron-ion velocities the normalized projected distance distribution $f_J(D)$ from the DR of a given rotational state J of HD^+ is completely determined (see Ref. [11] for a more rigorous treatment) by the kinetic energy release $E_k(J)$. For an ensemble of rotationally excited HD^+ ions we thus find

$$F(D, t) = (\alpha_{\mathrm{DR}}(t))^{-1} \sum_J \alpha_J P_J(t) f_J(D), \qquad (3)$$

where α_J denotes the DR rate coefficient of the rotational state J and $P_J(t)$ its population probability at time t.

In view of the counting statistics and the resolution in the D to E_k conversion it is not possible to reliably deduce the relative amplitudes of $f_J(D)$ for individual states from the measured PDDs. Instead, we combined adjacent J states into three groups, denoting the groups $\{J = 0, 1, 2\}$ by $\mu = 0$, $\{J = 3, 4\}$ by $\mu = 3$, and $\{J = 5, 6, 7\}$ by $\mu = 6$, respectively. Higher rotational states could be populated at least at short storage times but do not seem to contribute sizably to the DR rate (see Fig. 1). Denoting the average of the distribution functions $f_J(D)$ with $J \in \{\mu\}$ by $\tilde{f}_\mu(D)$, and the average of the DR rate coefficients α_J with $J \in \{\mu\}$ by $\tilde{\alpha}_\mu$, we can approximate Eq. (3) by

$$F(D, t) = \sum_\mu \tilde{F}_\mu(D, t) = \sum_\mu r_\mu(t) \tilde{f}_\mu(D), \qquad (4)$$

$$\text{with } r_\mu(t) = \frac{\tilde{\alpha}_\mu}{\alpha_{\mathrm{DR}}(t)} \hat{P}_\mu(t) \quad \text{and} \quad \hat{P}_\mu(t) = \sum_{J \in \{\mu\}} P_J(t).$$

In the data analysis we first fitted Eq. (4) to the measured PDDs inside the range $17 \text{ mm} \leq D \leq 21$ mm to deduce

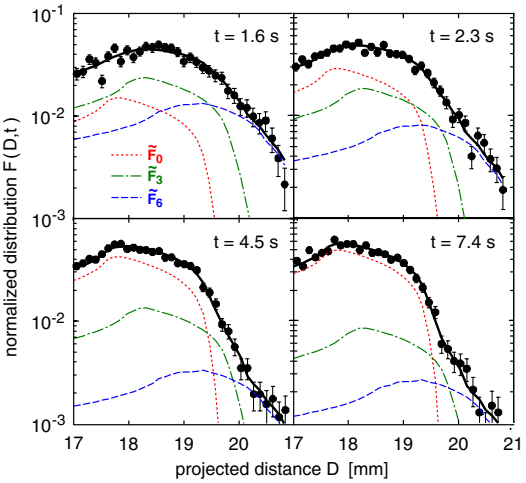

FIG. 1 (color online). Examples of projected distance distributions measured at different storage times and $n_e = 1.0 \times 10^7$ cm^{-3}. The broken lines are model calculations for three different groups of rotational states, while the solid line is the sum of these contributions after adjusting their relative heights to the data (see text for details).

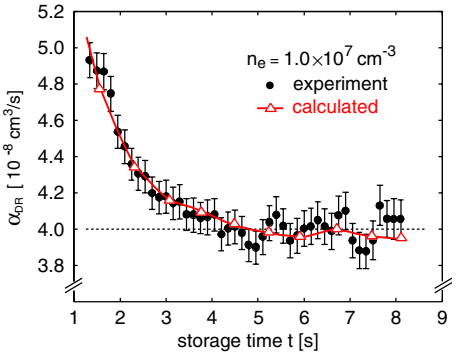

FIG. 2 (color online). Total DR rate coefficient measured as a function of storage time at "medium" electron density. The open triangles (connected by solid lines to guide the eye) are calculated using Eq. (5) after adjusting the DR coefficients $\tilde{\alpha}_\mu$ for the three groups of rotational states.

the time dependent relative amplitudes $r_\mu(t)$. The measured distributions are very well represented by these fits as exemplified in Fig. 1.

To determine the DR rate coefficients $\tilde{\alpha}_\mu$ we fitted in a second step the total DR rate coefficient $\alpha_{\mathrm{DR}}(t)$ measured at "medium" electron density of $n_e = 1.0 \times 10^7$ cm^{-3} (Fig. 2) by

$$\alpha_{\mathrm{DR}}(t) = \left(\sum_\mu r_\mu(t)/\tilde{\alpha}_\mu\right)^{-1}, \quad (5)$$

which follows from the definition of $r_\mu(t)$ and the normalization $\sum_\mu \hat{P}_\mu(t) = 1$. Using the relative amplitudes $r_\mu(t)$ determined for 10 time intervals between 1.6 to 8.2 s we find (statistical errors only)

$$\tilde{\alpha}_0 = 3.8 \pm 0.1, \quad \tilde{\alpha}_3 = 4.0 \pm 0.2, \quad \text{and} \quad \tilde{\alpha}_6 = 9.0 \pm 1.3$$

in units of 10^{-8} cm^3/s. The total DR rate coefficients resulting from this fit are shown by the open symbols in Fig. 2. Note that this result constitutes another example for the J dependence of the DR cross section of molecular hydrogen ions [5], and that these values compare favorably, in particular, when taking the error of the absolute DR scale of 20% into account, to the corresponding averaged values of 5.3, 4.0, and 10.3×10^{-8} cm^3/s, respectively, derived within the MQDT approach [16].

In the final analysis step we used $\tilde{\alpha}_\mu$ to determine $\hat{P}_\mu(t)$. Results are depicted in Fig. 3 for the three electron densities. For $t > 2$ s, $r_\mu(t)$ could be extracted reliably from the measured PDDs and the resulting $\hat{P}_\mu(t)$ clearly reveal that rotational cooling of the HD^+ ions takes place, the cooling getting faster with increasing density n_e of the electron beam. At shorter times the separation between $\tilde{F}_0(D)$ and $\tilde{F}_3(D)$ was hampered by the presence of $\tilde{F}_6(D)$, which is covering up the high distance tails of $\tilde{F}_0(D)$ and $\tilde{F}_3(D)$ most sensitive to J.

To investigate the role of SEC in the rotational cooling process, we calculated the time evolution of the rotational populations $P_J(t)$ of the vibrational ground state by solving the coupled set of differential equation

$$\dot{P}_J(t) = \sum_{J'}[M^r_{JJ'} + (l_e/C)n_e M^c_{JJ'}]P_{J'}(t). \quad (6)$$

Here the matrix M^r is due to the exchange of photons with the ambient radiation field; the matrix elements $M^r_{JJ'}$ are the Einstein coefficients, which can be readily taken from literature [17] assuming the radiation field to be given a Planck distribution with a temperature of 300 K. The matrix M^c describes the population change due to interactions with electrons; for $J > J'$ the matrix elements $M^c_{JJ'}$ are given by the SEC rate coefficients $c_{J,J'}$ leading from state J to state J', while for $J = J'$ the matrix elements are $-(\alpha_J + \sum_{J'<J} c_{J',J})$. The initial populations $P_J(t = 0)$ are assumed to be given by a Boltzmann distribution for an initial temperature T_i.

We first determined the evolution of $P_J(t)$ including only radiative processes and possible cooling effects through

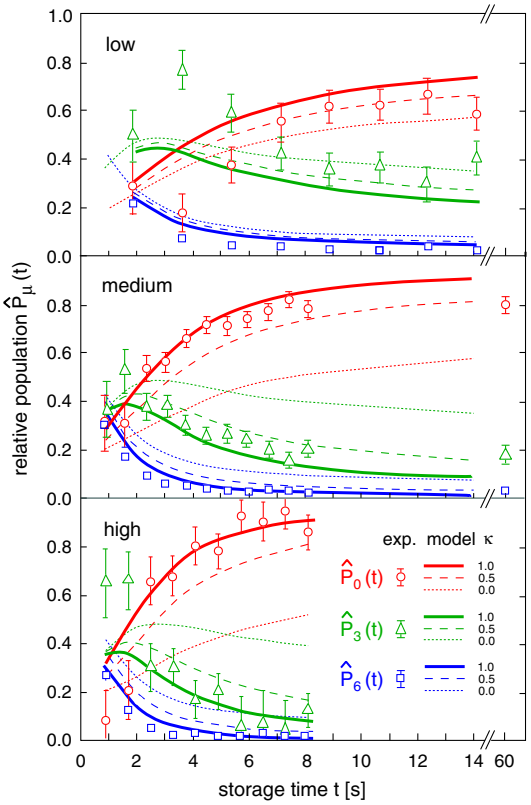

FIG. 3 (color online). Relative populations $\hat{P}_\mu(t)$ as a function of storage time which are extracted from the projected distance distributions measured at electron densities of 0.28 (low), 1.0 (medium), and 1.45×10^7 cm^{-3} (high). The lines are the results of our model calculations using the theoretical SEC rate coefficients given in Table I and multiplying them by a constant factor κ. The thick solid (thin dotted) lines are the resulting $\hat{P}_\mu(t)$ when including (neglecting) SEC, while the thin dashed lines are obtained using $\kappa = 0.5$.

J-dependent level depletion by DR. The resulting time dependence of $\hat{P}_\mu(t)$ is shown in Fig. 3 by the thin dotted lines ($\kappa = 0$) assuming the initial temperature to be $T_i = 1500$ K. These cooling curves are found to be essentially independent of the electron density and to be mainly governed by radiative processes only. The DR rate coefficients α_J in this calculation were set equal to the respective average values $\tilde{\alpha}_\mu$ determined above, while for $J \geq 8$ $\alpha_J = \tilde{\alpha}_6$ was used. However, due to the very low effect of the DR process on $P_J(t)$ the specific choice made for α_J turns out to be irrelevant as long as they stay within the limits given by $\tilde{\alpha}_\mu$. Moreover, calculations showed that the assumptions made on the initial level population are essentially washed out with increasing storage time; changes, e.g., of the initial temperature T_i by ± 300 K affect the individual $\hat{P}_\mu(t)$ values at $t = 1$ s by at most $\pm 15\%$, while at $t = 7.5$ s the T_i dependence is less than $\pm 2\%$. Rotational cooling by DR induced level depletion or by radiative processes alone clearly cannot reproduce the observed $\hat{P}_\mu(t)$ behavior.

TABLE I. Theoretical SEC rate coefficients (10^{-6} cm^3/s)

J	1	2	3	4	5	6	7	8	9	10
$c_{J,J-1}$	0.36	0.44	0.39	0.43	0.42	0.40	0.39	0.36	0.36	0.33
$c_{J,J-2}$		0.98	1.19	1.19	1.00	1.72	1.76	1.79	1.81	1.82

To include superelastic collisions in our cooling model we used IEC cross sections we calculated by combining R-matrix wave functions with the adiabatic nuclei rotation (ANR) approximation. These calculations followed those performed on H_2^+ [18] at a fixed HD^+ bond length of $2.0a_0$ except that they were carried out in $C_{\infty v}$ symmetry with a shifted center of mass which gave a dipole moment of $0.85D$. Note that the cross sections did not need to be corrected for threshold effects because the ANR approximation was shown to be valid down to threshold [8]. As observed previously for ions with moderate dipole moments ($\lesssim 1D$) [7], cross sections with $\Delta J = -1$ were found to be significantly smaller than those with $\Delta J = -2$. Note, moreover, that unlike the DR cross section, which is dominated at low energies by the $^1\Sigma_g^+$ symmetry of the electron-HD^+ complex and, within this symmetry, by the d-wave contribution, the $\Delta J = -1, -2$ SEC cross sections are both dominated by p-wave scattering. SEC rate coefficients were derived by integrating the cross sections over the flattened electron distribution. They are compiled in Table I for $\Delta J = -1, -2$ transitions; $\Delta J = -3$ and higher transitions are smaller by at least 2 orders of magnitude.

The time evolution of $\hat{P}_\mu(t)$ obtained by taking in addition the theoretical SEC rate coefficients given in Table I into account are shown by the thick solid lines ($\kappa = 1$) in Fig. 3. The calculated $\hat{P}_\mu(t)$ represent the data rather well, given that the only free parameter is the initial rotational temperature T_i chosen to be 1500 K, and even more so as at $t \approx 7.5$ s the calculation is basically independent of T_i as discussed above.

No attempt was made to fit individual or groups of SEC coefficients to the data. Instead, the overall sensitivity of the experiment on the SEC rate coefficients was estimated from $\hat{P}_\mu(t)$ curves obtained when multiplying all $c_{J,J'}$ by a constant factor κ; the thin dashed lines in Fig. 3 represent, e.g., the result for $\kappa = 0.5$, which clearly underestimates the measured cooling curves although it leads to a somewhat closer description of the $\hat{P}_\mu(t)$ values measured at "medium" electron density at $t = 60$ s. Moreover, we found that the effect of setting all $c_{J,J-1}$ coefficients equal to zero can be compensated by increasing the $c_{J,J-2}$ coefficients by about 15%. We also studied the influence of heating processes other than radiation induced onto the time evolution of $\hat{P}_\mu(t)$, primarily those caused by inelastic collisions with electrons in the merging sections of the electron beam with the ion beam (where relative electron-ion energies of up to 1.5 eV are available) and by the tails of the electron energy distribution in the straight target section. But neither these processes nor collisions of HD^+ with the residual gas where found to influence $\hat{P}_\mu(t)$ by more than a few percent. We conclude from these tests that the experiment verifies the theoretical $c_{J,J-2}$ coefficients, which dominate the rotational cooling process, to within an overall accuracy of about 30%.

In summary, we observe strong rotational cooling when rotationally hot HD^+ ions are subjected to cold electrons of $kT \approx 2.7$ meV (≈ 10 K). The cooling is due to superelastic collisions and is well described by theoretical rate coefficients obtained by combining the R-matrix approach with the ANR approximation, which predict the $\Delta J = -2$ coefficients to be dominant. These rate coefficients are of the order of $(1\text{–}2) \times 10^{-6}$ cm^3 s^{-1} and are thus of the same size as the vibrational ($\Delta v = -1$) SEC rates measured for H_2^+ [2]. The P_J distribution resulting after ≈ 7.5 s cooling at the highest measured electron densities corresponds to an HD^+ rotational temperature of about 125 K, which is well below the radiative equilibrium of 300 K reached only after more than 30 s of storage without electron cooling.

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