

Evidence for Subthermal Rotational Populations in Stored Molecular Ions through State-Dependent Dissociative Recombination

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We demonstrate that the dissociative recombination of D_2H^+ with low-energy electrons depends on the rotational energy of the molecular ion such that highly excited ions have a larger rate coefficient than colder ones. Observations on an ion beam continuously interacting with electrons at low relative velocity indicate that excited rotational levels are preferentially depleted which, in competition with radiative heating due to blackbody radiation, provides an opportunity for controlling the rotational temperature of stored molecules.

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Interactions of molecular ions at temperatures in the region of a few kelvin, where all rovibrationally excited states are essentially frozen out, play an important role as reaction steps in the chemical evolution of the interstellar medium [1] and other cold dilute plasmas. Among these reactions, the dissociative recombination (DR) between molecular cations and slow electrons [2] is a key process whose dependence on the internal molecular excitation has attracted particular attention [3–5]. It is hence of great interest to perform detailed single collision studies of electron interactions with molecular ions at rovibrational level populations corresponding to cryogenic temperatures (10–100 K).

Ion storage rings have proven to be efficient tools for electron-ion interaction studies at collision energies down to few meV [6]. By storage times ranging up to minutes, the vibrational excitation conditions of the interacting molecular ions could be made largely independent from their production, which is often linked with high internal excitation. In fact, radiative relaxation of stored molecular ions down to thermal equilibrium with the room-temperature environment in a magnetic storage ring has been demonstrated and followed in detailed experiments on the vibrational [7] and rotational [8] degrees of freedom. Thermal equilibrium at 300 K already yields a pure ground-state vibrational population for most ions of interstellar relevance, but it leaves a number of excited rotational states substantially populated. Lowering of the ambient temperature by cryogenic cooling has been demonstrated so far only for smaller scale electrostatic storage devices [9]. Thus, a further reduction of the rotational excitation in these experiments requires a subthermal population distribution of stored ions to be maintained in a warm (room-temperature) environment.

Here we present evidence that a subthermal rotational population distribution can be generated and maintained in a warm environment by the continuous interaction of stored molecular ions with electrons at low relative en-

ergies. The experiments use D_2H^+ ions which are shown to have a low-energy DR rate coefficient that depends significantly on their rotational state populations. The variations of the rate coefficient with the storage time and with the effective electron intensity indicate that the D_2H^+ rotational temperatures become subthermal, falling below the temperature of the ambient radiation field.

In the DR of H_3^+ and its isotopomers (such as D_2H^+) the capture of a low-energy electron initiates a fragmentation into neutral fragments. The triatomic hydrogen ion H_3^+ , and also its deuterated isotopomers, is central to the understanding of the chemical evolution of diffuse interstellar clouds [10,11]. The H_3^+ low-temperature DR rate coefficient has been one of the most controversial topics for the last 25 years, as experiments disagree by 4 orders of magnitude on its value [5], and theory is only now becoming able to provide reliable estimates [3,4]. Previous experiments performed with the ion storage ring technique [12] yielded DR rate coefficients for H_3^+ of $\sim 10^{-7}$ cm³/s for an electron temperature of 300 K, while with the afterglow technique recent experiments gave a value of $< 3 \times 10^{-9}$ cm³/s [13]. Studies performed at the storage ring TSR showed that H_3^+ ions undergo complete vibrational cooling after several seconds of storage [14] but that their rotational cooling is much slower; an average rotational excitation energy of 300 meV was measured even after 10 s of storage time [15]. In a corresponding measurement on D_2H^+ [16] the rotational excitation energy was found to be below ~ 50 meV after ~ 5 s of storage, as expected for the lower symmetry of this isotopomer (see below). More recently, evidence for the dependence of the DR rate coefficient on the rotational excitation of H_3^+ has been demonstrated at the CRYRING facility using a supersonic expansion ion source [11].

The present experiment was performed at the ion storage ring TSR located at the Max-Planck-Institut für Kernphysik in Heidelberg, Germany. A beam of D_2H^+

ions with a kinetic energy of 5.3 MeV was produced in a hot discharge ion source and injected in the TSR where it was stored and merged over 1.5 m (2.7% of the total 55.4 m circumference) with a cold electron beam, produced by the electron cooler. At matched electron and ion beam velocities, the electron current was 17.6 mA, yielding an electron density of $n_e = 1.1 \times 10^7 \text{ cm}^{-3}$ at longitudinal and transversal electron temperatures in the comoving reference frame of $kT_{\parallel} = 0.07 \text{ meV}$ and $kT_{\perp} = 12 \text{ meV}$, respectively. After injection the ions were precooled during a time $t_p \sim 5 \text{ s}$ at an electron beam energy set to match the ion velocity v_i . The collision energies are then determined essentially by the electron temperature kT_{\perp} . The time t_p is sufficient to achieve vibrational radiative relaxation, as the typical decay time of vibrationally excited D_2H^+ levels is of the order of 10 ms according to the calculated transition dipole moments [17]. Regarding the radiative decay rates of rotationally excited states within the vibrational ground state, these calculations give values of $\geq 1 \text{ s}^{-1}$ for excitation energies of $\geq 120 \text{ meV}$, in agreement with our earlier observations [16]. On the other hand, the same calculations show that the radiative rotational cooling slows down for lower excitation energies, reaching decay rates of $\leq 0.1 \text{ s}^{-1}$ at level energies of $\leq 60 \text{ meV}$ above the ground state. Hence, the D_2H^+ rotational distribution is expected to reach a blackbody-driven equilibrium at 300 K only on a time scale of several tens of seconds.

After the precooling period t_p , the electron-ion interaction energy was varied by changing the laboratory electron velocity v_e . Setting $v_e \neq v_i$ introduces a controlled kinetic energy E_d (detuning energy) in the electron-ion center-of-mass reference frame [18]. The energy E_d was switched on a ms time scale between cooling ($E_d = 0$, i.e., $v_e = v_i$), a measurement value $E_{d,m}$, and a reference energy $E_{d,r}$. To scan the energy dependence of the DR cross section, the level $E_{d,m}$ was changed for each new injection, while $E_{d,r}$ stayed fixed and was applied to perform a normalization to the ion current. The neutral fragments produced by the DR reaction were counted on an energy sensitive detector [18].

Absolute measurements of the DR rate coefficient α as a function of the electron detuning energy E_d were performed for storage time intervals of 5–15 and 30–60 s (see Fig. 1). During the precooling times of $t_p = 5 \text{ s}$ and 30 s, respectively, the electron cooler was kept permanently on cooling energy ($E_d = 0$). Afterwards, cooling was applied for 10/12 of the time and the levels $E_{d,m}$ and $E_{d,r}$ were set for time fractions of 1/12 ($\sim 25 \text{ ms}$) each. The DR rate at $E_{d,m}$ was normalized to the rate of background dissociation events measured at cooling, which was subsequently calibrated to the stored ion current with an estimated accuracy of $\pm 30\%$; together with the known electron density this provided the absolute rate coefficient scale. Remarkably, the low-energy DR rate coefficient α at $E_d < 0.15 \text{ eV}$ for short storage times (5–15 s) is larger

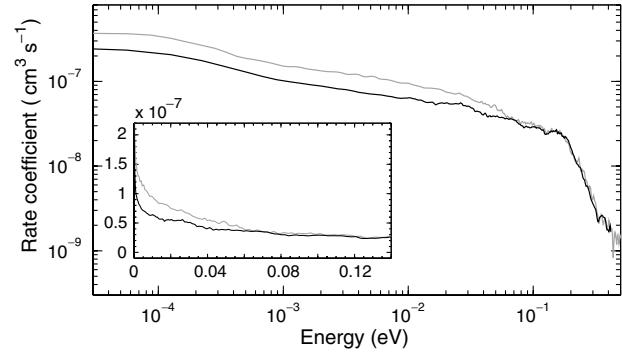


FIG. 1. Rate coefficient α for the DR of D_2H^+ as a function of electron energy E_d for two different storage time windows: $5 < t < 16 \text{ s}$ (grey) and $30 < t < 61 \text{ s}$ (black). The inset shows the low-energy range in linear scales.

than that for long storage times (30–60 s) by up to 65%. In the high energy region ($E_d > 0.15 \text{ eV}$) no storage time dependence of $\alpha(E_d)$ was found. Here, the energy dependence was similar to that observed for other triatomic hydrogen isotopomers [19]; a peak due to direct DR via a doubly excited electronic potential surface is observed close to 10 eV (not shown in Fig. 1) with a local maximum of $\alpha(E_d)$ amounting to $(1.6 \pm 0.5) \times 10^{-8} \text{ cm}^3/\text{s}$. The rate coefficient at this peak was continuously monitored during the energy scans by setting $E_{d,r} = 10 \text{ eV}$ and no variations of its size during the storage time were seen within the statistical errors ($\leq 4\%$). The only plausible explanation for the observed storage time dependence of the low-energy DR rate coefficient is that this quantity depends on the internal excitation of the D_2H^+ ions and that this excitation changes during the storage time. Considering the calculated radiative relaxation rates [17] summarized above, vibrational cooling should be already finished at all the storage times investigated here. The observed variations therefore indicate a *rotational* dependence of the low-energy D_2H^+ DR rate coefficient.

During the relevant storage times, the ions are expected to undergo the final phase of radiative cooling in the rotational degree of freedom, as discussed above, from excitation energies of $\leq 60 \text{ meV}$ down to the blackbody-driven equilibrium at 300 K. While this cooling can be one of the mechanisms behind our observations, also the continuous interaction of the stored ions with the copropagating electron beam must be taken into account. In particular, electron-impact rotational deexcitation could cause rotational cooling. This process was found to be the dominant mechanism for the vibrational cooling of stored H_2^+ and D_2^+ ions [20]. Heating and cooling by electron collisions at $E_d = 0$ would ultimately yield an equilibrium at the electron temperature T_{\perp} ($\sim 140 \text{ K}$ for the present experiment).

Changes in the population of rotational states have to be expected also from the selective depletion of states with a high DR rate. Indeed, the presence of low-energy

electrons was found to have a significant influence on the storage lifetime of the ions. While the $1/e$ decay time of the ion beam was ~ 17 s in the absence of the electron beam, this lifetime decreased to ~ 5 – 8 s, depending on the detailed conditions, when electron cooling was applied. This is in agreement with the absolute DR rate coefficients observed at low E_d which imply partial beam lifetimes against DR of 8 s for the early and 13 s for the late storage time window. Thus, the decay of the ion beam is substantially driven by the DR process, which will give rise to a change of the rotational state distribution if the DR rate coefficient α , as seen above, depends on the rotational state. In fact, the rotational states with low α will become more and more enhanced in the rotational distribution; in competition with radiative and collision-induced transitions, a new steady-state population will be established, whose effective temperature can, in principle, fall below that of the ambient radiation field ($T_{\text{br}} = 300$ K).

To shed more light on the mechanism leading to the observed time dependence of the state-averaged DR rate, the rate coefficient α at $E_d = 0$ was measured as a function of the storage time for different effective electron intensities (see Fig. 2). For this purpose the ratio \mathcal{R} between the storage time and the time spent by the ions in the electron beam at $E_d = 0$ was varied. \mathcal{R} is the product of the variable time fraction the electron beam is set to cooling energy and the spatial overlap fraction (0.027) of the electron beam. The collision energy E_d was switched on a ms time scale between zero (cooling) and $E_{d,r} = 10$ eV, where the DR rate is more than an order of magnitude smaller than at $E_d = 0$ and was found to be independent of the storage time as discussed above. The switching started after a precooling time of $t_p \sim 5$ s, where $E_d = 0$ was applied continuously. The DR count rate at 10 eV was used to normalize the measurement at $E_d = 0$, yielding again an absolute rate coefficient. In some measurements also the electron density n_e and hence the “breeding” efficiency of the electron beam as expressed by the product $\mathcal{R}n_e$ was varied.

The cooling ratio \mathcal{R} is found to have a significant effect on the time dependence and the equilibrium value of the low-energy DR rate coefficient α . For small electron breeding, \mathcal{R} was set to 0.45%, applying $E_d = 0$ for a time fraction of only $2/12$ (~ 50 ms within each switching period). In this case (open triangles in Fig. 2) the rate coefficient dropped from an initial value of $\alpha \approx 5 \times 10^{-7}$ cm³/s to an asymptotic value of $\alpha_{\text{br}} \approx 3.9 \times 10^{-7}$ cm³/s. For even smaller electron breeding, $\mathcal{R} = 0.22\%$ and 0.07% (not shown), no change of time dependence or asymptotic value was seen within the statistical uncertainty, indicating that the observed behavior of α is not due to electron interactions but rather a result of radiative thermalization. This assumption is supported by the radiative decay rates calculated in [17] (typically of order 0.03 s⁻¹), implying thermalization with the am-

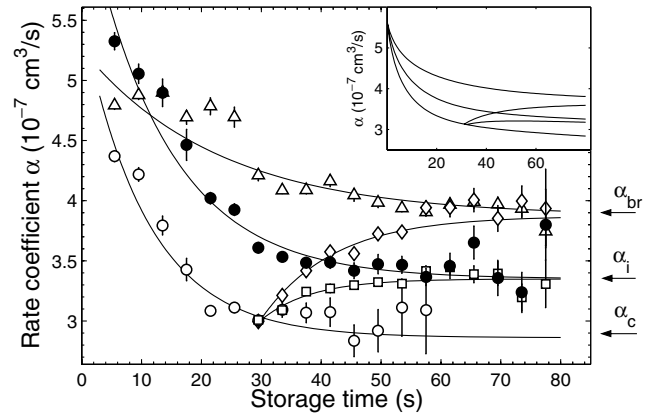


FIG. 2. DR rate coefficient α as a function of storage time and cooling ratio \mathcal{R} (see text): empty triangles: $\mathcal{R} = 0.45\%$, empty circles: $\mathcal{R} = 2.48\%$, empty diamonds: $\mathcal{R} = 0.45\%$ after 30 s of precooling, empty squares: $\mathcal{R} = 1.35\%$ after 30 s of precooling. The full circles are for $\mathcal{R} = 2.48\%$ with the electron current I_e reduced from 17.6 to 8.7 mA. The lines through the data points are to guide the eye. The inset shows the result of the model used to support our interpretation of the data (see text for details).

ambient blackbody radiation field at $T_{\text{br}} = 300$ K on a time scale of ~ 30 s. We consider that the equilibrium observed here is similar to that found in an earlier experiment [8] on CH^+ ions under comparable storage conditions, where temperatures close to $T_{\text{br}} = 300$ K were derived from rotationally resolved laser spectroscopy, demonstrating that radiative rotational cooling dominated over possible heating mechanisms such as residual gas collisions.

For the opposite case of strong electron breeding, \mathcal{R} was set to 2.48%, that is, cooling most of the time and stepping up to $E_{d,r}$ for a time fraction of $1/12$ only. This yields (open circles in Fig. 2) a much faster and stronger decrease of α , reaching now an asymptotic value of $\alpha_{\text{c}} \approx 2.9 \times 10^{-7}$ cm³/s after ~ 30 s of storage. The fact that stronger electron breeding leads to an asymptotic DR rate lower than α_{br} suggests that the rotational level populations reach a *subthermal* distribution (rotational temperature $T_c < T_{\text{br}}$) in the strong breeding case.

As an additional check we performed a measurement with a precooling time of $t_p = 30$ s in which $E_d = 0$ was applied continuously, almost equivalent to the strong breeding case; after 30 s the electron breeding was reduced by setting $\mathcal{R} = 0.45\%$. In this case (open diamonds in Fig. 2) the rate coefficient increased from a low level close to α_{c} up to $\sim \alpha_{\text{br}}$ within ~ 40 s. This suggests that the subthermal level populations can be maintained only by continuous electron interaction and that a blackbody-driven equilibrium reinstalls itself in the absence of such an interaction. The measurement also indicates that the level α_{c} is determined by an equilibrium between radiative heating and the net collisional cooling effect. Finally, intermediate electron breeding

was applied in two modes, setting $\mathcal{R} = 1.35\%$ at the full electron density n_e or $\mathcal{R} = 2.48\%$ at about half electron density ($n_e/2$). The data with ($\mathcal{R} = 2.48\%$, $n_e/2$) start at slightly higher α than the other measurements, probably because the initial electron cooling strength is reduced for the lower n_e , and then approach an intermediate level $\alpha_i \approx 3.4 \times 10^{-7} \text{ cm}^3/\text{s}$. Performing extended precooling ($E_d = 0$, full n_e continuously up to 30 s) and switching to ($\mathcal{R} = 1.35\%$, full n_e) for later storage times, we find an increase of the DR rate coefficient, in this case (within statistical errors) from α_c up to the same intermediate level α_i . Hence, intermediate electron breeding seems to be related to somewhat larger rotational temperatures T_i ($T_c < T_i < T_{\text{br}}$) as expected for an equilibrium between radiative heating and somewhat reduced collisional cooling. The fact that the same level α_i is reached despite the different time spent at the reference energy $E_{d,r}$ moreover demonstrates that electrons of 10 eV have no significant influence on the internal excitations.

To support our interpretation we have modeled the time dependence of α assuming a simple monotonous increase of the DR rate coefficient with the rotational excitation energy. The rotational levels listed in Ref. [17] were thermally populated for an initial rotational temperature of $kT_0 = 40 \text{ meV}$. The two parameters fixing a linear dependence of α on the rotational excitation energy E_{rot} were set to reproduce the measured asymptotic rate coefficient α_{br} for 300 K and to yield a value of $5.5 \times 10^{-7} \text{ cm}^3/\text{s}$ for the initial α at kT_0 (slope of $\alpha' = 0.94 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ K}^{-1}$). The level populations were obtained solving the coupled rate equations taking into account the radiative transition strengths of Ref. [17] and the selective depletion following from the assumed $\alpha(E_{\text{rot}})$. The average rate coefficients obtained from the population distributions as simulated for the various experimental procedures are shown in the inset of Fig. 2 and yield a good qualitative agreement with the observed time dependence. Electron-impact rotational (de-)excitation was not included in the model. Calculated rate coefficients exist only for H_3^+ [21] and the typical values are of the order of $1 \times 10^{-7} \text{ cm}^3/\text{s}$ for electrons at 100 K. For our conditions this corresponds to time scales of the order of $\sim 40 \text{ s}$, longer than the observed electron induced cooling time from Fig. 2. It hence appears that the (de-)excitation in electron collisions is not the main process that modifies the rotational distribution of the stored D_2H^+ ions.

In summary, our observations show a significant dependence of the low-energy DR rate coefficient of D_2H^+ ions on their rotational excitation and give strong evidence for rotational cooling of these ions by continuous interaction with electrons at meV collision energies, leading to subthermal level populations. In a general context, the control of the rotational temperature in stored ion

beams by electron collisions, in competition with black-body-driven radiative processes, is demonstrated. For radiatively inactive excitations it should be possible to manipulate the rotational temperature of stored ions considering the electrons as a thermal bath. Since advanced electron beam devices can reach beam temperatures down to 1 K, it is conceivable to cool rotations in molecular ions by electron interaction down to very low temperatures.

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