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Quantum-state-selective electron recombination studies suggest enhanced abundance of primordial HeH⁺

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The epoch of first star formation in the early universe was dominated by simple atomic and molecular species consisting mainly of two elements: hydrogen and helium. Gaining insight into this constitutive era requires thorough understanding of molecular reactivity under primordial conditions. We used a cryogenic ion storage ring combined with a merged electron beam to measure state-specific rate coefficients of dissociative recombination, a process by which electrons destroy molecular ions. We found a dramatic decrease of the electron recombination rates for the lowest rotational states of HeH⁺, compared to previous measurements at room temperature. The reduced destruction of cold HeH⁺ translates into an enhanced abundance of this primordial molecule at redshifts of first star and galaxy formation.

At the beginning of the universe, only small nuclei existed: mainly hydrogen, deuterium and helium. When temperatures lowered to ~2500 K, their recombination with electrons led to neutral atoms. Later, primordial molecules formed by radiative association and charge-exchange reactions (1): mainly H₂, HD, HeH⁺, and LiH. They are crucial for the formation of the first stars, since the collisional excitation of their rotational levels and subsequent radiative emission (2) can cool a gas cloud down to the low temperatures required for gravitational collapse. Critical for this radiative cooling is the molecular dipole moment. The dipole moment vanishes for the most abundant molecule H₂ and is only small (0.00083 D) for the isotopically asymmetric HD. But the dipole moments are large for HeH⁺ (1.66 D; HeH is unstable), HD⁺ (0.9 D), and LiH (5.98 D) (1, 3). As the relative D to He and Li to He elemental abundance ratios are ~10⁻⁴ and ~10⁻⁸, respectively, HeH⁺ moves into the focus. A number of astronomical searches for this elementary species have been unsuccessful (4, 5) before its very recent detection in a planetary nebula (6).

The underlying cosmological parameters and the outcome of Big Bang nucleosynthesis being known with great precision, uncertainties of the reaction rate coefficients are now perceived (1) as the only limitation on our understanding of primordial gas evolution. The relevant temperatures range from ~2500 K (redshift $z \sim 800$) down to ~20 K ($z \sim 6$) at the end of the cosmic reionization phase. Temperatures down to a few kelvin also apply to astrochemistry in the interstellar

medium of the contemporary universe (7); hence, molecular ions are crucial drivers of low-temperature gas-phase astrochemistry in all eras. Their abundance is often limited by dissociative recombination (DR) with electrons (8).

In this process, the ion captures a free electron while its internal degrees of freedom undergo excitation. The resulting neutral, excited compound dissociates in typically sub-pico-second times. The cross section of the exothermic DR reaction is strongly system-dependent, as possible excitation pathways – electronic, vibrational or rotational – vary. Extended studies (8–14) were performed on cold-electron reactions with HeH⁺. Ion storage rings with an internal, merged electron beam target were used (10–12) to measure DR of molecular ions at electron temperatures that reached below 20 K. These studies and related theoretical work (13–15) revealed the strong collision energy dependence of the cross section from predissociating molecular Rydberg states, formed when the colliding electron excites vibrations and rotations of the ion core. Despite the expected strong influence of rotational excitation, all measurements so far (9–12) were performed for HeH⁺ dominantly in excited rotational levels: through the molecular dipole moment, thermal equilibrium with the black-body radiation in the beam enclosure led to a rotational temperature of ~300 K. The present experiment, using a cryogenic ion storage ring, can finally address this rotational dependence.

Our measurements are performed in the recently completed electrostatic cryogenic ion storage ring CSR (16) at the

Max Planck Institute for Nuclear Physics, Heidelberg, Germany. Its vacuum chamber walls and all beam-guiding electrodes are cooled to ~ 6 K. HeH^+ ions from a discharge ion source are accelerated to 250 keV and injected into the cryogenic ring with four bending corners and interjacent linear sections (Fig. 1). The ions, circulating collision-free for hundreds of seconds (16–18), are merged in one of the linear sections with a quasi-monoenergetic electron beam with the same or a slightly detuned velocity (electron energy $E_0 = 27.32 \pm 0.06$ eV (SEM) at matched velocities). DR in the ~ 1 m long overlap region leads to neutral H and He atoms that separate from the electrostatically deflected ions and impinge on a position-sensitive, multi-hit counting detector (19). At the electron beam energy $E_e = E_0$ the HeH^+ ions collide with electrons of thermal energy spread (~ 2 meV). Choosing, however, $E_e > E_0$ the collision energy is detuned to $E_d = (E_e^{1/2} - E_0^{1/2})^2$ and easily variable. This yields (19) the energy-dependent DR rate coefficient $\alpha_{\text{DR}}(E_d)$.

As demonstrated recently (17, 18) rotationally excited hydride ions stored in the CSR relax by spontaneous emission of infrared photons along the energy ladder $E_J = BJ(J+1)$ in steps of $J \rightarrow J-1$, where J is the angular momentum quantum number and B is the rotational constant. For HeH^+ $B/k_B = 48.2$ K (k_B being the Boltzmann constant). From a comprehensive line list (2) we set up a radiative model for the HeH^+ rotational level populations as functions of ion storage time t . The radiation field in CSR is approximated by two components, 99% of the spectral energy density at the molecular transitions representing the 6 K wall temperature, and 1% of it representing inevitable radiation leaks from the outer (300 K) environment (19). In such conditions the population of the HeH^+ $J = 0$ level at equilibrium ($t \gg 10$ s) is 92%. In the earlier room-temperature studies (9–12) of HeH^+ , the equilibrium population was only $\sim 15\%$ for $J = 0$, with higher J levels populated much stronger (Fig. 1).

In the CSR, $>50\%$ population in $J = 0$ is reached at $t > 8$ s of storage. Vibrational excitation (v) relaxes much faster; similar to the previous storage-ring work (10–12), pure $v = 0$ population is ensured already for $t > 0.1$ s. The CSR result for the energy-dependent DR rate coefficient $\alpha_{\text{DR}}(E_d)$ at $10 \text{ s} < t < 50 \text{ s}$ is compared with the previous storage-ring results in Fig. 2, thus displaying the effect of reducing the rotational excitation. At 20% uncertainty in the overall scaling of our data, there are minor deviations between the CSR data and previous storage-ring results between ~ 0.07 and 1 eV. Strong deviations, however, occur at lower energies. For the rotationally cold ions, the DR rate first assumes a sharp resonant maximum at $E_d \sim 0.044$ eV ($E_d/k_B \sim 530$ K). Below

$E_d \sim 0.02$ eV ($E_d/k_B \sim 260$ K) the DR rate becomes much smaller (by a factor up to ~ 8) than for room-temperature and remains almost that low down to $E_d \sim 0.001$ eV ($E_d/k_B \sim 12$ K).

Significant rotational dependence for predissociating Rydberg resonances has been predicted (14, 15) for $\alpha_{\text{DR}}(E_d)$ in this energy range. We studied this through the storage-time dependence of the DR rate coefficient, $\alpha_{\text{DR}}(E_d, t)$. The rotational populations from the radiative cooling model reveal how the J -distribution is dominated by lower and lower levels as the storage time advances (Fig. 3A). The $\alpha_{\text{DR}}(E_d, t)$ data were analyzed in time slices adapted to some of the lower J (time slices I to IV for $J = 3$ to 0, see Fig. 3B). While in slice I the DR rate at low collision energies is similar to the room-temperature results, this level decreases as the ions cool rotationally. Moreover, later slices with dominating $J = 2$ or 1, respectively, indicate energy-shifted resonances below the strong peak of time slice IV.

All time-varying DR rates represent linear combinations of the time-invariant DR rates $\alpha_{\text{DR}}^J(E_d)$ for individual J levels, weighted by the average relative level populations in the various time slices. Using the data for 8 separate intervals between 0.1 and 45 s and the respective average level populations from the radiative model, we deduced (19) state-resolved rate coefficients $\alpha_{\text{DR}}^J(E_d)$ up to $J = 2$ and the average DR rate from the $J \geq 3$ levels contributing at early storage times (mainly $J = 3$ and 4). These data (Fig. 4A) show the dominance of a single near-Lorentzian peak for $J = 0$. Similar peaks with maxima downshifted in E_d are seen for $J \geq 1$, where an increase of the width points to unresolved peak structure. Moreover, starting from $J = 2$ the rate at $E_d < 0.01$ eV grows. Recent theory, such as figure 13a of Ref. (14), predicts a similar J -dependent peak structure at $\sim 0.01 - 0.07$ eV, but up to $10\times$ higher rates than the experiment at lower energy, especially for $J = 0$.

These energy and state resolved DR rates enable us to derive plasma rate coefficients for individual J s or fully thermal ensembles. We deconvolved (19, 20) the merged-beams DR rate coefficients $\alpha_{\text{DR}}^J(E_d)$ to yield DR cross sections in narrow energy bins. Subsequently we re-convolved these J -specific cross sections to obtain plasma rate coefficients $\alpha_{\text{DR,pl}}^J(T_{\text{pl}})$ (see Fig. 4B) for Maxwellian electron energy distributions of kinetic temperature T_{pl} . These results can be state-population weighted to obtain a rate coefficient for specified rotational temperatures T_{rot} or even for fully thermalized conditions, see $\alpha_{\text{DR,therm}}(T_{\text{rot}} = T_{\text{pl}})$ in Fig. 4B. Our results for $J = 0$ and $J = 1$ at < 80 K are factors of 15 to 80 lower

than the values (19) presently applied in early-universe models (21, 22) and those listed in astrochemistry databases (23–25). Compared with these previous data, even the enhanced $J = 2$ and $J \geq 3$ average rates are lower.

A recent study (22) (Fig. 2) shows that at redshifts $z < 15$ the only reactions essential for the abundance of HeH^+ are radiative association of H^+ and He for production and DR for destruction. Hence, the HeH^+ abundance from model calculations is inversely proportional to the applied DR rate coefficient. At these redshifts radiation temperature $T \sim 40$ K requires the $J \leq 1$ levels to dominate, while the gas temperature is $T_{\text{pl}} \leq 10$ K (26). Comparing for $T_{\text{pl}} = 10$ K the DR rate used by Ref. (22) with our $J = 0$ and $J = 1$ rates, population-averaged for $T = 40$ K, the estimated peak HeH^+ abundance at $z \sim 15$ increases by a factor of at least 20 above the previously calculated value (22) (Fig. 4). This strengthens the role of HeH^+ as a potential coolant in primordial star formation and also increases the chance to observe HeH^+ from the post-recombination era at low redshifts. Furthermore, higher abundance predictions for HeH^+ call for reinvestigating its role in smearing out the cosmic microwave background (27). For the HeH^+ observation in planetary nebula (6) high kinetic temperatures of $T_{\text{pl}} \approx 10^4$ K are relevant. The absolute HeH^+ DR rate of $3.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ used to interpret that observation (6) is compatible with our findings (19).

Considering the importance of resonant processes, our energy- and state-selective rate coefficients $\alpha_{\text{DR}}^J(E_d)$ offer a particularly clean, so far unavailable view on the mechanism of low-energy DR. We analyzed the emission velocities of the He and H fragments at the prominent resonance at 0.044 eV, using the position resolution of our coincidence detector, and compared it to the $E_d = 0$ behavior. Distributions $P(D)$ of the fragment distances D projected into the detector plane (Fig. 2, B and C) reflect the energy and the angular characteristic of the H and He atoms emitted in a DR reaction (19). For both E_d , the endpoints of $P(D)$ at $D \sim 27$ mm indicate an emission energy near 1.55 eV and confirm the well-known (28) fragmentation pathway into the atomic states 1^1S (ground state) for He and $n = 2$ for H . The shapes of $P(D)$, however, reveal different angular characteristics. At $E_d = 0$ (Fig. 2B) there is no distinct electron impact direction and the fragments are emitted isotropically. In contrast, at $E_d = 0.044$ eV (Fig. 2C) the collision direction is aligned with the beam axis and the data reveal a pure low-order multipole ($|Y_{10}|^2$) around this axis for the fragment directions. Based on the well-established axial-recoil approximation (29) this pure low-order multipole also applies to the DR cross section with respect to the internuclear axis, and (30) to the electron partial wave that drives the DR process. We find the DR resonance of $J = 0$ HeH^+ ions at 0.044 eV to be mostly driven by an electronic

partial wave with angular and magnetic quantum numbers $l = 1$, $m = 0$ (p_σ symmetry), whose importance was raised theoretically (15).

Our new accurate rate coefficient measurements consolidate the gas phase chemical data on HeH^+ that govern its abundance in the post-recombination era of the early universe. Moreover, the ability to obtain state-selective laboratory data for fundamental molecular reactions comes particularly timely, considering the imminent launch of the James Webb Space Telescope (31). Its search for the first luminous objects and galaxies after the Big Bang will benefit greatly from reliable predictions on early universe chemistry. Our data show that the rotational excitation can make a dramatic difference in low temperature reaction rates of small molecules.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Figs. S1 and S2
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Fig. 1. Dissociative recombination in the cryogenic storage ring CSR. (A) Scheme of the CSR ring structure with injected and stored HeH⁺ ion beam (red), merged electron beam (blue), reaction products (green) and particle detector. (B) Reaction scheme and position-sensitive detection of coincident fragments. (C) Equilibrium rotational state populations of HeH⁺ for previous studies (300 K) and the estimated radiation field in the CSR.

Fig. 2. DR for rotationally cold HeH⁺. (A) Blue dots: merged-beams rate coefficient α_{DR} as a function of the detuning energy E_d after relaxation to $>50\%$ $J = 0$ (this experiment, $10 \text{ s} < t < 50 \text{ s}$, mean $\pm$ SD); absolute scaling uncertainty $\pm 20\%$ (SEM). Red symbols: room-temperature data from Ref. (11) (squares, absolute scaling uncertainty $\pm 10\%$ SEM) and from Ref. (12) (triangles, scaled to Ref. (11) at 0.03 eV). (B) Fragment distance distribution projected into the detector plane for $E_d = 0$ (blue) with fit (19) for isotropic angular distribution (red). (C) Projected fragment distance distribution for $E_d = 0.044 \text{ eV}$ (blue) with fit (19) for a $|Y_{10}|^2$ angular distribution of the fragments (red). The angular dependences in (B) and (C) are indicated schematically.

Fig. 3. DR during the rotational relaxation of HeH^+ . (A) Relative rotational level populations as functions of ion storage time t from the radiative model (starting temperature: 3000 K; CSR radiation field: 99% at 6 K, 1% at 300K) for J as given and with time slices I–IV in which the dominant J varies from 3 to 0. (B) Rate coefficient $\alpha_{\text{DR}}(E_d)$ measured in the marked time slices (mean $\pm$ SD).

Fig. 4. Rotational-state selective DR rates for HeH^+ . (A) Merged-beams rate coefficients $\alpha_{\text{DR}}^J(E_d)$ for $J \leq 2$ and average for $J \geq 3$ (mainly 3 and 4; mean $\pm$ SD). The dashed lines mark the shift of the maximum as J increases. (B) Full lines: single- J plasma rate coefficients $\alpha_{\text{DR,pl}}^J(T_{\text{pl}})$ for $J \leq 2$ and average for $J \geq 3$ (mainly 3 and 4; mean with shaded areas as $\pm$ SD). Dotted: fully thermal rate coefficient $\alpha_{\text{DR,therm}}(T_{\text{rot}} = T_{\text{pl}})$. Dashed-dotted: values applied in early-universe models (21, 22) and astrochemistry databases (23–25). See (19) for further discussion, numerical fitting functions and parameters.