Dissociative recombination of highly enriched para-H$_3^+$

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The determination of the dissociative recombination rate coefficient of H$_3^+$ has had a turbulent history, but both experiment and theory have recently converged to a common value. Despite this convergence, it has not been clear if there should be a difference between the rate coefficients for ortho-H$_3^+$ and para-H$_3^+$. A difference has been predicted theoretically and could conceivably impact the ortho:para ratio of H$_3^+$ in the diffuse interstellar medium, where H$_3^+$ has been widely observed. We present the results of an experiment at the CRYRING ion storage ring in which we investigated the dissociative recombination of highly enriched ($\sim$83.6%) para-H$_3^+$ using a supersonic expansion source that produced ions with $T_{rot} \sim 60–100$ K. We observed an increase in the low energy recombination rate coefficient of the enriched para-H$_3^+$ by a factor of $\sim 1.25$ in comparison to H$_3^+$ produced from normal H$_2$ (ortho:para = 3:1). The ratio of the rate coefficients of pure para-H$_3^+$ to that of pure ortho-H$_3^+$ is inferred to be $\sim 2$ at low collision energies; the corresponding ratio of the thermal rate coefficients is $\sim 1.5$ at electron temperatures from 60 to 1000 K. We conclude that this difference is unlikely to have an impact on the interstellar ortho:para ratio of H$_3^+$. © 2009 American Institute of Physics. [DOI: 10.1063/1.3065970]

H$_3^+$, the simplest polyatomic molecule, plays a central role in the chemistry of the interstellar medium because it easily protonates most atoms and molecules.¹,² Consequently, understanding the formation and destruction pathways for this molecular ion under astrophysical conditions is of great importance. Dissociative recombination (DR), the recombination of molecular ions with electrons that leads to dissociation into neutral fragments, is the primary mechanism by which H$_3^+$ is destroyed in diffuse interstellar clouds.³ The search for the H$_3^+$ DR rate coefficient has had a somewhat turbulent history, with values that varied by orders of magnitude.⁴,⁵ The measurement of rotationally cold H$_3^+$ at CRYRING in 2002,⁶ together with complete dimensionality quantum mechanical calculations,⁷ has finally brought some level of closure to the debate. In fact, the CRYRING data were recently used to observationally determine the cosmic ray ionization rate in diffuse clouds.⁸ Theory,⁷ also predicted that ground-state ortho-H$_3^+$ recombines faster than the ground state of para-H$_3^+$ at low collision energies. To probe this difference, Kreckel et al.⁹ studied H$_3^+$ produced from both normal and highly enriched para-H$_2$, and found that para-H$_3^+$ had a higher DR rate coefficient (although the exact ortho:para ratio of H$_3^+$ in their source is unknown). A subsequent theoretical refinement¹⁰ was consistent with this observation. Unfortunately, recent experiments performed at TSR have not been able to replicate this difference.¹¹ Confirming and characterizing the difference in the DR rate coefficients of ortho- and para-H$_3^+$ are of great importance, not only because of the impact such knowledge can have on our ability to more precisely model astrophysical processes but also because of the basic physical insight we can gain regarding this simple yet pivotal molecular ion.

In the present experiment, the DR of highly enriched para-H$_3^+$ was studied at the CRYRING ion storage ring using a pulsed supersonic expansion ion source. This approach was motivated by the spin selection rules derived by Quack¹² and Oka,¹³ which imply that para-H$_3^+$ reacting with para-H$_2$ can only form para-H$_3^+$. We sought to enrich the fraction of para-H$_3^+$ as much as possible and furthermore to precisely measure this fraction in order to characterize the rate coefficient difference between ortho- and para-H$_3^+$.

An enriched >99.9% para-H$_2$ gas was produced using a modified closed-cycle ⁴He cryostat. The enrichment of the para-H$_2$ gas was measured using thermal conductivity¹⁴,¹⁵ and NMR. The gas was shipped to the experimental facility at the Manne Siegbahn Laboratory at Stockholm University in a Teflon-lined sample vessel. Tests indicated that the highly enriched para-H$_2$ gas stored in this vessel converted back to ortho-H$_2$ at a rate of $\sim 1.7$% per week. Therefore, the gas was ≥97% enriched in para-H$_2$ at the time of the experimental runs.

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The design and operation of the source have been covered in detail elsewhere.\textsuperscript{6} In short, the gas emerging from the source pinhole underwent collisional cooling in a supersonic expansion, and was ionized when passing an electrode held at approximately $-350$ V. About 1500 Torr of backing pressure was used to feed the source, which was pulsed for 400–800 $\mu$s. The source was spectroscopically characterized at the University of Illinois before and after the experiment at CRYRING. This was done in order to verify that our test gas and source conditions produced a plasma that was highly enriched in para-H$^3$, and at rotationally cold temperatures. We used continuous-wave (CW) cavity ring-down spectroscopy with a difference frequency laser to probe the ortho-H$^3$ $R(1,0)$ and the para-H$^3$ $R(1,1)^\alpha$ ground-state rovibrational transitions near 3.67 $\mu$m. Details regarding the difference frequency laser, the integration of the pulsed source with CW ring-down, as well as the source characterization itself will be presented elsewhere. The measured fraction of para-H$^3$ was $\sim$49.1% for normal H$_2$ and $\sim$74.7% for 97% para-H$_2$ enriched samples. Because we were seeking the highest fraction of para-H$^3$ possible, we experimented with dilutions in argon to reduce the number of H$_2^+ +$H$_2$ collisions, thereby reducing back-conversion from para- to ortho-H$^3$ in the plasma (see Ref. 16). We obtained the highest enrichment using a 1% dilution of para-enriched hydrogen in argon (by pressure), with a para-H$_2^+$ fraction of $\sim$83.6%. The rotational temperature of the ions was measured to be $\sim60$–100 K for all enrichments and dilutions.

Details regarding the experimental method at CRYRING are thoroughly discussed in Ref. 6 but a brief description is provided here for continuity. After exiting the source, the H$_2^+$ ions were mass selected, focused through ion optics floated at 30 kV, accelerated to 900 keV using a radio frequency quadrupole, and finally injected into the ring and accelerated to 13 MeV. The ions, having been rotationally cooled in the expansion, were stored in the ring for up to 5.6 s to allow vibrational relaxation to occur. During this relaxation period, the ions periodically passed through an electron cooler where they interacted with electrons at velocity matching conditions, leading to the translational cooling of the ions. As such, the electron cooler served the dual purpose of reducing the energy distribution of the ions, as well as providing a location where the DR could occur. The electron cooler cathode voltage was linearly ramped from 2965 to 1892 V over a 1 s interval, which covered the interaction energy range from $\sim0$ to $\sim30$ eV. The neutral DR products, no longer subject to the magnetic forces of the ring’s bending magnets, emerged tangentially from the ring and were counted by an ion-implanted silicon detector. Measurements were taken such that the rate coefficient, $\alpha_{\text{DR}}$, was measured as a function of the detuning energy, $E_d$, defined as the electron energy in the ion frame not including the electron thermal spread. The background contribution, originating from the interaction of the ion beam with residual gas in the ring, was corrected by subtracting counts until the relative difference between the trough centered at 2 eV and the peak at 10 eV was the same as that observed in the 2002 data. It is worth noting that this correction did not affect the rate coefficients at small interaction energies because of the magnitude of the DR signal in these regimes. In addition, the measured rate coefficients were corrected for the space charge of the electrons and the noncoaxial nature of the beams in the toroidal regions of the electron cooler.\textsuperscript{17,18}

We performed three experiments using three different sample gases. The first experiment used the 1% dilution of enriched para-H$_2$ in argon. The second experiment was run with normal H$_2$ gas in order to compare the performance of both the supersonic expansion source and the storage ring with the results from Ref. 6. The final experimental measurements were taken using the enriched para-H$_2$ with no argon dilution. The respective ion currents after acceleration were 8.16, 54, and 48 nA.

The results of these three runs are presented in Fig. 1(a). We do not include systematic uncertainty ($\sim16\%$) in our analysis because it did not change from experiment to experiment, and our focus is on the differences between the measurements. It is evident that the DR rate coefficient has a dependence on the spin modification of H$_2^+$. We observed the enriched para-H$_2^+$ produced from 97% para-H$_2$ to have a higher rate coefficient than that of the normal-H$_2$ at small $E_d$. The differences continue up to $\sim100$ meV, with a region of much smaller differences centered around 6 meV. The measurement using argon-diluted para-H$_2$, with a para-H$_2^+$ fraction of $\sim83.6\%$, shows a slight increase over that of the undiluted para-H$_2$ sample. Figure 1(b) shows the extrapolated rate coefficients for hypothetical pure ortho- and para-H$_2^+$ derived using the 83.6% and 49.1% para-H$_2^+$ results. The same extrapolated rate coefficients can be derived using the data from the 74.7% para-H$_2^+$ experiment.

The 2007 rate coefficients for normal hydrogen were larger for all $E_d$ than observed in the 2002 data, which might be due to inaccuracies in the ion current measurement during our experiment. Great care was taken in making the ring current measurements for the 2002 run. Consequently, we multiplied our data by a normalization factor of 0.65 which was based on a comparison of the 10 eV peak heights of the 2007 and 2002 experiments. Our objective was to observe relative differences in the DR rate between para-enriched H$_2^+$ and less enriched para-H$_2^+$ samples; therefore, the consistent

![Graph](image-url)
application of a multiplication factor to all of our data does not detract from our conclusions. A comparison with past experiments is presented in Fig. 2, and most structures above $10^{-2}$ eV are in good agreement.

The 2007 spectrum is structurally smoother below $10^{-2}$ eV compared with the 2002 data. The rate coefficient curve at low electron energy could show less structure due to the presence of rotationally hotter ions. The indirect DR mechanism, proceeding through intermediate Rydberg states, gives rise to resonant structure in the rate coefficient. An increase in the population of excited rotational states will increase the number of resonances, resulting in a smoother curve.

Our supersonic expansion source produced ions with $T_{rot} \sim 60–100$ K based on the spectroscopic characterization, which was slightly higher than the value of 20–60 K obtained with the same source in 2002. Perhaps this higher $T_{rot}$ combined with heating due to interactions with residual neutral molecules in the ring, led to the observed lack of structure in the cross section. That being said, experiments at TSR demonstrated that residual gas heating does not raise $T_{rot}$ by more than 100–200 K. It is important to note that although some excited rotational states may have contributed to our measurement, these states retain the para-to-ortho-$H_3^+$ distribution as measured spectroscopically; therefore, the comparison between DR reaction rate coefficients remains valid. Para-$H_3^+$ cannot be converted to ortho-$H_3^+$ by reactive collisions in the ring, as the only likely spin-changing reaction with residual $H_2$ molecules at these high collision energies is a proton hop. Any $H_3^+$ ions formed by this process would not be at an energy that could circulate in the ring and contribute to the measurement. Additionally, we determined that the uneven depletion of spin modifications due to the different rate coefficients would not significantly affect the ortho/para ratio over our storage timescales.

The thermal rate coefficients, $\alpha(T_e)$, were calculated by integrating the energy dependent DR cross section over a Maxwellian distribution of electrons (see Ref. 6) at a given electron temperature, $T_e$. To derive the absolute cross section from the measured rate coefficient, the deconvolution procedure described in Ref. 20 was used. Table I presents the values of $\alpha(T_e)$, normalized as described above. The thermal rate coefficient at 300 K for normal $H_2$ (49.1% para-$H_3^+$) of the current experiment is in excellent agreement with that of 2002; however, the higher $T_{rot}$ described earlier likely resulted in less agreement at lower electron temperatures [Fig. 3(a)]. Figure 3(b) shows the extrapolated values for 100% para-$H_3^+$ and 100% ortho-$H_3^+$.

Both the $E_e$-dependent rate coefficients and the thermal rate coefficients indicate that the DR of $H_3^+$ has a nuclear spin state dependence, with that of the para spin modification proceeding at a more rapid rate. The para-$H_3^+$ has a rate coefficient almost two times larger than ortho-$H_3^+$ at low electron temperatures, with a smaller difference (~1.5) at higher temperatures. Theory predicts differences that range from more than a factor of 10 down to unity between electron temperatures of ~0 and 300 K.

The relatively modest (by astrophysical standards) difference in the rate coefficients of ortho- and para-$H_3^+$ sug-

![FIG. 2. (Color online)](image)

Comparison of the normal H$_2$-fed H$_3^+$ DR rate coefficients using the supersonic expansion source in 2007 and 2002; both experiments were performed with a transverse electron thermal spread $(kT_{e,z})$ of 2 meV. Also included is a spectrum from TSR using the thermal cathode electron target with $kT_{e,z}=4$ meV (Ref. 9). Uncertainty bars are removed to facilitate comparison of 2002 and 2007 spectra.

![TABLE I. Thermal rate coefficients, $\alpha(T_e)$, measured in the current experiment for $T_{rot}=80\pm20$ K and $T_e=300$ K. These data are derived from the measured rate coefficients, normalized to the 2002 data by a factor of 0.65. The $\alpha(T_e)$ for $n$-$H_3$ is in good agreement with Ref. 6, $0.68\times10^{-7}$ cm$^3$ s$^{-1}$.](image)

<table>
<thead>
<tr>
<th>% para-$H_2$ feed</th>
<th>% para-$H_3^+$</th>
<th>$\alpha(T_e)$ ($10^{-7}$ cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\cdots$</td>
<td>0</td>
<td>5.52±0.77</td>
</tr>
<tr>
<td>25.0 (normal-$H_2$)</td>
<td>49.1±2.4</td>
<td>6.79±0.14</td>
</tr>
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<td>97.0±0.8</td>
<td>74.7±2.1</td>
<td>7.48±0.10</td>
</tr>
<tr>
<td>97.0±0.8 (Ar dilution)</td>
<td>83.6±1.9</td>
<td>7.65±0.16</td>
</tr>
<tr>
<td>$\cdots$</td>
<td>100</td>
<td>8.12±0.36</td>
</tr>
</tbody>
</table>

Spectroscopically determined after CRYRING measurements. Reported errors are 1σ.

Uncertainty is statistical.

Extrapolated values for pure ortho- and para-$H_3^+$.

![FIG. 3. (Color online)](image)

Thermal rate coefficients calculated for (a) normal $H_2$ (49.1% para-$H_3^+$) and for (b) the extrapolated 100% ortho- and para-$H_3^+$ results. Uncertainties are statistical. The dashed line represents the ratio of the thermal rate coefficients (para-$H_3^+/\text{ortho-}H_3^+$), with an arrow directing the reader to the appropriate axis.
suggests that DR is unlikely to be the dominant process in determining the ortho:para ratio of H$_3^+$ in the diffuse interstellar medium. An even more convincing argument is the fact that para-H$_3^+$ is more abundant than ortho-H$_3^+$ in diffuse clouds; yet we observe that para-H$_3^+$ has the higher DR rate coefficient. It is likely that the explanation for the interstellar ortho:para-H$_3^+$ ratio lies instead with the proton exchange reaction H$_3^+$ + H$_2$ → H$_2$ + H$_3^+$. Although this reaction has a rate coefficient roughly two orders of magnitude lower than DR, the reaction partner (H$_2$) is some four orders of magnitude more abundant than electrons in diffuse clouds.

Preparations are underway to refine our supersonic expansion source design in order to consistently achieve rotationally colder ions. In addition, work is scheduled at CRYRING to minimize residual gas heating so we can better observe structural details in the DR cross section. Together, these improvements should permit a more definitive measurement of the absolute $\alpha_{DR}$ for highly enriched para-H$_3^+$.

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