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The Ortho:para Ratio of H_3^+ in Laboratory and Astrophysical Plasmas

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Abstract. The discovery of H_3^+ in the diffuse interstellar medium has dramatically changed our view of the cosmic-ray ionization rate in diffuse molecular clouds. However, another surprise has been that the ortho:para ratio of H_3^+ in these clouds is inconsistent with the temperature derived from the excitation of H_2 , the dominant species in these clouds.

In an effort to understand this discrepancy, we have embarked on an experimental program to measure the nuclear spin dependence of the dissociative electron recombination rate of H_3^+ using the CRYRING and TSR ion storage rings. We have also performed the first measurements of the reaction $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_3^+$ below room temperature. This reaction is likely the most common bimolecular reaction in the universe, and plays an important role in interconverting ortho- and para- H_3^+ .

Finally, we have constructed a steady-state chemical model for diffuse clouds, which takes into account the spin-dependence of the formation of H_3^+ , its electron recombination, and its reaction with H_2 . We find that the ortho:para ratio of H_3^+ in diffuse clouds is likely governed by a competition between dissociative recombination and thermalization by reactive collisions.

Keywords: Interstellar Medium; Laboratory Plasmas; Nuclear Spin Modifications

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INTRODUCTION

The H_3^+ molecular ion is the cornerstone of interstellar chemistry. Because of the low proton affinity of H_2 , H_3^+ serves as a universal proton donor (“acid”), donating its extra proton to just about any atom or molecule it collides with. This initiates a network of ion-molecule reactions [1, 2] that is responsible for the formation of many of the ~ 150 known interstellar molecules [3]. H_3^+ was first detected in the interstellar medium in 1996 by Geballe and Oka [4] in two dense molecular clouds, thereby confirming this general picture of interstellar chemistry. However, it was quite a surprise when H_3^+ was subsequently discovered to be abundant in the diffuse interstellar medium towards Cygnus OB2 12 [5]. At first, many in the community suspected that this sightline did not actually consist of diffuse clouds, but the subsequent discovery of abundant H_3^+ towards ζ Persei [6] and in a large sample of diffuse clouds across the Galactic disk [7] demonstrated the ubiquity of H_3^+ in classical diffuse clouds. This high abundance is now understood to be the result of a large, previously unrecognized, flux of low-energy cosmic rays [8], which may be produced by supernova remnants such as IC 443 [9].

However, the subject of this contribution is not the abundance of H_3^+ , but rather the relative population of the ortho ($I = \frac{3}{2}$) and para ($I = \frac{1}{2}$) nuclear spin modifications. Much like H_2 , these two spin modifications are essentially different chemical species, as they cannot be interconverted by radiative or non-reactive processes. These spin modifications are rigorously linked by symmetry to the rotational states: ortho states have $K = 0 \pmod{3}$ and para have $K \neq 0 \pmod{3}$, where K is the projection of the rotational angular momentum onto the molecular symmetry axis. Consequently astronomical observations of absorption lines arising from the two lowest rotational states [$J = 1, K = 0$ (ortho) and $J = 1, K = 1$ (para)] directly probe the ortho:para ratio of H_3^+ . If the energy gap between these two levels is combined with the relative population to infer an excitation temperature, this excitation temperature is considerably lower than the kinetic temperature of the clouds, which is known from UV measurements of H_2 . [In diffuse clouds, the nuclear spin modifications of H_2 are thermalized by collisions with protons.]

In an effort to understand the non-thermal ortho:para ratio of H_3^+ in diffuse clouds, we have undertaken laboratory measurements probing the nuclear spin dependence of the dissociative recombination of H_3^+ with electrons, as well as the spin-changing chemical reaction of H_3^+ with H_2 . We have also developed a steady-state model of diffuse clouds that incorporates these two processes, along with H_3^+ formation. The following sections briefly describe these efforts.

H_3^+ DISSOCIATIVE RECOMBINATION

Theoretical calculations have predicted an order of magnitude difference in the rate coefficient of dissociative recombination (DR) of ortho- and para- H_3^+ [10]. If this prediction were correct, it would presumably have a significant effect on the ortho:para ratio of H_3^+ in diffuse clouds, where DR is the dominant destruction mechanism for this ion. Pioneering measurements using a 22-pole ion trap at the Test Storage Ring (TSR) in Heidelberg [11] revealed a small but measurable difference in the DR rate of samples of H_3^+ produced from normal H_2 (ortho:para=3:1) and from enriched para- H_2 ; however, in these experiments it was not possible to determine the ortho:para ratio of the H_3^+ .

Over the past several years, our group has been performing DR measurements using supersonic expansion discharge sources, which produce a sufficiently large number density of H_3^+ ions that their ortho:para ratio can be measured spectroscopically. In our lab at Illinois, we have developed widely tunable cw mid-infrared lasers by combining two visible or near-infrared lasers in a periodically poled lithium niobate (PPLN) crystal, which generates the difference frequency between the two lasers. Our first system combined a 1064 nm Nd:YAG laser with a tunable Ti:Sapphire laser; our second uses a 532 nm doubled Nd:YVO₄ laser and a tunable dye laser. In either case, we generate a fraction of a mW of radiation near 3.6 μm , and use this to perform “cw” cavity ringdown spectroscopy of our pulsed expansion discharge sources.

Our first effort utilized a source based on a solenoid valve, which was fed with either normal H_2 or nearly pure para- H_2 , generated in a home-made converter [12]. After spectroscopic characterization [13], this source was used for DR measurements at the CRYRING storage ring at the Manne Siegbahn Laboratory in Stockholm [14]. These experiments suggested a difference of only about a factor of two in the low-energy cross-section between ortho- and para- H_3^+ , but suffered from two drawbacks. First, the solenoid source was somewhat erratic in its behavior, leading to some worries about the temperature of the extracted ions. Second, the storage ring (which was subsequently decommissioned) may have suffered from a loss of energy resolution, as structure that had previously been observed in the cross section was no longer present in these measurements.

Recently, we have constructed a new source based on a piezoelectric valve, which is vastly better in terms of the consistency of its pulses. We have spectroscopically characterized the H_3^+ produced by this source, and then performed very high resolution DR measurements at the TSR in Heidelberg. These results [15] are largely consistent with the CRYRING measurements, but reveal a rich structure in the spin-dependent cross sections. At particular collision energies (e.g., 0.02 eV), there is nearly an order of magnitude difference between the DR cross section of ortho- and para- H_3^+ . However, overall the difference is modest; generally no more than about a factor of two. Furthermore, the DR cross section of para- H_3^+ is higher than that of ortho- H_3^+ , which clearly cannot explain the overabundance of para- H_3^+ in diffuse clouds. Obviously, some other effect must also be at play.

It should also be mentioned that the kinetic energy release of the DR fragments was measured at TSR, and these measurements suggest that the H_3^+ ions in the ring are considerably warmer than was measured spectroscopically near the nozzle of the ion source. We suspect that stray fields in the expansion region are accelerating the ions, inducing collisions with H_2 at energies of ~ 1 eV, which could rotationally excite the ions. Future experiments will aim to eliminate these fields in the expansion region, thereby enabling what will likely be the first measurements of truly rotationally cold H_3^+ ions.

CHEMICAL REACTION OF H_3^+ WITH H_2

Another process that should influence the ortho:para ratio of interstellar H_3^+ is the chemical reaction between H_3^+ and H_2 . Although the products of this reaction are also H_3^+ and H_2 , it is a chemical reaction because bonds can be broken and reformed, leading to a change in the nuclear spin modifications. This process is of fundamental importance, as it represents the simplest bimolecular reaction involving a polyatomic molecule; it is also the most common bimolecular reaction in the universe, occurring $\sim 10^{52}$ times per second in our galaxy alone.

This reaction has three possible outcomes. First, the protons may come out of the collision complex (H_5^+)* in the same sense that they entered it; we refer to this as the identity reaction. Second, it may appear that a proton has hopped from the reactant H_3^+ to the H_2 ; we call this the “proton hop,” and it has a statistical weight of 3 as there are 3 protons that can hop. Third, it may appear that protons have exchanged between the two reactants; this is called the “exchange,” and has a weight of $3 \times 2 = 6$. A major question surrounding this reaction is what is the branching ratio between the hop and the exchange, which we refer to as α . If the process were purely statistical (with complete scrambling of protons in the collision complex), one would expect $\alpha = 0.5$.

It is possible to study this reaction using spectroscopy because these different outcomes must obey selection rules based on the nuclear spin angular momentum [16]. For example, a reaction between para- H_3^+ and ortho- H_3^+ can only produce ortho- H_3^+ via the exchange channel. The first such measurements were made by the Oka group in the late 1990s [17] and implied a hop:exchange ratio of $\alpha \sim 2.4$ in a plasma at ~ 400 K. However, diffuse interstellar clouds are considerably colder ($T \sim 60$ K), so it is important to probe the temperature dependence of this branching ratio.

In our lab at Illinois, we have built a liquid-nitrogen cooled hollow cathode cell, based on a design provided by Takayoshi Amano. With this cell, we are able to measure the ortho:para ratio of H_3^+ produced from H_2 at various ortho:para ratios, at temperatures ranging from room temperature down to ~ 130 K. Our results will be presented in detail in a forthcoming paper, but they suggest that the hop:exchange ratio decreases with decreasing temperature, getting closer to the statistical value of 0.5. This is in line with chemical intuition, which suggests that at lower collision energies, the collision complex may live longer, leading to a more complete scrambling of the protons in the H_5^+ collision complex.

DIFFUSE CLOUD MODELS

In an effort to understand the origin of the observed ortho:para ratio of H_3^+ in diffuse interstellar clouds, we have constructed a steady state chemical model that considers the state-specific formation of H_3^+ through the reaction $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$, the dissociative recombination of H_3^+ , and the chemical reaction between H_3^+ and H_2 . For the latter reaction, we consider “ground-state – to all states” rate coefficients for each potential set of spin modifications: for example, k_{oppo} is the rate of ground-state ortho- H_3^+ reacting with ground-state para- H_2 to form any states of para- H_3^+ and ortho- H_2 . These rates are calculated using the microcanonical method developed by Park & Light [18], using a code generously provided by K. Park. We note that this method has been subsequently extended to deuterated systems by Hugo et al. [19], and these authors’ results agree with those of Park & Light for the fully hydrogenated system. We performed calculations for various input parameters, including the branching fraction S^{id} of the identity outcome and the branching ratio α between the hop and exchange outcomes. Our results will be presented in detail elsewhere [20], and here we only provide an overview of our results.

If we ignore the formation and destruction of H_3^+ and focus exclusively on the $\text{H}_3^+ + \text{H}_2$ reaction, the result of our model is that the ortho/para ratio of H_3^+ is fairly close to thermal equilibrium for a wide range of S^{id} and α . There are some significant deviations from the thermodynamic expectation; in particular, the fraction of para- H_3^+ can be below 50% for certain choices of the parameters, even for normal- H_2 . Nevertheless, the results of this calculation cannot come close to reproducing the astronomical observations, and we therefore conclude that this reaction does not (alone) determine the H_3^+ ortho/para ratio.

However, when we include the H_3^+ formation (from H_2^+) and the destruction by DR, we can reproduce the observed H_3^+ ortho/para ratio if we assume that the DR rates are the same for ortho- and para- H_3^+ and that the identity branching fraction $S^{id} \sim 0.9$. The large branching fraction of the identity outcome would suggest that the “reactive” collision rate is actually about an order of magnitude smaller than the total collision rate, which is assumed to be Langevin. If we instead adopt the theoretical DR predictions which show a large difference in the ortho- and para- H_3^+ DR rates [10], we are unable to reproduce the observed ortho/para ratio for any value of the parameters.

CONCLUSIONS

The effect of the nuclear spin modification of H_3^+ on dissociative recombination has now been probed by experiment, but the present experiments are imperfect in the sense that the H_3^+ ions in the storage ring are apparently not rotationally cold. Followup experiments, with rotationally cold ions, are desperately needed to pin down whether or not there is a significant difference between ortho- and para- H_3^+ DR. Our steady state model of diffuse clouds suggests there is not a large difference, but experimental verification (or contradiction!) of this is urgently needed.

The fundamental chemical reaction $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_3^+$ has now been probed at temperatures below room temperature, and these experiments suggest that the branching ratio between the hop and exchange outcomes approaches the statistical value of 0.5 at low temperatures. However, the present experiments only reach down to ~ 130 K, still much higher than the temperatures in diffuse clouds. Future measurements of this reaction in a cryogenic ion trap are critically needed.

A steady state model has been developed to consider the ortho/para ratio of H_3^+ in diffuse clouds, but this model is entirely dependent on rate coefficients calculated with a microcanonical statistical approach. Given the highly quantum mechanical nature of this system, there is reason to be concerned that these calculations may not be accurate, particularly at low temperatures. A more sophisticated theoretical treatment, ideally involving fully quantum reactive scattering calculations, would be very helpful in understanding this fundamental and ubiquitous bimolecular reaction.

In the future, once experiment and/or theory has resolved all of the uncertainties regarding the H_3^+ DR and the $\text{H}_3^+ + \text{H}_2$ reaction, it should be possible to use the observed ortho/para ratio of H_3^+ as a direct probe of the temperature of a diffuse interstellar cloud. This could be very important for the study of high extinction sightlines, where the usual methods for temperature determination (especially UV spectroscopy of H_2) are not feasible.

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