

Storage ring measurements of the dissociative recombination rate of rotationally cold H_3^+

B J McCall,¹ A J Huneycutt,² R J Saykally,² N Djuric,³ G H Dunn,⁴ J Semaniak,⁵
O Novotny,⁵ A Al-Khalili,⁶ A Ehlerding,⁶ F Hellberg,⁶ S Kalhori,⁶ A Neau,⁶
R Thomas,⁶ A Paal,⁶ F Österdahl⁶ and M Larsson⁶

¹ University of Illinois, 600 S. Mathews Ave., Urbana IL 61822, USA

² University of California, Berkeley CA 94720, USA

³ Jet Propulsion Laboratory, Pasadena CA 91109, USA

⁴ JILA, University of Colorado, Boulder CO 80309, USA

⁵ Swietokrzyska Academy, 25 406 Kielce, Poland

⁶ Stockholm University, S-106 91 Stockholm, Sweden

E-mail: bjmcCall@scs.uiuc.edu

Abstract. We present dissociative recombination measurements, using the CRYRING ion storage ring, of H_3^+ ions produced in a supersonic expansion discharge source. Before and after the CRYRING measurements, the ion source was characterized in Berkeley using infrared cavity ringdown spectroscopy, and was found to exhibit a typical rotational temperature of ~ 30 K. Our measurement of the dissociative recombination cross section using this ion source revealed resonances that had not been observed clearly in previous experiments that used rotationally hot ion sources. Based on the present measurements, we infer a thermal dissociative recombination rate coefficient for ions at interstellar temperatures of $\sim 2.6 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. Our results are in general agreement with theoretical calculations of the dissociative recombination cross section by Kokoouline and Greene. We will review the enigma of the abundance of H_3^+ in the diffuse interstellar medium, and discuss the impact of these experiments, especially in the context of the recent observation of H_3^+ towards ζ Persei.

1. Introduction

The dissociative recombination (DR) of H_3^+ is not only fundamentally important (as H_3^+ is the simplest polyatomic molecule), but is also of great importance to astrophysics. In diffuse interstellar clouds, electrons are produced by photoionization of atomic carbon by starlight, and the resulting electron abundance is high enough that DR is the dominant destruction mechanism for H_3^+ . The unexpected discovery [1,2] of abundant H_3^+ in diffuse clouds suggested a discrepancy of two orders of magnitude in the assumed value of either the H_3^+ DR rate coefficient, the electron fraction, the cosmic-ray ionization rate, or the size of the diffuse clouds. Of these quantities, only the H_3^+ DR rate can be pinned down by laboratory experiments; however, various experimental measurements have varied by as much as four orders of magnitude (see recent reviews by Larsson [3] Plasil *et al.* [4], and Oka [5]).

During the Fifth International Conference on Dissociative Recombination, held in Chicago in 2001, there was a great deal of discussion about the possible dependence of the H_3^+ DR rate on the ion's rotational quantum state. Larsson [6] presented data that had recently been obtained at the CRYRING ion storage ring in Stockholm showing indications of a dependence of the DR cross-section on the conditions in their hollow cathode discharge source. Following this presentation, one of us (McCall) was

discussing this issue with C. Michael Lindsay, and the idea of using a supersonic expansion discharge source for storage ring measurements was born. At this time, McCall had just begun a Miller Fellowship at UC Berkeley, and was working in Saykally's group. In the fall of 2001, Larsson visited Berkeley as a Visiting Miller Professor, and McCall, Larsson, Huneycutt, and Saykally resolved to construct a supersonic expansion ion source and use CRYRING to measure the DR rate of rotationally cold H_3^+ ions.

The remainder of this paper describes the construction and spectroscopic characterization of the supersonic expansion ion source, presents the results of the DR measurements performed at CRYRING, and discusses the implications of these results on the enigma of H_3^+ in diffuse interstellar clouds. A preliminary report on the storage ring measurements was published in [7], and a more detailed description is in press [8].

2. Supersonic expansion ion source

In a supersonic expansion, a "high" temperature gas at "high" pressure is adiabatically expanded into a vacuum, resulting in a jet of molecules that are internally cold but still in the gas-phase. Such sources have been used for molecular spectroscopy of stable molecules for decades, as reviewed by Levy [9]. The incorporation of a discharge with a supersonic expansion source to produce rotationally cold ions was pioneered by Engelking and coworkers [10] in the early 1980s, and is by now a standard tool for molecular spectroscopists.

In Berkeley, we (McCall, Huneycutt, and Saykally) constructed a supersonic expansion ion source designed to produce rotationally cold H_3^+ for storage ring experiments; our final source design is shown in figure 1. The heart of the source is a $500\ \mu\text{m}$ circular pinhole, which forms the nozzle for the expansion. Hydrogen gas (at ~ 2 atm of pressure) is pulsed through this nozzle by a poppet controlled by a solenoid valve, which produces pulses of gas $\sim 400\ \mu\text{s}$ in width. The repetition rate of the pulses can be varied over a wide range: for spectroscopic characterization, we used a 50 Hz repetition rate; for the DR measurements we use a ~ 0.1 Hz repetition rate. To produce H_3^+ from the H_2 , a discharge is struck between the plate containing the nozzle and a ring electrode (separated from the nozzle by an insulating spacer). The ring electrode is typically biased at approximately -800 V with respect to the nozzle.

In order to verify that the source produced rotationally cold H_3^+ ions, we characterized the expansion using infrared cavity ringdown laser absorption spectroscopy (figure 2). In short, a Nd:YAG laser is used to pump a tunable pulsed dye laser, operating around 660 nm. The dye laser light is then sent into a multipass cell containing a high pressure (~ 14 atm) of hydrogen gas, which redshifts the radiation through a stimulated Raman scattering process. After three Stokes shifts, pulses of tunable infrared radiation (near $3.6\ \mu\text{m}$) are produced. The infrared pulses are then sent into a cavity formed by two highly reflective ($R \sim 0.9998$) mirrors, and the radiation emerging from the other side of the cavity is

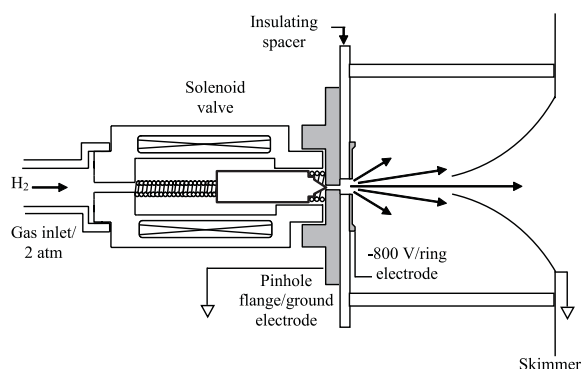


Figure 1. Cross-section of the supersonic expansion ion source (not to scale).

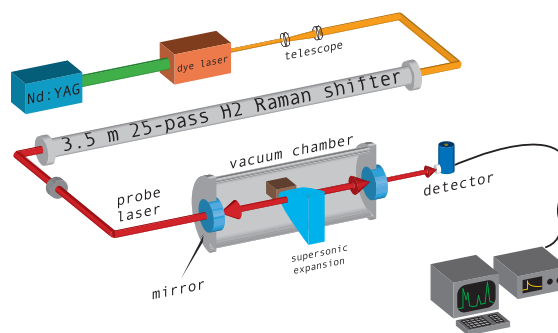


Figure 2. Infrared cavity ringdown laser absorption spectroscopy setup [11].

monitored with an InSb detector. The detector sees an exponential decay of the radiation, and the time constant of this decay is related to the total losses inside the cavity. When the supersonic expansion is placed inside the cavity, the ions produce additional losses at the frequencies of the H_3^+ transitions; thus, by scanning the dye laser we can record an absorption spectrum of the H_3^+ ions.

A typical cavity ringdown spectrum of the ion source is shown in figure 3, along with a spectrum of interstellar H_3^+ in the sightline towards ζ Persei [7], for comparison. The relative intensities of the $R(1,0)$ and $R(1,1)^u$ absorption lines of the H_3^+ fundamental band are similar in the laboratory spectrum and the interstellar spectrum, indicating that the supersonic expansion source is producing ions with a similar rotational distribution to that in the interstellar medium. These two transitions arise from the two lowest rotational levels, $J = 1, K = 0$ (ortho) and $J = 1, K = 1$ (para). The “temperature” defined by the relative intensity of these two lines is typically ~ 30 K when the source is operating normally. We also searched for the $R(2,2)^l$ transition from the next-lowest rotational level $J = 2, K = 2$, but we were unable to detect it. Given our sensitivity limit, our non-detection is consistent with a rotational temperature of < 50 K.

After an extended period of source operation at 50 Hz, we found that the source started producing H_3^+ ions with a higher temperature (sometimes in excess of 100 K). This higher temperature was obvious from a strengthening of the $R(1,0)$ transition, and was confirmed by observation of the $R(2,2)^l$ line. After some investigation, we determined that the transition to high temperature ion production was caused by deformation of the Teflon poppet that forms the seal with the pinhole nozzle. In order to guard against the possibility that the source had “heated up” during the course of the storage ring measurements, we spectroscopically characterized the source both before and after the storage ring measurements, to ensure the ions were produced at low temperature.

3. CRYRING measurements

The supersonic expansion ion source was first used at the CRYRING (Manne Siegbahn Laboratory, Stockholm) in May of 2002. When mounted on the end-station at CRYRING, the entire source assembly is floated to +30 kV, in order to give the ions an initial acceleration towards the ring. At that time, we had not yet implemented the skimmer shown in figure 1, and we found that arcing occurred from the source

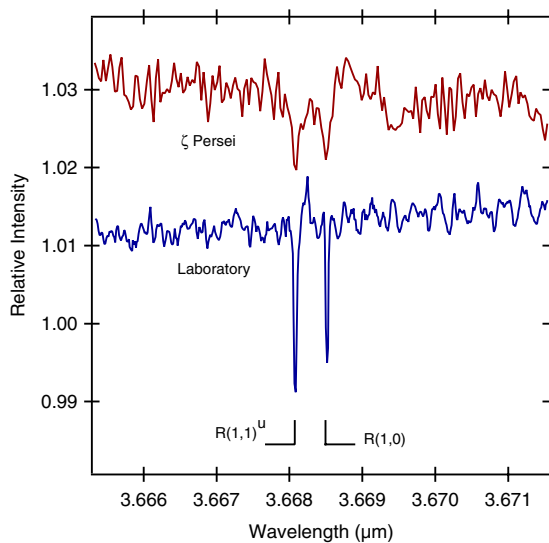


Figure 3. Spectra of H_3^+ in supersonic expansion ion source (lower trace) and towards ζ Persei [7] (upper trace).

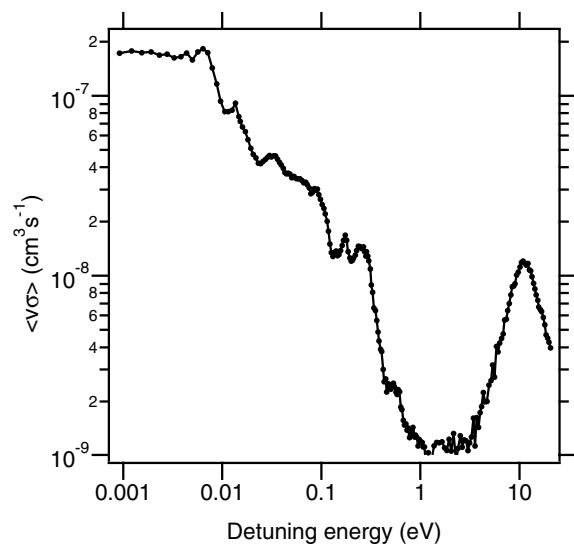


Figure 4. Dissociative recombination rate coefficient of H_3^+ produced in supersonic expansion source.

assembly to the nearest ground point every time the source fired. This arcing exceeded the current limit of the power supplies that held the source at +30 kV, and consequently the ions were not receiving the correct acceleration into the ring. While some data on the DR cross-section were collected, the statistics were very poor because of the difficulties with ion injection.

We interpreted this problem as due to the high ion current that was off the axis leading into the ring. To eliminate this off-axis current, we modified the source to include a skimmer, which was held at the same potential as the source body. The addition of the skimmer was not found to affect the temperature of the ions as measured spectroscopically upstream of the skimmer; our sensitivity was not high enough to measure the ion temperature after the skimmer.

In September 2002, we repeated the CRYRING measurements with the skimmer in place. Once sufficient statistics had accumulated, a remarkable amount of structure in the cross-section curve was immediately apparent. Figure 4 displays the final results of this run. Although the large peak near 10 eV had been well-known, the rest of the structure in this curve had never been seen in previous experiments with rotationally hot ions. We interpret this as evidence that the H_3^+ ions used in these DR measurements are, in fact, rotationally colder, such that the resonances due to individual quantum states are apparent (as fewer quantum states are populated).

During this experimental run, we were very much concerned about the possibility that the H_3^+ ions might be heated by electron impact in the electron cooler. The cross-sections for this process have since been published [12], but were not available at the time. To attempt to minimize such a heating effect, we performed a set of measurements in which the relative energy between ions and electrons was kept below the lowest threshold for electron impact excitation. To attempt to enhance such a heating effect, we also performed a set of measurements in which the relative energy between ions and electrons was kept just above threshold for 1.5 s, before making the cross-section measurements. These tests are described in more detail in [8], but we were not able to see any effect on the observed cross-section, which we interpret as an indication that this heating effect is not significant under the conditions of our experiment.

At about the same time as these measurements were performed, Chris Greene and Viatcheslav Kokoouline [13] had refined their theoretical calculations of the H_3^+ DR cross-section. As discussed in more detail in [8], the agreement between their calculations and our experiment is remarkably good (considering that experiment and theory have historically differed by orders of magnitude).

There remain some lingering uncertainties that make us hesitant to claim that we have definitively measured the DR cross-section of H_3^+ in its two lowest rotational levels, and that our value is exactly the right value for the interstellar case. If every detail of the theoretical calculations is to be counted on, the discrepancies between our experiment and the theory may indicate that some rotational excitation has occurred (either in the extraction from the ion source or in the ring itself). To take the most skeptical view, there is the added worry that the conditions in a storage ring (magnetic fields of ~ 300 Gauss and electron densities of $\sim 10^7 \text{ cm}^{-3}$) are wildly different from those in the interstellar medium (10^{-6} Gauss and 10^{-2} cm^{-3}). Additionally, some experiments [14] still seem to point to lower DR rate coefficients, and the discrepancies are yet to be understood.

Consequently, we do not consider the matter of H_3^+ DR to be a closed book, but we argue that the present results are the most appropriate ones to use in modeling H_3^+ in the interstellar medium, as they have been obtained under the well-controlled conditions of a storage ring, using ions that are known to be in the vibrational ground state and that are almost certainly much cooler rotationally than in any previous experiments.

4. Interstellar implications

Let us now consider the implications of these measurements for H_3^+ in the diffuse interstellar medium. In diffuse clouds (just as in dense clouds), H_3^+ is produced in a two-step process: cosmic-ray ionization of H_2 to form H_2^+ , followed by the fast ion-neutral reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$. The rate limiting step in the formation is the cosmic-ray ionization, and the rate of this step is expressed as $\zeta n(H_2)$, where ζ is the cosmic-ray ionization rate (usually taken to be $\sim 3 \times 10^{-17} \text{ s}^{-1}$), and $n(H_2)$ is the number density of H_2 .

The dominant destruction mechanism for H_3^+ is DR: $\text{H}_3^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}$ or $\text{H} + \text{H} + \text{H}$. The rate for this process can be written as $k_e n(\text{H}_3^+) n(\text{e})$, where k_e is the thermal rate coefficient for DR at the temperature of the diffuse cloud. If we take the temperature as that computed from the relative intensity of the $R(1,0)$ and $R(1,1)^u$ transitions in the diffuse clouds toward ζ Persei (reported in [7] and reproduced in figure 3), we find $T = 23$ K. By convolving the cross-section in figure 4 with a thermal distribution of electrons at 23 K, we find $k_e = 2.6 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. Incidentally, this value is about a factor of two lower than values obtained in storage ring measurements with rotationally hot H_3^+ .

The evolutionary timescales in diffuse clouds are much longer than the chemical timescales, and it is a very good approximation to assume that the cloud is in a chemical steady state: the rate of formation of H_3^+ is equal to the rate of destruction of H_3^+ . Equating the two rate expressions above, we find

$$n(\text{H}_3^+) = \frac{\zeta n(\text{H}_2)}{k_e n(\text{e})}. \quad (1)$$

The number density of H_3^+ is evidently a constant in diffuse clouds, as it is just the product of a ratio of two constants (ζ/k_e) and the reciprocal of the electron fraction $n(\text{e})/n(\text{H}_2)$, which is also a constant (that is, independent of density) in diffuse clouds. Consequently, we can write the observed column density of H_3^+ as $N(\text{H}_3^+) = n(\text{H}_3^+) L$, where L is the path length through the diffuse cloud. With this substitution, (1) can be rewritten as

$$\zeta L = k_e N(\text{H}_3^+) \frac{n(\text{e})}{n(\text{H}_2)}. \quad (2)$$

Let us consider the specific case of the ζ Persei cloud. In this sightline, ultraviolet measurements of H_2 [15] and of C^+ (which is a proxy for electrons) [16] have determined the electron fraction $n(\text{e})/n(\text{H}_2) = 3.8 \times 10^{-4}$. The spectrum in figure 3 implies that the H_3^+ column density is $N(\text{H}_3^+) = 8 \times 10^{13} \text{ cm}^{-2}$ [7]. Finally, the CRYRING experiments suggest $k_e = 2.6 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. Putting this together, we find $\zeta L \sim 8000 \text{ cm s}^{-1}$. This is a robust result, but it does not determine the individual values of ζ and L .

If we adopt the ‘‘canonical’’ value for the cosmic-ray ionization rate, $\zeta \sim 3 \times 10^{-17} \text{ s}^{-1}$, we derive a path length $L = 85$ parsecs (1 parsec $\sim 3 \times 10^{18} \text{ cm}$). This seems unrealistically long for a diffuse cloud, and given the total amount of hydrogen along the line of sight, this length would imply an unreasonably low average number density of only 6 cm^{-3} ! This seems to be out of the question. On the other hand, we could adopt an average number density inferred from the observed excitation of C_2 and CO molecules, or that derived from detailed cloud models that consider the relative abundance of H and H_2 [17]. Each of these methods has its own drawbacks, but all are consistent with an average number density between 100 and 500 cm^{-3} . If we adopt the value 250 cm^{-3} , this implies a path length of $L = 2.1$ parsecs. Plugging this into $\zeta L = 8000 \text{ cm s}^{-1}$, we derive $\zeta = 1.2 \times 10^{-15} \text{ s}^{-1}$, some forty times higher than the ‘‘canonical’’ value.

It has often been argued that such a high cosmic-ray ionization rate is inconsistent with observations of the OH column density (OH is formed following the charge exchange reaction $\text{H}^+ + \text{O} \rightarrow \text{O}^+ + \text{H}$, and the H^+ comes from cosmic-ray ionization of H). However, a recent chemical model calculation taking into account the endothermicity of this charge exchange reaction [18] has demonstrated that a higher than canonical value of ζ cannot be excluded based on the OH observations.

However, such a high value of ζ ($1.2 \times 10^{-15} \text{ s}^{-1}$) remains surprising. In particular, one wonders how this high value in diffuse clouds can be reconciled with the much lower value ($3 \times 10^{-17} \text{ s}^{-1}$) that has been inferred for dense clouds by many different measurements (including H_3^+ ! [19]). One interpretation (perhaps too simple) is that these observations are revealing the existence of a large flux of low energy cosmic rays, which have sufficient energy to penetrate into diffuse clouds but not enough to penetrate dense clouds. Another possible interpretation (John Scalo, private communication) is that cosmic rays have difficulty penetrating denser clouds due to magnetic effects.

5. Conclusions

Our dissociative recombination measurements (performed at CRYRING) using rotationally cold H_3^+ ions produced in a supersonic expansion ion source favor a DR rate coefficient of $2.6 \times 10^{-7} \text{ cm}^3\text{s}^{-1}$ for H_3^+ at a temperature of 23 K, about a factor of two lower than previous storage ring measurements with rotationally hot ions. For the first time, clear resonances are seen in the DR cross-section, and the results are in reasonable agreement with theoretical calculations [13].

Despite this apparent accord, we strongly encourage additional work on this key system, both experimentally and theoretically. Significant discrepancies remain between theory and experiment, and measurements using other techniques [14, e.g.] still yield considerably lower values of the DR rate coefficient. Because of the importance of H_3^+ DR both to fundamental molecular physics and to astrophysics, it is imperative that these discrepancies be resolved.

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