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Dissociative recombination of cold H_3^+ and its interstellar implications

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H_3^+ plays a key role in interstellar chemistry as the initiator of ion–molecule chemistry. The amount of H_3^+ observed in dense interstellar clouds is consistent with expectations, but the large abundance of H_3^+ seen in diffuse clouds is not easily explained by simple chemical models.

A crucial parameter in predicting the abundance of H_3^+ in diffuse clouds is the rate constant for dissociative recombination (DR) with electrons. The value of this constant has been very controversial, because different experimental techniques have yielded very different results, perhaps owing to varying degrees of rotational and vibrational excitation of the H_3^+ ions. If the value of this rate constant under interstellar conditions were much lower than usually assumed, the large H_3^+ abundance could be easily explained.

In an attempt to pin down this crucial rate constant, we have performed DR measurements at the CRYRING ion storage ring in Stockholm, using a supersonic expansion ion source to produce rotationally cold H_3^+ ions. These measurements suggest that the DR rate constant in diffuse clouds is not much lower than usually assumed and that the abundant H_3^+ must be due to either a low electron fraction or a high ionization rate.

Keywords: dissociative recombination; rate coefficient; cross-section; interstellar clouds; interstellar molecules; infrared spectroscopy

1. Introduction

As illustrated in figure 1, about 90% of all nuclei in the universe are hydrogen nuclei and most of the remaining 10% are helium nuclei. As helium is not chemically active, hydrogenic species (H, H_2 and H_3^+) are critically important species in the chemistry of interstellar medium. Owing to its strong 'acidity', H_3^+ plays a particularly vital role in chemistry, as it is able to donate its extra proton to just about any atom or molecule, thereby initiating a network of ion–neutral reactions that is responsible for the production of most of the known interstellar molecules (see figure 2). The importance of H_3^+ in interstellar chemistry was first highlighted by Herbst & Klemperer (1973) and Watson (1973).

Owing to the central role of H_3^+, it is important to understand the chemistry of this very simple species in order to facilitate the understanding of the larger picture of interstellar chemistry. However, H_3^+ is more difficult to observe than

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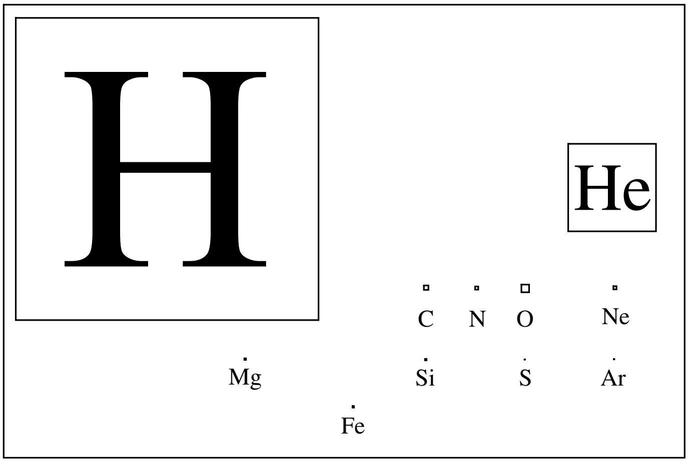

Figure 1. The 'astronomer's periodic table', wherein the area of each element corresponds to its abundance.

many molecules. Owing to its symmetric equilateral triangle equilibrium configuration, it possesses no permanent dipole moment and thus has no allowed rotational transitions (its forbidden rotational transitions are important in controlling its rotational excitation in low-density environments, but are so weak that they have not yet been spectroscopically detected). Consequently, the usual tools of radioastronomy are not applicable to H_3^+ (unless it is isotopically substituted). In addition, its only stable electronically excited state is a triplet state (the ground state is a singlet) with a linear geometry, so that the corresponding electronic transition is expected to be very weak. Therefore, neither UV nor optical spectroscopy can be applied to H_3^+.

This leaves vibrational spectroscopy as the only tool for spectroscopically characterizing H_3^+, either in the laboratory or in the interstellar medium. H_3^+ has two vibrational modes: the symmetric 'breathing' mode ν_1, which is infrared inactive; and the doubly degenerate 'stretch-bend' mode ν_2, which is infrared active with a band origin near 4 μm. It is the $\nu_2 \leftarrow 0$ band that has been used to discover H_3^+ in the interstellar medium. Infrared continuum radiation from background stars or embedded protostars passes through the interstellar clouds, where the individual rotation–vibration transitions of H_3^+ imprint absorption lines. After passing through the clouds, the starlight is collected by large telescopes and dispersed to reveal the signature of H_3^+ (figure 3).

(a) H_3^+ in dense clouds

Interstellar clouds are typically classified into dense molecular clouds and diffuse clouds (Snow & McCall 2006). Dense molecular clouds have typical number densities of 10^4–$10^6\,\mathrm{cm}^{-3}$ and temperatures of $\sim$20–30 K. In these clouds, almost all hydrogen atoms are in the form of H_2, and almost all carbon atoms are in the form of CO. H_3^+ is produced by 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 cosmic ray ionization is the rate-limiting step and it proceeds with a rate of $\zeta n(H_2)$, where ζ is usually assumed to be $\sim 3\times 10^{-17}\,\mathrm{s}^{-1}$. H_3^+ is destroyed by

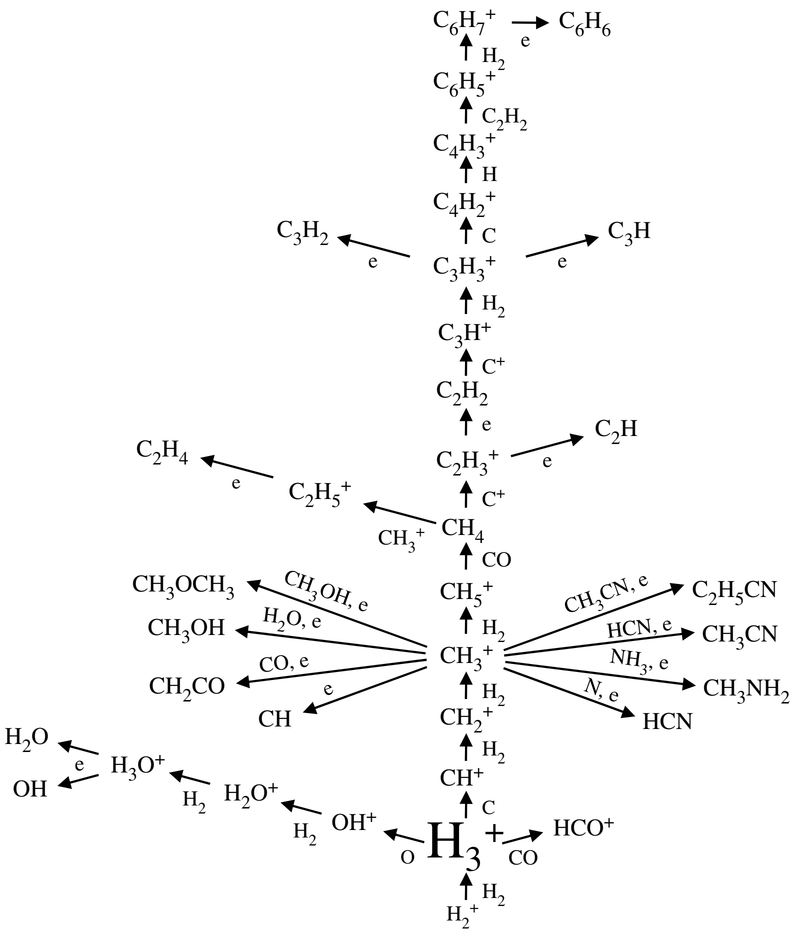

Figure 2. After being produced from H_2 by cosmic ray ionization, H_3^+ initiates a network of ion–neutral reactions that is responsible for the production of a wide variety of molecules.

chemical reactions with atoms and molecules other than H_2, dominantly by CO with a rate of $k_{CO}n(CO)n(H_3^+)$, where k_{CO} is the rate constant for the reaction $H_3^+ + CO \rightarrow HCO^+ + H_2$. In steady state, the rates of formation and destruction of H_3^+ must be equal, and we can solve for the number density of H_3^+,

$$n(H_3^+) = \frac{\zeta}{k_{CO}} \frac{n(H_2)}{n(CO)}. \tag{1.1}$$

Substituting $\zeta \sim 3\times10^{-17}\ s^{-1}$, $k_{CO}=2\times10^{-9}\ cm^3\ s^{-1}$ and $n(H_2)/n(CO) \sim 6700$, we find that $n(H_3^+) \sim 10^{-4}\ cm^{-3}$. There are two important things to note about this result. First, it is independent of the cloud density $n(H_2)$, because the ratio of H_2/CO is constant (all H atoms are in the form of H_2, all C atoms are in the form of CO). Second, the H_3^+ number density is very small, approximately one part per billion of the H_2 number density.

The infrared observations (figure 3) directly yield the column density $N(H_3^+) \sim 1$–$5\times10^{14}\ cm^{-2}$ in dense clouds (McCall *et al.* 1999). Since the column density is the integral of the number density along the line of sight, the absorbing

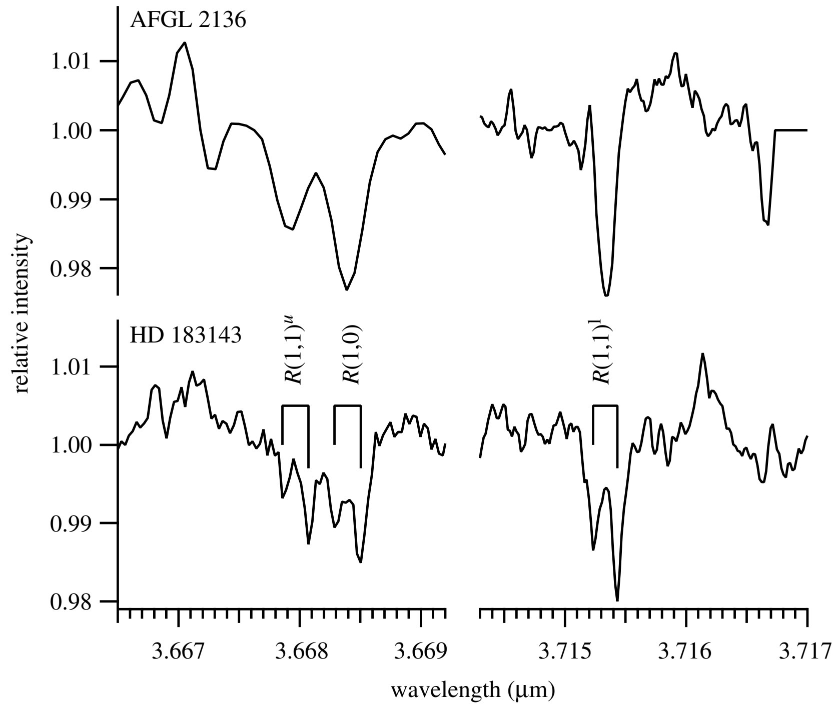

Figure 3. Spectra of H_3^+ in the dense cloud sightline AFGL 2136 (top, from McCall *et al.* 1999) and the diffuse cloud sightline HD 183143 (bottom, from McCall *et al.* 2002).

path length can be directly inferred as $L \sim N(H_3^+)/n(H_3^+)$, because $n(H_3^+)$ is a constant. This analysis yields path lengths of the order of 1 pc and resulting average number densities $\langle n(H_2) \rangle \sim N(H_2)/L$ of $\sim 10^5\ \mathrm{cm}^{-3}$, in agreement with our expectations for dense clouds. This agreement confirms the overall picture of H_3^+ chemistry in dense clouds and suggests that the adopted values of ζ and k_{CO} are probably correct.

(*b*) *H_3^+ in diffuse clouds*

Diffuse interstellar clouds have typical number densities of $\sim 10^1$–$10^3\ \mathrm{cm}^{-3}$ and higher temperatures of $\sim$50–100 K owing to the influence of starlight. The starlight also photodissociates H_2, leading to a mixture of H and H_2, and photoionizes C to C^+, producing abundant electrons. While H_3^+ is formed in the same way as in dense clouds, it is now dominantly destroyed by electrons, with a rate of $k_e n(H_3^+) n(e)$. Once again making the assumption of steady state, we can solve for $n(H_3^+)$

$$n(H_3^+) = \frac{\zeta}{k_e} \frac{n(H_2)}{n(e)}. \tag{1.2}$$

Substituting $\zeta \sim 3 \times 10^{-17}\ \mathrm{s}^{-1}$, $k_e = 5 \times 10^{-7}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ and $n(H_2)/n(e) \sim 2400$, we find that $n(H_3^+) \sim 10^{-7}\ \mathrm{cm}^{-3}$. This is approximately three orders of magnitude lower than in dense clouds and is also independent of the cloud density to the extent that $n(H_2)/n(e)$ is a constant.

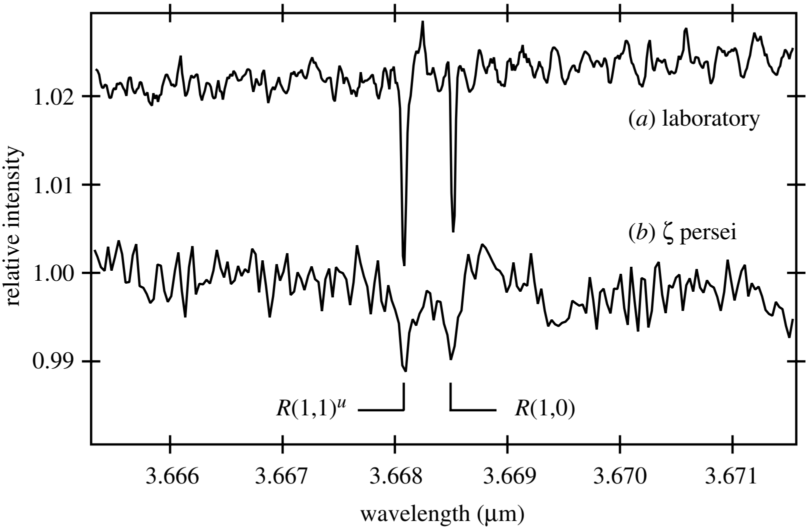

Figure 4. Spectra of H_3^+ produced (*a*) by the supersonic expansion ion source, and (*b*) in the line of sight towards ζ Persei, showing that the rotational distributions are similar. Adapted from McCall *et al.* (2003).

As can be seen in figure 3, the column density of H_3^+ observed in diffuse clouds is similar to that in dense clouds, which is very surprising, considering that the simple chemical model considered here predicts a number density that is 10^3 times lower. If the model is believed, this would imply that the path length must be 10^3 times longer in diffuse clouds or about 1 kpc. Such an absorption path length is difficult to accept, as it would imply a very low average number density (in conflict with other diagnostics of diffuse clouds). Furthermore, in the case of HD 183143 (figure 3), two distinct velocity components are seen in the H_3^+ spectrum, implying two distinct clouds along this line of sight, and this star is only about 1 kpc away.

It seems there is a serious problem with our simple chemical model of the H_3^+ number density. To explain these observations, $n(H_3^+)$ needs to be increased by approximately two orders of magnitude, so that the path length is consistent with other diagnostics. In order to increase $n(H_3^+)$, we need to lower the electron fraction $n(e)/n(H_2)$, lower the dissociative recombination (DR) rate constant k_e or raise the ionization rate ζ.

The recent observation of H_3^+ towards ζ Persei (figure 4; McCall *et al.* 2003) has ruled out the possibility of a lower electron fraction, at least in this sight line. Towards ζ Persei, the column densities of both H_2 (Savage *et al.* 1977) and C^+ (Cardelli *et al.* 1996) have been measured by ultraviolet spectroscopy, thereby determining $n(C^+)/n(H_2)$ and $n(e)/n(H_2)$, and the results are consistent with all carbon being photoionized, as expected. This is the first UV-bright sightline where H_3^+ has been detected (previous observations were restricted to more heavily reddened sightlines, where the flux is too low for UV spectroscopy).

These observations seem to rule out the possibility of a low electron fraction, with the possible caveat that the more heavily reddened sightlines could possibly still have a lower electron fraction (although this seems unlikely). This leaves only the ionization rate ζ and the DR rate constant k_e as the possible causes for the 'overabundant' H_3^+ in diffuse clouds.

2. Dissociative recombination of cold H_3^+

The rate constant k_e can be measured in the laboratory, so one might think that its value should not be suspect. However, as reviewed by Larsson (2000), Plašil *et al.* (2002) and Oka (2003), laboratory values of k_e have varied by as much as four orders of magnitude over the past 30 years. To make matters worse, theoretical calculations had yielded (until the work of Kokoouline & Greene (2003)) unreasonably low values of k_e, so they did not help in discriminating among the different experiments. Near the turn of this century (e.g. Larsson *et al.* 2003), it became widely recognized that the different experimental results were likely to be due to the lack of experimental control over the rotational and vibrational levels populated in the various plasmas used for the measurements. In the interstellar medium, almost all of the H_3^+ ions are in the lowest two rovibrational levels, and none of the experiments that had been conducted were really applicable to this situation.

A major advance in controlling the state distribution of molecular ions for DR measurements was the introduction of the ion storage ring method. At a storage ring such as the CRYRING facility in Stockholm, ions are produced in an external plasma source, extracted and mass selected, accelerated and then injected and stored in a ring consisting of a series of bending magnets. Ions can be stored as long as several tens of seconds, so that all ions will relax to their vibrational ground states by spontaneous emission. The DR measurement is made by overlapping a nearly mono-energetic electron beam with the ion beam and counting the number of neutral fragments (H and H_2) that fly out of the ring.

In addition to the benefit of the vibrational cooling, the storage ring technique has the advantage that it is also conceptually simple and does not require extensive modelling, in contrast to afterglow experiments. Furthermore, the electron–ion impact energy can be precisely controlled (by varying the velocity of the electron beam), thus enabling detailed measurements of the DR cross-section. However, a major limitation of this technique has been that hot plasma sources have traditionally been used to produce the ions. For a symmetric ion such as H_3^+, there is very little rotational cooling in the ring (as H_3^+ has only forbidden rotational transitions), and the rotational temperature of the ions remains high despite the vibrational cooling.

In order to study rotationally cold H_3^+ ions, we developed a new ion source that utilizes a supersonic expansion. In this source, high-pressure gas is pulsed through a small nozzle into the vacuum of the ring's endstation; as the gas rushes into vacuum, it expands adiabatically, converting the random thermal motions of the bulk gas into a directed supersonic flow out of the nozzle. The result is that the translational temperature of the gas is reduced to very low temperatures, and collisions in the expansion also cool the internal degrees of freedom of the molecules. Such sources have been used for many decades in spectroscopic studies of neutral molecules. To produce ions, a plasma is generated just downstream of the nozzle by placing a ring-shaped electrode (held at about -900 V) in front of the nozzle. More details of this ion source can be found in McCall *et al.* (2004).

This ion source was used to produce rotationally cold H_3^+ ions (with a rotational temperature of approx. 30 K) for DR measurements at CRYRING. Prior to the CRYRING run, the ions were spectroscopically characterized in Berkeley using infrared cavity ringdown laser absorption spectroscopy. This confirmed that the

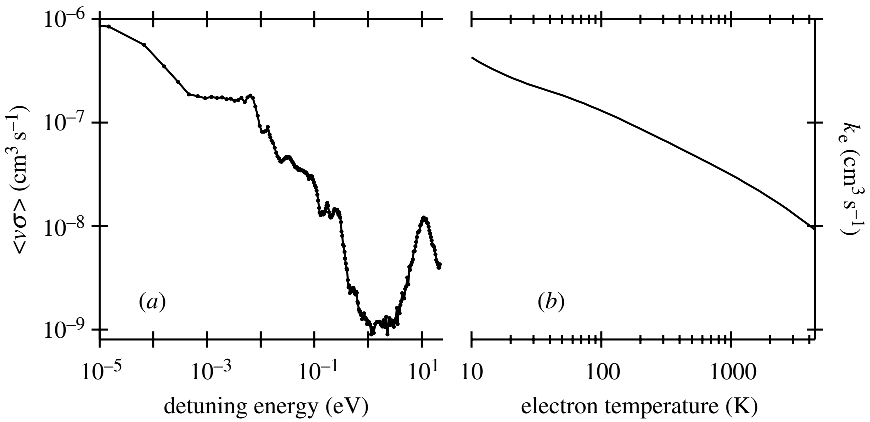

Figure 5. (*a*) Rate coefficient for dissociative recombination of rotationally cold H_3^+ as a function of detuning energy measured at CRYRING. (*b*) Thermal rate coefficient derived from CRYRING results. Adapted from McCall *et al.* (2003).

source produces H_3^+ ions with a rotational distribution similar to that in the interstellar medium (see figure 4). The results of the CRYRING measurements are shown in figure 5. Following the CRYRING run, the source was returned to Berkeley and the rotational temperature was again confirmed to be low.

The surprising result from the CRYRING study is that the DR rate coefficient for rotationally cold H_3^+ is about half that of the rate coefficient for rotationally hot H_3^+. Additionally, this study revealed, for the first time, structure in the cross-section curve (figure 5*a*), which can be interpreted as due to resonances in the recombination process. In previous measurements with hot H_3^+, so many quantum states were populated that the resonances were washed out; here, with only a few states populated, they are seen more clearly. The CRYRING results have since been confirmed by elegant experiments using an ion storage trap at the Test Storage Ring (TSR; Kreckel *et al.* 2005; Wolf *et al.* 2006) and are also largely consistent with recent theoretical calculations (Kokoouline & Greene 2003).

3. Interstellar implications

Coming back to the problem of 'overabundant' H_3^+ in diffuse clouds, there were three possible solutions proposed earlier: a lower electron fraction $n(\mathrm{e})/n(\mathrm{H_2})$; a lower DR rate coefficient k_e; or a higher ionization rate ζ. The observation of H_3^+ towards ζ Persei ruled out a low electron fraction, and the recent storage ring measurements rule out a low value of k_e (the change by a factor of 2 for rotationally cold H_3^+ is far from enough to solve the problem). This seems to point to a higher value of the cosmic ray ionization rate ζ.

Returning to equation (1.2) for the number density of H_3^+ in diffuse clouds, we can express $n(\mathrm{H_3^+}) = N(\mathrm{H_3^+})/L$ and solve for the product of the unknown quantities ζ and L;

$$\zeta L = k_\mathrm{e} N(\mathrm{H_3^+}) \frac{N(\mathrm{e})}{N(\mathrm{H_2})}. \tag{3.1}$$

In the case of the sightline towards ζ Persei, we have $N(H_3^+) = 8 \times 10^{13}$ cm^{-3} and $N(e)/N(H_2) = 3.8 \times 10^{-4}$. The value of k_e we adopt depends on the temperature of the electrons, which cannot be directly measured, but is probably the same as that of H_2 owing to the efficient Langevin collisions between electrons and the abundant H_2. Based on the observed ratio of $J=0$–1, the H_2 temperature is about 60 K (Le Petit *et al.* 2004). Adopting this as the electron temperature yields $k_e \sim 1.6 \times 10^{-7}$ cm^3 s^{-1}. Substituting into equation (3.1), we find $\zeta L \sim 5000$ cm s^{-1}.

The value of $\zeta \sim 3 \times 10^{-17}$ s^{-1}, which works well in explaining H_3^+ in dense clouds, would suggest a path length of $\sim$55 pc and an average number density (given $N_H = 1.6 \times 10^{21}$ cm^{-2}) of only $\sim$10 cm^{-3}, which is unreasonably low. It seems likely that the appropriate value for ζ in diffuse clouds is instead considerably higher. Various density diagnostics in this sightline suggest that the average number density is in the range of 150–500 cm^{-3}. If we adopt a density of 250 cm^{-3}, then the inferred path length is $\sim$2 pc, and the value of $\zeta \sim 8 \times 10^{-16}$ s^{-1}, roughly 25 times higher than the value in dense clouds. Even if we adopt a density as low as 100 cm^{-3}, we still find $\zeta \sim 3 \times 10^{-16}$ s^{-1}, 10 times higher than in dense clouds.

H_3^+ has also been observed in a number of other diffuse cloud sightlines (McCall *et al.* 2002). Although the electron fractions cannot be directly measured in these other sightlines (owing to the lack of UV flux), it seems likely that the carbon is mostly photoionized, because CO is observed not to be very abundant. If the carbon is mostly photoionized in all these sightlines, then the storage ring results imply that the value of ζ may be universally high in diffuse clouds, relative to dense clouds.

The cosmic ray flux at relevant energies ($\lesssim$2 MeV) cannot be directly measured in the Solar System, owing to the influence of the solar wind. Therefore, the only constraints we have on the appropriate value for ζ in diffuse clouds come from chemical arguments or theory. Newer chemical models (Liszt 2003, 2006; Le Petit *et al.* 2004) seem to indicate that an enhancement of ζ by an order of magnitude is plausible, and a recent theoretical calculation by Padoan & Scalo (2005) suggests that cosmic ray self-confinement may cause a higher ζ in diffuse gas than in dense gas.

4. Future directions

Although at first glance it might appear that the problem of H_3^+ in diffuse clouds, and that of the DR of H_3^+, is 'solved', there are still a number of open questions and there is much work left to be done.

In terms of the DR, there are lingering discrepancies between the experiments (both at CRYRING and TSR) and the theoretical calculations. These discrepancies suggest that either there is a problem with the theory, and/or that some fraction of the H_3^+ ions in the experiments is not rotationally cold. Further investigations into the rotational state distribution of the ions produced in the cold ion source, as well as the evolution of distribution in the storage ring, are clearly needed. Further refinement of the theoretical calculations is also desirable.

The calculations of Kokoouline & Greene (2003) predict a substantial difference in the DR cross-sections of the lowest *ortho* ($J=1$, $K=0$) and *para* ($J=K=1$) levels of H_3^+ at low collision energies. To test this prediction, storage ring measurements with pure *para*-H_3^+ should be made. A preliminary study by Kreckel *et al.* (2005), with only partially enriched *para*-H_3^+, indicates that there is a difference, but it is of the opposite sense than predicted by theory! This tantalizing result demands follow-up experiments, as well as a careful check of the theoretical results. In addition to the pure molecular physics interest, it is possible that this effect (if large enough) might influence the *ortho*/*para* ratio of H_3^+ in diffuse clouds.

On the observational side, it would be very interesting to observe H_3^+ in a large sample of classical diffuse cloud sightlines. Since k_e is now known, the column density of H_3^+ serves as a direct probe of the product ζL. Given the estimates of L from density diagnostics, it should be possible to measure ζ in many diffuse clouds and to see if the enhancement in ionization is indeed widespread or if it is confined to certain regions of the Galaxy. The simple and fundamental molecular ion H_3^+ may well turn into a sensitive probe for cosmic ray astrophysics!

It is a pleasure to acknowledge all my collaborators in this work. The astronomical observations and analysis were performed together with T. Oka (University of Chicago) and T. R. Geballe (Gemini Observatory). I also wish to thank the staff of UKIRT for their assistance with the observations. The ion source was constructed and the spectroscopic characterization performed together with A. J. Huneycutt in the laboratory of R. J. Saykally (University of California at Berkeley). The CRYRING measurements were made in collaboration with N. Djuric, G. H. Dunn, J. Semaniak, O. Novotny, A. Paal, F. Österdahl, A. Al-Khalili, A. Ehlerding, F. Hellberg, S. Kalhori, A. Neau, R. Thomas and M. Larsson. I also wish to thank the staff of the CRYRING for their expert assistance. While at Berkeley, B.J.M. was supported by the Miller Institute for Basic Research in Science. At Illinois, B.J.M.'s work is supported by grants from the National Science Foundation, the National Aeronautics and Space Administration, the American Chemical Society and the Camille and Henry Dreyfus Foundation.

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Discussion

A. Wolf (*Max Planck Institut fur Kernphysik, Heidelberg*). How well is the presence of cold, free electrons in the diffuse clouds, at the density inferred from the observed C^+ density, justified experimentally? A higher stationary electron energy or their binding that avoids their capability to recombine may explain the high H_3^+ abundance.

B. J. McCall. The electron density has not, of course, been directly measured. As for the electron energy, it is thought that electrons should quickly thermalize to the gas kinetic temperature through fast Langevin-type collisions with H and H_2. As for the free electron abundance, it is probably difficult to 'sink' a large fraction of the electrons by, for example, forming large molecular anions. The reason for this is that such large molecules must be made up of many heavy atoms (such as carbon), but yet there is one free electron for each carbon atom—so there cannot be enough large molecules to soak up all the electrons. A small depletion of electrons will not solve the H_3^+ problem; rather, something like 90–98% of them would have to be depleted.

S. Miller (*Department of Physics and Astronomy, University College London*). Are secondary electrons already taken into account in diffuse clouds, or could these provide another source of ionization?

B. J. McCall. The canonical value of the cosmic ray ionization rate already includes ionization due to secondary electrons.

R. N. Porter (*Department of Chemistry, SUNY Stony Brook*). I assume that in the dense clouds, the kinetic, vibrational and rotational temperatures are equilibrated. Can the same be said for the diffuse clouds?

B. J. McCall. Generally speaking, no. For example, the rotational excitation of molecules is governed by a balance between radiative and collisional effects, since the density is low enough that collisions do not always dominate. One must be careful to discriminate between observed excitation temperatures and the true kinetic temperature of the gas.

I. M. Mills (*Department of Chemistry, University of Reading*). Temperatures of 20 and 70 K in dense and diffuse clouds are much higher than that I would have naively expected. What is the explanation?

B. J. McCall. The temperature in dense clouds is determined by the balance between heating by cosmic rays and cooling by molecular line emission, and the kinetic temperature in quiescent dense clouds can range perhaps from 10 to 30 K. In diffuse clouds, the photoelectric effect (from starlight onto dust grains) injects hot electrons into the gas and cooling is achieved mainly by emission in fine structure lines of atoms, resulting in kinetic temperatures of roughly 50–100 K.

J. M. C. Rawlings (*Department of Physics & Astronomy, University College London*). I would just like to draw your attention to a recent paper by myself and one of my research students (Chris Lintott) in which we show that—if it is assumed that dark clouds are not quasi-static but are dynamically active—the equilibrium assumption used in deducing the cosmic ray ionization rate is not valid. As a result, ζ may be very different in dark clouds than what is usually inferred.

A. Dalgarno (*Department of Astronomy, Harvard-Smithsonian Center for Astrophysics*). Hartquist *et al.* (1978) that the ionization rate in dense clouds would be smaller than in diffuse clouds and gave resultant estimates of the magnitude of the difference.

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