Help!!! Theory for H_3^+ Recombination Badly Needed

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1. INTRODUCTION

A spectrum is haunting the field of dissociative recombination—the spectrum of H_3^+ in the diffuse interstellar medium. This spectrum, discussed in detail in a separate paper of this volume,[1] has revealed the surprisingly high abundance of H_3^+ in the diffuse interstellar medium. The intensities of the infrared absorption lines observed toward some 10 reddened visible stars correspond to H_3^+ column densities of $1–4\times10^{14}$cm^{-2}, which is one to two orders of magnitude higher than the value estimated from canonical laboratory and observational astrophysical parameters. The understanding of dissociative recombination is crucial in this estimate since it is the major destruction process of H_3^+ in the diffuse interstellar medium.

The abundance of hydrogen in space and the simplicity of hydrogen plasma chemistry allow us to narrow down possible sources causing the problem to the following three parameters: (1) the cosmic-ray ionization rate[2] of $\zeta\sim10^{-17}$ s^{-1}, (2) the ratio of electron number density n(e) to hydrogen number density n(H), x_e = n(e)/n(H) which is taken to be comparable to the relative carbon abundance $x_c\sim10^{-4}$ (because all carbon atoms are ionized), and (3) the rate constant of the H_3^+ dissociative recombination $k_e\sim10^{-7}$cm^{3}s^{-1}. The first two parameters, ζ and x_e are important astrophysical quantities, and the observed H_3^+ column densities should provide crucial information about them. Before we can do this, however, we need to understand the laboratory parameter k_e, and this is the subject of this paper. This is an important and general problem because the ubiquity of H_3^+ is being observed in cosmic plasmas, and it is an urgent one since H_3^+ is being observed rapidly in many astronomical sources.

In this paper I briefly sketch the plasma chemistry of H_3^+ in the diffuse interstellar medium and critically review the past and present studies of the H_3^+ dissociative recombination. Clearly it is presumptuous of a non-specialist to do the latter; this is an act of a man desperately needing help. (The number of exclamation marks in the title of this paper has increased with the successive announcements of the ACS meeting, and it is in logarithmic scale!) My cry of SOS is directed to theorists since k_e has been measured by many groups using several entirely different techniques.[3] They seem to give $k_e \sim 10^{-7} cm^3 s^{-1}$ at room temperature except for a few cases as we discuss in Section 3. On the other hand, theoretical studies give much lower values and seem to be in a more uncertain state of affairs.[4] Since laboratory experiments cannot be conducted in the extremely low density, field free condition of interstellar space, the following statement of Bates et al.[5] still applies. "Although several independent experiments provide strong evidence that the dissociative recombination coefficient of H_3^+ at 300K is around $1.5 \times 10^{-7} cm^3 s^{-1}$, an element of unease must remain as long as a theory seems to exclude this possibility."

2. CHEMISTRY OF H_3^+ IN THE DIFFUSE INTERSTELLAR MEDIUM

2.1 General remarks

Two special characteristics of interstellar chemistry are stressed here.

(i) Hydrogen and helium constitute 99.9% of interstellar atoms. Since He is not chemically active, interstellar chemistry is hydrogen dominated chemistry.

(ii) Ions are produced by ubiquitous cosmic-ray particles and stellar radiation and destroyed by electron recombination. Interstellar gas is in the state of weakly ionized plasmas.

H_3^+ has been observed in dense and diffuse clouds.[6]

(i) Dense (molecular) clouds have number density of $10^5 \sim 10^3 cm^{-3}$; they are gravitationally bound and are on their way to star formation. Stellar radiation does not penetrate the clouds. Stars are invisible and gas is in molecular form; hydrogen as H_2 and carbon as CO.

(ii) Diffuse clouds have a number density of $10^3 \sim 10^1 cm^{-3}$. Stars are visible through the clouds and hydrogen is a mixture of H and H_2. Carbon stays atomic and is ionized by star radiation since carbon has the lowest ionization potential among abundant species, i.e., H, H_2, He, C, N and O. This causes the high relative abundance of electrons in the clouds.

2.2 Ion chemistry of H_3^+

H_3^+ is produced by cosmic ray ionization of H_2

$$H_2 \xrightarrow{\text{C.R.}} H_2^+ + e \qquad (1)$$

followed by the ion-neutral reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (2)$$

with the typical Langevin rate constant[7] of $k_L = 2\times10^9 cm^3s^{-1}$. Since the rate of reaction (1), $\zeta \sim 10^{-17}s^{-1}$ is very much lower than the rate of reaction (2), $k_L n(H_2)$ for H_2 number density of clouds, (1) is the rate determining process and the production rate of H_3^+ (in cm^3s^{-1}) is given by $\zeta\, n(H_2)$.

The major destruction process is different in dense and diffuse clouds. In dense clouds H_3^+ is destroyed by proton hop reaction to CO,

$$H_3^+ + CO \rightarrow HCO^+ + H_2$$

with the rate of $k_L n(H_3^+)\, n(CO)$. In diffuse clouds H_3^+ is destroyed by electron recombination

$$H_3^+ + e \rightarrow \begin{cases} H + H + H \\ H_2 + H \end{cases} \qquad (3)$$

with the rate of $k_e\, n(H_3^+) n(e)$.

Equating the production and destruction rates, we obtain the steady state H_3^+ number density

$$n(H_3^+)_{dense} = \frac{\zeta}{k_L} \bullet \frac{n(H_2)}{n(CO)} \qquad (4)$$

for dense clouds, and

$$n(H_3^+)_{diffuse} = \frac{\zeta}{k_e} \bullet \frac{n(H_2)}{n(e)} \qquad (5)$$

for diffuse clouds. Therefore, if we assume a simple model that all hydrogen atoms are in the form of H_2 and all carbon atoms in the form of CO in dense clouds (which is valid), and hydrogen H_2 and carbon C^+ in diffuse clouds (which is not entirely valid and discussed later), $n(H_2)/n(CO) = n(H_2)/n(C^+) = n(H_2)/n(e)$ since they are simply half of the abundance ratio of hydrogen and carbon. We therefore have

$$\frac{n(H_3^+)_{diffuse}}{n(H_3^+)_{dense}} \sim \frac{k_L}{k_e} \sim 4 \times 10^{-3}$$

where the recombination rate constants recommended by Sundström et al,[8]

$$k_e = 4.6\times10^{-6}/(T/K)^{0.65}\ cm^3s^{-1} \qquad (6)$$

for temperature T in 30K and $k_L = 2\times10^{-9}cm^3s^{-1}$ which is temperature independent are used. Various uncertainties and assumptions in the simplified model leads to

$$n(H_3^+)_{diffuse} = (10^{-2} \sim 10^{-3})n(H_3^+)_{dense} \qquad (7)$$

2.3 Observed H_3^+ column densities and the mystery

Examples of H_3^+ column densities observed in dense and diffuse clouds are listed in Table I.

Table I. Observed column densities (in $10^{14}cm^{-2}$) of H_3^+ in dense and diffuse clouds.

Dense clouds[a]		Diffuse clouds[b]	
AFGL 2136	3.8	Cyg OB2 12	3.8
W33A	5.2	Cyg OB2 5	2.6
MonR2 IRS 3	1.4	HD183143	2.3
AFGL 961E	1.7	HD20041	3.5
AFGL 490	1.1	WR121	2.2

[a] from McCall et al.[9]
[b] from McCall et al.[10]

Clearly the column densities in dense clouds and diffuse clouds are comparable and on the order of $N(H_3^+) \sim 10^{14}cm^{-2}$.

Now Eqs. (4) and (5) demonstrate a special characteristic of H_3^+ as an astronomical probe; $n(H_3^+)$ does not depend on cloud density since $n(H_2)/n(CO)$ and $n(H_2)/n(e)$ are constant as long as we are discussing typical dense or diffuse clouds, as shown in Fig. 1.

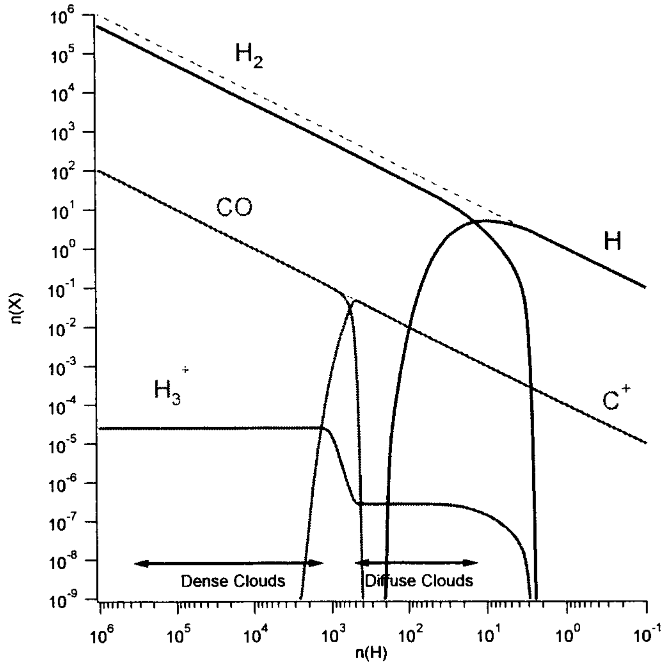

Fig. 1. Schematic diagram indicating number densities n(X) of key chemical species in dense and diffuse clouds relative to total hydrogen density n(H) (drawn by B. J. McCall).

This special property makes H_3^+ a powerful probe to measure cloud dimensions since the optical pathlength of a cloud L is simply given as a ratio of observed H_3^+ column density to estimated number density,

$$L = \frac{N(H_3^+)}{n(H_3^+)} \tag{8}$$

Thus using (4) we obtain a dimension of dense clouds $L_{dense} \sim$ lpc (3×10^{18}cm) which is in accord with astrophysical estimates.

The problem in diffuse clouds, however, is that since its H_3^+ column density is comparable to dense clouds, Eqs. (7) and (8) give $L_{diffuse} = (10^2 \sim 10^3)\ L_{dense} = 100\text{pc} \sim 1000$ pc. This is at least one order of magnitude higher than the canonical dimensions of diffuse clouds. If this is true, clouds occupy a sizeable fraction of the total distance from us to stars. Since clouds are not in general pencil shaped, our galaxy must be filled with H_3^+! Although this is a dream of H_3^+ aficionados like me, it runs into trouble with other observational evidence. For one thing such a huge low density, low temperature cloud cannot be in pressure equilibrium with surrounding gas.

2.4 More details and what ifs

Since hydrogen atoms are not all in the form of H_2 and carbon C^+, Eq. (5) can be elaborated as

$$n(H_3^+)_{\text{diffuse}} = \frac{\zeta}{k_e} \bullet \frac{f}{2} \bullet \frac{1}{1-\alpha} \bullet \frac{1}{z_C} \tag{9}$$

where f is a fraction of hydrogen atom in H_2

$$f \equiv \frac{2n(H_2)}{2n(H_2)+n(H)} = \frac{2n(H_2)}{n(\Sigma H)},$$

α is a fraction of carbon not in the form of C^+, and $z_C \equiv n(\Sigma C)/n(\Sigma H)$ is a fraction of total carbon in the gas phase. In our discussion in 2.2 and 2.3 we assumed $f = 1$ and $\alpha = 0$. By definition f is lower than 1 but cannot be much lower since H_2 is needed to produce H_3^+. Also a lower value of f simply makes the problem worse. There are electrons released from atoms other than carbon. This effect is not included in Eq. (9) but again it makes the problem worse. Solution of this mystery has to come from one of the four parameters in Eq.(9), i.e., k_e, ζ, α or z_C.

2.4.1 Rate constant of dissociative recombination; k_e

Clearly the simplest way out of this puzzle is to use the value of k_e which is lower by one to two orders of magnitude. However, in view of the good agreement of the laboratory values of $k_e \sim 10^{-7}\text{cm}^3\text{s}^{-1}$ at T=300, obtained by several different techniques, I do not want to use this escape route easily. The values of k_e are discussed in the next section. The value of k_e is smaller if the temperature of electrons is very high in interstellar space. This is highly unlikely, however, because of the large cross section of electron-neutral collisions which thermalize electrons rapidly.

2.4.2 Ionization rate; ζ

The puzzle can be explained if the ionization rate is one to two orders of magnitude higher than the canonical value of 10^{-17}s^{-1}. Since our argument is based on a comparison of dense and diffuse clouds, this difference has to be between the two categories of clouds. There is a possibility that a soft component of cosmic ray is shielded in dense clouds but penetrates the diffuse clouds, making the ionization rate higher in diffuse clouds than in dense clouds. This is a very interesting astrophysical problem. There are chemical arguments based on observational abundance of HD by O'Donnell and Watson[11] and OH by Hartquist et al.[12] that constrain the value of ζ to $\sim 10^{-17}\text{s}^{-1}$ although they may not be conclusive.

When H_3^+ was discovered in Cygnus OB2 No. 12 by McCall et al.,[13] Black[14] proposed that photo-ionization by intense X-ray from the extraordinarily bright star may make the ionization rate higher by two orders of magnitude. Gredel, Black and Yan[15] showed that the greatly enhanced ionization rate of $\zeta = (0.6\text{–}3)\times10^{-15}\text{s}^{-1}$ consistently explains the observations of C_2 and CN as well as our observation of H_3^+. However, this will not be a general solution since other stars which show large column densities of H_3^+ such as HD183143 and HD20041 are more ordinary stars.

2.4.3 States of carbon; α and z_C

The puzzle can be explained if z_C is much less than its canonical value due to depletion of carbon onto grains and large carbon molecules. This is not very likely in view of similar C/H ratio of 1.4×10^{-4} observed in diffuse clouds[16] and dense clouds.[17] The puzzle can be explained also if $\alpha \approx 1$, that is, if carbon atoms are mostly in neutral species. We have already confirmed observationally that a very small fraction of carbon atoms are in the form of CO in diffuse clouds;[10,13] therefore, carbon has to be in the form of a neutral atom. A model calculation by van Dishoeck and Black[18] shows it is unlikely to have carbon as a neutral atom without much CO nor C^+.

Both of these possibilities can be checked by observing spectra of C^+ and C directly. I am just writing a proposal to the Hubble Space Telescope to do these observations.

3. DISSOCIATIVE RECOMBINATION OF H_3^+

Since the discovery of the high efficiency of dissociative recombination by Biondi and Brown[19] in plasmas of H_2, N_2 and O_2, and Bates[20] theoretical estimate of dissociative recombination rate constants to be $10^{-7}\text{cm}^3\text{s}^{-1}$, a great many experiments have been conducted using many different experimental techniques and many theoretical works have been published. I summarize below experimental results published on H_3^+ recombination.

3.1 Experimental values of H_3^+ recombination rate constant

Dissociative recombination rate constants k_e at T=300K are listed in Table II.

Table II. Experimental rate constants of dissociative recombination of H_3^+

k_e (in $10^{-7} cm^3 s^{-1}$)	Method[a]	Authors	Year
25[b]	MA	Biondi, Brown[19]	1949
20[b]	MA	Richardson, Holt[21]	1951
3.4[b]	MA	Varnerin[22]	1951
<0.3[b]	MA	Persson, Brown[23]	1955
2.3	MA/MS	Leu, Biondi, Johnsen[24]	1973
2.5	IB	Peart, Dolder[25]	1974
2.1	MB	Auerbach et al.[26]	1977
1.5	IT	Mathur, Khan, Hasted[27]	1978
4.2	MB	McGowan et al.[28]	1979
1.6	FA	MacDonald, Biondi, Johnsen[29]	1984
<0.2	FALP	Adams, Smith, Alge[30]	1984
≤0.0001	FALP[c]	Smith, Adams[31]	1987
0.2	MB	Hus et al.[32]	1988
1.8	IR	Amano[33]	1988
≤0.0001	FALP	Adams, Smith[34]	1989
≤0.001	FALP	Smith, Adams, Ferguson[35]	1990
0.2	MB	Yousif et al.[36]	1991
1.5	FALP/MS	Canosa et al.[37]	1992
0.1~0.2	FALP	Smith, Ŝpanel[38]	1993
1.15	SR[d]	Larsson et al.[39]	1993
<2	IR/MS	Féher, Rohrbacher, Maier[40]	1994
	FALP	Gougousi, Johnsen, Golde[41]	1995
0.78	FALP/MS	Laubé et al.[42]	1998
<0.13	ISA	Glosík et al.[43]	2000
<0.03	ISA	Glosík[44]	2001

[a] MA: Microwave afterglow; MS: Mass Spectroscopy
IB: Inclined beam; MB: Merged beam
IT: Ion trap; FA: Flowing afterglow
LP: Langmuir probe; IR: Infrared spectrum
SR: Storage ring; ISA: Integrated stationary afterglow

[b] They are measurements under fairly high pressure of 1 to 50 Torr. Under higher pressure H_3^+ are clustered with H_2 in the form of $H_3^+(H_2)_n$.

[c] Adams and Smith advocated the low value also in refs. 45 and 46.

[d] There are other storage ring results which are in agreement with this.[47]

The period of 1947–1955 was that of discovery and establishment of the fast rate of dissociative recombination using microwave afterglow (MA). The measurements were done under high pressure of 1 to 50 Torr where some H_3^+ are clustered in the form of cluster cations $H_3^+(H_2)_n$. New experimental techniques of inclined beam (IB) and merging beam (MB), ion-trap (IT), and flowing afterglow (FA) were introduced from 1973–1984 which all gave k_e on the order of $10^{-7}cm^3s^{-1}$. The period of 1984–1990 saw a sudden plunge of k_e by four orders of magnitude to $10^{-11}cm^3s^{-1}$ reported by Smith and Adams[31] using the FA/Langmuir probe (FALP) method. This extremely low value, now retracted by the authors, seriously misled a generation of astrophysical model calculations. In 1988 Amano[33] published a paper titled "Is the dissociative recombination of H_3^+ really slow?" describing his measurement using spectroscopic techniques and restoring k_e to $\sim 10^{-7}cm^3s^{-1}$. It took a few years, however, before his value was accepted by the community. Since 1992 FALP experimental values have returned to $10^{-7}cm^3s^{-1}$ except the value by Smith which was revised to $10^{-8}cm^3s^{-1}$.[38] The year 1993 saw the advent of the novel and clean technique of merging beam using an ion storage ring by Larsson et al[39]. The value of k_e given in Eq. (6) has been obtained by this method and is now being used in model calculations. More in-depth review has been given by Larsson.[3] Very recently Glosík et al.[43] reported a low value of $<1.3\times10^{-8}cm^3s^{-1}$ and the value is getting even lower[44] to $<1.3\times10^{-9}cm^3s^{-1}$. This plunge of the upper limit of k_e is reminiscent of the period of 1984–1990. Does history repeat itself?

3.2 Relation to the mystery

The mystery of abundant H_3^+ in the diffuse interstellar medium will be immediately lessened if we adopt the value of Glosík et al.[43] However, I cannot accept their value easily since I do not understand the drastic dependence of k_e on number density of H_2 reported by them. They note that k_e changes from 1.3×10^{-8} to $1.5\times10^{-7}cm^3s^{-1}$ when H_2 number density is changed from 1×10^{11} to $2\times10^{12}cm^{-3}$. Such a drastic pressure dependence has not been reported in previous works except those in the earliest papers using microwave afterglow (MA) under higher pressure[19,21-23]. The values of k_e listed in Table II have been measured over a wide range of pressure, from the ultrahigh vacuum of storage ring[39] to near 1 torr pressure of hollow cathode.[33] The approximate constancy of the k_e value over this wide range of number density (about 10 orders of magnitude) is clearly in conflict with the drastic dependence of Glosík et al.[43] The dependence is hard to explain theoretically also since three-body collision with H_2 is not likely to be effective at the density of $10^{12}cm^{-3}$. Glosík et al.[43] stress "the excellent agreement" of their result and that of Smith and Španel,[38] but the latter experiment was conducted at H_2 density of $2\times10^{14}cm^{-3}$.

Merging beam experiments of Mitchell's group[32,36] conducted during the "depression" period gave $\sim10^{-8}cm^3s^{-1}$ but the value has been revised to $(1.2\pm0.2)\times10^{-7}cm^3s^{-1}$ (quoted in Laubé et al.[42]).

At this stage $10^{-7}cm^3s^{-1}$ at 300K and the value given in Eq.(5) are the experimental results to be adopted in astrophysical calculations. There remains uneasiness, however, since the laboratory experiments cannot be conducted in the low density, field free condition of interstellar space—the limitation laboratory astrophysicists always experience in trying to mimic nature. Even the cleanest ion storage ring experiment is conducted with an electron number density of $10^{-7}cm^{-3}$ and in a magnetic field of 300 Gauss.[48,49] The effect of stray Coulomb fields from other electrons and relativistic electric fields (although the magnetic field is parallel to ion velocity to a good approximation.) may not be completely dismissed. Hence the need of theoretical confirmation and the remark of Bates et al.[5] quoted earlier in Section 1.

4. THEORISTS, HELP!

Since the prescient paper by Bates and Massey[50] on the basic reactions in the upper atmosphere, the paper by Bates[51] ascribing the rapid neutralization of He to dissociative recombination to He_2^+, and the paper by Bates[20] on the estimate of k_e, a great many theoretical papers have been published. Theoretical results on H_3^+, however, seem to be in an uncertain state. Michels and Hobbs[52] presented theory which supported Adams and Smith and this influenced the acceptance of the extremely low k_e value by the community. The most recent results,[4,53] are still more than two orders of magnitude lower than the laboratory value of $10^{-7}cm^3s^{-1}$. Like Michels and Hobbs, they are based on the assumption of C_{2v} symmetry of H_3 during the dissociative process which is not in accord with the recent experimental results of Datz et al.[54] and Strasser et al.[55]

Dissociative recombination of H_3^+ in interstellar space is a clean, well defined process. The enigma is a fundamental problem with wide impact on various areas of astrophysics. In its generality this enigma of H_3^+ is reminiscent of the problem of its isoelectronic sibling H^- and the opacity of the Sun; observation and theory by Massey and Bates[56] were orders of magnitude off till it was finally clarified by Chandrasekhar and Breen.[57] This clarified the very general problem related to opacity of all main sequence stars. Likewise a conclusive theory of H_3^+ recombination will clarify a major uncertainty of interstellar chemistry. Extensive theoretical calculations are eagerly awaited.

Finally a word of caution. This astronomical mystery should not be taken to constrain the value of k_e in any definitive way. The assumed canonical astrophysical parameters may be wrong. It is even possible that clouds containing H_3^+ are indeed very large. *What we need is the TRUE value of* k_e *and not a value which explains the problem quickly.* To this end scientists in different disciplines need to work together. Physicists, chemists and astronomers of the world, unite!

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