EPJ Web of Conferences **84**, 06001 (2015)
DOI: 10.1051/epjconf/20158406001

Help!!! Theory for H_3^+ recombination still needed

Takeshi Oka

Department of Chemistry and Department of Astronomy and Astrophysics, the Enrico Fermi Institute, University of Chicago, 5735 South Ellis Ave., Chicago, IL 60637, USA

Abstract. In spite of the great progress in theoretical and experimental studies of the dissociative recombination (DR) of H_3^+ in the last decade, there still remain apparent discrepancies between them. They are counted out and the effect of magnetic fields used in the storage ring experiments is considered as a possible cause of the discrepancy. In addition, the high internal temperature of H_3^+ revealed by experiments at the Max Planck Institute of Nuclear Physics suggests a possibility that the current value of the DR rate constant may still be off by a significant factor.

In the meantime, the importance of the DR of in the H_3^+ diffuse interstellar medium has grown further as astronomical observations of H_3^+ developed rapidly in the last decade. It has been established that H_3^+ is the best probe to measure intensities of low energy cosmic rays. The rate constant for the DR of H_3^+ is crucial in the measurement. We still desperately need the theory for the dissociative recombination of H_3^+!

1. Introduction

The last time I attended this series of DR meetings was DR 2001 in Chicago, where I gave a talk with a title "Help!!! Theory for H_3^+ Recombination Badly Needed" [1]. The rate constant of the dissociative recombination (DR) of H_3^+ (hereafter k_e) is of primary importance for analyses of the H_3^+ spectra observed in the diffuse interstellar medium and I was desperate at that time since the best theoretical value in the year 2000 was off the experimental value by more than 2 orders of magnitude. In the meeting Chris Greene reported a new theory which looked very promising but the theoretical value was still off the experimental value by a factor of 10 [2].

In the last 12 years, there has been a great progress in theory by Kokoouline and Greene [3–5] and by dos Santos, Kokoouline and Greene [6]. Those theoretical calculations gave k_e which agreed well with the experimental values. Subsequently, an analytical theory by Jungen and Pratt followed [7, 8] which supported the results of [3–6].

In the laboratories, excellent agreement has been reached between the measurements of Larsson's group at the Manne Siegbahn Laboratory [9], and Wolf's group at the Max–Planck Institute of Nuclear Physics both in energy dependent resonant structure and in the absolute value of the cross section [10].

Nevertheless there still remain significant disagreements between theory and experiments [10–12]. In addition the recent experimental revelation of high internal temperature of H_3^+ [10–12] suggests that the currently used value of k_e [9] may still be off significantly. I discuss those problems in this paper.

During the 12 years since DR2001, astronomical observations and the understandings of interstellar H_3^+ have also made a great progress [13]. One of the most exciting developments has been that the cosmic ray ionization rate in interstellar space, which had been held to be on the order of $\zeta \sim 10^{-17}\,s^{-1}$ both observationally and theoretically for the previous 30 years, has been shown to be an order of magnitude higher in diffuse clouds in the Galactic disk [14] and two orders of magnitude higher near the Galactic center [15]. Such radical departure from the previous consensus initially met with skepticisms but the analysis was so straightforward and evidences so overwhelming [13, 16–18] that it is now becoming accepted. In these analyses, k_e of H_3^+ is the single laboratory parameter used. Since the cosmic rays are one of the most important and least understood phenomena of astrophysics, having sound understanding on the DR of H_3^+ is of vital importance.

I do not work on DR myself but I use it. In this talk I may sometime sound like a car buyer who complains about a car without understanding how a car works and without appreciating the enormous amount of work going into making a car. I also mention things that many of you know already. I apologize for it beforehand.

2. Remaining discrepancies

There still remain two apparent disagreements between the theory [2–6] and experiments [10–12]. Whether they are due to inadequacy of the theory or not remains to be seen. A possible source of the discrepancy may be the high magnetic field of 300–400 gauss used in the experiments. Recombination of H_3^+ proceeds through H_3 in Rydberg states which are sensitive to the magnetic field due to their magnetic dipole moment, and to the relativistic electric field due to their huge electric dipole moment proportional to n^2. The discrepancy between theory and experiment may be partly due to this. The effect of the magnetic field was considered earlier [19, 20] but not of the electric field. Since the laboratory experiment cannot be conducted under the field-free condition of interstellar space, it should eventually be the theoretical calculations which provide k_e for astrophysics of interstellar H_3^+. For this reason, we badly need accurate theory.

2.1 Energy dependent resonant structure

In a joint paper of experimentalists and theorists, Petrignani et al. [11] pointed out that the largest experimental resonance (A) at detuning energy of $E_d \sim 6.5\,\text{meV}(\sim 75\,\text{K})$ was not theoretically reproduced and the four theoretically expected resonances near 0.02. 0.03, 0.04, and 0.05 eV are not observed experimentally (Fig. 1). The latter resonances "are lying on and slightly below a rotational threshold supporting an infinite number of high-Rydberg states." [11] In general the theoretical results show many more sharp resonances than experiments. Some effect may be blurring the sharp resonances.

Would it be possible that those peaks are washed out by the magnetic field? The direct energy shifts due to Zeeman effect seem too small but the Stark effect due to the huge electric dipole moment of Rydberg H_3 might be large enough to broaden the resonances with the width on the order of 2 meV? During the electron capture, the electron moving toward H_3^+ may have a velocity component perpendicular to the magnetic field up to $v \sim e^2/\hbar$ and feel a high relativistic electric field of $B/137$ which for $B = 400$ gauss is $\sim 10^3$ V/cm. Would the electron capture under the electric field wash out the resonances? And would it create the big resonance at $E_d \sim 6.5$ meV?

2.2 k_e for para-H_3^+ and ortho-H_3^+

Theory predicts much higher k_e for para-H_3^+ than for ortho-H_3^+ [6] at low collision energy while experiments do not show this effect as decisively [10, 21] (Fig. 2).

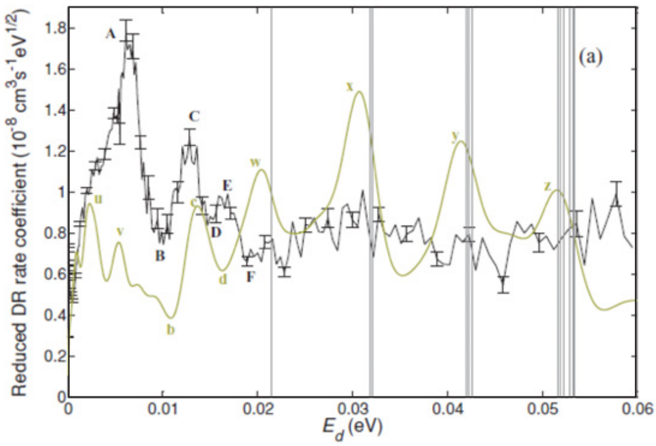

Figure 1. The H_3^+ DR rate constant k_e versus collision (detuning) energy compared with theoretical k_e calculated for the ions at 300 K. Vertical lines indicate ionization threshold for various initial ionic rotational levels. See [11] for more details.

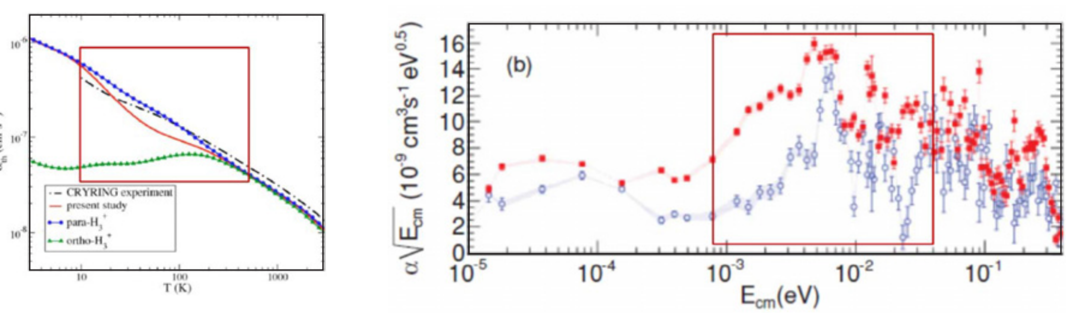

Figure 2. k_e for para-H_3^+ and ortho-H_3^+ theoretically calculated by dos Santos, Kokoouline, and Greene [6] (left) and experimentally observed by Kreckel et al. [10] (right), where red data give values for extrapolated "pure" para-H_3^+ and blue data for ortho-H_3^+. Rectangles represent collision energy from 10 K (0.8 meV) to 500 K (40 meV).

In Fig. 2, it is apparent that both the magnitude and collisional energy dependence of the ratio of k_e for para-H_3^+ and ortho-H_3^+ are different between theory and experiment. The direct magnetic effects of nuclear spin for $I = 1/2$ para-H_3^+ and $I = 3/2$ ortho-H_3^+ are negligible, and the large difference of k_e in the left of Fig. 2 must be the result of the difference in energy gap between two levels involved in the electron capture. Such difference may also be blurred due to Stark effect of the Rydberg H_3 with huge electric dipole moments in the relativistic electric field due to the magnetic field as discussed in the previous subsection.

Contrary to the storage ring experiments, stationary afterglow experiments by Glosik's group [22–24] have claimed that k_e for para-H_3^+ is much higher than for ortho-H_3^+ in agreement with the theory. Their ratio of k_e for para-H_3^+ and ortho-H_3^+ for the lowest temperature of 77 K is about 10 which is even *higher* than the theoretical value by more than a factor of 3! I take this result with a grain of salt. Unlike in the storage ring experiment in which only the directly interacting H_3^+ and electrons are involved, the afterglow experiments use He dominated plasmas with He/Ar/H_2 mixtures with typical compositions of $10^{17}/10^{14}/10^{14}$ cm^{-3}. Analyses of such plasmas are known to be notoriously difficult for their complexity. For one thing, the long lived metastable He* keep ionizing H_2 and producing H_3^+

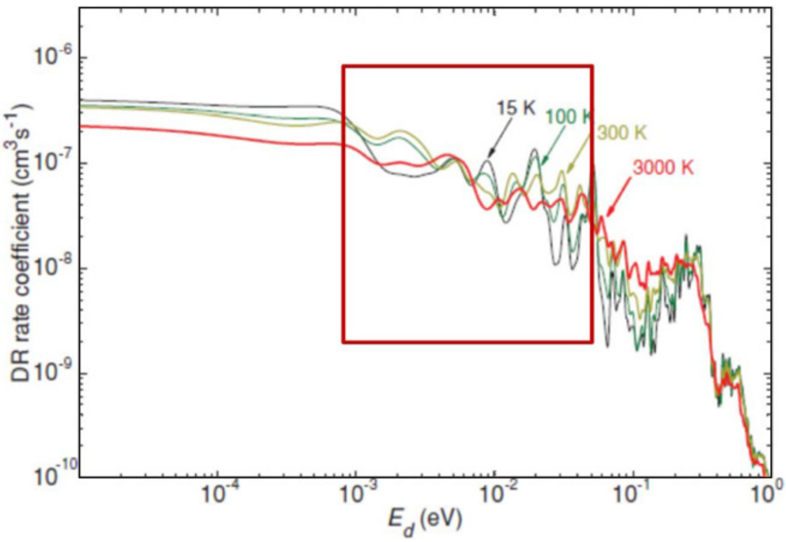

Figure 3. H_3^+ DR rate constants as theoretically predicted for 15, 100, 300, and 3000 K, The 15 K rate is calculated using a 1:1 ortho-to-para ratio [11]. The rectangle represents collision energy from 10 K (0.8 meV) to 500 K (40 meV).

(Penning ionization [25]) even after the microwave discharge is switched off. The Ar gas is perhaps added for the purpose of quenching the metastable He* but, with the quenching cross section less than 10 Å^2 [26], the quenching won't be complete with the Ar density of 10^{14} cm^{-3} in their experimental time scale of 100μs. The analyses in [22–24] considering only ortho- and para- species of H_2 and H_3^+, and electrons without taking into account the complexity of the He/Ar discharge may not be reliable.

3. High rotational temperature of H_3^+

Recently there has been a shocking revelation from the measurements of the total energy release upon DR that the rotational temperature of H_3^+ in the storage ring had been much higher than previously thought. Instead of the low rotational temperature of 20–60 K reported by McCall et al. [9], 380^{+50}_{-130} K has been given and claimed that this had been the lowest rotational temperature so far realized in storage-ring DR measurements on H_3^+ [11]. According to theoretical calculations by Petrignani et al. [11] shown in Fig. 3, k_e with rotational temperature of 300 K are higher than that with 15 K by a factor of ~2.6 at $E_d = 2.1$ meV (24 K) and of ~5.4 at $E_d = 28$ meV (320 K), and lower by a factor of ~2.0 at $E_d = 9.4$ meV (110 K). Figure 2 in dos Santos et al. [6] give different but qualitatively similar set of numbers.

These differences which vary with temperature tend to be averaged out to some extent but the difference in the rotational temperature between 20–60 K and 380 K may introduce the uncertainty in k_e up to a factor of perhaps 2. Since H_3^+ with higher rotational temperature tend to have higher rate of DR, the value of k_e by McCall et al. [9] which have been used in the analyses [14–18] of interstellar H_3^+ may have to be decreased somewhat.

4. Possible improvement in theory?

Concurrent to the theory by Kokoouline and Greene [3, 4], Tashiro and Kato [27, 28] studied dynamics of the predissociation of H_3 Rydberg states. Kato (now deceased) was of the opinion that the first-order perturbation treatment (Fermi's golden rule) of electron capture used by Kokoouline and Greene (and later by Jungen and Pratt [7, 8]) is not accurate when the resultant state is not a stationary state as the predissociating Rydberg state. (I thank Professor V. Kokoouline for pointing out to me after my talk that this effect had been taken into account in [4]).

Johnsen and Guberman [20] also point out that Tashiro and Kato proposed that initial electron capture occurs into high n ($n = 6$ or 7) states with low vibrational excitation which couples to low n states with high vibrational excitation and eventually reach the lowest $2sA_1'$ state which couples with the dissociative $2pE'$ state. This process was not considered in Kokoouline and Greene [3, 4] and Jungen and Pratt [7, 8] where only $l = 1$ p-states are considered since the $l = 0$ s-states are not directly involved in Jahn–Teller coupling.

Overall, I believe there remains much room for more improvement of the theory and I look forward to participation of ambitious theorist in further clarifying the problem of the dissociative recombination of H_3^+.

This research is supported by NSF grant AST 1109014.

References

[1] T. Oka, in *Dissociative Recombination of Molecular Ions with Electrons*, ed. by S. L. Guberman, Kluwer Academic/Plenum Publishers, New York, pp 209-220, (2003)
[2] C. H. Greene, V. Kokoouline, B. D. Esry, Ibid. pp 221-233
[3] V. Kokoouline, C. H. Greene, Phys. Rev. Lett. **90**, 133201 (2003)
[4] V. Kokoouline, C. H. Greene, Phys. Rev. A **68**, 012703 (2003)
[5] C. H. Greene, V. Kokoouline, Phil. Trans. R. Soc. A **364**, 2965 (2006)
[6] S. F. dos Santos, V. Kokoouline, C. H. Greene, J. Chem. Phys. **127**, 124309 (2007)
[7] Ch. Jungen, S. T. Pratt, Phys. Rev. Lett. **102**, 023201 (2009)
[8] Ch. Jungen, M. Jungen, S. T. Pratt, Phil. Trans. R. Soc. A **370**, 5074 (2012)
[9] B. J. McCall et al. Phys. Rev. A **70**, 052716 (2004)
[10] H. Kreckel et al. Phys. Rev. A **82**, 042715 (2010)
[11] A. Petrignani et al. Phys. Rev. A **83**, 032711 (2011)
[12] H. Kreckel et al. Phil. Trans. R. Soc. A **370**, 5088 (2012)
[13] T. Oka Chem. Rev. **113**, 8738 (2013)
[14] B. J. McCall et al. Nature **422**, 500 (2004)
[15] T. Oka et al. Astrophys. J. **632**, 882 (2005)
[16] M. Goto, et al. Astrophys. J. **688**, 306 (2008)
[17] T. Oka, Faraday Discuss. **150**, 9 (2011)
[18] N. Indriolo, B. J. McCall, Atrophys. J. **745**, 91 (2012)
[19] A. Wolf et al. Phil. Trans. R. Soc. A **364**, 2981 (2006)
[20] R. Johnsen, S. L. Guberman, in Adv. Atom. Mol. Optic. Phys. **76**, 126 (2010)
[21] B. A. Tom et al. J. Chem. Phys. **130**, 031101 (2009)
[22] J. Varju et al. Phys. Rev. Lett. **106**, 203201 (2011)
[23] P. Dohnal et al. J. Chem. Phys. **136**, 244304 (2012)
[24] P. Dohnal et al. Phil. Trans. R. Soc. A **370**, 5101 (2012)
[25] T. Oka, in *The Encyclopedia of Mass Spectrometry: Theory and Ion Chemistry*; **1** P. B. Armentrout, Ed.; Elsevier, Inc., San Diego, CA (2003)
[26] K. L. Bell, A. Dalgarno, A. E. Kingston, J. Phys. B **1**, 18 (1968)
[27] M. Tashiro, S. Kato, Chem. Phys. Lett. **354**, 14 (2002)
[28] M. Tashiro, S. Kato, J. Chem. Phys. **117**, 2053 (2002)