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Introductory remarks

By Takeshi Oka*

Department of Astronomy and Astrophysics and Department of Chemistry, The Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637, USA

The inspiring developments in astronomy, physics and chemistry of H_3^+ since 2000, which led to this Royal Society Discussion Meeting, are reviewed.

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1. First principle calculations

Rigorous theory for calculation of rovibrational energy levels of H_3^+ has been developed using the sub-microhartree accuracy potential energy surface by Kutzelnigg & Jaquet (2006), in which adiabatic and relativistic effects are included, and the hyperspherical coordinate formalism of Wolniewicz & Hinze (1994). The calculated energy level values by Schiffels and co-workers (Alijah & Hinze 2006) agree with experiment within 1 cm^{-1} up to *ca* 12 500 cm^{-1}. Only the non-adiabatic and quantum electrodynamical corrections are yet to be added. This situation may be compared to the *ab initio* theory of H_2 in 1975 (Kołos & Wolniewicz 1975). It has taken 30 years to progress from the two-particle to the three-particle problem.

Accurate potential energy surfaces for the triplet $a^3\Sigma_u^+$ state, the only bound electronic excited state of H_3^+, have been calculated and rovibrational levels of the lowest 19 vibrational states have been predicted (Alijah & Varandas 2006). Producing the triplet H_3^+ in a plasma will be a big challenge for experimentalists, since the dissociative triplet H_2 has to be protonated.

The enormously rich H_3^+ spectral lines near the dissociation limit reported by Carrington and colleagues remain unassigned. Tennyson and colleagues, however, have computationally discovered a series of H^+–H_2 asymptotic vibrational states which lie above the classical dissociation energy and have no analogue for diatomic molecules (Tennyson *et al.* 2006).

2. Laboratory spectroscopy

Close interplay between *ab initio* calculations and laboratory experiments has always been the cornerstone of the H_3^+ spectroscopy. Since 2000, the observed spectral range has been extended from 8200 to 13 700 cm^{-1} exceeding the barrier to

*t-oka@uchicago.edu

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linearity and entering into the visible (Gottfried 2006). This has provided a special challenge for theorists, since the region of linear H_3^+ has been sampled where its Hamiltonian has a singularity. The laboratory experiment has confirmed theory.

A new high-sensitivity spectroscopic technique using ion–neutral reactions called 'action spectroscopy' has been developed by Schlemmer & Gerlich and applied to H_3^+ and its isotopic species (Glosik *et al.* 2006). This method is also capable of providing state-specific information on chemical kinetics.

Sub-millimetre rotational spectra of H_2D^+ and HD_2^+ have been measured by Amano and co-workers (Amano 2006) which provided the key information for radio astronomical detection of HD_2^+, the crucial evidence for the ultrahigh deuterium fractionation (§7).

Schiller and colleagues have generated translationally very cold (approx. 20 mK) H_2^+, H_3^+ and isotopomers in an ion trap by sympathetic cooling of the molecular ions with laser-cooled Be^+ ions (Blythe *et al.* 2005). This opens a way to ultrahigh-resolution spectroscopy of H_3^+ and isotopomers enabling observations of their hyperfine structure and the Zeeman effect.

3. Dissociative recombination

Dissociative recombination (DR) with electrons is the major destruction mechanism of H_3^+ in the diffuse interstellar medium (ISM) and determining its accurate rate constant is essential for understanding the astrophysics of H_3^+. Larsson's group has studied rotationally cooled H_3^+ using ion-jet technique and obtained the value at the low temperature of interstellar space (McCall 2006). Subsequent experiments by Wolf and colleagues with the Test Storage Ring (TSR) using a cryogenic ion trap have confirmed the results and shown the first evidence for nuclear spin effect (Wolf *et al.* 2006). The experiment has also led to a better understanding of the nuclear dynamics in the DR of H_3^+ and deuterated species (Strasser *et al.* 2002, 2004).

There has been a great progress in the theoretical understanding of the H_3^+ DR. Kokoouline & Greene (2003) presented an extensive theoretical calculation fully taking into account the multidimensionality of the process including the Jahn–Teller effect and obtained a value which is more than two orders of magnitude higher than the best theoretical calculation of 2000. Finally, the theoretical and the experimental values of the storage ring experiment seem converging (Greene & Kokoouline 2006). Since this is an extremely important process governing the chemistry in the diffuse ISM, further experimental and theoretical studies are awaited.

The $H_2^+ + H^-$ ion-pair formation, instead of neutralization in electron recombination of H_3^+, has also been studied experimentally and theoretically (Larson *et al.* 2006).

4. Chemical kinetics

The rapid development of astronomical observations of H_3^+, H_2D^+ and HD_2^+, especially those related to the ultrahigh deuterium fractionation discussed in §7, has made it very important to have good understandings on the ion chemical kinetics of pure hydrogenic species and their deuterium variants. The extensive studies of the $H_mD_n^+$ $(m+n\leq 5)$ system made possible by the temperature variable

cryo-cooled 22-pole ion trap developed by Gerlich (1995) over years are providing crucial information at the low temperature of interstellar space (Gerlich *et al.* 2006). Fundamental ion–neutral reactions, $H^+ + H_2$, $H + H_2^+$, $H_2^+ + H_2$ and $H_3^+ + H_2$, and their deuterium variants, which play crucial roles in interstellar chemistry, have been studied. The ion trap has also been an essential element for the aforementioned action spectroscopy and the TSR studies of rotationally cooled H_3^+ DR.

The state-specific information on chemical kinetics at low temperature is the ultimate goal of the study to be used in molecular astrophysics. Recent introduction of spectroscopy to monitor reactions by Schlemmer *et al.* (see fig. 8 of Gerlich *et al.* (2006)) is the first experimental step towards this goal. Such experiment is also capable of providing the more subtle information on the change of *ortho* and *para* spin modifications in chemical reactions. The study on the *ab initio* potential energy surface for the $H_5^+ \rightarrow H_3^+ + H_2$ by Bowman and colleagues (Xie *et al.* 2005) is the first step towards the state-specific theoretical studies.

5. High abundance in diffuse clouds

Although it took many years to detect the first signal of interstellar H_3^+, subsequent observations have established its ubiquity. H_3^+ has been observed not only in dense molecular clouds where its presence had been anticipated but also in diffuse clouds. Contrary to the expectation from chemical model calculations, the extensive observations by McCall *et al.* (2002) of H_3^+ in diffuse clouds have established that the H_3^+ column density per unit visual extinction A_V in diffuse clouds is an order of magnitude higher in diffuse clouds than in dense clouds. In other words, the fractional abundance of H_3^+ relative to hydrogen is 10 times higher in diffuse clouds than in dense clouds. In addition, owing to the large volume, the total amount of the H_3^+ in a diffuse cloud is several orders of magnitude higher than in a dense cloud. Perhaps, most of the H_3^+ in the Universe are in diffuse clouds.

The surprising abundance of H_3^+ in diffuse clouds, especially in the classical optical sightline towards ζ Persei, has led to the idea that the cosmic ray ionization rate ζ is more than an order of magnitude higher in the diffuse cloud than in dense clouds (McCall *et al.* 2003; McCall 2006). Such a high value of ζ is beyond the limit previously set by HD and OH chemistry (Hartquist *et al.* 1978), but Liszt has argued that it is reasonable if neutralization of atomic ions on dust grains is properly taken into account, although 'many devils lurk in details of the chemistry of diffuse clouds' (Liszt 2006). A chemical model calculation in diffuse clouds towards ζ Persei has been presented (Le Petit *et al.* 2004).

6. The Galactic centre

Observations of H_3^+ in the Central Molecular Zone (CMZ) of the Galaxy by Geballe and Goto and colleagues have demonstrated high abundance of H_3^+ and the special nature of the gas in the CMZ (Geballe 2006). Large column densities of H_3^+ in the $(J,K)=(3,3)$ metastable rotational level, which is 361 K above the (1,1) ground level, have been discovered by Goto *et al.* (2002) demonstrating high temperature of the environment. Subsequent more extensive high-resolution

observation and analyses have revealed a vast amount of high-temperature (approx. 250 K) and low-density (approx. 100 cm^{-3}) gas in the CMZ (Oka *et al.* 2005). So far, the hot and diffuse gas has been observed towards eight young stars within 30 pc from the centre suggesting widespread existence of the gas. H_3^+ has emerged as a novel powerful probe to study the gas in the CMZ which provides information vital for understanding the great activity near the Galactic centre (GC). A model calculation on H_3^+ in hot and diffuse medium of the GC has been presented (Le Petit & Roueff 2006).

H_3^+ has also been observed towards an external galaxy IRAS 08572+3915 NW, where the spectrum is shifted by $z=0.0583$ owing to the expansion of the Universe (Geballe *et al.* 2006). This marks the beginning of the studies of extragalactic H_3^+.

7. Ultrahigh deuterium fractionation in pre-stellar cores

A remarkable manifestation of the fundamental role that H_3^+ plays in interstellar chemistry has been revealed in the observed ultrahigh deuterium fractionation in proto-stars. It has been shown by chemical model calculations that in pre-stellar cores with high density (greater than $10^6\,cm^{-3}$) and low temperature (10 K) where molecules other than H_2 and its deuterated species are highly depleted, HD becomes the main destroyer of H_3^+. The slightly exothermic reactions (owing to energy differences of zero-point vibrations of the reactants), $H_3^+ + HD \rightarrow H_2D^+ + H_2$, $H_2D^+ + HD \rightarrow HD_2^+ + H_2$ and $HD_2^+ + HD \rightarrow D_3^+ + H_2$, proceed efficiently owing to the low temperature resulting in number densities of H_3^+ isotopomers of the order $n(H_3^+) \leq n(H_2D^+) \leq n(HD_2^+) < n(D_3^+)$ in extreme cases (Roberts *et al.* 2003; Walmsley *et al.* 2004; Roberts & Millar 2006). Since nitrogen compounds, such as HN_2^+ and NH_3, are observed in the same region, this extreme case does not apply but the model calculations explain the observed highly deuterated molecules, such as D_2CO, ND_3 and D_2S, within the realm of gaseous chemistry.

Sub-millimetre detections of HD_2^+ (Vastel *et al.* 2006) in the pre-stellar core 16293E and L1544 and the observational and theoretical study of H_2D^+ in proto-planetary disks (Ceccarelli & Dominik 2006) give some observational support to the model calculation. Chemistry and kinematics of pre-stellar cores using H_3^+ and H_2D^+ has been studied (van der Tak 2006).

8. Dynamics in planetary ionospheres

Since its discovery in the auroral regions in Jupiter in 1989, the strong and pure H_3^+ emission spectrum has served as a powerful probe to study plasma activities in the ionosphere of Jupiter, Saturn and Uranus. Since H_3^+ is produced mainly from ionization of H_2 by high-energy electrons accelerated by Jupiter's magnetic field into Jovian atmosphere, the emission is a good indicator of energy input out of the magnetosphere to the planet. More recently, it has become increasingly clear that H_3^+ is not only a useful probe, but also an important driver of the thermosphere and ionosphere of the giant planet. The strong infrared emission serves as an efficient coolant and maintains the energy balance leading to the 'H_3^+ thermostat effect'. H_3^+ is also a major source of electric conductivity and participates in the dynamics of Jupiter's atmosphere through ion–neutral coupling (Miller *et al.* 2005, 2006).

The temperature of Jovian ionosphere is very high ($T \sim 1100$ K) that H_3^+ emission originating from $3\nu_2$ vibrational state ($T \sim 10\,000$ K) has been observed. Spectro-imaging observation of H_3^+ continues to provide new information on Jovian ionosphere (Lellouch 2006).

9. Thermalization

Thermalization of H_3^+ in interstellar space, planetary ionospheres and in laboratories through spontaneous emission and collisions determines vibrational and rotational distribution in each plasma. The infrared spontaneous emission of dipole-allowed vibrational transitions is essential for energy balance of Jovian plasmas, as mentioned earlier. The effect of such emission as coolant for primordial star formation has been examined (Glover & Savin 2006).

In addition to the ordinary dipole allowed vibrational transitions, H_3^+ has more subtle forbidden rotational transitions owing to breakdown of the geometrical symmetry (Pan & Oka 1986). Since the lifetime of their spontaneous emission is of the order of a month or shorter, they compete with collisions and lead to highly non-thermal rotational distributions (Oka & Epp 2004). Such distributions are observed both in the GC (Oka *et al.* 2005) and in the laboratory (Kreckel *et al.* 2002, 2004). The effect of the long-range Coulomb collisions between H_3^+ and electrons has been studied by Faure *et al.* (2006).

10. Related species

Dissociation dynamics of well-defined Rydberg states of H_3, the neutral counterpart H_3^+, have been studied experimentally and theoretically by Helm, Jungen and colleagues (Galster *et al.* 2005) and Continetti and colleagues (Laperle *et al.* 2004). Detailed information on the dissociation dynamics obtained from such studies is important for understanding DR of H_3^+, since the latter process starts from electron capture by H_3^+ into the H_3 Rydberg states. Theory of predissociation of H_3 Rydberg states (Tashiro & Kato 2002) and the Jahn–Teller effect (Rao *et al.* 2005) have been presented.

Turbiner & Vieyra (2006) have systematically studied one-electron molecular systems in a strong magnetic field and showed that, for a magnetic field comparable to that in the hydrogen atom, such as those found near neutron stars, both linear H_3^{++} with the field along the axis and equilateral triangle H_3^{++} with the field perpendicular to the plane have some stability. Jungen & Lehner have shown the existence of a short-lived Feshbach state of H_3^- by an *ab initio* calculation.

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