INTRODUCTION

Chemistry, astronomy and physics of H$_3^+$

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The great developments in the chemistry, astronomy and physics of H$_3^+$ since 2006, which have led to this Royal Society Theo Murphy Meeting, are reviewed.

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1. Spectroscopy and theory

The rovibrational spectroscopy of H$_3^+$ has served as the benchmark for the most rigorous ab initio theory. After the observation of the fundamental band [1], the spectroscopy of H$_3^+$ was extended to hot, overtone and combination bands reaching increasingly higher vibrational states. It took nearly 30 years to reach the visible region up to the energy level of 13921 cm$^{-1}$ above the ground level [2]. We stopped there, since, even with shot-noise-limited spectroscopy, we ran out of signal-to-noise ratio. It was timely that the new method of action spectroscopy [3] was developed and applied to H$_3^+$ spectroscopy by the group at the Max Planck Institute of Nuclear Physics [4]. This paradigm shift from photon counting to ion counting spectroscopy led them to go deeper into the visible up to the energy level of 16660 cm$^{-1}$ [5,6]. It will be possible to reach deeper into the near-ultraviolet if lasers are available.

Last year we also saw the first sub-Doppler spectrum of H$_3^+$ (J.-T. Shy 2012, unpublished data). It has narrowed the line-widths and increased the accuracy of frequency measurement by three orders of magnitude. The advent of the high-power optical parametric oscillator has made the experiment possible. The H$_3^+$ Lamb dip has also been observed using the noise-immune cavity-enhanced optical heterodyne velocity modulation spectroscopy technique very recently (B. J. McCall 2012, personal communication.).

The progress of theory has been equally remarkable. The sub-microhartree accuracy potential energy surface (PES) by Kutzelnigg’s school [7] has been superseded by the 10 nanohartree accuracy PES by Adamowicz and Pavanello [5,8]. The dynamical calculations by Pavanello, Polyansky et al. [9] based on the new PES have reduced the discrepancy between experiment and theory from a

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few cm$^{-1}$ to 0.1 cm$^{-1}$. In summary, the sensitivity of spectroscopy, accuracy of measurements, accuracy of the PES and agreement between theory and experiment have all been improved by two orders of magnitude within the last 6 years.

2. **Chemistry**

Ion chemistry at low temperature is a simple chemistry. Entropy plays a minor role and chemistry is governed by enthalpy. H$_3^+$ is a universal proton donor (acid) through the proton hop reaction, H$_3^+$ + X $\rightarrow$ H$_2$ + HX$^+$, as long as the proton affinity of X is higher than that of H$_2$, 4.39 eV. Most abundant interstellar atoms and molecules satisfy this condition, with the notable exceptions of He, N and Ne. O$_2$ is a borderline case since its proton affinity is only slightly (approx. 0.01 eV) less than that of H$_2$. If detectable, HO$^+_2$ will be a good tracer of interstellar O$_2$. Widicus Weaver *et al.* [10] theoretically studied the possibility of observing this ion. This ion has also eluded spectroscopic detection in the laboratory, in sharp contrast to its N$_2$ analogue, HN$_2^+$, which is observed strongly even from a minimum leak of the air into plasmas. Kluge *et al.* [11] have studied the proton transfer between H$_3^+$ and O$_2$ and used the reaction for action spectroscopy.

Along with the H$_3^+$-producing reaction, H$_2$ + H$_2^+$ $\rightarrow$ H$_3^+$ + H, the proton hop/exchange reaction H$_3^+$ + H$_2$ $\rightarrow$ H$_2$ + H$_3^+$ is the most fundamental prototype of ion-neutral reaction, which plays a central role in molecular astrophysics. This reaction is arguably the most frequently occurring chemical reaction in the Universe. The process does not qualify as a reaction in the usual chemical sense, since the reactants and products are the same, but it is a reaction with changes of enthalpy, since conversion between the ortho and para spin modifications of both H$_2$ and H$_3^+$ occurs. It is the major reaction that changes ortho-H$_2$ into para-H$_2$ in dense clouds. The process has been studied in detail in the laboratory [12–14], including its implication in interstellar space. The observed different spin temperature between H$_2$ (70 K) and H$_3^+$ (30 K) has been partly explained by such studies [14,15]. Plašil *et al.* studied production of H$_3^+$ through radiative association of H$^+$ to H$_2$ experimentally [16]. This reaction may play a role in primordial H$_3^+$ formation. They found abnormal temperature dependence in the rate of three-body association.

3. **Dissociative recombination**

Since the discovery of H$_3^+$ in the diffuse interstellar medium [17] and in the Galactic centre (GC) [18], the dissociative recombination (DR) of H$_3^+$ with an electron has become the most important chemical reaction for studying H$_3^+$ in the diffuse interstellar medium; it is by far the fastest destruction process of H$_3^+$ in those environments. The DR rate is the only laboratory parameter that enters in the determination of the cosmic ray ionization rate and the dimension of clouds from observed H$_3^+$ column densities.

Larsson [19] discusses the great developments in experiment and theory on the DR of H$_3^+$ in the last 10 years. Both discrepancies among experimental values of the DR rate constants, and those between experiment and theory, have been
greatly reduced. The advent of a low-temperature ion source has led to a near-perfect agreement between the experiments by both the CRYRING [20] and the TSR on the energy-dependent resonant structure [21] and the cross section [22].

There has been shocking news from the TSR group, however, that the temperature of the rotational energy of H$_3^+$, which was reported as very low (10–30 K), is actually fairly high, approximately 380 K [23, 24]. They concluded that ‘this is the lowest rotational temperature so far realized in storage-ring rate coefficient measurements on H$_3^+$’. According to the theoretical calculations by Dos Santos et al. [25] given in their fig. 2, this increase of temperature decreases the rate by a factor of approximately 2 at an electron energy of $10^{-3}$ eV but increases it by a factor of approximately 2 at $10^{-2}$ eV.

The theoretical advances in the last 10 years have also been great. After the discrepancy of orders of magnitude between theory and experiment in 2000 [26], introduction of the Jahn–Teller effect [27] made the theoretical value of the DR rate agree with experiment. Junge et al. [28] support the theoretical results through an analytical formalism [29]. Nevertheless, there are still two important disagreements between experiment and theory: (i) The theoretical and experimental resonant structures do not agree well [23]. (ii) The large difference of DR rates for ortho- and para-H$_3^+$ predicted by the theory is not observed experimentally [22, 24, 30]. For the latter, Glosik’s group has published papers that agree better with theoretical predictions [31, 32]. However, the chemistry in their He-dominated plasmas is extremely complicated because of the long-lived metastable He, which keeps ionizing H$_2$ and producing H$_3^+$; I find their analysis of ortho- to para-H$_3^+$ conversion without taking this into account unsatisfactory. The effect of three-body collision should also be taken into account [33]. Since it is impossible to simulate the low density and field-free condition of interstellar space in the laboratory, accurate theory is indispensable to finalize the DR rate constant. The current uncertainty of the DR rate constant by a factor of approximately 2–3 is unsatisfactory. My desperate cry for more theory [34] is still intact.

4. Cosmic rays

The most important information that H$_3^+$ provides as an astrophysical probe is the cosmic ray ionization rate. Before the advent of H$_3^+$ spectroscopy, H$^+$ with its spectroscopic surrogates of OH and HD were used. Although H$_3^+$ and H$^+$ are produced at similar rates by cosmic rays, the destruction of H$_3^+$ by the DR with electrons is 1000 times faster than that of H$^+$ by radiative recombination. The H$_3^+$ chemistry is very clean while for H$^+$ other competing processes, such as grain neutralization [35], make the analysis complicated. Extensive studies of diffuse clouds towards 50 sightlines in the Galactic Disc [36–38] have established that the mean value of the cosmic ray ionization rate of H$_2$ in diffuse clouds, $\zeta = 3.5 \times 10^{-16}$ s$^{-1}$, is an order of magnitude higher than that in dense clouds. They have also shown that the ionization rate and therefore the intensity of soft cosmic ray flux vary depending on the observed sightlines. For some sightlines that pass near supernova remnants IC 443, an ionization rate as high as $\zeta \sim 2 \times 10^{-15}$ s$^{-1}$ has been observed [39]. As discussed in the next section, ionization rate of this order of magnitude is observed everywhere near the GC. These high $\zeta$ values
observed by $\text{H}_3^+$ [40] initially met scepticism but are now getting accepted and assimilated into astrophysics. Much higher $\zeta$ values of the order of $10^{-13} \text{ s}^{-1}$ have appeared in the literature [41] based on X-ray and $\gamma$-ray observations.

Black [42] discusses $\text{H}_3^+$ at the interface between astrochemistry and astro-particle physics. He discusses relations between low-energy (less than 100 MeV) cosmic rays observed by $\text{H}_3^+$ and higher-energy (more than 1 GeV) cosmic rays observed by $\gamma$-rays from decay of $\pi^0$ mesons generated from molecular gas associated with supernova remnants. Based on the observed $\gamma$-ray flux, $\zeta$ values of $10^{-12} \text{ s}^{-1}$ over a path length of 3.4 pc are possible near supernova remnants [43]. They advocate that quadrupole infrared $\text{H}_2^+$ emission from 4 to 6 $\mu$m should be observable from such highly irradiated molecular gas. With an $\text{H}_2^+$ column density more than seven orders of magnitude less than that of $\text{H}_2$, it looks like a long shot but it may be observable by a space-borne high-resolution infrared spectrometer. Such observations along with that of $\text{H}_3^+$ may establish that supernova remnants are the sources of the cosmic rays [44]. Black also proposes emission lines of HeH$^+$ and Rydberg $\text{H}_3$ as possible future probes.

5. Galactic Centre

$\text{H}_3^+$ is most abundant in the Central Molecular Zone (CMZ), a region with a radius of approximately 200 pc of the GC [45]. The integrated intensities and therefore the column densities of $\text{H}_3^+$ observed towards stars in the CMZ are typically one to two orders of magnitude higher than towards other stars in the Galactic Disc [18]. Also the surface filling factor is practically 100 per cent. As long as we have bright stars suitable for $\text{H}_3^+$ spectroscopy, we always see $\text{H}_3^+$ with column densities of the order of $3 \times 10^{15} \text{ cm}^{-2}$. It seems that this region less than $10^{-5}$ in volume contains most $\text{H}_3^+$ in the Galaxy. This high abundance indicates a high ionization rate of $\text{H}_2$ ($\zeta \geq 10^{-15} \text{ s}^{-1}$) in the region. The observed total $\text{H}_3^+$ column density $N(\text{H}_3^+)$ is related to $\zeta$ as

$$\zeta L = 2k_e N(\text{H}_3^+) \left( \frac{n_C}{n_H} \right)_{SV} \frac{R_{C/H}}{f(\text{H}_2)},$$

where $L$ is the path length, $(n_C/n_H)_{SV}$ is the carbon to hydrogen ratio in the solar vicinity, $R_{C/H}$ is the increase of the C/H ratio from the solar vicinity to the GC, and $f(\text{H}_2)$ is the fraction of molecular hydrogen [40,46].

Geballe [47] discusses the amazing development of $\text{H}_3^+$ spectroscopy towards the GC in the last several years. The $\text{H}_3^+$ rotational levels composed of the lowest $(J, K) = (1, 1)$ para and $(1, 0)$ ortho levels, the high-lying (361 K) (3, 3) metastable level and the (2, 2) unstable level with a spontaneous emission lifetime of 27 days are ideal for studying the vast amount of warm ($T \sim 250$ K) and diffuse ($n < 100 \text{ cm}^{-3}$) gas in the CMZ. Such gas was revealed towards the brightest quintuplet star GCS 3-2 [40], eight stars from Sgr A* and 30 pc to the east [48], and much more widely from 140 pc west to 85 pc east [49]. For further extending the coverage of longitude, a systematic search for bright dust-embedded stars with smooth continuum suitable for $\text{H}_3^+$ spectroscopy is in progress. The presence of this new category of gas with a significant volume filling factor has radically changed the previous concept of the gas in the CMZ, which had been composed of three kinds.
of gas: dense molecular gas observed by radio emission, high-temperature ionized gas in the H II region and ultra-high-temperature plasma gas observed by X-rays.

The advent of the *Herschel Space Observatory* with its powerful heterodyne far-infrared spectrometer has led to revelations of many light hydride molecules. Lis *et al.* [50] discuss observation of hot H$_3$O$^+$ in metastable levels up to $J = K = 11$ towards Sgr B2(N). The excitation temperature determined from higher metastable levels is 519 K. This is lower than the temperature of iso-electronic NH$_3$ (1300 K) towards the same target [51] but it is surprisingly high, since H$_3$O$^+$ cools much faster than NH$_3$. While a collision between NH$_3$ and H$_2$ is a ‘physical’ collision in which both partners keep their identity throughout the process, a collision between H$_3$O$^+$ and H$_2$ is a ‘chemical’ collision in which the protons scramble. In the former, spin modifications (ortho and para) do not change while they do in the latter. Therefore, while metastable NH$_3$ needs to change $K$ by 3 to decay to lower levels, H$_3$O$^+$ can decay by changing $K$ by 1 with less energy change and hence higher probability. Moreover, the Langevin force between H$_3$O$^+$ and H$_2$ is one to two orders of magnitude stronger than the dispersion force between NH$_3$ and H$_2$. H$_3$O$^+$ cools one to two orders of magnitude faster than NH$_3$. Unlike OH$^+$ and H$_2$O$^+$, to be discussed in the next section, H$_3$O$^+$ exists mostly in dense clouds. It is most probably produced by protonation of O by H$_3$ followed by rapid hydrogen abstraction reactions. Lis *et al.* [50] suggest X-rays as the most likely source for the production and heating of H$_3$O$^+$.

### 6. Interstellar chemistry

There has been an avalanche of observations of strong rotational absorption spectra of hydride molecules, ions and radicals since the *Herschel Space Observatory* with the HIFI spectrometer opened the window on the 60–670 μm region. Many of the discovered molecules reside in diffuse clouds, which had been observed mostly by visible and infrared, and rotational spectroscopy played a relatively minor role. All of a sudden, rich information has been provided for diffuse molecular and atomic clouds. Gerin *et al.* [52] report observed spectra of C$^+$, CH, para-H$_2$O, HF and CH$^+$ towards the star-forming regions W49N and W51 with analyses and related model calculations. Major new information is the value of the fraction of molecular hydrogen, $f$(H$_2$), an important factor in the earlier-mentioned equation in §5 for the analysis of H$_3^+$.

It varies from 1 to less than 0.1 from diffuse molecular clouds to diffuse atomic clouds, depending on the molecules and velocities of the cloud components. Clouds with high $f$(H$_2$) contain abundant H$_3^+$ while others with very low $f$(H$_2$) do not since the charge exchange reaction H$_2^+$ + H → H$_2$ + H$^+$ will destroy H$_2^+$ before it reacts with H$_2$ to produce H$_3^+$. It has been observed that the velocity profiles of H$_2$O$^+$ [53] and $^{13}$CH$^+$ (E. Falgarone 2012, personal communication) towards Sgr B2 are similar to that of H$_3^+$ towards an infrared star 17 pc to the west of Sgr B2 [49], suggesting relations between and possible coexistence of the three molecular ions. The hydride spectrum also provides ionization rate in the environment. The analysis is not as clean as that of H$_3^+$, but the data can be collected much more widely and continuously using far-infrared dust emission than for H$_3^+$, which requires the rare presence of suitable stars.

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Although $\text{H}_3^+$ plays the central role in the chemistry of dense clouds and was first detected in dense clouds [54], it is the most powerful astrophysical probe for diffuse clouds. Instead the submillimetre-wave rotational spectra of its deuterated species, $\text{H}_2\text{D}^+$ and $\text{HD}^+_2$, have emerged as very powerful probes for cold ($T \sim 10\text{ K}$) and dense ($n \sim 10^6\text{ cm}^{-3}$) pre-stellar core regions. At such low temperature, $\text{H}_3^+$ abounds since its destroyers CO, O and others freeze out onto grains. The low temperature also shifts the chemical equilibrium from $\text{H}_3^+$ to $\text{H}_2\text{D}^+$, to $\text{HD}^+_2$ and to $\text{D}_3^+$, because of small enthalpy differences due to their zero-point vibrational energy. The resulting amazing deuterium fractionation exceeding $10^{15}$ was discussed in the last Royal Society Discussion Meeting on $\text{H}_3^+$ [55,56]. Van der Tak [57] discusses the rapid development of $\text{H}_2\text{D}^+$ and $\text{HD}^+_2$ spectroscopy for the studies of cold proto-stellar cores. He envisages a quantum jump in this field in the very near future; the up-coming ALMA interferometer will allow detection of $\text{H}_2\text{D}^+$ in pre-stellar cores and the SOFIA airborne observatory will allow detection of far-infrared spectra of both $\text{H}_2\text{D}^+$ and $\text{HD}^+_2$ from the ground rotational level. For warmer regions, puzzling observations of hydroxyl ions $\text{H}_2\text{O}^+$ led Van der Tak et al. [58] to observe strong HF emission.

In very insightful papers, Pagani et al. [59,60] extend the idea of the earlier seminal paper by Pagani et al. [61] and propose to measure the age of interstellar dark clouds by the appearance of deuterated ions, such as $\text{DCO}^+$ and $\text{DN}_2^+$. Because even a small fraction (less than 0.01) of ortho-$\text{H}_2$ with its high rotational energy of 170K suppresses deuterium fractionation from $\text{H}_3^+$ to $\text{H}_2\text{D}^+$, efficient deuterium fractionation would not occur until ortho-$\text{H}_2$, produced abundantly on grains, is nearly completely (approx. 0.001) converted to para-$\text{H}_2$ by proton exchange reactions with $\text{H}^+$ or $\text{H}_3^+$. Since this takes approximately 10 million years, comparable to the contraction time of pre-stellar cores, it serves as a clock to measure the age of pre-stellar cores. The age varies widely depending on star formation models, and the observed D/H ratios will give good test of the theories.

7. Planetary ionospheres

The ionospheres of giant planets are the only objects that have shown the emission spectrum of $\text{H}_3^+$. Intense infrared emission is seen from Jupiter and that from Uranus is equally intense considering its larger distance, while the emission from Saturn is orders of magnitude weaker and that from Neptune has not been detected yet in spite of repeated efforts [62]. The ionosphere of Uranus is very different from that of Neptune, although the planets are very similar in some other aspects. The three outer planets are the only objects that are close enough to us that their pole-to-pole profiles are observable with spatial resolution. Stallard et al. [63] present the remarkable differences in pole-to-pole profiles of $\text{H}_3^+$ emission from Jupiter, Saturn and Uranus and hence their magnetohydrodynamic activities; they involve similar processes but with different dominance. In all these three ionospheres, significant temporal variations of the emission intensity in variable time scales are observed, indicating the variations of the plasma temperature. Contrary to most atmospheric model studies, which assume steady states, their results demonstrate that the planets are far from equilibrium. Studies of these may lead to the understanding of the high temperature of their upper atmospheres.

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8. Early history

This issue celebrates the centennial of J. J. Thomson’s discovery of \( H_3^+ \) [64,65]. Kragh [66] gives the early history of the discovery of \( H_3^+ \) by Thomson, who thought it was the ionized form of the stable \( H_3 \) molecule. Its stability has been ‘explained’ by celebrated names like J. Stark and N. Bohr but was eventually rejected in the late 1930s. The interest in \( H_3 \) was revived when Herzberg observed the very broad spectrum of the unstable Rydberg \( H_3 \) in which \( H_3^+ \) is surrounded by a Rydberg electron [67]. In the meantime, the science of \( H_3^+ \) has been greatly developed, leading to subjects presented in this issue.

References

Introduction. Chemistry, astronomy and physics of H$_3^+$


