

## Introduction



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**Author for correspondence:**

Jonathan Tennyson  
e-mail: [j.tennyson@ucl.ac.uk](mailto:j.tennyson@ucl.ac.uk)

Hydrogen molecular ions:  
 $H_3^+$ ,  $H_5^+$  and beyond

Jonathan Tennyson and Steve Miller

Department of Physics and Astronomy, University College London,  
London WC1E 6BT, UK

JT, 0000-0002-4994-5238

Three decades after the spectroscopic detection of  $H_3^+$  in space, the inspiring developments in physics, chemistry and astronomy of  $H_n^+$  ( $n = 3, 5, 7$ ) systems, which led to this Royal Society Discussion Meeting, are reviewed, the present state of the art as represented by the meeting surveyed and future lines of research considered.

This article is part of a discussion meeting issue 'Advances in hydrogen molecular ions:  $H_3^+$ ,  $H_5^+$  and beyond'.

## 1. Background

In 1989, Drossart *et al.* [1] detected a strong spectroscopic signature of  $H_3^+$  in the southern aurora of Jupiter. Although  $H_3^+$  was known to exist on Jupiter from *in situ* measurements performed as part of the Voyagers' flybys [2,3], the observation contained two surprises. First, the emissions were from an overtone band that had yet to be characterized in the laboratory and instead relied on first principles, or *ab initio*, quantum mechanical predictions [4], and second the  $H_3^+$  emissions corresponded to a temperature of over 1000 K, about twice what was expected. These observations laid the seeds for many of the research themes of the intervening 30 years: the detection of  $H_3^+$  in active astronomical environments, its use as a probe revealing, often uniquely, detailed information about these environments, the close interplay between laboratory studies and astrophysics, and the study of  $H_3^+$  and its hydrogenated relatives  $H_5^+$  and  $H_7^+$  as benchmark quantum mechanical systems. All these themes are discussed below and are reflected in the articles that comprise this issue. Work on these topics has been the subject of three previous Royal Society Discussion Meetings held in 2000 [5], 2006 [6] and 2012 [7].

Similarly, the physics and astrophysics of  $\text{H}_3^+$  have been the subject of a series of reviews, notably by Oka [8,9], McNab [10] and the present authors [11–13].

Following its detection in the ionosphere of Jupiter,  $\text{H}_3^+$  was detected in the gas giants Uranus [14] and Saturn [15], but notably not in Neptune [16,17]. Long-running attempts by Oka [18] to detect interstellar  $\text{H}_3^+$  finally bore fruit with its detection in both the dense [19] and the diffuse [20] interstellar medium. The claimed serendipitous observation of  $\text{H}_3^+$  in the cooling remnants of supernova SN1987a [21] is supported by chemical models [22] but, of course, cannot be repeated. However, despite its perceived importance for cooling and stabilizing hot Jupiter exoplanets [23], there remains no definitive observation of  $\text{H}_3^+$  in either an exoplanet [24–26] or a brown dwarf [27].

The  $\text{H}_3^+$  molecular ion is the simplest stable molecular ion of hydrogen. It is rapidly formed by collisions between  $\text{H}_2$  and  $\text{H}_2^+$ . As outlined above, its presence in the interstellar medium and the ionospheres of gas giant planets is now well established, but careful studies of its spectra are providing valuable information on issues as diverse as the cosmic ray ionization rate in different environments [28] and wind speeds in planetary upper atmospheres [29]. Use of  $\text{H}_3^+$  to obtain these insights demands detailed knowledge of the properties of and processes involving the ion.

At the same time,  $\text{H}_3^+$  is the electronically simplest stable polyatomic molecule and therefore provides a benchmark system for testing high-accuracy *ab initio* methods [30]. While impressive accuracy has been achieved, calculations on the isoelectronic  $\text{H}_2$  molecule remain many orders of magnitude more accurate [31]; this problem is not directly due to issues with the multi-dimensional nuclear motion problem, which is capable of high-accuracy solution [32], but more to treating various subtle effects in many dimensions.

$\text{H}_5^+$  may seem superficially similar to  $\text{H}_3^+$  but it is an astructural or fluxional molecule: one for which there is facile conversion between multiple equilibrium geometries, leading to complicated and delocalized wave functions. The study of  $\text{H}_5^+$ , alongside the other key fluxional system  $\text{CH}_5^+$  [33,34], raises particular issues in terms of predicting and interpreting their spectral signatures.

Reactions between ionized and neutral hydrogenic species, such as  $\text{H}^+ + \text{H}_2$  or  $\text{H}_2^+ + \text{H}_2$ , are of importance for studies of hydrogen plasmas both on Earth and in the interstellar medium. These reactions also raise their own issues with fundamental physics. Modern experimental techniques, which provide the ability to study atoms and molecules at extremely low temperatures, allow these processes to be studied in increasing detail, which raises new challenges for theory to address.

The original discovery of  $\text{H}_3^+$  occurred over a century ago [26] but, as this issue demonstrates, there clearly remain a whole host of fundamental issues and their implications to be studied, both using and involving the molecular ions of hydrogen. In the introduction to the 1989 paper announcing the detection of  $\text{H}_3^+$  in the atmosphere of Jupiter, Drossart and his co-workers predicted: ‘Such strong  $\text{H}_3^+$  lines could be used in future ground-based monitoring of the Jovian auroral activity and to search for this molecule in the interstellar medium’ ([1], p. 539). The next subsection gives some indication of the considerable progress that has now been made in  $\text{H}_3^+$  studies of planetary atmospheres in the three decades since Jupiter first gave up its intriguing spectrum; the subsequent subsections then consider this for other aspects of  $\text{H}_n^+$ .

## 2. Current state of the art

### (a) Planets

In the last year, spectacular images of Jupiter’s auroral regions from the JUNO spacecraft in wavelengths sensitive to  $\text{H}_3^+$  have been added to those from the Cassini mission to Saturn to demonstrate just how powerful a tool this molecular ion can be for understanding the complex and dynamic processes that link a planet’s upper atmosphere with its magnetospheric environment. Indeed, since the first detection in 1989, nearly 200 papers have appeared in refereed journals making use of  $\text{H}_3^+$  either as a probe of planetary atmospheres themselves or as an indicator of magnetosphere–atmosphere interactions, or modelling how it should behave. The inclusion of no fewer than six papers in this issue alone [35–40] is testimony to the ongoing

activity in this area of research. So ground- and space-based observations of  $\text{H}_3^+$  spectra are in the process of revolutionizing our understanding of the upper atmospheres of the gas giants.

As well as the images produced by JUNO referred to above, its Jupiter InfraRed Auroral Mapper (JIRAM) [41] has also enabled the scientists associated with this instrument to study the spectra produced, in particular those taken when the spectrometer slit cuts across the limb of the planet. That makes it possible to produce the vertical altitude–intensity plots reported in the paper by Dinelli *et al.* [35]. Their analysis of the northern auroral region shows that the altitude of the peak  $\text{H}_3^+$  density is always greater than 750 km above the nominal 1 bar ‘surface’ of Jupiter and that generally there is some anti-correlation between high-density and high-temperature regions for which the ‘ $\text{H}_3^+$  thermostat’ [42] is only partially responsible.

Two papers look at Jupiter’s lower-latitude  $\text{H}_3^+$  emissions. Firstly, Drossart [36] presents a new analysis of ground-based spectral imaging observations of the mid- to low latitudes of Jupiter carried out using the ISAAC instrument on the European Southern Observatory’s (ESO’s) Very Large Telescope (VLT). There are clear fluctuations in the  $\text{H}_3^+$  emission on scales of some  $10^\circ$ , but this study is not able to tell whether the fluctuations are due to long-lasting structural effects—magnetospheric variations and/or inhomogeneities in charged particle precipitation—or temporal effects, most probably due to gravity waves, as postulated to account for the vertical temperature profile observed by the 1996 Galileo probe on its descent through the Jovian near-equatorial atmosphere [43]. Clearly, further studies are required to distinguish between structural and temporal variations, although, of course, both may be present.

Secondly, further insight into the Jovian lower latitudes is provided by the paper by Ray *et al.* [39], which discusses heating above the Great Red Spot (GRS), a massive tropical storm that has been raging for several centuries. Recently, ionospheric temperatures as high as 1600 K have been measured above the GRS [44], temperatures that pose challenging questions concerning the coupling between the lower and upper atmospheres of Jupiter. Ray *et al.* propose that there is sufficient coupling and co-location of stratospheric winds driven by the GRS anticyclone and the ionosphere that electric fields can be generated. Modelling shows that the Joule heating and ion drag associated with the currents generated by these fields may account for the elevated ionospheric temperatures above the GRS, a clear indication of one mechanism by which the lower and upper Jovian atmospheres can couple.

Ground-based observations in support of space missions have always been an important part of ensuring maximum scientific return for investment in multi-billion-dollar space missions. These can be preparatory observations, observations taken coincidentally with the missions themselves, and follow-up observations to investigate questions that remain once the spacecraft are no longer operating. Moving outwards in the Solar System, Stallard and co-workers provide a detailed analysis of spectra and spectral images of Saturn taken with the Keck telescope to coincide with the last orbits of the Cassini spacecraft in 2017 [40]. The properties of the auroral–polar regions averaged across  $\text{H}_3^+$  observations taken during the months of July and August show clear ion wind flow patterns and temperature and density enhancements. But the individual observations underlying these averages show up very detailed flows and arcs, and a changing pattern of auroral activity. Comparison of these observations with models highlights the fact that none so far available really matches the detailed observations, even if they can match the average behaviour.

Uranus has always been a challenging planet to understand: it rotates about an axis that is tilted so far that it is in the plane of the ecliptic, which means that for 21 years each rotational pole points more or less continuously at the Sun; its magnetic dipole, on the other hand, is tilted at an angle of  $59^\circ$  to the rotational axis and offset towards the south by about one-third of a planetary radius, which makes its magnetic interaction with the solar wind extremely variable on a daily and seasonal basis. Melin *et al.*’s analysis of 27 years of ground-based observations of Uranus [37] show that its average upper atmospheric temperature has cooled at a rate of just over 8 K per year from over 700 K when its  $\text{H}_3^+$  emission was first observed in 1992 [14] to closer to 500 K towards the end of 2018. But just why this is happening remains unresolved: given the number

of Uranus-like planets that have been found among the population of exoplanets, a dedicated mission is clearly indicated.

Two papers reporting modelling efforts give very much the state of the art. Firstly, Moore *et al.* [38] use calculated vertical profiles of planetary atmospheres to probe just how  $\text{H}_3^+$  temperatures, column densities and overall emission rates retrieved from observations can be affected by the detailed structure of the atmosphere. Both density and temperature gradients in the atmosphere play an important role. These authors conclude that  $\text{H}_3^+$  densities retrieved from observations represent a lower limit, and comparison with models is needed to get the ‘true’ densities represented by the observations. This needs to be borne in mind in interpreting observations, and their correlations with other parameters such as magnetospheric and solar conditions. It also needs to be remembered if and when, eventually,  $\text{H}_3^+$  is observed in an extrasolar planet. Although attempts to detect  $\text{H}_3^+$  in brown dwarfs or exoplanets have so far proved negative, the role of lightning in these bodies has been considered to be potentially important in making this possible at some future time [45,46]. Helling [47] here investigates how lightning and charge processes in brown dwarf and exoplanet atmospheres may lead to the production of  $\text{H}_3^+$  in observable quantities.

## (b) Interstellar medium

As in the gas giants,  $\text{H}_3^+$  is proving a unique window on the interstellar medium, although not through its emission spectrum but by way of absorption lines. These lines are produced when one or more stars have their light absorbed by the intervening gas clouds.  $\text{H}_3^+$  has shown itself to be a versatile probe of the local ionization rate by cosmic rays, and Oka [48] gives a straightforward argument as to why this should be the case, based on its ubiquity, the simple chemistry in which it participates, and the ‘concise’ nature of its infrared spectrum. It has been long assumed that the cosmic ray ionization rate,  $\zeta$ , was essentially constant throughout the Galaxy and of the order of  $10^{-17} \text{ s}^{-1}$ . But Oka explains how observations of  $\text{H}_3^+$  abundances in a variety of locations are showing that this is far from true and that the effective ionization rate due to cosmic rays varies hugely throughout the Galaxy, with values as large as  $(2-3) \times 10^{-14} \text{ s}^{-1}$  [48].

Following on from this, Ceccarelli and co-workers discuss the strong evidence that our own Solar System was born in a violent storm of energetic, ionizing rays, which should also have led to the formation of significant quantities of  $\text{H}_3^+$  [49]. They pay particular attention to the protocluster of young stars OMC-2 FIR4 to be found in the Orion Molecular Complex, and recent results from the Northern Extended Millimeter Array (IRAM-NOEMA), where the abundance of  $^{10}\text{Be}$  indicates that here  $\zeta$  may be as high as  $4 \times 10^{-14} \text{ s}^{-1}$ .  $\text{H}_3^+$  production in the nebula gas then leads to a rich harvest of molecules such as  $\text{HC}_3\text{N}$  and  $\text{HC}_5\text{N}$ , which can be used to map the region.

Observations of the Galactic central molecular zone (CMZ) using  $\text{H}_3^+$  have revealed the many complex structures present in this, in astronomical terms, crowded region [50]. Monitoring the metastable  $(J, K) = (3, 3)$  rotational state of  $\text{H}_3^+$  has exposed the presence of huge, warm ( $T \approx 250 \text{ K}$ ), diffuse clouds in the CMZ. As discussed by Geballe [51],  $\text{H}_3^+$  spectra are providing a wealth of information on the temperature, motion and distribution of the gas in the CMZ. The radial momentum inferred from these measurements is truly prodigious, exceeding that produced by thousands of core-collapse supernovae. It may be that this extraordinary activity may be associated with the super-massive black hole Sagittarius A\*, but that the expansion may cease in 1 million years, given the deceleration that the gravitational mass of the Galactic centre produces.

In less active regions of the Galaxy, fractionation can lead to extreme enhancements of deuterated  $\text{H}_3^+$ . Although  $\text{D}_3^+$  has yet to be observed in space, models suggest that under conditions appropriate to completely depleted, low-mass pre-protostellar cores, for which heavy elements such as C, N and O have vanished from the gas phase, it is possible for  $\text{D}_3^+$  to be the dominant molecular ion [52]! Owing to their permanent dipole moments, the asymmetrically substituted species  $\text{H}_2\text{D}^+$  and  $\text{D}_2\text{H}^+$  can be observed through their pure rotational spectrum. The interstellar detection of  $\text{H}_2\text{D}^+$  [53] and recently  $\text{D}_2\text{H}^+$  [54] provides a new handle on the

fractionation and other processes [55]. Surveys of  $\text{H}_2\text{D}^+$  distributions [56,57] are helping to provide information on the ages of interstellar clouds [58]. One crucial finding is that previous chemical models, which assumed that the H and D nuclear-spin states are completely scrambled when interstellar reactions occur, may not be correct in this assumption. Caselli *et al.* [55] find better agreement with observations of deuterated  $\text{NH}_3$  if a ‘proton hopping’ mechanism is put into the model.

### (c) Polyatomic ions

The  $\text{H}_5^+$  ion is a remarkable species. The delocalized wave function, which samples multiple minima, means that  $\text{H}_5^+$  is essentially astructural or fluxional. Special techniques are therefore required to simulate the  $\text{H}_5^+$  ion spectrum [59–61], and it shows unusual behaviour on isotopic substitution [62]. An interesting suggestion (T. Oka 2019, private communication) is that the many unassigned lines in the  $\text{H}_3^+$  spectrum recorded in a liquid-nitrogen-cooled discharge by Bawendi *et al.* [63] may actually belong to  $\text{H}_5^+$ . As discussed by Prosmi & Valdés [64] fully quantum mechanical treatments of the infrared spectrum of  $\text{H}_5^+$  are demanding but in progress.

Hydrogen ion clusters have been detected up to  $\text{H}_{99}^+$  [65]. However, it would appear that the higher hydrogen ionic species, which have the general formula  $\text{H}_{2n+1}^+$ ,  $n = 3, 4, \dots$ , are somewhat different from  $\text{H}_5^+$ . These appear to behave like clusters of  $\text{H}_2$  molecules nucleated round a central ion, probably  $\text{H}_3^+$  [66–68].

Ionic clusters with even numbers of protons,  $\text{H}_{2n}^+$ ,  $n = 2, 3, \dots$ , are generally thought to be less stable than their odd counterparts. However, such species are known and the  $\text{H}_6^+$  molecular ion has recently been generated in a pulsed-discharge supersonic expansion of hydrogen and mass-selected in a time-of-flight spectrometer, allowing its vibrational spectrum to be measured [69].

The  $\text{H}_5^+$  system itself is the intermediate in the proton exchange (or proton hopping) reaction between  $\text{H}_3^+$  and  $\text{H}_2$  discussed above; this is thought to lead to thermalization of  $\text{H}_3^+$  ortho/para (nuclear spin) ratios at low temperatures [70]. The rate of dissociative recombination (DR) of  $\text{H}_3^+$  was long a subject of controversy, which appears now to be substantially resolved [71]. Conversely measurements of the DR rate  $\text{H}_5^+$ , or more precisely for  $\text{D}_5^+$ , suggest that the situation is more straightforward, with a simple picture of the recombination process capturing the essential physics of the problem, as discussed by Larsson [72,73].

### (d) Laboratory

Laboratory studies involving the  $\text{H}_3^+$  system remain an active area motivated by the desire to understand the rich physics of this fundamental system and to provide key data for other studies, notably astrophysics.

The spectrum of  $\text{H}_3^+$  and its isotopologues have long acted as a benchmark for rigorous *ab initio* theory [31,74]. Highly accurate solution of the Born–Oppenheimer electronic Schrödinger equation [75] has shifted the emphasis towards study of corrections that go beyond this model, including the so-called Lamb shift due to quantum electrodynamics [76] and accurate treatment of non-adiabatic effects arising from failure of the Born–Oppenheimer approximation [77,78], as discussed by Amaral *et al.* [79].

The new-found ability to perform experiments at cool and ultracool temperatures has allowed collisions involving hydrogen ions to be explored with increasing accuracy with full quantum resolution [80]. The advances are driving the development of novel theories capable of studying low-energy collision processes; see the paper by McKemmish & Tennyson [81].

The  $\text{H}_3^+$  system itself has facets in its near-dissociation region that merit further investigation, including its near-dissociation spectrum, the possible presence of a whole series of weakly bound, long-range vibrational states [82] and exploring the nature of the  $\text{H}_3^+$  potential energy surface in the region above dissociation. In this region, there is interaction between surfaces which correlate with the two lowest dissociation asymptotes,  $\text{H}_2 + \text{H}^+$  and  $\text{H}_2^+ + \text{H}$ . The seam between these surfaces is now being probed using both photon processes and charge exchange; see Urbain *et al.*

[83]. Modelling these studies will require the extension of the accurate, global ground potential  $\text{H}_3^+$  potential energy surface [84,85] to forms which give multiple surfaces [86] accurately.

Cryogenic traps provide an environment for the study for the spectra of  $\text{H}_3^+$  and its isotopologues under very controlled conditions [87,88], which have also been used to probe complexes such as  $\text{He-H}_3^+$  [89].  $\text{H}_3^+$  is an active protonator of species that might otherwise be inert in the interstellar medium [90], and spectra of species such as  $\text{O}_2\text{H}^+$  can also be recorded in cryogenic traps [91], paving the way to possible astrophysical detection. The development of the new CSR (Cryogenic Storage Ring) further opens the way to astrochemical studies of species and processes involving molecular ions, as described by Kreckel *et al.* [92].

### 3. Future prospects

Thirty years after the original detection of the spectrum of  $\text{H}_3^+$  in space, there is still much to be done on the molecular hydrogen ions.  $\text{H}_3^+$  observations of the giant planets in our own Solar System have progressed so that it is now a routine probe of the atmospheres of Jupiter, Saturn and Uranus, enabling us to understand their behaviour over short (daily) and long (decadal) time scales. At some point in the future,  $\text{H}_3^+$  will be detected on Neptune, and we will be able better to understand the atmospheric differences that have made this planet ' $\text{H}_3^+$  dark' for so long. The detection of  $\text{H}_3^+$  itself in new environments such as the atmospheres of exoplanets and brown dwarfs remains a tantalizing possibility. While the presence of the weakly bound hydrogen dimer,  $(\text{H}_2)_2$ , is now well established in the atmospheres of Jupiter and Saturn [93], its much more stable protonated analogue  $\text{H}_5^+$  remains unseen.

The near-dissociation spectrum of  $\text{H}_3^+$  and its isotopologues, as characterized in great detail by Carrington, McNab and co-workers [94–99], remains unassigned [100] and poorly understood. This spectrum provides a clear link with  $\text{H}^+ + \text{H}_2$  reaction dynamics, which is now being probed in detail [101]. The elucidation of this spectrum would benefit from experimental studies performed under more controlled conditions such as the multiphoton near-dissociation spectra of water recorded by Rizzo and co-workers [102,103], which allow the observed resonance states to be rotationally assigned.

Treatment of the  $\text{H}_3^+$  vibration–rotation problem beyond the Born–Oppenheimer (BO) approximation remains a challenge. A number of studies have attempted to do this by adding corrections to a BO approach, with reasonable results [32,77,78,104]. Only recently has a fully non-BO treatment been attempted [105], but the results are very far from spectroscopic accuracy. It is notable that for the isoelectronic  $\text{H}_2$  problem both approaches now give excellent results, accurate to about  $10^{-4} \text{ cm}^{-1}$ . There is clearly more work to be done to get a proper beyond-BO treatment.

The above topics of course concern  $\text{H}_3^+$  only; for the higher ions these issues are substantially unexplored. They therefore present a whole host of issues for exploration in the laboratory and, possibly, astrophysically.

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