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

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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.

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 in the Voyagers' flybies [2,3], the observation contained two surprises. First, the emissions were from an overtone band that had yet to be characterised in the laboratory and instead relied on first principle, 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 intervening thirty 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 volume. Work on these topics were the subject of three previous Royal Society Discussion Meetings held in 2000 [5], 2006 [6] and 2012 [7]. Similarly, the physics and astrophysics of H_3^+ have been the subject of a series of reviews notably by Oka [8,9], McNab [10] and the present authors [11–13].

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Following its detection in the ionosphere of Jupiter, 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 H_3^+ finally bore fruit with its detection in both the dense [19] and the diffuse [20] interstellar medium. The claimed serendipitous observation of H_3^+ in the cooling remants of supernova SN1987a [21] is supported by chemical models [22] but, of course, cannot be repeated. However, despite its perceived importance for cooling and stablising hot Jupiter exoplanets [23] , there remains no definitive observation of H_3^+ in either an exoplanet [24–26] or a brown dwarf [27].

The H_3^+ molecular ion is the simplest stable molecular ion of hydrogen. It is rapidly formed by collisions between H_2 and H_2^+. As outlined above its presence the interstellar medium and the ionospheres of gas giant planets is now well established but carefully study of its spectra are providing valuable information on issues as diverse as the cosmic ray ionisation rate in different environments [28] and winds speeds in planetary upper atmospheres [29]. Use of H_3^+ to obtain these insights demands detailed knowledge of properties and processes involving the ion.

At the same time, 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 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.

H_5^+ may seem superficially similar to H_3^+ but is it an a structural or fluxional molecule: one for which there is facile conversion between multiple equilibrium geometries, leading to complicated and delocalised wavefunctions. The study of H_5^+, alongside the other key fluxional system CH_5^+ [33,34], raise their particular issues in terms of predicting and interpreting their spectral signatures.

Reactions between ionised and neutral hydrogenic species, such as $H^+ + H_2$ or $H_2^+ + H_2$, 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 study atoms and molecules at extremely low temperatures, allow these processes to be studies increasing detail which raises new challenges for theory to address.

The original discovery of H_3^+ occurred over a century ago [26] but, as this issue demonstrates, there clearly remains a whole host of fundamental issues and their implications to be studied, both using and involving the molecular ions of hydrogens.

2. Current state-of-the-art

(a) Planets

Steve: you will probably want to edit what I have written here.

Ground and space-based observations of H_3^+ spectra are in the process of revolutionising our understanding the of the upper atmospheres of the gas giants [35]. This has led to construction of detailed models of giant planet atmospheres [36] capturing the many physical processes which contribute to what is proving to be a highly complex picture.

Observations of polar H_3^+ emissions in Saturn have shown peaks which differ from those presented by H_2 [37] and that there is a persisant temperature asymmetry between the two region polars [38]. The latest results from Cassini's encounter with Saturn are discussed by Stallard [39].

Long-term monitoring H_3^+ emissions from Uranus have shown a persistent cooling over nearly three decades [40–45], punctuated only by a violent storm in 2014 [46]. Melin discusses possible explanations for these observations [47].

The arrival of the Juno space mission at Jupiter with its Jupiter InfraRed Auroral Mapper (JIRAM) instrument specifically tuned to monitor emissions from H_3^+ at spatial resolution way beyond what previously achievable is allowing the study of the Jovian upper atmosphere in unprecident detail [48,48]. Early discoveries include identication of complicated ionic auroral structure associated with the footprints of the major Jovian satellites. Mid-to-low lattide studies show H_3^+ heating which cannot be explained by insolation alone [49]; particurly intreaguing is the recent, unexplained detection of significant H_3^+ heating in upper atmosphere directly above the Great Red Spot [50]. These issues are discussed by Dinelli [51] and Ray [52].

As mentioned above, attempts to detecting H_3^+ in brown dwarfs or exoplanets have so far proved negative. However, the role lightning in these bodies has been considered for sometime [53,54]. Helling [55] considers how lightning and charge processes in brown dwarf and exoplanet atmospheres may lead to the production of H_3^+ in observable quantities.

(b) ISM

As in the gas giants, H_3^+ is proving a unique window on the interstellar medium. In particular, observations of the galactic central molecular zone (CMZ) using H_3^+ have revealed the many complex structures present in this, in astronomical terms, crowded region [56]. Monitoring the metastable $(J, K) = (3, 3)$ rotational state of H_3^+ has exposed the presence of huge, warm ($T \approx 250$ K), diffuse clouds in the CMZ. As discussed by Geballe [57], H_3^+ spectra are providing a wealth of information on the temperature, motion and distribution of the gas in the CMZ.

In less active regions of the galaxy fractionation can lead to extreme enhancements of deuterated H_3^+. Although 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 possible for D_3^+ to be the dominant molecular ion [58]! Due to their permanent dipole moments, the asymmetrically substited species H_2D^+ and D_2H^+ can be observed through their pure rotational spectrum. The interstellar detection of H_2D^+ [59] strand recently D_2H^+ [60] provides a new handle on the fractionation and other processes [61]. Surveys of H_2D^+ distributions [62,63] are helping to provide information on the ages of interstellar clouds [64].

H_3^+ has shown itself to be versatile probe of the local ionisation rate by cosmic rays. It long assumed that this rate was essentially constant throughout the galaxy but obseravations of H_3^+ abundances in a variety of locations are showing that this is far from true and that the effective ionisation rate due to cosmic rays varies hugely throughout the galaxy [65]. There is strong evidence that our own solar system was born in violent storm of energetic, ionising rays which should also have led to the formation of significant quantities of H_3^+ [66].

(c) Polyatomic ions

The H_5^+ ion is a remarkable species. The delocalised wavefunction which samples multiple minima has mean that it is essentially a structural of fluxional. Special techniques are therefore required to simulate the H_5^+ ion spectrum [67–69] and it shows unusual behaviour on isotopic substitution [70]. An interesting suggestion [71] is that the many unassigned lines in the H_3^+ spectrum recorded in a liquid nitrogen-cooled discharge by H_5^+. Quantum mechanical methods developed for computating spectra of H_5^+ are now being Bawendi *et al.* [72] may actually belong to extended H_7^+ ions [73].

Hydrogen ion clusters have been detected up to H_{99}^+ [74]. However, tt woudld appear that the higher hydrogen ionic species which have the general for H_{2n+1}^+, $n = 3, 4, \ldots$ rare somewhat different from H_5^+. These appear to behave like clusters of H_2 molecules nucleated round a central ion, probably H_3^+ [75–77].

Ionic clusters with even numbers of protons, H_{2n}^+, $n = 2, 3, \ldots$ are generally thought to be less stable than their odd counterparts. However, such species are know and the H_6^+ molecular ion has recently been generared in a pulsed-discharge supersonic expansion of hydrogen and mass-selected in a time-of-flight spectrometer allowing it vibrational spectrum to be measured [78].

The H_5^+ system itself is the the intermediate in the proton exchange reaction between H_3^+ and H_2 which is thought to lead to thermalisation of H_3^+ ortho/para ratios at low temperatures [79]. The rate of dissociative recombination (DR) of H_3^+ was long a subject of controversy which appears now to be subtantially resolved [80]. Conversely measurements of the DR rate H_5^+, or more precisely for D_5^+, suggest that the situation is more straightforward with a simple picture of the recombination process capturing the essential physics of the problem [81,82].

(d) Laboratory

Laboratory studies involving the 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 spectum of H_3^+ and its isotopologues have long acted as a benchmark for rigorous ab initio theory [31,83]. Highly accurate solution of the Born-Oppenheimer electronic Schrödinger equation [84] has shifted the emphasis towards study of corrections which go beyong this model including the so-called Lamb shift due to quantum electrodynamics [85] and accurate treatment of non-adiabatic effects arising from failure of the Born-Oppenheimer approximation [86–88].

The new-found ability to performe experiments at cool and ultracool temperatures has allowed collisions involving hydrogen ions to be explored with increasing accuracy with full quantum resolution [89]. The advanced are driving the development of novel theories capable of study low-energy collision processes. [90].

The H_3^+ system itself has facets in its near-dissociation region which meriting further investigation including its near-doissociation spectrum, the possible presence of a whole series of weakly bound, long-range vibrational states [91] and exploring the nature of H_3^+ potential energy surface in the region above dissociation. In this region there is interaction between surfaces which correlate with the two lowest dissocation asympotes, H_2+H^+ and H_2^++H. The seam between these surfaces is now being probed using both photon processes and charge exchange [92]. Modelling these studies will require the extension of accurate, global ground potential H_3^+ potential energy surface [93,94] to forms which give multiple surfaces [95] accurately.

Cryogenic traps provide an environment of the study of the spectra of H_3+ and its isotopologues under very controlled conditions [96,97] which have also been used to probe complexes such as $He - H_3^+$ [98]. H_3+ is an active protonator of species which might otherwise be inert in the interstellar medium [99] and spectra of species such as O_2H+ can also be recorded in crygenic traps [100,101] paving the way to possible astrophysical detection. The development of the new CSR (Cryogenic Storage Ring) further opens the way astrochemical studies of species and processes involving molecular ions [102].

3. Future prospects

Steve: do you wish to add other topics here?

Thirty years after the original detection of the spectrum of H_3^+ in space there is still much to be done on the molecular hydrogen ions. The detection of H_3^+ itself in new enviroments such as the atmospheres of exoplanets and brown dwarfs remains a tantelizing possibility. While the presence of the weakly bound hydrogen dimer, $(H_2)_2$, is now well established in the atmospheres of Jupiter and Saturn [103], its much more stable protonated analogue H_5^+ remains unseen.

The near dissociation spectrum of H_3^+ and its isotopologues as characterised in great detail by Carrington, McNab and co-workers [104–109] remins uncharacterised [110] and poorly understood. This spectrum provides clear link with H^+ + H_2 reaction dynamics which is now being probed in detail [111]. 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 Boyarkin, Rizzo and co-workers [112,113] which allow the observed resonances states to be rotationally assigned.

Treatment of the 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 [32,86,87,114]. Only recently has a fully non-BO treatment been attempted [115] but the results are very far from spectroscopic accuracy. It is notable that for the isoelectron H_2 problem both approaches now give excellent results, accurate to about 10^{-4} cm^{-1}. There is clearly more work to be done to get a proper beyond BO treatment.

The above topics of course concern H_3^+ only; for the higher ions represent are substantially unexplored. They therefore present a whole host of issues for exploration in the laboratory and, possibly, astrophysically.

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Authors' Contributions. For manuscripts with two or more authors, insert details of the authorsâĂŹ contributions here. This should take the form: 'AB caried out the experiments. CD performed the data analysis. EF conceived of and designed the study, and drafted the manuscript All auhtors read and approved the manuscript'.

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