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Spectroscopy of H_3^+ and its impact on astrophysics

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Abstract

Since the original laboratory detection of an H_3^+ spectrum 20 years ago, the search has been on for astronomical observations of this important and fundamental molecular ion. Successful detection of H_3^+ in gas-giant planets, supernova ejecta and the interstellar medium as well as the prospects for future observations are discussed. The role H_3^+ has in determining the atmospheric structure of both the gas giants and cool metal-free planets is explored.

Keywords: H_3^+ spectroscopy; Gas-phase molecular species; Atmospheric structure

1. Introduction

A large proportion of what we know about our Universe has been gleaned from the analysis of spectra. With our ability to obtain accurate spectra of fainter and cooler objects it is becoming increasingly apparent that much of the Universe is molecular. This has placed molecular spectroscopy at the forefront of many areas of astrophysical research.

A spectrum containing several well-resolved lines provides a unique fingerprint for a particular molecule. However much more information can be obtained from careful observations. Quantities of interest in various environments include the density of the molecule, its temperature, information on isotope ratios and distributions of nuclear-spin states. Doppler shifts and profiles can be used to determine systematic and turbulent velocity effects respectively. As many astronomical environments are not in local thermodynamic equilibrium (LTE), different aspects or portions of a molecular spectrum may contain information about effective temperatures which in turn are associated with different processes.

The complexity of the spectra of, particularly polyatomic, molecules means that a single molecule can provide a useful probe of several aspects of a problem simultaneously. To get the most out of such a situation it is necessary to have a good understanding of both the molecular spectroscopy and the astrophysical issues involved.

A good example of this is the H_3^+ molecule. Astronomically H_3^+ is formed rapidly following the ionization of molecular hydrogen. In molecular clouds the ionizing agent is mainly cosmic rays although uv photons may be important near the

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surface of the cloud. In planetary atmospheres electron-impact ionization is often more important. Ionization is followed by the reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H, \tag{1}$$

which occurs essentially at every collision. This means that H_3^+ is the dominant ion in cool molecular plasmas, which can be found in many locations in the Universe.

The H_3^+ molecular ion has long been thought to be responsible for much of the chemistry of the cool interstellar medium (ISM) [1,2]. However this proved frustratingly difficult to demonstrate [3,4]. Despite many attempts, it is only relatively recently that H_3^+ has been detected in the ISM [5]; in the meantime H_3^+ has been detected spectroscopically in environments where its presence had been less anticipated [6–10]. In this article we discuss how a detailed understanding of the spectroscopy of H_3^+ has led to significant advances in various fields and what the future may hold.

2. Spectroscopy of H_3^+

By molecular standards, H_3^+ is a simple system. It comprises three protons which share equally two electrons. Its equilibrium geometry is an equilateral triangle. But it is a fairly floppy system undergoing large-amplitude vibrational motion. For example H_3^+ can become linear at only about a third of its dissociation energy of 4.3 eV. For this reason H_3^+ spectra do not conform to many of the standard rules of spectroscopy and the analysis of observed spectra has relied heavily on ab initio theory [11].

No electronic spectrum of H_3^+ has ever been observed. The high symmetry of H_3^+ means that it has no permanent dipole and as a result no rotational spectrum has ever been observed either. However H_3^+ is predicted to have a weak, strongly J-dependent spectrum which arises from the small dipole created as the molecule distorts in response to rotatating about one particular axis [12,13]. Some astronomical consequences of this are discussed below.

This leaves infrared vibration–rotation spectra as the only present spectroscopy handle on the H_3^+ problem. Again because of its high symmetry, H_3^+ has only one infrared-active fundamental, a degenerate bending mode whose band origin lies at 2521 cm^{-1}. Fifteen lines in the ν_2 fundamental were originally observed by Oka [14], close to the ab initio predictions of Carney and Porter [15]. Fortunately most ν_2 transitions lie in the 3–4-μm region [20] which is in the L window in the Earth's atmosphere. This makes them amenable to ground-based astronomical observation. A comprehensive review of the laboratory spectroscopy of H_3^+ has been given by McNab [21].

3. Planetary

It took many years of searching before a spectrum of the only infrared-active fundamental of H_3^+, the bending mode, was detected in the laboratory by Oka [14]. Yet the first detection of an astronomical spectrum of H_3^+ was of an overtone spectrum [6]. This serendipitous detection was made during observations of H_2 quadrupole emissions in the aurora near the south pole of Jupiter. The spectrum was assigned largely on the basis of ab initio theoretical calculations [16]. Such calculations had predicted that overtone emissions should be strong [17].

The observation of an H_3^+ spectrum in Jupiter was not altogether a surprise, as H_3^+ has already been detected in situ by the charged-particle detector carried on the Voyager mission [18]. However the H_3^+ spectrum contained and continues to contain many surprises and much information. Initial fits to the H_3^+ spectrum of Drossart et al. [6] suggested a rotational temperature of about 1100 K. This temperature was significantly higher than that expected for Jupiter's aurora [19]. Similar temperatures were obtained by analysing vibrational state distributions [22,23] and the translational motion via Doppler profiles [24].

Interestingly, some models of H_3^+ in Jupiter's ionosphere suggest that the appearance that H_3^+ is thermalized in the Jovian ionosphere may be an illusion [25]. These models predict that the ground state should be overpopulated. This conclusion could be tested by observations of the weak ground-state pure-rotational spectrum. Such an observation would provide a sensitive test of both the collision rates used and the assumed conditions used in the model. Our estimates suggest that such a spectrum should be strong enough to observe in Jupiter's aurorae. Even though much of the spectrum lies at wavelengths unsuitable for ground-based observations, our estimates suggest that given the need for a significant quantity of H_3^+ it may well be that this rotational spectrum is observed first astronomically. Indeed we believe that Jupiter should give a clear signal.

Table 1 gives the intensity of some typical H_3^+ rotational transitions in the far infrared showing their strong sensitivity to effective temperature and suggesting that these lines are at least potentially observable. The tabulated lines not only give a useful series but also have upper energy levels ranging from 1680 cm^{-1} to 3725 cm^{-1}, which results in good sensitivity to temperature in the region of interest, $T = 600–1400$ K. Observation of transitions within the vibrational ground state of H_3^+ would give, for the first time, a population for this state and hence a proper H_3^+ column density. If the model predictions [25] that H_3^+ is only quasi-thermalized in Jupiter with overpopulation of the vibrational ground state are correct, then the intensities given in the table, which were derived assuming thermalized H_3^+, will be an underestimate.

Spectra of polyatomic molecules are often complicated with little obvious pattern. H_3^+ is no exception to this; indeed the earliest observation of H_3^+ emission from Jupiter was originally ascribed to at least three different species [26]. Complex spectra need careful interpretation. This is especially so with astronomical spectra where interpretation is often complicated by the relatively low resolution of the observation. H_3^+ spectra from Jupiter in the 3–4-μm region are bright. Jupiter can be seen to glow at the poles at wavelengths sensitive to H_3^+ [27]. In part this is due to the absorption of the incoming solar radiation at this wavelength by pressure-broadened methane lower in Jupiter's atmosphere.

Table 1
Intensity of pure rotational Q-branch H_3^+ emission lines for an observation of Jupiter at Earth with a $1'' \times 1''$ aperture as a function of H_3^+ rotational temperature

Line	λ (μm)	Intensity (W $m^{-2} \times 10^{-20}$)	
$J'K' \rightarrow J''K''$		800 K	1200 K
$6,2 \rightarrow 6,5$	22.665	3	4
$7,3 \rightarrow 7,6$	18.007	10	17
$8,4 \rightarrow 8,7$	15.011	6	14
$9,5 \rightarrow 9,8$	12.975	6	9
$10,6 \rightarrow 10,9$	11.499	9	42

How perfect this absorption is and whether the methane 'leaks' has been a subject of some debate. Thus, for example, Kim et al. [28] claimed to detect the signs of methane in Jupiter images while Baron et al. [27] analysing very similar images, specifically ruled this out. Our own analysis suggests that Kim et al.'s technique of removing the strong H_3^+ lines and then interpreting the remaining emissions as the signature of methane is incorrect. Associated with the strong, and well-characterized, H_3^+ emission lines are a large number of weaker transitions [29]. These are all that is required to explain behaviour of the observed spectra although the role of leaky methane remains a matter for discussion [30].

Whereas reliable H_3^+ rest frequencies are essential to confirm the presence of the molecular ion, most astrophysically interesting information, such as the effective temperatures discussed above, come from analysis of transition intensities. Transition intensities can be measured in the laboratory, but, even for stable species, it is often difficult to get accurate absolute, as opposed to relative, values. In the case of H_3^+ all spectra have been recorded using ions prepared in a discharge. Although it is possible to partially control the vibrational and rotational populations of the ions prepared by the discharge, it is very hard to determine individual state populations. This means that there are no experimental measurements of absolute line strengths for H_3^+ and all astronomical models rely on calculated intensities [20]. This situation is likely to continue for the foreseeable future. Fortunately ab initio calculations of H_3^+ spectra are becoming increasingly reliable [31,32], leading to the situation where frequencies are also calculated to sufficient accuracy for astronomical purposes.

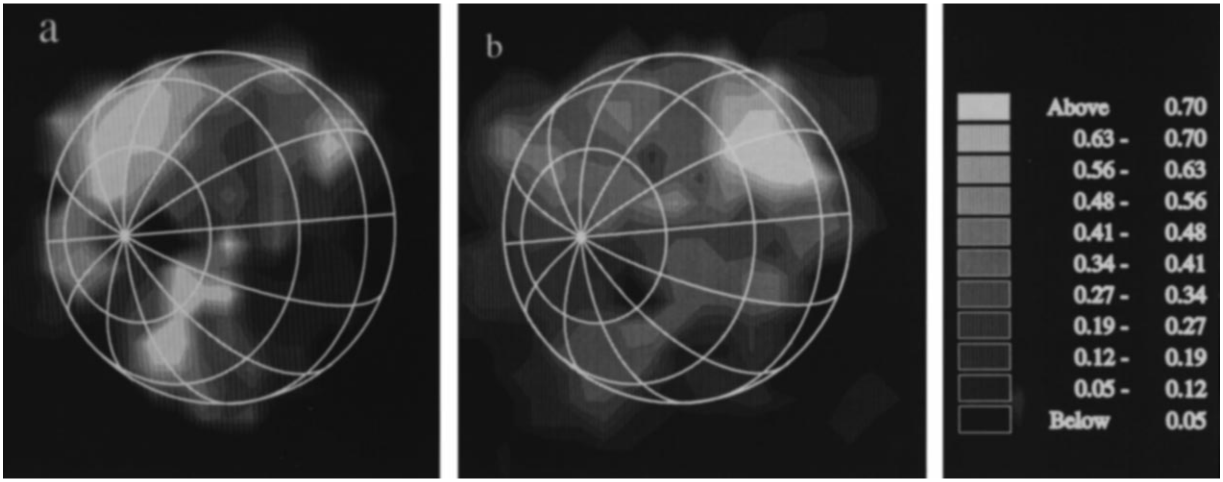

Fig. 1. Images of Uranus taken at the H_3^+ wavelength of 3.986 μm on (a) April 22, 1993 and (b) April 23, 1993. The emission is weak but can be seen to cover a large proportion of the planet, in contrast to Jupiter where bright emission is concentrated around the poles.

The Doppler effect can influence spectra in two ways: random, thermal motions lead to line broadening, whereas systematic motions lead to corresponding systematic shifts in line positions. Recent observations of H_3^+ emissions as a function of longitude by Rego et al. [33] showed, in some cases, pronounced Doppler shifts in the emissions. These shifts suggested supersonic motions and provided the first observational confirmation of a long-standing model of Jupiter's aurora [34].

Jupiter is not on the only gas giant from which H_3^+ emissions can be observed: spectra have been obtained from both Uranus [8] and Saturn [9]. Some interesting results are beginning to emerge from these studies [35]. For example, as shown in Fig. 1, the H_3^+ emission on Uranus is much more widespread and diffuse than it is on Jupiter. However it remains to be seen if the study of H_3^+ spectra on the other gas giants will prove as rewarding as it has done for Jupiter.

Initially, studies of H_3^+ emissions from Jupiter used the ion as an interesting spectroscopic tool to probe the physical environment of Jupiter's upper atmosphere. However it has become apparent that for both Jupiter [36] and Uranus [8] that H_3^+ emissions are actually an important component in the energy balance of the planet. This situation is similar to the atmospheres of cool stars whose properties and behaviour have long been known to be sensitive to the details of the spectra of their constituent molecules.

4. Stellar atmospheres etc

The spectra of cool stars are usually dominated by molecular absorptions, which are often difficult to model because of the sheer volume of laboratory or computed data that is required to synthesize reliable spectra at temperatures of 2000–4000 K [37]. The spectra of most cool stars local to us are dominated by absorptions due to molecules containing either oxygen or carbon, depending of the elemental abundance of the star.

However in the early Universe stars must have formed containing hydrogen and helium only. The spectra and chemistry of these 'metal-free' stars is very different [38]. Molecular hydrogen is a very inefficient absorber of infrared radiation and other means have to be found to explain the radiation transport in these bodies. It would appear that the dominant absorber of infrared photons is H^- [54]. However the stellar atmospheres are electrically neutral and in cool metal-free stars H_3^+, as the dominant hydrogenic molecular ion, is the ionic species that ensures charge neutrality. The number of electrons available for forming H^- is thus dependent on the amount of H_3^+ formed, which in models depends on the magnitude of the (temperature-dependent) partition function used.

It is possible to estimate the partition function of H_3^+ using measured or computed spectroscopic constants [40]. However H_3^+ is such an anharmonic species that these constants do not give a reliable model for the spectrum [39]. As it transpires, they do not give reliable values for the partition function above 1000 K. More detailed calculations, which explicitly sum all the energy levels of H_3^+ up to dissociation, result in a partition function bigger by more than an order of magnitude than the simplified treatment [41].

The spectrum of H_3^+ has yet to be observed in the atmosphere of any star; however models show that its partition function is an important parameter. Fig. 2 compares two models of the metal free magnetic white dwarf star WD1247 + 550 [38]. The model A used the less accurate and lower H_3^+ partition function of Chandra et al. [40], while model B uses more reliable value of Neale and Tennyson [41] which is some ten times larger at the relevant temperatures. The difference between the two models is striking: model B give a much better fit to the observed spectrum and predicts an atmospheric temperature a full 500-K lower than model A. H_3^+ itself is, of course, a significant absorber of infrared radiation. An extensive linelist of H_3^+ transitions has been calculated [29], but to our knowledge has not been included in the opacity function used to model cool metal-free stars.

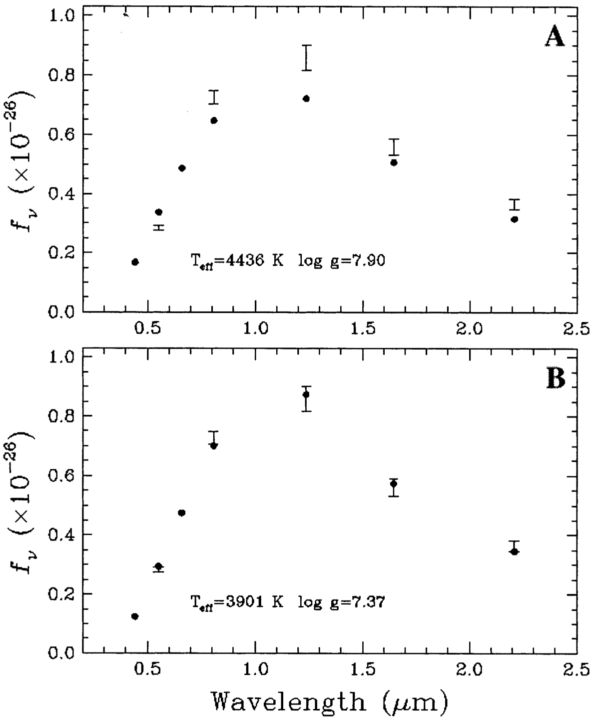

Fig. 2. Comparison of stellar models with different H_3^+ partition functions. Model A used the partition function of Chandra et al. [40]; model B used the partition function of Neale and Tennyson [41]. Besides the much improved fit given by model B, note that the effective stellar temperature is 500-K lower.

Supernovae explosions signal the death of massive stars. These rare events are thought to be the source of heavy elements. In 1987 the world was treated to an unusually good view of a nearby star exploded giving supernova 1987a. Astronomers rapidly trained telescopes on this event and, amongst other things, detailed infrared spectra of SN1987a were recorded as a function of time [42]. Analysis of spectra recorded about six months after the original explosion showed strong, blended emission features which matched closely with what one would expect for hot ($T \sim 2000$ K) H_3^+ [7]. Although the assignment of H_3^+ in the aftermath of SN1987a was supported by chemical models, it remained controversial. Recently Yan and Dalgarno [43] have constructed a much more detailed chemical, and in particular clumpy, model of the SN1987a ejecta. This model confirms the assignment of H_3^+ and successfully replicates its time dependence. In the absence of other plausible candidates for what is a strong spectrum, the assignment of H_3^+ in SN1987a must be regarded as secure.

5. Interstellar medium

H_3^+ has long been regarded as the main driver of chemical reactions in the ISM [1,2]. However, given the low temperatures prevalent in the ISM, the spectroscopy of H_3^+ in the ISM is (almost) non-existent. Soon after obtaining his first laboratory spectrum of H_3^+, Oka suggested searching for an infrared absorption spectrum of H_3^+ against starlight [44]. This observation is made difficult by the sparsity of the infrared spectrum of cold H_3^+, telluric absorptions in the infrared and the need for a suitably positioned star. A number of attempts to observe H_3^+ in this fashion failed [44–46]. In the meantime we proposed an alternative strategy of looking for H_3^+ emissions from warmer, possibly shocked, regions of the ISM. Searches based on this strategy also failed [47].

Recently, Geballe and Oka [5,48] successfully detected H_3^+ absorption against starlight in a number of dense molecular clouds. Much to the relief of the modeling community, these observations found H_3^+ column densities in the range expected by most chemical models. However further observations by Geballe, Oka and their coworkers [10,49] also found the clear spectra signature of H_3^+ in diffuse interstellar clouds. These much harsher environments were not expected to support column densities of H_3^+ close to those found in dense clouds, even when one allows for the much larger size of the diffuse clouds. Modeling these observations thus presents a real challenge.

So far all spectroscopic observations of H_3^+, both laboratory and astronomical, have relied on vibration–rotation spectra. Recently Black [50] has pointed out that two of the lower-lying, and hence weaker, rotational transitions of H_3^+ lie at long enough wavelengths to be observable from the ground. These are 4,4-3,1 at 7.261 cm^{-1} and 7,6-6,3 at 9.252 cm^{-1}. These frequencies come from the experimental energy levels compiled by Dinelli et al. [51], although it is Black's contention that these are not accurate enough for viable astronomical searches. More intriguing is Black's speculation that the transition at 217.8 GHz could well mase. Any maser action would of course significantly increase the possibility of observing what otherwise is expected to be a very weak transition.

Finally we should mention that deuterium-fractionation effects lead to a considerable overabundance of H_2D^+ in models of cold dense clouds [52]. Unlike H_3^+, H_2D^+ has a permanent dipole moment and hence strong pure-rotational spectrum. The search for this spectrum is also a story of difficult observations and false or tentative detections, although it does appear now that definitive observations have been made [53].

6. Conclusion

The era of H_3^+ astronomy is now truly upon us. From the original detection of H_3^+ spectra in the gas giants, the spectrum has now been observed in a variety of interstellar environments: dense molecular clouds, diffuse molecular clouds and a supernova ejecta. Furthermore H_3^+, even when invisible, has been shown to be important for energy-balance and radiative-transport considerations in both stellar and planetary atmospheres. These successes has led to suggestions where and how else one might observe H_3^+: interesting possibilities are in the atmospheres of 'giant Jupiters' orbiting other stars or via maser transitions in the interstellar medium. However given the history of this molecule, it would be no surprise if its spectrum was also present in places yet to be anticipated.

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