

# H<sub>3</sub><sup>+</sup> cooling in planetary atmospheres

Steve Miller,<sup>\*a</sup> Tom Stallard,<sup>b</sup> Henrik Melin<sup>b</sup>  
and Jonathan Tennyson<sup>a</sup>

Received 10th March 2010, Accepted 8th April 2010

DOI: 10.1039/c004152c

We review the role of H<sub>3</sub><sup>+</sup> in planetary atmospheres, with a particular emphasis on its effect in cooling and stabilising, an effect that has been termed the “H<sub>3</sub><sup>+</sup> thermostat” (see Miller *et al.*, *Philos. Trans. R. Soc. London, Ser. A*, 2000, **58**, 2485). In the course of our analysis of this effect, we found that cooling functions that make use of the partition function,  $Q(T)$  based on the calculated H<sub>3</sub><sup>+</sup> energy levels of Neale and Tennyson (*Astrophys. J.*, 1995, **454**, L169) may underestimate just how much energy this ion is radiating to space. So we present a new fit to the calculated values of  $Q(T)$  that is accurate to within 2% for the range 100 K to 10 000 K, a very significant improvement on the fit originally provided by Neale and Tennyson themselves. We also present a fit to  $Q(T)$  calculated from only those values Neale and Tennyson computed from first principles, which may be more appropriate for planetary scientists wishing to calculate the amount of atmospheric cooling from the H<sub>3</sub><sup>+</sup> ion.

## 1 Introduction

Infrared emission from H<sub>3</sub><sup>+</sup> has been detected in Jupiter,<sup>1,2</sup> Saturn<sup>3</sup> and Uranus,<sup>4</sup> but not—so far—in Neptune. For Jupiter, most of the emission comes from the auroral/polar regions, although there is a planet-wide glow: at mid-to-low latitudes, this cannot be explained by EUV ionisation alone,<sup>3</sup> but the exact cause(s) and their relative importance are not fully understood. Total H<sub>3</sub><sup>+</sup> emission from Jupiter is  $\sim 10^{13}$  W.<sup>4</sup> Saturn’s emission is a few percent of that of Jupiter, and is—again—concentrated around the poles as auroral activity.<sup>5</sup> For Uranus the situation is rather different: auroral emission is probably not more than 20% of the total, planetwide, and there is a glow that covers the entire disk. Again, uranian emission is a few percent that of Jupiter.<sup>6</sup> Taken together, however, these observations demonstrate that H<sub>3</sub><sup>+</sup> is an important constituent of giant planet atmospheres and ionospheres. An outstanding problem for the Solar System’s giant planets is how to account for their high exospheric temperatures, all of which are hundreds of degrees hotter than can be accounted for by the absorption of sunlight alone.<sup>7</sup> Amongst the leading candidates to explain these temperatures are gravity wave heating from the lower atmosphere<sup>8</sup> and the distribution of energy from the auroral/polar regions.<sup>9</sup> Neither explanation is without serious problems, however.<sup>10,11</sup>

The upper atmosphere of a planet such as Jupiter is an important interface between its space environment and the denser atmosphere below. In the Solar System, all planets are irradiated by the Sun and impacted upon by the Solar Wind, a stream of rarified plasma travelling at several hundred kilometres per

<sup>a</sup>Department of Physics and Astronomy, University College London, Gower Street, London, WC1E 6BT, U.K. E-mail: s.miller@ucl.ac.uk; j.tennyson@ucl.ac.uk; Fax: +44 20 7679 7155; Tel: +44 20 7679 2000

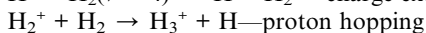
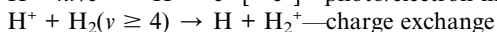
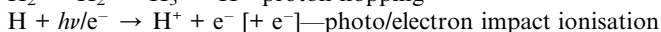
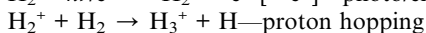
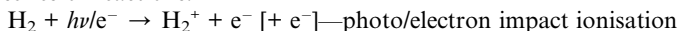
<sup>b</sup>Department of Physics and Astronomy, University of Leicester, University Road, Leicester, LE1 7RH, U.K. E-mail: tss@ion.le.ac.uk; hm@ion.le.ac.uk; Fax: +44 0116 252 2770; Tel: +44 0116 252 3575

second through interplanetary space with particle densities that range from a few million per cubic metre, at Earth, to  $\sim 100$  times less than that at Saturn. For magnetised planets, the interaction with the Solar Wind is mediated by a *magnetosphere*, a “teardrop-shaped” region of space dominated by the planetary magnetic field. For Earth, this magnetosphere stretches about 60 000 km in the direction of the Sun, and for about ten times this distance in the anti-Sun direction. For Jupiter, the corresponding distances are several million km and several hundred million. The precise values for both planets depend on the prevailing Solar Wind conditions, as densities and velocities—hence the pressure exerted on the planet’s magnetic field—can vary considerably. For Earth, most of the plasma that fills the magnetosphere itself comes from the Solar Wind. But for Jupiter and, to a lesser extent, Saturn, internal sources of plasma are also important: Io’s volcanoes for Jupiter; the rings and the emissions of Enceladus for Saturn.

## 2 $\text{H}_3^+$ in giant planet atmospheres

Since its first detection in the auroral regions of Jupiter,<sup>1,2</sup> the  $\text{H}_3^+$  molecular ion has been shown to play an important role in the upper atmospheres of giant planets.<sup>4,12</sup> These upper atmospheres are hydrogen dominated, with molecular hydrogen,  $\text{H}_2$ , predominating at lower levels, giving way to H atoms at the top. They are not convectively mixed, so individual species settle out with their own scale height, which is inversely proportional to their atomic or molecular weight. Giant planet atmospheres have  $\sim 10\%$  of He atoms, which are concentrated toward the bottom since they are twice as heavy as  $\text{H}_2$ . In the lower reaches of the upper atmosphere there may also be small amounts of other heavier species, such as hydrocarbons (especially methane, ethane and acetylene). Typically, pressures range from a microbar or so at the lower levels of the upper atmosphere, to picobars at the top. The corresponding temperature range can start from as low as 120 K, and rise to around 1500 K at the top. The pressure range between a few microbars and a few tenths of a nanobar, a region in which the temperature of the atmosphere rises monotonically with altitude, is known as the *thermosphere*. Above that is the *exosphere*, a region that blends into interplanetary space as atmospheric species escape the planet’s gravitational field. The exosphere is characterised by a (more or less) uniform temperature throughout.

In the upper atmosphere, solar extreme ultraviolet (EUV) radiation can cause ionisation of the atmospheric constituents. In the regions around the poles, various mechanisms can cause particles, such as electrons with energies of several kilovolts, to be accelerated along the magnetic field lines. Given enough energy in the direction towards the planet, these can precipitate into the atmosphere, creating further ionisation. Moreover, high-energy particles can often penetrate deeper into the atmosphere than EUV photons. The locations at which such precipitation occurs are often marked by bright auroral emissions: for Jupiter, these were first detected by Voyager spacecraft<sup>13</sup> and the International Ultraviolet Explorer satellite<sup>14</sup> in the EUV; the emissions were from H Lyman- $\alpha$  at 121.6 nanometres, and the Lyman and Werner bands of  $\text{H}_2$ . In hydrogen-rich atmospheres,  $\text{H}_3^+$  may be formed by a series of reactions:



Note that in the charge exchange, the difference in ionisation potential between H (13.6 eV) and  $\text{H}_2$  (15.4 eV) is made up by having the  $\text{H}_2$  molecule excited to the fourth vibrational energy level or above. These reaction sequences show that  $\text{H}_3^+$  is readily formed when hydrogen-rich atmospheres are ionised, so long as *molecular* hydrogen is also sufficiently abundant. The  $\text{H}_3^+$  infrared emission first detected for

Jupiter was auroral,<sup>2</sup> although it was being formed higher in the thermosphere than the corresponding EUV emission.<sup>15</sup> The overall impact of EUV radiation and particle precipitation is to produce a weakly ionised plasma that coexists with the thermosphere: this is known as the ionosphere, and there is strong coupling between the two.<sup>16</sup>

The exact composition of the ionosphere depends on a large number of factors, including the composition of the thermosphere and the depth to which photons and particles can penetrate, and the local time. Clearly, solar irradiation is only a factor during the hours of dawn until dusk, and during the nighttime photoionised ions will be expected to be lost to recombination with electrons. For a hydrogen rich atmosphere,  $\text{H}_3^+$  recombines dissociatively, at a rate of some  $10^{-8}$  to  $10^{-7}$   $\text{cm}^3 \text{s}^{-1}$ ,<sup>17</sup> which is much faster than radiative recombination, the mechanism that neutralises  $\text{H}^+$ . During the course of the night, therefore, the ionosphere produced by photoionisation will become less molecular and more atomic in character. At higher latitudes, however, where precipitation is the main ionising agent, much less change might be expected, at least at lower altitudes, where high energy particles tend to expend most of their energy.

As an ion,  $\text{H}_3^+$  is a charge carrier and it is affected by magnetic fields that do not directly affect the neutral thermosphere. Millward *et al.*<sup>18</sup> showed that  $\text{H}_3^+$  is the main charge carrier and provider of conductivity for the jovian auroral atmosphere: depending on the exact flux and individual energy of the electrons precipitating into the atmosphere, the height integrated Pedersen conductivity,  $\Sigma_P$ , varied from a few tenths of a mho to nearly 8 mho. This means  $\text{H}_3^+$  plays the major role in generating upper atmosphere Joule heating.<sup>19</sup> The same team also showed that  $\text{H}_3^+$  ion winds,<sup>20</sup> generated through the coupling of electric and magnetic fields, would create heating through ion drag.<sup>21</sup> At the same time, these ion winds also generated *neutral* winds that inhibited the transfer of energy from the auroral/polar regions to lower latitudes.<sup>11</sup> In auroral “events” the energy generated can be considerable,<sup>22</sup> however, and it may be that energy is transferred to lower latitudes under non-equilibrium conditions. Recent observations of Saturn’s auroral activity by Cassini show major changes on timescales of minutes to hours,<sup>23</sup> faster than the atmospheric response time, begging the question as to whether such planetary upper atmospheres are ever in “equilibrium”.

Melin *et al.*’s<sup>22</sup> study of a jovian auroral “event” in 1998 showed that the Joule heating and ion drag inputs to the overall energy budget increased by a factor of four over two days, leading to an excess energy in the atmospheric column of  $175 \text{ mW m}^{-2}$ . Integrated across the auroral/polar region, this amounts to an excess energy of  $\sim 10 \text{ TW}$ , roughly ten times the total EUV absorbed by the atmosphere planetwide. Melin’s study also showed that the heating due to increased precipitation associated with the event was balanced by an increase in the amount of infrared radiation emitted by  $\text{H}_3^+$ , which moderated the local temperature increase. This thermostat effect demonstrates the importance of  $\text{H}_3^+$  cooling in planetary atmospheres dominated by hydrogen.

### 3 $\text{H}_3^+$ cooling

Atomic hydrogen has only (relatively) energetic electronic transitions and therefore cannot cool planetary atmospheres where the temperature is much below  $8000 \text{ K}$ ;<sup>24</sup> and even then is rather inefficient. Thus it plays virtually no part in the thermal stability of planetary atmospheres in the Solar System. Molecular hydrogen is a homo-nuclear diatomic molecule, and its vibrational mode results in no change of dipole, so it is infrared inactive.  $\text{H}_2$  quadrupole transitions are known, but are weak, with Einstein  $A_{if}$  values between  $10^{-5}$  and  $10^{-7} \text{ s}^{-1}$ .<sup>25</sup>  $\text{H}_3^+$  is a stable though reactive molecule. It has two vibrational modes: a symmetric “breathing” stretch,  $\nu_1$  centred on  $3.1463 \mu\text{m}$ ; a doubly degenerate asymmetric stretch-bend,  $\nu_2$  centred on  $3.9662 \mu\text{m}$ . Of these, only  $\nu_2$  is infrared allowed. The  $\nu_2 = 1 \rightarrow 0$   $\nu_2$  fundamental

has an  $A_{\text{if}}$  coefficient of  $129 \text{ s}^{-1}$ .<sup>26</sup> The large molecular anharmonicity associated with this “floppy” molecule, however, means that transitions that are classically infrared inactive are also associated with large  $A_{\text{if}}$  values.<sup>27</sup> Thus the  $\nu_2 = 2 \rightarrow 0$   $2\nu_2(2)$  overtone has  $A_{\text{if}} = 145 \text{ s}^{-1}$ , making it  $\sim 10^9$  times more intense than the  $\text{H}_2$  ( $\nu = 1 \rightarrow 0$ ) quadrupole transitions that are found in the same spectral region, around  $2 \mu\text{m}$ . Even difference bands, such as the ( $\nu_1 = 1 \rightarrow 0$   $\nu_2 = 0 \rightarrow 1$ )  $\nu_1-\nu_2$  band centred on  $15.219 \mu\text{m}$ , have  $A_{\text{if}}$  values of  $\sim 1 \text{ s}^{-1}$ .<sup>26</sup> This means that  $\text{H}_3^+$  is capable of cooling throughout a wide temperature range from as low as  $200 \text{ K}$  up to several thousands of degrees, after which thermal dissociation becomes significant.

The  $\text{H}_3^+$  thermostat effect<sup>28</sup> noted above may not help with explaining the *higher* than expected thermospheric temperatures of the Solar System giant planets, but it has recently been shown to be extremely important in controlling the atmospheric stability of giant exoplanets. Using a three-dimensional global circulation model (3D GCM) developed for Jupiter and Saturn, Koskinen *et al.*<sup>29</sup> showed that it was possible to bring a Jupiter-like planet in to some 0.16 Astronomical Units (AU;  $1 \text{ AU} = 149\,598\,000 \text{ km}$ ) from the Sun, and—whilst the exospheric temperature increased from  $\sim 1300 \text{ K}$  to  $\sim 3800 \text{ K}$ —the planet remained Jupiter-like, insofar as the atmosphere was stable and its extent was  $\sim 6000 \text{ km}$ , less than 10% of the overall planetary radius. At this distance,  $\text{H}_3^+$  cooling was able to offset the increased heating due to EUV insolation. Bringing the planet just 3 million km closer to the Sun, however, to 0.14 AU results in the atmosphere becoming unstable, with temperatures at the top exceeding  $20\,000 \text{ K}$ , inflating to more than  $75\,000 \text{ km}$  (greater than a normal jovian radius), and escaping hydrodynamically. This process can be summarised as follows:

- 1) As a Jupiter-like planet orbits closer to a Sun-like star, the increased EUV flux has a tendency to heat the upper atmosphere;
- 2) But increased EUV also produces increased  $\text{H}_3^+$  densities by photoionisation;
- 3) The increased  $\text{H}_3^+$  cools the atmosphere, maintaining stability ...
- 4) ...until the planet is so close that increasing EUV heating overwhelms the  $\text{H}_3^+$  thermostat, whereupon...
- 5) ...the temperature increases sufficiently to dissociate  $\text{H}_2$ , and the “feedstock” for forming  $\text{H}_3^+$  is removed;
- 6) So a vicious spiral of increasing temperature, dissociating  $\text{H}_2$ , and non-formation of  $\text{H}_3^+$  occurs, leading to a rapidly heating and rapidly inflating atmosphere, with hydrodynamic escape.

The scenario outlined above explains why some of the closely orbiting exo-giants, such as HD189733B and HD209458B, have been found with very extended atmospheres<sup>30,31</sup> that show signs of escaping the planetary gravitational field, although escape rates are not considered large enough for the planet to evaporate entirely over the lifetime of a stellar system<sup>32</sup> (some 9 billion years, in the case of the Solar System).

The amount of  $\text{H}_3^+$  cooling will depend on the number of molecules and the average cooling per molecule. This latter may be calculated by computing the energy radiated in all the possible transitions between populated upper and lower states, weighted by some factor to take into account the fraction of molecules that are in the upper state at any time. Under conditions of Local Thermodynamical Equilibrium (LTE), the energy emitted in a single line is given by:

$$I(\omega_{\text{if}}, T) = g_{\text{f}} (2J_{\text{f}} + 1) \times hc\omega_{\text{if}} \times A_{\text{if}} \exp[-hcE_{\text{f}}/kT]/4\pi Q(T) \quad (1)$$

where  $g_{\text{f}}$  is the nuclear spin degeneracy,  $J_{\text{f}}$  the angular momentum, and  $E_{\text{f}}$  the energy, of the upper state.  $\omega_{\text{if}}$  and  $A_{\text{if}}$  are the energy and Einstein  $A$  coefficient of the transition, and the factor  $hc$  comes in if we wish to convert energies in wavenumbers to SI units.  $Q(T)$  is the partition function. The total cooling in this instance is then:

$$E(\text{H}_3^+, T) = \sum_{\text{if}} I(\omega_{\text{if}}, T) \quad (2)$$

Neale *et al.*<sup>33</sup> have produced an extensive and highly accurate linelist for the  $\text{H}_3^+$  molecular ion, and Melin and coworkers<sup>34,35</sup> have fitted the values of  $E(\text{H}_3^+, T)$  that result from Neale *et al.*'s<sup>33</sup> results for temperatures between 400 K and 3000 K; this temperature range covers limits below which  $\text{H}_3^+$  cooling is fairly insignificant ( $<10^{-21}$  W steradian<sup>-1</sup> molecule<sup>-1</sup>) or above which  $\text{H}_3^+$  formation is inhibited by the thermal dissociation of  $\text{H}_2$ . The fit is given by:

$$E(\text{H}_3^+, T) = -6.11904 \times 10^{-21} + 4.96694 \times 10^{-23} T - 1.443608 \times 10^{-25} T^2 + 1.60926 \times 10^{-28} T^3 - 3.87932 \times 10^{-32} T^4 \quad (3a)$$

for the range  $T = 400\text{--}900$  K, and

$$E(\text{H}_3^+, T) = -8.24045 \times 10^{-21} + 3.54583 \times 10^{-23} T - 8.66296 \times 10^{-26} T^2 + 9.76608 \times 10^{-29} T^3 - 1.61317 \times 10^{-32} T^4 \quad (3b)$$

for the range  $T = 900\text{--}3000$  K.

The values of  $E(\text{H}_3^+, T)$  thus produced are fully valid for LTE conditions. To a first approximation, they may be weighted by a non-LTE factor based on the population of vibrational levels:<sup>35</sup> for the gas (exo-)giants, this factor has been calculated by a detailed balance calculation making use of the method of Oka and Epp<sup>36</sup> and the vibration-only energy levels and  $A_{if}$  values of Dinelli *et al.*<sup>26</sup>

## 4 New fits of the partition function

Eqn (1) shows that the partition function  $Q(T)$  is an important input to the calculation of  $\text{H}_3^+$  cooling:  $E(\text{H}_3^+, T)$  depends inversely on  $Q(T)$ . Neale and Tennyson<sup>37</sup> calculated a partition function which was aimed particularly at studies at elevated temperatures and, in particular, for work on cool white dwarfs.<sup>38</sup> They published the values of  $Q(T)$  derived from their calculated ro-vibrational levels given by:

$$Q(T) = \sum_n g_n (2J_n + 1) \exp[-hcE_n/kT] \quad (4)$$

Neale and Tennyson (NT)<sup>37</sup> calculated states for angular momentum values of  $J = 0\text{--}20$ , with energies up to  $15\,000\text{ cm}^{-1}$  above the ground state from first principles. For higher energy states, they augmented their list by making use of an effective Hamiltonian. This increased the total number of energy levels that went into the summation by a factor of nearly 35, although this made only 0.4% difference to the value of  $Q(T)$  at 2000 K and just over 6% at 3000 K. Although more reliable theoretical models for the energy levels of  $\text{H}_3^+$  are now available,<sup>39</sup> the biggest problem with the NT partition function is actually due to the fit to  $Q(T)$ .

Since computing  $Q(T)$  over and over again for use in a variety of circumstances is time-consuming, these workers then fitted  $\log_{10}(Q(T))$ . This fit was used in the subsequent fits to  $E(\text{H}_3^+, T)$  by Melin and coworkers.<sup>36</sup> In Table 1, however, we show that the Neale and Tennyson ( $Q(\text{NT})$ ) functional form of  $Q(T)$  is a poor fit to their own values calculated from eqn (4) ( $Q(\text{all levels})$ ) at the lower temperatures important for planetary studies.

From Table 1 it is clear that the NT fit gets to within 10% of the actual values of  $Q(T)$  only for temperatures above  $\sim 800$  K, and to within 5% for temperatures above  $\sim 1400$  K. This means that  $Q(\text{NT})$  significantly overestimates  $Q(T)$  for much of the range of interest in planetary atmospheres. As a result, the cooling will be proportionately underestimated. To deal with this we have therefore refitted the values of  $Q(T)$  obtained from eqn (3), paying particular attention to the range from 400 K up to 3000 K. Our fit does not provide a universal set of parameters, but instead is divided into three regions: 100–1800 K; 1800–5000 K; 5000–10 000 K. Moreover, whereas Neale and Tennyson<sup>37</sup> fitted to  $\log_{10}[Q(T)]$ , our fit is to  $Q(T)$  itself, approximated by:

**Table 1** Partition function for H<sub>3</sub><sup>+</sup>: all levels—first principles + effective Hamiltonian

<i>T</i> /K	<i>Q</i> (all levels)	<i>Q</i> (NT)	<i>Q</i> (NT)/ <i>Q</i> (all levels)	<i>Q</i> (MSMT)	<i>Q</i> (MSMT)/ <i>Q</i> (all levels)
100	7.360	18.516	2.516	7.465	1.014
120	9.756	20.402	2.091	9.778	1.002
150	13.599	24.516	1.803	13.573	0.998
200	20.726	33.054	1.595	20.704	0.999
300	37.608	52.096	1.386	37.630	1.001
500	80.579	98.362	1.221	80.580	1.000
1000	245.762	264.504	1.076	245.781	1.000
1400	473.751	497.496	1.050	473.763	1.000
2000	1106.162	1151.482	1.041	1102.279	0.996
2400	1833.777	1911.053	1.042	1825.934	0.996
3000	3654.411	3824.257	1.046	3717.796	1.017
4000	10005.957	10450.312	1.044	10141.354	1.013
5000	23731.476	24389.597	1.028	23964.559	1.010
7000	91465.603	91740.611	1.003	91989.372	1.006
10 000	337371.359	341484.481	1.012	337087.391	0.999

$$Q(T) = A_0 + A_1T + A_2T^2 + A_3T^3 + A_4T^4 + A_5T^5 + A_6T^6 \quad (5)$$

The values obtained for the *A*s are:

$$T = 100\text{--}1800 \text{ K}$$

$$A_0 = -1.11391$$

$$A_1 = +0.0581076$$

$$A_2 = +0.000302967$$

$$A_3 = -2.83724 \times 10^{-7}$$

$$A_4 = +2.31119 \times 10^{-10}$$

$$A_5 = -7.15895 \times 10^{-14}$$

$$A_6 = +1.00150 \times 10^{-17}$$

$$T = 1800\text{--}5000 \text{ K}$$

$$A_0 = -22125.5$$

$$A_1 = +51.1539$$

$$A_2 = -0.0472256$$

$$A_3 = +2.26131 \times 10^{-5}$$

$$A_4 = -5.85307 \times 10^{-9}$$

$$A_5 = +7.90879 \times 10^{-13}$$

$$A_6 = -4.28349 \times 10^{-17}$$

$$T = 5000\text{--}10\,000 \text{ K}$$

$$A_0 = -654293.0$$

$$A_1 = +617.630$$

$$A_2 = -0.237058$$

$$A_3 = +4.74466 \times 10^{-5}$$

$$A_4 = -5.20566 \times 10^{-9}$$

$$A_5 = +3.05824 \times 10^{-13}$$

$$A_6 = -7.45152 \times 10^{-18}$$

Our results are also shown in Table 1 as *Q*(MSMT). Comparison with the values of *Q*(*T*) calculated from the full level summation (eqn (3)) shows that our three-region fit matches *Q*(*T*) to within 2% at all temperatures. This is a significant improvement over the original Neale and Tennyson fit, particularly in the 100–3000 K region of importance in planetary atmospheres; apart from a small temperature domain around 7000 K, our new fit is better at all temperatures from 100 K to 10 000 K.

## 5 Corrections to the $\text{H}_3^+$ cooling function, $E(\text{H}_3^+)$

The line list calculated by Neale *et al.*,<sup>33</sup> of necessity, includes only transitions between the levels that were calculated from “first principles”: while energy levels *may* be extended using effective Hamiltonians, it is not so straightforward to apply this to line strengths for which accidental degeneracies between levels, leading to level mixing, can cause otherwise infrared inactive transitions to “light up”. Moreover, the number of individual levels increases by a factor of 35 when states calculated from the effective Hamiltonian are included, leading to a potential increase in transitions by a factor of 1225. But this raises the question as to whether a partition function based on eqn (3) should be limited to just a sum over the first principles levels for use in calculating  $E(\text{H}_3^+)$ ; the logic is that if the sum over transitions is limited to a sum over first principles transitions, the population weighting in eqn (1),  $(g_i(2J_i + 1) \exp[-hcE_i/kT]/Q(T))$ , which feeds into the sum in eqn (2), should take this into account, at least as far as  $E(\text{H}_3^+)$  is a parameter to be fed into model atmospheres.

Table II shows the value of  $Q(T)$  calculated from eqn (3) using just the levels calculated from first principles. Comparison with the Neale and Tennyson fit to  $\log_{10}Q(T)$  shows clearly how this underestimates the full partition function above 3000 K, even allowing for the fact that the values of  $Q(\text{NT})$  overestimate the value of  $Q(\text{all levels})$ . We have also fitted the values of  $Q(\text{FP levels})$  to the same form as eqn (5). The resulting A parameters are:

$$T = 100\text{--}1800 \text{ K}$$

$$A_0 = -1.11391$$

$$A_1 = +0.0581076$$

$$A_2 = +0.000302967$$

$$A_3 = -2.83724 \times 10^{-7}$$

$$A_4 = +2.31119 \times 10^{-10}$$

$$A_5 = -7.15895 \times 10^{-14}$$

$$A_6 = +1.00150 \times 10^{-17}$$

$$T = 1800\text{--}5000 \text{ K}$$

$$A_0 = -378.621$$

$$A_1 = +0.839719$$

$$A_2 = -0.000349567$$

**Table 2** Partition function for  $\text{H}_3^+$ : first principle levels only

$T$	$Q(\text{FP levels})$	$Q(\text{NT})$	$Q(\text{NT})/$ $Q(\text{FP levels})$	$Q_{\text{FP}}(\text{MSMT})$	$Q_{\text{FP}}(\text{MSMT})/$ $Q(\text{FP levels})$
100	7.360	18.516	2.516	7.465	1.014
120	9.756	20.402	2.091	9.778	1.002
150	13.599	24.516	1.803	13.573	0.998
200	20.726	33.054	1.595	20.704	0.999
300	37.608	52.096	1.386	37.630	1.001
500	80.579	98.362	1.221	80.580	1.000
1000	245.762	264.504	1.076	245.781	1.000
1400	473.751	497.496	1.050	473.763	1.000
2000	1102.988	1151.482	1.044	1102.760	1.000
2400	1808.507	1911.053	1.042	1808.319	1.000
3000	3438.277	3824.257	1.057	3438.590	1.000
4000	7871.175	10450.312	1.044	7871.126	1.000
5000	14259.796	24389.597	1.112	14260.253	1.000
7000	30660.898	91740.611	2.992	30661.035	1.000
10 000	57504.066	341484.481	5.938	57503.198	1.000

$$\begin{aligned}
A_3 &= +5.17514 \times 10^{-8} \\
A_4 &= +7.79447 \times 10^{-11} \\
A_5 &= -1.63248 \times 10^{-14} \\
A_6 &= +9.60597 \times 10^{-19} \\
T &= 5000\text{--}10\,000 \text{ K} \\
A_0 &= +6200.41 \\
A_1 &= -4.55558 \\
A_2 &= +0.000805172 \\
A_3 &= +2.53004 \times 10^{-7} \\
A_4 &= -4.69402 \times 10^{-11} \\
A_5 &= +3.06177 \times 10^{-15} \\
A_6 &= -7.34376 \times 10^{-20}
\end{aligned}$$

Table 2 shows that this fit is 0.2% or better for the range from 120 K to 10 000 K. Since Melin's fit<sup>34</sup> for the  $E(\text{H}_3^+)$  values is based on dividing by  $Q(\text{NT})$ , it may be that it underestimates the actual  $\text{H}_3^+$  cooling by as much as 30% at 400 K, falling to a few percent at higher temperatures. This will tend, for instance, to alter atmospheric temperature profiles, with lower temperatures where  $\text{H}_3^+$  cooling is important than originally anticipated, and to move the exoplanet stability limit closer to the Sun, albeit by a few percent of the 21–24 million km proposed by Koskinen *et al.*<sup>29</sup>

## 6 Conclusions: The Europlanet modelling and data analysis facility

Since it has widespread applicability for planetary atmospheres and other astrophysical applications, a suite of programmes to calculate  $\text{H}_3^+$  cooling is now being grid-enabled as part of the European Modelling and Data Analysis Facility (EMDAF) under construction by Europlanet RI, the European Union funded network of planetary scientists (see <http://www.europlanet-ri.eu/research/jra3>). This programme suite will allow for non-LTE effects, and have the facility to take model atmospheres as inputs, as well as enabling grids of datapoints to be calculated. In this way, those computing the properties of hydrogen-rich environments may specify their own requirements to be provided “off the shelf” for incorporation in models as required. Given the discussion in Section 3, we can consider the impact of  $\text{H}_3^+$  cooling on the formation of our own Solar System. Although Jupiter is currently well outside of the Sun's “stability limit”, as far as the jovian atmosphere is concerned, solar EUV fluxes were much higher at earlier epochs. The “Sun-in-Time” project, which has looked at current exemplars of how our early Sun would have behaved, has produced a graph that shows the EUV flux of the Sun can be represented by:

$$\log_{10} [F_{\text{EUV}}(t)/F_{\text{EUV}}(4.58)] \sim 1.23 \times \log_{10} [4.58/t] \quad (66)$$

where  $t$  is the age of the Solar System in gigayears.<sup>40</sup> This would put Jupiter within the “stability” limit when the Sun was 15 million years old or less, during a critical period of atmospheric accretion. To date, the role that  $\text{H}_3^+$  cooling may have played in stabilising Jupiter around the 15 Myr period has not been modelled.

Finally we note that Sochi and Tennyson<sup>41</sup> have recently calculated a comprehensive linelist, partition function and cooling function for deuterated  $\text{H}_3^+$ ,  $\text{H}_2\text{D}^+$ . Cooling by  $\text{H}_2\text{D}^+$  could play an important role at lower temperatures where cooling by  $\text{H}_3^+$  becomes very inefficient: this may have an important bearing in the physics of stellar discs and planet formation,<sup>42</sup> and on star formation in the early universe.<sup>43</sup>

## References

- 1 L. M. Trafton, J. Carr, D. Lester and P. Harvey, in *Time Variable Phenomena in the Jovian System*, ed. M. J. S. Belton, R. A. West and J. Rahe, 1987, p. 229.
- 2 P. Drossart, *et al.*, *Nature*, 1989, **340**, 539.



- 3 D. Rego, S. Miller, N. Achilleos, T. S. Stallard, R. Prangé, M. Dougherty and R. D. Joseph, *Icarus*, 2000, **147**, 366.
- 4 S. Miller, *et al.*, *Philos. Trans. R. Soc. London, Ser. A*, 2000, **358**, 2485.
- 5 T. R. Geballe, M. F. Jagod and T. Oka, *Astrophys. J.*, 1993, **408**, L109.
- 6 L. M. Trafton, T. R. Geballe, S. Miller, J. Tennyson and G. E. Ballester, *Astrophys. J.*, 1993, **405**, 761.
- 7 R. V. Yelle and S. Miller, in *Jupiter: the Planet, Satellites and Magnetosphere*, ed. F. Bagenal, T. Dowling and W. McKinnon, 2004, p. 185.
- 8 L. A. Young, R. V. Yelle, R. E. Young, A. Sieff and D. B. Kirk, *Science*, 1997, **276**, 108.
- 9 J. H. Waite Jr., T. Cravens, J. Kozyra, A. F. Nagy and S. K. Atreya, *J. Geophys. Res.*, 1983, **88**, 6143.
- 10 K. I. Matcheva and D. F. Strobel, *Icarus*, 1999, **140**, 328.
- 11 C. G. A. Smith, A. D. Aylward, G. H. Millward, S. Miller and L. E. Moore, *Nature*, 2007, **445**, 399.
- 12 S. Miller, T. Stallard, C. Smith, G. Millward, H. Melin, M. Lystrup and A. Aylward, *Philos. Trans. R. Soc. London, Ser. A*, 2006, **A364**, 3121.
- 13 A. L. Broadfoot, *et al.*, *Science*, 1979, **204**, 979.
- 14 J. T. Clarke, H. W. Moos, S. K. Atreya and A. L. Lane, *Astrophys. J.*, 1980, **241**, L179.
- 15 J. T. Clarke *et al.*, in *Jupiter: the Planet, Satellites and Magnetosphere*, ed. F. Bagenal, T. Dowling and W. McKinnon, 2004, p. 639.
- 16 G. Millward, S. Miller, T. Stallard, A. Aylward and N. Achilleos, *Icarus*, 2005, **173**, 200.
- 17 M. Larsson, *Philos. Trans. R. Soc. London, Ser. A*, 2000, **A358**, 2433.
- 18 G. Millward, S. Miller, T. Stallard, A. Aylward and N. Achilleos, *Icarus*, 2002, **160**, 95.
- 19 S. Miller, A. Aylward and G. Millward, in *The Outer Planets and their Moons*, ed. T. Encrenaz, R. Kallenbach, T. C. Owen and C. Sotin, 2005, p. 319.
- 20 D. Rego, N. Achilleos, T. Stallard, S. Miller, R. Prange, M. Dougherty and R. D. Joseph, *Nature*, 1999, **399**, 121.
- 21 C. G. A. Smith, S. Miller and A. D. Aylward, *Ann. Geophys.*, 2005, **23**, 1379.
- 22 H. Melin, S. Miller, T. Stallard, C. Smith and D. Grodent, *Icarus*, 2006, **181**, 256.
- 23 T. Stallard, *et al.*, *Nature*, 2008, **456**, 214.
- 24 S. C. O. Glover and D. W. Slavov, *Mon. Not. R. Astron. Soc.*, 2009, **393**, 911.
- 25 J. Turner, K. Kirby-Docken and A. Dalgarno, *Astrophys. J. Suppl.*, 1977, **35**, 281.
- 26 B. M. Dinelli, S. Miller and J. Tennyson, *J. Mol. Spectrosc.*, 1992, **153**, 718; B. M. Dinelli, S. Miller and J. Tennyson, *J. Mol. Spectrosc.*, 1992, **156**, 243, erratum.
- 27 S. Miller, J. Tennyson and B. T. Sutcliffe, *J. Mol. Spectrosc.*, 1990, **141**, 104.
- 28 S. Miller, H. A. Lam and J. Tennyson, *Can. J. Phys.*, 1994, **72**, 760.
- 29 T. T. Koskinen, A. D. Aylward and S. Miller, *Nature*, 2007, **450**, 845.
- 30 A. Vidal Madjar, *et al.*, *Nature*, 2003, **422**, 143.
- 31 A. Vidal Madjar, *et al.*, *Astrophys. J.*, 2004, **604**, L69.
- 32 R. V. Yelle, *Icarus*, 2004, **170**, 167.
- 33 L. Neale, S. Miller and J. Tennyson, *Astrophys. J.*, 1996, **464**, 516.
- 34 H. Melin, PhD thesis, 2006, University of London.
- 35 H. Melin, S. Miller, T. Stallard and D. Grodent, *Icarus*, 2005, **178**, 97.
- 36 T. Oka and E. Epp, *Astrophys. J.*, 2004, **613**, 349.
- 37 L. Neale and J. Tennyson, *Astrophys. J.*, 1995, **454**, L169.
- 38 P. Bergeron, M. T. Ruiz and S. K. Leggett, *Astrophys. J. Suppl.*, 1997, **108**, 339.
- 39 O. L. Polyansky and J. Tennyson, *J. Chem. Phys.*, 1999, **110**, 5056.
- 40 I. Ribas, E. F. Guinan, M. Gudell and M. Audard, *Astrophys. J.*, 2005, **622**, 680.
- 41 T. Sochi and J. Tennyson, *Mon. Not. R. Astron. Soc.*, DOI: 10.1111/j.1365-2966.2010.16665.x.
- 42 C. Ceccarelli and C. Dominik, *Philos. Trans. R. Soc. London, Ser. A*, 2006, **364**, 3091.
- 43 D. R. Flower and G. Pineau des Forets, *Mon. Not. R. Astron. Soc.*, 2001, **323**, 672.