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Electron-impact rotational excitation of H_3^+: relevance for thermalization and dissociation dynamics

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Electrons are known to be efficient in rotationally exciting molecular ions in low-density astrophysical plasmas. Rotational excitation of molecular ions has also been shown to affect the measured values of dissociative recombination (DR) rate coefficients. Thus, electron collisions with H_3^+ are expected to play a significant role in thermalization and dissociation dynamics of this ion, both in the laboratory and in space. Using the molecular ***R***-matrix method combined with the adiabatic-nuclei-rotation approximation, we have computed new rate coefficients for the rotational excitation of H_3^+ by electrons at temperatures from 10 to 10 000 K. De-excitation rates are found to amount to a few $10^{-7}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ below 1000 K, i.e. comparable in magnitude to that of DR. In astrophysical environments where the electron fraction exceeds 10^{-4}, electron collisions are thus expected to contribute to the non-thermal rotational distribution of H_3^+. The competition between electron and neutral collisions is discussed in the context of recent observations of H_3^+ towards Galactic centre sources.

Keywords: H_3^+; molecular ions; electron–molecule collisions; dissociative recombination; rotational excitation; thermalization processes

1. Introduction

The discovery of H_3^+ in the diffuse interstellar medium has introduced a new enigma into interstellar chemistry, as the abundance of this ion is considerably larger than that predicted by the standard chemical models (McCall *et al.* 2003). However, these models are hampered by the uncertain values of (at least) three key parameters: the dissociative recombination (DR) rate of H_3^+ with electrons, the electron fraction and the cosmic ray ionization rate. Among these parameters, the DR rate has been the most controversial, because both different experimental techniques and theoretical calculations have yielded very different results for more than 40 years. Thanks to the recent experimental and theoretical efforts, however, storage ring measurements (McCall *et al.* 2004; Kreckel *et al.*

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2005) and theory (Kokoouline & Greene 2003) have now converged and demonstrated that the dissociation dynamics of rotationally cold H_3^+ is fast, with a rate constant larger than 10^{-7} cm^3 s^{-1} below 100 K. These results suggest that the DR rate in diffuse clouds is not much lower than previously assumed and that the abundant H_3^+ must reflect either a low electron fraction or a high ionization rate.

The electron abundance in the diffuse interstellar medium is rather uncertain, but it can be estimated by assuming that most electrons come from the photoionization of carbon atoms. In the particular line-of-sight towards ζ Persei, where H_3^+, H_2 and C^+ have been measured, the electron fraction $n(e^-)/n(H_2) = 3.8\times10^{-4}$ was employed by McCall *et al.* (2003) to infer a cosmic ray ionization rate 40 times larger than usually assumed. Such a high value for the ionization rate was also invoked by Oka *et al.* (2005) to model observations towards diffuse clouds near the Galactic centre. It should be noted that the physical conditions in the clouds, i.e. the temperature and the density, are also crucial parameters as these determine the excitation conditions of H_3^+ which, in turn, influence the DR process as observed in the storage ring measurements (Lammich *et al.* 2003, 2005). Thus, it appears that despite a simple and unique chemistry, the astronomical modelling of H_3^+ requires a detailed knowledge of all the microphysics processes that participate to the (de)population of its internal states, in particular the rotational levels observed through absorption lines, i.e. $(J, K) = (1,0)$ and (3,3) of *ortho*-H_3^+ and (1,1) of *para*-H_3^+.

Recently, Oka & Epp (2004) presented model calculations that simulated the thermalization of H_3^+ through spontaneous emission, caused by forbidden rotational transitions, and collisions with the most abundant partners, H_2 molecules. These authors derived collisional rates by using a simple analytical formula that assumes a Langevin capture rate, completely random selection rules and obeys detailed balance. Collisions between H_3^+ and H_2 are indeed chemical reactions in which five protons are scrambled and *ortho*/*para* conversions are expected to occur. In the absence of any rigorous dynamical (quantum or even classical) calculations, the collisional rates of Oka & Epp (2004) are expected to represent the essential characteristics of the collisional process. In particular, it should be noted that based on this model, Oka *et al.* (2005) were able to interpret the observed high population of H_3^+ in the (3,3) metastable level, as well as the absence in the (2,2) level, towards the central molecular zone (CMZ). Thus, a vast amount of high-temperature ($T\sim250$ K) and low-density ($n\sim100$ cm^{-3}) gas was discovered, providing useful informations for understanding the unusual activity near the nucleus of the Galaxy.

As recognized by Oka *et al.* (2005), species other than H_2 might contribute to the non-thermal rotational distributions of H_3^+. If collisions with hydrogen atoms are expected to have effects similar to those of H_2, the effects of helium and electron collisions were estimated by these authors to be mostly negligible. Therefore, the major source of inacurracy in the thermalization model was attributed to the H_2 collisional rate constants. Yet, in the diffuse interstellar medium, electron collisions can dominate the excitation of molecular ions even at the modest electron fractions, $n(e^-)/n(H_2)\sim10^{-4}$. This is because rate coefficients for electron-impact rotational excitation are usually about four orders of magnitude greater than the corresponding rates for excitation by

neutrals (Faure & Tennyson 2001, 2003). However, in the case of H_3^+, the situation is not standard because (i) collisions between H_3^+ and neutrals are reactive and their rate coefficients should be larger than those for standard inelastic ion–neutral collisions, and (ii) H_3^+ has no dipole and therefore collisions with electrons have rate coefficients smaller than those for standard electron–polar ion collisions. The rate coefficients for electron-impact rotational excitation of H_3^+ have been recently computed by two of us (Faure & Tennyson 2003). Based on these, electron effects for thermalization were estimated by Oka & Epp (2004) to be two orders of magnitude less than that of H and H_2. Given the large uncertainties on both the H_2 collisional rate constant and the electron fraction, we nevertheless believe that it is worth including electron collisional rates in any population model of H_3^+.

In the present paper, we propose to calculate the thermalization of interstellar H_3^+ by electron-impact alone, thus neglecting neutral collisions. Our objective is to assess the possibility that the electron contribution is able to drive the very non-thermal rotational distribution of H_3^+ observed towards diffuse clouds in the CMZ. The role of electrons in the rotational cooling and heating of H_3^+ during DR measurements is also discussed in the context of recent storage ring measurements. Section 2 briefly describes the theoretical approach employed to compute the rotational rate coefficients. The results are presented in §3, while conclusions are presented in §4.

2. Theory

State-resolved measurements of rotational excitation in electron–molecule collisions are extremely difficult, and to the best of our knowledge, there is no such data for molecular ions. As a result, population models including collisional processes can rely exclusively on theoretical estimates. The reference method for obtaining electron-impact excitation rates has been the Coulomb–Born (CB) approximation (Chu & Dalgarno 1974; Chu 1975). This approach assumes that the collisional excitation rates are determined by long-range interactions. A standard further approximation is to consider only the dominant long-range term. Within this model, the CB theory predicts that only single jumps in vibrational or rotational quanta are allowed for polar species. ***R***-matrix calculations combined with the adiabatic-nuclei-rotation (ANR) approximation have been applied to several molecular ions and have shown that the CB prediction is incorrect (see Faure & Tennyson 2003 and references therein). In particular, these ***R***-matrix studies have shown that the inclusion of short-range interactions can lead to significant population of higher rotational states, particularly $J=2$. On the other hand, the selection rules for H_3^+ were found to be consistent with the CB theory, implying that electron collisions essentially conserve the K quantum number and do not interconvert *para* and *ortho* forms. Complete details can be found in Faure & Tennyson (2002*a*,*b*).

The major approximation in these calculations is the use of the ANR method which assumes that the energies in the entrance and exit channels are independent of the rotational state, implying target state degeneracy. As a result, the ANR approximation is not expected to be accurate near a rotational threshold. In particular, ANR cross-sections do not go to zero below threshold.

The simplest way to correct this artefact is to force the cross-section at the threshold to zero by just multiplying the ANR cross-sections by a kinematic ratio, as suggested by Morrison & Sun (1995) in the case of diatomic neutral molecules. In the absence of any full calculations for molecular ions, this kinematic ratio was also applied in our previous works.

The recent DR study of Kokoouline & Greene (2003), based on a complete treatment of vibration and rotation of H_3^+ within the multichannel quantum-defect theory, has however provided the correct threshold law for rotational excitation. In particular, the probabilities for rotational excitation were found to be almost energy-independent from the first vibrational threshold down to the rotational threshold. As a result, rotational cross-sections were shown to be large and finite at threshold, in accordance with the Wigner threshold law for an attractive Coulomb field. By comparing our results with those of Kokoouline & Greene (2003), we have been able to check that the proper way to correct ANR cross-sections for ions is to replace the kinematic ratio of Morrison & Sun (1995) by a Heaviside step function which ensures that the cross-section is finite at threshold and is zero below. Complete details will be given in a forthcoming article. This new correction was shown to give a remarkable agreement (better than 2%) with the cross-sections of Kokoouline & Greene (2003). Obviously, it is significant only at temperatures close to thresholds and it was found to increase the rates by factors up to 3 at 100 K. New rate coefficients have been obtained for all transitions among the lowest 14 levels of H_3^+, i.e. up to the (5,4) level which is 865 cm^{-1} above the (1,1) level. These rates will be published elsewhere.

3. Results

Examples of rotational rate coefficients are presented in figure 1 along with the experimental DR rate coefficients of McCall *et al.* (2004). The rotational 'temperature' of H_3^+ in the CRYRING experiment was about 20–60 K, indicating that the only levels with significant population are the *para* (1,1) and *ortho* (1,0) levels. It can be noticed in figure 1 that the rotational excitation rates peak at relatively high temperatures, well above 100 K, as a consequence of the large rotational excitation energies of H_3^+ (e.g. 174 cm^{-1} for $(1,1)\rightarrow(2,1)$). As a result, rotational excitation rates are orders of magnitude lower than the DR rates below 100 K. On the other hand, rotational de-excitation and DR rates have comparable magnitude down to 10 K. This suggests that rotational cooling by electrons is an important mechanism in low-temperature DR experiments, while rotational heating is expected to occur only at larger temperature. Such effects have indeed been observed in recent storage ring experiments at the Test Storage Ring facility in Heidelberg (Lammich *et al.* 2005). A proper model of these measurements, in particular the time dependence of the DR rate as a function of cooling time, clearly requires the inclusion of electron collisional rates. However, it should be noted that if electron-impact rotational excitation is an important issue in the interpretation of storage ring experiments, the rotational excitation effects observed in storage rings or in the calculations of Kokoouline & Greene (2003) did not change the DR rates by factors larger than 2. This suggests that rotational excitation by electrons is not a major effect in the dissociation dynamics of H_3^+ at low temperatures.

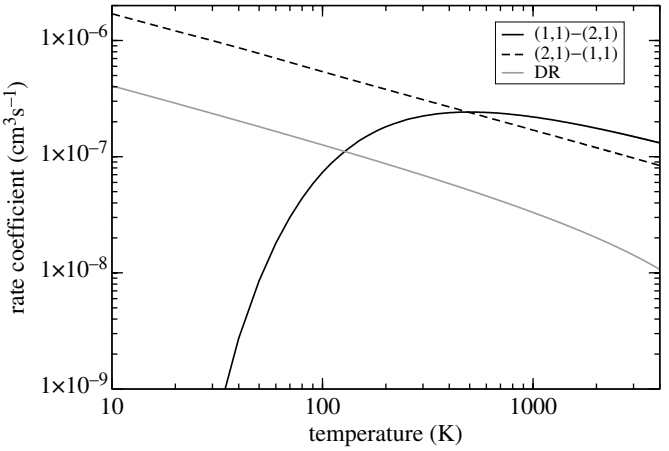

Figure 1. Rate coefficients as a function of temperature for electron–H_3^+ collisions. The solid and dashed lines denote typical rotational transitions for *para*-H_3^+. The grey line gives the power law fit of the experimental DR rate, as provided by McCall *et al.* (2004) from CRYRING ion storage ring measurements.

In their thermalization model for H_3^+ in the interstellar medium, Oka & Epp (2004) have discussed in detail the validity of the steady-state approximation. In typical diffuse clouds, they estimated the lifetime of H_3^+ as $t_{\rm life}\sim 1/(k_{\rm e}n({\rm e}^-))\sim 3\times10^8$ s with a typical electron density of $n({\rm e}^-)\sim 1.5\times 10^{-2}\,{\rm cm}^{-3}$ and a DR rate of $k_{\rm e}\sim 2\times10^{-7}\,{\rm cm}^3\,{\rm s}^{-1}$. Assuming a Langevin rate constant of *ca* $2\times10^{-9}\,{\rm cm}^3\,{\rm s}^{-1}$, they derived an average collision interval of *ca* 5×10^6 s in diffuse clouds with $n({\rm H}_2)\sim 100\,{\rm cm}^3$. Therefore, the lifetime of H_3^+ is two orders of magnitude larger than the time-scale of collisions (and spontaneous emission), allowing the steady-state approximation to be used. However, in the case of electron collisions alone, the average collision interval is comparable to the lifetime of H_3^+ since electron collisional rates are of the same order of magnitude as the DR rate. As a result, the DR process must be included in the population equations.

Let us consider the time evolution of an ensemble of H_3^+ ions formed at time $t=0$. The population equations including spontaneous emission, inelastic collisions and DR with electrons are given as

$$\frac{{\rm d}n(J,K;t)}{{\rm d}t}=\sum_{J',K'}\left[A_{J,K}^{J',K'}n(J',K';t)-A_{J',K'}^{J,K}n(J,K;t)\right]$$
$$+\sum_{J',K'}\left[k_{J,K}^{J',K'}n(J',K';t)-k_{J',K'}^{J,K}n(J,K;t)\right]n({\rm e}^-)-k_{\rm e}n({\rm e}^-)n(J,K;t). \tag{3.1}$$

These equations were integrated until $t_{\rm int}\gg t_{\rm life}$ and all levels are depopulated. In pratice, $t_{\rm int}=10\times t_{\rm life}$ was employed. Equation (3.1) was supplemented by

$$\frac{{\rm d}n_{15}(t)}{{\rm d}t}=\sum_{J,K}k_{\rm e}n({\rm e}^-)n(J,K;t), \tag{3.2}$$

where n_{15} represents the population that has become dissociated. In equation (3.1), $n(J, K; t)$ is the time-dependent population of the (J, K) rotational state, $A^{J',K'}_{J,K}$ are Einstein coefficients for spontaneous emission (taken from table 1 in Oka & Epp (2004)), $k^{J',K'}_{J,K}$ are the electron inelastic rate coefficients, k_e is the DR rate from McCall *et al.* (2004) and $n(e^-)$ is the electron abundance. The effective population ratios for this ensemble of ions were obtained from the time-averaged (normalized) populations $n(J, K)$

$$n(J,K) = \frac{1}{t_{\rm life}} \int_0^{t_{\rm int}} n(J,K;t)\mathrm{d}t. \tag{3.3}$$

Note that $t_{\rm life}$ depends not only on the electron density, but also on the electron temperature through the DR rate (which is assumed to be independent of the rotational level). At $t=0$, the populations were assumed at thermodynamic equilibrium at the selected kinetic temperature. In the present computation, starting conditions are obviously important to the final results. In particular, as discussed above, a major difference between electron and H or H_2 collisions is that the former do not interconvert *ortho* and *para* forms of H_3^+. As spontaneous emission also obeys this selection rule (Oka & Epp 2004), *ortho* and *para* forms are treated as separate species in our calculations. Rotational levels up to (5,4) have been included in the calculation and the coupled set of 15 first-order differential equations was solved using an extrapolation (Bulirsch-Stoer) algorithm (Press *et al.* 1992). The sum of the populations was checked and conserved up to nine digits.

We emphasize that a proper population model would actually require the inclusion of all state-dependent rates for the formation and destruction of H_3^+, which are unfortunately not known. In the present model, it is assumed that a 'chemical' steady-state has been achieved, implying that the rates of formation and destruction are equal. Indeed, the time-scale needed to achieve this steady-state in diffuse clouds was actually estimated by McCall *et al.* (2002) as *ca* 5×10^7 s for a density $n(H_2)=100\,\mathrm{cm}^{-3}$, which is significantly shorter than the lifetime of H_3^+.

The results are presented in figure 2, where the population ratio $n(3,3)/n(1,1)$ is plotted as a function of the electron abundance for a range of electron temperatures. These two levels have been shown to have comparable population towards the Galactic centre source GCS 3-2 (Oka *et al.* 2005). The observed range for the $-100\,\mathrm{km\,s}^{-1}$ clouds, which contain about half of the H_3^+ in the CMZ, is given by the shaded area. Electron abundances larger than $0.5\,\mathrm{cm}^{-3}$ are not considered, as these are not consistent with the relative population $n(3,3)/n(2,2)$, which was observed to be more than 4 towards GCS 3-2. It is found that our calculations are compatible with the observations for electron abundances lower than $0.5\,\mathrm{cm}^{-3}$ and temperatures in the range of approximately 200–300 K. It is interesting to note that assuming a typical electron fraction of approximately 10^{-4}, these results are perfectly consistent with those of Oka *et al.* (2005), i.e. a density $n(H_2)\sim10^2\,\mathrm{cm}^{-3}$ and $T\gtrsim250$ K. Furthermore, the relative population $n(1,0)/n(1,1)$ was found to lie in the range *ca* 0.3–0.7 in our calculations while the observed value is approximately 0.5. However, this latter value has a larger uncertainty because the (1,0) level was detected at lower spectral resolution.

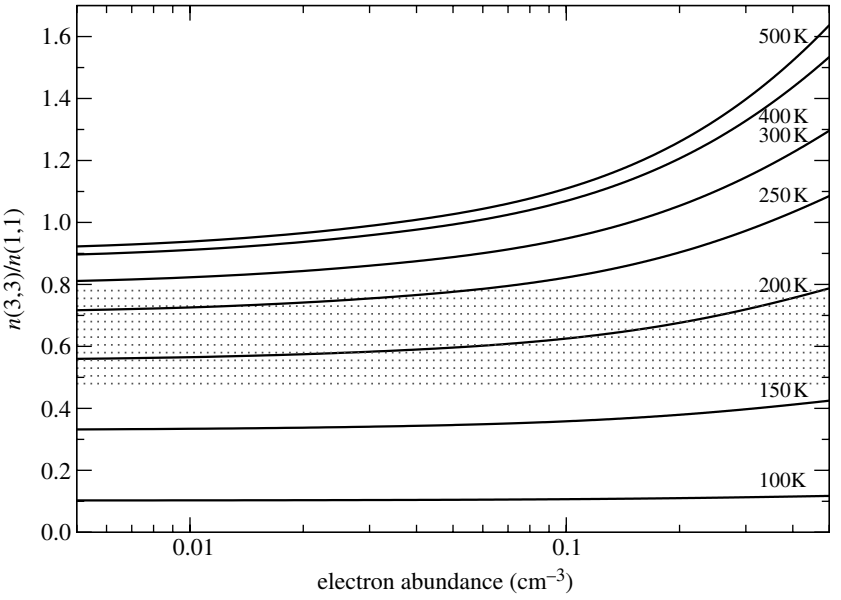

Figure 2. Calculated values of the population ratio $n(3,3)/n(1,1)$ as a function of electron abundance $n(e^-)$ for different electron temperatures T. The shaded area represents the observed range in the $-100\,\mathrm{km\,s^{-1}}$ clouds towards GCS 3-2, from Oka *et al.* (2005).

Finally, as collisions with H_2 are obviously of crucial importance, we included the H_2 collisional rates of Oka & Epp (2004) in our model for an electron fraction of 10^{-4}. We obtained results identical (within 1%) to those of Oka & Epp (2004), suggesting a negligible role for electron collisions at such electron fraction and for the assumed H_2 collisional rates. However, significant differences were obtained for larger electron fractions or, more spectacularly, smaller H_2 collisional rates. Thus, a decrease of the latter by a factor of 2 was found to affect population ratios by up to 50%. Therefore, we emphasize again that the major source of inacurracy in the thermalization model of H_3^+ is the H_2 collisional rates.

4. Conclusion

In summary, the current observational constraints are not yet strong enough to rule out the contribution of electrons in the thermalization of H_3^+ in the CMZ. In particular, the strongest constraint as given by the ratio $n(3,3)/n(1,1)$ is consistent with our model, which predicts density and temperature conditions similar to those inferred by Oka *et al.* (2005). We believe that further observations will help to reduce the uncertainties in the populations of the (1,1), (1,0), (2,2) and (3,3) levels. This should provide strong constraints on the relative role of electron and neutral collisions. In the absence of accurate H_3^+–H_2 collisional rates, we also strongly encourage the inclusion of electron collisional rates in any H_3^+ population model.

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