

Rate coefficients for electron-impact rotational excitation of H_3^+ and H_3O^+

Alexandre Faure^{*} and Jonathan Tennyson[†]

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

Accepted 2002 November 27. Received 2002 November 27; in original form 2002 October 8

ABSTRACT

Molecular **R**-matrix calculations are performed to obtain rotational excitation rate coefficients for electron collisions with the symmetric-top ions H_3^+ and H_3O^+ up to electron temperatures of 10 000 K. De-excitation rates and critical electron densities are also given. It is shown that short-range interactions, which are ignored in the standard Coulomb–Born theory, are crucial for studying electron-impact rotational excitation of molecular ions. In particular, our calculations show that electron collisions could help to create and maintain the predicted population inversion between the $(J, K) = (4, 4)$ and $(3, 1)$ levels of H_3^+ and populate the rotational levels of H_3O^+ up to the $(4, 1)$ level.

Key words: molecular data – molecular processes – ISM: molecules.

1 INTRODUCTION

Rate coefficients for the collisional excitation of molecular ions by electrons are crucial parameters for modelling the physical conditions of harsh astronomical environments such as diffuse interstellar clouds, where both ions and electrons are abundant (Black 1998). Amongst the molecular ions detected in such regions, the symmetric-top H_3^+ and H_3O^+ are two major species. H_3^+ is generally considered as a fundamental molecule of interstellar chemistry because it reacts efficiently with almost any neutral atom or molecule to initiate a complex network of ion–neutral reactions (Herbst 1995). The first detections of H_3^+ in interstellar space were made through infrared (vibration–rotation) transitions towards dense interstellar clouds (Geballe & Oka 1996). Subsequent observations revealed the presence of H_3^+ in diffuse clouds (McCall et al. 1998). The detection of H_3^+ in the diffuse interstellar medium was quite surprising because this ion is thought to be destroyed rapidly by dissociative recombination (DR) with electrons (van Dishoeck & Black 1986). Possible solutions to this problem have been suggested recently by McCall et al. (2002). H_3^+ is also crucial in determining the physical conditions in the upper atmospheres of the giant planets (Miller et al. 2000).

The hydronium ion H_3O^+ is another key species that plays a vital role in the oxygen chemistry network: its DR leads to the formation of OH and H_2O and it is believed to be the major source of water production in interstellar clouds (Phillips, van Dishoeck & Keene 1992). Moreover, since interstellar H_2O cannot be easily

observed from the Earth because of the water vapour in the atmosphere, its abundance is often determined from the abundance of H_3O^+ (Wooten et al. 1991). The far-infrared (rotation–inversion) detection of this ion in diffuse clouds located in the foreground of the Sagittarius B2 molecular cloud was recently reported (Goicoechea & Cernicharo 2001).

In diffuse environments, even at modest electron fractions, $n(\text{e})/n(\text{H}_2) \approx 10^{-5}$ to 10^{-4} , the electron collisions can dominate the excitation of the molecular ions. Rate coefficients for electron-impact rotational excitation are indeed about five orders of magnitude greater than the corresponding rates for excitation by the more abundant neutral partners, H and H_2 (e.g. Dickinson & Flower 1981). Since these parameters have yet to be measured experimentally, astronomical models 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; Dickinson & Muñoz 1977; Neufeld & Dalgarno 1989). 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.

Recent **R**-matrix studies on several linear molecular ions have shown that this prediction is incorrect (Sarpal & Tennyson 1993; Rabadán, Sarpal & Tennyson 1998b; Lim, Rabadán & Tennyson 1999; Faure & Tennyson 2001). In particular, the **R**-matrix calculations have shown that the inclusion of short-range interactions can lead to significant population of higher rotational states, particularly $J = 2$. Very recently, we have extended the theory presented in Rabadán, Sarpal & Tennyson (1998a) for the rotational excitation of linear molecular ions to the case of symmetric-top molecular ions (Faure & Tennyson 2002b). As in the linear case, rotational transitions with $\Delta J > 1$ were shown to have appreciable

^{*}Present address: Laboratoire d’Astrophysique, Observatoire de Grenoble, B.P. 53, 38041 Grenoble cedex 09, France.

[†]Author to whom correspondence should be addressed. E-mail: j.tennyson@ucl.ac.uk

cross-sections. Moreover, electron collisional selection rules were found to be consistent with the CB theory.

In this work, we present electron-impact rotational excitation rate coefficients as well as critical electron densities for the H_3^+ and H_3O^+ molecular ions. In Section 2, **R**-matrix calculations are described and the procedure used to obtain cross-sections is briefly introduced. In Section 3, we present and discuss our results. Conclusions are given in Section 4.

2 CALCULATIONS

2.1 R-matrix calculations

The H_3^+ and H_3O^+ wavefunctions were taken from the **R**-matrix calculations of Faure & Tennyson (2002a), where full details can be found. All calculations were performed at the equilibrium geometries of the molecular ions, which consist of an equilateral triangle with D_{3h} symmetry and a triangular pyramid with C_{3v} symmetry, respectively. The fixed-nuclei (FN) approximation is appropriate as previous **R**-matrix studies have shown that full inclusion of vibrational motion is unnecessary to obtain reliable rotational excitation rates (Rabadán et al. 1998a). However, these findings may not be valid in the context of H_3O^+ , which has a low-energy inversion mode; this will be discussed further below.

The H_3^+ model gives a ground-state quadrupole of $0.914 ea_0^2$, which is close to the theoretical value of $0.9188 ea_0^2$ calculated by Meyer, Botschwina & Burton (1986). The H_3O^+ ground-state dipole, computed at the molecular centre of mass, was found to be $0.6738 ea_0$, which can be compared to the value of $0.6459 ea_0$ computed by Swanton, Bacskay & Hush (1986).

The H_3^+ and H_3O^+ scattering models included respectively four and three target states, represented via configuration-interaction (CI) expansions. The close-coupling expansions were also augmented by terms representing correlation and polarization. Finally, the continuum functions were represented by Gaussian-type basis functions optimized to represent Coulomb functions, with $l \leq 4$ and energy below 68 eV (Faure et al. 2002).

2.2 Rotational cross-sections

The rotational excitation cross-sections were calculated following the procedure presented in Faure & Tennyson (2002b), where full details can be found. In this approach, the cross-section is expressed as a partial-wave expansion within the adiabatic nuclei rotation (ANR) approximation (Lane 1980). For low partial waves ($l \leq 4$), the cross-section is computed from the FN **T** matrices obtained via the **R**-matrix calculations. In the case of electron scattering from a polar molecular ion, the very long-range dipolar potential implies that the partial-wave expansion is only slowly convergent. In this case, the Coulomb–Born approximation is used to obtain the cross-section for the high partial waves not included in the FN **T** matrices. The total cross-section is then calculated as the sum of two contributions. For quadrupolar and higher multipolar interactions, the high- l contribution is negligible and the cross-section can be safely evaluated using FN **T** matrices only. Finally, the known unphysical behaviour of the cross-section near rotational thresholds, inherent in the ANR theory, is corrected using a simple kinematic ratio (Chandra & Temkin 1976). Note that threshold effects can only be included rigorously in a full rotational close-coupling calculation, which is impracticable at the collision energies investigated here (see below) owing to the excessively large number of open channels that would need to be considered.

For electron temperatures between 100 and 10 000 K, excitation rates are sensitive to collision energies in the range 0.001–10 eV. In practice, the cross-sections were calculated from a minimum value of $E_{\min} = 0.01$ eV. Below E_{\min} , the contribution to the cross-sections was estimated using the same low-energy extrapolation procedure as Rabadán et al. (1998b).

3 RESULTS AND DISCUSSION

The transition rates were obtained in the range 100–10 000 K assuming a Maxwellian velocity distribution for the electrons. For use in modelling, the temperature dependence of the transition rates, q , have been fitted using the standard form

$$q(T) = a(T/300)^b \exp(-c/T), \quad (1)$$

where T is in kelvin and q in $\text{cm}^3 \text{s}^{-1}$. It should be noted that the kinematic correction used to force the cross-sections to zero at threshold leads to rate coefficients that do not obey detailed balance at low temperature. De-excitation rates were therefore computed from the excitation ones using the detailed balance relation.

The critical electron density, n_{cr} , is defined as the density at which the collisional de-excitation rate is equal to the spontaneous radiative de-excitation rate:

$$n_{\text{cr}}(JK, T) = \sum_{J' \leq J} \frac{A(JK \rightarrow J'K')}{q(JK \rightarrow J'K')}. \quad (2)$$

At densities higher than n_{cr} , electron collisions will maintain rotational levels in Boltzmann equilibrium at the appropriate electron temperature.

3.1 H_3^+

As a consequence of the Pauli principle, which demands that the total wavefunction be antisymmetric with respect to permutation, the rotational levels with J even and $K = 0$ cannot be occupied in the vibrational ground state of H_3^+ (Bunker & Jensen 1998). The ground rotational state of this ion is, therefore, $(J, K) = (1, 1)$. Moreover, like the NH_3 molecule, H_3^+ has both ortho and para modifications, with $K = 3n$ ortho and $K = 3n \pm 1$ para. The level $(1, 0)$ is therefore very stable because ortho–para conversion is highly forbidden. Rate coefficients for rotational excitations starting from $(1, 1)$ and $(1, 0)$ are presented in Fig. 1.

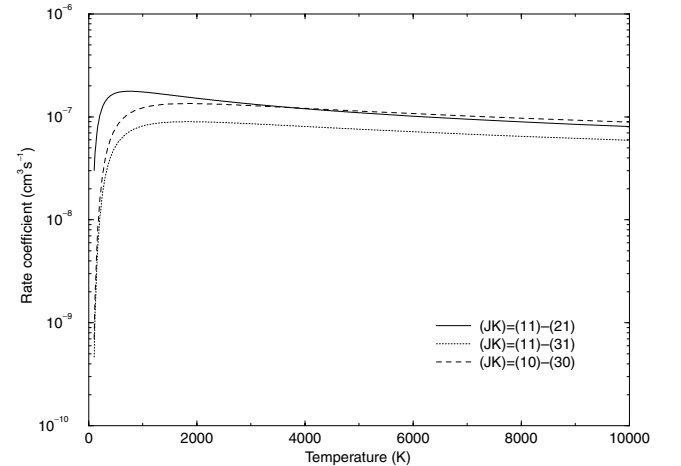


Figure 1. Rotational excitation rates for ortho- ($K = 0$) and para- H_3^+ ($K = 1$).

Table 1. Fitted parameters to the rate coefficients for ortho- ($K = 0$) and para- H_3^+ ($K = 1, 4$). Rates were fitted to equation (1). Powers of 10 are given in parentheses. Transitions are listed in increasing order of the initial state energy, E_{JK} , which was taken from Lindsay & McCall (2001).

Transition	E_{JK} (K)	a ($\text{cm}^3 \text{s}^{-1}$)	b	c (K)
(JK) = (11)–(21)	92.3	4.099 (–7)	–0.4425	321.4
(JK) = (11)–(31)	92.3	2.822 (–7)	–0.4124	737.8
(JK) = (11)–(44)	92.3	5.527 (–11)	–0.1892	633.4
(JK) = (10)–(30)	125.1	4.234 (–7)	–0.4124	737.7
(JK) = (21)–(11)	341.5	2.354 (–7)	–0.4250	53.34
(JK) = (21)–(31)	341.5	1.541 (–7)	–0.4289	459.4
(JK) = (21)–(44)	341.5	4.122 (–11)	–0.2169	393.6
(JK) = (31)–(11)	711.9	1.032 (–7)	–0.3532	37.98
(JK) = (31)–(21)	711.9	1.013 (–7)	–0.3968	48.59
(JK) = (31)–(44)	711.9	4.178 (–11)	–0.3628	–7.707
(JK) = (44)–(11)	722.3	1.922 (–11)	–0.2038	–6.652
(JK) = (44)–(21)	722.3	2.446 (–11)	–0.2413	11.36
(JK) = (44)–(31)	722.3	3.259 (–11)	–0.3641	–17.35
(JK) = (30)–(10)	743.7	1.549 (–7)	–0.3532	37.98

It can be noticed that, in contrast to H_2^+ (Faure & Tennyson 2001), transitions with $\Delta J = 1$ are allowed for H_3^+ when $K \neq 0$. Furthermore, rate coefficients for $\Delta J = 1$ transitions are larger than those for $\Delta J = 2$ transitions below 4000 K. We also observe that the rates peak at relatively high temperatures, between 700 and 2000 K, as a consequence of the large rotational excitation energies of H_3^+ (>0.021 eV). This illustrates the importance of the threshold correction for light molecular ions.

Rates for transitions with $|\Delta J| > 2$ or $\Delta K \neq 0$ were found to be small, as predicted by the CB theory (Faure & Tennyson 2002b). However, it is worth while to consider excitation up to the (J, K) = (4, 4) level because an astrophysical maser is predicted in the (4, 4) \rightarrow (3, 1) rotational transition of H_3^+ (Black 2000). As the (4, 4) level can be populated significantly by electrons only through $\Delta K = 3$ transitions (Faure & Tennyson 2002b), excitations from $K = 1$ only need to be considered. As shown in Table 1, the corresponding rate coefficients are small, typically around $10^{-11} \text{ cm}^3 \text{ s}^{-1}$. According to the calculations of Pan & Oka (1986), the Einstein A coefficient for the (4, 4) \rightarrow (3, 1) transition is $A = 4.1 \times 10^{-9} \text{ s}^{-1}$, which leads to critical densities larger than 30 cm^{-3} in the temperature range 100–10 000 K (see Table 2). As electron densities in the diffuse interstellar medium are generally below 1 cm^{-3} (e.g. Black & van Dishoeck 1991), the present calculations suggest that collisions with electrons might help to create and maintain the necessary population inversion.

The fitted parameters of equation (1) are given in Table 1 for all relevant transitions. All fits reproduce our data within 4 per cent in the temperature range $100 \leq T \leq 5000$ K. At higher temperature, the maximum discrepancy is less than 8 per cent except for the slow $\Delta K = 3$ transitions where the discrepancy reaches 15 per cent at 10 000 K.

For all transitions reported, the cross-sections were found to be entirely dominated by low partial waves. Dickinson & Muñoz (1977) already suggested that, in electron collisions where the long-range interaction is quadrupolar, short-range interactions must be included to obtain reliable results. The CB calculations were found to underestimate the cross-sections by a factor of about 2 (Faure & Tennyson 2002b).

Critical densities are given in Table 2. These were computed using Einstein A coefficients for spontaneous emission taken from the

Table 2. Critical electron density, n_{cr} , in cm^{-3} , as a function of temperature, for rotational levels in ortho- ($K = 0$) and para- H_3^+ ($K = 1, 4$). Powers of 10 are given in parentheses.

T (K)	(JK) = (21)	(JK) = (31)	(JK) = (30)	(JK) = (44)
100	3.1 (0)	3.1 (2)	2.7 (2)	3.72 (1)
200	3.3 (0)	3.4 (2)	3.1 (2)	4.62 (1)
300	3.6 (0)	3.7 (2)	3.4 (2)	5.22 (1)
400	3.8 (0)	4.0 (2)	3.6 (2)	5.59 (1)
500	4.1 (0)	4.2 (2)	3.8 (2)	6.09 (1)
1000	5.1 (0)	5.1 (2)	4.6 (2)	7.53 (1)
2000	6.7 (0)	6.5 (2)	5.7 (2)	9.24 (1)
3000	7.9 (0)	7.5 (2)	6.6 (2)	1.03 (2)
4000	9.0 (0)	8.5 (2)	7.4 (2)	1.10 (2)
5000	1.0 (1)	9.3 (2)	8.1 (2)	1.14 (2)
6000	1.1 (1)	1.0 (3)	8.8 (2)	1.18 (2)
7000	1.2 (1)	1.1 (3)	9.4 (2)	1.20 (2)
8000	1.3 (1)	1.2 (3)	1.0 (3)	1.22 (2)
9000	1.3 (1)	1.2 (3)	1.1 (3)	1.22 (2)
10000	1.4 (1)	1.3 (3)	1.1 (3)	1.23 (2)

calculations of Pan & Oka (1986). Note that the radiative selection rules for the forbidden rotational transitions are:

$$\Delta J = 0, \pm 1 \quad \text{and} \quad \Delta K = \pm 3. \quad (3)$$

3.2 H_3O^+

Like H_3^+ , H_3O^+ has both ortho and para modifications. Moreover, as we have frozen the molecular ions at their equilibrium geometries, the low-frequency inversion motion of H_3O^+ is neglected in our calculations (Faure & Tennyson 2002b). In this approximation, the $|+\rangle$ and $|-\rangle$ inversion states that belong to different rotational levels cannot be coupled, which leads to the selection rule $|+\rangle \leftrightarrow |+\rangle$ and $|-\rangle \leftrightarrow |-\rangle$. However, until inversion is explicitly included in a full rotational close-coupling calculation (currently not possible), the above selection rule must be treated with caution. In particular, such a rule was not observed in the close-coupling calculations of Offer & van Hemert (1992) for the rotational excitation of H_3O^+ by H_2 .

Rate coefficients for rotational excitations starting from (J, K) = (0, 0) $^-$, (1, 0) $^+$ and (1, 1) $^\pm$ are presented in Figs 2 and 3. Owing to nuclear spin statistics effects and to the $|+\rangle/|-\rangle$ selection

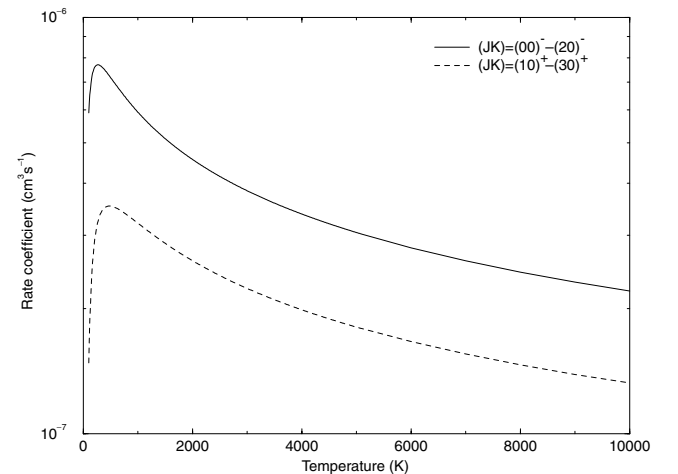


Figure 2. Rotational excitation rates for ortho- H_3O^+ .

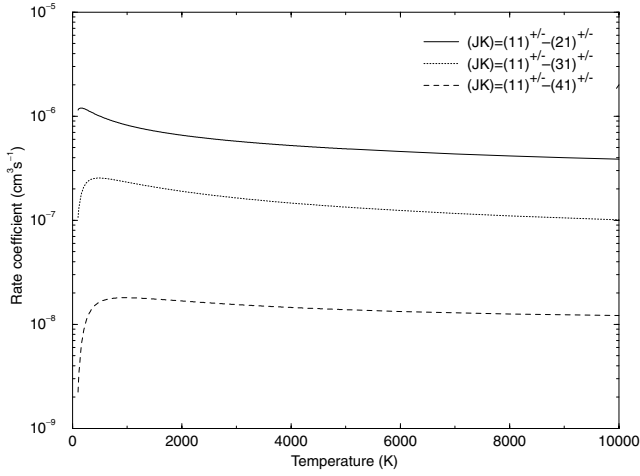


Figure 3. Rotational excitation rates for para- H_3O^+ .

rule, transitions with ΔJ odd are forbidden when $K = 0$ [an energy level diagram of H_3O^+ can be found in Phillips et al. (1992)]. As a result, transitions with $\Delta J = 2$ only are allowed in ortho- H_3O^+ ($K = 0$) whereas significant rates are found for transitions with $\Delta J = 1$ and $\Delta J = 3$ in para- H_3O^+ ($K = 1$). In particular, the (4, 1) level could be significantly populated by electron collisions. Note that transitions with $\Delta J = 3$ are negligible in standard CB theory (Faure & Tennyson 2002b).

Table 3. Fitted parameters to the rate coefficients for ortho- ($K = 0$) and para- H_3O^+ ($K = 1$). Rates were fitted to equation (1). Powers of 10 are given in parentheses. Transitions are listed in increasing order of the initial state energy, E_{JK} , which was taken from Pickett et al. (1998).

Transition	E_{JK} (K)	a ($\text{cm}^3 \text{s}^{-1}$)	b	c (K)
(JK) = (11) ⁺ -(21) ⁺	24.9	1.330 (-6)	-0.3567	52.77
(JK) = (11) ⁺ -(21) ⁺	24.9	1.330 (-6)	-0.3567	52.77
(JK) = (11) ⁺ -(31) ⁺	24.9	4.828 (-7)	-0.4396	205.9
(JK) = (11) ⁺ -(41) ⁺	24.9	3.622 (-8)	-0.3222	314.6
(JK) = (10) ⁺ -(30) ⁺	32.4	6.813 (-7)	-0.4541	210.2
(JK) = (00) ⁻ -(20) ⁻	79.6	1.170 (-6)	-0.4666	123.6
(JK) = (21) ⁺ -(11) ⁺	89.6	8.012 (-7)	-0.3584	-9.745
(JK) = (21) ⁺ -(31) ⁺	89.6	9.819 (-7)	-0.3273	97.96
(JK) = (21) ⁺ -(41) ⁺	89.6	4.727 (-7)	-0.4343	276.0
(JK) = (11) ⁻ -(21) ⁻	104.4	1.330 (-6)	-0.3567	52.77
(JK) = (11) ⁻ -(31) ⁻	104.4	4.828 (-7)	-0.4396	205.9
(JK) = (11) ⁻ -(41) ⁻	104.4	3.622 (-8)	-0.3222	314.6
(JK) = (21) ⁻ -(11) ⁻	167.9	8.012 (-7)	-0.3584	-9.745
(JK) = (21) ⁻ -(31) ⁻	167.9	9.819 (-7)	-0.3273	97.96
(JK) = (21) ⁻ -(41) ⁻	167.9	4.727 (-7)	-0.4343	276.0
(JK) = (20) ⁻ -(00) ⁻	175.0	2.311 (-7)	-0.4611	24.76
(JK) = (31) ⁺ -(11) ⁺	186.6	2.025 (-7)	-0.4306	40.18
(JK) = (31) ⁺ -(21) ⁺	186.6	7.066 (-7)	-0.3304	4.806
(JK) = (31) ⁺ -(41) ⁺	186.6	8.266 (-7)	-0.3081	133.5
(JK) = (30) ⁺ -(10) ⁺	194.0	2.843 (-7)	-0.4431	42.96
(JK) = (31) ⁻ -(11) ⁻	263.2	2.025 (-7)	-0.4306	40.18
(JK) = (31) ⁻ -(21) ⁻	263.2	7.066 (-7)	-0.3304	4.806
(JK) = (31) ⁻ -(41) ⁻	263.2	8.266 (-7)	-0.3081	133.5
(JK) = (41) ⁺ -(11) ⁺	315.7	1.209 (-8)	-0.3225	29.45
(JK) = (41) ⁺ -(21) ⁺	315.7	2.522 (-7)	-0.4178	40.02
(JK) = (41) ⁺ -(31) ⁺	315.7	6.482 (-7)	-0.3114	8.952
(JK) = (41) ⁻ -(11) ⁻	390.1	1.209 (-8)	-0.3225	29.45
(JK) = (41) ⁻ -(21) ⁻	390.1	2.522 (-7)	-0.4178	40.02
(JK) = (41) ⁻ -(31) ⁻	390.1	6.482 (-7)	-0.3114	8.952

We also observe that the rates peak at relatively low temperatures, below 700 K, as a consequence of the low rotational excitation energies of H_3O^+ (<0.025 eV). Rates for transitions with $|\Delta J| > 3$ or $\Delta K \neq 0$ were found to be negligible (Faure & Tennyson 2002b). The fitted parameters of equation (1) are given in Table 3 for all relevant transitions. All fits reproduce our data within 2 per cent in the whole temperature range, except for $\Delta J = 3$ transitions where the maximum discrepancy is less than 7 per cent.

As H_3O^+ has a substantial dipole (see Section 2.1), the long-range effects as given by the dipolar CB approximation are only slowly convergent. As a result, the high partial waves contribution was found to dominate the cross-sections for transitions with $\Delta J = 1$ and $K = K' = 0$ (Faure & Tennyson 2002b). When $K \neq 0$, however, low and high partial waves were found to compete with approximately the same order of magnitude. Cross-sections for transitions with $\Delta J > 1$ were found to arise purely from the low partial waves, as expected.

Critical densities for ortho- and para- H_3O^+ are given in Tables 4–6. These were computed using Einstein A coefficients for

Table 4. Critical electron density, n_{cr} , in cm^{-3} , as a function of temperature, for rotational levels in ortho- H_3O^+ . Powers of 10 are given in parentheses.

T (K)	(JK) = (20) ⁻	(JK) = (30) ⁺
100	3.92 (5)	3.60 (2)
200	4.92 (5)	4.13 (2)
300	5.69 (5)	4.60 (2)
400	6.33 (5)	5.02 (2)
500	6.91 (5)	5.40 (2)
1000	9.21 (5)	6.95 (2)
2000	1.25 (6)	9.27 (2)
3000	1.52 (6)	1.11 (3)
4000	1.74 (6)	1.26 (3)
5000	1.93 (6)	1.40 (3)
6000	2.11 (6)	1.53 (3)
7000	2.27 (6)	1.64 (3)
8000	2.42 (6)	1.75 (3)
9000	2.56 (6)	1.85 (3)
10000	2.70 (6)	1.94 (3)

Table 5. Critical electron density, n_{cr} , in cm^{-3} , as a function of temperature, for rotational levels in para- H_3O^+ (upper inversion levels). Powers of 10 are given in parentheses.

T (K)	(JK) = (21) ⁻	(JK) = (31) ⁻	(JK) = (41) ⁻
100	7.59 (4)	1.07 (5)	1.45 (5)
200	9.95 (4)	1.28 (5)	1.69 (5)
300	1.16 (5)	1.45 (5)	1.88 (5)
400	1.29 (5)	1.59 (5)	2.04 (5)
500	1.41 (5)	1.71 (5)	2.18 (5)
1000	1.82 (5)	2.16 (5)	2.71 (5)
2000	2.34 (5)	2.74 (5)	3.41 (5)
3000	2.70 (5)	3.14 (5)	3.89 (5)
4000	2.98 (5)	3.46 (5)	4.28 (5)
5000	3.22 (5)	3.73 (5)	4.59 (5)
6000	3.42 (5)	3.96 (5)	4.87 (5)
7000	3.61 (5)	4.17 (5)	5.12 (5)
8000	3.77 (5)	4.35 (5)	5.33 (5)
9000	3.92 (5)	4.52 (5)	5.54 (5)
10000	4.06 (5)	4.67 (5)	5.72 (5)

Table 6. Critical electron density, n_{cr} , in cm^{-3} , as a function of temperature, for rotational levels in para- H_3O^+ (lower inversion levels). Powers of 10 are given in parentheses.

T (K)	$(JK) = (31)^+$	$(JK) = (41)^+$
100	8.46 (1)	1.82 (3)
200	1.01 (2)	2.12 (3)
300	1.14 (2)	2.36 (3)
400	1.25 (2)	2.56 (3)
500	1.35 (2)	2.74 (3)
1000	1.70 (2)	3.40 (3)
2000	2.16 (2)	4.27 (3)
3000	2.48 (2)	4.88 (3)
4000	2.73 (2)	5.36 (3)
5000	2.94 (2)	5.76 (3)
6000	3.12 (2)	6.11 (3)
7000	3.28 (2)	6.42 (3)
8000	3.43 (2)	6.69 (3)
9000	3.56 (2)	6.94 (3)
10000	3.68 (2)	7.17 (3)

dipolar transitions, which for a symmetric-top molecule are given (in s^{-1}) by¹

$$A(JK \rightarrow J'K') = 2.026 \times 10^{-6} \nu^3 \mu^2 \frac{S(J'K', JK)}{(2J+1)}, \quad (4)$$

where

$$S(J'K', JK) = (2J'+1)(2J+1) \begin{pmatrix} J' & J & 1 \\ K' & -K & 0 \end{pmatrix}, \quad (5)$$

with ν and μ being the transition energy in cm^{-1} and the dipole moment of the molecule in atomic units (ea_0), respectively. Note that the radiative selection rules for dipolar radiation of a non-planar symmetric-top molecule are (Townes & Schawlow 1975)

$$\Delta J = 0, \pm 1, \quad \Delta K = 0 \quad \text{and} \quad |+\rangle \longleftrightarrow |-\rangle. \quad (6)$$

4 CONCLUSIONS

We have calculated electron-impact rotational excitation rates for the symmetric-top ions H_3^+ and H_3O^+ . These show that such collisions essentially conserve the K quantum number in these systems but can change J by up to three quanta. As these ions can only exist in environments where there are free electrons, and the excitation/de-excitation rates are large, it is important to include electron collisions in any population model of these species. In this context, we note the interesting suggestion by Black (2000) that H_3^+ might mase from its (4, 4) rotational level. As the radiative decay lifetime of this state is very long, state population models based purely on radiative

¹Equation (13) of Neufeld & Dalgarno (1989) has been corrected for typographical errors.

lifetimes are unlikely to be reliable without also considering electron collisions, the rates of which we provide here.

ACKNOWLEDGMENTS

This research has been supported by a Marie Curie Fellowship of the European Community programme Human Potential under contract number HPMF-CT-1999-00415. Part of the calculations were carried out on the workstations of the ‘Service Commun de Calcul Intensif de l’Observatoire de Grenoble’.

REFERENCES

- Black J., 1998, *Faraday Discuss.*, 109, 257
 Black J., 2000, *Phil. Trans. R. Soc. Lond. A*, 358, 2515
 Black J., van Dishoeck E. F., 1991, *ApJ*, 369, L9
 Bunker P. R., Jensen P., 1998, *Molecular Symmetry and Spectroscopy*. NRC Research Press, Canada
 Candra M., Temkin A., 1974, *Phys. Rev. A*, 13, 88
 Chu S.-I., 1975, *Phys. Rev. A*, 12, 396
 Chu S.-I., Dalgarno A., 1974, *Phys. Rev. A*, 10, 788
 Dickinson A. S., Flower D. R., 1981, *MNRAS*, 196, 297
 Dickinson A. S., Muñoz J. M., 1977, *J. Phys. B: At. Mol. Opt. Phys.*, 10, 3151
 Faure A., Tennyson J., 2001, *MNRAS*, 325, 443
 Faure A., Tennyson J., 2002a, *J. Phys. B: At. Mol. Opt. Phys.*, 35, 1865
 Faure A., Tennyson J., 2002b, *J. Phys. B: At. Mol. Opt. Phys.*, 35, 3945
 Faure A., Gorfinkiel J. D., Morgan L. A., Tennyson J., 2002, *Comput. Phys. Commun.*, 144, 224
 Geballe T. R., Oka T., 1996, *Nat*, 384, 334
 Goicoechea J. R., Cernicharo J., 2001, *ApJ*, 554, L213
 Herbst E., 1995, *Annu. Rev. Phys. Chem.*, 46, 27
 Lane N. F., 1980, *Rev. Mod. Phys.*, 52, 29
 Lim A., Rabadán I., Tennyson J., 1999, *MNRAS*, 306, 473
 Lindsay C. M., McCall B. J., 2001, *J. Mol. Spectrosc.*, 210, 60
 Meyer W., Botschwina P., Burton P., 1986, *J. Chem. Phys.*, 84, 891
 McCall B. J., Geballe T. R., Hinkle K. H., Oka T., 1998, *Sci*, 279, 1910
 McCall et al., 2002, *ApJ*, 567, 391
 Miller et al., 2000, *Phil. Trans. R. Soc. Lond. A*, 358, 2485
 Neufeld D. A., Dalgarno A., 1989, *Phys. Rev. A*, 40, 633
 Offer A. R., van Hemert M. C., 1992, *Chem. Phys.*, 163, 83
 Pan F. S., Oka T., 1986, *ApJ*, 305, 518
 Phillips T. G., van Dishoeck E. F., Keene J., 1992, *ApJ*, 399, 533
 Pickett H. M., Poynter R. L., Cohen E. A., Delitsky M. L., Pearson J. C., Muller H. S. P., 1998, *J. Quant. Spectrosc. Radiat. Transfer*, 60, 883
 Rabadán I., Sarpal B. K., Tennyson J., 1998a, *J. Phys. B: At. Mol. Opt. Phys.*, 31, 2077
 Rabadán I., Sarpal B. K., Tennyson J., 1998b, *MNRAS*, 299, 171
 Sarpal B. K., Tennyson J., 1993, *MNRAS*, 263, 909
 Swanton D. J., Bacskay G. B., Hush N. S., 1986, *Chem. Phys.*, 107, 9
 Townes C. H., Schawlow A. L. S., 1975, *Microwave Spectroscopy*. Dover Publications, New York
 van Dishoeck E. F., Black J. H., 1986, *ApJS*, 62, 109
 Wootten A., Turner B. E., Mangum J. G., Bogey M., Boulanger F., Combes F., Encrenaz P. J., Gerin M., 1991, *ApJ*, 380, L79

This paper has been typeset from a $\text{\TeX}/\text{\LaTeX}$ file prepared by the author.