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Electron-impact rotational excitation of symmetric-top molecular ions

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Abstract

We present electron-impact rotational excitation calculations for polyatomic molecular ions. The theory developed in this paper is an extension of the work of Rabadán *et al* (Rabadán I, Sarpal B K and Tennyson J 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 2077) on linear molecular ions to the case of symmetric-top species. The H_3^+ and H_3O^+ ions, as well as their deuterated forms D_3^+ and D_3O^+, are used as test cases and cross sections are obtained at various levels of approximation for impact energies up to 5 eV. As in the linear case, the widely used Coulomb–Born (CB) approximation is found to be unreliable in two major aspects: transitions with $\Delta J > 1$ are entirely dominated by short-range interactions and threshold effects are important at very low energies. Electron collisional selection rules are found to be consistent with the CB theory. In particular, dominant transitions are those for which $\Delta J \leqslant 2$ and $\Delta K = 0$.

1. Introduction

Electron scattering from polyatomic molecular ions is of fundamental interest in a variety of research fields such as plasma physics, atmospheric physics and astrophysics. At low energies, rotational excitation is a very important process by which electrons can control the populations of the rotational levels. In particular, collisions with electrons are thought to directly determine the radiative properties of the molecular ions in the diffuse interstellar medium (Neufeld and Dalgarno 1989, Lim *et al* 1999). Predictions of the emission intensities thus require cross sections for the excitation of the rotational levels by electrons.

Electron-impact excitation of neutral molecules has been widely studied both theoretically and experimentally (Gianturco and Jain 1986). Theoretical methods of calculating cross sections for rotational excitation have been investigated in considerable detail for diatomic

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(Morrison 1995) and polyatomic neutral molecules (e.g. Gianturco *et al* 1998a). In particular, it has been shown that electrons are very efficient in producing rotationally 'hot' molecules when the target exhibits a large dipole moment value (e.g. Gianturco *et al* 1998b). The corresponding rotational excitation of molecular ions is, however, more difficult to study experimentally and calculations have been traditionally performed using the limited Coulomb–Born (CB) approximation (e.g. Chu and Dalgarno 1974, Dickinson and Muñoz 1977). This approach assumes that the cross sections are determined by long-range interactions only. Recent R-matrix studies on linear molecular ions have shown that the CB approximation is not reliable for calculating vibrational or rotational excitation cross sections (Sarpal *et al* 1991, Rabadán *et al* 1998). In particular, rotational transitions with $\Delta J > 1$, which are neglected in a pure dipolar CB model, were found to have appreciable cross sections and were shown to be entirely dominated by short-range interactions. On the other hand, Faure and Tennyson (2001) found that the CB approximation is valid for $\Delta J = 1$ transitions when the molecular ion possesses a dipole moment greater than about 2D.

In this paper, we extend the formulation presented in Rabadán *et al* (1998) for the rotational excitation of linear molecular ions to the case of symmetric-top molecular ions. As plasma and astrophysics data are necessary for electron temperature up to about 10 000 K, rotational close coupling methods are impractical due to the excessively large number of open channels that would need to be considered. The present treatment of rotational excitation is therefore based on the adiabatic-nuclei-rotation (ANR) approximation (Lane 1980) with possible correction for threshold artefacts inherent in this approach. The theory is applied to the calculation of rotational excitation cross sections for the astronomically important molecular ions H_3^+ and H_3O^+ which have been detected recently towards diffuse interstellar clouds (McCall *et al* 1998, Goicoechea and Cernicharo 2001). Calculations are also presented for their deuterated forms D_3^+ and D_3O^+. The theoretical and computational treatment is introduced in the next section. Selection rules, in particular, are obtained for molecular ions with C_{3v} or D_{3h} symmetry. Section 3 presents our results and discussion. Conclusions are summarized in section 4.

2. Theory

2.1. Coulomb–Born approximation

In this work we follow the implementation of the CB theory for symmetric-top molecular ions presented in Chu (1975). The computational procedure is very similar to the linear case and details can be found in Rabadán and Tennyson (1998). We consider the following process:

$$\mathrm{e}^-(k) + ION(JKM) \rightarrow \mathrm{e}^-(k') + ION(J'K'M'), \tag{1}$$

where J is the angular momentum, K and M characterize the magnetic substates of J along the body-fixed (BF) and the space-fixed (SF) axes, respectively, and k (k') is the initial (final) momentum of the electron. The relation between k and k' is

$$k'^2 = k^2 + 2(E_{JK} - E_{J'K'}), \tag{2}$$

where the energy of the state (JK) is given in atomic units by

$$E_{JK} = BJ(J+1) + (A-B)K^2, \tag{3}$$

with A and B being the rotational constants.

The long-range interaction between the symmetric-top molecular ion and the electron can be represented in the form (Chu 1975)

$$V(r,\theta,\phi) = -\frac{1}{r} + \sum_{\lambda\nu} v_{\lambda\nu}(r) Y_{\lambda\nu}(\theta,\phi), \tag{4}$$

where (θ, ϕ) are the polar and azimuthal angles specifying the direction of the incident electron with respect to the BF frame. The potential $v_{\lambda\nu}(r)$ can be expressed in terms of a constant $M_{\lambda\nu}$ which depends on the multipole moment of the molecular ions:

$$v_{\lambda\nu}(r) = -\frac{1}{r^{\lambda+1}} M_{\lambda\nu}. \tag{5}$$

Note that for symmetric-top molecular ions with C_{3v} symmetry, the term $v_{\lambda\nu}(r)$ vanishes unless $|\nu| = 3n$ $(n = 0, 1, 2, \ldots)$.

The CB cross section for the transition $(JK) \to (J'K')$ is given by (Chu 1975)

$$\sigma^{\mathrm{CB}}(JK \to J'K') = \sum_{\lambda=1}^{\infty} \sigma^{\mathrm{CB}}_{\lambda,\nu=K-K'}(JK \to J'K'), \tag{6}$$

where

$$\sigma^{\mathrm{CB}}_{\lambda,\nu}(JK \to J'K') = 4\left(\frac{k}{k'}\right) M^2_{\lambda\nu}(2J'+1) \begin{pmatrix} J & J' & \lambda \\ K & -K' & -\nu \end{pmatrix}^2 \sum_{ll'} (2l+1)(2l'+1) \times \begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 |M^{-\lambda-1}_{ll'}|^2. \tag{7}$$

$M^{-\lambda-1}_{ll'}$ are the radial matrix elements defined as (Chu and Dalgarno 1974)

$$M^{-\lambda-1}_{ll'} = \frac{1}{kk'} \int_0^{\infty} F_{l'}(k'r) r^{-\lambda-1} F_l(kr)\,\mathrm{d}r, \tag{8}$$

where $F_l(kr)$ is the regular radial Coulomb function of angular momentum l.

The leading term in (6) which contributes for polar targets is the dipolar interaction. In this case, $\lambda = 1$, $\nu = 0$ and the summation in (7) can be evaluated exactly by closure (Chu and Dalgarno 1974):

$$\sigma^{\mathrm{CB}}_{10}(JK \to J'K') = \left(\frac{3}{4\pi^2}\right)\left(\frac{\pi}{k^2}\right)\mu^2(2J'+1) \begin{pmatrix} J & J' & 1 \\ K & -K' & 0 \end{pmatrix}^2 f_{E_1}(k, k'), \tag{9}$$

where μ is the dipole moment of the molecular ion and f_{E_1} is a function related to the E_1 nuclear Coulomb excitation that is given explicitly in Chu and Dalgarno (1974). It should be noted that, because of the properties of the $3j$ symbol, the dipolar cross section is non-zero only if $K = K'$ (which means that the dipolar interaction cannot induce rotation around the symmetric axis) and $J' = J \pm 1$. The selection rules for the dipolar interaction are therefore

$$\Delta J = \pm 1 \qquad \text{and} \qquad \Delta K = 0. \tag{10}$$

For the case of quadrupolar interaction, we have $\lambda = 2$, $\nu = 0$ and the cross section is given by (Chu 1975)

$$\sigma^{\mathrm{CB}}_{20}(JK \to J'K') = \frac{16}{5}\pi Q^2\left(\frac{k'}{k}\right)(2J'+1) \begin{pmatrix} J & J' & 2 \\ K & -K' & 0 \end{pmatrix}^2 \sum_{ll'} (2l+1)(2l'+1) \times \begin{pmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 |M^{-3}_{ll'}|^2, \tag{11}$$

where Q is the quadrupole moment of the molecular ion and $|M^{-3}_{ll'}|$ is the quadrupole radial matrix element which can be calculated using various formulas and recurrence relations (Chu 1975, Rabadán *et al* 1998). Note again the presence of the $3j$ symbol which implies that the quadrupolar interaction can only induce transitions with $\Delta K = 0$. Moreover, in the special case when K is zero, $J + J' + 2$ must be an even integer. The selection rules for the quadrupolar interaction are therefore

$$\begin{array}{l} \text{if } K \neq 0,\ \Delta J = \pm 1, \pm 2 \\ \text{if } K = 0,\ \Delta J = \pm 2 \end{array} \qquad \text{and} \qquad \Delta K = 0. \tag{12}$$

It should be noted that, although the dipolar cross section $\sigma_{10}^{\mathrm{CB}}$ is evaluated for an effectively infinite number of partial waves using (9), equation (7) is still needed to compute the low partial wave contribution and compare it with the same partial cross section obtained from body-frame T-matrices. Conversely, the quadrupole cross section $\sigma_{20}^{\mathrm{CB}}$ is only evaluated by direct summation using equation (11) which, fortunately, converges very rapidly (see section 2.3).

Rotational excitation cross sections induced by higher multipolar interactions ($\lambda \geqslant 3$) are usually much smaller than the dipolar and quadrupolar terms (Chu 1975) and will be neglected in this work. However, it is worth mentioning that the leading term that induces $\Delta K \neq 0$ transitions is due to the potential $v_{3,\pm 3}$ (octupolar interaction). In this case, the selection rules are

$$\Delta J = \pm 1, \pm 2, \pm 3 \qquad \text{and} \qquad \Delta K = \pm 3. \tag{13}$$

2.2. *Rotational cross sections from body-frame T-matrices*

Within the ANR approximation, the differential cross section for a symmetric-top molecule is (Jain and Thomson 1983a)

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(JK \to J'K'; \theta) = \frac{1}{(2J+1)} \frac{k'}{k} \sum_{MM'} |f(JKM \to J'K'M')|^2, \tag{14}$$

where $f(JKM \to J'K'M')$ is the BF scattering amplitude which has been converted into the SF frame. Using careful angular momentum algebra, equation (14) can be reduced to (Jain and Thomson 1983a)

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}(JK \to J'K'; \theta) = \frac{k'}{k} \sum_{L} A_L(JK \to J'K') P_L(\cos\theta), \tag{15}$$

where $P_L(\cos\theta)$ is the Legendre function. The A_L coefficients, which depend explicitly on products of T-matrix elements, have already been given many times in the literature (e.g. Gianturco and Jain 1986). The total (integral) rotational cross section follows immediately from (15):

$$\sigma^{\mathrm{TM}}(JK \to J'K') = \int \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi = 4\pi A_0. \tag{16}$$

The A_0 coefficient can be derived easily in a closed form (Jain and Thomson 1983a) and the total cross section can be written as

$$\sigma^{\mathrm{TM}}(JK \to J'K') = \frac{(2J'+1)\pi}{k^2} \sum_{jm_j} (2j+1) \begin{pmatrix} J & J' & j \\ K & -K' & m_j \end{pmatrix}^2 \sum_{ll'} |M_{ll'}^{jm_j}|^2 \tag{17}$$

with

$$M_{ll'}^{jm_j} = \sum_{mm'hh'p\mu} \bar{b}_{lhm}^{p\mu} \begin{pmatrix} l & l' & j \\ -m & m' & m_j \end{pmatrix} \bar{b}_{l'h'm'}^{p\mu} T_{lh,l'h'}^{p\mu} \tag{18}$$

where $T_{lh,l'h'}^{p\mu}$ are the BF T-matrix elements belonging to the μth component of the pth irreducible representation (IR) of the molecular point group, with h distinguishing between different elements with the same $(p\mu l)$. The $\bar{b}$ coefficients are discussed, for instance, in Gianturco and Jain (1986). Note that the total cross section σ^{TM} can also be expressed in terms of the SF T-matrix:

$$\sigma^{\mathrm{TM}}(JK \to J'K') = \frac{\pi}{(2J+1)k^2} \sum_{J_t l l'} (2J_t + 1) |T^{J_t}_{J'K'l',JKl}|^2, \tag{19}$$

where $J_t = J + l$ is the total angular momentum. Expression (19) is identical to the linear case (Rabadán *et al* 1998).

Jain and Thomson (1983b) have discussed selection rules for the transition $(J\tau M) \to (J'\tau' M')$ in asymmetric-top molecules (τ replaces K which is no longer a good quantum number). They found that transitions are allowed only between even τ states or between odd τ states which leads to the selection rule $\Delta\tau = 0, \pm 2, \pm 4, \ldots$ which, for a molecule like water, means that there is no interconversion between ortho and para states. From (17) and (18), it can be noticed that, because of the properties of the $3j$ symbols, transitions for which $K - K' \neq m' - m$ are forbidden. For symmetric-top molecules with C_{3v} or D_{3h} symmetry, the dominant $T^{p\mu}_{lh,l'h'}$ elements are those corresponding to $m - m' = 3n$ ($n = 0, 1, 2, \ldots$). Therefore, in contrast to the asymmetric-top case, the dominant rotational transitions for C_{3v} or D_{3h} molecules are those for which $\Delta K = 0, \pm 3, \pm 6, \ldots$. This result is consistent with the CB theory (see section 2.1) and with the selection rules observed experimentally in NH_3–rare-gas collisions (Oka 1968).

Moreover, for a non-polar molecule, the non-zero T-matrix elements are those for which $l + l'$ is even. If $K = K' = 0$ then $m_j = 0$ and equation (17) vanishes unless $J + J' + j$ is even. Because of the $3j$ relation (Brink and Satchler 1968),

$$\begin{pmatrix} l & l' & j \\ -m & m' & 0 \end{pmatrix} = (-1)^{l+l'+j} \begin{pmatrix} l & l' & j \\ m & -m' & 0 \end{pmatrix}, \tag{20}$$

the sum over (m, m') in (18) vanishes unless $l + l' + j$ is even. Therefore, j must be even and transitions must obey the selection rule $\Delta J = \pm 2, \pm 4, \ldots$, as predicted by the CB theory for the quadrupolar interaction (see equation (12)). Specific selection rules obtained for the H_3^+ and H_3O^+ ions will be given in section 3.

2.3. Final cross sections

The expression of σ^{TM} in (17) involves in principle infinite sums over the angular momenta (l, l') which characterize the T-matrix elements. As the number of partial waves included in the T-matrices is necessarily limited, the final cross section is obtained from the T-matrix cross section and completed with CB cross sections (Rabadán *et al* 1998):

$$\sigma(JK \to J'K') = \sigma^{\mathrm{TM}}(JK \to J'K') + \sigma^{\mathrm{CB}}(JK \to J'K') - \sigma^{\mathrm{PCB}}(JK \to J'K') \tag{21}$$

where $\sigma^{\mathrm{PCB}}(JK \to J'K')$ denotes the 'partial' CB cross section calculated using a few partial waves in (7): $l, l' \leqslant l_{\max}$, where $l_{\max}$ is the number of partial waves included in the T-matrices.

In the case of electron scattering from polar targets, the very long-range dipolar potential implies that a very large set of (l, l') indices needs to be included due to the very slow convergence of the partial wave expansion. However, for quadrupolar and higher multipolar transitions, the two CB terms almost cancel because equation (7) converges rapidly. In this case, the final cross section can be approximated by

$$\sigma(JK \to J'K') = \sigma^{\mathrm{TM}}(JK \to J'K'). \tag{22}$$

Table 1. Rotational constants (A_e and B_e in cm^{-1}), dipole (μ in Debye) and quadrupole (Q in atomic units) at the equilibrium geometry of the molecular ions. These values are used for the CB calculations.

Ion	A_e	B_e	μ	Q
H_3^+	21.94	43.88	0.00	0.914
D_3^+	10.98	21.96	0.00	0.914
H_3O^+	6.399	11.04	1.71	2.61
D_3O^+	3.202	5.632	1.55	2.69

2.4. Threshold effects

The rotational excitation cross sections discussed above have been obtained within the ANR approximation. The ANR method 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 at threshold. The simplest way to correct this artefact is to force the cross section at threshold to zero by just multiplying the ANR cross sections by the kinematic ratio k'/k (Chandra and Temkin 1976, Morrison 1995):

$$\tilde{\sigma}(JK \to J'K') = \frac{k'}{k}\sigma(JK \to J'K'). \tag{23}$$

Note, however, that the resulting ‘flux-corrected’ ANR cross sections do not necessarily obey the theoretical threshold laws (Morrison 1995).

3. Generation of T-matrices

The UK molecular R-matrix polyatomic code (Morgan *et al* 1998, Tennyson and Morgan 1999) was employed to compute the necessary BF K-matrices, which are related to T-matrices through the equation

$$\boldsymbol{T} = (1 + \mathrm{i}\boldsymbol{K})(1 - \mathrm{i}\boldsymbol{K})^{-1} - 1. \tag{24}$$

As shown by Rabadán *et al* (1998) in the case of the diatomic HeH^+ and NO^+ molecular ions, detailed (adiabatic and non-adiabatic) treatments of vibrational motion are unnecessary to obtain reliable rotational excitation cross sections. K-matrices were therefore computed within the fixed-nuclei approximation, which means that all calculations were performed at the equilibrium geometries of the molecular ions.

H_3^+ and H_3O^+ wavefunctions were taken from the calculations of Faure and Tennyson (2002a), where full details can be found. The equilibrium geometries of the molecular ions are, respectively, an equilateral triangle with D_{3h} symmetry and a triangular pyramid with C_{3v} symmetry. H_3^+ and H_3O^+ scattering models were constructed using the four and three lowest target states, respectively. The continuum orbitals were represented using the GTO basis set given by Faure *et al* (2002) which includes all angular momentum up to $l_{\max} = 4$ and is optimized to span energies below 5 Ryd. As the position of the centre of mass changes from H_3O^+ to D_3O^+, new scattering calculations were performed to obtain D_3O^+ wavefunctions using the same target and scattering models as H_3O^+. On the other hand, within the fixed-nuclei approximation, D_3^+ wavefunctions are identical to the H_3^+ ones. The molecular parameters used for the CB calculations are given in table 1.

As the R-matrix polyatomic code uses D_{2h} or lower symmetry, the scattering calculations were carried out in C_{2v} symmetry for H_3^+/D_3^+ and C_s symmetry for H_3O^+/D_3O^+. In order to compute rotational excitation cross sections, K-matrices were converted to the natural symmetries by mapping the C_{2v} and C_s channels to the D_{3h} and C_{3v} ones. However, as the available routines needed to compute equation (18) are implemented for the C_{3v} symmetry only (Sanna and Gianturco 1998), K-matrices for H_3^+/D_3^+ were finally downgraded to the C_{3v} symmetry.

4. Results and discussion

4.1. H_3^+ *and* D_3^+

H_3^+ is the simplest polyatomic molecule, consisting of only three protons (fermions) and two electrons. As a consequence of the Pauli principle, which demands that the total wavefunction be antisymmetric with respect to permutation, the $J = K = 0$ state of the vibrational ground state cannot be occupied (Oka 1992). Therefore, the ground rotational state of H_3^+ is the $(J = 1, K = 1)$ state and the next level is $(J = 1, K = 0)$ (Pan and Oka 1986). Moreover, like the NH_3 molecule, H_3^+ has both ortho- and para-modifications, with $K = 3n$ ortho and $K = 3n \pm 1$ para. On the other hand, D_3^+ is composed by three bosons and its lowest rotational level is $(J = 0, K = 0)$.

As expected from the selection rule derived in section 2.2 for non-polar species, transitions with $K = K' = 0$ are found to be forbidden except for $\Delta J = \pm 2, \pm 4, \ldots$. Cross sections are also found to be entirely dominated by low partial waves, as observed by Faure and Tennyson (2001) for the non-polar H_2^+. As a result, the T-matrix cross sections are essentially unaltered by augmenting them with CB calculations for higher partial waves. Cross sections for rotational transitions with $\Delta J = 1, 2$ and $\Delta K = 0$ in ortho- and para-H_3^+ are shown in figures 1(a), (b) and (c), respectively. Figure 1(d) gives cross sections for the lowest rotational excitation in D_3^+. The T-matrix calculations show that the CB approximation underestimates the cross sections by a factor of about 2. Our calculations also suggest that cross sections for $\Delta J = 1$ transitions are comparable to those for $\Delta J = 2$ transitions.

Figure 1 includes results of the T-matrix cross section with and without the threshold correction. It can be noticed that this correction leads to a significant difference in the cross sections below about 0.5 eV, in particular for H_3^+ which is lighter than D_3^+ and therefore has higher rotational excitation energies.

As none of our calculations included multipole moments higher than quadrupole, there can be no long-range contribution to $\Delta J > 2$ or $\Delta K \neq 0$ cross sections. This is consistent with the very rapid convergence observed for the $\Delta J = 2$ cross sections considered above. As illustrated in figure 2, cross sections for $\Delta J = 3, 4$ and $\Delta K = 3$ transitions are found to be about three orders of magnitude lower than the cross sections considered above.

In summary, propensity rules in H_3^+/D_3^+–electron collisions are found to be

$$\begin{array}{l} \text{if } K \neq 0,\ \Delta J = \pm 1, \pm 2 \\ \text{if } K = 0,\ \Delta J = \pm 2 \end{array} \qquad \text{and} \qquad \Delta K = 0, \tag{25}$$

which correspond to the quadrupolar selection rules derived from the CB theory (see section 2.1). It should be noted that radiative selection rules for the forbidden rotational transitions in H_3^+ are (Pan and Oka 1986)

$$\Delta J = 0, \pm 1 \qquad \text{and} \qquad \Delta K = \pm 3. \tag{26}$$

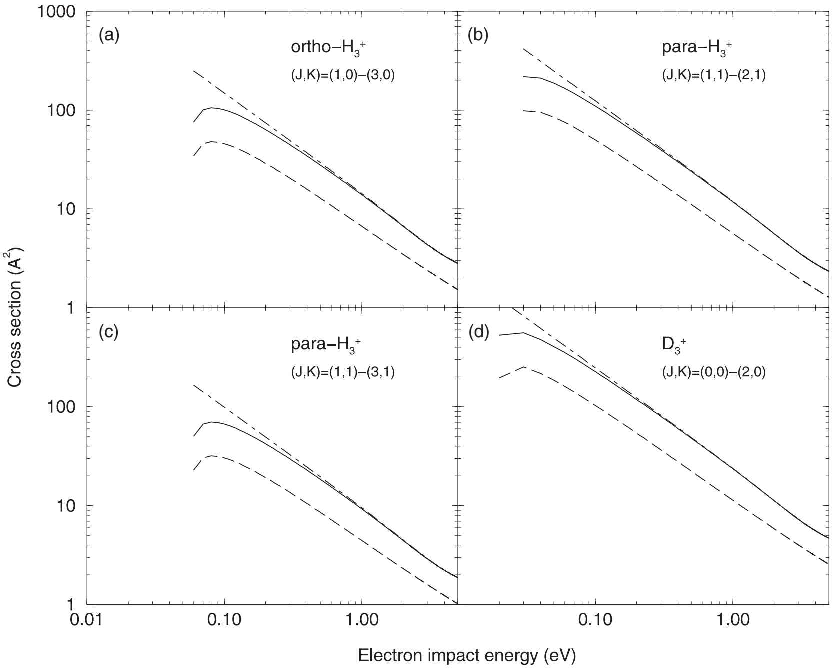

Figure 1. Rotational excitation cross sections for transitions with $\Delta J = 1, 2$ and $\Delta K = 0$ in ortho-, para-H_3^+ and D_3^+ by electron impact. The T-matrix results, with and without threshold correction, are represented by the solid and dot–dashed curves, respectively. The long-dashed curve denotes the CB results.

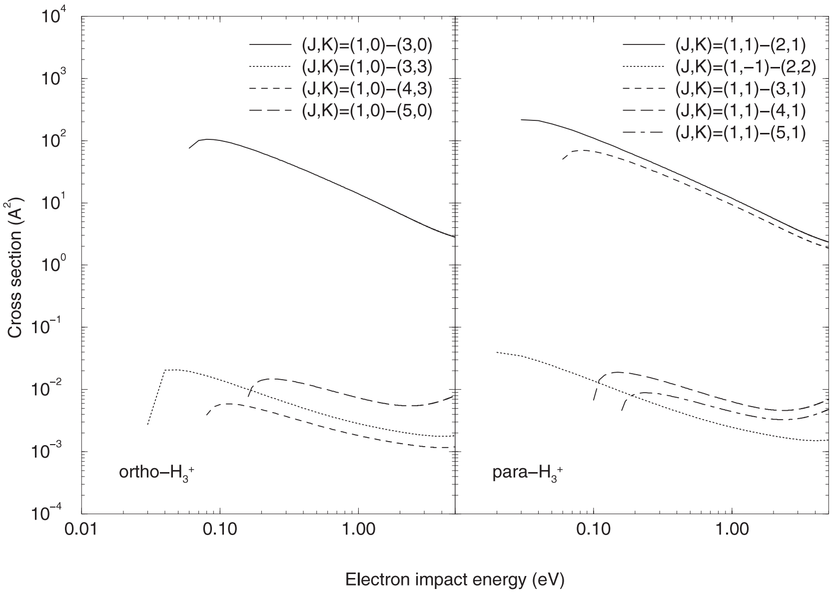

Figure 2. Rotational excitation cross sections for transitions with $\Delta J = 1, 2, 3, 4$ and $\Delta K = 0, 3$ in ortho- and para-H_3^+ by electron impact.

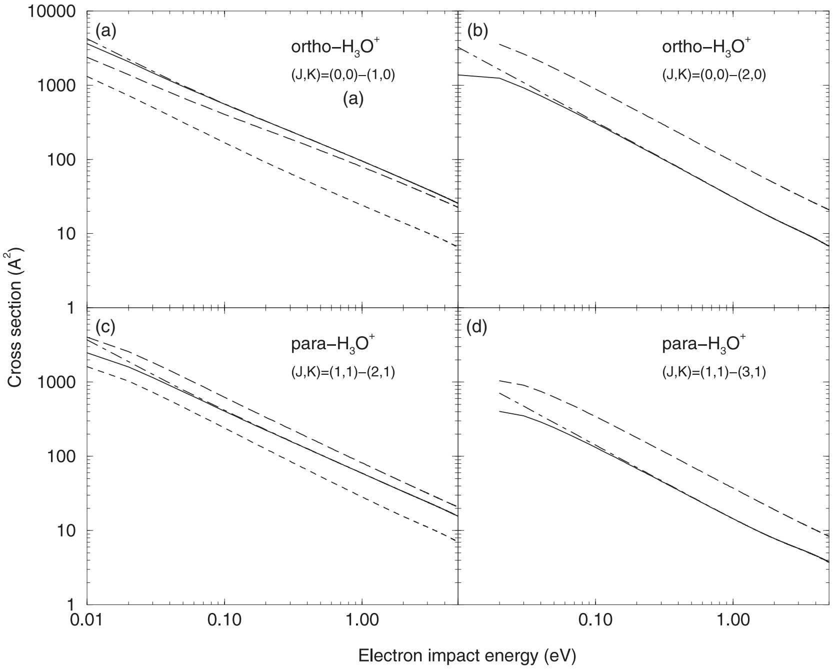

Figure 3. Rotational excitation cross sections for transitions with $\Delta J = 1, 2$ and $\Delta K = 0$ in ortho- and para-H_3O^+ by electron impact. (a) and (c): the solid curve denotes the T-matrix results augmented with CB calculations. The dot–dashed line gives the same model without threshold correction. The CB results are represented by the long-dashed curve and the dashed curve gives the T-matrix results. (b) and (d): the T-matrix results, with and without threshold correction, are represented by the solid and dot–dashed curves, respectively. The long-dashed curve denotes the CB results.

4.2. H_3O^+ and D_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 inversion motion of H_3O^+ is neglected in our calculations. This approximation is justified because the vibrational period for inversion is much longer than the duration of a collision. Explicit inclusion of inversion might, however, affect the collisional propensity rules, as shown by Rist *et al* (1992) for the NH_3–H_2 system.

As H_3O^+ has a substantial dipole (see table 1), the long-range effects as given by the dipolar CB approximation are only slowly convergent. In fact, the high partial waves contribution is found to dominate the cross sections for transitions with $\Delta J = \pm 1$ and $K = K' = 0$. When $K \neq 0$, however, both dipolar and quadrupolar interactions induce transitions with $\Delta J = \pm 1$ (see equation (12)). In this case, low and high partial waves contribute with approximately the same order of magnitude. Figures 3(a) and (c) gives results for $\Delta J = 1$ and $\Delta K = 0$ transitions in ortho- and para-H_3O^+, respectively. It can be noticed that the transition $(J, K) = (0, 0) \rightarrow (1, 0)$ is dominated by long-range effects and the final cross section is slightly larger than the pure CB calculation. On the other hand, short-range and long-range contributions compete for the transition $(J, K) = (1, 1) \rightarrow (2, 1)$ and the CB approximation slightly overestimates the cross section in this case.

As found for H_3^+/D_3^+, the $\Delta J = 2$ cross sections for ortho- and para-H_3O^+ arise purely from the low partial waves. Cross sections are shown in figures 3(b) and (d). Unlike H_3^+/D_3^+, however, the CB approximation was found to overestimate the cross sections significantly, by

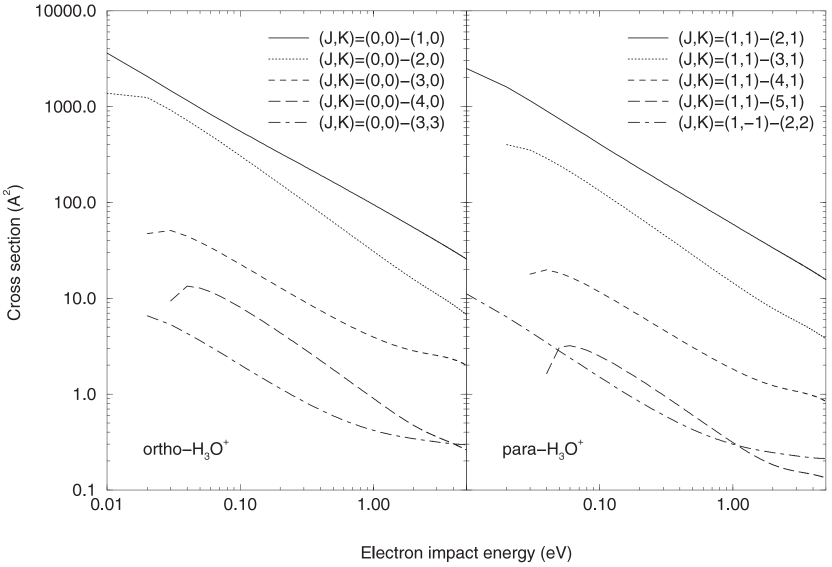

Figure 4. Rotational excitation cross sections for transitions with $\Delta J = 1, 2, 3, 4$ and $\Delta K = 0, 3$ in ortho- and para-H_3O^+ by electron impact.

a factor of about 3. This is a consequence of the large quadrupole of H_3O^+ (see table 1). Our calculations also suggest that $\Delta J = 1$ cross sections are larger than $\Delta J = 2$ cross sections by a factor of about 3.

Not surprisingly, due to the lower rotational excitation energies of H_3O^+ compared to H_3^+, threshold effects were found to be less pronounced. The threshold correction, however, remains important below about 0.1 eV. Figure 4 gives a comparison of $\Delta J = 1, 2, 3, 4$ and $\Delta K = 0, 3$ excitation cross sections for ortho- and para-H_3O^+. Unlike H_3^+/D_3^+, it can be noticed that $\Delta J = 3, 4$ cross sections are smaller than those for $\Delta J = 1, 2$ but by about one or two orders of magnitude 'only'. Finally, figure 5 gives results for D_3O^+. The small differences with H_3O^+ come from the slightly smaller dipole value (see table 1) and the lower rotational excitation energies.

In summary, propensity rules in H_3O^+/D_3O^+–electron collisions are found to be

$$\Delta J = \pm 1, \pm 2 \qquad \text{and} \qquad \Delta K = 0, \tag{27}$$

which can be compared to the radiative selection rules for dipole radiation of a nonplanar symmetric-top (Townes and Schawlow 1975):

$$\Delta J = 0, \pm 1, \qquad \Delta K = 0 \qquad \text{and} \qquad + \rightarrow -. \tag{28}$$

The last selection rule in (28) is needed to specify the inversion levels involved in a transition, which are neglected in this work.

5. Conclusions

In this paper, we have extended the theory presented in Rabadán *et al* (1998) for the rotational excitation of linear molecular ions to the case of symmetric-top molecular ions. Our approach, which includes short-range effects, has been applied to the calculation of rotational excitation cross sections for the astronomically important molecular ions H_3^+ and H_3O^+ and their

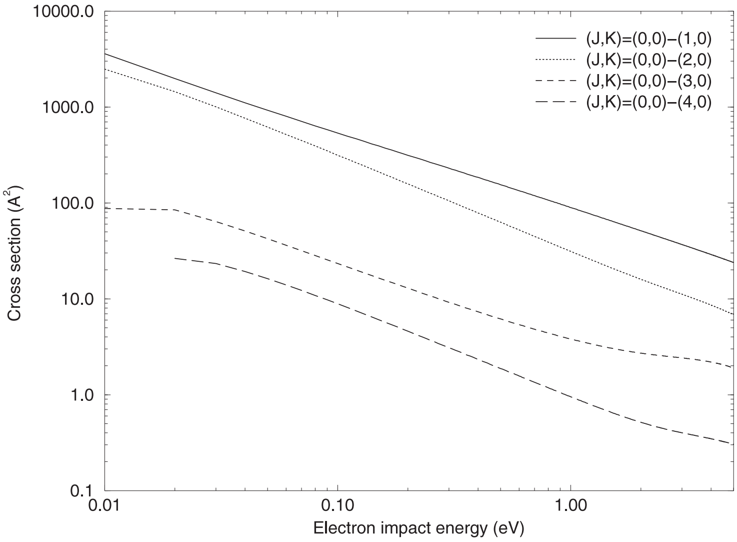

Figure 5. Rotational excitation cross sections for transitions with $\Delta J = 1, 2, 3, 4$ in D_3O^+ by electron impact.

deuterated forms D_3^+ and D_3O^+, at the equilibrium geometries of the ions. As in the linear case, the CB approximation is found to be unreliable in two major aspects: transitions with $\Delta J > 1$ are entirely dominated by short-range interactions and threshold effects are important for energies below a few tenths of electronvolt. Conversely, for the polar H_3O^+ and D_3O^+ ions, transitions with $\Delta J = 1$ and $K = K' = 0$ are dominated by long-range effects, as given by the CB theory. This feature is expected to depend on the magnitude of the dipole moment: for linear molecular ions, Faure and Tennyson (2001) have shown that the CB approximation is valid for $\Delta J = 1$ transitions when the ion has a dipole in excess of about 2D. The relatively small dipole moment of H_3O^+ (1.71D) means that long-range effects are insufficient to totally dominate $\Delta J = 1$ cross sections. In particular, short-range and long-range contributions are found to compete for transitions with $\Delta J = 1$ and $K \neq 0$.

Electron collisional selection rules are found to be consistent with the CB theory. In particular, dominant transitions are those for which $\Delta J \leqslant 2$ and $\Delta K = 0$. Moreover, in contrast to the linear case, transitions with $\Delta J = 1$ are allowed for non-polar ions such as H_3^+. As both H_3^+ and H_3O^+ have been detected in the diffuse interstellar medium where free electrons are important exciting species, rate coefficients for electron-impact rotational excitation are crucial for modelling the rotational spectra of these molecular ions. We are at present using the cross sections presented here to compute both rate coefficients and critical electron densities for astronomically important transitions of H_3^+ and H_3O^+, which includes extending the present work to higher rotational states (Faure and Tennyson 2002b). Finally, note that these rate coefficients might also help in the understanding of dissociative recombination measurements. In particular, current storage-ring experiments with rotationally hot H_3^+ ions appear to have a much larger rate than other experiments (Kokoouline *et al* 2001).

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