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R-matrix calculations for polyatomic molecular ions: electron scattering by H_3^+ and H_3O^+

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Abstract

Electron impact calculations are presented for H_3^+ and H_3O^+ at their equilibrium geometry using coupled states expansions. The *R*-matrix method is employed as it is very efficient for characterizing the many resonances found in electron–ion collisions. Positions, widths and symmetries are obtained for the lowest ten Feshbach resonances for each ion. These resonances are important for explaining features observed in dissociative recombination experiments at energies of 5–10 eV. In addition a broad shape resonance at about 4.5 eV is identified for H_3O^+. Electronic excitation cross sections are obtained in reasonable agreement with recent storage ring experiments.

1. Introduction

Collisions between electrons and molecules are of great interest, both from a purely fundamental viewpoint and in connection with many applications. For example, a detailed knowledge of these processes is crucial for the modelling of low-temperature plasmas such as those found in a number of astrophysical environments. Recent developments in both experiment and theory have emphasized the importance of polyatomic molecular ions in such environments. In particular, intensive work has been devoted to dissociative recombination (DR) which is the dominant destroyer of molecular ions in cool plasmas (e.g. Vejby-Christensen *et al* (1997), Kokooline *et al* (2001)). There has been considerable interest in the triatomic H_3^+ ion due to its importance in hydrogenic plasmas, particularly in modelling planetary atmospheres (Miller *et al* 2000) and the interstellar medium (Geballe 2000). The hydronium ion H_3O^+ is another key species which is believed to be the major source of water production in interstellar clouds (Phillips *et al* 1992). The discovery of both species in interstellar clouds (Wooten *et al* 1991, Geballe and Oka 1996) has provided direct observational evidence supporting the astronomical relevance of these molecular ions.

Until fairly recently, the main theoretical methods for treating electron collisions with non-linear molecules were based on the single-centre expansion approach, which has been successful for treating molecules with a central heavy atom, such as methane

(Gianturco *et al* 1995). A serious disadvantage of the single-centre method, however, is connected to its inability to treat electronic excited states of the target molecule. Procedures for computing electron impact electronic excitation necessarily rely on a multicentred representation of the target wavefunctions. The three major procedures currently in use are the complex Kohn variational method, the Schwinger variational method and the *R*-matrix method (see Huo and Gianturco (1995) for detailed descriptions). The *R*-matrix approach is particularly efficient as the most demanding part of any calculation, namely the description of the interaction inside the *R*-matrix sphere, need only be carried out once per symmetry and geometry, since it is independent of the scattering energy. This is a particular advantage for treating electron collisions with molecular ions as it allows the complicated resonance structures to be mapped out in detail at little extra computational cost.

In this paper, we are concerned with recent developments of the *R*-matrix method applied to electron impact excitation of H_3^+ and H_3O^+. The only available results for electron collisions with polyatomic molecular ions are those of Orel and co-workers who used the complex Kohn variational method to study the dissociative excitation (DE) and DR of H_3^+ (Orel 1992, Orel and Kulander 1993, Orel *et al* 1993). To our knowledge, there are no scattering calculations on any ion as complicated as H_3O^+. In the next section, the theoretical and computational treatment within the *R*-matrix approach is introduced. In section 3 cross sections and resonances are obtained and discussed. Conclusions are summarized in section 4.

2. Method

2.1. Polyatomic code

The application of the *R*-matrix method to electron collisions with diatomic molecular ions has been described in detail in previous papers (see, for example, Tennyson (1996), Rabadán and Tennyson (1997)). The *R*-matrix diatomic code is based on Slater-type orbitals (STOs) to represent the bound electronic orbitals and numerical orbitals to describe the continuum. The major change in the polyatomic code is the use of Gaussian-type orbitals (GTOs) to represent both target electrons and the continuum (Morgan *et al* 1998, Tennyson and Morgan 1999). The fundamental advantage of GTOs is that multicentred integrals can be evaluated in closed form. Following pioneering work by Nestmann and Peyerimhoff (1990), we have recently developed optimized GTO continuum basis sets to represent both Bessel and Coulomb functions within the finite region of a *R*-matrix sphere (Faure *et al* 2002). An interesting feature of this approach is that it is independent of the target molecule (except its charge) and only depends on the *R*-matrix radius and the range of scattering energies to be considered.

A related modification in the polyatomic code concerns the generation of the orthonormal set of molecular orbitals for the target-plus-electron system. The greater accuracy of integral evaluation for GTOs compared with STOs allows less stringent orthogonalization procedures. The present calculations are based on a mixture of Schmidt and symmetric (Löwden) orthogonalization procedures (Morgan *et al* 1997).

Finally, it should be noted that the polyatomic code uses D_{2h} or lower symmetry. Calculations for H_3^+ and H_3O^+ were therefore carried out in C_{2v} and C_s point groups, respectively.

2.2. H_3^+ target model

The equilibrium geometry of H_3^+ is an equilateral triangle with D_{3h} symmetry and a H–H bond distance of 1.65 a_0 (Herzberg 1987). The lowest four electronic states of H_3^+ are X^1A_1'

Table 1. Vertical energy excitations (in eV) for the H_3^+ target states. Also given are the results of: (a) Orel (1992) and (b) Talbi and Saxon (1988).

Electronic state		Vertical excitation		
D_{3h}	C_{2v}	This work	a	b
X^1A_1'	$^1A_1$	—	—	—
$^3E'$	$^3A_1 + {}^3B_2$	14.75	14.81	—
$^1E'$	$^1A_1 + {}^1B_2$	19.32	19.61	19.325
$^3A_2''$	$^3B_1$	20.78	20.73	—

(ground state), $^3E'$, $^1E'$ and $^3A_2''$. In C_{2v} symmetry, the doubly degenerate E′ states split into A_1 and B_2. Initial target wavefunctions were obtained from a full configuration interaction (CI) calculation in the large basis set of Orel (1992) of where the two lowest Gaussian exponents ($\alpha_s = 0.028$ and $\alpha_p = 0.04$) were removed. Indeed these small exponents were found to induce linear dependence with our continuum basis set. We followed Orel (1992) and extracted pseudo-natural orbitals (NOs) from the average of the density matrices for the six lowest states ($^1A_1$, $^3A_1$, $^3B_2$, $^1A_1$, $^1B_2$ and $^3B_1$). The final basis set consisted of the twelve NOs with the largest occupation, namely five a_1, three b_1, three b_2 orbitals and one a_2 orbital. Note that the target basis set of Orel (1992) consisted of four a_1, one b_1 and $2b_2$ NOs. The final target wavefunctions were obtained from a full CI calculation in our basis of NOs.

We obtained excitation energies in very good agreement with the results of Orel (1992) (see table 1), as expected from the similarity between our models. The transition dipole for the excitation $^1A_1' \rightarrow {}^1E'$ was found to be 1.0918 au, which is very close to the values of 1.0778 au and 1.0871 au computed by Orel (1992) and Talbi and Saxon (1988), respectively. The ground-state quadrupole was found to be 0.9104 au, which can be compared to the theoretical value of 0.9188 au calculated by Meyer *et al* (1986).

2.3. H_3O^+ target model

The equilibrium geometry of H_3O^+ is a triangular pyramid of C_{3v} symmetry. In the present work, we used the geometry of Miani *et al* (2001) which was optimized at the CCSD(T)/aug-cc-pVQZ level of theory. The bond length and angle values, $r(\mathrm{OH}) = 0.976\,56$ Å and $\mathrm{HOH} = 111.7464^\circ$, are in excellent agreement with the experimental values of $r(\mathrm{OH}) = 0.98$ Å and $\mathrm{HOH} = 111.3^\circ$ (Sears *et al* 1985). The lowest three electronic states of H_3O^+ are X^1A_1 (ground state), $^3A_1$ and $^1A_1$(II). Initial target wavefunctions were obtained from a complete-active-space (CAS) calculation augmented with single and double excitations in the basis set of Gorfinkiel *et al* (2002). This basis set was employed to study electron impact DE of the water molecule, which is isoelectronic to the hydronium ion. NOs were then extracted from the average of the density matrices for the two lowest states. The final basis set consisted of the eight NOs with the largest occupation, namely six a′ and two a″ orbitals. The final target wavefunctions were obtained from a CAS procedure in which the ten electrons of H_3O^+ were distributed according to the prescription $(1a'2a')^4\{3a'4a'5a'6a'1a''2a''\}^6$.

As shown in table 2, we obtained excitation energies in very good agreement with the accurate MRD-CI calculations of Roszak (1996). The ground-state dipole, computed at the molecular centre of mass, was found to be 0.6738 au, which can be compared to the value of 0.6459 au computed by Swanton *et al* (1986). The ground-state quadrupole was found to be 2.614 au.

Table 2. Vertical energy excitations (in eV) for the H_3O^+ target states. Also given are the results of: (a) Roszak (1996) and (b) Klein *et al* (1996).

Electronic state		Vertical excitation		
C_{3v}	C_s	This work	a	b
X^1A_1	X^1A'	—	—	—
$^3A_1$	$^3A'$	10.84	10.91	11.3
$^1A_1$(II)	$^1A'$(II)	11.77	11.62	11.9

2.4. Scattering model

At a fixed geometry, the wavefunction in the inner region defined by an R-matrix sphere of 10 a_0 has the form

$$\Psi_k = \sum_{ij} a_{ijk}\phi_i(x_1, \ldots, x_N)u_{ij}(x_{N+1}) + \sum_i b_{ik}\chi_i(x_1, \ldots, x_{N+1}), \tag{1}$$

where ϕ_i are target wavefunctions, $u_{ij}(x)$ are continuum orbitals and χ_i are two-centre quadratically integrable (L^2) functions constructed from the target occupied and virtual molecular orbitals. These last functions are important both for relaxing the enforced orthogonality between the target and continuum orbitals, and for representing short-range polarization effects not included in the truncated partial-wave expansion. The present calculations and most recent R-matrix calculations use natural orbitals (NOs) for the target molecular orbitals; orbitals from a multiconfiguration self-consistent-field (MCSCF) calculation could provide an alternative, possibly superior, starting point.

The H_3^+ and H_3O^+ scattering models include four and three target states, respectively. The continuum orbitals were represented using the GTO basis set given by Faure *et al* (2002) which includes all angular momenta up to $l = 4$ and is optimized to span energies below 5 Ryd. The present calculations include all continuum orbitals with $l \leqslant 4$. In the case of H_3^+, Orel (1992) investigated the convergence of the cross sections with the number of partial waves l and found that the T-matrix elements for $l > 4$, estimated from the Coulomb–Born approximation, are negligible.

3. Results and discussion

3.1. Electron–H_3^+ collisions

Earlier calculations on the electron impact DE of H_3^+ were performed by Orel (1992) for energies up to 21 eV, the threshold for excitation of the third excited electronic state. These calculations were carried out using the complex Kohn variational method at the equilibrium geometry of the ion. The fixed-nuclei excitation cross sections were found to be dominated by a series of sharp resonances, in apparent agreement with the experimental results of Yousif *et al* (1991). However, the final cross sections, averaged over the symmetric stretch vibrational motion of the ground state, were found to be structureless. In fact, recent heavy-ion storage ring measurements by Jensen *et al* (2001) did not reproduce the features observed by Yousif *et al* (1991) and a qualitative agreement with the final results of Orel (1992) was observed.

In the present study, we wished to make a detailed comparison with the work of Orel (1992). We therefore computed fixed-nuclei cross sections for excitation into the two lowest dissociative states of H_3^+, namely $^3E'$ and $^1E'$. Results are presented in figure 1. As observed by Orel (1992), excitation cross sections are dominated by a series of Feshbach resonances superimposed on a flat background whose magnitude is around 0.5 Å^2 in the energy ranges

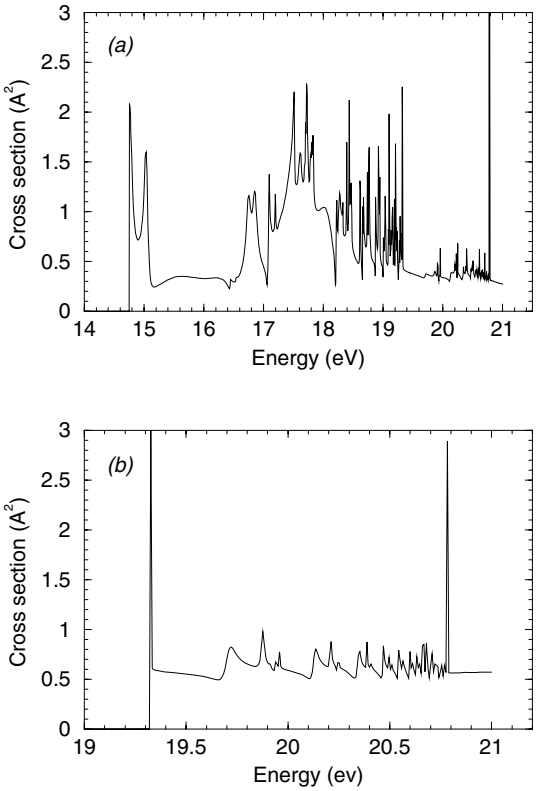

Figure 1. Total fixed-nuclei cross sections for excitations, (*a*) $X^1A_1 \rightarrow {}^3E'$ and (*b*) $X^1A_1 \rightarrow {}^1E'$ at the equilibrium geometry of H_3^+.

considered. This value is in good agreement with the recent DE measurements by Jensen *et al* (2001). An important difference with the results of Orel (1992), however, comes from the resolution of the *R*-matrix calculations: as explained in section 1, a fundamental advantage of the *R*-matrix approach is that the description of the system inside the *R*-matrix sphere is independent of the scattering energy. Very fine energy grids can hence be employed without difficulty. As shown in figure 1, the resonance peaks are perfectly defined, in marked contrast to the complex Kohn variational results. Orel (1992) chose to remove their structure by averaging over it. Since the better delineation of the resonances in our calculation leads to a clearly defined background contribution, we have not taken this path. However, it is likely that the inclusion of nuclear motion in the calculation would lead to considerable smoothing of the Feshbach resonance structures.

Following the work of Orel (1992), Orel and Kulander (1993) investigated the electron impact DR of H_3^+ in order to reproduce a broad peak observed experimentally near 9.5 eV (Larsson *et al* 1993, Jensen *et al* 2001). They showed that this peak is due to four H_3 resonance (autoionizing) states whose configuration in D_{3h} symmetry is $1a_1'1e'^2$ (Orel and Kulander 1993). In C_{2v} notation, these states become $^2A_1$ ($1a_1 2a_1^2$, $1a_1 2b_2^2$) and $^2B_2$ ($1a_1\{2a_1 1b_2\}^1$, $1a_1\{2a_1 1b_2\}^3$), where the superscripts 1 and 3 represent the spin coupling between $2a_1$ and $1b_2$ electrons. At the equilibrium geometry of the ion, the lowest $^2A_1$ and $^2B_2$ states correspond to the degenerate $^2E'$ components. For this geometry, the positions and widths of the ten lowest resonances were obtained by fitting the eigenphase sum to Breit–Wigner profiles (Tennyson

Table 3. Symmetry, resonance position (E_r in eV) and resonance width (Γ_r in eV) at the equilibrium geometry of H_3^+. Powers of ten are given in parentheses. Also given are the results of Orel and Kulander (1993) (the position of the third resonance taken from figure 2).

Symmetry		This work		Orel and Kulander (1993)	
D_{3h}	C_{2v}	E_r	Γ_r	E_r	Γ_r
$^2E'$	$^2A_1 + {}^2B_2$	9.12	6.4(−1)	9.1	6.4(−1)
$^2A_1'$	$^2A_1$	10.14	1.9(−1)	10.3	1.8(−1)
$^2A_2'$	$^2B_2$	11.11	8.6(−3)	≈11.2	—
$^2A_1''$	$^2A_2$	11.21	8.9(−2)	—	—
$^2A_2''$	$^2B_1$	11.53	1.1(−1)	—	—
$^2A_1'$	$^2A_1$	12.72	5.0(−2)	—	—
$^2A_1'$	$^2A_1$	12.84	1.2(−1)	—	—
$^2A_2'$	$^2B_2$	13.01	8.4(−2)	—	—
$^2A_1'$	$^2A_1$	13.02	2.5(−2)	—	—
$^2E'$	$^2A_1 + {}^2B_2$	13.12	1.2(−2)	—	—

Table 4. Symmetry, resonance position (E_r in eV) and resonance width (Γ_r in eV) at the equilibrium geometry of H_3O^+. Powers of ten are given in parentheses.

Symmetry		This work	
C_{3v}	C_s	E_r	Γ_r
$^2A_1$	$^2A'$	5.12	1.2(−2)
^2E	$^2A' + {}^2A''$	7.28	3.3(−2)
$^2A_1$	$^2A'$	8.34	2.3(−2)
^2E	$^2A' + {}^2A'$	8.55	7.0(−3)
$^2A_1$	$^2A'$	8.86	2.4(−3)
^2E	$^2A' + {}^2A''$	9.12	1.8(−3)
^2E	$^2A' + {}^2A''$	9.33	1.4(−3)
^2E	$^2A' + {}^2A''$	9.56	4.4(−4)
$^2A_1$	$^2A'$	9.63	8.6(−3)
^2E	$^2A' + {}^2A''$	9.70	3.6(−3)

and Noble 1984). As shown in table 3, our results are in very good agreement with the available results of Orel and Kulander (1993) and therefore support their interpretation of the DR experiments in the 9.5 eV region. We present parameters for eight higher resonances and would have little difficulty extracting parameters for further resonances from our calculations should they be of interest.

3.2. Electron–H_3O^+ collisions

Electron–H_3O^+ scattering calculations were performed for energies up to 12 eV, the threshold for excitation of the second excited electronic states. As can be observed from the eigenphase sums plotted in figure 2, a low-lying broad shape resonance with ^2E symmetry appears around 4–5 eV, followed above 5 eV by very narrow resonances with $^2A_1$ and ^2E symmetries. The ten lowest Feshbach resonances were fitted to Breit–Wigner profiles to obtain resonance positions and widths which are listed in table 4.

There are two notable differences between the H_3O^+ resonances and those calculated for H_3^+. The H_3O^+ resonances start at an energy 4 eV below those for H_3^+ and are significantly—approximately a factor of five—narrower. The lowering of energy is almost completely accounted for by the lower threshold for electronic excitation in H_3O^+ at 10.84 eV compared

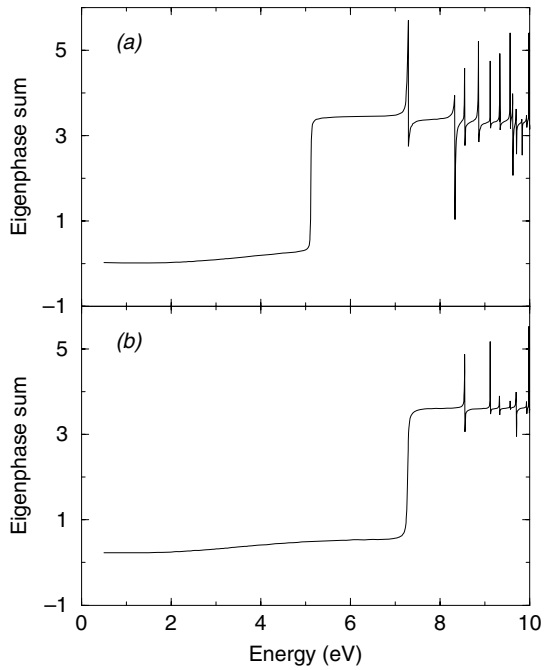

Figure 2. Eigenphase sums for electron–H_3O^+ collisions at the equilibrium geometry of the ion: (*a*) $^2A'$ symmetry, (*b*) $^2A''$ symmetry.

to 14.75 eV for H_3^+ suggesting that the quantum defects for the two systems are actually rather similar. The narrower resonances may also, at least in part, be a consequence of this reduced gap between the ground and first excited states in H_3O^+.

The DR and DE cross sections for H_3O^+ have been recently measured in the heavy-ion storage ring ASTRID (Vejby-Christensen *et al* 1997, Jensen *et al* 2000). As in the case of H_3^+, the DR cross section was found to display a strong and broad peak around 10 eV. This structure was attributed by Vejby-Christensen *et al* (1997) to capture into Rydberg states of H_3O pertaining to excited states of the molecular ion. These states lie around 11–17 eV above the ground state (see table 2 and Roszak (1996)). Given that we find that the resonance structure in H_3O^+ starts at 5 eV rather than the 9 eV found in H_3^+, one might have anticipated that the broad DR peak would also appear at lower energy. This is not so, but the DR cross section of H_3O^+ does show a small enhancement in the 5 eV region, a feature not displayed by the H_3^+ DR cross section. It is possible that this feature is caused by the lowest resonances and is small because they are narrow, but confirmation of this must await calculations which explicitly include dissociation.

Fixed-nuclei cross sections for excitation into the lowest excited state of H_3O^+ are presented in figure 3. As in the case of H_3^+, the cross section is dominated by a series of Feshbach resonances superimposed on a flat background whose magnitude is around 0.2 $Å^2$ in the energy range considered. This value is in good agreement with the DE measurements by Vejby-Christensen *et al* (1997). Vejby-Christensen *et al* (1997) also observe DE at energies below the vertical excitation threshold to electronic excitation. They attribute this to the presence of autoionizing resonances which can decay to electronically excited states. This mechanism is possible, but we note that DE via electronically excited states can occur at energies significantly below the vertical excitation threshold without the need to invoke resonances (Stibbe and Tennyson 1998, Trevisan and Tennyson 2001). This process involves

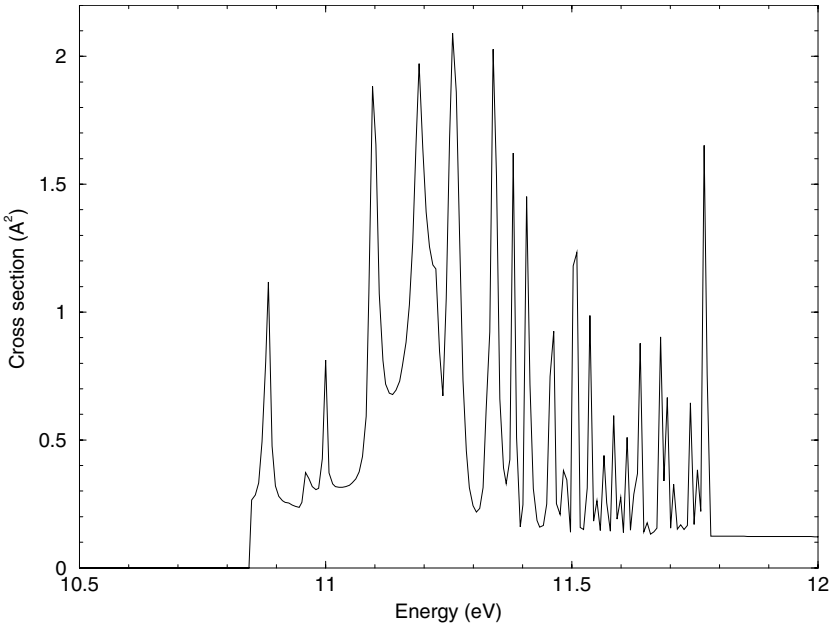

Figure 3. Total fixed-nuclei cross sections for the excitation $X^1A_1 \rightarrow {}^3A_1$ at the equilibrium geometry of H_3O^+.

excitation of the molecule in the region of the outer turning point of the vibrational state in question and can result in the lowering of the effective DE threshold for hydrogenic systems by about 3 eV, a figure consistent with the experimental observations.

Finally, it should be noted that MRD-CI calculations by Di Giacomo *et al* (1994) have shown that different structural geometries exist for the ground and for the excited electronic states of H_3O^+. In particular, some of the excited states were found to show planar geometries or small barriers between planar and pyramidal geometries. Structural effects might also play a role in the excitation process and detailed investigations will be necessary for a quantitative interpretation of the DR and DE measurements.

4. Conclusions

Electron impact calculations are presented for collisions with H_3^+ and H_3O^+. These are the first *R*-matrix calculations on scattering from polyatomic molecular ions and the first ever close-coupling calculations on a molecular ion as complicated as H_3O^+. The *R*-matrix method is well suited to studying such systems, as parameters for many resonances can be determined precisely at little computational cost. Furthermore, even the excited states of molecular ions are fairly compact, meaning that diffuse states, which can cause problems in *R*-matrix studies of electron impact electronic excitation of neutral molecules, are avoided.

Our electron scattering calculations for H_3^+ largely support the conclusions of Orel and co-workers (Orel 1992, Orel and Kulander 1993, Orel *et al* 1993) concerning the role of resonances in the DR of H_3^+ at energies above 9 eV. Our DE cross sections for this ion are in agreement with recent experimental determinations (Jensen *et al* 2001). For H_3O^+ we find that the resonances are both lower in energy and significantly narrower than those calculated for H_3^+. It is possible that these lower-lying narrow resonances explain the small feature in the experiments at about 5 eV but confirmation of this awaits a more extensive study which explicitly includes dissociative channels. Again our DE cross sections are in reasonable agreement with the

experimental determinations (Vejby-Christensen *et al* 1997). However, we suggest that it is not necessary to invoke a resonance mechanism to explain the observation that the effective threshold for DE lies below the threshold to vertical excitation.

Finally we note that both H_3^+ and H_3O^+ are astronomically important ions. Since electron impact rotational excitation is a key process for determining rotational populations and hence spectra of molecular ions in a variety of astrophysical locations, we are at present using the wavefunctions presented here to calculate rotational excitation cross sections (Faure and Tennyson 2002).

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