The role of the Jahn-Teller coupling in dissociative recombination of H$_3$O$^+$ and H$_3^+$ ions

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Abstract. We discuss the importance of the non Born-Oppenheimer Jahn-Teller coupling in the dissociative recombination of H$_3$O$^+$ and H$_3^+$ ions with low energy electrons. The coupling is known to be important for dissociative recombination of H$_3^+$, for which detailed and simplified theoretical models have been previously developed. In this study we discuss how the detailed theoretical model reproduces individual resonances in the experimental spectrum of H$_3^+$. We present a simplified theoretical model of the dissociative recombination of H$_3$O$^+$: Similarly to H$_3^+$, we consider the Jahn-Teller coupling as a key factor responsible for the capture of the electron into a Rydberg state associated with excited vibrational levels of the ion. We use a simplified Jahn-Teller model for highly symmetrical ions (not only for H$_3$O$^+$ and H$_3^+$) and adopt the normal mode approximation for the vibrational states of H$_3$O$^+$. Using the multi-channel quantum defect formalism and accurate ab initio calculations, we derive the cross sections for electron capture by the ion that is initially in the ground vibrational level. In our approximation, once the electron is captured by the ion, the autoionization probability is neglected compared to the predissociation probability. This allows us to evaluate the cross section for the dissociative recombination of H$_3$O$^+$ using just a few parameters obtained from ab initio calculation. The total cross section obtained is in good agreement with data from storage ring experiments.

1. Introduction

Reactive collisions of ionized species play an important role in the overall chemical evolution of the cold interstellar medium (ISM). One of the important charged species in the ISM, the hydronium ion H$_3$O$^+$ is formed by a chain of chemical reactions, starting with H$_3^+$ [1]

\[
\begin{align*}
O + H_3^+ &\rightarrow OH^+ + H_2 \\
OH^+ + H_2 &\rightarrow H_2O^+ + H \\
H_2O^+ + H_2 &\rightarrow H_3O^+ + H. 
\end{align*}
\]

The produced H$_3$O$^+$ molecular ion has a closed electronic shell and does not react with atomic or molecular hydrogen, but can be depleted by the dissociative recombination (DR) with electrons, which are also abundant in diffuse interstellar clouds. The ion was also observed in tails of comets. For example, observations by the spacecraft Giotto [2] reported the hydronium ions as
the most abundant ionic species in the comet Halley. It was suggested that in the inner coma of the comet, DR is the major mechanism of H$_3$O$^+$ destruction.

One of the products of dissociative recombination of H$_3$O$^+$ with electrons is water: In several experimental studies [1, 3, 4] it was demonstrated that H$_2$O is produced by the recombination of H$_3$O$^+$ with the branching ratio for the water pathway of about 18-33%: 33±8% in the older ASTRID experiment [1], 25±1% in the newer ASTRID experiment [4], and 18±5% in CRYRING experiment [3]. The slightly different results for the branching ratio in three experiments [1, 3, 4] could possibly be explained by a different population of excited rovibrational states of H$_3$O$^+$ in the storage rings. The water channel in DR of H$_3$O$^+$ is the reason that DR is believed to be the major source of water production in interstellar clouds [5, 6]. Therefore, understanding main mechanisms in DR of H$_3$O$^+$ is important for a correct evaluation of water abundance in the ISM. Finally, the dissociative recombination of H$_3$O$^+$ ions is thought to play an important role in the chemistry of the lean methane-oxygen flames [7], and in the electrical control of the instability of propane-air flames [8].

A theoretical description of dissociative recombination in H$_3$O$^+$ (and other polyatomic ions, in general) is complicated due to the large number of vibrational degrees of freedom and many electronic states of the neutral molecule H$_2$O that have to be included into the complete theoretical model. Theoretical methods for DR in triatomic molecular ions, H$_3^+$ [9, 10, 11], HCO$^+$ [12, 13], and LiH$_2^+$ [14] have been developed during the last decade, showing relatively good agreement with the experimental data. The structure of the H$_3^+$, HCO$^+$, and LiH$_2^+$ ions are similar in the way they recombine with electrons: They all have a closed electronic shell, so their dissociative resonant states lie above their ground electronic potentials such that the potential energy surfaces of the resonant electronic states do not cross the ionic potential surface in the Franck-Condon region. This makes direct DR impossible for such molecular ions. The dominant DR mechanism for these ions proceeds therefore through capturing an electron into a Rydberg state associated with a vibrationally excited ionic core.

A completely quantum-mechanical treatment that has been employed previously for DR in H$_3^+$ [10, 11, 15] requires the knowledge of the full electronic potential surfaces in a large configuration space, for both the ion and the neutral state. If used for H$_3$O$^+$, the treatment would require accurate ab initio calculations performed for the ground electronic state of the ion and for several excited electronic states of the neutral molecule H$_2$O for all vibrational degrees of freedom. Once the potential energy surfaces are available, one would have to do the vibrational dynamics in several dimensions, ideally along all six vibrational coordinates. Thus, the full completely quantum-mechanical treatment for indirect DR of polyatomic ions requires a massive computational effort in order to compute the DR cross section.

It is desirable to produce a simpler model, which takes into account only the key factors in the DR mechanism with the goal to give a correct estimate for the DR cross section. An important step forward for such simple DR theory for polyatomic ions was made in the previous study of DR in HCO$^+$ [12, 13] (both studies were based on the ideas suggested in Ref. [9]), for which the dissociative channels are not taken into account explicitly, and autoionization is neglected. Competition between autoionization and dissociation was discussed qualitatively in [12], where it was shown that autoionization should only slightly decrease the probability for dissociation after the electron is captured into a predissociated Rydberg state. On the other hand, that later treatment used ab initio calculations on the full configuration space, including different electronic couplings. Moreover, adiabatic vibrational states depending parametrically on the dissociative coordinates were computed, the procedure of channel elimination was performed and energies and widths of resonances were obtained. Finally an averaged cross section for electronic capture in any ionic vibrational state was computed. That simplified treatment was still quite complicated.

Jungen and Pratt [16, 17] made another step further in simplifying the treatments for both
H$_3^+$ [17] and HCO$^+$ [16], by considering solely the capture into the first excited doubly degenerate vibrational normal mode (harmonic approximation). This later approximation simplifies greatly the model and their results are in very good agreement with the more detailed approaches. Our study of DR of H$_3$O$^+$ will rely on the same basic principles discussed in Refs. [9, 12, 13, 16, 17], except that the H$_3$O$^+$ ion has two Jahn-Teller active normal modes. Before introducing the approach in detail, we start with a brief description of the H$_3$O$^+$ vibrational modes around the equilibrium position.

The simplified model discussed below provides the overall DR cross-section for H$_3$O$^+$. Resonances that would be present in high resolution experimental data can not be reproduced by this model. No high-resolution experimental data is available for DR of H$_3$O$^+$, but for H$_3^+$ such a high-resolution experimental DR spectrum is available. Therefore, the detailed theoretical model [10, 15, 11] developed previously can be used to check how theory can reproduce details in the DR spectrum. Another part of this study is devoted to a comparison of resonance features in the theoretical and experimental DR spectra.

This paper is organized in the following way. In the next section, we describe the vibrational normal modes of H$_3$O$^+$ and the Jahn-Teller interaction that couples the vibrational motion of the ion with the motion of the incident electron. In Section 3, we introduce the simplified theoretical model for calculation of the DR cross-section in closed-shell molecular ions of the $C_{3v}$ symmetry. In Section 4, we present new results on DR of H$_3^+$. Namely, we compare the resonances obtained in the complete theoretical model with resonances observed in the high-resolution DR experiment with H$_3^+$. In Section 5 we discuss obtained results and possible improvements of the theoretical treatment.

2. Vibrational modes of H$_3$O$^+$ and the Jahn-Teller model

In its equilibrium position, the H$_3$O$^+$ ion has a pyramidal shape, described by the $C_{3v}$ symmetry point group. However, the barrier for tunneling for the oxygen atom through the plane of the three hydrogen nuclei is quite weak, therefore $D_{3h}$ symmetry point group can be used for the qualitative analysis of vibrational modes. (For the $D_{3h}$ group, the expressions for vibrational normal modes do not depend on actual force constants of H$_3$O$^+$; the $C_{3v}$ normal modes do depend on the force constants). In this picture, the oxygen atom is situated in the middle of the equilateral triangle formed by the three hydrogen nuclei, at a distance $R_{OH}$ = 1.039Å. The normal modes in the $D_{3h}$ configuration are given in Ref. [18]. For our purposes we only need the expressions for the two doubly-degenerate modes $E'$: $Q_2$ and $Q_4$

\[
Q_{2x} = \sqrt{\frac{3}{12}}(2x_1 - x_2 - x_3 - \sqrt{3}y_2 + \sqrt{3}y_3),
\]
\[
Q_{2y} = \sqrt{\frac{3}{12}}(2y_1 - y_2 - y_3 + \sqrt{3}x_2 - \sqrt{3}x_3),
\]
\[
Q_{4x} = \sqrt{\frac{3m}{M + 3m}}x_o - \sqrt{\frac{M}{3(M + 3m)}}(x_1 + x_2 + x_3),
\]
\[
Q_{4y} = \sqrt{\frac{3m}{M + 3m}}y_o - \sqrt{\frac{M}{3(M + 3m)}}(y_1 + y_2 + y_3).
\]

In the above expressions, we used the Cartesian coordinates ($x_i$, $y_i$, $z_i$) of the three hydrogen nuclei $i$ = 1, 2, 3 with mass $m$, and the oxygen nucleus with coordinates ($x_o$, $y_o$, $z_o$) and mass $M$ ($z$-components do not contribute into $Q_2$ and $Q_4$). The $Q_2$ degenerate mode is similar to the asymmetric stretching of the H$_3$ triangle in H$_3^+$ with the fixed oxygen atom. The second degenerate normal mode $Q_4$ represents a motion of the oxygen in the $x$-$y$ plane.

In the study, we consider the H$_3$O$^+$ ion vibrating near its equilibrium configuration, therefore we need the normal coordinates at that specific configuration in the $C_{3v}$ point group symmetry.
Therefore, the character of the normal modes of the vibrational Hamiltonian by Bowman et al. to the energies for the lowest vibrational states obtained by a direct diagonalization of the normal modes obtained numerically by the standard normal modes analysis made using the MOLPRO package. The expressions above are provided just to give an idea about the character of the modes. For the simplicity of the discussion, we will use the same notations for the normal modes at the \( C_{3v} \) equilibrium configuration.

The frequencies of the four \( 2A_1 \oplus 2E \) normal modes of \( \text{H}_3\text{O}^+ \) are given in Table 1. The frequencies have been obtained from \textit{ab initio} calculations using the MOLPRO package [19] and are compared with accurate (beyond the normal mode approximation) calculations by Bowman et al. [20], who used the MULTIMODE code. The results agree well, with relative error less than 10%. In order of increasing frequencies, the first symmetric normal mode \( Q_1 \) is the so-called umbrella mode, the second doubly degenerate mode \( Q_2 = (Q_{2x}, Q_{2y}) \) represents the deformation, the third mode \( Q_3 \) represents the symmetric O-H stretching and finally, the fourth degenerate mode \( Q_4 = (Q_{4x}, Q_{4y}) \) is the antisymmetric O-H stretching.

| Representation | Present calculations | Bowman et al. [20] |
|----------------|---------------------|--------------------|
| \( \omega_1 \) | \( A_1 \) | 900 | 972 |
| \( \omega_2 \) | \( E \) | 1704 | 1639 |
| \( \omega_3 \) | \( A_1 \) | 3609 | 3405 |
| \( \omega_4 \) | \( E \) | 3705 | 3711 |

\textbf{Table 1.} Frequencies (in cm\(^{-1}\)) of \( \text{H}_3\text{O}^+ \) normal modes obtained in the present study compared to the energies for the lowest vibrational states obtained by a direct diagonalization of the vibrational Hamiltonian by Bowman et al. [20].

We now introduce the vibronic Jahn-Teller coupling in the \( \text{H}_3\text{O} \) radical. The \( \text{H}_3\text{O} \) electronic Rydberg states with non-zero projection \( \Lambda \) (more precisely, with \( \Lambda \neq 3k \) where \( k \) is an integer number) of the electronic angular momentum on the symmetry axis of the molecule are doubly degenerate at the equilibrium position of the ion (and any equilateral configuration of the three hydrogen nuclei). Such states with \( \Lambda \neq 0 \text{mod}3 \) belong to the \( E \) irreducible representation of the \( C_{3v} \) group. For any geometry different from equilateral, energies of the two electronic states split apart. The energy splitting between the two electronic states is linear with respect to \( Q_{2x}, Q_{2y}, Q_{4x}, \) and \( Q_{4y} \) [21]. Because the splitting between the two states is small or zero near the equilateral geometry, the non-Born-Oppenheimer interaction, Jahn-Teller coupling, between the vibrational and electronic motions is large or infinite. This coupling is responsible for the large probability of capturing the incident electron into a Rydberg state associated with an excited vibrational level. We include the Jahn-Teller coupling into the DR treatment using the parametrized Hamiltonian describing the coupled states suggested by Moffit and Liehr [22] and Longuet-Higgins [21]. The parametrized Hamiltonian is briefly discussed below.

We collectively denote all the nuclear and electronic coordinates by \( Q \) and \( q \) respectively and consider two degenerate electronic states \( \phi_+(q) \) and \( \phi_-(q) \) corresponding to two projections \( \Lambda = \pm 1 \) of the electronic angular momentum on the molecular symmetry axis. We also need two vibrational functions \( \chi^+(Q) \) and \( \chi^-(Q) \) corresponding to the vibrational motion along potential surfaces of the two electronic states. A solution of the vibronic equation is sought in the form

\[
\Psi = \chi^+_\lambda(Q)\phi_+(q) + \chi^-_\lambda(Q)\phi_-(q) .
\]
We consider only small displacements of the nuclei from the equilibrium position of the ion and assume at this point that the electronic states do not depend on small nuclear displacements. It is also assumed that there are no other electronic states, which are accidentally close in energy to the degenerate pair of states. This is needed to avoid any accidental perturbation of the two-state parametrized Hamiltonian. The electronic states in Eq. (3) transform according to

\[ C_3 \phi_\pm = \exp(\mp 2i\pi/3)\phi_\pm, \]
\[ \sigma_v \phi_\pm = \phi_\mp, \]

where \( C_3 \) is the rotation by \( 2\pi/3 \) around the molecular symmetry axis and \( \sigma_v \) the reflection through a vertical plane. Instead of the real normal coordinates \( Q_{2x}, Q_{2y} \) and \( Q_{4x}, Q_{4y} \), we will use the complex normal modes \( Q_1^+ \) and \( Q_1^- \) (\( Q_1^+ = Q_{1x} \pm iQ_{1y} \)) and polar normal modes \( \rho_1 \) and \( \varphi_1 \) \( (Q_{1x} = \rho_1 \cos \varphi_1, Q_{1y} = \rho_1 \sin \varphi_1) \) with \( i = 2, 4 \). The complex coordinates transform in the same way as the electronic functions in Eq. (4).

We need to solve the equation \( \hat{H}_{JT} \Psi = E \Psi \), with \( \hat{H}_{JT} = \hat{T}_{vib} + \hat{H}_{elec} \), where the vibrational \( \hat{T}_{vib} \) and electronic \( \hat{H}_{elec} \) parts of the Hamiltonian depend on the normal coordinates. We obtain the following form for the matrix \( \hat{H}_{elec} \) in the basis of the two electronic states

\[ \hat{H}_{elec} = W_0 \hat{I} + \hat{H}_{elec,Q_2} + \hat{H}_{elec,Q_4} \]  

with

\[ \hat{H}_{elec,Q_2} = \begin{pmatrix} \frac{1}{2}k_2\rho_2^2 & f_2\rho_2e^{-i\varphi_2} + g_2\rho_2^2e^{-2i\varphi_2} \\ f_2\rho_2e^{i\varphi_2} + g_2\rho_2^2e^{2i\varphi_2} & \frac{1}{2}k_2\rho_2^2 \end{pmatrix} \]

and with the similar expression for \( \hat{H}_{elec,Q_4} \) depending on \( \rho_4 \) and \( \varphi_4 \). In Eq. (6), \( \hat{I} \) is the \( 2 \times 2 \) identity matrix and \( W_0 \) is the energy of \( \text{H}_3\text{O} \) at the equilateral geometry. The one-dimensional normal modes \( Q_1 \) and \( Q_3 \) do not participate in the coupling between the degenerate electronic states. Therefore, the solutions of the two-state vibronic Hamiltonian can be written

\[ \Psi = \eta_1(Q_1)\eta_3(Q_3)(\eta^+(Q_2, Q_4)\phi_+(q) + \eta^-(Q_2, Q_4)\phi_-(q)). \]

If we set the coordinate \( \rho_1 = 0 \) (thus \( \hat{H}_{elec,Q_4} = 0 \)) but not \( \rho_2 \) and diagonalize the electronic Hamiltonian in Eq.(6) we obtain the electronic Born-Oppenheimer surfaces \( U_{a,b}(\rho_2, \varphi_2) \)

\[ U_{a,b}(\rho_2, \varphi_2) = W_0 + \frac{1}{2}k_2\rho_2^2 \pm \left[ f_2\rho_2 + \frac{1}{2}g_2\rho_2^2\cos(3\varphi_2) \right], \]

and the Born-Oppenheimer eigenfunctions

\[ \phi_a = \frac{1}{\sqrt{2}}[\phi_+e^{-i\varphi_2/2} + \phi_-e^{i\varphi_2/2}], \]
\[ \phi_b = \frac{1}{\sqrt{2}}[-i\phi_+e^{-i\varphi_2/2} + i\phi_-e^{i\varphi_2/2}]. \]

In a similar way, the Born-Oppenheimer energies and eigenstates can be obtained for the \( Q_4 \) degenerate mode.

If plotted as functions of two coordinates \( Q_{2x} \) and \( Q_{2y} \), the potential surfaces in Eq. (9) exhibit a conical intersection near the equilateral geometry \( \rho_2 = 0 \) with the minimum of energy situated at \( f_2^2/2k_2 \) below the energy of the intersection. The electronic potential surfaces obtained by \textit{ab initio} calculations exhibit the same behavior. This allows fitting the \textit{ab initio} data to the analytical behavior of Eq. (9). Therefore, the parameters \( k_i, f_i, g_i \), and \( W_0 \) of the Jahn-Teller coupling can be obtained from the \textit{ab initio} energies of excited electronic states of \( \text{H}_3\text{O} \).
Figure 1. (Color online) Effective quantum numbers of several excited electronic states of $\text{H}_3\text{O}$ as a function of the $Q_{4z}$ coordinate. The $Q_{4z}$ coordinate is plotted in units $\text{Å u}^{1/2}$, where u is the atomic mass unit, dalton. The figure gives also by red arrows effective quantum numbers obtained in Ref. [23] for equilibrium geometry of $\text{H}_3\text{O}^+$. A detailed comparison of the effective quantum numbers at the equilibrium is provided in Table 2. For higher states, the quantum defect $n - \nu$ is nearly independent on $n$. The independence of the quantum defect on $n$ is a confirmation of the accuracy of the present \textit{ab initio} calculation.

Table 2. Effective quantum numbers of several excited electronic states of $\text{H}_3\text{O}$ at the equilibrium of the ion obtained in Ref. [23] and this study.

| Electronic state | Ref. [23] | This study |
|-----------------|-----------|------------|
| $3sa_1$         | 1.616     | 1.432      |
| $3pe$           | 2.096     | 2.013      |
| $3pa_1$         | 2.306     | 2.274      |
| $4sa_1$         | 2.587     | 2.598      |
| $3de$           | 2.714     | 2.736      |
| $3de$           | 2.974     | 3.015      |
| $3da_1$         | 3.008     | 3.055      |
| $4pe$           | 3.128     | 3.113      |
| $4pa_1$         | 3.314     | 3.310      |
| $5sa_1$         | 3.562     | 3.604      |
| $4de$           | 3.682     | 3.706      |
| $4de$           | 3.980     | 4.016      |
| $4da_1$         | 4.008     | 4.016      |
| $5pe$           | 4.134     | 4.052      |
| $5pa_1$         | 4.313     | 4.143      |
| $6sa_1$         | 4.542     | 4.360      |

We use the quantum defect theory to calculate the DR cross-section. In this approach it is convenient to represent the \textit{ab initio} potential energy surfaces in the form of effective quantum numbers.
numbers $\nu(Q)$ or quantum defects $\mu(Q)$ that are related to the potential energies $U(Q)$ according to (in atomic units - a.u.)

$$U(Q) = U^+(Q) - \frac{1}{2[\nu(Q)]^2} = U^+(Q) - \frac{1}{2[n - \mu(Q)]^2},$$

(12)

where $U^+(Q)$ denotes the ionic potential and $n$ is the principal quantum number associated with the corresponding electronic state (with energy $U(Q)$). For excited electronic states the quantum defects $\mu(Q)$ are only weakly-dependent on $n$.

Figure 1 shows the $Q_{i\nu}$-dependence of effective quantum numbers obtained from \textit{ab initio} potential energy surfaces calculated in this study. The results at the equilibrium geometry of H$_3$O$^+$ are compared with \textit{ab initio} data from Ref. [23]. According to quantum defect theory, the quantum defects and the Jahn-Teller splitting for the excited electronic states should not depend on the principal quantum number. The results shown in the figure are in agreement with that. Because during the DR process, the electron is initially captured into a highly excited Rydberg state, we need to use the Jahn-Teller parameters obtained from the excited Rydberg states.

3. Simplified model for electronic capture and calculated cross section

We assume that the ion is initially in the ground vibrational level $v$ and we neglect the rotation of the ion. The energy of the ground vibrational level is chosen to be the origin of the total energy. The incident electron with kinetic energy $E_{el}$ arrives with the projection $\Lambda$ on the molecular symmetry. Using the approximation suggested in Ref. [12], we calculate the cross section $\langle \sigma \rangle$ for the electron capture, where $\langle \sigma \rangle$ means that we evaluate the cross section averaged over autoionization Rydberg resonances associated with the vibrational state $v'$. For this purpose, we use the element $\langle v', \Lambda' | \hat{S} | v, \Lambda \rangle$ of scattering matrix describing the $|v, \Lambda \rangle \rightarrow |v', \Lambda' \rangle$ scattering process

$$\langle \sigma \rangle = \frac{\pi}{2E_{el}} \left| \langle v', \Lambda' | \hat{S} | v, \Lambda \rangle \right|^2 \Theta((E_{v'} - E_v) - E_{el}).$$

(13)

The Heaviside function in Eq. (13) means that electron can only be captured into a Rydberg state attached to the vibrational state $v'$ with energy $E_{v'}$ if the total energy $E_v + E_{el}$ is smaller than $E_{v'}$. To evaluate the matrix element, we apply the vibrational frame transformation

$$\langle \sigma \rangle = \frac{\pi}{2E_{el}} \left| \int (v'|Q) S_{\Lambda',\Lambda}(Q) (Q|v) dQ \right|^2 \Theta((E_{v'} - E_v) - E_{el}),$$

(14)

where $S_{\Lambda',\Lambda}(Q)$ are elements of the clamped-nuclei scattering matrix $\hat{S}(Q)$. The quantities $S_{\Lambda',\Lambda}(Q)$ can also be considered as matrix elements of the same scattering operator $\hat{S}$ as in Eq. (13) but written in a different representation: $\langle Q', \Lambda' | \hat{S} | Q, \Lambda \rangle = S_{\Lambda',\Lambda}(Q) \delta(Q - Q')$. The matrix $\hat{S}(Q)$ depends on $Q$ and can be written in terms of the quantum defect matrix as $\hat{S}(Q) = \exp[2i\pi \hat{\mu}(Q)]$. For small vibrations, we can expand the quantum defect matrix to first order over small displacements $Q_i$ around $Q = 0$,

$$\hat{\mu}(Q) = \hat{\mu}(0) + \sum_i \left( \frac{\partial \hat{\mu}}{\partial Q_i} \right) Q_i.$$

(15)

Here and below, all partial derivatives are assumed to be taken at the equilibrium geometry of H$_3$O$^+$. Then, the scattering matrix is expressed as

$$\hat{S}(Q) = \exp[2i\pi \hat{\mu}(0)] \exp \left[ 2i\pi \sum_i \left( \frac{\partial \hat{\mu}}{\partial Q_i} \right) Q_i \right].$$

(16)
We expand the exponential term of the right side to first order

$$\hat{S}(Q) = \exp \left[ 2i\pi \hat{\mu}(0) \right] \left( \hat{I} + 2i\pi \sum \left( \frac{\partial \hat{\mu}}{\partial Q_i} \right) Q_i \right).$$  \hspace{1cm} (17)

In Eq. (14), the ionic vibrational functions in the bracket are orthogonal to each other. Therefore, the constant terms in Eq. (17) for the $\hat{S}(Q)$ matrix do not contribute to the cross section of Eq. (14). Hence, combining Eqs. (14) and (17) we obtain

$$\langle \sigma \rangle = \frac{2\pi^3}{E_{el}} \sum \left( \frac{\partial \mu_{\Lambda,\Lambda'}}{\partial Q_i} \right) \langle v'|Q_i|v \rangle |^2 \Theta(E'_e - E_e - E_{el}),$$  \hspace{1cm} (18)

where $\mu_{\Lambda,\Lambda'}(Q)$ is an element of the quantum defect matrix $\hat{\mu}(Q)$ written in the same representation as $S_{\Lambda,\Lambda'}(Q)$.

Equation (18) is quite general and can be used to calculate the cross section for the electron capture by different molecular ions. We now apply it to DR in $\text{H}_3\text{O}^+$ using the parameters of the Jahn-Teller coupling obtained above. These parameters are used below to construct the scattering matrix $\hat{S}(Q)$. Thus, they determine the $\text{H}_3\text{O}^+$ DR cross section. We will consider the symmetric normal modes $Q_1$ and $Q_3$, as well as the doubly degenerate normal modes $Q_2 = (\rho_2, \varphi_2)$ and $Q_4 = (\rho_4, \varphi_4)$ as the vibrational coordinates.

We start with an electronic state with potential

$$U(Q) = U^+(Q) - \frac{1}{2(n - \mu(Q))^2},$$  \hspace{1cm} (19)

and taking derivative with respect to $Q_i$, we obtain

$$\left( \frac{\partial \mu}{\partial Q_i} \right) = - \left( \frac{\partial v}{\partial Q_i} \right) = -\nu^3 \left( \frac{\partial U}{\partial Q_i} \right),$$  \hspace{1cm} (20)

The potential does not depend to first order on $Q_1$ or $Q_3$, i.e. $\left( \frac{\partial \mu_{\Lambda,\Lambda'}}{\partial Q_1} \right) = \left( \frac{\partial \mu_{\Lambda,\Lambda'}}{\partial Q_3} \right) = 0$, for any electronic states $\Lambda$ and $\Lambda'$. In the same way, using Eq. (9), we find that the potentials do not depend to first order on $\varphi_2$ and $\varphi_4$ near the equilateral geometries, i.e. $\left( \frac{\partial \mu_{\Lambda,\Lambda'}}{\partial \varphi_2} \right) = \left( \frac{\partial \mu_{\Lambda,\Lambda'}}{\partial \varphi_4} \right) = 0$.

Hence, in the first order of approximation, the only non-vanishing terms in Eq. (18) are the ones that depend on $\rho_2$ and $\rho_4$. Therefore, the main contribution into the electron capture is due to the Jahn-Teller coupling.

We assume that the incident electron has projection $\Lambda = -1$ on the molecular axis (Eqs. (3) and (6)), the final electronic state has projection $\Lambda' = 1$, once the electron is captured into a Rydberg state attached to an excited vibrational level of the ionic core. For the cross section calculation, we need to evaluate the derivatives $\partial \mu_{\Lambda',\Lambda}/\partial \rho_i$ at the equilibrium of the ion. Because the diagonal elements of $\hat{\mu}(Q)$ are the same, the derivative $\partial \mu_{\Lambda',\Lambda}/\partial \rho_i$ is equal to the derivative of eigenvalues $\mu_a(Q)$ and $\mu_b(Q)$ of $\hat{\mu}$. The derivatives $\partial \mu_a/\partial \rho_i$ and $\partial \mu_b/\partial \rho_i$ are obtained from $ab\ initio$ calculations (shown in Fig. 1) or directly using Eqs. (9) and (12) from the potential energy surfaces of the excited electronic states of $\text{H}_3\text{O}$ that are coupled by the Jahn-Teller interaction,

$$\left( \frac{\partial \mu_{-1,-1}}{\partial \rho_2} \right) = \frac{\partial U_a}{\partial \rho_2} |^{\nu^3}$$  \hspace{1cm} and  \hspace{1cm} $$\left( \frac{\partial \mu_{1,-1}}{\partial \rho_4} \right) = \frac{\partial U_a}{\partial \rho_4} |^{\nu^3}.$$  \hspace{1cm} (21)
As the last step of the treatment, we consider the vibrational states of $\mathrm{H}_3\mathrm{O}^{+}$ in the normal mode approximation and label them as $|v_1 v_2 v_3 v_4 \rangle$, where $l_2$ and $l_4$ are the vibrational angular momenta associated with the degenerate normal modes. The initial state of the ion is its ground vibrational state, thus $|j v_i \rangle = |j_0000 \rangle$. The only non-vanishing terms in the cross section (18) are $h_{01} \langle j_2 | j_0000 \rangle = 1$ and $h_{00} \langle j_4 | j_0000 \rangle = 1$. We use mass-scaled normal coordinates in these expressions, so the masses dropped out. The frequencies $\omega_i$ are given in Table 1. So, in this approximation the electronic capture can only occur into these two final vibrational states. Also, the cross section in Eq. (18) has to be multiplied by two because the final vibrational state is doubly degenerate. It gives the final DR cross section

$$
\sigma = \frac{2\pi^3}{E_{el}\omega_2} \left( \frac{\partial \nu_2}{\partial j_2} \right)^2 \Theta(\hbar \omega_2 - E_{el}) + \frac{2\pi^3}{E_{el}\omega_4} \left( \frac{\partial \nu_4}{\partial j_4} \right)^2 \Theta(\hbar \omega_4 - E_{el}).
$$

The derivatives $\partial \nu_i / \partial j_i$ are obtained from the dependencies $\nu_i(j_i)$ such as shown in Fig. 1. There are several electronic $e$ states that are doubly-degenerate at the equilateral configuration and that are split by the Jahn-Teller coupling once the $C_{3v}$ symmetry is lifted. These states can be considered as different superpositions of the hydrogen-like states $p$, $d\pi$, $d\delta$. As it is clear from Fig. 1 the Jahn-Teller coupling is not negligible between $d\pi$ states, for example. Therefore, the electron can be captured into these states. In Eq. (22) we account separately for the contribution from each such Jahn-Teller pair of electronic states. The final cross-section is plotted in Fig. 2. In that figure we also show the experimental DR cross section obtained in the CRYRING [3] and ASTRID [4, 24] storage rings.

![Figure 2.](image)

**Figure 2.** (Color online) Theoretical cross section for dissociative recombination of $\mathrm{H}_3\mathrm{O}^{+}$ with low-energy electrons. The experimental results from Refs. [3, 4, 24] are also given.

4. **Resonant $\mathrm{H}_3^+$ dissociative recombination**

Tests of the preceding simplified theoretical treatment of DR have been encouraging, in terms of predicting average recombination rates for increasingly complex polyatomic molecules. But it is still of interest to push theoretical and experimental capabilities to the greatest possible level of detail for some fundamental species like $\mathrm{H}_3^+$. To date it has not yet been possible to compare experiment and theory at the level of individual resonances in the spectrum. This is in part because even though this triatomic ion is the simplest, it is nevertheless predicted to have a spectrum dominated by a dense forest of resonances, which would require extremely high experimental resolution in order to test their positions, widths, and intensity profiles.

Some experimental evidence exists for the dense resonances in this energy range for the $\mathrm{e}+\mathrm{H}_3^+$ system, in the form of the near-threshold photoionization spectrum of metastable $\mathrm{H}_3$ that was
measured years ago by Helm and coworkers (see [25] and references therein). Photoionization is a different observable than dissociative recombination, of course, but it is well known that a resonance seen in one channel will have the same position and width in any other collision channel [26]. However, little experimental evidence exists to support this predicted dominance of resonance pathways for the DR observable. This is presumably in part because of the fact that collision experiments typically have a much greater energy bandwidth than laser photoionization experiments, which makes any given narrow resonance less pronounced in a DR experiment. A second reason is that many more symmetries are present in collision experiments, which are less selective in terms of final state angular momentum and parity channels than are photoionization experiments. It is worth noticing that the same level of theory that has been applied to the DR calculation for H$_3^+$ has also been shown [27] to describe the Helm photoionization experiments, with excellent agreement in the energy range where rotational autoionization dominates the decay, but somewhat more modest agreement in ranges where vibrational autoionization and predissociation dominate the resonance decay pathways. This concurrence of theory and experiment for high resolution photoionization measurements provides some additional confidence in the resonance properties predicted by theory, but since this concurrence is achieved only for one symmetry of the ortho species, it is not enough to conclude that all symmetries are predicted to have the correct resonance structure in the corresponding DR process occurring in the same energy range.

The level of theory has not been changed since the latest improvements were published in 2007 in [11]. However, some new thermal averages have been computed on a fine energy mesh, to explore the observability of resonance structures and their sensitivity to the ionic rotational temperature. The main results are being reported elsewhere, specifically in a joint experiment-theory publication [28], which includes a careful new analysis of the source ion rotational temperature. We show here one example of the level of agreement that is emerging from that study, plotted in Fig. 3 in the form of the reduced dissociative recombination rate coefficient, which is the DR rate coefficient multiplied by $\sqrt{E_d}$. The preliminary ionic rotational temperature relevant to the experimental results shown in this figure has been estimated to be 380 K. For the energy range shown, the theory has been computed for a rotational ion temperature of 100 K, a transverse temperature in the relative collision energy of 500 $\mu$K and a parallel temperature of 25 $\mu$K. At this ion temperature and electron beam energy resolution, signatures of resonances begin to emerge that are clearly identifiable. Modulations in the experiment, believed to have an ion temperature of approximately 300 K, do show some correlation with the theoretical modulations. While there remain discrepancies in the overall rate by a factor of 2-4 in some energy ranges, the overall agreement continues to be encouraging, even at this level of comparison, which is far more detailed than has been achieved previously. The energy range below that shown in the figure exhibits poorer agreement between theory and experiment, as is discussed in greater detail in Ref. [28].

Another positive advance in our understanding of H$_3^+$ dissociative recombination that has been achieved during the past few years has occurred in the context of afterglow experiments and their interpretation. Glosik and collaborators [29, 30, 31, 32, 33] have demonstrated through combined experimental and theoretical analysis that the neutralization process in plasma containing H$_3^+$, electrons, and ground state helium atoms is predominantly mediated by a three-body process involving He atoms. The three-body recombination rate at temperatures around 300 K tends to be in the range $K_3 \approx 1 - 10 \times 10^{-25}$ cm$^6$/s, which means that for He densities in the range $10^{17}$ to $10^{18}$ cm$^{-3}$, the effective rate of ternary recombination can compete with or even dominate over the binary recombination rate. Nevertheless, by extrapolating results to the limit of zero He density, the binary recombination rate for $e + H_3^+$ collisions has been obtained and good agreement has been found with both ab initio theory and storage ring experiments.
5. Discussion of the results and perspectives
We investigated the DR rate of $\text{H}_3\text{O}^+$ using the simplified theoretical model. In this model, we assume that once the electron is captured by the ion into a vibrationally excited level, the probability of autoionization is small compared to the predissociation probability. Therefore, we calculate the cross section for the electron capture. The non-Born-Oppenheimer Jahn-Teller interaction between the motion of the incident electron and the vibrational motion of the ion is the key ingredient in the present model. The obtained theoretical DR cross section is in good agreement with the results from the storage ring experiment by Neau et al. [3], which indirectly confirms that autoionization probability is indeed small compared to the predissociation probability.

In this model, the incident electron can excite only one quantum of degenerate vibrational modes of the ionic core. The excitation of higher vibrational levels is neglected. One possible simple improvement of the model would be to account for the excitation of higher vibrational levels of $E$ irreducible representation. In the present model it can be made if one considers the fact that the higher vibrational levels of the $E$ irreducible representation have small contributions from the $|01^100^0\rangle$ and/or $|00^001^1\rangle$ vibrational levels due to the anharmonicity of the ionic potential. This improvement will not change the cross section at low energy in a noticeable way, but it will give a non-zero cross section at incident electron energies above $h\omega_4$. The present theoretical cross section is identically zero above $E_{el} = h\omega_4$, although the experimental cross section is small but measurable.

We have also discussed the dissociative recombination of $\text{H}_3^+$, for which a detailed theoretical treatment has been developed. The overall theoretical cross section for the dissociative
recombination of $\text{H}_3^+$ is in good agreement with experimental data. Because the state of theory and experiment for DR of $\text{H}_3^+$ is such that they both provide information about positions of individual resonances, we compare detailed features in the experimental and theoretical DR spectra. The overall agreement is satisfactory but there are several regions in the spectrum where theory fails to reproduce experimental features.

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