Steric effect in H$_2$O$^+$ and H$_3$O$^+$ collision complexes

Charge transfer in O$^+$/H$_2$ and H$^+$/H$_2$O molecular ion systems

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Received: July 30th, 2005 / Revised version:

Abstract. The positive water and hydronium ions are of interest in a variety of chemical and biological applications. Here we study the steric effect in charge transfer collisions, i.e. the spatial dependence of single electron capture, in collisions mediated by these ions. In particular, the steric effect is demonstrated in the O$^+$(2D)/H$_2$ and H$^+$/H$_2$O charge transfer collisions in the energy range of 100 eV/u to 10 keV/u.

PACS. 34.70.+e charge transfer – 34.50.Gb electronic excitation and ionization of molecules; intermediate molecular states – 31.15.Ar ab initio calculations

1 Introduction

In charge-transfer collisions of atomic ions with molecules, the relative orientation of target and projectile as well as the details of potential energy surfaces are known to have a limited effect on the integral cross sections, at least in the keV/u energy range. Nevertheless, a considerable steric effect is evident even at those high energies when the differential cross sections or transition probabilities along particular collision trajectories are studied. These phenomena have been somewhat neglected in the past, due to both the experimental difficulties in orienting neutral molecular targets and theoretical complexity inherent in polyatomic collisional systems, which typically involves rovibrational motion of the colliding system in a number of coupled electronic states.

Owing to large collision velocities in the keV/u energy range, the period of (ro)vibrational motion of the target molecule is much larger than the collision time, and hence the nuclear geometry of the target can be kept fixed. In addition, the presence of long-range Coulomb interaction in ion-ion channels may dominate the details of local electronic structures, imposing thus a partial spherical symmetry on the system. That is often the reason why the integral charge transfer cross sections can be well estimated by using a few, if not a single one, orientation of the collisional molecular ion system. Much theoretical work has been devoted to the development and accuracy assessment of such approximations [1,2].

However, the electron capture process does depend on the orientation of the projectile and details of the potential energy surface, if either the collision trajectory or target orientation is resolved. It is the purpose of this paper to demonstrate the steric effect in the H$_2$O$^+$ and H$_3$O$^+$ systems. To that aim, we first study a central collision of O$^+$(2D)/H$_2$ and H$^+$/H$_2$O charge transfer collisions in the energy range of 100 eV/u to 10 keV/u.

The paper is organized as follows. In Section 2, the ab initio calculations and the electronic state close-coupling formalism are summarized along with references to previous work [3,4]. Section 3 then resolves the steric effect on electron capture probabilities and cross sections for the H$_2$O$^+$ and H$_3$O$^+$ collision intermediates and discusses the accuracy of the integral charge transfer cross sections. Concluding remarks close the paper in Section 4. Atomic units are used throughout the paper.

2 Theoretical Model

The potential energy curves (PEC) for H$_2$O$^+$ and H$_3$O$^+$ systems were obtained ab initio for the most general molecular symmetries by using the multireference single- and double-excitation configuration interaction (MRD-CI) method [5–8].

A gaussian (6s3p2d1f) basis contracted to [4s3p2d1f] was used for the hydrogen atom, while a (12s6p3d2f) basis

set contracted to [5s4p3d2f] was employed for the oxygen atom. All basis sets are of the cc-pVQZ type [9]. In addition, a diffuse [2s2p2d] basis centered at oxygen atom is employed to describe the Rydberg electronic states of the water molecule.

The selection threshold and the number of configurations are $2.0 \times 10^{-7}$ a.u. and 500, 000 for $\text{H}_2\text{O}^+$, and $8.0 \times 10^{-7}$ a.u. and 200, 000 for $\text{H}_3\text{O}^+$, respectively. The effect of all unselected configurations is checked by using the perturbative energy extrapolation procedure [8]. The resulting highly correlated wavefunctions are used to obtain the nonadiabatic coupling matrix elements by a numerical differentiation method [10]. The origin of electronic coordinates is placed at the molecular center of mass for all geometries.

In the case of $\text{H}_2\text{O}^+$, the internuclear distance of hydrogen atoms was fixed at 1.4 and 1.6, to estimate the effect of hydrogen molecular vibrations. The potential energy surfaces for the doublet states (asymptotically corresponding to the metastable $\text{O}^+ (\Sigma^+ D,^2 P)$) ions were projected along three $\text{O}^+$ lines passing through the center of the H-H line at the angles $\gamma = 0, \pi/4$ and $\pi/2$.

In case of $\text{H}_3\text{O}^+$, the target water molecule is fixed at the equilibrium geometry. The trajectories of impacting proton are perpendicular to the plane of water molecule $[x, y]$, which they intersect at: (1) the oxygen atom ($z$-direction approach), (2) on the OS line, where $S$ is the center of H-H line, or (3) the OP line, where OP and OS are perpendicular in-plane lines. Nuclear geometry is invariant with respect to an inversion along the OS line. Potential energy curves and nonadiabatic couplings were obtained for three magnitudes of the impact parameter relative to the oxygen atom, $b = 0.9$, 1.8, and 3.6. The geometry of the collision is shown in Fig. 1.

The collision dynamics at the keV energy range is given by coupled equations [1, 3] in the above basis of electronic-state amplitudes $f_n^\Gamma$ on potential energy surfaces $\Gamma$ labelled by the impact parameters $b$,

$$ \left[ \frac{d}{dz} - \frac{E_n(R) - E_0}{v} \right] f^{\Gamma}_n(z; \Gamma) = \sum_{n'} c_{nn'} f^{\Gamma}_{n'}(z; \Gamma). \tag{1} $$

Here $v$ is the velocity, $z = vt$ is the coordinate along projectile’s trajectory, $R = (b^2 + z^2)^{1/2}$, $c_{nn'}$ is the coupling matrix and $E_0$ is the collision energy. The equations are solved for the initial condition $f^{\Gamma}_{n'}(\pm \infty) = \delta_{nn'}$. The cross section formula for electron capture in the general case is obtained by integration over the plane of impact parameters and averaging over the molecular orientations $\Gamma$ as appropriate,

$$ \sigma_{nn'} = \int db \int d\phi \int_0^{\infty} \left| f^{\Gamma}_{n'}(\infty; \Gamma) \right|^2 \Gamma. \tag{2} $$

Details of the above formulation for ion-atom collisions ($J^b \rightarrow J^\circ$, single PEC $\Gamma$) can be found in Refs. [1, 11–14]; the ion-diatomic collision case is dealt with e.g. in Refs. [2, 15–17] (PEC are parameterized by one angle $\gamma$). In the present ion-triatomic case, $\text{H}^+\text{H}_2\text{O}$ collision, the molecular plane is aligned perpendicular to the proton beam, and hence each value of the impact parameter corresponds to its potential energy surface $\Gamma$. Introducing polar coordinates for the impact parameter vector, $(b, \phi)$, the cross section formula then reads

$$ \sigma_{\perp} = 2 \int_0^\infty \int_0^{\pi} \int_0^{\infty} db \int_0^{\pi} d\phi \Gamma(b, \phi; R(b, z \rightarrow \infty)). \tag{3} $$

### 3 Steric Effect in the Electron Capture

Based on the MRD-CI potential energy curves and couplings, we solved the coupled equations (1) along the collision trajectories and for target orientations defined in Section 2. The next two subsections discuss the steric effect seen in the resulting charge transfer probabilities.

#### 3.1 Collision of $\text{O}^+ (\Sigma^+ D)$ with $\text{H}_2$

Figure 2 (upper panel) displays the manifold of doublet $\text{H}_2\text{O}^+$ potential energy curves, which asymptotically correspond to $\text{O}^+ (\Sigma^+ D,^2 P)$ states, or $\text{O}$ states in the electron capture channel. Excited states of $\text{H}_2/\text{H}_2^+$ are also included. The PEC passing through the target center are shown for two angles between $\gamma = \pi/4$ (dashed line, $A'$ and $A''$ symmetry) and $\gamma = \pi/2$ (full line, $A_1$, $A_2$, $B_1$, $B_2$ symmetry). Although both groups of PEC are similar for [HH] $\sim 2.5$ (polarization interaction), substantial differences arise at lower collision distances. Owing in part to symmetry reasons, the PEC for $\gamma = \pi/4$ have higher energies than those for $\gamma = \pi/2$. The lower panel of Fig. 2 shows the cross section for electron capture from the $\text{O}^+ (\Sigma^+ D)$ projectile in fixed-$\gamma$ approximation [4, 15, 16]. The steric effect can clearly be resolved in Fig. 2. On the other hand, since $\gamma = \pi/4$ is the middle value interpolating the extreme cases $\gamma = \pi/2$ and $\gamma = 0$, the range of the steric
Fig. 2. Electron capture cross section for collisions of O\textsuperscript{+} (\textsuperscript{2}D) with the H\textsubscript{2} molecule using fixed-\(\gamma\) potential energy surfaces for \(\gamma = \pi/2\) and \(\gamma = \pi/4\).

The effect is only about 30\% of the total cross section value for keV energies. This is a very reasonable accuracy for the O\textsuperscript{+} (\textsuperscript{2}D) charge transfer cross sections that vary in the experiments by a factor of 2 [18–20].

A detailed discussion of the integral cross sections for electron capture on H\textsubscript{2} by O\textsuperscript{+} (\textsuperscript{2}D, \textsuperscript{2}P, \textsuperscript{4}S) can be found in Ref. [3,4] along with a comparison to recent measurements [21, 22].

3.2 Collision of H\textsuperscript{+} with H\textsubscript{2}O

The potential energy curves for the proton beam intersecting water molecular plane on the OS line (\(\phi = 0\)) and the OP line \(\phi = \pi/2\) are shown in the upper and lower panel of Fig. 3, respectively. The labels correspond to the vertical ordering of PEC for the four different impact parameter values and the initial (dashed line) and final (full line) collision channels. As the impact parameter increases, the energy difference diminishes, converging to the asymptotic energy gain value \(E(\text{H}_2\text{O}) - E(\text{H}_2\text{O}^+) + 0.5\), which is approximately 0.0467. The absolute values of the non-adiabatic coupling between the initial and final state is shown in Fig. 4 for all values of impact parameters and \(\phi = 0, \pi/2\).

Solving the coupled equations (1) along the H\textsuperscript{+} beam, we obtained the electron capture probability for each straight-line trajectory. These are plotted in Figs. 5 and 6, respectively, demonstrating a marked steric effect along each trajectory. Except for \(b = 0\), the angle between \(\text{RO-}\text{H}^+\) (connecting the oxygen atom and the impacting proton) and the plane of water molecule varies in the full range from \(-\pi/2\) through 0 to \(\pi/2\), scanning the potential energy surface in a complex way. The probabilities of electron capture for \(\phi = 0\) and \(\phi = \pi/2\) exhibit oscillations as a function of energy, the frequency of which diminishes when \(b\) increases. Although for any fixed value of energy the capture probability substantially differs between \(\phi = 0\) and \(\phi = \pi/2\), the overall behavior (frequency of oscillations, relative heights of the peaks) is similar, except for the highest value of the impact parameter considered here, \(b = 3.6\). This similarity between the two cases can be explained analytically e.g. in the 2-state exponential model, since the asymptotic energy separation is small and the coupling vanishes quite slowly both for \(\phi = 0\) and \(\phi = \pi/2\).

Finally, let us estimate the variation of the unresolved electron capture cross section in the case of perpendicular collisions, based on Eq. (3). To perform the integral over the entire plane of impact parameters with high accuracy, the present 10-point grid may still be quite inaccurate.
The most natural choice is $s_\perp(0,\cdot)$, hereafter referred to as the central collision. In mathematical terms, the diabatic matrix $V(b,\phi,z)$ is approximated by $V(0,\cdot,z)$ for $0 \leq b < R_t$, where $R_t$ is the size of the transition region. Variation in the values of $s_\perp(b_0,\phi_0)$ (for $b_0$'s falling in the transition region and arbitrary $\phi_0$'s) then indicates the accuracy of the central collision approximation. We also note that the value $s_\perp(0,\cdot)$ corresponds to the fixed-$\gamma$ approximation, which has been used extensively [23–25]. The resulting cross section estimates, $s_\perp(0,\cdot)$ and $s_\perp(1.8,0.0)$ are shown in Fig. 7 along with experimental values for single electron capture by the proton on the water molecule. The experimental cross sections can be well reproduced by $s_\perp(0,\cdot)$ in accordance with our experience and previous work [4,23–25]; the size of the steric effect on the electron capture cross section is also much smaller as compared to the transition probabilities along particular collision trajectories.

4 Concluding Remarks

In this paper, we have first discussed the steric effect in the charge transfer collisions of the metastable $O^+(2D)$ ion with $H_2$. The steric effect in the keV range of collision energies, defined as the cross section ratio for the $H^+ + H_2O(X) \rightarrow H(1s) + H_2O^+(X)$ and $H^+ + H_2O^+(X) \rightarrow H(1s) + H_2O(X)$ reactions, varies...
in the range of 30% of the orientation-unresolved cross section, an effect which falls within the error bars of most electron capture experiments. We further observed a marked steric effect in the electron capture probabilities for individual rays in an H\(^+\) beam oriented perpendicular to the plane of the H\(_2\)O target molecule. The steric characteristics of charge transfer probabilities are pronounced in the entire energy range studied, i.e. 100 eV/u to 10 keV/u. A numerical criterion was developed to assess the variation of the cross section integral based on a sample of projectile trajectories from the beam. Using this theoretical criterion and the experimental data available, it was demonstrated that the central collision approximation yields a very reasonable value of the capture cross section.

Acknowledgements

This work was supported in part by the Japan Society for the Promotion of Science (JSPS), the Japanese Ministry of Science, Sports, Culture and Education (MEXT), and by the grant BU 450/7-3 of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. L. Pichl acknowledges support by a JSPS Grant-in-Aid, Max Planck Society, and the Academic Frontier Program by MEXT. Special thanks are due to Prof. T. Kasai.

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