Experimental study for dissociative electron attachment to water molecule in the $^2B_1$ resonance

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Abstract. The dynamics of the dissociative electron attachment (DEA) to water via the first resonances, $^2B_1$, is investigated by using a modified Coltrims spectrometer for imaging dissociation dynamics. The dissociation channel of $H^-$ ion is found to be $H^- + OH^{(2)\Pi}$, and the negative ions are observed to be ejected out perpendicular to the incident electron direction, which agree with previously reported measurements. For the channel of $O^-$ ion, however, the ion yields are found to be an order of magnitude smaller than what have been reported in the literature.

1. Introduction

Free electron collisions with chemical species, such as molecules and molecular ions, can lead to a variety of interesting reactions such as electronic, vibrational, and rotational excitation, as well as dissociation. Low energy ($\leq 20\text{eV}$) electron collision can lead to dissociative electron attachment (DEA) to molecules. This phenomena has been known to have an importance in the field of radiation damage, where in a biological system external radiation deposited in the system creates a large number of secondary free electrons with relatively low energy. These electrons can cause DEA with neighboring molecules such as water [L Sanche et al. (2005)].

Recently DEA to water attracts attention for gaining the basic knowledge of a mean of controlling chemical reactions. As we will see, the angular distribution of $H^-$ ions from this resonance has strong dependence on the incident electron direction, which indicates the formation of the resonance state of a water molecule also strongly depends on not only the incident electron energy but also its direction. These characteristics of the resonant state can possibly give rise to control of the dissociation of the molecule, or even control of the dissociation of a specific bond. Site specific fragmentation of molecules at the hydrogen site was reported recently [Prabhudesai et al. (2008)]. It was found the DEA properties of the OH bond leading $H^-$ ion in a water molecule appears to maintain even in larger molecules such as CH$_3$COOH, and CH$_3$CH$_2$COOH. Despite of their importance, the DEA study to water molecule has been mainly focused on measuring accurate cross section and identifying the accurate locations of the resonances, and the study for its dissociation dynamics is rare. We think it is necessary to make detailed measurements of the DEA dynamics of water to reveal the dissociation processes involved in each resonances. Thus the present study of the $^2B_1$ resonance is a part of ongoing set of investigations on dissociation dynamics of all resonances.
2. Experiments

In this experiment a modified Coltrims spectrometer together with a low energy electron beam and an ion extraction electrode both in a pulsed mode, and an effusive water source are used to measure the full angular distribution and kinetic energy release of negative ions arising from water DEA. The modified Coltrims spectrometer consists of an ion extraction electrode flanking the interaction region, a series of electrodes, and two dimensional position sensitive detector. The series of electrodes constitutes an electrostatic lens system creating the ion acceleration region, ion focus region, and ion drift region. The effusive molecular source is a syringe with a 0.5mm opening. It is mounted under the center of the extraction electrode which has a hole for the path of the molecular beam.

The interaction region is formed between the extraction electrode and a grounded electrode, which is the first electrode of the ion acceleration region, with a meshed 1.0 inch hole for the path of the ions. The mesh prevents the electric fields from leaking. An aluminum cylinder encloses the spectrometer as a noise shield. The electron and molecular beam intersect at right angles, the time-of-flight axis is along the molecular beam direction. The base vacuum of the experiment is maintained at few times \(10^{-8}\) Torr while the experiments are conducted with the typical background pressure of \(10^{-7}\) Torr.

Detecting negative ions arising from DEA process imposes a technical challenge in controlling low energy electrons through the extracting electric field region, eliminating noise from stray electrons. And also an effusive water source we have used inevitably leads to uncertainty in the initial position and momentum of the target molecules. In order to control the low energy electron, we have used a magnetic field \((\sim 20\text{G})\) produced by a pair of Helmholtz coils to collimate and guide the electron beams. We have found the presence of a magnetic field of moderate strength shifts impact position of the ions on the detector in accordance with the mass of ions. To eliminate noise from stray electrons, we have applied finely tuned electric pulses to the electron gun and the extraction electrode. These pulses are properly set to control the widths of the electron beam and the extraction electric field, as well as the delay time between them. Only after this delay, is the electric pulse applied to the extraction electrode to prevent it from altering the electron beam path. We optimized the pulse timing to prevent the electron beam straying into the spectrometer but still to extract most of the negative ions. We have also used two shielding boxes to enclose the spectrometer and detector separately to minimize the interference of the pulsing field with the detector. To alleviate the uncertainty of the initial position and velocity of the target molecules, caused by the effusive water source, we employed an electrostatic lens system in the Coltrims spectrometer. The lens system focuses the ion trajectories with respect to the initial momentum of the ions, hence the ion impact positions on the detector are independent of initial uncertainty of position.

The two dimensional position sensitive detector consists of two microchannel plates (MCP) in 80mm diameter and a delay-line anode detector. The signals from the detector are amplified and fed to a six channel computer automated measurement and control (CAMAC) - based time to digital converter(TDC). The digitized ion flight time and impact positions on the detector are stored separately using the event-by-event data acquisition, from which the momentum vector \((P_x,P_y,P_z)\) is calculated. The two dimensional position sensitive detector together with the ion extraction scheme we employed ensures full \(4\pi\) solid angle detection of the ion yields with high sensitivity.

3. Results

3.1. \(H^-\) channel of \(^2B_1\) resonance

Fig.1 shows the momentum images of \(H^-\) ions, \(P_{\text{longitudinal}}\) vs. \(P_{\text{transverse}}\), at 6.8eV, 7.3eV, and 7.8eV incident electron energy. The electron direction is from the bottom to the top in
each figure. One can see the momentum distribution of the $H^-$ ions has a distinctive yields

**Figure 1.** The momentum sphere of $H^-$ ions produced in he $^2B_1$ resonance. From left (a): At incident electron energy 6.8eV, (b): At 7.3eV, and (c): At 7.8eV. The distribution becomes broader as with the increase of the electron energy, indicating the increase of the internal energy in the OH fragments. The ion ejection direction is predominantly perpendicular to the electron direction, and it does not change even with the increase of the internal energy in OH.

**Figure 2.** Left (a): The kinetic energy release of $H^-$ ions at three incident electron energies in the same range. The peak position does not progressive appreciably, though the width of the distribution widens with the increase of the electron energy. Right (b): The angular distribution of $H^-$ ions in the same electron energy range. The distributions’ peak angle does not change in this resonance.

in the direction perpendicular to the electron beam, and the width of the distribution increases with the electron energy. It indicates that the fragment OH increases its internal energy or vibrational excitation with the increase of the electron energy. Similar results were observed in previous experiments [Belic et al. (1981)].

Fig2 (a) shows the kinetic energy distribution of $H^-$ (referred as $K_{H^-}$), and Fig2 (b) shows the angular distribution of $H^-$ at the same incident electron energy rage. $\Theta$ indicates the angle between the incident electron and ejected $H^-$ direction. One can see that the width of the kinetic energy distribution widens with the electron energy, but the peak position does not increase significantly, which indicates the electron energy is transferred mostly to the internal energy of OH. The angular distribution shown is that of the $H^-$ ions at the peak of the energy.
distribution within $\sim\pm0.5$eV range in Fig2 (a). The most probable kinetic energy release found as the peak positions of Fig2 (a) agree well with previously reported work [Belic et al.(1981)] [N Bhargava Ram et al.(2008)]. The angular distribution peaks in this resonance are found near $100^\circ$, which also agree well with theoretical prediction [D.Haxton et al.(2008)], and previous experiments [Belic et al.(1981), N Bhargava Ram et al.(2008)].

3.2. $O^-$ channel of $^2B_1$ resonance

Fig.3 shows the momentum image, $P_{\text{longitudinal}}$ vs.$P_{\text{transverse}}$, of the $O^-$ ions from DEA to water(and from $O_2$) at 6.8eV, 7.3eV, and 7.8eV incident electron energy. The data was obtained simultaneously with the $H^-$ measurements. The incident electron goes from the bottom to the top as before. The fuzzy small rings at the center in each figures are the images of the $O^-$ ions from $H_2O$ molecule targets, the outer denser rings are the images of the $O^-$ ions from the residual $O_2$ background gas. The resonance energy of DEA to $O_2$ molecule ($\sim7$eV) overlaps to the $^2B_1$ resonance. Considering the known cross section of $O^-$ from $O_2$ and the pressure in the experimental chamber, the cross section of $O^-$ from $H_2O$ is very small. Fig4(a) shows the kinetic energy release, $K_{O^-}$, of $O^-$ ions in the same electron energy range. One can see there is a long tail on the higher energy releasee side. Since energetically possible dissociation is two-body breakup in this resonance, this broad kinetic energy distribution is considered to indicate the existence of a wide range of internal energy in $H_2$ fragments. Surprisingly, however, one can see that neither the peak kinetic energy nor distribution width increase with the increase of the incident electron energy, 1eV. The two-body dissociation would show either the increase of the peak kinetic energy due to the increase in the translational energy of $O^-$ and $H_2$, or the increase in the width of the energy distribution due to the increase in the internal energy in $H_2$.

The angular dependence in Fig4(b) shows that $O^-$ ions dissociate almost isotropically in this electron energy range. The angular distribution is plotted for the $O^-$ ions at the peak of the kinetic energy distribution in Fig4(a).

4. Discussion

4.1. $H^-$ channel of $^2B_1$ resonance

The angular distribution of $H^-$ ions has been predicted [D.Haxton et al.(2008)]. The calculation was carried out based on the entrance amplitude under the axial recoil approximation.
Figure 4. Left (a): Total energy distribution of $O^-$ from $H_2O$, at incident electron energy 6.8eV, 7.3eV, and 7.8eV. The peak is found on the low kinetic side, below 0.7eV, and the peak position does not move with the increase of the electron energy. There is a long tail toward the higher energy side, indicating excitation of the internal energy of $H_2$ fragments. Right (b): Angular distribution of $O^-$ ions at the peak of (a). Unlike the $H^-$ angular distribution, $O^-$ ions exhibit isotropic distributions. $O^-$ and $H^-$ ions were measured simultaneously in this experiment.

and the constant-eigenmode approximation. It is shown in Fig5 The angular distributions of

Figure 5. Calculated angular distribution of $H^-$ from the $^2B_1$ resonance. It is calculated under the constant eigenmode assumption and the axial recoil approximation. Angle Theta represents the angle between the incident electron direction and $H^-$ ejection direction.

our experimental results for $H^-$ shown in Fig2(b) agree well with theory. One can also see that the peak positions of these distributions remain at the same angle within this resonance. These observations show that the assumption of the axial recoil approximation and the constant-eigenmode approximation is well justified; the dissociation dynamics is a fast O-H bond rupture, and no angular motion is involved. Also the angular distribution of $H^-$ is found not to depend on the final internal energy of the OH fragment.

4.2. $O^-$ channel of $^2B_1$ resonance

Theoretical prediction shows that the angular distributions of $O^-$ ions via the $^2B_1$ resonance should be directional [D.Haxton(2009)]. Our measurements however show fairly isotropic distributions. Our experimental results also show that the $O^-$ ion yields from the DEA to
H$_2$O molecules are considerably smaller than what has been reported (∼1/40 of the yields of H$^-$ ions). On the other hand, we have also observed abundant O$^-$ ions from the residual O$_2$ background gas. The O$^-$ ion yields from the O$_2$ background gas are found to be few hundred times larger than those from the H$_2$O targets, and the vacuum of our experimental system is kept at few times 10$^{-7}$ Torr during experiment. We, therefore suspect that a majority of the O$^-$ yields, which has been considered as the production via the DEA to water in previous experiments, would have been produced from the DEA to O$_2$ molecules; e$^- +$ O$_2$ → O$^-$ + O. The branching ratio between H$^-$ and O$^-$ yields are shown in Fig.6. Comparison of the yields of both ions shows that the branching ratio of H$^-$ to O$^-$ ions in our experimental results is close to a few hundred.

Figure 6. Branching ratio of H$^-$ to O$^-$ from the incident electron energy 6.3eV to 12.3eV. Both H$^-$ and O$^-$ ions were collected simultaneously. The ratio at ∼6eV is about an order of magnitude larger than previously known value, ∼40.

5. Conclusion
The DEA process to gaseous water in the $^2$B$_1$ resonance was studied by means of a modified Coltrim spectrometer. The angular distribution of H$^-$ ions is found to be in a good agreement with previous works. The dissociation dynamics involved in the H$^-$ production is a simple O-H bond rupture, and the final state of the OH fragment does not affect the angular distribution of H$^-$ ion. We have been able to obtain for the first time the momentum distribution, angular distribution, and kinetic energy release of O$^-$ ions in this resonance. Our data suggests that the O$^-$ ion yields in this resonance are about an order of magnitude smaller than the available data in the literature.

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6. References
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