Velocity Map Imaging of H$^-$ Ions from Dissociative Electron Attachment to H$_2$O

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Abstract. The velocity map imaging (VMI) technique developed recently for dissociative electron attachment (DEA) experiments is improvised further to study the formation of H$^-$ ions. The experiment is used to study DEA to water molecules at the 6.5 eV and 8.5 eV resonances. The kinetic energy and angular distribution of the H$^-$ ions arising from this resonance are compared with those in the existing experimental and theoretical data.

1. Introduction
Dissociative attachment of electrons to organic molecules has been attracting a great deal of attention recently due to its importance in radiation induced structural and chemical modification of cellular DNA [1]. It has been shown that electrons with energies below 20 eV play a dominant role in damaging DNA [2]. This, along with the fact that about 10$^4$ of such electrons are produced per MeV of the energetic particles constituting the radiation[3], has spurred a variety of electron collision experiments on organic molecules in gas as well as in condensed phase[4]. The importance of water molecule in this context arises from two perspectives. The first one is that water is the largest constituent in biological tissue and the creation of any free radicals from water could affect the tissue. And the second one is related to our recent observation that electron attachment to big molecules may be modeled in terms of the electron attachment to their smaller constituents. We found that electron attachment arising from core-excited resonances show a functional group dependence leading to site specific fragmentation. This is a manifestation of the electron attachment properties of the smaller subsystems being maintained even when they are part of the bigger molecules [5]. One example of this is the O-H group which appears to have similar electron attachment properties whether it is part of water molecule or of a big molecule. Electron impact studies on water are also important from the point of view of the storage of spent nuclear fuel [6].

Several measurements have been reported on DEA to H$_2$O, showing the presence of three resonances, yielding H$^-$, O$^-$ and OH$^-$ ions at around 6.5, 8.2, and 12 eV electron energy [7]. Of these, H$^-$ is the dominant ion with the maximum cross section at 6.5 eV. The kinetic energy spectra and the angular distributions of H$^-$ ions from the DEA process have been measured to understand the dynamics of the process as well as to identify the quantal state of the resonances [8, 9]. These measurements were carried out in the conventional turn table arrangement using an electrostatic analyzer. The kinetic energy spectra of H$^-$ showed that the DEA process leads to the formation of the OH in various excited states. These measurements also provided the cross sections for the formation of
OH in specific vibrational levels as a function of the incident electron energy. The theoretical calculations for the DEA process in general are too complex. Though there are a few calculations reported for some molecules identifying the resonances, there have been few on the dynamics of the dissociation process of the resonances. There have been recent reports on the dynamics of the DEA process in H$_2$O leading to the $^2$B$_1$, $^2$A$_3$ and $^2$B$_2$ resonances of water anion [10, 11, 12]. These calculations show partial agreement with the experimental results of the position of the resonance, vibrational excitation of the OH fragment and the cross sections. Considering the importance of these calculations as a model for the DEA to polyatomic molecules in general, and for the case of H$_2$O in particular, there is a need for further measurements on the kinetic energies and angular distributions of the fragment ions from H$_2$O. In view of this, we have used our newly developed velocity map imaging technique to study the DEA process in H$_2$O.

2. Experimental

The newly developed VMI experiment for DEA studies and its performance in imaging O$^-$ from O$_2$ has been reported before [13]. However, using it to image the lighter H$^-$ ions needed careful evaluation since the experiment involved a magnetic field over a fairly large volume, used for collimating the electron beam. Moreover, since the ions are produced continuously over an extended period of time followed by a finite time delay before they are extracted; there could be a dependence on the mass of the ion being imaged when their kinetic energies are appreciable. This problem would be worst for H$^-$ ions due to their small mass. For a given initial kinetic energy, the H$^-$ ion cloud will bloom to a size four times that of the O$^-$ cloud within a specific time interval. By reducing the width of the electron gun pulse and the delay between the electron pulse and the extraction pulse, we try to reduce the size of the H$^-$ cloud. We also found that it was necessary to increase the operating voltages, which needed further modifications of the apparatus. We give below a brief description of the technique employed, and the modifications done to the previous experiment, in carrying out the present measurements.

As described previously [13], the present experiment employs a time sliced velocity map imaging similar to the one developed by Kitsopoulos and co-workers [14]. The notable feature of this experiment is its adaptation to work with low energy electron beams. This entailed operating the spectrometer with relatively low voltages. The other important feature of this experiment is the use of a Wedge and Strip based position read-out; thereby doing away with the CCD camera based read-out. This feature allows the recording of individual ions for their arrival time and position simultaneously, enabling the time slicing without pulsing the detector bias.

The experiment uses a magnetically collimated and pulsed electron beam produced by thermionic emission from a heated tungsten filament. The grid electrode of the three element gun is negatively biased in order to cut off the electron beam. It is over ridden by a positive voltage pulse in order to get the pulsed electron beam. The repetition rate and width of the electron pulse is controlled by suitably changing the electrical pulse applied to the grid. A pair of Helmholtz coils kept outside the vacuum chamber produces a uniform magnetic field of about 50 Gauss for collimating the electron beam. The electron current is monitored using a Faraday cup kept beyond the interaction region. The molecular target is produced as an effusive beam from a capillary array mounted at the centre of the pusher electrode used for ion extraction and along the axis of the time of flight spectrometer used for velocity map imaging. The electron beam intersects the target molecular beam at right angles. The base vacuum in the experiment is maintained at a few times 10$^{-6}$ Torr, while the experiments are conducted with typical background pressure of 10$^{-6}$ Torr.

The ion imaging spectrometer consists of a pair of extraction electrodes (pusher and puller) flanking the interaction region, a lens electrode, the flight tube and a 2-dimensional position sensitive detector (PSD). The imaging spectrometer assembly is identical to what was described earlier [13], except for a fine wire-mesh mounted on the puller electrode, to prevent any field penetration from the lens electrode and the flight tube into the interaction region. The ion extraction pulse is applied with a finite delay after the electron pulse. While working with O$^-$ from O$_2$, an electron pulse width of 200 ns followed by a delay of 100 ns for the extraction pulse was found to be optimum, as far as the imaging
was concerned. O\textsuperscript{−} from \ce{O_2} are produced with kinetic energy up to 3 eV. The H\textsuperscript{−} from \ce{H_2O} are also expected to have energy in the same range, but the corresponding velocities of H\textsuperscript{−} would be a factor of 4 larger as compared to those of O\textsuperscript{−}. This could have a bearing on the imaging process that employs the delayed extraction as we have employed. The width of the electron pulse and the extraction delay are reduced to optimize the focusing of H\textsuperscript{−} ions. In order to have reasonable time averaged electron beam current, the electron pulse width is kept at 100 ns. We also notice that reduction of pulse width tended to worsen the electron energy resolution. The delay in the extraction is also kept at 50 ns for operational convenience. Under these conditions, and the geometry that was fixed in the previous measurement \cite{13}, we need to increase the operating voltages of the imaging system. This tends to cause unwanted leakage of electric field into the interaction region from the flight tube side and vice versa. This problem is overcome by fixing a fine wire-mesh on the aperture on the puller electrode. The ion optics is further optimized under the new conditions, using trajectory calculations followed by actual experiment. The voltages in the simulation and experiment are found to be in fairly good agreement. The voltages used to carry out the experiment are 40 V on the pusher, 26 V on the lens electrode and 190 V on the flight tube. The ion extraction pulse is maintained at 1\,µs as in the previous experiment. The experiment is carried out with a pulse repetition rate of 20 KHz. The time averaged electron beam current under these conditions is typically a few hundreds of pA.

The PSD used in the experiment is made up of a Z-stack of three micro-channel plates of 50 mm in diameter and a Wedge and Strip anode. The arrival time of each ion at the detector along with the position information is stored separately using the list mode data acquisition \cite{15}. The delayed extraction provides appropriate time spread for time sliced velocity imaging. The central time sliced image of the Newton sphere of ions is obtained by selecting appropriate time window during analysis of the list mode data. This time sliced image corresponds to the ions ejected in a plane parallel to the detector and containing the electron beam axis. This image provides the necessary information on the velocity distribution of the ions.

It is found that the presence of the magnetic field does have an effect on the imaging of H\textsuperscript{−} ions. The most noticeable one is the shift of the entire image away from the centre of the detector. However, this does not cause any undue problem, as the entire image is found to be within the usable area of the detector. The second problem is the marginal distortion in the image from the expected circular geometry. No attempt is made to correct this.

One of the important benefits of the modifications that we have carried out in the present experimental condition is the linearity in the relationship between the velocity and the radius of the velocity map image over a larger velocity ranges. This is verified by determining the radii of the images of O\textsuperscript{−} from \ce{O_2} over the range of electron energies covering the resonance from 4 to 9 eV. Due to finite energy resolution of the electron beam and the DEA cross section not being the same throughout the energy range, the raw data overestimates the radii of the ion images at electron energies below the centre of the resonance, and underestimates that at electron energies above the centre of the resonance. This is rectified by convoluting the electron beam energy profile at the given energy with an ideal ion yield curve, and using the electron energy corresponding to the peak of this function to obtain the kinetic energy of the concerned ion. Using such a procedure with the measured data on O\textsuperscript{−} from \ce{O_2}, the linearity of the radius with initial velocity of the ions is confirmed. With the new voltage conditions and the modified electrodes the VMI of O\textsuperscript{−} from \ce{O_2} is taken and found to be in good agreement with the previous measurements. It also appears that the presence of the wire mesh on puller electrode does not cause any noticeable blurring of the ion image.

3. Results and Discussion
The ion yield curve as a function of electron energy obtained in the setup used is given in figure 1. A typical time-of-flight spectrum of H\textsuperscript{−} ions is given in figure 2. A central slice of 50 ns is selected for obtaining the velocity map image.
3.1. First resonance at 6.5 eV

The velocity map image obtained at the peak of the first resonance at 6.5 eV is shown in figure 3. From this figure, it is clear that the ions are ejected at about right angles to the electron beam with the range of energies starting from zero. The angular distribution of $\text{H}^-$ ions is obtained by integrating the ion counts over the entire range of the radial coordinate and over a 10 degree angular range in the velocity map image. The intensity distribution thus obtained is shown as a function of angle with respect to the electron beam direction in figure 4 along with the other previous measurements [8, 9].
Figure 4. Angular distribution of H$^-$ ions at 6.5 eV electron energy. Previous results are shown for comparison. The data are normalized at 90°. (● Belic et al.$^9$ ▲ Trajmar et al.$^8$ □ our experiment.)

It is clear from the figure that the present results are in good agreement with the earlier reported measurements, including the position of the maximum of the distribution, which is at 100°. Based on the results for H$_2$S by Azria et al.$^{[16]}$, and the observed angular distribution for H$_2$O, Belic et al.$^9$ concluded that the resonant state involved should be $^2B_1$. It is found that p-wave is the lowest allowed partial wave that on capture gives transition from the neutral state of $A_1$ symmetry to the negative ion state of $B_1$ symmetry in the $C_{2v}$ point group $^{[15]}$. In the case of H$_2$S, Azria et al.$^{[16]}$ had shown that for $A_1$ to $B_1$ transition, the DEA differential cross section peaks around 90° with respect to electron beam. (For a molecule of $C_{2v}$ symmetry like H$_2$O, and the neutral state being of $A_1$ symmetry, Azria et al.$^{[16]}$ had shown that the angular distribution would peak at 90° for a transition to $B_1$ symmetry with p-wave capture, which is the lowest allowed partial wave. Similar conclusion could be drawn from the work by Read $^{[17]}$, where he discusses the angular distribution of resonantly scattered electrons from molecules of all possible point groups.) Belic et al.$^9$ have argued that the peak in the angular distribution at 100° may be due to a distortion of the incident electron wave from the plane wave due to direct potential scattering whereas Haxton et al.$^{[11]}$ conclude that this results from the mixing of partial waves in the resonant electronic T matrix.

The intensity distribution along the radius of the image shows the kinetic energy distribution of H$^-$ ions, which in turn represents vibrational and rotational excitation of the OH fragment. In this context, one would expect discrete rings in the kinetic energy distribution corresponding to these vibrational and rotational excitations. Belic et al.$^9$ have reported observing clear peaks corresponding to the vibrational excitation of the OH fragment. However, we are unable to see these rings distinctly in the present VMI data due to the poorer (finite) energy resolution of the electron beam, which is about 0.5 eV.

Though the energy resolution is not sufficient to clearly see the vibrational levels, we attempt to retrieve the intensity distribution of vibrational excitation in the following way. For a given radius the intensity distribution is integrated over the entire angular range of 360°. This is done assuming that angular distribution is independent of the vibrational excitation of the OH fragment. The kinetic energy of the H$^-$ ions is calibrated using the data of O$^-$ from O$_2$ taken at the peak of its excitation function i.e. at 6.5eV electron energy. Based on the bond dissociation energy of O$_2$ and the electron affinity of O, the expected kinetic energy of O$^-$ at the electron energy of 6.5 eV is 1.42 eV. This measured radius of the O$^-$ image corresponding to this energy is then used to normalize the kinetic energy distribution of H$^-$. The distribution thus obtained is shown in figure 5. It is seen from the figure
that the ion kinetic energy peaks at 1.8 eV. This is in conformity with the measurements by Belic et al. [9]. The distribution is then fitted for contributions corresponding to excitation of various allowed vibrational levels of the OH fragment. (In this, the individual contributions of each vibrational level which is energetically possible are considered.) The contributions of allowed vibrational excitations are taken as Gaussians with the same width, but different heights. The width and the heights are used as free parameters and the best fit for them is obtained. The fit provided a standard deviation of 0.3 eV that matches with electron energy spread.

![Figure 5. Kinetic energy distribution of H⁻ from H₂O at 6.5 eV electron energy.](image)

| Vibrational Level | Theory \(^\text{a}\) | Earlier exp \(^\text{b}\) | Present exp. |
|-------------------|------------------|-----------------|-------------|
| 0                 | 1                | 1               | 1           |
| 1                 | 1.08             | 0.83            | 0.82        |
| 2                 | 0.60             | 0.30            | 0.57        |
| 3                 | 0.04             | 0.07            | 0.32        |
| 4                 | -                | -               | 0.25        |

\(^\text{a}\)Haxton et al.[10]  
\(^\text{b}\)Belic et al.[9]

The contribution of each of the vibrational level is given in table 1 along with those measured by Belic et al.[9] and the theoretical calculations of Haxton et al.[10]. It is seen that the contribution of higher vibrational levels in our measurements is larger than those reported by Belic et al. [9] and Haxton et al. [10]. It may be noted that Belic et al. [9] had optimized their spectrometer for relatively energetic ions (around 1.7 eV). They found that the transmission of their ion kinetic energy analyzer in the range of 1 to 3 eV was constant within 20%. No information was provided for the transmission below 1 eV. However, it is expected that the transmission at low energies decreases considerably in the conventional energy analyzers. Unlike the conventional energy analyzers, the transmission for a VMI spectrometer is constant throughout the energy range starting from zero, except for energies large enough to leave the image out of bound of the detector. Thus the kinetic energy distribution obtained at low energies in the present experiment is expected to be more reliable. It is interesting to note that calculated peak in the cross section for the H⁻ channel is at 6.8 eV [10] instead of the measured 6.5 eV. One reason for this shift may be the underestimation of the cross sections for excitation of higher vibrational levels in OH at lower electron energies.
3.2. Second resonance at 8.5 eV

The velocity image of the hydride ions obtained at the second resonance is shown in figure 6. The only existing measurements of angular and energy distribution of H⁻ ions from DEA to water at 8.5 eV incident electron energy is by Belic et al. [9], who used a 127° electrostatic analyser for measuring angle and energy of the H⁻ ions. The data obtained by our VMI technique however does not agree with the measurements of Belic et al. [9]. Under the same experimental conditions, the angular distribution at the first resonance (6.5 eV) matches well with earlier measurements but not at the second resonance. The comparison with the measurement of Belic et al. [9] is shown in figure 7. The H₂O⁻ ion at 8.5 eV is known to proceed through the \(^2\)A\(_1\) symmetry state [9, 12].

![Figure 6. VMI of H⁻ from DEA to H₂O at 8.5eV electron energy.](image)

![Figure 7. Angular distribution of H⁻ ions at 8.5 eV electron energy. The data are normalized at 90°. Present data (■) compared with the results of Belic et al.[9](●)](image)
Our angular distribution data appear to have a fairly broad peak centred at about 80°, (in the vicinity of 90°, which is typically characteristic of B1 symmetry state), with fairly large intensity intensity in the forward and backward scattering angles. An attempt to fit the angular distribution data with the spherical harmonics shows that the anion state includes capture of s, p and d partial waves from the incident electron beam. A detailed analysis and further measurements are being carried out. Currently, we make no conclusion on this observation.

Like in the case of the first resonance at 6.5 eV, we have obtained the kinetic energy distribution of H− ions at second resonance at 8.5 eV (figure 8) and attempted to retrieve the OH fragment vibrational state intensities on the similar lines as in section 3.1. The kinetic energy calibration is done using the data of O− from O2 taken at 8.5 eV. Comparison with Belic’s [9] measurements are shown in table 2.

![Figure 8. Kinetic energy distribution of H− ions from H2O at 8.5 eV electron energy](image)

| Vibrational Level | Earlier exp b | Present exp. |
|-------------------|---------------|--------------|
| 0                 | 1.00          | 1.00         |
| 1                 | 1.91          | 2.93         |
| 2                 | 2.06          | 6.94         |
| 3                 | 1.36          | 10.28        |
| 4                 | 0.85          | 7.98         |
| 5                 | 0.60          | 7.34         |
| 6                 | 0.50          | 4.84         |
| 7                 | 0.41          | 3.44         |
| 8                 | 0.28          | 1.06         |
| 9                 | 0.16          | 0.49         |

bBelic et al. [9]

From table 2, we observe that the relative intensities of the vibrational levels in our experiment are considerably different from that reported by Belic et al. [9]. In their experiment, the H− ions were observed at 50° with respect to the electron beam and the analyzer optics was focused for H− energies.
at 3 eV. Theoretical calculations to determine the $\text{H}^-$ production at a given kinetic energy via the $^2\text{A}_1$ resonance state at 8.5 eV electron energy has been done by Haxton et al. [12]. Their results are in reasonably good agreement with those of Belic et al. [9]. We are in the process of making further measurements to substantiate our finding.

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