



# Absolute cross sections for dissociative electron attachment to NH<sub>3</sub> and CH<sub>4</sub>

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## ABSTRACT

Dissociative electron attachment (DEA) cross sections for NH<sub>3</sub> and CH<sub>4</sub> are measured in a crossed beam apparatus with special care to eliminate discrimination due to kinetic energy and angular distribution of the fragment ions. The cross sections are put on absolute scale using the relative flow technique. The absolute cross sections for the formation of H<sup>-</sup> and NH<sub>2</sub><sup>-</sup> from ammonia and H<sup>-</sup> and CH<sub>2</sub><sup>-</sup> from methane are compared with available data from literature. It is seen that the present results are considerably different from what has been reported before. We also compare the cross sections of the H<sup>-</sup> channel from these molecules along with that from H<sub>2</sub>O to those from organic molecules containing alkyl, amino and hydroxyl groups to examine the extent to which the recently observed functional group dependence in the DEA contributes.

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## 1. Introduction

Dissociative electron attachment (DEA) is an important tool to study the excited states of molecular negative ions apart from the information it provides on the electron–molecule interactions. The radicals and negative ions that result from DEA are important to the chemistry of plasmas and planetary atmospheres, and to astrochemistry. DEA has been shown to be the prime process in the chemical basis of radiation biology. In these contexts the measurement of absolute cross sections for DEA is very important. The absolute cross sections also lead to significant insight into the dynamics of the DEA process.

The DEA cross section,  $\sigma_{\text{DEA}}$  may be written in terms of the capture cross section,  $\sigma_c$  and the survival probability  $p(\varepsilon)$  for the case of diatomic system as [1]

$$\sigma_{\text{DA}}(\varepsilon) = \sigma_c(\varepsilon)p(\varepsilon) \quad (1)$$

$$p(\varepsilon) = \exp\left(-\int_{R_e}^{R_c} \frac{\Gamma_a(R)}{\hbar v(R)} dR\right) \cong \exp\left(-\frac{\tau_d}{\tau_a}\right) \quad (2)$$

where, with  $\Gamma_a$  the autodetachment width,  $v(R)$  the velocity of separation of the products and  $\tau_a$  and  $\tau_d$  are the autodetachment time and dissociation time respectively.  $R_e$  is the equilibrium internuclear separation of the neutral molecule and  $R_c$  is the crossing point of the negative ion potential energy curve with that of the neutral curve, beyond which autodetachment is not energetically possible.

From these equations we can see that the DEA cross section is very sensitive to the lifetime against autodetachment, the potential energy surface of the negative ion as well as its Franck Condon overlap with the initial electronic state of the target neutral molecule. The autodetachment width is a function of the nuclear coordinates. Strong coupling between the electronic and nuclear degrees of freedom dominates the eventual DEA cross sections. The strong isotope effect seen in the DEA process can be understood from this behavior [2]. This also explains the large increase in DEA cross sections if the neutral molecule is in a vibrationally excited state before the electron collision. Several orders of magnitude increase in DEA cross sections have been observed in some of the molecules, just by heating them to several hundred degrees Kelvin prior to electron collision [3].

It was expected that each molecule would have its own unique negative ion resonances as well as the DEA pattern depending on

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the electron–molecule interaction potential and the negative ion state of the molecule concerned. However, the recent observation of functional group dependence in DEA [4] have shown that the basic features of electron attachment to methane, ammonia and water are carried forward to the alkyl, amino and hydroxyl groups respectively in bigger organic molecules. These observations showed that the formation of  $H^-$  is the dominant channel in these molecules and these resonances occur in a specific energy range depending on the C–H, O–H or N–H site involved in the electron capture process. The results were explained as due to the excitation of a valence electron at the particular site resulting in the localization of charge and energy at that site and subsequent dissociation [4]. Functional group dependence and the resultant site specific fragmentation have been observed for several big organic molecules [5–7]. It may also be noted that similarity in electron attachment to water and its alkyl derivatives was observed in the electron transmission measurements by Mathur and Hasted [8]. They had also observed that the electron transmission spectra of benzene derivatives are largely uniform and resemble that of benzene, despite large differences in symmetry [9]. It is also seen that the compilation of data on resonances in aromatic molecules and heterocyclic molecules shows distinctly similar resonance positions in them. [10].

The realization of the functional group dependent DEA provides a boost to the area of electron controlled chemistry as it provides a way of selectively fragmenting a molecule at a given site using electron energy as a control parameter. However, as is expected in the complex dynamics of DEA, functional group dependence may appear only in terms of similar resonance energies, but not in terms of absolute cross sections. Though similarity in absolute cross sections is not expected, a comparison of the absolute cross sections within O–H containing molecules like carboxylic acids and alcohols show similar values [7]. However, they are quite different in what is observed from  $H_2O$ . In this context, it is pertinent to make a similar comparison of the absolute DEA cross sections from the alkyl sites in these molecules with those of methane and of those from the amine sites to those of ammonia. We also note that reliable DEA cross sections for various fragmentation channels in methane and ammonia are not available to date. Also theoretical calculations of DEA for these molecules are nonexistent.

Qualitative aspects of DEA to ammonia have been studied by several workers in terms of identifying the fragment ions and obtaining the ion yield curves as a function of the electron energy [11–15]. These measurements have identified  $H^-$  and  $NH_2^-$  ions as the major products of the DEA arising from two resonances with peak positions at about 5.7 eV and 10.5 eV respectively. Stricklett and Burrow [16] have carried out high resolution measurements on the lower energy resonance using the electron transmission as well as total ion measurements. They found the anion yield curve to be superimposed with a vibrational level structure of the resonant state indicating that the resonance has a long lifetime against autodetachment. Tronc et al. [15] measured the ion yield curves for  $H^-$  and  $NH_2^-$  ions at high energy resolution and observed similar vibrational excitation structure in them. They have also measured the kinetic energy and angular distribution of these fragment ions and identified the lower energy resonance as due to a Feshbach resonance of  $^2A_2'$  ( $D_{3h}$ ) symmetry. As noted by Stricklett and Burrow [16] earlier, Tronc et al. [15] explain the observed vibrational level structure as due to predissociation of the Feshbach state by an overlapping broad  $\sigma^*$  shape resonance.

Though there exist several ion yield curve measurements [11–15] for  $H^-$  and  $NH_2^-$  ions from ammonia the only absolute cross sections are those reported by Sharp and Dowell [17] and Compton et al. [18]. These two groups have reported the total ion cross sections and the partial cross sections for the formation of  $NH_2^-$ .

These sets of measurements show between them a discrepancy of as much as a factor of two in the cross sections.

As for  $CH_4$ , though there exists a fairly large body of experimental and theoretical studies on low energy electron scattering [19], there is very little data existing on the DEA process. Relative ion yield measurements have been reported by Smith [20] and Trepka and Neuert [21]. The only absolute cross section data are the total ion measurements by Sharp and Dowell [22].

Ammonia is important in the context of engineering applications such as plasma reactors for waste treatment or plasma surface treatment. Ammonia and methane are important constituents of outer planets and comets. It is expected that they play a major role in the synthesis of bigger organic molecules in the interstellar medium, particularly the molecules of life [23–25]. The formation of amino acids by the irradiation of ultraviolet light and high energy electron beams on mixtures of ice containing ammonia and other small molecules has been experimentally demonstrated [24,25]. In a similar experiment, acetic acid molecules have been produced by high energy electron irradiation on binary ice mixtures of methane and carbon dioxide ices at low temperature [26]. It is believed that the DEA due to secondary electrons plays a major role in the production of reactive radicals, which eventually lead to the formation of the amino acids. Methane is a crucial minor component of the earth's atmosphere. It is also crucial for applications involving plasma deposition of diamond like carbon films, diamond films and preparation of carbon nanotubes apart from its role in edge plasmas for fusion devices [27].

## 2. Measurements

Our measurements are done in a crossed beam geometry in which the electron beam intersects an effusive molecular beam from a capillary array. The set up has been described earlier [28–30]. However, for the sake of completeness a brief description is given here. The schematic of the experimental set up is shown in Fig. 1. The electron beam is produced by thermionic emission from a heated tungsten filament mounted behind a cathode of Pierce geometry. The 'grid' electrode following the Pierce element is used to pulse the beam. This is done by initially cutting off the DC beam by a suitable negative voltage on the grid with respect to the filament and overriding it with a positive pulse of finite duration. The typical pulse duration in the present experiments was 300 ns. A shielded Faraday cup with a positive bias of about 35 V is used to monitor the electron beam current. The electron beam is collimated by a magnetic field produced by a pair of compact solenoids mounted inside the vacuum chamber. The current of about 1 A produces a magnetic field of about 50 Gauss in a small volume

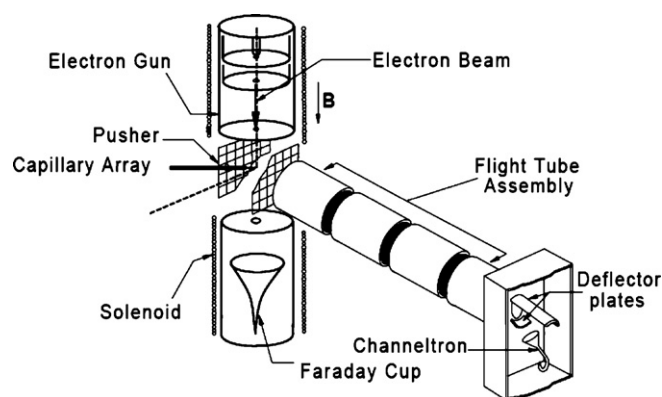


Fig. 1. Schematic of the experiment.

containing the electron gun, the interaction region and the Faraday cup. The ions produced in the interaction region are extracted out using a pulsed electric field produced between two molybdenum wire meshes flanking the interaction region. The wire meshes, having 90% transparency, are 30 mm × 50 mm in extent and separated from each other by 10 mm. These are mounted in such a way that the interaction point is right in the geometric center of the two wire mesh combination. The extracted ions from the interaction region enter a segmented flight tube made up of four cylindrical tubes of 30 mm diameter and varying lengths. Together they form an electrostatic lens, which focuses the diverging beam of ions entering it to the channel electron multiplier mounted at the opposite end and operated in the pulse counting mode. The pulsed extraction field and the segmented flight tube ensure complete collection and detection of the ions independent of their mass, kinetic energies and angular distribution. The detailed discussion on the optimization and care of such a system for cross section measurements have been discussed earlier [28,29] and are carefully followed in the present experiments. The electron energy resolution in the measurements is about 0.5 eV.

One of the additional problems in the present measurements was the contribution due to the background water vapor. This was reduced by baking the gas line and the vacuum chamber to a temperature of about 100 °C, before the measurements. In addition, a liquid nitrogen cooled baffle was used along with the diffusion pump. These provided a base vacuum of a few times  $10^{-8}$  Torr. During measurements, the needle valve and the gas line introducing the gaseous targets into the vacuum chamber were heated to a temperature of about 90 °C. The interaction region including the capillary array was at a temperature of about 70 °C, due to the heating caused by the magnetic coils used for collimating the primary electron beam. The background pressure in the chamber during the experiment was kept at about  $5 \times 10^{-6}$  Torr.

The measurements were carried out in two steps. In the first step, a specific anion was selected using appropriate time window in the time of flight mass spectrometer and the ion yield measured as a function of electron energy. In the data acquisition system that we used, we could simultaneously record the ion yield curves for two different anions along with the electron beam current [28,31]. This allowed accurate normalization of the ion yield curves with the electron beam current. In the second step, the cross sections at the resonance peaks in the yield curves were determined using the relative flow technique [28,32] using  $O^-$  from  $O_2$  [33] as the standard. The cross sections at the peaks were then used to normalize the respective ion yield curves to obtain the absolute cross sections.

The overall uncertainty in the present measurements is estimated to be a maximum of  $\pm 15\%$ . The major contribution to this comes from the uncertainty in the cross section for  $O^-$  from  $O_2$ , which is used as the standard for normalization of the cross sections. The uncertainty in that data is  $\pm 10\%$  [33]. The possible systematic errors arising from the collection and detection efficiency of the ions have been minimized as discussed elsewhere [28]. The systematic error due to the limited electron energy resolution could not be estimated, but is assumed to be small since the resonances in these molecules are found to be relatively broad. The statistical errors in our measurements are mainly arising from the ion count rate. This has been minimized while carrying out normalization of the cross sections to absolute values using the relative flow technique by collecting data for sufficiently long time.

### 3. Results and discussion

Sharp and Dowell [17] and Compton et al. [18] have studied the DEA to  $NH_3$  and  $ND_3$ . A total ion tube and a magnetic mass ana-

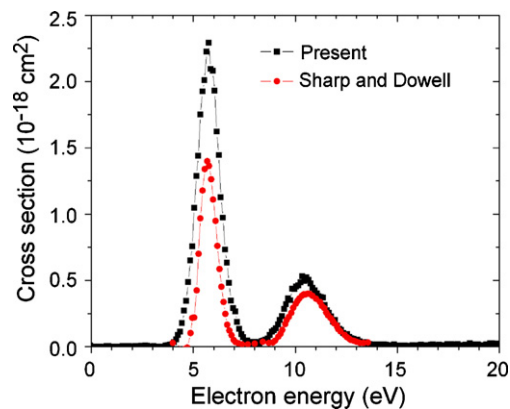


Fig. 2. Cross sections for the formation of  $H^-$  from ammonia (squares, present data; circles, retrieved from Sharp and Dowell [17] using the total ion and the  $NH_2^-$  cross sections).

lyzer were employed by Sharp and Dowell for those studies. They obtained the absolute cross sections for total ion production by normalizing the measured negative ion current in their total ion tube with that for the formation of positive ions at 85 eV. The absolute cross sections for the formation of  $NH_2^-$  were obtained in an indirect way using the magnetic mass analyzer after normalization with the total ion current. Compton et al. used a time of flight mass spectrometer and a total ion tube for their measurements. In addition to  $H^-$  and  $NH_2^-$ , the presence of very weak signal from  $NH^-$  has been reported by Compton et al. at the second resonance, while Sharp and Dowell too did not rule out the presence of very weak signal due to this fragment. We find  $H^-$  and  $NH_2^-$  as the dominant ions in our measurements. We are unable to identify the presence of any  $NH^-$  due to limited mass resolution. Our measured absolute cross sections for the formation of  $H^-$  are given in Fig. 2. In the figure we also provide the  $H^-$  cross sections estimated from the work of Sharp and Dowell by subtracting their  $NH_2^-$  cross sections from their total ion cross sections. In a similar way, the cross sections for the  $H^-$  channel were obtained from the data of Compton et al. [18] at the first resonance peak, and are given in Table 1, along with the results of Sharp and Dowell [17] and the present ones. The positions of the peaks in the present measurements are found to be at 5.7 eV and 10.5 eV respectively, and are in excellent agreement with the results from Sharp and Dowell. As for the absolute cross sections, the results of Sharp and Dowell are only 60% of the present results where as those by Compton et al. are higher by 30% at 5.7 eV. The difference in cross sections at the second resonance appears to be within the combined experimental uncertainties.

The data for the  $NH_2^-$  channel are shown in Fig. 3. The peak positions for this channel are found to be at 5.9 eV and 10.3 eV respectively in the present measurements as compared to 5.65 eV and 9.8 eV respectively found by Sharp and Dowell [17]. Compton et al. [18] also find the  $NH_2^-$  channel peaking at 5.7 eV for the first resonance. They also obtain a rather broad peak above 9 eV and stretching beyond 13 eV. Our data on absolute cross sections at the lower energy resonance agree very well with that of Sharp and Dowell but is 60% lower as compared to that of Compton et al. At the higher energy resonance the present results are about a factor of two larger as compared to Sharp and Dowell, but agree with those of Compton et al. within the combined experimental uncertainties.

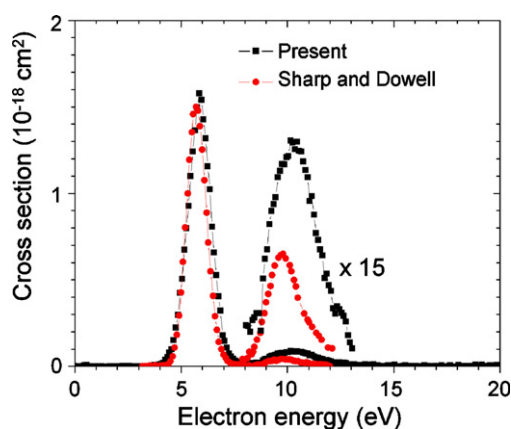
The total ion cross sections from the present measurements are compared with those of Sharp and Dowell and Compton et al. in Fig. 4. The positions of the two peaks in the three sets of data, including the present one, appear to agree well with each other at 5.7 eV and 10.5 eV respectively. At the first resonance, the measurements by Sharp and Dowell give values about half of those reported by

**Table 1**  
DEA cross sections for ammonia

Fragment negative ion	Present results		Sharp and Dowell [17]		Compton et al. [18]	
	Resonance position (eV)	Cross section ( $10^{-18} \text{ cm}^2$ )	Resonance position (eV)	Cross section ( $10^{-18} \text{ cm}^2$ )	Resonance position (eV)	Cross section ( $10^{-18} \text{ cm}^2$ )
$\text{H}^-$	5.7	2.3	5.65	1.4	5.7	3.1 <sup>a</sup>
	10.5	0.5	10.5	0.38		
$\text{NH}_2^-$	5.9	1.6	5.65	1.5	5.7	2.63
	10.2	0.09	9.8	0.043 <sup>b</sup>	10.6	0.076
Total ion	5.7	3.9	5.7	2.9	5.7	5.74
	10.5	0.6	10.5	0.42	10.6	0.47

<sup>a</sup> Estimated by us using the total ion and the  $\text{NH}_2^-$  channel cross sections from their measurements.

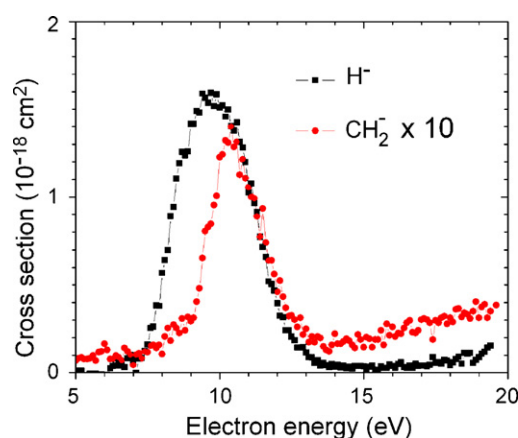
<sup>b</sup> Table 1 in Sharp and Dowell [17] lists the cross section at 10.5 eV as  $0.046 \times 10^{-18} \text{ cm}^2$ , which does not appear to be consistent with the data in their Fig. 5.



**Fig. 3.** Cross sections for the formation of  $\text{NH}_2^-$  from ammonia (squares, present data; circles, Sharp and Dowell [17]).

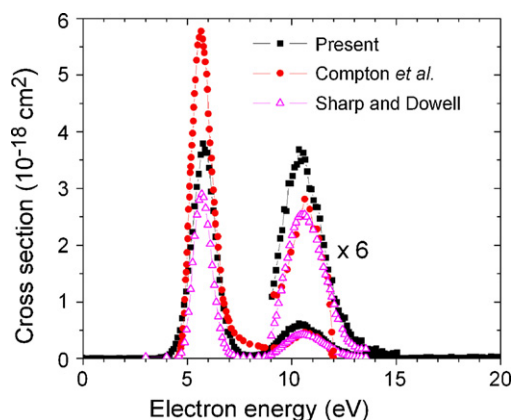
Compton et al., where as the present results are in between. At the second resonance, the results from Sharp and Dowell and Compton et al. appear to agree well with each other, but have considerably lower values as compared to our data. The ratio of the cross sections at the first resonance to that at the second resonance is 6.5 for our data, 6.9 for Sharp and Dowell and 12.2 for Compton et al.

Ion yield curves from methane have been reported by Smith [20] and Trepka and Neuert [21]. They have shown the dominant ions from methane due to DEA to be  $\text{H}^-$  and  $\text{CH}_2^-$ . We also observe these two channels as the dominant ones in our measurements, though due to limited mass resolution we cannot rule out the presence of  $\text{CH}^-$ . The cross sections for the  $\text{H}^-$  and  $\text{CH}_2^-$  channels are given in

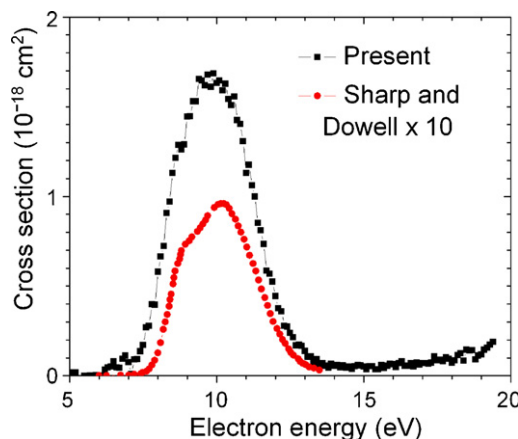


**Fig. 5.** Cross sections for the formation of negative ions from methane (squares,  $\text{H}^-$ ; circles,  $\text{CH}_2^-$ ). The  $\text{CH}_2^-$  data have been multiplied by a factor of 10.

Fig. 5 and in Table 2. The  $\text{H}^-$  channel appears to have a fairly broad peak centered at 9.8 eV, whereas the  $\text{CH}_2^-$  channel has a relatively narrow peak centered at 10.4 eV. The cross sections for the  $\text{CH}_2^-$  channel are an order of magnitude smaller than those for the  $\text{H}^-$  channel. Fig. 6 shows the total ion cross sections from the present measurements along with those by Sharp and Dowell [22]. Sharp and Dowell obtained a broad peak with signatures of two separate processes. The first one they attributed to the  $\text{H}^-$  channel and the second one to the  $\text{CH}_2^-$  channel based on the data by Trepka and Neuert [21]. This is consistent with the present results. However, it appears that their measurements have underestimated the cross



**Fig. 4.** Total DEA cross sections for ammonia (squares, present data; circles, Compton et al. [18]; triangle, Sharp and Dowell [17]).



**Fig. 6.** The total DEA cross sections for methane (squares, present data; circles, Sharp and Dowell [22]). The data from Sharp and Dowell are multiplied by a factor of 10.



**Table 2**  
DEA cross sections for methane

Fragment negative ion	Present results		Sharp and Dowell [22]	
	Resonance position (eV)	Cross section ( $10^{-18}$ cm <sup>2</sup> )	Resonance position (eV)	Cross section ( $10^{-18}$ cm <sup>2</sup> )
H <sup>-</sup>	9.8	1.6		
CH <sub>2</sub> <sup>-</sup>	10.4	0.14		
Total ion	9.9	1.7	10.2	0.095

sections for the H<sup>-</sup> channel by almost a factor of 20. This is manifested as the difference, by a similar factor, in the total ion cross sections as seen in the figure. This appears to be a typical case of discrimination due to the kinetic energy of the ions.

The cross section measurements for a dissociation process, whether for dissociative ionization or attachment, have been known to suffer from errors due to discrimination of energetic ions resulting from dissociation. The kinetic energy of the particles can be larger in dissociative ionization as compared to dissociative attachment. But, the strong anisotropies in the angular distribution of fragments generally observed in dissociative attachment make it more susceptible to the kinetic energy dependent discrimination. While the discrimination can be very acute in partial cross section measurements where one has to use a mass spectrometer, even a total ion measurement technique can suffer from this problem. It may be noted that, in general, almost all the mass spectrometer arrangements and the total ion tube experiments extract ions at right angles to the electron beam direction. Thus the angle dependent discrimination gets acute if the ions are ejected preferentially in the backward and forward directions. There are instances reported in the literature where while the accuracy of a measurement for a particular molecule was cross checked or the measurement normalized to absolute values, using cross sections for another molecule taking care that the kinetic energies of the fragments in both instances were very similar, the fact that the angular distributions in the two cases might have been quite different was overlooked. In such cases, it is likely that systematic errors due to ion discrimination effect still persist. The apparatus that we have employed makes use of a pulsed electron beam and pulsed ion extraction technique along with a segmented time of flight mass spectrometer, and is aimed at eliminating the above ion discrimination effects. As mentioned above, Sharp and Dowell used a total ion tube to determine the total ion cross sections. In that technique, the ions follow trochoidal paths in crossed electric and magnetic fields to the detector. Hence, their detection depends on their initial direction and kinetic energy. Also they normalized their cross sections using the cross section for positive ion formation at 85 eV for ammonia. We believe that the discrimination of ions depending on their kinetic energy and angular distribution may be the reason for the lower cross section values determined by them. It may be noted that the maximum kinetic energy of H<sup>-</sup> ions estimated, based on the bond dissociation energy and the electron affinity of H, at the two resonances could be as much as 1.8 eV and 6.3 eV respectively. It is possible that the ion extraction field used by Sharp and Dowell was insufficient to extract all the ions. The difference in their cross section values from ours for NH<sub>2</sub><sup>-</sup> at the 10.5 eV resonance may also be due to ion discrimination effect. The cross sections for NH<sub>2</sub><sup>-</sup> were determined by Sharp and Dowell using a magnetic mass analyzer. The ions were extracted into this analyzer at 90° to the electron beam. The expected maximum kinetic energies for NH<sub>2</sub><sup>-</sup> ions, again based on the bond dissociation energy and the electron affinity, are about 0.12 eV and 0.4 eV for electron energies of 5.7 eV and 10.5 eV respectively. It may be surprising that even a kinetic energy of 0.4 eV leads to discrimination effects. We believe that these effects in this case are enhanced since our ongoing measurements on angular distribution of ions from ammonia

indicate that at the 10.5 eV resonance NH<sub>2</sub><sup>-</sup> is ejected dominantly in the forward direction.

Compton et al. used a total ion tube and a linear time of flight spectrometer to measure the total cross sections and the partial cross sections respectively from NH<sub>3</sub> and ND<sub>3</sub>. Unlike the data by Sharp and Dowell, the cross section values obtained by Compton et al are higher than our values. We believe that this difference between our data and those of Compton et al. may be due to combination of systematic errors in their measurements. The presence of errors due to kinetic energy discrimination in their data could be seen from the fact that the ratio of the total ion cross sections for the 5.7 eV resonance to that of 10.5 eV resonance is more than a factor of 12 as compared to 6.5 in our data. This clearly indicates discrimination of ions with larger kinetic energies produced at 10.5 eV, as compared to those produced at 5.7 eV. The ion discrimination effect should have lowered the cross sections that they obtained. However, overall the cross sections obtained by them are relatively high. It is difficult to identify the reason for this. The only way this could have happened is if they have underestimated the gas pressure and/or the electron current. It may be noted in this context that measurements on H<sub>2</sub>O from the same lab using a similar set up gave relatively larger cross sections [34]. They mention that their set up was tested by cross checking the O<sup>-</sup> data from O<sub>2</sub>. They also claim reliability of their measurements based on the partial cross section data for the formation of ND<sub>2</sub><sup>-</sup> from ND<sub>3</sub>. The ND<sub>2</sub><sup>-</sup> cross sections were obtained by normalization using O<sup>-</sup> from N<sub>2</sub>O, assuming that the ion kinetic energies and the masses of the two ions are the same. However, the O<sup>-</sup> ions from N<sub>2</sub>O have kinetic energies ranging up to 1 eV with maximum intensity at 0.38 eV [35] as against a maximum kinetic energy of 0.12 eV for ND<sub>2</sub><sup>-</sup> from ND<sub>3</sub> at the electron energy of 5.7 eV. Also the angular distribution of O<sup>-</sup> ions from N<sub>2</sub>O peaks in the forward and backward directions making its efficient detection far more difficult. Thus it is very likely that Compton et al. would have heavily overestimated the cross sections for the ND<sub>2</sub><sup>-</sup> channel by using the linear time of flight spectrometer and normalization with O<sup>-</sup> from N<sub>2</sub>O. Considering this, the consistency check that they have used may be in error.

For the case of methane, the total cross sections were obtained by Sharp and Dowell [22] using a total ion tube. The cross sections were normalized to absolute values using the electron impact ionization cross section at 85 eV. They appear to have missed out the contribution from H<sup>-</sup> to their total ion cross section by as much as a factor 20 in comparison to our results. The contribution from the CH<sub>2</sub><sup>-</sup> channel in their total ion cross section also is lower, but differs from our only by about 50%. We are unable to identify any reason other than ion discrimination effects in their measurements for the lower cross sections obtained by them. The relative differences in the cross sections for H<sup>-</sup> and CH<sub>2</sub><sup>-</sup> from ours are also indicative of kinetic energy discrimination since H<sup>-</sup> ions take away most of the excess kinetic energy.

As mentioned in Section 1, one of the motivations for the present measurements was to investigate the extent of the functional group dependence recently observed in DEA [4]. It is seen that the DEA features for the H<sup>-</sup> channel in H<sub>2</sub>O, NH<sub>3</sub> and CH<sub>4</sub> show up in bigger molecules containing O–H, N–H, and C–H sites respectively. It is also seen that the H<sup>-</sup> channel dominates the DEA process in all

**Table 3**Comparison of DEA cross sections for the H<sup>-</sup> channel from the O–H, N–H, and C–H sites in various molecules

Molecule	O–H site		N–H site		C–H site	
	Electron energy (eV)	Cross section (10 <sup>-20</sup> cm <sup>2</sup> )	Electron energy (eV)	Cross section (10 <sup>-20</sup> cm <sup>2</sup> )	Electron energy (eV)	Cross section (10 <sup>-20</sup> cm <sup>2</sup> )
H <sub>2</sub> O [34]	6.5	460				
NH <sub>3</sub> [present]			5.7	230		
CH <sub>4</sub> [present]					9.8	160
CH <sub>3</sub> COOH [7]	6.7	20			9.1	13 <sup>a</sup>
C <sub>2</sub> H <sub>5</sub> COOH [7]	6.7	8.8			9.1	9 <sup>a</sup>
CH <sub>3</sub> OH [7]	6.4	7.6			10.2	4.3 <sup>a</sup>
C <sub>2</sub> H <sub>5</sub> OH [7]	6.4	7.5			9.3	2.8 <sup>a</sup>
C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> [7]			5.2	5.2		

The source for the cross sections for molecules other than ammonia and methane are shown next to the molecule.

<sup>a</sup> There is some contribution from the O–H sites at these energies.

these molecules. We note that the DEA cross sections for both NH<sub>3</sub> and CH<sub>4</sub> in our measurements are in the range of 10<sup>-18</sup> cm<sup>2</sup>, with the H<sup>-</sup> channel being the dominant one. Comparison of the H<sup>-</sup> channel cross sections for these two molecules along with those of H<sub>2</sub>O [34] and several other organic molecules for which absolute cross sections are available [7] is given in Table 3. It is seen that the H<sup>-</sup> channel from H<sub>2</sub>O also has cross sections of the order of 10<sup>-18</sup> cm<sup>2</sup>, where as for all other molecules these cross sections are significantly lower. Specifically, the peak cross section for the formation of H<sup>-</sup> from water appears to be about two orders of magnitude larger as compared to that from the O–H site in the alcohols and acids. Such difference also exists between ammonia and the N–H sites in isopropyl amine, and between methane and the C–H sites in alcohols and acids. Qualitatively, one expects considerable difference in the DEA cross sections based on the survival probabilities, which are dependent on the autodetachment lifetime of the resonance, the potential energy surfaces and the Franck–Condon factors between the neutral state and the negative ion state. As discussed in Section 1, the DEA cross sections can change dramatically with changes in these parameters. Considering all this, it may not be surprising that there are large differences in the magnitude of cross sections from similar sites in different molecules. Nevertheless, two features of the DEA process in these molecules compel us to investigate other aspects contributing to the cross sections. The first one is that except for the three precursor molecules of the three functional groups, all other molecules show very similar magnitude for the H<sup>-</sup> channel from a given type of bond [7]. The second feature is that in all these cases we are looking at two-body type dissociation with almost the same reduced mass.

Apart from the 'survival probability' it is the capture cross section that contributes to the DEA cross section as given in Eq. (1). What is the extent to which the capture cross sections change from the precursor molecules of the functional groups to the bigger molecules, where those functional groups are present? The functional group dependence observed is based on valence electron excitation, leading to the formation of Feshbach resonances. It is the valence excitation at a particular site that gives the characteristic resonance for that site. The situation is almost identical to having similar optical excitations in molecules containing the same functional group. The optical absorption cross sections for these molecules are of the order of 10<sup>-17</sup> cm<sup>2</sup> within a factor of three for water, methane, ammonia, methanol, formic acid and acetic acid [36] in the bands corresponding to the valence excitation we are considering. Since the dipole transition dominates even in excitation by charged particles, we may assume that the probability for the formation of Feshbach resonances in these molecules to have very similar values. However, what separates the electron collision process from the optical excitation may be the dynamics of

the site selective electron attachment. In order to get captured, it is expected that the electron has to be physically close to the particular site. Though the resonance capture occurs only at the given site, the electron undergoes scattering at other parts of the molecule as well. Included in this is elastic scattering, which generally dominates all others. This process may greatly reduce the available amplitude of the incoming electron wave packet, leading to much lower capture cross sections at a given site. If indeed, such a process plays a role in DEA, it is possible that the cross section for DEA for a particular site may decrease as the molecule gets bigger. Also, depending on whether the particular site is on the outer periphery of a molecule or shielded within by other parts of the molecule, the cross section may change dramatically. This may have important consequences in DEA to biological molecules. It may be pointed out that an electron rescattering model has been recently proposed to explain the observed enhancement in damage to DNA films on electron irradiation [37]. In that model it is shown that the probability for the electron interaction with the spatially extended DNA molecule is increased when the electrons approaching the molecule perpendicular to its long axis is scattered elastically.

#### 4. Conclusion

We have obtained accurate partial and total cross sections for DEA to ammonia and methane, which are important from the point of view of various applications. H<sup>-</sup> formation is found to be the dominant channel in the DEA process in these molecules. The cross sections are in the range of 10<sup>-18</sup> cm<sup>2</sup>, like in the case of H<sub>2</sub>O. The measured partial and total cross sections are considerably different from previous measurements. Our analysis shows that the previous measurements may have suffered from systematic errors, with the dominant contribution coming from ion kinetic energy discrimination. An attempt is made to analyze the effects of the observed functional group dependence in DEA in organic molecules by comparing the absolute cross sections for the H<sup>-</sup> channel from the O–H, N–H, and the C–H sites in the bigger molecules with those from H<sub>2</sub>O, NH<sub>3</sub> and CH<sub>4</sub> respectively. It is seen that the cross sections from the organic molecules are smaller by about two orders of magnitude. One possible reason for this could be the resultant effect of the site specific nature of the electron capture process and the nonresonant scattering by other parts of the molecules.

#### References

- [1] T.F. O'Malley, Phys. Rev. 150 (1966) 14.
- [2] L.G. Christophorou, Electron-molecule Interactions and Their Applications – Vol I, Academic Press, Orlando, Florida, 1984.
- [3] E. Illenberger, in: E. Illenberger, J. Momigny (Eds.), Gaseous Molecular Ions: An Introduction to Elementary Processes Induced by Ionization, Steinkopff/Springer, Darmstadt/New York, 1992.

- [4] V.S. Prabhudesai, A.H. Kelkar, D. Nandi, E. Krishnakumar, *Phys. Rev. Lett.* 95 (2005) 143202.
- [5] S. Ptasinska, S. Deniff, V. Grill, T.D. Mark, E. Illenberger, P. Scheier, *Phys. Rev. Lett.* 95 (2005) 093201.
- [6] B.C. Ibanecu, O. May, A. Monney, M. Allan, *Phys. Chem. Chem. Phys.* 9 (2007) 3163.
- [7] V.S. Prabhudesai, A.H. Kelkar, D. Nandi, E. Krishnakumar, *J. Chem. Phys.* 128 (2008) 154309.
- [8] D. Mathur, J.B. Hasted, *Chem. Phys. Lett.* 34 (1975) 90.
- [9] D. Mathur, J.B. Hasted, *J. Phys. B* 9 (1975) L31.
- [10] J.B. Hasted, D. Mathur, in: L.G. Christophorou (Ed.), *Electron Molecule Interactions and Their Application*, vol. 1, Academic Press, 1984, p. 1.
- [11] M.M. Mann, A. Hustrulid, J.T. Tate, *Phys. Rev.* 58 (1940) 340.
- [12] K. Krauss, *Z. Naturforsch* 16a (1961) 1378.
- [13] C.E. Melton, *J. Chem. Phys.* 45 (1966) 4414.
- [14] J.E. Collin, M.J. Hubin-Fraskin, L. D'Or, *Proceedings of conference held in Berlin, 1967*, in: *Advances in Mass Spectrometry*, vol.4, Institute of Petroleum, London, 1968, p. 713.
- [15] M. Tronc, R. Azria, M.B. Arfa, *J. Phys. B: At. Mol. Opt. Phys.* 21 (1988) 2497.
- [16] K.L. Stricklett, P.D. Burrow, *J. Phys. B: At. Mol. Opt. Phys.* 19 (1986) 4241.
- [17] T.E. Sharp, J.T. Dowell, *J. Chem. Phys.* 50 (1969) 3024.
- [18] R.N. Compton, J.A. Stockdale, P.W. Reinhardt, *Phys. Rev.* 180 (1969) 111.
- [19] C.T. Bundschu, J.C. Gibson, R.J. Gulley, M.J. Brunger, S.J. Buckman, N. Sanna, F.A. Gianturco, *J. Phys. B: At. Mol. Opt. Phys.* 30 (1997) 2239.
- [20] L.G. Smith, *Phys. Rev.* 51 (1937) 263.
- [21] L.v. Trepka, H. Neuert, *Z. Naturforsch* 18a (1963) 1295.
- [22] T.E. Sharp, J.T. Dowell, *J. Chem. Phys.* 46 (1967) 1530.
- [23] J.M. Greenberg, *Surf. Sci.* 500 (2002) 793.
- [24] M.P. Bernstein, J.P. Dworkin, S.A. Sandford, G.W. Cooper, L.J. Almandola, *Nature* 416 (2002) 401.
- [25] P.D. Holtom, C.J. Bennet, Y. Osamura, N.J. Mason, R.I. Kaiser, *Astrophys. J.* 626 (2005) 940.
- [26] C.J. Bennet, R.J. Kaiser, *Astrophys. J.* 660 (2007) 1289.
- [27] W.L. Morgan, *Plasma Chem. Plasma Process.* 12 (1992) 477.
- [28] D. Nandi, S.A. Rangwala, S.V.K. Kumar, E. Krishnakumar, *Int. J. Mass Spectrom.* 205 (2001) 111.
- [29] E. Krishnakumar, K. Nagesha, *Rapid Commun. Mass Spectrom.* 9 (1995) 336.
- [30] D. Nandi, E. Krishnakumar, A. Rosa, W.F. Schmidt, E. Illenberger, *Chem. Phys. Lett.* 373 (2003) 454.
- [31] S.V.K. Kumar, T.S. Anathakrishnan, E. Krishnakumar, V.S. Ashoka, S.K. Kataria, *Rev. Sci. Instrum.* 75 (2004) 2711.
- [32] S.K. Srivastava, A. Chutjian, S. Trajmar, *J. Chem. Phys.* 63 (1975) 2659.
- [33] D. Rapp, D.D. Briglia, *J. Chem. Phys.* 43 (1965) 1480.
- [34] P. Rawat, V.S. Prabhudesai, G. Aravind, M.A. Rahman, E. Krishnakumar, *J. Phys. B: At. Mol. Opt. Phys.* 40 (2007) 4625.
- [35] M. Tronc, F. Fiquet-Fayard, C. Schermann, R.I. Hall, *J. Phys. B: At. Mol. Opt. Phys.* 10 (1977) L459.
- [36] M.B. Robin, *Higher Excited States of Polyatomic Molecules*, vol. III, Academic Press, New York, 1983.
- [37] L.G. Caron, L. Sanche, *Phys. Rev. Lett.* 91 (2003) 113201.