

Dissociative electron attachment to formic acid

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Abstract

Dissociative electron attachment to formic acid (HCOOH) is studied in a crossed beams experiment using mass spectrometric detection of the product ions in the electron energy range 0–15 eV, including the measurement of absolute cross-sections. Unlike the previous reports, we observe the formation of H^- from this molecule, in addition to the fragment negative ions namely O^-/OH^- and HCOO^- , which were observed earlier. The absolute cross-sections indicate that H^- formation is one of the important DEA channels in this molecule.

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1. Introduction

Dissociative electron attachment to formic acid has been reported recently from the point of understanding the behaviour of simple organic molecules under electron collisions [1–3]. These measurements were motivated by the recent observations of small organic molecules in astrophysical objects and the realization that low energy electrons play a major role in radiation damage in bio-molecules. Specific to the case of formic acid, it is one of the organic molecules found in the interstellar medium [4,5]. Traces of formic acid have been detected in the coma of Hale–Bopp comet [6]. Recently, the traces of formic acid were observed in the extensively studied massive star forming region in Orion nebula (Orion-KL) [7,8] and in the Orion molecular clouds (OMC-1) [9] as well as from the SGR B2 [10] which is another massive star forming region in the Sagittarius. Also the detection of formic acid and other simple organic molecules in the IRAS 16293–2422 region

[11], which is a young stellar object has added the general interest in the role of such organic molecules in the chemical processes in star forming regions. All these findings have made the study of interaction of formic acid with free electrons important from Astrophysics point of view. Since carboxylic acids are part of the basic building blocks of various bio-molecular structures [12], their observation in astrophysical objects may have significance to Astrobiology. The electron collision processes on these molecules are important due to possible role of electron-induced chemistry in the formation of bigger biological molecules.

The previous measurements on the DEA to the formic acid [2,3] showed three different resonances peaking at energies 1.25, 7.5 and above 8 eV yielding HCOO^- , OH^- and O^- , respectively, with a ratio of 240:10:1. Absolute cross-sections were also estimated for these channels. The resonance yielding the formate ion, HCOO^- was found to have a sharp onset and having structures on the high energy tail. It is not clear if these structures are due to the vibrational levels of the formate ion as suggested by them or due to different shape resonances. Another striking result of these measurements

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was the absence of H^- channel. It may be noted that the subsequent measurements using the same technique, on similar but bigger organic acids [3,13] have also not shown the formation of H^- . The strong points of these measurements are that they are carried out at high electron energy resolution and good enough mass resolution of 1 amu. However, in these experiments relatively weak electric fields are used to extract the ions along with a quadrupole mass spectrometer for mass analysis. As was pointed out [2], these experiments strongly discriminate against translational energies of the ions. Since H^- ions will carry almost all the kinetic energy of the dissociation process, it is important that the presence of this channel is investigated using a different, but appropriate technique. Moreover, the possibility exists that energetic H^- ions from the acid, if present, could contribute to the chemistry of the environment in which the acid molecule is present.

It is now known that the secondary electrons in the energy range of 0–20 eV produced in the interaction of the high energy radiations with matter are one of the most important species, which bring about the most dramatic physical and chemical changes in the cells. This particular feature has been demonstrated in the form of a single and double strand breaking of the supercoiled DNA on interaction with low energy electrons [14]. In this study, it has been shown that one of the major channels through which this damage takes place is the H^- channel. The importance of H^- channel in DEA to individual DNA bases has also been demonstrated earlier [15]. More recently, electron attachment to ascorbic acid [16] has shown the presence of H^- channel. Since formic acid is the simplest model system to be studied in order to understand the response of more complex bio-molecules like amino acids and proteins to various radiation environments, we felt it necessary to look at the DEA process in this molecule using our apparatus, which is optimized for absolute cross-section measurements and complete collection and detection of all the ions irrespective of their initial kinetic energies and angular distributions.

Our measurements using this apparatus show that the formation of H^- is one of the important channels in the DEA process in formic acid. Moreover, based on the analysis of measurement technique and kinematics, we point out that the structure seen in the $HCOO^-$ cross-sections cannot be due to vibrational excitation of that ion as proposed earlier [2].

2. Experimental

The experimental arrangement has been discussed earlier [17–19]. However, for the sake of completeness a brief description is given below. An effusive molecular beam was allowed to interact with a magnetically colli-

dated and pulsed electron beam derived from a hairpin filament. Typical energy resolution of the electron beam is 0.5 eV. The negative ions formed in the interaction region were extracted using a fairly high, pulsed electric field (typical pulse height ~ 200 V/cm and duration 5 μ s) delayed with respect to the electron pulse by about 100 ns. This ensured complete extraction of all the negative ions formed in the interaction region irrespective of their initial kinetic energies and angular distributions. The Time-of-Flight (ToF) technique was used for the ion transport and detection using channel electron multiplier. In the ToF mass-spectrometer, the flight tube is segmented into four sections and different voltages are applied to each of these sections, making them into an electrostatic lens assembly. This lens is optimized in such a way that all the ions entering it are transported to the end of the flight tube, irrespective of their transverse energy and angle of entry. The high field pulsed extraction and the segmented ToF allows collection and mass analysis of all the ions formed in the interaction region without discrimination, irrespective of their mass, kinetic energy and angular distribution [20].

The single collision condition was ensured by keeping the background pressure not more than 5×10^{-6} torr and hence the pressure in the molecular beam was not more than few times 10^{-4} torr. The needle valve used for introducing the gas and the gas line was heated to about 50 °C. The interaction region including the capillary array was at a temperature of 70 °C due to heating by the magnet coils used for collimating the electron beam. We believe that at this temperature formic acid will be predominantly in the monomer form and very little of the dimers would be present [14]. The contribution to the H^- signal from the background water vapour was suppressed using a cold trap inside the vacuum chamber. The cross-sections were put on the absolute scale using the relative flow technique [17].

The formic acid with a stated minimum purity of 98% was obtained from Riedel-de Haen. In order to get rid of water vapour possibly present in the sample, the acid in the bulb was pumped using a rotary pump till its volume reduced to one third before carrying out the experiments.

3. Results and discussion

A typical mass spectrum of the formic acid consisted of H^- , O^-/OH^- and $HCOO^-$. Due to poor mass resolution of the segmented ToF mass-spectrometer, we could not separate out the O^- and OH^- mass peaks. The absolute cross-sections for the formation of $HCOO^-$ and OH^-/O^- are given in Figs. 1 and 2. Previous measurements [2,3] showed the $HCOO^-$ ion yield curve having a sharp onset at 1.15 eV with the peak position at 1.25 eV. We find the peak in the ion yield curve at

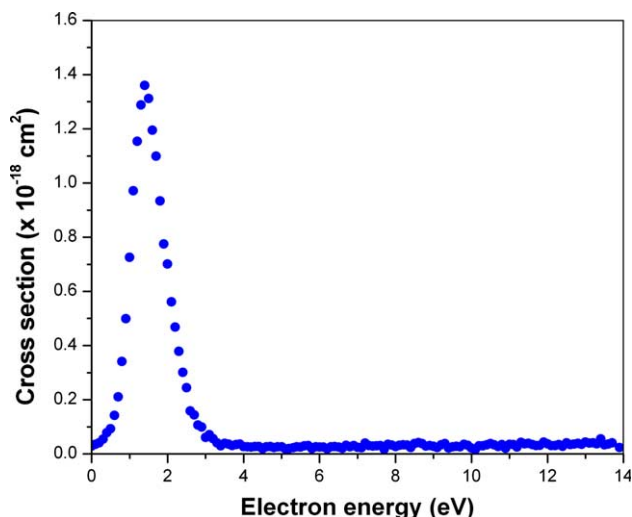


Fig. 1. Absolute cross-section of HCOO^- from HCOOH as function of electron energy.

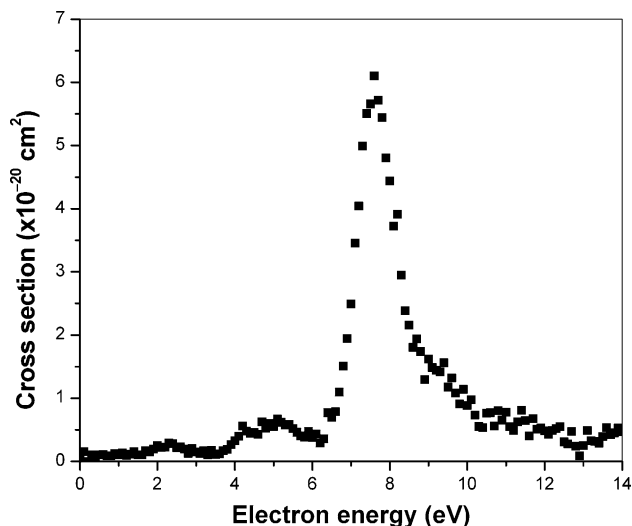


Fig. 2. Absolute cross-section of O^- and OH^- from HCOOH as a function of electron energy.

1.4 eV, and with a slower onset. This could be due to the relatively poor energy resolution in our experiment. The ion yield curve for the O^-/OH^- ions in the present measurements show a peak at 7.6 eV followed by a shoulder at 9.3 eV. This compares well with the ion yield curves from the earlier measurements [2,3], where they observed a peak at 7.5 eV in the OH^- channel and a peak about 9 eV in the O^- channel with an intensity of about one-tenth that of the OH^- channel. We also observed relatively weak structure for the combined O^- and OH^- channel at lower electron energies, which have not been seen in earlier reports. We find that the peak in the 4–6 eV region appears only when we introduce formic acid in the interaction region and hence we attribute it to be due to this molecule. The peak below 4 eV

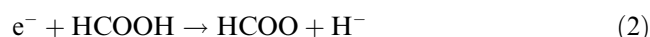
is seen even without any formic acid in the target region and hence is due to some impurity.

The cross-section for HCOO^- channel at the peak energy of 1.4 eV was found to be $1.4 \times 10^{-18} \text{ cm}^2$ and that for combined O^- and OH^- channels at the peak energy of 7.6 eV was found to be $6.1 \times 10^{-20} \text{ cm}^2$. The cross-sections for HCOO^- channel and combined O^- and OH^- channels are in agreement with the earlier estimated cross-sections. Because of the sharp onset of the ion channel, we may have underestimated the cross-section for HCOO^- channel due to poor energy resolution to some extent. These values are on a little lower side as compared to the previously estimated cross-sections [3].

Apart from the above mentioned fragment negative ion channels, we also observed H^- formation as an important channel in the DEA process. This channel shows a main peak at 7.3 eV with a shoulder at about 9 eV as shown in Fig. 3. The absolute cross-section for the main peak is measured to be $1.2 \times 10^{-19} \text{ cm}^2$ and at the high energy shoulder to be $4.9 \times 10^{-20} \text{ cm}^2$.

In all the above measurements, the estimated random error inclusive of the uncertainty in the cross-section for O^- from O_2 used for normalization [21] is estimated to be about 15% at the resonant peaks. The cross-sections were found to be reproducible within a deviation of 5%.

There are two possible channels through which H^- could be formed as given below:



Using available thermochemical data, we have calculated the appearance energy for H^- in these two channels. In the case of channel (1), the thermodynamic threshold for the reaction is calculated using the available data. The enthalpy of formation of COOH^+ , i.e.

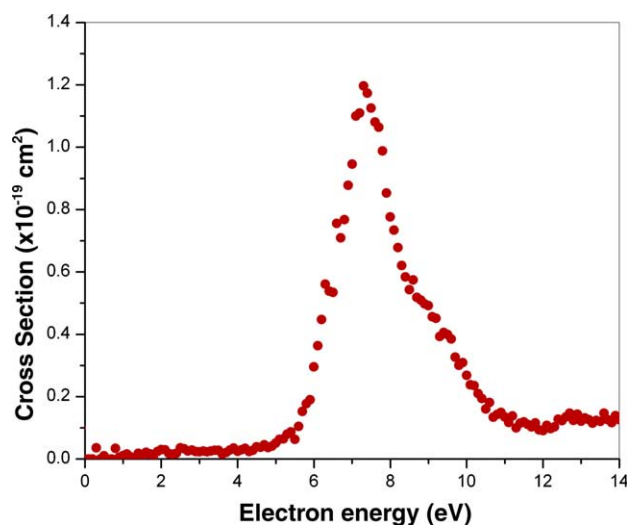


Fig. 3. Absolute cross-section for H^- from HCOOH as a function of electron energy.

$\Delta H_f(\text{COOH}^+) = 597 \pm 8 \text{ kJ/mol}$ [22] and the ionization energy of COOH is $791 \pm 1 \text{ kJ/mol}$ [23]. Hence, $\Delta H_f(\text{COOH})$ becomes $-194 \pm 9 \text{ kJ/mol}$. Knowing the $\Delta H_f(\text{H}) = 218 \pm 0.006 \text{ kJ/mol}$ [24], $\Delta H_f(\text{HCOOH}) = -378.6 \text{ kJ/mol}$ and electron affinity of H ($\text{EA}(\text{H}) = 0.75 \pm 0.004 \text{ eV}$) [25] the appearance energy for H^- is found to be $3.43 \pm 0.1 \text{ eV}$. For channel (2), the bond dissociation energy of $D(\text{HCOO}-\text{H}) = 4.54 \pm 0.23 \text{ eV}$ [2] and the electron affinity for H gives the appearance energy for H^- to be $3.79 \pm 0.23 \text{ eV}$. Within the limited energy resolution in the present experiment, we find the appearance energy for H^- to be about 5.5 eV . This high appearance energy and the fact that most of the ion intensity appears after 6 eV as compared to the calculated thermodynamic threshold indicate that the channels leading to H^- formation will have considerable excess energy. We do not know how much of this excess energy goes into internal excitation of the neutral fragments or their further break up. If all the excess energy appears as kinetic energy, almost all of it will be taken away by the H^- ions due to their low mass. Hence, it is not surprising that the previous measurements failed to observe H^- formation as the apparatus was found to be discriminating ions of large kinetic energy [2].

Considering the electron energy at which the resonances in the H^- channel occur, they appear to be core excited resonances. This is supported by the absorption spectrum of formic acid, which shows the first strong band starting from 55000 cm^{-1} [26]. The first band in the $55000\text{--}61000 \text{ cm}^{-1}$ has been assigned as a valence shell $n'_0 \rightarrow \pi^*_3$ excitation, where n'_0 is the second lone-pair orbital on the keto oxygen atom aligned with the $\text{C}=\text{O}$ axis. The resonance at 7.3 eV may be attributed to a core excited resonance. In a similar way, the broad shoulder at 9.3 eV may be explained as due to a different core excited resonance in accordance with the absorption spectrum in this energy range. We also note that the two resonances seen in the H^- channel appear to decay through the OH^- and O^- channels, respectively. Since both OH^- and H^- appear at the same resonance (about 7.5 eV), one may argue that the H^- formation is exclusively occurring from the OH part of the molecule and not from the CH part. However, the presence of O^- channel in the second resonance does not rule out a possible contribution to H^- from the CH part of the molecule.

The previous measurements by Pelc et al. [2,3] showed sharp structure with an energy spacing of 340 meV in the HCOO^- ion yield curve. These reports discounted the possibility of assigning this ion to COOH^- (which has an expected appearance energy of $0.63 \pm 0.2 \text{ eV}$, calculated using the thermodynamic data mentioned earlier and $\text{EA}(\text{COOH}) = 3.499 \text{ eV}$ [27] as in the case of H^- above) due to the sharp onset seen in the ion yield curve. Because of relatively poor resolution, we do not observe a sharp onset in the cross-sections and

find the peak to have shifted to 1.4 eV , instead of the 1.25 eV as observed earlier by Pelc et al. We are also unable to see the structure observed by them in the HCOO^- ion yield curve, again due to relatively poor energy resolution. This sharp structure was attributed to vibrational excitation in the HCOO^- ion, though the possibility of several closely spaced shape resonances was also not ruled out. Under the assumption that only one resonance is involved, the structure in the ion yield curve could be attributed to the vibrations of either the resonant or the fragments. Experimentally, these two possibilities may be resolved depending on whether the ions are detected in their entirety irrespective of their kinetic energies or only those ions of near-zero energies as shown in the case of CO_2 [28]. Pelc et al. [2] have used similar arguments for the case of HCOO^- . They found that the ion extraction in their apparatus is efficient only for ions of low energy as their measurements on O^- from CO_2 yielded results similar to that obtained by Dressler and Allan [28] for the case of near-zero kinetic energy ions. However, it may be noted that in the case of DEA to formic acid, unlike the case of O^- from CO_2 , the mass ratio of the fragments HCOO^- and H are far too large and hence all the formate ions will necessarily have very little energy. For example, for a total kinetic energy of 1 eV , the formate ion will have only about 23 meV as kinetic energy, which is almost the same as thermal energy at room temperature. Thus, in the measurements of Pelc et al., it is very likely that all the formate ions are detected. Hence, the structure they observed in the ion yield curve in HCOO^- cannot be due to vibrational excitation of the HCOO^- fragment ion. We believe that the observed structure is due to vibrations in the HCOOH^{-*} resonant state as observed in the high resolution electron transmission spectroscopy earlier [29]. The possibility that the structure is due to different resonances may also be ruled out on the basis of the study on the lowest empty orbital in HCOOH using electron transmission spectroscopy and virtual orbital calculations [30].

To conclude, we have measured the absolute cross-sections for the fragment ion formation in DEA to formic acid. We observe the formation of H^- as an important channel in the DEA process, through core excited resonances. We also point out that the structure observed in the HCOO^- ion yield curve is most probably due to excitation of vibrational levels of the negative ion resonance rather than vibrational excitation of the fragment ion.

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References

- [1] A. Pelc, W. Sailer, P. Scheier, N.J. Mason, T.D. Märk, *Eur. Phys. J. D.* 20 (2002) 441.
- [2] A. Pelc, W. Sailer, P. Scheier, M. Probst, N.J. Mason, E. Illenberger, T.D. Märk, *Chem. Phys. Lett.* 361 (2002) 277.
- [3] A. Pelc, W. Sailer, P. Scheier, N.J. Mason, E. Illenberger, T.D. Märk, *Vacuum* 70 (2003) 429.
- [4] J. Ellder, P. Friberg, A. Hjalmarsen, B. Hoeglund, W.M. Irvine, L.E.B. Johansson, H. Olofsson, G. Rydbeck, O.E.H. Rydbeck, *Astrophys. J.* 242 (1980) L93.
- [5] W.M. Irvine, P. Friberg, N. Kaifu, Y. Kitamura, K. Kawaguchi, *Astrophys. J.* 342 (1989) 871.
- [6] D. Bockelee-Morvan, D.C. Lis, J.E. Wink, D. Despois, J. Crovisier, R. Bachiller, D.J. Benford, N. Biver, P. Colom, J.K. Davies, E. Gerard, B. Germain, M. Houde, D. Mehringer, R. Moreno, G. Paubert, T.G. Phillips, H. Rauer, *Astron. Astrophys.* 353 (2000) 1101.
- [7] S.-Y. Liu, J.M. Girart, A. Ramijan, L.E. Synder, *Astrophys. J.* 576 (2002) 255.
- [8] S.-Y. Liu, D.M. Mehringer, L.E. Snyder, *Astrophys. J.* 552 (2001) 654.
- [9] J.M. Hollis, J.A. Pedelty, L.E. Synder, P.R. Jewell, F.J. Lovas, P. Palmer, S.-Y. Liu, *Astrophys. J.* 588 (2003) 353.
- [10] G. Winnewisser, E. Churchwell, *Astrophys. J. Lett.* 200 (1975) L33.
- [11] S. Cazaux, A.G.G.M. Tielens, C. Ceccarelli, A. Castets, V. Wakelam, E. Caux, B. Parise, D. Teyssier, *Astrophys. J. Lett.* 593 (2003) L51.
- [12] G.A. Kumar, Y. Pan, C.J. Smallwood, M.A. McAllister, *J. Comput. Chem.* 19 (1998) 1345.
- [13] Andrzej Pelc, Wolfgang Sailer, Pau Scheier, Tilmann D. Märk, Eugen Illenberger, *Chem. Phys. Lett.* 392 (2004) 465.
- [14] B. Boudaiffa, P. Cloutier, D. Hunting, M.A. Huels, L. Sanche, *Science* 287 (2000) 1658.
- [15] H. Abdoul-Carime, P. Cloutier, L. Sanche, *Radiat. Res.* 155 (2001) 625.
- [16] Hassan Abdoul-Carime, Eugen Illenberger, *Chem. Phys. Lett.* 390 (2004) 481.
- [17] E. Krishnakumar, K. Nagesha, *J. Phys. B* 25 (1992) 1645.
- [18] D. Nandi, S.A. Rangwala, S.V.K. Kumar, E. Krishnakumar, *Int. J. Mass Spectrom.* 205 (2001) 111.
- [19] D. Nandi, E. Krishnakumar, A. Rosa, W.-F. Schmidt, E. Illenberger, *Chem. Phys. Lett.* 373 (2003) 454.
- [20] E. Krishnakumar, K. Nagesha, *Rapid Commun. Mass Spectrom.* 9 (1995) 336.
- [21] D. Rapp, D.D. Briglia, *J. Chem. Phys.* 43 (1965) 1480.
- [22] The NIST Chemistry WebBook, Available from: <http://web-book.nist.gov/>.
- [23] B. Ruscic, M. Schwartz, J. Berkowitz, *J. Chem. Phys.* 91 (1989) 6780.
- [24] M.W. Chase Jr., *NISTJANAF Thermochemical Tables*, fourth ed., *J. Phys. Chem. Ref. Data*, Monograph 9 (1998) 1.
- [25] K.R. Lykke, K.K. Murray, W.C. Lineberger, *Phys. Rev. A* 43 (1991) 6104.
- [26] Melvin Robin Higher Excited States of Polyatomic Molecules, vol. II, Academic Press, New York, 1975.
- [27] E.H. Kim, S.E. Bradforth, D.W. Arnold, R.B. Metz, D.M. Neumark, *J. Chem. Phys.* 103 (1995) 7801.
- [28] R. Dressler, M. Allan, *Chem. Phys.* 92 (1995) 449.
- [29] M. Tronc, M. Allan, F. Edard, in: J. Geddes, H.B. Gilbody, A.E. Kingston, C.J. Latimer, H.R.J. Walters (Eds.), *Electronic and Atomic Collisions*, North-Holland, 1987, p. 335.
- [30] K. Aflatoon, B. Hitt, G.A. Gallup, P.D. Burrow, *J. Chem. Phys.* 115 (2001) 6489.