

Calculations of electron impact ionization cross section for simple biomolecules: Formic and acetic acids

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Abstract. Cross sections for single electron-impact ionization of formic acid (HCOOH) and acetic acid (CH₃–COOH) are calculated using the binary-encounter-Bethe model in the energy range from the ionization threshold up to 4000 eV. The present results are compared with available experimental and theoretical data.

1 Introduction

The large interest in the low energy electron (LEE) interactions with biomolecules is related to the fact that such electrons can induce significant number of single and double strand breaks in the DNA [1], and thus play an important role in the ionizing radiation damage to the living cells. On the other hand, LEE interactions with the living cell, the DNA or its large components proceed in many different direct and indirect processes. Therefore, for complete physical description of all events leading to the living cell damage induced by ionizing radiation comprehensive studies on the LEE collisions with the molecular analogues of the living cells subunits and their building blocks are necessary. Moreover, ionizing radiation damage to the living cell is usually modelled with the Monte Carlo track structure codes, in which the complete set of cross sections for ionizing particles collision with the constituents of the cell are needed as input data. In the present contribution we provide cross sections for electron-impact ionization of formic acid (HCOOH) and acetic acid (CH₃–COOH). Both acids can be treated as the simplest building blocks of more complex biomolecules like amino acids. Experimental studies on the electron interactions with formic and acetic acids are not so numerous and have been focused mainly on the dissociative electron attachment (DEA) process [2–3]. Recently, other than DEA processes induced by electron impact on the formic acid have been reported. Differential elastic cross sections (DCS) at incident electron energies from 1.8 to 50 eV have been measured over 1–130° scattering angle range using a crossed electron-target beam apparatus by Vizcaino et al [4]. The same authors presented integral and momentum cross sections derived from measured DCS [4]. Differential and momentum transfer cross sections for elastic scattering of low energy electrons by *trans* formic acid have been calculated with the Schwinger multichannel method with pseudopotentials in the static-exchange plus polarization approximation [5]. Total and ionization cross sections for electron impact on formic acid have been calculated [6] using the multicenter group additivity rule for energies ranging from the ionization threshold to 2000 eV.

Ionization and dissociation processes due to electron and proton impact on formic acid have been studied experimentally by Pilling *et al* [7,8].

The objective of the present work is to provide total cross section for electron impact ionization for formic and acetic acids over a wide energy range starting from the ionization threshold up to 4 keV.

2 Computational procedures

The theoretical approach and computational procedures used in the present work are the same as those in our previous studies [9,10]. Electron-impact ionization cross sections have been obtained with the binary-encounter-Bethe (BEB) method [11]. The electron-impact ionization cross section per molecular orbital is given by:

$$\sigma^{BEB} = \frac{S}{t+u+1} \left[\frac{\ln t}{2} \left(1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t+1} \right], \quad (1)$$

where $u = U/B$, $t = T/B$, $S = 4\pi a_0^2 N R^2 / B^2$, $a_0 = 0.5292 \text{ \AA}$, $R = 13.61 \text{ eV}$, and T is the energy of impinging electrons. Finally, the total cross section for electron-impact ionization was obtained as the sum of σ^{BEB} for all molecular orbitals. The electron binding energy B , kinetic energy of the orbital U , and orbital occupation number N , were obtained for the ground states of the molecules with the Hartree-Fock method using the Gaussian code [12] and Gaussian 6-311G(d) basis set. Because the valence orbital energies obtained in this way usually differ slightly from experimental ones, we performed also the outer valence Green function (ROVGF) calculations of correlated electron affinities and ionization potentials [13] with the Gaussian code [12]. It has been shown [11] that ionization cross sections obtained for many polyatomic molecular targets reproduce well experimental data usually with discrepancies lower than 10%. Moreover, while the BEB formula is the semiempirical one, all quantities necessary to obtain the ionization cross section can be obtained with molecular structure *ab initio* codes [11].

3 Results

Total cross sections for electron-impact ionization of formic and acetic acids at selected collision energies are listed in Table 1. The energy dependencies of these cross sections are also shown in Fig. 1 and Fig. 2, respectively. In the BEB calculation of the ionization cross sections we have used the following energies of the first ionization potential, calculated with the Gaussian code [12]: 11.46 eV for HCOOH and 10.84 eV for CH₃-COOH. For formic acid ionization cross section maximum of $5.26 \times 10^{-20} \text{ m}^2$ is located at 95 eV while the ionization cross section maximum of $7.88 \times 10^{-20} \text{ m}^2$ for acetic acid is peaked at 90 eV.

In Fig. 1 the present cross section for electron-impact ionization of formic acid is compared with the total ionization cross sections derived by Vinodkumar *et al* [6] and measured by Pilling *et al* [8]. There is a very good agreement between the present data and experimental total ionization cross sections [8]. On the other hand the discrepancy in the magnitude of the present data and theoretical cross sections by Vinodkumar *et al* [6] can be easily seen. The observed discrepancy can be related to the different theoretical methods used in the cross section calculations. The ionization data of Vinodkumar *et al* [6] has been derived from inelastic total cross section obtained with the multicenter group additivity rule [6]. It is well known fact that cross sections for electron scattering from molecules obtained with additivity rule can be overestimated especially at the low collision energy range [9]. Moreover, calculated the same

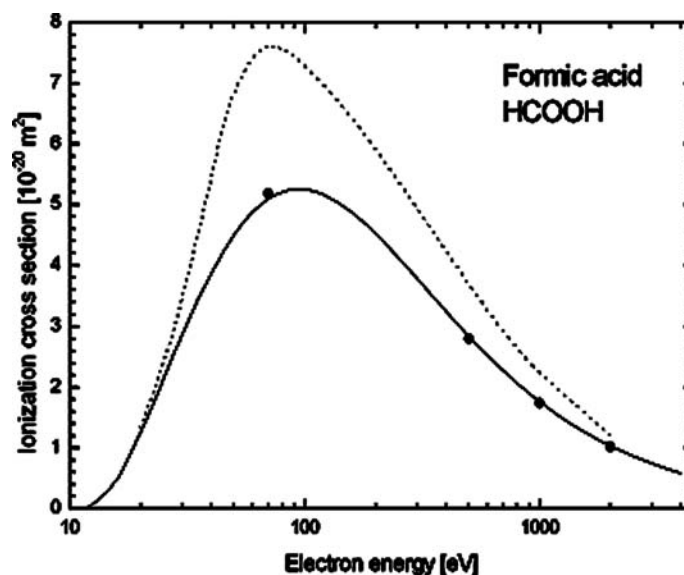


Fig. 1. Cross section for electron-impact ionization of formic acid: (•), total experimental [8], (···) Vinodkumar *et al* [6]; (—), present results.

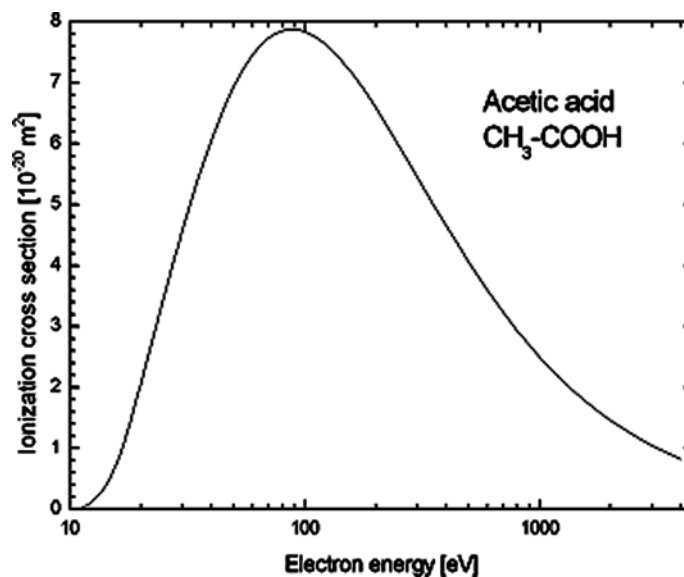


Fig. 2. Cross section for electron-impact ionization of acetic acid: (—), present results.

way [10] as in the present contribution, ionization cross sections for tetrahydrofuran (THF) and tetrahydrofurfuryl alcohol (THFA) combined with the respective elastic integral cross sections [10] reproduce very well experimental absolute total cross sections for THF and THFA [11].

Table 1. Total cross section for electron impact ionization of formic and acetic acids in units of 10^{-20} m^2 .

Energy (eV)	HCOOH	CH ₃ -COOH	Energy (eV)	HCOOH	CH ₃ -COOH
10.84		0.0	65	5.00	7.62
11.0		0.011	70	5.09	7.73
11.46	0.0		75	5.16	7.80
11.5	0.0025	0.045	80	5.21	7.85
12.0	0.033	0.081	85	5.24	7.87
12.5	0.065	0.316	90	5.25	7.88
13	0.117	0.201	95	5.26	7.86
13.5	0.176	0.267	100	5.25	7.84
14	0.235	0.341	110	5.22	7.76
14.5	0.294	0.437	120	5.17	7.66
15	0.358	0.549	140	5.03	7.41
15.5	0.432	0.673	160	4.87	7.14
16.0	0.507	0.803	180	4.70	6.87
16.5	0.592	0.933	200	4.53	6.60
17.0	0.685	1.09	220	4.36	6.34
17.5	0.785	1.24	250	4.13	5.99
18.0	0.883	1.40	270	3.99	5.77
18.5	0.980	1.56	300	3.79	5.47
19.0	1.08	1.73	350	3.49	5.03
19.5	1.17	1.89	400	3.24	4.65
20.0	1.26	2.04	450	3.03	4.33
21.0	1.44	2.35	500	2.84	4.05
22.0	1.61	2.64	600	2.52	3.60
23.0	1.78	2.91	700	2.28	3.24
24.0	1.95	3.18	800	2.07	2.94
25.0	2.12	3.44	900	1.91	2.70
26.0	2.28	3.68	1000	1.77	2.50
27.0	2.44	3.91	1200	1.54	2.18
28.0	2.59	4.13	1400	1.37	1.94
29.0	2.73	4.34	1600	1.24	1.75
30.0	2.86	4.54	1800	1.13	1.59
35.0	3.43	5.40	2000	1.04	1.46
40.0	3.87	6.05	2500	0.866	1.22
45.0	4.22	6.56	3000	0.746	1.05
50.0	4.50	6.95	3500	0.657	0.924
55.0	4.71	7.24	4000	0.588	0.827
60.0	4.88	7.46			

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