

Total, direct and dissociative electron impact ionization cross sections of the acetylene molecule

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The total electron impact ionization cross sections of the acetylene molecule have been measured in the incident electron energy range from threshold to 1000 eV. These results are compared with other existing data, obtained by direct measurements of this molecular property or by indirect ones, *via* the partial ionization cross sections for the formation of different ions. Using three semiempirical equations, the total ionization cross sections were calculated and compared to available data, too. Direct and dissociative ionization cross sections were also calculated by a semiempirical equation and compared to existing data.

Keywords: electron, acetylene molecule, ionization, cross sections, dissociative ionization.

INTRODUCTION

The present measurements of the electron impact total ionization cross sections of the acetylene (C₂H₂) molecule were initiated by two recent papers on partial ionization cross section measurements, those of Zheng and Srivastava¹ and Tian and Vidal.²

There are two reviews on the status of the knowledge of ionization cross sections for hydrocarbons, by de Heer³ and by Tawara *et al.*⁴ The total ionization cross sections for acetylene were measured by Tate and Smith⁵ in the incident electron energy range from the threshold to 750 eV, by Gaudin and Hagemann⁶ between 100 eV and 1000 eV, by Gomet⁷ from the threshold to 500 eV and by Azria and Fiquet-Fayard⁸ from the threshold to 100 eV. Recent measurements by Djurić *et al.*,⁹ from the threshold to 200 eV, have been reported but not published, since it was felt that some additional calibration procedures and cross checks of the target gas pressure were necessary.

The total ionization cross section values of both Zheng and Srivastava¹ and Tian and Vidal,² obtained by summing partial ionization cross sections, are higher than those measured directly by total charge collection in a parallel plate interaction

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chamber.^{5,7,8} This difference can come either from systematic errors in the total charge collection method, or in the methods used for the partial ionization cross section measurements.

Calculated total ionization cross sections have so far been published by Margreiter *et al.*,¹⁰ who developed an analytical formula based on a classical equation of Gryzinski,¹¹ the results of which are consistent with data of Gaudin and Hagemann.⁶

Our intention was to find the cause of the differences among the available sets of data by measuring carefully the total ionization cross section in a parallel plate interaction chamber.

EXPERIMENTAL

In the present experiment, total ionization cross sections were measured using a parallel plate interaction chamber,⁵ basically the same as described in detail by Kurepa *et al.*¹² The interaction chamber ion collection part was the same as in the earlier experiment, except that in front of and behind the parallel plate assembly three pairs of split electrodes were introduced with decreasing gaps toward the center of the interaction chamber (Fig. 1). They were added in order to reduce the inhomogeneity of the electric field as seen by the electron beam while entering and leaving the ion collection region. Their influence was analyzed and proved by an electron ray tracing program. We believe that this improved the knowledge of the incident electron beam energy inside the interaction region, as well as the ion collection efficiency.

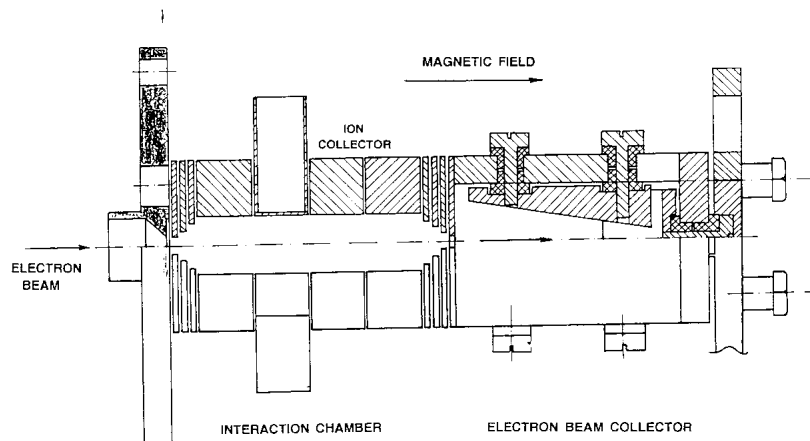


Fig. 1. Scheme of the interaction chamber region of the experimental apparatus used in the present experiments.

The second improvement introduced recently was a new eight segment solenoid with different number of windings, calculated and made following the approach of Overshott and Smith.¹³ The magnetic field distribution was investigated by a Hall probe.¹⁴ This increased the length of the homogeneous magnetic field region inside which the trochoidal electron monochromator,¹⁵ the parallel plate interaction chamber with the two sets of three split-electrodes and the incident electron beam collectors are housed. The consequence was that the electron beam intensity could be kept constant during its energy scanning over a quite wide energy range.

The absolute target gas pressures were determined by a capacitance manometer (MKS, Model 170-6M) and a spinning rotor manometer (MKS, Model SRG-2), both calibrated by the manufacturer,

who claims the exact pressure values to be known with a relative error of ± 0.02 (± 2 %). The relative variations of the gas pressure were monitored by an ionization gauge (Granville-Phillips), and the gas purity checked by a quadrupole mass filter (A.I.G. 50). The temperature of the target gas was measured and monitored inside the interaction chamber by a thermocouple thermometer, to within ± 0.5 K.

The whole apparatus and its operation was thoroughly checked before and after the final acetylene cross section measurements with argon as the target gas. The reason is that its cross sections are well known from recent accurate measurements,¹⁶ that confirm earlier data obtained with the present apparatus.¹² They agree even better with our values obtained during the calibration procedure (with a relative error of ± 5 %),¹⁷ the difference between the two being within 2 %.

CALCULATION OF CROSS SECTIONS

Three semiempirical equations have been used to calculate cross sections, in order to compare their applicability and results with experimentally available data. The first is the classical encounter approximation,¹¹ from which the single ionization cross section is calculated by

$$\sigma_{i,1} = 4\pi a_0^2 \xi_n (\epsilon_{i,H}/\epsilon_{i,n})^2 \left[\frac{u-1}{u} \right]^{3/2} f(u) \quad (1)$$

where a_0 is the Bohr radius, while $\epsilon_{i,H}$ and $\epsilon_{i,n}$ are the ionization potential of the H atom, and the binding energy of the electron in the energy state with the principal quantum number n , respectively. The number of electrons in the subshell with quantum numbers n and l , is denoted by $\xi_{n,l}$. The function $f(u)$ is the form factor

$$f(u) = \frac{1}{u} \left[\frac{(u-1)}{(u+1)} \right] \left\{ \frac{2}{3} \left(1 - \frac{1}{2u} \right) \ln [2.7 + (u-1)^{1/2}] \right\} \quad (2)$$

where $u (= \epsilon_0/\epsilon_{i,n})$ is the normalized incident electron energy ϵ_0 .

The second method¹⁰ is an improved classic equation. It allows calculations of total electron impact ionization cross sections from known properties of the atoms included in the molecule. In this approach, the formula for the total single ionization cross section of an atom is given by

$$\sigma_{i,1} = \sum \pi g_{n,l} < r_{n,l} >^2 \xi_{n,l} f(u) \quad (3)$$

where $< r_{n,l} >^2$ is the mean radius squared of the shell with quantum numbers n and l , and $g_{n,l}$ are weighed factors determined by a fitting procedure using reliable experimental data. In this expression the multiplication factor $(4\pi a_0^2)$ in the original equation was substituted by $(g_{n,l} < r_{n,l} >^2)$, and the term $(\epsilon_{i,H}/\epsilon_{i,n})^2$ omitted.

Apart of these two methods, we also used the semiempiric equation

$$\sigma_{i,\text{tot}} = \sum_{i=1}^n a_i \xi_i \frac{\ln(u)}{\epsilon_0 \epsilon_{i,n}} \{ 1 - b_i \exp [-c_i (u-1)] \} \quad (4)$$

derived by Lotz.^{18,19} The values of parameters a_i , b_i and c_i depend on the orbital from which the electron is ejected.²⁰ Equation (4) was originally derived for calculations of electron impact ionization cross sections of atoms. It is often used

in papers and review papers to interpret measured cross sections of atoms and ions, but also to predict them for atomic species where measurements do not exist, or are very difficult to perform.

The acetylene molecule in the ground state has a $D_{\infty h}$ symmetry, with the electron configuration $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (3\sigma_g)^2 (1\pi_u)^4 - ^1\Sigma_g^+$.^{21,22} Acetylene can be treated as two CH fragments bound to form the molecule, as is standard procedure in molecular structure analysis.²³ In each fragment most of the electronic charge is located around the carbon atom. In an approximate method, the cross section calculation could be approached by treating the two CH fragments as a quasi-nitrogen atom. The ionization cross sections for them can be calculated using Eq. (4) with binding energies of electrons in C_2H_2 molecular orbitals and then

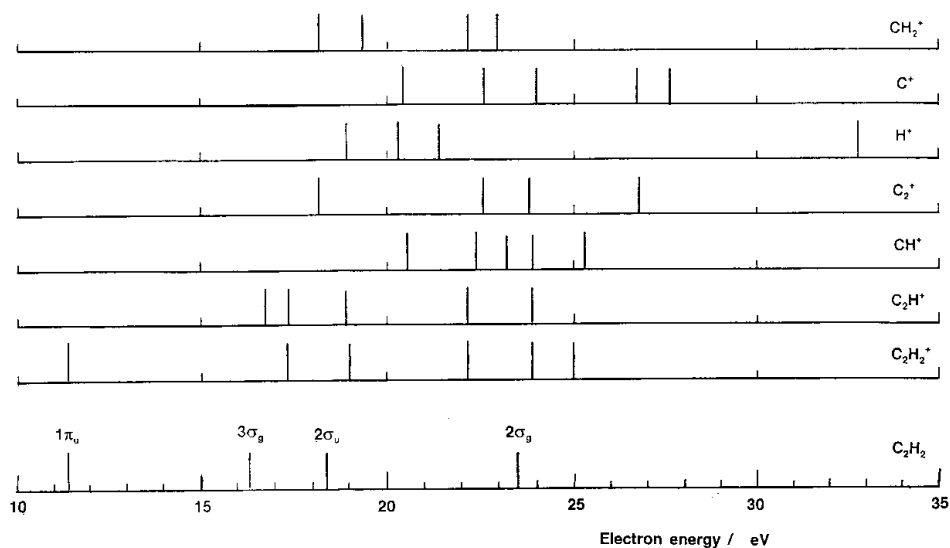


Fig. 2. Graphical representation of the acetylene molecule electron binding energies as measured by Dibeler and Walker,²⁴ Cavell and Allison²⁶ and Cavell,²⁷ Reutt *et al.*,²⁵ Pratt *et al.*,²⁶ Cha *et al.*,²⁷ and appearance potentials of various ions as determined by Tate *et al.*,³³ Williams and Hamill,³⁴ Davister and Loch³⁵ and Zheng and Srivastava.¹

summed to get the corresponding value for the C_2H_2 molecule. The orbital occupation number ξ_i was chosen to be equal to the number of electrons in a particular molecular orbital.

Electron binding energies in different orbitals of the acetylene molecule were measured by photoelectron spectrometry. The value for the electron ejection from the $(1\pi_u)^4$ molecular orbital was determined by different authors to be 11.398 ± 0.005 eV,²⁴ 11.403 ± 0.003 eV,²⁵ and 11.400 ± 0.0004 eV,²⁶ respectively. For the next orbital, $(3\sigma_g)^2$, binding energies of 16.36 eV,²⁸ 16.297 ± 0.005 eV²⁵ and 16.250 ± 0.005 eV²⁷ were obtained. And for the $(2\sigma_u)^2$ orbital a binding energy of 18.38 eV was measured.²⁸ For the $(2\sigma_g)^2$ orbital a value of 23.50 eV was obtained,²⁹

while a value of 291.14 eV for both the $(1\sigma_u)^2$ and $(1\sigma_g)^2$ orbitals was measured,³⁰ since it was impossible to distinguish the difference between the two. All these binding energies are shown graphically in the lower part of Fig. 2.

For each molecular orbital of the acetylene molecule a cross section was calculated, which we call "the orbital electron ejection cross section". These ejection cross sections could then be compared with different experimentally obtained values. The innermost orbitals $(1\sigma_u)^2$ and $(1\sigma_g)^2$ are essentially C(1s) atomic orbitals. Since their binding energies are much larger than all the others, contributions of ejecting these electrons to the total ionization cross section calculated from Eq. (4) was neglected.

TABLE I. Electron impact total ionization cross sections of the acetylene molecule, in units of 10^{-20} m^2

Electron energy/eV	Present results	Electron energy/eV	Present results
12	0.072	100	4.76
14	0.53	150	4.21
16	1.01	200	3.70
18	1.45	250	3.27
20	1.84	300	2.92
22	2.19	350	2.63
24	2.52	400	2.40
26	2.80	450	2.21
28	3.06	500	2.06
30	3.29	550	1.91
40	4.15	600	1.80
50	4.59	650	1.68
60	4.82	700	1.59
70	4.90	750	1.49
75	4.91	800	1.42
80	4.90	900	1.30
90	4.85	1000	1.20

TOTAL IONIZATION CROSS SECTIONS

In the present work the total ionization cross sections were measured in the energy range from the threshold up to 1000 eV. the results are listed in Table I. In order to show more clearly the difference between different sets of earlier measurements and the present one, comparisons were calculated in form $\{[\sigma_{i,\text{tot}}(X) - \sigma_{i,\text{tot}}(\text{JLDK})]/\sigma_{i,\text{tot}}(\text{JLDK})\} \cdot 100$, *i.e.*, as percentages, and are presented in Fig. 3. As can be seen, the present results are in best agreement with the values of Tate and Smith⁵ and Azria and Fiquet-Fayard,⁸ with differences within $\pm 5 \%$. The data of Gaudin and Hagemann⁶ are lower by between 10 % and 5 %, the difference decreasing with increasing electron energy. Those of Gomet⁷ are much higher, with

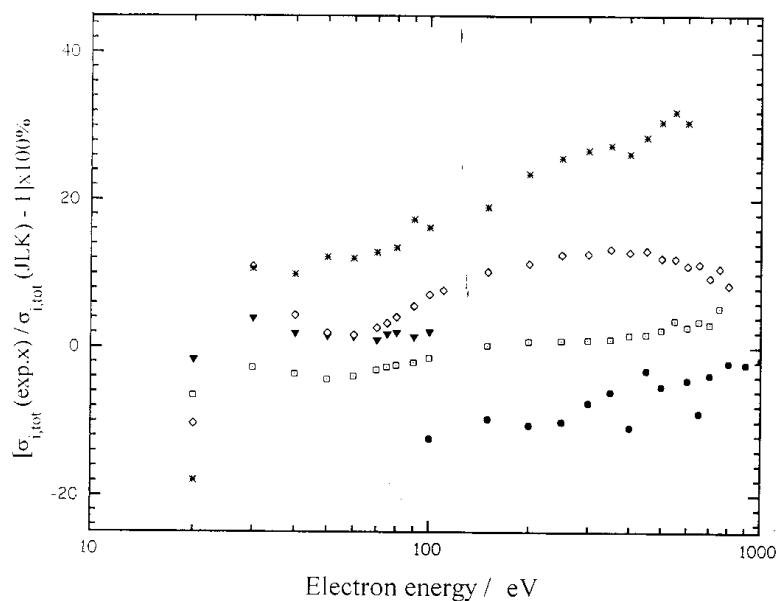


Fig. 3. Comparison of the experimentally determined electron impact total ionization cross sections for the acetylene molecule of various authors to the present data: \square - Tate and Smith¹; \bullet - Gaudin et Hagemann⁶; Δ - Gomet⁷; \blacktriangledown - Azria and Fiquet-Fayard⁸; \diamond - Zheng and Srivastava¹; $*$ - Tian and Vidal².

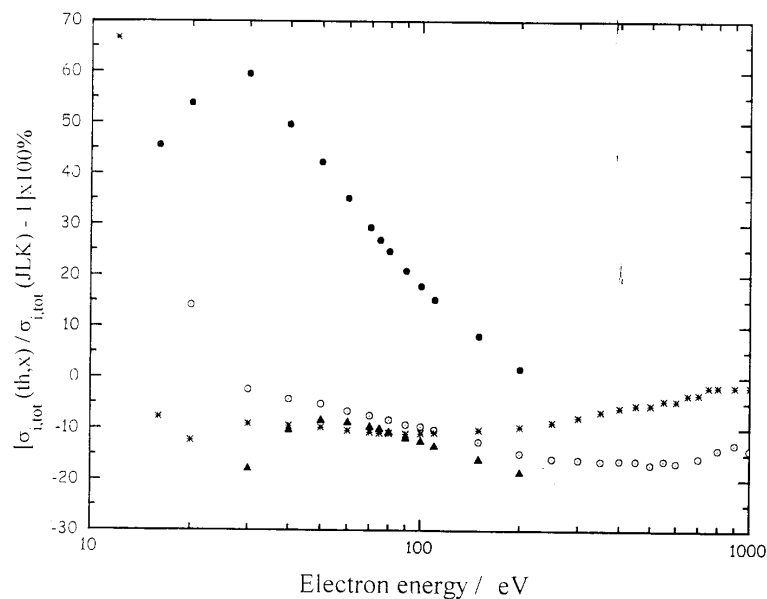


Fig. 4. Comparison of the calculated electron impact total ionization cross sections by various semiempirical or theoretical equations for the acetylene molecule to the present measured data: \bullet - Gryzinski¹¹; \circ - Lotz⁸ (present calculation); Δ - Margeiter *et al.*¹⁰; $*$ - Kim *et al.*¹⁸.

dramatic changes, which prove that the cross section curve is also very different in form. The results of Zheng and Srivastava¹ and Tian and Vidal,² obtained by summing partial ionization cross sections, are higher by about 10 % and 20 %, respectively, with different forms of the cross section curves as well.

The total ionization cross section calculated using the Gryzinski's equation,¹¹ that of Margreiter *et al.*¹⁰ and the Lotz's equation¹⁸ are shown in Fig. 4 also as the percent difference from the present set of values. The results of very recent calculations by Kim *et al.*³⁰ by the BEB (Binary Encounter Bethe) method are also compared to our data. The calculations of Kim *et al.*³⁰ gave the best agreement, the difference being mostly within 10 %. The next best calculated values were those obtained by the Lotz's equation,¹⁸ which agree with the experimental values to within 15 %. Calculations using the Gryzinski's equation¹¹ gave results substantially different from our measured data. Those calculated by the equation of Margreiter *et al.*¹⁰ agree better, but in both these cases the cross section curves have forms different from the experimental one.

PARENT ION FORMATION CROSS SECTIONS

Basic knowledge about the processes of parent ion ($C_2H_2^+$) formation from the acetylene molecule comes from photoelectron spectroscopy. The mass selected yield of the $C_2H_2^+$ ion curve,²⁴ shows a stepwise rise at a photon energy of 11.398 eV, with autoionization features superimposed upon the steps. It has been suggested that parent ions in the ground state $X^2\Pi_u$ are formed, but that a predissociation process could be in competition. The ionization yield at an energy of 16.74 eV is unity, while at 21.21 eV it drops to 0.092.

Photoionization mass spectrometry²⁸ proved that after ejection of an electron from the $3\sigma_g$ molecular orbital, at an energy of 16.36 eV, a broader photoelectron band appears, implying that some bonding character was disturbed. This was assigned to excitation of $C\equiv C$ and $C-H$ stretching modes of the parent ion. Plessis and Marmet,³² on the other side, were the only ones to find that this energy corresponds to the appearance potential of the C_2H^+ ion.

Additional evidence for parent ion formation processes comes from electron impact appearance potential measurements in mass spectrometry experiments. The results of some of them are presented graphically in Fig. 2, to corroborate our approach to the calculations. The first, around 11.40 eV, obtained by different authors, is closely related to the measured electron binding energy of the $1\pi_u$ orbital.

The electron ejection cross section calculated for the valence molecular $1\pi_u$ orbital and the $3\sigma_g$ orbital were summed and compared with the experimentally obtained partial ionization cross sections for the formation of the parent ion by Tate *et al.*,²⁹ Gaudin and Hagemann,⁶ Zheng and Srivastava¹ and Tian and Vidal.² The results are presented in Fig. 5 as percent differences from the data of Tate *et al.*,³³ which were chosen as the most reliable ones, since the total cross sections obtained

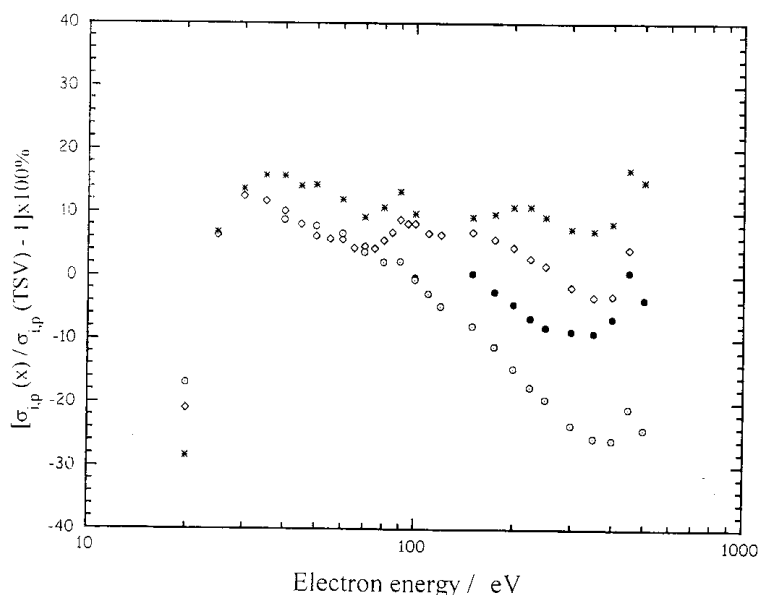


Fig. 5. Comparison of the experimentally determined electron impact partial ionization cross sections for the formation of the parent ion C_2H_2^+ of the acetylene molecule to data of Tate *et al.*³³; * - Gaudin and Hagemann⁶; \diamond - Zheng and Srivastava¹; * - Tian and Vidal²; \circ - Lotz¹⁸ (present calculation).

by this group⁵ were in excellent agreement with the present ones. As can be seen from Fig. 5 the partial ionization cross section curves of different experimental measurements have different shapes. The measurements of Zheng and Srivastava¹ agree with those of Tate *et al.*³³ to within $\pm 15\%$. Those of Gaudin and Hagemann⁶ are lower by about 10 % at higher energies. The measurements of Tian and Vidal,² which are more than 10 % higher, show the biggest difference. The cross sections calculated by the Lotz's equation¹⁸ show very big differences both in the cross section values and the shape of the cross section curve.

DISSOCIATIVE IONIZATION

Other ions formed in dissociative processes following an electron impact with the C_2H_2 molecule: C_2^+ , CH^+ , C^+ , H^+ , CH_2^+ , and C_2H^+ , all have appearance potentials higher than 18.38 eV, the binding energy of the electron in the $2\sigma_u$ orbital (see Fig. 2). Branching ratios for different dissociative ionization processes have been only crudely derived from experimental data, and are known only for a few incident photon energies.²¹

On the basis of data, available from photoelectron mass spectrometry, it was concluded that the ejection of an electron from any of the inner molecular orbitals of the acetylene molecule, except the outermost $1\pi_u$ and $3\sigma_g$ ones, leads to dissociative ionization into one of the possible dissociation channels. In order to corroborate this assumption, electron ejection from the next two orbitals, $2\sigma_u$ and $2\sigma_g$,

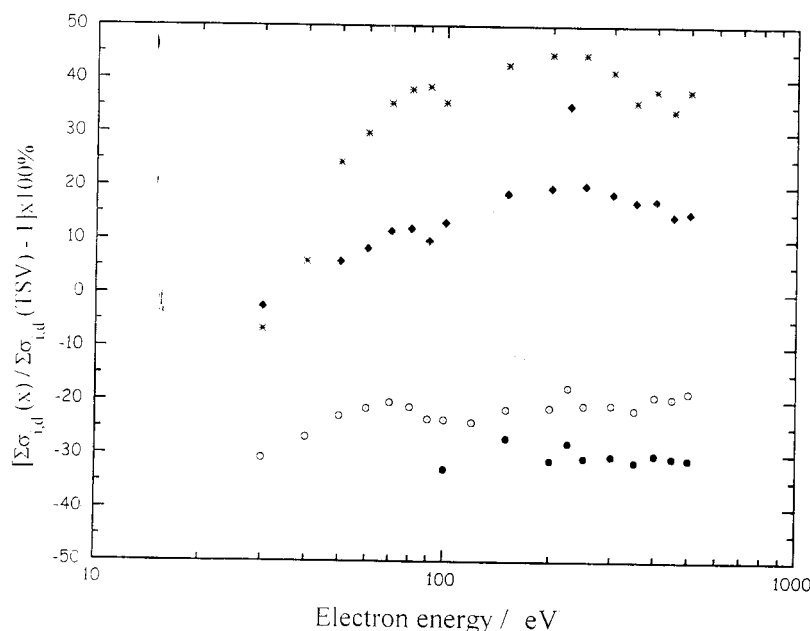


Fig. 6. Comparison of the experimentally determined, and calculated electron impact total partial ionization cross sections for dissociative processes of the acetylene molecule to the data of Tate *et al.*³³ ●- Gaudin and Hagemann;⁶ ◇- Zheng and Srivastava;¹ *- Tian and Vidal²; ○- Lotz¹⁸ (present calculation).

have been calculated using the Lotz's equation,¹⁸ summed and then compared to the sums of all partial ionization cross sections, except to the one for the formation of the parent ion, as measured by Tate *et al.*,³³ Gaugin and Hagemann,⁶ Zheng and Srivastava¹ and Tian and Vidal.² The results are presented in Fig. 6 in the form of percent differences to the values of Tate *et al.*³³ The data of Zheng and Srivastava¹ are higher by up to 20 %, depending on the incident electron energy, while the values of Gaudin and Hagemann⁶ are 30 % lower. The biggest difference is in the data of Tian and Vidal,² since they are higher by even 40 %. The values calculated by the Lotz's equation¹⁸ are lower than the experimental ones of Tate *et al.*³³ by around 20 %, which is acceptable for this type of approximate calculation.

CONCLUSIONS

Careful examination of the data presented in Fig. 3 leads to conclusion that the existing sets of measurements of the total electron impact ionization cross sections of the acetylene molecule are still not sufficiently consistent. The differences in the cross section values between the present measurements, and those of Tate and Smith,⁵ Azria and Fiquet-Fayard⁸ are within ± 5 %, which is acceptable. The shapes of cross section curves are, however, different, which is rather strange since the same method, total charge collection, was used in all three of these

experiments.

The calculated total ionization cross section by Kim *et al.*³¹ by the BEB method, and by the Lotz's equation,¹⁸ as can be seen from Fig. 4, are also in good agreement with experiments.

The situation is worse in the case of the partial ionization cross section for the formation of the parent molecular ion. The differences are much bigger (see Fig. 5), especially in the forms of the cross section curves. It seems obvious that serious problems do exist in the efficiencies of ion extraction in experiments of this kind.

The differences are also very big in cross sections for dissociative ionization processes, as can be seen from Fig. 6. Strangely enough, in this case the difference in the shapes of the cross section curves is less pronounced.

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ИЗВОД

ЕФЕКТИВНИ ПРЕСЕЦИ ЗА ТОТАЛНУ, ДИРЕКТНУ И ДИСОЦИЈАТИВНУ ЈОНИЗАЦИЈУ МОЛЕКУЛА АЦЕТИЛЕНА УДАРОМ ЕЛЕКТРОНА

ГОРАН ЈОСИФОВ, ДРАГАН ЛУКИЋ, НАДА БУРИЋ И МИЛАН КУРЕПА

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Тотални пресеци за јонизацију молекула ацетилена мерени су у домену енергија упадних електрона од прага до 1000 eV. Ови резултати упоређени су са другим постојећим подацима, добијеним непосредним мерењима ове молекулске особине, или посредним мерењима преко парцијалних пресека за јонизацију уз настанак различитих јона. Применом трију семиемпиријских једначина прорачунати су тотални пресеци за јонизацију и упоређени са расположивим експерименталним подацима. Пресеци за непосредну и дисоцијативну јонизацију такође су прорачунати применом семиемпиријских једначина и упоређени са постојећим подацима.

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