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Cross sections of the electron impact dissociative ionization of CO, CH₄ and C₂H₂

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Abstract. The cross sections of the electron impact ionization and dissociative ionization of CO, CH₄ and C₂H₂ have been measured for electron energies from threshold to 600 eV. The present values agree with the previous measurements where a complete collection of the resulting ions has been demonstrated experimentally. However, for the processes where no complete collection has been demonstrated, the present results are usually higher if the ions are produced with higher kinetic energy. The present measurement demonstrates the complete collection of the ions experimentally and the results are thus believed to be reliable. The disagreement between the present results and the previous ones is explained by noting the kinetic energy distributions of the fragment ions.

1. Introduction

The cross sections of the electron impact ionization and the dissociative ionization of the atoms and molecules are important in modelling plasma processes and understanding the production of ions and the extensive ion–molecule reactions in atmospheric science. In order to get the cross section data, almost all the existing mass spectroscopic techniques have been applied which include quadrupole mass spectrometers (QMS) [1–5], time-of-flight (TOF) mass spectrometers [6–8], fast-neutral-beam techniques together with energy analysers [9–14], cycloidal mass spectrometers [15, 16], double-focusing section field mass spectrometers [17, 18], etc. To obtain reliable cross section values, it is necessary to demonstrate the complete collection of all the ions produced in a particular ionization or dissociative ionization process. This is especially true for the ions produced in the dissociative ionization of molecules which usually attain the kinetic energy of a few electronvolts, and very easily escape collection. A QMS has the advantage of high mass resolution. However, the ions in the QMS move on complicated trajectories under the radio frequency electric field. The transmission efficiency of the ions is thus mass and energy dependent. Although the mass-dependent transmission of the ions can be calibrated [19], the energy-dependent transmission is almost impossible to calibrate since the kinetic energy of the ions is dependent on the particular electron energy, the mass of the ions, and the dissociation channels. The fast-neutral-beam technique of Wetzel *et al* [9, 11] and Tarnovsky *et al* [14] has the advantage of access to unstable molecules such as radicals [14] and metastable particles [11]. The complete collection of the ions is checked by deflecting the ion beam and observing the deflection curves. The experiment has demonstrated the complete collection for the direct ionization of atoms and molecules. However, for ions produced by the dissociation of

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molecules, the experiment showed incomplete collection. In order to obtain the cross sections for the fragment ions, the authors made a correction to the detected ion current. The correction factors are achieved through the deflection curves [12]. The measurement is thus indirect and unreliable. The recent work of Lindsay *et al* [20] on the dissociative ionization of SO_2 also suggested the inaccuracy of the correction in the fast beam measurement to the energetic fragment ions. The double-focusing sector field mass spectrometer developed by Märk and co-workers has very high mass resolution, but the system discriminates seriously against the energetic ions and the collection efficiency decreases by about two orders of magnitude for ions with kinetic energies from thermal energy to 10 eV [18]. In order to get more accurate values, the authors correct the collection efficiency relying on the calculated collection efficiency. In this correction the kinetic energy of the ions must be known. Since this kinetic energy is determined by many factors, as already mentioned, the correction process is complicated which makes the results unreliable [18]. Because of the different advantages and disadvantages in the different techniques, the agreement between the different results is not satisfactory. The argument for the disagreement is usually focused on whether energetic fragment ions are completely collected or not. However, without a direct demonstration of the complete collection of all the ions, the measurement is of limited value. To our knowledge, for measuring the partial cross sections only the very recent work of Straub *et al* is conclusive [20–24] except those measurements with a focusing TOF mass spectrometer developed recently by the present authors [25]. In the work of Straub *et al*, the ions are detected by a position-sensitive detector, the complete collection of the ions is demonstrated by observing the local distribution of the ions. In the focusing TOF mass spectrometer of the present work, the complete collection is checked by observation of the deflection curves. If a flat top on the deflection curves is observed, we have demonstrated that we collected all the ions.

In this paper we will report the measurement of the cross sections of the ionization and the dissociative ionization of CO , CH_4 , C_2H_2 at the electron energies from threshold to 600 eV. CO is important because after H_2 it is the most abundant molecule in the interstellar medium and an important constituent in stellar and planetary atmospheres and comets. CH_4 is important in chemistry, in discharge phenomena and also in stellar atmospheres. C_2H_2 is also an important molecule since it is the simplest molecule among the hydrocarbons. It is also present in the interstellar medium and plays an important role in plasma physics and in the semiconductor industry. The knowledge of the dissociative ionization of these molecules will help us to understand the chemistry in the interstellar medium and the plasma dynamics.

Cross sections for the electron impact ionization and dissociative ionization of CO have been measured by Vaughan [27], Defrance and Gomet [28], Hille and Märk [29] with a double focusing mass spectrometer, Orient and Srivastava with a QMS and Freund *et al* [11] with a fast beam technique. Among them, only Freund *et al* demonstrated the complete collection for the parent ion. CH_4 has been measured with the cycloidal mass spectrometer by Adamczyk *et al* [15], with a QMS by Chatham *et al* [2], Orient and Srivastava [4], and recently by the present authors [26], with the fast beam technique by Tarnovsky *et al* [14] and with a short-path TOF mass spectrometer by Straub *et al* [24]. The work of Tarnovsky *et al* is reliable for the parent ions, only that of Straub *et al* demonstrated the complete collection for all the ions. The cross sections for the dissociative ionization of C_2H_2 have been measured with a magnetic sector by Gaudin and Hagemann [30] and with a QMS and TOF mass spectrometer by Zheng and Srivastava [7]. None of the latter measurements demonstrated the complete collection in the experiments. We will compare our measurements with previous results, especially with those where a complete collection has been demonstrated experimentally.

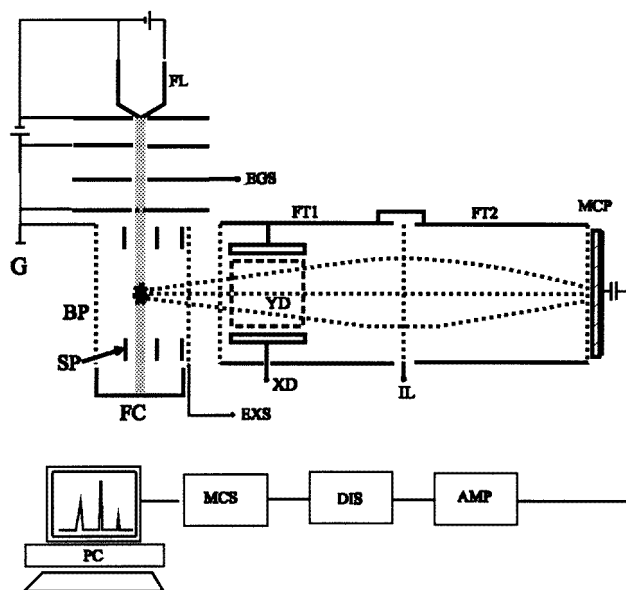


Figure 1. Experimental arrangement of the TOF mass spectrometer. FL—filament, EGS—electron gun switch, FC—Faraday cup, G—ground, BP—backing plate, SP—shield plate, EXS—ion extraction switch, YD—Y deflector, XD—X deflector, FT1—flight tube 1, FT2—flight tube 2, IL—ion lens, MCP—microchannel plate, AMP—amplifier, DIS—discriminator, MCS—multichannel scaler, PC—personal computer.

2. Experimental

The experimental set-up of figure 1 has been described in detail in a previous paper [25] except for some minor modifications. Briefly, a continuous molecular beam is crossed with a pulsed (100 ns) electron beam at right angles. As a modification a skimmer with a diameter of 1.27 mm was added below the needle. The top of the needle is about 2 cm above the skimmer and the skimmer is about 6 cm above the electron beam. Experiments show that with the skimmer the molecular beam is significantly narrowed. The interaction region is less than $4\text{ mm} \times 4\text{ mm} \times 4\text{ mm}$, which is thus much smaller than that in our previous work on CO_2 [25]. Consequently the complete collection can be achieved more easily. Since the skimmer and the needle are far from the interaction region, the extraction field of the mass spectrometer is not distorted, the mass resolution of the mass spectrometer has been greatly improved. About 100 ns after the decay of the electron beam, a pulsed extraction field is applied, the ions are thus extracted into a specially designed focusing time-of-flight (FTOF) mass spectrometer. The shield plates in the interaction region of the FTOF make the extraction mesh perform as a plano-convex lens, which focuses the ions close to the axis of the FTOF mass spectrometer when the ions leave the ion source region, and also makes the divergence angle smaller than that in a normal extraction system. The flight tube of the FTOF mass spectrometer is segmented into two tubes of identical length, with a fine mesh in between. The fine mesh performs as a symmetrically spherical lens when the voltage applied to it is about 1.3–1.4 times of the voltage on the flight tubes. It makes the detection plane the image of the acceleration plane. In the experiments the voltage applied to the extraction mesh is typically -0.6 kV , that on the flight tubes is -1.27 kV , and that on the focusing mesh is -1.70 kV . Experimentally the complete collection of the ions is

verified by deflecting the ion beam, and observing the deflection curves. If a flat top can be observed in the deflection curve, we conclude that all the ions have been collected by the detector.

The absolute cross sections of the molecules are obtained by normalizing the ion counts to those of a well known gas such as argon. First, the ion counts of argon are recorded for electron energies with a particular backing pressure. Second, the molecules to be measured are used with the same backing pressure and all other experimental conditions are kept unchanged and the ion counts of these molecules are also recorded. The pressure of the molecules in the small chamber above the needle is kept low enough so that the gas flow is in the effusive flow region. The absolute partial cross sections (e.g. C^+ from CH_4) are obtained by

$$\sigma_{C^+} = \frac{I_{C^+}}{I_{Ar^+}} \sigma_{Ar^+}, \quad (1)$$

where I is the number of counts. Argon is used as the reference gas because its ionization cross section has been well established. In this work, the very recent result of Straub *et al* has been taken as the reference value [21].

The CO used in our experiment has a purity of 99.995%, CH_4 of 99.995%. However, the purity of acetylene is only about 99%.

The errors in the cross sections of the fragment ions relative to the total values originate mainly from the data fluctuations in the measurements. Usually we make at least five independent measurements and get the data fluctuations from these independent measurements. The electron current measurements, the electron gun reproducibility and the pressure measurements do not contribute to the error of the relative measurements since all the ions are measured at the same time. The counts from the background gas are measured without the molecular beam and are usually less than 2% of the total count rate and are subtracted from the total count rate. In determining the absolute cross sections, the error of the pressure measurements (less than $\pm 2\%$) and the uncertainty of the cross sections of the reference gas ($\pm 3.6\%$) will contribute in addition. The electron gun reproducibility will also contribute to the error just like the absolute data fluctuations. Assuming that the backing pressure is the same, the gas density in the interaction region is the same for different gases. This assumption may cause some error, but it does not affect the measurement for the cross sections of the fragment ions relative to that of the total values. The general error in the measurements is on the order of 10% if the cross section value is higher than $1 \times 10^{-17} \text{ cm}^2$, otherwise it is on the order of 15%.

3. Results and discussion

In this section the results of the cross sections for CO, CH_4 , C_2H_2 will be presented. Previous results will also be included for comparison and discussion. The total cross section is the summation of the partial values with consideration of the charge.

3.1. CO

A typical mass spectrum of the fragments of CO at 200 eV is shown in figure 2. The observed fragments include the parent ion CO^+ , singly charged fragments such as O^+ , C^+ and doubly charged fragments such as CO^{2+} , O^{2+} and C^{2+} . We can see that the mass peaks of O^+ , C^+ , O^{2+} and C^{2+} are broadened because these fragments carry usually a few electronvolts of kinetic energy. The complete collection of all the ions is demonstrated by

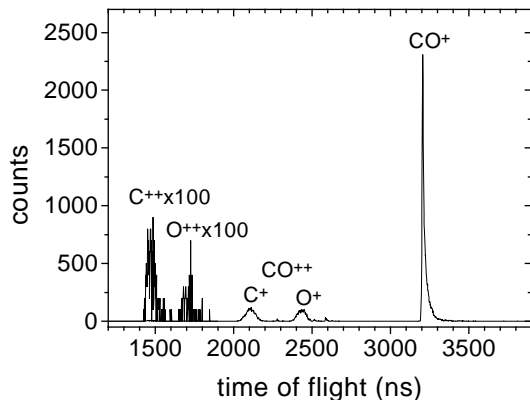


Figure 2. Mass spectrum of CO at an electron energy of 200 eV.

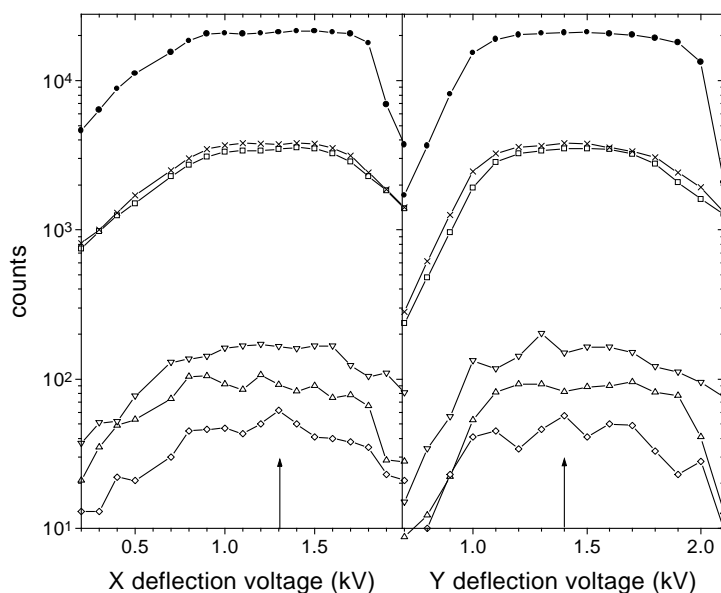


Figure 3. The ion counts produced by the dissociative ionization of CO at an electron energy of 200 eV versus the X and Y deflection voltages. (—●—) CO⁺; (—△—) CO₂⁺; (—□—) O⁺; (—×—) C⁺; (—◇—) O₂⁺; (—▽—) C₂⁺. All the voltages should be considered to be negative. The deflection voltage is fixed to the position indicated by the arrow when the voltage in the perpendicular direction is adjusted. For the cross section measurements the deflection voltages are fixed to both the arrow positions.

the deflection curves in figure 3 which were measured at an electron energy of 200 eV. The voltage in one direction is adjusted and that in the perpendicular direction is fixed to the voltage shown with the arrow in the corresponding graph. We can see that the count rate of the parent ion is constant with the X deflection voltage from −0.9 to −1.7 kV and the Y deflection voltage from −1.2 to −1.8 kV. The counts decrease strongly at the shoulders. There the deflection curves for C⁺ and O⁺ are broader, because the average kinetic energy of these fragments are much larger. However, they still show a flat top for the X deflection voltage from −1.0 to −1.5 kV and the Y deflection voltage from −1.2 to −1.5 kV. The

Table 1. The ionization cross sections for electron impact on CO.

Electron energy (eV)	CO ⁺ (10 ⁻¹⁶ cm ²)	C ⁺ (10 ⁻¹⁷ cm ²)	O ⁺ (10 ⁻¹⁷ cm ²)	CO ²⁺ (10 ⁻¹⁹ cm ²)	O ²⁺ (10 ⁻¹⁹ cm ²)	C ²⁺ (10 ⁻¹⁹ cm ²)
600	0.86	1.27	1.04	3.35	1.77	7.08
550	0.92	1.34	1.11	3.29	2.16	7.57
500	0.98	1.44	1.20	3.31	2.00	7.62
450	1.02	1.56	1.28	3.72	2.41	8.16
400	1.12	1.73	1.45	4.50	2.66	9.04
350	1.19	1.93	1.62	4.57	2.45	9.78
300	1.30	2.18	1.78	5.48	3.34	11.0
275	1.35	2.27	1.91	5.85	3.35	11.6
250	1.43	2.46	2.06	6.69	3.38	11.9
225	1.51	2.65	2.24	7.45	3.35	12.1
200	1.54	2.78	2.33	6.97	3.67	12.5
175	1.63	3.01	2.45	8.51	3.45	12.4
150	1.69	3.17	2.55	7.88	2.41	11.6
125	1.74	3.31	2.58	8.60	1.84	9.44
100	1.82	3.37	2.58	8.21	0.73	5.39
90	1.82	3.27	2.47	7.57	0.51	4.44
80	1.81	3.20	2.26	6.22	0.23	2.43
70	1.78	2.95	1.91	5.34		0.96
60	1.72	2.66	1.53	2.63		0.4
50	1.63	2.21	1.04	0.85		
45	1.53	1.90	0.64			
40	1.45	1.46	0.38			
35	1.33	1.10	0.20			
30	1.04	0.57	0.03			
25	0.74	0.31				
20	0.32					
17.5	0.14					

counts of the doubly charged ions of CO²⁺, O²⁺ and C²⁺ show higher fluctuations, but generally, they are constant with the X deflection voltage from -0.9 to -1.6 kV and the Y deflection voltage from -1.2 to -1.7 kV. Hence, the deflection curves prove that the diameters of the ion beams are much smaller than the effective diameter of the detector and all the ions are therefore completely collected if the deflection voltages are set to the positions indicated by the arrows, i.e. X deflection voltage at -1.3 kV and Y deflection voltage at -1.4 kV.

The cross section values for the ionization and dissociative ionization are tabulated in table 1 and illustrated in figure 4. The results of Rapp and Englarnder-Golden [31], Hille and Märk [29], Orient and Srivastava [4] and Freund *et al* [11] are included for comparison. As pointed out by Hille and Märk, the earlier results of Vaughan [27] and Defrance and Gomet [28] are not accurate and have therefore not been included. For the parent ion (figure 4(a)) the present results differ from the results of Hille and Märk and the more reliable measurements of Freund *et al* by less than 5%. Hence they are in excellent agreement. The result of Orient and Srivastava lies about 15% above our results and those of Hille and Märk and Freund *et al*, but still agree with each other within the combined error limits.

The results for the doubly charged parent ion are shown in figure 4(a), multiplied by a factor of 50, together with the result of Hille and Märk [29]. Our result is about 30% lower than theirs. Earlier work shows that the doubly charged molecular ion CO²⁺ is produced in

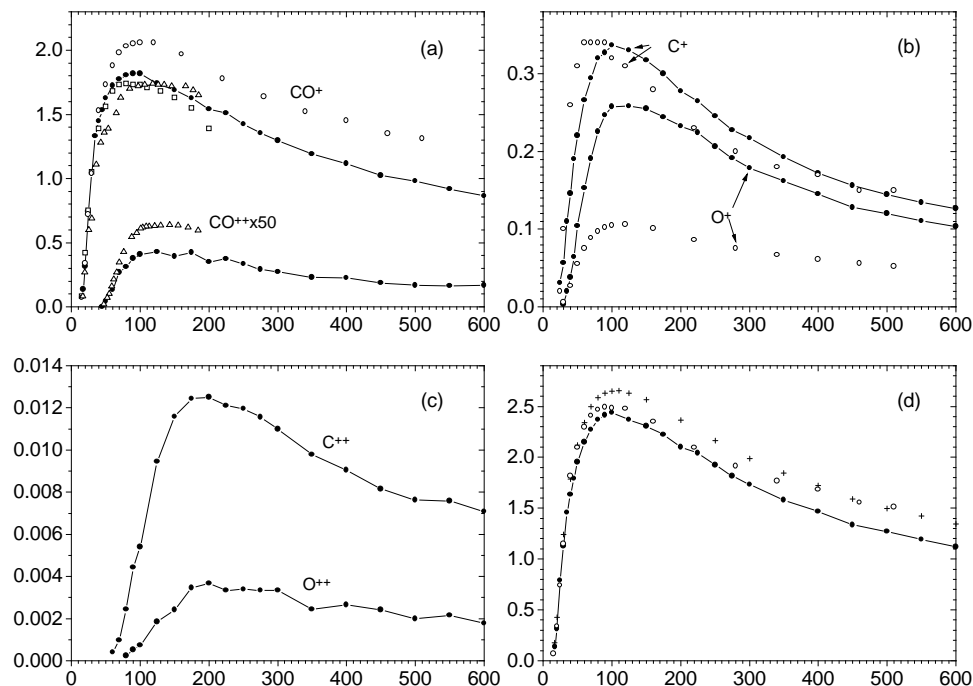


Figure 4. Cross sections of the electron impact ionization and dissociative ionization of CO. The X-axis of all the graphs is in units of eV, the Y-axis is in units of 10^{-16} cm². (a) CO⁺ and CO²⁺ (multiplied by 50). (b) C⁺ and O⁺. (c) C²⁺ and O²⁺. (d) Total cross section. (—●—) this work, (□) the results of Freund *et al* [11], (○) Orient and Srivastava [4], (△) Hille and Märk [29], and (+) Rapp and Englander-Golden [31] are included.

a quasistable electronic state which dissociates spontaneously by unimolecular decay with a mean lifetime of 5–30 μ s [32, 33]. From figure 2 we see that the time between the formation and the detection of CO²⁺ is about 2 μ s. In the work of Hille and Märk the time from the formation to the collection is about 10 μ s, our result should thus be higher than that of Hille and Märk. The uncertainty of the measurement of Hille and Märk is 30%, we believe that our result is accurate within the stated uncertainty under the present experimental conditions.

The cross sections for the singly charged fragments C⁺ and O⁺ are shown in figure 4(b). The only previous results are QMS measurements of Orient and Srivastava [4]. For C⁺ the present result agrees with that of Orient and Srivastava within the combined error limits, whereas the shape of the present result differs. The maximum in the present measurement lies at an electron energy of 100 eV. However, the maximum in the work of Orient and Srivastava lies at an electron energy of about 80 eV which is even smaller than that of the parent ion and seems unlikely. Since in this work all the ions are measured at the same time, we believe that the relative shape of the present measurement is accurate. In strong contrast to C⁺, the present O⁺ value exceeds the result of Orient and Srivastava by a factor of 2.5. The different behaviours in the two measurements can be explained if we note the kinetic energy distributions of the two fragments. The kinetic energy distributions of C⁺ and O⁺ dissociated from CO have been measured by Loch, as shown in figures 1 and 3 in [34]. At 100 eV most of the C⁺ ions are produced with a kinetic energy of less than 1 eV. However, most of the O⁺ ions are produced with a kinetic energy above 1 eV. The

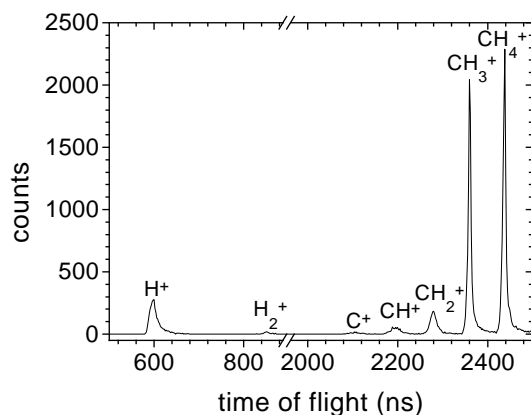


Figure 5. Mass spectrum of CH_4 at an electron energy of 200 eV.

energetic ions cannot be transmitted by the quadrupole mass spectrometer of Orient and Srivastava and thus escape collection. This conclusion is further supported by the work of Knudsen *et al* [35]. These authors measured the cross sections of dissociative ionization of CO by protons and antiprotons impact, they found a better agreement of their results with the electron impact data of Orient and Srivastava [4] for C^+ , whereas a result of a factor of 3 above that of Orient and Srivastava for O^+ . This discussion also supports the conclusion in our previous work on CO_2 [25].

The results for the doubly charged fragments C^{2+} and O^{2+} are shown in figure 4(c). To our knowledge no previous data exist. The appearance potential of C^{2+} lies at 60 ± 3 eV, whereas that of O^{2+} lies at 72 ± 3 eV.

The total cross section for CO is shown in figure 4(d), together with the results of Rapp and Englander-Golden, and Orient and Srivastava. Our results lie about 9% below the result of Rapp and Englander-Golden, but are in excellent agreement with their relative shape. The shape of Orient and Srivastava is different from this work and that of Rapp and Englander-Golden. All the measurements still agree with each other within the combined error limits.

3.2. CH_4

The typical mass spectrum of CH_4 is shown in figure 5. We can see that all the ions are well resolved. The TOF width of the mass peak of CH_4^+ is about 10 ns. The ionic fragments include CH_4^+ , CH_3^+ , CH_2^+ , CH^+ , C^+ , H_2^+ and H^+ . The deflection curves with respect to the X and Y deflection voltages are illustrated in figure 6. For the ions of CH_n^+ ($n = 0-4$), the total counts show a very good flat top with the X deflection voltage between -0.9 and -1.6 kV and the Y deflection voltage between -1.1 kV and -1.8 kV. The H^+ counts show a flat top for the X deflection voltage between -1.0 and -1.5 kV and the Y deflection voltage between -1.2 and -1.6 kV. The shoulders of the deflection curves for H^+ are broader than those of CH_n^+ ($n = 0-4$), suggesting that the average kinetic energy of H^+ is much larger than that of CH_n^+ ($n = 0-4$). The counts of H_2^+ have higher fluctuations, but generally the counts are also constant within the fluctuations for the X deflection voltage between -1.0 and -1.6 kV and the Y deflection voltage between -1.2 and -1.6 kV. The deflection curves show that in the present experiment all the ions from the ionization and dissociative ionization are collected.

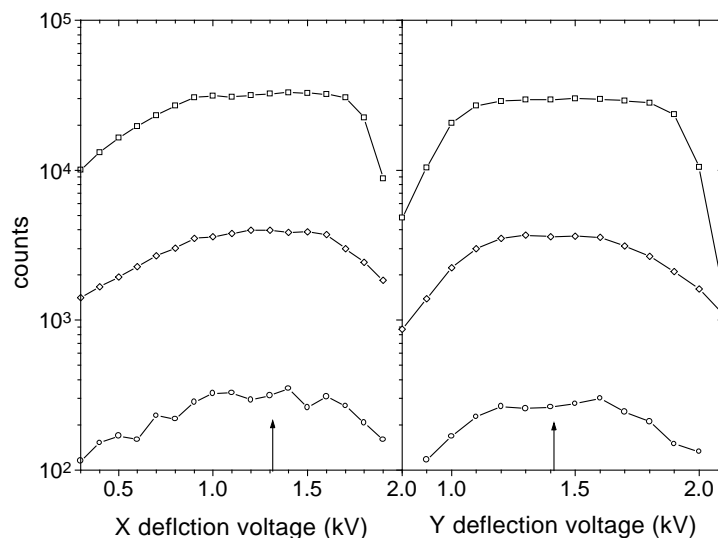


Figure 6. The ion counts produced by the dissociative ionization of CH₄ at an electron energy of 200 eV versus the *X* and *Y* deflection voltages. (—□—) ΣCH_n^+ ($n = 0-4$); (—○—) H_2^+ ; (—◇—) H^+ . All the voltages should be considered to be negative. The deflection voltage is fixed to the position indicated by the arrow when the voltage in the perpendicular direction is adjusted. For the cross section measurements the deflection voltages are fixed to both the arrow positions.

The cross section values are tabulated in table 2. For comparison, our results together with the previous results are also illustrated in figure 7, which includes our previous measurements [26], the data of Straub *et al* [24], Tarnovsky *et al* [14], Orient and Srivastava [4], Chatham *et al* [2] and Adamczyk *et al* [15]. For CH_4^+ (figure 7(a)). All the measurements are distributed within about $\pm 12\%$ in amplitude. Our results lie in the middle and differ from the measurements of Tarnovsky *et al* [14] and Straub *et al* [24] by less than 5% in amplitude. For CH_3^+ (figure 7(b)), the results of Orient and Srivastava [4] and the previous work with a QMS by the present authors lie above the present values. The present results differ from the results of Straub *et al* by about 6%. For CH_2^+ (figure 7(b)) our result is above all the other measurements. However, it agrees with the results of Straub *et al* and Tarnovsky *et al* within the error limits. For CH^+ (figure 7(c)) and C^+ (figure 7(d)), the results from different measurements are distributed within about $\pm 30\%$ of the amplitude. The discrepancy between the present results and those of Adamczyk *et al* [15], Chatham *et al* [2] and Orient and Srivastava [4] exceeds the error limits. Our work agrees with that of Straub *et al* within 10% and both results lie above the other measurements.

For H_2^+ (figure 7(c)) the present results exceed those of Adamczyk *et al* and of Chatham *et al* by a factor of 2. For H^+ (figure 7(e)) our results exceed their results by a factor of 4. However, in both cases our results agree again with those of Straub *et al* within 5% in amplitude.

The kinetic energy of the fragments due to dissociative ionization of CH₄ has been measured by Apell and Kubach [36], Lochter *et al* [37] and Ben-Itzhak *et al* [38]. The measurements show a large number of protons produced by the dissociative ionization of methane with a kinetic energy above 1 eV. These energetic protons may escape collection in the work of Adamczyk *et al* and Chatham *et al*. The average kinetic energy of H_2^+

Table 2. The ionization cross sections for electron impact on CH₄.

Electron energy (eV)	CH ₄ ⁺ (10 ⁻¹⁶ cm ²)	CH ₃ ⁺ (10 ⁻¹⁶ cm ²)	CH ₂ ⁺ (10 ⁻¹⁷ cm ²)	CH ⁺ (10 ⁻¹⁷ cm ²)	C ⁺ (10 ⁻¹⁸ cm ²)	H ₂ ⁺ (10 ⁻¹⁸ cm ²)	H ⁺ (10 ⁻¹⁷ cm ²)
600	0.74	0.62	1.19	0.42	1.47	0.99	0.29
550	0.79	0.66	1.28	0.49	1.63	1.14	0.42
500	0.84	0.70	1.34	0.52	1.90	1.20	1.56
450	0.89	0.73	1.46	0.58	2.02	1.30	1.73
400	0.96	0.80	1.63	0.67	2.39	1.49	1.95
350	1.03	0.87	1.76	0.77	2.78	1.73	2.21
300	1.14	0.96	2.07	0.90	3.33	1.95	2.57
275	1.18	1.00	2.15	0.95	3.57	2.15	2.75
250	1.26	1.06	2.31	1.06	4.11	2.28	3.04
225	1.34	1.12	2.47	1.17	4.44	2.59	3.30
200	1.38	1.14	2.63	1.23	4.85	2.78	3.58
175	1.45	1.20	2.79	1.36	5.35	2.99	3.79
150	1.50	1.24	2.98	1.48	5.66	3.35	4.17
125	1.58	1.32	3.26	1.65	6.20	3.52	4.48
100	1.67	1.40	3.48	1.84	6.87	3.84	4.71
90	1.71	1.43	3.63	1.89	6.79	3.77	4.71
80	1.72	1.43	3.62	1.87	6.44	3.85	4.42
70	1.71	1.42	3.54	1.81	5.72	3.78	4.10
60	1.69	1.39	3.39	1.74	5.15	3.48	3.46
50	1.68	1.36	3.12	1.57	4.26	2.81	2.58
45	1.63	1.31	2.94	1.37	3.68	2.30	2.05
40	1.62	1.29	2.67	1.20	2.72	1.20	1.41
35	1.53	1.21	2.08	0.71	1.42	0.61	0.80
30	1.41	1.08	1.32	0.34	0.64	0.20	0.48
25	1.00	0.69	0.56	0.15	0.09		0.10
20	0.47	0.28	0.30				
17.5	0.26	0.14	0.10				

measured by Ben-Itzhak *et al* is around 2 eV which is apparently too high for complete collection in the earlier work. The average kinetic energies of CH⁺ and C⁺ are in the range 0.1–0.3 eV. However, the present measurement and the work of Straub *et al* show that our previous work [26], the work of Orient and Srivastava and Chatham *et al* in QMS and the work of Adamczyk in cycloidal mass spectrometer cannot collect all the ions.

The total ionization cross section of CH₄ is shown in figure 7(f) together with the results of Rapp and Englander-Golden [31], Nishimura and Tawara [39] and Straub *et al* [24]. All the results agree within the mutual error limits.

3.3. C₂H₂

The mass spectrum of C₂H₂ at the electron energy of 200 eV is shown in figure 8. The ionic fragments include C₂H₂⁺, C₂H⁺, C₂⁺, CH⁺ + C₂H₂²⁺, C⁺ + C₂²⁺ and H⁺. No other doubly charged fragments are observed. We cannot resolve CH⁺ from C₂H₂²⁺, as well as C⁺ from C₂²⁺, since they have the same *m/e* value. The mass peaks of C⁺ and CH⁺ are broadened because of the kinetic energy associated with the ions during the dissociation. Hence the two masses are not completely resolved. This will contribute about 3% to the measurements of these two mass peaks, but does not affect the total value of the two peaks. The deflection curves are shown in figure 9. As in the cases of CO and CH₄, all the mass peaks show a flat top in a particular range of the deflection voltages demonstrating the

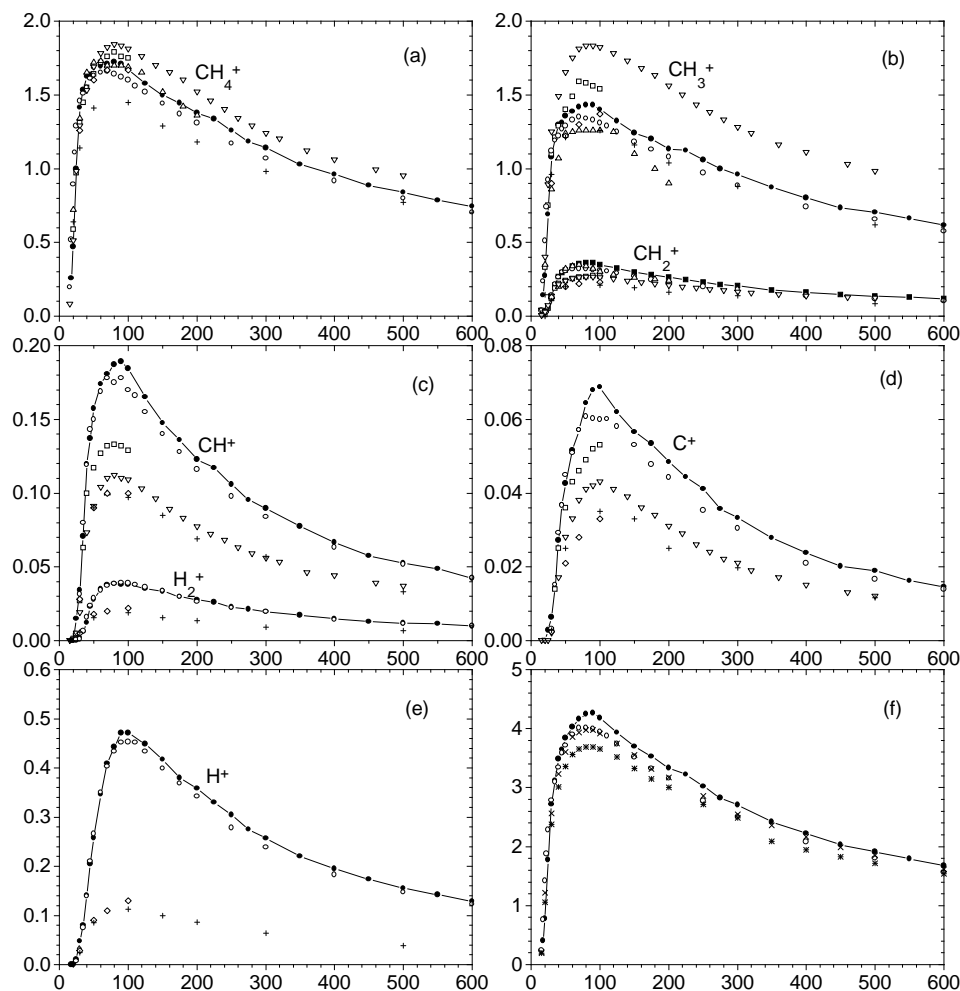


Figure 7. Cross sections of the electron impact ionization and dissociative ionization of CH_4^+ . The X-axis of all the graphs is in units of eV, the Y-axis is in units of 10^{-16} cm^2 . (a) CH_4^+ . (b) CH_3^+ and CH_2^+ . (c) CH^+ and H^+ . (d) C^+ . (e) H^+ . (f) Total cross section. (—●—) the present work, (□) the previous results of the present authors, (○) the results of Straub *et al* [24], (△) Tarnovsky *et al* [14], (▽) Orient and Srivastava [4], (◇) Chatham *et al* [2], (+) Adamczyk *et al* [15], (*) Rapp and Englander-Golden [31] and (×) Nishimura and Tawara [39] are shown.

complete collection of all the ions.

The cross sections for C_2H_2 are tabulated in table 3 and illustrated in figure 10. The previous cross section measurements of Gaudin and Hagemann [30] and Zheng and Srivastava [7] are also included. For the ions with two carbon atoms (figure 10(a)), our results show excellent agreement with the recent results of Zheng and Srivastava [7]. The earlier results of Gaudin and Hagemann are generally lower than our results by about 15%, but still agree with our results within the combined error limits.

For $\text{CH}^+ + \text{C}_2\text{H}_2^{2+}$ (figure 10(b)) generally the present result agrees with the result of Zheng and Srivastava within the combined error limits, but at the peak position, our value lies above theirs by about 30%. The earlier work of Gaudin and Hagemann lost a lot

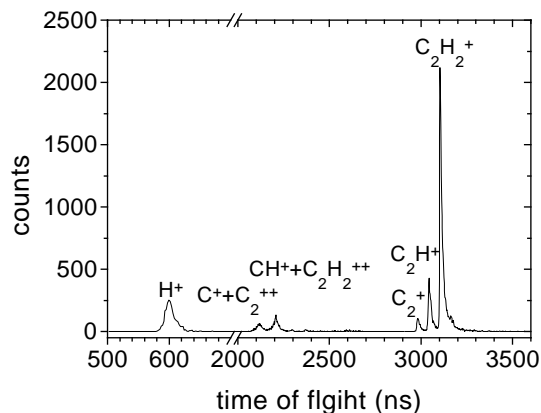


Figure 8. Mass spectrum of C_2H_2 at an electron energy of 200 eV.

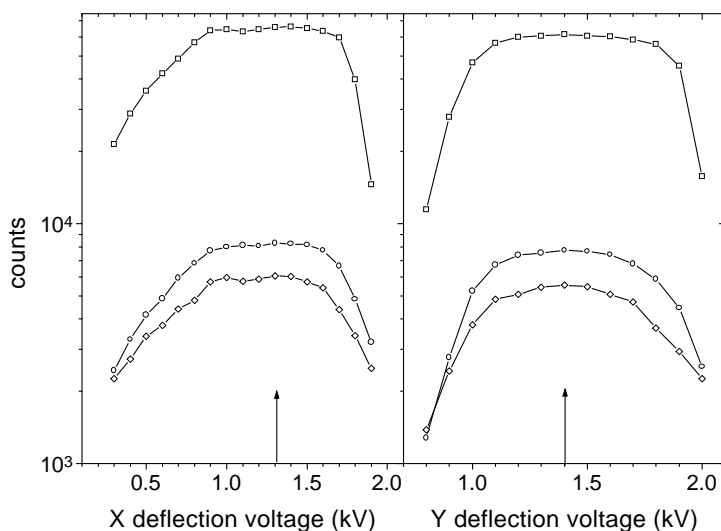


Figure 9. The ion counts produced by the dissociative ionization of C_2H_2 at an electron energy of 200 eV versus the X and Y deflection voltages. $(-\square-)$ $C_2H_2^+ + C_2^+ + C_2^+$; $(-\circ-)$ $C_2H_2^+ + C_2^+ + CH^+ + C^+$; $(-\diamond-)$ H^+ . All the voltages should be considered negative. The deflection voltage is fixed to the position indicated with the arrow when the voltage in the perpendicular direction is adjusted. In the cross section measurements the deflection voltages are fixed to both the arrow positions.

of energetic ions in their detection. For $C^+ + C_2^{2+}$ (figure 10(c)) our results exceed all the previous results at least by a factor of 3 in the peak range. The relative shape of Gaudin and Hagemann is close to the present measurement. The different behaviours of $CH^+ + C_2H_2^{2+}$ and $C^+ + C_2^{2+}$ in the work of Zheng and Srivastava and the present can be explained again by the different kinetic energy distributions of the two groups of ions. As measured by Davister and Loch [40, 41], most of the $CH^+ + C_2H_2^{2+}$ ions are produced with kinetic energies below 1 eV. However, a considerable number of $C^+ + C_2^{2+}$ are produced with kinetic energies above 1 eV. The energetic part of $C^+ + C_2^{2+}$ might be lost in the collection of Zheng and Srivastava [7].

Table 3. The ionization cross sections for electron impact on C₂H₂.

Electron energy (eV)	C ₂ H ₂ ⁺ (10 ⁻¹⁶ cm ²)	C ₂ H ⁺ (10 ⁻¹⁷ cm ²)	C ₂ ⁺ (10 ⁻¹⁷ cm ²)	CH ⁺ (10 ⁻¹⁷ cm ²)	C ⁺ (10 ⁻¹⁷ cm ²)	H ⁺ (10 ⁻¹⁷ cm ²)
600	1.64	3.23	0.70	1.12	0.70	1.35
550	1.75	3.46	0.77	1.23	0.78	1.44
500	1.85	3.70	0.85	1.34	0.84	1.66
450	1.95	3.89	0.89	1.48	0.91	1.73
400	2.09	4.28	0.99	1.64	1.02	1.94
350	2.26	4.62	1.10	1.86	1.15	2.22
300	2.46	5.09	1.24	2.13	1.33	2.60
275	2.54	5.38	1.34	2.25	1.43	2.78
250	2.69	5.67	1.44	2.45	1.59	3.06
225	2.84	5.96	1.55	2.63	1.74	3.37
200	2.95	6.23	1.67	2.89	1.89	3.51
175	3.04	6.56	1.79	3.12	2.02	3.75
150	3.17	6.88	1.94	3.37	2.18	4.03
125	3.28	7.14	2.08	3.65	2.30	4.27
100	3.47	7.62	2.26	3.95	2.40	4.43
90	3.58	7.98	2.37	4.05	2.37	4.40
80	3.59	7.91	2.35	4.08	2.21	4.20
70	3.54	7.93	2.34	3.87	2.02	3.79
60	3.54	7.86	2.28	3.57	1.76	3.22
50	3.50	7.52	2.13	2.99	1.36	2.47
45	3.38	7.26	1.96	2.49	1.10	1.91
40	3.30	6.79	1.76	2.03	0.76	1.32
35	3.15	6.42	1.45	1.45	0.44	0.80
30	2.90	5.21	0.82	0.78	0.20	0.45
25	2.49	3.15	0.22	0.12		0.20
20	1.44	0.75				
17.5	0.85					

For H⁺ (figure 10(c)), the only previous result comes from Zheng and Srivastava. Our results are above theirs by about 15%, but agree with theirs within the mutual error limits of the two experiments, whereas the shape of our measurement differs from theirs. Compared with the group of C⁺ + C₂²⁺ the H⁺ ions are more energetic [42]. The reason why Zheng and Srivastava can detect more H⁺ may be caused by the fact that these authors collected H⁺ with a segmented TOF mass spectrometer, whereas they collected C⁺ + C₂²⁺ with a QMS which lost more energetic ions. In the mass spectra of C₂H₂ we also observed minor peaks at m/e of 27, 15 and 14 which also appeared in the mass spectrum of Zheng and Srivastava [7]. Those at $m/e = 27$ and $m/e = 15$ may come from other isotopes or impurities. The one at $m/e = 14$ may have a contribution from the dissociative ionization of C₂H₂. If this is true, the cross section is smaller than 3×10^{-18} cm² at the electron energy of 200 eV. We also do not exclude the production of H₂⁺, but the cross section is smaller than 5×10^{-19} cm² at the electron energy of 200 eV.

The total cross section is shown in figure 10(d), together with the results of Gaudin and Hagemann and Zheng and Srivastava. Our result agrees with that of Zheng and Srivastava. The result of Gaudin and Hagemann is smaller than our result by 20%, but still agrees within the combined error limits.

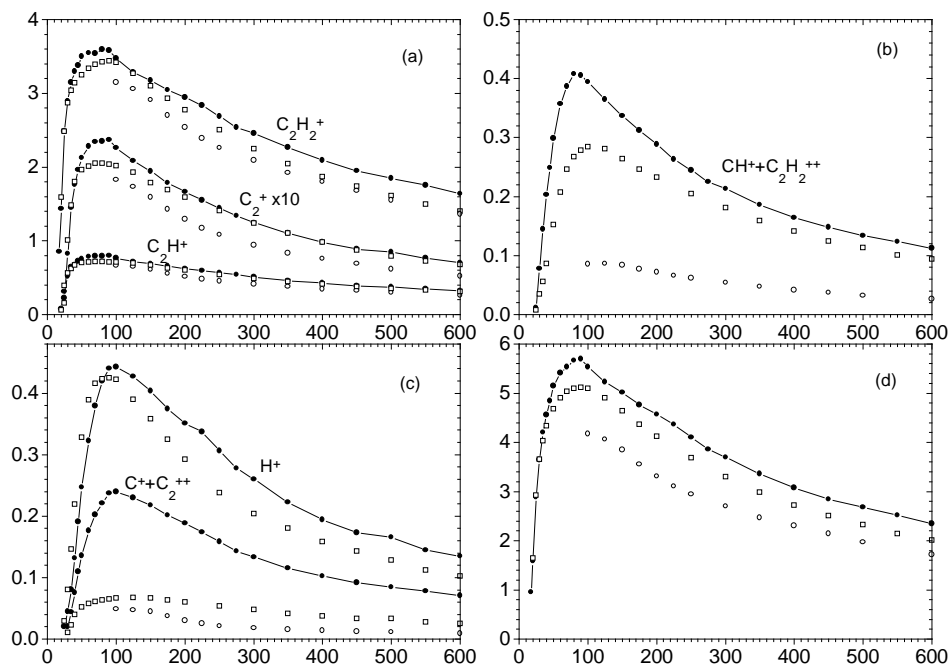


Figure 10. Cross sections of the electron impact ionization and dissociative ionization of C_2H_2 . The X-axis of all the graphs is in units of eV, the Y-axis is in units of 10^{-16} cm^2 . (a) $C_2H_2^+$, C_2H^+ and C^+ (multiplied by 10). (b) $CH^+ + C_2H_2^{2+}$. (c) $C^+ + C_2^{2+}$ and H^+ . (d) Total cross section. (—●—) the present work, (\square) the results of Zheng and Srivastava [7], (\circ) Gaudin and Hagemann [30] are included for comparison.

4. Conclusions

The cross sections of the electron impact ionization and dissociative ionization of CO, CH_4 and C_2H_2 have been measured, as we think, conclusively for electron energies from the threshold to 600 eV. The special design of the experiment makes the tolerance for the detection system to the kinetic energy of the ions much higher and allows us to demonstrate that we have collected all the produced ions by observing the deflection curves. For all the fragments we have obtained good deflection curves. In the case of CO, for the direct ionization our results agree with the previous results within the experimental uncertainties. However, for the energetic fragments, our results exceed the previous results by a factor of 2.5. The doubly charged fragments of C^{2+} and O^{2+} have been measured for the first time. In the case of CH_4 , the previous results except those of Straub *et al* [24] are lower than our results for small fragment ions. Our results show excellent agreement with the measurement of Straub *et al*. In the case of C_2H_2 , the present results are higher than the previous results for the light fragment ions. The disagreement between the present measurements and the previous ones are explained by noting the kinetic energy distributions of the fragment ions; the previous measurements usually lost the energetic ions, thus have lower values.

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