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Cross sections of electron impact ionization of ethylene

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Abstract

The cross sections of the direct as well as the dissociative electron impact ionization of ethylene have been measured for electron energies from the threshold to 600 eV. The complete collection of the ionic fragments has been verified directly in the experiment. The total cross section values from the present work have been compared with previous experimental results. All the data generally show excellent agreement. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years much attention has been paid to simple hydrocarbon molecules because of their existence in interstellar space [1] and their role in plasma processing where the structures and dissociation dynamics of these molecules [2] are of interest. For understanding the behavior of these molecules in the interstellar environment and in plasma processing, different kinds of data on the interaction of these molecules with electrons and photons are required. This is one of the reasons why the photoionization and electron impact ionization of the hydrocarbon molecules are of great interest both theoretically as well as experimentally [3–6]. Electron impact ionization data for small hydrocarbon molecules are rare. For instance, the available data on the electron impact ionization of ethylene are only from the total ionization cross section measurements of Rapp and Englander-Golden for electron energies from threshold to 145 eV [7], Schram et al. from 0.6–12 keV [8] and Nishimura and Tawara from the threshold to 3 keV [4]. No data exist so far on the partial cross sections of the electron impact dissociative ioniza-

tion of ethylene into different ionic fragments.

The present work on the measurement of the partial cross sections of the electron impact dissociative ionization of ethylene is intended to fill that gap. The cross sections of the electron impact dissociative ionization of ethylene have been measured with a specially designed focusing time-of-flight mass spectrometer [9,10]. The focusing characteristics of the time-of-flight mass spectrometer exceed the collection capability of a normal Wiley-McLaren design. The ions with an initial kinetic energy of 15 eV can be collected by the detector without discrimination. Furthermore, the complete collection of the ionic products is verified experimentally by observing the deflection curves. No calibration of the dependence of the collection efficiency on either mass or the kinetic energy of the ions is required during the measurement. Hence the results are believed to be reliable.

2. Experiment

The experimental apparatus has been described in detail in previous papers [9,10]. Briefly, a continuous

molecular beam is crossed with a pulsed electron beam (100 ns) at right angles. The molecular beam is produced by a gas flow from a long needle with a diameter of 0.4 mm passing through a skimmer. The top of the needle is about 2 cm above the skimmer and the skimmer is about 6 cm above the electron beam. The interaction region is less than 4 mm $\times$ 4 mm $\times$ 4 mm. About 100 ns after the decay of the electron beam a pulsed voltage is applied to the extraction mesh of the mass spectrometer. The ions are extracted into a specially designed focusing time-of-flight (FTOF) mass spectrometer. The shield plates in the interaction region of the FTOF mass spectrometer cause the extraction mesh to perform as a plane-convex lens, which focuses the ions close to the axis of the FTOF mass spectrometer after the ions leave the ion source region. It also reduces the divergence angle with respect to the extraction system of a normal Wiley-McLaren TOF mass spectrometer. 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 spherically symmetrical lens if the voltage applied to it is about 1.3–1.4 times the voltage on the flight tubes. The detection plane is thus 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 detection signal. If a flat top can be observed in the deflection curve, we conclude that all the ions have been collected by the detector, which is
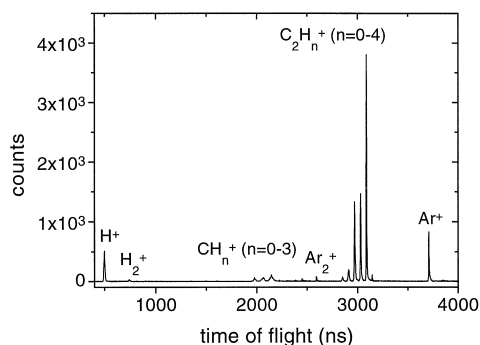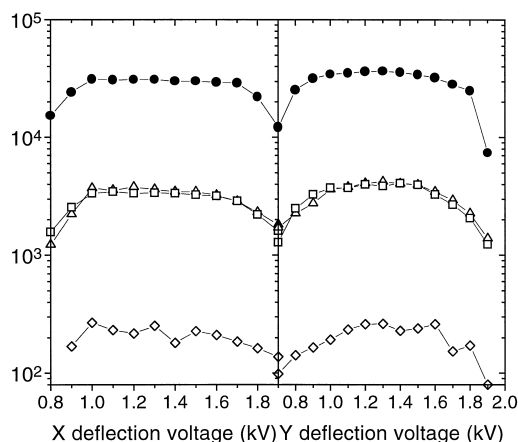

Fig. 2. The ion counts produced by the dissociative ionization of C_2H_4 at an electron energy of 200 eV versus the X and Y deflection voltages. $(-\bullet-)$ $\Sigma C_2H_n^+$ $(n=0-4)$; $(-\square-)$ ΣCH_n^+ $(n=0-3)$; $(-\diamond-)$ H_2^+; $(-\triangle-)$ H^+. All the voltages should be considered 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 arrow positions.

a microchannel plate with a diameter of 37 mm (Hamamatsu 1208-3DS).

The absolute cross sections of ethylene are obtained by normalizing the ion counts to those of a well-known gas, like argon. Initially the ion counts of argon are recorded for electron energies with a particular backing pressure. Then 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 C_2H_4) are obtained by

$$\sigma_{C^+} = \frac{I_{C^+}}{I_{Ar^+}} \sigma_{Ar^+}, \tag{1}$$

where I is the number of counts. The normalization is done at different backing pressures at the electron energy of 200 eV. As the backing pressure decreases, the obtained total cross section of ethylene converges to a final value, which fluctuates within $\pm 2\%$ of the total value, if we reduce the backing

Fig. 1. Mass spectrum of C_2H_4 at an electron energy of 200 eV.

pressure further. Argon is used as the reference gas because its ionization cross section has been well established. In this work, the recent result of Straub et al. has been taken as the reference value [11]. The errors in the cross sections of the fragment ions relative to the total values originate mainly from the data fluctuations, the gas pressure fluctuations in the measurements, and the other isotopes of carbon. Usually we make at least 5 independent measurements and obtain the data fluctuations from these independent measurements. The counts from the background gas are measured without the molecular beam and are usually less than 5% of the total count rate and are subtracted from the total count rate. Unless otherwise stated, the error of the relative value of the partial cross sections with respect to the total cross section is about 6%. The normalization of the data caused an error of 6%. The error of the absolute cross sections are believed to be about 10%.

3. Results and discussion

A typical time-of-flight mass spectrum of the mixture of ethylene and Ar at an electron energy of 200 eV is shown in Fig. 1. The ionic fragments of ethylene include H_n^+ ($n = 1$–2), CH_n^+ ($n = 0$–3) and $C_2H_n^+$ ($n = 0$–4). On the right side of the $C_2H_4^+$ peak there is also a minor peak, which is caused by the other isotope of carbon, the corresponding ionic product is $^{13}C^{12}CH_4^+$. From the total counts of this peak we can deduce the error caused by the isotopic impurity in the measurements. From Fig. 1 we see that all the mass peaks are well resolved. The most abundant products are the parent ions, $C_2H_4^+$. The mass peaks of CH_2^+, CH^+ and C^+ are broadened significantly by the initial kinetic energies of the two fragments, but they are still well resolved in the present work. These peaks are also superimposed on the doubly ionic products, $C_2H_4^{++}$, $C_2H_2^{++}$ and

Table 1
The dissociative ionization cross sections (in units of 10^{-16} cm^2) for electron impact on C_2H_4

Energy (eV)	$C_2H_4^+$	$C_2H_3^+$	$C_2H_2^+$	C_2H^+	C_2^+	CH_3^+	CH_2^+	CH^+	C^+	H_2^+	$H +$	Total
600	0.775	0.573	0.472	0.0640	0.0206	0.00500	0.0933	0.0297	0.0227	0.00859	0.138	2.24
550	0.829	0.603	0.504	0.0661	0.0188	0.00519	0.0990	0.0328	0.0264	0.00929	0.154	2.39
500	0.865	0.628	0.538	0.0726	0.0221	0.00544	0.100	0.0364	0.0288	0.0115	0.172	2.52
450	0.913	0.665	0.563	0.0797	0.0255	0.00650	0.107	0.0410	0.0317	0.0114	0.179	2.67
400	0.999	0.720	0.617	0.0897	0.0296	0.00615	0.127	0.0487	0.0341	0.0133	0.217	2.95
350	1.06	0.782	0.664	0.102	0.0342	0.0058	0.140	0.0521	0.0401	0.0161	0.242	3.19
300	1.15	0.845	0.730	0.116	0.0407	0.0103	0.158	0.0661	0.0512	0.0190	0.274	3.53
275	1.22	0.882	0.772	0.127	0.0423	0.00746	0.172	0.0692	0.0508	0.0191	0.293	3.72
250	1.30	0.937	0.825	0.137	0.0456	0.0110	0.189	0.0791	0.0582	0.0212	0.330	4.00
225	1.35	0.965	0.864	0.150	0.0515	0.0107	0.198	0.0877	0.0664	0.0228	0.359	4.20
200	1.39	0.988	0.890	0.155	0.0559	0.0101	0.213	0.0924	0.0683	0.0235	0.387	4.35
175	1.49	1.05	0.943	0.178	0.0661	0.0109	0.233	0.105	0.0781	0.0268	0.428	4.70
150	1.56	1.09	0.983	0.200	0.0736	0.0114	0.251	0.116	0.0822	0.0311	0.471	4.96
125	1.61	1.11	1.03	0.211	0.0747	0.0133	0.271	0.117	0.0851	0.0346	0.509	5.16
100	1.73	1.18	1.10	0.235	0.0823	0.0125	0.286	0.134	0.0901	0.0365	0.521	5.51
90	1.76	1.20	1.12	0.245	0.0792	0.0154	0.293	0.143	0.0857	0.0362	0.503	5.57
80	1.80	1.19	1.14	0.260	0.0753	0.0140	0.289	0.135	0.0788	0.0357	0.472	5.59
70	1.77	1.15	1.11	0.255	0.0693	0.0154	0.283	0.122	0.0682	0.035	0.405	5.39
60	1.75	1.14	1.11	0.232	0.0648	0.0140	0.253	0.107	0.0571	0.0283	0.353	5.20
50	1.74	1.09	1.06	0.224	0.0540	0.0112	0.211	0.0845	0.0447	0.0212	0.254	4.89
45	1.72	1.06	1.03	0.203	0.0443	0.0112	0.186	0.0721	0.0341	0.015	0.199	4.68
40	1.70	1.03	1.00	0.183	0.0328	0.0101	0.165	0.0536	0.0199	0.0126	0.157	4.47
35	1.62	0.957	0.909	0.122	0.0197	0.00810	0.118	0.0351	0.0176	0.00771	0.0992	3.99
30	1.52	0.829	0.751	0.0688	0.00685	0.0800	0.0855	0.0230	0.0115	0.00628	0.0602	3.50
25	1.24	0.579	0.474	0.0431		0.00460	0.0512	0.0187	0.00513			2.56
20	0.627	0.218	0.201	0.0153								1.21
17.5	0.274	0.0952	0.0929									0.502

C_2^{++}, respectively. Another doubly charged product, $C_2H_3^{++}$, was observed in the works of Plessis and Marmet [12,13], but it does not appear as an obvious mass peak in the present work.

The ion counts versus the deflection voltages are shown in Fig. 2, in groups of $\Sigma C_2H_n^+$ ($n = 0$–4), ΣCH_n^+ ($n = 0$–3), H_2^+ and H^+. We can see that all the groups show constant counts for the X deflection voltage from -1.0 to -1.6 kV and the Y deflection voltage from -1.1 to -1.6 kV. In the measurement of the cross sections we set the X and Y deflection voltages at -1.3 and -1.4 kV, respectively. We thus guaranteed experimentally that all the ions are collected at the detector with equal efficiency, which is just determined by the transmission of the meshes and the physical area of the microchannel plate.

The cross section values for electron energies from threshold to 600 eV are tabulated in Table 1 and are shown in Figs. 3–5, respectively. The data which are available for comparison are only the total cross section values from the measurements of Rapp and Englander-Golden [7], Schram et al. [8] and Nishimura and Tawara [4]. No partial cross section data exist.

The results for the electron impact direct and dissociative ionization of C_2H_4 into the ionic products of $C_2H_n^+$ ($n = 0$–4) are shown in Fig. 3. Typical error bars are also included. We can see that the cross section values for $C_2H_n^+$ ($n = 1$–4) maximize at electron energies of about 80 eV, whereas those for the C_2^+ peak maximize at electron energies of 100 eV.
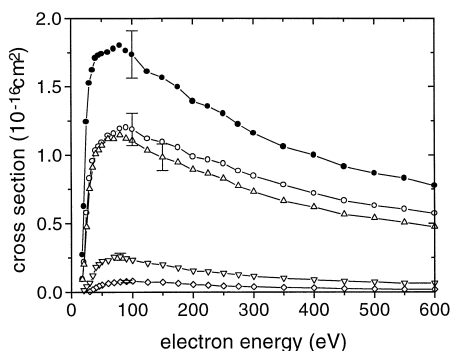
Fig. 3. Cross sections for the electron impact direct and dissociative ionization of C_2H_4 into the fragments of $C_2H_n^+$ ($n = 0$–4). $(-\bullet-)$ $C_2H_4^+$, $(-\circ-)$ $C_2H_3^+$, $(-\triangle-)$ $C_2H_2^+$, $(-\bigtriangledown-)$ C_2H^+, $(-\diamond-)$ C_2^+.
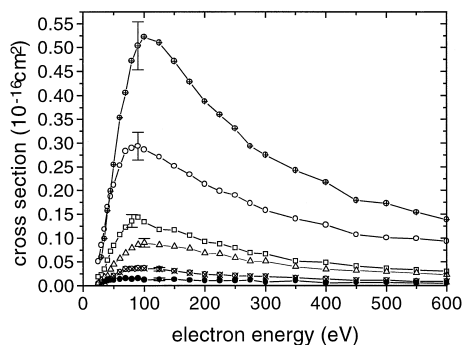

Fig. 4. Cross sections for the electron impact dissociative ionization of C_2H_4 into the fragments of CH_n^+ ($n = 0$–3) and H_n^+ ($n = 1, 2$). $(-\bullet-)$ CH_3^+, $(-\circ-)$ CH_2^+, $(-\square-)$ CH^+, $(-\triangle-)$ C^+, $(-\oplus-)$ H_2^+, $(-\otimes-)$ H^+.
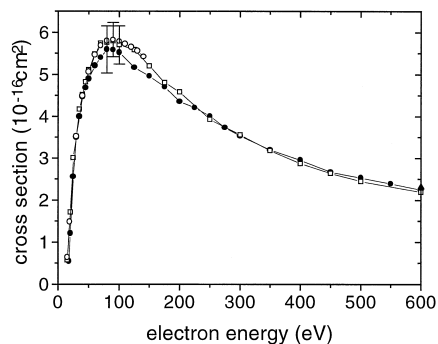

Fig. 5. Total cross sections of the electron impact direct and dissociative ionization of C_2H_6. $(-\bullet-)$ the present work, $(-\square-)$ Nishimura and Tawara [4], $(\triangle)$ Schram et al. [8], $(-\circ-)$ Rapp and Englander-Golden [7].

The fragments of CH_n^+ ($n = 0$–3) are more energetic than the group of C_2H_n ($n = 0$–4), their mass peaks are considerably broadened by the initial kinetic energy associated with dissociation. The cross sections shown in Fig. 4. The production of CH_3^+ is related to the breaking of the $C = C$ bond and the H-atom rearrangement after the ionization of the ethylene molecule. This process has a smaller probability than the direct breaking of a $C = C$ bond. The cross sections for CH_3^+ are thus less than 5% of the production of CH_2^+. In this case the isotopic isomer of $^{12}CH_2^+$, namely $^{13}CH_3^+$, contributes significantly to the count rate of $^{12}CH_3^+$. From Fig. 1 we know that the count of $^{13}C^{12}CH_4^+$ is about 2% of that of $^{12}C_2H_4^+$. In calculating the cross sections for CH_3^+ we reduced its count by 1% with respect to that of

CH_2^+. In this manner we hope that we can obtain more accurate data for CH_3^+, the uncertainty for CH_3^+ is expected to be less than 20%. For the other products the isotope impurity causes uncertainties less than 2% of the measurements, the general uncertainties are not affected by the isotopic impurity. CH_2^+ is the most abundant ionic fragment among the ionic products with a single C atom. Its cross section peaks at 90 eV.

The relative abundance of the hydrogen products H_n ($n = 1, 2$) is even higher than that of the products with a single C atom, as also shown in Fig. 4. The isotopic impurity does not cause an error. The cross sections peak at about 100 eV.

The fragments of $C_2H_3^{++}$ and C_2H^{++} do not show obvious mass peaks in the measurement. We estimate that the cross section for $C_2H_3^{++}$ is smaller than 2×10^{-18} cm^2 at the electron energy of 200 eV. Those for C_2H^{++} are even smaller.

The total cross sections are shown in Fig. 5 together with the measurements of Rapp and Englander-Golden [7], Schram et al. [8] and Nishimura and Tawara [4]. Generally all the available data agree with each other within $\pm 4\%$. The present results are about 4% lower than the results of Rapp and Englander-Golden and of Nishimura and Tawara at 100 eV. At electron energies above 300 eV all the data show excellent agreement.

4. Conclusions

The cross sections of the electron impact ionization as well as the dissociative ionization of ethylene have been measured for electron energies from threshold to 600 eV using the focusing time-of-flight mass spectrometer. The complete collection of the ionic fragments has been verified directly in the experiment. No calibration on either mass or energy

dependent transmission of the system is required. The total cross section values from the present work have been compared with previous experimental results. All the data generally show excellent agreement with each other. We hope that this work fills the gap on the cross sections of the electron impact dissociative ionization of C_2H_4.

Acknowledgements

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