Total electron impact ionization cross sections for simple hydrocarbon molecules

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Abstract. Total electron impact ionization cross sections for CH_4, C_2H_4, C_2H_6, C_3H_6 (cyclopropane and propene) and C_3H_8 were determined in the energy range from threshold to 3 keV. Results are compared with the available data. The measured cross sections are found to correlate strongly to the total electron number and the molecular dipole polarizability. In connection with the total number of molecular electrons and the molecular dipole polarizability, two scaling methods for the total ionization cross sections are presented. The isomer effect is also discussed.

1. Introduction

Simple hydrocarbon molecules have received much interest in the field of the molecular physics as a prototype of polyatomic molecules. Whereas they have been watched as an important constituent in the planetary and cometary atmosphere, and also as a dominant material in the field of the plasma processing, they also play an important role in edge plasmas of magnetically confined high temperature hydrogen plasma (Tawara and Phaneuf 1988). For understanding the behaviour of these molecules in space and laboratory, various reliable absolute cross sections are needed. Among these quantities, the total ionization cross section Q_i is fundamentally important for studing the interaction between electrons and molecules. Furthermore Q_i serves as a normalization standard for various partial ionization cross sections.

Rapp and Englander-Golden (1965) measured Q_i for CH_4 (threshold to 1 keV) and C_2H_4 (threshold to 145 eV). Schram *et al* (1966) reported Q_i for many hydrocarbons (CH_4–C_6H_6, 0.6–12 keV). Recently Duric *et al* (1991) determined Q_i for CH_4, C_2H_6 and C_3H_8 (threshold to 240 eV). These three groups used three pairs of linearly arranged parallel plate ion collectors and a magnetically confined linear electron beam. On the other hand, Orient and Srivastava (1987) measured the partial ionization cross sections for CH_4 (threshold to 510 eV) using a crossed beam method. They obtained absolute values by normalizing the sum of relative partial cross sections to a known Q_i of inert gas by means of a relative flow technique. Adamczyk *et al* (1966, CH_4, 20–2000 eV), Chatham *et al* (1984, CH_4 and C_2H_6, threshold to 400 eV) and Grill *et al* (1993, C_3H_8, threshold to 950 eV) reported the partial and total ionization cross sections. The latter experimental groups measured relative partial cross sections and then they normalized

their relative total cross sections to the absolute values of one of the former groups at a specific energy.

Many experimental studies of the electron impact ionization for hydrocarbons had been done at relatively low energies. However, data at high energies are still insufficient in quantity (Tawara *et al* 1992). Of those many experimental studies, only Schram *et al* compared the results with the optical data. The results of Rapp and Englander-Golden, and those of Schram *et al* have often been referred to as standard values of Q_i. However the agreement between them is not so satisfactory in the electron energy range overlapped. The former group reported Q_i, only for CH_4 and C_2H_4 as hydrocarbon molecules. Therefore more systematic measurements over the wide energy range are desirable for investigating general features in electron-molecule collisions and also for many relevant fields. The target species and the energy range in the present work are chosen from this point of view.

2. Experimental

2.1. Apparatus

Among various experimental apparatuses for Q_i measurements, a parallel plate ion collector method with a magnetically confined linear electron beam is the simplest in principle. In the present study, we constructed an apparatus of such a type which is shown in figure 1. It consists of an electron beam source (EBS), a collision cell (CC) and an electron collector (EC). Electrons from an iridium filament are accelerated
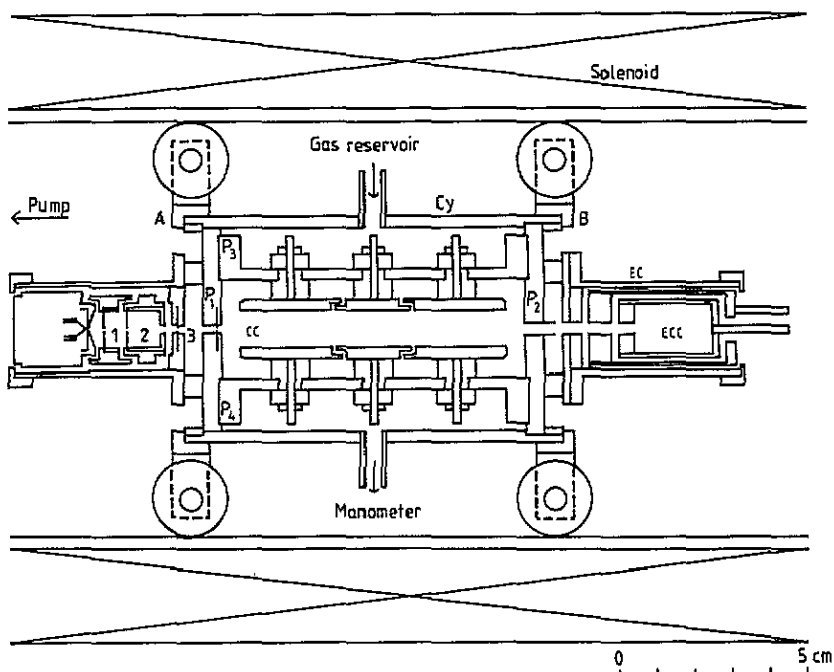
Figure 1. Cross sectional view of the experimental apparatus for total ionization cross section measurement: EBS, electron beam source; 1, 2 and 3, electrodes; CC, collision cell; EC, electron collector; ECC, electron collection cylinder; A and B, clasping rings.

through electrodes 1, 2 and 3 to CC and EC. Each electrode has a molybdenum aperture of diameter 0.5, 1.0 and 1.0 mm for beam collimation, respectively. The voltage on the electrodes 1 and 2 with respect to the filament was adjusted to get maximum current at EC. Throughout the present study, the electron current was limited to below 4 nA. The electrodes and their enclosure are made of non-magnetic stainless steel (type 310S). Each element is insulated by rings of boron nitride. The collision cell is enclosed by a cylinder Cy and two circular plates P_1 and P_2 (all made of type 310S) on both sides of Cy. The plate P_1 has a molybdenum circular aperture 1 mm in diameter, meanwhile the plate P_2 has a rectangular opening 3 mm in height, 10 mm wide and 8 mm in thickness, which ensures complete transmission of even the lowest energy electrons to EC. Three pairs of parallel plates (27, 20 and 27 mm in length) are fixed through insulators (alumina) on plates P_3 and P_4 made of corrosion-resistant aluminium alloy, which are in turn fixed on P_1 and P_2. The central pair are used as ion collector and the remaining serve as the field corrector which ensures a uniform field for the collection of ions formed along the electron beam.

A calibrated thermistor is mounted on P_3 to monitor the temperature of CC. The target gas is introduced from a gas reservoir through a needle valve and its pressure is monitored by a capacitance manometer (Baratron 390H). The final electron collector system (EC) consists of three coaxial cylinders (non-magnetic stainless steel (type 310S) and is covered with gold plated copper alloy plate) with the same size of opening (3 mm × 10 mm) as that of P_2. The innermost cylinder, ECC, is used for measuring the incident electron and is biased at +300 eV with respect to the ground potential for complete collection, the intermediate cylinder shields the precipitation of the field applied on ECC and monitors the charged particles and finally the outermost cylinder is grounded. The central axis of this system is arranged on the centre of the opening on P_2. The axes of EBS and CC are arranged coaxially. The assembly including EBS and CC is guided to the central region of an axially symmetric and uniform magnetic field by four wheels put on clasping rings A and B. The magnetic field (456 G) is provided by a solenoid (40 cm in length) around a cylindrical vacuum chamber. The vacuum chamber made of non-magnetic stainless steel (type 304), 11 cm inner diameter, and 66 cm in length is evacuated down to several times 10^{-7} Torr by a 6 in oil diffusion pump with liquid nitrogen trap.

2.2. Procedure

The ion collection efficiency of the present apparatus is examined by measuring ratios I_i/I_e, where I_i and I_e represent slow secondary ion and primary electron current, respectively, as a function of the field strength (V_d) applied on the ion collector for each target molecule. The ratios I_i/I_e increase with increasing V_d and reach constant values at above about 20 V cm^{-1}. All target molecules showed similar trend in V_d-dependence. Then, $V_d = 26$ V cm^{-1} is selected as a sufficient field strength for complete collection of slow secondary ions formed along the electron beam in CC.

The electron energy calibration is done by comparing the observed appearance potential with the available ionization potentials (Sharon 1992) for CH_4, C_2H_4, C_2H_6, C_3H_6 (cyclopropane and propene) and C_3H_8 referred as 12.51, 10.51, 11.52, 9.86, 9.73 and 10.95 eV, respectively. In this study, the value Q_i corresponds to the total positive charge production. Therefore a n-times ionized ion is measured as n times singly charged ions.
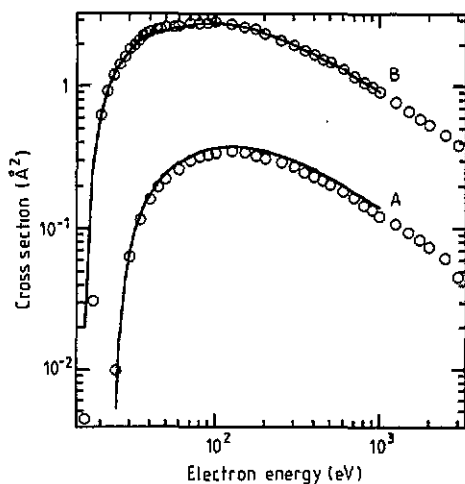
Figure 2. Electron impact ionization cross sections (Å^2) of helium A and argon B as a function of electron energy: O, This work; ——, Rapp and Englander-Golden.

The value Q_i is given as

$$Q_i = \frac{I_i}{pLI_e} \tag{1}$$

where I_i is the secondary ion current, I_e is the primary electron current at ECC, p is the target gas pressure in number density and L is the effective path length of electrons in the ion collector. Measurements of Q_i are performed under sufficiently low target gas pressure to maintain single collision conditions. These conditions are examined by measuring $I_i/(I_e p)$ as a function of p at the electron energy of 100 eV. Throughout this study, the target gas was adjusted in the range between 0.1 and 0.15 mTorr. The pressure in the vacuum chamber was kept below several times 10^{-6} Torr when CC was filled up to 0.15 mTorr.

As a preliminary test of the apparatus, Q_i for He and Ar were measured in the energy range from threshold to 3 keV. For both atoms, $V_d = 6$ V cm^{-1} was used for the positive charge collection. The measured results are shown in figure 2, curves A and B with the experimental data of Rapp and Englander-Golden. The present results for He are lower by about 10% than theirs, meanwhile, the two results for Ar agree excellently. The dipole transition moments squared M_i^2 are derived from the measured data and are listed in table 1 with values obtained from the available data of the optical oscillator strengths of He(Chan *et al* 1991) and of Ar(Cullen *et al* 1989).

2.3. Error estimation

The temperature of the capacitance manometer head was controlled at 45 °C. The temperature of CC rose to about 50 °C mainly due to the power dissipation of the

Table 1. M_i^2.

He		Ar	
This work	Optical	This work	Optical
0.49	0.53	4.8	3.35

magnetic coil. Although the thermal transpiration effect was corrected, the contribution of this effect to the estimation of the target pressure is small. The electron path length is taken to be the geometrical length of the central parallel plate as 2.0 cm with 0.5% uncertainty. Increase of the electron path length due to the effect of the electric field and the magnetic field is negligible in this experimental condition. The uncertainties in reading of p, I_t and I_e are 3, 3 and 3%, respectively. Then, the resultant systematic uncertainties are estimated to be 8%.

3. Results

The present results are listed in table 2. The results for each molecule are compared with the available data in figure 3(a)–(d) and table 2.

3.1. Methane

Figure 3(a) shows a comparison of the present Q_i with some available data. The values of Rapp and Englander-Golden (1965) agree very well with this work over the energy range overlapped. Schram *et al* (1966) also measured Q_i at higher energies which were lower than the present values by about 15%. Adamczyk *et al* (1966) reported partial cross sections over a wide energy range. The values of their Q_i were determined by summing up their partial cross sections. Their values are smaller than ours by about 15% on average. The data reported by Chatham *et al* (1984) agree well with our results within experimental errors. The results of Orient and Srivastava (1987) agree very well with ours in the energy range between 40 and 100 ev. However, their values become larger than ours at energies above 100 eV. Recent results of Duric *et al* are about 8% lower at energies above 35 eV and considerably higher at energies below 20 eV. Among these measurements, the relatively large discrepancy in Q_i near threshold energy may be attributed to the calibrated electron energies because Q_i increases very steeply in this energy region.

3.2. Ethene

Figure 3(b) shows the present results together with those of Rapp and Englander-Golden (1965), and of Schram *et al* (1966). Agreement among these results is very good except for those near the threshold energy region. This discrepancy should be caused by reasons similar to that in methane.

3.3. Ethane

The present results are shown in figure 3(c) together with those of Schram *et al* (1966), Chatham *et al* (1984) and Duric *et al* (1991). The data reported by Schram *et al* (1966) and Chatham *et al* agree with ours within experimental errors. The values of Duric *et al* are lower by about 9% than ours at energies above 30 eV. At energies near threshold, Q_i of Chatham *et al* and of Duric *et al* are considerably higher than the present results.

3.4. Cyclopropane and propane

Cyclopropane and propene, isomers of each other, have the same number of constituent atoms but different chemical structures. The present results for propene are slightly

Table 2. Total electron impact ionization cross sections (Å^2). The numbers in parentheses indicate statistical errors in %.

$E(\text{eV})$	CH_4	C_2H_4	C_2H_6	C_3H_6 Cyclopropane	C_3H_6 Propene	C_3H_8
10				0.034 (12)	0.093 (4.4)	
12		0.097 (4.7)	0.074 (16.3)			0.206 (2.3)
12.5				0.312 (5.4)	0.498 (3.6)	
15	0.209 (1.6)	0.581 (2.8)	0.618 (1.1)	1.04 (4.1)	1.26 (2.5)	1.14 (1.3)
17.5	0.693 (1.2)	1.15 (1.6)	1.39 (1.3)	1.97 (2.1)	2.15 (1.6)	2.30 (6.0)
20	1.22 (0.4)	1.71 (1.4)	2.24 (4.1)	2.61 (2.5)	3.07 (1.7)	3.31 (4.7)
25	2.01 (1.2)	3.01 (1.2)	3.48 (2.1)	4.27 (0.7)	4.54 (2.7)	5.21 (2.9)
30	2.56 (1.9)	3.52 (1.8)	4.45 (1.5)	5.36 (3.0)	5.54 (0.7)	6.47 (1.9)
35	2.96 (0.9)	4.17 (2.7)	4.94 (3.7)	6.13 (3.6)	6.42 (1.5)	7.37 (3.1)
40	3.23 (1.8)	4.52 (1.6)	5.41 (3.5)	6.71 (2.8)	7.18 (1.5)	8.00 (3.0)
45	3.49 (0.7)	4.82 (0.7)	5.84 (2.6)	7.42 (2.6)	7.54 (1.0)	8.54 (0.3)
50	3.60 (2.0)	5.11 (3.3)	6.04 (1.5)	7.84 (3.0)	8.00 (1.8)	9.22 (2.2)
60	3.86 (2.7)	5.48 (2.7)	6.67 (1.5)	8.27 (1.8)	8.42 (3.2)	9.79 (2.7)
70	3.93 (1.9)	5.74 (0.3)	6.93 (2.1)	8.48 (2.1)	8.82 (1.2)	10.09 (1.2)
80	3.98 (2.0)	5.76 (2.0)	6.86 (1.6)	8.83 (2.8)	9.04 (2.7)	10.20 (3.3)
90	3.98 (2.3)	5.79 (1.5)	6.84 (2.4)	8.87 (1.4)	9.17 (3.4)	10.24 (2.9)
100	3.92 (3.0)	5.70 (1.4)	6.89 (0.7)	8.27 (2.0)	9.02 (2.1)	10.23 (1.8)
125	3.75 (1.4)	5.58 (2.2)	6.53 (1.3)	8.30 (1.0)	8.62 (1.7)	9.90 (3.5)
150	3.55 (2.0)	5.20 (2.1)	6.32 (2.7)	8.10 (2.2)	8.14 (1.9)	9.36 (1.7)
175	3.32 (2.3)	4.80 (3.4)	5.98 (1.8)	7.29 (1.8)	7.83 (3.7)	8.84 (4.2)
200	3.17 (1.5)	4.58 (1.7)	5.68 (1.1)	7.25 (1.2)	7.34 (3.4)	8.35 (1.9)
250	2.86 (1.4)	3.92 (3.1)	5.01 (1.9)	6.59 (3.4)	6.78 (2.4)	7.80 (5.8)
300	2.55 (2.3)	3.56 (2.3)	4.60 (1.1)	5.88 (0.9)	5.99 (3.5)	6.84 (1.2)
350	2.36 (1.8)	3.18 (1.6)	4.18 (1.4)	5.34 (0.9)	5.48 (3.5)	6.25 (3.9)
400	2.17 (2.3)	2.87 (1.0)	3.86 (1.5)	4.88 (2.1)	4.95 (0.8)	5.78 (2.1)
450	1.99 (0.3)	2.64 (2.8)	3.47 (1.6)	4.56 (2.3)	4.66 (2.2)	5.26 (3.6)
500	1.85 (3.2)	2.45 (2.2)	3.33 (1.7)	4.33 (0.9)	4.50 (2.6)	4.93 (1.8)
600	1.62 (0.9)	2.19 (1.9)	3.03 (2.0)	3.77 (1.9)	3.96 (1.9)	4.33 (1.2)
700	1.44 (3.7)	1.96 (1.7)	2.71 (2.1)	3.51 (3.4)	3.61 (1.7)	3.99 (2.3)
800	1.33 (1.2)	1.75 (3.2)	2.38 (2.5)	3.12 (2.6)	3.18 (0.6)	3.67 (5.3)
900	1.22 (1.4)	1.63 (2.6)	2.25 (2.9)	2.77 (0.9)	2.98 (0.9)	3.27 (0.5)
1000	1.13 (1.2)	1.52 (2.3)	2.03 (3.8)	2.58 (0.7)	2.79 (3.1)	3.05 (1.8)
1250	0.937 (0.7)	1.28 (3.2)	1.75 (3.6)	2.17 (1.2)	2.34 (1.2)	2.64 (2.3)
1500	0.818 (3.8)	1.11 (6.6)	1.52 (3.5)	1.97 (0.9)	2.06 (2.8)	2.27 (1.4)
1750	0.747 (3.0)	1.03 (2.5)	1.37 (2.2)	1.76 (5.4)	1.87 (2.6)	2.06 (3.2)
2000	0.660 (1.2)	0.908 (2.1)	1.22 (2.3)	1.56 (2.1)	1.67 (1.1)	1.88 (5.4)
2500	0.552 (5.9)	0.767 (2.7)	1.08 (2.7)	1.36 (2.4)	1.42 (3.1)	1.62 (2.5)
3000	0.435 (3.7)	0.678 (1.9)	0.899 (3.6)	1.16 (1.8)	1.24 (3.0)	1.39 (1.6)

higher, particularly at lower energies, than those for cyclopropane (see table 2). A similar isomer effect in total electron scattering cross sections for these molecules has been observed experimentally (Nishimura and Tawara 1991). Results of Schram *et al* (1966) also show the same trend (see table 3). Table 3 shows a comparison of the present results for cyclopropane and propene with those of Schram *et al* in the energy range overlapped.

3.5. Propane

The present results are compared with those of Schram *et al* (1966), Duric *et al* (1991) and Grill *et al* (1993) in figure 3(*d*). Agreement between the present results and those
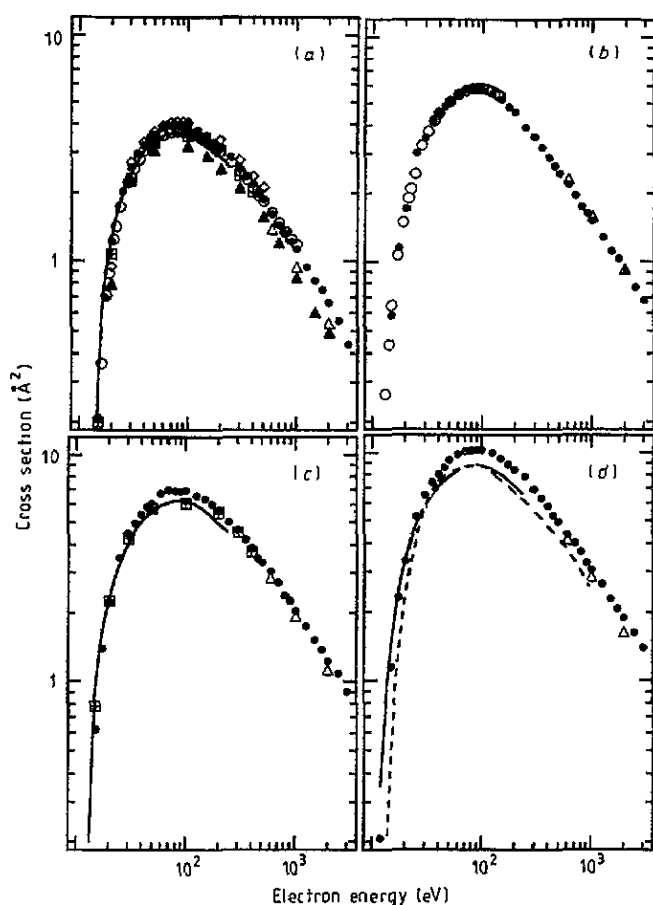
Figure 3. Electron impact ionization cross sections (Å^2) of methane (a), ethene (b), ethane (c) and propane (d) as a function of electron energy: ●, This work; ○, Rapp and Englander-Golden; △, Adamczyk *et al*; △, Schram *et al*; ⊞, Chatham *et al*; ◇, Orient and Srivastava; ——, Duric *et al*; ..., Grill *et al*. Note that the data of Rapp and Englander-Golden, Schram *et al*, Duric *et al* and the present work were taken with the parallel ion collector method and the others were normalized to the known cross sections by summing partial cross sections.

Table 3. $Q_i(\text{Å}^2)$.

	Cyclopropane			Propene		
E(eV)	600	1000	2000	600	1000	2000
This work	3.77	2.58	1.56	3.96	2.79	1.67
Schram	3.41	2.28	1.32	3.70	2.52	1.44

of Schram *et al* is good only at 600 eV but their data are much lower than the present results at higher energies. The data of Duric *et al* are higher at low energies and increase more slowly than the present results. The recent results of Grill *et al*, nomalized to those of Duric *et al* at 100 eV, are considerably lower than the present data, but the energy dependences are similar to each other.

4. Discussion

At sufficiently high electron energies, the asymptotic Bethe Formula for Q_i (Miller and Platzman 1957) is given by

$$Q_i = \frac{4\pi a_0^2 R}{E} M_i^2 \ln \frac{4EC_i}{R} \tag{2}$$

where E is the electron energy, a_0 is the first Bohr radius of atomic hydrogen, R is the Rydberg energy, M_i^2 is the square of the dipole matrix elements and C_i is a constant. The value M_i^2 is expressed as

$$M_i^2 = \int_{IP}^{\infty} \frac{R}{E} \frac{df}{dE} dE \tag{3}$$

where df/dE is the differential oscillator strength and E is the excitation energy. Since M_i^2 includes collision processes both with and without any secondary electron liberation from excited molecules, M_i^2 was defined by Schram et al (1966) as

$$M_i^2 = \int_{IP}^{\infty} \eta(E) \frac{R}{E} \frac{df}{dE} dE \tag{4}$$
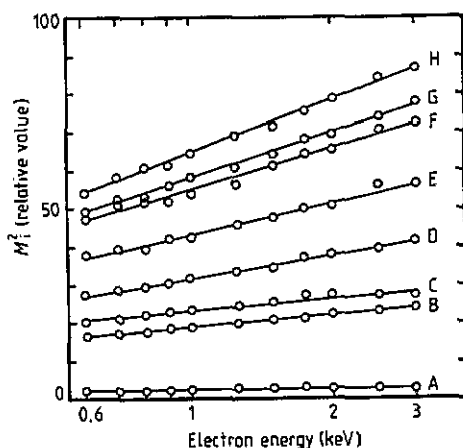
where $\eta(E)$ is the ionization efficiency.

Figure 4. Platzman plot for helium, argon and various hydrocarbons: A, helium; B, argon; C, methane; D, ethene; E, ethane; F, cyclopropane; G, propene; H, propane.

Figure 4 shows the Platzman plots at energies between 0.6 and 3 keV for all the molecules investigated. Values of M_i^2 can be determined by fitting the above expression to the present results and are listed in table 4 along with those of Schram et al (1966). Values of Adamczyk et al (0.7–2 keV) were recalculated by the present authors based on their results.

The optical values of M_i^2 in table 4 have been evaluated based on the data reported by Samson and Haddad (1988) for CH_4, by Schoen (1962) for C_2H_4, C_2H_6, cyclopropane, propene and C_3H_8. The values for hydrocarbon molecules except for CH_4 may include large uncertainties as data are available only in a limited photon energy range. For CH_4, the present M_i^2 seems to be in reasonable agreement with others by electron impact as well as optical data. Yet the deviation between the present results of M_i^2 and

Table 4. M_i^2.

| | CH$_4$ | C$_2$H$_4$ | C$_2$H$_6$ | C$_3$H$_6$ | | C$_3$H$_8$ |
				Cyclopropane	Propene	
This work	4.8	9.3	12	16	17	20
Schram	4.28	7.32	8.63	10.2	12.0	13.8
Adamczyk	4.15					
Optical	4.56	4.31	6.26	8.19	8.15	7.60

those of optical increases with increasing molecular weight. More or less, the results of Schram *et al* (1966) shows a similar trend. Backx and Van der Wiel (1975) pointed out that electron data obtained using apparatus with magnetic field often gives larger values of M_i^2 than optical data. For checking the experimental data, more extensive photoabsorption and photoionization cross sections over a wide energy range are needed.

For all molecules and over the energies examined, Q_i should strongly correlate to the total number of electrons z, and also to the molecular dipole polarizability α. The values of Q_i/z and Q_i/α are listed in tables 5 and 6.

Table 5. Ratio (Q_i/z) of the cross section Q_i ($\mathring{A}^2$) to the total number of molecular electrons z versus electron energy (eV).

| E(eV) | CH$_4$ | C$_2$H$_4$ | C$_2$H$_6$ | C$_3$H$_6$ | | C$_3$H$_8$ | Average (%) |
				Cyclopropane	Propene		
20	0.076	0.061	0.075	0.062	0.073	0.075	0.070 (9.9)
25	0.13	0.11	0.12	0.10	0.18	0.12	0.12 (9.3)
30	0.16	0.15	0.15	0.13	0.13	0.15	0.15 (8.3)
40	0.20	0.16	0.18	0.16	0.17	0.18	0.18 (8.6)
50	0.22	0.18	0.20	0.19	0.19	0.21	0.20 (7.4)
100	0.24	0.20	0.23	0.21	0.21	0.23	0.22 (7.0)
200	0.20	0.16	0.19	0.17	0.17	0.19	0.18 (8.6)
500	0.12	0.087	0.11	0.10	0.11	0.11	0.11 (10)
1000	0.071	0.054	0.067	0.061	0.066	0.069	0.065 (9.5)
2000	0.041	0.032	0.041	0.037	0.040	0.043	0.039 (10)
3000	0.027	0.024	0.030	0.028	0.030	0.032	0.029 (10)

Table 6. Ratio (Q_i/α) of the cross section Q_i ($\mathring{A}^2$) to the molecular polarizability α ($\mathring{A}^3$) versus electron energy (eV).

| E(eV) | CH$_4$ | C$_2$H$_4$ | C$_2$H$_6$ | C$_3$H$_6$ | | C$_3$H$_8$ | Average (%) |
				Cyclopropane	Propene		
20	0.47	0.40	0.50	0.46	0.49	0.53	0.48 (9.2)
25	0.78	0.71	0.78	0.75	0.73	0.83	0.76 (5.6)
30	0.99	0.83	1.00	0.95	0.88	1.03	0.95 (8.1)
40	1.25	1.06	1.21	1.19	1.15	1.27	1.19 (6.4)
50	1.39	1.20	1.35	1.39	1.28	1.47	1.35 (7.0)
100	1.51	1.34	1.54	1.54	1.44	1.63	1.50 (6.6)
200	1.22	1.08	1.27	1.28	1.17	1.33	1.23 (7.3)
500	0.71	0.58	0.74	0.77	0.72	0.78	0.72 (9.7)
1000	0.44	0.36	0.45	0.46	0.45	0.48	0.44 (9.1)
2000	0.25	0.21	0.27	0.28	0.27	0.30	0.26 (12)
3000	0.17	0.16	0.20	0.20	0.20	0.22	0.19 (12)

At energies above 20 eV, Q_i/z and Q_i/α show nearly the same values at each electron energy for all molecules tested. This indicates that the total number of molecular electrons and molecular polarizability play a decisive role in determining total ionization cross sections. If a similar comparison is made for alkanes and alkenes, these features become clearer.

The oscillator strength relates to some fundamental quantities through a number of sum rules $S(n)$ which are expressed in the general form (Massey and Burhop 1969) as

$$S(n) = \sum_i (E_i)^n f_i + \int (E)^n \frac{\mathrm{d}f}{\mathrm{d}E}\,\mathrm{d}E. \tag{5}$$

E_i and E are energies of the discrete and the continuous state of target (measured from the ground state). The terms f_i and $\mathrm{d}f/\mathrm{d}E$ are the oscillator strength and the differential oscillator strength, respectively. In connection with the present work, we take the following three terms, $S(0)$, $S(-1)$ and $S(-2)$, which give the total number of electrons in the target molecule z, the squared dipole transition matrix element as shown in equation (2) and the value proportional to the molecular dipole polarizability, respectively. For $S(0)$, the first term in equation (5) is less than 2 for most atoms and molecules. Therefore, we can neglect that term in $S(0)$ for polyatomic molecules. Then Q_i/z can be written as

$$Q_i/z \propto \int_{IP}^{\infty} \eta(E) \frac{R}{E} \frac{\mathrm{d}f}{\mathrm{d}E}\,\mathrm{d}E \Big/ \int_{IP}^{\infty} \frac{\mathrm{d}f}{\mathrm{d}E}\,\mathrm{d}E. \tag{6}$$

Now we define $\overline{E^{-1}}$ as

$$\overline{E^{-1}} = \int_{IP}^{\infty} \frac{R}{E} \frac{\mathrm{d}f}{\mathrm{d}E}\,\mathrm{d}E \Big/ \int_{IP}^{\infty} \frac{\mathrm{d}f}{\mathrm{d}E}\,\mathrm{d}E. \tag{7}$$

If the numerator and the denominator in equation (7) have similar distributions with

Table 7. $\overline{E^{-1}}$.

			C_3H_6			
CH_4	C_2H_4	C_2H_6	Cyclopropane	Propene	C_3H_8	Average (%)
0.043	0.033	0.039	0.035	0.036	0.042	0.038 (12.5)

respect to the energy E, $\overline{E^{-1}}$ should be independent of molecules. As shown in table 7, this is the case in the hydrocarbon molecules studied. The numerator and the denominator in equation (7) are evaluated from the photoionization and photoabsorption cross sections, respectively, For this purpose, the data of Samson and Haddad (1988) for CH_4, and of Schoen (1962) for C_2H_4, C_2H_6, cyclopropane, propene and C_3H_8 are used. The results for hydrocarbons are listed in table 7. The values of $\overline{E^{-1}}$ are nearly constant for all molecules. These support the usefulness of Q_i/z.

In the approximate value of $S(-2)$ for polyatomic molecules, we can neglect the term of Σ in equation (5). Then as the molecular dipole polarizability α can be

written as

$$\alpha \propto \int_{IP}^{\infty} \left(\frac{R}{E}\right)^2 \frac{df}{dE} dE. \tag{8}$$

Then we get the following expression:

$$Q_i/\alpha \propto \int_{IP}^{\infty} \eta(E) \frac{1}{E} \frac{df}{dE} dE \bigg/ \int_{IP}^{\infty} \left(\frac{1}{E}\right)^2 \frac{df}{dE} dE. \tag{9}$$

Hence we define $\overline{E'}$ as

$$\overline{E'} = \int_{IP}^{\infty} \eta(E) \frac{1}{E} \frac{df}{dE} dE \bigg/ \int_{IP}^{\infty} \left(\frac{1}{E}\right)^2 \frac{df}{dE} dE. \tag{10}$$

As well as the discussion of Q_i/z, if $\eta(E)(df/dE)$ _and_ df/dE of the compared molecules have similar distributions with respect to E, then $\overline{E'}$ should be on a constant value at a given electron energy. To check this assumption, values of $\eta(E)(df/dE)$ are evaluated using the same data as in the case of Q_i/z and listed in table 8 where the value for CH_4

Table 8. $\overline{E'}$.

| CH$_4$ | C$_2$H$_4$ | C$_2$H$_6$ | C$_3$H$_6$ | | C$_3$H$_8$ | Average (%)(CH$_4$ |
			Cyclopropane	Propene		excluded)
21.7	13.5	13.6	12.3	14.2	12.6	13.2 (5.2)

is excluded because of its special behaviour. As listed in table 8, values of $\overline{E'}$ are nearly equal for all molecules except for CH_4. This may be attributable to the small value of α of CH_4.

The above two results may suggest that the incident electron recognizes not only all electrons in a molecule but also its structure of electron cloud (polarizability) even at sufficiently high energies. This feature also should serve as approximate indices of the consistency among Q_i for similar molecules.

Cyclopropane and propene are isomers, as mentioned above. For both molecules, Q_i themselves at a given energy show only slight differences (see table 2). On the other hand, Q_i/α differs considerably even below 0.5 keV (see table 5) but becomes nearly equal above 1 keV. This indicates that Q_i/α is more sensitive than Q_i/z for isomers at low incident electron energy.

5. Concluding remarks

In the present work, it is found that at sufficiently high electron energies, the Bethe formula for the electron impact total ionization is found to be fitted very well to the present results. Therefore Q_i at higher energies can be known accurately from the Bethe formula with experimentally determined constants.

The Platzman plot should be used, based on data at sufficiently high energies, namely more than several ten times the ionization potential. Otherwise, the incorrect values of M_i^2 would be deduced. Therefore more systematic investigations at high energies would be desirable.

The molecular dipole polarizability, α, and the total number of electron, z, hitherto neglected in electron collision data analysis, are found to play an important role in determining total electron impact ionization cross sections. As we have shown in tables 6 and 7, better scalings for Q_i/z and Q_i/α, not Q_i themselves, are found among various hydrocarbon molecules.

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