Electron scattering by CH_4 molecules at intermediate energies (400–5000 eV)

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Total cross sections for electron scattering by CH_4 molecules in the energy range 400–5000 eV have been measured with experimental errors of about 3%. The method was based on a transmission-beam technique, and a detailed error source analysis is included. Present results have been compared with available experimental and theoretical data. The dependence on electron energy of the total cross sections obtained shows an asymptotic behavior with increasing energies, in agreement with the Born-Bethe approximation. In addition, an analytical formula is provided to extrapolate total cross sections to higher energies. Finally, total cross-section values have been partitioned into elastic and inelastic (ionization and neutral dissociation) processes. [S1050-2947(98)07502-7]

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I. INTRODUCTION

In recent years, the interest in total cross-section (σ_T) determinations for electron-molecule collisions at intermediate energy (0.1–10 keV) has increased [1–4]. Accurate measurements in this range require extremely good angular and energy resolution to avoid effects due to forward-scattered electrons. From the theoretical point of view, the high variety of open channels at these energies demands the use of approaches based on complex optical potentials [5], and, in some cases, requires applying additive rules for electron-molecule scattering [6–8]. Although this energy range is of special interest in the search for systematic relations between σ_T and other molecular parameters, experimental data for energies above 500 eV are scarce. For electron-CH_4 collisions we have only found experimental σ_T results, for energies above 500 eV, in the work of Zecca *et al.* [9], obtained by means of a Ramsauer-type device [10]. In previous works [3,4], serious discrepances between results obtained by this technique and those given by the present experimental setup have been found for energies above 1500 eV. These considerations have prompted the present work.

In this work experimental total cross sections for e-CH_4 scattering in the energy range 400–5000 eV are obtained by using a transmission beam technique. The experimental errors are estimated to be approximately 3%. A detailed error source analysis is made, paying special attention to those arising from forward scattered electrons. The dependence of σ_T on electron energy is compared with theoretical predictions and especially with the energy dependence derived from the Born-Bethe approximation [11–13]. A simple formula to extrapolate cross section values to higher energies is obtained by assuming an asymptotic behavior of σ_T as a function of energy, according to the Born-Bethe theory. Finally, total cross-section values are partitioned into the possible constituent processes (elastic, ionization) and neutral dissociation) in accordance with the partial cross sections available in the literature. Semiempirical fits of these values are also given.

II. EXPERIMENT

A. Experimental setup

The experimental setup was described previously [3,4], and will be only briefly mentioned here. A 1-mm-diameter electron beam is generated by an electron gun operating at typical beam currents of 10^{-13} A. Pressure in the gun was maintained less than 10^{-5} Torr during the measurements. The collision chamber is defined by two apertures 1 mm in diameter, separated by a distance (L) which can be changed from 70 to 127 mm according to the experimental requirements, and the gas pressure in the chamber measured with an absolute capacitance manometer (MKS Baratron 127A). The energy of the emerging electrons from the gas cell is analyzed by means of an electrostatic hemispherical spectrometer of 81.9-mm mean radius and 1-mm-diameter entrance and exit apertures. The spectrometer energy resolution is better than 1 eV (full width at half maximum) for incident energies ranging from 300 to 5000 eV with a maximum angular acceptance of the entrance aperture of 3.5×10^{-5} sr. The transmitted electrons are detected by a channeltron electron multiplier operating in a single-pulse mode. The pressure in the region of the energy analyzer and detector was maintained at less than 10^{-5} Torr during the measurements.

B. Procedure

The method is based on the measurement of the electron beam attenuation through the gas cell. The recorded beam intensity (I) follows the law

$$I = I_0 \exp(-nL\sigma_T), \tag{1}$$

where I_0 is the intensity of the primary beam, L is the interaction region length, n is the molecular density and σ_T is the total cross section; n was obtained from the measurement of pressure and temperature in the gas cell. Each measurement was processed by plotting on a semilogarithmic scale the measured I/I_0 values as a function of pressure in the gas cell, for at least ten different values ranging from 2 to 70 m Torr. The experimental points obtained in this way lie on a straight line, the slope of which gives the total cross section.

TABLE I. Experimental and theoretical total cross sections (in units of a_6^2) for electron scattering from CH_4.

Electron energy (eV)	Experimental values					Theoretical data	
	This work	Ref. [9]	Ref. [17]	Ref. [18]	Ref. [19]	Ref. [5]	Ref. [7]
400	13.4	13.9	12.8	13.2	13.2	11.1	14.1
450		12.6					
500	11.2	11.4			11.1	9.31	11.5
600		9.68				8.05	9.68
640	9.27						
700		8.89				7.10	8.32
800		7.89				6.36	7.29
850	7.53						
900		7.07					6.72
1000	6.60	6.36				5.27	6.31
1250	5.46	5.18					
1500	4.80	4.32					
1750	4.27	3.68					
2000	3.82	3.19				2.87	
2250	3.50	2.87					
2500		2.56					
2600	3.13						
2750		2.31					
3000	2.79	2.10				1.98	
3250		1.98					
3500	2.48	1.85					
4000	2.22	1.58				1.51	
4500	2.04						
5000	1.87					1.18	

C. Error source analysis

The accuracy of the pressure measurements was assumed to be better than 1% (manufacturer's data). To ensure that pressure gradients did not contribute to the experimental errors, the pressure was measured at several points along the cell. Measurements have been carried out for electron currents ranging from 10^{-13} to 10^{-15} A. For this current range no dependence of σ_T on electron intensity was found. Each measurement was repeated at least five times with the same experimental conditions, to ensure statistical uncertainties of less than 2%. The length of the collision chamber was changed from 70 to 127 mm, and the measured σ_T values were found to be in agreement within the statistical uncertainties (i.e., 2%). This result indicates that our measured length (L) corresponds to the actual absorption length and that possible multiscattering effects are negligible for these experimental conditions.

Special attention was paid to avoid errors arising from forward electron scattering. As pointed by several authors [14,15], electrons scattered in the forward direction can be the main error source at high impact energies if they are not efficiently discriminated.

Equation (1) represents the ideal case in which the beam is infinitely narrow and the solid angle subtended by the detector is zero. Blaaw *et al.* [14] incorporated the small-angle scattering contribution to Eq. (1), giving a method to estimate an upper limit to the error contribution of the electrons scattered into the detection angle. For experiments such as the present one, in which the energy resolution allows one to eliminate the inelastic scattering contribution, this limit is determined by the elastic differential cross section, extrapolate to zero angle, and the mean acceptance angle of the detector. However, in a recent work [16], we showed by means of a Monte Carlo electron transport simulation that this error contribution can be more important than the predictions of Ref. [14], even in experiments with reasonable angular resolution. The results of these calculations for transmission experiments show that the correlation to σ_T for this effect increases exponentially with energy. However, for the conditions of the present work, a maximum error contribution from the elastic forward scattering at 5000 eV of less than 0.4% has been obtained. By combining the partial error components mentioned above, we have a total error of 3% for the present measurements.

III. RESULTS

A. Total cross sections

The measured total cross sections for electron scattering by CH_4 molecules in the energy range 400–5000 eV are given in Table I, together with the previous experimental [9,17–19] and theoretical [5,7] values for comparison. All experimental data in general show good agreement, within the error limits, for energies between 400 and 1250 eV. For energies above 1250 eV the only previous measurements [9] deviate from those given in the present work, reaching dis-

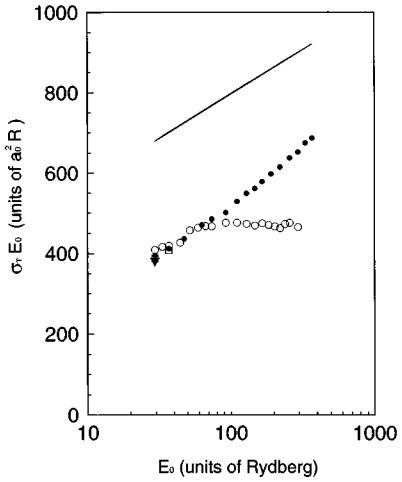

FIG. 1. $\sigma_T E_0$ in a $a_0^2\,R$ units plotted vs E_0 in R units. ●: present experimental results. □: measurements from Ref. [19]. ○: experimental results of Ref. [9]. ▼: experimental result of Ref. [17]. +: experimental value given in Ref. [18]. —: Born-Bethe approximation in the framework of the independent-atom model.

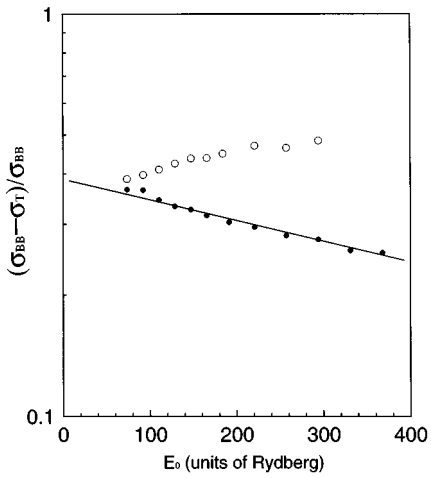

FIG. 2. Relative difference between the experimental total cross sections (σ_T) and those predicted by the Born-Bethe approximation (σ_{BB}) vs electron incident energy (in Rydberg units). ●: from the present experimental results. ○: from the experimental results of Ref. [9].

crepancies of about 30% at 4000 eV. Calculations by Jain and Baluja [5], obtained by means of molecular complex optical potentials, are systematically lower than the experimental values. However, similar calculations obtained by applying additive rules to atomic data up to 1000 eV [7] show an excellent agreement with the experimental results.

The energy range considered in this work is of special interest to check the suitability of the calculations based on the Born-Bethe approximation [11–13]. As described previously [3,4], Born-Bethe total cross sections (σ_{BB}), in the framework of the independent-atom model, can be obtained by applying a sum rule [6–8] to atomic calculations [11,13]. In accordance with this, σ_{BB} for electron scattering by CH_4 is given by the expression:

$$\frac{\sigma_{BB}}{a_0^2}\frac{E_0}{R}=365+94.5\ln\frac{E_0}{R}-123\frac{R}{E_0}+\cdots, \qquad (2)$$

where E_0/R is the incident energy in Rydberg units and a_0 is the Bohr radius. In order to study the dependence of the total cross section on the electron energy for the energy range of this experiment, we made a Bethe plot $[(\sigma_T E_0)/(a_0^2 R)$ versus $\ln(E_0/R)]$, which includes the present results and all the experimental values available in the literature (see Fig. 1). As may be seen, the σ_T dependence on the electron energy agrees for all the experimental values given for energies less than 1250 eV. For higher energies the values of Zecca *et al.* [9] showed a clearly different behavior than those of the present work. The Born-Bethe energy dependence given by Eq. (2) is also shown in Fig. 1.

B. High-energy behavior

The valid energy range of the Born-Bethe approximation can be checked by studying the relative difference between σ_{BB} values and the corresponding experimental ones as a function of energy. Figure 2 is a semilogarithmic plot of $(\sigma_{BB}-\sigma_T)/\sigma_{BB}$ versus E_0/R for energies above 1000 eV, obtained by using the present σ_T values and those of Zecca *et al.* [9] for comparison. As may be seen in this figure, while the relative differences with the Born-Bethe calculations decrease for our values with increasing energies, those of Zecca *et al.* [9] increase when the energy increases. Our data lie on a straight line, which may be fitted by the following exponential function:

$$\frac{\sigma_{BB}-\sigma_T}{\sigma_{BB}}=0.395\exp\left[-\frac{1}{800}\frac{E_0}{R}\right]. \qquad (3)$$

Thus total cross sections for high electron energies ($E_0 > 1000$ eV) can be obtained from the following formula:

$$\sigma_T=\left[1-0.395\exp\left(-\frac{1}{800}\frac{E_0}{R}\right)\right]\sigma_{BB}, \qquad (4)$$

where σ_{BB} is given by Eq. (2). This expression reproduces to a good approximation the present experimental results for electron energies from 1000 to 5000 eV, and can be used to extrapolate σ_T values to higher energies.

This result implies that, according to Eq. (2), σ_T varies with energy as a sum of E_0^{-1} and $E_0^{-1}\ln E_0$ terms, for energies ranging from 1.5 to 5 keV. However, the energy dependence proposed by Zecca *et al.* [9] for this energy range was only proportional to E_0^{-1}. If we compare the extrapolated σ_T value at 5 keV given by the E_0^{-1} formula of Zecca *et al.* [9] with that deduced from the present results [Eq. (4)], a discrepancy on the order of 40% is found. The origin of this discrepancy is not known and therefore more theoretical or experimental data for energies above 1.2 keV are needed to clarify this disagreement. Recently, Joshipura and Vinodkumar [20], found that their calculated total cross sections for electron-molecule collisions at energies above 100 eV can be analytically represented by the following expression:

$$\frac{\sigma_T}{a_0^2}=A[E_0]^{-B}, \qquad (5)$$

where the parameters A and B are given in Ref. [20] for some molecules. In the case of CH_4, their values are 1258

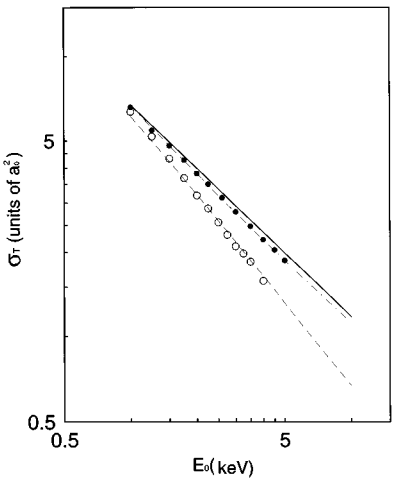

FIG. 3. The energy dependence of total cross sections from 1 to 10 keV. ●: present experimental results. ○: experimental results of Ref. [9]. -·-: the energy dependece given by Eq. (4). ---: the energy dependence deduced by Zecca *et al.* [9] -: energy dependence deduced from the calculations of Ref. [20].

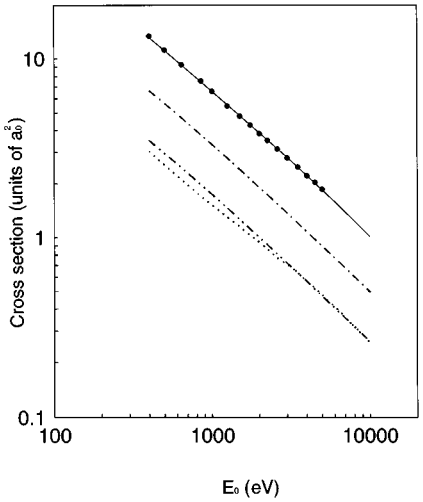

FIG. 4. Partitioning of total cross sections. ●: present experimental results. -: fit given by Eq. (4). -·-: ionization cross section (7). -···-: neutral dissociation cross section (8). ··· : elastic cross section (12).

and 0.757, respectively, when E_0 is given in eV. As may be seen in Fig. 3, the values deduced from Eq. (5) show an excellent agreement, within 6%, with those of the present energy dependence formula [Eq. (4)] for the whole energy range.

IV. PARTITIONING OF TOTAL CROSS SECTIONS

A. Inelastic scattering

As may be deduced from the work of Ref. [21], no bound electronic state of CH_4 is known. All the electronic excitations lead to dissociation in which two or more fragments are produced. For this reason, we can divide the inelastic channels into two groups: processes leading to neutral dissociation or to ionization.

All the measured total ionization cross sections (σ_{ion}), for energies above 100 eV, show an energy dependence in agreement with the Born-Bethe theory:

$$\frac{\sigma_{\text{ion}}}{a_0^2}\frac{E_0}{R}=4\pi M_i^2\,\ln\left(4C_i\,\frac{E_0}{R}\right). \tag{6}$$

In Ref. [22], values for the parameters M_i^2 and C_i are given obtained by fitting their experimental results to the Eq. (6), the values obtained being 4.28 and 1.278 $(\text{R})^{-1}$, respectively. A similar fit for the results of experiments performed at energies below 1000 eV [23,24] gives values of M_i^2 approximately 50% higher. However, the high-energy measurements (0.1–2.7 MeV) of Rieke and Prepejchal [25] give a value of 4.23 for this parameter, which is in excellent agreement with that of Ref. [22]. Other values, derived from oscillator strength distributions, are 3.84 and 3.77, given in Refs. [26] and [27], respectively. From measurements of photoionization cross sections a value of 4.2 can be deduced (see Ref. [22]). Finally, a new assessment of the M_i^2 value can be obtained by applying the additivity rule to the ionization cross sections [28] of the constituent atoms. By using the atomic data of Ref. [29], we obtained a value of 3.7. Taking into consideration all the above-mentioned results for energies higher than 1000 eV, we can consider the values of Schram *et al.* [22] as a good approximation to the constants M_i^2 and C_i, which agree, within 12%, with those obtained by different methods. For these conditions Eq. (6) can be written as

$$\frac{\sigma_{\text{ion}}}{a_0^2}\frac{E_0}{R}=53.8\,\ln\left(\frac{E_0}{R}\right)+13.21. \tag{7}$$

Concerning neutral dissociation, i.e., dissociation of CH_4 into neutral fragments, the corresponding cross sections (σ_{diss}) can be estimate by assuming the conclusions of the experiment of Winters [30] and applying the partial ionic fragmentation probabilities measured by Adamczyk *et al.* [31] to the total σ_{Ion} given by Eq. (6). Accordingly, the neutral dissociation cross section is given by

$$\frac{\sigma_{\text{diss}}}{a_0^2}\frac{E_0}{R}=28.3\,\ln\left(\frac{E_0}{R}\right)+6.96. \tag{8}$$

The total inelastic cross section (σ_{Inel}) can be obtained by adding Eqs. (7) and (8), giving

$$\frac{\sigma_{\text{Inel}}}{a_0^2}\frac{E_0}{R}=82.1\,\ln\left(\frac{E_0}{R}\right)+20.2. \tag{9}$$

The cross-section values deduced from Eqs. (7), (8), and (9) are plotted in Fig. 4.

B. Elastic scattering

Semiempirical data for the elastic cross section in the energy range 400–5000 eV can be deduced by subtracting the values given by Eq. (9) from the experimental total cross sections. In order to obtain an analytical expression for the elastic cross section, we take into consideration the high-energy behavior. For energies where the Born approximation is valid, the total elastic cross section (σ_{el}^B) can be written

$$\frac{\sigma_{\rm el}^B}{a_0^2}\frac{E_0}{R}=\pi\left[A_{\rm el}+B_{\rm el}\frac{R}{E_0}+C_{\rm el}\left(\frac{R}{E_0}\right)^2+\cdots\right]. \quad (10)$$

The constants $A_{\rm el}$, $B_{\rm el}$, and $C_{\rm el}$ are defined for atoms in Ref. [11], and were extended to molecular targets by Bonham and Fink [32]. In the first Born approximation, $A_{\rm el}$ can be written as a function of the elastic differential cross sections:

$$A_{\rm el}=2\int_0^\infty\left(\frac{d\sigma}{d\Omega}\right)K\,dK, \quad (11)$$

where K is the momentum transfer. This equation can be evaluated by means of the elastic differential cross sections calculated by Sharma and Tripathi [33] from their molecular coherent scattering factors. For high energies, the term of $C_{\rm el}$ in Eq. (10) can be neglected, and $B_{\rm el}$ can be evaluated from the atomic data given in Ref. [11]. In these conditions the total elastic cross section of CH_4 for high-energy incident electrons is given by

$$\frac{\sigma_{\rm el}^B}{a_0^2}\frac{E_0}{R}=193.2-123\frac{R}{E_0}+\cdots\ . \quad (12)$$

Following a procedure similar to that described for the total cross section, an analytical expression can also be obtained for the elastic part, giving

$$\sigma_{\rm el}=\left[1-0.62\exp\left(-\frac{1}{185}\frac{E_0}{R}\right)\right]\sigma_{\rm el}^B, \quad (13)$$

where $\sigma_{\rm el}^B$ is given by Eq. (12). The elastic cross section obtained in this way is plotted in Fig. 4.

V. CONCLUSIONS

Total electron-scattering cross sections for the CH_4 molecule have been measured in the energy range from 400 to 5000 eV. The experimental values obtained agree well, within the experimental errors, with previously published values in the energy range from 400 to 1250 eV. Above 1250 eV the only previously published measurements of Zecca *et al.* [9] deviate from the present ones outside the quoted error limits, the discrepancy being larger for increasing energies. The energy dependence above 1 keV deduced from the present σ_T values is in agreement with the results of the Born-Bethe theory in the framework of the independent atom model, and with the recent calculations of Joshipura and Vinodkumar [20]. The total cross sections have been partitioned into constituent processes. In the energy range of this work, the inelastic collisions can be described in terms of the Born-Bethe theory. However, to reproduce the energy dependence of the elastic part a corrective term to the Born formula is required, as shown in Eq. (13).

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