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Energy dependence of the total cross section for electron scattering by chloromethanes in the energy range 0.5–10 keV

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The energy dependence of the total cross section for electron scattering by methane and its chloride compounds has been studied by considering the latest experimental results and those predicted by the Born-Bethe theory. A simple analytical expression depending on the number of electrons and the polarizability of the target is proposed for these molecules. The energy dependence given by this formula shows an asymptotic behavior for increasing energy in better agreement with the Born-Bethe theory. The inconsistency with the Born-Bethe theory of the two-parameter formula given recently by Karwasz *et al.* has also been shown.

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Cross-section values for electron scattering over a wide energy range are required in many scientific and technological applications (astrophysics, atmospheric physics, detector response simulations). Analytical or empirical expressions reproducing data accurately are very useful in computational work related with these applications. In particular, chloromethanes play an important role in environmental studies of the destruction of the stratospheric ozone. For these reasons, an extensive paper devoted to the determination of the total cross sections (σ_T) for electron scattering by these molecules has been recently published by Karwasz *et al.* [1]. In this paper, a two-parameter formula for the energy dependence of σ_T is deduced from their measurements of the attenuation of a circular electron beam in a Ramsauer-type apparatus [2] for electron energies ranging from 75 to 4000 eV. However, for energies above 1 keV, important aspects have not been taken into consideration in the empirical fits of Ref. [1], as will be discussed in this paper.

At electron energies above 1 keV, previous measurements carried out in the mentioned apparatus for other molecules (N_2, CO, CO_2, NH_3, and CH_4) gave systematically lower values than those obtained in linear transmission beam experiments [3–6], reaching discrepancies of about 40% at 4 keV. We have shown [5] that the effect of the forward scattering is the most important source of systematic errors in transmission measurements at high energy, even in experiments with a reasonable angular resolution, and could be the origin of this discrepancy. As can be seen in Ref. [5], the angular acceptance of the detector combined with a zero angle extrapolation of the differential cross section is not enough to define the contribution of the elastic scattering to this error source, and a Monte Carlo simulation of the electron transport showed that in two experiments with similar detection angle, about 10^{-5} sr, this contribution can differ by a factor of 10 at 3 keV. The angular acceptance quoted in Ref. [1], about 10^{-4} sr, is worse than that considered in [5], and the circular trajectories of the electrons in the magnetic field make more difficult the definition of an effective angular resolution, so that the contribution of electrons elastically scattered into the detection angle must be more important in this case. Moreover, the situation in the experiment of Ref. [1] is even worse because the energy resolution of the magnetic spectrometer used is not sufficient to discriminate against the contribution of the inelastic scattering to this error. It is well known that differential ionization and electronic excitation cross sections of molecules by electron impact are strongly peaked in the forward direction at these energies [7]. Therefore, the energy resolution of $\Delta E/E \cong \frac{1}{16}$ used in [1] is clearly insufficient for the energy range considered here. Accurate transmission measurements at these energies require at least that the energy resolution of the detector allows one to discriminate against the main inelastic channels (ionization, electronic excitation, neutral dissociation), i.e., $\Delta E/E \cong 1/1000$ for energies of about 4 keV. The advantages of linear systems combined with electrostatic spectrometers to achieve this requirement at high electron energies has been discussed elsewhere [8]. As a consequence of a poor energy and angular resolution, the apparent total cross section measured in transmission experiments tends to be less than the true value. Consequently, the energy dependence deduced from these apparent values corresponds to a higher slope than expected.

On the other hand, Karwasz *et al.* [1] claim that their two-parameter formula for high energies is supported by the Born approximation. However, they take into account in their argument only elastic scattering of electrons from a Coulomb potential giving an energy dependence of the cross section proportional to E^{-1}. However, in the energy range studied here, inelastic processes add an important contribution to the total cross section, so that an additional term, proportional to $E^{-1}\ln E$, should appear in the expression of the total cross section. The application of the Born model for electron scattering to inelastic processes was introduced by Bethe [9] and reconsidered later by Inokuti [10]. In this combined Born-Bethe (BB) theory the total cross section can be written as a function of the electron energy (E) as

$$\sigma_T^{\mathrm{BB}} = A_T E^{-1} + B_T E^{-1} \ln E + C_T E^{-2} + \cdots , \qquad (1)$$

TABLE I. Born-Bethe parameters of Eq. (1) for methane and its chloride compounds.

Molecule	A_T	B_T	C_T
CH_4	10.08	1.209	-0.0074
CH_3Cl	24.37	1.988	-0.0607
CH_2Cl_2	38.69	2.768	-0.1139
$CHCl_3$	53.00	3.548	-0.1672
CCl_4	67.30	4.327	-0.2205

where E is the electron energy in keV and A_T,B_T,C_T are constants related to internal dynamic properties of the targets (see Refs. [11],[12]). For electron-molecule collisions at high energy, where the independent-atom model [13] applies, and taking into account the optical theorem for the forward scattering amplitude, these parameters can be deduced from those of the constituent atoms. We have calculated these constants for Cl, C, and H from the atomic wave functions deduced by a Hartree-Fock procedure [14]. The results for the parameters in Eq. (1) obtained in this way for methane and chloromethanes are shown in Table I. It is well known that the Born-Bethe theory overestimates the total cross sections in the energy range considered here [6], and especially the elastic part. Therefore, as expected, the total cross section given by Eq. (1) with the parameters of Table I is higher than the experimental one even at 10 keV. However, as this formulation is valid for other applications at higher energies, we can consider Eq. (1) as a correct asymptotic behavior for the energy dependence of σ_T. The consistency of the energy dependence proposed in Ref. [1] with this asymptotic behavior can be checked by studying the relative differences between the σ_T values given in [1] and those calculated with Eq. (1), i.e., $(\sigma_T^{\mathrm{BB}}-\sigma_T)/\sigma_T^{\mathrm{BB}}$, as a function of the incident energy. These differences, in percentage, are plotted for methane in Fig. 1. As this figure shows, the relative difference between the experimental values of Ref. [1] and those given by the Born-Bethe theory increases with energy, reaching discrepancies almost 50% at 4 keV in the case of methane. This points out that the E^{-1} dependence derived from their experimental values is in contradiction with the asymptotic behavior predicted by the Born-Bethe theory. However, by using the experimental data of Ref. [6], these deviations decrease with energy giving an asymptotic behavior in better agreement with the Born-Bethe theory. A similar situation has been found for chloromethanes.

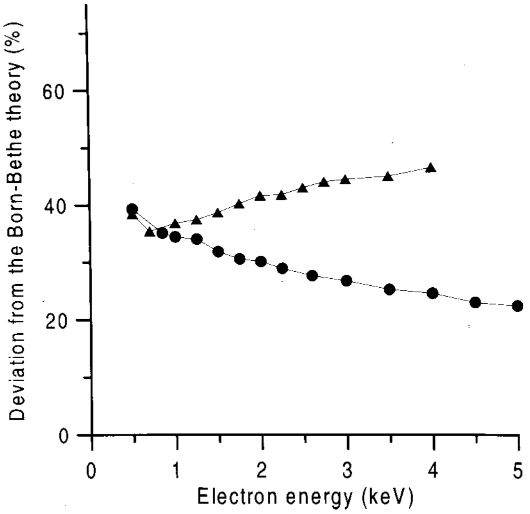

FIG. 1. Relative difference, in percentage, between the experimental total cross sections and those calculated in the Born-Bethe theory by means of Eq. (1) for methane. ▲ corresponds to data given in Ref. [1], and ● to measurements from Ref. [6].

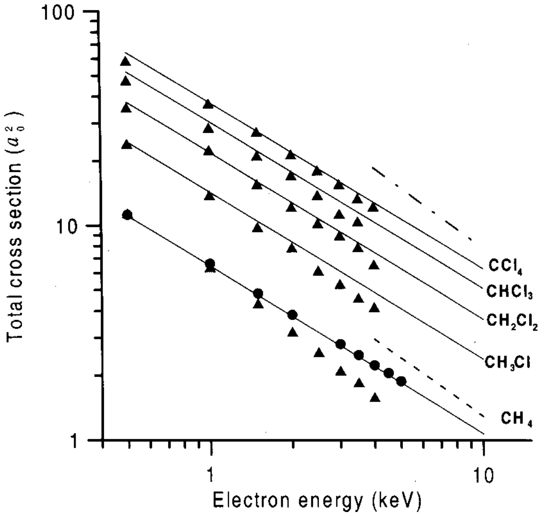

FIG. 2. Total cross section in atomic units (a_0^2) for electron scattering by methane and its chloride compounds for energies ranging from 0.5 to 10 keV. ▲, experimental data given in Ref. [1]; ●, measurements from Ref. [6]; ——, present empirical values; -----, Born-Bethe calculations for CH_4; -·-·-·, Born-Bethe calculations for CCl_4.

There are no other experimental or theoretical total cross-section values available in the literature for chloromethanes at energies above 1 keV. However, in a recent article [15] we proposed an empirical expression for σ_T of some molecules that was based on our measurements performed in a linear-transmission-beam configuration. This formula can be expressed as a function of the molecular polarizabilities (α) and the number of target electrons (Z) as follows:

$$\sigma_T=(0.4Z+0.1\alpha+0.7)E^{-0.78}, \qquad (2)$$

where α and σ_T are given in atomic units (a_0^3 and a_0^2, respectively) and E in keV. By using the molecular polarizabilities given in Ref. [16], empirical values of the total cross section for electron scattering by chloromethanes can be obtained from Eq. (2). These results are plotted in Fig. 2 together with experimental data from Refs. [1],[6]. In order to show the energy dependence predicted by the Born-Bethe theory, results of this theory are also plotted for CH_4 and CCl_4 at high energies (above 3 keV). As this figure shows, although Eq. (2) is an empirical fit of the experimental results for other molecules [15], and for the moment does not have any physical meaning, it gives total cross-section values that are in excellent agreement with the experimental ones at energies about 1 keV and provides an asymptotic behavior for higher energies that seems to approach the Born-Bethe theory. However, data of Ref. [1] for high energies deviate from those of Eq. (2), leading to an asymptotic behavior proportional to E^{-1} which is in contradiction with the Born-Bethe theory [Eq. (1)]. The energy above which this deviation is appreciable depends on the size of the target, and for CH_4 it begins at 1 keV reaching discrepancies of 40% by 4 keV. In the case of CCl_4 this effect begins to be appreciable at 4 keV. As a consequence of this, the atomic values deduced in Ref. [1] by applying their ''additivity rule'' to the molecular ones present the same problem at high energies. Therefore, the E^{-1} dependence for the total cross section for electron scattering from C, H, F, Si, S, and Cl at high energies proposed in Ref. [1] is in clear contradiction with atomic data available in the literature [17] and with our recent studies of electron scattering by atoms at intermediate and high energies [18,19].

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