

A New Semi-Empirical Method for Total Cross Sections of Electron Scattering from Spherical Polyatomic Molecules at 30–5000 eV *

SHI De-Heng(施德恒)^{1,2,3**}, LIU Yu-Fang(刘玉芳)², SUN Jin-Feng(孙金锋)^{2,3},
YANG Xiang-Dong(杨向东)³, ZHU Zun-Lue(朱遵略)^{2,3}

¹Department of Physics, Xinyang Teachers' College, Xinyang 464000

²Department of Physics, Henan Normal University, Xinxiang 453007

³Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065

(Received 2 June 2004)

Electron scattering from spherical polyatomic molecules in the intermediate and high energy range is studied by employing the developed semi-empirical formula for electron scattering from simple diatomic molecules. The total cross sections of electron scattering from CF₄ and CCl₄ are obtained over the incident energy range 30–5000 eV. The quantitative total cross sections are compared with the measurements and with the other calculations wherever available including the results derived from the additivity rule model and the correlated optical potential [Chin. Phys. Lett. 21 (2004) 474], and good agreement is obtained over the incident energy range 30–5000 eV. It is shown that the calculations derived from the semi-empirical formula are much closer to the measurements than other calculations. Finally, some quantitative information of the single Yukawa potential is also obtained.

PACS: 34.80.Bm, 34.80.-i

It is well known that electron–molecule scattering presents a more complex problem than the corresponding electron–atom scattering due to its multi-centre nature, the lack of a central symmetry (in the case of polyatomic and hetero-nuclear molecules) and its nuclear motion. Therefore, for electron–molecule scattering, in order to obtain more accurate total cross sections (TCSs), researchers have presented many approaches.^[1–3] In the intermediate and high energy range, since almost all inelastic channels (rotational, vibrational, electronic excitation and ionization process, etc.) are open, a conventional close-coupling theory for electron–molecule scattering is almost impossible to carry out. Thus, great discrepancies of TCSs exist between theories and measurements at intermediate and high energies.

Recently, many approximate methods, such as the additivity rule (AR) model,^[4,5] the semi-empirical formula for simple diatomic molecules,^[5] the two-parameter formula,^[6] and the spherical complex optical potential (SCOP),^[7] have been proposed. In this Letter, we concentrate on the semi-empirical formula for simple diatomic molecules, and develop it into equations suitable for calculations of spherical polyatomic molecules such as CF₄ and CCl₄.

If we carefully notice the TCSs derived from the AR model,^[8,9] we will find the relations between TCS and the incident energy of electron.^[8] The relations are identical with the first Born approximation.^[10] That is to say, if $E \rightarrow \infty$, then

$$\sigma_T(E) \rightarrow AE^{-1}. \quad (1)$$

Consulting the energy dependence in the Born approximation formula, and analysing a large number of experimental data and theoretical calculations, we hold that the following fitting formula for the total cross sections of electron scattering from diatomic molecules in the intermediate and high energy range is approximately

$$\sigma_T(E) = \frac{d\sigma_0}{d + C\sigma_0 E}, \quad (2)$$

where E is the collision energy of the incident electron in eV; C is a fitting parameter; $\sigma_T(E)$ is the TCS at energy E , and d (Å) and σ_0 (Å²) are the two free parameters for a particular molecule, which can be fitted by two points of energy and the corresponding total cross sections; σ_0 is the TCS which corresponds to zero impact energy.

Let $C = 3 \times 10^{-4}$ (eVÅ)⁻¹. By using Eq. (2), we have fitted the TCS of electrons scattering from CO, NO, O₂, HCl and N₂ and found $d \approx 2r_0$ for diatomic molecules.^[5] This means that the TCS of electron scattering from diatomic molecule depends on the internuclear distance r_0 between the two atoms. In the formula, we treat the e–molecule interactions as a hard sphere potential with radius r_0 . Therefore, the TCS of zero energy would be equal to $4\pi r_0^2$.^[10] We obtain an alternative semi-empirical formula,

$$\sigma_T(E) = \frac{4\pi r_0^2}{1 + C \cdot 2\pi r_0 E}. \quad (3)$$

Now the total cross sections depend on a unique parameter r_0 which is a well-known physical–chemical parameter. Equation (3) can be used to estimate the TCSs immediately to meet the urgent diatomic need

* Supported by the National Natural Science Foundation of China under Grant No 10174019.

** Email: scattering@sina.com.cn

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of data, and be suitable for the TCS calculations of all the diatomic molecules.

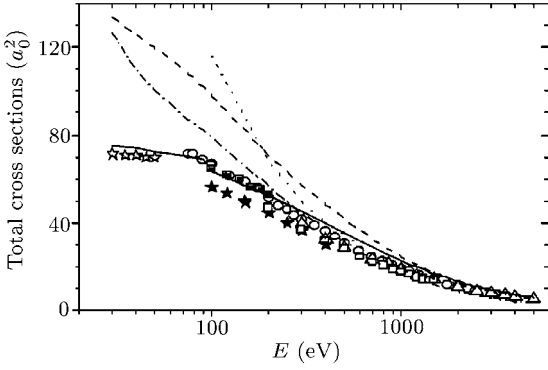


Fig. 1. Total cross sections for e- CF_4 scattering. Theoretical results: dot-dashed line, correlated results;^[12] dashed line, uncorrelated results;^[12] solid line, present; dotted line, Manero *et al.*^[6] Experimental results: circles, Zecca *et al.*;^[13] triangles, Manero *et al.*;^[6] closed stars, Sueoka *et al.*;^[14] closed squares, Szmytkowski *et al.*;^[15] open squares, Ariyasinghe;^[16] open stars, Tones.^[17]

In contrast to the diatomic molecules, CF_4 and CCl_4 have five atoms and have a trigonal pyramidal shape, and the maximum scale along the bond axis between the central atom and any other one (that is to say, the C-F bond for CF_4 and C-Cl for CCl_4) equals the bond length r_0 . Therefore, we set $d = 2r_0$ and

also treat the interactions of electron with CF_4 and CCl_4 roughly as a ‘hard sphere’ potential with radius of r_0 for Eq. (2) which neglects their long-distance interactions of electron with CF_4 and CCl_4 . Thus, we hold that Eq. (3) for TCSs of electron scattering from CF_4 and CCl_4 over the intermediate and high energy range is appropriate.

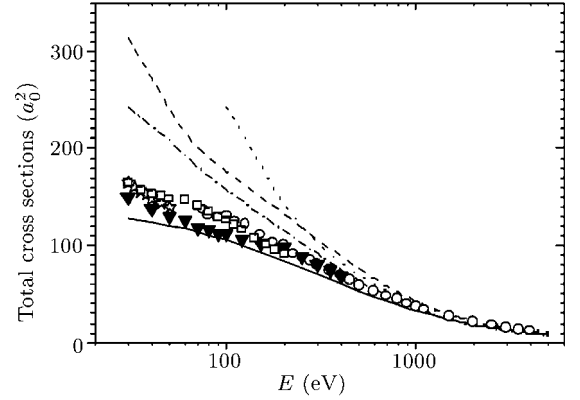


Fig. 2. Total cross sections for e- CCl_4 scattering. Theoretical results: dot-dashed line, correlated results;^[18] dashed line, uncorrelated results;^[18] solid line, present; dotted line, Garcia *et al.*^[19] Experimental results: circles, Zecca *et al.*;^[13] closed triangles, Hamada *et al.*;^[20] stars, Jones;^[17] squares, Szmytkowski *et al.*^[15]

Table 1. Total cross sections for electron scattering from CF_4 and CCl_4 in units of a_0^2 .

Energy (eV)	CF_4	CCl_4	Energy (eV)	CF_4	CCl_4	Energy (eV)	CF_4	CCl_4	Energy (eV)	CF_4	CCl_4
30.0	62.91	127.5	300.0	22.50	70.13	1200.0	13.70	28.06	2200.0	9.55	16.84
40.0	52.44	123.7	400.0	20.99	60.12	1300.0	13.13	26.31	2400.0	9.00	15.59
50.0	44.96	120.2	500.0	19.67	52.60	1400.0	12.60	24.79	2600.0	8.52	14.51
60.0	39.35	116.9	600.0	18.53	46.76	1500.0	12.12	23.38	2800.0	8.08	13.58
70.0	34.98	113.7	700.0	17.50	42.09	1600.0	11.69	22.15	3000.0	7.69	12.76
80.0	31.49	110.7	800.0	16.58	38.26	1700.0	11.25	21.05	3500.0	6.85	11.08
90.0	28.63	107.9	900.0	15.75	35.07	1800.0	10.86	20.04	4500.0	6.43	8.77
100.0	26.24	105.2	1000.0	15.00	32.38	1900.0	10.50	19.13	4000.0	7.16	9.79
200.0	24.23	84.15	1100.0	14.32	30.06	2000.0	10.16	18.30	5000.0	5.84	7.94

Using Eq. (3) and values of $r_0 = 1.323 \text{ \AA}$ for CF_4 and $r_0 = 1.767 \text{ \AA}$ for CCl_4 ,^[11] we have calculated the TCSs of electron scattering from the two spherical polyatomic molecules CF_4 and CCl_4 at 30–5000 eV. These calculations together with the available measurements, recent theories by employing correlated complex optical model potential, and the empirical results given by Manero *et al.*^[6] and Garcia *et al.*^[19] are shown in Figs. 1 and 2, respectively. At the same time, the present semi-empirical calculations are listed in Table 1. Atomic units are employed throughout this paper unless otherwise specified.

Now we start by discussing the TCS for e- CF_4 scattering. Figure 1 shows the present TCS results together with the calculations derived from the complex optical model potential correlated and uncorrelated by the concept of bonded atom^[12] at 30–5000 eV,

and the measurements given by Zecca *et al.*^[13] at 75–4000 eV, Manero *et al.*^[6] at 300–5000 eV, Sueoka *et al.*^[14] at 100–400 eV, Szmytkowski *et al.*^[15] at 100–200 eV, Ariyasinghe^[16] at 100–1500 eV, Jones^[17] at 30–50 eV, and the empirical results given by Manero *et al.*^[6] at 100–5000 eV. From Fig. 1, we can easily see that the present TCSs of electron scattering from CF_4 obtained from Eq. (3) agree well with all the measurements^[6,13–17] at the corresponding energies. The results also agree well with the data derived from the potential correlated by the concept of bonded atom above 100 eV,^[12] and agree well with the calculations derived from the empirical formula given by Manero.^[6] However, there is bad agreement between the data derived from the potential uncorrelated by the concept of bonded atom and all the measurements below 1000 eV. The discrepancies between

the measurements and the calculations derived from the empirical formula given by Manero^[6] is too large to bear! Therefore, we can say that Eq. (3) is completely suitable for the calculations of the TCSs of e-CF₄ scattering.

Figure 2 shows the present e-CCl₄ TCS results together with the correlated and uncorrelated calculations^[18] at 30–5000 eV, the empirical values given by Garcia *et al.*^[19] at 100–5000 eV, the measurements of Zecca *et al.*^[13] at 75–4000 eV, Szymkowski *et al.*^[15] at 30–200 eV, Jones^[17] at 30–50 eV, and Hamada *et al.*^[20] at 30–400 eV. Obviously, the present results obtained from Eq. (3) agree well with all the measurements above 60 eV, and also agree well with recent calculations.^[18] Below 100 eV, the present results are lower than all the measurements, but much closer to all the measurements than the correlated and uncorrelated calculations obtained by the method given in Ref. [18]. For example, the largest discrepancies between the measurements of Ref. [20] and the present results, and between the measurements of Ref. [13] and the present results are 14.9% and 16.3%, respectively, whereas the largest discrepancies between the measurements of Ref. [20] and the correlated calculations, and between the measurements of Ref. [13] and the correlated calculations are 61.4% and 29.4%, respectively.

We can see from Figs. 1 and 2 that the values given by Garcia *et al.*^[6,19] are much higher than all the measurements at 100–400 eV, whereas the uncorrelated calculations are even higher than all the measurement at 30–800 eV. At the same time, the present results are much closer to the measurements than the correlated calculations^[18] below 150 eV. Thus, our present results are encouraging.

The discrepancies between the values derived from the semi-empirical formula and the measurements are exhibited in Figs. 1 and 2. The reason is that we treat the interactions of electron with CF₄ and CCl₄ roughly as a ‘hard sphere’ potential with radius of r_0 . This approximation only considers the short-range interactions of electrons with CF₄ and CCl₄ and neglects the long-range interactions. The leading term of the long-range interactions is $-\alpha_0/r^4$ (α_0 is the polarizability). For non-polar molecules, the next important long-range term is the dynamical effects in the dipole polarization interaction. Since the long-range interactions are different from each other, so the discrepancies remain and differ from each other.

From the above calculations and discussion of e-CF₄ and e-CCl₄ scattering, we easily see that Eq. (3) can give very accurate TCS results. Some qualitative explanations of relations between Eq. (3) and the Yukawa potential with the bond length are presented in the following. Yukawa proposed a model potential for the nucleon interaction on the basis of meson

theory,

$$V(r) = -\frac{V_0}{r}e^{-\frac{r}{a}}. \quad (4)$$

Zecca *et al.*^[21] found that the TCS can be well approximated by a single or a double Yukawa potential. They also obtained quantitative information on strength V_0 and in the range a of some molecular scattering potential, but the values of V_0 and a rely on the measurements. If we treat the e-molecule interactions as a single Yukawa potential, then the TCS can be well expressed by^[10]

$$\sigma_T(E) = \frac{4\pi V_0^2}{a^2 \left(a^2 + \frac{2mE}{\hbar^2} \right)}. \quad (5)$$

Comparing Eq. (2) with Eq. (5), we can gain the magnitudes of a and V_0 , i.e.

$$a = \sqrt{\frac{m}{C\pi r_0 \hbar^2}}, \quad (6)$$

$$V_0 = \frac{m}{C\pi \hbar^2}. \quad (7)$$

Equation (6) shows that the applicable range of the single Yukawa potential depends on the bond length of CF₄ and CCl₄. From Eq. (7), we can find that the strength of the single Yukawa potential is a constant and does not depend on the physical-chemical parameters of CF₄ and CCl₄.

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