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Ramsauer–Townsend minimum in electron scattering from CF$_4$: modified effective range analysis

Kamil Fedus[a] and Grzegorz P. Karwasz

Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5/7, 87-100 Toruń, Poland

Abstract. Elastic cross sections for electron scattering on tetrafluoromethane (CF$_4$) from 0 up to 5 eV energy are analyzed using semi-analytical approach to the modified effective range theory (MERT). It is shown that energy and angular variations of differential, integral and momentum transfer cross sections can be parameterized accurately by six MERT coefficients up to the energy region of the resonant scattering. In particular, the model is used to determine the depth and the position of the Ramsauer–Townsend minimum as well as the s-wave scattering length. Moreover, we investigate the influence of the dipole polarizability value on the predictions of present model. To further validate our approach, the elastic data are combined with the Born-dipole cross sections for vibrational excitations as the input data for Monte Carlo simulation of electron swarm coefficients.

1 Introduction

Carbon tetrafluoride (CF$_4$) is used for etching Si and SiO$_2$ from the beginning of nano-electronics era [1]. It is a great source of reactive species needed for plasma processing of materials. However, it could be also a reason of some undesirable effects such as enlarging the etched paths. This is due to the peculiarity of the cross sections for electron scattering: high thresholds for the ionization and relatively large contribution from the dissociation into unstable neutral and ionized fragments, see review papers on cross section for e^--CF$_4$ collisions by Bonham [2], Christophorou et al. [3], Karwasz et al. [4] or Sakai [5]. Nevertheless, as recently showed [6], CF$_4$ in appropriate mixtures with other gases (O$_2$, He, C$_4$F$_8$) can be used for preparation of nanowires of SiGe and Si as thin as 20 nm in diameter. Obviously, to avoid laboratory try-and-error procedures, theoretical modeling of plasma is desirable.

The very low-energy collisions (below 1 eV), apparently, seem to be less important in plasma processing than the inelastic processes starting at few eV such as dissociation and ionization. On the contrary, it is the Ramsauer–Townsend minimum of the integral elastic cross sections at 0.3 eV that defines the overall temperature of Ar-based discharges with practical applications in lighting [7]. Moreover, the elastic collisions are of primary importance in numerical modeling of plasma, particularly at low temperatures. In this paper we discuss the very low-energy electron elastic scattering on CF$_4$. Relatively, few papers explored this problem. The

first relative measurements of total cross sections by David Field's group [8] (repeated later by Lunt et al. [9]) indicated the presence of Ramsauer–Townsend (R-T) minimum somewhere at 0.15 eV. However, the evidence was not clear since the same energy regime corresponds to excitation thresholds for bending (symmetric ν_2 at 0.054 eV and asymmetric ν_4 at 0.078 eV) and stretching (symmetric ν_1 at 0.112 eV and asymmetric ν_3 at 0.157 eV) vibrational modes. Due to the high transition dipole moments of CF$_4$ molecule the vibrational scattering channel may become the leading contribution to the total cross sections. Therefore, the separation of the two contributions: elastic one and vibrational one at low energies, is essential. Unfortunately, later absolute measurements of total cross sections were not carried out at such low energies: Gdańsk laboratory stopped at 0.4 eV [10], Jones [11] at 1 eV and Tokyo group at 1.5 eV [12]. Only the measurement of differential elastic cross sections (DCS) down to 0.3 eV by Mann and Linder [13] helped to confirm the presence of R-T minimum in integral elastic cross sections (IECS). This minimum was derived from experimental data using the modified effective range theory (MERT), as formulated in sixties of last century by O'Malley et al. [14]. MERT allows to extrapolate measured cross sections down to ultra-low energies which are inaccessible experimentally. Another evidence for the presence of R-T minimum in IECS was brought by the analysis of electron transport parameters measured in swarm experiments (i.e., a cloud of electrons adrift in external electric field through relatively dense CF$_4$ gas) by Curtis et al. [15] and Hayashi [16]. However, swarm-derived IECS in both experiments

^{a} e-mail: kamil@fizyka.umk.pl (corresponding author)

do not agree on the energy position, the width and the depth of minimum.

The theoretical research on the low-energy e^--CF_4 collisions are even more scarce than experimental ones. Although there are several high-quality theoretical works for energies just above 1 eV [17–21] to the best of our knowledge, only Isaacs et al. [22] and Gianturco and Willner [23] computed scattering cross sections at much lower energies. Both models predict the presence of R-T minimum, but they do not agree, either with the experiments and with each other, on the exact position of this minimum.

In the present work we re-analyze available experimental data of elastic cross sections for e^--CF_4 collisions using a new approach to MERT as proposed by Idziaszek and Karwasz [24] and applied successfully for noble gases and some molecules (H_2, CH_4) [25,26]. In the original MERT formulation by O'Malley et al. [14] the scattering phase shift of partial wave with given angular momentum is expanded into the energy series known as the effective range expansion. In contrast to the original approach, in the present work we take into account the exact contribution of the long-range polarization potential ($\sim r^{-4}$) to the phase shifts, while the effective range approximation is applied exclusively to unknown short-range interaction. This allows to extend the applicability of MERT almost up to the threshold for electronic excitation, while the original MERT [14] (where contributions of both long and short-range parts of interaction are approximated) is valid only at ultra-low energies (much below 1 eV) as proved by Buckman and Mitroy [27] for noble gases and Chang [28] for nonpolar molecules. In this work we show that a new approach to MERT can be used to describe elastic cross sections for e^--CF_4 collisions up to such high energy as 5 eV, i.e., just below the threshold for resonant scattering. To validate our approach the MERT-derived momentum transfer cross section (MTCS) in the region of R-T minimum is combined with vibrational cross sections calculated using Born-dipole approximation as input data for METHES Monte Carlo collision code [29] in order to calculate electron drift coefficients.

In the following section we will briefly describe our current theoretical methodology to derive elastic cross section for e^--CF_4 collisions at low energies, while in Sect. 3, we report our analysis. Section 4 summarizes our conclusions.

2 Theoretical model

A semi-analytical approach to MERT, originally introduced by O'Malley et al. [14], has been discussed in details in our previous papers [24,25]. Therefore, only a brief description will be given here. MERT analytical expression for partial wave scattering phase shift induced by the spherical part of the long-range dipole polarization potential is given by the following expression (in atomic units) [14]:

$$\tan \eta_l = \frac{m_l^2 - \tan \delta_l^2 + \tilde{B}_l \tan \delta_l (m_l^2 - 1)}{\tan \delta_l (1 - m_l^2) + \tilde{B}_l (1 - m_l^2 \tan^2 \delta_l)}, \quad (1)$$

where l is the angular momentum quantum number and $\delta_l = \frac{\pi}{2}(\nu_l - l - \frac{1}{2})$. Here m_l and ν_l denote the energy-dependent parameters which have to be determined numerically for each partial wave using the procedures described in Refs. [24,25]. Parameter $\tilde{B}_l$ is related to the phase shift that is induced by the unknown short-range potential. O'Malley et al. [14] showed that this parameter can be approximated by the effective range expansion:

$$\tilde{B}_l = B_l(0) + \frac{1}{2} R^* R_l k^2 + \cdots, \quad (2)$$

where k is a wavenumber, B_l is the zero energy contribution, R_l can be interpreted as the effective range for a given partial wave and $R^* = \alpha^{1/2}$ with α being the dipole polarizability. In the particular case of $l = 0$, B_0 can be expressed in terms of A_0, the s-wave scattering length, as $B_0 = -R^*/A_0$.

Using this semi-analytical model we verified below that in the energy range $E \leq 5$ eV (i.e., below resonance), the leading contributions come from s, p and d partial waves ($l = 0, 1, 2$), while the contributions of higher partial waves are small and they are not modified by the short-range forces due to very high centrifugal barriers associated with large l numbers. Therefore, the scattering phase shifts experienced by higher partial waves are described by taking only the leading order contribution in the energy dependence of scattering phase shifts:

$$\tan \eta_l(k) = \frac{\pi \alpha k^2}{8(l - 1/2)(l + 1/2)(l + 3/2)}, \quad \text{for } l > 2. \quad (3)$$

We found that the k^4 terms appearing in phase shifts induced by pure long-range forces (due to charge-induced dipole and quadrupole moments) as presented by Ali and Fraser [30] give only minor contribution and since the quadrupole polarizability of CF_4 is still unknown, these terms were omitted. Moreover, due to the lack of permanent dipole moment the rotational excitation can be neglected.

Integral elastic (σ_{IE}), momentum transfer (σ_{MT}) and differential elastic ($\frac{d\sigma}{d\omega}$) cross sections are calculated using the standard partial wave expansions:

$$\sigma_{IE} = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l + 1) \sin^2 \eta_l(k) \quad (4)$$

$$\sigma_{MT} = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (l + 1) \sin^2[\eta_l(k) - \eta_{l+1}(k)] \quad (5)$$

$$\frac{d\sigma}{d\omega} = \frac{1}{k^2} |\sum_{l=0}^{\infty} (2l + 1) \exp \eta_l \sin \eta_l(k) P_l(\cos \theta)|^2 \quad (6)$$

where θ is the scattering angle and $P_l(x)$ are the Legendre polynomials. In the zero energy limit both integral elastic and momentum transfer cross sections can be expressed by the s-wave scattering length:

$$\sigma_{IE}(k) \approx \sigma_{MT}(k) = 4\pi A_0^2, \quad \text{for } k \to 0. \qquad (7)$$

Substituting Eqs. 1–3 into Eqs. 4–6 one gets relations which can be fitted to experimental data in order to determine the unknown parameters of the effective range expansion of $\tilde{B}_l(k)$.

3 Results

There are only three measurements of elastic differential scattering cross sections (DCS) for e^--CF_4 collisions. Sakae et al. [31] measured the DCS for incident electron energies between 75 and 700 eV and for scattering angles between $5°$ and $135°$. Boesten et al. [32] measured the DCS in the energy range of 1.5–100 eV and over the scattering angles of $15° - 130°$. Mann and Linder [13] measured the DCS in the energy range 0.3–20 eV for scattering angles from $10°$ to $105°$. In all three works [13,31,32] experimental DCS were extrapolated to $0°$ and $180°$ scattering angles and the integral (IECS) and momentum transfer (MTCS) elastic cross sections were estimated by simple integration procedures. In addition Mann and Linder [13] applied original MERT to their low-energy DCS ($E < 1$ eV) in order to estimate IECS for the energies between 0.001 and 0.5 eV. Later the similar MERT extrapolation was done by Lunt et al. [9] to their low-energy (normalized) experimental total cross sections between 0.01 and 0.175 eV. However unlike Mann and Linder, MERT analysis done by Lunt et al. did not give the s-wave scattering phase shift passing through the zero for any energy. The latter effect is responsible for the presence of R-T minimum in IECS. It has to be also added that both earlier MERT analysis [9,13] used dipole polarizability $\alpha = 25.9a_0^3$ measured by Miller et al. [33]. However, more recent works indicate on much lower value between 19 and 20 a_0^3, see the paper by Olney et al. [34] and references therein. We show below that such a huge difference in dipole polarizability have an important impact on the results of the MERT extrapolation of cross sections toward the zero energy.

In Fig. 1 we present the results of present MERT fits to experimental DCS by Mann and Linder [13] and Boesten et al. [32] using $\alpha = 19.5a_0^3$ and $\alpha = 25.9a_0^3$. We have developed a numerical procedure to fit the model simultaneously to all considered experimental datasets in order to optimize the derivation of parameters in the effective range expansion (Eq. 2). The derived parameters are given in Table 1. We found that model is able to reconstruct experimental data within their error bars up to the energy of 5 eV independently on polarizability. At higher energies the resonant scattering occurs and the coupling between elastic and vibrational scattering channels, which may affect the dipole polarizability,

imposes limitation for the applicability of the present model. Present MERT fit is also compared in Fig. 1 with complex Kohn calculations of Isaacs et al. [22]. The agreement is relatively good except very low scattering angles ($\theta < 10°$) where MERT predicts a slight rise of DCS. This kind of rise is expected at low energies for highly polarizable quasi-spherical systems such as CF_4 where the electron interaction with the electric dipole induced in molecule is dominant. If polarization potential is sufficiently strong, its long-range nature ($\sim r^{-4}$) should result in efficient scattering of incoming charged particles at very low angles. Present MERT results are in agreement with such expectation since the rise of DCS at low angles is larger for higher α.

In Fig. 2 we show how the MERT-derived s-wave scattering length (A_0) changes with the value of dipole polarizability (α). The scattering length decreases almost linearly from $-2.0a_0$ to $-3.06a_0$ with the rise of α. This is reflected in much higher integral s-wave cross section for larger α at energies below 1eV—as shown in the inset of Fig. 2. On the other hand, the s-wave cross section is weakly sensitive to α for energies higher than 1eV—so in the energy regime where most of fitted data reside. Independently on polarizability, the present MERT predicts the presence of minimum in the s-wave cross section. The polarizability affects only the position and the depth of minimum—higher α shifts the minimum toward higher energies making it shallower.

In Table 2 we compare presently derived range for s-wave scattering length ($-2.0a_0$ to $-3.06a_0$) with other estimates available in the literature. Present values are consistent with MERT analysis done by Mann and Linder [13] and Lunt et al. [9]. Moreover, we stay in agreement with quantum-mechanical calculations of Gianturco and Willner [23]. However, the value of $-3.0a_0$ reported in the latter work was obtained considering $\alpha = 19.6a_0^3$, while here the same result was achieved for $25.9a_0^3$. Theoretical calculations by Tossell and Davenport [35] as well as the analysis of experimental photoionization spectra by Evans et al. [36] predict much larger IECS in the zero energy limit. Additionally, for comparison we give also in Table 2 the only available estimation (to the best of our knowledge) of scattering length for positron collisions with CF_4 provided by Nishimura and Gianturco [37]. Surprisingly, the value obtained by these authors is lower in absolute magnitude than results for electrons. Generally, the comparison of positron and electron scattering data for different atomic and molecular targets [25,38,39] shows opposite results—the positron scattering length is much larger in absolute value due to much stronger polarization effects at low energies that enhance significantly the interaction between the projectile and the target. Strong attractive polarization can lead to virtual positronium formation [40] or even to the formation of positron bound state with molecule [41]. Present MERT model can be used to estimate the positron scattering length once some elastic data on positron scattering from CF_4 will be available at few eV. We have already proven that present approach to MERT works
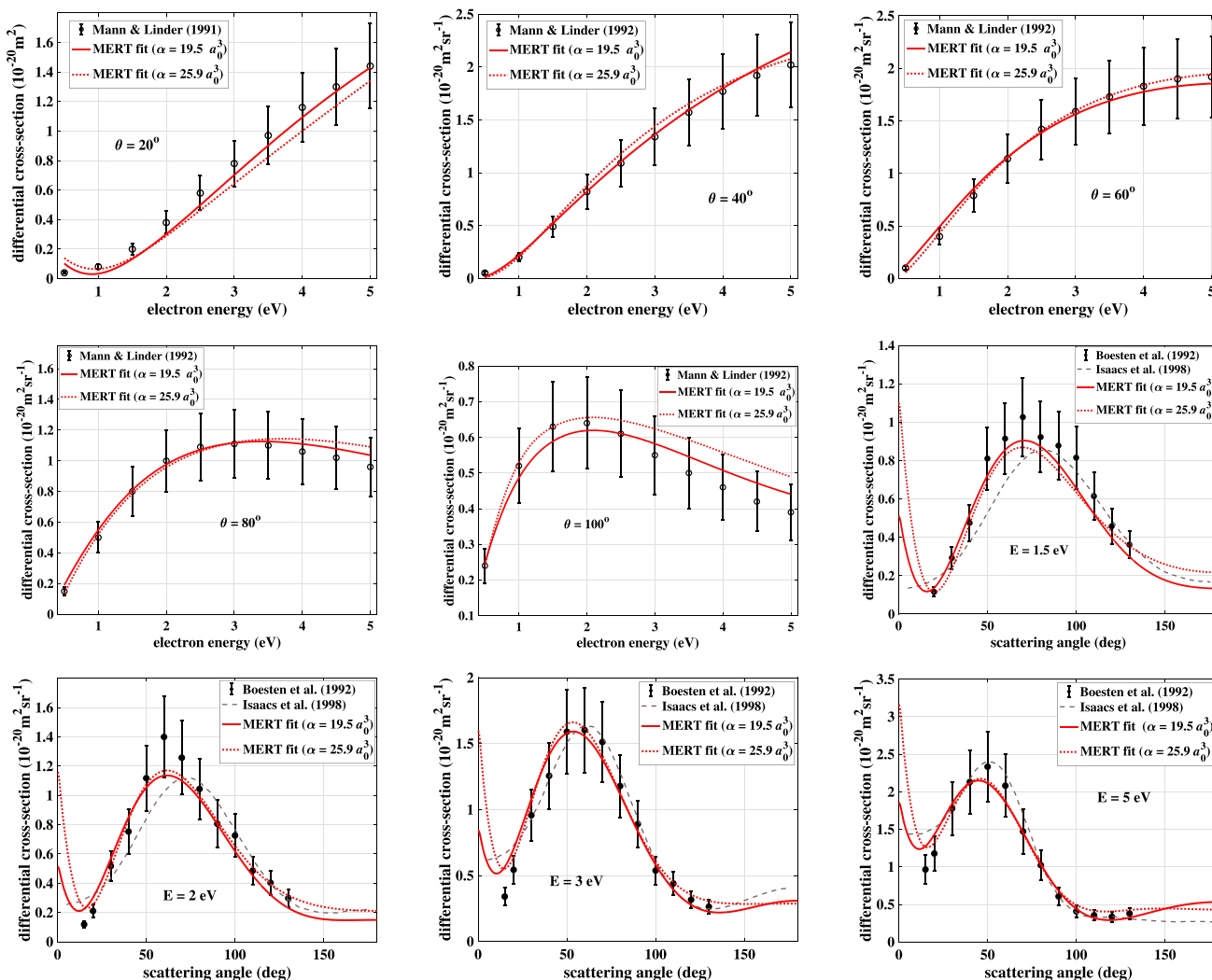
Fig. 1 MERT simultaneous fit (solid lines with $\alpha = 19.5a_0^3$ and dotted lines with $\alpha = 25.9a_0^3$) to elastic differential cross-section datasets measured by Mann and Linder [13] and Boesten et al. [32] for electron energies below 5 eV. Present fit is compared with complex Kohn calculations (dashed lines) of Isaacs et al. [22]

Table 1 Parameters of the effective range expansion defined in Eq. 2 for s, p and d partial waves (i.e., for $l = 0$, 1 and 2) in electron scattering from CF_4. Parameter A_0 denotes the s-wave scattering length

$\alpha(a_0^3)$	$A(a_0)$	B_1	B_2	$R_0(a_0)$	$R_1(a_0)$	$R_2(a_0)$
19.5	-2.001	-0.608	-0.178	1.176	0.020	0.042
25.9	-3.077	-0.781	-0.073	0.587	-0.067	-0.079

for positron collisions at the same energy range as for electrons [24,25,42].

In Fig. 3 we present the energy dependence of scattering phase shifts for s, p and d partial waves and the corresponding IECS and MTCS (for $\alpha = 19.5a_0^3$). The s-wave phase shift passes through the zero at energy of 0.185 eV clearly indicating on the presence of R-T minimum. Interestingly, the p-wave phase shift crosses the zero slightly above 1eV, while the d-wave phase shift passes through the zero at around 10 eV (not shown in Fig. 3), i.e., at the maximum of resonant scattering

if we extend our calculations to higher energies. In the resonance region the s-wave phase shift approaches the value of $\pi/2$.

In the terms of position and deepness of R-T minimum, MERT-derived IECS and MTCS are much different than quantum mechanical calculations by Isaacs et al. [22] and Gianturco and Willner [23] as well as swarm-derived cross sections by Curtis et al. [15] and Hayashi [16], as shown in Fig. 3. On the other hand, present MERT for $\alpha = 19.5a_0^3$ stays in good agreement with elastic cross sections recommended by Christophorou
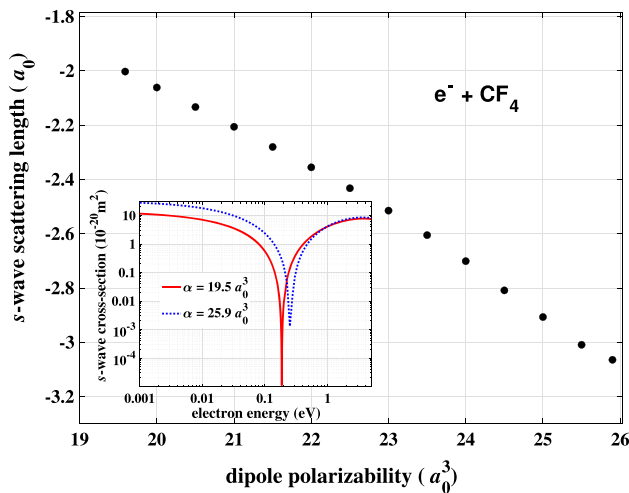
Fig. 2 MERT-derived s-wave scattering length (A_0) as a function of dipole polarizability (α). The inset presents integral s-wave cross section in the region of Ramsauer–Townsend minimum calculated using two extreme values: $\alpha = 19.5a_0^3$ and $\alpha = 25.9a_0^3$

et al. [3]. This is not surprising since this recommendation was based on available experimental DCS: below 0.5 eV they propose to use MERT analysis done by Mann and Linder [13], while above 1 eV they fitted a line to mean values of three integrated DCS datasets [13,31,32]. Between 0.5 eV and 1 eV, where no integral data were available, the interpolation was done to connect the region of R-T minimum with higher energies. In the present paper we validate this recommendation on the basis of more stronger principles showing that available low and high energy experimental data describing e^--CF$_4$ elastic collisions are consistent with each other within the frame of present MERT model.

Figure 4 shows selected integral cross sections including all available total cross sections (TCS) measured below 5 eV. Relative TCS by Lunt et al. [9] measured in region of R-T minimum are normalized to absolute TCS by Szmytkowski et al. [10] at 1 eV. The sharp rise of TCS with increasing energy starting at 0.16 eV is related to the excitation of asymmetric stretching

vibrational mode ν_3. This mode has relatively large infrared (IR) activity. Non-negligible contribution to TCS comes also from electron impact excitation of asymmetric bending mode ν_4; however, this mode is much weaker than ν_3—this is consistent with its lower IR activity. The other two modes: symmetric stretching and bending (ν_1 and ν_2, respectively) are expected to be characterized by much lower cross sections and they cannot be distinguished experimentally from their asymmetric counterparts [3]. The only direct measurements of integral vibrational cross sections in the near threshold region (i.e., below 1 eV) for ν_3 mode were reported by Marler et al. [43,44] (for both electron and positron impact excitation). The subsequent quantum calculations by Franz et al. [45] confirms this experimental finding. Both experiment and theory show that vibrational cross sections can be quite well described by the Born-dipole model (with the dipole strength determined from infrared absorption data). This is consistent with conclusions reached earlier by Mann and Linder [46] and Boesten [32] who measured vibrational DCS in the near threshold region. Therefore, we follow here the recommendations of other authors [3,44] to describe cross sections for excitation of ν_3 and ν_4 modes by the Born-dipole approximation. According to this approach the integral cross section for electron impact excitation of ν vibrational mode is given by the following relation (in atomic units):

$$\sigma_{ICS}^{vib}(\nu \to \nu') = \frac{8\pi}{3k^2} g_\nu \left|\langle\nu'|D|\nu\rangle\right|^2 \log \frac{k+k'}{|k-k'|}. \quad (8)$$

Here k and $k' = \sqrt{k^2 - \omega_\nu}$ are the initial and final electron momenta, ω_ν is the initial energy of the ν mode and g_ν is its degeneracy. The quantity $|\langle\nu'|D|\nu\rangle|$ is the dipole transition strength. For optically active modes the latter (in atomic units) can be determined from infrared absorption measurements [47] using

$$|\langle\nu'|D|\nu\rangle| = 0.2487\sqrt{\frac{A_\nu[\text{km/mol}]}{g_\nu\omega_\nu[\text{cm}^{-1}]}}, \quad (9)$$

Table 2 Presently determined electron−CF$_4$ scattering length (A_0 in Bohr length units a_0) compared to available semiempirical and theoretical results. For comparison the only available estimation of positron−CF$_4$ scattering length is also given

| Reference	Scattering length (a_0)
Electrons:	
Present MERT with $\alpha = 19.5a_0^3$	-2.00
Present MERT with $\alpha = 25.9a_0^3$	-3.06
Lunt et al. [9], original MERT below 1eV with $\alpha = 25.9a_0^3$	-2.22
Mann and Linder [13] , original MERT below 1eV with $\alpha = 25.9a_0^3$	-2.36
Gianturco and Willner [23], quantum-mechanical calculations (with $\alpha = 19.6a_0^3$)	-3.00
Evans et al. [36], analysis of photoionization spectra	-3.40
Tossell and Davenport [35], MS-Xα calculations	≈ -4.77
Positrons:	
Nishimura and Gianturco [37], quantum-mechanical calculations (with $\alpha = 19.6a_0^3$)	≈ -1.83
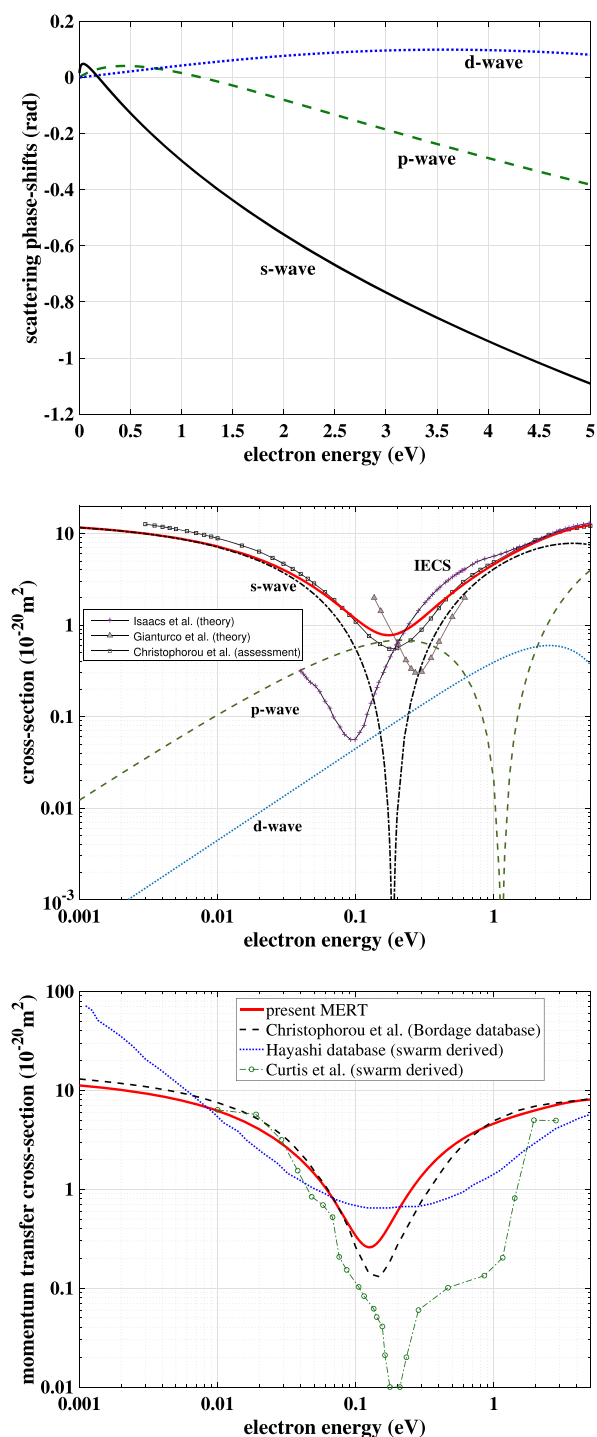
Fig. 3 MERT-derived (with $\alpha = 19.5a_0^3$) scattering phase shifts for s, p and d partial waves and corresponding integral elastic (IECS) and momentum transfer (MTCS) cross sections in the region of Ramsauer–Townsend minimum (solid lines). The contribution of particular partial waves to IECS is also presented. Present calculations using $\alpha = 19.5a_0^3$ are compared with other results including IECS and MTCS by Isaacs et al. [22], Gianturco and Willner [23], Hayashi [16], Curtis et al. [15] and Christophorou et al. [3] (the latter data are recommended by Bordage et al. [50])
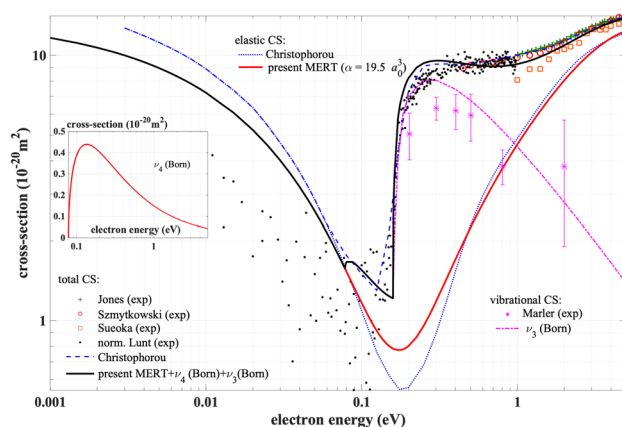
Fig. 4 Selected integral cross sections for electron scattering on CF_4 in the region of Ramsauer–Townsend minimum. *Elastic*: present MERT (for $\alpha = 19.5a_0^3$) and recommended by Christophorou et al. [3]. *Vibrational excitation*: experimental data of Marler et al. [43,44] and Born-dipole approximation calculation using infrared measurements [47] to fix the dipole transition strength for ν_3 stretching mode. The inset presents the Born-dipole approximation for ν_4 bending mode. *Total*: present elastic MERT $+ \nu_3$(Born)$+ \nu_4$ (Born) is compared with recommendation of Christophorou et al. [3] and experimental data of Jones [11], Szmytkowski et al. [10], Sueoka et al. [12] and Lunt et al. [9] normalized to Szmytkowski et al. at 1eV

where A_ν (in km/mol units) is the integrated IR intensity.

In the present work we used A_ν and ω_ν values provided by Bishop and Cheung [47]: 935.3 km/mol and 1283 cm^{-1} for ν_3 mode and 12.3 km/mol and 632 cm^{-1} for ν_4 mode. Both ν_3 and ν_4 are triply degenerate [3]. The Born-dipole vibrational cross section were added to MERT-derived IECS in order to determine total cross section (TCS). The obtained result for $\alpha = 19.5a_0^3$ remains in very good agreement with available experimental TCS below 5 eV, see Fig. 4.

A stringent test for the reliability of recommended cross sections is to use them as input in a calculation of electron transport through a dense gas in a uniform electric field where multiple scattering takes place. Correct cross sections for all possible scattering processes combined with reliable numerical procedures should provide transport coefficients such as drift velocity, the transverse (D_T) and longitudinal (D_L) diffusion coefficients in agreement with swarm experiments. Electron swarm techniques allow to determine the transport parameters much more precisely [48] than the electron beam techniques (where only single scattering occurs) allows for determination of the scattering cross sections. Therefore, the transport parameters are frequently used to test different cross-section "sets." However, the problem of uniqueness is the main drawback of such a test since different cross-section "sets" can sometimes lead to "the same transport" parameters. Consequently, in the case of CF_4, few different complete cross-section databases have been proposed in the past
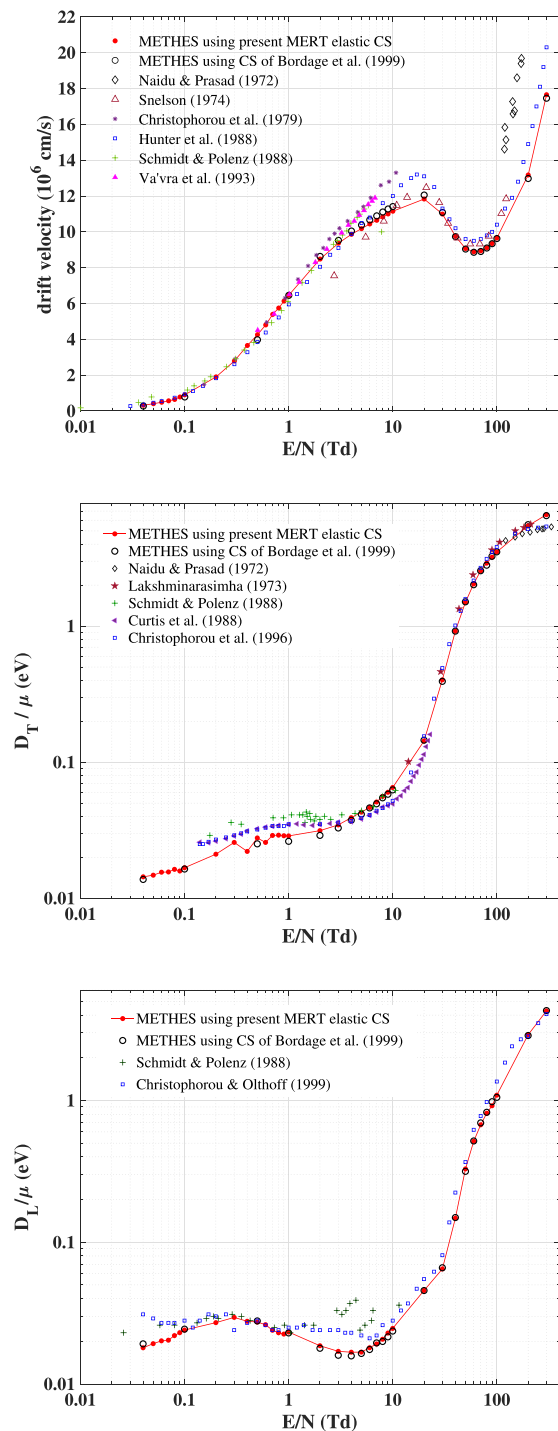
Fig. 5 Swarm parameters: drift velocity, ratio of transverse (D_T/μ) and longitudinal (D_L/μ) diffusion coefficients to electron mobility as a function of reduced electric field (E/N) transporting electrons through CF_4 gas. Present Monte Carlo calculations using METHES code [29] with present MERT elastic cross sections (CS) and other CS from Bordage database [50] are compared with experimental data: Naidu and Prasad [52], Snelson [53], Christophorou et al. (1979 [54], 1996 [3] and 1999 [55]), Hunter et al. [56], Schmidt and Polenz [57], Va'vra et al. [58] Curtis et al. [15] and Lakshminarasimha et al. [59]

[16,49,50]—see LXCat Web site (https://us.lxcat.net/home/) where a large number of swarm-related data are assembled. In particular, Bordage et al. [50] showed that the cross-section "set" recommended by Christophorou et al. [3] is consistent with available experimental electron drift coefficients. Additional check of this "set" was also done by Vasenkov [51]. The recommended cross sections determined by Christophorou were constructed almost purely from the results of electron beam experiments. In Fig. 5 we show the results of present Monte Carlo calculations of drift velocity, transverse and longitudinal diffusion coefficients as a function of reduced electric field using METHES code [29]. To the best of our knowledge, so far this Monte Carlo code was tested for CF_4 [29] using only the Hayashi cross-section database [16]. Here as the input data we used the original cross-section "set" from Bordage database and the same "set" with MTCS replaced by presently derived MERT data (for $\alpha = 19.5a_0^3$) in the region of Ramsauer–Townsend minimum (i.e., below 5 eV). Both results are in perfect agreement with each other demonstrating that the difference in MTCS shown in Fig. 3 does not affect the swarm analysis significantly. Moreover, present calculations remain in very good agreement with swarm experimental data [52–59] even for very low electric field despite the lack of contribution from superelastic collisions in METHES code. Interestingly, the inclusion of this phenomenon was necessary in multiterm Boltzmann analysis of transport parameters in Ref. [50] in order to avoid unphysical results.

4 Summary

In this paper we showed that the modified effective range theory (MERT) in the form proposed by Idziaszek and Karwasz [24] can be used to describe elastic differential, integral and momentum transfer cross sections for electron collision with such complex molecule as CF_4 in relatively wide energy range: from zero up to 5 eV, i.e., just below energy regime for the resonant scattering. The only available experimental elastic cross sections of Mann and Linder [13] and Boesten et al. [32] were proven to be consistent with each other within the frame of this single theoretical approach in the entire energy range under consideration. In this way we provide a simple tool allowing to extrapolate e^--CF_4 elastic cross sections measured accurately at higher energies down to very low-energy regions that are hardly accessible by experiments (and very difficult for sophisticated quantum-mechanical computations). In particular, we confirmed the presence of Ramsauer–Townsend minimum in integral cross sections at very low energies. Presently derived elastic data in the region of R-T minimum are consistent with the extensive assessment of $e^- - CF_4$ cross sections done by Christophorou et al. [3]. The effect of R-T minimum is not visible clearly in total cross sections (TCS) because it is accompanied by strong excitation of asymmetric vibrational modes of CF_4 molecule. Due to the relatively large

transition dipole amplitudes associated with these excitations, the Born-dipole approximation is sufficient to describe vibrational cross sections in the near threshold region. The consistency check of recommended elastic and vibrational data was done through the calculation of electron swarm parameters using Monte Carlo METHES code [29]. Knowledge of partitioning into the elastic and vibrational channels at low energies, as proved here, should be useful in models of plasma etching [60].

Due to some ambiguities in the literature regarding the value of dipole polarizability of CF_4 molecule, we also tested how this quantity affects the current model, in particular with regard to the estimation of cross sections toward zero energy. We found that MERT-derived s-wave scattering length decreased almost linearly from $-2.0a_0$ to $-3.06a_0$ with the rise of polarizability from $19.5a_0^3$ to $25.9a_0^3$. Estimated range for the scattering length remains consistent with some other predictions available in the literature.

Present MERT can be also useful in estimation of positron cross sections down to zero energy once some data for elastic scattering will be measured at few eV. Positron beams with energy of about 1eV are easily accessible with currently available techniques (see, e.g., [61–63]). Since CF_4 is used as a buffer gas in positron traps, reliable cross sections for low-energy $e^+ - CF_4$ collision are necessary to study positron transport in CF_4 environment in order to improve the efficiency of positron trapping techniques [64]. Present MERT can be a great asset in the search for benchmark cross sections describing low-energy positron-CF_4 scattering.

Author contributions

K. F. developed numerical procedures, performed the computations and wrote the manuscript. G.K. provided some initial ideas and participated in editing the manuscript. Both authors discussed the results and contributed to the final article.

References

1. J.L. Mauer, J.S. Logan, L.B. Zielinski, G.C. Schwartz, J. Vac. Sci. Technol. **15**(5), 1734 (1978)
2. R.A. Bonham, Jpn. J. Appl. Phys. Part 1 **33**, 4157 (1994)
3. L.G. Christophorou, J.K. Olthoff, M.V.V.S. Rao, J. Phys. Chem. Ref. Data **25**, 1341 (1996)
4. G.P. Karwasz, R.S. Brusa, A. Zecca, Riv. Nuovo Cim. **24**(4), 1–101 (2001). https://doi.org/10.1007/BF03548896
5. Y. Sakai, Appl. Surf. Sci. **192**, 327 (2002)
6. Junjie Li et al., Materials **13**(3), 771 (2020)
7. V.A. Godyak, R.B. Piejak, Phys. Rev. Lett. **65**, 996 (1990)
8. D. Field, J.P. Ziesel, P.M. Guyon, T.R. Govers, J. Phys. B At. Mol. Opt. Phys. **17**, 4565 (1984)
9. S.L. Lunt, J. Randell, J.-P. Ziesel, G. Mrotzek, D. Field, J. Phys. B At. Mol. Opt. Phys. **31**, 4225 (1998)
10. C. Szmytkowski, A.M. Krzysztofowicz, P. Janicki, L. Rosenthal, Chem. Phys. Lett. **199**, 191 (1992)
11. R.K. Jones, J. Chem. Phys. **84**, 813 (1986)
12. O. Sueoka, S. Mori, A. Hamada, J. Phys. B At. Mol. Opt. Phys. **27**, 1453 (1994)
13. A. Mann, F. Linder, J. Phys. B At. Mol. Opt. Phys. **25**, 533 (1992)
14. T.F. O'Malley, L. Spruch, L. Rosenberg, J. Math. Phys. **2**, 491 (1961)
15. M.G. Curtis, I.C. Walker, K.J. Mathieson, J. Phys. D Appl. Phys. **21**, 1271 (1988)
16. M. Hayashi, *Electron collision cross sections for molecules determined from beam and swarm data.* in *Swarm Studies and Inelastic Electron-Molecule Collisions,* eds. L.C. Pitchford, B.V. McKoy, A. Chutjian, and S. Trajmar, (Springer-Verlag, New York, 1987)
17. W.M. Huo, Phys. Rev. A **38**, 3303 (1988)
18. C. Winstead, Q. Sun, V. McKoy, J. Chem. Phys. **98**, 105 (1993)
19. A.P.P. Natalense, M.H.F. Bettega, L.G. Ferreira, M.A.P. Lima, Phys. Rev. A **52**, R1 (1995)
20. F.A. Gianturco, R.R. Lucchese, N. Sanna, J. Chem. Phys. **100**, 6464 (1994)
21. M.T.N. do Varella, A.P.P. Natalense, M.H.F. Bettega, M.A. Lima, Phys. Rev. A **60**, 3684 (1999)
22. W.A. Isaacs, C.W. McCurdy, T.N. Rescigno, Phys. Rev. A **58**, 309 (1998)
23. F.A. Gianturco, K. Willner, Phys. Rev. A **75**, 062714 (2007)
24. Z. Idziaszek, G.P. Karwasz, Phys. Rev. A **73**, 064701 (2006)
25. K. Fedus, G.P. Karwasz, Z. Idziaszek, Phys. Rev. A **88**, 012704 (2013)
26. K. Fedus, G. Karwasz, Eur. Phys. J. D **68**, 93 (2014)
27. S.J. Buckman, J. Mitroy, J. Phys. B At. Mol. Opt. Phys. **22**, 1365 (1989)
28. E.S. Chang, J. Phys. B At. Mol. Opt. Phys. **14**, 893 (1981)
29. M. Rabie, C.M. Franck, Comput. Phys. Comm., **203**, 268 (2016); METHES code downloaded from http://www.lxcat.net/download/METHES
30. M.K. Ali, P.A. Fraser, J. Phys. B At. Mol. Phys. **10**, 3091 (1977)

31. T. Sakae, S. Sumiyoshi, E. Murakami, Y. Matsumoto, K. Ishibashi, A. Katase, J. Phys. B At. Mol. Opt. Phys. **22**, 1385 (1989)
32. L. Boesten, H. Tanaka, A. Kobayashi, M.A. Dillon, M. Kimura, J. Phys. B At. Mol. Opt. Phys. **25**, 1607 (1992)
33. C.K. Miller, B.J. Orr, J.F. Ward, J. Chem. Phys. **74**, 4858 (1981)
34. T.N. Olney, N.M. Cann, G. Cooper, C.E. Brion, Chem. Phys. **223**, 59 (1997)
35. J. A. Tossell, J. W. Davenport, J. Chem. Phys. **80**, 813 (1984); J. A. Tossell and J. W. Davenport, J. Chem. Phys. **83**, 4824 (1985) (erratum)
36. C.M. Evans, E. Morikawa, G.L. Findley, J. Phys. B At. Mol. Opt. Phys. **34**, 3607 (2001)
37. T. Nishimura, F.A. Gianturco, J. Phys. B At. Mol. Opt. Phys. **37**, 215 (2004)
38. G.P. Karwasz, Eur. Phys. J. D **35**, 267 (2005)
39. C.M. Surko, G.F. Gribakin, S.J. Buckman, J. Phys. B At. Mol. Opt. Phys. **38**, R57 (2005)
40. D.G. Green, J.A. Ludlow, G.F. Gribakin, Phys. Rev. A **90**, 032712 (2014)
41. G.F. Gribakin, J.A. Young, C.M. Surko, Rev. Mod. Phys. **82**, 2577 (2010)
42. K. Fedus, J. Franz, G.P. Karwasz, Phys. Rev. A **91**, 062701 (2015)
43. J.P. Marler, C.M. Surko, Phys. Rev. A **72**, 062702 (2005)
44. J.P. Marler, G.F. Gribakin, C.M. Surko, Nucl. Inst. Meth. Phys. Res. B **247**, 87 (2006)
45. J. Franz, I. Baccarelli, S. Caprasecca, F.A. Gianturco, Phys. Rev. A **80**, 012709 (2009)
46. A. Mann, F. Linder, J. Phys. B At. Mol. Opt. Phys. **25**, 545 (1992)
47. D.M. Bishop, L.M. Cheung, J. Phys. Chem. Ref. Data **11**, 119 (1982)
48. L.C. Pitchford, L.L. Alves, K. Bartschat, S.F. Biagi, M.C. Bordage, A.V. Phelps, C.M. Ferreira, G.J.M. Hagelaar, W.L. Morgan, S. Pancheshnyi, V. Puech, A. Stauffer, O. Zatsarinny, J. Phys. D Appl. Phys. **46**, 334001 (2013)
49. D. Slovetsky, A. Deryugin, Chem. Plasm. (Russ) **13**, 240 (1987)
50. M.-C. Bordage, P. Ségur, L.G. Christophorou, J.K. Olthoff, J. Appl. Phys. **86**, 3558 (1999)
51. A.V. Vasenkov, J. Appl. Phys. **85**, 1222 (1999)
52. M.S. Naidu, A.N. Prasad, J. Phys. D Appl. Phys. **5**, 983 (1972)
53. R. A. Snelson, Ph. D. thesis, University of Liverpool (1974)
54. L.G. Christophorou, D.L. McCorkle, D.V. Maxey, J.G. Carter, Nucl. Inst. Meth. **163**, 141 (1979)
55. L.G. Christophorou, J.K. Olthoff, J. Phys. Chem. Ref. Data **28**, 967 (1999)
56. S.R. Hunter, J.G. Carter, L.G. Christophorou, Phys. Rev. A **38**, 58 (1988)
57. B. Schmidt, S. Polenz, Nucl. Inst. Meth. Phys. Res. A **273**, 488 (1988)
58. J. Va'vra, P. Cole, J. Kadyk, J. Wise, Nucl. Inst. Meth. Phys. Res. A **324**, 113 (1993)
59. C.S. Lakshminarasimha, J. Lucas, D.A. Price, Proc. IEE **120**, 1044 (1973)
60. Y.-R. Zhang, S. Tinck, P. De Schepper, Y.-N. Wang, A. Bogaerts, J. Vac. Sci. Technol. A **33**(2), 021310 (2015)
61. G.P. Karwasz, M. Barozzi, M. Bettonte, R.S. Brusa, A. Zecca, Nucl. Inst. Meth. Phys. Res. B **171**, 178 (2000)
62. J.P. Sullivan, C. Makochekanwa, A. Jones, P. Caradonna, S.J. Buckman, J. Phys. B At. Mol. Opt. Phys. **41**, 081001 (2008)
63. J.R. Danielson, D.H.E. Dubin, R.G. Greaves, C.M. Surko, Rev. Mod. Phys. **87**, 247 (2015)
64. A. Banković, S. Dujko, S. Marjanović, R.D. White, Z.L. Petrović, Eur. Phys. J. D **68**, 127 (2014)