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PARAMETRIC POTENTIAL CALCULATIONS FOR SCATTERING OF ELECTRONS (1—100 eV) FROM CS_2 AND C_2H_2 MOLECULES

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Cross sections have been calculated for electron scattering by CS_2 and C_2H_2 molecules. Two-centre, parametric, optical potential was employed for description of interaction between projectile and the molecule. Calculations were performed for electron impact energies from 1 to 100 eV and for this entire energy region a reasonable agreement with experiment was obtained.

1. Introduction

The scattering of electrons and positrons on molecules has attracted considerable theoretical interest in recent years. This is due, in part, to increasing number of the experimental data which are in hands and to very efficient computational techniques which can be now applied to the scattering problem.

Distinct advance in theoretical treatment of processes which occur when projectile interacts with a molecule is visible for simple targets for which numerous near ab initio calculations have been recently made (for references see in: Gianturco et al.$^{1)}$, Jain and Thompson$^{2)}$, Morrison et al.$^{3)}$). In case of more complex systems progress is not so rapid and only very few calculations have been reported for polyatomic molecules.

In majority of recently performed theoretical investigation on electron and positron scattering by molecules, a multipole expansion of the interaction potential in one-centre spherical coordinate system (cf. the review by Lane$^{4)}$) was successfully employed. The basic difficulty with the single-center expansion method is its very slow convergence for more complex molecules. On the other hand, two-centre coordinates have been applied in the case of scattering on homonuclear diatomic molecules (Nagahara$^{5)}$, Hara$^{6,7)}$, Darewych et al.$^{8)}$, Bell$^{9)}$), for which two-centre expansion seems to be more natural. The two-centre approach was also employed in calculations of cross sections for scattering of electrons on some polyatomic (Shimizu$^{10)}$), and polar (Takayanagi and Itikawa$^{11)}$) molecules.

In the present work we apply a model, two-centre, parametric optical potential to calculate the electron scattering cross sections on linear, symmetric molecules of CS_2 and C_2H_2. For e^--CS_2 system, the elastic scattering computations have already been performed by Lynch et al.$^{12)}$ with the use of continuum-multiple-scattering model; however, at low energies their results are considerably different from the experiment. For C_2H_2 no integral elastic or total cross section calculations are known to date in the low-intermediate energy range. Present calculations reproduce the experimental data quite satisfactorily. Preliminary results have already been reported (Szmytkowski$^{13,14)}$).

2. *Method*

The construction of the effective potential employed for the electron — linear symmetrical molecule system is based on the assumption that the interaction between a projectile and a target can be represented by a two-centre field. This approximation seems to be more realistic for polyatomic-symmetrical molecules in which the majority of the molecular charge is concentrated on two atoms (eg. sulphur atoms in CS_2 molecule).

In the case of two-centre field the scattering problem can be treated in terms of the prolate spheriodal coordinates fixed at the molecule with z-axis coincident with the molecular axis:

$$\zeta = (r_1 + r_2)/2R, \qquad \eta = (r_1 - r_2)/2R \quad \text{and} \quad \varphi,$$

where r_1 and r_2 are the distances from each of the two force centres to the incoming particle, φ is the azimuthal angle and $2R$ is the fixed separation between these centres.

The effective potential which in the present calculations approximates the interaction between the incident electron and molecule, written in spheroidal coordinates, is represented as (SI units are used):

$$U(\zeta, \eta) = -\frac{e^2}{4\pi\varepsilon_0} \cdot \frac{2Z\zeta \cdot f(\zeta)}{R(\zeta^2 - \eta^2)} - \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{\alpha C(\zeta)}{2R^4(\zeta^2 - 1)(\zeta^2 - \eta^2)} +$$

$$+ i\frac{U^A(\zeta)}{\zeta^2 - \eta^2} = \frac{U(\zeta)}{\zeta^2 - \eta^2}. \tag{1}$$

The first term in expression (1) describes the two-centre short-range electrostatic potential, in which the screening term $f(\zeta)$ is of the form (Allis and Morse[15]), Fisk[16]), Stier[17]))

$$f(\zeta) = \begin{cases} \dfrac{(\zeta\zeta_k - \zeta^\nu)(\zeta_k - \zeta)}{\zeta(\zeta_k - 1)^2} & \text{for } \zeta < \zeta_k, \\ 0 & \text{for} \zeta > \zeta_k \end{cases} \tag{2}$$

with $\nu = 0$, 1 and 2, respectively. $Z \cdot e$ is the effective charge placed in each of the centres. ζ_k in (2) represents the boundary of coulombic interaction region (spheroidal boundary of molecule). The second term in expression (1) simulates the induced adiabatic polarization potential. Its asymptotic form is modified, at short distances, with cut-off function

$$C(\zeta) = [1 - \exp(-(\zeta - 1)/(\zeta_c - 1))]^6, \tag{3}$$

where α is the static molecular dipole polarizability and ζ_c is an adjustable cut-off parameter. An imaginary part of the potential (1) is responsible for the inelastic processes.

Substitution of the wavefunction of the scattered particle, written in the form of $\Psi(\zeta, \eta, \varphi) = X(\zeta)\, Y(\eta)\, \Phi(\varphi)$, into the Schrödinger equation yields a set of equations:

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\varphi^2} + m^2\right)\Phi_m(\varphi) = 0, \tag{4a}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}\eta}(1 - \eta^2)\frac{\mathrm{d}}{\mathrm{d}\eta} - \varkappa^2\eta^2 - \frac{m^2}{1 - \eta^2} + \lambda_{ml}(\varkappa)\right) Y_{ml}(\eta, \varkappa) = 0, \tag{4b}$$

$$\left(\frac{\mathrm{d}}{\mathrm{d}\zeta}(\zeta^2 - 1)\frac{\mathrm{d}}{\mathrm{d}\zeta} + \varkappa^2\zeta^2 - \frac{m^2}{\zeta^2 - 1} - \frac{2m_e R^2}{\hbar^2} \cdot U(\zeta) - \lambda_{ml}(\varkappa)\right) X_{ml}(\zeta, \varkappa) = 0, \tag{4c}$$

where m_e is the mass of electron and $\varkappa^2 = k^2R^2 = (2m_e E/\hbar^2) \cdot R^2$, E is the incident energy. $\Phi_m(\varphi)$ is single-valued only if m is zero or an integer, and $\lambda_{ml}(\varkappa)$ is the separation constant which is determined so that the angular functions $Y_{ml}(\eta, \varkappa)$ are regular at $\eta = \pm 1$. The suffix l corresponds to the azimuthal quantum number in the spherically symmetric case ($R \to 0$).

The calculation of the phase shifts is carried out by using the variable-phase approach (Calogero[18])). The solution of (4c) gives complex phase shifts for the complex potential. If $\gamma_{ml}(\zeta, \varkappa)$ and $a_{ml}(\zeta, \varkappa)$ are, respectively, the real and imaginary parts of the complex phase-shift function, then we can write first-order coupled differential equations in terms of $\gamma_{ml}(\zeta, \varkappa)$ and $a_{ml}(\zeta, \varkappa) = \exp[-2_g \alpha_{ml}(\zeta, \varkappa)]$:

$$\frac{\mathrm{d}a_{ml}(\zeta, \varkappa)}{\mathrm{d}\zeta} = \frac{1}{2\varkappa} \cdot [V^K_{ml}(\zeta, \varkappa)\, F_{ml}(\zeta, \varkappa) + V^A_{ml}(\zeta, \varkappa)\, H_{ml}(\zeta, \varkappa)], \tag{5a}$$

$$\frac{\mathrm{d}\gamma_{ml}(\zeta, \varkappa)}{\mathrm{d}\zeta} = \frac{1}{4\varkappa \cdot a_{ml}(\zeta, \varkappa)} \cdot [V^A_{ml}(\zeta, \varkappa)\, F_{ml}(\zeta, \varkappa) - V^K_{ml}(\zeta, \varkappa)\, H_{ml}(\zeta, \varkappa)], \tag{5b}$$

with the boundary conditions $a_{ml}(1, \varkappa) = 1$ and $\gamma_{ml}(1, \varkappa) = 0$.

$$F_{ml}(\zeta, \varkappa) = [1 - a^2_{ml}(\zeta, \varkappa)] \cdot \sin 2\,[\varkappa(\zeta - 1) + \gamma_{ml}(\zeta, \varkappa)], \tag{6a}$$

$$H_{ml}(\zeta, \varkappa) = 2\,[1 + a^2_{ml}(\zeta, \varkappa)] \cdot \sin^2[\varkappa(\zeta - 1) + \gamma_{ml}(\zeta, \varkappa)] - - [1 - a_{ml}(\zeta, \varkappa)]^2. \tag{6b}$$

$V^R(\zeta, \varkappa)$ and $V^A(\zeta, \varkappa)$ are related to real and imaginary parts of the potential $U(\zeta)$, respectively, and are of the form

$$V^R_{ml}(\zeta, \varkappa) = \frac{1}{\zeta^2 - 1}\left\{\lambda_{ml} - \varkappa^2 + \frac{m^2 - 1}{\zeta^2 - 1} - \frac{2}{a_0}\left[2Z \cdot R \cdot \zeta \cdot f(\zeta) + + \frac{a \cdot C(\zeta)}{2R^2(\zeta^2 - 1)}\right]\right\}, \tag{7a}$$

$$V^2_{ml}(\zeta, \varkappa) = -\omega \cdot (\zeta - 1) f(\zeta) (E - IP)^{9/2} \cdot \Theta(E - IP). \tag{7b}$$

a_0 is the Bohr radius, $f(\zeta)$ and $C(\zeta)$ are defined by (2) and (3), respectively, IP is the ionization potential of target and ω is an adjustable parameter. Here $\Theta(x)$ is a function defined by

$$\Theta(x) = \begin{cases} 0, & x \leq 0 \\ 1, & x > 0. \end{cases}$$

The scattering matrix S is then written as

$$S_{ml} = a_{ml}(\infty) \cdot \exp[2i\gamma_{ml}(\infty)],$$

where $a_{ml}(\infty) = \lim\limits_{\zeta \to \infty} a_{ml}(\zeta, \varkappa)$ and $\gamma_{ml}(\infty) = \lim\limits_{\zeta \to \infty} \gamma_{ml}(\zeta, \varkappa)$, and the corresponding elastic σ_{el}, absorption σ_{abs}, and total σ_{tot} cross sections can be written as

$$\sigma_{el}(E) = \frac{\pi}{k^2} \sum_{m,l} |1 - S_{ml}(E)|^2, \tag{8a}$$

$$\sigma_{abs}(E) = \frac{\pi}{k^2} \sum_{m,l} (1 - |S_{ml}(E)|^2), \tag{8b}$$

$$\sigma_{tot}(E) = \sigma_{el}(E) + \sigma_{abs}(E). \tag{8c}$$

Equations (5a—b) were integrated numerically up to $m = 5$ and the obtained phase shifts were used to calculate the respective cross sections. For higher energies the convergence of the cross section is rather slow and near 100 eV the terms of $m > 5$ should be included. The ending point of the integration, $\zeta_{end} = 200$, was chosen so that the phase shifts were insensitive to any further increase in ζ_{end}.

Values of some parameters in expressions (7a—b), such as ionization potentia' IP, internuclear distance R and dipole polarizability α, were taken from Herzberg[19], and Landolt-Börnstein[20]. As the boundary of coulombic interaction region, we used the value $\zeta_k = (2R + 2 \langle r \rangle)/2R$, were $\langle r \rangle$ is the calculated mean distance of the valence electrons from their atom nucleus placed in one of the centre of potential (Radzig and Smirnov[21]). Parameters IP, R, α and ζ_k, established in this way, were treated as constants throughout the calculations.

The preliminary value of effective charge number Z was estimated similarly as in Stier[17] and Fisk[16], while ζ_c was taken equal to ζ_k. The final values of Z and ζ_c (usually not differing by much from the initial ones) were chosen to reproduce the experimental low-energy features of cross section (the resonant maximum for N_2, CO_2 and C_2H_2 and minimum for CS_2). Parameter ω was determined by fitting the calculated absorption cross section $\sigma_{abs}(E)$ to the experimental total cross section for inelastic processes (usually σ_{ion} only).

The values of parameters used in the calculations are presented in Table 1. The same values were employed in the whole range of energy. The variations of Z and ζ_c values, in the range of ± 0.1 as compared with those of Table 1, do not change the calculated cross sections remarkably.

TABLE 1.

	CS_2	C_2H_2
ζ_k	1.7	2.2
ν	0	2
Z	3.5	1.6
ζ_c	1.4	2.0
ω		0.2

Adjustable parameters of the effective potential used for calculations of cross sections presented in Figs. 1 and 2.

The procedure described above was tested on N_2 and CO_2 molecules. The results for electron scattering fairly well reproduced the general energy dependence of experimental data along with the characteristic resonant peaks at 2.3 eV in N_2 and around 3.8 eV in CO_2 (Szmytkowski[19]).

3. *Results*

Fig. 1 shows our e^--CS_2 elastic cross sections (σ_{el}) as a function of electron energy along with the elastic calculations of Lynch et al.[12] and the experimental measurements of Sohn et al.[22]. It can be seen that our calculated results reproduce the general features of the experimental data resonably. Around 6 eV, however, the calculated cross section is greater than both the elastic cross section of Sohn et al.[22] and the absolute, experimental total cross section of Szmytkowski[23]. The resulting peak, superimposed on a very broad hump is not resonant in character but is due to a cumulative effect of a few components of different m.

Calculations of Lynch et al.[12], performed with the use of continuum-multiple-scattering model, predicted the presence of a very strong shape resonance in the vicinity of 1.8 eV. However, no such structure was visible in the very recent elastic and vibrational excitation spectra of Sohn et al.[22]. Only a very weak resonance effects around energy 1.8 eV were seen previously in the electron transmission spectra by Burrow (unpublished, see Ziesel et al.[24]) and Dressler et al.[25] and in the threshold electron spectra by Dance et al.[26]. From the analysis of influence of the effective potential magnitude on the total cross section it follows that the serious discrepancy between calculations of Lynch et al.[12] and the experiment below 2.5 eV may be attributed to their too attractive potential in the low energy region. Above 15 eV the present results agree quite closely with the theoretical values of Lynch et al.[12].

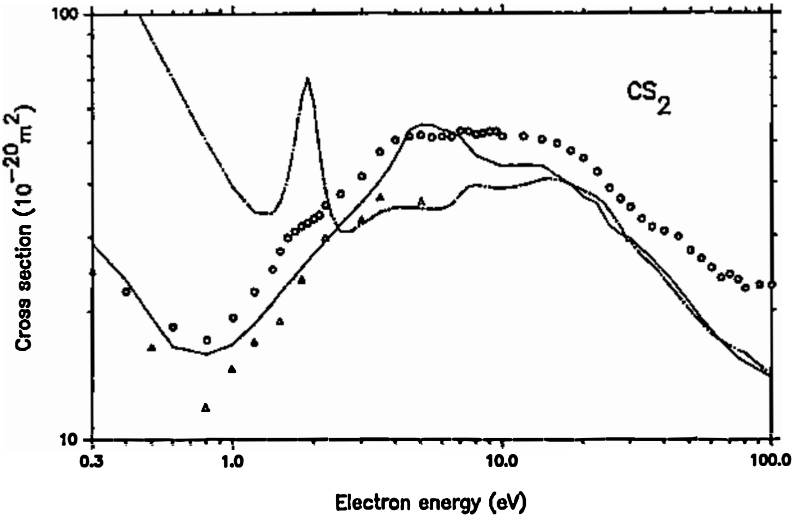

Fig. 1. e$^-$-CS$_2$ cross sections. Theory: —·—, Lynch et al.[12], vibrationally elastic; ——, present calculations, elastic. Experiment: △ △ △, Sohn et al.[22], integrated elastic (normalized); ○ ○ ○, Szmytkowski[23], absolute total.

In Fig. 2, we compare our calculated total cross sections (elastic + absorption) for e$^-$-C$_2$H$_2$ scattering (centers of the potential are placed on carbon nuclei) with the absolute experimental measurements of Brüche[27] and normalized data of Sueoka and Mori[28]. In general, calculated cross sections follow closely the pattern of the experimental results with the main resonant maximum around 2.6 eV. Because laboratory cross sections of the dominant inelastic processes were not available for the fitting the absorption cross section (σ_{abs}) was calculated with the use of the same value of parameter ω which fits the calculated cross sections to experimental (ionization) data for CO$_2$ molecule[14]. It is worth noting, that inclusion of the absorption potential reduces the magnitude of elastic cross section by a significant amount.

Concluding, we reported computations of low- and low- intermediate energy cross sections for electron scattering on CS$_2$ and C$_2$H$_2$ molecules. With the employed model of the interaction between the projectile and the target we reproduced the main features of experimental data. Simplicity of calculations alllow to study how the potential changes influence the shape and magnitude of the cross section. Once the experimental cross section for electron scattering is reproduced, the same parameters (only ζ_c must be slightly reduced) can be used for estimation of positron scattering cross sections below positronium formation threshold (Szmytkowski[13,14]). The preliminary results for C_2H_6 suggest applicability of the method to more complex molecule.

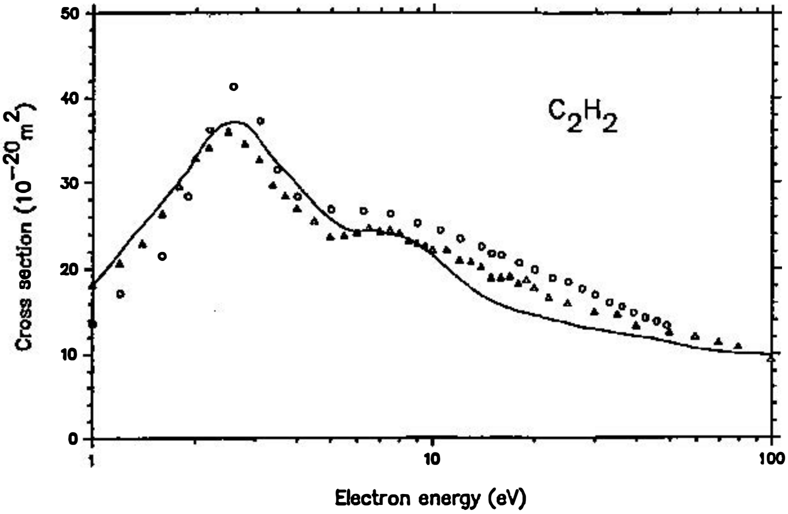

Fig. 2. e$^-$-C_2H_2 cross sections. Experiment: O O O, Brüche[27], absolute total; △ △ △, Sucoka and Mori[28], total (normalized). Theory: ——, present calculations, totat (elastic + absorption).

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RAČUN RASPRŠENJA ELEKTRONA (1—100 eV) NA MOLEKULAMA CS_2 i C_2H_2 KORISTEĆI PARAMETARSKI POTENCIJAL

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Računati su udarni presjeci za raspršenje elektrona na molekulama CS_2 i C_2H_2. Optički potencijal, parametarski, na dva centra, koristili smo za opis interakcije projektila i molekule. Računi su izvedeni za elektronske sudarne energije od 1 do 100 eV. Za cijeli interval energije dobiveno je dobro slaganje s eksperimentom.