ELECTRON SCATTERING CROSS SECTION OF CH_4; A MULTIPLE SCATTERING CALCULATION

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The total cross section of CH_4 molecules for elastic electron scattering is calculated by a multiple scattering method. The scattering potential includes the following terms: a static potential calculated with the X_α method, a free electron gas exchange potential, and a polarization term for which two variants have been used. The results are discussed and compared with previous calculation and experimental total cross section data.

Introduction

Total cross sections for electron-molecule collisions have been investigated experimentally for many years.

Theoretical results which reproduce the characteristic behaviour of the total cross section for elastic electron scattering on polyatomic molecules have been published, however, only recently. One of the difficulties in calculations arises due to the complexity of the multiple scattering effects, even in the rigid molecule approximation.

In this paper we present results on the total cross section of the electron-methane molecule elastic scattering. The method used here is a modified version of the multiple scattering calculations developed by JOHNSON [1] for determining bound electronic states. Namely, it is a generalized partial wave analysis proposed by DEMKOV and RUDAKOV [2] and extended for a cluster of muffin-tin potentials by ZIESCHE and JOHN [3]. A somewhat different formulation of the scattering problem was proposed by DILL and DEHMER [4, 5].

The details of the scheme of present calculations is described in [6] and this formalism of the multiple scattering problem has been applied for the electron SF_6 molecule scattering [6, 7].

In the following, first we describe the construction of the static molecule potentials for the methane molecule, then present the calculated total cross sections comparing them with experimental data [8—11] and previous calculation [12].

Model

For construction of the potential seen by the scattered electron, as a first step, a self-consistent multiple scattering $X\alpha$ calculation was performed for the rigid CH_4 molecule with the parameters of ref. [13].

The molecular field is partitioned into three types of muffin-tin regions:
The atomic region consists of atomic spheres of radii b_p around the p-th atomic nucleus at R_p ($p=C, H^{(1)}, \ldots$). The potential V_p in the p-th atomic sphere is taken to be spherically symmetric. The atomic region is enclosed in a sphere of radius b_0, the so-called Watson sphere, centered in this case at R_c. In the interatomic region — the region outside the atomic spheres and inside the Watson sphere — the potential $\bar{V}$ is constant. The outer region is the region outside the Watson sphere, where the potential V_0 is assumed to be spherically symmetric.

The exchange part of the self-consistent $X\alpha$ molecular potential was changed to a more detailed free-electron exhange potential [14]:

$$V_x(r) = -\frac{4}{\pi} K_F \cdot F(K/K_F) \tag{1}$$

where

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| . \tag{2}$$

The maximum momentum K_F is expressed by the electron density $\varrho(r)$ of the target as

$$K_F(r) = [3\pi^2 \varrho(r)]^{1/3} . \tag{3}$$

For the momentum K of the electron with kinetic energy E, Hara [15] used the following approximation:

$$K^2(r) = E + I + K_F^2(r) \tag{4}$$

which is reasonable at small r. In our case, *i.e.* for CH_4 the ionization potential I has the value of 1.14 Ry [11]. Eqs. (1—4) give the so called Hara free electron gas exchange (HFEGE) potential [16].

The obvious way to correct Eq. (4) for large r is to remove the ionization energy:

$$K^2(r) = E + K_F^2(r) \tag{5}$$

giving a more attractive exchange potential. Combining Eq. (5) with Eqs. (1—3) gives the asymptotically adjusted free electron gas exchange (AAFEGE) potential [16].

The scattering potentials were constructed with the AAFEGE approximation outside of the Watson sphere and with HFEGE approximation inside of it.

To include polarization effects we first added a polarization potential of the form

$$V_{\mathrm{pol}}(r) = -\frac{\alpha}{r^4} \left(1 - e^{-\frac{r}{r_0}}\right)^6 \tag{6}$$

centered on the carbon site, where α is the static molecular polarizability ($\alpha=17.5$ for methane [17]). This type of polarization potential was suggested by GIANTURCO and THOMPSON [12] who chose the "cut-off" r_0 to be 0.84 by fitting calculated total cross sections to experimental data. In this way they could reproduce the experimental total cross section satisfactorily. The potential constructed in this way will be referred to as potential I. We performed the calculation with another type of potential (potential II) as well. Here the dipole part $-\alpha/r^4$ of the "true" polarization potential was added to the potential in the outer region. Inside the Watson sphere we simply modified the potential by $-\frac{\alpha}{b_0^4}$ in the interatomic and in the hydrogen regions.

Results and Discussion

In the wave function of the scattered electron mixed of partial waves with different angular momenta the $l=6$ term gave the highest contribution to be taken into account in our calculations.

The total scattering cross section calculated with potential I does not even qualitatively reproduce the results of Ref. [12] or the experimental results of Ref. [11]. This discrepancy is due to the polarization which is clearly overestimated having a deep minimum within the carbon site. In fact, as mentioned by GIANTURCO and THOMPSON [12], the polarization potential of Eq. (6) is essentially chosen by appeal to experiment and not to the polarization effect itself.

Potential II with a more flat polarization, as described in the previous section, produces the total scattering cross section plotted in Fig. 1; for comparison the recent experimental values of [11] are also given. The total cross section is a sum

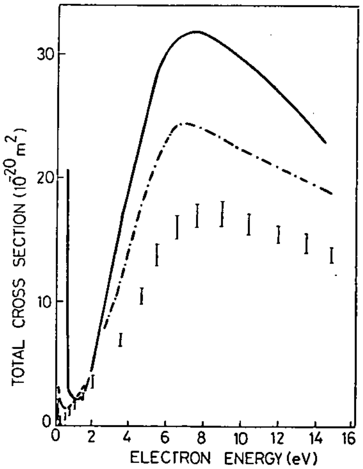

Fig. 1. Total scattering cross section calculated with potential II (solid line). Experimental values of Ref. [11] (error bars), Ref. [9] (dashed line) Ref. [10] (dash-dotted line)

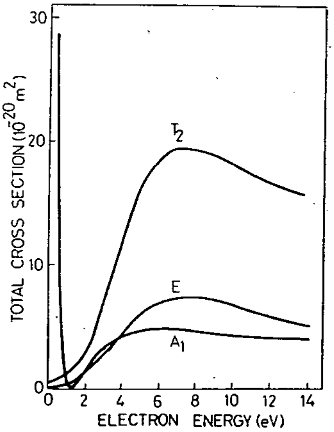

Fig. 2. The cross sections of different symmetry for potential II.

of contributions of cross sections belonging to the A_1, E, T_2 irreducible representations (IR) of the T_d symmetry group of the CH_4 molecule. (The other two IRs do not appreciably contribute in this energy range.) This decomposition is shown in Fig. 2. It can be seen that the broad maximum near 7.5 eV is dominated by T_2 symmetry. The minimum in Fig. 1 at 1.2 eV is in qualitative agreement with the experimental total cross section. At low energies there appears a sharp increase of A_1 origin in accord with the calculation in [12].

These results show that an essential point in the calculations is the choice of the potential seen by the scattered electron. The muffin-tin approximation, on one hand, turns out to be appropriate for molecular calculations and for electron scattering on 'nearly spherical' molecules, *e.g.* on SF_6 [6]. As to the exchange and especially the polarization part of the potential on the other hand we are left to rough approximations.

Nevertheless, the characteristic features of the experimental total cross section for electron-methane elastic scattering can be reproduced. Better agreement, however, can be achieved by using more reasonable potentials; this needs further investigations.

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СЕЧЕНИЕ ЭЛЕКТРОННОГО РАССЕЯНИЯ CH_4: РАСЧЕТ МЕТОДОМ МНОГОКРАТНОГО РАССЕЯНИЯ

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Рассгитано полное сечение молекулы CH_4 для упругого электронного рассеяния методом многократного рассеяния. Потенциал рассеяния состоит из следующих частей: статический потенциал рассчитанный методом X_α, обменной потенциал типа свободного электронного газа и поляризационный член, для которого было применено два варианта. Обсуждаются результаты и сравниваются с предыдушими рассчетами и с экспериментальными сечениями.