

## Scattering of low-energy electrons by $\text{TiCl}_4$ , $\text{GeCl}_4$ , $\text{SiCl}_4$ and $\text{CCl}_4$ : a comparison of elastic cross sections

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Received 6 June 2000, in final form 28 September 2000

**Abstract.** We report results of calculations of low-energy electron scattering by  $\text{TiCl}_4$ . Our calculations employed the Schwinger multichannel method implemented with norm-conserving pseudopotentials (Bettega *et al* 1993 *Phys. Rev. A* **47** 1111) at the fixed-nuclei static-exchange approximation. We compare the elastic integral, differential and momentum transfer cross sections of  $\text{TiCl}_4$  with those of  $\text{CCl}_4$ ,  $\text{SiCl}_4$  and  $\text{GeCl}_4$ . Similarities and differences in the cross sections for these molecules are discussed. We also discuss the role of the inner atom and the chlorine atom in the scattering process. To the best of our knowledge, this is the first *ab initio* calculation on electron scattering by  $\text{TiCl}_4$  and  $\text{GeCl}_4$  molecules. We have also calculated the ionization cross section for these molecules using the binary-encounter Bethe model and estimated the inelastic cross section for  $\text{CCl}_4$ ,  $\text{SiCl}_4$  and  $\text{GeCl}_4$ , where measured total cross sections are available.

### 1. Introduction

$\text{TiCl}_4$  is a gas with increasing technological use. It is a source of Ti, and of its compounds, for the coating of surfaces and the preparation of catalysts [1–9]. Recent density functional [10] and complete *ab initio* calculations [11] exist, with enough sophistication to determine the magnitude of the interaction. Due to the importance of this molecule in plasma-enhanced chemical vapour deposition, knowledge of  $\text{e}^-$ – $\text{TiCl}_4$  scattering data is warranted.

$\text{TiCl}_4$  has the same valence electronic configuration as  $\text{XCl}_4$  ( $\text{X} = \text{C}, \text{Si}, \text{Ge}$ ), although atomic titanium has  $3\text{d}^24\text{s}^2$  and the X atoms have  $\text{s}^2\text{p}^2$  for the valence electronic configuration. Despite the intrinsic importance of the  $\text{e}^-$ – $\text{TiCl}_4$  collision process itself, it would be interesting to compare the  $\text{TiCl}_4$  electron scattering cross sections with those of  $\text{XCl}_4$  ( $\text{X} = \text{C}, \text{Si}, \text{Ge}$ ), in order to look for similarities and differences in their elastic cross sections.

Among these molecules, there are theoretical and experimental results for elastic and rotationally inelastic scattering of electrons by  $\text{CCl}_4$  and  $\text{SiCl}_4$ . The MS- $\text{X}\alpha$  was applied by Tossell and Davenport [12] to calculate elastic cross sections by  $\text{CX}_4$  and  $\text{SiX}_4$  ( $\text{X} = \text{H}, \text{F}, \text{Cl}$ ) for the 0–8 eV energy scattering range. A model complex optical potential was used by Jiang *et al* [13] to calculate total cross sections for a series of molecules, including  $\text{CCl}_4$ , for energies from 10 eV to 1000 eV. Curik *et al* [14] used a model exchange potential to study elastic electron

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**Table 1.** Distance XCl for the different molecules.

Molecule	X–Cl (Å)
CCl <sub>4</sub>	1.767
SiCl <sub>4</sub>	2.019
GeCl <sub>4</sub>	2.113
TiCl <sub>4</sub>	2.185
HCl	1.275

collisions with CF<sub>4</sub> and CCl<sub>4</sub>. Previously we have obtained elastic and rotationally inelastic cross sections for CCl<sub>4</sub> and SiCl<sub>4</sub> [15, 16], obtained with the Schwinger multichannel method with pseudopotentials (SMCPP) [17]. Experimental total cross sections for CCl<sub>4</sub> [18–20], SiCl<sub>4</sub> [21] and GeCl<sub>4</sub> [22] are also available. Recently, the energy dependence of the total cross section for electron scattering by chloromethanes has been investigated by Garcia and Blanco [23], in the energy range from 0.5 up to 10 keV. In this paper we present the results of electron-scattering cross section calculations for TiCl<sub>4</sub> and GeCl<sub>4</sub>. Our calculations employed the SMCPP method at the fixed-nuclei static-exchange approximation, for energies from 5 eV up to 30 eV, where polarization effects are not too important. We are looking for similarities and differences in the cross sections of these molecules. As the Cl<sup>−</sup> ion is much bigger than the positive ion, one may suspect that the cross section is dominated by the four anions and depends little on the cation C<sup>4+</sup>, Si<sup>4+</sup>, Ge<sup>4+</sup> or Ti<sup>4+</sup>. On the other hand, the molecular sizes of the four molecules are different (as shown in table 1) and that may be a reason for the different cross sections.

Elastic, inelastic and ionization cross sections are a very important piece of information for plasma modellers. In order to estimate the inelastic cross section for these molecules, from our elastic results and from the experimental total cross sections, we also present the total ionization cross section for CCl<sub>4</sub>, SiCl<sub>4</sub>, GeCl<sub>4</sub> and TiCl<sub>4</sub>, obtained by applying the binary-encounter Bethe (BEB) model [24]. The BEB method has been used successfully in calculations of total ionization cross sections of polyatomic molecules [25].

## 2. Methods

The electron elastic cross sections were calculated by means of the Schwinger multichannel method (SMC) [26, 27]. This is a variational method for the scattering amplitude that can be made very precise if the wavefunctions for the many channels are well described. To render the calculation feasible on currently available computers we have been using pseudopotentials [17], i.e. assuming that, for the beam energies we explore, the atomic cores are rigid, do not mix with and are not polarizable by the beam and valence electrons, and are describable by effective, though non-local, potentials. The use of pseudopotentials (effective potentials) to beam energies of up to 30 eV has proved very successful. Apparently any of the many pseudopotentials available in the literature will do for the energy range being considered [28], but systematically we use the BHS expressions [29].

Our application of the SMC to these tetrahalides assumed no polarization of the targets, in the following sense. The SMC scattering amplitude has the expression

$$[f_{\vec{k}_i, \vec{k}_f}] = -\frac{1}{2\pi} \sum_{m,n} \langle S_{\vec{k}_f} | V | \chi_m \rangle [A^{(+)-1}]_{mn} \langle \chi_n | V | S_{\vec{k}_i} \rangle$$

where  $|S_{\vec{k}_i}\rangle$  and  $|S_{\vec{k}_f}\rangle$  are the input and output channels, that is the ground state target molecule with  $N$  electrons plus the incoming (or outgoing) electron.  $V$  is the interaction potential

between the molecule and the extra electron of the beam. The operator  $A^{(+)}$  is well discussed in the references already quoted. The vectors  $|\chi_m\rangle$  are a complete set of  $(N + 1)$  -electron states. The approximations made in the SMC refer mainly to the space of vectors  $|\chi_m\rangle$ . In our case we use

$$|\chi_m\rangle = \mathcal{A}\{|\Phi\rangle|\varphi_m\rangle\}$$

where  $|\Phi\rangle$  is the target ground state,  $|\varphi_m\rangle$  are an as complete as possible set of one-electron wavefunctions and  $\mathcal{A}$  is the antisymmetrizer. Thus in our approximation we are not letting the target be polarized by the beam electrons. This sort of approximation is well known and it is defective when the incoming electrons are slow enough to appreciably deform the target. Frequently it is said that a lack of polarization causes errors at energies below 7 eV [16].

The ionization cross sections were calculated by means of the binary-encounter Bethe model [24]. The expression for the ionization cross section per molecular orbital is given by

$$\sigma_{\text{BEB}}(T) = \frac{S}{t + u + 1} \left[ \frac{\ln t}{2} \left( 1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t + 1} \right]$$

where  $T$  is the incident electron energy,  $t$  and  $u$  are normalized energies,  $t = T/B$  and  $u = U/B$ ;  $B$  is the binding energy and  $U$  is the electron kinetic energy of the molecular orbital,  $S = 4\pi a_0^2 N R^2 / B^2$ , where  $N$  is the orbital occupation number,  $a_0 = 0.5292 \text{ \AA}$  and  $R = 13.61 \text{ eV}$ . The total ionization cross section is obtained by summing  $\sigma_{\text{BEB}}(T)$  over the molecular orbitals that satisfy  $T > B$ .

Our calculations were performed in the fixed-nuclei static-exchange approximation at the experimental equilibrium geometries (table 1). The basis functions we used for Ti and Ge were obtained according to [30] and are shown in table 2. We also show in table 2 the basis set for Cl, used only in  $\text{GeCl}_4$  calculations and also obtained according to [30]. The Cl basis used in  $\text{TiCl}_4$  calculations and the basis set for the previous calculations on the other molecules are shown in [16]. As in previous studies [16, 31], we have not included in the calculations the symmetric combination of functions  $[(x^2 + y^2 + z^2) \exp(-\alpha r^2)]$  in order to eliminate the linear dependence in the basis set.

**Table 2.** Cartesian Gaussian function exponents for Ti, Ge and Cl.

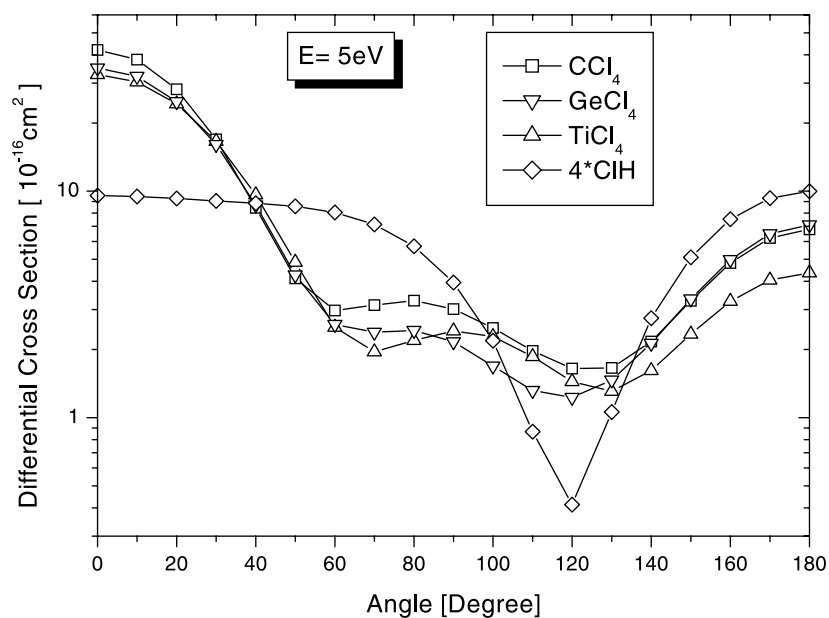
	Ti		Ge	Cl
Type	Exponent	Type	Exponent	Exponent
s	1.103 464	s	2.429 279	8.997 332
s	0.608 360	s	1.000 450	2.155 809
s	0.156 812	s	0.542 241	0.805 058
s	0.055 347	s	0.148 198	0.339 912
s	0.010 628	s	0.019 957	0.063 508
p	0.376 338	s	0.005 212	0.019 227
p	0.223 876	p	1.677 720	2.344 123
p	0.100 119	p	0.270 291	0.902 071
p	0.046 818	p	0.091 598	0.345 005
p	0.024 131	p	0.034 666	0.120 979
d	9.441 681	p	0.011 682	0.027 029
d	3.116 683	d	0.287 583	1.554 031
d	1.106 055	d	0.090 705	0.311 512
d	0.382 464			
d	0.117 024			

The binding energies  $B$  and the kinetic energies  $U$  used in the calculation of  $\sigma_{\text{BEB}}(T)$  for these molecules were obtained using the package GAMESS [32] in an RHF calculation with a 3-21G(3d) basis set.

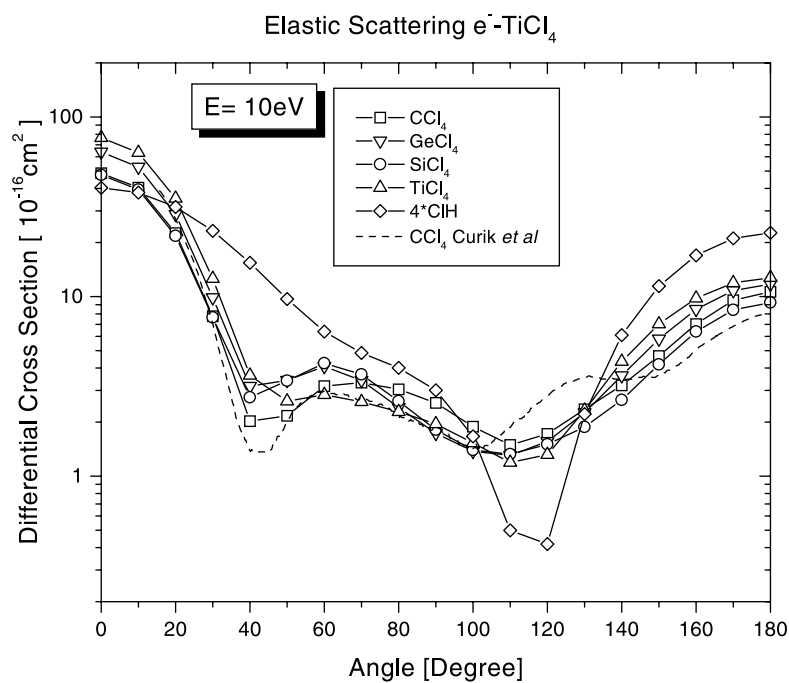
### 3. Results and discussion

In figures 1–5 we present the elastic differential cross sections (DCS) for the four molecules. One notes that the curves are similar, with maxima and minima located at the same angles. To understand the reason for this similarity, we also plot four times the differential cross section of an artificial molecule constructed from a single Cl surrounded by four centres of charge  $0.25e$ , distributed in a tetrahedron. With this procedure we obtained a closed-shell ‘CIH’ molecule, with the hydrogen atom divided into four parts, tetrahedrally distributed; this configuration of charges has no permanent dipole moment and simplifies the calculation (closed-shell molecule). Figure 6 shows the DCS for this artificial ‘CIH’ molecule for different sizes of the tetrahedron. For all energies the results are quite similar, suggesting that the scattering is mostly due to the chlorine atom. For purposes of comparison, we show in figures 2 and 3 the results of [14] for  $\text{CCl}_4$ , obtained by solving the Schrödinger equation with a parameter free model potential. At 10 eV, the DCS of Curik *et al* show a structure around  $120^\circ$  not seen in our results, although there is agreement in shape among both results. At 15 eV one can also find agreement in shape, except for angles above  $140^\circ$ , where the DCS of Curik *et al* remain below ours.

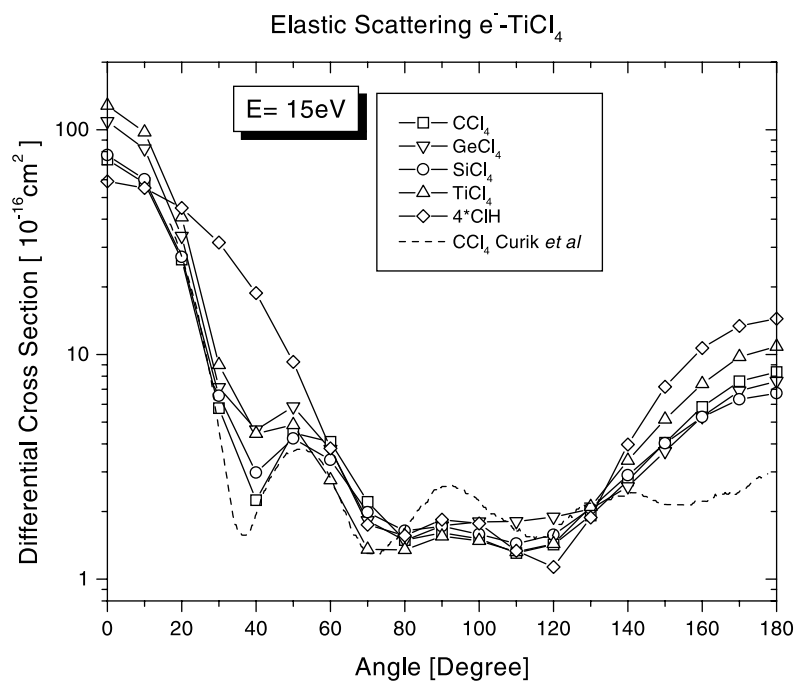
At high impact energies, four times the DCS of the ‘CIH’ molecule is very similar to the differential cross section of the tetrachlorides (for energies above 15 eV, ‘CIH’ shows two of the three minimum structures). The conclusion is then very simple: with the possible exception of



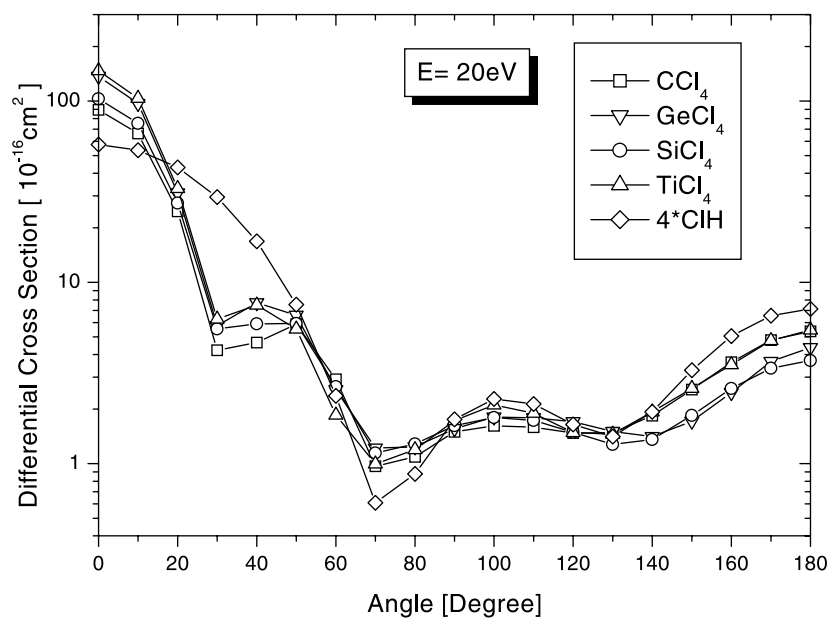
**Figure 1.** Elastic differential cross sections of the four tetrachlorides and four times the cross section of symmetrized CIH at 5 eV impact energy.



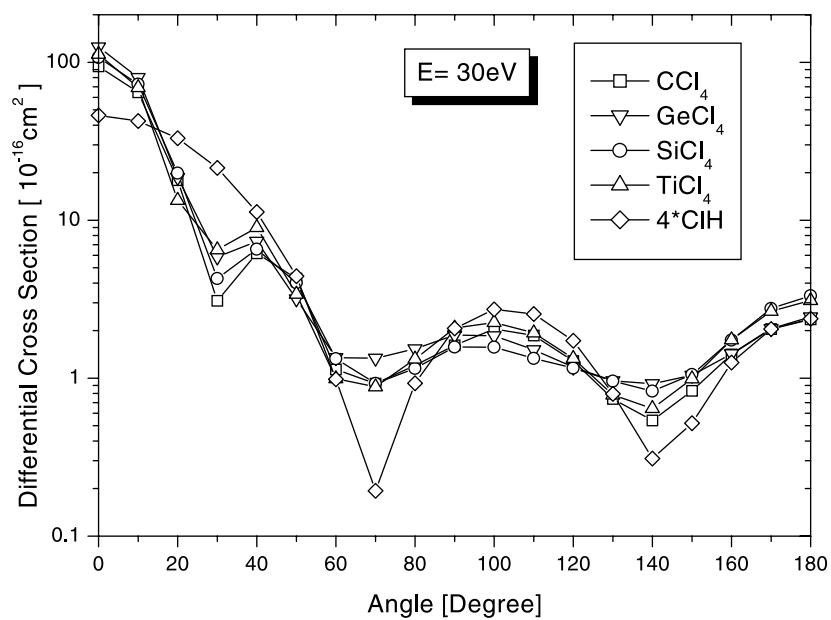
**Figure 2.** Elastic differential cross sections of the four tetrachlorides and four times the cross section of symmetrized ClH at 10 eV impact energy.



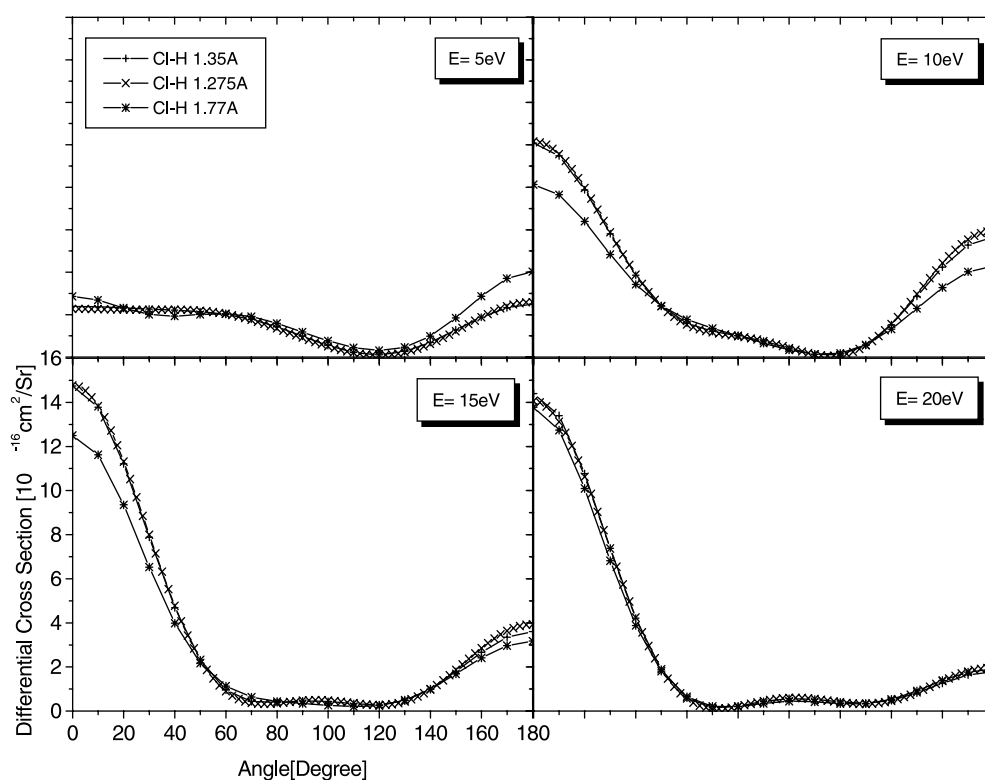
**Figure 3.** Elastic differential cross sections of the four tetrachlorides and four times the cross section of symmetrized ClH at 15 eV impact energy.



**Figure 4.** Elastic differential cross sections of the four tetrachlorides and four times the cross section of symmetrized ClH at 20 eV impact energy.



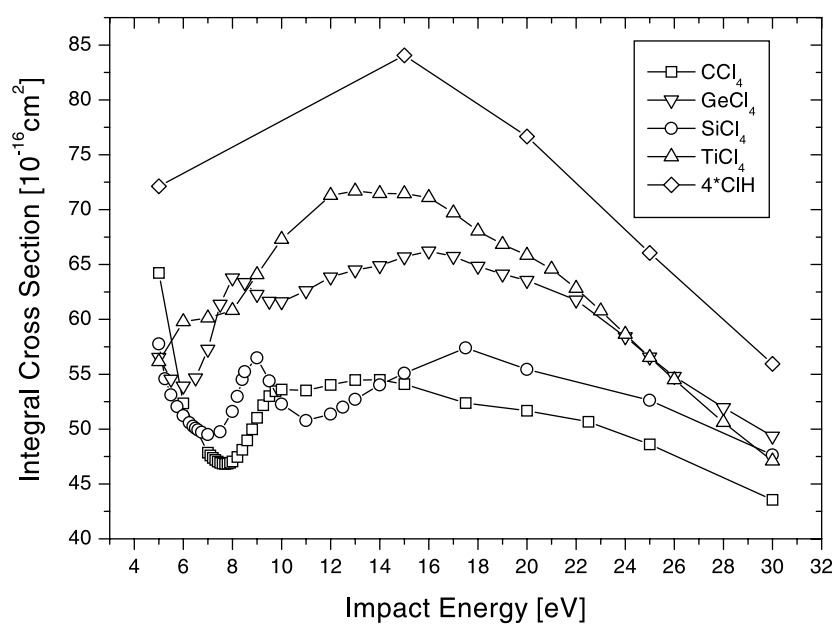
**Figure 5.** Elastic differential cross sections of the four tetrachlorides and four times the cross section of symmetrized ClH at 30 eV impact energy.



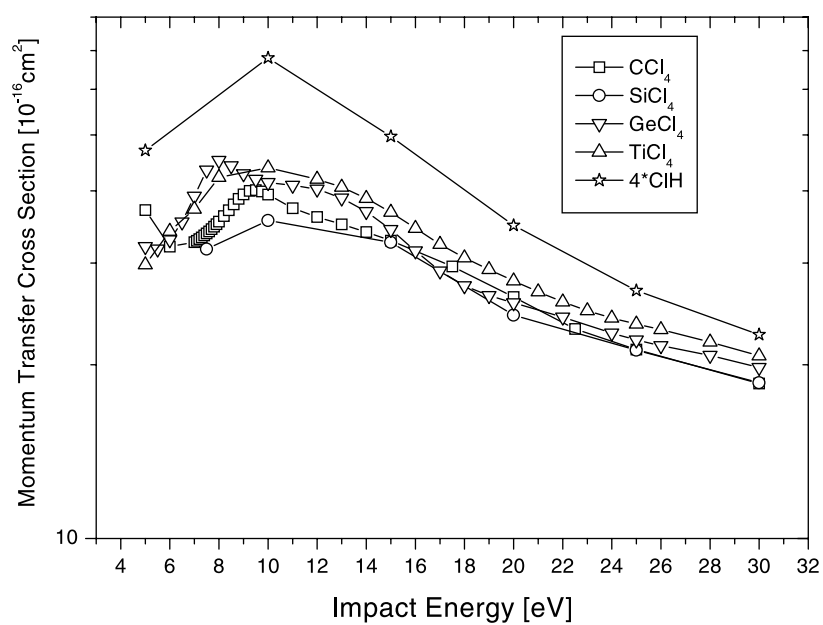
**Figure 6.** Elastic differential cross sections of the different sizes of the tetrahedron of the 'ClH' molecule.

the forward scattering (small angles), the four  $\text{Cl}^-$  scatter independently, with no interference among them, with no dependence on their mutual distance, and no shading of the others or hiding the incident electron beam from the ions behind. The cations are so small that they make no appreciable contribution to the cross section (at least for angles greater than zero). However, these effects seem to be important at lower energies.

For forward scattering, that is, at low scattering angles, where the higher partial waves contribute, we are able to see some important differences in figures 1–5 (observe that we are using a logarithmic scale so that the differences at zero scattering angle are relatively important). The differences seen in figures 1–5 between the differential cross sections of 'ClH' and  $\text{XCl}_4$  are expected, once the  $\text{XCl}_4$  molecules are able to couple higher angular momenta than 'ClH'. The DCS is then integrated in two different ways. First, we calculated the integral elastic cross section to obtain the curves of figure 7. There one notes different cross sections for the four halides, especially in the region between 5 and 20 eV. In this region, the cross sections follow roughly the hierarchy of molecular sizes, though  $\text{CCl}_4$  being appreciably smaller than the other halides has a larger cross section in some energy ranges. Secondly, we include a factor of  $(1 - \cos \theta)$  in the integrand to obtain the momentum transfer cross section. The factor is zero at  $\theta = 0$  so that it eliminates the contribution of the forward scattering. The result is shown in figure 8 where one sees that the  $\text{XCl}_4$  molecules become similar again. Also, one can see that for high energies four times the momentum transfer cross section of the 'ClH' molecule becomes closer to the results of  $\text{XCl}_4$  molecules, for the reason discussed above.

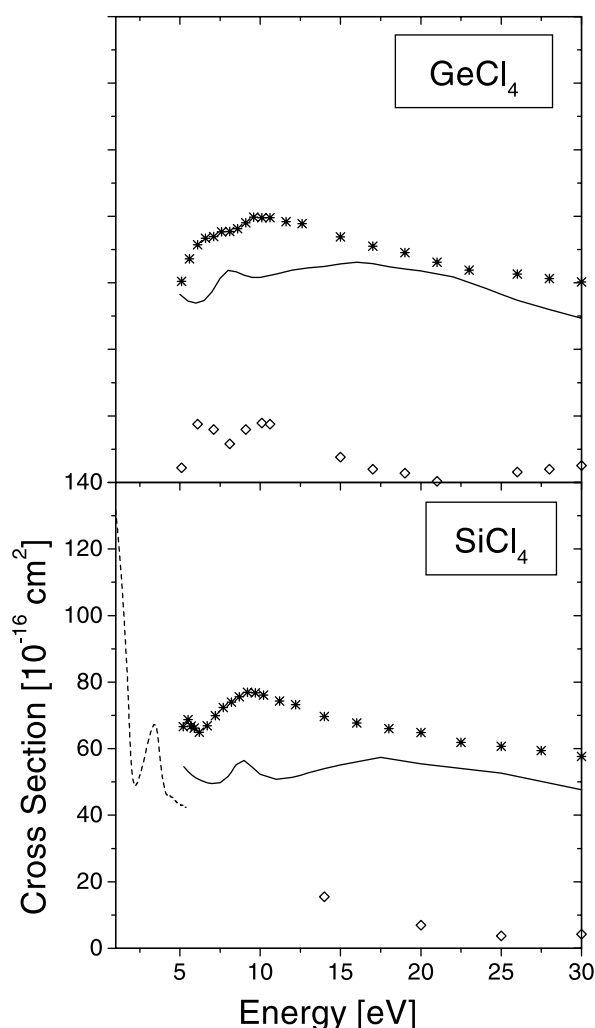


**Figure 7.** Elastic integral cross sections of the four tetrachlorides and four times the cross section of symmetrized ClH.



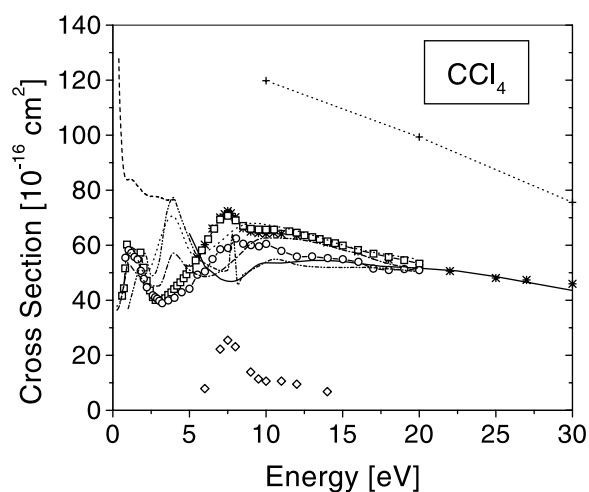
**Figure 8.** Elastic momentum transfer cross sections of the four tetrachlorides and four times the cross section of symmetrized ClH.



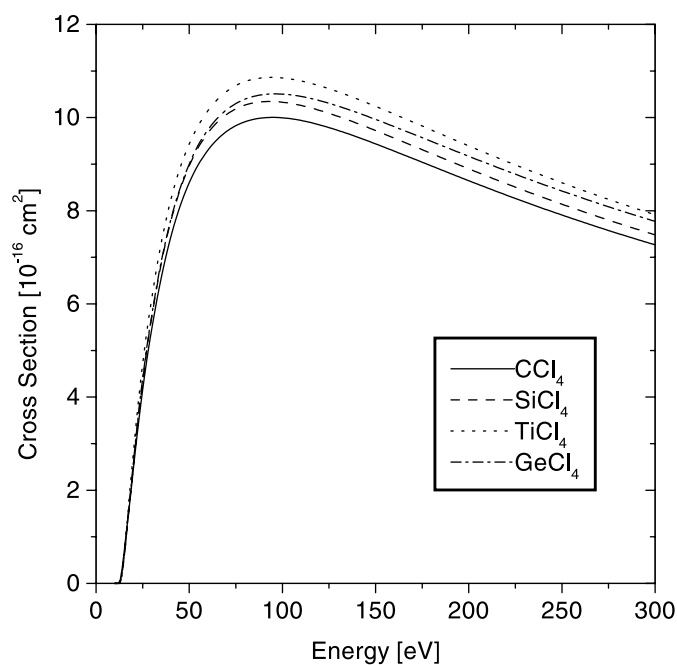


**Figure 9.** Our elastic integral cross sections for  $\text{GeCl}_4$  and  $\text{SiCl}_4$  (full curves); elastic integral cross sections of [12] (broken curve); measured total cross sections from [22, 21] for  $\text{GeCl}_4$  and  $\text{SiCl}_4$ , respectively (stars); estimated inelastic cross sections (open diamonds).

In figures 9 and 10 we present our elastic cross sections along with the measured total cross sections for  $\text{CCl}_4$ ,  $\text{SiCl}_4$  and  $\text{GeCl}_4$  from [18, 21, 22] and theoretical MS- $X\alpha$  results of [12]. We also show in figure 10 the theoretical results of [13, 14], our previous results of [15] and the total cross section of [19, 20]. The shape of the elastic cross section and the total cross section for each one of these molecules is similar. For  $\text{CCl}_4$  (figure 10), our cross sections follow the shape of the theoretical results of [14] and the experimental total cross sections. The results of Jiang *et al* remain above all of the curves. In figures 9 and 10 we also present the estimated inelastic cross sections for these molecules, obtained through the differences of the total cross section and the elastic plus total ionization cross section, which are presented in figure 11 for the four tetrachlorides.



**Figure 10.** Present elastic integral cross sections (full curves) and present estimated inelastic cross sections (open diamonds); elastic cross integral cross sections of [12] (broken curve); measured total cross sections of [18] (stars); measured total cross sections of [20] (open circles); measured total cross sections of [19] (open squares); elastic integral cross section of [14] using their SMCE SEP approximation (dotted curve); elastic integral cross section of [14] using their HFEGE SEP approximation (chain curve); elastic integral cross section of [15] (double-dotted chain curve); elastic integral cross section of [33] (dotted curve with plus).



**Figure 11.** Total ionization cross sections of the four tetrachlorides.

#### 4. Summary

We conclude our findings in the following way. The tetrahedral chlorides all have similar elastic cross sections away from the forward direction. At high impact energies the cross section is due only to the  $\text{Cl}^-$  ions scattering independently and incoherently. Furthermore, one cannot note the effects of shading and hiding behind that one would expect from a geometrical optics cross section. Only for angles very near those of forward scattering do the molecules present different cross sections, which barely follow a hierarchy of molecular sizes. We also presented the total ionization cross sections for these tetrachlorides and estimated the inelastic cross sections for  $\text{CCl}_4$ ,  $\text{SiCl}_4$  and  $\text{GeCl}_4$ . This is an important piece of information for plasma modellers.

#### Acknowledgments

The authors acknowledge support from the Brazilian agency Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). DLA acknowledges support from the Brazilian agency CAPES through the Universidade Federal do Maranhão (UFMA) PICD programme, MHFB acknowledges Professors Carlos M de Carvalho and Ivo A Hümmelgen (PADCT-620081/97-0 CEMAT) for computational support at Departamento de Física-UFPR. Our calculations were performed at CENAPAD-SP, at CENAPAD-NE and at DF-UFPR.

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