

Polarization effects in the elastic scattering of low-energy electrons by XH_4 ($X = C, Si, Ge, Sn, Pb$)

M. H. F. Bettega

Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531-990 Curitiba, Paraná, Brazil

M. T. do N. Varella and M. A. P. Lima

Instituto de Física “Gleb Wataghin,” Universidade Estadual de Campinas, Caixa Postal 6165, 13083-970 Campinas, São Paulo, Brazil

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We report integral and differential cross sections for elastic scattering of electrons by XH_4 ($X = C, Si, Ge, Sn, Pb$) molecules for energies between 3 and 10 eV. We use the Schwinger multichannel method with pseudopotentials [Bettega *et al.*, Phys. Rev. A **47**, 1111 (1993)] at the static-exchange and static-exchange plus polarization approximations. We compare our results with available theoretical and experimental results and find very good agreement. In particular, our results show Ramsauer-Townsend minima for all XH_4 molecules.

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I. INTRODUCTION

Elastic collision of low-energy electrons with CH_4 , SiH_4 , and GeH_4 has been the subject of several experimental [1–16] and theoretical [17–32] works. Among these molecules, CH_4 is the most investigated, followed by SiH_4 and then by GeH_4 . The other two molecules of this series, SnH_4 and PbH_4 , have received very little attention. In the theoretical side, most studies have been concerned with the Ramsauer-Townsend minimum that appears in the elastic cross section of CH_4 , SiH_4 , and GeH_4 at very low energies (in general, below 1 eV). These studies have employed *ab initio* methods [17,20–23,25,32] and methods based on model polarization potentials [18,19,26–31]. There are also studies which considered higher energies and used the static-exchange approximation [17,21,22,32].

In the present paper, we report elastic integral, and differential cross sections for electron scattering by XH_4 molecules. We used the Schwinger multichannel (SMC) method with pseudopotentials at the static-exchange (SE) and static-exchange plus polarization (SEP) approximations. Our calculations were mostly carried out for energies between 3 and 10 eV. Polarization is included in a sufficient amount to give results that are comparable with other calculations and with experiment in this energy range.

II. THEORY

The SMC method [33–35] and its implementation with pseudopotentials [36] have been described in detail in several publications. Here we will describe only the relevant points concerning the present work.

The SMC method is a variational method which results in the following expression for the scattering amplitude:

$$f(\vec{k}_f, \vec{k}_i) = -\frac{1}{2\pi} \sum_{m,n} \langle S_{\vec{k}_f} | V | \chi_m \rangle (d^{-1})_{mn} \langle \chi_n | V | S_{\vec{k}_i} \rangle, \quad (1)$$

where

$$d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle \quad (2)$$

and

$$A^{(+)} = \frac{\hat{H}}{N+1} - \frac{(\hat{H}P + P\hat{H})}{2} + \frac{(VP + PV)}{2} - VG_p^{(+)}V. \quad (3)$$

In the above equations, $|S_{\vec{k}_{i,f}}\rangle$ is a solution of the unperturbed Hamiltonian H_0 and is a product of a target state and a plane wave, V is the interaction potential between the incident electron and the electrons and nuclei of the target, $|\chi_m\rangle$ is a set of $(N+1)$ -electron Slater determinants [configuration state functions (CSF's)] used in the expansion of the trial scattering wave function, $\hat{H} = E - H$ is the total energy of the collision minus the full Hamiltonian of the system, with $H = H_0 + V$, P is a projection operator onto the open-channel space defined by the target eigenfunctions, and $G_p^{(+)}$ is the free-particle Green's function projected on the P space. The (direct) configuration space is constructed as

$$\{|\chi_i\rangle\} = \{\mathcal{A}(|\Phi_1\rangle \otimes |\varphi_i\rangle)\}, \quad (4)$$

where $|\Phi_1\rangle$ is the target ground-state wave function, described at the Hartree-Fock level of approximation, $|\varphi_i\rangle$ is a one-electron function, and \mathcal{A} is the antisymmetrizer. To take polarization into account, the configuration space is enlarged by including CSF's of the type

$$\{|\chi_i\rangle\} = \{\mathcal{A}(|\Phi_j\rangle \otimes |\varphi_u\rangle)\}, \quad j \geq 2, \quad (5)$$

where $|\Phi_j\rangle$ are virtual states of the target obtained from the ground state by single excitations, and $|\varphi_u\rangle$, as before, is a one-electron function. To construct the $|\Phi_j\rangle$ states, we made single excitations from the occupied orbital to a compact set of polarized orbitals [23,37]. These orbitals are defined by

$$|\varphi_{i,\mu}\rangle = \sum_{j \in \text{virtuals}} \frac{\langle \varphi_j | x_\mu | \varphi_i \rangle}{E_j - E_i} |\varphi_j\rangle, \quad (6)$$

TABLE I. Bond Lengths (R) for XH_4 (Å).

System	R
CH ₄	1.085
SiH ₄	1.480
GeH ₄	1.527
SnH ₄	1.711
PbH ₄	1.754

where $|\varphi_i\rangle$ is an occupied orbital, x_μ is a component of the dipole moment operator, and j runs over the Hartree-Fock virtual orbitals. An orthonormal set of orbitals is constructed using the Schmidt orthogonalization procedure, from the polarizing orbitals and the residual scattering orbitals. All polarized and virtual orbitals are used as scattering orbitals.

III. COMPUTATIONAL DETAILS

The cross sections were computed by the Schwinger multichannel method, along with the *norm-conserving* pseudopotentials of Ref. [38], at the SE and SEP approximations at the ground-state equilibrium geometry shown in Table I. For the central atoms, the basis set used in our bound state and scattering calculations are shown in Table II and were obtained according to a variational procedure described in Ref. [39]. The basis set for the hydrogen used in the calculations of GeH₄, SnH₄, and PbH₄ is shown in Table III. For the hydrogen in the CH₄ calculations, we included one extra s -type function with exponent 0.03 and used one p -type function with exponent 0.15, and for SiH₄ we used one p -type function with exponent 1.0. For the XH_4 molecules but methane, we included three s -type functions (with exponents equal to 1.6, 0.4, and 0.1) at chargeless centers. These centers, together with the hydrogens, complete the cube centered at the X atom. With these sets, we obtained 1532 CSF's for CH₄, 1988 CSF's for SiH₄, and 2360 CSF's for GeH₄, SnH₄, and PbH₄. The polarizabilities for the above mol-

TABLE III. Cartesian Gaussian functions for H .

Type	Exp.	Coefficient
s	13.3615	0.130844
	2.0133	0.921539
p	0.4538	1.0
	0.1233	1.0
	0.4538	1.0
	0.1233	1.0

ecules are shown in Table IV, and are calculated using the sum-over-states method [40].

IV. RESULTS AND DISCUSSION

We show in Figs. 1 and 2 our calculated integral cross sections (ICS) for XH_4 between 3 and 10 eV. We present the ICS obtained at the SE and SEP approximations for the purpose of comparison. In Fig. 1 we compare our ICS for CH₄, SiH₄, and GeH₄ with other theoretical calculations and with experimental data. For CH₄ our results show good agreement with the theoretical results of Lengsfeld *et al.* [23], Althorpe *et al.* [28], and Machado *et al.* [29] and with the experiments of Ferch *et al.* [4] and Lohmann and Buckman [5]. For SiH₄, there is good agreement between our results and the theoretical results of Sun *et al.* [25] and Lee *et al.* [30]. Good agreement is also found between theory and experiment of Wang *et al.* [8] and Szmytkowski *et al.* [15]. For GeH₄, the theoretical results of Lee *et al.* [31] lie above ours and above the total cross section of Szmytkowski *et al.*, and do not show the broad shape resonance. The results of Jain *et al.* agree in magnitude with the results of Lee *et al.* but show the broad structure. The reason why both, the results of Lee *et al.* and Jain *et al.*, seem to be overestimated will be discussed below. Our results agree in shape with the integrated cross section of Dillon *et al.* [11] and total cross section of Mozejko *et al.* [14].

TABLE II. Cartesian Gaussian for the X atoms.

Type	C Exp.	Si Exp.	Ge Exp.	Sn Exp.	Pb Exp.	Coefficients
s	2.648201	2.683331	2.429279	1.593439	3.394634	1.0
	0.578047	1.321474	1.000450	0.784579	0.825517	1.0
	0.176324	0.309926	0.542241	0.434812	0.526215	1.0
	0.034012	0.115275	0.148198	0.119889	0.158800	1.0
	0.013014	0.023236	0.019957	0.013993	0.046794	1.0
		0.005734	0.005212	0.004644	0.013081	1.0
p	3.823468	0.344268	1.677720	2.592850	2.269577	1.0
	0.835457	0.123883	0.270291	0.822731	0.668937	1.0
	0.193432	0.045674	0.091598	0.211766	0.210801	1.0
	0.042745	0.012853	0.034666	0.062991	0.064993	1.0
d			0.011682	0.012170	0.015564	1.0
	0.662246	1.8	0.457112	1.296389	2.148486	1.0
	0.171029	0.6	0.195662	0.183128	0.142802	1.0
		0.2	0.036696	0.068350	0.056799	1.0

TABLE IV. Calculated and experimental values for the polarizabilities (a_0^3) of XH_4 .

System	Calculated	Experimental
CH_4	17.67	17.50 (Ref. [41])
SiH_4	31.91	31.90 (Ref. [42])
GeH_4	39.67	44.35 (Ref. [31])
SnH_4	51.36	
PbH_4	58.74	

In Figs. 3 and 4, we present the differential cross sections (DCS) for CH_4 at 3 eV, 5 eV, 7.5 eV, and 10 eV. In Fig. 3, we compare our results with the theoretical results of Lengsfeld *et al.* [23] and Machado *et al.* [29] and with the experimental data of Tanaka *et al.* [1], Mapstone and Newell [10], Curry *et al.* [2], and Bundschu *et al.* [16]. There is good agreement between the theoretical curves and the experimental points, except for the fact that the results of Machado *et al.* present a rise for angles below 30° , which agrees with the experimental data of Bundschu *et al.* At 3 eV, our DCS present the same shape as that of the others shown in this figure, but is larger for angles below 100° . In Fig. 4, we compare our SEP and SE results, which shows that for CH_4 , polarization is

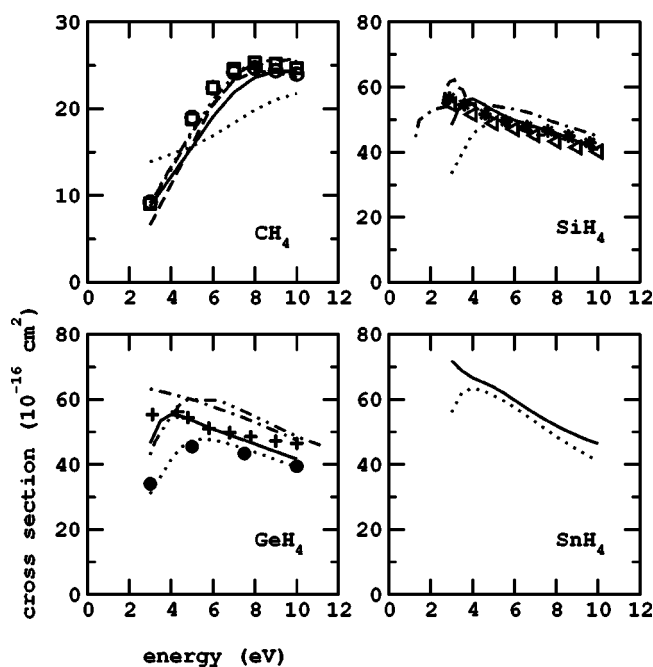


FIG. 1. Integral cross section for XH_4 . Solid line, results including polarization effects; dotted line, results at the static-exchange approximation; dashed line, results of the complex Kohn method (CKVM) calculations from Ref. [23] for CH_4 and from Ref. [25] for SiH_4 ; dotted-dashed line, results of the Schwinger iterative method (SVIM) calculations from Ref. [29] for CH_4 , Ref. [30] for SiH_4 , and Ref. [31] for GeH_4 ; dashed-dotted-dotted line, results of model potential calculations from Ref. [28] for CH_4 and from Ref. [26] for GeH_4 . Experiments are circles from Ref. [4] and squares from Ref. [5] for CH_4 ; triangles from Ref. [8] and stars from Ref. [15] for SiH_4 ; filled circles from Ref. [11] and crosses from Ref. [14] for GeH_4 .

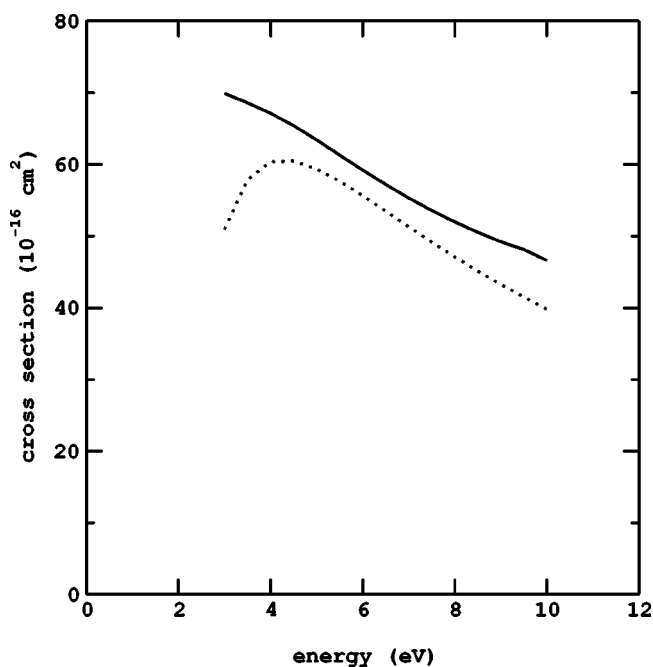


FIG. 2. Integral cross section for PbH_4 . Solid lines, results including polarization effects; dotted line, results at the static-exchange approximation.

important for almost all impact energies below 10 eV.

The DCS for SiH_4 at 3 eV, 5 eV, 7.5 eV, and 10 eV are shown in Figs. 5 and 6. In Fig. 5, we compare our SEP results with results of Sun *et al.* [25] and Lee *et al.* [31] and

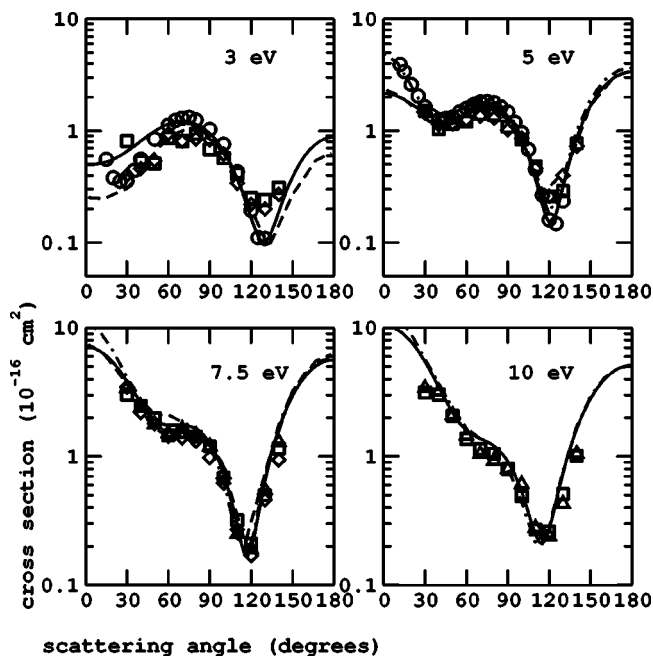


FIG. 3. Differential cross section for CH_4 at 3, 5, 7.5, and 10 eV. Solid line, results including polarization effects; dashed line, results of CKVM calculations; dotted-dashed line, results of the SVIM calculations. Experiments are squares from Ref. [1], diamonds from Ref. [10] (at 3.2, 4.2, and 7.9 eV), triangles from Ref. [2], and circles from Ref. [16].

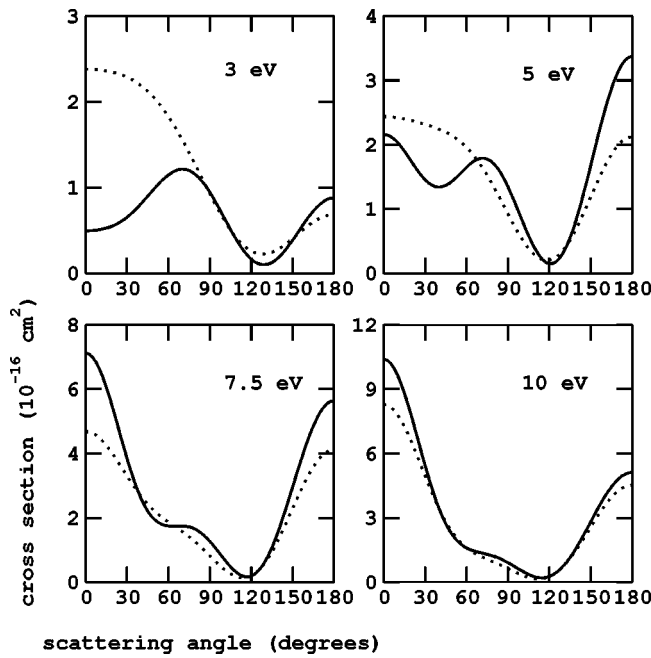


FIG. 4. Differential cross section for CH_4 at 3, 5, 7, 5, and 10 eV. Solid line, results including polarization effects; dotted line, results at the static-exchange approximation.

with the experimental data of Sohn *et al.* [6]. Our results agree very well with the complex Kohn results of Sun *et al.*, except at 3 eV, where small discrepancies are seen. At 7.5 eV and 10 eV, the results of Lee *et al.* also show a rise for angles below 30° . Our results also agree very well with the experiments of Sohn *et al.* Figure 6 shows our SEP and SE results. For this molecule, polarization effects seem to be important only for impact energies below 5 eV. At this energy and

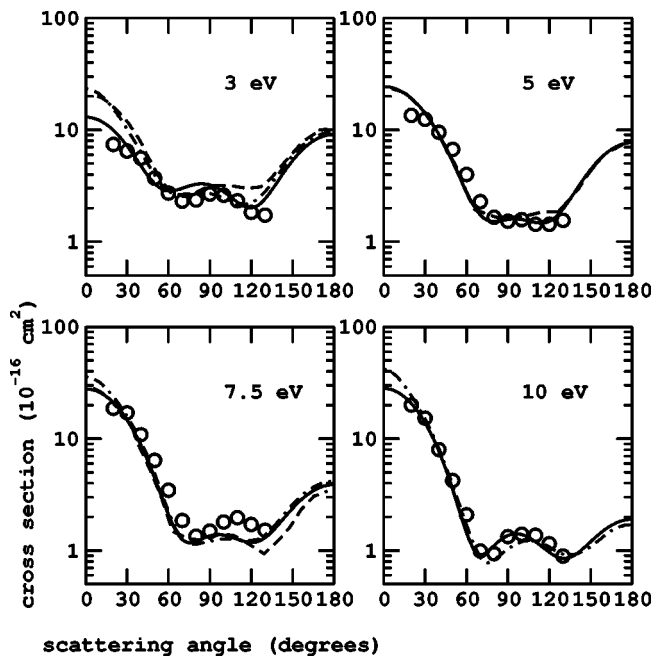


FIG. 5. As in Fig. 3 for SiH_4 , except circles are results from Ref. [9].

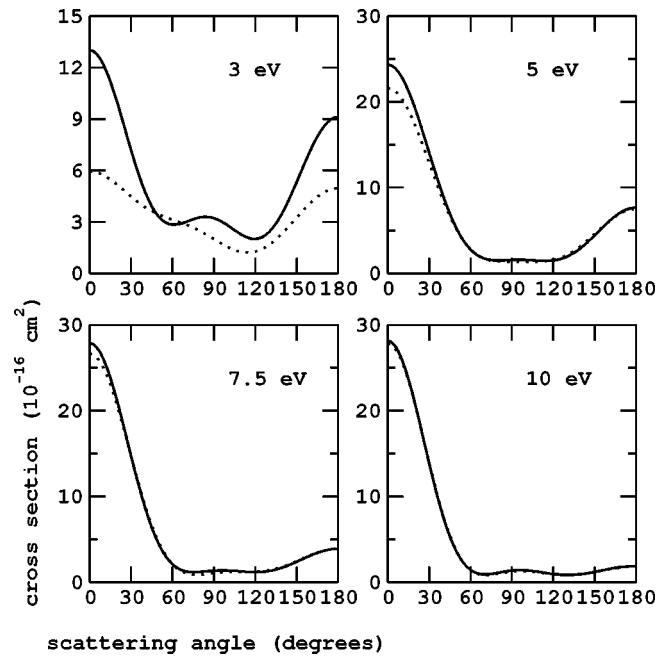


FIG. 6. As in Fig. 4 for SiH_4 .

above it, the SEP and SE DCS show very little discrepancies (and only at small angles).

The DCS for GeH_4 are shown in Figs. 7 and 8. In Fig. 7, we show our calculated SEP DCS along with the results of Jain *et al.* [26], Lee *et al.* [31], and Dillon *et al.* [11]. The agreement between our results and the experimental DCS of Dillon *et al.* is very good. Our DCS agree in shape with the DCS of Lee *et al.* but differ in magnitude, mainly at 3 eV and 5 eV. Our results also show some discrepancies with the

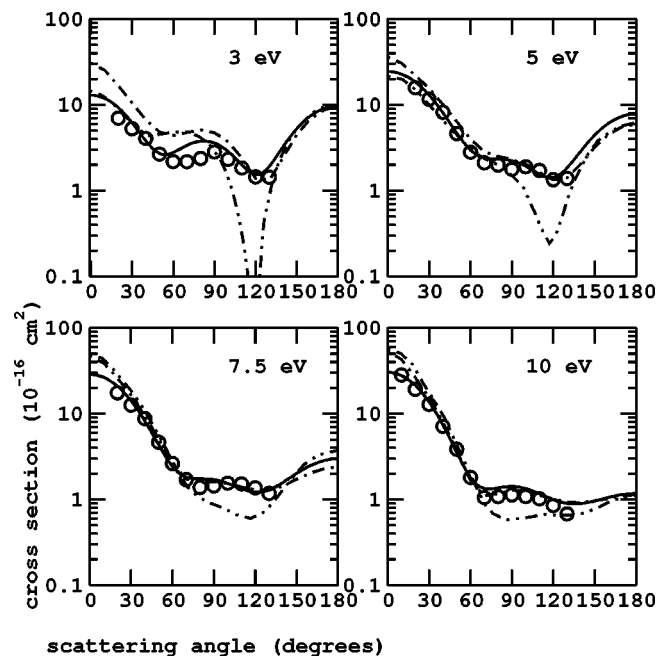
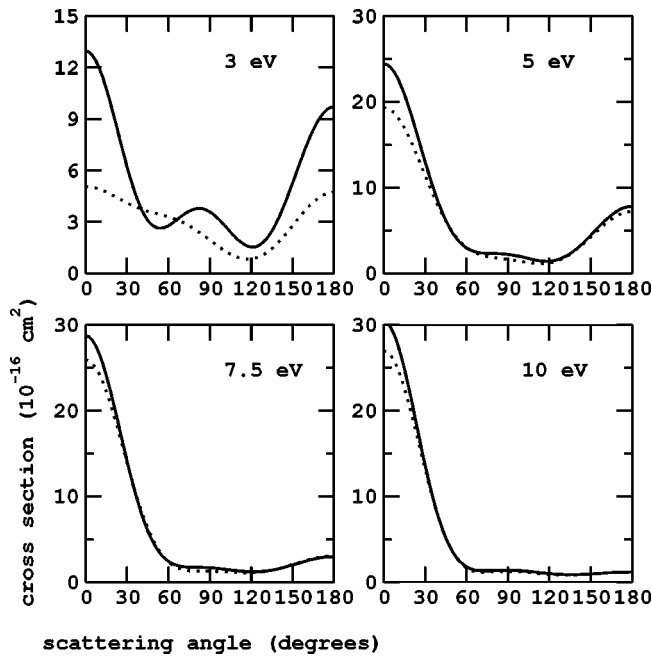
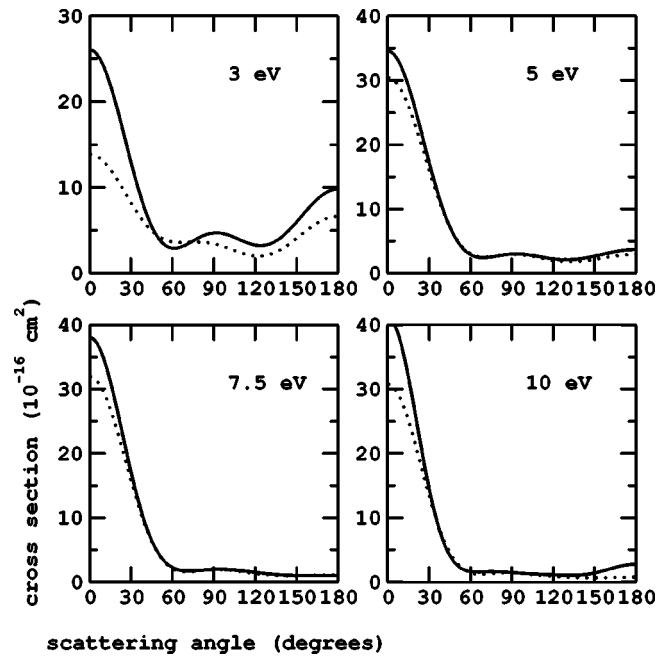


FIG. 7. As in Fig. 3 for GeH_4 , except circles are results from Ref. [11] and the dashed-dotted-dotted lines are results from Ref. [26].

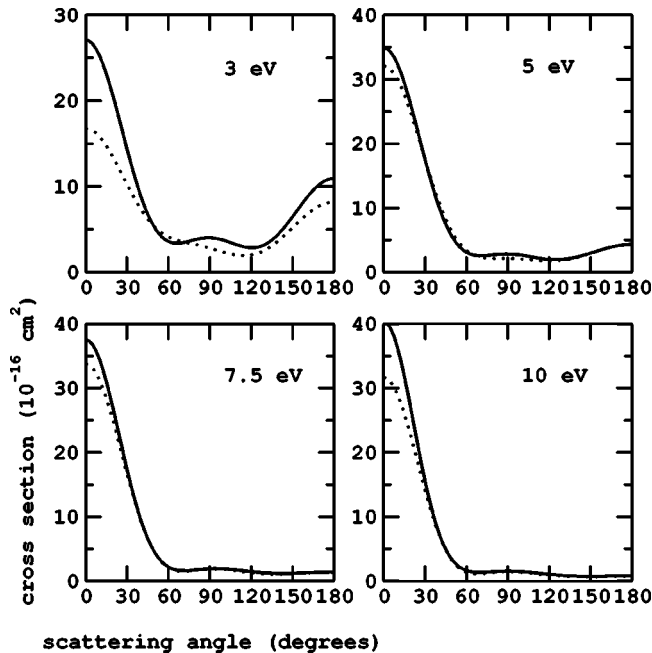
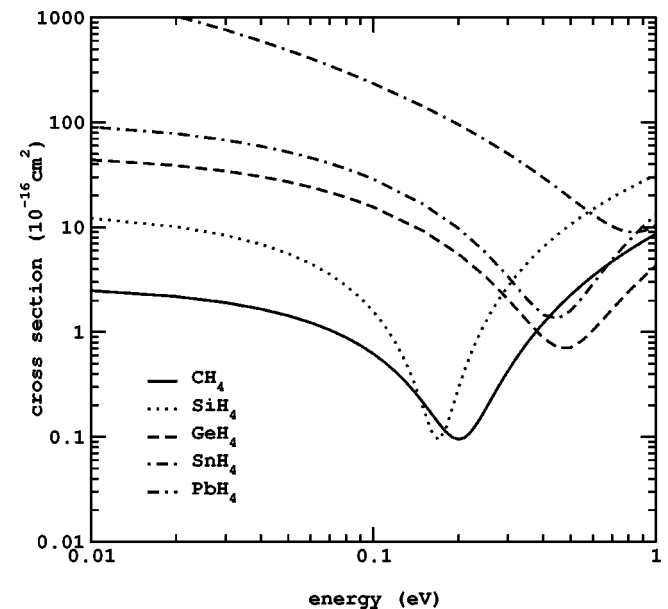
FIG. 8. As in Fig. 4 for GeH₄.FIG. 10. As in Fig. 4 for PbH₄.

results of Jain *et al.*, which show a deep minimum especially at 3 eV and 5 eV. The DCS of Lee *et al.* and Jain *et al.* show the same behavior at the forward direction, being greater than ours in magnitude (since we are using a logarithmic scale, this difference is minimized by this scale). This rise in the forward direction may be due to the long-range part of the model polarization potential used by both methods, which behaves as $-\alpha_0/2r^4$, where α_0 is the polarizability. We believe that the contribution of the DCS at low scattering angles is responsible for the raise of the ICS of Jain *et al.* and Lee *et al.* seen in Fig. 1. Figure 8 compares our SEP and SE

DCS. As for SiH₄, polarization seems to be important for GeH₄ for energies below 5 eV.

In Figs. 9 and 10, we show our SEP and SE DCS for SnH₄ and PbH₄. For these molecules, the SEP and SE DCS are very close at higher impact energies (5 eV and above), except near the forward-scattering direction, where the long-range polarization potential (determined by the polarizability) plays a major role.

From the differential cross-section plots, we may observe that, in general, polarization emphasizes the *d*-wave character of the DCS for the heavier systems. We have also investigated the ICS for all XH₄ molecules at lower energies (be-

FIG. 9. As in Fig. 4 for SnH₄.FIG. 11. Integral cross section for XH₄ at energies below 1 eV.

low 3 eV), and show these results in Fig. 11. According to our results, all XH_4 molecules present Ramsauer-Townsend minima, even though their position and magnitude should be significantly affected by a more elaborate description of polarization. For example, our calculations place the Ramsauer-Townsend minimum for CH_4 , SiH_4 , and GeH_4 around 0.2 eV, 0.15 eV, and 0.45 eV, respectively. For CH_4 , this value is placed too low in energy, since the value reported by other calculations [23,28,29] and by experiment [4,6,28] is around 0.4 eV. For SiH_4 , the value reported by Sun *et al.* is around 0.3 eV, while Lee *et al.* reported the value of 0.2 eV for this molecule [25,30]. For GeH_4 , Lee *et al.* reported the value of 0.6 eV [31] for the Ramsauer-Townsend minimum. In fact, from Table IV, we see that the calculated polarizabilities become worse as the size of the molecule grows, which would significantly affect the cross sections below 1 eV, where the minima are found.

V. SUMMARY

We have presented elastic integral and differential cross sections for elastic scattering of electrons by XH_4 molecules.

Our calculations included polarization effects and our results agree very well with other theoretical results and with experiments available in the literature in the energy range between 3 and 10 eV. Our results show that polarization effects are important for all XH_4 molecules. According to our results, all XH_4 molecules present Ramsauer-Townsend minima.

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