Electronic excitation of XH_4 $(X=C,Si,Ge,Sn,Pb)$ by electron impact

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We calculate integral cross sections for the electronic excitation to the $^3T_2$ states of XH_4 $(X=C,Si,Ge,Sn,Pb)$ by electron impact. This is the lowest-lying excited state of these molecules. Our results were obtained with the Schwinger multichannel method with pseudopotentials at the two-state level of approximation. In the case of CH_4 we compare our results with previous results of an all-electron calculation obtained at the same level of approximation, in which case we found an excellent agreement between the two calculations. Though these molecules are very similar, after discarding the cores, as the pseudopotential technique does, the inelastic cross sections are very distinctive and do not have a monotonic behavior with increasing proton number Z of the central atom. [S1050-2947(98)09706-6]

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The implementation of pseudopotentials into the Schwinger multichannel method (SMC) [1] makes it possible to calculate cross sections of molecules otherwise inaccessible by all-electron methods [2]. In the case of the molecules we are dealing with, the pseudopotential calculation of the cross sections of PbH_4 is no more complicated or time consuming than that of CH_4, while by all-electron methods PbH_4 is unreachable. Although pseudopotentials could do much to the cross-section calculations, their use was slow in the literature but, nowadays, aside from the SMC, the Kohn method [3,4] has also been adapted to pseudopotentials.

In this paper we present integral cross sections for the electronic excitation of XH_4 $(X=C,Si,Ge,Sn,Pb)$ to the $^3T_2$ states at the two-state level of approximation, using pseudopotentials. The pseudopotentials are normally derived from the ground state of atoms [5]. Therefore, for a calculation with an excited state, it is advisable to test the pseudopotential technique itself by comparing the results with those of an all-electron calculation. Only for CH_4 we found calculated excitation cross sections at this level of approximation [6], and the agreement between these results and our results is excellent. We also compare our two-state cross sections for CH_4 and SiH_4 with the results of more sophisticated calculations of Refs. [6–8]. All the calculations were performed with the Schwinger multichannel method.

The SMC [1] and its version with pseudopotentials [2] have been discussed in earlier works, and we review here only those aspects of the method related to the two-state approximation being used. The SMC method is a multichannel extension of the Schwinger variational principle. Actually it is a variational approximation for the scattering amplitude, where the scattering wave function is expanded in a basis of $(N+1)$-particle Slater determinants. The coefficients of this expansion are then variationally determined. The resulting expression for the scattering amplitude in the body frame is

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

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 these equations, the solution $S_{\vec{k}_i}$ of the unperturbed Hamiltonian H_0 is the product of a target state and a plane wave, V is the interaction potential between the incident electron and the target, χ_m is an $(N+1)$-electron Slater determinant 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. A two-state approximation means that P is reduced to a sum of the ground state plus the first excited triplet state $^3T_2$. Similarly, to define the configuration space $|\chi_n\rangle$ we add to the representations of the N-particle ground state plus $^3T_2$ a fairly complete set of single-particle wave functions representing the scattered electron, and antisymmetrize.

With the choice of Cartesian Gaussian functions to represent the molecular and scattering orbitals, all the matrix ele-

TABLE I. Cartesian Gaussian functions for H.

Type	Expt.	Coefficient
s	13.3615	0.130844
s	2.0133	0.921539
s	0.4538	1.0
s	0.1233	1.0
p	1.0000	1.0

TABLE II. Cartesian Gaussian for the X atoms.

Type	C Expt.	Si Expt.	Ge Expt.	Sn Expt.	Pb Expt.	Coefficient
S	7.979510	2.683331	2.429279	1.593439	1.463700	1.0
	3.277998	1.321474	1.000450	0.784579	0.987842	1.0
	0.520826	0.309926	0.542241	0.434812	0.361598	1.0
	0.168132	0.115275	0.148198	0.119889	0.128466	1.0
	0.041465	0.023236	0.019957	0.013993	0.012124	1.0
	0.019352	0.005734	0.005212	0.004644	0.004628	1.0
P	4.985125	0.344268	1.677720	2.592850	1.384797	1.0
	1.382734	0.123883	0.270291	0.822731	0.965722	1.0
	0.416258	0.045674	0.091598	0.211766	0.192039	1.0
	0.118249	0.012853	0.034666	0.062991	0.058663	1.0
D	1.8	0.8	2.4	2.4	2.4	1.0
	0.6	0.2	0.8	0.8	0.8	1.0
	0.2		0.2	0.2	0.2	1.0

ments arising in Eq. (1) can be computed analytically, except those from $\langle \chi_m | V G_P^{(+)} V | \chi_n \rangle$ (named VGV), that are evaluated by numerical quadrature [9].

The pseudopotential we use is that of Ref. [5]:

$$\hat{V}_{PP}(r) = \hat{V}_{core}(r) + \hat{V}_{ion}(r), \quad (4)$$

with

$$\hat{V}_{core}(r) = -\frac{Z_v}{r} \left[\sum_{i=1}^{2} c_i^{core} \mathrm{erf}[(\alpha_i^{core})^{1/2} r] \right], \quad (5)$$

and

$$\hat{V}_{ion}(r) = \sum_{n=0}^{1} \sum_{j=1}^{3} \sum_{l=0}^{2} A_{njl} r^{2n} e^{-\alpha_{jl} r^2} \sum_{m=-l}^{+l} |lm\rangle\langle lm|, \quad (6)$$

where Z_v is the valence charge of the atom and in this application it is equal to 4 for the C, Si, Ge, Sn, and Pb. The coefficients c_i^{core}, A_{njl}, and the decay constants α_i^{core} and α_{jl} are all tabulated in Ref. [5].

In all-electron calculations, even for small molecules, a large number of two-electron integrals must be evaluated. This limits the size of molecules in scattering calculations. Using pseudopotentials, we need shorter basis sets to describe the target and scattering and consequently the number of two-electron integrals is smaller than in the all-electron case. The reduction in the number of these integrals allows the study of bigger molecules than those reachable by all-electron techniques.

The Cartesian Gaussian functions that we used in the description of the target and in the expansion of the scattering

TABLE III. Cartesian Gaussian for the chargeless centers.

Type	Expt.	Coefficient
S	1.6	1.0
	0.4	1.0
	0.1	1.0

wave function are shown in Table I for hydrogen, in Table II for the X atoms, and in Table III for the chargeless centers, which, with the H sites, complete the cube centered at the X atom. In these tables, coefficients different from 1.0 (one) mean that the corresponding Gaussians are contracted. The Gaussians of Table II were generated by the procedure described in Ref. [10].

For each molecule, the Slater determinant describing the ground state $^1A_1$ is constructed with the valence a_1 and t_2 orbitals made of pseudo wave functions with zero nodes, the core orbitals being replaced by the pseudopotential. For example, the core orbitals replaced by the pseudopotential are $1a_1$ for CH_4; $1a_1$, $2a_1$ and $1t_2$ for SiH_4; $1a_1$, $2a_1$, $1t_2$, $3a_1$, $2t_2$, $3t_2$, and $1e$ for GeH_4; $1a_1$, $2a_1$, $1t_2$, $3a_1$, $2t_2$, $3t_2$, $1e$, $4a_1$, $4t_2$, $5t_2$, and $2e$ for SnH_4. For PbH_4 there are 39 core orbitals replaced by the pseudopotential.

The triplet excited state $^3T_2$ is constructed by promoting one electron of the valence t_2 orbital (hole) to the lowest unoccupied a_1 orbital (particle). The a_1 orbital (particle) is an improved virtual orbital (IVO) with one node [11]. The values for the vertical excitation energies are presented in Table IV and the experimental interatomic distances of the equilibrium ground state, used in our calculations, are in Table V.

In Fig. 1(a) we show the integral excitation cross section to the $^3T_2$ state of CH_4, obtained with pseudo and all-

TABLE IV. Excitation energies for XH_4 (eV).

System	This work	Previous calculation	Experiment
CH_4	10.84	10.86 [a]	8.8 [c]
SiH_4	9.85	9.88 [b]	8.7 [d]
GeH_4	9.40		
SnH_4	8.57		
PbH_4	7.48		

[a]Reference [6].
[b]Reference [7].
[c]Reference [13].
[d]Reference [14].

TABLE V. Bond lengths for XH_4 (a_0).

System	Experiment
CH_4	2.05
SiH_4	2.80
GeH_4	2.89
SnH_4	3.23
PbH_4	3.31

electron potentials [6]. The results are identical, which encourages us to extend the pseudopotential technique to the calculation of the excitation cross section of the other molecules. For completeness we also show results for three- and seven-state all-electron calculations of Ref. [6] and four-state all-electron calculations of Ref. [8]. These earlier works [6,8] have shown that for CH_4 the coupling of the degenerate triplet states is very strong and that of the triplets and singlets are relatively weak. Gil *et al.* [8] also indicated that the seven-state cross sections are not converged and that the convergence process is very slow. Figure 1(b) compares our two-state pseudopotential results with four- and seven-state all-electron results of Ref. [7] for SiH_4. For energies above 16 eV the excitation cross section of the triplet state in-

FIG. 2. Electronic excitation cross section to the $^3T_2$ states of XH_4 ($X=$C,Si,Ge,Sn,Pb).

creases from two- to four-state calculation and decreases back in the seven-state approximation. This is also an evidence of the slow convergence of multichannel coupling. Although the two-state calculation may give only qualitative results, it represents a first step towards the solution of the problem. Especially if we consider that the multichannel convergence in electron-molecule scattering is still an open problem in the literature and one needs to rely on two-state calculations to begin the solution of the problem. We therefore present in Fig. 2 the two-state integral excitation cross sections for all the molecules of the family. The curves may
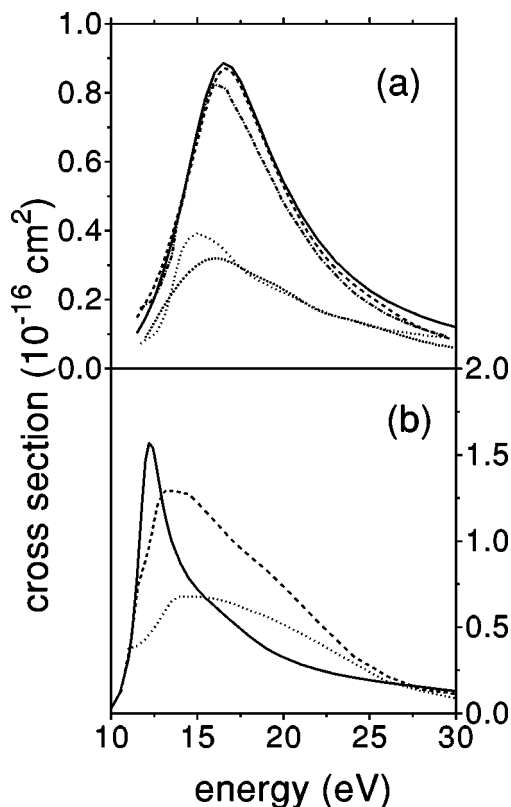

FIG. 1. (a) Electronic excitation cross section to the $^3T_2$ states of methane. Present two-state pseudopotential results, solid line; two-state all-electron results of Ref. [6], dashed line; three-state all-electron results of Ref. [6], dotted-dashed line; seven-state all-electron results of Ref. [6], dotted line; four-state all-electron results of Ref. [8], short-dashed line. (b) Electronic excitation cross section to the $^3T_2$ states of silane. Present two-state pseudopotential results, solid line; four-state all-electron results of Ref. [7], dashed line; seven-state all-electron results of Ref. [7], dotted line.
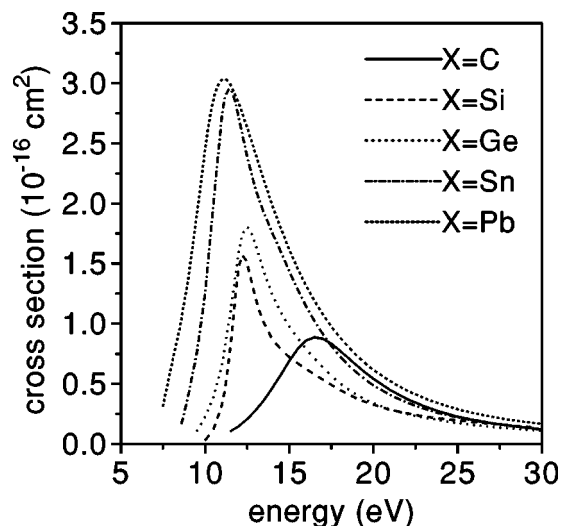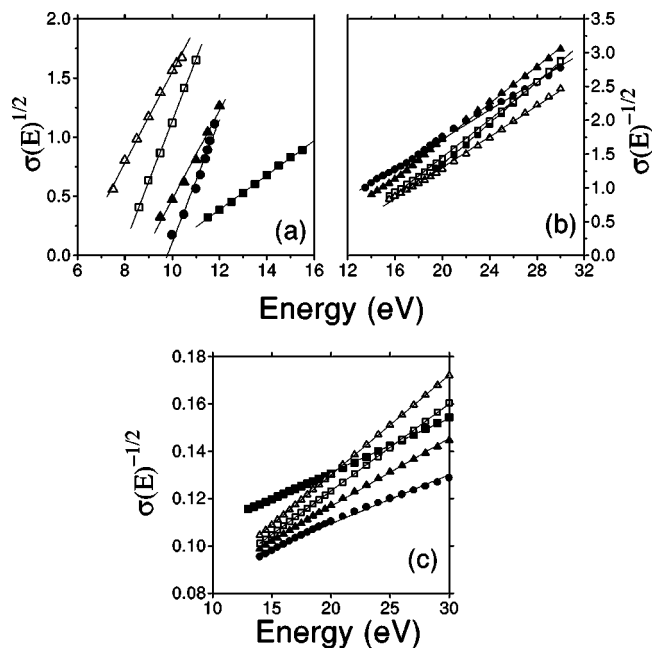

FIG. 3. (a) Least-squares fit of a straight line to $\sigma(E)^{1/2}$, for the *excitation* cross sections of XH_4 at *low* energies. (b) Least-squares fit of a straight line to $\sigma(E)^{-1/2}$, for the *excitation* cross sections of XH_4 at *high* energies. (c) Least-squares fit of a straight line to $\sigma(E)^{-1/2}$, for the *elastic* cross sections of XH_4 at *high* energies. For all plots: CH_4, filled squares; SiH_4, filled circles; GeH_4, filled triangles; SnH_4, open squares; PbH_4, open triangles. The units of σ are 10^{-16} cm^2.

TABLE VI. Fitting constants of Fig. 3 for XH$_4$.

System	a	b	c	d	f	g
CH$_4$	1.36487	0.14591	1.69736	0.15223	0.08538	0.00228
SiH$_4$	5.08505	0.51933	0.43823	0.10790	0.06795	0.00207
GeH$_4$	3.29457	0.37668	1.04989	0.13740	0.05916	0.00287
SnH$_4$	4.05286	0.51892	1.30790	0.13810	0.04954	0.00368
PbH$_4$	2.29135	0.38422	0.98795	0.11427	0.04556	0.00422

be grouped into three classes: PbH$_4$ and SnH$_4$, GeH$_4$ and SiH$_4$, and CH$_4$ which is clearly distinct from the other molecules. These classes correspond to the classes of bond length in Table V, suggesting that excitation cross sections, obtained at the two-state level of approximation, are also mostly a matter of molecular size for the families with the same chemical bonding and similar geometries. To investigate this point further, and to determine the law of cross section decaying at higher energies, and the law of buildup at lower energies, we made least-square fits of polynomials to the curves of Fig. 2. We found that, at lower energies E, the excitation cross section σ grows according to the law

$$\sigma^{1/2}(E) = bE - a$$

as shown in Fig. 3(a), and at higher energies it decays as

$$\sigma^{-1/2}(E) = dE - c$$

as shown in Fig. 3(b). The behavior at higher energies follows the same law as the elastic cross sections,

$$\sigma^{-1/2}(E) = gE + f$$

obtained at this two-state calculation, shown in Fig. 3(c), but, while the elastic cross section lines keep a clear pattern of increasing slope with increasing proton number of the central atom, the inelastic cross section lines of Fig. 3(b) have no simple relation. The fitting constants a, b, c, d, f, and g are shown in Table VI.

To summarize, we calculated the electron $^3T_2$ excitation cross section for XH$_4$ (X = C,Si,Ge,Sn,Pb) thus completing a previous work on the elastic cross section [12]. After verifying for CH$_4$ that the pseudopotential results coincided with those from an all-electron calculation, even for the excitation cross sections, we could apply the pseudopotential technique to calculate the other molecules of the family. We found that the excitation cross section has a high energy decay similar to that of the elastic cross section, but it does not follow a clear pattern of atomic number dependence.

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