Valence Electronic Structure and Internal Rotation Barrier of the Molecules XH_3YH_3 (X, Y = C, Si, Ge) by a Pseudopotential Method

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Abstract: The valence electronic structure of XH_3YH_3 molecules (X, Y = C, Si, Ge) is determined by nonempirical calculations. A pseudopotential method is used within the self-consistent field approximation. The method is first checked on CH_3CH_3 and CH_3SiH_3 for which comparisons with all-electron calculations are available. For all the molecules of the series, valence molecular orbitals and internal rotation barriers are calculated and discussed. The calculated values are in good agreement with experimental data when the latter are known.

I. Introduction

It is often interesting to examine the evolution of chemical and physical properties for a series of similar molecules in which one of the atoms is replaced by the next atom in the same column of the periodical system. Generally, experiments allow us to carry out this type of study, but this is less easy with ab initio calculations of quantum chemistry. In most cases, numerous technical difficulties restrict the use of these calculations to the study of molecules containing only the atoms of the first two rows of the periodic table. For this reason, it is essential to develop simpler theoretical methods. In this paper, we have used a nonempirical pseudopotential method to determine valence molecular orbitals and internal rotation barriers for the series of molecules XH_3YH_3 (X, Y = C, Si, and Ge).

The basic principle of pseudopotential methods[1] is to replace atomic cores by the appropriate potentials in such a manner that only valence electrons can be explicitly treated in molecular calculations. This results in a great saving of computational time, which increases with the atomic number of the atoms of the molecule. This technical advantage is accompanied by the following conceptual advantage: the core-valence electron separation allows us to introduce into the calculations the well-known chemical idea that most of the chemical properties of a molecule depend on the valence electronic structure of the constituent atoms.

The use of pseudopotential methods in quantum chemistry is recent, and their molecular applications are yet scarce.[2-5] We have developed techniques which allow us to calculate, in a rigorous manner, entirely theoretical pseudopotentials for all the atoms of the periodical system.[6] Very similar techniques have been developed simultaneously by Melius et al.[3] The efficiency of our pseudopotential method has already been demonstrated in the calculation of the valence electronic structure of various molecules for which we have successfully studied the following quantities: valence molecular orbital energies, bond lengths, bond angles, vibrational force constants.[7]

The present work pursues two goals: first, it is a new test of the efficiency of our pseudopotentials by comparison with similar all-electron calculations and with experimental results when available; second, the theoretical knowledge of the valence molecular orbitals of this series of molecules leads to new results, useful for the interpretation of their photoelectron or vacuum ultraviolet spectra. Moreover, the systematic calculation of the barrier height of these ethane-like molecules allows us to obtain a set of values completing the experimental estimates or confirming them.

At the present time, there is no simple method for obtaining such information on molecules containing heavy atoms such as Si and Ge. In addition to their well-known technical difficulties, all-electron ab initio calculations present the inconvenience of obtaining rotation barrier values of a few kilocalories per mole from the total energy difference between two conformers with the absolute values of their energies being very high. Semiempirical methods such as CNDO are easy to handle, but these appear to be limited because of their wide and various parametrizations specifically adapted to reproduce either ground state or electronic excited state molecular properties; thus recent CNDO calculations of the barrier heights of methylsilane and disilane[8] give the proof of their inadequacy by the dispersion of the results according to the choice of the parameters used. Moreover, it has been shown that CNDO methods lead to an erroneous origin of rotation barriers.[9,10] Our conviction is that pseudopotential methods are well adapted to the determination of an internal rotation barrier.

In section II, we recall the essential features of our pseudopotential method. In section III, we give the results concerning the valence molecular orbitals and in particular we study the shift of the highest occupied orbitals in the molecules of this series. Section IV is devoted to internal rotation barriers.

II. Pseudopotential Method

Let us imagine a molecule containing m atoms A, B, ... Its N_v valence electrons are described by the valence pseudo-Hamiltonian:

$$\mathcal{H}_{ps} = \sum_{i=1}^{N_v}\left[-\tfrac{1}{2}\Delta(i) - \sum_{A=1}^{m} W_{ps,A}(i)\right] + \sum_{i<j}^{N_v}\frac{1}{r_{ij}} \qquad (1)$$

where $W_{ps,A}$ is the pseudopotential associated with the core of A. For a given atom, we have

$$W_{ps} = -\frac{z}{r} + \sum_{l} W_{R,l}(r)P_l \qquad (2)$$

$z = N_v$ which is the net charge of the ion consisting of the core electrons and the nucleus of the atom; P_l denotes the projection operator over the lth subspace of spherical harmonics and $W_{R,l}(r)$ is a function characterizing the atom.

The function $W_{R,l}(r)$ is defined by

$$W_{R,l} = \frac{B_{1,l}}{r} + \frac{B_{2,l}}{r^2} \qquad (3)$$

where the parameters $B_{1,l}$ and $B_{2,l}$ are determined by a least-squares method so that the lowest eigensolutions of the atomic pseudo-Hamiltonian are in coincidence with the valence atomic orbital energies and pseudo-orbitals which

Table I. $B_{1,l}$ and $B_{2,l}$ Parameter Set (au)

Atom	l	$B_{1,l}$	$B_{2,l}$
C	0	−0.637 53	1.177 15
	1		−0.049 32
Si	0	−0.977 30	2.373 54
	1	−0.480 28	1.383 70
Ge	0	−1.050 96	2.519 64
	1	−0.615 45	1.745 07

Table II. Slater Atomic Orbital Exponents

Atom	Orbital	Exponents
C	2s	1.6083
	2p	1.5679
Si	3s	1.6344
	3p	1.4284
Ge	4s	2.0109
	4p	1.6951
H bonded to C	1s	1.2
H bonded to Si	1s	1.0
H bonded to Ge	1s	1.0

Table III. Geometries Used in Our Calculations

Molecules	Bond lengths, Å		Bond angles, deg	
CH_3CH_3	C–C	1.535	HCH	109.8
	C–H	1.093		
CH_3SiH_3	C–Si	1.867	HCH	107.7
	C–H	1.093	HSiH	108.2
	Si–H	1.485		
CH_3GeH_3	C–Ge	1.945	HCH	108.4
	C–H	1.083	HGeH	109.3
	Ge–H	1.529		
SiH_3SiH_3	Si–Si	2.320	HSiH	109.8
	Si–H	1.480		
SiH_3GeH_3[a]	Si–Ge	2.357	HSiH	108.2
	Si–H	1.485	HGeH	109.3
	Ge–H	1.529		
GeH_3GeH_3	Ge–Ge	2.410	HGeH	109.8
	Ge–H	1.527		

[a] See ref 15; for the other molecules, see ref 16.

Table IV. Valence Molecular Orbital Energies and Total Energies of Ethane and Methylsilane in Their Staggered Conformation (au)

Molecule	Pseudopotential calculations		All-electron Hartree–Fock calculations	
CH_3CH_3	$1e_g$	−0.496	$1e_g$	−0.5150[a]
	$3a_{1g}$	−0.524	$3a_{1g}$	−0.5361[a]
	$1e_u$	−0.615	$1e_u$	−0.6273[a]
	$2a_{2u}$	−0.839	$2a_{2u}$	−0.8588[a]
	$2a_{1g}$	−1.040	$2a_{1g}$	−1.040[a]
	Total valence energy −14.5104		Total energy −78.991 15[a]	
CH_3SiH_3	3e	−0.479	$7a_1$	−0.453 02[b]
	$7a_1$	−0.485	3e	−0.465 00[b]
	2e	−0.590	2e	−0.567 40[b]
	$6a_1$	−0.744	$6a_1$	−0.711 35[b]
	$5a_1$	−0.987	$5a_1$	−0.951 94[b]
	Total valence energy −12.6810		Total energy −330.227 68[b]	

[a] Minimal Slater basis set calculation, see ref 17. [b] Extended Gaussian basis set calculation, see ref 18.

are atomic nodeless orbitals obtained from the true Hartree-Fock orbitals. Once the pseudo-orbitals are determined according to our criterion (for more details see ref 6), a unique set of parameters ($B_{1,l}$, $B_{2,l}$) is obtained for each atom which is involved in our calculations. The values of these parameters are given in Table I.

For an l symmetry valence orbital, there are generally inner core orbitals of the same symmetry. In this case, it is noticed that the parameters $B_{1,l}$ have negative values whereas the parameters $B_{2,l}$ have positive values. That means that the pseudopotential is repulsive near the nucleus and attractive for moderately large r values according to the valence pseudo-orbital shape that looks like the true orbital in the atomic valence region and decreases monotonically in the core region.

The total valence energy E_{tot} of a molecule is given by the sum of the valence electronic energy E_{elec} obtained from the resolution of the eigenvalue equation associated with the valence pseudo-Hamiltonian $\mathcal{H}_{\mathrm{ps}}$, and of the coulombic repulsion energy between the atomic cores

$$E_{\mathrm{tot}} = E_{\mathrm{elec}} + \sum_{A<B} z_A z_B / R_{AB} \qquad (4)$$

where z_A and z_B are the net charges of the atomic cores A and B, respectively. R_{AB} is the distance between the two atoms A and B.

A classical Hartree-Fock calculation allows us to determine valence molecular orbitals and total valence energy for the system described by the pseudo-Hamiltonian $\mathcal{H}_{\mathrm{ps}}$; we use a minimal basis set of atomic Slater orbitals expanded in uncontracted Gaussian lobe functions at the rate of three spherical Gaussian functions for an s orbital and three spherical Gaussian functions per lobe for a p orbital. The details of this expansion have already been published.[5,11] Atomic Slater orbital exponents used in our calculations are listed in Table II. For all atoms excepting the H atom, these values are those optimized with free atoms by Clementi and Raimondi.[12] For a H atom bonded to C or Si, rounded-off exponent values have been chosen from previously optimized calculations on methane[13] and silane.[14] The same orbital exponent has been taken for H, bonded to Si or Ge.

In all our calculations, the geometry of the molecules is the experimental one; bond lengths and bond angles are gathered in Table III.

III. Valence Molecular Orbitals

All the calculations presented in this section have been carried out for the staggered conformation of the molecules.

All-electron Hartree-Fock calculations have been performed on ethane[17] and methylsilane.[18] Table IV compares our results with these calculations. A good agreement is observed particularly for ethane for which the all-electron calculation has been carried out with a valence basis set similar to ours. This agreement, which has been observed for several other molecules,[5-7] constitutes the proof of the adequacy of our pseudopotential method to give good valence molecular orbital levels.

It is known that the occupied valence molecular orbitals obtained with Hartree-Fock calculations are of importance because of Koopmans' theorem[19] which associates the various ionization potentials of the molecule with the energies of these orbitals. For this reason, the frontier orbital, i.e., the highest occupied orbital, is most particularly interesting. In the case of ethane, calculation and experimentation (photoelectron spectrum[20] and vacuum ultraviolet spectrum[21]) show that the frontier orbital is of the symmetry e_g; however, this orbital is very close to the uppermost orbital of symmetry a_{1g}. Sandorfy[21] points out that the order of these orbitals can easily be reversed and that this particular feature must play a fundamental part in the chemical properties of ethane and its derivatives. In the case of methylsilane, Liskow and Schaefer[18] have carried out all-electron calculations with various basis sets; in all cases, they obtain the same molecular orbital ordering as in ethane, except for the frontier orbital which is an orbital of

Table V. Valence Molecular Orbital Energies and Total Valence Energies (au)[a]

Molecule	CH_3CH_3		CH_3SiH_3		CH_3GeH_3		SiH_3SiH_3		SiH_3GeH_3		GeH_3GeH_3	
Orbital energies	e_g	−0.496	e	−0.479	a_1	−0.472	a_{1g}	−0.444	a_1	−0.447	a_{1g}	−0.442
	a_{1g}	−0.524	a_1	−0.485	e	−0.481	e_g	−0.489	e	−0.487	e_g	−0.488
	e_u	−0.615	e	−0.590	e	−0.588	e_u	−0.535	e	−0.533	e_u	−0.533
	a_{2u}	−0.839	a_1	−0.744	a_1	−0.749	a_{2u}	−0.736	a_1	−0.741	a_{2u}	−0.745
	a_{1g}	−1.040	a_1	−0.987	a_1	−0.987	a_{1g}	−0.851	a_1	−0.857	a_{1g}	−0.863
Total valence energy	−14.5104		−12.6810		−12.5524		−10.8861		−10.7616		−10.6310	

[a] All the molecules are in their staggered conformation.

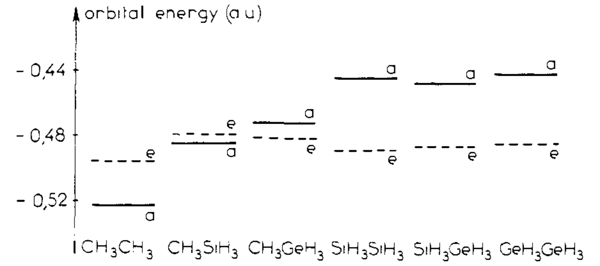

Figure 1. Relative position of the frontier orbitals from the results of Table V.

symmetry a_1, and they draw the attention of spectroscopists to this fact. Our pseudopotential calculation on methylsilane leads to a frontier orbital of symmetry e (see Table IV). We must, however, notice that pseudopotential and all-electron calculations give nearly degenerate a_1 and e orbitals; therefore, as in ethane, the inversion of these levels can be obtained very easily.

We have carried out calculations on the complete series XH_3YH_3 in order to obtain new information on the nature of the frontier orbital. Valence molecular orbital energies and symmetries are given in Table V. We notice a change in the symmetry of the frontier orbital from methylgermane onwards; Figure 1 gives the relative positions of this frontier orbital for all the molecules of the series. It may be noticed that the energy of the orbital of symmetry e remains almost unchanged from one molecule to the other; its value stays in a narrow range of about 0.4 eV. This is not true concerning the energy of the orbital of symmetry a_1; its value increases monotonically for the series CH_3XH_3 when we go from X = C to X = Ge; thus, this a_1 orbital shifts slightly above the degenerate e orbital. For the three other molecules of the series, however, the a_1 orbital is clearly above the e orbital and the difference between their energies is about 1 eV.

These results suggest that methylsilane and methylgermane should behave like ethane: the a_1 and e orbitals are very near and they can be easily reversed. On the contrary, this inversion will probably be unreasonable for the other molecules of the series.

In order to connect the previous results with the properties of the X-Y and X-H bonds, it is interesting to pursue a straightforward analysis of the Fock operator F in the basis set of the molecular orbitals localized on the X-Y and X-H bonds. These orbitals, denoted by ϕ_{XY} and ϕ_{XH}, are constructed with the sp^3 hybrid orbitals of the X and Y atoms, and the 1s orbital of H. In the cases of ethane and disilane for instance, we have obtained the following results: $\langle\phi_{CC}|F|\phi_{CC}\rangle = -0.74$ au and $\langle\phi_{SiSi}|F|\phi_{SiSi}\rangle = -0.58$ au, while $\langle\phi_{CH}|F|\phi_{CH}\rangle = -0.69$ au and $\langle\phi_{SiH}|F|\phi_{SiH}\rangle = -0.60$ au. It can be seen that the energy of the orbital localized on the X-X central bond increases more rapidly than the energy of the orbital localized on the X-H bond when we go from X = C to X = Si. These results are in good agreement with the evolution of experimental lengths and energies of the X-X and X-H bonds for X = C and then X = Si.

Table VI. Internal Rotation Barriers (kcal/mol)

Molecule	Pseudo-potential calculation	Exptl value	All-electron calculation value
CH_3CH_3	3.19	2.928 ± 0.025[a]	3.3[g]
CH_3SiH_3	1.40	1.665 ± 0.050[b]	1.437[h] 1.44[i]
CH_3GeH_3	1.22	1.239 ± 0.025[c]	
SiH_3SiH_3	1.05	~1[d] ~1.1[e]	
SiH_3GeH_3	1.02	~1.1[e]	
GeH_3GeH_3	1.09	1.490 ± 0.200[f]	

[a] S. Weiss and G. E. Leroi, *J. Chem. Phys.*, 48, 962 (1968). [b] D. R. Herschbach, *ibid.*, 31, 91 (1959). [c] V. W. Laurie, *ibid.*, 30, 1210 (1959). [d] H. S. Gutowsky and E. O. Stejskal, *ibid.*, 22, 939 (1954). [e] A. P. Cox and R. Varma, *ibid.*, 46, 2007 (1967). [f] J. E. Griffiths and G. E. Walrafen, *ibid.*, 40, 321 (1964). [g] R. M. Pitzer and W. N. Lipscomb, *ibid.*, 39, 1995 (1963) (minimal Slater basis set calculation). [h] C. S. Ewig, W. E. Palke, and B. Kirtman, *ibid.*, 60, 2749 (1974) (minimal Slater basis set calculation). [i] A. Veillard, *Chem. Phys. Lett.*, 3, 128 (1969) (extended Gaussian basis set calculation).

IV. Rotation Barriers

In all our rotation barrier calculations, bond angles and bond lengths are the same in the two staggered and eclipsed molecular conformations. Our calculations predict the staggered conformation to be more stable for all the molecules in the series. The calculated barriers are given in Table VI where they are compared with experimental values. All the calculated values are in good agreement with the experimental data; this is all the more satisfactory as the order of magnitude of the studied barriers is small.

In the series CH_3XH_3, the calculated barrier decreases regularly from X = C to X = Ge, in agreement with experimental observations. Furthermore one can correlate the barrier height to the C-X bond length; experiment leads to a linear correlation for the complete series X = C, Si, Ge, Sn.[15] Figure 2 shows that our calculations account for the same correlation; the barrier height decreases linearly with the C-X bond length. For this CH_3XH_3 series, the experimental values are known with accuracy. The deviation between the calculated and the experimental value is at the highest 0.27 kcal/mol. These differences do not exceed those that can be obtained with all-electron Hartree-Fock calculations carried out on the two first molecules of the series (cf. Table VI). Particularly for the methylsilane molecule, for which we obtain the furthest value from the experimental one, the all-electron Hartree-Fock calculations do not give better results than ours whether they have been done with minimal[22] or very extended[23] basis sets. We must also note the drawback of all-electron calculations used to obtain small barriers for molecules containing heavy atoms: the absolute value of the total energy is very high and the calculation of the barrier obtained by the difference of the two total energies of the conformers needs more and more accuracy in the integral evaluation. This problem has been emphasized in the calculation of the rotation barrier of

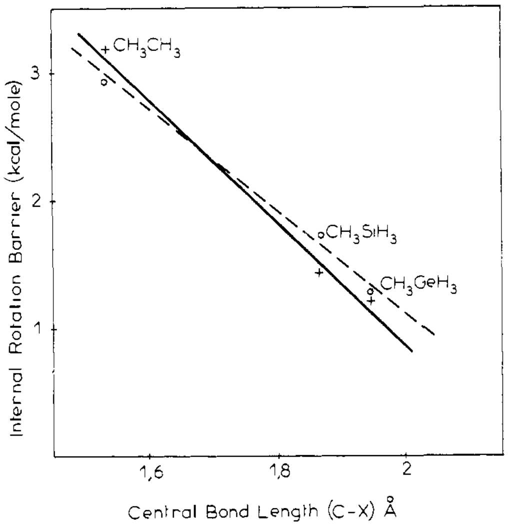

Figure 2. Variation of the barrier height as a function of the C-X bond length: (+) calculations performed with the pseudopotential; (O) experiment (see references in Table VI).

methylsilane by Veillard[23] and Ewig et al.[22] With the use of pseudopotentials, this drawback considerably disappears; indeed, these calculations provide the total valence energy of the molecule which is a small part of the total energy. In the series XH_3YH_3 studied here, we remark that this valence energy is always of the same order of magnitude whatever the atomic number of the atoms X and Y may be (cf. Table V). This value has to be compared with the total energy value of about 4000 au that would have been obtained in an all-electron calculation of the digermane molecule.

The calculated barrier height of about 1 kcal/mol is almost the same for the three other molecules SiH_3SiH_3, SiH_3GeH_3, and GeH_3GeH_3. The experimental values are here less accurate than those obtained for the series CH_3XH_3: the barrier is known with an accuracy of ±0.2 kcal/mol for digermane and is only estimated for disilane and silylgermane. We note that our calculations corroborate the values of the barrier heights of these two molecules. Inasmuch as our results in the series CH_3XH_3 are of good quality, we think that our calculations of the barriers in the molecules SiH_3SiH_3, SiH_3GeH_3, and GeH_3GeH_3 contribute useful information to help the present insufficiency of experiment.

We have carried out our calculations in the simplest conditions: minimal Slater basis set without exponent optimization and rigid rotor approximation. We think that these working conditions are justified by the conclusions that had been reached in all-electron calculations previously made on ethane. Most of the significant results have been gathered in Tables VII and VIII, and allow us to conclude that: (i) the barrier height is obtained correctly whatever the choice and the extent of the basis set may be (see ref 25 and Table VII); (ii) the optimization of the geometries for each staggered or eclipsed conformation only slightly improves the results (cf. Table VIII). These conclusions, available for the ethane molecule, cannot be extended to any molecule (H_2O_2 for example) but they can be applied to ethane-like molecules. Particularly for such tetracoordinate compounds it does not seem necessary to extend the atomic s and p basis set to d orbitals for Si and Ge atoms. Table IX gathers the various all-electron calculations performed on the methylsilane molecule and shows that this is a reasonable approximation.

Table VII. Influence of the Basis Set on the Ethane Barrier in ab Initio All-Electron Calculations within the Rigid Rotor Approximation

Basis set	Barrier kcal/mol
16 Slater orbitals	3.3[a]
34 Gaussian functions	2.88[b]
52 Gaussian functions	3.45[b]
72 Gaussian functions	3.31[c]
86 Gaussian functions	3.6[d]
110 Gaussian lobes	2.52[e]
122 Gaussian functions	3.65[f]

[a] R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, 39, 1995 (1963). [b] L. Pedersen and K. Morokuma, *ibid.*, 46, 3941 (1967). [c] W. E. Palke, *Chem. Phys. Lett.*, 15, 244 (1972). [d] E. Clementi and D. R. Davis, *J. Chem. Phys.*, 45, 2593 (1966). [e] W. H. Fink and L. C. Allen, *ibid.*, 46, 2261 (1967). [f] A. Veillard, *Chem. Phys. Lett.*, 3, 128 (1969).

Table VIII. Influence of the Geometry Optimization on the Ethan Barrier in ab Initio All-Electron Calculations

	Barrier, kcal/mol	
Basis set	Fixed geometry	Optimized geometry
Minimal Slater basis set	3.5[a]	3.3[b]
Extended Gaussian basis set	3.65[c]	3.07[c]
Bond orbital	2.6[d]	3.1[e]

[a] R. M. Pitzer, *J. Chem. Phys.*, 47, 965 (1967). [b] R. M. Stevens, *ibid.*, 52, 1397 (1970). [c] A. Veillard, *Chem. Phys. Lett.*, 3, 128 (1969). [d] O. J. Sovers, C. W. Kern, R . M. Pitzer, and M. Karplus, *J. Chem. Phys.*, 49, 2592 (1968). [e] R. M. Stevens and M. Karplus, *J. Am. Chem. Soc.*, 94, 5140 (1972).

Table IX. Influence of d Atomic Orbitals on the Methylsilane Barrier in ab Initio All-Electron Calculations

Basis set	Barrier, kcal/mol
Extended Gaussian basis set C(s,p,d) Si(s,p,d) H(s,p)	1.440[a]
Minimal Slater basis set C(s,p) Si(s,p) H(s)	1.437[b]
Minimal Slater basis set C(s,p) Si(s,p,d) H(s)	1.567[b]

[a] A. Veillard, *Chem. Phys. Lett.*, 3, 128 (1969). [b] C. S. Ewig, W. E. Palke, and B. Kirtman, *J. Chem. Phys.*, 60, 2749 (1974).

As the minimal Slater basis set is expanded in Gaussian lobe functions, one can question the ability of this basis set for calculating small rotation barriers of a few kilocalories per mole. Indeed the lobe representations of p orbitals differ a little from pure spherical harmonics, and the energy of a molecule like ethane depends on the coordinate system that is used. In order to verify that this point is without a marked effect on the calculated rotation barrier, three calculations of the ethane molecule have been performed with the C-C bond in the directions [1, 0, 0], [1, 1, 0], and [1, 1, 1]. The calculated rotation barriers were found to differ less than 0.02 kcal/mol and the valence molecular orbital energies were in agreement better than 0.003 eV.

Under these working conditions, our results show that the core electrons do not seem to play an important part in the existence of the rotation barrier. This result agrees well with the study of Magnasco and Musso who have frozen the core electrons in their analysis of the rotation barrier of ethane.[26] This conclusion should lead to an interesting simplification in the theoretical analysis of the rotation barrier. Indeed it is well known that the rotation barrier is correctly reproduced in an all-electron calculation with a simple Slater determinant, and that the correlation effects add only a small correction.[27] Various analyses have been provided at this level.[28] The simplest one, worked out by Sovers et al.,[29] has considerably clarified the situation by showing the prominent part played by the antisymmetrization of the wave function in the existence of the rotation barrier. This result which is invariant with regard to the used basis set and the geometry optimization of the molecule[30] has also been obtained for the methanol molecule.[31] It is necessary however to carry out more detailed analyses of the origin of the rotation barrier in terms of local contributions. Magnasco et al.[32] and Christiansen et al.[33] have given the various contributions due to the orthogonalization or nonorthogonalization of the localized molecular orbitals on the CH bonds and to the presence or absence of the exchange terms. Daudey et al.[10] and Musso et al.[26] have proposed a partition of the total energy of the molecules in one-, two-, and three-body terms. In view of our very satisfactory results, the previous analyses should be reexamined with pseudopotential techniques that allow to separate explicitly the core and valence terms and to treat molecules containing any light or heavy atom in the periodic table.

V. Conclusion

The pseudopotential method has been used to determine, for the series XH_3YH_3 (X, Y = C, Si, Ge): (i) the nature of the frontier orbital and (ii) the height of the rotation barrier. We have obtained good agreement between our results and other all-electron ab initio calculations in the cases of ethane and methylsilane for which such calculations have been done. In other respects, the agreement between our calculations and the experimental results, when the latter are known, is good. Our calculations provide new information on the nature of the frontier orbital that can be correlated to spectroscopic properties through Koopmans' theorem. This work is also the first theoretical calculation of the rotation barriers in a full "ethane-like" series of molecules. When the experimental values of these barrier heights are known, the agreement is very satisfactory when they are not, our calculations give a reasonable estimate of the barrier height value.

The results presented in this paper also confirm the efficiency of pseudopotential methods. The appearance of these methods in quantum chemistry marks a critical step toward the possibility of studying systematically, by entirely theoretical methods, the various valence properties of molecules.

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