

All-Electron *ab Initio* Calculations on Tetramethyltin

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Received: January 3, 1994; In Final Form: March 31, 1994*

All-electron *ab initio* (nonrelativistic) calculations on tetramethyltin, $\text{Sn}(\text{CH}_3)_4$, have been carried out at the SCF, MP2, and MP4 levels of theory. At the MP4 correlation level the Sn–C bond distance is predicted to be 2.144 Å, in excellent agreement with experiment. Our calculations indicate that useful results can be obtained even at the SCF level, due to a possible cancellation of relativistic and correlation effects, provided that a good quality basis set for the metal is employed.

Introduction

The gas-phase geometrical structure of the tetramethyl derivatives of the heavy elements of the 14th (IVA) column of the periodic table has long been established: the electron diffraction data on $\text{M}(\text{CH}_3)_4$, $\text{M} = \text{Si},^1 \text{Ge},^2 \text{Sn},^3$ and $\text{Pb},^4$ unequivocally show that these molecules have a practically perfect tetrahedral distribution of the methyl groups. Hartree–Fock *ab initio* full electron calculations of Almlof and Faegri⁵ with first-order relativistic corrections concerning mass–velocity and Darwin terms on the $\text{M}(\text{CH}_3)_4$ systems show fair agreement with experimental results. In particular, it appears that the relativistic corrections are responsible for a shortening by 0.018 and 0.045 Å of the equilibrium M–C bond distance of $\text{Sn}(\text{CH}_3)_4$ and $\text{Pb}(\text{CH}_3)_4$, respectively. Nevertheless, in the Almlof–Faegri (AF) paper⁵ there is no hint of the role of correlation effects vs relativistic effects.

Table 1 presents ratios r of the radial expectation values $\langle R \rangle$ of the valence $n\text{p}_{3/2}$ orbitals to the $n\text{p}_{1/2}$ valence orbitals, as well as ratios of the nonrelativistic to the relativistic radii of the maximum radial density of the IVA(14) column of the periodic table from Dirac–Fock atom calculations.⁶ Table 1 shows that relativistic effects do not practically influence the extension of C and Si systems; they affect mildly Ge and Sn but affect severely the Pb atom. Focusing on Sn alone, the numbers of Table 1 indicate a $\sim 4\%$ contraction of the radial distribution function of either the 5s or $5\text{p}_{1/2}$ distributions due to relativity. The $5\text{p}_{3/2}$ distribution remains essentially unaffected due to the higher angular momentum of this function. Assuming an equal participation of the valence orbitals in bonding, the weighted average of 5s, $5\text{p}_{1/2}$, and $5\text{p}_{3/2}$ predicts a $\sim 2\%$ size contraction of the Sn atom due to relativistic effects as contrasted to a $\sim 14\%$ for the Pb atom.

Hypothesizing that the bearing of relativity on chemical effects of the Sn atom is approximately of the same order as the size effects, i.e., $\sim 2\%$, it seems that meaningful results for a system as heavy as Sn can be extracted without considering the complications of relativistic methodologies. In addition, $\text{Sn}(\text{CH}_3)_4$ is a closed (singlet) system; therefore, spin–orbit effects can be considered as practically quenched.

With the purpose of understanding the effects of correlation alone, we performed all-electron *ab initio* calculations at the HF (SCF), MP2, and MP4 levels on the tetramethyltin, $\text{Sn}(\text{CH}_3)_4$, molecular system. The available accurate experimental results

TABLE 1: Ratio, $r = \langle R \rangle_{n\text{p}_{3/2}} / \langle R \rangle_{n\text{p}_{1/2}}$, of the Radial Expectation Values (R) of the Valence $n\text{p}_{3/2}$ and $n\text{p}_{1/2}$ Orbitals and Ratios $r_{\text{max}}(ns)$, $r_{\text{max}}(n\text{p}_{3/2})$, and $r_{\text{max}}(n\text{p}_{1/2})$ of the Nonrelativistic to the Relativistic Radii of Maximum Radial Density of the 14-Elements $X(n)$, Where n Is the Principal Quantum Numbers^a

$X(n)$	r	$r_{\text{max}}(ns)$	$r_{\text{max}}(n\text{p}_{3/2})$	$r_{\text{max}}(n\text{p}_{1/2})$
C(2)	1.000 53	1.000 88	0.999 95	1.000 49
Si(3)	1.002 73	1.002 35	0.998 52	1.001 18
Ge(4)	1.016 12	1.016 52	0.998 84	1.015 09
Sn(5)	1.040 84	1.042 58	0.999 40	1.038 57
Pb(6)	1.143 90	1.136 24	0.998 53	1.134 66

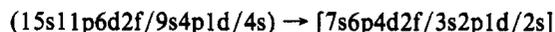
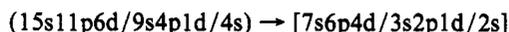
^a Relativistic Dirac–Fock values from ref 6.

on this molecule allow for a critical comparison of theoretical vs experimental numbers.

Basis Sets: Methodology

For the Sn atom the $15\text{s}11\text{p}6\text{d}$ basis set of Strömberg et al. was employed,⁷ contracted to $7\text{s}6\text{p}4\text{d}$ according to Raffennetti.⁸ The calculated atomic energy of the ground ^3P state of Sn is -6022.2108 hartrees (reproducing exactly the Strömberg result), 0.721 hartree higher than the corresponding Hartree–Fock limit.⁹ Despite the large absolute energy difference between the two energy values, the percentage error of our basis is $\sim 0.01\%$ with respect to the HF limit, typical of a double-zeta quality basis. This was augmented by a set of two seven-component f functions with exponents⁵ 0.5 and 1.2.

The basis set for carbon is the $9\text{s}4\text{p}$ of Duijneveldt¹⁰ contracted to $3\text{s}2\text{p}$ according to Raffennetti⁸ and augmented by a d set of polarization functions ($a_d = 0.55$). The hydrogen basis is Huzinaga's¹¹ 4s contracted to 2s as recommended by Raffennetti.⁸ In order to investigate the effect of polarization functions on the hydrogens, exploratory SCF calculations were performed with an additional set of p functions ($a_p = 0.8$). Collectively, our basis sets run as follows



the larger basis set comprising of 260 primitives and 139 contracted Cartesian Gaussian functions. Although the role of H-polarization functions is not negligible, it was found (*vide infra*) that the overall influence of f functions was more significant.

* Abstract published in *Advance ACS Abstracts*, June 1, 1994.

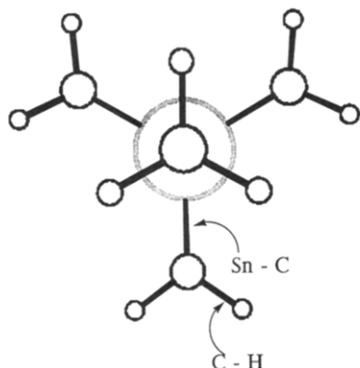


Figure 1. Conformational model considered in the present investigation. Hydrogen atoms are staggered with respect to the methyl groups.

Valence correlation effects (42 valence electrons) were taken into account at the MP2 and MP4 perturbation levels. Notice that for the Sn atom 14 electrons, namely, $4d^{10}5s^25p^2$, were taken into consideration as valence electrons. Full geometry optimizations were done using analytical gradient methods under T_d symmetry constraints at the SCF and MP2 levels of theory. In addition, a point by point geometry optimization was performed on the Sn-C bond distance at the MP4 level, keeping the rest of the geometrical parameters frozen at the MP2 optimal geometry. Finally, force constants and frequencies were calculated by full normal-coordinate analysis via analytical first and second derivatives at the SCF level and in two different basis sets. Moreover, MP2 and MP4 Sn-C force constants were determined by parabolic fitting of three energy values bracketing the minimum.

In all our calculations the $\text{Sn}(\text{CH}_3)_4$ model that has been employed is that of the hydrogens being staggered with respect to the other three methyl carbons (Figure 1). The experimental³ indications are that the methyl groups rotate rather freely around the Sn-C bonds, and in essence, the relative orientations of these groups do not seem to influence the main geometrical features of the organotin system.

All our computations were performed with the GAUSSIAN 92 set of codes¹² using the CONVEX-3800 computer supported by the NCSR DEMOKRITOS Super Computer Center. Exploratory calculations were done with the GAMESS set of codes¹³ using the SUN SPARC station-10 of the Physical Chemistry Laboratory.

Results and Discussion

To the best of our knowledge, the present study is the first that allows for correlation effects on the $\text{Sn}(\text{CH}_3)_4$ molecule. As was already mentioned, the calculations of AF⁵ are at the SCF level corrected to first order for relativity (*vide supra*), while geometrical parameters published by Pople and co-workers¹⁴ on this system are at the SCF(STO-3G) level. Pseudopotential calculations have been reported,^{15,16} though, with the purpose of obtaining the photoelectron spectrum of the tetramethyltin molecule. No geometries have been reported in these calculations.

Table 2 condenses all our calculated results along with the most recent experimental findings³ in the gas phase. For comparison, the theoretical results of AF⁵ are also included. First, we observe that our SCF(+p) energy is practically the same as the SCF energy reported by AF; the rather small difference of ~ 0.01 Å of the $r_{\text{Sn-C}}$ bond distance at this level is probably due to the unoptimized values of the $r_{\text{C-H}}$ and $\angle\text{HCSn}$ of these researchers. Notice also that although the energy lowering due to polarization p functions on the H atoms is much larger than the energy lowering due to the f functions on Sn, SCF(+p) *vs* SCF(+f) in Table 2, the effect of the latter on the Sn-C bond distance is much more pronounced. With the assumption that the f functions are also more significant at the MP2 and MP4 level of computation, the p functions were not considered in more

detail. At all levels of calculation C-H bond distances and the $\angle\text{HCSn}$ angle are in good agreement with the experimental results;³ relativistic effects do not influence directly the geometry of the methyl groups.

Taking into account the size of the $\text{Sn}(\text{CH}_3)_4$ system and the fact that our Sn basis set is significantly distant from the HF limit, the Sn-C bond length at the SCF level could be considered in modest agreement with the experimental results. From Table 2 we observe that, by increasing the basis set size, the Sn-C bond length decreases as expected. Assuming that basis set effects are additive, going from SCF to SCF(+f) and SCF(+f+p) the Sn-C bond distance should end up at $r_{\text{Sn-C}} \sim 2.158$ Å. This number is longer than the r_{exp} by ~ 0.014 Å only. By further increasing the basis set size of Sn toward the HF limit, the Sn-C bond distance would certainly become shorter. This, in turn, would possibly make the agreement between experimental and theoretical $r_{\text{Sn-C}}$ values quite good. It is pertinent to emphasize at this point that our SCF results on the $r_{\text{Sn-C}}$ length are just the opposite from the accumulated common experience; i.e., SCF bond lengths obtained through reasonable basis sets are always shorter than corresponding (accurate) experimental or high quality theoretical results.

The above thoughts can be rationalized on the basis of relativistic effects on the Sn atom. We can write quite generally that

$$r_{\text{exp}} \approx r_{\text{HF}} + \delta r_{\text{corr}} + \delta r_{\text{rel}}$$

where r_{HF} , δr_{corr} , and δr_{rel} are HF limit bond length, correction of the r_{HF} with respect to exact correlation effects, and correction due to relativistic effects, respectively, assuming independence of the δr_{corr} and δr_{rel} corrections. Generally speaking, δr_{corr} and δr_{rel} have opposite signs, namely, $\delta r_{\text{corr}} > 0$, $\delta r_{\text{rel}} < 0$. In the present case of the Sn system, our previous estimate of a $\sim 2\%$ relativistic shrinkage cancels out a typical δr increase of the same size due to correlation. Therefore, $r_{\text{exp}} \approx r_{\text{HF}}$.

From Table 2 we can see that the effect of f functions on the Sn atom is markedly pronounced at the MP2(+f) level of calculation. The very large correlation drop between MP2 and MP2(+f), ~ 200 mhartrees, comes from the metal atom alone and is due to angular correlation of the five 4d electron pairs. The pure valence ($5s^25p^2$) MP2 correlation of Sn is ~ 15 mhartrees, contrasted to the ~ 17 mhartrees of the MP2(+f) number. At this point, it is interesting to report that the four-electron Sn CISD (SCF+1+2) correlation with and without f functions is ~ 22 and ~ 25 mhartrees, respectively, as computed by the MELD set of codes.¹⁷

We turn now to the MP n geometrical properties, i.e., MP2, MP2(+f), and MP4(+f) (Table 2). Concerning the C-H bond length, our final result at the MP4(+f) level is in excellent agreement with the experimental value.³ As far as the Sn-C bond is concerned, at all levels of MP correlation we observe a bond length shortening as compared to the SCF results, with the final MP4(+f) value being in perfect agreement with the experimental value.³ Some comments are in order here: (a) The MP4(+f) Sn-C length was obtained with the rest of the geometrical parameters frozen at the MP2(+f) optimized values. (b) There is an oscillatory behavior of the MP(+f) values with respect to the SCF(+f) one, converging to the, apparently correct, experimental result. (c) Although the agreement between theoretical vs experimental findings seems in perfect agreement, the Sn-C bond potential is extremely "soft" around the equilibrium at all computational levels, the SCF included. This can be seen clearly from Figure 2, where the MP2(+f) Sn-C potential energy curve is presented, showing that within a $\Delta r_{\text{Sn-C}}$ range of ~ 0.05 Å around the formal minimum the energy changes by only ~ 1 mhartree. Recent X-ray crystallographic results¹⁸ on the $\text{Sn}(\text{CH}_3)_4$ molecule at low temperature (158 K) corroborate our conclusions on the softness of the Sn-C bond: the crystal structure

TABLE 2: Absolute Energies E (hartrees), Bond Distances R_e (Å), Angles (degrees), Net Mulliken Charges q_{Sn} , Mean Dissociation Energies $D_{e,\text{Sn-C}}$ (kcal mol⁻¹), and Force Constants $k_{\text{Sn-C}}$ (mdyn Å⁻¹) of Tetramethyltin, Sn(CH₃)₄, in the Ground [¹A₁] State in Different Methodologies

method	E	$r_{\text{Sn-C}}$	$r_{\text{C-H}}$	$\angle\text{HCSn}$	q_{Sn}	$D_{e,\text{Sn-C}}$	$k_{\text{Sn-C}}$
SCF	-6180.6838	2.168	1.097	111.6	+1.91	43.2	2.51
SCF(+f) ^a	-6180.6918	2.161	1.096	111.6	+1.80	44.3	2.62
SCF(+p) ^b	-6180.7243	2.165	1.093	111.2	+1.88	43.1	
MP2 ^c	-6181.3621	2.159	1.100	111.6		64.4	
MP2(+f) ^{a,c}	-6181.5628	2.135	1.108	111.6		66.3	2.66 ^e
MP4(+f) ^{a,c}	-6181.6384	2.144	1.108 ^d	111.6 ^d		64.5	2.67 ^e
experimental		2.144 ± 0.003 ^f	1.117 ± 0.009 ^f	112.0 ± 1.6 ^f		52.0 ^g	2.32 ^h
AF ⁱ							
SCF	-6180.73	2.174	1.094 ^j	109.47 ^j			
SCF + (rel) ^k	-6323.0	2.156	1.094 ^j	109.47 ^j			2.54

^a A set of two seven-component *f* "polarization" functions were added to the basis of the Sn atom only, ref 5. ^b *p* functions with a 0.8 exponent were added to the basis of the H atoms only. ^c MP n , n th-order Møller–Plesset perturbation, ref 14. ^d MP2 values. ^e Determined by parabolic fitting. ^f Reference 3. ^g Reference 19. ^h Reference 22. ⁱ Almlf–Faegri, ref 5. ^j Nonoptimized ("standard") values. ^k First-order relativistic correction with respect to the SCF wave function.

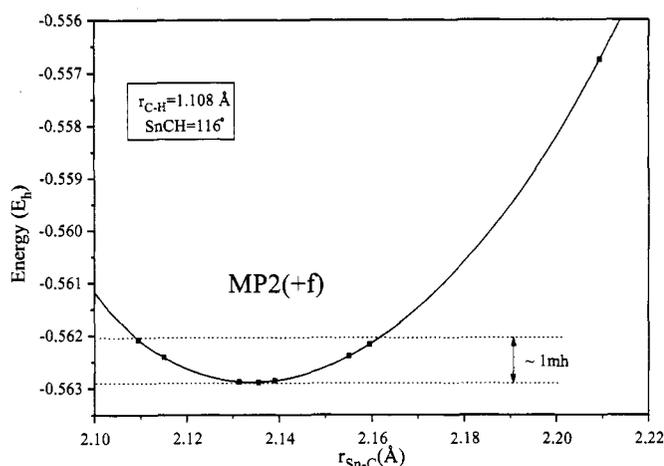


Figure 2. Energy dependence of Sn(CH₃)₄ molecule as a function of Sn–C bond distance at the MP2(+f) level of theory. Notice that the energy has been shifted by 6181 hartrees.

reveals that three of the Sn–C bonds are equivalent with a bond length of 2.146 Å, with the fourth Sn–C bond compressed significantly by ~0.04 Å due to packing forces. (d) Finally, we should not forget that a series of approximations are involved in the present calculations, the most serious of all being the quality of the Sn atom basis set.

From Table 2 it is seen that the Sn(CH₃)₄ molecule is bound with respect to its ground-state fragments, Sn(³P) + 4CH₃(²A₂''), by 177.2 kcal mol⁻¹ (SCF(+f)) and 258.0 kcal mol⁻¹ (MP4(+f)), corresponding to mean bond dissociation energies, $D_{\text{Sn-C}}$, of 44.3 and 64.5 kcal mol⁻¹, respectively. Both these numbers are at variance with the experimental mean dissociation energy¹⁹ of 52.0 kcal mol⁻¹. In an attempt to explore a possible source of error, a basis set superposition correction (BSSC) was tried by using the counterpoise method. Notwithstanding the pitfalls of this method,^{20,21} a BSSC of ~16 kcal mol⁻¹ was computed at the SCF(+f) level with the Sn atom in its ³P ground state, thus changing the previous computed SCF(+f) and MP4(+f) $D_{\text{Sn-C}}$'s to ~40 and ~60 kcal mol⁻¹, respectively. Expecting the BSSC to be larger at the MP4 than the SCF level of theory, the corrected MP4 binding energy should be less than 60 kcal mol⁻¹, thus rendering the theoretical result in better agreement with experiment.

Our SCF calculated force constant, $k_{\text{Sn-C}}$, is in agreement with the SCF relativistic result of AF⁵ (Table 2). Improving the quality of the calculation by either increasing the basis set size on the metal or introducing correlation at MP2(+f) and/or MP4(+f) level makes the $k_{\text{Sn-C}}$ larger and the agreement with the experimental value²² worse. The percentage error with respect to the experimental $k_{\text{Sn-C}}$ on going from SCF to SCF(+f) to MP2(+f) to MP4(+f) is ~8%, ~13%, ~15% and ~15%,

TABLE 3: Harmonic Frequencies (cm⁻¹) Calculated at the SCF and SCF(+f) Levels of Theory (See Text) vs Experimental Values

sym	description	SCF	SCF(+f)	exp ^a
A ₁	skeletal symmetrical stretching	537.4	543.7	508
A ₁	CH ₃ symmetrical deformation	1371.2	1370.2	1205
A ₁	CH ₃ symmetrical stretching	3130.5	3130.6	2915
E	skeletal distortion	133.6	131.1	157
E	CH ₃ distortion	825.2	819.1	768
E	CH ₃ rocking	1564.3	1563.7	1445
E	CH ₃ deformation	3226.1	3225.4	2987
T ₁	CH ₃ stretching (inactive)	3225.9	3225.2	2987
T ₁	CH ₃ deformation (inactive)	1562.1	1561.6	1445
T ₁	CH ₃ rocking (inactive)	707.0	699.6	768
T ₂	CH ₃ stretching	3226.8	3225.4	2987
T ₂	CH ₃ stretching	3128.8	3128.9	2915
T ₂	CH ₃ deformation	1573.7	1573.4	1445
T ₂	CH ₃ deformation	1356.4	1355.3	1194
T ₂	CH ₃ rocking	829.6	820.0	768
T ₂	skeletal stretching	556.1	560.0	530
T ₂	skeletal distortion	160.5	159.0	157

^a Experimental values taken from ref 23.

respectively. We again observe the major role of the *f* functions on the tin atom. Notice, however, that the MP2 and MP4 force constants have been obtained through a three-point parabolic fitting process.

Table 3 reports SCF and SCF(+f) normal-mode frequencies of the Sn(CH₃)₄ molecule, obtained by the analytical evaluation of first and second derivatives. The mean percentage error with respect to the experimental values²³ is about 9%, with the computed values being in all cases but two, larger than the experimental ones. From the values listed we observe that the *f* functions reinforce skeletal stretching while not having any practical influence on skeletal distortions.

Net Mulliken charges calculated at the SCF level and presented in Table 2 indicate that there is a considerable charge transfer from the metal to the (four) methyl groups, thus rendering the Sn–C bond of significant ionic character. This can be "intuitively" interpreted on the basis of electronegativity difference between the tin and the carbon atoms, $\Delta\chi^{\text{P}} \approx 0.8$ in the Pauling scale. The presence of *p* functions on the hydrogens and the *f* functions on the metal do not cause any serious changes of the charge distributions.

Concluding Remarks

Our results clearly show that useful numbers can be extracted by *ab initio* nonrelativistic calculations for as heavy an element as tin. At the MP4(+f) level of theory, calculated geometrical parameters are in excellent agreement with experiment, but certainly this is due to some cancellation of errors. At the same level of theory force constants and mean dissociation energies are

overestimated by ~10–15% due to rather low quality basis set of the metal. Relativity does not interfere significantly in the force constant as is evidenced from the AF⁵ calculations.

Our calculations further show that very useful results can be obtained at the SCF level, provided that the tin atom is described by a high quality basis set. This is rather caused as was previously discussed by the cancellation between relativistic and correlation effects.

Acknowledgment. Computing resources that made this work possible were generously provided by the Super Computer Center of the NCSR DEMOKRITOS. We thank Mr. A. Kalemios for his general help in the early stages of the present study. A.M. is an adjunct member of the Physical Chemistry Institute of NCSR DEMOKRITOS.

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