Table VI. *Ab Initio* Electric-Field Gradients and Molecular Quadrupole Moments, in Atomic Units, for KrF_2. The Kr–F Bond Distances are in Bohr Radii. SCF, TCSCF, and 993 Refer to the Calculations Involving 1, 2, and 993 Configurations

R	Quadrupole moment			Field gradient at Kr			Field gradient at F		
(Kr–F)	SCF	TCSCF	993	SCF	TCSCF	993	SCF	TCSCF	993
3.00	−12.21	−12.10	−11.87	9.217	8.658	8.134	1.055	1.085	1.060
3.25		−12.67	−12.39		8.401	7.934		1.363	1.304
3.50	−13.66	−12.84	−12.70	9.431	7.275	7.243	1.515	1.713	1.570
3.75		−12.28	−12.76		4.959	6.040		2.132	1.841
4.50		−10.01	−11.08		0.345	1.595		2.725	2.550
5.00		−9.72	−10.14		0.074	0.461		2.794	2.743
5.50		−9.62	−9.78		0.046	0.167		2.822	2.806
6.00		−9.58	−9.64		0.043	0.084		2.835	2.828
7.00		−9.54	−9.55		0.030	0.035		2.844	2.841
10.00		−9.52	−9.52		0.005	0.005		2.846	2.844

(2) A maximum exists in the linear symmetric KrF_2 potential curve, which results from an avoided crossing of an attractive ionic curve and a repulsive covalent curve. (3) The single configuration model fails to give a stable KrF_2 molecule but does give fairly good approximations to such molecular properties as electric quadrupole moment and electric-field gradient at the nuclei. (4) Two-configuration SCF and valence excited CI calculations give repulsive potential curves with a point of inflection. However, they also give reasonably good approximations for quadrupole moment and field gradient. Finally (5) the details of binding in KrF_2 depend on complicated electron-correlation effects which must be treated with sophisticated forms of wave functions. These effects are not included in the relatively simple SCF, TCSCF, or valence-shell configuration interaction models.

Acknowedgments. We thank Dr. N. Bartlett, Dr. A. D. McLean, and Dr. R. K. Nesbet for helpful discussions.

Sign of the Dipole Moment and Other Properties of Methylsilane

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Abstract: Nonempirical electronic structure calculations have been carried out on CH_3SiH_3 in its staggered form. A flexible basis set of contracted Gaussian functions was used. The present self-consistent-field calculations predict the electric dipole moment to be 0.58 D, $+$C Si$-$. This result is in good agreement with the experimental magnitude, 0.73 D, but disagrees with simple electronegativity arguments concerning the polarity of carbon–silicon bonds. However, Shoemaker and Flygare have recently argued on the basis of molecular Zeeman experiments that the sign of the dipole moment should be $+$C Si$-$. The predicted sign of the molecular quadrupole moment agrees with experiment, but the quantitative agreement in magnitude is poor. The *ab initio* sign of the dipole moment is not consistent with atomic charges obtained from a Mulliken population analysis of the wave function. The electronic structure of CH_3SiH_3 is discussed and several other molecular properties are reported.

Methylsilane is one of the simplest stable molecules containing a carbon–silicon bond. The absolute value of the dipole moment of CH_3SiH_3 has been known for some time to be 0.73 D.[1–3] Since carbon is usually considered to be more electronegative than silicon (2.5 for C as opposed to 1.8 for Si on Pauling's scale[4]), it might appear reasonable to assume that the electric dipole moment of methylsilane points toward the carbon, that is, $-$C Si$+$. However, recent molecular Zeeman effect measurements by Shoemaker and Flygare[5] have challenged this assumption. If the dipole moment is $-$C Si$+$, Shoemaker and Flygare find the molecular quadrupole moment along the C–Si axis to be $+(11.74 \pm 0.46) \times 10^{-26}$ esu cm^2. However, if the dipole is oriented $+$C Si$-$, the quadrupole moment is $-(6.31 \pm 0.46) \times 10^{-26}$ esu cm^2. Citing several arguments, Shoemaker and Flygare conclude that $-(6.31 \pm 0.46)$ is the correct value of the quadrupole moment and hence that the dipole moment of CH_3SiH_3 points toward silicon, *i.e.*, $+$C Si$-$. Shoemaker and Flygare close their communication[5] with "the large difference between the two choices (of the quadrupole moment) should make an *ab initio* calculation useful in the differentiation."

The only previous *ab initio* calculations on CH_3SiH_3 of which we are aware are those of Veillard.[6] Veil-

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Table I. Assumed Cartesian Coordinates, in Bohr Radii, of the Atoms in Methylsilane[a]

Atom	x	y	z
H_1	−1.69164	0.97669	4.24476
H_2	1.69164	0.97669	4.24476
H_3	0.0	−1.95534	4.24476
C	0.0	0.0	3.53379
Si	0.0	0.0	0.0
H_4	0.0	2.64588	−0.96302
H_5	2.29140	−1.32294	−0.96302
H_6	−2.29140	−1.32294	−0.96302

[a] The geometry is described in terms of bond angles and bond distances in the text.

lard's interest was in the barrier to internal rotation, which he predicted to be 1.44 kcal/mol, in good agreement with experiment,[7] 1.71 kcal. In the present paper we report *ab initio* calculations on methylsilane in an attempt to predict reliable values of the electric dipole and quadrupole moments. Several other molecular properties are also reported, and, in addition the electronic structure of the molecule is discussed *per se*.

Details of the Calculations

The basis set used was of double-zeta-plus-polarization[8] quality. For carbon, we used Dunning's (4s,2p) contraction[9] of Huzinaga's (9s,5p) primitive Gaussian basis.[10] For polarization, six d-like functions (xx, yy, zz, xy, xz, and yz) with Gaussian exponent α = 0.75 were added. The basis set on carbon is thus designated C(4s,2p,1d). For each hydrogen atom, Huzinaga's 4s primitive Gaussian set was contracted to 2s and a set of p functions (α = 1.0) added. The H atom basis is thus H(2s,1p). For silicon, we used Dunning's (7s,4p) contraction[11] of Veillard's (12s,9p) primitive set.[12] Finally a set of 3d functions (α = 0.6) was added to complete the silicon basis, Si(7s,4p,1d). The full SiH_3CH_3 basis is thus comprised of 72 contracted functions, constructed from 117 primitive Gaussians. The

Table II. Some SCF Properties of CH_3SiH_3 as a Function of Basis Set[a]

	Basis set		
Property	1 C(4s,2p) Si(7s,4p) H(2s)	2 C(4s,2p,1d) Si(7s,4p,1d) H(2s)	3 C(4s,2p,1d) Si(7s,4p,1d) H(2s,1p)
Total energy (hartrees)	−330.22769	−330.28191	−330.29929
Dipole moment, D, +C Si−	0.50	0.56	0.58 (0.73)[b]
Quadrupole moment, 10^{-26} esu cm^2	−0.68	−0.63	−0.62(−6.31 ± 0.46) or 11.74 ± 0.46[c])
Atomic populations			
H(bonded to C)	0.811	0.820	0.881
C	6.847	6.781	6.607
Si	13.249	13.286	13.138
H(bonded to Si)	1.156	1.158	1.204

[a] Experimental values are in parentheses. [b] References 1, 2, and 3. [c] Reference 5.

Table III. Orbital Energies, Potential Energies, Kinetic Energy, and Virial Theorem for Methylsilane[a]

	Basis set 1	2	3
Total energy	−330.22768	−330.28190	−330.29928
Potential energy	−660.50779	−660.48761	−660.47875
One-electron potential energy	−910.24244	−910.48915	−910.54465
Two-electron potential energy	186.92873	187.19652	187.25998
Nuclear repulsion energy	62.80592	62.80592	62.80592
Kinetic energy	330.28009	330.20479	330.17945
$-V/T$	1.99984	2.00023	2.00036
Orbital energies			
$1a_1$	−68.7824	−68.7664	−68.7646
$2a_1$	−11.2166	−11.2145	−11.2165
$3a_1$	−6.1382	−6.1177	−6.1148
$4a_1$	−4.2447	−4.2243	−4.2216
$5a_1$	−0.95194	−0.94745	−0.94651
$6a_1$	−0.71135	−0.70057	−0.69835
$7a_1$	−0.45302	−0.45537	−0.45361
1e	−4.2447	−4.2247	−4.2217
2e	−0.56740	−0.56639	−0.56397
3e	−0.46500	−0.46864	−0.46761

[a] The three different basis sets are described in Table II and the text.

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[9] T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).

[10] S. Huzinaga, *ibid.*, **42**, 1293 (1965).

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[12] A. Veillard, *Theor. Chim. Acta*, **12**, 405 (1968).

computations were carried out using a modified[13] version of POLYATOM.[14,15] The complete self-consistent-field (SCF) calculation (including the listing and computation of one- and two-electron integrals and the SCF iterations required for convergence) using the 72 contracted function basis required 15 min of CDC 7600 computer time.

The geometry chosen for the calculations was close to the experimental geometry. The assumed geometry (with experimental values[2] in parentheses) was

$$R(\text{C–Si}) = 1.87\ \text{Å}\ (1.8668 \pm 0.0005\ \text{Å})$$

$$R(\text{C–H}) = 1.10\ \text{Å}\ (1.093 \pm 0.005\ \text{Å})$$

$$R(\text{Si–H}) = 1.49\ \text{Å}\ (1.484 \pm 0.005\ \text{Å})$$

$$\text{H–C–Si angle} = 110°\ (111.2 \pm 0.5°)$$

$$\text{C–Si–H angle} = 110°\ (110.7 \pm 0.5°)$$

C_{3v} geometry was assumed and only the staggered geometry considered. The Cartesian coordinates corresponding to our assumed geometry are given in Table I.

Results

We first consider the effect of polarization basis functions on the calculated total energy, dipole moment, and Mulliken atomic populations of CH_3SiH_3. These results are seen in Table II.

For comparison, the lowest SCF energy obtained by Veillard[6] for staggered methysilane was −330.23234. The fact that our final SCF energy is 0.06695 hartree lower is primarily due to the improved[9,11] contraction of the s and p Gaussians centered on C and Si. Table II shows that the deletion of hydrogen 2p functions from the basis set raises the SCF energy by 0.01738 hartree. The further deletion of carbon and silicon d functions raises the SCF energy an additional 0.05422 hartree. The total energy lowering obtained from both kinds of polarization functions, 0.07160, can be compared to that obtained[16] for the diatomic closed-shell species SiO, 0.0833 hartree. From an energy standpoint, it is seen that polarization basis functions are no more important in methylsilane than in neighboring diatomic molecules.

The three calculations in Table II yield the same sign of the dipole moment, +C Si−, and rather close agreement as to the magnitude of μ. The final value, 0.58 D, is 79% of the experimental value, and the deviation from experiment, 0.15 D, is about as small as can reasonably be expected from a Hartree–Fock calculation. If our calculated SCF dipole moment were of the wrong sign, then the error in μ would be $(0.58 + 0.73) = 1.31$ D. Experience suggests[8] that an error of this magnitude from the present type of calculation is unlikely. Thus we conclude, in agreement with Shoemaker and Flygare,[5] that the sign of the dipole moment of CH_3SiH_3 is +C Si−.

Our calculated quadrupole moments are more difficult to reconcile with experiment than the dipole moments. All three of the calculated quadrupole moments along the molecular axis are small and negative.

Table IV. Properties of Methylsilane[a]

Property	Basis set C(4s,2p) Si(7s,4p) H(2s)	Basis set C(4s,2p,1d) Si(7s,4p,1d) H(2s,1p)
First moments of the electronic charge distribution (10^{-8} cm)		
$\langle x \rangle$	0.0	0.0
$\langle y \rangle$	0.0	0.0
$\langle z \rangle$	−0.682	−0.667
Second moments of the electronic charge distribution (10^{-16} cm^2)		
$\langle xx \rangle$	−9.52	−9.42
$\langle yy \rangle$	−9.52	−9.42
$\langle zz \rangle$	−31.66	−31.54
Third moments (10^{-24} cm^3) of the electronic charge distribution		
$\langle yyy \rangle$	−1.74	−1.72
$\langle zzz \rangle$	−18.74	−18.74
$\langle xxy \rangle$	1.74	1.72
$\langle xxz \rangle$	1.26	1.22
$\langle yyz \rangle$	1.26	1.22
Potential at each nucleus (au)		
$\Phi(H_1)$	−1.0807	−1.0943
$\Phi(C)$	−14.7463	−14.7403
$\Phi(Si)$	−49.2572	−49.2736
$\Phi(H_4)$	−1.1033	−1.1263
Diamagnetic shielding (au)		
$\langle 1/r_{H_1} \rangle$	−8.0478	−8.0614
$\langle 1/r_C \rangle$	−20.7263	−20.7202
$\langle 1/r_{Si} \rangle$	−52.6626	−52.6789
$\langle 1/r_{H_4} \rangle$	−8.1551	−8.1781
Force at each nucleus (au)		
$F_x(H_1)$	−0.0525	−0.0004
$F_y(H_1)$	0.0303	0.0002
$F_z(H_1)$	0.0326	0.0053
$F_z(C)$	0.0727	0.0108
$F_z(Si)$	0.0364	0.0350
$F_y(H_4)$	0.0886	0.0019
$F_z(H_4)$	−0.0332	−0.0021
Electric field gradient at each nucleus (au)		
$q_{xx}(H_1)$	−0.1615	−0.1526
$q_{yy}(H_1)$	0.0566	0.0506
$q_{zz}(H_1)$	0.1049	0.1020
$q_{xy}(H_1)$	0.1888	0.1760
$q_{xz}(H_1)$	0.1382	0.1271
$q_{yz}(H_1)$	−0.0798	−0.0734
$q_{xx}(C)$	−0.0588	−0.0770
$q_{yy}(C)$	−0.0588	−0.0770
$q_{zz}(C)$	0.1176	0.1540
$q_{xx}(Si)$	−0.0569	−0.0647
$q_{yy}(Si)$	−0.0569	−0.0647
$q_{zz}(Si)$	0.1137	0.1294
$q_{xx}(H_4)$	0.0942	0.0737
$q_{yy}(H_4)$	−0.1534	−0.1201
$q_{zz}(H_4)$	0.0591	0.0464
$q_{yz}(H_4)$	0.0890	0.0701

[a] H_1 is bonded to carbon and H_4 is bonded to silicon.

The negative sign means that the electronic contribution to θ is larger than the nuclear contribution. In our largest calculation, the nuclear contribution is +105.64 and the electronic contribution -106.26×10^{-26} esu cm^2. This means, assuming the experimental θ of Shoemaker and Flygare is the correct value, that our calculated value of $\langle Z^2 \rangle$ is in error by 5.69×10^{-26} esu cm^2. Although such an error is by no means inconceivable, experience suggests that it is unlikely.[17]

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We hasten to point out that our predicted value of θ, -0.62×10^{-26} esu cm^2, is in much worse agreement with the alternate experimental quadrupole moment, that obtained assuming the dipole moment is $-$C Si$+$. Thus our calculated quadrupole moments, although in poor agreement with experiment, do support Shoemaker and Flygare's interpretation of their data.

The Mulliken atomic populations seen in Table II suggest that d functions do not change the qualitative features of the electronic structure of CH_3SiH_3. Despite the sign of the dipole moment, all three calculations predict (in the admittedly naive point-charge picture) carbon to be negatively charged and silicon to be positively charged, by 0.862 electron in our final calculations. This seeming inconsistency can be partially rationalized by the fact that the H atoms bonded to carbon are "positively charged" while the three hydrogens bonded to Si withdraw electrons, yielding a negative charge in the Mulliken picture. However, in the final reckoning, the analysis of the dipole moment using the Mulliken charges is not meaningful, since it yields a $-$C Si$+$ value of μ, which is inconsistent with that obtained as the expectation value of the dipole moment operator.

$$\mu = \sum_{k \text{ nuclei}} Z_k \mathbf{R}_k - \int \psi^* \left(\sum_{i \text{ electrons}} \mathbf{r}_i \right) \psi \, d\tau$$

It is also worthwhile to report the populations associated with the polarization basis functions. The carbon d orbitals have a population of 0.059, while the silicon d orbitals have a larger population, 0.128. For comparison, earlier calculations[18] of an analogous type on SiH_4 yielded a Si d function population of 0.108 electron. The p functions centered on each H atom adjacent to carbon carried a population of 0.019 electron, while those adjacent to Si were less important, 0.009 electron.

The poor agreement between calculated and experimental quadrupole moments led us to carry out an additional calculation at the precise experimental geometry, which differs as much as 0.007 Å in bond lengths from that assumed in Table I. No polarization functions were used since we were looking for qualitative improvements. Thus the basis set was that labeled "1" in Table II. The total energy obtained was -330.22801 hartrees, or 0.00033 hartree lower than the original calculation. The calculated dipole moment was 0.60 D, compared to the original calculation 0.50, and experimental 0.73. However, the quadrupole moment was -0.49×10^{-26} esu cm^2, in slightly poorer agreement with experiment than the original calculation. Thus, it would appear that the discrepancy between experimental and theoretical values of the quadrupole moment of CH_3SiH_3 is a real one.

Table III contains a summary of the present energetic results. Of primary interest here are the orbital energies, which may be associated with ionization potentials *via* Koopmans' theorem.[19] The interpretation of Table III is aided by the realization that the 1e, 2e, and 3e orbitals are doubly degenerate; *i.e.*, they are each occupied by four electrons. All three calculations predict the same ordering of orbital energies with the $7a_1$ orbital being the highest occupied. We hope that our calculations will provide a useful qualitative guide to the photoelectron spectroscopy[20] of methylsilane.

Some additional computed properties of CH_3SiH_3 are seen in Table IV. Conversion factors between atomic units and conventional units are given in an earlier paper.[17] The calculated second moments, third moments, potentials, and diamagnetic shieldings are quite insensitive to basis set. We should note that the second and third moments are computed relative to the center of mass, and the reported values can be used[21] to obtain the diamagnetic susceptibility and octupole moment tensors. The forces on the nuclei, particularly the forces on the hydrogen atoms, are greatly reduced by the addition of polarization functions to the basis. Since the force on each atom will be zero for the exact wave function at equilibrium geometry, this is one respect in which the larger basis set yields a superior wave function. The change in calculated electric field gradients with addition of polarization functions varies from ~5% for $q(H_1)$ to 30% for the carbon field gradients. Experience suggests that the field gradients computed with our largest basis set are within ~20% of the true Hartree-Fock values. The Hartree-Fock field gradients in turn are probably within 20% of the exact values.

Acknowledgments. We thank Professor W. H. Flygare for suggesting this problem and Dr. Graham Blackman for helpful discussions. This work was supported in part by the National Science Foundation, Grant GP-31974 and was performed under the auspices of the U. S. Atomic Energy Commission.

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