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Ab Initio Structure, Force Constants, and Vibrational Frequencies of Methylsilane and Silane

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Abstract: We have predicted the vibrational spectra and the associated force fields for methylsilane and silane using basis sets of double-ζ and double-ζ-plus polarization quality. The calculations were performed by using standard gradient methods. For methylsilane our calculations suggest that the silicon–carbon bond length should be about 0.03 Å longer than the experimental value derived from microwave measurements. Our calculations also support the orginal assignment of a dipole moment which points in the direction +CSi–. We believe our force field for methylsilane to be the most complete to date and compare it to the chemically similar force field for ethane. Our calculations show that for a number of modes the methyl group force constants are insensitive to the presence of the silyl group on the other end of the molecule. Although we have found the geometries to be rather insensitive to the presence of polarization functions, the calculated force fields for the silyl group are much more sensitive than the correponding force fields for the methyl group.

In recent years the value of ab initio calculations in the refinement of experimental force fields has become well established.[1,2] A number of investigators have published force fields for a variety of small molecules. Most of these, however, have been restricted to molecules containing first-row atoms. For example, Pople et al. have recently published an extensive list of frequencies at the 3-21G level.[3] Investigations of the structure and force fields for molecules containing silicon have also appeared. Schlegel et al. have published an ab initio vibrational minimal basis set spectrum of silaethylene.[4] More recently Hoffmann, Yoshika, and Schaefer[5] have investigated the molecular structures and have predicted the vibrational frequencies of silaacetylene at the SCF and CI levels. The study by Schlegel shows that silaethylene exhibits a structure and vibrational spectrum similar to that found in ethylene. Silaacetylene, however, shows very little resemblance to acetylene since the acetylene-like structure lies over 60 kcal above the most stable isomer, and contains two imaginary frequency modes.[5]

On the basis of these latest investigations it appears that the structure and force fields of molecules which contain silicon–carbon multiple bonds are qualitatively different from those found in molecules which contain only single bonds. In this report we present the results of our investigation of the structure and force fields for silane, SiH_4, and methylsilane, SiH_3CH_3. Although these molecules resemble their first-row counterparts, methane and ethane, relatively little is known about their force fields. A recent reinvestigation[6] of the vibrational spectrum of silane has refined the Si–H bond length and confirmed the positions of the fundamental frequencies. The force field, however, is based on much older data.[7]

The structure of methylsilane has been established from several microwave investigations,[8,9] while the vibrational spectrum has been the subject of both low-resolution[10] and high-resolution studies.[11] To the best of our knowledge there does not exist a complete force field for methylsilane in the literature. Although a preliminary force field by Duncan[12a] was based on high-resolution data, the latter force field of Clark and Weber[12b] was able to refine only 15 of the 36 possible force constants, with the remainder set to 0. In constrast the vibrational force fields for methane and ethane are much better established. On the basis of very recent high-resolution data, combined with ab initio force field calculations, Duncan et al. have published a revised force field for ethane.[13] In this investigation we have included in our comparison the force field parameters of both methylsilane and ethane because of their structural similarity. Our investigation has tried to focus on the differences and similarities between these two force fields. Of particular theoretical interest has been the effect of inclusion of polarization functions in the treatment of these molecules.

Theoretical Approach

In this work we have located the theoretically predicted equilibrium geometries and evaluated the harmonic force constants at the SCF level of theory. Several investigations have demonstrated that this level of theory offers a sound and reliable description of geometries and force constants for many molecules of the first row.[1,2,14] Much less information is known about the behavior of molecules containing second-row atoms. Even if an SCF description is good, previous investigations of molecular geometries have shown that second-row atoms are much more sensitive to the presence of polarization functions in the basis set.[15] In addressing these questions we have sought to predict the geometry and the force field for both silane and methylsilane using basis sets with and without polarization functions and have compared our results with parallel calculations on the well-known molecules of methane and ethane. All of the calculations reported here have been carried out with the GRADSCF program system.[16]

The calculations on silane were performed with two basis sets. The first we call split-valence and denote it as Si[5s3p]; H[2s]. The silicon basis was the McLean and Chandler contraction[17] as

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derived from the primitive (12s8p) basis of Huzinaga, while the hydrogen basis was the [2s] contraction derived by Dunning from the (4s) primitive basis.[18] The second basis set we termed DZP and is denoted by Si[5s3p1d]; H[3s1p]. In this basis set we used the [3s] contraction of the (5s) primitive set[19] on the hydrogen atoms and included polarization functions on both the silicon and hydrogen atoms. The calculations on methylsilane were performed with three basis sets which we label as split, split + d, and DZP. The set labeled split consisted of the split-valence basis denoted above on the silicon atom, while for carbon we used the Pople-derived[20] [3s2p] basis contracted from (10s4p) primitive set and commonly refered to as 6-31G, with the hydrogen basis the [2s] contraction used also on silane. The split + d basis consisted of the above named set augmented with a set of d-type polarization functions on the silicon and carbon atoms. The third and largest basis set, which we labeled DZP, can be described as Si[6s4p1d]; C[4s2p1d]; H[3s1p]. This basis was constructed by using the [6s4p] contraction for silicon derived from the (13s9p) primitive set and contracted by the same authors as the split-valence primitive set.[17] The carbon atom was described by using the double-ζ [4s2p] basis as contracted by Dunning[18] from the (9s5p) primitive set of Huzinaga. In cases where polarization functions were added, for both carbon and silicon a set of six d functions was added with exponents of $\alpha_d(\mathrm{C}) = 0.8$ and $\alpha_d(\mathrm{Si}) = 0.5$. These values were obtained from optimized values using a DZP basis on either methane or silane, respectively. The hydrogen atom was augmented by a set of p functions with exponent $\alpha(\mathrm{H}) = 1.1$.

The geometry and force constant calculations were performed by using standard gradient methods,[1,21] where both the energy and the analytic gradient are evaluated simultaneously. For each of the molecules considered we have evaluated the matrix of second derivaties in a Cartesian coordinate representation. The force constants were evaluated by the finite difference techniques described previously.[13,21c] The Cartesian coordinates of each molecule were displaced by using a two-point central difference formula with a step size of 0.01 au. Thus, each column of the matrix of second derivaties was calculated as the difference between two displaced Cartesian gradient vectors. This was done at each of the equilibrium geometries predicted by the respective basis sets. As usual the frequencies and the normal modes were determined by diagonalizing the mass weighted force constant matrix. In order to extract the force constants in terms of internal coordinates we evaluated the appropriate B matrix[22] for each molecule which in turn was used to transform the force constants from a Cartesian to an internal or symmetry coordinate representation. This transformation not only serves to remove any redundancies in the coordinate system but also provides a set of physically meaningful potential parameters. Although angle redundancies have been removed, the angle bending coordinates have not been scaled. Thus, stretching force constants are in units of mdyn/Å; stretch bend force constants are in units of mdyn, while bending force constants are in units of mdyn Å.

A complete description of the force constants requires us to specify the internal coordinates and their linear combinations which form the symmetry coordinates. For tetrahedral molecules we have used the standard set[7] of ten internal coordinates which were used to form the four symmetry coordinates which transform as A_1, E, the two T symmetry modes. For methylsilane we have used the coordinates defined in Table I and have combined them to form the symmetry coordinates listed in Table II. A comparison of both set of molecules in this symmetry-adapted internal coordinate representation facilitates the assignment of the spectra and, as the discussion in the next section shows, allows us to focus on the differences and similarities in the bonding environment.

Table I. Definition of Internal Coordinates for SiH_3–CH_3

$Q_1 = R(\mathrm{Si{-}C})$	$Q_{14} = \beta(\mathrm{H_3{-}Si{-}C})$
$Q_2 = R(\mathrm{Si{-}H_3})$	$Q_{15} = \beta(\mathrm{H_4{-}Si{-}C})$
$Q_3 = R(\mathrm{Si{-}H_4})$	$Q_{16} = \beta(\mathrm{H_5{-}Si{-}C})$
$Q_4 = R(\mathrm{Si{-}H_5})$	$Q_{17} = \beta(\mathrm{H_6{-}C{-}Si})$
$Q_5 = R(\mathrm{C{-}H_6})$	$Q_{18} = \beta(\mathrm{H_7{-}C{-}Si})$
$Q_6 = R(\mathrm{C{-}H_7})$	$Q_{19} = \beta(\mathrm{H_8{-}C{-}Si})$
$Q_7 = R(\mathrm{C{-}H_8})$	
$Q_8 = \alpha(\mathrm{H_3{-}Si{-}H_4})$	$Q_{20} = \tau(\mathrm{H_3{-}Si{-}C{-}H_6})$
$Q_9 = \alpha(\mathrm{H_3{-}Si{-}H_5})$	$Q_{21} = \tau(\mathrm{H_3{-}Si{-}C{-}H_7})$
$Q_{10} = \alpha(\mathrm{H_4{-}Si{-}H_5})$	$Q_{22} = \tau(\mathrm{H_3{-}Si{-}C{-}H_8})$
$Q_{11} = \alpha(\mathrm{H_6{-}C{-}H_7})$	$Q_{23} = \tau(\mathrm{H_4{-}Si{-}C{-}H_6})$
$Q_{12} = \alpha(\mathrm{H_6{-}C{-}H_8})$	$Q_{24} = \tau(\mathrm{H_4{-}Si{-}C{-}H_7})$
$Q_{13} = \alpha(\mathrm{H_7{-}C{-}H_8})$	$Q_{25} = \tau(\mathrm{H_4{-}Si{-}C{-}H_8})$
	$Q_{26} = \tau(\mathrm{H_5{-}Si{-}C{-}H_6})$
	$Q_{27} = \tau(\mathrm{H_5{-}Si{-}C{-}H_7})$
	$Q_{28} = \tau(\mathrm{H_5{-}Si{-}C{-}H_8})$

Table II. Definition of Symmetry Coordinates for SiH_3–CH_3 (C_{3v})[a]

A_1	$S_1 = Q_1$	Si–C stretch
	$S_2 = Q_2 + Q_3 + Q_4$	SiH_3 stretch
	$S_3 = Q_5 + Q_6 + Q_7$	CH_3 stretch
	$S_4 = (Q_8 + Q_9 + Q_{10}) - (Q_{14} + Q_{15} + Q_{16})$	SiH_3 def
	$S_5 = (Q_{11} + Q_{12} + Q_{13}) - (Q_{17} + Q_{18} + Q_{19})$	CH_3 def
E	$S_6 = 2Q_2 - Q_3 - Q_4$	SiH_3 stretch
	$S_7 = 2Q_5 - Q_6 - Q_7$	CH_3 stretch
	$S_8 = 2Q_{10} - Q_8 - Q_9$	SiH_3 bend
	$S_9 = 2Q_{13} - Q_{11} - Q_{12}$	CH_3 bend
	$S_{10} = 2Q_{14} - Q_{15} - Q_{16}$	SiH_3 rock
	$S_{11} = 2Q_{17} - Q_{18} - Q_{19}$	CH_3 rock
A_2	$S_{12} = Q_{20} + Q_{21} + Q_{22} + Q_{23} + Q_{24} + Q_{25} + Q_{26} + Q_{27} + Q_{28}$	torsion

[a] The symmetry coordinates have been normalized by the square root of the sum of the squares of the coefficients given in this table.

Molecular Geometries

The ability to predict the molecular vibrational spectrum as well as the force field is predicated on the choice of the reference geometry. Our approach requires us to use the equilibrium geometry predicted with our theoretical model. We have summarized our calculated geometries and energies for both silane, SiH_4, and methylsilane, SiH_3CH_3, in Table III. As can readily be seen, there is very little variation in the geometry for each molecule as we improve the basis sets. For silane the split-valence basis set predicts essentially quantitative agreement with the experimentally[6] accepted values. Previous calculations on SiH_4 by Collins et al.[15] have shown that the Si–H bond is insensitive to the inclusion of d functions with both minimal and polarized minimal basis sets. These calculations have predicted a bond which is 0.06 Å shorter than experiment. They had also optimized the geometry of methylsilane and found a silicon–crbon bond which is only 0.001 Å shorter than experiment. Our calculations show the opposite trend in that we predict the silicon–carbon bond to be 0.02 Å longer than the experimentally derived value, even with the largest basis set. We beleive that the short bond lengths found with the minimal and polarized minimal basis sets are the result of basis set superposition error. As we increase the size of the basis set we observe the anticipated shortening of the silicon–carbon bond in methylsilane, while the remaining geometrical parameters remain essentially unchanged. Previous studies have shown that polarization functions are particularly important for geometry predictions in cases where second-row atoms are involved.[23] In this case we find the silicon–carbon bond to be much

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Table III. Summary of Calculated Geometries and Energies for Silane and Methylsilane

coordinate	geometry[a] split	split + d	DZP	exptl[b]
	Methylsilane			
R(Si-C)	1.907	1.884	1.880	1.867
R(Si-H)	1.487	1.470	1.476	1.485
R(C-H)	1.084	1.087	1.085	1.093
α(H-Si-H)	108.2	108.4	108.2	108.3
α(H-C-H)	108.0	107.7	107.8	107.7

basis	energy, au	μ, debyes
	Methylsilane	
split	-330.205933	0.685
split + d	-330.274036	0.692
DZP	-330.309183	0.669
expt[b]		0.73

basis	energy	R(Si-H)
	Silane	
split	-291.169558	1.482
DZP	-291.234046	1.474
exptl[c]		1.481

[a] Bond lengths in angstroms, angles, and degrees. [b] Reference 9. [c] Reference 6.

less sensitive to the presence of polarization functions. Our experience with molecules containing first-row atoms, however, has shown that as we increase the size of the basis set, the bond lengths become shorter at the SCF level relative to the experimentally accepted values.[14] Although we do show a shortening of the silicon–carbon bond as the basis set is improved, all of our values remain above the value found in the microwave experiments.[9] Our calculations would suggest that the silicon–carbon bond length previously established[9] is indeed too short. As a crude model we can compare the methyl C–C bond lengths from some typical hydrocarbons such as ethane, propene, and propyne with those found in the analogous silicon-containing compounds. The Si–C bond length in silylacetylene (1.821 Å)[24] is 0.362 Å longer than the correponding carbon–carbon single bond (1.459 Å)[25] in propyne. Likewise the Si–C bond is 0.352 Å longer than the carbon–carbon bond if we compare vinylsilane (1.853 Å)[26] with propene (1.501 Å).[27] Following the classical ideas which date back to Pauling,[28] one arrives at a value of 1.13 Å for the covalent bond radius of the SiH_3 moiety, i.e., 0.358 Å longer than that of the methyl group (half of the carbon bond length in ethane, 1.54 Å). This argument predicts a silicon–carbon bond in methylsilane to be about 1.90 Å. Although this analysis is based on a very approximate model, it does point out that the predicted bond lengths are substantially longer than the value of 1.867 Å currently accpeted. Our calculations suggest that either electron correlation should decrease the bond length, which previous experience would dictate as unlikely, or that the experimental value should be revised. It is generally accepted that electron correlation increases the predicted bond lengths for most first-row molecules.[29,30] Furthermore the recent work by Schaefer et al. on SiH_2CH_2 has shown that correlation does increase the predicted bond length in this unusual and controversial molecule, relative to the value predicted at the SCF level.[31]

Table IV. SiH_4 Comparison of Experimental and Calculated (Harmonic) Vibrational Spectra

asign		description	exptl	split	DZP
A	ν_1	sym stretch	2185[a]	2297, 2179	2375, 2253
E	ν_2	asym bend	972[a]	1052, 998	1060, 1006
T	ν_3	asym stretch	2189[a]	2281, 2164	2361, 2240
	ν_4	asym bend	913[a]	975, 924	1028, 975
		Calculated (Harmonic) Force Constants			
$F_{1,1}$		sym stretch	2.84[b]	3.132	3.347
$F_{2,2}$		deg bend	0.404[b]	0.481	0.483
$F_{3,3}$		T stretch	2.742[b]	2.959	3.167
$F_{4,4}$		T bend	0.496[b]	0.573	0.627
$F_{3,4}$			-0.03[b]	-0.136	-0.116

[a] Frequencies in cm^{-1}, ref 6. [b] Reference 7.

We would like to conclude this section by addressing the question of the sign and magnitude of the dipole moment in methylsilane. On the basis of relative electronegativities, chemical intuition would suggest that the electric dipole moment of methylsilane should point toward the carbon atom, that is, –CSi+. Over 10 years ago Shoemaker and Flygare[32] had challenged this assumption on the basis of molecular Zeeman effect measurements. Citing several arguments they concluded that the dipole moment points toward the silicon atom, i.e., +CSi–. Subsequent ab inito calculations by Liskow and Schaefer[33] supported this assignment. All three of our calculations also support this direction, even though it seems contrary to chemical intuition, and predict a magnitude which is in very good agreement with experiment. The direction of the dipole moment of methylsilane is less surprising when one considers the internal polarization of the SiH and the CH bonds. As pointed out by Shoemaker and Flygare[32] the CH bond dipole has –C–H+ polarity, while the SiH bond has a polarity of +SiH–. Both of these values are based on known octapole moment of methane and silane, respectively. A vector sum of these bond dipoles, even in the presence of a +Si–C– moment, would yield a resulting vector pointing towards the silicon atom.

Vibrational Spectra and Force Fields

In our previous investigation on three-membered rings[14] we had suggested a model in which we chose to scale the diagonal force constants by a uniform scale factor in order to account for the lack of electron correlation in the SCF wave function while leaving the off-diagonal coupling force constants unchanged. This is in contrast to the viewpoint adopted by others in the field who have tried to fit ab initio force fields by employing a number of scale factors for both the diagonal as well as the off-diagonal force constants to the experimentally observed spectra.[1,2] Thus, in all of our tables which contain vibrational frequencies for a given basis set, where two columns appear the first column refers to the raw ab initio frequencies, while the second results from a scaling by a factor of 0.9 of the diagonal force constants in the internal symmetry-adapted representation.

The vibrational spectrum of silane is now well-known. The IR[6] as well as the Raman[34] spectra have been recorded and analyzed by a number of investigators. Unfortunately there does not exist a set of harmonized experimental frequencies for direct comparison with our calculated values which we present in Table IV, where we have included our predicted force field and have compared our spectrum with that obtained by Kattenberg and Oskam.[6] Our calculations show generally good agreement at the split-valence level, while at the DZP level the predicted frequencies are uniformly too high. The only previous investigations of the force field is that of Schlegel, Wolfe, and Bernardi,[35] who have used both

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Table V. Calculated (Harmonic) Vibrational Frequencies for SiH_3–CH_3 (C_{3v})

assign		description	split	split + d	exptl,[a] ν
A_1	ν_1	CH_3 stretch	3195, 3031	3195, 3030	2929
	ν_2	SiH_3 stretch	2269, 2152	2402, 2279	2169
	ν_3	CH_3 def	1478, 1396	1458, 1378	1264
	ν_4	SiH_3 def	1005, 952	1054, 998	946
	ν_5	Si–C stretch	712, 675	733, 696	701
A_2	ν_6	torsion	183, 173	207, 196	183
E	ν_7	CH_3 stretch	3279, 3109	3265, 3096	2982
	ν_8	SiH_3 stretch	2246, 2133	2382, 2260	2166
	ν_9	CH_3 bend	1621, 1537	1607, 1525	1430
	ν_{10}	SiH_3 bend	1036, 980	1060, 1002	946
	ν_{11}	CH_3 rock	1007, 965	980, 940	871
	ν_{12}	SiH_3 rock	582, 538	574, 527	545

[a] Frequencies in cm^{-1}, ref 11.

Table VI. Calculated Harmonic Force Constants of SiH_3–CH_3 (C_{3v})

		description	split	C_2H_6(4-31G)	split + d	C_2H_6(6-31G**)
A_1	$F_{1,1}$	Si–C stretch	3.031	4.873	3.216	4.950
	$F_{2,2}$	SiH_3 stretch	3.020	5.867	3.386	5.833
	$F_{3,3}$	CH_3 stretch	5.895	5.867	5.885	5.833
	$F_{4,4}$	SiH_3 def	0.589	0.709	0.634	0.671
	$F_{5,5}$	CH_3 def	0.626	0.709	0.589	0.671
	$F_{1,2}$		0.082	0.136	0.098	0.138
	$F_{1,3}$		0.047	0.136	0.062	0.138
	$F_{1,4}$		−0.144	−0.390	−0.134	−0.325
	$F_{1,5}$		−0.280	−0.390	−0.199	−0.325
	$F_{2,3}$		0.014	0.013	0.014	0.010
	$F_{2,4}$		0.075	0.172	0.063	0.135
	$F_{2,5}$		−0.021	−0.022	−0.025	−0.027
	$F_{3,4}$		−0.017	−0.022	−0.020	−0.027
	$F_{3,5}$		0.175	0.172	0.140	0.135
	$F_{4,5}$		0.018	0.030	0.022	0.032
E	$F_{6,6}$	SiH_3 stretch	2.878	5.698	3.228	5.670
	$F_{7,7}$	CH_3 stretch	5.805	5.698	5.755	5.670
	$F_{8,8}$	SiH_3 bend	0.562	0.730	0.581	0.693
	$F_{9,9}$	CH_3 bend	0.680	0.730	0.668	0.693
	$F_{10,10}$	SiH_3 rock	0.574	0.818	0.623	0.782
	$F_{11,11}$	CH_3 rock	0.564	0.818	0.496	0.782
	$F_{6,7}$		−0.015	−0.032	−0.013	−0.029
	$F_{6,8}$		−0.101	−0.212	−0.086	−0.162
	$F_{6,9}$		0.0	−0.004	0.0	−0.006
	$F_{6,10}$		0.096	0.139	0.086	0.115
	$F_{6,11}$		0.030	0.054	0.031	0.057
	$F_{7,8}$		−0.014	−0.004	−0.016	−0.006
	$F_{7,9}$		−0.191	−0.202	−0.157	−0.162
	$F_{7,10}$		0.038	0.054	0.042	0.057
	$F_{7,11}$		0.157	0.139	0.144	0.115
	$F_{8,9}$		−0.005	−0.005	−0.009	−0.005
	$F_{8,10}$		−0.075	−0.035	−0.097	−0.023
	$F_{8,11}$		−0.027	0.006	−0.032	0.004
	$F_{9,10}$		−0.004	0.006	0.0	0.004
	$F_{9,11}$		0.0	−0.035	0.020	−0.023
	$F_{10,11}$		0.188	0.170	0.197	0.175

the minimal STO-3G and the split-valence 4-31G basis sets. Their results at the 4-31G level show force constants that are somewhat smaller than our split-valence results. If we compare our force constants with those of Duncan and Mills[7] we find the largest discrepancy in the degenerate interaction force constant $F_{3,4}$ where we calculate a value of −0.116, while the accepted value is −0.03. The effect of polarization functions is found to be very strong for the two stretching modes and quite unlike that found for molecules containing first-row atoms.[14] Surprisingly, we have found the geometry to be rather insensitive to the presence of polarization functions.

On the basis of geometrical considerations alone, methylsilane can be considered as the union of two simple subgroups. The SiH_3 part looks very much like the SiH_3 portion of silane, while the methyl group resembles the methyl group in methane. The two groups are separated by a chemical bond of about 1.9 Å in length. In analogy to ethane, methylsilane is known to adopt a staggered conformation and thus belongs to the point group C_{3v}. Thus, methylsilane should exhibit 12 vibrational modes, 5 of A_1 symmetry, 6 degenerate E type vibrations, and an A_2 torsinal mode. We have calculated the vibrational spectrum of methylsilane with two basis sets, the split-valence and the split + d basis, which included polarization functions only on the heavy atoms. The resulting spectra are presented in Table V. As suggested above, some of the vibrational modes should resemble the spectrum of ethane while others should resemble the vibrations in silane.

If we accept this analogy, it proves useful to compare our calculated harmonic frequencies with the most recent values

Table VII. Comparison of Vibrational Frequencies for Various Deuterated SiH_3–CH_3 Split + d Level

assign		d_0		SiD_3–CH_3		SiH_3–CD_3	SiD_3–CD_3
		calcd	exptl[a]	calcd	exptl[a]	calcd	calcd
A_1	ν_1	3030	2929	3030	2923	2279	2183
	ν_2	2279	2169	1627	1558	2183	1627
	ν_3	1378	1264	1377	1262	1077	1075
	ν_4	998	946	762	741	996	751
	ν_5	696	701	664	652	644	622
A_2	ν_6	196		178		162	139
E	ν_7	3096	2982	3096	2982	2299	2297
	ν_8	2260	2166	1637	1577	2257	1636
	ν_9	1525	1403	1525	1401	1105	1105
	ν_{10}	1002	946	890	825	1001	748
	ν_{11}	940	871	720	668	822	709
	ν_{12}	527	545	420	430	454	380

[a] Frequencies in cm^{-1}, ref 11.

derived by Duncan on ethane.[13] In the A_1 symmetry block we find the methyl group stretching frequency of 3030 cm^{-1} while the experimental harmonic value for ethane is 3042 cm^{-1}. The methyl group deformation is predicted to lie at 1378 cm^{-1}, somewhat lower than the value of 1417 cm^{-1} found in ethane. In the degenerate E block the methyl stretch and bend modes are predicted to lie at 3096 and 1525 cm^{-1}, respectively, in quantitative agreement with the E_g and E_u values found in ethane. Our calculations do show that the degenerate methyl rock lies closer to the E_u value of 822 cm^{-1} than the E_g value of 1214 cm^{-1} found in ethane. As we had found in silane, the calculations show a very pronounced shift in frequencies for the SiH_3 group when polarization functions are included in the basis set. If we compare the changes in the calculated spectrum between the two basis sets, we find that the methyl stretching motions are almost insensitive to the presence of polarization functions while the bends are softened. In contrast, modes that involve the SiH_3 group all increase in frequency when polarization functions are added, even though the geometry seems to be insensitive to basis set changes. As noted above, the predicted force field is a function of the geometry chosen. In general it has been observed that shorter bond lengths produce larger stretching force constants.[1] The observed basis set dependence of the frequencies and force constants for methylsilane and silane is quite significant, and cannot be attributed to the slight decrease in the predicted bond lengths of the Si–H and C–H bonds. This is especially true since changes in geometry on the order of 0.01 Å are also observed for hydrocarbons such as ethane, once polarization functions are included, with much smaller changes in the force constants as the discussion in the following paragraphs indicates.

It has often proven useful to compare the calculated ab initio force fields with experimentally derived values. As we had mentioned above the existing experimental force fields are incomplete. Since we find these data difficult to compare, we do offer for comparison our calculated force fields with two basis sets in Table VI and compare these results with our previous calculations[36] on ethane at the 4-31G and 6-31G** levels. A comparison of the force constants reveals that the silicon–carbon stretch diagonal force constant is much smaller than the corresponding carbon–carbon bond in ethane. Within the A_1 symmetry block we do observe that the methyl group symmetric stretch is nearly the same in methylsilane and ethane. However, as our discussion above of the calculated spectra revealed, we do note that pronounced effect of polarization functions in terms of the diagonal force constants which include the silicon atom. No such changes are observed in the ethane molecule. If we turn our attention to the interaction force constants, we find that they are in general smaller in methylsilane than in ethane. We do find qualitative agreement in the value of the constant $F_{3,5}$ (CH_3 str/CH_3 def) between methylsilane and ethane, which further indicates that the internal motions of the CH_3 group are not appreciably perturbed by the presence of the SiH_3 group on the other end of the molecule. Surprisingly, we do find the interaction force constants $F_{1,4}$ and $F_{1,5}$, involving the silicon–carbon stretch and the deformation of the SiH_3 and the methyl groups, are much smaller in methylsilane than in ethane. We could try to rationalize the reduced magnitude of these interaction force constants as a result of the lower values found for the diagonals. We believe that such arguments are tenuous at best since as our discussion of the degenerate E block indicates, some of the interactions remain just as large in methylsilane as they are in ethane. These interaction force constants also show much greater sensitivity to polarization functions than most of the other off-diagonal force constants.

A comparison of the force constants in the degenerate E block reveals some of the differences between methylsilane and ethane. Although diagonal force constants which involve the methyl group show similarities when we compare them with ethane, the magnitude of the methyl bend and rock force constants is reduced when we compare the two molecules. We do find that the methyl rock diagonal force constant is smaller than the methyl bend in methylsilane, in constrast to that observed in ethane. As in the A_1 symmetry block, we find almost quantitative agreement in the methyl interaction force constants $F_{7,9}$ and $F_{7,11}$. The longer central bond in methylsilane is probably responsible for the fact that we calculate two of the interaction force constants to be 0 within the precision of our calculation. Surprisingly, this increased distance does not seem to affect the interaction between the SiH_3 rock/CH_3 rock since we calculate these force constants to have a very similar magnitude in methylsilane and ethane.

As a final prediction we have calculated the vibrational spectra of various deuterated species for methylsilane which we present in Table VII and compare these with the experimental assignment of Wilde.[11] The frequencies are derived from a force field where the diagonals have been scaled. These data on isotopic frequency shifts further support the independence of the SiH_3 and the methyl group in this simple, yet quite interesting molecule.

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(36) Komornicki, A. to be published.

(37) **Note Added in Proof**: We have recently become aware of a new microwave investigation of methylsilane (Wong, M.; Ozier, I.; Meerts, W. L. *J. Mol. Spectrosc.* **1983**, *102*, 89) where these authors have produced a structure which is in very close agreement with the older works of Kilb and Pierce.[9] Furthermore, these authors have derived a value of 1.864 Å for the Si–C bond length which is slightly shorter than that from the older microwave work. While we still believe that our theoretical data and arguments are sound, a resolution of this bond length discrepancy will require further theoretical investigation.