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The Equilibrium Structure and Torsional Potential Energy Function Of Methanol and Silanol

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The molecular parameters of methanol, CH_3OH, and its silicon analogue silanol, SiH_3OH, have been determined in large-scale ab initio calculations using the coupled-cluster method, CCSD(T), and basis sets of double- through (partly) quintuple-zeta quality. The properties studied included the equilibrium structure, spectroscopic constants, potential energy functions for internal rotation, and harmonic force fields of both molecules. The effects of core−electron correlation and of small-amplitude vibrations on the calculated molecular parameters were investigated. The molecular parameters determined for methanol are found to be in good agreement with the experimental data. The accuracy of the theoretical predictions for silanol can be assessed.

I. Introduction

Methanol, CH_3OH, is one of the best spectroscopically characterized molecules whose methyl group undergoes internal rotation around the CO bond.[1] In contrast, there is almost no experimental data on its silicon analogue silanol, SiH_3OH. Silanol is highly reactive even in argon matrixes (at 17 K),[2] and only one absorption band has been observed so far in its low-resolution infrared spectra. This band was tentatively assigned to the SiO stretching mode.[2] A large number of unidentified lines, which may be due to hydroxysilylene (HSiOH) or silanol, were observed in the millimeter wave spectrum of a silane−oxygen plasma.[3] The structural parameters and spectroscopic constants of the SiH_3OH molecule are therefore known only from theoretical studies. Moreover, as silanol can serve as a simple molecular model of the hydroxyl group on the outer surface of silica-containing materials (for example, the acidic terminal hydroxyls of zeolites),[4] its structure and electronic properties are of interest.

The aim of this study is to predict the basic properties of methanol and silanol—namely, the structure and shape of the potential energy surface—by state-of-the-art theoretical methods. As shown below for methanol, this can be accomplished to remarkably high accuracy by using extensively correlated electronic wave functions in conjunction with large one-particle basis sets. Given the quality of the computed electronic wave function, it can be expected that a similar accuracy has been achieved for silanol as well. Therefore, the results of this paper may be helpful in a further analysis of the rotational−vibrational spectra of silanol. The results may also serve as high-level benchmark data for the evaluation of density functional theory (DFT) for silicates and related materials of industrial interest.

There are a number of theoretical studies on methanol, and the results of several ab initio calculations have been reported, spanning the level of theory from the self-consistent field to the coupled-cluster method (see refs 5−13 and references therein). To the best of the author's knowledge, the most advanced ab initio study has been performed by Florian et al.[11] The structure and harmonic force field of the molecule were determined using the coupled-cluster method, CCSD(T),[14−17] with the split-valence 6-311G(3df, 2p) basis set.[18] Vibrational transition intensities in the infrared and Raman spectra were predicted at lower levels of theory. The results of high-level calculations were compared with those obtained with density functional methods.

The theoretical studies on silanol are less numerous.[5,19−25] The most advanced ab initio calculations so far were performed by Sauer and Ahlrichs[5] and by Nicholas and Feyereisen.[24] Sauer and Ahlrichs determined the structural parameters of methanol and silanol using the coupled-pair functional method (CPF)[26] with the partly quadruple-ζ basis set of *spdf* quality. Nicholas and Feyereisen studied the structure of silanol by the second-order Møller−Plesset perturbational approach[27] with the series of the correlation-consistent basis sets[28,29] up to quadruple-ζ *spdf* quality. The cubic anharmonic force fields for methanol and silanol were calculated[5,19] at the self-consistent field level (SCF)[30] with the double-ζ plus polarization basis set.

II. Method of Calculation

In this study, the molecular parameters of methanol and silanol were calculated using the coupled-cluster method, including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T).[14−17] The one-particle basis sets used are the correlation-consistent polarized valence basis sets, cc-pV*n* Z.[28,29] The quality of the basis sets employed ranges from double-ζ (n = D) through triple-ζ (n = T) to quadruple-ζ (n = Q). To investigate further the effects of the extension of the basis set, we performed additional calculations in which the quintuple-ζ (n = 5) basis set was used for silicon while the cc-pVQZ basis set was used for oxygen and hydrogen. This basis set is referred to hereafter as Q/5. The largest one-particle basis sets thus consist of a (6*s*3*p*2*d*1*f*)/[4*s*3*p*2*d*1*f*] set for hydrogen, a (12*s*6*p*3*d*2*f*1*g*)/[5*s*4*p*3*d*2*f*1*g*] set for carbon and oxygen, and a (20*s*12*p*4*d*3*f*2*g*1*h*)/[7*s*6*p*4*d*3*f*2*g*1*h*] set for silicon. Only the spherical harmonic components of polarization functions *d*−*h* were used. In the correlation treatment involving only the valence electrons, the 1*s*-like core orbitals of the carbon and oxygen atoms and the

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TABLE 1: Equilibrium Molecular Parameters of Methanol, Determined by the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ
r(CO) (Å)	1.4206	1.4209	1.4194
r(CH) (Å)	1.1089	1.0928	1.0914
r(OH) (Å)	0.9666	0.9595	0.9577
β (deg)	110.90	110.51	110.34
δ (deg)	3.91	3.69	3.59
∠(COH) (deg)	106.28	107.42	107.98
energy + 115 (hartrees)	−0.420759	−0.550767	−0.588915

1*s*-,2*sp*-like core orbitals of the silicon atom were excluded from the active space.

The core-related correlation effects were investigated using the correlation-consistent polarized core-valence basis set of triple-ζ quality, cc-pCVTZ.[31,32] The basis set is obtained by augmenting the standard cc-pVTZ basis set with a (2*s*2*p*1*d*) set for carbon and oxygen[31] and a (2*s*2*p*2*d*1*f*) set for silicon.[32] The exponents of the augmenting functions were determined by optimizing the total core−valence correlation energy in the atoms.[31,32] In the correlation treatment involving the core and valence electrons, only the 1*s*-like orbital of the silicon atom was excluded from the active space.

The ab initio calculations were performed using the MOLPRO-2000 package of programs.[33,34]

III. Results and Discussion

For the sake of comparison with the experimental spectroscopic studies on methanol,[1,35−41] we assumed that the methyl group in the calculations had C_{3v} symmetry, with the C_3 symmetry axis lying in the COH plane and tilting toward the CO bond. The structure of the methyl group in methanol is thus determined by three parameters, namely, the CH bond length, the angle β between the CH bond and the C_3 symmetry axis, and the angle δ between the C_3 symmetry axis and the CO bond. The methyl group was allowed to rotate around the C_3 symmetry axis, and the internal rotation angle τ is defined as the dihedral angle between the plane through one of the CH bonds and the C_3 symmetry axis and the plane of COH.

The calculated equilibrium molecular parameters of methanol are given in Table 1. As could be expected, the equilibrium structure was found to be of C_s symmetry, with the staggered conformation of the methyl group ($\tau = 0°$). Changes in the molecular parameters for larger one-particle basis sets can be estimated by using various extrapolation techniques.[42−46] These extrapolation schemes make use of simple relations between a molecular property and a cardinal number *n* assigned to the cc-pV*n* Z basis set. The schemes employed in this work included an exponential function,[42] an exponential/Gaussian function,[43] and two Schwartz-type extrapolation formulas.[44,45] The average of the four extrapolated values was taken as the best estimate of a molecular property. Extension from the cc-pVQZ to cc-pV5Z basis set would thus lower the total energy by ∼13 mhartrees. The total energy lowering at the limit of the infinite basis set could be estimated to be ∼21 mhartrees. Likewise, extension of the one-particle basis set beyond the cc-pVQZ level should not decrease the calculated bond lengths by more than ∼0.001 Å. The angles β and δ are estimated to be accurate to ∼0.1°, while the valence angle COH to ∼0.3°.

The effects of local-symmetry constraints on the methyl group were investigated in the calculation with the cc-pVTZ basis set when all the constraints were relaxed. In comparison with the results in Table 1, complete optimization of the structural parameters affects substantially only the CH bond lengths, the differences being −0.0039 and 0.0020 Å for the CH bond in and out of the symmetry plane, respectively. The structure of the COH moiety was determined to be identical. The "relaxed" structure of methanol is more stable than the "constrained" one by only 0.020 mhartrees (4 cm^{-1}). In light of the errors due to limitations in the electronic wave function (incompleteness of the one-particle basis set and some neglected correlation effects), this difference is completely irrelevant and lends plausibility to the applied model of the methanol molecule.

TABLE 2: Equilibrium Structural Parameters of Methanol, Determined at the CCSD(T)/cc-pCVTZ Level of Theory

	valence only (V)[a]	all electrons (A)[b]	A−V
r(CO) (Å)	1.4206	1.4185	−0.0021
r(CH) (Å)	1.0926	1.0914	−0.0012
r(OH) (Å)	0.9591	0.9583	−0.0008
β (deg)	110.50	110.53	0.03
δ (deg)	3.67	3.66	−0.01
∠(COH) (deg)	107.42	107.51	0.09
energy + 115 (hartrees)	−0.555338	−0.659088	−0.103750

[a] Correlating only the valence electrons. [b] Correlating all the electrons.

TABLE 3: Molecular Parameters for the Eclipsed Conformation of Methanol, Determined by the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ
r(CO) (Å)	1.4253	1.4248	1.4232
r(CH) (Å)	1.1084	1.0923	1.0910
r(OH) (Å)	0.9636	0.9571	0.9555
β (deg)	111.07	110.63	110.48
δ (deg)	1.64	1.60	1.62
∠(COH) (deg)	106.71	107.77	108.37
ΔE[a] (cm^{-1})	508	381	356

[a] ΔE is the energy difference between the eclipsed and staggered (equilibrium) conformations.

The core−electron correlation effects have been investigated by comparing the results of calculations correlating only the valence electrons with those when all the electrons were correlated. The molecular parameters determined for the equilibrium conformation of methanol are given in Table 2. Inclusion of the core-related effects decreases the calculated bond lengths by 0.001−0.002 Å and changes only insignificantly the valence angles.

Table 3 lists the molecular parameters calculated for the eclipsed conformation of methanol ($\tau = 60°$), corresponding to the top of the potential energy barrier to internal rotation. In comparison with the equilibrium conformation, the largest change in the structural parameters occurs for the tilt angle δ, which is predicted to narrow by nearly 2°. The calculated barrier to internal rotation changes with the quality of the basis set, the barrier height decreasing by a factor of 1.4 on going from the cc-pVDZ to cc-pVQZ basis set. At the limit of the infinite one-particle basis set, the barrier to internal rotation is estimated to be 345 ± 5 cm^{-1}. The core-related effects on the structural parameters were determined to be the same as those for the equilibrium conformation. The core-related correction to the barrier to internal rotation appeared to be negligible, decreasing the barrier height by merely 0.8 cm^{-1}.

The best estimate of the molecular parameters of methanol at the CCSD(T) level of theory can be determined by adding the changes in the parameters due to the core−electron correlation effects (A−V) to the complete-basis-set limits determined with the valence cc-pV*n* Z basis sets (using the four extrapolation techniques mentioned above). The equilibrium

TABLE 4: Structural Parameters and Spectrosopic Constants of Methanol

			experimental		
	r_e[a]	r_z[a]	r_s[b]	r_z[c]	r_0[d]
r(CO) (Å)	1.416	1.424	1.421	1.428	1.427
r(CH) (Å)	1.090	1.099	1.094	1.098	1.096
r(OH) (Å)	0.956	0.953	0.963	0.975	0.956
β (deg)	110.3	110.3	110.4	109.8	109.9
δ (deg)	3.5	3.6	3.2	3.4	3.3
∠(COH) (deg)	108.4	108.9	108.0	107.6	108.9
A (MHz)	129114	127720			127523
B (MHz)	24960.9	24651.6			24690.2
C (MHz)	24064.1	23787.2			23759.7
D_{ab} (MHz)	−133	−176			−125
F (cm^{-1})	27.68	27.88			27.654
ρ	0.807	0.812			0.8102

[a] Theoretical values are calculated as described in the text. [b] Ref 37. [c] Ref 38. [d] The structural parameters are taken from ref 35, and the effective spectroscopic constants are taken from ref 39.

structural parameters (r_e) calculated in this way are given in Table 4. To account for the vibrational effects, we added the nuclear motion corrections. These were calculated by Hill et al.[19] using the cubic anharmonic force field determined at the SCF/DZP level of theory. The vibrational corrections, as listed in Table 7 of ref 19, were added to the estimated equilibrium structural parameters, yielding the average structure in the ground vibrational state (r_z). The calculated structural parameters are compared with the experimental substitution structure (r_s),[37] the average structure (r_z),[38] and the effective structure (r_0).[35] It is believed that the equilibrium structure of a molecule is most closely approximated by the substitution structure. On the other hand, the average structure is close to the effective structure. Uncertainties in the experimental structural parameters of methanol are estimated to be as large as 0.005 Å for the bond lengths and 0.5° for the valence angles.[47] The calculated values fall within the experimental error bars, except for the OH bond length. However, it should be noted that due to large anharmonicity and mass effects, the OH and CH bond lengths are the most difficult structural parameters to determine precisely from the experimental data. For the effective OH bond length, two distinctly different experimental values are quoted, 0.956 and 0.945 Å in refs 35 and 47, respectively.

A direct comparison between the theoretical and experimental data can be made by calculating the values of the spectroscopic constants. For the methanol molecule, these were calculated in the internal-axis system (IAM).[35,48] The set of spectroscopic constants determined in this work includes the effective rotational constants A, B, C, and D_{ab}, the reduced torsional constant F, and the moment-of-inertia ratio ρ. As shown in Table 4, the calculated average rotational constants A, B, C, and D_{ab} differ from the experimental effective values by 197, −39, 28, and −51 MHz, respectively. The agreement between the calculated and observed constant F is less satisfactory, whereas the constant ρ is nicely reproduced. As for the experimental structural parameters, the values of the experimental spectroscopic constants are not consistent to the accuracies quoted by various authors. For example, the rotational constant A was determined to be 127 523, 127 588, and 127 536 MHz in refs 39, 40, and 41, respectively. The torsional constant F was determined in the same references to be 27.654, 27.633, and 27.645 cm^{-1}, respectively. Nevertheless, differences between the calculated and experimental values of the spectroscopic constants are still 1 order of magnitude larger than the experimental uncertainties. It should be noted, however, that changes in the bond lengths and valence angles to within the accuracy of the theoretical predictions result in changes of the spectroscopic constants of a few tens of megahertz. These changes can fully account for the discrepancies between the theoretical and experimental data. In this respect, the estimated equilibrium structure of methanol in Table 4 is likely the most accurate prediction available. A final comparison of the equilibrium structural parameters of methanol awaits the experimental and/or theoretical determination of the rotation−vibration interaction constants. For a molecule having 12 vibrational degrees of freedom, this is certainly a formidable task, given the condition that the experimental and theoretical treatments should account for interactions between the large-amplitude internal rotation and small-amplitude vibrations.

TABLE 5: Harmonic Frequencies ω of Methanol, Determined at the CCSD(T)/cc-pVTZ Level of Theory for the Equilibrium Conformation

symm[a]	ω (cm^{-1})	PED × 100[b]
A''	305.1	100 torsion
A'	1065.2	52 CO stretch, 27 asym HCO bend, 20 COH bend
A'	1096.5	50 CO stretch, 35 asym HCO bend, 14 COH bend
A''	1173.4	95 asym HCO bend
A'	1394.0	64 COH bend, 27 asym HCO bend
A'	1487.8	98 sym HCO bend
A''	1507.1	96 asym HCH bend
A'	1523.4	84 asym HCH bend, 11 asym HCO bend
A'	3019.0	99 sym CH stretch
A''	3081.5	100 asym CH stretch
A'	3101.4	99 asym CH stretch
A'	3864.3	100 OH stretch

[a] Symmetry in the C_s point group. [b] Potential energy distribution; only contributions greater than 10 are quoted.

As a first step in this direction, the harmonic force field of methanol was calculated at the CCSD(T)/cc-pVTZ level of theory. The harmonic frequencies and potential energy distribution determined for the equilibrium conformation are given in Table 5.[49] The potential energy distribution is given in terms of local-symmetry valence coordinates. Almost all the normal vibrations appeared to be characteristic, except for two modes of A' symmetry at 1065 and 1097 cm^{-1}. These normal vibrations consist of combinations of vibrations along the CO stretching, HCO rocking, and COH bending valence coordinates. Unfortunately, there are neither experimental harmonic frequencies nor force fields for comparison. The harmonic force fields of methanol reported by Serrallach et al.[50] and Cruz et al.[51] were calculated using the observed (anharmonic) fundamentals. Therefore, the force fields and frequencies determined experimentally are contaminated by anharmonicity effects. This is clearly seen when the calculated and experimental frequencies of the OH and CH stretching modes are compared, the differences being as large as 100−200 cm^{-1}. Anharmonicity also affects the torsional vibration, as this mode in methanol is a large-amplitude motion.

The potential energy function for internal rotation, $V(\tau)$, can be expressed as the Fourier series[48]

$$V(\tau) = (V_3/2)(1 - \cos 3\tau) + (V_6/2)(1 - \cos 6\tau) + (V_9/2)(1 - \cos 9\tau) + \cdots \quad (1)$$

Since the expansion coefficient V_9 for the main methanol isotopomer was found experimentally[39] to be merely 1.0 cm^{-1}, the higher-order terms were neglected, and only the expansion coefficients V_3 and V_6 were determined in this study. The structural parameters were optimized additionally for the intermediate, skew conformation of methanol with the torsional angle $\tau = 30°$. The total energy was computed with the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets to be −115.419538, −115.549847, and −115.588052 hartrees, respectively. As the V_6 term in eq 1 vanishes for the eclipsed conformation, the expansion coefficient V_3 becomes equal to the barrier height and thus amounts (see Table 3) to 508, 381, and 356 cm^{-1} for the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, respectively. The expansion coefficient V_6 was then calculated to be 14, 12, and 11 cm^{-1}, respectively. When the core−electron correlation effects discussed above were included, the expansion coefficients were found at the complete-basis-set limit to be $V_3 = 344$ cm^{-1} and $V_6 = 11$ cm^{-1}.

The effects of the small-amplitude vibrations can be studied in a first approximation by considering the dependence of the harmonic frequencies on the torsional coordinate τ.[52,53] Within the Born−Oppenheimer-type approximation, the effective potential energy function for internal rotation, $V^{\mathrm{eff}}(\tau)$, can be written as

$$V^{\mathrm{eff}}(\tau) = V(\tau) + \sum_i \omega_i(\tau)\left(\upsilon_i + \frac{1}{2}\right) \quad (2)$$

where the sum runs over the 11 small-amplitude vibrations of methanol and ω_i and υ_i are respectively the harmonic frequency and vibrational quantum number. In addition to the harmonic frequencies discussed above, the harmonic force field and frequencies were determined[49] also for the eclipsed and skew conformations of methanol. For the main isotopomer in the ground state of the small-amplitude vibrations ($\upsilon_i = 0$), the second term in eq 2 was determined to be 11 157, 11 170, and 11 184 cm^{-1} for $\tau = 0°$, 30°, and 60°, respectively. The effective expansion coefficients are thus calculated to be $V_3^{\mathrm{eff}} = 371$ cm^{-1} and $V_6^{\mathrm{eff}} = 10$ cm^{-1}. The calculated parameter V_3^{eff} is in good agreement with experimental values for the CH_3OH molecule: 373.59,[39] 373.13,[40] and 373.37 cm^{-1}.[41] On the other hand, the calculated parameter V_6^{eff} is 1 order of magnitude greater (and of a different sign) than the experimental values of −1.6,[39] −1.0,[40] and −0.9 cm^{-1}.[41] The reason for such a discrepancy may be that the calculated effective expansion coefficients include neither contributions from the potential energy anharmonic nor kinetic energy coupling terms. For the perdeutero methanol isotopomer, CD_3OD, the second term in eq 2 was determined to be 8349, 8356, and 8364 cm^{-1} for $\tau = 0°$, 30°, and 60°, respectively. The effective expansion coefficients are thus calculated to be $V_3^{\mathrm{eff}} = 359$ cm^{-1} and $V_6^{\mathrm{eff}} = 10$ cm^{-1}. The experimental values of the parameters were determined[54] to be 362.21 and −2.2 cm^{-1}, respectively. The change in the torsional barrier height upon deuteration is thus nicely reproduced.

TABLE 6: Equilibrium Molecular Parameters of Silanol, Determined by the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	Q/5[a]
r(SiO) (Å)	1.6968	1.6595	1.6525	1.6481
r(SiH) (Å)	1.4906	1.4828	1.4799	1.4793
r(OH) (Å)	0.9663	0.9581	0.9560	0.9562
β (deg)	109.81	109.76	109.64	109.69
δ (deg)	4.13	3.82	3.71	3.71
∠(SiOH) (deg)	113.49	116.38	117.74	117.91
energy + 366 (hartrees)	−0.484108	−0.619759	−0.660327	−0.664867

[a] cc-pV5Z for silicon and cc-pVQZ for the other atoms.

TABLE 7: Equilibrium Structural Parameters of Silanol, Determined at the CCSD(T)/cc-pCVTZ Level of Theory

	valence only (V)[a]	all electrons (A)[b]	A−V
r(SiO) (Å)	1.6517	1.6483	−0.0034
r(SiH) (Å)	1.4800	1.4768	−0.0032
r(OH) (Å)	0.9575	0.9568	−0.0007
β (deg)	109.83	109.82	−0.01
δ (deg)	3.81	3.81	0.00
∠(SiOH) (deg)	116.78	116.87	0.09
energy + 366 (hartrees)	−0.627978	−0.970288	−0.342310

[a] Correlating only the valence electrons. [b] Correlating all the electrons, except the 1s electrons of the silicon atom.

Analogous calculations were performed for the silanol molecule. The molecular parameters for the equilibrium (staggered) conformation are given in Table 6. In comparison with methanol, substitution of carbon by silicon results in the lengthening of the SiO and SiH bonds by about 0.2 and 0.4 Å in reference to the corresponding CO and CH bonds. The SiOH valence angle is also about 10° larger than the COH valence angle. The other structural parameters remain nearly the same as those for the methanol molecule. By using the four extrapolation techniques mentioned above, we find that the extension from the cc-pVQZ to cc-pV5Z basis set (for all the atoms) would lower the total energy by ∼14 mhartrees, nearly 3 times larger than the energy lowering for the Q/5 basis set. The total energy lowering at the limit of the infinite basis set could be estimated to be ∼23 mhartrees. As for methanol, with respect to the extension of the one-particle basis set, the calculated bond lengths, the angles β and δ, and the SiOH valence angle are estimated to be accurate to about 0.001 Å, 0.1°, and 0.5°, respectively.

In the context of the gas-phase acidity of silanol, it is interesting to compare the calculated total electronic energy with that reported by Nicholas and Feyereisen[24] for the MP2/cc-pVQZ(-g) level of theory. For the cc-pVQZ basis set, the total energy for the equilibrium conformation of silanol is calculated to be −366.626115 and −366.660327 hartrees at the MP2 and CCSD(T) levels, respectively. For the cc-pVQZ basis set without polarization *g* functions, the total energy was determined at the MP2 level to be −366.618478 hartrees.[24] The contribution due to the *g* functions amounts thus to 7.6 mhartrees at the MP2 level. The inclusion of higher-order electron correlation effects through the CCSD(T) framework lowers the total energy by 34.2 mhartrees. This is a quite substantial contribution, as compared to the estimated total energy lowering of ∼23 mhartrees on going from the cc-pVQZ to the infinite basis set.

The core−electron correlation effects on the molecular parameters are illustrated by the results in Table 7. The calculated changes in the structural parameters of silanol due to inclusion of the core-related effects parallel closely those determined for methanol.

TABLE 8: Molecular Parameters for the Eclipsed Conformation of Silanol, Determined by the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	Q/5[a]
r(SiO) (Å)	1.6977	1.6602	1.6532	1.6486
r(SiH) (Å)	1.4907	1.4830	1.4801	1.4794
r(OH) (Å)	0.9649	0.9569	0.9550	0.9551
β (deg)	109.94	109.89	109.77	109.81
δ (deg)	0.59	0.65	0.70	0.68
$\angle$(SiOH) (deg)	113.23	116.08	117.48	117.60
ΔE^b (cm^{-1})	228	175	155	151

[a] cc-pV5Z for silicon and cc-pVQZ for the other atoms. [b] ΔE is the energy difference between the eclipsed and staggered (equilibrium) conformations.

TABLE 9: Structural Parameters and Spectrosopic Constants of Silanol

	r_e[a]	r_z[a]
r(SiO) (Å)	1.646	1.650
r(SiH) (Å)	1.475	1.484
r(OH) (Å)	0.954	0.944
β (deg)	109.6	109.6
δ (deg)	3.7	3.4
$\angle$(SiOH) (deg)	118.6	119.5
A (MHz)	78054	77487
B (MHz)	13895.1	13807.4
C (MHz)	13654.9	13579.3
D_{ab} (MHz)	−273	−218
F (cm^{-1})	29.23	30.27
ρ	0.901	0.906

[a] Theoretical values are calculated as described in the text.

The molecular parameters determined for the eclipsed conformation of silanol are given in Table 8. As for methanol, the largest change in the structural parameters upon internal rotation occurs for the tilt angle δ, which is predicted to narrow to only 0.7°. At the limit of the infinite one-particle basis set, the barrier to internal rotation is estimated to be 143 ± 5 cm^{-1}. The calculated barrier height is thus a factor of 2.4 smaller than that determined for methanol. On the other hand, such a high torsional barrier for silanol is surprisingly in contrast to the disiloxane molecule, $H_3SiOSiH_3$, for which the silyl groups were found both experimentally[55] and theoretically[56] to rotate nearly freely around the SiO bonds. At the CCSD(T)/cc-pVTZ level of theory, the expansion coefficient V_3 of the torsional potential energy function for disiloxane was predicted[56] to be merely 9 cm^{-1} at equilibrium. It was found, however, to increase steeply with a decreasing SiOSi angle, being 55 cm^{-1} at an SiOSi angle of 130°. Therefore, the high torsional barrier for silanol is likely connected to the equilibrium valence angle SiOH of 118°, which is predicted to be by about 30° narrower than the equilibrium valence angle SiOSi for disiloxane. For the main silanol isotopomer, the vibrational harmonic correction (see below) to the barrier height was determined to be only 4 cm^{-1}, and the effective expansion coefficient V_3^{eff} is thus estimated to be 147 cm^{-1}.

The best molecular parameters of silanol at the CCSD(T) level of theory were determined as described above for methanol. The predicted equilibrium (r_e) and average (r_z) structural parameters are given in Table 9. The vibrationally averaged parameters were calculated by adding the nuclear motion corrections, determined by Hill et al.,[19] to the estimated equilibrium parameters. Table 9 lists also the spectroscopic constants of silanol calculated in the internal-axis system. Given the quality of the computed electronic wave function, it can be expected that the predicted equilibrium and average spectroscopic constants are as accurate as those found for methanol. In conjunction with the calculated barrier to internal rotation, the spectroscopic constants can be used to predict the rotational−torsional spectrum of silanol and thus to assign the high-resolution spectra.

TABLE 10: Harmonic Frequencies ω of Silanol, Determined at the CCSD(T)/cc-pVTZ Level of Theory for the Equilibrium Conformation

symm[a]	ω (cm^{-1})	PED × 100[b]
A″	198.4	98 torsion
A′	694.9	76 asym HSiO bend, 24 SiOH bend
A″	725.0	100 asym HSiO bend
A′	858.3	73 SiO stretch, 18 SiOH bend
A′	925.4	48 SiOH bend, 22 SiO stretch, 16 asym HSiO bend
A″	974.5	99 asym HSiH bend
A′	982.8	91 asym HSiH bend
A′	1011.1	92 sym HSiO bend
A″	2247.5	100 asym HSi stretch
A′	2249.9	57 sym HSi stretch, 43 asym HSi stretch
A′	2254.1	57 asym HSi stretch, 43 sym HSi stretch
A′	3915.9	100 OH stretch

[a] Symmetry in the C_s point group. [b] Potential energy distribution; only contributions greater than 10 are quoted.

The harmonic force field of silanol was calculated at the CCSD(T)/cc-pVTZ level of theory, and the frequencies and potential energy distribution determined for the equilibrium conformation are given in Table 10.[49] As for methanol, almost all the normal vibrations appeared to be characteristic, except those of both totally symmetric SiH stretching modes and the mode of *A*′ symmetry at 925 cm^{-1}. The latter normal vibration consists of a combination of vibrations along the SiOH bending, SiO stretching, and HSiO rocking valence coordinates. Experimentally, only one fundamental absorption band of silanol has been observed so far in low-resolution infrared spectra in argon matrixes.[2] This band was tentatively assigned to the SiO stretching mode and was observed at 859, 851, 874, and 850 cm^{-1} for the SiH_3OH, $SiH_3{}^{18}OH$, SiD_3OD, and $SiD_3{}^{18}OD$ isotopomers, respectively. The harmonic frequencies of the SiO stretching mode for these isotopomers are predicted here to be 858, 829, 883, and 859 cm^{-1}, respectively. For the main isotopomer, the calculated frequency is very close (likely fortuitously) to the observed fundamental. The predicted harmonic D and ^{18}O isotopic shifts are, however, substantially overestimated. The reason for this is not clear.

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References and Notes

(1) Moruzzi, G.; Winnewisser, B. P.; Winnewisser, M.; Mukhopadhyay, I.; Strumia, F. *Microwave, Infrared, and Laser Transitions of Methanol: Atlas of Assigned Lines from 0 to 1258 cm*$^{-1}$; CRC Press: Boca Raton, FL, 1995, and references therein.
(2) Withnall, R.; Andrews, L. *J. Phys. Chem.* **1985**, *89*, 3261.
(3) Bogey, M.; Delcroix, B.; Walters, A.; Guillemin, J. *J. Mol. Spectrosc.* **1996**, *175*, 421.
(4) Sauer, J.; Ugliengo, P.; Garrone, E.; Saunders, V. R. *Chem. Rev.* **1994**, *94*, 2095.
(5) Sauer, J.; Ahlrichs, R. *J. Chem. Phys.* **1990**, *93*, 2575.
(6) Lee, T. J.; Rice, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 8247.
(7) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.
(8) Bakkas, N.; Bouteiller, Y.; Loutellier, A.; Perchard, J. P.; Racine, S. *J. Chem. Phys.* **1993**, *99*, 3335.
(9) Bauschlicher, C. W., Jr.; Partridge, H. *Chem. Phys. Lett.* **1993**, *215*, 451.
(10) Chung-Philips, A.; Jebber, K. A. *J. Chem. Phys.* **1995**, *102*, 7080.

(11) Florian, J.; Leszczynski, J.; Johnson, B. G.; Goodman, L. *Mol. Phys.* **1997**, *91*, 439.

(12) Rolke, J.; Zheng, Y.; Brion, C. E.; Shi, Z.; Wolfe, S.; Davidson, E. R. *Chem. Phys.* **1999**, *244*, 1.

(13) Xu, L.-H.; Lees, R. M.; Hougen, J. T. *J. Chem. Phys.* **1999**, *110*, 3835.

(14) Čižek, J. *J. Chem. Phys.* **1966**, *45*, 4256.

(15) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(16) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(17) Scuseria, G. E.; Lee, T. J. *J. Chem. Phys.* **1990**, *93*, 5851.

(18) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(19) Hill, J.-R.; Sauer, J.; Ahlrichs, R. *Mol. Phys.* **1991**, *73*, 335.

(20) Nicholas, J. B.; Winans, R. E.; Harrison, R. J.; Iton, L. E.; Curtiss, L. A.; Hopfinger, A. J. *J. Phys. Chem.* **1992**, *96*, 10247.

(21) Darling, C. L.; Schlegel, H. B. *J. Phys. Chem.* **1993**, *97*, 8207.

(22) Stave, M. S.; Nicholas, J. B. *J. Phys. Chem.* **1993**, *97*, 9630.

(23) Bleiber, A.; Sauer, J. *Chem. Phys. Lett.* **1995**, *238*, 243.

(24) Nicholas, J. B.; Feyereisen, M. *J. Chem. Phys.* **1995**, *103*, 8031.

(25) Cypryk, M. J. *Organomet. Chem.* **1997**, *545*−*546*, 483.

(26) Ahlrichs, R.; Scharf, P.; Ehrhardt, C. *J. Chem. Phys.* **1985**, *82*, 890.

(27) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(28) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(29) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(30) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(31) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572.

(32) Peterson, K. A.; Dunning, T. H., Jr. Private communication.

(33) MOLPRO-2000 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson.

(34) Hampel, C.; Peterson, K. A.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1.

(35) Venkateswarlu, P.; Gordy, W. *J. Chem. Phys.* **1955**, *23*, 1200.

(36) Lees, R. M.; Baker, J. G. *J. Chem. Phys.* **1968**, *48*, 5299.

(37) Gerry, M. C. L.; Lees, R. M.; Winnewisser, G. *J. Mol. Spectrosc.* **1976**, *61*, 231.

(38) Iijima, T. *J. Mol. Struct.* **1989**, *212*, 137.

(39) Xu, L.-H.; Hougen, J. T. *J. Mol. Spectrosc.* **1995**, *173*, 540.

(40) Duan, Y.-B.; Wang, L.; Wu, X. T.; Mukhopadhyay, I.; Takagi, K. *J. Chem. Phys.* **1999**, *111*, 2385.

(41) Duan, Y.-B.; McCoy, A. B.; Wang, L.; Takagi, K. *J. Chem. Phys.* **2000**, *112*, 212.

(42) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.

(43) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410.

(44) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 669.

(45) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

(46) Feller, D.; Sordo, J. A. *J. Chem. Phys.* **2000**, *113*, 485.

(47) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619.

(48) Lin, C. C.; Swalen, J. D. *Rev. Mod. Phys.* **1959**, *31*, 841.

(49) Calculated values of the force constants can be obtained upon request from the author.

(50) Serrallach, A.; Meyer, R.; Günthard, Hs. H. *J. Mol. Spectrosc.* **1974**, *52*, 94.

(51) Cruz, F. C.; Scalabrin, A.; Pereira, D.; Vazquez, P. A. M.; Hase, Y.; Strumia, F. *J. Mol. Spectrosc.* **1992**, *156*, 22.

(52) Hougen, J. T.; Bunker, P. R.; Johns, J. W. C. *J. Mol. Spectrosc.* **1970**, *34*, 136.

(53) Hoy, A. R.; Bunker, P. R. *J. Mol. Spectrosc.* **1979**, *74*, 1.

(54) Mukhopadhyay, I.; Sastry, K. V. L. N.; Winnewisser, M. *Spectrochim. Acta A* **1998**, *54*, 1375.

(55) Durig, J. R.; Flanagan, M. J.; Kalasinsky, V. F. *J. Chem. Phys.* **1977**, *66*, 2775.

(56) Koput, J. *J. Phys. Chem.* **1995**, *99*, 15874.