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Equilibrium Structure and Vibrational−Rotational Energy Levels of the X^2A' SiOH/HSiO Radical System

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The equilibrium structures and anharmonic force fields of the SiOH and HSiO radicals in their $^2A'$ ground electronic state have been determined from large-scale ab initio calculations using the coupled-cluster method, RCCSD(T), with basis sets of double- through quintuple-ζ quality. The vibrational−rotational energy levels of both species were calculated by the perturbational and variational approach, and the spectroscopic constants were then determined. The rotational and centrifugal distortion constants of the HSiO radical are in good agreement with the experimental data. The predicted spectroscopic constants of the SiOH radical can be useful in the future detection of this species by vibrational−rotational spectroscopy.

1. Introduction

The SiOH and HSiO radicals are interesting species because of their involvement as possible reactive intermediates in chemical vapor deposition processes (silicon deposition and etching reactions). The SiOH radical can also serve as the simplest model of the isolated hydroxyl group of silica. Both radicals have been detected in the gas phase only by neutralization−reionization mass spectrometry.[1] The rotational spectrum of the HSiO radical was measured in the millimeter wave region and unambiguously assigned;[2] however, the corresponding spectrum of the SiOH radical could not be identified. Likewise, only the HSiO radical was proven by electron-spin-resonance spectroscopy to exist in solid argon and neon.[3] Surprisingly though, the HSiO radical was predicted in ab initio calculations[1,4−10] to be thermochemically less stable than the SiOH radical.

The energy difference, including the zero-point vibrational energy, between the SiOH and HSiO radicals was predicted to be 6.4 kcal/mol at the MP4//MP2/6-311G(3df,3pd) level,[1] 6.2 kcal/mol at the G-2 level,[9] and 9.8 kcal/mol at the CCSD(T)/TZ2P(f,d)+diff level of theory.[10] The energy barrier for the isomerization reaction SiOH → HSiO was determined to be 35.9 kcal/mol at the MP4//MP2/6-311G(3df,3pd) level[1] and 33.9 kcal/mol at the CCSD(T)/TZ2P(f,d)+diff level.[10] As a result, Srinivas et al.[1] concluded that both the SiOH and HSiO radicals “do indeed exist in the gas phase”, whereas Yamaguchi et al.[10] suggested that “the SiOH molecule should be spectroscopically detectable once it is formed”.

To our knowledge, the latter conclusion has not been confirmed experimentally to date. Therefore, the present study has been undertaken with the aim of predicting the spectroscopic properties of the SiOH radical to the highest possible accuracy and of assisting future experimental studies by vibrational−rotational spectroscopy. In this paper, we report the anharmonic force fields of the SiOH and HSiO radicals determined in ab initio calculations near the one- and *N*-particle basis-set limits as well as the corresponding vibrational−rotational energy levels calculated by the perturbational and variational approaches. The results presented may also serve as high-level benchmark data for the evaluation of density functional theory (DFT) for molecules containing the Si−O linkage.

2. Method of Calculation

The molecular parameters of the SiOH and HSiO radicals were calculated using the spin-restricted coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, RCCSD(T).[11−13] The coupled-cluster wave function was based on spin-restricted Hartree−Fock (RHF) molecular orbitals as a reference wave function. The one-particle basis sets employed were the correlation-consistent polarized valence basis sets of double- through quintuple-ζ quality, cc-pVDZ through cc-pV5Z.[14,15] The largest basis set, cc-pV5Z, consists of a (20s12p4d3f2g1h)/[7s6p4d3f2g1h] set for silicon, a (14s8p4d3f2g1h)/[6s5p4d3f2g1h] set for oxygen, and a (8s4p3d2f1g)/[5s4p3d2f1g] set for hydrogen. Only the spherical harmonic components of polarization d through h functions were used. In the correlation treatment involving only the valence electrons, the 1s-like orbital of the oxygen atom and the 1s- and 2sp-like orbitals of the silicon atom were excluded from the active space.

The core-related correlation effects were investigated using the correlation-consistent core-valence basis sets, cc-pCV*n*Z.[16,17] The basis sets of triple- and quadruple-ζ quality were employed. The cc-pCV*n*Z basis set is obtained by augmenting the standard cc-pV*n*Z basis set with a set of tight functions. The largest basis set applied, cc-pCVQZ, is obtained by augmenting the cc-pVQZ basis set with a (3s3p3d2f1g) set for silicon[17] and with a (3s3p2d1f) set for oxygen.[16] In the correlation treatment involving the core and valence electrons, only the 1s-like orbital of the silicon atom was excluded from the active space.

The RCCSD(T) calculations were performed using the MOLPRO 2000 package of ab initio programs.[18]

Vibrational−rotational energy levels of the SiOH and HSiO radicals were determined by the perturbational approach. For the SiOH species, the energy levels were also calculated variationally. Within the perturbational approach, the energy levels and spectroscopic constants were determined using the standard perturbational formulas for vibrational−rotational energy levels.[19,20] Within the variational approach, the energy

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TABLE 1: Equilibrium Molecular Parameters of X^2A' SiOH and HSiO Determined Using the RCCSD(T) Method and Various cc-pVnZ Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
SiOH				
r(SiO) (Å)	1.7048	1.6639	1.6553	1.6510
r(OH) (Å)	0.9703	0.9620	0.9601	0.9601
$\angle$(SiOH) (deg)	113.78	116.23	117.91	118.39
energy + 364 (hartrees)	−0.635019	−0.751782	−0.786096	−0.797619
HSiO				
r(SiO) (Å)	1.5738	1.5401	1.5328	1.5280
r(HSi) (Å)	1.5372	1.5254	1.5207	1.5194
$\angle$(HSiO) (deg)	118.84	119.79	119.74	119.84
ΔE^a (cm^{-1})	4921	4464	4057	3757

[a] ΔE is the energy difference between the equilibrium configurations of both isomers.

levels were calculated using the 6D vibration−rotation Hamiltonian of a triatomic molecule developed by Carter and Handy.[21−24] The Hamiltonian consists of an exact representation of the kinetic energy operator and a representation of the potential energy operator in terms of valence curvilinear coordinates. Vibrational basis set functions were formed as products of the contracted 2D stretching functions and 1D bending functions. For each value of the total angular momentum quantum number $J = N \pm S$, where N and S are the rotational and spin quantum numbers, respectively, the secular matrix was constructed using the vibrational functions and the rotational symmetric-top functions. The matrix elements were evaluated by numerical quadrature. The secular matrix was then diagonalized to obtain the vibrational−rotational-spin energy levels.

3. Results and Discussion

The ground electronic state of the SiOH or HSiO radical is a doublet A′ state (in the C_s symmetry point group). The calculated equilibrium structural parameters and total energies are given in Table 1. As in the previous theoretical studies,[1,4−10] the SiOH radical was found to be more stable than the HSiO radical. With increasing basis-set size, the calculated energy difference between the equilibrium configurations of both isomers decreases from 4921 (cc-pVDZ) to 3757 cm^{-1} (cc-pV5Z). Changes in the calculated molecular parameters beyond the quintuple-ζ basis set can be estimated using the exponential/Gaussian extrapolation formula.[25] For the SiOH radical, the total energy lowering from the cc-pV5Z to the cc-pV6Z basis set is computed in this way to be ∼4 mhartrees, whereas that to the infinite basis set is estimated to be ∼7 mhartrees. The energy difference between both isomers is computed to be 3650 cm^{-1} for the cc-pV6Z basis set, whereas the complete-basis-set (CBS) limit is estimated to be 3580 cm^{-1} (10.2 kcal/mol). The RCCSD(T)/CBS energy difference determined in this work is thus midway between the values calculated in the previous ab initio studies: 8.4 kcal/mol at the MP4//MP2/6-311G(3df,3pd) level,[1] 8.4 kcal/mol at the G-2 level,[9] and 12.1 kcal/mol at the CCSD(T)/TZ2P(f,d)+diff level.[10]

Using the same extrapolation scheme, changes in the equilibrium structural parameters beyond the quintuple-ζ basis set were estimated to about ±0.002 Å for the SiO bond length, ±0.001 Å for the OH and HSi bond lengths, and ±0.2° for the SiOH and HSiO valence angles. To investigate the effects of diffuse functions, additional calculations were performed with the augmented correlation-consistent basis sets, aug-cc-pVnZ.[26] For the largest basis set employed, aug-cc-pVQZ, inclusion of the diffuse functions insignificantly affects the calculated values of the structural parameters, with changes being smaller than the above-mentioned uncertainties. Therefore, these values can be assigned as reliable error bars for the calculated equilibrium structural parameters.

TABLE 2: Core-Related Corrections $(A - V)^a$ to the Equilibrium Molecular Parameters of X^2A' SiOH and HSiO Determined Using the RCCSD(T) Method and Various cc-pCVnZ Basis Sets

	cc-pCVTZ	cc-pCVQZ
SiOH		
r(SiO) (Å)	−0.0027	−0.0044
r(OH) (Å)	−0.0007	−0.0008
$\angle$(SiOH) (deg)	0.12	0.15
energy (hartrees)	−0.342819	−0.379289
HSiO		
r(SiO) (Å)	−0.0028	−0.0043
r(HSi) (Å)	−0.0020	−0.0028
$\angle$(HSiO) (deg)	−0.23	−0.25
ΔE^b (cm^{-1})	129	103

[a] Difference between the value determined correlating all of the electrons except Si 1s (A) and the value determined correlating only the valence electrons (V). [b] ΔE is the energy difference between the equilibriulm configurations of both isomers.

The core-related effects were computed as differences between the molecular parameters determined in calculations correlating only the valence electrons and those when the valence and core electrons were correlated, both calculations performed with the same one-particle core-valence basis set. The results obtained with the cc-pCVTZ and cc-pCVQZ basis sets are given in Table 2. Inclusion of the core-related effects decreases the equilibrium SiO and HSi bond lengths substantially, whereas the OH bond length is only slightly affected. The energy difference between both isomers increases by about 100 cm^{-1}.

The best estimate of the structural parameters of both isomers can be determined by adding the changes in the parameters due to the core-related correlation effects (cc-pCVQZ of Table 2) to the values determined with the largest valence basis set (cc-pV5Z of Table 1). The equilibrium structural parameters of the SiOH radical are estimated in this way to be $r_e(\mathrm{SiO}) = 1.646$ Å, $r_e(\mathrm{OH}) = 0.959$ Å, and $\angle_e(\mathrm{SiOH}) = 118.5°$. Likewise, the equilibrium structural parameters of the HSiO radical are estimated to be $r_e(\mathrm{SiO}) = 1.523$ Å, $r_e(\mathrm{HSi}) = 1.516$ Å, and $\angle_e(\mathrm{HSiO}) = 119.6$ °.

To characterize both isomers further, the potential energy surfaces were determined by computing the total energy in the vicinity of the equilibrium configurations at 203 points for the SiOH radical and at 137 points for the HSiO radical. The energies were determined with the cc-pV5Z basis set to an accuracy of better than 10^{-8} hartrees. The potential energy surfaces were then approximated by 3D expansions along the internal valence coordinates. The curvilinear displacement coordinates $\Delta q = q - q_e$ were used,[27] where q and q_e are, respectively, instantaneous and equilibrium values for the bond lengths and valence angles. The coordinate for the SiO stretching mode is referred to as Δr_1. The coordinate for the OH or HSi stretching mode is referred to as Δr_2, whereas that for the SiOH or HSiO bending mode is referred to as $\Delta\alpha$. The potential energy surfaces were approximated by a Taylor expansion

$$V(\Delta r_1, \Delta r_2, \Delta\alpha) = \frac{1}{2}\sum_{ij} f_{ij}\, s_i s_j + \frac{1}{6}\sum_{ijk} f_{ijk}\, s_i s_j s_k + \frac{1}{24}\sum_{ijkl} f_{ijkl}\, s_i s_j s_k s_l + \cdots \quad (1)$$

TABLE 3: Calculated Anharmonic Force Fields (in aJ Å^{-n})[a] of X^{2}A′ SiOH and HSiO

	SiOH	HSiO		SiOH	HSiO
f_{11}	4.7892	8.4340	f_{1111}	135.63	253.29
f_{22}	8.2852	2.2049	f_{2222}	362.51	43.40
f_{aa}	0.3129	0.4995	f_{aaaa}	−0.44	−1.72
f_{12}	−0.0022	0.1082	f_{1222}	2.37	−0.19
f_{1a}	0.2880	0.1752	f_{1aaa}	−0.20	0.97
f_{2a}	0.1239	0.0129	f_{2aaa}	0.90	0.32
f_{111}	−26.925	−50.843	f_{1112}	0.56	−0.86
f_{222}	−58.724	−11.762	f_{111a}	0.07	1.91
f_{aaa}	−0.497	0.153	f_{222a}	−1.67	0.16
f_{122}	0.274	0.145	f_{1122}	−2.00	0.65
f_{1aa}	−0.158	−0.595	f_{11aa}	−0.78	−1.11
f_{2aa}	−0.077	−0.361	f_{22aa}	0.68	−0.72
f_{112}	−0.250	−0.219	f_{12aa}	0.29	0.48
f_{11a}	−0.581	0.155	f_{122a}	0.97	−0.20
f_{22a}	−0.169	0.003	f_{112a}	0.10	0.32
f_{12a}	−0.105	−0.146			

[a] Coordinates Δr_1 and Δr_2 are in angstroms; $\Delta\alpha$ is in radians.

TABLE 4: Fundamental and Harmonic Wavenumbers (in cm^{-1}) and the Ground-State Rotational and Quartic Centrifugal Distortion Constants (in MHz) of X^{2}A′ SiOH and HSiO

	SiOH	HSiO	
	calcd[a]	calcd[a]	exptl[b]
ν_1	3667	1828	
ν_2	869	1166	
ν_3	743	622	
ω_1	3851	1961	
ω_2	881	1181	
ω_3	776	651	
A	817 400	317 310	312 105
B	16 871	19 861	19 887.01
C	16 482	18 613	18 605.42
Δ_N	0.0268	0.0240	0.02475
Δ_{NK}	2.57	1.12	1.309
Δ_K	1095	133	147
δ_N	0.0005	0.0019	0.00220
δ_K	1.22	0.89	1.28

[a] Determined by the pertubational approach using the anharmonic force fields given in Table 3. [b] From the analysis of the rotational spectrum in ref 2.

where $\{s_i\}$ are the coordinates Δr_1, Δr_2, and $\Delta\alpha$. The expansion coefficients f were determined from a least-squares fit of eq 1 to the computed total energies. The optimized values of the force constants, representing the complete quartic anharmonic force fields of both isomers, are listed in Table 3. The root-mean-square deviations of the fits were about 4 μhartrees (0.9 cm^{-1}). The calculated potential energy surfaces were modified by replacing adjusted values of the equilibrium structural parameters with the "best" estimates discussed above. The modified anharmonic force fields were then used to determine the vibrational−rotational energy levels by the perturbational approach.

The calculated fundamental wavenumbers and spectroscopic constants of the main isotopomers of the SiOH and HSiO radicals are given in Table 4. All of the normal modes of both isomers appeared to be characteristic. The ν_1, ν_2, and ν_3 modes correspond to the OH/HSi stretching, SiO stretching, and SiOH/HSiO bending vibrations, respectively. The normal modes of the HSiO radical were found to interact via the Fermi-type resonances. Resonance of the type $2\omega_i \approx \omega_j$ occurs for the ν_3 and ν_2 modes, with the off-diagonal element of the energy matrix predicted to be 6.8 cm^{-1}. Resonance of the type $\omega_i + \omega_j \approx \omega_k$ occurs for the ν_2, ν_3, and ν_1 modes, with the off-diagonal element of the energy matrix predicted to be 11.8 cm^{-1}.

The calculated rotational and quartic centrifugal distortion constants of the HSiO radical are in good agreement with those determined by Izuha et al.[2] The predicted rotational constants B and C are within ±20 MHz of the experimental values, whereas the rotational constant A is overestimated by as much as 5 GHz. However, A appeared to be very sensitive to small changes in the equilibrium structural parameters. Varying the HSi bond length by ±0.001 Å results in a change in A of ∓0.4 GHz, whereas varying the HSiO angle by ±0.2° results in a still larger change of ±1.5 GHz. The corresponding changes in B and C are smaller than ∓10 MHz. Varying the SiO bond length by ±0.002 Å influences all of the rotational constants to a similar extent, about ±40 MHz. The calculated changes in the rotational constants are thus consistent with the uncertainties in the predicted equilibrium structural parameters discussed above. The discrepancy in A may also result from the inability of the quartic force field and/or second-order perturbational approach to account fully for the anharmonicity of the HSiO bending vibration (see below). The equilibrium parameters calculated by Izuha et al.,[2] r_e(SiO) = 1.5286 Å and $\angle_e$(HSiO) = 116.8°, differ significantly from those predicted in this study, r_e(SiO) = 1.523 Å and $\angle_e$(HSiO) = 119.6°. This is likely due to the equilibrium HSi bond length of 1.4971 Å, which was assumed by Izuha et al.[2] following the CISD/TZ2P(f,d)+diff calculation by Yamaguchi et al.[10] The equilibrium HSi bond length is estimated here at the RCCSD(T)/spdfgh level of theory to be substantially longer, r_e(HSi) = 1.516 Å. The harmonic wavenumbers for the SiO stretching and HSiO bending modes were calculated by Izuha et al.[2] to be 1180 and 555 cm^{-1}, respectively. The former value is identical, whereas the latter value is smaller than those calculated here at the RCCSD(T)/spdfgh level by as much as 100 cm^{-1}. For comparison, the harmonic wavenumbers for the SiO stretching and HSiO bending modes were predicted at the CISD/TZ2P(f,d)+diff level[10] to be 1256−1272 and 713−723 cm^{-1}, respectively.

A similar analysis performed for the SiOH radical indicated that the predicted rotational constant A was also very sensitive to small changes in the equilibrium structural parameters. Varying the OH bond length by ±0.001 Å or the valence angle SiOH by ±0.2° results in a change in the constant A of ∓1.7 or ±3.7 GHz, respectively. The corresponding changes in constants B and C do not exceed ±5 MHz. As for the HSiO radical, varying the SiO bond length by ±0.002 Å results in similar changes in all of the rotational constants by about ±40 MHz.

Note that the equilibrium structural parameters and fundamental wavenumbers predicted in this study for the HSiO radical are quite different from those determined previously[28] for the silaformyl anion, HSiO$^-$. The equilibrium structural parameters of the silaformyl anion were calculated at the CCSD(T)/spdfgh level of theory to be r_e(SiO) = 1.563 Å, r_e(HSi) = 1.609 Å, and $\angle_e$(HSiO) = 106.0 °. The ν_1, ν_2, and ν_3 fundamentals were determined to be 1440, 1049, and 791 cm^{-1}, respectively. Electron attachment $HSiO + e^- \rightarrow HSiO^-$ thus results in a substantial lengthening of the SiO and HSi bonds and a narrowing of the HSiO angle. The changes in the fundamental wavenumbers seem to reflect those in the corresponding equilibrium structural parameters. Using the results of our previous study,[28] the adiabatic electron affinity of the HSiO radical at 0 K is calculated at the CCSD(T)/cc-pV5Z level to be 1.967 eV. An upper limit for the electron affinity of the HSiO radical was estimated experimentally by Gronert et al.[29] to be 1.1 eV.

To assist in future experimental determinations of the equilibrium rotational constants, Table 5 lists the predicted

TABLE 5: Vibration−Rotation Interaction Constants (in MHz) of X^2A' SiOH and HSiO Determined by the Perturbational Approach

	$i = 1$	$i = 2$	$i = 3$
SiOH			
α_i^A	39 590	1670	−112 040
α_i^B	17.7	122.6	−28.7
α_i^C	34.0	114.1	25.2
HSiO			
α_i^A	12 320	1408	−13 060
α_i^B	21.9	135.1	−83.6
α_i^C	56.7	122.5	44.8

TABLE 6: Fundamental Term Values (in cm^{-1}) and the Ground-State Rotational and Quartic Centrifugal Distortion Constants (in MHz) of X^2A' SiOH and SiOD[a]

	SiOH	SiOD
$E(1, 0, 0)$	3694	2714
$E(0\ 1, 0)$	871	857
$E(0, 0, 1)$	739	560
A	826 940	447 680
B	16 873	15 679
C	16 471	15 082
Δ_N	0.0266	0.0225
Δ_{NK}	3.07	0.89
Δ_K	2169	573
δ_N	0.0008	0.0014
δ_K	1.89	1.35

[a] Determined by the variational approach, the term values are labeled by the (v_1, v_2, v_3) vibrational quantum numbers.

values of the vibration−rotation interaction constants of the SiOH and HSiO radicals. For the SiOH species, the rotational constant *A* strongly depends on the excitation of the SiOH bending mode (ν_3).

For the SiOH radical, the vibrational−rotational energy levels were also calculated by the variational approach. The internal coordinates for the SiO and OH stretching modes were chosen as Simons−Parr−Finlan coordinates[30] $s = (r - r_e)/r$, where r and r_e are the instantaneous and equilibrium bond lengths, respectively. For the SiOH bending mode, a curvilinear displacement coordinate from a linear SiOH reference configuration was used. The potential energy surface was approximated by a Taylor expansion analogous to that given by eq 1. The expansion coefficients[31] were determined from a least-squares fit using the same set (203 data points) of the computed total energies. As for the perturbational approach, the adjusted "equilibrium" SiO and OH bond lengths at the linear SiOH reference configuration were corrected for the effects of core-electron correlation. The vibrational−rotational-spin energy levels were then calculated variationally for the rotational quantum number $N = 0-4$. The spin-doubling splittings were averaged out, and the predicted vibrational−rotational term values were used to calculate the spectroscopic constants. The rotational and centrifugal distortion constants were determined by fitting the averaged rotational energy levels of the ground vibrational state using Watson's Hamiltonian in the *A* represention.[32]

Table 6 lists the predicted fundamental term values and the ground-state spectroscopic constants for the main isotopomer, SiOH, and for the deuterated species, SiOD. The largest differences between the variational and perturbational approach occur for the fundamental term value of the OH stretching mode and for the spectroscopic constants related to rotation about the molecular *a* axis, *A* and Δ_K. This is likely the result of approximations inherent to the applied second-order perturbational method and large anharmonicities of the ν_1 and ν_3 modes.

TABLE 7: Equilibrium Molecular Parameters of X^2A' SiOH and HSiO Determined at the RHF, CASSCF, and MRCI+Q Levels of Theory Using the cc-pV5Z Basis Set

	RHF	CASSCF	MRCI+Q
SiOH			
r(SiO) (Å)	1.6256	1.6620	1.6645
r(OH) (Å)	0.9399	0.9652	0.9650
∠(SiOH) (deg)	121.83	115.74	114.87
energy + 364 (hartrees)	−0.411909	−0.509693	−0.790203
HSiO			
r(SiO) (Å)	1.4852	1.5276	1.5319
r(HSi) (Å)	1.4903	1.4956	1.5196
∠(HSiO) (deg)	123.86	123.04	119.76
ΔE^a (cm^{-1})	6266	1640	2791

[a] ΔE is the energy difference between the equilibrium configurations of both isomers.

The above-discussed large sensitivity of the rotational constant *A* to small changes in the equilibrium structural parameters suggests that the differences in the spectroscopic constants reflect the level of sophistication of the perturbational and variational treatment of the SiOH bending vibration. The predicted SiO stretching fundamental of the SiOD species (857 cm^{-1}) is quite close to the wavenumber of a strong infrared absorption band appearing at 868 cm^{-1} on photolysis of SiD_4 and O_3 in solid argon.[33] This band was tentatively assigned by Withnall and Andrews[33] to the SiOD radical. The ^{18}O isotopic shift of the SiO stretching fundamental is predicted here to be −28 cm^{-1}, being slightly larger than the experimentally observed shift of −24 cm^{-1}.[33]

Turning to the energetics of the SiOH and HSiO radicals, the vibrational corrections can be calculated. Using the perturbational approach, the zero-point vibrational energies of the SiOH and HSiO species were determined to be 2724 and 1870 cm^{-1}, respectively. The zero-point vibrational energy of the SiOH species was calculated variationally to be 2715 cm^{-1}. Including the correction for the effects of core-electron correlation discussed above, the energy separation between the SiOH and HSiO radicals at 0 K is thus computed to be 2830 cm^{-1} (8.1 kcal/mol). This value is midway between the previous best estimates of Srinivas et al.[1] (6.4 kcal/mol), Darling and Schlegel[9] (6.2 kcal/mol), and Yamaguchi et al.[10] (9.8 kcal/mol).

Finally, it is interesting to examine the character of the electronic wave functions of the SiOH and HSiO radicals. The coupled-cluster $\mathcal{T}_1$ diagnostic[34] was determined for the equilibrium configurations of the SiOH and HSiO radicals to be 0.016 and 0.034, respectively. The latter value suggests that the nondynamical correlation effects may be important for the HSiO species. Therefore, the equilibrium structures and energetics of both isomers were investigated using both a single- and multireference approach. The multireference treatment included the complete active space self-consistent-field (CASSCF) approach[35] and the internally contracted multireference configuration interaction (MRCI).[36,37] In these calculations, the reference wave function consisted of a full valence complete active space. The wave function thus included all of the excitations of the 11 valence electrons in the 9 molecular orbitals corresponding to the valence atomic sp orbitals of the silicon and oxygen atoms and the 1s orbital of the hydrogen atom. The multireference Davidson correction[38] to the calculated energy (MRCI+Q) was employed to account approximately for the effects of higher excitations. The results of calculations at the spin-restricted Hartree−Fock (RHF) level and both of the multireference levels of theory are presented in Table 7. Surprisingly though, the nondynamical correlation effects appeared to be more important for the SiOH radical than for the HSiO radical. On going from the RHF to CASSCF level, the equilibrium SiO and OH bond lengths of the SiOH species increase by as much as 0.036 and 0.025 Å, respectively. The corresponding change in the equilibrium SiOH angle amounts to −6.1°. For the HSiO species, inclusion of the nondynamical correlation effects substantially changes only the equilibrium SiO bond length, which increases by 0.042 Å. The CI weight of the SCF configuration in the CASSCF wave function was found to be quite high—0.964 and 0.942 for the SiOH and HSiO species, respectively. The excited-state configurations appeared to be only moderately important. For the SiOH radical, the weights of the leading configurations $(9a')^2 \rightarrow (11a')^2$ and $(2a'')^2 \rightarrow (3a'')^2$ are both 0.006. For the HSiO radical, there is only one important configuration: $(2a'')^2 \rightarrow (3a'')^2$ with a weight of 0.011. Inclusion of the dynamical correlation effects through the MRCI+Q framework appeared to be important only for the HSiO radical. On going from the CASSCF to MRCI+Q level, the equilibrium HSi bond length increases by 0.024 Å, whereas the equilibrium HSiO angle changes by −3.3°. The weights of the reference wave functions in the MRCI wave functions were found to be 0.927 and 0.930 for the SiOH and HSiO species, respectively. Therefore, it is resonable to conclude that the single-reference coupled-cluster approach, including single through triple excitations, applied in this study seems to be adequate for describing the electronic structure of the SiOH and HSiO radicals. Inclusion of both nondynamical and dynamical correlation effects significantly changes the energy separation between the SiOH and HSiO radicals. The energy difference was calculated to be larger than 6200 cm^{-1} (17.9 kcal/mol) at the RHF level. It decreases by a factor 3.8 on going from the RHF to CASSCF level and increases by a factor 1.7 on going from the CASSCF to MRCI+Q level. The energy separation calculated at the MRCI+Q/cc-pV5Z level is smaller than that determined at the RCCSD(T)/cc-pV5Z level by nearly 1000 cm^{-1}.

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