Anharmonic Force Fields and Accurate Thermochemistry of H_2SiO, *cis*-HSiOH, and *trans*-HSiOH

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The energetics, structure, and anharmonic force fields of the isomers H_2SiO, *cis*-HSiOH, and *trans*-HSiOH have been studied using coupled cluster methods and basis sets of up to spdfgh quality and including inner-shell correlation. Inner polarization functions on Si were found to be of crucial importance for the correct reproduction of computed properties. At the basis set limit at 0 K, the H_2SiO isomer is more stable than the two others by about 0.5 kcal/mol. *cis*-HSiOH is marginally more stable than *trans*-HSiOH (0.05 kcal/mol); deuteration shifts the equilibrium toward the trans form. The computed fundamentals for the {H,D} and {^{16}O,^{18}O} isotopomers closely track the experimental ones in an argon matrix, except for a few reassignments which impose themselves. Our best computed geometry for H_2SiO, $r(SiH) = 1.4733$ Å, $r(SiO) = 1.5140$ Å, and $\theta(HSiH) = 111.97°$, agrees within experimental error with the most recent determination. Using a recently proposed Schwartz-type extrapolation, we obtain the following $\sum D_0$ values (including core correlation, atomic spin−orbit splitting, and anharmonic zero-point energy): SiO 189.9, SiH_2 (a $^3B_1$) 124.5 kcal/mol, SiH_2 (X $^1A_1$) 145.80 kcal/mol, and H_2SiO 292.6 kcal/mol, which we expect to be accurate to about 0.3 kcal/mol. The former three agree with experiment to within the latter's uncertainty but have smaller error bars. As a byproduct, we obtain a basis set limit for the singlet−triplet splitting in silylene, $T_0 = 21.35 \pm 0.1$ kcal/mol. To assist future gas-phase infrared and microwave studies on silanone and hydroxysilylene, computed anharmonic spectroscopic constants for all species concerned have been presented, and complete anharmonic force fields are available as Supporting Information.

I. Introduction

While formaldehyde, H_2CO, and its aldehyde and ketone derivatives do not require an introduction to any chemist, much less is known about their silicon analogues, H_2SiO (silanone) and the silanones.

Two isomers of hydroxysilylene, HSiOH, were tentatively identified in an argon matrix by Ismail et al.[1] This identification was bolstered by further experiments by Withnall and Andrews,[2] who also identified the H_2SiO molecule. They were aided in their assignment by small basis set SCF frequency calculations by Kudo and Nagase.[3] The first high-resolution rotational spectrum of H_2SiO was reported in 1994 by Bailleux et al.,[4] who were aided in their search by two ab initio studies, specifically a CCSD/TZ2P(f,d) (coupled cluster with all single and double substitutions[5]) computed geometry by Ma and Schaefer (MS)[6] and SCF level ab initio values[7] for the centrifugal distortion constants. In a followup on that study, Bogey et al.[8] obtained a gas-phase geometry of H_2SiO for the first time.

There has been some controversy in the literature about the relative energies of the three isomers H_2SiO, *cis*-HSiOH, and *trans*-HSiOH, which are nearly isoenergetic. Early ab initio studies[3,9−12] suggested that HSiOH would be more stable than H_2SiO. Darling and Schlegel,[13] using the semiempirical Gaussian-2 (G2) model,[14] first suggested that H_2SiO might actually be more stable, and MS arrived at the same conclusion. However, the energy difference of 0.5 kcal/mol would normally be regarded as within the error limits of the largest calculations they performed, which were at the CCSD(T) (i.e., CCSD with a quasiperturbative account for connected triple excitations[15]) level with a basis set of spdf quality. In addition, MS suggested that, contrary to previous assumptions, *cis*-HSiOH would be slightly more stable than *trans*-HSiOH and that the bands assigned by WA to *trans*-HSiOH actually belong to *cis*-HSiOH and conversely. One answer to the question as to why *cis*-HSiOH and *trans*-HSiOH could not be found in the gas phase was proposed by Ma, Allinger, and Schaefer (MAS),[16] who found that *cis*-HSiOH forms a strongly bonded dimer.

The tendency of H_2SiO to polymerize has been known for some time.[17,18] It has greatly plagued the ongoing effort (for example, ref 19) of the Milstein group at the Weizmann Institute to synthesize substituted silanones.

Besides the potential usefulness of silanones as organic reagents[20] and the interest from a theoretical chemistry point of view, [Si,O,H] systems in general are presumed to play a role in ionospheric[21] and interstellar[22] chemistry, as well as in recent developments in thin silicon plasma film etching technology[23] and the synthesis of ceramic powders.[24] Furthermore, silanone is implied as a possible intermediate in the combustion of silane.[13]

The purpose of the present paper is two-fold. The first is to offer accurate quartic force fields for the three isomers to assist further spectroscopic work. It has been shown repeatedly (for example, refs 25, 26) that CCSD(T) calculations with large basis sets can yield fundamental frequencies to within a few cm^{-1}, thus enabling unambiguous assignments in all but the most

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cluttered spectra. The second is a study of the relative energetics and thermochemistry of the species concerned near the basis set limit.

II. Methods

All coupled cluster calculations were carried out using the MOLPRO[27] ab initio package, release 96.4 with the tripu and scfpr0 patches installed,[28] running on a DEC Alpha 500/500 workstation and an SGI Origin 2000 minisupercomputer at the Weizmann Institute of Science. These calculations employed the implementation by Hampel et al.[29] of the CCSD(T) electron correlation method.[15,30] The acronym stands for coupled cluster with all single and double substitutions[5] augmented by a quasiperturbative account for triple excitations.[15] From extensive studies (see ref 31 for a review) this method is known to yield total energies very close to the exact solution within the given basis set as long as nondynamical correlation effects are not overly prominent. The $\mathcal{T}_1$ diagnostic[32] is used here as a gauge for the importance of such effects.

Calculations including only valence correlation were carried out using correlation consistent polarized n-tuple-ζ (cc-pVnZ) basis sets of Dunning and co-workers.[33,34] The contracted basis set sizes for [second-row/first-row/hydrogen] atoms are [4s2p1d/3s2p1d/2s1p] for the cc-pVDZ (double-ζ) basis set, [5s4p2d1f/4s3p2d1f/3s2p1d] for the cc-pVTZ (triple-ζ) case, [6s5p3d2f1g/5s4p3d2f1g/4s3p2d1f] for the cc-pVQZ (quadruple-ζ) case, and [7s6p4d3f2g1h/6s5p4d3f2g1h/5s4p3d2f1g] for the cc-pV5Z (quintuple-ζ) basis set. For brevity, we shall denote these basis sets VDZ, VTZ, VQZ, and V5Z throughout the paper.

Considering that H_2SiO is a fairly polar molecule, additional calculations were carried out using the cc-pVnZ+aug(O) basis set, which is a combination of the regular cc-pVnZ basis set for H and Si with the aug-cc-pVnZ (augmented cc-pVnZ[35]) basis set on O. The "aug" refers to the addition of a single diffuse function of each angular momentum to the cc-pVnZ basis set. For brevity, these basis sets will be referred to in the present work as AVTZ, AVQZ, and AV5Z.

In previous work on SO_2[26] and some second-row diatomics,[36] it was found that the addition of inner polarization functions (IPFs) to the second-row atoms was essential for obtaining high-accuracy results. In the present work, the IPFs were chosen in two ways. The first involves gradual basis set saturation with even-tempered sequences of hard d and f functions. The exponents are chosen as $2.5^n\alpha$, where α is the highest exponent of that angular momentum present in the parent basis set. Such basis sets are indicated, for example, as VQZ+2d1f for a VQZ basis set with two extra hard d and one extra hard f functions on silicon.

The second choice involves merely adding the hardest d function from the V5Z basis set (which is nearly optimum for the effect[36]) to the VDZ, VTZ, and VQZ basis sets. This is denoted by the acronyms VDZ+1, VTZ+1, and VQZ+1, with V5Z+1 and V5Z being equivalent by definition. Since this function appeared to recover a large share of the effect in previous work in second-row molecules,[36] it offered an option for keeping the basis set size in the anharmonic force field calculations down to a tractable size.

Core correlation was included using the Martin-Taylor basis set.[37] This is generated by completely uncontracting the VTZ basis set and adding a single high-exponent p function and two even-tempered series, one of three d functions and another of two f functions. The exponents are defined as $3^n\alpha$ (rounded to the nearest integer or half-integer), where α represents the highest exponent of that angular momentum already present in the VTZ basis. For first-row compounds, it was found[38] that such a basis set recovers essentially the complete effect of core correlation. It was also successfully applied to assess the core correlation effect on the properties of various electronic states of the SiN molecule[39] and on the anharmonic force field of SO_2. For brevity, CCSD(T)/Martin-Taylor calculations with only the valence electrons correlated are denoted CCSD(T)/MTnocore, while in CCSD(T)/MTcore calculations, all orbitals except for the silicon (1s)-like orbital (which lies too deep to interact appreciably with the valence shell) have been correlated.

Geometry optimizations were carried out by repeated multivariate parabolic interpolation with step sizes of 0.001 bohr or radian, to a convergence threshold of about 10^{-5} bohr or radian. Quartic force fields for *cis*- and *trans*-HSiOH were set up by finite differences in the valence coordinates. For H_2SiO (the "as-" isomer), we used the symmetry coordinates $S_{1,5} = (r(\mathrm{SiH}_1) \pm r(\mathrm{SiH}_2))/\sqrt{2}$, $S_2 = R(\mathrm{SiO})$, $S_{3,6}$ $(\theta(\mathrm{OSiH}_1) \pm \theta(\mathrm{OSiH}_2))/\sqrt{2}$ and S_4 the angle between the Si=O bond and the HSiH plane. Step sizes of 0.01 Å or radian were used. The displaced geometries were generated, and the transformation of the internal coordinate force field to Cartesian coordinates was carried out, with the aid of the INTDER program.[40] A vibrational second-order perturbation theory analysis[41] was then carried out using a modified version of SPECTRO.[42,43]

In addition, some calculations were carried out for comparison using the B3LYP (Becke 3-parameter-Lee−Yang−Parr[44,45]) density functional[46,47] method as implemented in Gaussian 94.[48] While not yielding the kind of accuracy that has come to be expected from large basis set CCSD(T) calculations, it has been shown to yield harmonic frequencies (for example, ref 49) and infrared intensities[50] in very good agreement with experiment for most molecules.

III. Results and Discussion

A. Spectroscopy. *1. SiO ($X\ ^1A_1$).* To obtain a realistic assessment of the accuracy that can be achieved, we will briefly consider the SiO diatomic, for which very accurate rovibrational constants are available.[51] The relevant data can be found in Table 1. (For detailed references on the great astrophysical importance of this molecule, see ref 52. The unique electrical properties of SiO have been the subject of considerable theoretical interest.[53])

The anharmonic constant $\omega_e x_e$ remains fairly constant across basis sets from VTZ on up and, therefore, will not be considered further. Basis set dependence in the rovibrational coupling constant α_e mainly reflects the latter's dependence on r_e. Our discussion will therefore focus on ω_e and r_e.

At the CCSD(T)/VTZ level, r_e is 0.0168 Å too long and ω_e 16.7 cm^{-1} too low. Enlarging the basis set to VQZ reduces these errors by 0.0094 Å and -6.2 cm^{-1}; going one step further to V5Z still leaves r_e 0.0060 Å too long, but ω_e is now only 2.2 cm^{-1} too low. Given however that SiO is a very polar molecule ($\mu_e = 3.088$ D[51]), the use of AVnZ basis sets would appear mandatory. At first sight, this appears to worsen agreement with experiment for the lower terms in the series: errors in r_e are $+0.0192$ (AVTZ), $+0.0112$ (AVQZ), and $+0.0631$ (AV5Z) Å, and those in ω_e -26.9 (AVTZ), -10.0 (AVQZ), and -3.7 cm^{-1} (AV5Z).

While agreement for AV5Z is quite satisfactory, we are obviously unable to calculate a quartic force field with such a large basis set for H_2SiO, let alone the less symmetric *cis*- or *trans*-HSiOH species. Even adding a single inner polarization function, however, greatly improves basis set convergence, particularly in r_e: the VTZ+1 results are 0.0089 Å too long for r_e and 8.3 cm^{-1} too low for ω_e, bringing results within the 10

TABLE 1: CCSD(T) Basis Set Calibration for the Properties of the SiO($X^1\Sigma^+$) Diatomic

	D_e (kcal/mol)	r_e (Å)	ω_e (cm^{-1})	α_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
VTZ	180.80	1.526 55	1224.9	0.004 88	5.83
VTZ+d	182.87	1.519 09	1233.2	0.004 96	5.91
VQZ	187.07	1.520 06	1235.4	0.004 91	5.85
VQZ+d	187.95	1.517 06	1236.5	0.004 91	5.79
VQZ+2d	188.27	1.516 33	1237.8	0.004 91	5.79
VQZ+2d1f	188.45	1.515 43	1238.2	0.004 94	5.80
V5Z	189.88	1.515 68	1239.4	0.004 93	5.85
V5Z+2d1f	190.23	1.514 62	1240.4	0.004 93	5.83
V∞Z[a]	194.14	1.48 83			
V∞Z+dfg...	191.71	1.51 42			
AVTZ	182.97	1.528 98	1214.7	0.004 92	5.84
AVTZ+d	184.92	1.522 19	1221.6	0.004 96	5.82
AVQZ	188.08	1.520 93	1231.6	0.004 93	5.86
AVQZ+2d1f	189.45	1.516 38	1234.9	0.004 95	5.82
AV5Z	190.38	1.516 05	1237.9	0.004 93	5.85
AV5Z+2d1f	190.71	1.515 03	1238.9	0.004 94	5.83
AV∞Z	193.87	1.4983			
AV∞Z+dfg...	191.53	1.5143			
VTZ+1	183.16	1.518 58	1233.2	0.004 93	5.86
VQZ+1	188.01	1.516 91	1236.7	0.004 91	5.80
V∞Z+1	191.99	1.4991			
AVTZ+1	185.25	1.521 57	1222.7	0.004 93	5.84
AVQZ+1	189.07	1.517 67	1233.3	0.004 93	5.82
AV∞Z+1	191.57	1.513 9			
MTnocore	185.48	1.513 51	1244.7	0.004 96	5.94
MTcore	186.21	1.509 31	1250.9	0.004 99	5.99
best estimate[b]	192.72	1.4949	1245.6[e]		
best estimate[c]	192.30	1.5099	1243.1[e]		
best estimate[d]	192.44	1.5101	1245.1[e]		
expt[f] [51]	192.9	1.509 739	1241.557	0.005 037 7	5.966

[a] V∞Z denotes VnZ+1 (n =T,Q,5) results extrapolated to the infinite-basis set valence correlation CCSD(T) limit using the formula[54] $A + B/(n + 1/2)^C$, and analogously for similar acronyms. [b] V∞Z+1 (n = T,Q,5) results together with difference between MTcore and MTnocore results. [c] The same with AV∞Z. [d] The same using AVTZ+d, AVQZ+2d1f, and AV5Z+3d2f1g results. [e] Largest basis set in series plus ω (MTcore) − ω (MTnocore). [f] The effect of atomic spin−orbit splitting has been removed from the results for D_e.

cm^{-1} accuracy bracket usually achieved for first-row compounds[31] at a quite small additional computational cost. For VQZ+1, this drops to +0.0072 Å and −4.9 cm^{-1}, respectively.

From comparing CCSD(T)/MTcore and CCSD(T)/MTnocore calculations, we find that the differential effect of inner-shell correlation amounts to −0.0042 Å on r_e and +6.2 cm^{-1} on ω_e. Actually, the CCSD(T)/MTcore bond length is only 0.0004 Å shorter than the experimental value. It should be noted that the basis set requirements for inner-shell correlation and inner polarization are quite similar, at least as far as the d and f functions are concerned. Therefore, the MT basis can be considered converged in the inner polarization effect as well, and the exaggerated ω_e (by 9.3 cm^{-1}) at the CCSD(T)/MTcore level reflects mainly the absence of diffuse functions which were seen above to lower ω_e. A "best estimate" result can be obtained by carrying out an extrapolation to the valence-correlation basis set limit using, for example, the Schwartz-type three-point extrapolation[54] $A + B/(l + 1/2)^C$, (with l the maximum angular momentum present in the basis set), then adding in the inner-shell correlation as an additive correction.

Extrapolations on a series that does not include both inner polarization functions and diffuse functions are seen to overcorrect severely because these effects are partially accounted for in the larger basis sets but barely in the smaller ones, leading to an artificially large final basis set increment. By contrast, convergence with the AVnZ+1 series is quite smooth, and the best estimates $r_e = 1.5099$ Å and $\omega_e = 1243.1$ cm^{-1} are within −0.0002 Å and +1.5 cm^{-1}, respectively, of experiment. Extrapolation on the VTZ+d, VQZ+2d1f, and V5Z+2d1f series yields a similar result. It is therefore clear that the intrinsic error of the CCSD(T) method for these properties is quite small, despite the rather strong nondynamical correlation effects ($\mathcal{T}_1 = 0.039$). Given that, on one hand, the $\mathcal{T}_1$ values of 0.031 and 0.023 for *cis*- and *trans*-HSiOH indicate weaker and much weaker nondynamical correlation effects, respectively, than in SiO, and, on the other hand, that basis set convergence should improve in the bond order series Si≡O, Si═O, Si−O, it would appear that the methods considered in the present work are adequate for the task at hand.

2. H_2SiO. To the author's knowledge, this is the first ab initio anharmonic vibrational study on any isomer of H_2SiO published in the open literature.

Computed geometries and fundamentals of H_2SiO as a function of the basis set are given in Table 2 in the interest of compactness, anharmonic spectroscopic constants are given only for the highest level of theory considered in this work (CCSD(T)/VQZ+1) in Table 3.

At the CCSD(T)/VTZ level, we find a strong $\omega_4 \approx \omega_6$ Coriolis resonance along the *A* axis (just like in formaldehyde[55]), as well as a weak one $\omega_3 \approx \omega_4$ along the *B* axis. Computed rotational properties become qualitatively absurd unless the former resonance is taken into account.

Contrary to the convoluted Fermi resonance picture in formaldehyde, we here find only a strong $\nu_3+\nu_2 \approx \nu_1$ interaction, as well as a rather weak $2\nu_3 \approx \nu_1$ resonance. Therefore, there is no real problem here with a vibrational treatment by second-order pertubation theory.

The only vibrational bands observed by Withnall and Andrews (WA) for H_2SiO were the Si═O stretch at 1202 cm^{-1} and a band at 697 cm^{-1}, which they assigned to either the $OSiH_2$ wag or the SiH_2 rock, with their preferred assignment being the rock. Our computed fundamentals for Si═O stretch, $OSiH_2$ wag, and H_2 Si rock are 1190.2, 688.4, and 675.1 cm^{-1}, which seems to confirm the WA assignment for the upper band but to indicate that the lower band may be the out-of-plane band

TABLE 2: Basis Set Convergence at the CCSD(T) Level of Computed Fundamentals (cm^{-1}) and Geometry (Å, deg) of H_2SiO[a]

	VTZ	VTZ+1	AVTZ+1	VQZ	VQZ+1	AVQZ+1	AVQZ+2d1f	MTnocore	MTcore	best	expt
$\nu_2+\nu_3$	2185.5	2198.3	2185.2	2194.8	2198.4						
ν_1	2153.2	2152.7	2151.2	2162.3	2162.0						
ν_2	1190.2	1200.6	1189.9	1200.0	1202.9						
ν_3	991.8	996.5	992.5	991.3	992.9						
ν_4	688.4	693.1	693.2	690.3	691.6						
ν_5	2174.7	2174.8	2177.1	2184.2	2186.2						
ν_6	675.1	678.6	675.1	678.5	679.5						
r(SiH)	1.482 00	1.478 86	1.479 00	1.479 11	1.478 00	1.478 09	1.477 72	1.477 08	1.473 26	1.473 26	1.472 ± 0.002
r(SiO)	1.531 89	1.523 47	1.526 62	1.525 46	1.522 09	1.522 95	1.521 64	1.518 33	1.513 98	1.513 98	1.515 ± 0.002
θ (HSiH)	111.278	111.320	111.674	111.794	111.764	111.869	111.857	111.427	111.537	111.967	112.0 ± 0.2

[a] The experimental geometry[8] is an r_m geometry, which should[78] be close to an r_e geometry.

TABLE 3: Best Computed Zero-Point Energies (cm^{-1}), Harmonic Frequencies (cm^{-1}), Anharmonicity Constants (cm^{-1}), Rotational Constants (MHz), Rovibrational Coupling Constants (kHz), Quartic (kHz) and Sextic (Hz) Centrifugal Distortion Constants, and Coriolis Interaction Constants (cm^{-1}) for H_2SiO, *cis*-HSiOH, and *trans*-HSiOH

	H_2SiO CCSD(T)/VQZ+1	*cis*-HSiOH CCSD(T)/AVTZ+1	*trans*-HSiOH CCSD(T)/AVTZ+1
ZPE[a]	4032.9	4449.5	4528.7
ω_1	2254.1	3857.8	3851.2
ω_2	1218.9	1958.9	2034.1
ω_3	1010.3	969.7	971.1
ω_4	699.8	854.6	851.8
ω_5	2268.1	752.5	808.8
ω_6	686.4	628.6	670.0
X_{11}	−18.269	−84.737	−83.987
X_{12}	−1.671	0.490	−1.346
X_{13}	−17.531	−8.726	−3.205
X_{14}	−6.824	−0.830	−0.545
X_{15}	−69.337	−2.641	−7.484
X_{16}	−6.418	−12.517	−7.597
X_{22}	−5.232	−34.717	−34.976
X_{23}	−2.208	−13.317	−12.269
X_{24}	−4.204	−0.315	1.624
X_{25}	0.989	−8.271	−8.730
X_{26}	−3.808	−3.643	−7.649
X_{33}	0.500	−3.050	−8.515
X_{34}	−0.777	−3.186	−4.326
X_{35}	−12.680	−20.093	−16.487
X_{36}	−3.661	−3.959	−12.100
X_{44}	−0.211	−4.604	−4.717
X_{45}	−8.637	−1.378	−4.215
X_{46}	4.721	−2.856	−3.620
X_{55}	−17.299	−4.009	−1.190
X_{56}	−5.062	−2.562	0.895
X_{66}	0.126	−8.106	−11.164
k_{133}	−56.997		
k_{123}	34.687		
k_{233}		32.754	
A_e	167 460.75	172 034.00	175 220.47
B_e	18 538.25	16 270.68	16 260.74
C_e	16 690.57	14864.79	14879.87
α_1^A	2189.687	1612.552	2190.622
α_2^A	38.403	3861.909	3581.095
α_3^A	−1069.415	−3397.666	−4180.876
α_4^A	1788.287	48.632	−70.005
α_5^A	1432.597	−3400.632	−2279.054
α_6^A	−2127.760	1658.024	1714.927
α_1^B	20.554	27.224	19.271
α_2^B	103.853	−21.955	−12.128
α_3^B	−100.294	−14.355	−23.316
α_4^B	99.564	121.738	128.343
α_5^B	27.092	23.007	18.569
α_6^B	−54.852	28.665	40.450
α_1^C	37.873	34.331	31.438
α_2^C	93.972	4.147	10.283
α_3^C	25.917	36.687	22.940
α_4^C	−16.548	109.663	110.851
α_5^C	28.672	28.017	40.930
α_6^C	32.838	−3.357	2.862
Z_{64}^A	−6.396 60		
Z_{65}^A		3.219 41	−3.993 82
Z_{65}^B		0.979 07	0.936 39
Z_{43}^C		−0.311 46	−0.291 73
Δ_J	0.016 92	0.022 08	0.022 04
Δ_K	8.481 34	7.027 39	6.262 88
Δ_{JK}	0.583 69	0.342 72	0.395 96
δ_J	0.001 91	0.001 95	0.001 86
δ_K	0.368 38	0.226 01	0.236 00
Φ_J	0.004 93	−0.005 24	−0.006 93
Φ_K	1488.545	1066.843	690.465
Φ_{JK}	8.650	2.953 81	3.088 21
Φ_{KJ}	−60.588	17.693	34.957
ϕ_J	0.003 46	0.002 41	0.001 76
ϕ_{JK}	4.454 28	1.573 53	1.610 07
ϕ_K	469.759	223.394	239.089

[a] Includes the Dunham offset E_0.[79]

TABLE 4: CCSD(T)/VQZ+1 and Experimental Fundamentals for H_2SiO Isotopomers

	$H_2\,Si^{16}\,O$	$H_2\,Si^{18}\,O$	$D_2\,Si^{16}\,O$	$D_2\,Si^{18}\,O$
$\nu_2+\nu_3$	2198.4	2174.3		
ν_1	2162.0	2141.8	1577.7	1576.7
ν_2	1202.9	1162.9	1189.5	1148.0
ν_3	992.9	989.4	718.5	716.9
ν_4	691.6	690.4	530.8	529.3
ν_5	2186.2	2186.1	1597.9	1595.9
ν_6	679.5	676.0	529.0	524.5
expt[2]				
ν_2	1202	1162	1189	1147
ν_4[a]	697	694	533	530

[a] Assigned to ν_6 (antisymm. bend) by WA[2] based on computed HF/6-31G* frequencies[3] scaled by 1/1.126.

("wag") rather than the antisymmetric bend ("rock"). We will return to this issue below.

Adding a single hard d function has a noticeable effect on the computed spectroscopic properties. The SiH stretching fundamentals are not significantly affected, but the Si═O stretching frequency moves up by 10 cm^{-1} and the bending frequencies move up by lesser amounts. As a result, $\nu_2+\nu_3$ moves up by 13 cm^{-1}. The Si═O bond length is shortened by 0.009 Å, while the SiH bond length is shortened by a more modest 0.003 Å. The bond angle is not significantly affected. The basis set effects on the Si═O bond distance and stretching frequency are, incidentally, very similar to those seen for the corresponding quantities in the SiO diatomic (Table 1).

In addition adding diffuse functions on oxygen opens up the bond angle by some 0.35° and lengthens the Si═O bond distance by 0.0032 Å. (This particular effect, in our experience, tends to be seriously overestimated relative to a VTZ basis set, and it is necessary to move up to a VQZ basis set, to see a consistent set of numbers.) The principal effect on the harmonic frequencies is that the Si═O stretch is brought down again by 11 cm^{-1}, but this is again an artifact of the poor underlying VTZ basis set.

The addition of a hard d function to the VQZ basis set has a more modest effect than in the case of the VTZ basis set. As far as the fundamentals go, it is mainly manifested in a blue shift of 3 cm^{-1} of the Si═O stretch (and of 3.6 cm^{-1} on $\nu_2+\nu_3$). The bond angle and *r*(SiH) are not appreciably affected, but *r*(SiO) is shortened by 0.0034 Å. The convergence behavior from VTZ+1 to VQZ+1 is altogether more pleasing than that from VTZ to VQZ. The most conspicuous differences between VTZ+1 and VQZ+1 are increases of 9 and 11 cm^{-1}, respectively, in the symmetric and antisymmetric SiH stretching fundamentals; in addition, the bond angle opens up by some 0.44°, incidentally about the same effect as adding diffuse functions on O to the VTZ basis set. (It was noted before[37] that the basis set effects on bond angles of polar molecules strongly overlap between the VTZ to VQZ and VTZ to AVTZ increments.)

Turning to the isotopic shifts (Table 4), we see that the four isotopic Si═O stretching bands are in essentially perfect agreement with the matrix IR values of WA. The second band observed by WA can now unequivocally be identified as the out-of-plane mode rather than the antisymmetric bend, and the computed-observed difference of about 5 cm^{-1} is within the error margin of the calculations but may also contain some matrix effect. (The opposite assignment, to the antisymmetric bend, was made by WA on the basis of scaled SCF frequencies[3] of 721 cm^{-1} for the out-of-plane mode and 699 cm^{-1} for the antisymmetric bend. This serves as a good illustration of the pitfalls of using SCF frequencies to discriminate between

TABLE 5: B3LYP/VTZ Harmonic Frequencies (cm^{-1}) and Infrared Intensities (km/mol, in parentheses) of Silicic Acid, H_2SiO_3, and of the H_2SiO Isomers Considered in This Work[a]

$H_2Si^{16}O_3$
313.8(b_2, 80), 323.4(a_1, 0.8), 360.8(b_1, 27), 412.0(a_2), 481.8(b_1, 255), 824.0(a_1, 19), 836.5(b_2,179), 905.8(a_1,175), 1021.1(b_2, 96), 1286.1(a_1, 177), 3858.0(b_2, 272), 3859.5(a_1,2)
$H_2Si^{18}O_3$
300.7(b_2, 72), 309.6(a_1, 0.7), 354.3(b_1, 29), 408.7(a_2), 479.7(b_1, 247), 779.5(a_1, 20), 818.8(b_2,196), 899.2(a_1,166), 1002.8(b_2, 73), 1247.7(a_1, 173), 3845.6(b_2, 265), 3846.8(a_1,2)
$D_2Si^{16}O_3$
296.0(b_2, 78), 301.2(a_1, 1.7), 325.1(b_1, 17), 312.2(a_2), 384.3(b_1, 168), 822.2(a_1, 45), 662.3(b_2, 37), 678.6(a_1, 78), 986.5(b_2, 196), 1285.5(a_1, 170), 2808.0(b_2, 165), 2810.9(a_1,0.9)
$D_2Si^{18}O_3$
284.9(b_2, 71), 290.6(a_1, 1.4), 324.3(b_1, 14), 307.7(a_2), 376.2(b_1, 165), 778.1(a_1, 40), 649.5(b_2, 45), 669.7(a_1, 75), 961.3(b_2, 182), 1247.1(a_1, 165), 2790.5(b_2, 158), 2792.9(a_1,0.9)

$H_2Si^{16}O$
684.9(b_2,65), 697.4(b_1,56), 1003.7(a_1,43), 1223.9(a_1,70), 2219.4(a_1,45),2235.8(b_2,144)
$H_2Si^{18}O$
681.3(b_2,62), 696.2(b_1,54), 1000.4(a_1,37), 1182.6(a_1,72), 2219.4(a_1,44), 2235.8(b_2,144)
$D_2Si^{16}O$
531.7(b_2,52), 534.3(b_1,44), 722.4(a_1,26), 1208.8(a_1,48), 1596.2(a_1,39), 1619.3(b_2,90)
$D_2Si^{18}O$
527.2(b_2,49),532.7(b_1,43),720.9(a_1,25), 1166.3(a_1,48),1595.2(a_1,37),1619.3(b_2,89)

cis-$HSi^{16}OH$
638.0(a_2,133), 743.0(a',132), 846.6(a',93), 966.5(a',59), 1903.1(a',428), 3836.2(a',70)
cis-$HSi^{18}OH$
635.2(a'',132), 740.3(a',147), 818.7(a',66), 961.5(a',59), 1903.1(a',428), 3823.5(a',68)
cis-$DSi^{16}OD$
473.2(a'',72), 530.2(a',48), 843,4(a',131), 732.1(a',35), 1370.1(a',227), 2793.5(a',47)
cis-$DSi^{18}OD$
469.4(a'',70), 529.9(a',49), 817.4(a',117), 722.1(a',37), 1370.1(a',227), 2775.8(a',44)

trans-$HSi^{16}OH$
676.9(a'',56), 812.0(a',32), 842.2(a',137), 967.2(a',134), 1985.4(a',354), 3837.2(a',102)
trans-$HSi^{18}OH$
674.5(a'',55), 804.8(a',119), 818.8(a',39), 962.3(a',133), 1985.4(a',355), 3824.6(a',100)
trans-$DSi^{16}OD$
494.6(a'',30), 586.8(a',13), 839.0(a',144), 723.4(a',67), 1429.8(a',187.4), 2793.7(a',61)
trans-$DSi^{18}OD$
491.3(a'',30), 585.7(a',14), 809.8(a',131), 717.4(a',67), 1429.8(a',187), 2776.1(a',59)

[a] Modes for minor isotopomers were ordered according to the band of the major isotopomers with which the normal mode overlaps most.

assignments to two fairly close bands. Even the fairly inexpensive B3LYP/cc-pVTZ frequencies in Table 5 lead to the correct assignment: it should be remembered, however, that neither the B3LYP nor the CCSD(T) method even existed at the time of the WA study.)

While computer time limitations precluded us running a complete anharmonic force field with even larger basis sets, we did manage to perform some additional geometry optimizations. Improving the basis set from VQZ+1 to AVQZ+1 results in r(Si═O) being lengthened by 0.0009 Å and the angle opening up by 0.1°. Adding additional hard polarization functions to Si to obtain an AVQZ+2d1f basis set, however, results in r(Si═O) being shortened by 0.0013 Å again and r(SiH) by 0.0004 Å. The bond angle appears to be converged.

As expected for a second-row compound, there is a rather appreciable core correlation contribution to the geometry: r(SiO) and r(SiH) are predicted to be shortened by 0.0043 and 0.0038 Å, respectively, by core correlation, while θ (HSiH) opens up by a further 0.11°. The CCSD(T)/MTcore bond distances, $r(\mathrm{SiO}) = 1.5140$ Å and $r(\mathrm{SiH}) = 1.4733$ Å, are actually within the error bars of the r_m distances of Bogey et al.,[8] 1.515 ± 0.002 and 1.472 ± 0.002 Å, respectively. Concerning the bond angle, the MT basis set is simply not flexible enough in the diffuse region: adding the core correlation contribution to the computed CCSD(T)/AVQZ+2d1f angle, we obtain a best estimate of 111.97°, in excellent agreement with the Bogey et al. value of $112.0 \pm 0.2°$. Using this geometry in conjunction with the CCSD(T)/VQZ+1 force field yields the rotational and centrifugal distortion constants given in Table 6. The relative errors in our computed rotational constants are seen there to be +0.2% for A_0, +0.06% for B_0, and +0.08% for C_0. The large centrifugal distortion constant Δ_K is computed near the upper end of the experimental uncertainty: the other quartic centrifugal constants are computed in good agreement with experiment. The discrepancy with earlier, lower-level, calculated results[7,16] reflects mainly the strong geometry dependence of the quantities concerned. Comparison for the sextic constants is a little more difficult since only a partial set was obtained experimentally, and therefore the constants given may actually include contributions from other constants not included in the rotational model.

TABLE 6: Computed and Observed Ground-State Rotational Constants (MHz) and Quartic (kHz), and Sextic (Hz) Centrifugal Distortion Constants for H_2SiO

	SCF/DZP[7]	MAS[16a]	best estimate, this work	expt[4]
A_0	168 774	166 896	167 008.1	166 657(2)
B_0	18 890	18 542	18 690.2	18 679.390(6)
C_0	16 938	16 638	16 756.9	16 742.774(6)
Δ_K	7650	7872	8580.3	7500(940)
Δ_{JK}	504	504	594.69	602.47(2)
Δ_J	15.1	15.5	17.454	17.522(2)
δ_K	316	329	375.75	413(3)
δ_J	1.7	1.8	1.9788	2.0811(25)
Φ_{JK}	6.0		8.9823	4.76(7)
Φ_{KJ}	−42.6		−63.527	−47.7(3)

[a]Equilibrium rotational constants CCSD/TZ2P(f,d); centrifugal distortion and vibrational corrections SCF/TZ2P.

It is noteworthy that the computed vibrational anharmonicities appear to be quite stable with respect to the basis set. Thus, a

TABLE 7: Basis Set Convergence of CCSD(T) Computed Fundamentals (cm^{-1}) and Geometry (Å, deg) for *cis*-HSiOH and *trans*-HSiOH

		VTZ	VTZ+1	AVTZ	AVTZ+1	VQZ/VTZ	expt[2]
cis							
ν_1	υ(OH)	3692.5	3694.0	3675.8	3676.2	3695.5	3661
ν_2	υ(SiH)	1907.5	1908.9	1891.2	1891.0	1896.5	1882
$2\nu_3$		1866.9	1865.8	1858.9	1857.9	1869.0	1846
$\nu_3+\nu_5$		954.7	955.1	938.9	939.0	945.0	938
ν_3	θ syn	851.6	855.5	835.7	841.1	854.5	847
ν_4	υ(SiO)	851.6	855.5	835.7	841.1	854.5	723
ν_5	θ anti	737.8	735.4	729.7	727.0	733.1	723
ν_6	τ	609.9	611.3	600.6	599.6	604.4	596
r(SiH)		1.541 61	1.538 17	1.540 49	1.537 12	1.536 92	
r(SiO)		1.664 73	1.656 52	1.669 92	1.661 79	1.657 50	
r(OH)		0.960 37	0.960 26	0.961 65	0.961 52	0.958 61	
θ(HSiO)		98.076	98.209	97.851	97.990	98.058	
θ(SiOH)		116.552	116.944	117.601	117.982	117.842	
trans							
ν_1	υ(OH)	3692.5	3694.0	3675.8	3676.2	3691.8	
ν_2	υ(SiH)	1872.5	1871.5	1878.8	1877.0	1956.6	
ν_3	θ syn	954.7	955.1	938.9	939.0	932.2	
ν_4	υ(SiO)	851.6	855.5	835.7	841.1	851.1	
ν_5	θ anti	737.8	735.4	729.7	727.0	790.9	
ν_6	τ	609.9	611.3	600.6	599.6	634.3	
r(SiH)		1.541 61	1.538 17	1.540 49	1.537 12	1.525 81	
r(SiO)		1.664 73	1.656 52	1.669 92	1.661 79	1.668 85	
r(OH)		0.960 37	0.960 26	0.961 65	0.961 52	0.961 35	
θ(HSiO)		98.076	98.209	97.851	97.990	94.780	
θ(SiOH)		116.552	116.944	117.601	117.982	112.574	

set of CCSD(T)/VQZ+1 harmonic frequencies combined with CCSD(T)/VTZ anharmonicities would yield excellent fundamentals, obviating the need for a costly CCSD(T)/VQZ+1 quartic force field. As discussed elsewhere,[56] there generally *is* appreciable basis set dependence beyond VTZ for CH, NH, and OH stretching anharmonicities. Our predicted band origins for the unobserved fundamentals, as well as the complete set of anharmonic constants given in Table 3, should therefore prove useful to experimentalists studying the vibrational spectroscopy of silanone.

3. *cis- and trans-HSiOH.* We shall now turn to the *cis*-HSiOH isomer (Table 7). The addition of a hard d function to the VTZ basis set appears to have only a limited effect on the fundamental frequencies, although the geometry is substantially affected. The addition of a set of diffuse functions on O, however, very significantly alters the computed spectrum. It would be expected to alter the OH stretch and the SiOH bend strongly, and the SiO stretch to a lesser extent, but since strong mixing exists between HOSi and HSiO bends, and in addition ν_2 (the SiH stretch) is in strong Fermi resonance with $2\nu_3$, the entire vibrational spectrum ends up being affected, by as much as -16 or -17 cm^{-1} in ν_1, ν_2, ν_3, and ν_4. The CCSD(T)/AVTZ+1 harmonic frequencies agree well with the matrix bands of WA, which they ascribed to the trans isomer but were reassigned to the cis isomer by Ma and Schaefer. The latter assignment can now be regarded as definitively confirmed.

The largest discrepancy with the observed frequencies, 15 cm^{-1}, is for the OH stretch. It should be noted that Dateo et al.[57] found a breakdown of vibrational second-order perturbation theory for the NH stretch in bent HNO, which is not all that dissimilar to the OH stretch in HSiOH. As in that work, the problem is expected to disappear with deuteration.

Tendencies in the frequencies of the trans isomer are similar to those in the cis isomer.

We will consider the isotopic substitution patterns at the CCSD(T)/AVTZ+1 level (Table 8). The isotopic shifts of the cis isomer upon ^{18}O substitution closely track those observed for the trans isomer by WA. Likewise, it is not hard to assign bands for the lower vibrations of the deuterium isomers. ν_2 is calculated to be in Fermi resonance with $\nu_3+\nu_5$: no evidence of a resonance doublet is found in the spectra of WA, although assignments to one of the two partners can readily be made in both cases (1352 cm^{-1} for DSiOD to $\nu_3+\nu_5$ and 1359 cm^{-1} for $DSi^{18}OD$ to ν_2). The discrepancy between the bands assigned to ν_1 for these two isotopomers by WA, 2667 and 2651 cm^{-1}, and the present calculations is however too large to be ascribed to errors in the calculations, particularly since, as noted above, second-order vibrational PT is not expected to break down in this case. There is however a very close correspondence between our calculations and two bands (2710 cm^{-1} for DSiOD and 2694 cm^{-1} for $DSi^{18}OD$) ascribed by WA to the OH stretch of silicic acid. Incidentally, the 3677 and 3667 cm^{-1} absorptions, ascribed by WA to the $\{H,^{16}O\}$ and $\{H,^{18}O\}$ isotopomers of silicic acid, also agree much better with our calculated ν_1 for the corresponding isotopomers of *cis*-HSiOH than the 3661 and 3649 bands assigned by WA. It therefore appears, unless an unusually large matrix effect is at play, that ν_1 for the four isotopomers should be reassigned. Actually, WA noted that the 3677 and 3667 cm^{-1} bands were accompanied by satellites of comparable intensity at 3682 and 3670 cm^{-1}, which at first sight would appear to be consistent with two nearly degenerate OH stretches in H_2SiO_3. Computing power limitations preclude us from carrying out a study on the anharmonic force field of H_2SiO_3 at the present time, but we did manage to carry out a B3LYP/VTZ calculation of the harmonic frequencies and double-harmonic intensities. We found (Table 5), like Dixon and Gole[58] at the SCF level, that the a_1 and b_2 OH stretching modes were nearly degenerate: however, we also found that the intensity of the a_1 mode is nearly 2 orders of magnitude smaller than that of the b_2 mode and that this basically remains the case for all isotopomers considered here. Hence, only one would be visible under normal circumstances, which would make one partner of each satellite pair available for assignment to *cis*-HSiOH, viz. *cis*-$HSi^{18}OH$. Have the cis and trans forms both been observed? Ismail et al.[1] and WA both saw doubling-up of the ν_3 and ν_4 bands upon deuteration, which they ascribed

TABLE 8: CCSD(T)/AVTZ+1 and Observed Isotopic Fundamental Frequencies (cm^{-1}) for *cis*-HSiOH and *trans*-HSiOH

		HSi^{16}OH	HSi^{18}OH	HSi^{16}OD	HSi^{18}OD	DSi^{16}OD	DSi^{18}OD
cis							
ν_1	υ(OH)	3676.2	3664.7	2713.4	2696.7	2713.1	2696.4
ν_2	υ(SiH)	1891.0	1888.1	1885.1	1884.7	1372.8	1369.3
$2\nu_3$		1857.9	1851.1	1782.8	1775.7		
$\nu_3+\nu_5$						1354.7	1332.0
ν_3	θ syn(c)	939.0	934.2	896.9	893.3	718.2	709.0
ν_4	υ(SiO)	841.1	813.4	836.9	807.9	838.4	812.5
ν_5	θ anti(d)	727.0	724.7	566.7	564.1	523.4	523.2
ν_6	τ	599.6	597.1	489.6	486.4	450.2	446.7
trans							
ν_1	υ(OH)	3673.1	3661.6	2709.8	2693.2	2709.7	2693.2
ν_2	υ(SiH)	1950.0	1950.0	1950.8	1950.7	1423.6	1421.8
ν_3	θ syn(c)	929.9	925.1	881.1	877.6	705.3	699.4
ν_4	υ(SiO)	836.9	810.7	834.4	805.9	834.7	806.2
ν_5	θ anti(d)	788.4	784.7	618.3	615.6	573.4	572.3
ν_6	τ	632.7	630.6	515.1	512.5	469.2	466.3
expt[2] (our assignment)							
H_2SiO_3[a]		3682	3670			2714	2698
cis ν_1[a]		3677	3667			2710	2694
b		3661	3649	(2667)			(2651)
cis ν_2		1882	1878				1359
cis $2\nu_3$		1846	1842				
cis $\nu_3+\nu_5$						1352	
cis ν_3		938	933			716	
cis ν_4		847	820			843	817
trans ν_4						837	809
cis ν_5		723	720			523	
cis ν_6		596	594			448	445
expt[1] (our assignment)							
cis ν_2		1881.9	1880.0	1872.3	1872.0		1362.2
cis $2\nu_3$		1847.1	1841.8				
cis $\nu_3+\nu_5$						1354.5	
cis ν_3		937.0	932.1	895.8	892.3	715.1	706.2
trans ν_3				881.4	877.9	700.7	695.3
cis ν_4		850.0	823.1	845.4	816.7	847.0	820.9
trans ν_4				840.5	812.1	840.7	812.3
cis ν_5		722.6	720.0	563.2	560.5	521.2	
cis ν_6		595.2	593.6	489.8	486.9	447.3	444.0

[a] Or conversely. [b] Originally assigned by WA to "*trans*"-HSiOH. [c] Strongly mixed, larger component θ (SiOH). [d] Strongly mixed, larger component θ (SiOH).

to the presence of the second isomer. Although in the case of the HSiOD and HSi^{18}OD isotopomers our band ordering is reversed compared to the other isotopomers, our computed results (Table 8) are largely consistent with this observation, even though this leaves the question unanswered as to why none of the other bands have been observed. Computed intensities at the B3LYP/VTZ level (Table 5) do not readily suggest a reason for this, although this could be due to the limitations of the B3LYP method and/or the double-harmonic approximation for infrared intensities.

B. Relative Energies. All relevant data are given in Table 9. We shall first investigate the relative energies using different electron correlation methods with the VTZ basis set.

At the SCF level, H_2SiO lies some 8 kcal/mol above the two other structures, which are found to be nearly isoenergetic, with the cis structure being about 0.2 kcal/mol more stable than the trans structure. Introducing electron correlation favors trans over cis and brings H_2SiO closer in energy to HSiOH. At the MP2 level, these effects are exaggerated, in particular that on H_2SiO, which is spuriously found to be more stable than either *cis*- or *trans*-HSiOH. The latter is not surprising given the quite different importance of nondynamical correlation effects in both molecules. While the $\mathcal{T}_1$ diagnostic, proposed by Lee and Taylor[32] as a measure of the importance of nondynamical correlation, has a value of about 0.023 for *cis*- and *trans*-HSiOH—which suggests mild nondynamical correlation—the corresponding value for H_2SiO is 0.032, which suggests a somewhat more pronounced departure from the single-reference regime. The CCSD results are actually closer to SCF than to MP2 in this case, again illustrating the observation (for example, ref 59) that in cases with moderately strong nondynamical correlation effects SCF provides a more balanced treatment than low-order perturbation theory. Introducing connected triple excitations shifts the equilibrium toward H_2SiO by about 1.8 kcal/mol, leaving an $H_2SiO \leftrightarrow$ *cis*-HSiOH isomerization energy of about 3.3 kcal/mol at the CCSD(T)/VTZ level.

As expected, oscillation in the cis−trans energy difference is rather less pronounced, with MP2 and CCSD(T) yielding essentially identical isomerization energies. Since the electronic structures of the two isomers are so similar, MP2 yields good results even though $\mathcal{T}_1$ is somewhat outside the "fail-safe margin" for MP2 of about 0.02.[31]

Rather noteworthy is the excellent performance of the B3LYP density functional method, which yields as−cis and cis−trans isomerization energies of 2.8 and −0.1 kcal/mol, respectively, in very good agreement with the corresponding CCSD(T) results of 3.3 and −0.2 kcal/mol.

Let us now turn to the basis set convergence behavior at the CCSD(T) level. As seen in Table 9, the convergence of the as−cis isomerization energy using standard V*n*Z basis sets is quite slow: VDZ 5.61, VTZ 3.27, VQZ 1.72, V5Z 0.72 kcal/mol. By contrast, adding a single high-exponent d function greatly speeds up convergence: VDZ+1 2.61, VTZ+1 1.58, VQZ+1 1.01, V5Z+1 (identical with V5Z) 0.72 kcal/mol. A

TABLE 9: Total Energies (hartrees) and Isomerization Energies (kcal/mol) of H_2SiO, *cis*-HSiOH, and *trans*-HSiOH. Zero-Point Energies in cm^{-1}

	E (H_2SiO)	E (cis)	E (trans)	as−cis	cis−trans
SCF/VTZ	−364.979 899	−364.992 602	−364.992 318	7.97	0.18
MP2/VTZ	−365.343 112	−365.341 096	−365.341 452	−1.27	−0.22
CCSD/VTZ	−365.352 924	−365.360 960	−365.361 114	5.04	−0.10
CCSD(T)/VTZ	−365.369 052	−365.374 265	−365.374 595	3.27	−0.21
B3LYP/VTZ	−365.965 774	−365.970 162	−365.970 255	2.75	−0.06
CCSD(T)/					
VDZ	−365.242 345	−365.251 279	−365.251 965	5.61	−0.43
VTZ	−365.369 052	−365.374 265	−365.374 595	3.27	−0.21
VQZ	−365.407 684	−365.410 426	−365.410 682	1.72	−0.16
V∞Z(DTQ)	−365.424 630	−365.425 487	−365.425 730	0.54	−0.15
V5Z	−365.421 471	−365.422 611	−365.422 893	0.72	−0.18
V∞Z(TQ5)[a]	−365.429 121	−365.428 803	−365.429 138	−0.20	−0.21
VDZ+1	−365.252 804	−365.256 960	−365.257 518	2.61	−0.35
VTZ+1	−365.374 768	−365.377 281	−365.377 553	1.58	−0.17
VQZ+1	−365.410 028	−365.411 636	−365.411 879	1.01	−0.15
V∞Z+1(DTQ)	−365.424 367	−365.425 365	−365.425 626	0.63	−0.16
V5Z+1	−365.421 471	−365.422 611	−365.422 893	0.72	−0.18
V∞Z+1(TQ5)	−365.426 969	−365.427 763	−365.428 097	0.50	−0.21
AVDZ	−365.269 063	−365.279 423	−365.280 172	6.50	−0.47
AVTZ	−365.377 679	−365.382 095	−365.382 550	2.77	−0.29
AVQZ	−365.410 816	−365.413 253	−365.413 605	1.53	−0.22
AV∞Z(DTQ)	−365.425 363	−365.426 828	−365.427 127	0.92	−0.19
AVDZ+1	−365.279 102	−365.284 849	−365.285 518	3.61	−0.42
AVTZ+1	−365.383 248	−365.385 086	−365.385 493	1.15	−0.26
AVQZ+1	−365.413 298	−365.414 601	−365.414 935	0.82	−0.21
AV∞Z+1(DTQ)	−365.425 485	−365.426 919	−365.427 225	0.90	−0.19
MTcore	−365.734 730	−365.736 489	−365.736 683	1.10	−0.12
MTnocore	−365.389 525	−365.390 739	−365.390 982	0.76	−0.15
best ΔE_e				0.84	−0.18
ZPE(H,H)[b]	4032.9	4449.3	4528.0	−1.19	0.22
ZPE(H,D)[c]	3112.0	3772.1	3838.8	−1.89	0.19
ZPE(D,D)[d]	2576.0	3369.7	3422.4	−2.27	0.15
ΔE_0(H,H)[b]				−0.35	0.05
ΔE_0(H,D)[c]				−1.05	0.01
ΔE_0(D,D)[d]				−1.43	−0.03

[a] The notation V∞Z(TQ5) refers to the result of a geometric extrapolation[60] to CCSD(T)/VTZ, CCSD(T)/VQZ, and CCSD(T)/V5Z results, and similarly. [b] H_2SiO vs *cis*- and *trans*-HSiOH. [c] HDSiO vs *cis*- and *trans*-HSiOD. [d] D_2SiO vs *cis*- and *trans*-DSiOD.

geometric extrapolation following Feller,[60] $E(l) = E_\infty + AB^{-l}$, yields an infinite-basis limit of 0.63 kcal/mol based on the VDZ+1, VTZ+1, and VQZ+1 points; based on the VTZ+1, VQZ+1, and V5Z(+1) points, the extrapolated limit is 0.50 kcal/mol. A Schwartz-type extrapolation,[54] $E(l) = E_\infty + A/(l + 1/2)^B$, yields the somewhat lower value of 0.33 kcal/mol from the largest three basis sets. Repeating the extrapolation from the AVDZ+1, AVTZ+1, and AVQZ+1 points (we were unable to complete AV5Z+1 calculation for the cis and trans isomers) leads to a somewhat higher limit of 0.90 kcal/mol.

As expected, basis set convergence for the cis−trans energy difference is rather more rapid. Geometric extrapolations from the V{D,T,Q}Z+1, AV{D,T,Q}Z+1, and V{T,Q,5}Z+1 series all yield very similar values of −0.16, −0.19, and −0.21 kcal/mol, respectively: a Schwartz-type extrapolation to the three largest basis sets yields −0.24 kcal/mol. In other words, the trans isomer is slightly more stable than the cis isomer if zero-point energy (ZPE) is not included.

Inclusion of the latter does change the picture. We will first consider the effect of core correlation. Since complete geometry optimizations could not be carried out for the cis and trans isomers with all electrons correlated, we have evaluated these contributions at the CCSD(T)/VQZ reference geometries. We thus found that the cis isomer is favored by 0.03 kcal/mol over the trans isomer and that the H_2SiO isomer is disfavored by 0.34 kcal/mol over the cis isomer. The most profound effect is however exercised by zero-point energy: this shifts the cis−trans equilibrium by 0.22 kcal/mol toward the cis structure, and the as−cis equilibrium by 1.34 kcal/mol toward the as structure.

We thus find at 0 K that the H_2SiO isomer is the most stable one, 0.35 kcal/mol below the cis structure, and that the latter is itself marginally more stable (0.05 kcal/mol) than the trans structure. Upon single and double deuteration, respectively, the as−cis equilibrium shifts even further to H_2SiO, with energy differences of −1.05 kcal/mol for HDSiO versus HSiOD and −1.43 kcal/mol for D_2SiO versus *cis*-DSiOD. For the cis−trans equilibrium, the shifts are smaller, but nevertheless have a qualitative effect on the equilibrium: −0.01 kcal/mol for *cis*-HSiOD versus *trans*-HSiOD and +0.03 kcal/mol for *cis*-DSiOD versus *trans*-DSiOD.

While we cannot claim that our computed relative energies are accurate to 0.01 kcal/mol, the isotopic contributions (being derived from accurate anharmonic force fields) may well be, and given the degree of convergence that has been established in the electronic component of the relative energy, it is quite unlikely that the qualitative picture given here—*as*-H_2SiO as the global minimum and a cis−trans energy difference small enough for isotopic contributions to be dominant—would change with further improvement of the level of theory.

If the isomerization reaction were to proceed at an appreciable rate, the shift in equilibrium would appear to explain why at 15 K only the cis isomer is visible for the {H,H} isotopomer, but both cis and trans structures are observed for the {H,D} and {D,D} isotopomers. However, a recent semiclassical dynamics study[61] concluded, in contradiction to earlier work,[62] that the tunneling probability is negligible and “[their] results cannot explain the fact that only one isomer of HSiOH was observed in the matrix studies”. These authors[61] speculate on

TABLE 10: Atomization Energies and Other Thermochemical Quantities (kcal/mol) for H_2SiO, SiO, SiH_2 (a $^3B_1$), and SiH_2 (X $^1A_1$). All Calculated Values at the CCSD(T) Level

	H_2SiO	SiO	SiH_2 (a $^3B_1$)	SiH_2 (X $^1A_1$)	ΔE^a	$T_e{}^b$
AVTZ+d	295.28	184.92	129.88	150.00	19.52	20.12
AVQZ+2d1f	302.17	189.45	132.41	152.74	19.70	20.32
AV5Z+3d2f1g	303.82	190.74	132.90	153.33	19.82	20.43
limit	304.71	191.61	133.10	153.62	19.99	20.52
spin−orbit	0.66	0.66	0.43	0.43	0.43	0.00
limit rel	304.05	190.95	132.67	153.19	19.56	20.52
MTcore	296.50	186.21	129.94	150.64	19.65	20.70
MTnocore	296.41	185.48	130.50	150.76	19.57	20.26
core corr	0.09	0.72	−0.56	−0.11	0.08	0.45
$\sum D_e$	304.14	191.67	132.11	153.08	19.64	20.97
ZPE	11.53	1.77	7.65	7.27	−2.11	−0.38
$\sum D_0$	292.61	189.90	124.46	145.80	21.75	21.35
ΔH°_f(0 K)	−22.26	−22.81	86.90	65.56		
expt ΔH°_f(0 K)		-23.1 ± 1.4^{63}	86.6 ± 0.7^{76}	65.6 ± 0.7^{76}		21.0 ± 0.7^{76}

[a] For the reaction $Si(^3P) + H_2SiO(X\ ^1A_1) \rightarrow SiO(X\ ^1\Sigma^+) + SiH_2(a\ ^3B_1)$. [b] Singlet−triplet splitting in SiH_2.

a number of factors involving the matrix that might accelerate tunneling: clearly, further dynamical work would be desirable. In addition, as pointed out by a referee, the electrostatic energy between the very polar solute and the induced dipoles of the matrix atoms may well exceed the isomerization energies computed above.

C. Thermochemistry. Using AVTZ+d, AVQZ+2d1f, and AV5Z+3d2f1g basis sets for $l = 3, 4, 5$, respectively, the Schwartz-type extrapolation $A + B/(l + 1/2)^\alpha$ proposed by the present author[54] yields a valence basis set limit for D_e(SiO) of 191.61 kcal/mol, of which the extrapolation itself accounts for only 0.9 kcal/mol. The differential contribution of Si(2s,2p) and O(1s) correlation, evaluated using the MT basis set, amounts to only 0.72 kcal/mol, which nearly cancels out with the atomic spin−orbit correction of −0.66 kcal/mol. We thus obtain D_e = 191.67 kcal/mol or, after deducting the zero-point energy of 1.77 kcal/mol (regardless of whether our best computed or the observed[51] ω_e and $\omega_e x_e$ are used), D_0(SiO) = 189.9 kcal/mol, in the lower half of the error bar of the accepted experimental value[63] value of 190.4 ± 1.4 kcal/mol. This value is itself an average of four experimental determinations: of those, the Knudsen cell determination 190.2 ± 1.4 kcal/mol of Drowart et al.[64] is the closest to the present calculation and has the smallest error bar. Both the present calculated and the experimental values are substantially higher than those derived from the G2 theory[65] energies of Darling and Schlegel,[13] 188.8 kcal/mol. The value using the older and less sophisticated G1 theory[66] determined in that work, 190.2 kcal/mol, is fortuitously in excellent agreement with the present determination. A revised value of the heat of formation of Si(g) has recently been proposed by both Grev and Schaefer[67] and by Ochterski et al.:[68] 108.1 ± 0.5 kcal/mol. Using this value rather than the JANAF value[69] of 106.6 ± 1.9 kcal/mol, we derive ΔH°_f (SiO) = −22.8 kcal/mol. The fairly poor value obtained using the BAC-MP4[70] bond additivity scheme, −26.7 ± 3.8 kcal/mol,[71] is probably to a large extent due to the rather strong nondynamical correlation effects in this molecule ($\mathcal{T}_1 = 0.039$), for which a method based on fourth-order many-body perturbation theory (MP4[72]) is liable to fail.

For H_2SiO, the same procedure yields a valence correlation limit for TAE_e of 304.71 kcal/mol, of which again only 0.9 kcal/mol is accounted for by the extrapolation. Again a correction for atomic spin−orbit splitting of −0.66 kcal/mol applies: interestingly, the contribution of inner-shell correlation nearly vanishes in this case, 0.09 kcal/mol. If we consider that dissociation of the Si═O bond would create O(^{3}P) and SiH_2 (a $^3B_1$) fragments at infinite distance, our result is in accord with the substantial negative core correlation contribution to TAE, −0.54 kcal/mol, found by Grev and Schaefer[67] for SiH_2 (a $^3B_1$). Using the MT basis set, we obtain the nearly identical result, −0.56 kcal/mol, for the same quantity.

Our best computed TAE_e for H_2SiO amounts to 304.14 kcal/mol; combined with our CCSD(T)/VQZ+1 zero-point energy of 11.53 kcal/mol, we finally obtain TAE_0 = 292.61 kcal/mol. This is rather higher than the G1 and G2 theoretical values obtained from Table 2 in ref 13, 291.09 and 291.41 kcal/mol, respectively. On the basis of previous experience,[25,54] we expect our computed value to be accurate to about ±0.3 kcal/mol. We readily derive ΔH°_f = −22.3 kcal/mol: as for experimental values, only a crude estimate of −27.5 kcal/mol at 298 K is available.[74]

As a byproduct of the present study, we obtained the TAE for the SiH_2 (a $^3B_1$) molecule. Of the extrapolated valence-only basis set limit of 133.10 kcal/mol, only 0.20 kcal/mol comes from the extrapolation. Inclusion of the core correlation effect of −0.55 kcal/mol and the spin−orbit correction of −0.43 kcal/mol leads to TAE_e =132.11 kcal/mol. The anharmonic zero-point energy of SiH_2, 7.65 kcal/mol, was taken from the work of Gabriel et al.,[75] who calculated CEPA-1/[11s8p4d2f/4s3p1d] quartic force fields of the X $^1A_1$ and a $^3B_1$ states of SiH_2. This finally leads to TAE_0 = 124.46 kcal/mol, or ΔH°_f = 86.9 kcal/mol. The latter value falls within the error margin of the mass spectroscopic determination of Berkowitz et al.,[76] 86.6 ± 0.7 kcal/mol. (It should be noted that the thermochemical cycle leading to this value did not involve Si(g) and therefore is not affected by errors in the heat of formation of Si(g).) Our computed TAE_0 and the one extracted from the experimental ΔH°_f of SiH_2, H(g), and Si(g), 124.8 ± 0.7 kcal/mol, are both significantly higher than the computed G1[66] and G2[65] theory values of 123.2 and 123.8 kcal/mol.

We may also consider the isogyric reaction

$$Si(^3P) + H_2SiO(X\ ^1A_1) \rightarrow SiO(X\ ^1\Sigma^+) + SiH_2(a\ ^3B_1) \quad (1)$$

the reaction energy of which can be taken as a measure for the difference in strength between a double and a triple Si═O bond. As seen from Table 10, the reaction energy of that reaction converges quite rapidly with the basis set, changing only from 19.52 kcal/mol at the CCSD(T)/AVTZ+d level to 19.82 kcal/mol at the CCSD(T)/AV5Z+3d2f1g level. The value from our extrapolated basis set limits is 19.99 kcal/mol or, after spin−orbit correction, 19.56 kcal/mol. Inner-shell correlation affects the value by 0.08 kcal/mol, leading to a bottom-of-the-well energy difference, ΔE_e, of 19.64 kcal/mol. We thus finally obtain an energy change at absolute zero, ΔE_0, of 21.74 kcal/mol. Combining this with the experimental heats of formation of Si(g), SiH_2 (g), and SiO(g), we obtain $\Delta H°_f$ (H_2SiO(g)) = −23.1 ± 1.7 kcal/mol, which serves as a consistency check on our directly calculated value.

For the sake of completeness, we will also consider SiH_2 (X $^1A_1$). The extrapolated valence correlation basis set limit amounts to 153.62 kcal/mol, only 0.29 kcal/mol of which comes from the extrapolation itself. The core correlation contribution is quite different from that for the triplet state: −0.11 kcal/mol, in essentially complete agreement with the −0.10 kcal/mol previously reported by Grev and Schaefer.[67] Also adding in the atomic spin−orbit correction term leads to $TAE_e = 153.19$ kcal/mol: together with the zero-point energy of 7.27 kcal/mol from Gabriel et al.[75] we obtain $TAE_0 = 145.80$ kcal/mol or $\Delta H°_f = 65.6$ kcal/mol, the latter in perfect agreement with the Berkowitz et al.[76] value of 65.6 ± 0.7 kcal/mol as well as with the best extrapolated value of Grev and Schaefer. (The G1[66] and G2[65] theoretical values, 146.9 and 147.1 kcal/mol, are substantially higher.) Our best result for the a → X electronic excitation energy T_0, 21.35 kcal/mol, is again in excellent agreement with Berkowitz et al., 21.0 ± 0.7 kcal/mol, and slightly higher than the value of Grev and Schaefer (21.14 kcal/mol). Given the fact that these latter authors found that CCSD(T) reproduced the full CI benchmark value (in a DZP basis set) of Bauschlicher and Taylor[77] to within 0.07 kcal/mol, the presently computed T_e may well be the most accurate value available.

IV. Conclusions

The energetics, structure, and anharmonic force fields of the isomers H_2SiO, *cis*-HSiOH, and *trans*-HSiOH have been studied using coupled cluster methods and large basis sets. Effects of inner-shell correlation were taken into account.

Inner polarization functions on Si were found to be of crucial importance for the correct reproduction of computed properties.

At the basis set limit at 0 K, the H_2SiO isomer is more stable than the two others by about 0.5 kcal/mol. *cis*-HSiOH is marginally more stable than *trans*-HSiOH (0.05 kcal/mol); single and double deuteration change this to 0.01 and −0.03 kcal/mol, respectively. In view of the smallness of these values, it should be stressed that convergence with respect to both basis set and electron correlation method has been established.

The conclusion by Ma and Schaefer that the bands assigned by Withnall and Andrews to *trans*-HSiOH in fact belong to *cis*-HSiOH has been confirmed beyond reasonable doubt. The computed fundamentals for the {H,D} and {^{16}O,^{18}O} isotopomers closely track the experimental ones, except for the OH stretch, for which a reassignment of a band previously assigned to H_2SiO_3 has been proposed.

Our best computed geometry, r(SiH) = 1.4733 Å, r(SiO) = 1.5140 Å, and θ(HSiH) = 111.97°, is in perfect agreement with a recent experimental determination[8] r(SiH) = 1.472 ± 0.002 Å, r(SiO) = 1.515 ± 0.002 Å, and θ(HSiH) = 112.0 ± 0.2°. This kind of agreement requires both the addition of several inner polarization functions to the Si basis set and the inclusion of inner-shell correlation. Computed rotational constants are in excellent agreement with experiment.

Using CCSD(T)/AVTZ+d, CCSD(T)/AVQZ+2d1f, and CCSD(T)/AV5Z+3d2f1g energies in conjunction with a Schwartz-type three-point extrapolation[54] of the form $A + B/(l + 1/2)^C$ (with l = 3, 4, 5, respectively), as well as including inner-shell correlation and our best anharmonic zero-point energy, we obtain the following atomization energies at 0 K: SiO 189.9, SiH_2 (a $^3B_1$) 124.5 kcal/mol, SiH_2 (X $^1A_1$) 145.80 kcal/mol, and H_2SiO 292.6 kcal/mol, which we expect to be accurate to about 0.3 kcal/mol. Heats of formation, based on a revised heat of formation[67,68] of Si(g), are SiO −22.8 kcal/mol, SiH_2 (a $^3B_1$) + 86.9 kcal/mol, SiH_2 (X $^1A_1$) +65.6 kcal/mol, H_2SiO −22.3 kcal/mol. The former three values are within the error limits of the experimental values, −23.1 ± 1.4, 86.6 ± 0.7, and 65.6 ± 0.7 kcal/mol.

To assist future gas-phase infrared and microwave studies on silanone and hydroxysilylene, computed anharmonic spectroscopic constants for all species concerned have been presented.

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Supporting Information Available: Quartic force fields in Cartesian, internal, and normal coordinates of the species involved, as well as computed spectroscopic constants for deuterated isotopomers, are available on the Internet World Wide Web (WWW) at http://theochem.weizmann.ac.il/web/papers/h2sio.html. Parties not possessing WWW access can request the material by e-mail to comartin@wicc.weizmann.ac.il.

Note Added in Proof: After acceptance of the present paper, some additional references were kindly brought to the author's attention by Dr. Miriam Karni (Technion). Schwarz and coworkers[80,81] detected HSiOH and H_2SiO in separate experiments using ionization−reneutralization techniques and found that no interconversion exists between these isomers, which is consistent with a very high barrier (about 50 kcal/mol) for their isomerization. In addition, a comparative study of H_2XO and Me_2XO (X = C, Si, Ge, Sn, Pb) was carried out by Schleyer and coworkers[82] at the B3LYP, MP2, and CCSD(T) levels with basis sets of valence double-ζ plus polarization quality and relativistic effective core potentials.

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