Assignment of the Vibrational Spectra of Polysilane and Its Oligomers

C. X. Cui and Miklos Kertesz*

Department of Chemistry, Georgetown University, Washington, D.C. 20057

Received July 22, 1991; Revised Manuscript Received October 21, 1991

ABSTRACT: The dynamical properties of polysilane (also, polysilylene) have been studied by the scaled quantum mechanical oligomer force field (SQMOFF) approach. The analysis of the vibrational spectrum of polysilane is based on the assignments of the available vibrational spectra of small polysilane oligomers, Si_2H_6, Si_3H_8, and Si_4H_{10}, on the basis of the scaled ab initio force fields at the 6-31G basis set level. The phonon dispersion curves of *all-trans-* and *gauche*-polysilanes have been obtained. The calculated vibrational spectrum of polysilane indicates that polysilane is most likely in a disordered form, where trans and gauche segments are randomly distributed. The experimental Raman spectrum of polysilane has been assigned on the basis of the present calculations.

I. Introduction

Polysilane (PS) and its derivatives have attracted considerable attention in recent years due to their spectroscopic and semiconducting properties, not to mention their potentially valuable practical applications as useful materials.[1] Progress in their research has reached the stage at which fundamental structural details are being determined.[1] Experimental measurements of their structures have been performed,[2] and their structural and conformational properties have been extensively studied theoretically by empirical force field, semiempirical, and ab initio quantum chemical approaches.[3]

The vibrational spectrum of PS has been the subject of several recent publications[4] with the aim of providing basic understanding of the physical and chemical properties of PS. Such work has been often conducted in connection with the analysis of the local bonding environment of H in a-Si (amorphous silicon) and a-Si:H (hydrogenated amorphous silicon). The basic issue has been how to assign the SiH stretching, SiH_2 rocking, SiH_2 bending, SiH_2 wagging, and SiH_3 deformation vibrational modes. (See Figure 1.) The observed vibrational modes at 630, 890, and 2100 cm^{-1} for the SiH_2 group have been assigned to the rocking, bending, and stretching modes for a-Si and a-Si:H alloys, which are very close to the observed values of 630, 909, and 2115 cm^{-1} for PS.[4a] These assignments are based on comparison of the spectra of PS oligomers with those of PS. However, the spectra of these oligomers have not yet been fully assigned.[4] Detailed studies of the dynamical properties of PS have not been carried out yet, especially the effects of conformation on its vibrational spectrum.

In this work we analyze the vibrational spectrum of PS beginning with the assignment of the vibrational spectra of PS oligomers from the smallest Si_2H_6 to Si_4H_{10} at the 6-31G level. Then, the ab initio scaled quantum mechanical oligomer force field (SQMOFF) approach[5] will be applied to PS to extrapolate the vibrational frequencies and intensities for the perfect *all-trans-* and *gauche*-polysilanes. This method provides an unbiased assignment and has been proven to produce reliable frequencies and qualitatively acceptable intensities for a number of different polymers.[5] These calculations provide new insights into the dynamical properties of PS and relate its vibrational spectrum to its conformation.

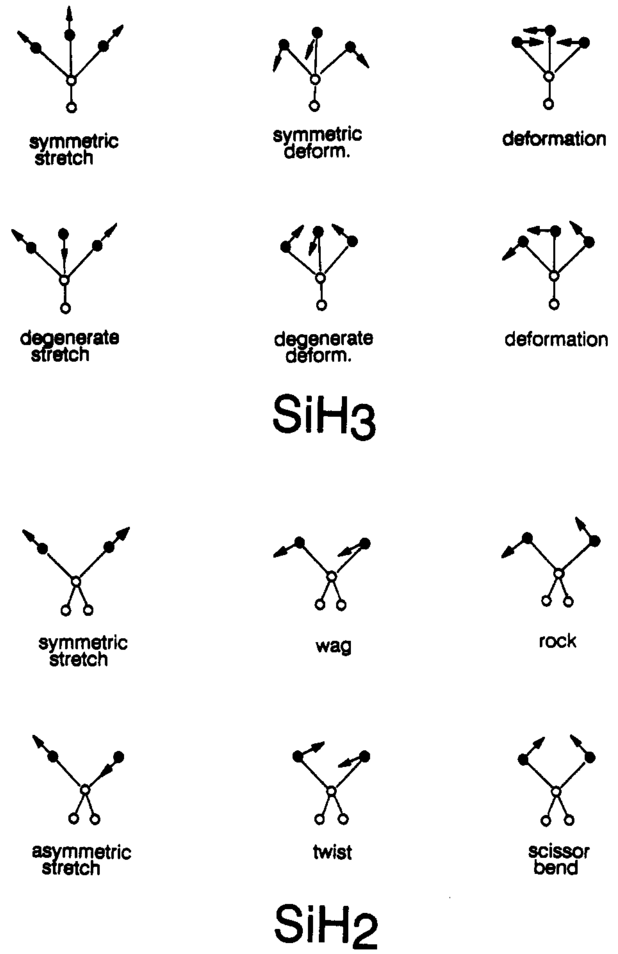

Figure 1. Descriptions of vibrational modes of SiH_2 and SiH_3 groups. Open circles are silicon; filled ones are hydrogen.

II. Method

It is well-known that ab initio calculations at the modest basis set level can produce very reasonable vibrational frequencies if they are used in conjunction with force constant scaling.[6] The 6-31G double-ζ quality basis[7] set has been used throughout the present work. The reliability of this basis set for the present purpose can be assessed by the calculated vibrational frequencies and intensities of PS oligomers, Si_2H_6, Si_3H_8, and Si_4H_{10}, for which experimental vibrational spectra and relative intensities are available.[8]

Table I
Calculated Vibrational Spectrum of Si_2H_6 at the 6-31G Level together with the Experimental Values

expt[a]	calcd, cm^{-1} unscaled	calcd, cm^{-1} scaled[b]	intensity[c]	descripn
		IR-Active Modes		
E_u 379 m	420	400	38	SiH_3 rock
A_{2u} 844 s	898	856	679	SiH_3 deformn
E_u 940 s	1011	964	137	SiH_3 deformn
A_{2u} 2154 vs	2250	2145	216	SiH stretch
E^u 2179 vs	2270	2164	401	SiH stretch
		Raman-Active Modes		
A_{1g} 432 vs	439	418	41	SiSi stretch
E_g 628 w	676	644	26	SiH_3 rock
A_{1g} 920 m	967	922	9	SiH_3 deformn
E_g 941 w	999	952	97	SiH_3 deformn
E_g 2155 s	2260	2154	239	SiH stretch
A_{1g} 2163 vvs	2266	2160	543	SiH stretch
rms error	71	14		

[a] Experimental data from ref 8; intensities are rated as w (weak), m (medium), s (strong), vs (very strong), and vvs (very very strong). [b] Uniform scaling with a scaling factor of 0.9533. [c] IR and Raman intensities in km/mol and Å^4/amu, respectively.

Table II
Calculated Vibrational Spectrum of Si_3H_8 at the 6-31G Level together with the Experimental Values

expt[a]	calcd, cm^{-1} unscaled	calcd, cm^{-1} scaled[b]	intensity[c] IR	intensity[c] Raman	descripn
A′ 112 w	112	107	2	3	SiSi bend
A″	353	337	36	0	SiH_2 rock
A′ 392 s	389	371	1	56	SiSi stretch
A′ 447 s (IR)	467	445	3	27	SiSi stretch
A″ 468 s (IR)	468	446	0	1	SiH_3 deformn
A′	499	476	35	0	SiH_3 deformn
A′ 565 w	610	582	15	24	SiH_3 deformn
A″ 584 m (IR)	636	606	15	12	SiH_3 deformn
A″ 704 s (IR)	769	733	0	48	SiH_2 twist
A′ 716 s (IR)	776	740	380	0	SiH_2 wag
A′ 876 s (IR)	924	881	430	7	SiH_3 deformn
A″	941	897	244	12	SiH_3 deformn
A′ 926 m	986	940	2	67	SiH_2 scissor
A″	1001	954	0	90	SiH_3 deformn
A″	1006	959	122	3	SiH_3 deformn
A′	1006	959	47	0	SiH_3 deformn
A′	1012	965	126	41	SiH_3 deformn
A′ 2130 m	2242	2137	140	71	SiH stretch
A″	2250	2145	20	254	
A′	2254	2149	174	1	
A″	2262	2156	0	27	
A′ 2148 s	2264	2158	77	611	
A′	2265	2159	151	105	
A′	2269	2163	246	287	
A″ 2150 s (IR)	2270	2164	527	62	
rms error	68	17			

[a–c] See Table I.

The scaled quantum mechanical oligomer force field is based on the k-dependent dynamical matrix $\mathbf{F}(\mathbf{k})$ which can be expressed as

$$\mathbf{F}(\mathbf{k}) = \boldsymbol{F}(0) + \sum_{l} \exp(i\mathbf{k}al)\boldsymbol{F}(l) \qquad (1)$$

The central block (interactions within the middle SiH_2 repeat unit) of the force constant matrix of Si_5H_{12} is taken as $\boldsymbol{F}(0)$ and the interaction force constant matrix block between the central and the first neighboring repeat units as $\boldsymbol{F}(1)$, and so on. Then, the $\mathbf{k}$-dependent version of Wilson's method[9] is used to obtain the vibrational frequencies and normal modes of PS.[5] The IR intensities and Raman scattering activities of PS can be obtained from the dipole moment and polarizability derivatives[7] with respect to Cartesian coordinates taken from the middle repeat unit of Si_5H_{12}.[5]

More details including convergence properties of the above approach have been discussed elsewhere.[5] Usually the second-nearest-neighbor approximation in (1) can be considered fully converged[5] in the sense that in this approximation the errors of the calculation are dominated by other effects, such as interchain interactions, choice of the basis set, and inherent limitations of the empirical scaling process.[6] This approach is empirical in so far as scaling parameters are used to obtain the best overall agreement with experiment in full analogy with successful molecular vibrational calculations.[6] In this work we used only one uniform scaling factor as a parameter. This scaling factor is found by minimizing the mean square root difference between the experimental vibrational frequencies of Si_2H_6 and the corresponding theoretical frequencies. The intensities are determined without any empirical adjustable parameter and should be, at this level of theory, only qualitatively correct.

III. Oligomers

We are primarily interested in the vibrational motions of the SiH_2 groups because PS is built up from SiH_2 units. The descriptions of vibrational modes related to SiH_2 and SiH_3 groups are shown in Figure 1. The calculated vibrational frequencies and intensities for Si_2H_6, Si_3H_8, and Si_4H_{10} together with our assignments are listed in Tables I–III. The uniformly scaled vibrational frequencies in Table I agree reasonably well with the observed frequencies for Si_2H_6. The largest error between the calculated and observed frequencies is 23 cm^{-1}, which is within the error found for typical molecules by Pulay's more sophisticated scaling method.[6a] Therefore, the uniform scaling method[6b] will be used throughout the present work due to its simplicity. The trends in the intensities are poor, as observed generally with ab initio calculations of similar quality.

The SiH_2 rocking mode is predicted to be at 337 cm^{-1} for Si_3H_8, which is not observed experimentally because its intensity is too weak. The vibrational frequencies of similar modes for Si_4H_{10} are calculated to be 320 (IR) and 368 cm^{-1} (Raman). Our finding is different from the earlier assignment of this mode. Vora et al.[4a] assigned their observed 630-cm^{-1} Raman line of PS to this mode. Obviously, such an assignment is questionable at least if PS is in an all-trans conformation. More discussions about this Raman line will be made in connection with the discussion of conformational effects on the vibrational spectrum of PS.

The vibrational frequency of the SiH_2 wagging mode for Si_3H_8 is calculated to be 740 cm^{-1}, and the observed value is 714 cm^{-1}. The two SiH_2 wagging modes for Si_4H_{10} are calculated to be 694 cm^{-1} (IR) and 780 cm^{-1} (Raman). The observed IR line is at 692 cm^{-1}, and the Raman scattering activity (3 Å^4/amu) of the SiH_2 wagging mode is weak, making it difficult to observe. Our calculations do not support the previous assignment[4e] of the 845-cm^{-1} line as the SiH_2 wagging motion.

The SiH_2 twisting mode for Si_3H_8 was observed at 704 cm^{-1} while the calculated value is 733 cm^{-1}. The theoretical values of two similar modes for Si_4H_{10} are 693 cm^{-1} (IR) and 753 cm^{-1} (Raman), and the corresponding observed values are 657 cm^{-1} (IR) and 744 cm^{-1} (Raman), respectively.

The SiH_2 scissor mode is very localized. The calculated frequency is 940 cm^{-1} for Si_3H_8, and the corresponding observed value is 926 cm^{-1}. The theoretical frequencies

Table III
Calculated Vibrational Spectrum of Si_4H_{10} at the 6-31G Level together with the Experimental Values

expt[a]	calcd, cm^{-1} unscaled	calcd, cm^{-1} scaled[b]	intensity[c]	descripn
		IR-Active Modes		
A_u	336	320	39	SiH_2 rock
B_u 422 s	438	418	0	SiSi stretch
A_u 465 s	497	474	15	SiH_3 rock
B_u 478 m	522	498	88	SiH_3 rock
A_u 657 s	727	693	7	SiH_2 twist
B_u 692 s	728	694	622	SiH_2 wag
B_u 874 s	926	883	738	SiH_3 deformn
B_u 933 m	989	943	62	SiH_2 scissor
A_u	1004	957	119	SiH_3 deformn
B_u	1010	963	232	SiH_3 deformn
B_u	2241	2136	238	SiH stretch
A_u	2253	2148	45	
B_u	2257	2152	259	
B_u	2267	2161	455	
A_u 2144 s	2270	2164	645	
		Raman-Active Modes		
A_g 139 vw	136	130	10	SiH_3 rock
A_g 361 s	374	357	75	SiSi stretch
B_g	386	368	0	SiH_2 rock
A_g 465 m	481	459	45	SiSi stretch
A_g 542 vw	583	556	28	SiH_3 rock
B_g	616	587	18	SiH_3 rock
B_g 744 w	790	753	74	SiH_2 twist
A_g	818	780	3	SiH_2 wag
A_g 869 w	935	891	15	SiH_3 deformn
A_g 917 m	987	941	91	SiH_2 scissor
B_g	1003	956	98	SiH_3 deformn
A_g	1008	961	44	SiH_3 deformn
A_g 2120 s	2244	2139	102	SiH stretch
B_g 2143 s	2247	2142	272	
A_g	2264	2158	787	
B_g	2265	2159	165	
A_g	2266	2160	454	
rms error	64	16		

[a–c] See Table I.

Table IV
Optimized Geometry of Si_2H_6 (D_{3d})

Bond Length (Å)
Si–Si 2.370 (2.331)[a]
Si–H 1.494 (1.492)[a]

Bond Angle (deg)
Si–Si–H 110.4 (110.3)[a]

[a] Experimental data from Beagley et al.[2e]

Table V
Optimized Geometry of Si_3H_8 (C_{2v})[a]

Bond Length (Å)
Si1–Si2 2.376
Si1–H 1.494, 1.494
Si2–H 1.495

Bond Angle (deg)
Si1–Si2–Si1′ 113.0
H–Si1–Si2 110.3
H–Si2–Si1 109.0

Dihedral Angle (deg)
H–Si1–Si2–Si1′ 59.8
H–Si2–Si1–H 58.7

[a] Si1 and Si1′ are related by symmetry.

Table VI
Optimized Geometry of Si_4H_{12} (C_{2h})[a]

Bond Length (Å)
Si1–Si2 2.376
Si2–Si2′ 2.381
Si1–H (in plane) 1.493
Si1–H (out of plane) 1.493
Si2–H 1.496

Bond Angle (deg)
Si1–Si2–Si2′ 112.9
H–Si1–Si2 (in plane) 110.6
H–Si1–Si2 (out of plane) 110.1
H–Si2–Si2′ 108.9

Dihedral Angle (deg)
H–Si1–Si2–Si2′ 59.8
H–Si2–Si2′–Si1′ 58.4

[a] Si1 and Si1′ are related by symmetry.

Table VII
Optimized Geometry of Si_5H_{14} (C_{2v})[a]

Bond Length (Å)
Si1–Si2 2.377
Si2–Si3 2.380
Si1–H (in plane) 1.494
Si1–H 1.494
Si2–H 1.495
Si3–H 1.496

Bond Angle (deg)
Si1–Si2–Si3 112.9
Si2–Si3–Si2′ 113.2
H–Si1–Si2 (in plane) 110.3
H–Si1–Si2 110.4
H–Si2–Si3 108.8
H–Si3–Si3 109.1

Dihedral Angle (deg)
H–Si1–Si2–Si3 59.8
H–Si2–Si3–Si2′ 58.5
H–Si3–Si2–Si1 58.4

[a] Si2 and Si2′ are related by symmetry.

of the SiH_2 scissor modes for Si_4H_{10} are 943 cm^{-1} (IR) and 941 cm^{-1} (Raman), while the observed values are 933 cm^{-1} (IR) and 917 cm^{-1} (Raman). Thus, on the basis of these oligomer data, it is natural to preliminarily assign the 909-cm^{-1} Raman line of PS to the SiH_2 scissor motion. This assignment will be confirmed in the next section.

The SiH stretching modes have been predicted to have frequencies around 2150 cm^{-1}, which is in very good agreement with the available experimental values and the earlier assignments for this vibrational band of PS.[4,8]

The vibrational frequencies of the SiSi stretch mode have been calculated for the three oligomers to fall between 360 and 460 cm^{-1}, similar to the experimental results on oligomers. The corresponding polymer bands have also been assigned to the SiSi stretch[4] in concordance with the oligomer data and our polymer predictions to be discussed in the next section.

The optimized geometries for Si_2H_6, Si_3H_8, Si_4H_{10}, and Si_5H_{12} at the 6-31G level are listed in Tables IV–VII. The agreement between the theoretical and experimental spectra of the silanes is satisfactory, and only one empirical parameter has been used. We now turn to the vibrational spectrum of infinite polysilane.

IV. Regular *all-trans*-Polysilane

The calculated vibrational frequencies and intensities of *all-trans*-PS are listed in Table VIII. The geometry of *all-trans*-PS is taken from the previously calculated values using the crystal orbital approach.[3i] We have used a unit cell of SiH_2 and a screw axis of symmetry. This corresponds to $3 \times 3 = 9$ phonon branches. The helical angle is defined to be the angle θ for the screw operation $S(\theta)$, which means a rotation through θ, followed by a translation by h. More details concerning helical symmetry in quantum chemistry can be found in ref 3h. Only spectroscopically active modes[5,9] are listed in Table VIII, which

Table VIII
Calculated Vibrational Spectrum of *all-trans*-Polysilane at the 6-31G Level Based on the SQMOFF Approach

	calcd, cm^{-1}			
expt[a]	unscaled	scaled[b]	intensity[c]	descripn
	IR-Active Modes			
B_{1u}	326	311	11	SiH_2 rock
A_u	576	549	0.02	SiH_2 twist
B_{3u}	634	604	268	SiH_2 wag
B_{2u} 905	1000	953	58	SiH_2 scissor
B_{2u} 2100	2244	2139	123	SiH s-stretch
B_{1u} 2100	2264	2158	125	SiH a-stretch
	Raman-Active Modes			
A_g	433	413	15	SiSi stretch
B_{1g} 480	492	469	12	SiSi stretch
B_{3g}	558	532	2	SiH_2 rock
B_{2g}	807	769	27	SiH_2 twist
B_{1g}	848	808	0.01	SiH_2 wag
A_g 909	990	943	25	SiH_2 scissor
A_g 2115	2245	2140	91	SiH s-stretch
B_{3g} 2155	2255	2150	167	SiH a-stretch
rms error[d]	114	36		

[a] Reference 4a. [b,c] See Table I. [d] Not counting the 630-cm^{-1} band; see text.

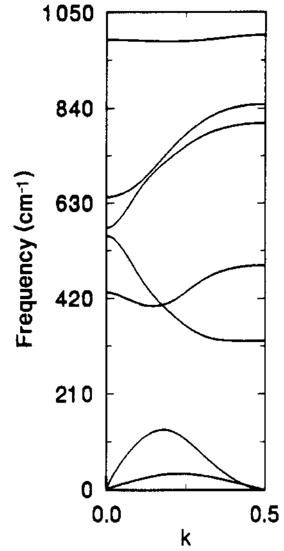

Figure 2. Scaled phonon dispersion curves of *all-trans*-polysilane by the oligomer approach at the 6-31G level using a uniform scaling factor of 0.9533. (**k** is in $2\pi/h$ units.)

Table IX
Selected Scaled Force Constants Used for Polysilane, Based on Si_5H_{12} at the 6-31G Level

descripn	force constant[a]
Diagonal Elements of **F**(0)	
SiSi stretch (R1)	1.539 (1.838)
SiSiSi bend (R2)	0.584
SiSiSi torsion (R3)	0.473
SiH stretch (R4)	2.646 (2.692)
SiSiH bend (R5)	0.630 (0.396)
SiSiSiH torsion (R6)	0.584
Off-Diagonal Elements of **F**(0)	
R3/R5	0.113
R2/R5	−0.081
R1/R5	0.081
Elements of **F**(1)	
R2/R2	0.113
R1/R2	0.091
R1/R6	−0.061
R2/R5	0.128
R2/R6	0.160
R3/R4	0.054
R3/R5	−0.160
R3/R6	−0.234

[a] Stretching, bending, and torsional force constants in mdyn/Å, mdyn/rad., and mdyn/rad., respectively. Force constants with absolute values less than 0.05 are not listed. The numbers in parentheses are the corresponding empirical force constants for Si_2H_6.[8a]

correspond to the modes of the phonon dispersion curves at **k** = 0 and **k** = $\theta/h = \pi/h$ in Figure 2. The calculated SiSi stretching, SiH stretching, and SiH_2 scissor vibrational frequencies of *all-trans*-PS are in good agreement with the experimental observations for PS and its oligomers. Generally, there is agreement with the earlier assignments[4] in that the 480-cm^{-1} band is SiSi stretch and the 2115-cm^{-1} band is SiH stretch. The 909-cm^{-1} band has been assigned earlier as SiH_2 bending,[4] which occurs in our calculations at 940–950 cm^{-1} and corresponds to a SiH_2 scissoring motion. However, we cannot find any spectroscopically allowed frequency close to the observed 630-cm^{-1} band.[4a] This band might be related to changes in conformation or disorder effects as discussed below. This also accounts for the fact that the RMS error is relatively large, even without the 630-cm^{-1} band.

The two lowest phonon dispersion curves in Figure 2 correspond to the longitudinal and transverse acoustic modes. The slopes of these at **k** = 0 determine the longitudinal and transverse sound velocities and the ultimate longitudinal elastic (Young's) modulus, Y. We estimate Y in the 40–100-GPa range using

$$Y = \omega_z^2 hm/A\pi^2$$

where h is the length of a translation vector, A the area of the cross section of the polymer, m the total mass of the translational unit cell, and ω_z the intercept of the tangent of the longitudinal acoustic branch at the zone edge, π/h. Y has a large uncertainty because A is not known precisely, and the **k** = 0 region of the acoustic branches is the most inaccurate region of the calculated phonon dispersion curve.[5]

In general, four phonons should have zero frequencies for a polymer, which correspond to the translational motions of polymers in the X, Y, and Z directions plus a rotational motion around the screw or translation axis. (Let us assume that this is the Z axis.) When a polymer has a 2-fold screw axis of symmetry, the two phonons corresponding to the translational motion in the Z direction and rotation around the Z axis will have the wave vector of **k** = 0 while the translational motions in the X and Y directions will have the wave vector of **k** = π/h. This is why the two lowest phonon dispersion curves in Figure 2 touch the frequency axis at **k** = 0 and **k** = π/h, respectively. For the all-gauche conformation, assuming a helical conformation, the lowest branch has zero frequency at **k** = $\pm\theta/h$ corresponding to pure translations in the X–Y plane.

Some selected force constants are listed and compared with data from the literature in Table IX.

Interchain interactions will have the largest effect on the phonon dispersion at **k** $\neq$ 0 but otherwise low-energy vibrations. As shown by Strobl and Eckel,[10] the inclusion of interchain interaction can be estimated to affect Young's modulus of polyethylene by about 20%, which would indicate a reduction by about 10% of the vibrational frequencies of the longitudinal acoustic branch.

V. Conformational and Disorder Effect

It is well-known that PS is very flexible. The barrier between all-trans and gauche conformations is merely 0.9 kcal/mol, as calculated by the ab initio crystal orbital

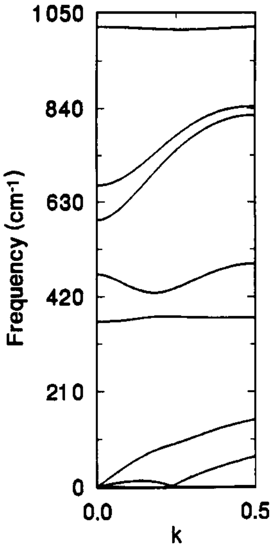

Figure 3. Scaled phonon dispersion curves of *gauche*-polysilane by the oligomer approach at the 6-31G level using a scaling factor of 0.9533. The narrow well-localized SiH stretching branches around 2140 cm^{-1} are not shown.

approach.[3i] Such flexibility has a significant effect on the photoelectron spectroscopies of silane compounds.[1i] The conformational change of PS with temperature is believed to be responsible for the observed thermochromism of PS.[1]

PS samples are not single crystals and do not have long-range order. Therefore, the IR and Raman selection rules of infinite regular polymers are not satisfied exactly.[5,11] It is reasonable to assume that PS is disordered where trans and gauche segments are distributed randomly. In this case, since the polymer has no symmetry, all vibrational modes become spectroscopically active.

The broadness of the Raman bands of PS indicates that PS has some intrinsic disorder. The bandwidth of the SiSi stretching mode is about 60 cm^{-1}, the band around 630 cm^{-1} (assigned here as SiH$_2$ wagging and twisting) has a width of about 110 cm^{-1}, and the 900-cm^{-1} (SiH$_2$ scissor) band is about 45 cm^{-1} wide.

A possible approach to the present problem of randomness is to calculate vibrational frequencies and intensities for many possible conformations and employ a statistical treatment. As a first approximation to this problem we use the phonons of two regular conformations, those of the *all-trans-* and *gauche*-polysilanes, in representing vibrations of random PS. Due to the perturbations caused by the disorder all phonons for *all-trans-* and *gauche*-polysilane become spectroscopically active, which will be used to mimic the vibrational density of states (DOS) of conformationally disordered PS.

The force constants in internal coordinates from *all-trans*-Si$_5$H$_{12}$ have been used to construct the dynamical matrix of *gauche*-PS. Such construction of the force constant matrix has been demonstrated to be reliable by MNDO-AM1 calculations.[3i] This transferability of the $F(l)$ matrix has been demonstrated by the fact that the largest difference between the frequencies obtained for *gauche*-PS using the oligomer approach on the basis of the all-trans oligomer (Si$_7$H$_{16}$) versus the gauche oligomer (Si$_7$H$_{16}$) is less than 5 cm^{-1} at the MNDO-AM1 level. The geometry of helical PS is taken from the previous calculated result, which has a helical angle (θ) of 83.9°.[3i] Actually a slight change in geometry does not affect significantly the vibrational frequencies. The calculated phonon dispersion curves are shown in Figure 3. The way in which the two lowest phonon dispersion curves run in the Brillouin zone (BZ) is similar to that of the two corresponding phonon dispersion curves of *all-trans*-PS. The differnce is that for the latter the two lowest phonon dispersion curves touch the **k** axis at **k** = 0 and θ/h, where θ is the helical angle. This difference can be understood on the basis of a group theoretical analysis, which shows that the translational motion along the screw axis and rotation around the screw axis have the wave vector of **k** = 0 while the translational motions in the X and Y directions have the wave vector of **k** = θ/h.

Table X
Calculated Vibrational Spectrum of *all-gauche*-Polysilane at the 6-31G Level by the SQMOFF Approach

calcd (Raman), cm^{-1}			calcd (IR), cm^{-1}		
unscaled	scaled[a]	intensity[b]	unscaled	scaled[a]	intensity
48	46	10	104	99	4
104	99	11	374	357	26
139	133	11	439	418	6
369	352	20	473	451	12
372	355	24	668	637	159
374	357	26	735	701	15
439	418	6	770	734	156
484	461	3	1014	967	117
591	563	104	2239	2134	81
735	701	97	2247	2142	190
770	734	53	2256	2151	82
821	783	118			
843	804	45			
1014	967	39			
1019	971	37			
1020	972	39			
2239	2134	64			
2247	2142	32			
2242	2137	65			
2256	2151	66			
2263	2157	31			

[a] Scaled frequencies with a scaling factor of 0.9533. [b] IR and Raman intensities in km/mol and Å^4/amu, respectively.

The calculated Raman and IR spectra of PS with a helical angle of 83.9° are listed in Table X. The intensities are calculated by the use of the dipole moment and polarizability derivatives from the middle repeat unit of Si$_5$H$_{12}$, which have been rotated to the orientation of the SiH$_2$ unit of the helical PS. The spectroscopically active modes are those at **k** = 0, θ/h, and $2\theta/h$ according to the selection rules for perfect helical polymers.[5,10]

The vibrational densities of states for *all-trans-* and *gauche*-polysilanes are presented in Figure 4 together with the experimental Raman spectra[4a] for a comparison. The phonon densities of states are obtained by the formula

$$\mathrm{DOS}(\upsilon) = \sum_j w_j \exp\left(-\frac{[\upsilon - \upsilon_j]^2}{2\sigma}\right) \qquad (2)$$

where σ is the half-width of a Gaussian function, w_j is the number of phonon modes between frequencies υ_j and $\upsilon_j + \sigma$. σ was taken as 2.5 cm^{-1}. The number of **k** points used is 200 which are uniformly distributed in the BZ.

The experimental Raman spectrum of PS cannot be compared quantitatively with the calculated phonon density of states even though we assumed that all normal modes are spectroscopically active, because of the variations of the Raman scattering activities for the different normal modes. A statistical treatment along the lines of Tasumi and Zerbi[12] will be required to quantitatively mimic the spectrum of disordered polysilane. A further refinement would require inclusion of interchain interactions. No doubt, the sharp spikes in the calculated density of states (van Hove singularities) would be

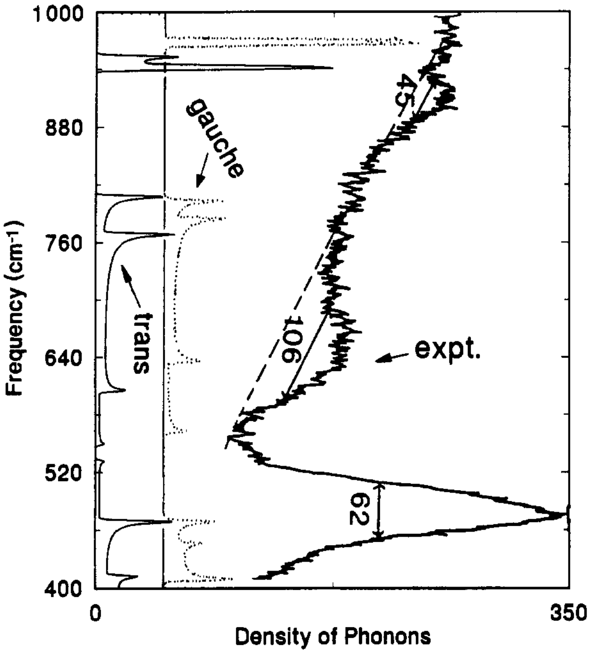

Figure 4. Calculated densities of phonons for *all-trans-* and *gauche*-polysilane together with the experimental Raman[4a] spectrum. Calculated phonon frequencies have been scaled with a factor of 0.9533. The dashed and solid lines represent the phonon densities of states for gauche and all-trans conformations, respectively. The numbers in the experimental Raman spectrum indicate the half-widths of the peaks.

broadened due to interchain interactions. This, as well as conformational disorder effects and the fact that we display the density of states without regard for the variation of intensity as a function of normal modes, distorts the calculated curves. What remains comparable, then, is the location of the bands, which qualitatively correspond to the experimental Raman spectrum of a mixture of mostly $(SiH_2)_n$ and some $(SiH)_n$, and cross-linking cannot be excluded. Especially, the broad distribution of phonons between 600 and 800 cm^{-1} can be related to the corresponding widely broadened band of the observed Raman spectrum. The normal modes lying between 600 and 800 cm^{-1} can be assigned as SiH_2 wagging and twisting, as can be seen from Table VIII. Thus, the observed peak at 630 cm^{-1} can be attributed to the SiH_2 group wagging and twisting motions rather than the rocking motion.[4a]

VI. Conclusion

A new assignment of the Raman spectrum of polysilane has been given on the basis of ab initio calculations performed on PS oligomers. The assignment begins with the analysis of the vibrational spectra of the PS oligomer, and then the extrapolation is made using our newly developed SQMOFF approach[5] to obtain the vibrational spectra of infinite *all-trans-* and *gauche*-polysilanes. The major difference between the present and earlier assignments of the Raman spectrum of PS concerns the broad line at 630 cm^{-1}. The earlier study assigned this line to the rocking motion of the SiH_2 group while the present work assigned it to the mixing of wagging and twisting motions.

The present calculations show that it is impossible to assign the vibrational spectrum to a single all-trans or gauche conformation. This finding provides an independent confirmation to the generally accepted assumption that polysilane is disordered, conformationally and via cross-linking. We anticipate that further practical applications of the SQMOFF approach will provide accurate enough IR and Raman spectral assignments to make vibrational spectroscopy a more useful structural tool for polymer research.

Acknowledgment. This research has been supported by a grant from the U.S. Air Force Office of Scientific Research (Grant 89-0229).

References and Notes

(1) (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) Zeigler, J. M. *Synth. Met.* **1989**, *28*, C581. (c) Trefonas, P.; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 823. (d) Pitt, C. G. In *Homoatomic Rings, Chains and Macromolcules of Main-Group Elements*; Rheingold, A. L., Ed.; Elsevier: New York, 1977. (e) West, R.; David, L. D.; Djurovich, P. I.; Stearley, K. L.; Srinivasan, K. S. V.; Yu, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 7352. (f) Kepler, R. G.; Zeigler, J. M.; Harrah, L. A.; Kurtz, S. R. *Phys. Rev.* **1987**, *B35*, 2818. (g) West, R.; Wolff, A. R.; Peterson, D. J. *J. Radiat. Curing* **1986**, *13*, 35. (h) Hofer, D. C.; Miller, R. D.; Wilson, C. G.; Neureuther, A. R. *P. Soc. Photo. Opt. Inst.* **1984**, *469*, 108. (i) Miller, R. D.; Michl, J. *Chem. Rev.* **1990**, *89*, 1359.

(2) (a) McCrary, V. R.; Sette, F.; Chen, C. T.; Lovinger, A. J.; Robin, M. B.; Stohr, J.; Zeigler, J. M. *J. Chem. Phys.* **1988**, *88*, 5925. (b) Kuzmany, H.; Rabolt, J. F.; Farmer, B. L.; Miller, R. D. *J. Chem. Phys.* **1986**, *85*, 7413. (c) Lovinger, A. J.; Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2657. (d) Schilling, F. C.; Bovey, F. A.; Lovinger, A. J.; Zeigler, J. M. *Bull. Am. Phys. Soc.* **1988**, *33*, 657. (e) Beagley, B.; Conrad, A. R.; Freeman, J. M.; Monaghan, J. J.; Norton, B. G.; Holywell, G. C. *J. Mol. Struct.* **1972**, *11*, 371. (f) See ref 1i and references therein.

(3) (a) Damewood, J. R., Jr.; West, R. *Macromolecules* **1985**, *18*, 159. (b) Welsh, W. J.; Damewood, J. R., Jr.; West, R. *Macromolecules* **1989**, *22*, 2947. (c) Farmer, B. L.; Rabolt, J. F.; Miller, R. D. *Macromolecules* **1987**, *20*, 1161. (d) Ortiz, J. V.; Mintmire, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 4522. (e) Mintmire, J. W. *Mater. Res. Soc. Symp. Proc.* **1989**, *141*, 235. (f) Mintmire, J. W. *Phys. Rev.* **1989**, *B39*, 13350. (g) Teramae, H.; Takeda, K. *J. Am. Chem. Soc.* **1989**, *111*, 1281. (h) Cui, C. X.; Kertesz, M. *J. Am. Chem. Soc.* **1989**, *111*, 4216. (i) Cui, C. X.; Karpfen, A.; Kertesz, M. *Macromolecules* **1990**, *23*, 3302. (j) Takeda, K.; Teramae, H.; Matsumoto, N. *J. Am. Chem. Soc.* **1986**, *108*, 8186. (k) Springborg, M. *Phys. Rev. B* **1989**, *40*, 7839.

(4) (a) Vora, P.; Solin, S. A.; John, P. *Phys. Rev.* **1984**, *B29*, 3423. (b) Brodsky, M. M.; Cardona, M.; Cuomo, J. J. *Phys. Rev.* **1977**, *B16*, 3556. (c) Lucovsky, G.; Nemanich, R. J.; Knights, J. C. *Phys. Rev.* **1979**, *B19*, 2064. (d) Furukawa, S.; Matsumoto, N.; Toriyama, T.; Yabumoto, N. *J. Appl. Phys.* **1985**, *58*, 4658. (e) Furukawa, S.; Matsumoto, N. *Phys. Rev. B* **1985**, *31*, 2114.

(5) Cui, C. X.; Kertesz, M. *J. Chem. Phys.* **1990**, *93*, 5257.

(6) (a) Fogarasi, G.; Pulay, P. *Vib. Spectra Struct.* **1985**, *14*, 125 and reference therein. (b) Saebo, S.; Random, L.; Scheafer, H. F., III *J. Chem. Phys.* **1983**, *78*, 845.

(7) Frisch, M. J.; Binkley, J. S.; Sclegel, H. B.; Ragavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowitz, F.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D.; Fluder, E. M.; Pople, J. A. GAUSSIAN 86, Gaussian Inc., Pittsburgh, PA, 1986.

(8) (a) Durig, J. R.; Church, J. S. *J. Chem. Phys.* **1980**, *73*, 4784. (b) Feher, F.; Fisher, H. *Naturwissenschaften* **1969**, *51*, 461. (c) Spanier, E. J.; MacDiarmid, A. G. *Inorg. Chem.* **1962**, *1*, 432. (d) Gokhale, S. D.; Jolly, W. L. *Inorg. Chem.* **1965**, *3*, 946.

(9) Decius, J. C.; Hexter, R. M. *Molecular Vibrations in Crystals*; McGraw-Hill: New York, 1977.

(10) Strobl, G. R.; Eckel, R. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 913.

(11) (a) *Vibrational Intensities in Infrared and Raman Spectroscopy*; Person, W. B., Zerbi, G., Eds.; Elsevier Scientific: New York, 1982. (b) Zerbi, G. *Appl. Spectrosc. Rev.* **1969**, *2*, 193.

(12) Tasumi, M.; Zerbi, G. *J. Chem. Phys.* **1968**, *48*, 3813.