

INFRARED ANALYSIS OF ORGANOSILICON COMPOUNDS: SPECTRA-STRUCTURE CORRELATIONS

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The infrared spectrum reveals vibrations of atoms in molecules. The beauty of the spectrum is the close and accessible relationship between infrared bands and molecular structure. Certain groups of atoms have characteristic vibration frequencies which persist in different compounds. These groups (i.e. Si-OCH₃, C=O, Si-CH=CH₂, BF₄⁻) are the very kind of functional groups chemists are interested in. This is why infrared spectroscopy is an indispensable tool for organosilicon research.

The positions of infrared bands characteristic of some organosilicon groups are shown in the following table. Ideally, these correlations should be used for liquids or solutions. Infrared band positions for a crystalline solid often show shifts and splitting when compared with band positions of the sample in the liquid state. However, non-crystalline solids (amorphous polymers, glasses) tend to have infrared spectra that are similar to their solution spectra.

These spectra-structure correlations are the result of work by many investigators. Major contributions have been made by A. Lee Smith and his colleagues at Dow Corning Corporation. In addition to previously-published data, we have included some correlations based on our experience in the analysis of organosilicon compounds.

There is increasing interest in carbon-containing silicon compounds as precursors of high-performance ceramics. Accordingly, the table gives data on the infrared bands of some silicon-containing ceramics.

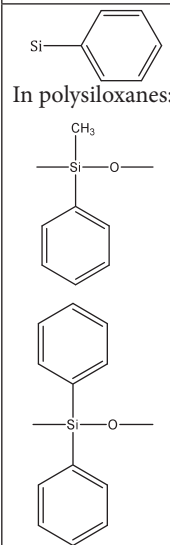
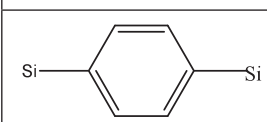
This table presents *empirical* correlations between spectra and structure. The table does not show the types of vibrations (stretching, bending, rocking etc.) that give rise to the infrared bands. Empirical correlations can guide the chemist who is using infrared to follow the course of the reaction, to analyze a commercial product, or to identify an unknown. The correlations become even more useful if the chemist learns the vibrational origins of the bands. The chemist then will be in a better position to anticipate interferences by other groups. Knowledge of the vibrational origins also will help the chemist to understand shifts in a group frequency caused by strain in a bond, coupling of vibrations, or change in the electronegativity of neighboring atoms.

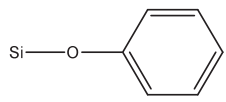
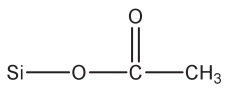
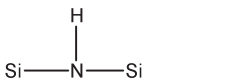
The references list three excellent reviews of spectra-structure correlations for organosilicon compounds. Each review contains some discussion of the molecular vibrations associated with the infrared bands. The reviews also offer a quick way to locate the original literature for many of the correlations.

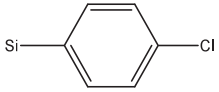

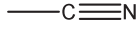
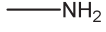

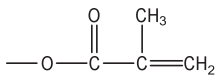
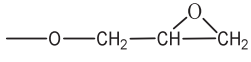
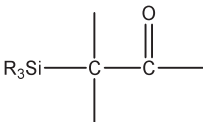
References

1. D. R. Anderson in "Analysis of Silicones," A. Lee Smith, editor, Wiley-Interscience, New York, 1974, Chapter 10.
2. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 3rd ed., Chapman and Hall, London, 1975, Chapter 20.
3. A. Lee Smith, *Spectrochim. Acta* **1960**, 16, 87.

Group	Frequency in cm ⁻¹	Comments
Si-CH ₃ In polysiloxanes: <div style="display: flex; flex-direction: column; align-items: center; margin-top: 10px;"> $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{Si}-\text{O}- \\ \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-\text{O}- \\ \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \\ \text{O} \\ \\ \text{CH}_3-\text{Si}-\text{O}- \\ \\ \text{O} \end{array}$ </div>	1275-1245, 865-750 (M) 1250, 840, 755 (D) 1260, 860 (weak), 800 (T) 1270, 780-760	The Si-CH ₃ group is easily recognized by a strong, sharp band at about 1260 cm ⁻¹ together with one or more strong bands in the range 865-750 cm ⁻¹ . Some (CH ₃) ₃ Si- compounds show a 1250 cm ⁻¹ band split into two components with the weaker component often appearing as a shoulder on the higher frequency side of the band. Blocks of dimethyl D units show a relatively weak band at 860 cm ⁻¹ . In many copolymers containing dimethyl D units (random or alternative, not block), the 860 cm ⁻¹ band shifts to 845 cm ⁻¹ and becomes stronger.
Si-CH ₂ CH ₃	1250-1220, 1020-1000, 975-945	The 1250-1220 cm ⁻¹ Si-CH ₂ band is much weaker than the analogues 1260 cm ⁻¹ Si-CH ₃ band.
Si-CH ₂ (CH ₂) _x CH ₃	1220-1170	As the alkyl group becomes longer, the Si-CH ₂ - band moves to lower frequency; <i>n</i> -propyl, 1220-1200 cm ⁻¹ ; <i>n</i> -butyl, 1200-1190 cm ⁻¹ ; longer chains, 1190-1170 cm ⁻¹

Group	Frequency in cm^{-1}	Comments
$\text{Si}-\text{CH}=\text{CH}_2$	1600, 1410, ca. 1010, ca. 960	If other alkenyl groups and aryl groups are absent, C—H bands at 3060 and 3020 cm^{-1} help to identify $\text{Si}-\text{CH}=\text{CH}_2$.
$\text{Si}-\text{CH}_2-\text{CH}=\text{CH}_2$	1640-1630, 1190-1140, 990, 930 (appears as shoulder in some compounds), 920-890	The isomeric group, $\text{Si}-\text{CH}=\text{CH}-\text{CH}_3$, shows a different pattern with a strong band at 970 cm^{-1} due to <i>trans</i> —CH=CH—.
$\text{Si}-\text{C}\equiv\text{CH}$	3300 (C-H), 2040 ($\text{C}\equiv\text{C}$)	These are strong, narrow bands. In $\text{Si}-\text{C}\equiv\text{C}-\text{Si}$ compounds the 3300 cm^{-1} band is absent, and the $\text{C}\equiv\text{C}$ band is so weak that it is difficult to identify.
 <p>In polysiloxanes:</p>	<p>1600-1590, 1430, 1130-1110, 1030, 1000, 760-710, 700-690</p> <p>730, 700 Intensities approx. equal</p> <p>740, 720, 700 Intensities increase as frequency of band decreases</p>	<p>The 1430 cm^{-1} band is so narrow that its intensity in a recorded spectrum is greatly influenced by the resolution of the spectrometer and the scanning speed. When two phenyl groups are attached to the silicone, the strong 1120 cm^{-1} band usually is split into a doublet. The 1030 and 1000 cm^{-1} bands, normally weak, become much stronger in cyclotrisiloxanes. Specific Si-phenyl compounds often can be identified by the pattern in the range 760-690 cm^{-1}, where there is a strong band in the region 700-710 cm^{-1} and one to three weak, medium or strong bands in the region 760-710 cm^{-1}.</p>
$\text{Si}-\text{O}-\text{Si}$	1130-1000	Siloxanes show one or more very strong infrared bands in the region of 1130-1000 cm^{-1} . Disiloxanes and small-ring cyclosiloxanes show a single Si—O—Si band. As the siloxane chains become longer or branched, the Si—O—Si absorption becomes broader and more complex, showing two or more overlapping bands. A band associated with Si-O rocking can be observed at 455 cm^{-1} .
$\text{R}_3\text{SiOSiR}_3$ disiloxanes	1080-1040	Some unusual shifts in the disiloxane band: $\text{Cl}_3\text{SiOSiCl}_3$, 1115 cm^{-1} (inductive effect); $(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2$, 920 cm^{-1} (strained ring).
$[\text{R}_2\text{SiO}]_3$ cyclic trimers	1020-1010	Cyclic trimers, tetramers, and pentamers have a single Si—O—Si band. As the ring becomes larger (D_6 , D_7 , etc), the Si—O—Si band gradually widens and splits.
$[\text{R}_2\text{SiO}]_{4-5}$ cyclic tetramers and pentamers	1090-1075	
$[(\text{CH}_3)_2\text{SiO}]_x$ Poly(dimethylsiloxane)	1090, 1020	Long chains of dimethyl D units show very strong, distinct bands of about equal intensity at 1090 and 1020 cm^{-1} .
$[\text{RSiO}_{1.5}]_{8, 10, \text{ or } 12}$	1130-1115	
$[\text{RSiO}_{1.5}]_x$	1160-1000	Polysiloxanes made up of T units $[\text{RSiO}_{1.5}]_x$, often show a broad, structureless absorption covering the entire region 1160-1000 cm^{-1} . In other preparations of all-T polymers, there are two distinct bands — one at about 1130 cm^{-1} , the other at about 1040 cm^{-1} .
$\text{Si}-\text{CH}_2-\text{Si}$	1080-1040	The disilylmethylene band is strong and sharp. The sharpness helps distinguish it from Si—O—Si bands.
$\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}$	1180-1120	This is a strong, sharp band. Caution: The band does not appear in this range when the disilylethylene group is part of a strained ring.
	1135	Compounds containing the <i>p</i> -substituted silphenylene group show a strong, sharp band at 1135 cm^{-1} .

Group	Frequency in cm^{-1}	Comments
Si—H	2280-2080, 950-800	The Si—H group is readily identified by a strong band in the range 2280-2080 cm^{-1} . There usually is no interference from other bands in this part of the spectrum. The exact position of the 2280-2080 band is very sensitive to the electronegativity of the groups attached to the silicon. (For details, see the references.)
Si—H in amorphous silicon	2150-2000	Si—H bands at three or more frequencies in the range 2150-2000 cm^{-1} have been found in amorphous silicon (a-Si). There still is some uncertainty about the correlations between these band positions and the nature of the other groups on the Si atom.
Si-F	1030-820	SiF ₂ and SiF ₃ compounds show two bands in this range.
Si—Cl	625-425	SiCl ₂ and SiCl ₃ compounds usually show two bands in this range.
Si—OH	3690 (free OH), 3400-3200 (hydrogen-bonded OH), 950-810	Isolated Si—OH groups on silica show a sharp band at 3750 cm^{-1} [R.S. McDonald, <i>J. Phys. Chem.</i> 62 , 1168 (1958)]. Free silanol groups in organo silicon compounds show a sharp band at about 3690 cm^{-1} . Aryl silanols show slightly lower frequencies than alkyl silanols. Two ways to tell the difference between Si—OH and C—OH: The free Si—OH band at 3390 cm^{-1} is at a significantly higher frequency than the free C—OH band. Si—OH compounds show absorption, often a single broad band, in the range 950-810 cm^{-1} .
Si-OD	2742	This band is observed after D ₂ O exchange with isolated Si-OH in silica.
Si—O—Metal	1000-900	Silanolates show a strong band in the range 1000-900 cm^{-1} . Si—O—Ti compounds show a strong band at ca. 925 cm^{-1} .
Si—OR	1110-1000	Si—alkoxy compounds have one or more strong bands in the 1110-1000 cm^{-1} range. If siloxane is present in a sample, the 1110-1000 cm^{-1} band is apt to be masked by strong Si—O—Si absorption. In such cases, the alkoxy group often can be identified by using other bands.
Si—OCH ₃	2840 (sharp), 1190, 1100-1080 (strong)	
Si—OCH ₂ CH ₃	1170-1160, 1100 and 1075 (strong doublet), 970-940	
Si—OCH ₂ CH ₂ CH ₃	1155(weak), 1100 and 1085 (strong doublet), 1020	
Si—OCH(CH ₃) ₂	1385 and 1370 (sharp, well-defined doublet), 1175, 1140-1110, 1055- 1030 (strongest band in the set), 890	
	1240, 975	The phenoxy group attached to silicon has strong bands at about 1240 and 975 cm^{-1} .
	1770-1725, 1370, 1260-1195, 1050-1000, 970-925	Two of these bands are sensitive to the number of acetoxy groups attached to a silicon atom. The correlations are not perfect, but here are the tendencies: In the interval 1770-1725 cm^{-1} , as the number of acetoxy groups increases, the band shifts to higher frequency. In the interval 1260-1195 cm^{-1} , as the number of acetoxy groups increases, the band shifts to lower frequency.
Si—NH ₂	3500-3390 (NH ₂ , doublet in this interval), 1550-1540	Tris(trimethylsilyl)amine (also called nonamethyltrisilazane, "NMTS") has a strong Si—N—Si band at 915 cm^{-1} .
	3390 (NH, single band), 1200-1150, 950-920	
Si—N ₃	2180-2120	Compounds containing the azide group attached to silicon have a strong N=N=N band in the interval 2180-2120 cm^{-1} . See W. R. Peterson, <i>Reviews on Silicon, Germanium, Tin and Lead Compounds</i> 1974 , <i>1</i> , 193.
Si—N=C=O	2280	Trimethylsilylisocyanate has a very strong —N=C=O band at 2280 cm^{-1} . This band position is close to the high frequency end of the range 2275-2250 cm^{-1} for N=C=O attached to carbon.
Si—CH ₂ CH ₂ CF ₃	1210, 1130, 1070, 1025, 900	The 1210 cm^{-1} band is the strongest one of the set.
Si—CH ₂ Cl	1395, 1180	

Group	Frequency in cm^{-1}	Comments
	1580, 1485, 1380, 1090, 1015, 810	These are strong, narrow bands.
$(\text{RO})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{X}$ where X is  Cl  $\text{C}\equiv\text{N}$  NH_2  SH  	1310, 910, 860 2245($\text{C}\equiv\text{N}$), 1190-1175 3370 and 3290 (NH_2 , weak doublet), 1595 (broad, weak) 2560 (S—H, weak) 1720 (C=O), 1640 (C=C) 3045 (C—H of three-membered ring, weak), 1250	Silanes having this general formula, where X is a reactive group, are used as coupling agents. For some of these silanes, the infrared spectrum is dominated by bands of the $(\text{RO})_3\text{Si}$ -part of the structure, and bands due to the reactive group are not obvious. In such cases, it often is a good idea to hydrolyze the trialkoxysilane to the resin, $[\text{O}_{1.5}\text{SiCH}_2\text{CH}_2\text{CH}_2\text{X}]_n$, and to record the infrared spectrum of the resin. This eliminates the many bands due to Si—OR and replaces them with one or two broad Si—O—Si bands. When 3-aminopropyl compounds are hydrolyzed in air, the $-\text{NH}_2$ group reacts with carbon dioxide and water, and one gets a resin containing $-\text{NH}_3^+ \cdot \text{HCO}_3^-$ [see S. R. Culler, H. Ishida, and J. K. Koenig, <i>Appl. Spect.</i> 1984 , 38, 1]. This salt structure is characterized by the following bands: 3400-2000 (several broad bands), 1640 (shoulder), 1575 (strong), 1480 cm^{-1} (strong).
	1725-1660	In compounds having a carbonyl group β to silicon C=O frequency in 10-20 cm^{-1} lower than that of the carbon analog. This is attributed to the inductive effect of the $\text{R}_3\text{SiC}-$ group. [see G. L. Larson, D. Hernandez, I. Montes de Lopez-Cepero and L. E. Torres, <i>J. Org. Chem.</i> 1985 , 50, 5260 and references therein for examples of these kinds of molecules]
Si=C (silenes)	ca. 1000	$(\text{CH}_3)\text{HSi}=\text{CH}_2$, stable at 35°K in argon mixture, has a strong band at 989 cm^{-1} due to Si=C stretch (see C. A. Arrington et al., <i>J. Am. Chem. Soc.</i> 1984 , 106, 525; and G. Raabe et al., <i>J. Am. Chem. Soc.</i> 1986 , 108, 671. For a good summary of all the Si=C infrared results reported to date, see the review by A. G. Brook and K. M. Baines in <i>Advances in Organometallic Chemistry</i> 1986 , 25. Solid silenes of the type $[(\text{CH}_3)_3\text{Si}]_2\text{Si}=\text{C}[\text{OSi}(\text{CH}_3)_3]\text{R}$, where R is a bulky group, are stable at room temperature in the absence of air. These silenes show a strong band at 1135-1130 cm^{-1} probably due to the Si—O—C stretch in the Si—O—C=Si group (see A. G. Brook et al., <i>J. Am. Chem. Soc.</i> 1982 , 104, 5667.
CERAMICS Silicon carbide Silicon nitride Silicon dioxide	ca. 800 ca. 840 ca. 1100	Silicon carbide occurs in the bewildering number of crystal modifications. It also occurs as amorphous material (a-SiC). We do not have detailed spectra-structure correlations for these forms. We expect that the different forms will have small differences in the infrared spectra, but that all forms of SiC will show strong absorption at or near 800 cm^{-1} . Amorphous Si_3N_4 has a strong, broad absorption band at ca. 840 cm^{-1} . All forms of SiO_2 show a strong band at 1110-1080 cm^{-1} . In addition to this strong band, there are other bands that help to identify the kind of SiO_2 : α -Quartz (a crystal form of SiO_2)—1170 (sharp band on the slope of the strong 1080 band), 800 and 780 (well-defined, sharp doublet), and 695 cm^{-1} . <i>Cristobalite</i> (another crystal form)—1200 (a narrow shoulder or "step"), 795, and 620 cm^{-1} . <i>Amorphous silica</i> (includes silica gel, silica glass, "fused quartz", precipitated silica, and fumed silica)—ca. 1220 (a very broad shoulder) and 810-800 cm^{-1} . The 810-800 cm^{-1} absorption of amorphous silica is broader and weaker than the 800 cm^{-1} region bands of α -quartz and cristobalite.