Vibration Frequencies and Binding Forces in Some Silicate Groups

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Frequency formulas for some atomic groups occurring in silicates (Si_2O_7, Si_3O_9 ring, SiO_3 chain, SiO_2 network) are computed, using simplified force systems, and force constants are calculated. The strong force between the O atoms connecting the SiO_4 groups of the Si_3O_9 ring is especially remarkable. Further observations are necessary to indicate the choice of less simple force systems.

I. INTRODUCTION

THE main structure elements in building the crystal lattice of silicates are tetrahedral SiO_4 groups, which may be either isolated as in the orthosilicates or connected with one another by common O atoms as in building an Si_2O_7 group from two connected tetrahedra. Connection at all corners will result in the structure found, for instance, in quartz, SiO_2. Connection of SiO_4 groups so as to form a ring of tetrahedra occurs in the crystals of benitoite ($BaTiSi_3O_9$) or beryl ($Al_2Be_3Si_6O_{18}$).

The infra-red reflection spectra of all silicates[1] contain two reflection maxima near 1000 and 500 cm^{-1}, which have been interpreted as the two active frequencies of a tetrahedral point group. In addition to these, there may occur other maxima corresponding to other particular features of the crystal lattice. Of special interest is the reflection band at 750-850 cm^{-1}—the so-called ring-band—which occurs whenever there is a ring-forming connection. This band has originally been interpreted as a pulsation vibration of the tetrahedron which somehow might have been activated in ring structures, while being inactive in a single tetrahedron.

Certain theoretical considerations[2] have indeed led to the prediction that connected SiO_4 groups should give two active frequencies at wave numbers near those of a single group. These same considerations, however, rule out the possibility of the activation of the pulsation vibration in symmetrical groups such as Si_6O_{18}, thus invalidating the above-mentioned interpretation of the ring-band as an activated pulsation.

One of the objects of the present investigation was to shed more light on the connection between the ring-band and ring-structure. To this end I have computed, as the most simple example, the vibrations of the Si_3O_9 group as found in benitoite. It will indeed be seen that a frequency at the observed wave numbers is to be expected; this frequency is dependent on the binding force between the connecting atoms in the ring. Also the spectrum of wollastonite ($CaSiO_3$) can be accounted for in terms of Si_3O_9 vibrations.

The vibrations of the Si_2O_7 group in thortveitite ($Sc_2Si_2O_7$) and those of a linear chain of SiO_4 groups, as it occurs, somewhat distorted, in silicates of the pyroxene type (e.g., diopside, $CaMgSi_2O_6$) are also calculated. For comparison, the vibrations of the isolated SiO_4 group (e.g., in zircone, $ZrSiO_4$) and those of quartz are considered.

In the following sections are presented the frequency formulas developed in this investigation.

The theory gives statements about the forces within the groups, but at present all such statements are of a qualitative character. For complete quantitative statements, we should have a complete set of binding forces; this is not possible, however, since observational data are not sufficient to determine the entire force system unambiguously. The calculations would, moreover, become extremely involved.

We have assumed a special central force system, retaining forces only between Si and the O atoms and, in some cases, between the connecting O atoms. Only for Si_2O_7 a valence-force system has been used. The general method need not be discussed here beyond the fact that group theoretical methods and symmetry coordinates have been used. Our symmetry coordinates are defined in a somewhat different manner from those of Howard and Wilson[3] who introduced symmetry coordinates first. Our coordinates are defined as

$$q = \sum_i (a_i x_i + b_i y_i + c_i z_i),$$

where x_i, y_i, z_i are "point-coordinates" described in the figures; the constants a_i etc., are determined in applying symmetry operations (linear transformations with coefficients given by group theoretical considerations). These coordinates are not necessarily normal coordinates, but those of one species are orthogonal to those of other species. They are similar to the coordinates of Bhagavantam,[4] but differ from them by a more consequent application of group theory and in not excluding translations and rotations, which is more convenient in the case of complicated molecules.

In general, the approximate character of the calculations suggests that we must not attach too great an importance to the special numerical values. As long as there are no more observations (Raman effect, separa-

[1] C. Schaefer, F. Matossi, and K. Wirtz, Zeits. f. Physik **89**, 210 (1934); F. Matossi and H. Krueger, *ibid.* **99**, 1 (1936); C. Schaefer and M. Schubert, Zeits. f. techn. Phys. **3**, 201 (1929).
[2] F. Matossi and R. Mayer, Naturwiss. **33**, 219 (1946).

[3] J. B. Howard and E. B. Wilson, Jr., J. Chem. Phys. **2**, 620 (1934).
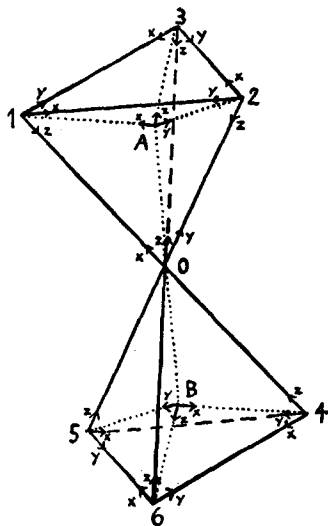[4] S. Bhagavantam and T. Venkatarayudu, Proc. Ind. Acad. Sci. **A9**, 224 (1939).

FIG. 1. Si_2O_7 group.

$A, B =$ Si atoms at the centers$\}$of regular tetrahedra;
$0, 1 \cdots 6 =$ O atoms at the corners$\}$
$x, y, z =$ point coordinates.

tion of the different vibration directions in the infra-red spectrum), we cannot make a more definite statement about the forces in silicate-groups, and we must be

content with the result that it is possible, even with simplified force assumptions, to obtain reasonable correspondence between observed and theoretical frequencies. As in many other cases where vibrational analysis does not or cannot furnish complete information, the data obtained should be considered more as the statement of a problem than as a result.

II. FREQUENCY FORMULAS

The force constants k_i are defined by the potential energy ϕ written as $\phi = \frac{1}{2}\Sigma k_i\Delta_i^2$ ($\Delta_i =$ distance changes) and are always designated in the following manner:

$k_1 =$ force between Si and free O atoms,
$k_2 =$ force between Si and connecting O atoms,
$k' =$ force between connecting O atoms (in SiO_4, free O atoms);
$d =$ bond-bending force at Si in Si_2O_7, assumed to be equal for all angles $O-Si-O$.

M is the mass of the Si atom, m is the mass of the O atoms; $\omega = 2\pi\nu$, ν being the frequency.

a. Si_2O_7 Group, Symmetry Group D_{3d}

Species A_{1g} (inactive, polarized Raman lines):

$$\omega_1^2 + \omega_2^2 + \omega_3^2 = (1/m + 1/3M)k_1 + k_2/M + (2/m + 16/3M)d,$$

$$\omega_1^2\omega_2^2 + \omega_2^2\omega_3^2 + \omega_3^2\omega_1^2 = k_1k_2/Mm + (2/m^2 + 6/Mm)k_1d + 2k_2d/Mm,$$

$$\omega_1^2\omega_2^2\omega_3^2 = 2k_1k_2d/Mm^2.$$

Species A_{2u} (active with vibration parallel to threefold axis, no Raman lines):

$$\omega_6^2 + \omega_7^2 + \omega_8^2 = (1/m + 1/3M)k_1 + (2/m + 1/M)k_2 + (2/m + 16/3M)d,$$

$$\omega_6^2\omega_7^2 + \omega_7^2\omega_8^2 + \omega_8^2\omega_6^2 = (2/m^2 + 5/3Mm)k_1k_2 + (2/m^2 + 6/Mm)k_1d + (4/m^2 + 38/3Mm)k_2d,$$

$$\omega_6^2\omega_7^2\omega_8^2 = (4/m^3 + 14/Mm^2)k_1k_2d.$$

Species E_g (inactive, depolarized Raman lines):

$$\omega_{10}^2 + \omega_{11}^2 + \omega_{12}^2 = (1/m + 4/3M)k_1 + (7/2m + 11/3M)d,$$

$$\omega_{10}^2\omega_{11}^2 + \omega_{11}^2\omega_{12}^2 + \omega_{12}^2\omega_{10}^2 = (7/2m^2 + 8/Mm)k_1d + (9/4m^2 + 3/Mm)d^2,$$

$$\omega_{10}^2\omega_{11}^2\omega_{12}^2 = (9/4m^3 + 6/Mm^2)k_1d^2.$$

Species E_u (active with vibration perpendicular to threefold axis, no Raman lines):

$$\omega_{14}^2 + \omega_{15}^2 + \omega_{16}^2 = (1/m + 4/3M)k_1 + (13/2m + 11/3M)d,$$

$$\omega_{14}^2\omega_{15}^2 + \omega_{15}^2\omega_{16}^2 + \omega_{16}^2\omega_{14}^2 = (13/2m^2 + 12/Mm)k_1d + (39/4m^2 + 11/Mm)d^2,$$

$$\omega_{14}^2\omega_{15}^2\omega_{16}^2 = (39/4m^3 + 24/Mm^2)k_1d^2.$$

All other frequencies are zero.

The oscillations are described by the following symmetry coordinates, expressed in the "point coordinates" of Fig. 1. The properties of the vibration patterns of any species are obtained in putting zero all coordinates not belonging to this species.

Species A_{1g}: $\quad x_A+y_A+z_A+x_B+y_B+z_B, \quad \sum\limits_{i=1}^{6}(x_i+y_i), \quad \sum\limits_{i=1}^{6}z_i.$

Species A_{1u}: $\quad \sum\limits_{i=1}^{6}(x_i-y_i).$

Species A_{2g}: $\quad \sum\limits_{i=1}^{3}(x_i-y_i)-\sum\limits_{i=4}^{6}(x_i-y_i).$

Species A_{2u}: $\quad x_0+y_0+z_0, \quad x_A+y_A+z_A-x_B-y_B-z_B,$

$$\sum\limits_{i=1}^{3}(x_i+y_i)-\sum\limits_{i=4}^{6}(x_i+y_i), \quad \sum\limits_{i=1}^{3}z_i-\sum\limits_{i=4}^{6}z_i.$$

Species E_g (two sets):

$q:\quad \begin{cases} 2x_A-y_A-z_A+2x_B-y_B-z_B, & x_1-x_3+x_4-x_5+y_1-y_2+y_4-y_6, \\ x_2-x_3-x_5+x_6-y_2+y_3+y_5-y_6, & 2z_1-z_2-z_3+2z_4-z_5-z_6; \end{cases}$

$q':\quad \begin{cases} y_A-z_A+y_B-z_B, & x_1-x_3-x_4+x_5-y_1+y_2+y_4-y_6, \\ x_2-x_3+x_5-x_6+y_2-y_3+y_5-y_6, & z_2-z_3+z_5-z_6. \end{cases}$

Species E_u (two sets):

$q:\quad \begin{cases} 2x_0-y_0-z_0, & 2x_A-y_A-z_A-2x_B+y_B+z_B, & x_1-x_3-x_4+x_5+y_1-y_2-y_4+y_6, \\ x_2-x_3+x_5-x_6-y_2+y_3-y_5+y_6, & 2z_1-z_2-z_3-2z_4+z_5+z_6, \end{cases}$

$q':\quad \begin{cases} y_0-z_0, & y_A-z_A-y_B+z_B, & x_1-x_3+x_4-x_5-y_1+y_2-y_4+y_6, \\ x_2-x_3-x_5+x_6+y_2-y_3-y_5+y_6, & z_2-z_3-z_5+z_6. \end{cases}$

Only frequencies belonging to E_u and A_{2u} are observed, but these species could not be identified separately from the experiments.

FIG. 2. Si$_3$O$_9$ group.
(a) view along the threefold axis;
(b) view along one twofold axis;
$A, B, C=$ Si atoms; 1, 2 $\cdots$ 9 $=$ O atoms;
$<3B2=\psi(\cos\psi=-\frac{1}{3})$, $<32B=\chi=\frac{\pi}{2}-\frac{\psi}{2}$.

b. Si$_3$O$_9$ Group, Symmetry Group D_{3h}

Species A_1' (inactive, polarized Raman lines):

ω_1, ω_2, ω_3 are given by

$$\begin{vmatrix} \alpha & \beta & \gamma \\ \beta & \delta & 0 \\ \gamma & 0 & \epsilon \end{vmatrix}=0 \quad \text{with}$$

$$\alpha=-\tfrac{1}{2}M\omega^2+\tfrac{1}{3}(k_1+k_2),$$

$$\beta=\left(\frac{\sqrt{2}}{3}-\frac{\sqrt{3}}{4}\right)k_2, \quad \gamma=-(\tfrac{2}{3})^{\frac{1}{2}}k_1,$$

$$\delta=-\frac{3m}{4}(1-\cos\varphi)\omega^2+\frac{15-6(6)^{\frac{1}{2}}}{8}k'+\frac{59-4(6)^{\frac{1}{2}}}{8}k_2,$$

$$\epsilon=-2m\omega^2+2k_1, \quad \varphi=2\chi-\frac{\pi}{3}, \quad \cos\chi=(\tfrac{2}{3})^{\frac{1}{2}}.$$

Species A_2' (inactive, no Raman lines):

$$\omega_6{}^2=(4/3M+32/9m[1+\cos\varphi])k_2.$$

Species A_2'' (active with vibration parallel to threefold axis, no Raman lines):
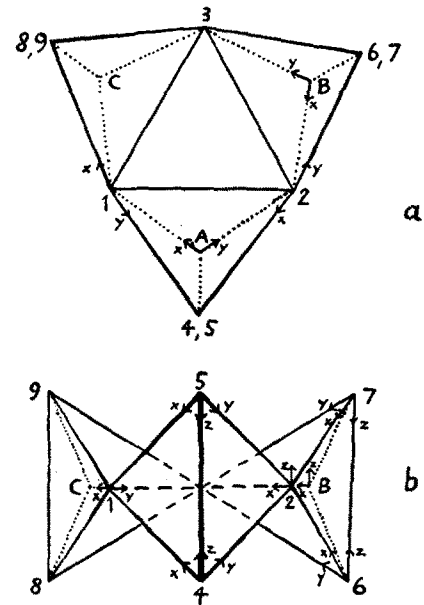
$$\omega_9{}^2=(1/m+4/3M)k_1.$$

Species E' (active with vibration in ring-plane, depolarized Raman lines):

ω_{13}, ω_{14} are given by

$$\begin{vmatrix} -3m(1+\cos\varphi)\omega^2+\left(\dfrac{59}{12}+2(6)^{\frac{1}{2}}\right)k_2+\dfrac{21+6(6)^{\frac{1}{2}}}{8}k' & -\left(\sqrt{3}+\dfrac{4\sqrt{2}}{3}\right)k_2 \\[2mm] -\left(\sqrt{3}+\dfrac{4\sqrt{2}}{3}\right)k_2 & -4M\omega^2+\dfrac{16}{3}k_2 \end{vmatrix}=0;$$

ω_{15}, ω_{16}, ω_{17} are given by

$$\begin{vmatrix} \alpha & -\beta & \gamma \\ -\beta & \eta & 0 \\ \gamma & 0 & \epsilon \end{vmatrix} \quad \text{with} \quad \eta=-3m(1-\cos\varphi)\omega^2+\left(\frac{59}{12}-2(6)^{\frac{1}{2}}\right)k_2+\frac{15-6(6)^{\frac{1}{2}}}{8}k',$$

Species E'' (inactive, depolarized Raman lines):

$$\omega_{20}{}^2=4k_1/3M.$$

All other frequencies are zero. E' is the only species to which observed frequencies belong in benitoite (Fig. 2).

The symmetry coordinates are:

Species A_1': $\displaystyle\sum_{i=1}^{3}(x_i+y_i)$, $\displaystyle\sum_{i=A}^{C}(x_i+y_i)$, $\displaystyle\sum_{i=4}^{9}(x_i+y_i)$, $\displaystyle\sum_{i=4}^{9}z_i$.

Species A_1'': $\displaystyle\sum_{i=2}^{4}[(x_{2i}-y_{2i})-(x_{2i+1}-y_{2i+1})]$.

Species A_2': $\displaystyle\sum_{i=1}^{3}(x_i-y_i)$, $\displaystyle\sum_{i=A}^{C}(x_i-y_i)$.

Species A_2'': $\displaystyle\sum_{i=2}^{4}[(x_{2i}+y_{2i})-(x_{2i+1}+y_{2i+1})]$, $\displaystyle\sum_{i=1}^{3}z_i$, $\displaystyle\sum_{i=A}^{C}z_i$, $\displaystyle\sum_{i=2}^{4}(z_{2i}-z_{2i+1})$.

Species E':

q: $\begin{cases} 2x_2-x_1-x_3, & 2y_2-y_1-y_3, & 2x_C-x_A-x_B, & 2y_C-y_A-y_B, \\ 2x_8+2x_9-x_4-x_6-x_5-x_7, & 2y_8+2y_9-y_4-y_6-y_5-y_7, & 2z_8+2z_9-z_4-z_6-z_5-z_7; \end{cases}$

q': $\begin{cases} x_1-x_3, & y_1-y_3, & x_A-x_B, & y_A-y_B, \\ x_4-x_6+x_5-x_7, & y_4-y_6+y_5-y_7, & z_4-z_6+z_5-z_7. \end{cases}$

Species E'':

q: $\begin{cases} 2z_2-z_1-z_3, & 2z_C-z_A-z_B, & 2x_8-2x_9-x_4-x_6+x_5+x_7, \\ 2y_8-2y_9-y_4-y_6+y_5+y_7, & 2z_8-2z_9-z_4-z_6+z_5+z_7; \end{cases}$

q': z_1-z_3, z_A-z_B, $x_4-x_6-x_5+x_7$, $y_4-y_6-y_5+y_7$, $z_4-z_6-z_5+z_7$.

c. Chain, Symmetry Group C_{2v}

The chain is treated as a crystal lattice of the symmetry group C_{2v} with a translation period in one direction only (Fig. 3).

Species A_1 (active with vibration parallel y_0, polarized Raman lines):

$$\omega_1{}^2=(1/m+4/3M)k_1,$$

$$\omega_2{}^2+\omega_3{}^2=(1/m+2/3M)k_1+(4/9m+2/3M)k_2,$$

$$\omega_2{}^2\omega_3{}^2=(4/9m^2+26/27Mm)k_1k_2.$$

Species A_2 (inactive, depolarized Raman lines):

$$\omega_8{}^2 = (4/9m + 4/3M)k_2.$$

Species B_1 (active, vibration parallel x_0, depolarized Raman lines):

$$\omega_{12}{}^2 = \omega_1{}^2,$$

$$\omega_{13}{}^2 + \omega_{14}{}^2 + \omega_{15}{}^2 = \left[\left(Mm - \frac{7}{12}m^2\right)k_1 + \left(\frac{14}{9}Mm - m^2\right)k_2 + (4Mm - 3m^2)k'\right] \Big/ (Mm^2 - \tfrac{3}{4}m^3),$$

$$\omega_{13}{}^2\omega_{14}{}^2 + \omega_{14}{}^2\omega_{15}{}^2 + \omega_{15}{}^2\omega_{13}{}^2 = \left[\left(\frac{14}{9}M - \frac{20}{27}m\right)k_1k_2 + \left(4M - \frac{7}{3}m\right)k_1k' + \frac{8}{9}Mk_2k'\right] \Big/ (Mm^2 - \tfrac{3}{4}m^3),$$

$$\omega_{13}{}^2\omega_{14}{}^2\omega_{15}{}^2 = 28Mk_1k_2k'/27m(Mm^2 - \tfrac{3}{4}m^3).$$

Species B_2 (active, vibration parallel z_0, depolarized Raman lines):

$$\omega_{20}{}^2 = (14/9m + 4/3M)k_2.$$

The observations do not allow to separate the active vibrations.

The symmetry coordinates are:

Species A_1: $y_0 + y_1$, $x_a + x_b + y_a + y_b$, $z_a + z_b$, $x_3 + x_5 + y_3 + y_5$, $x_2 + x_4 + y_2 + y_4$, $z_3 + z_5$, $z_2 + z_4$.

Species A_2: $y_0 - y_1$, $x_a + x_b - y_a - y_b$, $x_3 + x_5 - y_3 - y_5$, $x_2 + x_4 - y_2 - y_4$.

Species B_1: $x_0 - x_1$, $z_0 + z_1$, $x_a - x_b + y_a - y_b$, $z_a - z_b$, $x_2 - x_4 + y_2 - y_4$, $x_3 - x_5 + y_3 - y_5$, $z_2 - z_4$, $z_3 - z_5$.

Species B_2: $x_0 + x_1$, $z_0 - z_1$, $x_a - x_b - y_a + y_b$, $x_3 - x_5 - y_3 + y_5$, $x_2 - x_4 - y_2 + y_4$.

d. SiO$_4$ and SiO$_2$

The frequency formulas for the complicated SiO_2 structure are not computed with the general method.[5] For our purpose, the following approximation may be sufficient. If two atomic groups are connected by a common O atom which is an inversion center, then the frequency formulas for the connected system are the same as those of the single system, but in which the mass m' of the connecting atom is changed[2] successively to $m'/2$ and to ∞. Thus the frequency formulas for Si_2O_7 may be obtained from those for a Y_3XZ molecule. Now, in the case of quartz, we have not one but four points common to SiO_4 groups, and these connecting points are not inversion centers. Nevertheless, it has been considered a possible approximation to obtain the frequencies of quartz by substituting into the formulas of the isolated SiO_4 group first $m/2$ and then ∞ for m. This treatment cannot, of course, account for all observed frequencies.

For the frequencies of the SiO_4 group, we use the central-force formulas of Dennison-Schaefer,[6] in which k is an additional force constant related to linear terms of the potential energy. These formulas give the following frequencies:

Species A_1 (inactive, completely polarized Raman lines):

$$\omega_1{}^2 = (1/m)k_1 + (4/m)k'.$$

Species E (inactive, depolarized Raman lines):

$$\omega_2{}^2 = (1/m)k' - (1/m)k.$$

Species F_2 (active, depolarized Raman lines):

$$\omega_3{}^2 + \omega_4{}^2 = \left(\frac{4}{3M} + \frac{1}{m}\right)k_1 + \frac{2}{m}k' - \left(\frac{32}{3M} + \frac{2}{m}\right)k;$$

$$\omega_3{}^2\omega_4{}^2 = \frac{8m + 2M}{3Mm^2}(k_1k' - 5k_1k - 8k'k - 8k^2).$$
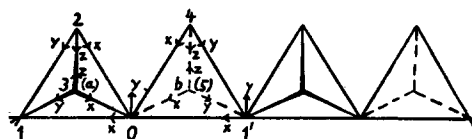
FIG. 3. Chain of SiO$_4$ groups.

a, b = Si atoms at the centers} of regular tetrahedra;
0, $1 \cdots 6$ = O atoms at the corners}

3 and a above} drawing plane;
5 and b below}

z coordinates of a and b are perpendicular to the drawing plane, directed to the points 3 and 5, respectively.

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[5] For β-quartz, the calculation has been accomplished by J. Barriol, J. de phys. et rad. **7**, 209 (1946).

[6] D. M. Dennison, Astrophys. J. **62**, 84 (1925); C. Schaefer, Zeits. f. Physik **60**, 586 (1930).

TABLE I. Frequencies and binding forces for several silicate groups.

Group	Frequencies (cm⁻¹) (Observed = Infra-red reflection maxima, in parentheses: Raman effect data of zircone)						Force constants (10⁵ dynes/cm) k_1	k_2	k' or d	k
SiO₄	obs.	944–894	770*	455(440)	300*(360)					
	calc.	924	770	450	260		4.0	—	0.38	−0.26
zircone		ω_3	ω_1	ω_4	ω_2					
	* calculated from combination bands									
Si₂O₇	obs.	980–860	587	486	435					
	calc.*	915	610	490			2.0	3.0	0	—
thortveitite		1190	750	585			3.0	5.0	0	—
		1110	760	585	425	290	200			
							3.0	4.0	0.2(d)	—
		ω_6	ω_{14}	ω_7	ω_{15}	ω_8	ω_{16}			
	* species A_{2u} and E_u									
Si₃O₉	obs.*	1065–930		768	500–462	385				
	calc.*	1000		740	535	340	4.0	4.0	4.0	—
benitoite		ω_{13}		ω_{15},ω_{16}	ω_{14}	ω_{17}				
		1080	870	770	565	355	5.0	4.5	5.4	—
		ω_{13}	ω_{15}	ω_{16}	ω_{14}	ω_{17}				
	* species E'									
Si₃O₉	obs.	1090	920	630	550					
	calc.*	970	900	635	510	255	5.0	4.0	3.0	—
wollastonite		ω_9, ω_{13}	ω_{15}	ω_{16}	ω_{14}	ω_{17}				
	* species A_2'' and E'									
SiO₃-chain	obs.	1120	970–930			565	520			
	calc.*	1050	1000	920	870	600	520	4.5	4.0	0	—
diopside		ω_{13}	ω_{20}	$\omega_{1,12}$	ω_2	ω_{14}	ω_3			
	* species A_1, B_1, B_2									
SiO₂	obs.	1200–1120	1015	800	690	480	385			
	calc.*	1100	1090		700	595	370	—	4.0	0.38	−0.26
quartz		ω_3'	ω_1'		ω_∞'	ω_4'	ω_2'			
	calc.**	1270	1215	817		538	382	—	4.5	0.7	—
	obs.**		263	128						
	calc.**		292	216						
	* from zircone frequencies and forces ** according to Barriol (see reference 5)									

Substituting $m/2$ for m, we obtain

$$\omega_1'^2 = 2\omega_1^2, \quad \omega_2'^2 = 2\omega_2^2,$$

$$\omega_3'^2 + \omega_4'^2 = \left(\frac{4}{3M} + \frac{2}{m}\right)k_1 + \frac{4}{m}k' - \left(\frac{32}{3M} + \frac{4}{m}\right)k;$$

$$\omega_3'^2 \omega_4'^2 = \frac{16m + 8M}{3Mm^2}(k_1 k' - 5k_1 k - 8k'k - 8k^2).$$

For $m = \infty$, we obtain

$$\omega_\infty'^2 = (4/3M)k_1 - (32/3M)k.$$

Neglecting k, we do not obtain consistent numerical results, and it may be asked, whether neglecting such terms may not involve essential discrepancies in the other cases too. It is not easy to give a reliable answer to this question; but it can be said that, according to experience, simpler force-systems always give good results with complicated molecules and bad ones for simple molecules.

III. BINDING FORCES

Comparison of calculated and observed frequencies will give the values of the force constants only if the interpretation of the observed spectra is correct. It is not possible, in certain cases, to obtain an unambiguous correspondence between observed and calculated frequencies, resulting in more than one possible solution for the force constants. The results of the comparison of calculated and observed frequencies are summarized in Table I.

It is seen that a reasonable interpretation of the spectra is possible by choosing the force constants so that at least one of the major forces k_1 or k_2 has the same value in all groups. But as mentioned before, the ambiguity of the results prevents a sure assertion. Sometimes, only the general structure of the spectrum is represented by the theoretical values, the actual values of the frequencies leading to impossible force constants. Improvements might be accomplished by introducing more complete force systems, but as long as new experiments do not give some indications for them,

it is virtually impossible to do this. Some remarks to the particular groups have to be made:

Si_2O_7

At first sight, the first solution seems to be the best one, but the force constants are unreasonably low compared with those of the other groups: In all other solutions there is no such good agreement between observed and calculated values. A not unreasonable substitute is the last combination of force constants which is not inconsistent with the observed spectrum although it is far from being ideal. The effect of the neglection of the bond-bending force is clearly seen in the second solution; cutting off the low frequencies and changing the remaining force constants.

Si_3O_9

The main feature of the proposed solutions is the large value of k'. It has been impossible to find solutions with substantially smaller forces k'. Which one of the two solutions should be preferred is hard to say. Regarding the desirable connection with the other groups, the first one should be selected, but the second one gives a better description of the higher frequencies. The observation of ω_9, which has not yet been made because of the crystallographic orientation of the benitoite sample, would at once give a decision and lead to further elucidation; it is to be expected at 865 or 970 cm^{-1} for $k_1 = 4$ or 5, respectively.

The large value of k' might be ascribed to the special structure of the group. It is not impossible that the formation of a ring may alter the binding forces considerably, or rather that ring-formation will occur only if there are such forces. Insofar as a frequency at about 750 appears within a considerable range of the force constants, it might be considered as characteristic of the structure itself and designated as ring-band as suggested before (of course, not every band at this frequency is a ring-band).

There are reasonable combinations of force constants that do not give a frequency near 750, e.g., the values $k_1 = 5.0$, $k_2 = 4.0$, $k' = 3.0$ lead to the frequencies given in Table I for wollastonite. It is remarkable that wollastonite ($CaSiO_3 = Ca_3Si_3O_9$) on the one side has Si_3O_9 rings but on the other side lacks the "ring-band" in the spectrum, if not the very weak band at 630 shall be acknowledged as this band. Our result for the just mentioned force constants shows that there need not be a contradiction of the wollastonite spectrum to our other interpretations. But there is no explanation for the change of k' in the wollastonite ring.

SiO_3 chain

With exception of ω_{13}, the frequency values are rigorously or practically independent of k'; therefore also larger k' values might be possible. But here as in Si_2O_7, the introduction of bond-bending forces might change some k values. Furthermore it must be realized that the chain of Fig. 3 is idealized, only more or less twisted chains occurring in the actual lattices.

SiO_2

Our approximation method does not claim to give unrefutable results for quartz, but nevertheless it is remarkable that it accounts reasonably well for the shift from ω_3 of SiO_4 to ω_3' of SiO_2; the vibration pattern of just this frequency approximately obeys the conditions for the applicability of our method. At present, we cannot decide which of the calculated frequencies corresponds to the observed one at 800 cm^{-1}. It may be that this frequency is not at all included in our treatment. The frequency values of Barriol, which are obtained from a more rigorous treatment similar to that used here for the other silicate groups, are not very satisfactory either although a frequency near 800 appears. Saksena[7] obtains different force constants for a valence force system from a computation of the totally symmetric vibrations. His values are: $k_2 = 5.065$, $d_{Si-O-Si} = 0.512$, $d_{O-Si-O} = 0.949$. The Raman-active species are calculated by Barriol with reasonable agreement with observation.

Finally, it must again be warned not to rely on the presented results as providing physical constants, because of the inherent incompleteness of this as every vibrational analysis of complicated molecules. However, it is my opinion that the results indeed show that a reasonable interpretation of the silicate spectra is possible even if simplified force systems are used and if it is assumed that the forces in the different groups are not quite independent of one another. But only further experiments can test the proposed solutions and lead to improvements and to indications whether the neglection of forces in some cases might have been too detrimental.

[7] B. D. Saksena, Proc. Ind. Acad. Sci. A16, 270 (1942).