When the current is increasing exponentially, $i(t)=i(0)\exp(t/\theta)$ so that Eq. (A1) becomes

$$1=\gamma[m_{+}\exp(-T_{+}/\theta)+G]. \tag{A3}$$

When the electrode spacing is fixed, γ and m_{+} are functions of V. The quantity G is a function of V and ξ (which contains θ implicitly). The following are typical of the expansions to first order of these functions about their breakdown values:

$$\begin{aligned}
V&=V_b+\Delta V,\\
\gamma&=\gamma_b+(d\gamma/dV)_b\Delta V=\gamma_b+(1/pd)[d\gamma/d(E/p)]_b\Delta V,\\
G&=G_b+(\partial G/\partial V)_b\Delta V+(\partial G/\partial\xi)_b\Delta\xi,\\
\xi&=[(Ap+Bp^2+1/\theta)/D]^{\frac{1}{2}}\\
&=\xi_b+(1/2\xi_bD)(1/\theta),\\
\exp(-T_{+}/\theta)&=1-T_{+}/\theta.
\end{aligned}$$

Recall the breakdown criterion $1=\gamma_b[m_{+b}+G_b]$. When expressions such as the ones we have listed are substituted into Eq. (A3), Eq. (8) of the text follows.

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Theory of the Optical Properties of Quartz in the Infrared

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A theoretical study has been carried out of the eight nondegenerate optical vibrations of α quartz including the problem of their infrared and Raman intensities. The investigation consists of three parts: First, the atomic motions and frequencies are calculated on the basis of a valence force model. It is shown that the 207 cm^{-1} vibration involves atomic motions very similar to those of the α-β transformation. Secondly, a general discussion is given of infrared absorption in complex crystals, which shows that in quartz the intensities are determined by the atomic motions through 12 effective charge parameters. The intensities are calculated in good agreement with experiment on the assumption of a 2-charge model suggested by the valence nature of quartz. It is shown that a 1-charge model, the usual model for an ionic crystal, cannot account for the observed intensities. Finally, the relative Raman intensities are calculated with no adjustable parameters in good agreement with experiment on the basis of a simple assumption about the atomic polarizabilities. The calculation accounts for the surprising weakness of the 1082-cm^{-1} stretching vibration in the Raman effect. The three parts of the investigation are mutually dependent, since the infrared and Raman intensities depend in an essential way upon the atomic motions corresponding to each frequency. It is shown that a consideration of the Raman intensities as well as the usual comparison of frequencies is required to determine the bending constants of the valence force model. It is inferred from the success of the calculations that the three principal assumptions of the present work, namely the valence force model for the vibrations, the 2-charge model for the infrared intensities, and the simple Raman model, are all applicable for quartz.

I. INTRODUCTION

THIS paper is concerned with the fundamental lattice vibrations of α quartz and the intensities of these vibrations in infrared absorption and Raman scattering. The range of these intensities extends over more than an order of magnitude, so that in some cases a fundamental frequency exhibits a weaker effect than a combination frequency. An adequate explanation of this phenomenon would be very desirable both from the standpoint of practical spectroscopy and of the basic physics of dielectric crystals. The problem of relating the intensities to the corresponding vibrations may be called the *effective charge* problem. The problem is to determine an effective charge and an effective polarizability coefficient[1] for each atom in the unit cell such that all crystal vibrations have the correct infrared and Raman intensities. This problem is essentially trivial in the diatomic cubic crystals where the effective charge is a single parameter which can be adjusted to give the measured intensity of the single fundamental optical vibration. The problem then remains of explaining the effective charge in terms of the atomic polarizabilities, which may be called the *local field* problem.[2] In complicated crystals, however, the effective charge problem itself may be formidable. The effective charges become tensors, and the total number of independent components of all these tensors is the number of fundamental lattice vibrations active in the infrared.

It might appear that the effective charge problem in quartz with its 16 fundamental vibrations is hopelessly complicated. Furthermore, the problem cannot be approached until something is known or assumed about the nature of the vibrations. Nevertheless some progress has been made on the problem, notably by Saksena and associates. Saksena and Bhatnagar[3] have attempted

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[1] The effective charge is sometimes called the dipole derivative, the derivative of the electric moment with respect to the displacement of a certain atom. The polarizability coefficient is the derivative of the polarizability with respect to the displacement of a certain atom. For a discussion of the effective charge as the term is used here see H. Callen, Phys. Rev. **76**, 1394 (1949).

[2] The local field problem in this sense has been treated by: B. Dick and A. Overhauser, Phys. Rev. **112**, 90 (1958); J. Hanlon and A. Lawson, *ibid.* **113**, 472 (1959); B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949).

[3] B. D. Saksena and S. S. Bhatnagar, Proc. Indian Acad. Sci. **A30**, 308 (1949).

to predict the relative intensities of the four infrared active-Raman inactive vibrations of quartz on the basis of normal modes of vibration previously calculated by Saksena.[4] Qualitative agreement with reflectivity measurements was claimed, but the actual strengths of the resonances were not known at the time, and no proper comparison with experiment could be made. More recently Stepanov and Prima[5] have calculated frequencies and intensities for β quartz and several mineral silicates. Some calculations have been reported for the intensities in molecules.[6–8] In particular Rollefson and Havens[7] have made a careful theoretical and experimental study of CH_4 and report great discrepancies between the calculated and measured intensities of the infrared bands. Similar discrepancies were found by Bell *et al.*[8] who considered certain bending vibrations in the molecules of a number of benzene derivatives. All of these calculations are based on the rather drastic assumption that the tensor effective charge can be approximated by a scalar representing a point charge residing on and moving with the ion. The sizeable discrepancies between calculated and measured intensities are probably[7] due to this assumption.

An experimental investigation of the intensities of the infrared active fundamental vibrations of quartz has recently been completed.[9] With the information provided by this investigation it now becomes possible to treat the effective charge problem in quartz. It is proposed in the present work that the infrared intensities in quartz can be accounted for on the basis of a simple kind of tensor effective charge suggested by a valence bond picture of the quartz crystal. Comparisons between theory and experiment are presented for the four infrared active–Raman inactive vibrations based upon new calculations of the normal modes of vibration. The Raman intensities reported by Krishnan[10] for these vibrations are found to be consistent with a scalar polarizability coefficient which depends only on the Si-O distance. The local field problem is not considered in this paper beyond pointing out that the effective charges obtained seem physically reasonable. Detailed consideration is given to the problem of calculating the normal modes of vibration and to the physical nature of the modes.

Of particular interest is the mode of wave number 207 cm^{-1} which is Raman active–infrared inactive. According to Raman and Nedungadi[11] the excitation of this vibration with increasing temperature is responsible for the α-β phase transformation in quartz at 575°C. Narayanaswamy[12] has reported that as the transformation temperature is approached, the Raman line at 207 cm^{-1} broadens remarkably, shifts to lower frequency, and ultimately disappears. It is therefore of considerable interest to compare the appropriate calculated mode of vibration with the motions of atoms in the α-β transformation. This comparison is presented here and reveals a striking similarity.

Two approaches have been proposed for understanding the essential features of the vibration spectra of quartz. Matossi[13] has attempted to account for the vibration frequencies of several silicate minerals including quartz by considering the SiO_4 tetrahedron. All silicates exhibit infrared bands near 1000 and 500 cm^{-1} which are interpreted as the two active frequencies of the tetrahedron. The tetrahedron also has inactive frequencies corresponding to wave numbers near 770 and 360 cm^{-1}. Matossi points out that bands are observed in quartz near all four of these frequencies. In spite of this superficial correspondence of frequencies the normal modes of quartz cannot be deduced in any straightforward way from those of the tetrahedron. Barriol[14] has suggested that the vibrations of quartz may be in first approximation the same as those of β quartz. Because of the higher symmetry of β quartz it is much easier to calculate its modes and frequencies, and these can be assigned to the appropriate symmetry species of quartz.[14,15] This approach provides an attractive explanation for the intensities of the doubly degenerate (species E) infrared lines. In β quartz there are eight doubly degenerate vibrations, four of which are inactive in the infrared spectrum. This suggests that of the eight doubly degenerate vibrations in quartz four should be weak and four should be strong in agreement with experiment.[9] The same argument applied to the eight nondegenerate vibrations, however, does not give results in agreement with experiment. Both the central force model of Barriol and the valence force model of Saksena and Narian[15] predict zero frequency for the vibration corresponding to the 207-cm^{-1} Raman line. It seems therefore that the β-quartz model cannot be used to discuss the relationship of this vibration to the α-β transformation. Since neither of these approaches is suitable for quantitative calculations they will not be considered further in this paper.

In the present work it is proposed that the vibrations of quartz are best understood by considering the motions of the O atoms relative to their Si neighbors. The valence bond picture of quartz suggests that the O atom may vibrate with respect to its neighbors along three mutually orthogonal directions with quite different frequencies. Therefore the normal modes are expanded

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[4] B. D. Saksena, Proc. Indian Acad. Sci. **A22**, 379 (1945).

[5] B. I. Stepanov and A. M. Prima, Optika i Spektroskopiya 4, 734 (1958).

[6] D. M. Dennison, Phil. Mag. 1, 216 (1926).

[7] R. Rollefson and R. Havens, Phys. Rev. **57**, 710 (1940).

[8] R. P. Bell, H. W. Thompson, and E. E. Vago, Proc. Roy. Soc. (London) **192**, 498 (1948).

[9] W. G. Spitzer and D. A. Kleinman, Phys. Rev. **121**, 1324 (1961).

[10] R. S. Krishnan, Nature **155**, 452 (1945).

[11] C. V. Raman and T. M. K. Nedungadi, Nature **144**, 147 (1940).

[12] P. K. Narayanaswamy, Proc. Indian Sci. Sci. **A28**, 417 (1948).

[13] F. Matossi, J. Chem. Phys. **17**, 679 (1949).

[14] J. Barriol, J. phys. radium **7**, 209 (1946).

[15] B. D. Saksena and H. Narian, Proc. Indian Acad. Sci. **A30**, 128 (1949).

in terms of these O motions combined with appropriate Si motions. The normal modes and frequencies are obtained on the assumption of the usual valence force model[16] previously used for quartz by Saksena.[17] For simplicity, consideration is limited to the eight nondegenerate modes of vibration. The effective charge problem in quartz divides itself naturally into three parts, the normal modes, the infrared intensities, and the Raman intensities, which are treated in Secs. II, III, and IV, respectively.

II. NORMAL MODES OF VIBRATION

Formulation

A projection of the atoms in a unit cell of quartz onto the basal plane (normal to the triad axis) is shown in Fig. 1. The atoms are numbered according to the notation of Saksena[18] where numbers 1, 2, 3 are Si and 4 through 9 are O atoms. The Cartesian coordinates of each atom are given in Table I, referred to the x, y axes shown in Fig. 1 and a z axis normal to the basal plane, based on data furnished by Wyckoff.[19] Also given in Table I are the Cartesian components of the unit vectors $\boldsymbol{\varrho}$ between neighboring Si and O atoms associated with the tetrahedron of atom 1. Since some of these atoms are not part of the unit cell of Fig. 1 their numbers are primed. It may be noted that the Si atoms do not lie at the hexagonal vertices in the basal plane. In the α-β transformation the Si atoms move out to the vertices and the O atoms move to planes bisecting the angles between the Si atoms. The projection of the motion of atom 4 is shown by the heavy arrow in Fig. 1. Table II gives the atomic displacements of the Si 1 tetrahedron in the α-β transformation.

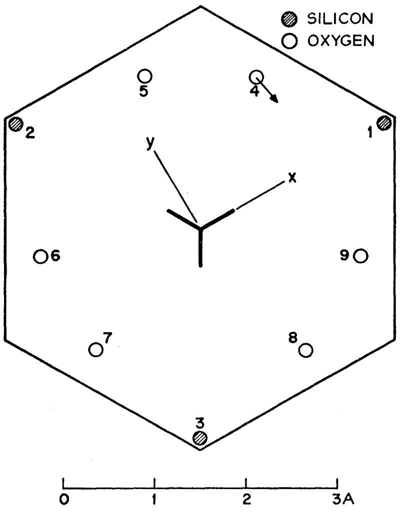

FIG. 1. Projection of the atoms of the unit cell of quartz onto the basal plane. The arrow shows the α-β transformation.

The symmetry elements of quartz are a triad screw-axis normal to the basal plane through the origin of Fig. 1 and diad axes through each Si atom intersecting the triad axis. The unit cell has the symmetry group D_3 if displacements of the translation lattice are considered equivalent to the identity operation. Saksena[18] has shown that the 24 vibrational degrees of freedom of the unit cell can be classified according to symmetry as follows[20]: four of *species* A_1, nondegenerate totally symmetric Raman active–infrared inactive; four of *species* A_2, nondegenerate Raman inactive–infrared active in the extraordinary ray; eight of *species* E, doubly degenerate Raman active–infrared active in the ordinary ray. These vibrations correspond to the vibrations of quartz having the periodicity of the lattice, the so-called *optical vibrations*.

TABLE I. Cartesian coordinates in angstroms of the atoms according to the numbering of Fig. 1. Also given are the unit vectors $\boldsymbol{\varrho}$ representing the bonds belonging to silicon tetrahedron 1.

Atom	x	y	z
1 silicon	2.280	0	0
2	−1.140	1.974	−1.796
3	−1.140	−1.974	1.796
4 oxygen	1.368	1.155	0.647
5	0.316	1.760	−2.443
6	−1.684	0.607	−1.149
7	−1.684	−0.607	1.149
8	0.316	−1.760	2.443
9	1.368	−1.155	−0.647
$1 \rightarrow 4\,\boldsymbol{\varrho}$	−0.566	0.720	0.402
$1 \rightarrow 9$	−0.566	−0.720	−0.402
$1 \rightarrow 6'$	0.586	0.379	−0.716
$1 \rightarrow 7'$	0.586	−0.379	0.716
$4 \rightarrow 3'$	−0.036	0.694	0.716
$9 \rightarrow 2'$	−0.036	−0.694	−0.716
$6' \rightarrow 2''$	0.341	0.850	−0.402
$7' \rightarrow 3''$	0.341	−0.850	0.402

Therefore, it must be possible to reduce the problem of determining the frequencies ω to two secular equations of degree 4 in ω^2 and one of degree 8. This reduction is best done by writing the equations of motion in terms of *symmetry coordinates*, which are linear combinations of the coordinates of all the atoms in the unit cell so constructed as to form bases for the symmetry species. If the species occurs only once in the vibrations the symmetry coordinate is also a normal coordinate. In other cases the symmetry coordinates are not necessarily normal coordinates but linear combinations of normal coordinates of the same species. Nevertheless, the hope exists that one might intuitively construct symmetry coordinates which are approximately normal

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[16] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), Chap. II, Sec. 4.

[17] B. D. Saksena, Proc. Indian Acad. Sci. **A16**, 270 (1942).

[18] B. D. Saksena, Proc. Indian Acad. Sci. **A12**, 93 (1940).

[19] R. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951).

[20] The notation follows that of Herzberg (see reference 16). The term *species* designates an irreducible representation of the symmetry group. Species A_1 and A_2 are called class A and B, respectively, in the notation of Saksena (see reference 18).

modes, although this is more difficult in crystals than in molecules. Saksena[18] has given symmetry coordinates for quartz and diagrams showing the corresponding atomic motions. It does not appear that any consideration of the atomic motions went into the construction of these symmetry coordinates, so they probably have no physical significance.

It is convenient to refer to the atomic displacements corresponding to a symmetry coordinate as a *symmetry mode*. A symmetry mode j is specified by a set of vectors $\mathbf{q}_j{}^\alpha$ which gives the displacement of each atom α of the unit cell. An arbitrary displacement may be expanded in the symmetry modes

$$\mathbf{x}^\alpha = \sum_j \mathbf{q}_j{}^\alpha Q_j, \tag{1}$$

where Q_j are the *symmetry coordinates* of the arbitrary displacement. The $\mathbf{q}_j{}^\alpha$ may be chosen orthogonal to one another such that

$$\sum_\alpha m^\alpha \mathbf{q}_j{}^\alpha \cdot \mathbf{q}_k{}^\alpha = \mu_j \delta_{jk}, \tag{2}$$

TABLE II. Atomic displacements in the α-β transformation.

Atom	x (A)	y (A)	z (A)
1	0.17	0	0
4	0.08	−0.32	0.25
9	0.08	0.32	−0.25
6′	0.23	0.23	0.25
7′	0.23	−0.23	−0.25

where m^α is the mass of the αth atom and the sum is over the unit cell. The constants μ_j, which specify the normalization, may be considered to be the masses of the symmetry modes. For orthogonal modes the symmetry coordinates are given by

$$Q_j = \sum_\alpha (m^\alpha/\mu_j) \mathbf{q}_j{}^\alpha \cdot \mathbf{x}^\alpha. \tag{3}$$

If the symmetry coordinates are given in the form

$$Q_j(\mathbf{x}^\alpha) = \sum_\alpha \mathbf{v}_j{}^\alpha \cdot \mathbf{x}^\alpha, \tag{4}$$

where the components of $\mathbf{v}^\alpha$ are constant coefficients, then the orthogonality relation (2) takes the form

$$\sum_\alpha (m^\alpha)^{-1} \mathbf{v}_j{}^\alpha \cdot \mathbf{v}_k{}^\alpha = \mu_j{}^{-1} \delta_{jk}. \tag{5}$$

If (5) is satisfied, the mode vectors are

$$\mathbf{q}_j{}^\alpha = (\mu_j/m^\alpha) \mathbf{v}_j{}^\alpha. \tag{6}$$

The orthogonality relation for symmetry modes is written in the form (2) since this is the relation satisfied by the normal modes of vibration. It is not essential that the symmetry modes be orthogonal. For nonorthogonal modes the Q_j are defined by (1), but (3) is not valid. The equations of motion for the Q_j can be obtained, however, without obtaining explicit expressions of the form (4) for Q_j.

TABLE III. Unit vectors $\boldsymbol{\xi}$, $\boldsymbol{\eta}$, $\boldsymbol{\zeta}$ for the three types of O motion·

Atom		$\boldsymbol{\xi}$	$\boldsymbol{\eta}$	$\boldsymbol{\zeta}$
4	x	0.860	−0.317	−0.404
	y	−0.042	0.744	−0.667
	z	0.510	0.588	0.626
5		0.466	−0.802	0.375
		−0.724	−0.098	0.682
		0.510	0.588	0.626
6		−0.393	−0.486	0.780
		0.766	−0.646	−0.017
		0.510	0.588	0.626
7		0.393	0.486	−0.780
		0.766	−0.646	−0.017
		0.510	0.588	0.626
8		−0.466	0.802	−0.375
		−0.724	−0.098	0.682
		0.510	0.588	0.626
9		−0.860	0.317	0.404
		−0.042	0.744	−0.667
		0.510	0.588	0.626

The *normal modes* of vibration can be written

$$\mathbf{n}_k{}^\alpha = \sum_j \mathbf{q}_j{}^\alpha Q_{jk}, \tag{7}$$

where the sum extends over only the symmetry modes of a particular species, and Q_{1k}, Q_{2k}, $\cdots$, Q_{jk}, $\cdots$ satisfy the equations of motion for a frequency eigenvalue ω_k. Regardless of whether the symmetry modes are orthogonal, the normal modes must satisfy

$$\sum_\alpha m^\alpha \mathbf{n}_k{}^\alpha \cdot \mathbf{n}_l{}^\alpha = m_k \delta_{kl}, \tag{8}$$

where m_k may be considered the mass of the kth mode. An arbitrary displacement may be expanded in the normal modes

$$\mathbf{x}^\alpha = \sum_k \mathbf{n}_k{}^\alpha N_k, \tag{9}$$

where the N_k are the *normal coordinates* of the displacement.

As a starting point for the present work, predicted motions for the O atoms of quartz were used to construct new symmetry modes. Each O atom is bonded to two Si atoms with bonds of nearly equal length making an angle of 144°. If $\boldsymbol{\varrho}$ and $\boldsymbol{\varrho}'$ are unit vectors pointing along the bonds toward the Si atoms, the vectors $\boldsymbol{\varrho}+\boldsymbol{\varrho}'$, $\boldsymbol{\varrho}-\boldsymbol{\varrho}'$, and $\boldsymbol{\varrho}\times\boldsymbol{\varrho}'$ define three mutually orthogonal directions which are designated ξ, η, and ζ respectively. The unit vectors $\boldsymbol{\xi}$, $\boldsymbol{\eta}$, and $\boldsymbol{\zeta}$ for each O atom of Fig. 1 are given in Table III. The sign of each vector has been chosen to make all the z components positive. It may be expected intuitively that the O atoms move along one of these three directions in many of the normal modes of vibration. In particular, the highest frequency mode in any species should involve motions of the η type, since this motion stretches and compresses the bonds. Also the lowest frequency mode should be of the ζ type which does not change the bond lengths. Therefore, symmetry modes constructed from the $\boldsymbol{\xi}$, $\boldsymbol{\eta}$, and $\boldsymbol{\zeta}$ vectors might be expected to have physical significance. Although symmetry modes for species E can be constructed from these vectors, consideration here will be limited for simplicity to species A_1 and A_2.

Four symmetry modes are required to represent the most general vibration of species A_1. Three of these can be O motions of the ξ, η, ζ types, and the fourth must involve Si motion along the radial direction in the x, y plane. If $\mathbf{r}$ is a unit vector in the x, y plane in the outward radial direction representing Si motion, the symmetry modes for A_1 can be designated r, ξ, η, ζ. These modes are orthogonal according to (2) and have the masses 84.18, 96, 96, and 96, respectively, if m^α is expressed in atomic weights. In constructing the ξ, η, ζ modes care must be taken to choose the correct sign for the vectors of Table III for each atom. For A_1 the symmetry modes are defined by

$$\begin{aligned}(A_1):\quad \mathbf{q}_\xi{}^\alpha &= +\boldsymbol{\xi}^\alpha \quad \text{for} \quad \alpha=4,6,8\\ &= -\boldsymbol{\xi}^\alpha \quad \text{for} \quad \alpha=5,7,9;\end{aligned}$$

similarly for $\boldsymbol{\eta}$, $\boldsymbol{\zeta}$;

$$\mathbf{q}_r{}^\alpha=\mathbf{r}^\alpha \quad \text{for} \quad \alpha=1,2,3, \tag{10}$$

where ξ, η, ζ are given in Table III and the atoms are numbered as in Fig. 1.

The sets of $\boldsymbol{\xi}$, $\boldsymbol{\eta}$, $\boldsymbol{\zeta}$ vectors given in Table III constitute symmetry coordinates for A_2 with the signs as given. It will be noticed, however, that in these modes all of the O atoms move in the same sense along the z axis so that the center of gravity of the unit cell is not at rest. If only four symmetry modes are to be used, it is essential that they be orthogonal to a rigid motion of the unit cell along the z axis. To keep the center of gravity at rest a Si motion along z can be combined with the O motions of ξ, η, ζ. A fourth symmetry mode is needed to represent tangential motion of the Si atoms around the triad axis. If $\mathbf{t}$ is a unit tangential vector in the counterclockwise sense of rotation, the A_2 symmetry modes can be written

$$\begin{aligned}(A_2):\quad \mathbf{q}_\xi{}^\alpha &= \boldsymbol{\xi}^\alpha &&\text{for} \quad \alpha=4,5,\cdots 9\\ &= -(2m_s/m_0)\xi_z{}^\alpha\mathbf{z} &&\text{for} \quad \alpha=1,2,3;\end{aligned}$$

similarly for $\boldsymbol{\eta}$, $\boldsymbol{\zeta}$;

$$\mathbf{q}_t{}^\alpha=\mathbf{t}^\alpha \quad \text{for} \quad \alpha=1,2,3, \tag{11}$$

where $\mathbf{z}$ is a unit vector in the z direction, and m_s, m_0 are the atomic weights of Si and O, respectively. These modes are less convenient than those of (10) because $\mathbf{q}_\xi{}^\alpha$, $\mathbf{q}_\eta{}^\alpha$, $\mathbf{q}_\zeta{}^\alpha$ are not mutually orthogonal, although they are orthogonal to $\mathbf{q}_t{}^\alpha$. The main difficulty introduced by the nonorthogonality is that the secular equation for the frequencies is more difficult to reduce to polynomial form. It turns out that the nonorthogonality does not seriously interfere with the characterization of the normal modes in terms of the O motions.

The kinetic energy expressed in symmetry coordinates is

$$T=\tfrac{1}{2}\sum_{ij}\mu_{ij}\dot{Q}_i\dot{Q}_j, \tag{12}$$

where

$$\mu_{ij}=\sum_\alpha m^\alpha \mathbf{q}_i{}^\alpha\cdot\mathbf{q}_j{}^\alpha. \tag{13}$$

For orthogonal modes $\mu_{ij}=\delta_{ij}\mu_j$. The kinetic energy for the A_1 symmetry modes (10) is given by

$$T_{A_1}=\tfrac{1}{2}\mu_r\dot{Q}_r{}^2+\tfrac{1}{2}\mu(\dot{Q}_\xi{}^2+\dot{Q}_\eta{}^2+\dot{Q}_\zeta{}^2), \tag{14}$$

where $\mu_r=84.18$ and $\mu=96$ measured in atomic weights. For the A_2 symmetry modes (11)

$$\begin{aligned}T_{A_2}=\tfrac{1}{2}\mu_t[\dot{Q}_t{}^2&+(0.339)\dot{Q}_\xi{}^2+(0.450)\dot{Q}_\eta{}^2+(0.510)\dot{Q}_\zeta{}^2\\ &+2(0.391)\dot{Q}_\xi\dot{Q}_\eta+2(0.479)\dot{Q}_\eta\dot{Q}_\zeta\\ &+2(0.416)\dot{Q}_\xi\dot{Q}_\zeta]+\tfrac{1}{2}\mu(\dot{Q}_\xi{}^2+\dot{Q}_\eta{}^2+\dot{Q}_\zeta{}^2),\end{aligned} \tag{15}$$

where $\mu_t=84.18$.

The potential energy will be written as the sum of three terms

$$V=V_s+V_{b,\mathrm{Si}}+V_{b,\mathrm{O}}, \tag{16}$$

representing the stretching of bonds, the bending of the Si bond angles, and the bending of the O bond angles, respectively. If $\boldsymbol{\varrho}$ is a unit vector representing some bond, and $\mathbf{x}_\rho$ and $\mathbf{x}_\rho{}'$ are the atomic displacements at the two ends of the bond, the stretching energy may be written

$$V_s=\tfrac{1}{2}K\sum_\rho[(\mathbf{x}_\rho-\mathbf{x}_\rho{}')\cdot\boldsymbol{\varrho}]^2, \tag{17}$$

where the sum is over all bonds with one end terminating on a Si atom of the unit cell. The change in the angle θ between two bonds, $\boldsymbol{\varrho}$ and $\boldsymbol{\varrho}'$, of an atom may be written as

$$\begin{aligned}\Delta\cos\theta=[\boldsymbol{\varrho}-\boldsymbol{\varrho}'(\boldsymbol{\varrho}\cdot\boldsymbol{\varrho}')]\cdot(\mathbf{x}_{\rho'}-\mathbf{x})d^{-1}&\\ +[\boldsymbol{\varrho}'-\boldsymbol{\varrho}(\boldsymbol{\varrho}\cdot\boldsymbol{\varrho}')](\mathbf{x}_\rho-\mathbf{x})d^{-1},&\end{aligned} \tag{18}$$

where d is the Si-O distance $=1.60$ A, $\boldsymbol{\varrho}$ and $\boldsymbol{\varrho}'$ extend outward, $\mathbf{x}_\rho$ and $\mathbf{x}_{\rho'}$ are the displacements of the respective neighbors, and $\mathbf{x}$ is the displacement of the atom. The bending energies may then be written

$$\begin{aligned}V_{b,\mathrm{Si}}&=\tfrac{1}{2}K'\textstyle\sum_{\mathrm{Si}}(\Delta\cos\theta)^2d^2,\\ V_{b,\mathrm{O}}&=\tfrac{1}{2}K''\textstyle\sum_{\mathrm{O}}(\Delta\cos\theta)^2d^2,\end{aligned} \tag{19}$$

where $\sum_{\mathrm{Si}}$ is over all Si bond angles (six for each Si atom), and $\sum_{\mathrm{O}}$ is over all O atoms of the unit cell. Expressions for V_s, $V_{b,\mathrm{Si}}$, and $V_{b,\mathrm{O}}$ in terms of symmetry coordinates are obtained by substituting the appropriate $\mathbf{x}^\alpha$ from (1) for $\mathbf{x}$, $\mathbf{x}_\rho$, $\mathbf{x}_\rho{}'$, $\mathbf{x}_{\rho'}$ in (17), (18), and (19). The general form for the equations of motion in terms of T and V is

$$\frac{d}{dt}\frac{\partial T(\dot{Q})}{\partial\dot{Q}_j}=-\frac{\partial V(Q)}{\partial Q_j}. \tag{20}$$

A_1 Modes

Consider first a pure stretching model in which $V=V_s$. This model should be a good approximation for the highest frequency normal mode. For the A_1 symmetry coordinates

$$\begin{aligned}V_s=\tfrac{1}{2}K[3.98Q_r{}^2&+10.86Q_\eta{}^2\\ &+1.164Q_\xi{}^2+2(6.57)Q_rQ_\eta],\end{aligned} \tag{21}$$

where very small terms in Q_rQ_ξ and $Q_\eta Q_\xi$ have been neglected. Since Q_ζ does not appear in V_s, it is a normal coordinate belonging to zero frequency in the pure stretching model. Also Q_ξ is a normal coordinate since it enters T_{A_1} and V_s only as $\dot{Q}_\xi^2$ and Q_ξ^2. The equations for Q_r and Q_η are

$$\begin{bmatrix} 3.98K-\mu_r\omega^2 & 6.57K \\ 6.5K & 10.86K-\mu\omega^2 \end{bmatrix}\begin{bmatrix} Q_r \\ Q_\eta \end{bmatrix}=0. \tag{22}$$

The solutions and frequencies are

$$\begin{bmatrix} -1.65 \\ 1.00 \end{bmatrix};\quad \omega^2=0, \tag{23}$$

and

$$\begin{bmatrix} 0.69 \\ 1.00 \end{bmatrix};\quad \omega_4^2=K\left(\frac{3.98}{\mu_r}+\frac{10.86}{\mu}\right), \tag{24}$$

where ω is 2π times the frequency. The mode (24) is to be identified with the highest A_1 wave number[18] 1082 cm^{-1}, which gives for the stretching force constant

$$K=4.32\times10^5 \text{ dyne/cm}. \tag{25}$$

The normal modes of vibration will be denoted by $\mathbf{n}_1$, $\mathbf{n}_2$, $\mathbf{n}_3$, $\mathbf{n}_4$ in order of increasing frequency. It is assumed temporarily that $\mathbf{n}_4$ is given correctly by the pure stretching model:

$$\mathbf{n}_4=C[(0.69)\mathbf{q}_r+\mathbf{q}_\eta], \tag{26}$$

where C is a normalization factor to be specified later. The other three modes given by the stretching model will be used as the basis for $\mathbf{n}_1$, $\mathbf{n}_2$, $\mathbf{n}_3$ in a calculation which includes Si and O bending forces. This procedure has the advantage of reducing the secular equation from fourth to third order for the determination of the bending constants K' and K''. Therefore let new symmetry modes be defined by

$$\mathbf{q}_\zeta,\mathbf{q}_\xi,\mathbf{q}_\delta=[(-1.65)\mathbf{q}_r+\mathbf{q}_\eta],\quad \mathbf{q}_4=\mathbf{n}_4, \tag{27}$$

which are orthogonal and have masses $\mu_\zeta=\mu_\xi=96$, $\mu_\delta=325$, and $\mu_4=136C^2$, respectively. The kinetic energy in coordinates Q_ζ, Q_δ, Q_ξ is

$$T_{A_1}=\tfrac{1}{2}(\mu_\xi\dot{Q}_\zeta^2+\mu_\delta\dot{Q}_\delta^2+\mu_\xi\dot{Q}_\xi^2), \tag{28}$$

and the three potential energy terms are

$$\begin{aligned} V_s&=\tfrac{1}{2}K(1.164)Q_\xi^2,\\ V_{b,\mathrm{Si}}&=\tfrac{1}{2}K'[(51.6)Q_\delta^2+(26.2)Q_\xi^2\\ &\qquad+(20.6)Q_\zeta^2+2(6.03)Q_\delta Q_\xi\\ &\qquad\quad+2(7.44)Q_\zeta Q_\delta-2(15.3)Q_\zeta Q_\xi],\\ V_{b,\mathrm{O}}&=\tfrac{1}{2}K''[(1.36)Q_\delta^2+(7.47)Q_\xi^2+2(3.18)Q_\delta Q_\xi]. \end{aligned} \tag{29}$$

The normal modes are the solutions of the matrix equation

$$\begin{bmatrix} 20.6K'-\mu_\xi\omega^2 & 7.44K' & -15.3K' \\ 7.44K' & 51.6K'+1.36K''-\mu_\delta\omega^2 & 6.03K'+3.18K'' \\ -15.3K' & 6.03K'+3.18K'' & 1.164K+26.2K'+7.47K''-\mu_\xi\omega^2 \end{bmatrix}\times\begin{bmatrix} Q_\zeta \\ Q_\delta \\ Q_\xi \end{bmatrix}=0. \tag{30}$$

If we define the dimensionless quantities

$$\lambda=K/K',\quad \epsilon=K''/K',\quad f=\omega/\omega_4,\quad\text{and}\quad z=\lambda f^2, \tag{31}$$

then the secular equation for the frequencies can be written

$$a_0-a_1z+a_2z^2-z^3=0, \tag{32}$$

where

$$\begin{aligned} a_0&=0.978+0.517\epsilon+0.0944\lambda+0.00262\epsilon\lambda,\\ a_1&=4.165+1.156\epsilon+0.175\lambda+0.00196\epsilon\lambda,\\ a_2&=4.020+0.510\epsilon+0.0754\lambda. \end{aligned} \tag{33}$$

The cubic equation (32) may be solved easily by trial and adjustment when values have been chosen for λ and ϵ.

A number of calculated frequencies and the experimental ones[10,18] are given in Table IV. All of the cases calculated satisfy the condition that the product of the calculated frequencies equals the product of the measured frequencies. This condition provides a relation between λ and ϵ:

$$a_0(\lambda,\epsilon)=0.000734\lambda^3. \tag{34}$$

The quality of agreement between calculated and measured frequencies can be estimated by the quantity

$$D=\sum[1-(f/f_{\mathrm{exp}})]^2. \tag{35}$$

Outside the range of λ, ϵ indicated in Table IV, D increases rapidly.

The normal modes have been calculated for two of the cases of Table IV, $\lambda=15$, $\epsilon=0$ and $\lambda=12$, $\epsilon=-1.6$. The significance of negative ϵ will be discussed later. It is convenient to normalize the normal modes to have a mass of 100 (atomic weight), i.e., $m_k=100$ in (8) and $C=1.36^{-\frac{1}{2}}$ in (26). The normalized modes obtained from (30) for $\lambda=15$, $\epsilon=0$ are given in Table V along with the calculated and observed frequencies expressed in wave numbers. The normalized mode vectors for each atom in the unit cell are given in Table VI in the Cartesian coordinates of Table I and Fig. 1. These vectors are to be considered dimensionless.

TABLE IV. Calculated frequencies $f=\omega/\omega_4$ for several choices of the bending force constants. The deviation D is defined in (35).

	Calculated						Experimental
λ	10	12	13	14	15	16	
ϵ	−2.2	−1.6	−1.0	−0.5	0	1.0	
f_1	0.180	0.194	0.199	0.198	0.199	0.194	0.191
f_2	0.308	0.295	0.295	0.292	0.289	0.289	0.329
f_3	0.487	0.467	0.466	0.469	0.469	0.487	0.432
D	0.024	0.017	0.019	0.022	0.024	0.031	

It may be readily verified from Table VI that they satisfy (8) with $m_k=100$. The normalized modes for $\lambda=12$, $\epsilon=-1.6$ are given in Table VII. No figures are given here to show the normal modes because it is very difficult to exhibit graphically their essential properties.

The validity of the approximation of separating out the highest frequency stretching mode will now be examined. The equations of motion (20) for the normal coordinates $N_1, \cdots, N_4$ corresponding to the normalized modes $\mathbf{n}_1, \cdots, \mathbf{n}_4$ of Table VI and the valence force system $\lambda=15$, $\epsilon=0$ may be written

$$\begin{bmatrix} 81.5-2.11\varphi^2 & -0.443 & -1.81 & 0.411 \\ -0.443 & 17.8-2.08\varphi^2 & 0 & 0 \\ -1.81 & 0 & 6.70-2.09\varphi^2 & 0 \\ 0.411 & 0 & 0 & 3.09-2.09\varphi^2 \end{bmatrix} \times \begin{bmatrix} N_1 \\ N_2 \\ N_3 \\ N_4 \end{bmatrix} = 0, \tag{36}$$

where $\varphi^2=\omega^2 m_0/K'$. The off-diagonal terms in the first row and column connect the pure stretching mode $\mathbf{n}_4$ to the other three modes through the Si bending force. By expanding the secular determinant of (36) into polynomial form it can readily be shown that the effect of the off-diagonal terms on the frequencies is completely negligible. By perturbation theory it can be shown that the greatest effect on the normal modes is a 2% mixing of modes 4 and 2:

$$\mathbf{n}_4 \to \mathbf{n}_4-0.024\mathbf{n}_2, \quad \mathbf{n}_2 \to \mathbf{n}_2+0.024\mathbf{n}_4. \tag{37}$$

The procedure leading to (30) is therefore justified.

A_2 Modes

The normal modes and frequencies of species A_2 can be calculated by using as a basis the symmetry modes given by (11). Since three of the four symmetry modes are not mutually orthogonal, the secular equation will be more complicated in this case than for the A_1 modes. The kinetic energy for the A_2 symmetry modes (11) is given by (15). The potential energy terms V_s and $V_{b,\mathrm{Si}}$ are given by

$$\begin{aligned} V_s=\tfrac{1}{2}K\{&1.324Q_t^2+0.683Q_\zeta^2+8.44Q_\eta^2+1.055Q_\xi^2 \\ &-2(0.0274)Q_tQ_\zeta-2(0.674)Q_tQ_\eta \\ &+2(0.660)Q_tQ_\xi+2(2.16)Q_\zeta Q_\eta \\ &+2(0.690)Q_\zeta Q_\xi+2(1.876)Q_\eta Q_\xi\}, \\ V_{b,\mathrm{Si}}=\tfrac{1}{2}K'\{&4.78Q_t^2+13.79Q_\zeta^2+2.80Q_\eta^2+11.16Q_\xi^2 \\ &+2(2.29)Q_tQ_\zeta+2(0.729)Q_tQ_\eta \\ &-2(3.94)Q_tQ_\xi+2(6.19)Q_\zeta Q_\eta \\ &+2(8.14)Q_\zeta Q_\xi+2(4.01)Q_\eta Q_\xi\}. \end{aligned} \tag{39}$$

It will be assumed that $V_{b,\mathrm{O}}=0$ corresponding to the case $\lambda=15$, $\epsilon=0$. The normal modes and frequencies are then solutions of the equations

$$\begin{bmatrix} 24.6-g^2 & 2.29 & -9.38 & 5.96 \\ 2.29 & 24.0-1.65g^2 & 38.6-0.479g^2 & 18.5-0.416g^2 \\ -9.38 & 38.6-4.79g^2 & 129-1.59g^2 & 32.2-0.391g^2 \\ 5.96 & 18.5-0.416g^2 & 32.2-0.391g^2 & 27.0-1.48g^2 \end{bmatrix} \times \begin{bmatrix} Q_t \\ Q_\zeta \\ Q_\eta \\ Q_\xi \end{bmatrix} = 0, \tag{40}$$

where $g^2=\omega^2 m_s/K'$ and m_s is the mass of the Si atom (absolute units). The secular equation in polynomial form is

$$128\,883-42\,845g^2+4109g^4-126g^6+g^8=0, \tag{41}$$

and the roots of this equation are $g^2=5.20$, 10.79, 28.0, and 82.1. The frequencies obtained are compared with the observed frequencies[9] in Table VIII. Also given are the normal modes, which are normalized according to (8) with $m_k=100$. The normal modes are orthogonal, although this is not so easy to verify in the form given in Table VIII. In Table IX the normal mode vectors for each atom are given in Cartesian form, from which the orthonormality can readily be verified.

It will be seen from Table VIII that the agreement between calculated and observed frequencies is poorer than was obtained for A_1. The deviation defined by (35) has the value $D=0.07$, and the wave number product is 1.1×10^{11} cm^{-4} compared with the observed value of 1.5×10^{11}. The valence force constants were chosen to make the highest frequency and the frequency product of A_1 agree exactly with experiment. In A_2 no adjustable parameters are used, so that the poorer agreement is not surprising. The maximum fractional error in Table VIII is for the 364-cm^{-1} mode for which $|(\nu_{\mathrm{calc}}/\nu_{\mathrm{obs}})-1|=0.18$.

TABLE V. Normal modes for the three lowest A_1 frequencies (wave numbers $\tilde{\nu}$ given in cm^{-1}) with $\lambda=15$, $\epsilon=0$.

	1	2	3
$\tilde{\nu}_{\mathrm{calc}}$	215	313	507
$\tilde{\nu}_{\mathrm{obs}}$	207	356	467
Q_ζ	0.706	0.584	−0.446
Q_δ	−0.347	0.433	0.0171
Q_ξ	0.372	0.260	0.917

Discussion

Normal modes and frequencies of species A_1 and A_2 have now been obtained for a valence model. The highest frequency A_1 mode and the stretching constant

TABLE VI. Normal modes of vibration (A_1) in Cartesian form. The normalization is chosen to make the masses of (8) equal to 100 atomic weight units.

Mode		1	2	3	4
$\tilde{\nu}_{\mathrm{obs}}$ (cm)$^{-1}$		207	356	467	1082
1	x	0.573	−0.714	−0.028	0.589
	y	0	0	0	0
	z	0	0	0	0
2		−0.286	0.357	0.014	−0.294
		0.496	−0.619	−0.024	0.510
		0	0	0	0
3		−0.286	0.357	0.014	−0.294
		−0.496	0.619	0.024	−0.510
		0	0	0	0
4		0.145	−0.150	0.963	−0.270
		−0.745	−0.078	0.272	0.635
		0.428	0.753	0.199	0.502
5		−0.716	0.007	−0.246	0.684
		−0.246	−0.168	0.970	0.084
		−0.428	−0.753	−0.198	−0.502
6		0.573	0.143	−0.717	−0.415
		0.497	−0.091	0.699	−0.551
		0.428	0.753	0.199	0.502
7		0.573	0.143	−0.717	−0.415
		−0.497	0.091	−0.699	0.551
		−0.428	−0.753	−0.199	−0.502
8		−0.716	0.007	−0.246	0.684
		0.246	0.108	−0.970	−0.084
		0.428	0.753	0.199	0.502
9		0.145	−0.150	0.963	−0.270
		0.745	0.078	−0.272	−0.635
		−0.428	−0.753	−0.199	−0.502

K were obtained directly by fitting the experimental wave number 1082 cm^{-1} with $K'=K''=0$. [We will identify modes throughout the rest of the paper with their wave number, the units (cm^{-1}) being understood.] It was subsequently shown that this is a valid procedure. The remaining A_1 frequencies are in reasonable agreement with experiment as shown in Table IV providing K', K'' are within the acceptable range. Since the deviation D is slowly varying in this range it is difficult to determine K', K'' more precisely from a consideration of frequencies alone. The calculated A_1 frequencies agree with experiment to within 12%, which is typical of the accuracy of valence force calculations for mole-

TABLE VII. Normal modes for the three lowest A_1 frequencies with $\lambda=12$, $\epsilon=1.6$.

	1	2	3
$\tilde{\nu}_{\mathrm{calc}}$ (cm^{-1})	210	319	505
$\tilde{\nu}_{\mathrm{obs}}$ (cm^{-1})	207	356	467
Q_ζ	0.743	0.293	−0.636
Q_δ	−0.238	0.500	−0.0451
Q_ξ	0.546	0.330	0.795

TABLE VIII. Normal modes for the four A_2 frequencies with $\lambda=15$, $\epsilon=0$.

	1	2	3	4
$\tilde{\nu}_{\mathrm{calc}}$ (cm^{-1})	298	433	697	1190
$\tilde{\nu}_{\mathrm{obs}}$ (cm^{-1})	364	495	778	1080
Q_ι	0.008	0.544	0.935	0.147
Q_ζ	−0.845	−0.303	0.167	0.009
Q_η	0.124	0.300	−0.047	−0.894
Q_ξ	0.523	−0.673	0.397	0.007

TABLE IX. Normal modes of vibration (A_2) in Cartesian form. The normalization is chosen to make the masses of (8) equal to 100 atomic weight units.

Mode		1	2	3	4
$\tilde{\nu}_{\mathrm{obs}}$ (cm^{-1})		364	495	778	1080
1	x	0	0	0	0
	y	0.008	0.543	−0.935	−0.141
	z	0.215	0.405	0.319	−0.568
2		−0.007	−0.471	0.809	0.122
		−0.004	−0.272	0.467	0.071
		0.215	0.405	0.319	−0.568
3		0.007	0.471	−0.809	−0.122
		−0.004	−0.272	0.467	0.071
		0.215	0.405	0.319	−0.568
4		0.751	−0.552	−0.289	−0.275
		0.634	0.453	0.163	0.646
		−0.189	−0.357	−0.279	0.497
5		−0.172	−0.666	−0.285	−0.696
		−0.966	0.251	0.169	−0.085
		−0.189	−0.357	−0.279	0.497
6		−0.924	−0.118	0.003	−0.423
		0.334	−0.702	−0.332	−0.561
		−0.189	−0.357	−0.279	0.497
7		0.924	0.118	−0.003	0.423
		0.334	−0.702	−0.332	−0.561
		−0.189	−0.357	−0.279	0.497
8		0.172	0.675	0.285	0.696
		−0.966	0.251	0.169	−0.085
		−0.189	−0.357	−0.279	0.497
9		−0.751	0.552	0.289	0.275
		0.634	0.453	0.163	0.646
		−0.189	−0.357	−0.279	0.497

TABLE X. Comparison of calculated and observed wave numbers (in cm^{-1}) for species A_1 and A_2.

Observed	Present work	Saksena[a] (1942)	Saksena[b] (1945)	Barriol[c] (β Quartz)
A_1				
1082	1082	1082	1087	1200
466	507	484	508	466
356	313	330	310	272
207	215	208	195	0
A_2				
1080	1190		1160	1190
778	697		809	660
495	433		489	400
364	298		149	318

[a] See reference 17.
[b] See reference 4.
[c] See reference 14.

cules.[21] The calculated A_2 frequencies without further adjustment of force constants agree within 18%. The arbitrary choice of $\lambda=15$, $\epsilon=0$ in Tables VI and IX, which give the Cartesian components of the normal modes, is an acceptable one and has the advantage of simplifying the model and the calculations.

For purposes of comparison the frequencies calculated here for $\lambda=15$, $\epsilon=0$ are listed in Table X along with the observed frequencies[9] and the calculated frequencies of Saksena (1942),[17] Saksena (1945),[4] and Barriol.[14] The significance of the work of Barriol on β quartz has already been discussed in the Introduction. The most extensive calculations in the literature on quartz are those of Saksena. For the A_1 modes the present work is in substantial agreement with Saksena (1945), which was based upon a valence force model including O-O repulsion. The force constants were obtained by fitting the elastic constants c_{33} and c_{31}, and the frequency expressions $\sum\omega_j^2$ and $\sum'\sum'\omega_i^2\omega_j^2(i\neq j)$ using the A_1 frequencies. The A_2 frequencies were calculated for the same force constants. Three of the A_2 frequencies are in somewhat better agreement with experiment than the present work. The lowest frequency, however, is very much in disagreement with experiment. The normal modes belonging to these frequencies are not given. Although Saksena does not comment on this fact, his earlier paper (1942) on the frequencies and normal modes of A_1 reported much better agreement with experiment. The modes which he obtained for A_1 are not in agreement with the present work.

The force constants for quartz along with those for several silicate minerals and several molecules containing Si or O are given in Table XI. The first two rows give the results obtained here for the extreme cases of Table IV, $\lambda=16$, $\epsilon=1$ and $\lambda=10$, $\epsilon=-2.2$. The bending constants are listed in the form $(\sin^2\theta')K'$ to agree with the customary definition for the bending force constant.[16] The Si bond angles are considered to be all equal to $\theta'=109°$, and the O bond angle is $\theta''=144°$. The next three rows give results obtained in various calculations by Saksena *et al.* The sixth row gives a result reported by Matossi from qualitative considerations on the SiO tetrahedra in quartz. The remaining data on minerals and simple molecules containing Si and O are included for comparison. It will be seen that the K obtained here agrees well with that of Matossi[13] and Barriol[14] but is considerably smaller than that of Saksena.[3,15,17] The Si bending constant $(\sin^2\theta')K'$ is in reasonable agreement with those found in molecules but much smaller than that of Saksena. The O bending constant $(\sin^2\theta'')K''$ is much smaller than either Saksena's or those found in simple molecules.

TABLE XI. Summary of information on force constants relevant to quartz.

Material	K (10^5 dynes/cm)	$(\sin^2\theta')K'$ (10^5 dynes/cm)	$(\sin^2\theta'')K''$ (10^5 dynes/cm)	Reference
Quartz	4.32	0.24	0.093	present work
	4.32	0.39	−0.33	
Quartz	5.065	0.9491	0.5116	17
	5.01	0.51	0.41	3
	4.98	0.61	0.18	15
Quartz	4.5	...	...	13
β Quartz	4.48	...	...	14
Zircone	4.0	...	...	13
SiH_4	2.8	0.19	...	16
$SiCl_4$	3.8	0.16	...	16
SiF_4	7.2	0.25	...	16
H_2O	...	...	0.69	16
Cl_2O	...	...	0.41	16
F_2O	...	...	0.55	16

Of particular interest is the negative K'', which according to Table IV gives optimum agreement with measured frequencies. It may at first seem surprising that negative bending force constants are allowable in the theory. This may be understood by considering the potential energy as a function of bond angle for oxygen. The potential energy would presumably have a minimum at some angle near $\theta''\sim 90°$ corresponding to covalent bonding of the p electrons.[22] At some angle $\theta''\sim 135°$ the potential energy has an inflection point, and at $\theta''=180°$ it has a maximum. Since the bending force constant is the second derivative of the potential energy it must be positive near $\theta''\sim 90°$, zero at the inflection point, and negative for greater angles. The bond angle in the molecules H_2O, Cl_2O, F_2O is about $\theta\sim 105°$ where $(\sin^2\theta'')K''$ should be positive and large. In quartz, on the other hand, $\theta''=144°$ where $(\sin^2\theta'')K''$ should be small and possibly negative.

Symmetry modes for quartz were proposed by Saksena[18] as a first step toward understanding the optical vibrations. He originally assigned observed frequencies to these symmetry modes, but his later calculations[4,17,23] showed that they are not approximate normal modes. Saksena's symmetry modes,[24] chosen with a view of the symmetry of the unit cell, consist of Si and O motions normal to and in the basal plane. It is possible, however, that the motions of the individual atoms are determined less by the symmetry of the unit cell than by the local environment of the atoms. This point of view is supported by the similarities in the spectra of quartz and vitreous silica.[25] A con-

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[21] Wilson, Decius, and Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), p. 174.

[22] Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), Sec. 12b.

[23] B. D. Saksena, Proc. Indian Acad. Sci. **A19**, 357 (1944).

[24] The symmetry coordinates given by Saksena (see reference 18) have been verified except for modes $Q_{14'}$ and $Q_{15'}$, where the expression given for $Q_{14b'}$ is actually $Q_{15b'}$ and that given for $Q_{15b'}$ is actually $Q_{14b'}$.

[25] I. Simon and H. O. McMahon, J. Chem. Phys. **21**, 23 (1953).

sideration of the O motions in the Si-O-Si unit leads to the symmetry modes based on the $\boldsymbol{\xi}$, $\boldsymbol{\eta}$, $\boldsymbol{\zeta}$ vectors of Table III.

The η motion, which is in the Si-O-Si plane in the direction from one Si to the other, involves the greatest potential energy of stretching. The highest frequency A_1 mode (24) consists of this motion combined with a radial Si motion in the basal plane. This is the only type of Si motion allowed in species A_1. These two motions combine in two ways, one of which is the high frequency mode n_4 given by (26), and the other is essentially a rigid rotation of the Si-O-Si unit denoted by q_δ in (27). As shown in Table V this latter motion is important in the 356 mode. The 207 and 467 modes may be characterized as ζ and ξ modes, respectively. The ζ motion would be expected to have a low frequency since it is normal to the Si-O-Si plane and therefore does not stretch the bonds. The potential energy of the ξ motion contains large contributions from both stretching and Si bond bending. Thus the ξ, η, ζ motions of O provide a simple and satisfactory way of characterizing the 207, 467, and 1082 vibrations of species A_1.

The 356 mode of A_1 cannot be well characterized in the ξ, η, ζ scheme. Saksena[18] suggested that this mode is an O motion along the triad axis. According to Table VI the O motion is in substantial agreement with Saksena's prediction, and there is also a large radial Si motion.

For the A_2 modes it is necessary to combine with the ξ, η, ζ motions an axial Si motion. The modes are given in Table VIII in terms of the ξ, η, ζ coordinates, which include the axial Si motion, and a coordinate representing the tangential motion of Si atoms in the basal plane. The normal modes are given in Table VIII, which must be interpreted with some care, since the ξ, η, ζ symmetry modes are not mutually orthogonal. Nevertheless the 1080 mode can be characterized as an η mode, which is the expected result. The 778 is a tangential Si motion in the basal plane. The lowest frequency A_2 mode 364 has an appreciable contribution from the ξ motion as well as the ζ motion, which accounts for its frequency being considerably higher than that of the lowest frequency A_1 mode. Neither the 364 nor the 495 is simply characterized in the ξ, η, ζ scheme, although the dominant contributions are ζ and ξ respectively. It is evident from Table IX, however, that these modes involve radial and tangential O motions, respectively.[26]

α-β Transformation

It has long been known[11,12,18] that the lowest frequency A_1 mode 207 is associated in some way with the α-β transformation at 575°C. Saksena[18] at first suggested that this mode is a radial Si motion in the basal plane, but his later calculations did not confirm that this motion is a normal mode. According to the present work this mode is best described as a motion of O atoms normal to the plane of the Si-O-Si unit. The vectors of Table VI for the 207 mode may be compared with the vectors of Table II giving the displacements in the α-β transformation for the atoms of the tetrahedron of atom 1. The directions of motion and the relative magnitudes of the Si and O motions are in remarkable agreement. This establishes the connection between this mode and the transformation. There is of course no requirement that the mode agree exactly with the transformation displacements. When the other modes of Table VI are compared with Table II they are seen to be unrelated to the transformation.

III. THE INFRARED INTENSITIES

General Theory

The theory of infrared absorption in crystals has been given by Lax and Burstein.[27] The general expression for the electric moment to first order in the atom displacements may be written

$$\mathbf{M}=\sum\nolimits_\alpha B^\alpha \mathbf{x}^\alpha, \tag{42}$$

where the tensor (dyadic) B^α is the effective charge for atom α and the sum extends over one unit cell. If Ω is the volume of the unit cell, the polarization is $\mathbf{M}/\Omega$. The real susceptibility χ and conductivity σ are defined by

$$\mathbf{M}\Omega^{-1}=\left(\chi+\frac{1}{2\pi i\nu}\sigma\right)\mathbf{E}, \tag{43}$$

where χ, σ are tensors and $\mathbf{E}$ is an electric field with the time dependence $\exp(2\pi i\nu t)$. When the displacements are expressed in the normal coordinates according to (9), then (42) becomes

$$\mathbf{M}=\sum\nolimits_k N_k \sum\nolimits_\alpha B^\alpha \mathbf{n}_k{}^\alpha. \tag{44}$$

In the presence of the field $\mathbf{E}$ the equations of motion for the N_k are

$$\sum\nolimits_k m^\alpha \mathbf{n}_k{}^\alpha\left(\frac{d^2N_k}{dt^2}+4\pi^2\nu_k{}^2N_k\right)=\boldsymbol{\nabla}^\alpha(\mathbf{E}\cdot\mathbf{M}), \tag{45}$$

where $\boldsymbol{\nabla}^\alpha$ is the gradient operator on the coordinates of atom α. By means of (8) and (44) this can be written

$$\frac{d^2N_k}{dt^2}+4\pi^2\nu_k{}^2N_k=m_k{}^{-1}\mathbf{E}\cdot\sum\nolimits_\alpha B^\alpha\mathbf{n}_k{}^\alpha. \tag{46}$$

The solution to (46), when damping has been introduced in the usual way, is

$$N_k=\frac{1}{4\pi^2m_k}\,\frac{1}{(\nu_k{}^2-\nu^2)+i\gamma_k\nu\nu_k}\mathbf{E}\cdot\sum\nolimits_\alpha B^\alpha\mathbf{n}_k{}^\alpha, \tag{47}$$

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[26] It is interesting to note that the 778 and 364 are essentially the symmetry modes $Q_{8'}$ and $Q_{6'}$ respectively, of Saksena (see reference 18) while the O motion in the 495 agrees with his $Q_{9'}$. However, to $Q_{8'}$, $Q_{6'}$, $Q_{9'}$ he assigns the wave numbers 364, 777, and 1149 cm^{-1}.

[27] M. Lax and E. Burstein, Phys. Rev. **97,** 39 (1955).

where γ_k is the width for the kth normal vibration in the notation of reference 9. From (43), (44), and (47) one obtains in dyadic notation

$$\chi+\frac{1}{2\pi i}\sigma=\sum_k \frac{1}{4\pi^2\Omega m_k}\frac{1}{(\nu_k{}^2-\nu^2+i\gamma_k\nu\nu_k)} \times(\sum_\alpha B^\alpha\mathbf{n}_k{}^\alpha)(\sum_\alpha B^\alpha\mathbf{n}_k{}^\alpha). \tag{48}$$

Separating real and imaginary parts gives

$$\begin{aligned}\chi&=\sum_k \rho_k\nu_k{}^2\frac{\nu_k{}^2-\nu^2}{(\nu_k{}^2-\nu^2)^2+\gamma_k{}^2\nu^2\nu_k{}^2},\\ \sigma&=\sum_k \rho_k\nu_k{}^2\frac{2\pi\gamma_k\nu^2\nu_k}{(\nu_k{}^2-\nu^2)^2+\gamma_k{}^2\nu^2\nu_k{}^2},\end{aligned} \tag{49}$$

where the strength ρ_k of the kth vibration is the tensor (dyadic notation)

$$\rho_k=\frac{1}{4\pi^2\Omega m_k\nu_k{}^2}(\sum_\alpha B^\alpha\mathbf{n}_k{}^\alpha)(\sum_\alpha B^\alpha\mathbf{n}_k{}^\alpha). \tag{50}$$

For the simple case of an isotropic diatomic crystal this reduces to the usual form[28]

$$\rho=e^{*2}/(4\pi^2\Omega m^*\nu^2), \tag{51}$$

where e^* is the effective charge[1] and m^* the reduced mass. It will be seen from (8) that m_k is an arbitrary normalization constant, but the choice of normalization does not affect ρ_k.

The electrical neutrality and symmetry of the crystal impose restrictions on the B^α. The neutrality condition is

$$\sum_{\mathrm{Si}} B^\alpha+\sum_{\mathrm{O}} B^\alpha=0. \tag{52}$$

Symmetry requires

$$B^\beta=TB^\alpha\tilde{T}, \tag{53}$$

where T is any symmetry operation, and $\boldsymbol{\beta}=T\boldsymbol{\alpha}$ with the atomic indices considered as position vectors in the unit cell. Symmetry enables $B^{(2)}$, $B^{(3)}$ to be determined from $B^{(1)}$, and $B^{(5)},\cdots,B^{(9)}$ to be determined from $B^{(4)}$ in the notation of Fig. 1. The xy, yx, xz, zx components of $B^{(1)}$ vanish because the atom lies on a diad axis, but there is no such restriction on $B^{(4)}$. It may be noted that there is no requirement that B^α be symmetric. Both sums in (52) have the form

$$\sum_{\mathrm{Si}} B^\alpha=\begin{bmatrix} a & 0 & 0\\ 0 & a & 0\\ 0 & 0 & b\end{bmatrix}. \tag{54}$$

Therefore, (52) imposes two conditions on the 14 components of $B^{(1)}$ and $B^{(4)}$ allowed by symmetry, leaving a total of 12 independent effective charge components for quartz. There are also 12 infrared active normal vibrations, so that the effective charge problem in principle has a unique solution.

Two-Charge Model

Quartz is classified[29] as a valence crystal primarily because the number of nearest neighbors of each atom is equal to the ordinary chemical valence of that atom. Other reasons for this classification are its hardness, high-cohesive energy, low-electrical conductivity, and the fact that silicon comes from the center of the periodic table. On the other hand quartz might also be considered an ionic crystal because of its strong infrared absorption and because O is highly electronegative.[30] The covalent and ionic properties of quartz may be expected to give rise to two distinct kinds of effective charges, which are conveniently designated *ionic* and *valent* charges. Since the ionic charges are regarded as residing on and moving with the atoms, they have the form

$$B_{\mathrm{Si}}(\text{ionic})=eqI,\quad B_{\mathrm{O}}(\text{ionic})=-\tfrac{1}{2}eqI, \tag{55}$$

where I is the unit dyadic and e is the electronic charge. The valent charges can be simply represented in terms of a single parameter if the assumption is made that the polarization of the Si-O bonds depends only upon the interatomic distance. In this case

$$\begin{aligned}B_{\mathrm{Si}}{}^\alpha(\text{valent})&=-eQ\sum{}^{(\alpha)}\boldsymbol{\varrho}\boldsymbol{\varrho}\\ B_{\mathrm{O}}{}^\alpha(\text{valent})&=eQ\sum{}^{(\alpha)}\boldsymbol{\varrho}\boldsymbol{\varrho},\end{aligned} \tag{56}$$

where $\sum^{(\alpha)}$ is the sum over the unit neighbor vectors $\boldsymbol{\varrho}$ of atom α. Each term of the form $\pm eQ\boldsymbol{\varrho}\boldsymbol{\varrho}$ gives rise to a moment directed along the bond and proportional to the strain of the bond. On the basis of these considerations it is proposed that the effective charges in quartz can be represented in terms of two parameters q, Q

$$\begin{aligned}B^\alpha&=eqI-eQ\sum{}^{(\alpha)}\boldsymbol{\varrho}\boldsymbol{\varrho} &&\text{silicon,}\\ B^\alpha&=-\tfrac{1}{2}eqI+eQ\sum{}^{(\alpha)}\boldsymbol{\varrho}\boldsymbol{\varrho} &&\text{oxygen.}\end{aligned} \tag{57}$$

The components of the symmetric dyadics $\sum^{(\alpha)}\boldsymbol{\varrho}\boldsymbol{\varrho}$

TABLE XII. Components of the symmetric dyadics $\Sigma^{(\alpha)}\boldsymbol{\varrho}\boldsymbol{\varrho}$ introduced in (56).

Atom	xx	xy	xz	yy	yz	zz
1	1.328	0	0	1.324	0.036	1.350
2	1.325	−0.00173	−0.0312	1.327	−0.018	1.350
3	1.325	0.00173	0.0312	1.327	−0.018	1.350
4	0.321	−0.432	−0.253	1.000	0.786	0.675
5	1.204	0.078	−0.807	0.1166	−0.174	0.675
6	0.456	0.510	−0.554	0.865	−0.612	0.675
7	0.456	−0.510	0.554	0.865	−0.612	0.675
8	1.204	−0.078	0.807	0.1166	−0.174	0.675
9	0.321	0.432	0.253	1.000	0.786	0.675

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[28] W. G. Spitzer, D. Kleinman, and D. Walsh, Phys. Rev. **113**, 127 (1959).

[29] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 60.

[30] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), p. 93.

based on the $\boldsymbol{\rho}$ vectors of Table I are given for each atom in Table XII.

The normal modes of species A_2 given in Table IX are so normalized that m_k corresponds to 100 atomic weight units, or $m_k = 1.67\times10^{-22}$ g. It follows that

$$(e^2/\pi\Omega m_k) = 3.9\times10^{24}\ \mathrm{sec}^{-2}. \tag{58}$$

It is convenient to define an experimental quantity

$$S_k^{\mathrm{exp}} = 4\pi\rho_k\nu_k^2/3.9\times10^{24}, \tag{59}$$

which is readily obtained from Table XVI of reference 9. According to (50), S_k^{exp} should agree with the quantity

$$S_k^{\mathrm{calc}} = (\textstyle\sum_\alpha B^\alpha \mathbf{n}_k^\alpha)(\sum_\alpha B^\alpha \mathbf{n}_k^\alpha). \tag{60}$$

Actually S_k^{calc} as defined by (60) is a dyadic, but it has only one nonvanishing component if $\mathbf{n}^\alpha$ is a mode of species A_2. It is evident from (57) and (60) that S^{calc} is a quadratic form in q, Q. The coefficients of q^2, $2qQ$, Q^2 in the zz component of S_k^{calc} are given in Table XIII for each A_2 mode. These coefficients have been computed in a straightforward manner from the $\mathbf{n}_k^\alpha$ of Table IX and the $\sum^{(\alpha)} \boldsymbol{\rho}\boldsymbol{\rho}$ of Table XII. The fourth column of Table XIII gives S_k^{calc} for the choice

$$q = +3, \quad Q = +3. \tag{61}$$

The last column gives the experimental values S_k^{exp}. A graphical comparison of the calculated and experimental infrared frequencies and intensities is shown in Fig. 2.

TABLE XIII. Comparison of calculated and observed infrared intensities for the A_2 frequencies. The quantities S^{exp} and S^{calc} are defined in (59) and (60).

$\tilde{\nu}_k$ (cm^{-1})	q^2	$2qQ$	Q^2	S_k^{calc}	S_k^{exp}
1080	10.2	−24.9	60.7	190	180
778	3.20	− 1.99	1.24	4	14
495	5.24	− 0.385	0.028	40	37
364	1.47	0.251	0.043	18	21

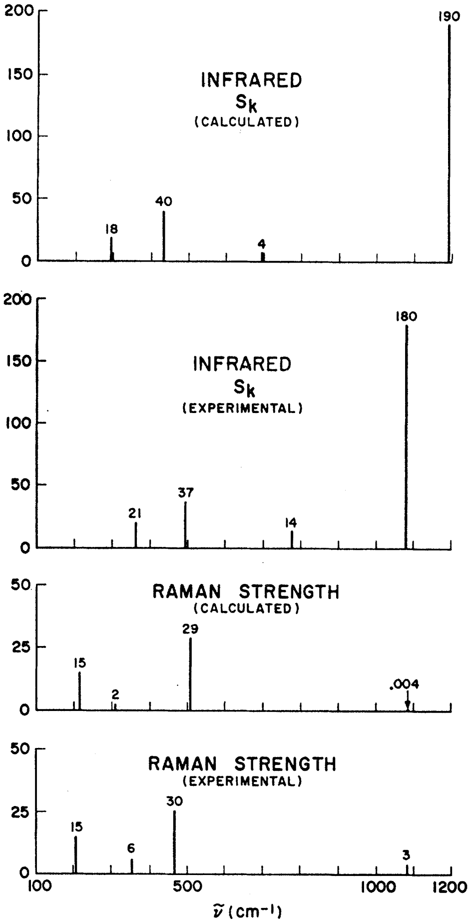

FIG. 2. A comparison of the calculated and experimental infrared and Raman intensities and frequencies.

Discussion

It will be seen in Table XIII that the theory accounts for the weakness of the 778 and accounts quantitatively for the other intensities of species A_2. The agreement is noteworthy since the calculation depends both upon the two-charge assumption (57) and the calculated normal modes of Table IX. The modes 495 and 364 may be considered ionic in the sense that their intensity is derived primarily from the ionic effective charge q. The value of q^2 is therefore determined by the intensities of these modes. The value of Q is obtained from q and the intensity of the 1080. This causes the 778 to be given the least accurately of all the modes, but this is not surprising since its small intensity is due to the large negative value of the $2qQ$ interference term. The effective charge parameters q, Q must be of the same sign, and their magnitudes are fixed by S^{exp} to within about 10%. It is of interest that good agreement with experiment is not obtained by considering only the ionic effective charge. If one sets $q \neq 0$, $Q = 0$ the 364 becomes the weakest mode, and the 1080 is only twice as strong as the 495, only three times as strong as the 778. The conclusion that the ionic effective charge by itself cannot account for the observed infrared intensities concurs with the findings of Dennison,[6] Rollefson and Havens,[7] and Bell *et al.*,[8] on simple molecules. The two-charge model used here for quartz may be equally applicable for molecules, although this has not been investigated.

It is not to be expected that q, Q can be readily interpreted in terms of electron densities on the atoms or in the bonds. For the cubic ionic crystals the number of extra electrons residing on the negative ion can be immediately determined from an expression given by Szigeti[2]

$$n_e = 3q/(\epsilon_0 + 2) \quad \text{(cubic)}, \tag{62}$$

where ϵ_0 is the dielectric constant at optical frequencies. The factor $3/(\epsilon_0+2)$ arises from solving the local field problem for cubic crystals. There is no treatment of the local field problem for quartz, and no formula like (62) is available. If nevertheless (62) is applied it gives the result that each oxygen atom carries one extra electron.

The valent effective charge parameter Q may be interpreted as a measure of the derivative of the ionic charge with respect to small changes in the Si-O distance. Changes in the ionic charge as the atoms vibrate may be regarded as changes in the polarization of the Si-O bonds and produce electric moments along the bonds. Since q, Q have the same sign, (57) shows that the ionic effective charge decreases as the Si-O distance is increased. If (62) is applied to Q it gives the result that the ionic charge changes by two electrons per unit strain of the bond for small strains. These elementary considerations suggest that the values (61) obtained for q, Q are physically reasonable.

IV. THE RAMAN INTENSITIES

General Theory

The Raman effect considered here arises from the dependence of the electric susceptibility χ on the atomic displacements from equilibrium.[31] The nature of the interaction can be deduced quickly from the semi-classical theory of radiation. Let the incident and scattered electron waves be represented by

$$\begin{aligned} \mathbf{E}_I(r,t) &= \mathbf{E}_I \exp(i\mathbf{k}_I\cdot\mathbf{r}-i\omega_I t) \\ \mathbf{E}_S(r,t) &= \mathbf{E}_S \exp(i\mathbf{k}_S\cdot\mathbf{r}-i\omega_S t). \end{aligned} \tag{63}$$

The energy of interaction with the crystal is

$$W=E_S{}^*\chi E_I \exp[i(\mathbf{k}_I-\mathbf{k}_S)\cdot\mathbf{r}-i(\omega_I-\omega_S)t], \tag{64}$$

where χ is the dyadic susceptibility. To first order in the displacements, χ may be written

$$\chi=\chi_0+\textstyle\sum_j \chi_j N_j, \tag{65}$$

where χ_0 is the static susceptibility, χ_j is a dyadic coefficient, and N_k is the normal coordinate for the jth normal mode of vibration. The intensity of the jth mode for Raman scattering is proportional to the square of the matrix element of N_j which is

$$|\langle N_j\rangle|^2=\frac{\Omega}{V}\frac{\hbar}{2m_j\omega_j}\left[1+\frac{1}{\exp(\hbar\omega_j/kT)-1}\right], \tag{66}$$

where V/Ω is the number of unit cells in the crystal. The absolute intensities of Raman lines are usually unknown, but (66) is important in comparing the relative intensities of Raman lines of different frequencies.

The Raman intensity of the jth mode is also proportional to $|\chi_j|^2$ which must satisfy certain requirements of symmetry.[32] In the usual theory of Raman effect in crystals it is assumed that the light is of such long wavelength that it interacts only with phonons having the periodicity of the crystal, the optical normal modes of vibration. In this case the unit cells of the crystal may be regarded as molecules having the symmetry of the point group of the crystal. If a molecule has no symmetry all vibrations are Raman active. In a symmetric molecule, however, some vibrations may be Raman inactive, which is to say that χ_j vanishes for those vibrations.

The symmetry properties of the modes for Raman scattering are easily formulated as follows: The susceptibility dyadic must transform according to the relation

$$\chi'=T^{-1}\chi T, \tag{67}$$

where T is an orthogonal transformation of coordinates. In (67), χ and T may be represented by 3×3 matrices. The operation of T on a function of the atomic coordinates $\mathbf{r}$ may be defined by the relation

$$Tf(\mathbf{r})=f(T^{-1}\mathbf{r}). \tag{68}$$

If now T is an operation of the point group of the crystal χ' can be written

$$\chi'=\chi(N(\mathbf{r}')), \tag{69}$$

where $\mathbf{r}'=T^{-1}\mathbf{r}$ represents the atomic coordinates in the transformed system, and N represents the set of normal coordinates. From (67), (68), and (69) is obtained the fundamental symmetry requirement on χ:

$$\chi(TN)=T^{-1}\chi(N)T. \tag{70}$$

This shows that the static part of χ must be invariant to the symmetry operations, as is well known. The first-order part of χ must obey the relations

$$\textstyle\sum_j \chi_j TN_j=\sum_k N_k T^{-1}\chi_k T. \tag{71}$$

The selection rules for the first-order Raman effect follow from the application of the orthogonality relations of group representations to (71). The result may be simply stated as follows: The only nonvanishing components of χ_j are those which form a basis for the species of N_j. The form of χ_j for the Raman active species A_1 and E of quartz has been given by Saksena.[18,33]

Simple Stretching Model

It is generally found in the Raman spectra of simple molecules that stretching modes have larger intensities than bending modes. This tendency might be expected to hold also in a valence crystal such as quartz. The Raman intensities reported by Krishnan[10] are given in the fifth column of Table XIV. It is at first surprising

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[31] See reference 16, Chap. III, Sec. 1.

[32] G. Placzek, *Handbuch der Radiology* (Verlag Julius Springer, Berlin, 1934), Vol. 6, 2nd Ed., Part II.

[33] Saksena (see reference 18) has distinguished three kinds of χ_j for species E which he calls E_1, E_2, E_3. This distinction is not a necessary consequence of theory.

TABLE XIV. Comparison of calculated and observed Raman intensities for the A_1 frequencies.

$\tilde{\nu}_j$ (cm^{-1})	$F(\nu_j)$	χ_j^2	$\chi_j^2F(\nu_j)$	Krishnan[a]
1082	0.9	0.004	0.004	3
467	2.4	12	29	30
356	3.3	0.7	2	6
207	7.3	2.1	15	15

[a] See reference 10.

to observe that the stretching mode 1082 is the weakest of all the modes. It will be shown, however, that the observed intensities can be accounted for on the basis of a simple model. Let it be assumed that each atom has an isotropic (scalar) polarizability which depends only upon the distances of its nearest neighbors. With this assumption χ_j can be written, except for a non-essential factor,

$$\chi_j=\sum\nolimits_\alpha \sum\nolimits^{(\alpha)} \boldsymbol{\varrho}^\alpha\cdot\mathbf{n}_j{}^\alpha, \tag{72}$$

where $\sum^{(\alpha)}$ has been defined under (57), and $\sum_\alpha$ is over all atoms of the unit cell. It is convenient to express the relative intensities by the quantity $\chi_j^2F(\nu_j)$, where $F(\nu)$ is the essential factor from (66):

$$F(\nu)=\frac{10^3}{\tilde{\nu}}\left[1+\frac{1}{\exp(\hbar\omega/kT)-1}\right], \tag{73}$$

$\tilde{\nu}$ being the wave number. The calculation of χ_j is straightforward from the $\boldsymbol{\varrho}^\alpha$ of Table I and the $\mathbf{n}_j{}^\alpha$ of Table VI. The calculated values of $F(\nu_j)$, χ_j^2, and $\chi_j^2F_j$ are given in Table XIV. A graphical comparison of theory and experiment is shown in Fig. 2.

Discussion

It will be evident from Table XIV that this simple model gives the correct order of the intensities, the correct ratio of the two strongest intensities, and adequately accounts for the weakness of the 1082 vibration. This weakness is the result of cancellation in (72) between bonds which are compressed and bonds which are stretched. Since the stretching model is reasonable in view of the Raman intensities observed in molecules,[34] the excellent agreement here obtained with experiment supports the validity of the normal modes for species A_1 given in Table VI. Although it was earlier suggested that the choice $\lambda=15$, $\epsilon=0$ for the bending constants, upon which Table VI is based, is convenient and proper but essentially arbitrary, positive evidence favoring this choice can be adduced from the Raman intensities. The calculations of Table XIV have been repeated for the modes of Table VII based upon the bending force constants $\lambda=12$, $\epsilon=-1.6$. The 1082 is, of course, exactly the same for the two cases. The theoretical intensities obtained in the order of decreasing frequency are $\chi_j^2F(\nu_j)=0.004$, 21, 15, 32. These results are in disagreement with experiment in regard to the ratio of the intensities of the two strongest vibrations.

It may be of interest to report briefly on the results obtained with two other models for the vibrational Raman effect. Let it be assumed that the Raman effect is due to the O atoms which have an isotropic polarizability depending only on the angle between the bonds to the two neighboring Si atoms. We then write, except for a non-essential factor,

$$\chi_j=\sum\nolimits_{\mathrm{O}} \Delta\cos\theta_j, \tag{74}$$

where $\Delta\cos\theta$ is given by (18). This model gives $\chi_j^2F(\nu_j)=0.5$, 41, 13, 8 in order of decreasing frequency. This model correctly predicts the strongest and weakest vibrations, but comparison with experiment decidedly favors the stretching model. Calculations were also made for a more sophisticated model which leads to anisotropic χ_j dyadics. It was hoped that this model would predict the polarization properties of the Raman scattering reported by Saksena.[18] Let it be assumed that the vibrational Raman effect arises from a modulation of the energy gap by the vibrations. This modulation could arise from the changes in Si-O distance and also from the changes in ionic charge implied by the nonvanishing valent charge parameter Q. It may further be supposed that in the presence of an electric wave the polarization induced by the vibration would be in the direction of the bond and the resultant polarization would be the sum of the contributions of each bond. The mathematical expression of these assumptions, except for a non-essential factor, is

$$\chi_j=\sum\nolimits_\alpha \sum\nolimits^{(\alpha)} (\boldsymbol{\varrho}\cdot\mathbf{n}_j{}^\alpha)\boldsymbol{\varrho}\boldsymbol{\varrho}, \tag{75}$$

where $\boldsymbol{\varrho}^\alpha$ is always regarded as extending outward from atom α to the neighboring atom. Calculation shows that this model fails completely to account for the weakness of the 1082 vibration.

V. SUMMARY

In this paper the fundamental lattice vibrations of species A_1 and A_2 of quartz have been discussed in considerable detail. The physical description of each of these 8 vibrations is given in the discussion part of Sec. II, and the modes are given in Tables VI and IX. An interesting result of this study is the discovery that the bending force constant for O in quartz may be negative. It is not possible, however, from a consideration of frequencies alone to fix the bending force constants very closely. Evidence from the Raman intensities favors the choice zero for the oxygen bending constant. The relationship of the 207 vibration of species A_1 to the α-β transformation is exhibited directly by comparing the calculated displacements of this mode with those of the transformation.

The effective-charge problem has been treated on the

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[34] See reference 16, Chap. III, Sec. 3.

basis of a two-charge model. The physical meaning of the two-charge parameters is briefly discussed in Sec. III. By a suitable choice of the two parameters satisfactory agreement is obtained for the intensities of the four A_2 vibrations as shown in Table XIII. The Raman intensities of the four A_1 vibrations have been calculated on the basis of a simple model in Sec. IV. With no adjustable parameters satisfactory agreement with experiment is obtained for the relative intensities as shown in Table XIV. The theoretical and experimental strengths and frequencies for both the Raman and infrared are summarized and compared graphically in Fig. 2.

It has been customary to demonstrate the validity of the valence-force model entirely from the calculated frequencies. Such a comparison is shown in Table X. However, in the present work it has been shown that the Raman intensities are more sensitive to the normal modes than are the frequencies. Evidently the infrared intensities are also very sensitive to the normal modes. Therefore the successful calculation of the intensities constitutes a much stronger confirmation of the normal modes and the valence-force model than just a comparison of frequencies. The picture of quartz as a valence crystal is further substantiated by the success of the two-charge model in representing the effects of the twelve charges allowed by symmetry.

There remains the task of applying these techniques to the modes of species E. Much could be learned from such a study, since these modes are active in both infrared and Raman effects, and the experimental intensities are now known.[9] It would be interesting to test the β-quartz theory for the infrared intensities of the E modes suggested in the Introduction. Looking beyond the interest in quartz itself, we hope that these ideas will prove helpful in the general understanding of the vibrational spectra of molecules and valence crystals.

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Effect of Dislocations on Self-Diffusion in Germanium

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The effect of dislocations on the rate of diffusion of radioactive Ge^{71} in intrinsic germanium single crystals has been studied at temperatures near 740°C. The dislocations were introduced by either of two methods: (A) distorting the surface by lapping under pressure, thus producing a network of dislocations; (B) bending the specimens so as to introduce up to 2×10^6 parallel edge dislocations per cm^2. Both deformation treatments produce an enhancement of self-diffusion relative to that in undeformed crystals. In both cases the diffusion can be described in terms of an enhanced volume diffusion with apparent diffusion coefficients up to 38% larger than the value for undeformed intrinsic specimens.

INTRODUCTION

THE role of dislocations in enhancing atom diffusion has not been demonstrated clearly. One method by which information has been sought is in the study of diffusion along small-angle tilt boundaries, using the Burgers model to describe the boundary in terms of individual dislocations. It was Hoffman and Turnbull[1,2] whose observations implied that the rate of self-diffusion in silver along grain boundaries may, indeed, be explained by defining an intrinsic diffusivity for dislocation pipes. Somewhat contradictory to this are the findings of others, particularly Smoluchowski and co-workers.[3] Their measurements indicate that the effect of individual dislocations is inconsequential in all systems which they studied. The role of an array of parallel edge dislocations which do not form a boundary was first studied by Hendrickson and Machlin.[4] An appreciable enhancement of diffusion due to the dislocations was reported. Their results were later contradicted, however, by Murray[5] of the same laboratory who had tried to duplicate and extend them. Finally, for the case of a random network of dislocations, Hart[6] and Mortlock[7] suggested that single crystals at low temperatures may exhibit enhanced diffusion, but without a change in the mathematical form of the concentration profile. The resulting diffusion constant at low temperatures should then be larger than that found by the extrapolation of high-temperature data. Tomizuka[8] claims that the curvature in the Arrhenius

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[1] D. Turnbull, *Report of Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 203.

[2] R. E. Hoffman, Acta Met. 4, 97 (1956).

[3] R. Smoluchowski, *Report of Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 147.

[4] A. A. Hendrickson and E. S. Machlin, J. Metals **6**, 1035 (1954).

[5] G. T. Murray, thesis, 1958, Columbia University, New York, (unpublished).

[6] E. W. Hart, Acta Met. **5**, 598 (1957).

[7] A. J. Mortlock, Acta Met. **8**, 132 (1960).

[8] C. T. Tomizuka, Acta Met. **6**, 660 (1958).