

Theory of the vibrational spectra of some network and molecular glasses

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(Received 30 November 1973)

A theory of the vibrational spectra of glasses is presented, and equations are derived specifically for the Raman intensities. The theory is applicable to glasses of the oxide type [such as glasses in the system $M_2O-L O-SiO_2-Al_2O_3-B_2O_3$ (where M is an alkali and L is an alkaline earth)], as well as to molecular glasses. It is shown when the vibrational spectrum of a glass will resemble that of a crystal of similar composition and that such a resemblance may be consistent with considerable disorder of the glass. It is found that some optically active modes are localized about a few atoms while others are extended, i.e., involve the cooperative vibrations of a large number of atoms of the glass. The widths of the peaks of the vibrational spectra are shown to increase with increasing glassy disorder. It is calculated that Raman spectroscopy is sensitive to heterogeneities on a scale of tens of angstroms in oxide glasses, making it a potentially valuable analytic tool for glass research. The theory is applied specifically to calculate the Raman spectra of Na_2O-SiO_2 and K_2O-SiO_2 glasses and crystals and agreement with experiment is good. The existence of several moderately strong peaks in the glass spectra which are very weak in the crystal spectrum is successfully predicted. It is shown that the presence of extra peaks is expected to be a general feature of the vibrational spectra of glass.

INTRODUCTION

Oxide glasses are of considerable technological importance as well as of purely scientific interest, and many of their properties have been investigated.¹ But while much use is made of oxide glasses, their behavior is scarcely understood on the atomic level. For example, nearly all the low-temperature properties of vitreous silica are not understood even qualitatively.^{2,3} In silicate, aluminosilicate, and borosilicate glasses there are important physical phenomena not found in crystals such as the mixed alkali effect^{1,4} and the boron anomaly^{1,5} for which no acceptable explanation has yet been offered.

The primary reason for this lack of understanding is that the structure of glass is not known. But while the elucidation of glass structure is an important problem there are few experimental techniques which permit a direct investigation of this structure. The usual methods of structural analysis of crystals depend on the presence of order over hundreds of interatomic spacings and are not readily applicable to glasses where no such order exists. X-ray diffraction patterns of glass can be analyzed to yield correlation functions for atomic positions which are probably accurate up to distances of about 10 Å over which atomic correlations seem to extend. From such correlation functions information about short-range order and possible molecular structures existing in the glass can be obtained. Some cases for which this has been applied with varying degrees of success include silica,^{6,7} silicates,^{8,9} amorphous tetrahedrally bonded semiconductors,¹⁰ vitreous Se,¹¹ the amorphous As-Te,¹² and As-Se (Ref. 13) systems as well as disordered metallic alloys.¹⁴

Other information about the structure of amorphous systems can be gleaned from physical and thermodynamic properties such as ac and dc conductivity,¹⁵ sound absorption,^{2,16} magnetic relaxation,¹⁷ viscosity,^{1,18} thermal conductivity,^{2,19} and so forth.

Another experimental technique which has provided some information about glass structure is vibrational spectroscopy.²⁰ There have been a number of studies of the vibrational spectra of silicate glasses, notably those by Simon,²¹ Haas,²² Sweet and White,²³ Etchpare,²⁴ Tobin and Baak,²⁵ Stolen,²⁶ and the large amount of data from Soviet workers.²⁷ In general it has been concluded from these studies that SiO_4 units are the building blocks of silicate glasses and that the short-range order of the glasses is much like that in various crystalline silicates. This is in agreement with x-ray data. Similar conclusions have been reached for phosphate glasses,²⁸ BeF_2 ,²⁹ alkali germanates,³⁰ glycerol,³¹ and many other systems. The infrared spectra of lunar glasses³² have provided clues to their thermal histories. Work has also been done in amorphous Te,³³ As_2S_3 ,³⁴⁻³⁶ As_2Se_3 ,³⁶ where in some cases Raman spectra clearly indicate the existence of some well-defined structural units. In amorphous tetrahedrally bonded semiconductors³⁷ the similarity of crystalline and amorphous short-range order has been observed, as well as some V-V bonding in III-V compounds.³⁸

Much more information probably could be obtained from the vibrational spectra if there existed a theory of the relationship between the lattice vibrations and the vibrational spectra of disordered solids. Several people have taken steps in this direction. Shuker and Gammon³⁹ have related the vi-

brational spectrum to the density of states of the solid but it is difficult to apply their results directly to glass structure. Gaskell⁴⁰ tried to relate the widths of the peaks in the vibrational spectra to a distribution of bond angles, an approach that directly connects structure and spectrum. Gaskell assumed that one could calculate the vibrational spectrum from small molecular units using periodic boundary conditions. Assuming that the width of the peaks in the glass vibrational spectrum is due to a distribution of units with fluctuating bond angles, he determined a distribution of bond angles by fitting a calculated spectrum to an observed one. Gaskell's idea is similar in spirit to the approach of this article. Similar (but by no means identical) assumptions underlie the molecular model of Lucovsky and Martin⁴¹ for chalcogenide glasses.

The most dramatic demonstration of structural units in a glass by Raman spectroscopy was made by Krogh-Moe,⁴² who showed that the existence of B_3O_6 groups in B_2O_3 glass is consistent with the extremely narrow (width less than 10 cm^{-1}) line at 808 cm^{-1} in the Raman spectrum of B_2O_3 glass. He calculated that the particular frequency of the B_3O_6 group is independent of coupling between such groups. His calculation can be justified on the basis of the theory developed here.

Mention must also be made of the work of Bell *et al.*,⁴³ who have computed the frequency spectrum of a model of vitreous silica. They have presented some very interesting results about the nature of the lattice vibrations of a three-dimensional random network, especially as regards mode localization, but they did not report the infrared or Raman spectra of their model.

In this article a theory of the high-frequency lattice vibrations of glasses of the oxide type is developed and applied to a realistic case. The development of the theory was motivated by the references given above as well as by the measurements described below which show that the vibrational spectra of glasses, and in particular the Raman spectra, contain sufficient detail to provide information about glass structure. An important prediction of the theory is that Raman spectroscopy is sensitive to small-scale heterogeneities in glasses, an idea that has some experimental support.⁴⁴

Recently the Raman spectra of a number of binary alkali silicate glasses and crystals have been measured in this laboratory by the author and White. The details of these measurements and the conclusions will be presented separately. However, it will be useful to outline some of the results as they provided much of the stimulus for the theoretical developments reported in the body of this article.

Glasses of composition $M_2O-xSiO_2$, $M = \text{Li, Na, K}$ and $1 \leq x \leq 4$, were made from high-purity SiO_2 (Supersil, obtained from the Pennsylvania Glass

Sand Corp.) and reagent-grade alkali carbonates. The powders were well mixed in the desired proportions and melted in Pt crucibles in a SiC resistance furnace at temperatures between 1200 and 1300 °C. The melts were stirred several times during melting and rods 1–3 mm in diameter were drawn after 1–72-h melting. Spectra of the rods were measured on a Spex model 1401 double-grating spectrometer at a scattering angle of 90°. The excitation source was an RCA ionized argon laser. All spectra were run on the blue (488.0 nm, 300 mW) and green (514.5 nm, 260 mW) lines and spectra were identical for both excitation frequencies. At least two spectra from each of three rods were run for each composition. No detectable change in Raman spectra occurred for different melting times (so long as the melts were clear) or for glasses of the same composition but different batches. It did not even matter whether or not the melts were completely bubble free. These glasses have high transition temperatures and spectra were not influenced by heating due to the laser beam. Highly soluble metasilicates were run immediately after drawing rods, but no attempt was made to determine the effect of absorbed water on the spectra.

Disilicate and metasilicate glasses were crystallized by heating at a temperature about 50 °C below the melting point for several days.

It has been found that the spectra of the glasses are similar to those of crystalline silicates, as shown in Figs. 1 and 2. The general features of the glass spectra are (a) the strong peaks in the crystal spectrum appear in the spectra of glasses of similar composition, where the frequencies may be shifted somewhat. In spite of considerable broadening the peaks are still well defined. (b) Some peaks and shoulders appear in the glass spectrum alongside the strong peaks but are not seen or are very weak in the corresponding crystal spectrum. (c) The low-frequency peaks of the crystal spectrum become a nearly featureless continuum in the glass spectrum.

The 1100-cm^{-1} peak appears in the spectra of all glasses except the pure metasilicate ($x = 1$). Figure 3 shows the width of the 1100-cm^{-1} peak as a function of composition. All curves have minima at approximately the disilicate composition. This composition is expected to be most ordered, while compositions on either side of the disilicate should show more disorder due to random crosslinking of various molecular units. Thus the peak widths increase as x becomes greater than or less than 2. These curves of Fig. 3 strongly suggest that the peak width of the Raman spectra increases with increasing disorder of the Si-O framework of the glass.

Further, for given alkali concentration the fact that the peak width increases as the radius of the alkali decreases, as seen in Figs. 1–3, is inter-

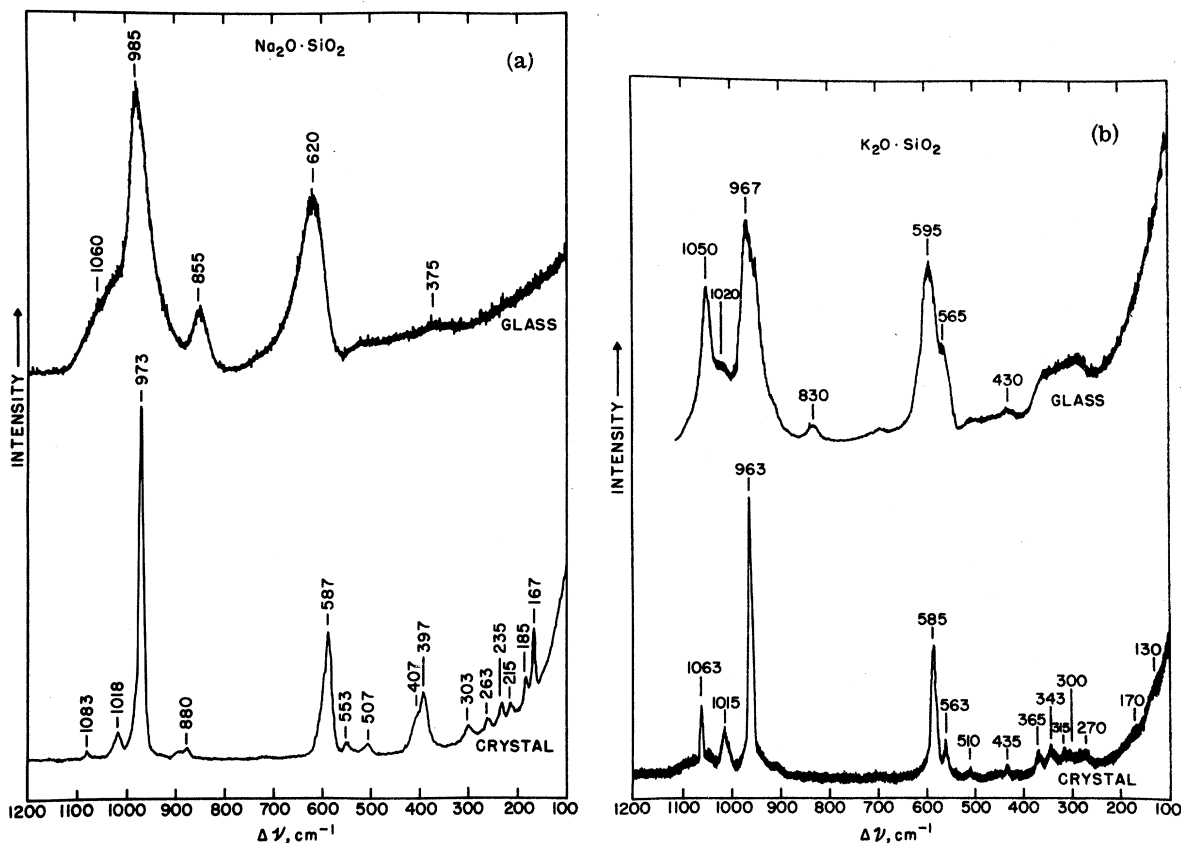


FIG. 1. (a) Raman spectra of $\text{Na}_2\text{O}-\text{SiO}_2$ crystal and glass; (b) Raman spectra of $\text{K}_2\text{O}-\text{SiO}_2$ crystal and glass.

preted to mean that the silica network becomes more disordered as the size of the modifier is decreased. The tentative explanation for this is that the smaller alkalis can shield the nonbridging oxygens and so lower the free energy even with considerable disorder. The important point is that the alkali ions affect the peak width, for the high-frequency peaks at any rate, only insofar as they affect the order of the silica network. The alkali ions are weakly coupled to the oxygen ions and their vibrations appear to have little direct effect on the Raman spectrum at the higher frequencies.

The combination of the Raman spectra and crystallization behavior of binary-alkali-silicate glasses is not consistent with a polycrystallite model. Quite simply, the rate of crystallization in binary alkali silicates decreases markedly in the direction $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$. As seen in Figs. 2 and 3 the order of the glass increases in the direction $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$, while just the opposite is expected to be true for a polycrystallite. Changes in the spectra as a function of composition can be explained qualitatively by a random-network-type structural model applied to the silica framework. In this model the silicons are approximately tetrahedrally coordinated by

oxygens and these tetrahedra are linked at the vertices to form a network. The amount of disorder increases as the correlation in position and relative orientation of the tetrahedra increases, and this appears to be related to the size of the alkali. Consequently, the short-range order in the glass is some greater or lesser distortion of crystalline short-range order, depending on the composition. These conclusions are consistent with present ideas of glass structure.^{1,7,45}

There is another aspect of Raman spectroscopy which makes it a very attractive tool for glass research. It appears that the Raman spectra are sensitive to heterogeneities in glass whose characteristic dimensions are of the order of tens of angstroms. Theoretical support for this idea is presented in Sec. V. Some experimental results which support the idea are (a) In amorphous zirconia, Keramidas and White⁴⁶ detected crystallites whose characteristic dimensions were about 35 Å by Raman spectroscopy. (b) Brawer and White detected phase separation in the system $\text{K}_2\text{O}-\text{SiO}_2$ by Raman spectroscopy. Unsuccessful attempts by Charles⁴⁷ to detect such phase separation by electron microscopy have placed an upper limit on the size of the

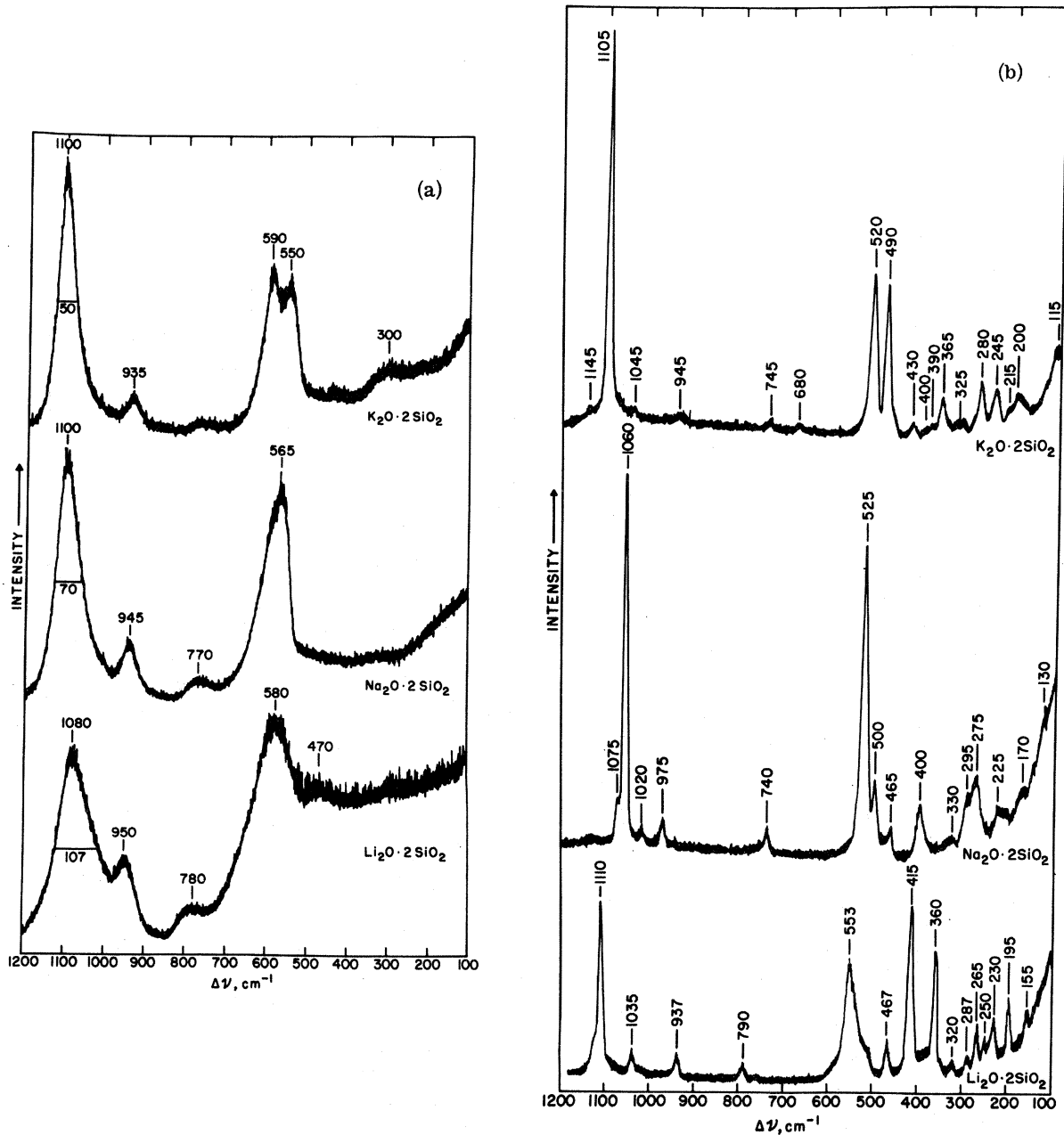


FIG. 2. (a) Raman spectra of alkali disilicate glasses; (b) Raman spectra of alkali disilicate crystals.

separated regions as less than 100 Å.

There has been a large amount of work on the Raman and infrared spectra of very small crystallites in a polycrystallite material.⁴⁸⁻⁵¹ In these approaches, changes of spectra due to surface effects are detected. End effects also allowed Tuinstra and Koenig⁵² to detect very small particle size in glassy carbon. The detection of small glassy heterogeneous regions by Raman spectroscopy is based on a principle different from detecting end effects,

as discussed in Sec. V.

The above discussion shows that it is possible to obtain structural information about glasses from the Raman spectra. Therefore it would be useful to have a general theoretical treatment of the vibrational spectra of glasses of the network type, such as the silicates, germanates, borates, and others, and such a theory is developed in this article.

In order for a theory to be applicable one must have a useful model of the atomic interactions in the

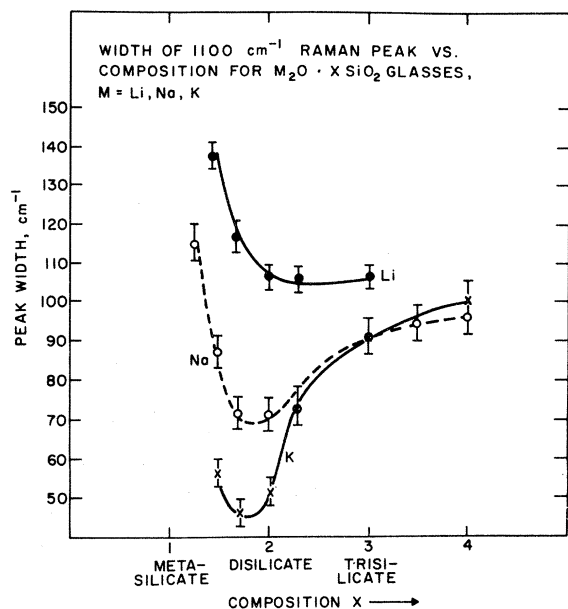


FIG. 3. Width of the 1100-cm^{-1} peak in the glass Raman spectra as a function of glass composition. Compositions are $M_2O \cdot xSiO_2$, where M is the alkali ion.

system under consideration. For the vibrational spectra and dispersion relations of some silicates, a model with atoms interacting via nearest-neighbor harmonic forces gives reasonable agreement with experiment.⁵³⁻⁵⁵ This model is adopted here. The extension of the theory to include long-range Coulomb forces can be accomplished within the framework of the theory.

In general terms, then, this article presents a method of calculating the Raman spectra of certain disordered structures in which the atoms interact with nearest-neighbor harmonic forces. The treatment is general enough to be applicable to network glasses of the oxide type as well as to molecular glasses such as nitrates,¹ but will not apply to glasses like amorphous Si or Ge.

The following points are dealt with by the theory.

(a) It is shown under what conditions the glass spectrum will resemble the spectrum of a related crystal. In some disordered solids such as amorphous Ge (Refs. 37 and 41) or Ca-stabilized ZrO_2 ,⁵⁷ the Raman spectrum bears little relation to crystal spectra, while for many oxide glasses, glass and crystal spectra are similar (Figs. 1 and 2).

(b) Some qualitative principles are formulated which can be applied to the Raman spectra of glasses. At present, the state of the art appears to be that the Raman spectrum of one single glass is informative only as it is compared to the spectra of other related glasses and crystals. It is important to develop a framework in which such comparisons

can be made.

(c) In order to determine some information on glass structure, one would assume a model of the structure and then calculate its vibrational spectrum according to the prescription given here. If the calculated spectrum matches the observed one, then the structural model has some degree of validity. In general, different structures are expected to lead to similar results, so the theory cannot be used to determine a unique structure.

This paper is composed of seven sections. In Secs. I-IV the equations of motion of the glass lattice are approximated and formulas for the Raman spectrum are derived. In Sec. V the results of this treatment are summarized together with some qualitative conclusions about the Raman spectra of glasses including the size of the heterogeneities to which it is sensitive. In Sec. VI the theory is applied to the Raman spectra of crystalline and glassy alkali metasilicates. The interatomic-force constants and polarizabilities are chosen by matching the calculated and observed crystal spectra. Then the silica network is disordered and the Raman spectrum again calculated. The only parameters in the glass calculation are structural. The frequencies and polarizabilities are computed directly with no *ad hoc* adjustments. In Sec. VII the results of the calculations of Sec. VI are summarized and the conclusions drawn.

I. EQUATIONS OF MOTION OF GLASS

According to present concepts,^{1,5,7,43,45} glasses such as the inorganic oxides consist of networks in which glass formers such as the metals Si, B, Ge, and Al are bonded with strong partially covalent and partially ionic bonds to electronegative atoms such as oxygen. Analysis of x-ray patterns shows that structures such as BO_3 triangles and SiO_4 tetrahedra are found. These structures are not exactly tetrahedral or triangular, and small deviations are common.

In this article we will be concerned with the structure of this network. Modifier ions such as the alkalis and alkaline earths may also be present, clustering somehow about the nonbridging oxygens. The vibration frequencies of the modifiers are usually two to four times smaller than the frequencies of the strong optically active vibrations of the oxide network. Thus the presence of the modifiers in a variety of different equilibrium positions⁵⁸⁻⁶⁰ is taken into account in a phenomenological way by assuming fluctuating force constants between some of the network atoms and stationary modifiers. Only the motion of the oxide framework is studied here.

The structure of many glasses can be represented as in Fig. 4, where the large circles represent a collection of atoms and will be called a *structural unit*, or *unit* for short. The solid lines represent

bonds between atoms in different units. These bonds can be of any magnitude relative to the bonds between atoms within the same unit. If these interunit bonds are very weak compared to the intraunit bonds, one has a molecular solid. This is generally *not* the case for inorganic oxide glasses, where the intraunit and interunit bonds are the same metal-oxide bonds. In spite of this, as will be shown, it is a good approach to use as a starting point a molecular solid.

The individual units may be joined in one, two, or three dimensions and either regularly or irregularly. A possible two-dimensional disilicate glass is shown in Fig. 5, where the nonbridging oxygens are not shown and where some structural units are surrounded by dotted circles. In alkali metasilicate M_2O-SiO_2 and disilicate $M_2O-2SiO_2$ the units have the composition Si_2O_6 and Si_2O_5 , respectively. In B_2O_3 glass the natural structural unit appears to be a B_3O_6 unit.⁵

The structural unit is a generalization of the idea of the unit cell of a crystal. *It is important that one can physically construct the glass from these units.* The reason is that the atomic displacements are expanded in terms of the normal modes of the individual units. Thus in silicates an SiO_4 tetrahedron cannot be used as a structural unit since the glass cannot be constructed from such units. Similarly, BO_3 units cannot be used in borates and AsS_3 and AsO_3 units are unsatisfactory in arsenic glasses.

The structural units need not have the same composition or the same average properties. For silicates of composition $Na_2O-xSiO_2$, where $1 < x < 2$,

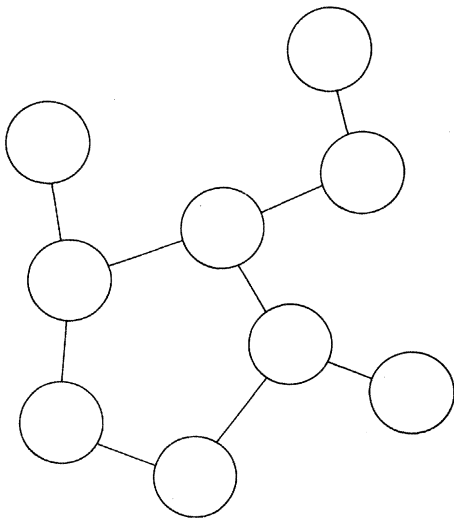
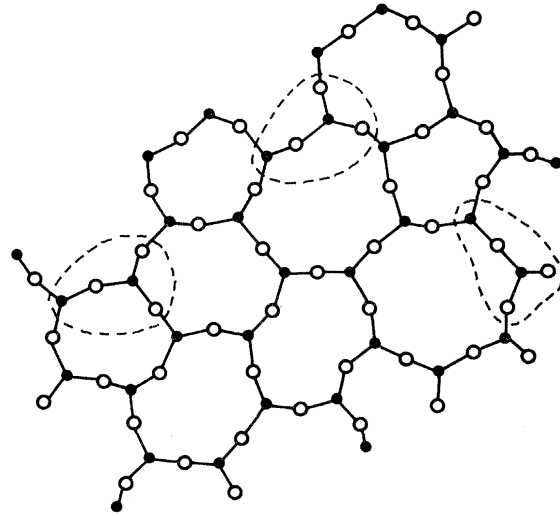


FIG. 4. Schematic model of network glass. Open circles are structural units and signify a collection of atoms. Lines represent bonds between atoms in neighboring structural units.



• SILICON
○ OXYGEN

FIG. 5. Two-dimensional schematic model of a disilicate glass. Open circles are oxygens, shaded circles are Si. Nonbridging oxygens are not shown. Several structural units are surrounded by dotted lines.

there are on the average $2/x$ nonbridging oxygens per silicon. Thus, at the very least, the glass must be made up of Si_2O_5 and Si_2O_6 structural units. In the case where all structural units are the same (on the average) our equations reduce to those of a crystal in the limit of vanishing disorder when all structural units become identical. When the units are the same on the average, one can define a *crystal corresponding to the glass* as one which has a unit cell whose structure is an average over all the structural units of the glass. Such a crystal will be referred to as the *corresponding crystal*. Actually, the corresponding crystal may be a fictitious creation which may not exist in nature and whose existence may in fact be impossible. For such cases the heuristic definition of the corresponding crystal is given a mathematically precise definition following Eq. (4).

Let \vec{n} label the units. \vec{n} is a scalar integer for one dimension, or a vector in two or three dimensions. Let l label the atoms within the units. There are $M+3$ atoms in each unit and N units in the glass.

The equations of motion of the atoms in the harmonic approximation are

$$m(l) \frac{d^2}{dt^2} X_\alpha(\vec{n}, l, t) = \sum_{\beta, \vec{n}', l'} V_{\alpha\beta}(\vec{n}, l | \vec{n}', l') X_\beta(\vec{n}', l', t), \quad (1)$$

where

$$(x_1, x_2, x_3) = (x, y, z).$$

$V_{\alpha\beta}$ is the force-constant matrix and $m(l)$ is the mass of the l th atom. It is assumed that central and noncentral harmonic forces act between nearest neighbors. It is possible to extend this theory to more general cases, as will be discussed later.

It is useful in some cases to define a zeroth-order force-constant matrix $v^{(0)}$ as

$$v_{\alpha\beta}^{(0)} = V_{\alpha\beta} - \Delta V_{\alpha\beta}. \quad (2)$$

For example, consider the case of Fig. 6, where a unit is shown coupled to three other units. The atoms 1, 2, 3, all lie within the n th unit and the angles ϕ_1, ϕ_2, ϕ_3 are in general all different and fluctuate from unit to unit. It may be desirable to have $v^{(0)}$ describe the case where all the angles ϕ_i are equal or where some natural symmetry condition is met, while fluctuations in ϕ_i are absorbed in ΔV . $v^{(0)}$ is not the same for all units but only has some sort of uniformity in the angles ϕ_i . In the above example, $v^{(0)}$ is useful when the ϕ_i are the angles between two bonds, one an interunit and the other an intraunit bond. Other cases may occur when the interunit force constants vary.

For network glasses this viewpoint of a glass as separate units bonded together is feasible only when there are more interatomic bonds within a unit than bonds between a unit and all its neighbors. This immediately eliminates amorphous Si and Ge from consideration. The silicates and borates fall nicely within this approximation.

Since each unit is considered a molecular entity, it is reasonable to use as a zeroth-order solid the individual units. This means the displacements $X_\alpha(\vec{n}, l, t)$ of the (\vec{n}, l) th atom will be expanded in terms of orthonormal basis states for the \vec{n} th unit. There are different ways of determining these basis states.

In the case of a small amount of disorder one would use the basis states u_α satisfying

$$\begin{aligned} -E(\vec{n}, \mu)^2 m(l) u_\alpha(\vec{n}, l; \mu) \\ = \sum_{\vec{n}', l', \beta} v_{\alpha\beta}^{(0)}(\vec{n}, l | \vec{n}', l') u_\beta(\vec{n}', l'; \mu). \end{aligned} \quad (3)$$

Note the presence of \vec{n} and not \vec{n}' in the u_β on the right-hand side of (3). The basis states are calculated with periodic boundary conditions, so there is a dynamical link with adjacent units. This approximation is useful only when there are correlations in the configurations and positions of neighboring units.

In the case of a lot of disorder, when there is little correlation in the relative positions of neighboring units, one would use basis states calculated from the equations

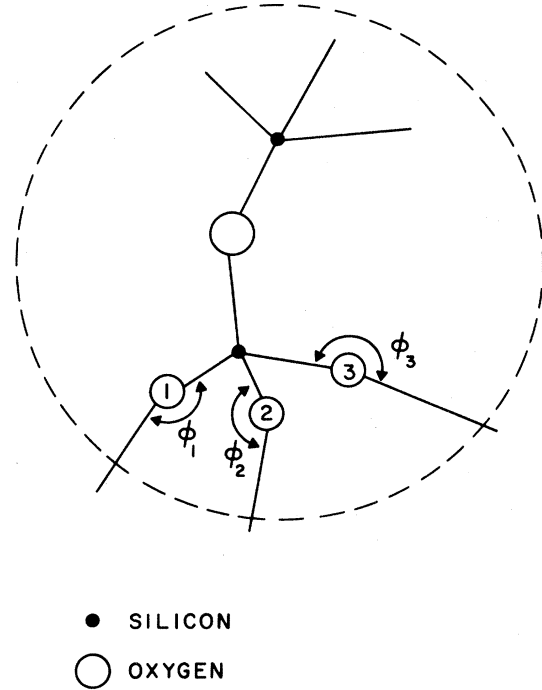


FIG. 6. Structural unit for vitreous silica. Variations of ϕ_i should be incorporated into ΔV as explained following Eq (2).

$$\begin{aligned} -E(\vec{n}, \mu)^2 u_\alpha(\vec{n}, l; \mu) m(l) \\ = \sum_{l', \beta} v_{\alpha\beta}^{(0)}(\vec{n}, l | \vec{n}, l') u_\beta(\vec{n}, l'; \mu). \end{aligned} \quad (4)$$

Note that in (4) the $v^{(0)}$ has no \vec{n}' in its argument. These equations put in no dynamical link to neighboring units. The basis states of one unit are calculated assuming all its neighbors are constrained to be at rest. Long-range Coulomb forces can be absorbed into E^2 .

The manner in which the spectrum of the corresponding crystal is determined depends on the circumstances. If there is an obvious crystal structure to use (meaning that the glass is clearly a distortion of this particular crystal), then one calculates its optically active modes from Eq. (3) in the usual manner for any crystal. Otherwise the optically active modes of the corresponding crystal are calculated from Eq. (3) using $\langle v_{\alpha\beta}^{(0)} \rangle$ instead of $v_{\alpha\beta}^{(0)}$, where $\langle \dots \rangle$ denotes an ensemble average over the random variables in the force-constant matrix. This can be done only if all the units are, on the average, the same.

The u 's obey the orthonormality conditions

$$\sum_{\alpha, \mu} m(l) u_\alpha(\vec{n}, l; \mu) u_\alpha(\vec{n}, l'; \mu) = \delta_{l, l'}, \quad (5)$$

$$\sum_{\alpha, l} m(l) u_{\alpha}(\tilde{n}, l; \mu) u_{\alpha}(\tilde{n}, l; \mu') = \delta_{\mu, \mu'} . \quad (6)$$

$$X_{\alpha}(\tilde{n}, l, t) = \sum_{\mu} q(\tilde{n}, \mu, t) u_{\alpha}(\tilde{n}, l; \mu) . \quad (7)$$

Since the u 's form a complete set, the X_{α} may be expanded:

Putting (7) into (1), the equations of motion are

$$\frac{d^2}{dt^2} q(\tilde{n}, \mu_0, t) = -\Omega(\tilde{n}, \mu_0)^2 q(\tilde{n}, \mu_0, t) + \sum_{\mu' (\neq \mu_0)} \psi(\tilde{n}, \mu_0, \mu') q(\tilde{n}, \mu', t) + \sum_{\tilde{n}', \mu'} \beta(\tilde{n}, \mu_0 | \tilde{n}', \mu') [q(\tilde{n}', \mu', t) - q(\tilde{n}, \mu', t)] , \quad (8)$$

where

$$\beta(\tilde{n}, \mu_0 | \tilde{n}', \mu') = \sum_{\substack{\alpha, \beta \\ l, l'}} u_{\alpha}(\tilde{n}, l; \mu_0) V_{\alpha\beta}(\tilde{n}, l | \tilde{n}', l') u_{\beta}(\tilde{n}', l'; \mu') . \quad (9)$$

The value of ψ depends on whether one uses Eq. (3) or (4) for the basis states. For the case of more disorder [Eq. (4)], we have

$$\psi(\tilde{n}, \mu_0, \mu') = \sum_{\alpha, \beta, l} u_{\alpha}(\tilde{n}, l; \mu_0) [V_{\alpha\beta}(\tilde{n}, l | \tilde{n}, l) - v_{\alpha\beta}^{(0)}(\tilde{n}, l | \tilde{n}, l)] u_{\beta}(\tilde{n}, l; \mu') + \sum_{\tilde{n}' (\neq \tilde{n})} \beta(\tilde{n}, \mu_0 | \tilde{n}', \mu') , \quad (10a)$$

whereas for the case of more order [Eq. (3)], we have

$$\psi(\tilde{n}, \mu_0, \mu') = \sum_{\alpha, \beta, \tilde{n}', l'} u_{\alpha}(\tilde{n}, l; \mu_0) [V_{\alpha\beta}(\tilde{n}, l | \tilde{n}', l') u_{\beta}(\tilde{n}', l'; \mu') - v_{\alpha\beta}^{(0)}(\tilde{n}, l | \tilde{n}', l') u_{\beta}(\tilde{n}, l'; \mu')] , \quad (10b)$$

while in both cases

$$\Omega(\tilde{n}, \mu_0)^2 = E(\tilde{n}, \mu_0)^2 - \psi(\tilde{n}, \mu_0, \mu_0) . \quad (11)$$

We note that $\psi(\tilde{n}, \mu, \mu')$ as given by Eqs. (10) is not symmetric, i. e.,

$$\psi(\tilde{n}, \mu, \mu') \neq \psi(\tilde{n}, \mu', \mu) .$$

For our purposes this form is satisfactory but for some cases it may be necessary to rewrite Eqs. (8)–(11) so that ψ is symmetric.

It is now desired to approximate Eq. (8) and thus to determine the nature of those solutions which are relevant to the vibrational spectra.

In general, for all \tilde{n} and the modes μ_0 of interest, the relations

$$\begin{aligned} |\beta(\tilde{n}, \mu_0 | \tilde{n}', \mu')| &\ll \Omega(\tilde{n}, \mu_0)^2 , \\ |\psi(\tilde{n}, \mu_0, \mu')| &\ll \Omega(\tilde{n}, \mu_0)^2 \end{aligned} \quad (12)$$

will hold.

Equations (12) are crucial to the ensuing discussion and must be true for the theory developed here to be applicable. They will not be true for all modes μ . They will obviously hold for the high-frequency modes of molecular solids such as alkali nitrates and carbonates. In Sec. VI Eqs. (12) are shown to hold very well for the high-frequency modes of a model of metasilicate glass. Equations (12) also imply that Raman spectroscopy can be used as an analytic tool for glass research, as discussed in Sec. V.

If (12) holds, then Eq. (8) describes a lattice of harmonic oscillators coupled weakly to each other. If all $\beta(\tilde{n}, \mu | \tilde{n}', \mu') = 0$, Eq. (8) reduces to N uncoupled sets of equations. In each set there are the

coupled equations

$$\begin{aligned} \frac{d^2}{dt^2} q(\tilde{n}, \mu_0) &= -\Omega(\tilde{n}, \mu_0)^2 q(\tilde{n}, \mu_0) \\ &+ \sum_{\mu' (\neq \mu_0)} \psi(\tilde{n}, \mu_0, \mu') q(\tilde{n}, \mu') , \end{aligned} \quad (13)$$

which describe the variations of the n th unit uncoupled from its neighbors. (ψ becomes symmetric in the limit of vanishing β .) The secular equation for (13) must then be solved to get the modes for each unit (this may not be necessary in practice). Equation (13) is the molecular solid approximation discussed above.

In general $\beta \neq 0$, so all the modes are coupled and scatter into each other. Because of the weak-coupling (12) the individual units will execute many vibrations at their resonant frequencies before being damped by motions of their neighbors. The widening of the peaks in the glass spectrum is of order ψ and Eqs. (12) imply the peaks will be fairly sharp. This means that if the solutions to (4) are similar to the solutions of (3) for the corresponding crystal the Raman intensities and frequencies of the normal modes of the glass will resemble those of the corresponding crystal.

Consider now any two modes for which, for most \tilde{n} and \tilde{n}' ,

$$\begin{aligned} |\Omega(\tilde{n}, \mu_0)^2 - \Omega(\tilde{n}, \mu')^2| &\gg |\beta(\tilde{n}, \mu_0 | \tilde{n}', \mu')| , \\ |\Omega(\tilde{n}, \mu_0)^2 - \Omega(\tilde{n}, \mu')^2| &\gg |\psi(\tilde{n}, \mu_0, \mu')| . \end{aligned} \quad (14)$$

These modes μ_0 and μ' will, to a good approximation, be uncoupled. For the first part of this discussion the inequalities (14) are presumed to hold for *all* the modes of the solid. Later on the case of two modes close together is considered.

We note that nothing we have done so far requires that all the units be the same. If they are not all the same, however, Eqs. (14) will hold only for some special modes.

Thus as a first step in approximating Eq. (8) the quantities $\beta(\vec{n}, \mu | \vec{n}', \mu')$ and $\psi(\vec{n}, \mu, \mu')$ are ignored for $\mu \neq \mu'$.

The quantity β fluctuates about a nonzero mean, in general. Define the average

$$\bar{\beta}(\mu_0) = \langle \beta(\vec{n}, \mu_0 | \vec{n}', \mu_0) \rangle, \quad (15)$$

where $\langle \dots \rangle$ is the ensemble average over all units. It will be shown that only this average $\bar{\beta}$ need be considered and that fluctuations in β are of secondary importance.

Then Eq. (8) can be approximated by the M equations (for the M optically active modes):

$$\frac{d^2}{dt^2} q(\vec{n}, \mu_0) = -\Omega(\vec{n}, \mu_0)^2 q(\vec{n}, \mu_0) + \bar{\beta}(\mu_0) \sum_{\vec{n}'}^{(nn)} [q(\vec{n}', \mu_0) - q(\vec{n}, \mu_0)], \quad (16)$$

where (nn) means the sum is over nearest neighbors only. The validity of the approximations leading to (16) will be discussed as the behavior of (16) is analyzed.

Equation (16) describes individual oscillators, each with a different resonance frequency, and all coupled uniformly by $\bar{\beta}(\mu_0)$. In this approximation the disorder is taken into account only in the variation of Ω^2 with \vec{n} . Implicit in Ω^2 is the fluctuating coupling between units, as seen from the defining equation (11), as well as fluctuating force constants due to modifiers.

Equation (16) is identical (apart from the second-order time derivative) to the tight-binding Hamiltonian used for electronic properties. An equation similar to (16) has been analyzed by Anderson⁶¹ who gives considerable insight into its behavior.

In Eq. (16), $\Omega(\vec{n}, \mu_0)$ fluctuates about a mean $\Omega_0(\mu_0)^2$ with variance $\sigma(\mu_0)$. That is,

$$\langle \Omega(\vec{n}, \mu_0)^2 \rangle = \Omega_0(\mu_0)^2, \quad (17)$$

$$\langle [\Omega(\vec{n}, \mu_0)^2 - \Omega_0(\mu_0)^2]^2 \rangle = \sigma(\mu_0)^2. \quad (18)$$

Equations (12) means that $\sigma \ll \Omega_0^2$ (henceforth, for the sake of brevity, the explicit μ_0 dependence will be dropped where no confusion can result).

Let $p(\vec{n}, t)$ be the time-dependent polarizability of the \vec{n} th unit (we discuss the Raman spectrum in this article. One can carry through the discussion with very little changes for the case of the infrared absorption). A classical bond-stretching model is

employed in which the polarizability of a bond is proportional to its change in length from the equilibrium value:

$$p(\vec{n}, t) = \sum_{\beta, l, l'} Q_\beta(\vec{n}, l, l') [X_\beta(\vec{n}, l, t) - X_\beta(\vec{n}, l', t)] + \frac{1}{2} \sum_{\beta, l, l', \vec{n}'} R_\beta(\vec{n}, l | \vec{n}', l') [X_\beta(\vec{n}, l, t) - X_\beta(\vec{n}', l', t)], \quad (19)$$

where the Q term gives the polarizability within each unit while the R term gives that due to inter-unit bonds. The $\frac{1}{2}$ is used so that when the polarizability is summed over \vec{n} , each interunit bond is counted only once.

Here Q can be written explicitly as

$$Q_\beta(\vec{n}, l, l') = \frac{r_\beta(\vec{n}, l) - r_\beta(\vec{n}, l')}{|\vec{r}(\vec{n}, l) - \vec{r}(\vec{n}, l')|},$$

where $\vec{r}(\vec{n}, l)$ is the equilibrium position of the (\vec{n}, l) th atom. There is a similar expression for R . The proportionality constant has been set equal to unity for convenience.

It is useful to define

$$\alpha(\vec{n}, \mu_0) = \sum_{\beta, l, l'} Q_\beta(\vec{n}, l, l') [u_\beta(\vec{n}, l; \mu_0) - u_\beta(\vec{n}, l'; \mu_0)] + \sum_{\beta, l, l', \vec{n}'} R_\beta(\vec{n}, l | \vec{n}', l') u_\beta(\vec{n}, l; \mu_0) \quad (20)$$

as a polarizability of μ_0 th mode due strictly to the \vec{n} th unit and without reference to neighboring units. This is the quantity which will appear in all the final expressions derived here.

The vibrational spectrum is determined from the approximate equations of motion (16). The relative values of the parameters where a reasonably accurate calculation can be made are

- (i) $\bar{\beta} \ll \sigma/4d$,
- (ii) $\bar{\beta} \geq \sigma$,

where d is the number of dimensions of the network.

It is well known that Eq. (16) has a quite different behavior depending on whether (i) or (ii) holds.^{61,62} In general, the two types of behavior can occur for the same glass but different modes μ_0 , regardless of which set of basis states, Eq. (3) or Eq. (4), is used.

It is useful to note here that Eq. (16) has in it the seeds of various observed phenomena. Consider the case of enough disorder so that Eq. (4) is used to calculate the basis states. Suppose that the polarizabilities $\alpha(\vec{n}, \mu_0)$ from Eq. (20) are different for these basis states than they are for those of the corresponding crystal which are calculated using periodic boundary conditions, Eq. (3). Modes which are inactive, or very weak, for the corresponding

crystal may become stronger in the glass so that peaks may appear in the glass spectrum which do not appear in the crystal spectrum. This is shown to occur for the particular example. The peaks in the glass spectrum may be widened by the disorder (fluctuating Ω) and several peaks close together may blend into one. Peak heights in glass and corresponding crystal may be quite different due to differing polarizabilities and peak widths. Modes which are very strong (very weak) Raman scatterers in the corresponding crystal will probably be very strong (weak) scatterers in the glass and this is what is most striking when one compares the glass and crystal spectra of Figs. 1 and 2.

II. CASE OF $\bar{\beta} \ll \sigma/4d$

In this case the oscillators are simply taken to be independent of each other. The Raman intensity at angular frequency ω is

$$I(\omega) = \left\langle \sum_{\vec{n}} \delta(\omega - \Omega(\vec{n}, \mu_0)) \alpha(\vec{n}, \mu_0)^2 \right\rangle, \quad (21)$$

where α is given by (20). The use of (20) for the polarizability follows from the fact that the motion of neighboring units is uncorrelated, as discussed below. A classical model is assumed in which the radiation-matter interaction is described by one scalar parameter—the polarizability—and the sample size is presumed negligible compared to the wavelength of the incident radiation. Thus the frequency of the excitation source appears only in the constant of proportionality which has been set equal to unity in Eq. (20).

Formula (21) holds for each mode μ_0 such that the condition $\bar{\beta}(\mu_0) \ll \sigma(\mu_0)/4d$ is satisfied. If α is small, the mode will be a weak scatterer and possibly not observable. The shape of the peak in the spectrum is determined both by fluctuations in α and fluctuations in Ω^2 , so the peak shapes may not directly give the distribution of frequencies.

The result (21) holds strictly for $\bar{\beta} = 0$. For non-zero $\bar{\beta}$ each oscillator interacts with its neighbors and thus will have a certain lifetime for vibrating at the frequency ω . Say the lifetime is τ . Then

$$\left. \frac{d}{d\bar{\beta}} I(\omega) \right|_{\bar{\beta}=0} \sim \left. \frac{d}{d\bar{\beta}} \frac{1}{\tau} \right|_{\bar{\beta}=0}. \quad (22)$$

The lifetime τ is now estimated for very small $\bar{\beta}$.

Suppose that at time $t=0$ all the atoms of the lattice are at rest at their equilibrium positions except the \vec{n}_0 th, which is displaced one unit and released from rest. Because of the weak coupling (12) the \vec{n}_0 th oscillator will initially vibrate in harmonic motion at its resonant frequency $\Omega(\vec{n}_0)$. A periodic force of frequency $\Omega(\vec{n}_0)$ then acts on the neighbors of the \vec{n}_0 th oscillator. Because of this force the neighbors begin to oscillate at frequency $\Omega(\vec{n}_0)$. Since $\bar{\beta} \ll \sigma$, the chances are that the reso-

nant frequency Ω of any neighbor of the \vec{n}_0 th oscillator will be far from $\Omega(\vec{n}_0)$ so that

$$|\Omega^2 - \Omega(\vec{n}_0)^2| \gg \bar{\beta}.$$

Then the amplitude of a neighbor for vibrations at the frequency $\Omega(\vec{n}_0)$ is a factor of the order $\bar{\beta}/\sigma$ smaller than the amplitude of the \vec{n}_0 th oscillator. The argument may be continued so that at some site \vec{n}' the amplitude of the atomic vibrations at frequency $\Omega(\vec{n}_0)$ will be about $(\bar{\beta}/\sigma)^{|\vec{n}' - \vec{n}_0|}$. Therefore the vibrations of the \vec{n}_0 th oscillator are localized.

Eventually a distance $|\vec{r} - \vec{n}_0|$ away one will come to the \vec{r} th oscillator of frequency $\Omega(\vec{r})$ such that

$$|\Omega(\vec{r})^2 - \Omega(\vec{n}_0)^2| \leq \bar{\beta}, \quad (23)$$

and hence near the resonance frequency of the \vec{n}_0 th oscillator. The \vec{r} th oscillator can be driven at resonance by its neighbor, which is driven by its neighbor and so on back to the original one, so that energy may then leak away from \vec{n}_0 . The lifetime for this is on the order of

$$\frac{2\Omega(\vec{n}_0)}{\bar{\beta}} \left(\frac{\bar{\beta}}{\sigma} \right)^{|\vec{r} - \vec{n}_0|}.$$

For small $\bar{\beta}$ the average value of $|\vec{r} - \vec{n}_0|$ such that (23) holds is proportional to q^{-1} , where

$$q = \int_{[\Omega(\vec{n}_0)^2 - \bar{\beta}]^{1/2}}^{[\Omega(\vec{n}_0)^2 + \bar{\beta}]^{1/2}} d\omega P(\omega) \cong \left(\frac{\bar{\beta}}{\Omega(\vec{n}_0)} \right) P(\Omega(\vec{n}_0))$$

and $P(\omega)$ is the probability that any oscillator has resonant frequency ω . Thus the lifetime of the oscillator is proportional to

$$\left(\frac{\bar{\beta}}{\sigma} \right)^{[\Omega(\vec{n}_0)/\bar{\beta} P(\Omega(\vec{n}_0))] \times \text{const}} \quad (24)$$

as $\bar{\beta} \rightarrow 0$. Consequently,

$$\left. \frac{d^{(j)}}{d\bar{\beta}^{(j)}} I(\omega) \right|_{\bar{\beta}=0^+} = 0 \quad (25)$$

for all orders of derivative j .

Equations (24) and (25) indicate that even for finite but small $\bar{\beta}$ the result (21) will be satisfactory approximation to the Raman spectrum when the modes are localized. It is clear from the discussion that the lifetime (24) will be small when nearest neighbors have such different frequencies that they vibrate independently of one another. If an atom has n neighbors, the probability that no neighbor has frequency within $\bar{\beta}$ of a given one is

$$(1 - \bar{\beta}/\sigma)^n.$$

This must be close to unity for (21) to be valid, so that

$$n\bar{\beta}/\sigma \ll 1. \quad (26)$$

This result can be given a physical interpretation. For many cases $n=2d$ for d dimensions, and $4\bar{\beta}d$ is the bandwidth, in frequency squared, of a

crystal with all $\Omega(\vec{n})$ the same. The condition (26) is then

$$2\bar{\beta}d/\sigma \ll 1, \quad (27)$$

which states that the frequencies of neighbors are so different that no band is formed and waves cannot propagate. Since, from (24) and (25), $I(\omega)$ increases in width only very slowly with $\bar{\beta}$, Eq. (21) will be accurate so long as (27) is obeyed.

The discussion leading to (25) is a heuristic treatment of Eq. (16) in the case $\bar{\beta}/\sigma$ is very small. A very elegant treatment of this equation has been given in the paper by Anderson.⁶¹ Anderson obtains the result that there is no transport of energy for values of $\bar{\beta}/\sigma$ smaller than a certain critical value, at least in three dimensions. On the other hand, the above argument presumes a small but finite lifetime for nonzero $\bar{\beta}$ which is estimated in (24). In any event both approaches indicate that Eq. (21) is a satisfactory approximation to the Raman spectrum in the limit of small $\bar{\beta}$.

III. CASE WHEN $\bar{\beta} \gtrsim \sigma$

As $\bar{\beta}$ increases, the oscillators are coupled together by springs which become more and more incompressible. For optically active modes it becomes energetically favorable for the oscillators to vibrate in phase at a single average frequency, in order not to compress the connecting springs. Thus, neglecting fluctuations in polarizability, $I(\omega)$ is expected to become narrower as $\bar{\beta}$ increases.

In terms of the discussion of Sec. II, when $\bar{\beta} \gtrsim \sigma$, it is certain that many neighboring oscillators will have their squared resonant frequencies within $\bar{\beta}$ of each other. Bands are formed and there will then be a rapid transfer of energy from one oscillator to its neighbors, then to their neighbors, and so on, via nonlocalized lattice waves.

In the limit $\bar{\beta} \gtrsim \sigma$, the fluctuations in $\Omega(\vec{n})^2$ are a perturbation on a uniform system. The oscillators will tend to vibrate cooperatively and the zeroth-order eigenstates are the traveling waves $e^{i\vec{k}\cdot\vec{n}}$ (in the case of a regular arrangement of units) rather than the opposite extreme of highly localized modes.

In general, the units will not be regularly arranged and the zeroth-order eigenstates of Eq. (16) will be the eigenfunctions of the matrix

$$\begin{aligned} M(\vec{n}, \vec{n}') &= 1 && \vec{n}, \vec{n}' \text{ nearest neighbors} \\ &= -C && \vec{n} = \vec{n}', \quad C = \text{number of neighbors} \\ &= 0, && \text{otherwise.} \end{aligned} \quad (28)$$

Let the eigenfunctions of this matrix be $v(\vec{k}, \vec{n})$, where \vec{k} labels the eigenvalues $\nu_{\vec{k}}^2$. There is always an eigenvalue $\nu_0^2 = 0$ for $v(0, \vec{n}) = 1$ which we take as corresponding to $\vec{k} = 0$. All other eigenvectors are orthogonal to this one.

For small $\nu_{\vec{k}}^2$ the v are approximately plane waves and \vec{k} is an approximate wave vector. This is because the eigenfunctions of the matrix (28) for small \vec{k} describe long-wavelength sound waves propagating in a disordered continuum.

Expand

$$q(\vec{n}, t) = \frac{1}{\sqrt{N}} \sum_{\vec{k}} h_{\vec{k}}(t) v(\vec{k}, \vec{n}). \quad (29)$$

Writing the polarizability (20) as

$$\alpha(\vec{n}, \mu) = \bar{\alpha}(\mu) + \Delta\alpha(\vec{n}, \mu), \quad (30)$$

$$\bar{\alpha}(\mu) = \langle \alpha(\vec{n}, \mu) \rangle, \quad (31)$$

we have for the net polarizability

$$\sum_{\vec{n}} p(\vec{n}, t) = N\bar{\alpha} h_0(t) + \frac{1}{\sqrt{N}} \sum_{\vec{n}, \vec{k}} \Delta\alpha(\vec{n}) v(\vec{k}, \vec{n}) h_{\vec{k}}(t). \quad (32)$$

Taking the Fourier transform, the Raman intensity is

$$\begin{aligned} I(\omega) &\sim \bar{\alpha}^2 \text{Im} \langle h_0(\omega + i\epsilon) \rangle \\ &+ \sum_{\vec{k}} \left\langle \left(\frac{1}{\sqrt{N}} \sum_{\vec{n}} \Delta\alpha(\vec{n}) v(\vec{k}, \vec{n}) \right)^2 \text{Im} h_{\vec{k}}(\omega + i\epsilon) \right\rangle. \end{aligned} \quad (33)$$

If $\bar{\alpha}^2 \gg \langle \Delta\alpha^2 \rangle$, the first term will dominate and the Raman peak will be sharp. If, on the other hand, $\langle \Delta\alpha^2 \rangle \gg \bar{\alpha}^2$, then the second term will dominate and one has, ignoring correlations between $h_{\vec{k}}$ and the $\Delta\alpha$ term,

$$I(\omega) \sim \langle \Delta\alpha(\vec{n})^2 \rangle g(\omega),$$

which is proportional to the density of states $g(\omega)$. This second case has been dealt with by Shuker and Gammon.³⁹ The magnitude of the density-of-states term may be estimated as follows. The net bandwidth in Ω for d dimensions is $2\bar{\beta}d/\Omega_0$, where Ω_0 is the center of the band, so the density of states can be taken as approximately the square distribution:

$$\begin{aligned} g(\omega) &\cong \Omega_0/2\bar{\beta}d, && -\bar{\beta}d/\Omega_0 \leq \omega \leq \bar{\beta}d/\Omega_0 \\ &= 0, && \text{otherwise.} \end{aligned}$$

Then the peak height due to the density of states is approximately

$$C \langle \Delta\alpha^2 \rangle \Omega_0 / 2\bar{\beta}d, \quad (34)$$

where C is a constant of order unity.

The first term of (33) is expected to be more important than the second term for network glasses because the well-defined molecular units are likely to have well-defined polarizabilities. Thus we determine $\langle h_0 \rangle$ for Eq. (16).

The ensemble average $\langle h_0 \rangle$ is estimated by expanding and resumming the resolvent using well-known techniques.⁶³ In the usual quasiphonon picture

$$\langle h_0(\omega) \rangle \cong \frac{1}{\Omega_0^2 - \omega^2 - 2i\Gamma\Omega_0}. \quad (35)$$

Then the first term of (33) gives a contribution to the Raman intensity

$$I(\omega) = C \frac{\bar{\alpha}^2}{\pi} \frac{\Gamma}{(\Omega_0 - \omega)^2 + \Gamma^2}. \quad (36)$$

The mode μ_0 contributes a sharp peak, of width Γ , to the Raman spectrum. The height of the peak is equal to

$$C \frac{\bar{\alpha}^2}{\pi} \frac{1}{\Gamma},$$

where C is the same constant as in (34).

The equations for the $h_{\vec{k}}(\omega)$ are

$$(\omega_{\vec{p}}^2 - \omega^2) h_{\vec{p}}(\omega) = \sum_{\vec{n}, \vec{k}} v(\vec{p}, \vec{n})^* \Delta(\vec{n}) v(\vec{k}, \vec{n}) h_{\vec{k}}(\omega), \quad (37)$$

where

$$\Omega(\vec{n})^2 = \Omega_0^2 + \Delta(\vec{n}), \quad (38)$$

$$\omega_{\vec{k}}^2 = \Omega_0^2 + \nu_{\vec{k}}^2. \quad (39)$$

In the usual way, one then defines the diagonal matrix

$$D_{\vec{k}} = \left\langle \left\langle \frac{1}{\mathcal{H}_{0+} - V - \omega^2} \right\rangle_{\vec{k}\vec{k}} \right\rangle, \quad (40)$$

where

$$\mathcal{H}_{0+} = \omega_{\vec{p}}^2 \delta_{\vec{k}, \vec{p}}, \quad (41)$$

$$V_{\vec{p}\vec{k}} = \frac{1}{\sqrt{N}} \sum_{\vec{n}} v(\vec{p}, \vec{n})^* \Delta(\vec{n}) v(\vec{k}, \vec{n}). \quad (42)$$

Then

$$D_{\vec{k}} = \langle h_{\vec{k}} \rangle \quad (43)$$

and, in the usual way, one finds

$$D_{\vec{k}} = \frac{1}{\omega_{\vec{k}}^2 - \omega^2 - \Sigma_{\vec{k}}}, \quad (44)$$

$$\Sigma_{\vec{k}} = - \langle V_{\vec{k}\vec{k}} \rangle_i + \sum_{\vec{k}_1} \langle V_{\vec{k}, \vec{k}_1} D_{\vec{k}_1} V_{\vec{k}_1, \vec{k}} \rangle_i + \dots, \quad (45)$$

where $\langle \dots \rangle_i$ means that only irreducible diagrams are used in computing the ensemble average.⁶³

Let ω be near Ω_0 . Then in the quasiphonon approximation

$$\Sigma_{\vec{k}} \cong R_{\vec{k}}(\omega) + 2i\Gamma_{\vec{k}}(\omega)\Omega_0, \quad (46)$$

where $R_{\vec{k}}$ and $\Gamma_{\vec{k}}$ are real and, as will be seen,

$$\Gamma_{\vec{k}}(\Omega_0) \ll \Omega_0.$$

Then we have

$$D_{\vec{k}}(\omega) \cong \frac{1}{\Omega_0^2 + \nu_{\vec{k}}^2 - \omega^2 - R_{\vec{k}}(\omega) - 2i\Gamma_{\vec{k}}(\omega)\Omega_0}. \quad (47)$$

From (43), $\langle h_0 \rangle$ has the form (35). It therefore remains to calculate Γ_0 . The $\vec{k}=0$ modes are on a band edge and, in general, the frequency spectrum is singular there. Thus the usual Born approxi-

mation to Eqs. (45) with δ functions for frequencies is not valid. The first approximation is instead to use (47) for $D_{\vec{k}}$ in the second term on the right-hand side of (45). Similar approximations have been used to calculate sound absorption⁶⁴ and the frequency spectrum of disordered crystals.⁶⁵ (See also the self-consistent equation of Abou-chacra *et al.*⁶²)

The use of $D_{\vec{k}}$ self-consistently removes the singularity at the band edge. Physically it puts into the scattering the finite lifetime of the final state. Then we have

$$2\Gamma_{\vec{p}}\Omega_0 = \frac{\sigma^2}{N} \sum_{\vec{k}} \frac{2\Gamma_{\vec{k}}(\omega)\Omega_0 |v(\vec{k}, \vec{n})|^2 |v(\vec{p}, \vec{n})|^2}{(\Omega_0^2 + \nu_{\vec{k}}^2 - \omega_0^2 - R_{\vec{k}})^2 + (2\Gamma_{\vec{k}}\Omega_0)^2} \quad (48)$$

and a similar equation for $R_{\vec{k}}$.

If Γ is small enough [see Eq. (53)] then the most important terms in (48) are for $|\vec{k}| \ll 1$, i. e., for small $|\vec{k}|$. That is, the $k=0$ mode mixes only with nearby modes so that it is lightly damped. For small $|\vec{k}|$ it is sufficient for our purposes to let

$$\begin{aligned} \Gamma_{\vec{k}} &\sim \Gamma_0, \\ R_{\vec{k}} &\sim 0, \\ \nu_{\vec{k}}^2 &\sim \beta k^2. \end{aligned} \quad (49)$$

Also for small $|\vec{k}|$ the continuum approximation holds for the eigenvectors and eigenvalues of (28), so \vec{k} is a wave vector and $|v(\vec{k}, \vec{n})| \sim 1$ to order k^2 . Thus for

$$\omega^2 = \Omega_0^2 \quad (50)$$

we have

$$2\Gamma_0\Omega_0 = \sigma^2 \int \frac{d\vec{k}}{(2\pi)^d} \frac{2\Gamma_0\Omega_0}{\beta^2 k^4 + (2\Gamma_0\Omega_0)^2} \quad (51)$$

for d dimensions. The solution to (51) is

$$\begin{aligned} \Gamma_0 &= \frac{\sigma}{4^{2/3}\Omega_0} \left(\frac{\sigma}{4\beta} \right)^{1/3} & d=1 \\ &= \frac{\sigma}{4\Omega_0} \left(\frac{\sigma}{4\beta} \right) & d=2 \\ &= \frac{\sigma}{\pi^2\Omega_0} \left(\frac{\sigma}{4\beta} \right)^3, & d=3. \end{aligned} \quad (52)$$

The results are valid only when terms $|\vec{k}| \ll 1$ are most important in (48). This is true when $2\Gamma_0\Omega_0$ is much less than the maximum value of $\nu_{\vec{k}}^2$, so that

$$2\Gamma_0\Omega_0 \ll 4\bar{\beta}d$$

for d dimensions.

Consider now what happens when β fluctuates. In the region $\bar{\beta} \ll \sigma/4d$ it was possible to ignore $\bar{\beta}$ entirely in the result (21) for the Raman intensities, so we may safely ignore its fluctuations. (The RMS of the fluctuations of β are expected to be of the order $\bar{\beta}$ itself.)

In the case $\bar{\beta} \geq \sigma$, Eq. (37) has an extra term,

$$V'_{\vec{k}, \vec{p}} \sim \frac{1}{N} \sum_{\vec{n}'} \Delta\beta(\vec{n}') e^{i\vec{n}' \cdot (\vec{k} - \vec{p})} |\vec{k}| |\vec{p}| h_{\vec{k}}(\omega), \quad (53)$$

where

$$|\vec{k}|, |\vec{p}| \ll 1,$$

$$\Delta\beta(\vec{n}) \sim \sum_{\vec{n}'}^{(nn)} \beta(\vec{n}', \mu_0 | \vec{n}', \mu_0) - \bar{\beta}(\mu_0),$$

and

$$v(\vec{k}, \vec{n}) \sim e^{i\vec{k} \cdot \vec{n}}$$

were used, which is valid for small $|\vec{k}|$. It is seen that $V'_{\vec{k}, 0}$ vanishes, so (53) gives no contribution to Σ_0 [see (45)]. This is to be expected on physical grounds. In the $k=0$ modes all the atoms vibrate in phase with approximately the same amplitude. Thus $q(\vec{n}) - q(\vec{n}')$ is small for these modes.

IV. CASE OF TWO MODES CLOSE TOGETHER

In the case that Eqs. (14) are not well satisfied it is necessary to take into account the interaction of different modes. This is particularly true if one of the modes has a large polarizability and the other a small one, since the mixing of states can alter the polarizability of the weak mode a great deal. In this section we deal with a special case which will be useful for the metasilicate glass, which is considered in Sec. V. In this case the silica network is one dimensional, so n is a scalar integer and each unit has two neighbors.

Consider two modes $\mu = 1, 2$ so that

$$\beta(n, 2 | n \pm 1, 2) = 0. \quad (54)$$

It is assumed that

$$\Omega(n, 2) > \Omega(n, 1)$$

for all n . There is non-negligible coupling between

the two modes of the same unit and between modes $\mu = 1$ of the n th unit and mode $\mu = 2$ of the $n+1$ st unit. That is, it is valid to set

$$\beta(n, 1 | n+1, 2) = 0. \quad (55)$$

Defining

$$\psi_1(n) \equiv \psi(n, 1, 2) - \sum_{n'}^{(nn)} \beta(n, 1 | n', 2), \quad (56)$$

$$\beta_2(n) \equiv \beta(n, 1 | n-1, 2) = \beta(n-1, 2 | n, 1), \quad (57)$$

Eq. (8) for the two modes becomes

$$\begin{aligned} \frac{d^2}{dt^2} q(n, 1) = & -\Omega(n, 1)^2 q(n, 1) + \psi_1(n) q(n, 2) + \beta_2(n) \\ & \times q(n-1, 2) + \bar{\beta}(1) \sum_{n'}^{(nn)} [q(n', 1) - q(n, 1)], \end{aligned} \quad (58)$$

$$\begin{aligned} \frac{d^2}{dt^2} q(n, 2) = & -\Omega(n, 2)^2 q(n, 2) + \psi_1(n) q(n, 1) \\ & + \beta_2(n+1) q(n+1). \end{aligned}$$

In (58), $\beta(n, 1 | n \pm 1, 1) \equiv \bar{\rho}(1)$.

In the system under consideration the following inequalities are satisfied:

$$\begin{aligned} |\psi_1(n)| & \leq 5 |\Omega(n, 1)^2 - \Omega(n, 2)^2|, \\ |\beta_2(n)| & \leq 3 |\Omega(n, 1)^2 - \Omega(n, 2)^2|, \\ |\bar{\beta}(1)| & < |\psi_1|, |\beta_2|. \end{aligned} \quad (59)$$

Therefore the modes are weakly coupled. It is a simple matter to transform Eqs. (58) to the form (16) by using ordinary two-state perturbation theory and using the approximations (59) to simplify the results. It is not necessary to carry out this process explicitly here. The results are given below.

The equations of motion are

$$\frac{d^2}{dt^2} a(n, 1) = -M_1(n, n-1)^2 a(n, 1) + [\bar{\beta}(1) + \langle \beta_2(n) h_2(n-1, 1) \rangle] \sum_{n'}^{(nn)} [a(n', 1) - a(n, 1)], \quad (60)$$

$$\frac{d^2}{dt^2} a(n, 2) = -M_2(n+1, n)^2 a(n, 2) + \langle \beta_2(n) h_1(n, 2) \rangle \sum_{n'}^{(nn)} [a(n', 2) - a(n, 2)], \quad (61)$$

where the a 's are the transformed normal coordinates which are linear combinations of the original q 's. We have

$$M_p(n, n-1)^2 = \frac{1}{2} [\phi_1(n)^2 + \phi_2(n-1)^2] + \frac{1}{2} (-)^p \{ [\phi_1(n)^2 - \phi_2(n-1)^2]^2 + 4\beta_2(n)^2 \}^{1/2}, \quad (62)$$

$$f_1(n, n-1, \rho) = \frac{1}{S_p(n, n-1)},$$

$$f_2(n, n-1, \rho) = \left(\frac{1}{S_p(n, n-1)} \right) \frac{\beta_2(n)}{\phi_2(n)^2 - M_p(n, n-1)^2}, \quad (63)$$

$$S_p(n, n-1) = \left\{ 1 + \left[\left(\frac{\beta_2(n)}{\phi_2(n)^2 - M_p(n, n-1)^2} \right)^2 \right] \right\}^{1/2},$$

$$W_p(n)^2 = \frac{1}{2} [\Omega(n, 1)^2 + \Omega(n, 2)^2] + \frac{1}{2} (-)^p \{ [\Omega(n, 1)^2 - \Omega(n, 2)^2]^2 + 4\psi_1(n)^2 \}^{1/2}, \quad (64)$$

$$h_1(n, \delta) = \frac{1}{N_6(n)} \left(\frac{\psi_1(n)}{\Omega(n, 1)^2 - W_6(n)^2} \right), \quad (65)$$

$$h_2(n, \delta) = \frac{1}{N_6(n)},$$

$$N_6(n) = \left[1 + \left(\frac{\psi_1(n)}{\Omega(n, 1)^2 - W_6(n)^2} \right)^2 \right]^{1/2}, \quad (66)$$

$$\phi_{6_0}(n)^2 = W_{6_0}(n)^2 - \beta_2(n)h_1(n, \delta_0)h_2(n-1, \delta_0) - \beta_2(n+1)h_1(n+1, \delta_0)h_2(n, \delta_0).$$

The polarizabilities $A(\vec{n}, \rho)$ of the ρ th mode ($\rho = 1, 2$) for the \vec{n} th unit are found from (20), using (60) and (61). One must expand in terms of the eigenfunctions (63) and use Eqs. (59). It is straightforward to show that

$$A(n, \rho) \cong \alpha(n, \rho) + \sum_{\mu} \alpha(n, \mu) f_{\mu}(n, n-1, \rho)(1 - \delta_{\mu, \rho}) + \sum_{\mu} \alpha(n, \mu) h_{\mu}(n, \rho)(1 - \delta_{\mu, \rho}), \quad (67)$$

where fluctuations in α and f from unit to unit have been ignored.

In the case that

$$\beta(n, 2 | n-1, 1) \neq 0,$$

$$\beta(n, 1 | n-1, 2) = 0,$$

$$\beta(n, 2 | n, 2) \neq 0,$$

$$\beta(n, 1 | n, 1) \neq 0,$$

there is an additional term

$$\bar{\beta}(2) \sum_{n'}^{(nn)} [a(n', 2) - a(n, 2)] \quad (68)$$

added to (61) while in all equations, $n-1$ ($n+1$) is replaced by $n+1$ ($n-1$). All this does is to put neighbors that were on the right-hand to the left-hand side and vice versa. Equation (67) can make a significant difference in mode intensities.

V. DISCUSSION OF RESULTS

Here the results of Secs. I–IV are summarized. Some of the implications of the theory for using Raman spectroscopy as an analytic tool for glass research are discussed.

Assume the structural units are the same on the average. Then the vibrational spectra of a network glass will be qualitatively similar to the spectrum of a corresponding crystal so long as (a) the basis states given by Eq. (4) are similar to the basis states of the corresponding crystal [which are solutions to Eqs. (3)]. (b) The inequalities (12) are very well satisfied, and the inequalities (14) are at least a fair approximation.

The points of similarity in glass and crystal spectra are (i) the peaks that are strong (weak) in the crystal spectrum are expected to be strong

(weak) in the glass spectrum. (ii) The widths of the peaks of the glass spectrum will be much smaller than the central frequencies of the peaks, so the peaks will be well defined.

This similarity will persist even though there may be considerable structural disorder in the glass. Thus the fact that the glass spectrum is similar to that of a crystal in no way implies that the glass is a polycrystal or even that it is highly ordered. It means merely that the disorder is a perturbation on the vibrations of some structural unit. The similarity of the spectra is quite striking for the binary alkali silicates as seen in Figs. 1 and 2. See also the results for chalcogenide glasses.⁴¹

If the inequalities (14) are satisfied, each mode can be treated independently. The width and scattering intensity of a particular mode depends on the ratio of the RMS deviation of the squared frequency Ω^2 to the average coupling constant $\bar{\beta}$. If this ratio is large the vibrations are localized and the Raman intensity is calculated from Eq. (21). The limit of validity of (21) is given by Eq. (26). If the ratio is less than unity, the most important optically active vibrations are cooperative and extend over many atoms. The Raman intensities are calculated from Eqs. (36) and (52). Equation (34) gives the contribution of fluctuating polarizabilities to the Raman intensities.

It is of interest that varying degrees of localization were observed by Bell *et al.* for the vibrations of their model of vitreous silica.⁴³

There are two quantities of the vibrational spectra which are subject to interpretation—the peak widths and their intensities. It is quite clear from the derived equations that the smaller the $\sigma(\mu)$ the smaller the peak widths. Moreover, from Eqs. (8)–(11) it may be concluded that σ will decrease with decreasing disorder of the lattice. Therefore it is concluded that *the greater the disorder of the lattice the greater the widths of the peaks.* This agrees with what one would intuitively expect and, as discussed in the Introduction, has been shown to be the case, experimentally, for the binary alkali silicates.

The above statement is not trivial in light of a possible alternate viewpoint that glass is a disordered crystal, so the peak widths result from a

breakdown of selection rules making all modes of the crystal optically active. (This point of view is tempting when the glass structural unit and the crystal unit cell are similar.) This statement implies that there is an upper bound to the peak widths given by the appropriate bandwidths of the corresponding crystal, so that the spectrum would reflect the density of states of the crystal. This is not the case with some oxide glasses, either experimentally or theoretically. For example, there is no *a priori* limit, apart from Eqs. (12), to the width of a Raman peak given by Eq. (21). Experimentally, Fig. 3 shows that the peak widths can become very large. On the other hand, a density-of-states treatment is likely to be valid for amorphous IV-IV and III-V semiconductors.³⁷⁻⁴¹

The polarizabilities of some modes of the glass may be different from the polarizabilities of respective modes of the corresponding crystal. This can come about in two ways.

(a) For the case of much disorder, the polarizabilities of the modes calculated from Eq. (4) may be different from those calculated by Eq. (3).

(b) The interaction of modes may change the polarizabilities as described by Eq. (67). In this case modes whose frequencies lie near strongly scattering modes may appear in glass spectra.

In neither of these cases is it particularly useful to think of the increase of polarizabilities as arising from a breakdown of selection rules because of the disorder. Rather the function of the disorder is to change the boundary conditions for the secular equation used to calculate the basis states so that (4) is used instead of (3). Physically, the nature of the average dynamic coupling between adjacent units is altered, so that the zeroth-order vibrations are different in glass and crystal. As shown in the calculation of Sec. VI, it is entirely possible that the new peaks in the glass spectrum will be relatively sharp, due to an extended nature.

One general conclusion that can be drawn is that *disorder may produce an increase of polarizabilities of modes which, in the absence of disorder, are very weak or unobservable*. Therefore the appearance of peaks in the glass spectrum, where none appears in the spectrum of the corresponding crystal, indicates glasslike disorder.

This principle can be of use in interpreting Raman spectra in practice. Consider, for example, some sample consisting mostly of crystal and a small amount of glass, such as might be found in a heat-treated aluminosilicate or in a moon rock. Suppose the spectrum of the pure crystal is composed of a few very large peaks and a number of small peaks. In the glass of the same composition as the crystal, the polarizabilities of some weak modes may be greater than for the crystal, while for the larger peaks the change is not so drastic.

Thus in the spectrum of the mixed sample some smaller peaks may appear to grow at the expense of the larger peaks, and some smaller peaks may even blur together, particularly at lower frequencies. This type of spectrum change indicates the presence of small amounts of glass in some apparently crystalline samples. This has been observed in albite by Sweet.⁶⁶

Perhaps the most important deduction of the theory is of the scale of disorder detectable by Raman spectroscopy. The Raman spectrum of a glass with sufficient disorder that $\bar{\beta}/4\sigma \ll 1$ is a linear superposition of the spectra of the various units [see Eq. (21)]. For extended modes the surface is of considerable importance and for these modes our conclusions are only qualitative. Suppose now that the glass consists of two regions of different structures, say, regions 1 and 2. The regions can both be amorphous (as would be the case for phase separation) or one region can be amorphous and one crystalline, and so forth. Let there be N_i units totally within the i th region. Then each of these N_i units will contribute a Raman spectrum characteristic of the i th region.

Let N_s be the number of units on the surface of the region, i. e., the number that are part in one region and part in another. These will presumably have a spectrum intermediate between the spectra of the two regions.

Now let $I_1(\omega)$ and $I_2(\omega)$ be the scattering intensities at frequency ω per unit, typical of the regions 1 and 2, respectively. If for a given frequency interval

$$N_i I_i(\omega) \gg \frac{1}{2} N_s [I_1(\omega) + I_2(\omega)], \quad (69)$$

then the Raman spectrum of the glass in that interval will be a superposition of the spectra of the two regions with a small contribution from the boundaries.

Suppose that at frequency ω one has

$$I_2(\omega) \ll I_1(\omega), \quad (70)$$

so only region 1 contributes strongly. Then it is sufficient that

$$N_s/N_i \lesssim 0.2, \quad i=1, 2 \quad (71)$$

so that Raman spectroscopy is expected to be sensitive to heterogeneities on the scale of five or more structural units. For silicates, this is about 20 Å and larger.

It is to be noted that the contribution to the Raman spectrum of the highly localized modes of even very small regions is expected to be the same as for large regions. Thus the sensitivity predicted here is qualitatively different from the detection of a distorted Raman spectrum of small particles due to surface effects.

VI. RAMAN SPECTRUM OF ALKALI METASILICATE

In this section we report a calculation of the Raman spectra of alkali metasilicate M_2O-SiO_2 crystal and glass. Crystals are easily obtained for $M=Li, Na,$ and K , while glasses can be obtained for $M=Na, K$.

The structures of Li and Na metasilicate crystals have been reported in the literature.^{67,68} There are one-dimensional silica chains, of composition $(Si_2O_6)_n$ parallel to the c axis. The silicons are approximately tetrahedrally coordinated by oxygens. These "tetrahedra" are joined at the vertices to form chains, so two oxygens of each tetrahedron are bonded to two silicons and are called bridging oxygens while the other two oxygens are bonded to only one silicon and are called nonbridging oxygens (NBO's). The angle between the two Si-NBO bonds is found to be greater than the tetrahedral angle.

The chains are held together by ionic NBO-alkali-NBO bonds, where in both Li and Na metasilicate the alkalis are approximately fourfold coordinated. Here we concern ourselves only with the silica chain. The NBO-alkali bonds are neglected. The rationale for this is that the alkali-NBO bonds are much weaker than the strong Si-O bonds. For example, the activation energy for alkali diffusion in silicate glasses of high alkali content is about 18 cal/mole, while that for migration of nonbridging oxygens is some 60 kcal/mole and for viscous flow in silica over 150 kcal/mole.¹ So for the higher-frequency vibrations (greater than 500 cm^{-1}) the motion of the atoms of an isolated chain is of paramount importance. This is discussed in more detail later on. We also study a somewhat idealized chain here in which all the silicons are tetrahedrally coordinated.

The unit cell for the idealized metasilicate chain is shown in Fig. 7. The angle γ is taken to be 133° , the value found in the crystal. All bridging oxygens lie in the $Z=0$ plane and the NBO's lie symmetrically on either side of this plane.

Frequencies are in units of

$$(1/2\pi)(k/m_0)^{1/2} = 730\text{ cm}^{-1},$$

where $k = 5 \times 10^5$ dyn/cm is the central Si-O stretching force constant and m_0 is the mass of the oxygen atom. The noncentral Si-O force constant is $0.17k$, as estimated by Saskena.^{53,54} The noncentral force constant has a small effect (less than 10%) on the frequencies and polarizabilities of interest. The force constant resisting deformation of the Si-O-Si angle is 10^4 dyn/cm,³⁷ and is neglected.

The optically active modes of the crystal are calculated for the unit cell of Fig. 7 from Eq. (3), which is the usual secular equation. The eigenstates are then used in Eq. (20) to calculate the polarizabilities of the modes.

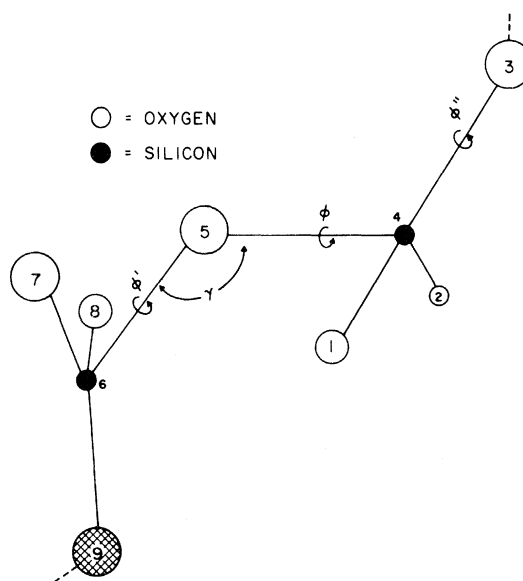


FIG. 7. Unit cell of idealized metasilicate chain. Shaded circles are Si, open circles are oxygen. Atoms 9 and 10 are in neighboring cells. Atoms 3-6 all lie in the x - y plane. Atoms 8 and 2 are above this plane, and atoms 2 and 7 are below it. Silicons are exactly tetrahedrally coordinated. Si-O-Si angle $\gamma = 133^\circ$.

To calculate the polarizabilities, a distinction was made between Si-bridging-oxygen bonds and Si-NBO bonds. Let $a(\mu)$ and $b(\mu)$ be the contributions to the polarizability, Eq. (20), of all Si-bridging-O and Si-NBO bonds, respectively. Then we write

$$\alpha(\mu) = b(\mu) + x a(\mu), \quad (72)$$

where, for the crystal, α does not depend on n . The parameter x gives the relative importance of Si-bridging-O to Si-NBO bonds.

It is found, on solving the secular equation, that

$$b(0.87) = 0.81, \quad a(0.87) = 1.2,$$

$$b(1.3) = -2.2, \quad a(1.3) = 1.2.$$

The calculated eigenfrequencies in reduced units are given in Table I, and the polarizabilities are given for $x=0.4$, the value appropriate for Na_2O-SiO_2 . Only the two modes with frequencies 0.87 and 1.3 have reasonably large values of $a(\mu)$ and $b(\mu)$, and these are consequently identified as the two strongest peaks in the crystal spectrum at 587 and 973 cm^{-1} , respectively.

The value of $x=0.4$ was calculated for Na metasilicate as follows. Let $\Gamma(\nu)$ be the measured peak width of the mode of frequency ν . For Na_2O-SiO_2

$$\Gamma(0.87) = 20\text{ cm}^{-1}, \quad \Gamma(1.3) = 10\text{ cm}^{-1}.$$

Then x is determined from the equation

TABLE I. Computed optically active modes of crystalline metasilicate chain.

Mode	Frequency (reduced units)	Frequency (cm ⁻¹)	Polarizability (arbitrary units)
1	0.278	202	0
2	0.316	231	0.54
3	0.332	246	0.001
4	0.412	305	0
5	0.412	305	0
6	0.436	322	0
7	0.476	346	0
8	0.482	352	0.07
9	0.504	368	0.09
10	0.583	425	0
11	0.609	444	0.35
12	0.633	462	0.005
13	0.657	480	0
14	0.855	620	1.4
15	1.12	810	0.0004
16	1.16	848	0.015
17	1.30	950	1.6
18	1.38	1000	0
19	1.38	1001	0
20	1.54	1120	0.006
21	1.60	1170	0.07

$$\frac{[b(0.87) + xa(0.87)]^2 / \Gamma(0.87)}{[b(1.3) + xa(1.3)]^2 / \Gamma(1.3)} = \frac{1}{3.5}, \quad (73)$$

where 1/3.5 is the observed ratio of the heights of the 587- and 973-cm⁻¹ peaks in the Na₂O-SiO₂ spectrum. For K₂O-SiO₂ it is found that $x=0.35$.

The calculated spectrum for $x=0.4$ is shown in Fig. 8 and is to be compared with Fig. 1. In Fig. 8 the two strong peaks are drawn as Lorentzians with the measured widths and calculated intensities. (The value of x was of course determined, so the calculated intensities equal the measured ones for these two peaks.) The calculated intensities of all other modes except two are then found to be smaller by a factor of at least 400 than the intensity of the 630-cm⁻¹ mode, and hence cannot be drawn on the scale of the figure. Their positions are shown as short vertical lines. The two small peaks at low frequencies were arbitrarily assumed to have widths of 15 cm⁻¹. They cannot be identified with any particular feature of the measured spectrum because the motion of the alkalis is not negligible in the low-frequency region.

The calculated frequencies of the two strong modes are 630 and 950 cm⁻¹, an error of about 3.5% from the measured values for Na metasilicate.

Thus the model used here gives reasonable agreement with experiment for the crystalline metasilicates and in particular is unambiguous as to mode assignments for the strong modes.

It is interesting to consider the change of frequencies of the optically active modes as a function of the Si-O-Si angle γ . Figure 9 shows the various optical frequencies as a function of γ for the higher-frequency modes. There is a very large change in the strong 600-cm⁻¹ mode and very little change in the frequency of the strong 950-cm⁻¹ mode. This is consistent with the results of Gaskell.⁴² Figure 9 also shows that it is a fair approximation to calculate the spectrum of alkali metasilicate from a unit cell in which $\gamma=180^\circ$, as was done elsewhere.

Consider now the metasilicate glass. The similarity of the crystal and glass spectra is a strong indication that the glass and crystal have the same basic structure. That is, the glass must be composed of silica chains in which the Si atoms are approximately tetrahedrally coordinated by oxygens and in which there are two NBO's per tetrahedron. This model is assumed here, and the remainder of this section gives the results of calculations of the effect of different types of disorder on the Raman spectrum. The only parameters entering into the calculation are structural. The force constants and polarizabilities are the ones determined from the crystal spectrum, as described above.

The structural units of the glass are the same Si₂O₆ units which comprised the unit cells of the crystal. For all units let there now be completely free rotation of tetrahedra about Si-bridging-O bonds. In terms of Fig. 7 the angles ϕ , ϕ' , ϕ'' , ... are completely random. For now, the Si-O-Si angles are taken to be constant at 133° throughout the chain.

Since considerable disorder is introduced in the chain, the basis states are calculated from Eq. (4). The details are given in the Appendix. The polarizabilities are calculated from the basis states using Eq. (20). The averages and RMS deviations of the quantities in Eqs. (8)-(11) are given in the Ap-

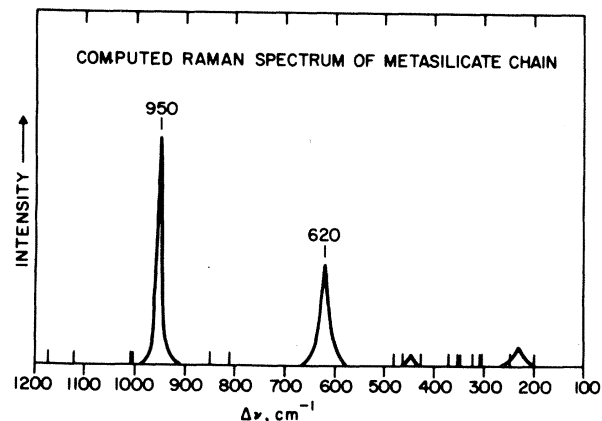


FIG. 8. Calculated Raman spectrum of crystalline metasilicate chain.

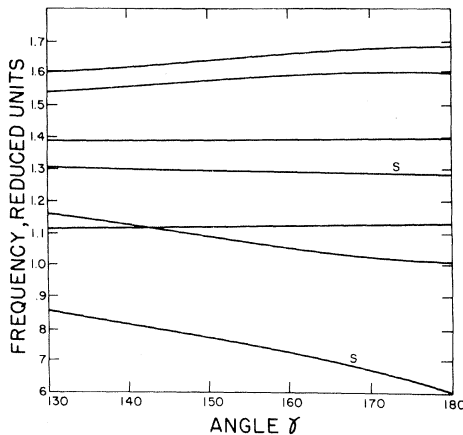


FIG. 9. Variation of the high-frequency modes of the crystalline metasilicate chain with Si-O-Si angle γ . Frequencies are in reduced units. Modes marked S give the two strong peaks of the Raman spectrum.

pendix. Only the nine modes of highest frequency are considered, and these are labeled 1-9.

As seen in the Appendix, the inequalities (12) are very well satisfied for these modes, and Eqs. (14) are approximately satisfied for modes 4-9 inclusive. For all modes the RMS deviation of $E(n, \mu)$ is extremely small, so the variation of $\Omega(n, \mu)^2$ is determined principally by the $\psi(n, \mu, \mu)$ term in Eq. (11).

There is a clear correspondence between modes 4-9 and the six highest-frequency modes of the crystal as given in Table I.

The mode of frequency 1.3 (mode 5) is still the strongest, so it will dominate the glass spectrum as it does the crystal spectrum.

The polarizabilities of modes 4 and 8 are more than a factor of 10 greater for the glass than for the crystal (see Table I). Their Raman intensities are therefore increased by a factor of more than 100. As seen in Fig. 1, $\text{Na}_2\text{O-SiO}_2$ glass has a shoulder at 1050 cm^{-1} and a peak at 850 cm^{-1} , and these features are consequently associated with modes 8 and 4, respectively. The increase in polarizability is a significant prediction of the theory, and physically it may be attributed to a change in the nature of the zeroth-order basis states because of the disorder, as discussed in Sec. V.

Modes 1-3 are so strongly coupled as to change their identities completely from those given by the eigenstates of Eq. (4). These modes blend together to form a strong broad feature in the glass spectrum around 600 cm^{-1} .

Modes 6, 7, and 9 have negligible polarizabilities. Their interactions with nearby modes are small, and so these modes make a negligible contribution to the Raman spectrum of either crystal

or glass.

The Raman spectrum of the model then seems qualitatively similar to the measured spectrum of the glass, but, as will be seen, there are considerable differences as well.

To take account of the coupling of the modes, Eqs. (58) are solved for the pairs of modes (5, 8), (3, 4), and (4, 5). The approximations of Sec. IV are appropriate for these modes. The RMS deviations of $\Omega(n, \mu)^2$ are altered by less than 0.01 due to the interaction of modes. The values of the coupling constants $\bar{\beta}$ and polarizabilities $\bar{\alpha}$, as calculated from (60), (61), and (67), are changed significantly for some cases. The final result of this calculation is that the modes 4, 5, and 8 are described by Eq. (16) using the values

$$\begin{aligned} \sigma(4) &= 0.065, & \bar{\beta}(4) &= 0.042, & \bar{\alpha}(4) &= 0.28, \\ \sigma(5) &= 0.015, & \bar{\beta}(5) &= 0.006, & \bar{\alpha}(5) &= 1.5, \\ \sigma(8) &= 0.1, & \bar{\beta}(8) &= 0.001, & \bar{\alpha}(8) &= 0.25. \end{aligned} \quad (74)$$

Equation (28) applies to modes 5 and 8, so the Raman intensities are calculated from Eq. (20). On the other hand, $\sigma(4) \sim \bar{\beta}(4)$, so that the Raman intensities of mode 4 are calculated from Eqs. (36) and (52). The vibrations of modes 5 and 8 are localized, while the optically active vibrations of mode 4 are extended.

The result of this calculation is shown in Fig. 10. The Raman spectrum of a metasilicate chain in the harmonic approximation used here, disordered so that γ is constant but the angles $\phi, \phi', \phi'', \dots$ are random, has the following characteristics: a very weak and broad peak at 1100 cm^{-1} , two very sharp peaks (widths less than 5 cm^{-1}) at 950 and 875 cm^{-1} , and a broad feature around 600 cm^{-1} shown by the dotted line. This dotted line is a crude estimate of the contributions of modes 1 and 2. Therefore, while the disorder is sufficient to increase the polarizability of modes 4 and 8, it does not widen the

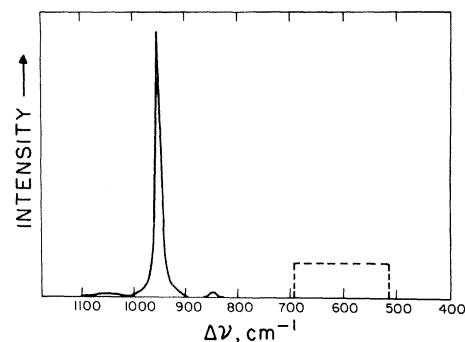


FIG. 10. Computed Raman spectrum of metasilicate chain disordered so that the angles $\phi, \phi', \phi'', \dots$ are random but the SiO_4 tetrahedra are not distorted.

peak of mode 5.

Suppose now that γ varies in addition to the randomness of the angles $\phi, \phi', \phi'', \dots$. It is found that if $\gamma = 150^\circ \pm 20^\circ$ the RMS deviations of $\Omega(n, \mu)^2$ for modes $\mu = 4, 5$ are altered less than 0.01 from the values given previously. A calculation using the basis states of the crystal with $\gamma = 133^\circ$ shows that the matrix elements $\psi(n, \mu, \mu')$ are not significantly altered from the results of the Appendix by the additional variation in γ . No study was made of the variation of polarizabilities.

The small effect of so much disorder on mode 5 is contrary to what might be intuitively expected. A similar result was found by Gaskell.⁴¹ The fluctuations in ψ are due to a fluctuating coupling between atom 3 of one unit and atom 6 of a neighbor (see Fig. 7). For mode 5 it turns out that the displacements of atoms 3 are small and therefore so is the variation in Ω^2 .

In the glass, the NBO's are joined to alkalis by force constants which presumably fluctuate from one NBO to another.⁵⁸⁻⁶⁰ This can widen the peaks as well. It is now shown that this effect is small.

The vibration frequency of Na in silicate glasses is about 300 cm^{-1} , while the frequency of K is less.⁶⁹ Then assuming one alkali bonded to one NBO, the NBO-Na force constant is

$$\bar{k} \sim \left(\frac{300}{750}\right)^2$$

on the average. Assume the distribution of NBO-alkali force constants is Gaussian with $1/e$ value of $\frac{1}{2}\bar{k}$. Then

$$\langle k^2 - \bar{k}^2 \rangle \sim \frac{1}{8}\bar{k}^2.$$

If u is the average displacement of an NBO, $u \sim 0.3$, the net RMS fluctuation due to the four NBO-alkali bonds is

$$(1/\sqrt{2})\bar{k}u^2 \sim 0.01,$$

where a factor of 2 enters because the four bonds are independent. This variation is a very small amount.

Clearly the only way to widen mode 5 is to distort the units in some other way—in particular, the disorder must include a distortion of the tetrahedra themselves. The tetrahedra may be distorted by rotating Si-NBO bonds (keeping the Si atoms fixed) through an angle $\Delta\theta$. Such a rotation adds an additional term $\Delta\psi(n, \mu, \mu')$ to $\psi(n, \mu, \mu')$. Assuming that $\Delta\theta$ is Gaussian distributed, the probability distribution of $\Delta\psi$ for $\mu = \mu'$ is

$$P(\Delta\psi) = \frac{1}{2KE(\mu)\sqrt{\pi}} e^{-\Delta\psi^2/4K^2E(\mu)^2}, \quad (75)$$

where

$$E(4) = 0.2, \quad E(5) = 0.3,$$

$$E(8) = 0.1, \quad K = \frac{1}{6},$$

where

$$\langle \Delta\theta^2 \rangle = \frac{1}{2}K^2.$$

Here the RMS deviation is 7° . The small distortion of the tetrahedra leads to a half-width for the 950-cm^{-1} peak of 50 cm^{-1} , the experimentally observed width. For all modes 1-9 (apart from 6 and 7) E is between 0.1 and 0.3.

Combining the widening due to Eq. (75) with that due to a randomness of $\phi, \phi', \phi'', \dots$, but γ fixed at 133° , the modes 4, 5, and 8 are described by Eq. (16), where now

$$\sigma(4) = 0.073, \quad \sigma(5) = 0.07, \quad \sigma(8) = 0.1.$$

The values of $\bar{\beta}$ are given in (74). The small distortion of the tetrahedra has a negligible effect on the polarizabilities.

Therefore $\sigma(5) \gg \bar{\beta}(5)$ and $\sigma(8) \gg \bar{\beta}(8)$, so the Raman scattering from modes 5 and 8 is calculated from Eq. (21), while $\sigma(4) \sim \bar{\beta}(4)$ and the Raman intensity of mode 4 is calculated from Eq. (36).

The lattice vibrations for modes 5 and 8 are highly localized, while those of mode 4 are extended.

The total Raman spectrum for the high-frequency region is given by the sum of the contributions of the 3 modes $I_\mu(\nu)$ in reduced units

$$I_4(\nu) = \frac{0.08}{\pi} \frac{0.018}{(\nu - 1.19)^2 + (0.018)^2},$$

$$I_5(\nu) = \frac{54.25}{\sqrt{\pi}} e^{-(\nu - 1.3/0.04)^2}.$$

I_8 was calculated directly from Eq. (21) and no explicit functional form was determined.

The spectrum is shown in Fig. 11. It is quite similar to the spectrum of Na metasilicate. The conclusions about the structure of Na and K metasilicates to be drawn from these calculations are discussed in Sec. VII.

VII. CONCLUSIONS

Several aspects of the calculation of Sec. VI are now discussed. A model of atoms interacting with nearest-neighbor harmonic forces adequately describes the metasilicate chain. The similarity between the computed spectrum and the measured ones for crystalline Na and K metasilicates is striking.

As has been pointed out, the essential similarity of the glass and crystal spectra argues for a basic similarity of structure in that the glass is composed of chains of approximate tetrahedra linked at the vertices. It is found that distorting the tetrahedra has a large effect on the spectrum. If the tetrahedra were too distorted, the crystal and glass spectra would be more dissimilar, and this is evidence for a similarity of structures.

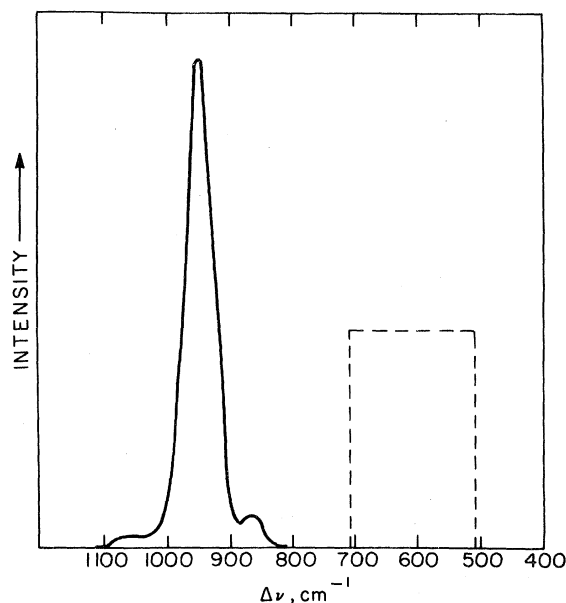


FIG. 11. Computed Raman spectrum of metasilicate chain disordered so that the angles ϕ , ϕ' , ϕ'' , ... are random and the SiO_4 tetrahedra are distorted.

The distortion of SiO_4 tetrahedra is not unreasonable. In very few alkali-silicate structures are there perfect tetrahedra, but rather distortion is the rule rather than the exception.^{67,68,70} Only in pure SiO_2 do there seem to be perfect SiO_4 tetrahedra.

The calculations reported in the Appendix show that the inequalities (12) are well satisfied. Therefore for purposes of calculating the Raman spectrum it is a useful point of view to consider the unit as the elementary vibrating quantity.

The mechanisms by which the disorder alters the Raman spectrum are

(a) The polarizabilities of modes 4 and 8 are increased, because the basis states are calculated from Eqs. (4) instead of (3). The mixing with modes 5 and 3 also affects the polarizabilities. It is seen that the presence of an extra peak in the glass spectrum indicates considerable disorder.

(b) Modes 1-3 and 8 are widened considerably by disordering a chain of tetrahedra, leaving the tetrahedra themselves undistorted.

(c) The width of the strong 950-cm^{-1} peak is increased *only* when the tetrahedra themselves are distorted.

(d) The NBO-alkali bonds have a small effect on the peak widths.

(e) The less the disorder the smaller the widths of the Raman peaks.

There is reasonable agreement between the calculated spectrum and the measured one of Na meta-

silicate glass. For the calculated spectrum the intensities of modes 4 and 8 are two orders of magnitude greater for the glass than for the corresponding crystal. Therefore increases in polarizabilities, and hence the appearance of extra peaks in the glass spectrum, are a natural result of the calculation. It is proposed that modes 4 and 8 correspond, respectively, to the 855-cm^{-1} peak and the 1050-cm^{-1} shoulder observed in the spectrum of Na metasilicate glass. Further, mode 3 appears at 730 cm^{-1} , where there is a small peak in the measured spectrum.

For the case of Na metasilicate the calculations show that not only is there rotational disorder (angles ϕ , ϕ' , ϕ'' , ... random) but distortion of the tetrahedra. Actually, there must also be a distribution of Si-O-Si angles. The free-energy change for distortion of the tetrahedra is certainly far greater than for variation of the Si-O-Si angles. This can be seen from the force constants. The Si-O noncentral force constant is 0.85×10^5 dyn/cm, while the force constant resisting bending of the Si-O-Si angle is about 10^4 dyn/cm,⁷¹ a factor of 8 smaller. Therefore it is easier to distort Si-O-Si angles, than tetrahedra. Although no force constants are available, it is probably easier to rotate tetrahedra about Si-bridging-O bonds than to distort them. Consequently, the various types of disorder should occur simultaneously.

Another type of disordering which was not considered is the fluctuation of Si-O force constants, which were presumed constant in the glass and which could accompany structural disorder. Moreover, the effect of Coulomb forces was not considered. These omissions make the calculations presented here only qualitative. However, all the qualitative ideas expressed here, which are consistent with the calculation of Sec. VI, are expected to carry through, unaltered, to the case of more detailed calculation. The reason for this is that even in the general case Eqs. (14) should still be a good first approximation.

The differences between the K and Na metasilicate glass spectra may be attributed to a difference in the short-range order of the silica chains in the two glasses. This is in agreement with the results of the Raman spectra of other silicates (see Figs. 1-3) which show that, in general, the K silicate glasses are more ordered glasses than the Na silicate glasses.

The presence in the K metasilicate glass spectrum of fairly sharp peaks of small intensity, as well as of a relatively narrow peak at 600 cm^{-1} , argues for much less fluctuation of the angles ϕ , ϕ' , ϕ'' , ... than in Na metasilicate. The smallness of the 850-cm^{-1} peak is also consistent with this, since the intensities of the smaller peaks should decrease with decreasing disorder. More-

TABLE II. Various quantities which appear in the equations of motion of the metasilicate chain, disordered so that the angles ϕ , ϕ' , ϕ'' , ... are random but the tetrahedra are not distorted.

(μ, μ')	$\bar{\beta}_2(\mu, \mu')$	$\Delta\beta_2$	$\bar{\beta}_1(\mu, \mu')$	$\Delta\beta_1$	$\bar{\psi}_1(\mu, \mu')$	$\Delta\psi_1$	$\bar{E}(n, \mu)$	ΔE	$\alpha(n, \mu)$	$\Delta\alpha$
(1, 1)	0.025	0.036	0.025	0.036	0	0.02	0.78	0.02	+0.98	0.04
(1, 2)	-0.03	0.18	0.02	0.02	0.02	0.03				
(2, 2)	-0.01	0.078	-0.01	0.078	0.07	0.15	0.87	0.002	-0.83	0.1
(2, 3)	0.02	0.02	0.03	0.14	0.15	0.08				
(3, 3)	-0.054	0.056	-0.054	0.056	0.12	0.07	1.04	0.015	+0.65	0.06
(3, 4)	0.035	0.04	-0.07	0.075	-0.08	0.045				
(4, 4)	0.051	0.043	0.051	0.043	0.04	0.025	1.21	0.006	+0.13	0.09
(4, 5)	-0.02	0.025	0.035	0.03	-0.025	0.015				
(5, 5)	0.011	0.011	0.011	0.011	0.015	0.011	1.25	0.008	+1.5	0.02
(5, 6)	0	0	0	0	0	0				
(6, 6)	0	0	0	0	0	0	1.38	0.005	0.02	0.01
(6, 7)	0	0	0	0	0	0				
(7, 7)	0	0	0	0	0	0	1.38	0.004	0.01	0.01
(7, 8)	0	0	0	0	0	0				
(8, 8)	0.0017	0.0038	0.0017	0.0038	0.15	0.1	1.48	0.006	0.39	0.009
(8, 9)	0	0	0.02	0.01	-0.05	0.03				
(9, 9)	0.003	0.005	0.003	0.005	0.014	0.016	1.57	0.005	0.06	0.04

over, the narrowness of the 950-cm⁻¹ peak indicates a smaller distortion of the tetrahedra than in Na metasilicate. On the other hand, the large peak at 1050 cm⁻¹ in the glass is surprising. Therefore, the features of the spectrum are generally consistent with K metasilicate being more ordered than Na metasilicate. Moreover, the absence of any appreciable amount of crystallinity in K metasilicate glass may be inferred from the absence of a sharp spike sticking out of the 975-cm⁻¹ peak. Probably in this glass the silica chains are sufficiently disordered so as not to lie parallel in crystalline configuration. The different equilibrium positions of the alkalis then lead to a slight distortion of the tetrahedra.

ACKNOWLEDGMENT

The author gratefully acknowledges many invaluable discussions with Professor W. B. White.

APPENDIX

Here the numerical values of various quantities appearing in Eqs. (8)–(11) are given for the metasilicate chain. The average and RMS variations were calculated for both ϕ and ϕ' , varying in steps of 30°. The matrix $v^{(0)}$ varies with ϕ and ϕ' , but for each ϕ and ϕ' , the bond joining angles 8 and 10

was chosen to lie in the 3-4-5 plane. The variation of the angle ϕ'' was incorporated into $\Delta V_{\alpha\beta}$. It turns out that for the high-frequency modes the central force constant is of overriding importance. Since the component of $\vec{u}(6)$ along the 6-9 bond varied by less than 10% for all ϕ and ϕ' , this variation was neglected in comparison with the other variations.

We use the abbreviations

$$\bar{\beta}_2(\mu, \mu') = \langle \beta(n, \mu | n-1, \mu') \rangle,$$

$$\bar{\beta}_1(\mu, \mu') = \langle \beta(n, \mu | n+1, \mu') \rangle.$$

Therefore

$$\bar{\beta}_2(\mu, \mu') = \bar{\beta}_1(\mu', \mu),$$

and similarly for the RMS deviations, so it is necessary to give only $\bar{\beta}_2$. Also we define

$$\psi_1(n, \mu, \mu') = \psi(n, \mu, \mu') - \sum_{\mu''}^{(nn)} \beta(n, \mu | n', \mu''),$$

$$\psi_1(n, \mu, \mu') = \psi_1(n, \mu', \mu).$$

For any A , let

$$\Delta A \equiv \langle (A^2 - \bar{A}^2) \rangle^{1/2}.$$

The results are tabulated in Table II.

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