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Vibrational dynamics in ^{18}O-substituted vitreous SiO_2

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We report the polarized Raman spectra of vitreous $Si^{18}O_2$ prepared by steam oxidation of Si in $H_2{}^{18}O$. This yields the $^{16}O \rightarrow {}^{18}O$ isotope shifts for all Raman- and nearly all infrared-active modes. The shifts of network vibrations agree very well with the predictions of a recently introduced nearest-neighbor central-force ideal continuous-random-network model, and thus confirm the utility of that simple model. The unexplained Raman-active "defect" lines reported at 495 and 606 cm^{-1} in ordinary fused silica are shown to involve little or no silicon motion.

INTRODUCTION

Bulk vitreous silica (v-SiO_2) is perhaps the most studied of all network glasses, yet its properties are by no means well understood.[1-3] Although the continuous-random-network model for v-SiO_2 involving corner-sharing SiO_4 tetrahedra was proposed by Zachariasen[4] in 1932, the details of the structure of v-SiO_2 are not yet agreed upon,[5-7] and techniques for elucidating the structure are still evolving. One area of evolution is in the development of theoretical methods for deducing glass structure from vibrational spectra.[8-13]

In experimental tests of models of molecular structure, vibrational spectroscopists have often used the method of isotopic substitution, in which one atomic species is replaced by an isotope of different mass. This creates a new material whose geometrical structure and interatomic forces are identical with those of the original. The observed changes in vibrational spectra must then be accounted for only by the known change in mass of the specific atomic species, else the structure or force model is clearly inadequate. We have carried out this procedure for v-SiO_2 for the first time by measuring the polarized Raman spectra of samples in which we have substituted heavy oxygen (^{18}O) for the lighter ^{16}O that occurs almost exclusively in normal material. The vibrational frequencies that we report are useful for testing present and future models of the structure and interatomic forces in v-SiO_2, as we shall illustrate.

Our v-$Si^{18}O_2$ samples were free-standing *films* about 10 μm thick, prepared by steam thermal oxidation of Si for 14 days at 900 °C in 10 atm of $H_2{}^{18}O$.[14] The preparation procedures are as described by Mikkelsen and Galeener,[15] except for the use of $H_2{}^{18}O$ in place of ordinary water. (It is notable that although the oxidation was carried out using $H_2{}^{18}O$ in a sealed ordinary silica ampoule, the spectra show no evidence for incorporation of ^{16}O from the ampoule into the growing film.) Raman spectra were obtained by focusing 514.5-nm Ar^+-ion laser radiation into one edge of the film, and collecting the scattered light in the 90° scattering configuration, illustrated schematically in Fig. 1. Excellent signal-to-noise ratios (up to 1000) were achieved. Details of the Raman spectroscopic procedures (to be associated with Fig. 1) are given by Galeener and Mikkelsen,[16] who have demonstrated that the Raman spectra of steam thermal oxide made with $H_2{}^{16}O$ are identical to those of bulk melt-quenched v-$Si^{16}O_2$ (apart from increased line strength at 970 and 3695 cm^{-1} caused by increased OH content in the thermal oxide). On this basis, we take the Raman spectra to be presented in this paper as equivalent to those that would be obtained from melt-quenched bulk v-$Si^{18}O_2$, were it available.[17]

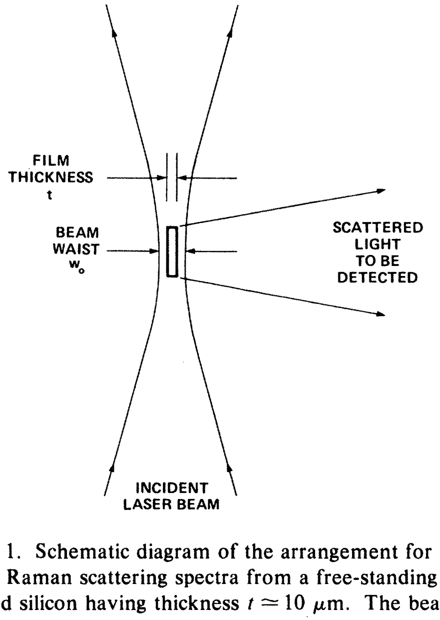

FIG. 1. Schematic diagram of the arrangement for obtaining 90° Raman scattering spectra from a free-standing *film* of oxidized silicon having thickness $t \simeq 10$ μm. The beam is focused to a spot diameter $w_0 = 10-15$ μm.

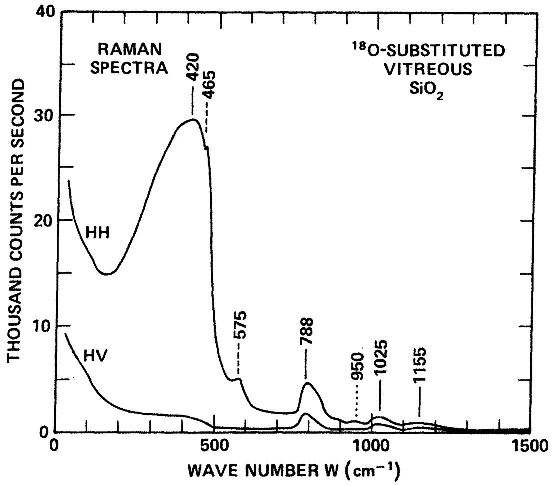

FIG. 2. The polarized Raman spectra of a thick film of v-$Si^{18}O_2$ produced by steam thermal oxidation of Si, using $H_2{}^{18}O$.

OBSERVATIONS

The polarized Raman spectra of $Si^{18}O_2$ from 30 to 1500 cm^{-1} are shown in Fig. 2. They are qualitatively similar to spectra reported for v-$Si^{16}O_2$ (cf. Refs. 11 and 18), but differ quantitatively in the *frequencies* of the features marked by vertical lines. For brevity, spectra obtained from 1500 to 4500 cm^{-1} are not shown. The omitted spectra reveal an ^{18}O-H vibrational line with peak strength of 500 counts per second at 3680 cm^{-1}, having the same linewidth and polarization properties as the ^{16}O-H line seen in normal steam oxide[15] at 3695 cm^{-1}. These spectra also exhibit second-order (2-phonon) features between 1500 and 2400 cm^{-1} that have the same relation to first-order lines as has already been reported[19] for normal v-$SiO^{16}O_2$. The spectra from 1500 to 4500 cm^{-1} display no features indicating the presence of Si-H bonds, free water, or impurities other than OH, and except for isotopic shifts are very similar to those reported elsewhere[18] for v-$Si^{16}O_2$. Infrared (ir) spectra are not presented because they are complicated by thin-film interference phenomena, and because all but one of the principal first-order ir lines are also seen in the Raman spectra.

ANALYSIS

We shall discuss the first-order features with the aid of Table I, in which the lines are grouped into three categories according to their physical origin: network, defect, or OH impurity content. The network peaks are labeled ω_i in Table I, as defined in Ref. 11, where their origin in motions of the basic network is demonstrated and explained. They are marked by *solid* vertical lines in Fig. 2. The defect lines are marked by *dashed* vertical lines in Fig. 2, and are labeled D_1 and D_2 in Table I. They were first ascribed to network defects by Stolen, Krause, and Kurkjian[7] in 1970; the precise nature of these "defects," whether due to broken bonds, microcrystals, etc., is the subject of much inquiry,[20–26] on which the present study sheds new light. (We note without ex-

TABLE I. Comparison of observed positions (cm^{-1}) of first-order Raman spectral features in vitreous $Si^{18}O_2$ with those in vitreous $Si^{16}O_2$. Also shown are values calculated using the nearest-neighbor central-force ideal continuous-random-network dynamical model developed in Ref. 11. Values in parentheses ( ) are estimated differently, as explained in the text. *Comparison of columns (c) and (d) shows that the network isotope shifts are predicted remarkably well by the central-force model.*

		Observations			Calculations		
Label	Origin of feature	(a) $Si^{18}O_2$	(b) $Si^{16}O_2$	(c) $\Delta = (a) - (b)$	(d) $\Delta = (e) - (f)$	(e) $Si^{18}O_2$	(f) $Si^{16}O_2$
ω_1	Network	420	450	−30	−26	424	450
ω_3	Network	788	800	−12	−14	786	800
ω_4 (TO)	Network	1025	1065	−40	−40	(1001)	(1041)
ω_4 (LO)	Network	1155	1200	−45	−45	1131	1176
D_1	Defect	465	495	−30	. . .	. . .	. . .
D_2	Defect	575	606	−31	. . .	. . .	. . .
w_1	Si−(OH)	950	970	−20	(−32)	. . .	. . .
w_2	O−H	3680	3695	−15	(−13)	. . .	. . .

planation that D_1 *appears* to be weaker in v-Si^{18}O$_2$ than in v-Si^{16}O$_2$). The lines caused by incorporation of "water" are labeled w_1 and w_2, and are due to essentially Si-(OH) and O-H motions, respectively, as discussed in Refs. 18 and 21; w_1 is marked by the *dotted* vertical line in Fig. 2, and w_2 is off scale to the right.

The observed positions of all first-order lines for Si^{18}O$_2$ are listed in column (a) of Table I, while those for v-Si^{16}O$_2$ prepared under the same conditions are given in column (b). (The latter are the same as reported in Ref. 11.) The observed shift Δ induced by substitution of ^{18}O for ^{16}O is given in column (c).

In the first four rows of column (d), we present the isotope shifts calculated using the nearest-neighbor central-force ideal continuous-random-network (NN-CF-ICRN) model developed in Ref. 11. They are in remarkable agreement with the observations in column (c), and thus tend to support the structure, force-constant approximation, and symmetry assignments used in the NN-CF-ICRN model. In particular, strong support is added to the assertion that ω_1 represents symmetric stretch (SS) motion of the bridging oxygen atoms, *with the Si atoms virtually at rest.* (For SS motion in the ideal network structure, each oxygen atom moves along the bisector of the bridging oxygen angle $\theta=\angle$Si-O-Si, in phase with all other oxygen atoms.)

The theoretical network isotope shifts (d) were calculated as follows. The ω_i in column (b) were used as in Table III of Ref. 11 to deduce NN-CF-ICRN parameters for v-Si^{16}O$_2$, with the results that $\theta=130°$ and the central force constant $\alpha=545$ N/m. Using these parameters and the following equations

$$\omega_1^2=(\alpha/M_{\rm Ox})(1+\cos\theta)\ , \tag{1}$$

$$\omega_3^2=(\alpha/M_{\rm Ox})(1+\cos\theta)+(4\alpha/3M_{\rm Si})\ , \tag{2}$$

$$\omega_4^2({\rm LO})=(\alpha/M_{\rm Ox})(1-\cos\theta)+(4\alpha/3M_{\rm Si})\ , \tag{3}$$

with $M_{\rm Ox}=16$ and $M_{\rm Si}=28$ as the atomic masses of oxygen and silicon, one calculates three of the theoretical frequencies in column (f). The fourth frequency (in parentheses) is estimated as $\omega_4({\rm TO})=\omega_4({\rm LO})-135$ cm^{-1}, since 135 cm^{-1} is the TO-LO splitting observed[27] in v-Si^{16}O$_2$. The predicted frequencies for Si^{18}O$_2$ are obtained using Eqs. (1)–(3) and the same parameters, except for substituting 18 as the atomic mass of oxygen. The results are listed in column (e), using $\omega_4({\rm TO})=\omega_4({\rm LO})-130$ cm^{-1} (since the observed TO-LO splitting in Si^{18}O$_2$ is 130 cm^{-1}). The differences between columns (e) and (f) are then taken as the theoretically predicted isotope shifts, entered in column (d).

Since the precise structures responsible for the defect lines D_1 and D_2 are not known, we cannot *derive* theoretical values for the isotope shifts. Nevertheless, it is notable that the shift of each line is the same as that of ω_1, SS stretch motion of bridging oxygen atoms in the network. One *cannot* conclude from this that the defect lines also are due to SS motion of bridging oxygen atoms (in the defect structures) although this is a hypothesis we are considering. The same shift would be incurred for any vibration involving little Si motion. In any such case, the oxygen frequency will be given by an equation of the form $\omega^2=C/M_{\rm Ox}$, where C represents unspecified quantities that are not changed by the ^{18}O substitution. This equation has the same form as Eq. (1), for example, and leads to prediction of precisely the same isotope shifts as does Eq. (1), namely, $\Delta=\omega'-\omega\simeq\omega(M_{\rm Ox}-M_{\rm Ox}')/2M_{\rm Ox}'$, where primes indicate the quantities after isotopic substitution. Specific examples might be the dangling oxygen atoms assumed in the nonbridging oxygen defect model considered by several authors,[7,20,21,24] or the three-bonded oxygen defect suggested by Lucovsky[24] [see, e.g., Eqs. (15) and (19) in Ref. 24]. We conclude that the isotope shifts of D_1 and D_2 are consistent with vibrations in which there is mainly oxygen motion, and little silicon motion; *they are inconsistent with the absence of oxygen motion.*

Isotope shifts for the lines associated with OH content (w_1 and w_2) are estimated as follows, and listed in column (d) in parentheses. Since ω_2 occurs at frequencies much higher than other vibrations in the glass, the motion of H against O can be treated approximately as decoupled from the rest of the system. This means that $\omega_2^2\simeq C/\mu$ where $\mu=(M_{\rm Ox}^{-1}+M_{\rm H}^{-1})^{-1}$ is the reduced mass of the O-H system. It follows that $(w_2'/w_2)^2=\mu/\mu'$, and one predicts $\Delta=-13$ cm^{-1}, as given in column (d). This is in good agreement with the observation that $\Delta=-15$ cm^{-1}, and tends to verify use of the simple dynamical formula employed here. It is also in reasonable agreement with the 10- and 12-cm^{-1} shifts reported[28] for the high-frequency modes of ^{18}O substituted H$_2$O. Since w_1 occurs in the midst of the network frequencies, it is unlikely that the motion (described approximately as movement of the OH unit against the Si atom) is effectively decoupled from the rest of the network. If one nevertheless assumes decoupling and uses $\mu=(M_{\rm OH}^{-1}+M_{\rm Si}^{-1})^{-1}$, one finds that $\Delta\simeq-32$ cm^{-1}, the value listed in column (d) of Table I. The 50% excess of this estimate over the observed value of -20 cm^{-1} is taken as evidence for appreciable involvement of other atoms in the w_1 motion, particularly the three oxygen atoms which bridge the $\equiv$Si$-$(OH) system to the rest of the network.[29]

CONCLUDING COMMENTS

The shifts in vibrational frequencies of v-SiO$_2$ upon substitution of ^{18}O for ^{16}O have been successfully measured and interpreted quantitatively. The results illustrate the utility of using Raman studies of various forms of the steam thermal oxide of Si to provide new information about the vibrational dynamics and structure of v-SiO$_2$, and they encourage application of the Raman[16] and sample preparation[15] techniques to other substances. It is important that only very small quantities of isotopes are needed. The successful prediction of isotope shifts for lines associated with the basic network structure adds support for use of the central-force network dynamics model.[10–13] The ease with which that model is applied illustrates its present utility, and provides impetus for further attempts to generalize the model, and improve its accuracy by including noncentral forces.[30] The isotope shifts of the Raman-active defect lines normally seen at 495 and 606 cm^{-1} strongly suggest that these vibrations consist primarily of oxygen motion in the defect structures. All of the observed shifts provide an isostructural test of present and future (refined) structural and dynamical models. The abundance of valuable information provided by this Raman study suggests that an attempt be made to produce and study v-SiO$_2$ in which ^{28}Si has been replaced by, e.g., ^{30}Si. This would be particularly valuable for ascertaining the limited extent of Si motion involved in ω_1, D_1, and D_2.

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