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Detection of LO modes in glass by infrared reflection spectroscopy at oblique incidence

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The occurrence of longitudinal-transverse splittings in the optic-vibrational-mode frequencies of partially ionic glasses has previously been observed in several glass systems and was also theoretically confirmed. The transverse-optic (TO) and longitudinal-optic (LO) components are usually derived from near-normal infrared-specular-reflectivity spectra by Kramers-Kronig analysis, and the TO frequencies often coincide with minima in the transmission spectrum. The approximate positions of the high-frequency LO modes of vitreous silica (v-SiO$_2$) and two more ionic modified fluoride glasses based on ZrF$_4$ (ZBLA glass) and ZnF$_2$-CdF$_2$ (ZnCd glass) have been directly obtained from infrared-external-specular-reflectivity spectra at oblique incidence. Fourier-transform infrared reflectivity spectra were recorded at incidence angles between 10° and 70° off normal, and the results are compared with Kramers-Kronig analysis of the near-normal (10°) incidence data and polarized Raman spectra of the same glasses. The reflection spectra at $\gtrsim 50°$ off normal contained peaks corresponding very approximately to the LO vibrational modes, while the peaks in the Raman spectra did not generally coincide with either TO or LO frequencies of the glasses. The high-frequency LO modes were experimentally observed at 1286, ~607, and 617 cm^{-1}, for v-SiO$_2$, ZBLA, and ZnCd glasses, respectively, compared to Kramers-Kronig values calculated at 1266, 625, and ~623 cm^{-1}, respectively. Ionicity was found to be an important factor in determining the extent of LO-TO splittings. The original Berreman argument for the case of transmission through thin crystal films may be extended to reflection from bulk glasses.

I. INTRODUCTION

Vibrational spectroscopy has been one of the most useful methods for studying the structure of glass.[1] Namely, infrared (ir) and Raman spectroscopies, particularly the former, are experimental techniques already available in many glass research laboratories. Although vibrational spectroscopy methods do not usually give direct structural information, they can be very useful for probing terminal or weakly coupled bridging anions in terms of short-range order. Moreover, vibrational spectra may be compared with calculations based on models of the glass structure in order to yield more direct short-range or, to some extent, intermediate-range structural data.

The present paper is particularly concerned with ir reflection spectra of bulk glasses, from which the fundamental optical constants n (real refractive index) and k (dimensionless imaginary part of the complex refractive index or extinction coefficient) may be derived by Kramers-Kronig analysis of near-normal-incidence data.[2] In this fashion the real part of the complex dielectric constant ϵ_1 and imaginary part ϵ_2 may be computed and peaks in ϵ_2 and $\epsilon_2/(\epsilon_1^2+\epsilon_2^2)$ correspond to TO and LO split frequencies, respectively. In the transverse vibrations, the atomic displacements are perpendicular to the direction of periodicity of the elastic wave (that of the wave vector $\mathbf{k}$), whereas in the longitudinal vibrations the displacements are parallel to the wave vector. Although the physical meaning of this is clear for crystals, in the case of glasses, where $\mathbf{k}$ is not a well-defined quantity, the significance of such splittings at the atomic level is still unclear.

LO-TO splittings were first proposed to occur in v-GeO$_2$ and v-SiO$_2$ in order to explain certain pairs of peaks in their Raman spectra.[3] Since then, such frequency splittings have also been observed in other oxide glasses such as v-P$_2$O$_5$,[4] v-As$_2$O$_3$,[5] and v-B$_2$O$_3$,[6] in chalcogenide glasses such as v-GeS$_2$,[7] or v-As$_2$S$_3$ and v-As$_2$Se$_3$,[5] and also in more ionic halide glasses such as v-BeF$_2$,[8] HfF$_4$-based glasses,[9] and v-ZnCl$_2$.[10] In crystals these splittings arise as a result of long-range Coulomb forces which are a consequence of the internal electric field created by the motions of the ions during the vibrations. In glasses there is also some theoretical support for this,[11,12] in particular from the work of de Leeuw and Thorpe,[13] who used the equation of motion method to calculate the optical response of a computer-generated random network with 1536 ions and, by introducing long-range Coulomb forces in an exact way, obtained LO-TO split-vibrational-mode frequencies. Phillips,[14] on the other hand, has maintained that LO-TO splittings imply a macroscopic polarization accompanying the vibrational modes which is not possible in the continuous random-network model of glass structure.[15] He assigned the vibrational spectra of v-SiO$_2$ in terms of a paracrystalline model, including a large density of $>\mathrm{Si}=\mathrm{O}$ bonds on internal surfaces, where LO-TO pairs would be physically possible under certain conditions. The continuous random-network model is accepted as valid in the framework of the present paper.

Because of the transverse character of electromagnetic radiation, in conventional transmission spectroscopy at normal incidence only TO modes can be detected. Near-normal-incidence reflectivity data contain information

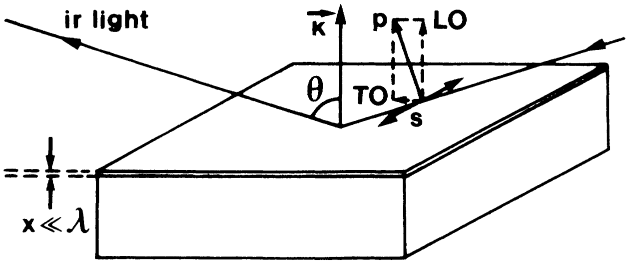

FIG. 1. Directions of *s* (perpendicular) and *p* (parallel) components of radiation incident oblique to the surface of a thin film (perpendicular to the phonon wave vector **k**).

about both fundamental optical constants *n* and *k*, but these have to be extracted from the reflectivity spectra, for example, by Kramers-Kronig data manipulations. It was shown by Berreman[16] that transmission spectra of crystal films at ~30° off normal incidence allowed the detection of LO modes, and this has also been observed for thermal v-SiO_2 thin films, in both transmission[17] and multiple internal reflection.[18] Berreman's argument[16] consisted in showing that, in crystal thin films, zone-center (long-wavelength) phonons have wave vector **k** perpendicular to the film surface, such that normal-incidence radiation can only interact with TO vibrations (parallel to the surface), whereas the *p*-polarized component of oblique incident radiation has subcomponents parallel and perpendicular to the film surface, which can excite both TO and LO phonons, respectively, as shown schematically in Fig. 1. Almeida, Guiton, and Pantano[19] suggested recently that this argument can be extended to the case of bulk samples, and the high-frequency LO mode of bulk v-SiO_2 was detected by diffuse-reflectance Fourier-transform infrared spectroscopy (DRIFTS), where the incidence angle varied between ~20° and 70°. This work led to the original idea on which the present paper is based.

This paper presents external-specular-reflectance measurements at oblique incidence on oxide and halide glasses. The positions of the TO and LO vibrational modes are determined by Kramers-Kronig analysis of near-normal-incidence ir reflectivity, and they are compared with the off-normal-incidence ir reflectivity and Raman data. The influence of ionicity on the extent of the splittings, structural implications, and possible technological consequences are also discussed.

II. EXPERIMENT

Three different glass compositions were studied in this work. Clear bulk v-SiO_2 was obtained from Quartz Scientific, Inc. (Fairport Harbor, OH) in the form of 1.5-mm-thick polished disks. ZBLA glass (57 mol % ZrF_4–35 mol % BaF_2–3 mol % LaF_3–5 mol % AlF_3) was prepared by melting high-purity anhydrous fluorides in a glove box, according to previously published procedures,[20] and the samples were polished in the form of parallelepipeds ~5 mm thick. ZnCd glass (35 mol % ZnF_2–15 mol % CdF_2–25 mol % BaF_2–6 mol % LaF_3–7 mol % AlF_3–12 mol % LiF) was prepared by a similar procedure, but higher quenching rates had to be used, and the final thickness of these samples, after polishing, was ~1–2 mm.

Infrared spectra were measured for all glass samples in a Nicolet 5DXC FTIR spectrometer (in the middle ir) or a Nicolet 20F spectrometer (in the far ir), both equipped with a DTGS detector. Each spectrum was the result of co-adding 500 scans collected at 4 cm^{-1} resolution, in the external-specular-reflectance mode, by means of a SPECAC variable-angle attachment, at incidence angles ϕ between 10° and 70° off normal, using unpolarized radiation. All reflection measurements were referenced to an aluminum mirror, and they were carried out at room temperature.

Polarized Raman spectra were measured with a Spex 1403 double monochromator equipped with holographic gratings, at 4 cm^{-1} resolution, using a Spectra-Physics 2016 argon-ion laser for excitation at 488.0 or 514.5 nm, with ~100 mW power at the sample and a Hamamatsu photomultiplier detector. Measurements were performed in the 90° scattering geometry, in the polarized (HH) and depolarized (HV) configurations,[1] at room temperature.

III. RESULTS AND DISCUSSION

A. Spectral data

Figure 2 shows the reflectance spectra of bulk v-SiO_2 as a function of the incidence angle. As the angle varies from 10° to 70° off normal, minor changes occur in the lower-frequency regime, and simultaneously there are major changes at high frequencies. The minor variations consist of a shift in the lower-frequency peak from 479 to 492 cm^{-1} and the growth of a weak band near 611–619 cm^{-1} (barely visible for $\phi < 50°$), together with a gradual smoothing of the ~787-cm^{-1} peak. The major changes occur in the high-frequency region above 1000 cm^{-1}, and the discussion will be concentrated in this region. As the angle ϕ increases beyond 10°, the high-frequency shoulder increases both in intensity and frequency, from about 1232 to 1286 cm^{-1}. For $\phi > 50°$ the shoulder actually becomes stronger than the peak on its low-frequency side, whose position has an almost negligible increase from 1123 to 1128 cm^{-1}, when ϕ goes from 10° to 60°. (The 60° curve is not shown in the figure.) The data for 70° were obtained near the limit of the reflectance attachment capabilities and are therefore less reliable.

The high-frequency region of the v-SiO_2 spectrum has been attributed to an antisymmetric stretching vibration of the oxygen atoms along a line parallel to the adjacent Si-Si direction plus Si cation motion in unspecified directions,[21] designated by AS(*C*). Lucovsky and Galeener[7] calculated, by Kramers-Kronig analysis of near-normal ir reflectivity data, TO and LO split frequencies at approximately 1067 and 1265 cm^{-1}, respectively. Lucovsky, Wong, and Pollard[22] and Pai *et al.*,[23] on the other hand, have proposed an alternative explanation in terms of two

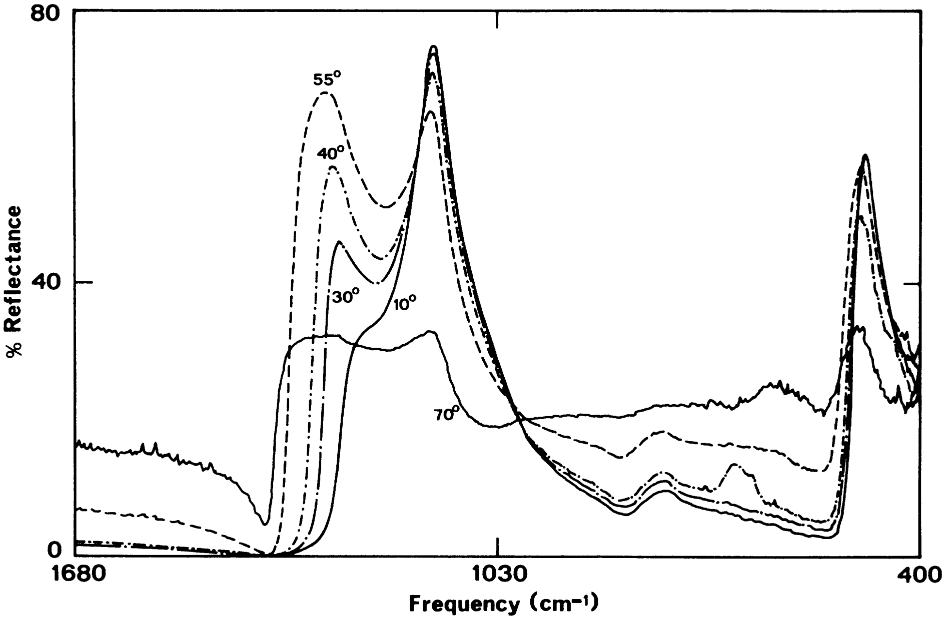

FIG. 2. Specular reflectivity spectra of v-SiO$_2$ at different angles of incidence ($\phi = 10°$, 30°, 40°, 55°, and 70° off normal).

vibrational modes, recently analyzed quantitatively by Kirk:[24] (1) an AS$_1$ mode where adjacent oxygens move in-phase, as in the original interpretation,[21] and (2) an AS$_2$ mode where adjacent oxygens move out of phase. According to Kirk,[24] the TO and LO frequencies are 1076 and 1256 cm^{-1} for AS$_1$, respectively, whereas they are ~ 1200 and ~ 1160 cm^{-1} for the AS$_2$ inverted TO-LO pair, respectively. Even if the latter interpretation is correct, the AS$_2$ motion is weakly ir active and the reflectance spectra of Fig. 2 show essentially only the AS$_1$ motions. Moreover, Philipp[25] has shown, in his calculations of the transmittance and reflectance spectra of v-SiO$_2$ films at different incidence angles, that the high-frequency shoulder observed in both spectra at normal incidence clearly evolves to a well-defined peak, at incidence angles $\phi \geq 60°$, located at ~ 1260 cm^{-1} for 500-nm-thick films.

Figure 3(a) shows the near-normal-incidence (10° off normal) and the 55° off-normal-incidence reflectance spectra of v-SiO$_2$. The latter is very similar to the diffuse-reflectance (DRIFTS) spectrum of the same material in bulk form and particularly as a neat powder.[19] Figure 3(b) shows the TO and LO spectra of v-SiO$_2$, which were calculated from the near-normal-incidence data by Kramers-Kronig analysis, using a computer-based fast-Fourier-transform (FFT) routine (Spectra Calc, Galactic Industries) on a personal computer. Although this FFT algorithm is essentially qualitative, because of the way in which wing corrections are treated,[26] the results of Fig. 3(b) are in good agreement with those of Galeener and Lucovsky,[3] showing that the FFT method is acceptable, in particular for deriving the *positions* of the TO and LO peaks. The agreement is especially good in the case of the LO spectrum, which is of main concern in this work, where the major peaks occurred at 509 and 1266 cm^{-1}, compared to ~ 488 and 1265 cm^{-1} in Galeener and Lucovsky's paper[3] or to 508 and 1260 cm^{-1} in a recent work of Almeida, Guiton, and Pantano,[27] where numerical integration was performed in a mainframe computer and proper wing corrections were employed. Only the intensities are not quantitatively accurate, and therefore they are not included in the figure. Peak widths could also be affected to some extent by the FFT algorithm. The calculated LO-TO splitting for the AS(C) vibration was 163 cm^{-1}. Figure 4 shows the polarized Raman spectra of v-SiO$_2$, with the calculated TO and LO positions superimposed.

Figure 5 shows the reflectance spectra of ZBLA glass as a function of the incidence angle ϕ. Some variations in the intermediate-frequency range and major changes at higher frequencies may be observed. The intermediate-frequency peak position increases from 244 to ~ 285 cm^{-1} as ϕ varies from near-normal incidence (10° off normal) to 60° off normal. The major changes at higher-frequency consist essentially of (1) a shift in the dominant reflection peak from 530 to ~ 559 cm^{-1}, when ϕ varies from 10° to 50° off normal (above this angle, the peak position is no longer clear), with a simultaneous intensity increase, and (2) a large increase in the intensity of the high-frequency reflectivity shoulder (barely visible in the 10° spectrum) and a shift in its position from ~ 600 to 610 cm^{-1}, as ϕ varies from 10° to 60° off normal, with a value of 630 cm^{-1} for $\phi = 70°$ (not shown in the figure). For $\phi > 50°$ the high-frequency shoulder becomes stronger than the lower-frequency peak, similar to the case of v-SiO$_2$. As it was done for this glass, the discussion will also concentrate on the high-frequency region of the ZBLA spectrum. The dominant, high-frequency ir-absorption band has been attributed[1,28,29] to AS(*C*) motions of bridging F atoms along the Zr-Zr direction, with simultaneous Zr cation motion in the opposite direction, the character of this vibration being somewhat similar to that of the AS(*C*) mode of vitreous silica; the main differences probably lie in a larger bridging angle for the Zr-F-Zr bridges, a larger coordination number for the Zr cation compared to Si and the occurrence of nonbridging F atoms around Zr, whereas Si is surrounded only by bridging oxygens in SiO_2. Figure 6(a) shows the 10° and 50° off-normal reflectance spectra of ZBLA glass, and Fig. 6(b) shows the corresponding TO and LO spectra, calculated from the near-normal-incidence (10°) data by Kramers-Kronig analysis. The AS(*C*) TO-LO mode splitting was 96 cm^{-1}, smaller than for the corresponding mode of the more covalent SiO_2 glass, although larger on a percentage frequency basis. Finally, Fig. 7 shows the polarized Raman spectra of ZBLA glass with the calculated TO and LO positions superimposed.

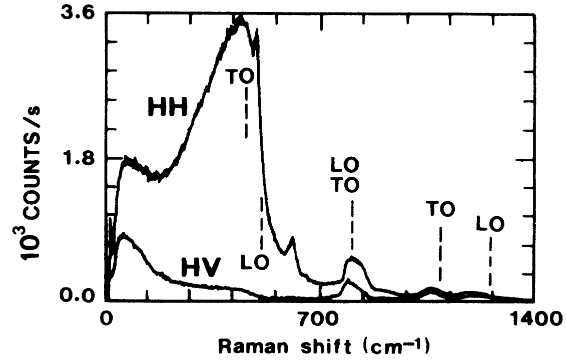

FIG. 4. Raman spectra of v-SiO_2 in the polarized (HH) and depolarized (HV) configurations.

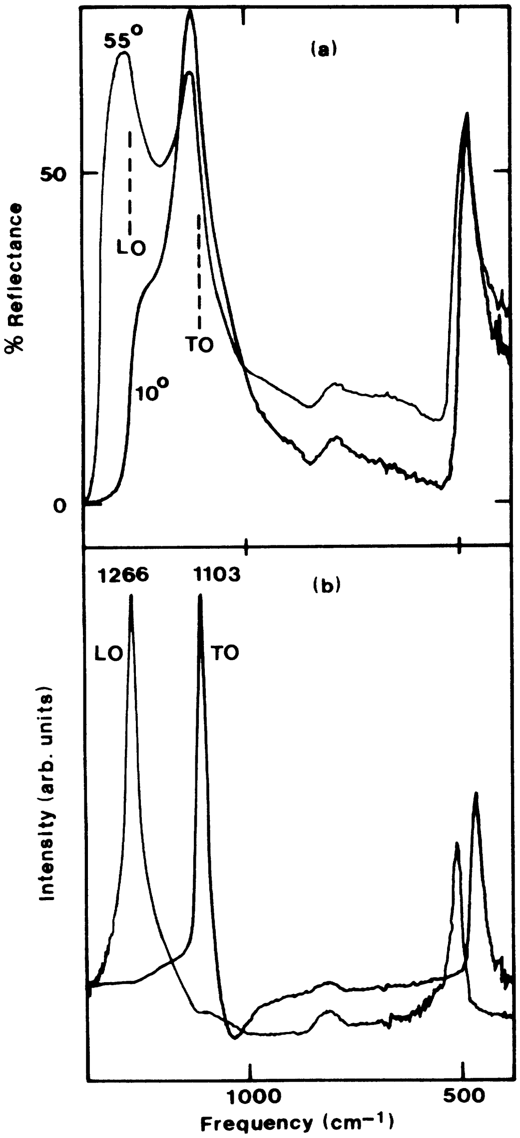

FIG. 3. ir spectra of v-SiO_2: (a) experimental specular reflectivity at 10° and 55° off normal; (b) TO and LO spectra, calculated from the experimental 10° curve.

Figure 8(a) shows the reflectance spectra of the even more ionic ZnCd glass at 10° and 55° off normal. The 10° spectrum is dominated by a low-frequency band at ~238 cm^{-1}; there is also an intermediate-frequency shoulder at ~397 cm^{-1} plus a very weak peak at ~608 cm^{-1}. For $\phi = 55°$, however, the two major vibrational features have merged into a very broad band of modes centered at around 330 cm^{-1} and extending until about 600 cm^{-1}, whereas the high-frequency weak peak had a major intensity increase and is now positioned at 617 cm^{-1}. Although the structure of ZnF_2-CdF_2-based glasses is just beginning to be studied, it appears[30] that the dominant peak at ~238 cm^{-1} in the near-normal reflectance spectrum (which is Raman active and depolarized as seen in Fig. 9) is due to an antisymmetric stretching of *F* atoms in Cd-F-Cd(Ba) bridging sequences, whereas the ~397-cm^{-1} shoulder (Raman active and polarized) may be due to symmetric stretching of *F* atoms in Zn-F-Zn bridges; the symmetric stretching of nonbridging *F* atoms about Zn is not active in the ir. The "bridging" and "nonbridging" designations, very common in glass terminology, are used here in spite of the largely ionic character of the bonding in these glasses. Figure 8(b) shows the corresponding TO and LO spectra, calculated from the 10° reflectance data of ZnCd glass by Kramers-Kronig analysis. This highly ionic glass apparently exhibits very large TO-LO splittings, assuming that the TO-LO pairs are 390–623, 274–459, and 148–326 cm^{-1}, respectively. The intermediate-frequency ir-active mode at ~397 cm^{-1} (near-normal incidence) exhibits a splitting of ~233 cm^{-1}, which is especially large on a percentage frequency basis; the lower-frequency ir modes have also very large splittings of 185 and 178 cm^{-1}, respectively.

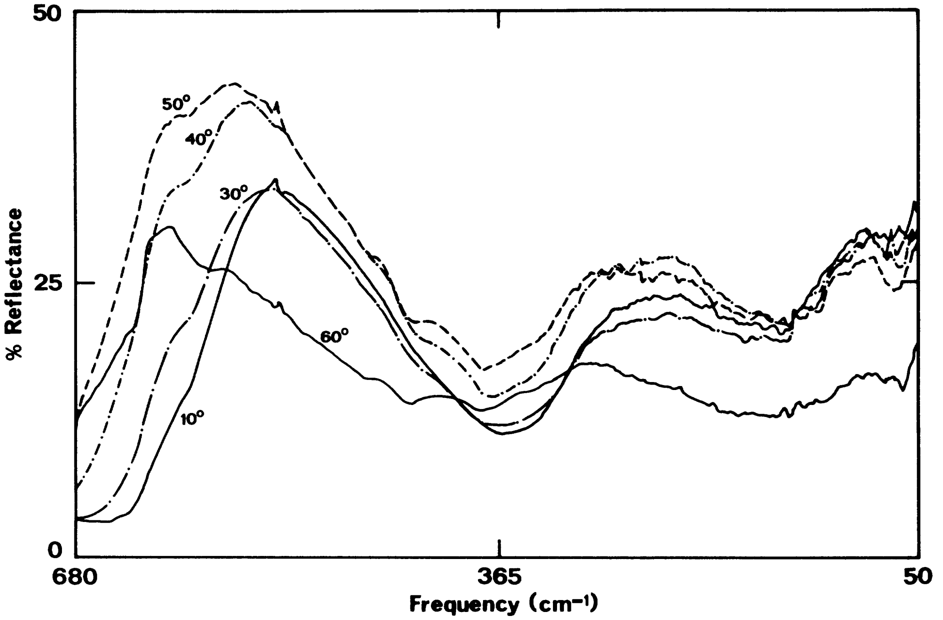

FIG. 5. Specular reflectivity spectra of ZBLA glass at different angles of incidence (ϕ = 10°, 30°, 40°, 50°, and 60° off normal).

The very weak mode at ~ 608 cm^{-1} in the near-normal-incidence ir reflectance spectrum is probably an incipient LO mode, similar to the high-frequency shoulder in the spectrum of v-SiO$_2$. Figure 9 shows the polarized Raman spectra of the ZnCd glass with the TO and LO positions superimposed. All the relevant spectral data concerning the three different types of glasses are given in Table I.

It is important to stress that the changes observed in the reflectance spectra of the glasses as the incidence angle ϕ is varied are real and do not arise as a result of experimental artifacts. In fact, the penetration depth[31] of the reflected radiation, i.e., the depth inside the sample at which the ir light intensity falls to $1/e$ of its initial value, is equal to $1/\alpha$ for normal-incidence radiation, where α is the absorption coefficient. For example, for v-SiO$_2$, α reaches an absolute maximum, near 1090 cm^{-1}, of $\sim 4\times10^4$ cm^{-1},[25] corresponding to a penetration depth of ~ 0.25 μm for normal incidence, at the peak frequency. This value will decrease to some extent for off-normal incidence, and it is conceivable that a compacted surface layer due to polishing (~ 100 nm) could have some influence on the reflectivity spectra at higher ϕ values. However, the fact that similar changes are found in the transmission spectra of v-SiO$_2$ films at off-normal incidence,[17,32,33] in the reflectivity spectra of modified silicate glasses,[34] and in the DRIFTS spectrum of v-SiO$_2$

TABLE I. ir and Raman scattering data for SiO$_2$, ZBLA, and ZnCd glasses (peak frequencies are in cm^{-1}).[a]

v-SiO$_2$			ZBLA			ZnCd		
ir			ir			ir		
10°	55°	Raman	10°	50°	Raman	10°	55°	Raman
~1232(sh)	1283	1188(dep)	~600(sh)	610	576(pol)	608	617	562(pol)
1123	1128	1063(dep)	529	559	478(pol)	~397	~400	384(pol)
786	781	796(dep)	245	264	388(dep)	238	~330	231(dep)
479	848	602(pol)	85	~90	327(dep)			52(dep)
		488(pol)			260(dep)			
		433(pol)			190(dep)			
		52(dep)			45(dep)			

[a] Nomenclature: sh, shoulder; pol, polarized peak; and dep, depolarized peak.

powder[19] shows that this is not an experimental artifact. The present spectral behavior was previously found in the ir reflectance of modified alkali and alkaline-earth silicate glasses,[35] but it was not discussed. Also, some samples of unpolished ZBLA and ZnCd glass exhibited the same ir reflectance behavior as a function of ϕ. Finally, in order to further prove the previous point, the reflectance of v-SiO_2, ZBLA, and ZnCd glasses was calculated at different ϕ values, using the n and k spectra derived from near-normal-incidence data by Kramers-Kronig analysis and the Fresnel formulas[31] for oblique incidence. These spectra were generally found to be in qualitative agreement with the experimental data. As an example, Fig. 10 shows the calculated reflectance spectra of v-SiO_2 at 10°

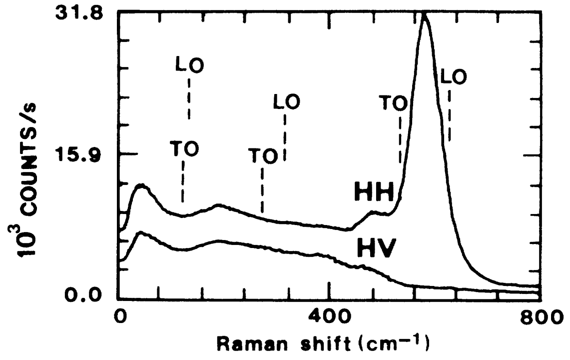

FIG. 7. Raman spectra of ZBLA glass in the polarized (HH) and depolarized (HV) configurations.

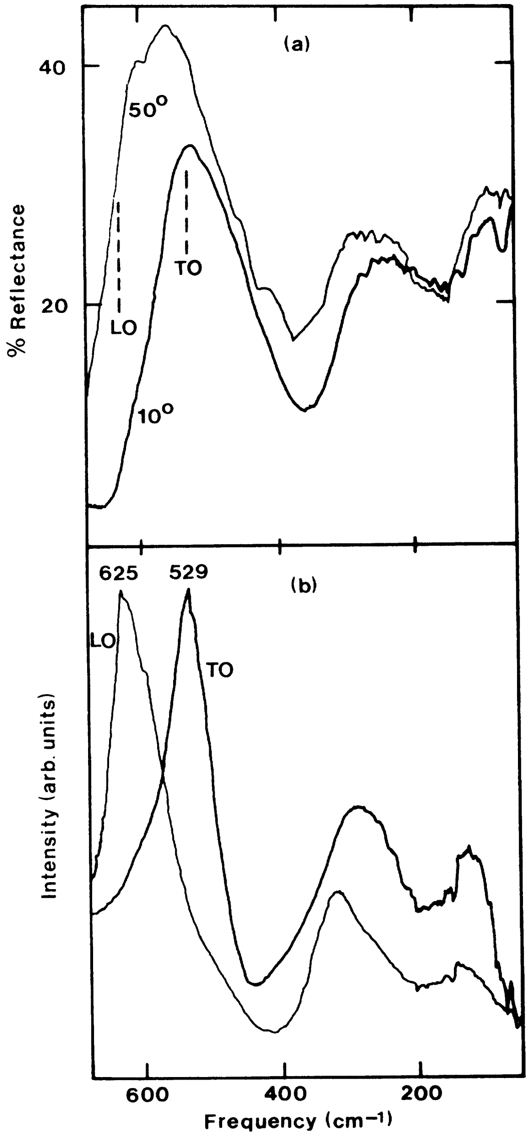

FIG. 6. ir spectra of ZBLA glass: (a) experimental specular reflectivity at 10° and 50° off normal; (b) TO and LO spectra, calculated from the experimental 10° curve.

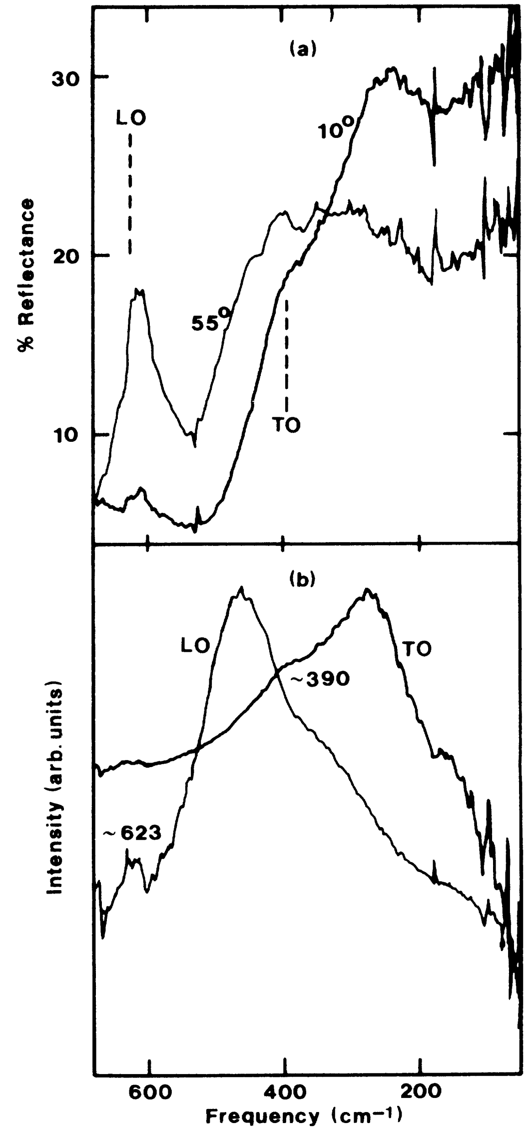

FIG. 8. ir spectra of ZnCd glass: (a) experimental specular reflectivity at 10° and 55° off normal; (b) TO and LO spectra, calculated from the experimental 10° curve.

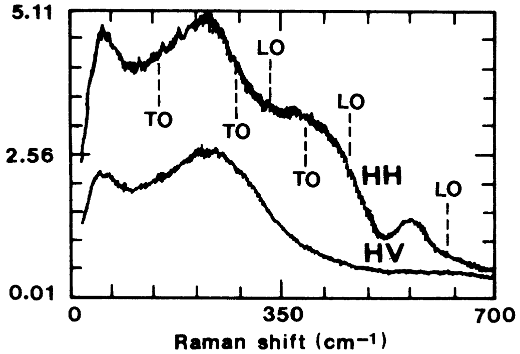

FIG. 9. Raman spectra of ZnCd glass in the polarized (HH) and depolarized (HV) configurations.

and 70° off-normal incidence. Although even the calculated 10° spectrum is somewhat different from the experimental curve of Fig. 3(a) at high frequency (because of the FFT algorithm used in the Kramers-Kronig analysis), it is clear that an increase in ϕ leads to a dramatic increase in the intensity of the high-frequency shoulder, whereas the shape of the other spectral features remains basically unchanged. This confirms the experimental observation of only the highest-frequency LO mode, which in turn rules out the possible presence of experimental artifacts, which would affect the low-frequency region as well.

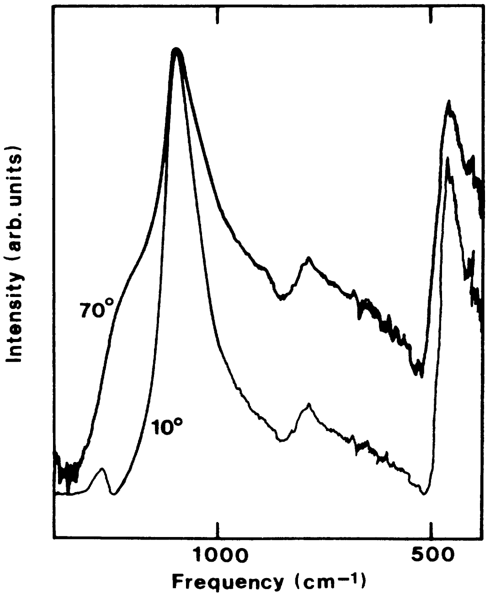

FIG. 10. Calculated ir reflectivity spectra of v-SiO$_2$ at 10° and 70° off-normal incidence.

B. TO-LO splittings in glass

The occurrence and physical explanation of TO-LO splittings in crystals is well established.[36] Glasses, however, are isotropic solids where the vibrational modes do not possess a well-defined wave vector, particularly for the more delocalized, lower-frequency modes.[1] Therefore, the physical meaning of TO-LO splittings in glass, at the atomic level, is not clear at present. Nevertheless, they appear to occur, on both experimental and theoretical grounds. The pioneering work of Berreman[16] showed that, for thin crystal films of thickness $\ll\lambda$, there are two types of phonons with $\mathbf{k}\sim 0$—TO and LO—and the LO component can be detected by transmission measurements at oblique incidence. This observation was later demonstrated for transmission through thin glass films as well.[17] The present work shows that external-specular-reflection measurements on bulk glasses at oblique incidence are able to achieve a similar result. The model of Payne and Inkson[12] considers that any vibrational mode in a glass generates a uniform effective electric field which is a combination of a local field (in both the TO and LO modes) and a macroscopic field (only in the LO vibration). This uniform effective field, generated by long-range Coulomb attractions, acts as an ordering force which tends to orient the dipoles in a particular direction.[12]

Figure 3 clearly shows that the high-frequency peaks in the oblique-incidence reflectance spectrum of v-SiO$_2$ reproduce quite accurately the calculated TO-LO splitting (155 cm^{-1} for $\phi=55°$ versus a calculated value of 163 cm^{-1}). The agreement was not as good for the lower-frequency pairs, which have smaller splittings and did not exhibit split peaks in the oblique-incidence reflectance spectrum, perhaps in part because those glass vibrations have the least well-defined wave vector. Also, the reflectance peaks corresponding to the high-frequency TO-LO pair had slightly higher frequencies than the calculated modes. This raises the fundamental question of the relationship between the two high-frequency reflectance peaks at oblique incidence and the TO and LO modes. For a given vibrational mode of a crystal at normal incidence, the broad reflectance maximum is bound at low and high frequency by the TO and LO peaks, respectively.[36] In the present case it appears that the lower-frequency peak of the oblique-incidence spectra at 1123–1128 cm^{-1} is the same peak found at normal incidence, whose frequency is higher than the maximum in the extinction coefficient k (1103 cm^{-1}), because of the anomalous dispersion of the refractive index; the somewhat broader peak at $\sim$1232–1286 cm^{-1} virtually coincides with the LO peak of Fig. 3(b), which was also broader than the corresponding TO peak. The $\sim$1232–1286-cm^{-1} band is located very close to the LO frequency, because this value falls beyond the region of large anomalous dispersion of the refractive index, in a frequency domain where n is approximately constant ($\sim$1). Attempts at fitting the reflectance envelope between $\sim$845 and 1380 cm^{-1} with mixtures of Gaussian or Lorentzian components did not lead to satisfactory results, and more than seven bands of oscillators were need-ed in order to produce a reasonable fit. The difference between the frequencies of the two oblique-incidence reflectance peaks is found to increase with ϕ: For v-SiO$_2$ it starts at ~ 109 cm^{-1} for $\phi = 10°$ and it levels off at ~ 158 cm^{-1} for $\phi \geq 60°$, a value similar to the calculated TO-LO splitting of 163 cm^{-1} for the high-frequency vibrational mode of v-SiO$_2$.

The generalized Lyddane-Sachs-Teller relation[36] may be written in the form

$$\frac{\epsilon_0}{\epsilon_\infty} = \prod_i \left[\frac{\omega_{\mathrm{LO},i}}{\omega_{\mathrm{TO},i}} \right]^2 , \tag{1}$$

where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants, respectively, and $\omega_{\mathrm{LO},i}$ and $\omega_{\mathrm{TO},i}$ are the LO and TO frequencies of mode i, respectively. This equation applies to any crystal, but not necessarily to a glass. However, the "crystal-like" behavior of the vibrational modes of the present glasses suggests that one should, in principle, be able to extract ϵ_0 from the measured visible refractive index and observed TO-LO splittings. In the case of v-SiO$_2$, for which $\epsilon_\infty = n_D^2 = 2.126$,[37] the approximate TO and LO frequencies obtained from reflectivity at $\phi = 55°$ were 1283 and 1128 cm^{-1}, corresponding to the only observed split TO-LO pair, and Eq. (1) gives $\epsilon_0 = 2.75$, compared to an experimental value[37] of 3.78. The agreement is not good, because only one split pair was observed for the glass at oblique incidence. However, if one uses the Kramers-Kronig calculated values for the two split TO-LO pairs of the glass at 1266 and 1103 cm^{-1} and 509 and 463 cm^{-1}, Eq. (1) gives $\epsilon_0 = 3.39$, already in reasonable agreement with the experimental value of 3.78. This suggests that the Lyddane-Sachs-Teller relation remains approximately valid in the case of glasses.

Figure 4 shows that, contrary to previous suggestions,[3] the Raman peak positions of v-SiO$_2$, within the experimental error, do not appear to coincide with either the TO or LO components, except in the case of the ~ 787-cm^{-1} mode, where the coincidence might be fortuitous; the agreement is especially poor in the LO case. The reason for this may be that there are in fact no pure TO or LO vibrations in glasses, which is consistent with the absence of a well-defined phonon wave vector and is suggested by the shape of the TO and LO spectra—e.g., in the high-frequency region of Fig. 3(b), the TO component of the AS(C) mode appears to have some admixture of the LO component (as evidenced by the shoulder on the high-frequency side of the 1103-cm^{-1} TO peak) and vice versa.

In the case of ZBLA glass, Fig. 6 shows that again the high-frequency peaks in the oblique-incidence reflectance spectrum reproduce approximately the high-frequency TO-LO splitting, although not as clearly as in the case of v-SiO$_2$. For the lower-frequency modes, TO-LO pairs could not be detected at oblique incidence, as was the case with v-SiO$_2$. Finally, the Raman spectra of Fig. 7 show an even worse agreement between the Raman peak positions and TO-LO pair frequencies than in the case of v-SiO$_2$. A similar conclusion was reached by Gervais *et al.*[38] for the case of several modified silicate glasses.

The reflectance data of ZnCd glass at oblique incidence resemble those of v-SiO$_2$ more than ZBLA, especially with respect to the high-frequency modes, where a clear peak appears at 617 cm^{-1} for $\phi = 55°$, which was essentially absent for $\phi = 10°$. Again no TO-LO splittings are detectable for the lower-frequency modes in the oblique-incidence spectrum. Finally, in the Raman spectra of Fig. 9, the agreement between the Raman peak positions and TO-LO frequencies was again quite poor. Presumably, the occurrence of any extra peaks[3] in the Raman spectra of glasses, if any, should preferably be assigned in terms of genuine vibrational modes, rather than LO components.

The degree of ionicity of the bonding involved is expected to be a factor in determining the extent of the TO-LO frequency splittings. This appears quite noticeable in the case of ZnCd glass, for which the overall ionicity of bonding (based upon the difference in electronegativity between fluorine and the major metallic species involved) was largest. This glass had a relatively structureless ir reflectance at near-normal incidence ($\phi = 10°$) and a Raman spectrum which was largely coincident with the ir spectrum, which are features characteristic of highly ionic glasses where well-defined anionic structural units are difficult to identify. The TO-LO splittings of the highest-frequency mode of each of the glasses studied were 163 cm^{-1} for v-SiO$_2$, 96 cm^{-1} for ZBLA, and 233 cm^{-1} for ZnCd glass. These $\Delta\nu$ values may be compared on a similar scale by ratioing them to the corresponding TO frequencies, and these $\Delta\nu/\nu_{\mathrm{TO}}$ ratios were 0.148, 0.182, and 0.597 for each of the above glasses, respectively. This shows that ionicity plays an important role in determining the extent of TO-LO splittings in glass, probably by increasing the value of the macroscopic electric field[12] during the LO vibrations. This effect is especially obvious when one compares the covalent network glass SiO$_2$ ($\Delta\nu/\nu_{\mathrm{TO}} = 0.148$) with the highly ionic modified ZnCd glass ($\Delta\nu/\nu_{\mathrm{TO}} = 0.597$). The effective charges e_s^* carried by the ions during the vibrations may be calculated for a diatomic material by an expression due to Szigeti.[39] A good measure of ionicity is then the ratio between this effective charge and nominal ionic charge $z_0 e$, given by

$$\frac{e_s^*}{z_0 e} = \frac{3[\mu(\omega_{\mathrm{LO}}^2 - \omega_{\mathrm{TO}}^2)\epsilon_{\mathrm{vac}}\epsilon_\infty V]^{1/2}}{z_0 e(\epsilon_\infty + 2)} , \tag{2}$$

where μ is the reduced mass of the ions for a given vibrational mode exhibiting TO-LO splitting, ϵ_{vac} is the dielectric constant of vacuum, and V is the volume corresponding to one formula unit of the material. If one applies Eq. (2) to the high-frequency TO-LO pair of v-SiO$_2$ (measured density and refractive index at 25 °C were $\rho = 2224$ kg m^{-3} and $n_D = 1.4588$, respectively), one obtains $e_s^*/z_0 e = 0.50$. This is close to Pauling's[40] Si—O ionicity (51%), and it corresponds to effective charges of $+2$ on the Si atom and -1 on the oxygen. The Szigeti model can be applied with less confidence in the case of the halide glasses studied. For ZBLA glass, where ZrF$_4$ can be considered the glass network former,[28] one may take the formula unit as containing one Zr atom. In this case the 25 °C values of $\rho=4604$ kg m^{-3} and $n_D=1.5173$ measured for ZBLA glass in this work lead to $e_s^*/z_0e=0.51$ for the high-frequency TO-LO split pair, corresponding to effective charges of $+2.04$ on the Zr atom and -0.51 on the fluorine atom. The ionicity value, although slightly larger than that of v-SiO$_2$, is considerably lower than Pauling's Zr—F ionicity (82%). In the case of the ZnCd glass (measured $\rho=5038$ kg m^{-3} and $n_D=1.5061$), where a single network former cannot be identified,[30] this role being played by both ZnF$_2$ and CdF$_2$ at least, Eq. (2) leads to $e_s^*/z_0e>1$ for a formula unit containing 0.7 Zn and 0.3 Cd atoms and the Szigeti model is clearly no longer applicable. The above calculations indicate, however, that the glass ionicities I scale in fact as I (ZnCd) $\gg I$ (ZBLA) $> I$ (SiO)$_2$.

Berreman's rationale[16] was originally derived for transmission through thin crystal films. The fact that high-frequency LO modes can clearly be detected in external-specular-reflectivity spectra of glasses at oblique incidence suggests that the former argument can be extended to bulk samples as well. In fact, in such reflectance measurements, the incident radiation will always see a thin film at the surface of a bulk specimen, with a thickness determined by the depth of penetration of the ir radiation in the frequency range of each particular vibrational mode, which is roughly equal to the reciprocal of the absorption coefficient $1/\alpha=\lambda/4\pi k$. For example, for v-SiO$_2$ at $\lambda\sim10$ μm, this depth is ~0.25 μm, which is much smaller than λ, as required by Berreman's rationale.[16] The corresponding values for ZBLA glass at $\lambda\sim19$ μm and for ZnCd glass at $\lambda\sim25$ μm are of the order of 0.85 and 2.0 μm, respectively. The incident radiation interacts mostly with this film, for which there are TO and LO vibrations, respectively perpendicular and parallel to a "wave vector" **k** perpendicular to the film surface.

Based on the previous discussion, the present behavior of the glass specular reflectivity at oblique incidence would appear to be quite general, but this still needs experimental confirmation. So far, in addition to the glasses presently studied, such behavior was also observed for modified silicate glasses.[34] Among the three different types of materials tested in the present work, the detection of a LO mode at oblique incidence was less clear for ZBLA glass than for the other two glasses, and it should again be stressed that this phenomenon was only observed for the highest-frequency vibrational mode of each glass. In the case of crystalline materials, the behavior first reported by Berreman[16] in cubic crystals was also recently observed in different anisotropic crystals.[41–43] The "crystal-like" behavior of certain vibrational modes of glass, particularly the highest-frequency ones, which most clearly exhibit TO-LO splittings, suggests that these are characteristic of some degree of intermediate-range order in the glass. Since this is in apparent disagreement with a larger degree of localization associated with the higher-frequency modes, compared to the lower-frequency vibrations, reported, for example, for v-SiO$_2$,[44] it probably indicates that the better defined wave vector of the former vibrational modes is the predominant factor. Also, Berreman's condition[16] that the film thickness must be $\ll\lambda$, i.e., that the ir depth of penetration must be $\ll\lambda$, is more clearly fulfilled for the highest-frequency modes of larger extinction coefficient in the case of SiO$_2$ and ZBLA glasses.

The present findings might, in principle, have some technological implications, namely, those related to the transparency of ir optical components such as ir transparent glass windows. These, however, are used at frequencies much higher than those which correspond to the vibrational fundamentals, and therefore the appearance of strong LO peaks at oblique incidence may not be a problem. On the other hand, if overtones of those fundamentals or of fundamental vibrations involving impurities such as OH or hydrogen-related impurities are considered, increased absorption may be found at large off-normal-incidence angles. In any case, in addition to the effect of larger optical path, e.g., for radiation falling on an ir window at oblique incidence, Fresnel's equations predict that, in regions where $k\sim0$, the value of the transmission plateau will decrease at oblique incidence when ϕ increases, particularly for ϕ larger than $\sim60°$, because of increasing reflection losses. This behavior was indeed experimentally confirmed.[34]

IV. CONCLUSIONS

The occurrence of TO-LO splittings appears to be a general feature of the optical vibrations of glass. Essentially, only TO modes are found in normal-incidence transmission measurements or reflectance spectra at near-normal incidence. It was shown that the high-frequency LO modes of three different types of glasses, both modified and nonmodified, could be detected by ir external specular reflectance at oblique incidence for $\phi\leq70°$ off normal, in the form of new shoulders or peaks which were almost invisible at near-normal incidence. This was done without the need for complex data treatment. The LO frequencies were found to be approximately correct by comparison with Kramers-Kronig analysis of near-normal-incidence data. The Raman peaks of the same glasses did not generally coincide with either the TO or LO component positions. The classical Berreman argument for transmission through thin crystal films was extended to the case of reflection from bulk glasses. The present findings could have some adverse consequences for ir-transmitting glass components when used at oblique incidence, although it is not known how general the present type of behavior is.

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