

Reply to "Comment on 'Infrared-reflectance spectra of heat-treated, sol-gel-derived silica'"

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Previously reported infrared spectra of amorphous SiO₂ have been discussed in order to clarify the origin of the shoulder at $\sim 1200\text{ cm}^{-1}$ in the transmission spectra and of the high-frequency band at $\sim 1260\text{ cm}^{-1}$ in the reflection spectra. Infrared measurements at oblique incidence with *s*- and *p*-polarized light show that the high-frequency response of silica (between ~ 1000 and 1300 cm^{-1}) originates from two coupled modes AS₁ and AS₂. The polarization characteristics indicate that the features at $\sim 1200\text{ cm}^{-1}$ and $\sim 1260\text{ cm}^{-1}$ have different origin and that it is appropriate to attribute to them TO (AS₂) and LO (AS₁) character, respectively. This assignment was found to be consistent with the infrared-reflectance measurements at oblique incidence reported by Almeida [Phys. Rev. B **45**, 161 (1992)] and with those at nearly normal incidence reported by Kamitsos *et al.* and analyzed by Kramers-Kronig transformation [Phys. Rev. B **48**, 12 499 (1993)]. The two-mode interpretation of the high-frequency response of silica was found to be consistent with the trends of the effective transverse-optic and longitudinal-optic frequencies, which were calculated using the second-moment expressions of Noh and Sievers [Phys. Rev. Lett. **17**, 1800 (1989)]. [S0163-1829(96)04818-7]

Discussion about the origin of the shoulder at $\sim 1200\text{ cm}^{-1}$ (designated by SH), which is measured in the absorption or transmission spectrum of amorphous SiO₂ at normal incidence, has led to considerable disagreement. Bertoluzza *et al.*,¹ and Almeida and Pantano² have attributed this shoulder to the longitudinal-optic (LO) component of the asymmetric (AS) vibration of Si-O-Si bridges, with the corresponding transverse-optic (TO) pair being responsible for the strong absorption at $\sim 1080\text{ cm}^{-1}$. In an alternative approach, Gaskell and Johnson,³ Lucovsky and co-workers,^{4,5} and Kirk⁶ have proposed that the AS motion gives rise to an in-phase (AS₁) and to an out-of-phase (AS₂) mode. The AS₁ mode is optically active, while the AS₂ one is inactive, but becomes activated by disorder-induced coupling with the strong AS₁ mode. A key result of the work of Kirk⁶ was that the overall strength of these coupled modes is constant and any increase of the strength of AS₂ occurs at the expense of the AS₁ mode. The LO-TO frequency pair for the AS₁ mode was measured at $1256\text{--}1076\text{ cm}^{-1}$, while the LO-TO splitting for the AS₂ mode was found inverted at $1160\text{--}1200\text{ cm}^{-1}$.⁶ It was therefore concluded that the SH absorption feature represents the TO response of the AS₂ mode.⁶

In a recent study, Kamitsos *et al.*⁷ (designed by KPK) presented infrared reflectance (11° off-normal) and Raman spectra of bulk SiO₂ gels, which were treated at selected temperatures; air dried at room temperature (sample A) and heated at 650°C (sample B), as well as 1000°C (sample C). The purpose of that work was to investigate the vibrational response of SiO₂ glass, while changing the silicate network connectivity through appropriate heat treatments. The spectra of the imaginary part of the complex dielectric function ϵ'' , which were obtained by Kramers-Kronig transformation of the reflectance spectra, showed well-defined shoulders at $\sim 1200\text{ cm}^{-1}$. While the intensity of the $\sim 1200\text{ cm}^{-1}$ shoulder decreases with increasing temperature of treatment, the sum of the infrared activity of the bands at 1080 cm^{-1} and $\sim 1200\text{ cm}^{-1}$ remains practically constant. On the basis of

these results for SiO₂ gels KPK (Ref. 7) suggested that the behavior of the $\sim 1200\text{ cm}^{-1}$ shoulder in the ϵ'' spectra is consistent with its assignment to the TO component of the AS₂ mode.³⁻⁶

It is now proposed by Almeida⁸ that strong experimental evidence for attributing LO character to the SH absorption feature at $\sim 1200\text{ cm}^{-1}$ is provided by the reflectance spectra of Fig. 2 in Ref. 9. It has been argued that it is this SH feature which shows strong activation with reflection at oblique incidence.⁸ Regarding this point, we would like to emphasize that (a) the high-frequency reflectance shoulder does not appear at 1200 cm^{-1} . It appears in the range $1232\text{--}1285\text{ cm}^{-1}$ as the angle of incidence varies from 10° to 55° , and (b) the enhancement of this high-frequency reflectance shoulder with increasing angle of incidence φ can be well understood on the basis of the Berreman effect.¹⁰ This effect refers to the observation of features at LO frequencies, in addition to those at TO frequencies, when transmission or reflection spectra are measured with *p*-polarized light at oblique incidence, the coupling of the LO modes with the electric-field vector being proportional to $\sin^2\varphi$.¹⁰ Therefore, the enhancement of the reflectance feature measured in the range $1232\text{--}1285\text{ cm}^{-1}$ with increasing φ , as observed by Almeida,⁹ can be attributed to the enhanced participation of the LO component of the AS₁ mode, which has been measured at 1256 cm^{-1} .⁶ The analogous effect on the $\sim 480\text{ cm}^{-1}$ peak is manifested only by a small frequency upshift, because of the considerably smaller LO-TO splitting of this mode.^{6,7}

The Berreman effect has been observed for amorphous SiO₂ by a number of workers^{6,11-15} in both reflection and transmission measurements at oblique incidence. Careful consideration of the published results shows that the high-frequency reflectance feature in the range $1230\text{--}1285\text{ cm}^{-1}$ (depending on the angle of oblique incidence) and the $\sim 1200\text{ cm}^{-1}$ absorption shoulder (transmission with normal incidence, or ϵ'' spectra) have different origins. This is

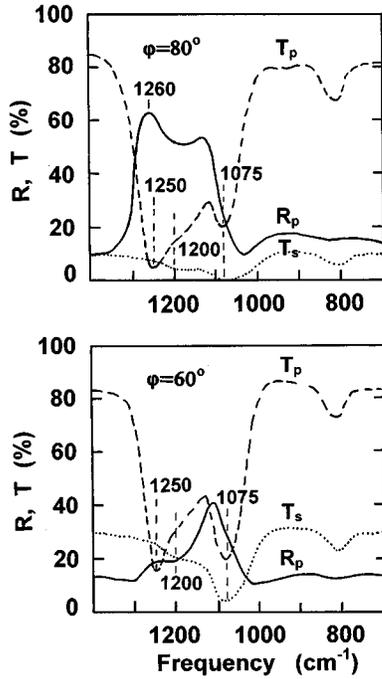


FIG. 1. Transmission and reflectance curves for light polarized parallel (p) and perpendicular (s) to the plane of incidence of a $0.5\text{-}\mu\text{m}$ -thick $\alpha\text{-SiO}_2$ film on Si, for each of the specified angles of incidence. [Redrawn from H. R. Philipp, *J. Appl. Phys.* **50**, 1053 (1979)].

clearly shown, for example, in the transmission spectra of amorphous SiO_2 with oblique incidence (60° and 80°) reported by Philipp,¹¹ and redrawn in Fig. 1 for the reader's convenience. The s -polarized transmission spectra, T_s , reveal a deep minimum at 1075 cm^{-1} and a shoulder at $\sim 1200\text{ cm}^{-1}$ in the high-frequency range. According to the Berreman effect, both features have TO character and indicate the presence of two modes in this frequency range; AS_1 : 1075 cm^{-1} and AS_2 : 1200 cm^{-1} . Besides these features, the p -polarized transmission curves, T_p , show an additional deep minimum at $\sim 1250\text{ cm}^{-1}$, which is quite well separated from the $\sim 1200\text{ cm}^{-1}$ shoulder. The relative intensity of the $\sim 1250\text{ cm}^{-1}$ band increases with φ , and this is also reflected in a corresponding increase of the peak at $\sim 1260\text{ cm}^{-1}$ in the R_p reflectance curve (Fig. 1). These data demonstrate very clearly that the feature at $\sim 1250\text{ cm}^{-1}$ has LO character (AS_1 mode), while the ones at 1075 and $\sim 1200\text{ cm}^{-1}$ have TO character. It is noted that the LO component of the inverted AS_2 mode [$\sim 1160\text{ cm}^{-1}$ (Refs. 6 and 7)] should also contribute to the T_p and R_p curves.

Additional evidence for the nature of peaks in the high-frequency range of silica can be obtained by employing the analytical expressions derived by Noh and Sievers¹⁶ for the second moments of the transverse and longitudinal responses,

$$\langle \omega^2 \rangle_t = \left\{ \int_0^\infty d(\ln\omega) \omega^2 \text{Im}[\varepsilon(\omega)/\varepsilon_\infty] \right\} \times \left\{ \int_0^\infty d(\ln\omega) \text{Im}[\varepsilon(\omega)/\varepsilon_\infty] \right\}^{-1} \quad (1)$$

and

$$\langle \omega^2 \rangle_l = \left\{ \int_0^\infty d(\ln\omega) \omega^2 \text{Im}[-\varepsilon_\infty/\varepsilon(\omega)] \right\} \times \left\{ \int_0^\infty d(\ln\omega) \text{Im}[-\varepsilon_\infty/\varepsilon(\omega)] \right\}^{-1}, \quad (2)$$

where $\varepsilon(\omega)$ is the dielectric function and ε_∞ is the high-frequency dielectric constant. The application of the above expressions requires integration of the data in the frequency range of interest ($1000\text{--}1350\text{ cm}^{-1}$), assuming that other types of modes of silica are well apart from this frequency range. Under this condition, one can calculate effective transverse (ω_t) and longitudinal (ω_l) frequencies by taking the square root of the corresponding second moments.¹⁷

We have applied this approach to our data for silica gels,⁷ to the data of Galeener and Lucovsky for $v\text{-SiO}_2$ (Ref. 18) and to the data of Almeida *et al.* for silica gel and $v\text{-SiO}_2$.¹⁹ The calculated effective transverse and longitudinal frequencies in the range of interest are given in Table I. For the purpose of comparison we have included also TO and LO frequencies of the AS_1 and AS_2 modes discussed previously by KPK.⁷ As shown in Table I the ω_t and ω_l frequencies are not constant; they vary systematically with heat-treatment temperature of the gel and approach eventually the corresponding frequencies of $v\text{-SiO}_2$. It is found also that ω_t is between the TO frequencies of the AS_1 and AS_2 modes, while ω_l is between the LO frequencies of the same modes. In the case of strong disorder-induced coupling which leads to comparable strengths of the AS_1 and AS_2 modes [air-dried at room-temperature (RT) SiO_2 gel], it is observed that ω_t and ω_l are almost the averages of the TO and LO frequencies, respectively, of the two modes. When the coupling is reduced, as in $v\text{-SiO}_2$, ω_t is very close to the TO frequency of the strongest AS_1 mode and ω_l approaches the LO frequency of AS_1 . Therefore, the trends exhibited by ω_t and ω_l are well understood in terms of the two coupled AS_1 and AS_2 modes proposed by a number of workers.³⁻⁶ Since the optical activity in the range $1000\text{--}1350\text{ cm}^{-1}$ is proportional to $\langle \omega^2 \rangle_l - \langle \omega^2 \rangle_t$, we have calculated this quantity and present the results in the last row of Table I. It is evident that the optical activity, or oscillator strength in the range of interest, increases upon increasing the heat-treatment temperature of the gel. This trend can be attributed to the enhancement of the network connectivity, through the development of Si-O-Si bridges with heat treatment of the gel.⁷

The above analysis suggests that in the case of a simple one-component glass it is legitimate to obtain TO and LO frequencies from the peaks of the $\text{Im}[\varepsilon(\omega)]$ and $\text{Im}[-1/\varepsilon(\omega)]$ responses,¹⁸ as it was done by KPK for SiO_2 gels.⁷ In fact, the validity of this approach was demonstrated recently by Kim *et al.* for the case of B_2O_3 glass.²⁰ They showed that the original Lyddane-Sachs-Teller (LST) relation,

$$\varepsilon_0/\varepsilon_\infty = \prod_{j=1}^N \omega_{lj}^2/\omega_{tj}^2, \quad (3)$$

is valid, with ω_{tj} and ω_{lj} being determined directly from the $\text{Im}[\varepsilon(\omega)]$ and $\text{Im}[-1/\varepsilon(\omega)]$ spectra, respectively. However, for a more complicated two-component glass,

TABLE I. Calculated effective transverse (ω_t) and longitudinal (ω_l) frequencies (cm^{-1}) for the range 1000–1350 cm^{-1} of SiO_2 gels and $v\text{-SiO}_2$. For the purpose of comparison, the TO and LO frequencies of the AS_1 and AS_2 modes are included (Ref. 7). The last row of the table gives the values of the quantity $\langle \omega^2 \rangle_l - \langle \omega^2 \rangle_t$ (in 10^5 cm^{-2}) for the same frequency range.

Mode	SiO_2 gel ^a			$v\text{-SiO}_2$ ^c	SiO_2 gel ^d	$v\text{-SiO}_2$ ^d
	RT ^b	650 °C ^b	1000 °C ^b			
AS_1 TO	1103	1083	1097	1063		
ω_t	1148	1118	1115	1076	1120	1090
AS_2 TO	1208	1193	1200	1200		
AS_1 LO	1215	1230	1255	1256 ^e		
ω_l	1164	1167	1228	1245	1196	1230
AS_2 LO	1115	1118	1170	1160 ^e		
$\langle \omega^2 \rangle_l - \langle \omega^2 \rangle_t$	0.4	1.1	2.6	3.9	1.8	3.2

^aFrom the data reported by KPK (Ref. 7).

^bTreatments of air-dried SiO_2 gels.

^cFrom the data reported by Galeener and Lucovsky (Ref. 18).

^dFrom the data reported by Almeida, Guiton, and Pantano (Ref. 19).

^eFrequencies reported by Kirk (Ref. 6).

$x\text{BaO}-(1-x)\text{B}_2\text{O}_3$, for which the corresponding spectra result from extensively overlapping bands, they had to apply the generalized LST relation of Noh and Sievers,¹⁶

$$\varepsilon_0 / \varepsilon_\infty = \langle \omega^2 \rangle_l / \langle \omega^2 \rangle_t, \quad (4)$$

where the second moments were obtained by integrating Eqs. (1) and (2) in the entire infrared range.

Almeida⁸ has also compared the infrared spectra of an air-dried SiO_2 gel (sample AGP), measured by Almeida *et al.*¹⁹ (20° off-normal incidence), with those of samples A, B, and C measured by KPK (Ref. 7) at nearly normal incidence (11° off-normal). The fact that gel samples prepared in different laboratories show differences in infrared reflectivity can be attributed to surface finish⁸ and also to porosity⁷ effects. There are other instances where differences in infrared reflectivity have been also observed. For example, porous Vycor glass (Corning 7930) exhibits a reflectivity as high as 20% (at 1090 cm^{-1}) according to Almeida *et al.*,¹⁹ but the same type of material measured by Murray and Greytak²¹ shows a corresponding reflectivity of only ~4%.

On the basis of comparison of the high-frequency (1000–1300 cm^{-1}) TO and LO profiles, Almeida⁸ concluded that the AGP sample looks like a KPK sample that has been treated between 650 and 1000 °C. We would like to add that this conclusion is supported also by the level and profile of the AGP reflectivity (between those of KPK samples B and C), as well as by the calculated ω_t and ω_l frequencies given in Table I. This comparison leads also to the conclusion that the KPK samples exhibit TO and LO profiles which are compatible with their corresponding reflectivity. In that respect, the suggestion made by Almeida⁸ that errors may have been introduced by the Kramers-Kronig transformation and could have affected the TO and LO profiles of the KPK samples, does not seem to be substantiated. In fact, if such errors were indeed introduced one would expect them to affect also the lower-frequency spectral range, and not only the high-frequency (1000–1300 cm^{-1}) envelope.

A useful way of checking the accuracy of the Kramers-Kronig transformation is provided by the general sum rule,

$$\int_0^\infty d(\ln \omega) \omega^2 \text{Im}[-\varepsilon_\infty / \varepsilon(\omega)] = \int_0^\infty d(\ln \omega) \omega^2 \text{Im}[\varepsilon(\omega) / \varepsilon_\infty]. \quad (5)$$

As typical examples, we have treated the data for a SiO_2 gel⁷ (KPK sample B, heat-treated at 650 °C) and for $v\text{-SiO}_2$ (Ref. 18) according to Eq. (5). For both materials the integration of the data has been performed in the range 200–1400 cm^{-1} . In the case of SiO_2 gel, the left-hand-side integral of Eq. (5) equals $1.8 \times 10^5 \text{ cm}^{-2}$, while the right-hand-side integral gives $2.2 \times 10^5 \text{ cm}^{-2}$. For $v\text{-SiO}_2$, the results are $8.4 \times 10^5 \text{ cm}^{-2}$ and $8.1 \times 10^5 \text{ cm}^{-2}$, respectively. These findings show that the general sum rule is obeyed quite well, and thus the results of the Kramers-Kronig transformation should be accurate.

The experimental conditions (method of preparation and heat treatment) employed by KPK have certainly determined the level of reflectivity and profile of each sample. However, the observed spectral differences between samples A, B, and C are solely due to the different heat-treatment temperatures. As discussed extensively elsewhere,⁷ the relatively low reflectivity of samples A and B is due to their porous structure that originates from a high concentration of Si-OH groups. As the temperature of treatment is increased these groups condense into Si-O-Si bridges, and this was demonstrated by Raman spectroscopy. The increasing network connectivity with temperature is also manifested by larger LO-TO splitting of the rocking ($\sim 455 \text{ cm}^{-1}$), bending ($\sim 805 \text{ cm}^{-1}$), and AS_1 ($\sim 1075 \text{ cm}^{-1}$) modes of Si-O-Si bridges.⁷ On the contrary, the LO-TO splitting of the disorder-induced AS_2 ($\sim 1200 \text{ cm}^{-1}$) mode was found to decrease with heat treatment.

The above discussion of previously reported spectra of silica, including those of heat-treated SiO₂ gels and amorphous films measured with *s*- and *p*-polarized light, leads to the conclusion that the high-frequency (1000–1300 cm⁻¹) infrared response is due to the presence of two coupled

modes (AS₁ and AS₂). This model is consistent also with the trends exhibited by the effective transverse and longitudinal frequencies calculated from the corresponding second moments. Therefore, the assignment of TO (AS₂) character to the SH absorption feature is well documented.

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