Curve-fitting of Raman spectra of silicate glasses

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Abstract

A procedure for deconvolution of complex Raman spectra of amorphous materials (*e.g.*, silicate glass and melt) is described. The line shapes and quality of the fits are determined statistically after correction for the temperature- and frequency-dependence of the Raman intensities. In the fitting routine, intensity, half-width and position (frequency) of all bands are treated simultaneously as unconstrained variables. The number of lines fitted to a spectrum is also treated statistically by numerical minimization of the squares of the deviations between the observed and the calculated Raman envelopes and by maximizing the randomness of the residuals. It is assumed, however, that all bands are symmetric.

Introduction

Raman spectroscopy has proved a powerful tool for determining important features of the structure of amorphous materials such as silicate melts and glasses (*e.g.*, Brawer, 1975; Lucovsky, 1979; Brawer and White, 1975, 1977; Verweij 1979a,b; Furukawa *et al.*, 1978, 1981; Furukawa and White, 1980; Virgo *et al.*, 1980; Mysen *et al.*, 1980, 1981). It has been shown that melts of petrological significance, containing a small number of coexisting structural units, give rise to established numbers and positions of relevant Raman bands. Because each structural unit can be characterized in terms of the number of nonbridging oxygens (NBO) per silicon, most of these interpretations have been based on (1) the similarity of the topology of spectra with the same NBO/Si and (2) systematic relations between the raw Raman spectra and NBO/Si of the melt.

The information acquired from raw Raman spectra is, however, somewhat uncertain as the Raman bands tend to be broad and may also shift in frequency as a function of polarization of the relevant *T*–O bonds. These shifts may be induced, for a given vibration, by type and abundance of polarizing cations, by the nature of the *T* cation (tetrahedral cation), by *T*–O distance, by the number of nonbridging oxygens in a given tetrahedron, and by *T*–O–*T* angles. Several of these features when inferred by interpretation of the Raman spectra depend on the model of the melt structure. Furthermore, rigorous theoretical treatment of the spectra is not always possible in amorphous materials that are devoid of long-range order. In view of these limitations, a statistical approach has been adopted in which no constraints on the line-parameters (intensity, half-width and position), or on the number of bands fitted, have been imposed.

The value of fits thus obtained has been tested with the aid of spectra from a range of chemical compositions. This compositional range was chosen so as to introduce significant changes of as many of the variables known to affect the Raman spectra as possible. It has been shown that this approach to curve-fitting of Raman spectra of silicate melts and glasses yields internally consistent models of the anionic structure of such materials.

Experimental procedure

Rigorous curve-fitting requires digitized spectra. In this study, spectra were collected with an automation system designed and built at the Geophysical Laboratory. The main element of this system is a minicomputer, which is interfaced to a photon counter and to the slit and wavelength drives of the Raman spectrometer. This computer is programmed to step the spectrometer through the desired wavelength range, measure the photon count, and store the resulting spectrum on a floppy disk. As the spectra are accumulated they are simultaneously displayed on a graphics terminal for visual inspection.

Before curves may be fitted to the spectra it is

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necessary to correct the data for the dependence of the scattered intensity on temperature and frequency (Long, 1977). In the present experiments, in which only relative intensities have been considered, a correction factor of the form employed by Long (1977) will be used:

$$R = \nu_0^3 \, [-\exp(-hc/kT) + 1]\nu/(\nu_0 + \nu)^4, \quad (1)$$

where ν_0 and ν are the frequencies of the exciting line and Raman shift, respectively. In order to obtain a corrected spectrum, the measured intensities have been multiplied by R from equation (1). No instrumental corrections are included. An example of a corrected and an uncorrected spectrum of a binary metal oxide-silica glass is shown in Figure 1.

Spectra have been deconvoluted with a computer program. This program, based on the technique of Powell and Fletcher (1963) and Powell (1964a,b), is the result of a combined effort of several laboratories, mainly Argonne National Laboratories, Harwell Laboratories, and the University of Chicago. Its development was initiated by S. L. Ruby and J. R. Gabriel (S. Hafner, personal communication, 1981). In the present study the program was modified to minimize the squares of the deviations between the observed and calculated Raman envelopes with Gaussian line shapes (χ^2). The main advantage of the program is that convergence is quite rapid compared with other refinement techniques, and the method may be used with several linear or nonlinear constraints (a copy of the program is available upon request from the authors). The results reported here do not, however, involve the use of constraints on any of the line parameters. Consequently, intensity, half-width and position (frequency) of each band within a fitted spectrum are independent variables determined exclusively by the computer program.

The line shapes of bands

The nature of a Raman band is a function of a number of properties, such as the type of vibration, scattering geometry, optical properties of the detection system, and polarization of the bond in question. Determination of such properties is beyond the scope of this presentation. Furthermore, for curve-fitting of silicate glasses and melts the large half-width (commonly $\geqslant 50$ cm^{-1} compared with $\leqslant 5$ cm^{-1} for spectra of crystalline materials) of the individual bands and their general topology most likely depend on properties such as distribution of
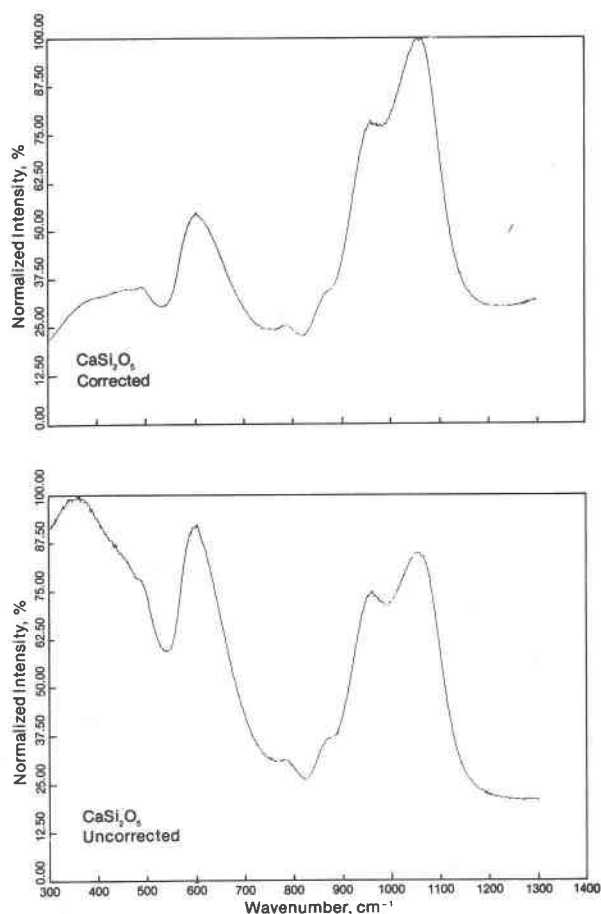

Fig. 1. Raman spectra of quenched CS2 melt with and without corrections for temperature- and frequency-dependent scattering intensities.

bond angles and bond distances in the glass. The distribution function that describes a given band from a glass may, therefore, be the distribution of bond angles rather than the distribution of the scattered light from a local molecular configuration. For silicate melts it appears reasonable to expect that the ranges of values of bond angles and bond distances are wider than in crystalline materials. Consequently, the halfwidth of a given band in the spectrum from a melt is greater than for the same band derived from a crystalline material. In fact, trends in halfwidths as a function of intensive and extensive variables may yield structural information about the silicate melt or glass (Brawer and White, 1975). If it is assumed that these expanded ranges result from thermal agitation, a Boltzmann type distribution may be expected. In the present report, it is assumed that the distribution may be described with symmetric Gaussian functions. This
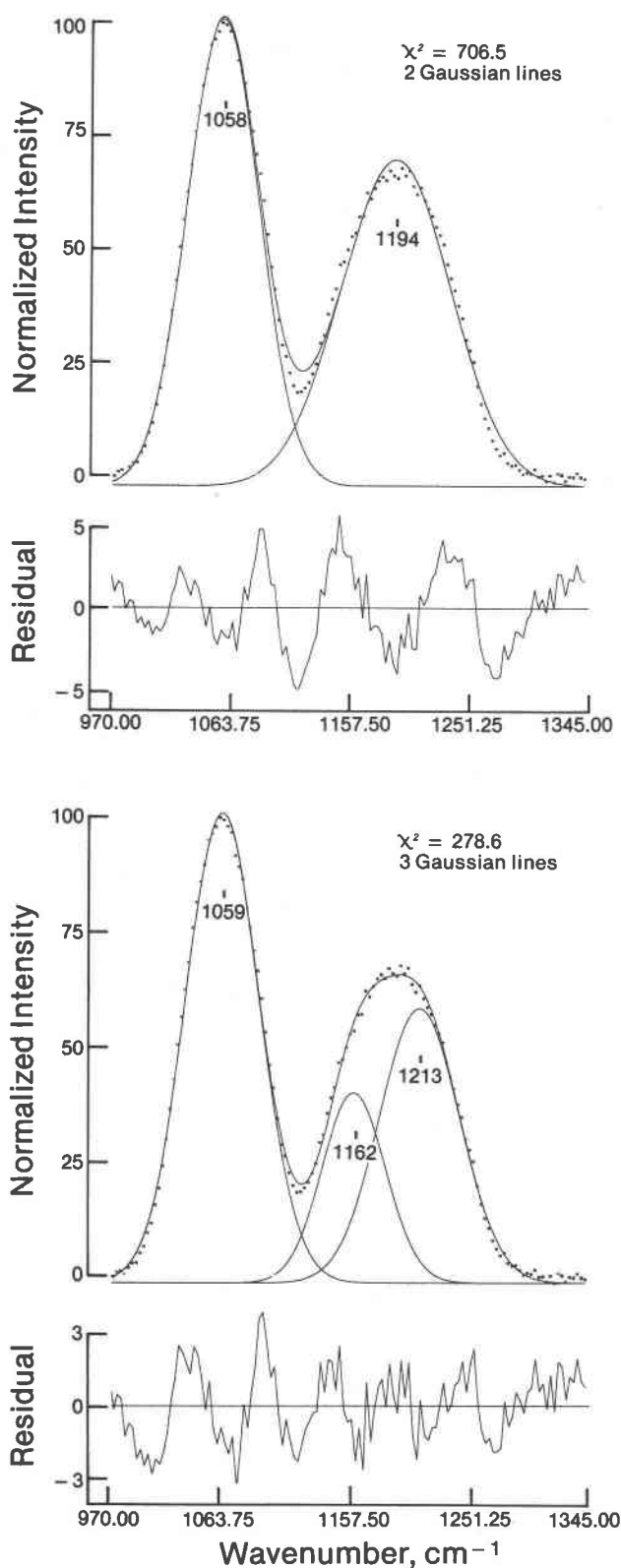
Fig. 2. High-frequency envelope of fitted spectra of vitreous SiO$_2$ as a function of number of lines.

is considered a reasonable assumption if, in fact, one is observing a Boltzmann distribution of the light-scattering elements in the silicate melts and glasses.

Neither of these assumptions can be tested independently. Many Raman bands in the raw spectra are asymmetric. However, it is suggested here, as also done, for example, by Hartwig (1977) for H$_2$O in vitreous silica, that such asymmetries are due to the superimposition of several bands with different line parameters. The goal in the present study is to separate those bands.

One of the relevant tests of distribution of Si–O–Si angles in amorphous silicate materials may be found in Soules (1979) and Gaskell and Tarrant (1980) for vitreous SiO$_2$. Those authors concluded that the angle distribution is asymmetric. Consequently, on the basis of a single three-dimensional structure for vitreous SiO$_2$, one might expect to find asymmetric Raman bands. High-resolution electron microscopy of such materials (Gaskell, 1975; Gaskell and Mistry, 1975) reveals, however, that even an apparently simple compound like vitreous SiO$_2$ consists of more than one type of structure. Furthermore, the Raman spectrum of vitreous SiO$_2$ cannot be interpreted on the basis of a single structure unless the unlikely long-range order is invoked (Mammone *et al.*, 1981; Seifert *et al.*, 1981). With more than one three-dimensional structure, the asymmetry observed by Soules (1979) and Gaskell and Tarrant (1980) may be understood. This reasoning also shows, however, that independent data on Si–O–Si angles in a presumed simple structure such as that of vitreous SiO$_2$ may have several interpretations.

Whether the presence of asymmetric bands in a Raman spectrum is due to the fact that individual bands are asymmetric or whether the asymmetry is due to the superimposition of several symmetric bands with different line-parameters can only be tested with detailed knowledge of the structure of the material. For silicate melts and glasses, such information does not exist. It seems reasonable to *assume*, however, that the bands will be symmetric. Inasmuch as this conclusion cannot be proven, it remains an assumption.

It is also assumed that the individual bands have Gaussian line shape. With these two assumptions, the Raman spectra of silicate melts and glasses have been fitted statistically with *no additional* constraints or assumptions. At present, the only available test for these assumptions is the internal con-

sistency of structural models thus derived and the extent to which such models can be used to predict physical and chemical properties of silicate melts. A very brief summary of important structural features will be presented below. Relationships between structure and properties may be found in Mysen *et al.* (1980, 1981, 1982).

Number of bands

In deconvoluting a given envelope it is necessary to determine the number of bands to be included. In the absence of other information, initial fitting is carried out with the number of bands indicated by the topology of the Raman spectra (maxima and inflections). The high-frequency envelope of the spectrum of vitreous SiO_2 indicates the presence of two bands, for example (Fig. 2).

The computer routine, when the spectrum is fitted with three rather than two bands, places the third band near 1157 cm^{-1} in vitreous SiO_2 and near 960 cm^{-1} in vitreous GeO_2 (Figs. 2 and 3). The existence of a third band is not clearly indicated by the topology of the high-frequency envelopes. It is noted, however, that if only one band near 1190 cm^{-1} were included, it would be asymmetric and would show a distinctly flat maximum. Inclusion of

a third band resulted in a 60% reduction of χ^2. It is suggested, therefore, that three bands make up the high-frequency envelopes in the Raman spectra of vitreous SiO_2 and GeO_2. The existence of a band near 1160 cm^{-1} and one near 1210 cm^{-1} in place of only one near 1190 cm^{-1} was interpreted by Seifert *et al.* (1981) to be due to two six-membered, interconnected rings in the three-dimensional network structure. The rings differ in Si–O–Si angle by about 5° when the band position is calculated with the central-force model of Sen and Thorpe (1977).

Another example of improvement of the fit, by starting with a minimum number of bands and increasing this number until no further improvement in χ^2 occurs, is exemplified by the high-frequency envelope of quenched AS50 melt (NaAl-Si$_4$O$_{10}$; Figure 4). The form of the high-frequency envelope indicates that two bands, at 1078 and 1161 cm^{-1}, respectively, may be present. The quality of the fit, as indicated by the significant (Hamilton, 1965) decrease in χ^2 and the randomness of the residuals, is improved systematically until six lines are inserted. The structural interpretation of the six-line fit in conjunction with the rest of the spectrum (see Seifert *et al.*, 1981) is consistent with other spectra of melts on the join NaAlSiO$_4$–SiO$_2$ (Seifert
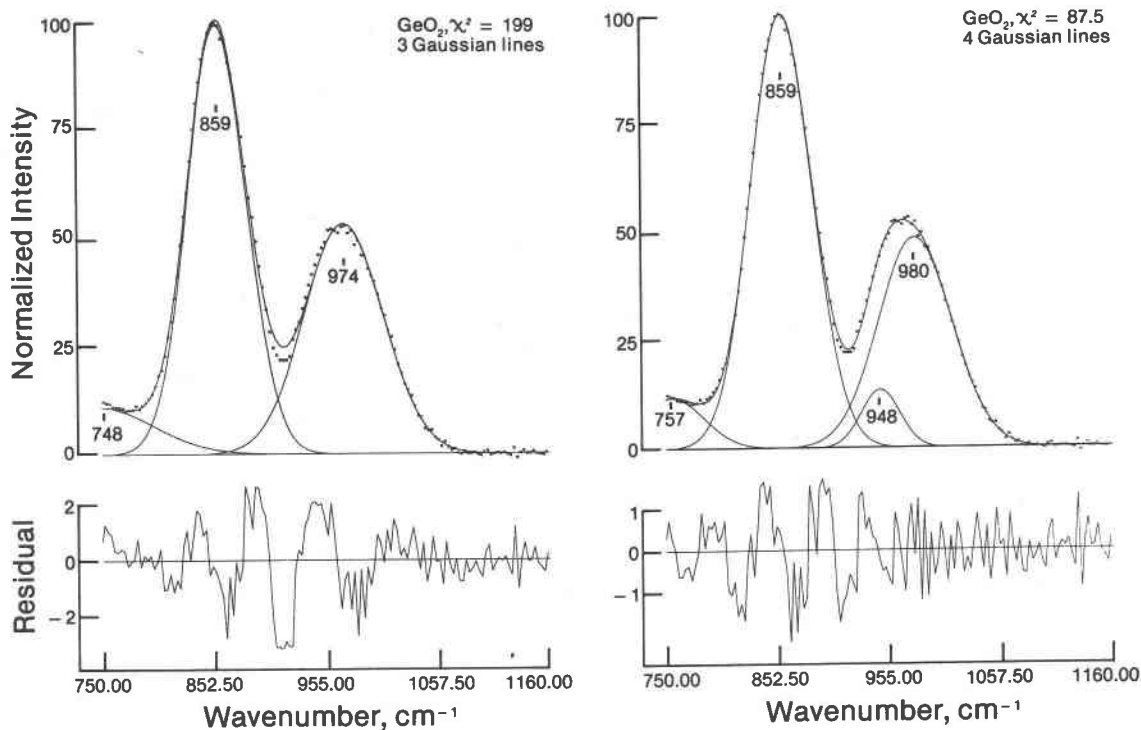

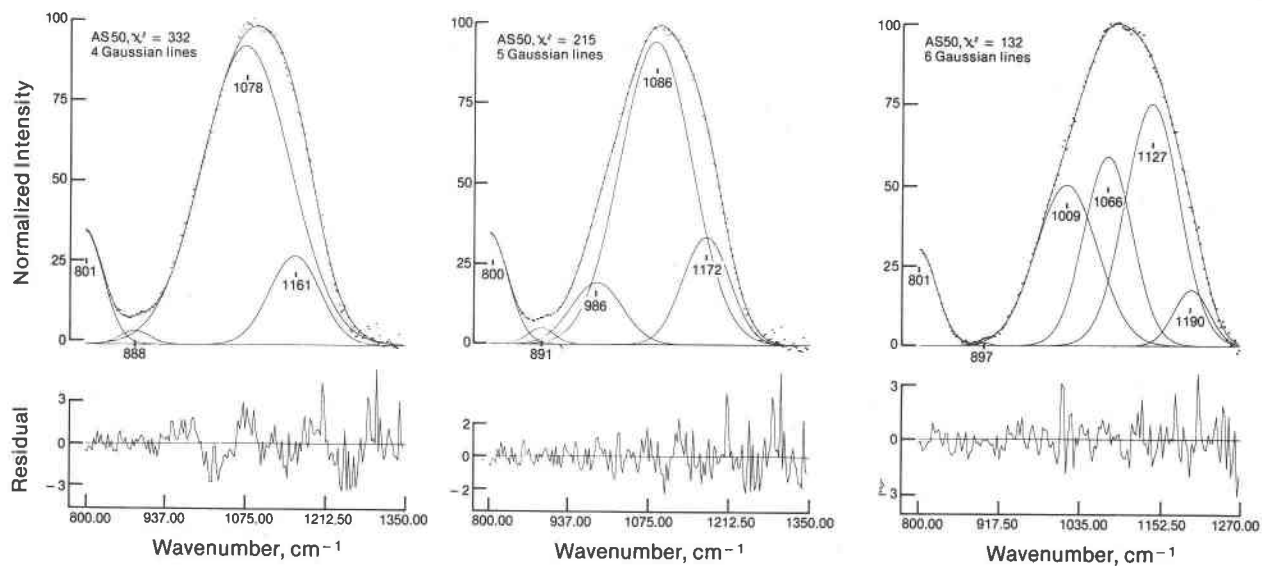Fig. 3. High-frequency envelope of fitted spectra of vitreous GeO_2 as a function of number of lines.

Fig. 4. Fitted high-frequency envelopes of three-dimensional aluminosilicate melt AS50 ($NaAlSi_4O_{10}$) as a function of the number of lines.

et al., 1981; see also Figure 5), whereas the fit with five or less bands (with the exception of Ne) is not. When the number of bands is increased beyond six they cannot be fitted without constraints on line shapes (half-width and intensity) or line positions (frequency). This interpretation, based exclusively on statistical tests on the quality of the fits (Hamilton, 1965), is also consistent with thermochemical data on the system (Flood and Knapp, 1968; Navrotsky *et al.,* 1980). These relations would not be obtained with other than six lines (five lines for Ne).

Raman spectra of glasses on binary metal oxide-silica joins in the frequency range between 800 and 1200 cm^{-1} are dominated by bands that stem from symmetric stretch vibrations (Verweij, 1979a, b; Brawer and White, 1975, 1977; Furukawa and White, 1980; Mysen *et al.,* 1980, 1982; Furukawa *et al.,* 1981). These bands tend to be narrower and better defined in the raw Raman spectra than those resulting from antisymmetric stretch vibrations of bridging oxygens, as indicated by the spectra in Figures 2 and 6.

An example of the use of statistical tests of the quality of the deconvoluted spectra of melts that contain nonbridging oxygens is shown in Figure 6. Composition CS2 ($CaSi_2O_5$) has bulk NBO/Si = 1. A two-line fit (excluding the 779 cm^{-1} band) indicates two bands, at 965 and 1064 cm^{-1}, respectively. A better fit, also indicated by the topology of the high-frequency envelope, includes a band at 861 cm^{-1}.

The bands at 861 and 956 cm^{-1} may be interpreted as due to symmetric stretch vibrations in structural units with NBO/Si = 4 and 2, respectively (Brawer and White, 1977; Furukawa *et al.,* 1978, 1981; Virgo *et al.,* 1980). The frequency of symmetric stretch vibrations increases with decreasing NBO/Si of the structural unit (Furukawa *et al.,* 1981; Brawer and White, 1975). The 1058 cm^{-1} band might be interpreted as one with NBO/Si between 1 and 0. It is, however, known that the symmetric stretch band of sheet-type units occurs near 1100 cm^{-1} (Brawer and White, 1975; Verweij, 1979a,b; Furukawa *et al.,* 1981). It is unlikely, therefore, that the fitted 1058 cm^{-1} band is a single band.

Insertion of a fourth band does lower the value of the χ^2 somewhat, but does not alter the shape and frequency of the 1058 cm^{-1} band significantly. Furthermore, there is no clear interpretation for the 1010 cm^{-1} band that occurs in the four-line fit.

Inclusion of more bands results in a significant (Hamilton, 1965) lowering of χ^2, and the residuals become randomly distributed. Both the five- and the six-line fit have structural interpretations consistent with the interpretations of other compositions on the join CaO–SiO_2 and other metal oxide-silica joins, and most important, this solution can be interpreted consistently with the other bands occurring in the spectrum of $CaSi_2O_5$ glass. The interpretations are: 864 cm^{-1} band, symmetric stretch from an SiO_4^{4-} unit; 906 cm^{-1} band, symmetric stretch
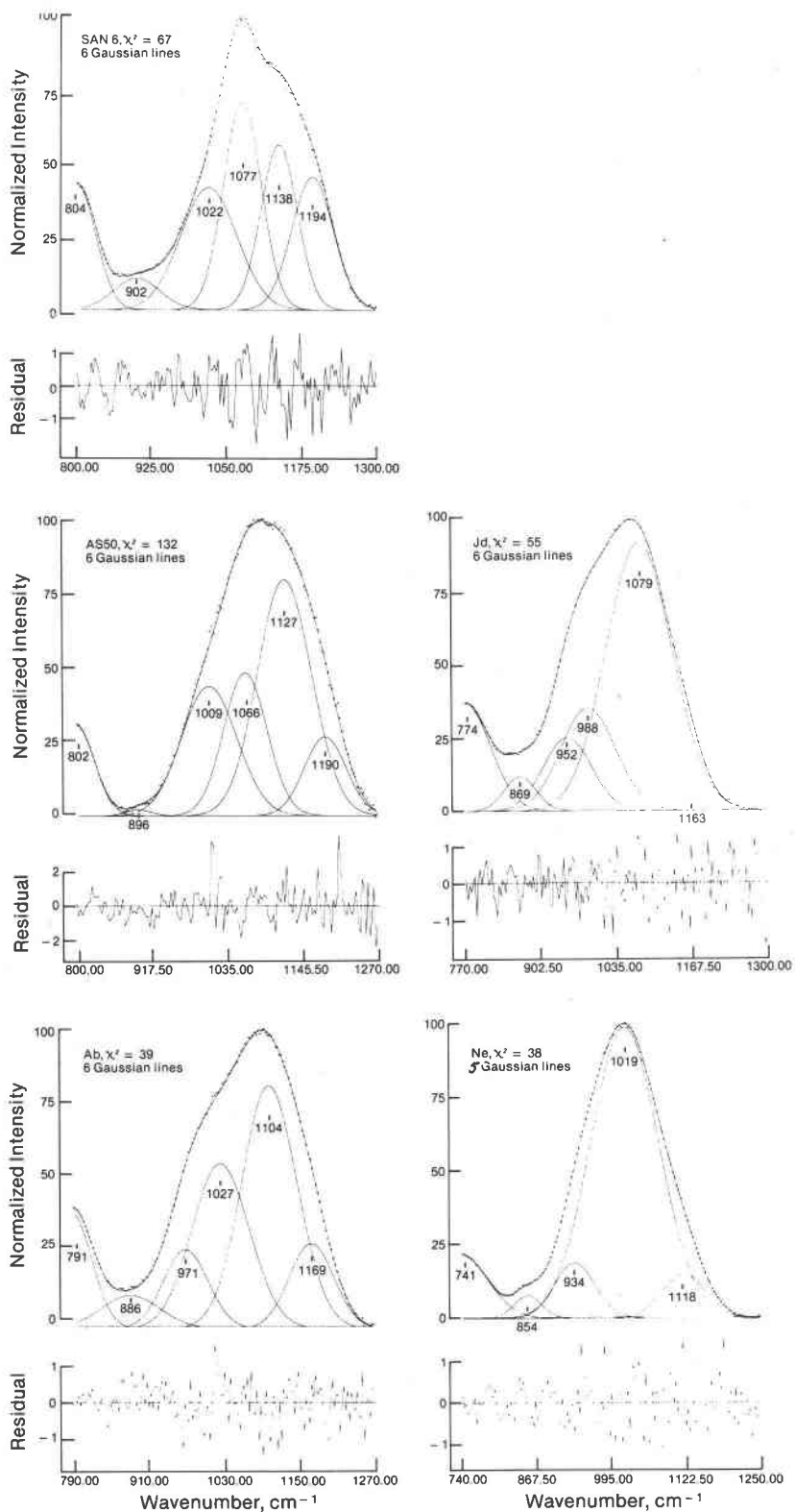
Fig. 5. Best fit of high-frequency envelopes of spectra for melts on the join $SiO_2NaAlSiO_4$. SAN 6, $Al/(Al + Si) = 0.125$; AS50, $Al/(Al + Si) = 0.200$; Ab, $Al/(Al + Si) = 0.250$; Jd, $Al/(Al + Si) = 0.333$; Ne, $Al/(Al + Si) = 0.500$.
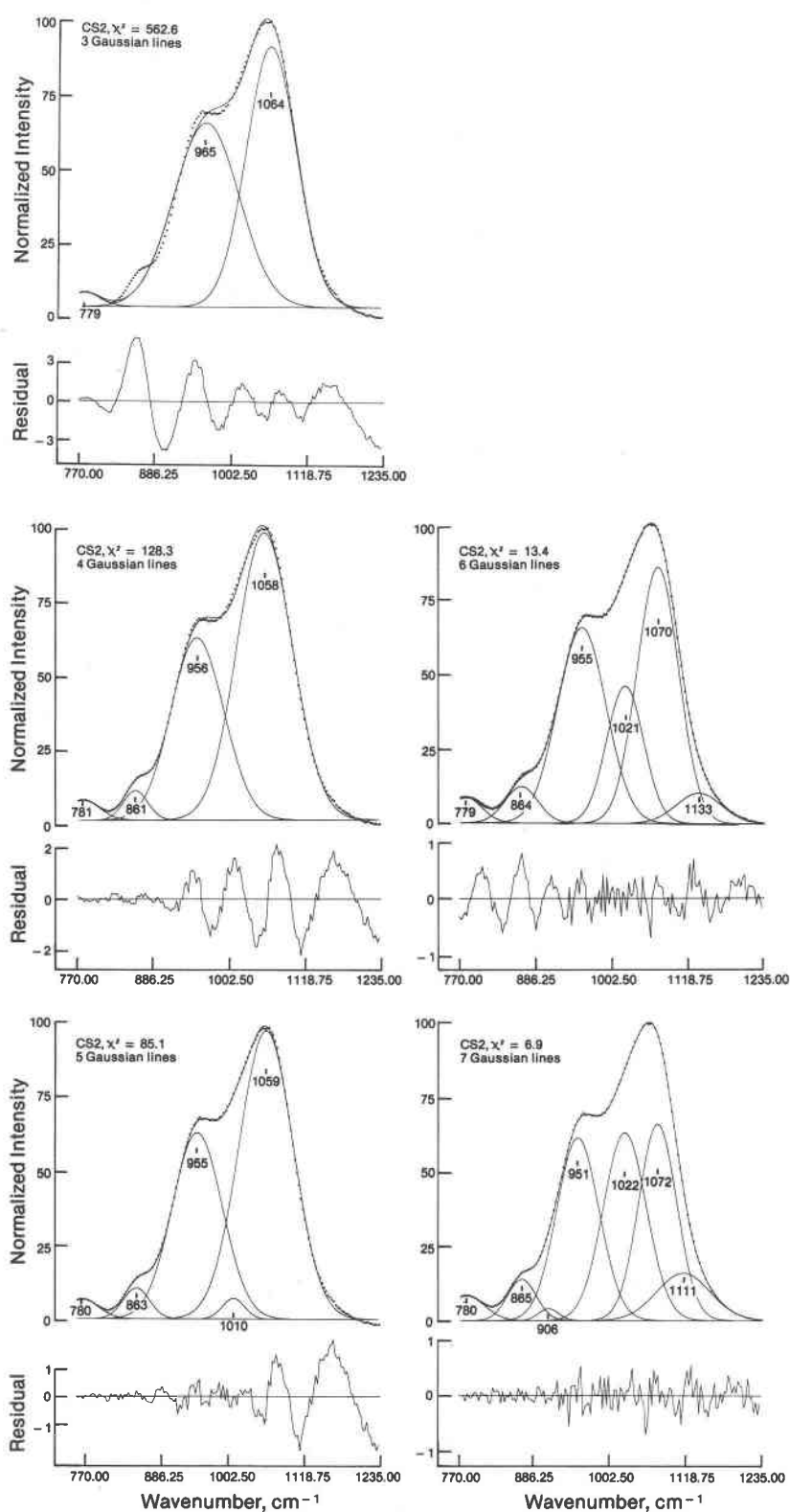
Fig. 6. Relationships between quality of the fit and the number of lines in the high-frequency envelope of melt of $CaSi_2O_5$ composition (CS2).
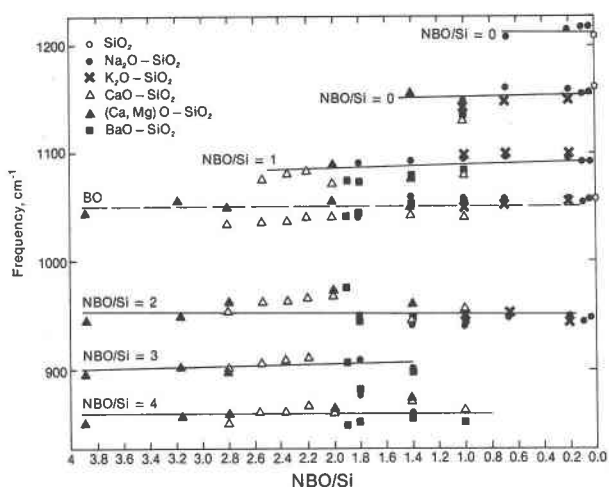
Fig. 7. Summary of results on line positions (frequency) of symmetric stretch bands determined with the fitting procedure discussed in the text for binary silicate melt compositions on the joins SiO_2–Na_2O, SiO_2–K_2O, SiO_2–CaO, SiO_2–$(Ca,Mg)O$, and SiO_2–BaO.

from an $Si_2O_7^{6-}$ unit; 951 cm^{-1} band, from an SiO_3^{2-} unit; 1072 cm^{-1} band, from an $Si_2O_5^{2-}$ unit (see Brawer, 1975; Lazarev, 1972; Verweij, 1979a,b; Furukawa et al, 1978, 1981; Mysen et al., 1980). The 1111–1133 cm^{-1} band (the exact frequency depends on the number of bands fitted) most likely corresponds to that of the W4 vibration observed in vitreous SiO_2 (Sen and Thorpe, 1977; Galeener, 1979). The existence of this band together with associated W1, W2, and W3 bands (Sen and Thorpe, 1977; see Mysen et al., 1980) at lower frequencies indicates that three-dimensional network units are present in $CaSi_2O_5$ glass. The 1022 cm^{-1} band may be considered an antisymmetric stretch vibration (W2 in the terminology of Sen and Thorpe, 1977) stemming from bridging oxygens (with no regard for structural units) in the melt.

More than seven bands cannot be fitted without constraints on line parameters. The philosophy behind the approach discussed here is that none of the line-parameters (half-width, intensity and position) of any of the bands should be constrained. As already mentioned, it is assumed that the lines are symmetric and of Gaussian line shape. No additional assumptions and no subjective judgment are involved, however, in fitting such bands to the envelopes. With this philosophy in mind it is inferred that the spectrum of CS2 melt requires only seven bands in this particular frequency range. The model of CS2 melt thus derived with only statistical tests (Hamilton, 1965) on the quality of the decon-

voluted spectrum is also consistent with a more general model of melt structure of binary metal oxide-silica melts (Virgo et al., 1980; Mysen et al., 1980; Furukawa et al., 1981). A summary of the positional data on stretch vibrations obtained for a number of compositions with the present procedure is shown in Figure 7.

Area ratios and abundance of structural units

In order to understand the crystallization behavior of silicate melts, as well as properties such as viscosity, density, and compressibility, it is necessary to know the proportions of the structural units that occur in the melt. Such information can be obtained from deconvoluted Raman spectra of relevant compositions provided that area ratios of individual bands can be related to relative abundance of the associated structural units.

The area ratios may be calculated from a set of deconvoluted spectra of melts with different bulk NBO/Si but the same types of coexisting structural units. Melt compositions on the join CaO–SiO_2 (Table 1) will be used as an example. Deconvoluted high-frequency envelopes of the relevant Raman spectra are shown in Figure 8. The area ratios from Figure 8 may be related to the abundance of structural units giving rise to the stretch vibrations with the Raman bands in Figure 8.

The relative intensity of each band (Fig. 8) is, however, a function of scattering properties of the appropriate bonds in the structural units (see Long,

Table 1. Composition of starting materials and comparison of theoretical with measured ratio of nonbridging oxygens per tetrahedral cations.

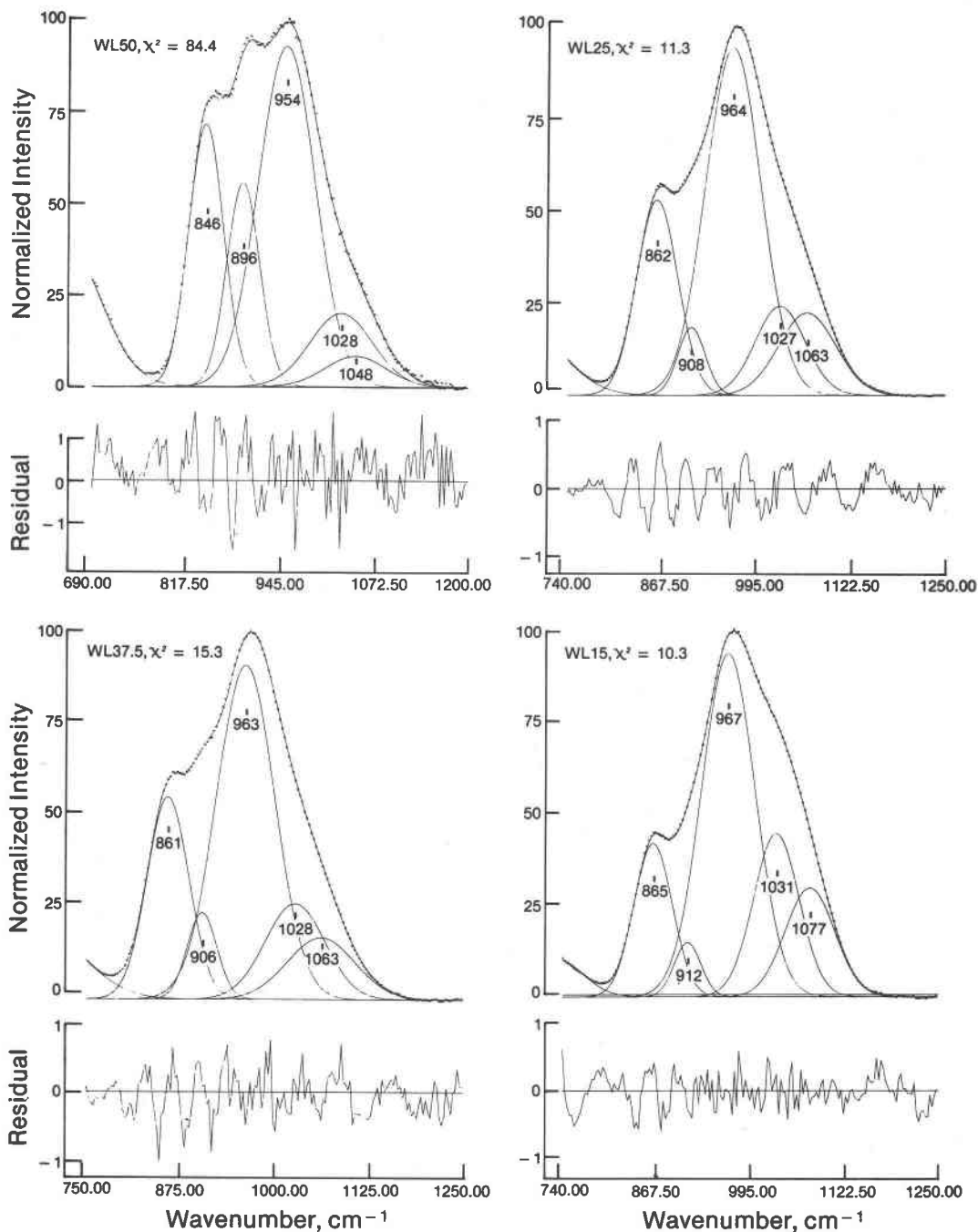|	WL50	WL37.5	WL25	WL15
	Weight percent oxide			
SiO_2	43.30	45.41	47.51	49.19
CaO	56.70	54.59	52.49	50.81
	Normalized cross sections			
[a]SiO_4^{4-}		1.456		
[a]$Si_2O_7^{6-}$		1.401		
[a]$Si_2O_6^{4-}$		0.428		
[a]$Si_2O_5^{2-}$		2.500		
	NBO/Si			
Theoretical NBO/Si	2.81	2.58	2.37	2.21
Calculated NBO/Si	2.78	2.51	2.44	2.23

Fig. 8. Fitted high-frequency envelopes of Raman spectra of melts on the join SiO_2–CaO used in the calculation of results shown in Table 1.

1977, for discussion of effects). Normalized Raman cross sections, which include geometric properties and polarizability of the relevant bonds, may be determined empirically from sets of Raman spectra.

The procedure involves simultaneous solution of a number of linear equations, (i). This method requires acquisition of spectra from at least i–1 compositions. Normalized cross sections, a_i, are then related to A_i, the relative area of i, and are mass-balanced with the ratio of nonbridging oxygens per tetrahedral cation, n_i, so that the sum of n_i is equal to the bulk NBO/T:

$$\Sigma\, a_i n_i A_i = \text{NBO}/T, \qquad (2)$$

$$\Sigma\, a_i A_i = 1, \qquad (3)$$

and

$$\Sigma \, x_i = A_i a_i, \qquad (4)$$

where x_i is the mole fraction of species i.

Inasmuch as area ratio determinations have small, but finite, uncertainties (approximately 5%), the equations are not always amenable to rigorous solution. Consequently, least-squares minimization is preferred.

An example of the results that may be obtained is given in Table 1 for compositions in the system $CaO–SiO_2$ and NBO/Si > 2. It can be seen from the data in Table 1 that the calculated NBO/T from the mole fractions of the structural units is within 3% of the theoretical value (calculated from the stoichiometry of the bulk composition). It is concluded, therefore, that deconvolution of Raman spectra of amorphous materials provides data that can be used to determine proportions of structural units in silicate melts.

Acknowledgments

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