OH groups in the glass must be bound to a species with a vibration near 1000 cm⁻¹, either an Si-O or Al-O bond, or a TOT linkage (Newman et al., 1986; Pichavant et al., 1992; McMillan et al., 1993). Consistent with this assignment, the infrared and Raman spectra of hydrous SiO₂ glasses contain a peak at 970 cm⁻¹, due to stretching or bending of Si-OH groups in the glass SiO₄ and Wallatium. In 1976, Harwig and Ram 1977, Nyssen and Virgo (1996), McMillan and Bernede (1996) (see Chapter 4). A similar feature appears near 900 cm⁻¹ in the spectra of hydrous aluminosilicate glasses, which could be due to either a terminal Al-OH species, or to a protonated Al-OH linkage (Kohn et al., 1989a; McMillan et al., 1993; Sykes and Kubicki, 1993) (Chapter 4).

If this 900 cm⁻¹ band is in fact due to a protonated Al-OH linkage, and the water dissolution model proposed by Kohn et al. (1989a) is correct (see Chapter 4), there should be Na⁺⁺. OH⁻ species present in the hydrous glass, presumably as hydration complexes (Pichavant et al., 1992). The vibrations contributing to the 4500 cm⁻¹ combination band then only represent one half of the OH species present, with the result that the determined value for the molar absorptivity (see below) is in error by a factor of two. It is interesting that there is an overtone band near 4000 cm⁻¹ in the infrared spectra of hydrous aluminosilicate glasses (Solper, 1982a,b; Neustadt et al., 1986) (Fig. 12) which has not been satisfactorily assigned. This could be due to the combination of the O-H stretching vibration with that of a metal-oxygen stretching (e.g. Na-O stretching, such a complex (Pichavant et al., 1992). This observation would not, however, affect either the conclusions or the analysis results obtained by Solper and colleagues, because the molar absorptivity values obtained in those studies are all internally consistent, and return correct values for the total water content.

CO₂, CO, and CO₂⁻. Carbon-oxygen species form the second major class of volatiles analyzed routinely by quantitative FTIR spectroscopy. The diatomic molecule CO has no characteristic absorption at 2345 cm⁻¹, and is visible in infrared and Raman spectra. From micro-Raman studies, this species is known to be present in CO₂-CO fluid inclusions (Bergman and Dubessy, 1984). However, it is unlikely that molecular CO is an important dissolving species in silicate melts, based on the experimental findings of Pawley et al. (1992) on basaltic liquids in equilibrium with CO₂-CO₂ fluids.

Carbon dioxide forms a linear symmetric molecule in the gas phase. The expected vibrational modes include the symmetric (ν₁) and asymmetric (ν₃) CO stretching modes, and a doubly degenerate O=O bending mode (ν₄). The symmetric stretching vibration ν₁ is only Raman active, whereas ν₂ and ν₃ are only infrared active. As expected, the infrared spectrum of CO₂ shows two strong absorption bands due to the ν₁ and ν₂ vibrations, at 2349 and 667 cm⁻¹, respectively (Herrberg, 1945). However, the observed Raman spectrum shows two strong peaks in the CO₂ stretching region, near 1388 and 1286 cm⁻¹ (Fig. 15). These two peaks are due to Fermi resonance between the ν₁ fundamental and the first overtone of the bending vibration, ν₂ (Herrberg, 1945). The normally weak ν₂ overtone gains a large component of the character of the ν₁ vibration through the Fermi coupling, and becomes strongly Raman active (Herrberg, 1945). The frequencies of both components are affected by this vibrational coupling, in that both move away from the positions of their unperturbed components. The result is two new vibrational modes (denoted ν₄ and ν₂), each of which has a partial character of both the ν₁ and ν₂ components.

The relative intensities of the ν₁ and ν₄ species are less than the ν₂ and ν₃ components of the Fermi doublet of CO₂ is critically dependent on the angle of 106°, which is extremely sensitive to the molecular geometry and to any intermolecular interactions. The relative

### Figure 15

**Raman spectrum of CO₂ vapor in the CO-stretching region from a fluid inclusion in a quartz crystal.** The two strongest peaks are the ν₁ (ν₂) and low-frequency (ν₄) components of the ν₁/ν₂ Fermi doublet of normal isotopic CO₂ used in quaternary studies. Weaker peaks due to the Fermi doublet of 13CO₂ are also present (Howard, 1974). An additional peak at 1490 cm⁻¹ is due to a 'hot band' transition from the first excited state of the bending vibration (the 010 → 110 transition; Hersberg, 1945).

**Raman shift (cm⁻¹)**

| 1550 | 1500 |
| 1450 | 1400 |
| 1350 | 1300 |
| 1250 | 1200 |

### Figure 16

**Vibrational modes of the free CO₂ molecule, with trigonal D₃h symmetry.** The frequencies given are those measured in aqueous solution. The totally symmetric stretching vibration is only Raman active, the out-of-plane bend (ν₂) only appears in the infrared spectrum, and the other vibrations are infrared and Raman active. Disrotation of the molecular bonds results in splitting of the asymmetric stretch (ν₁) into two components, and the symmetric stretch may become weakly infrared active.
Quantitative vibrational spectroscopy

Infrared absorption: theory. Because this is the primary technique used in determination of volatile species concentration via FTIR spectroscopy, it is important to understand the theoretical basis for the method.

When a beam of infrared light with incident intensity \( I_0 \) (this is the incident intensity) is passed through a sample of thickness \( d \) (which is conventionally given in cm), it is attenuated at the vibrational frequency \( v \) by interaction with the absorbing species in the sample. The transmitted intensity \( I \) is given by:

\[
I = I_0 e^{-\alpha d}
\]

(6)

The constant \( \alpha \) is known as the absorption coefficient associated with the infrared active vibrational mode with frequency \( \nu \), and its magnitude reflects the degree of infrared activity of that mode. Within a harmonic model, the theoretical expression for the net absorption coefficient for a collection of \( N \) molecules per unit volume is given by (Stuehr, 1971):

\[
\alpha = \frac{N}{d} \left( \frac{\pi \nu}{3 \hbar} \right)^2 \frac{d\nu}{d\alpha}
\]

(7)

Here \( m^* \) is the reduced mass of the molecule, \( n \) is the quantum number of the lower vibrational energy level, \( v \) is the vibrational frequency, and \( \hbar \) is the speed of light. The magnitude of the absorption coefficient also depends upon the square of the change in molecular dipole moment during the vibrational displacement, as defined above. In this expression, \( \alpha \) is independent of temperature and frequency, for a given vibrational mode (Saele, 1971). This is no longer strictly true for the vibrations of real anharmonic molecules, for which \( \alpha \) becomes temperature dependent, and the vibrational transitions for even a single molecule are spread over a band of frequencies.

For quantitative analysis applications, it is usual to work in decimal logarithms, and the corresponding intensity expression becomes

\[
I = I_0 10^{-\alpha d}
\]

(8)

The decadic absorption coefficient is \( K \), with \( K = 2.303 \times 10^4 \). For quantitative analysis of a sample containing a uniform concentration of the absorbing species \( c \) moles per liter, the corresponding expression is the Bouger-Beer-Lambert law:

\[
I = I_0 e^{-Kc b}
\]

(9)

The parameter \( c \) is known as the extinction coefficient, with \( c = \text{K/mole units} \). The transmittance of the infrared beam through the sample is given by

\[
T = \frac{I}{I_0}
\]

(10)

usually expressed as a percentage. In an FTIR experiment (see below), it is usual to plot a blank spectrum to account for the spectral response of the spectrometer system, and absorption by any species in the sample compartment environment (e.g., water vapor in the air, etc.). The transmittance of the blank is

\[
T = \frac{I}{I_0}
\]

(11)

The absorbance due to the species of interest is then given by

\[
A = \log \left( \frac{I_0}{I} \right)
\]

\[
A = \log \left( \frac{I}{I_0} \right)
\]
For a completely (cosine) distribution of disks, as found in a volatile-bearing glass, the orientation factor is 0.33.

From comparison of values for the 0.4 to 9.1 micron continuum obtained for different hydrous minerals and glasses, the amplitude of the extinction coefficient of similar material in the optical region is approximately 100,000,000 cm⁻² per cc of 100% mainstream 500°C. The measured minima and maxima in parallel and perpendicular polarization are largely parallel to the strength of the admittance factor (1/1.3).

Potential application of the technique. The basic instrumentation required for the procedure is a spectrophotometer equipped with suitable accessories to cover the spectral region of interest. While it is desirable to obtain data at 0.4 to 10.0 microns, the information obtained at 0.4 to 1.0 microns is more readily available due to the availability of the necessary optical instrumentation and the sensitivity of the equipment to small changes in the optical properties of the sample. The sensitivity of the equipment to small changes in the optical properties of the sample is such that the signal-to-noise ratio is typically 100:1. The signal-to-noise ratio is typically 100:1, and the sensitivity of the equipment to small changes in the optical properties of the sample is such that the signal-to-noise ratio is typically 100:1.

The technique is applicable to the determination of the optical properties of hydrous minerals and glasses, and it is also applicable to the determination of the optical properties of minerals and glasses that are isotropic. The technique is applicable to the determination of the optical properties of hydrous minerals and glasses, and it is also applicable to the determination of the optical properties of minerals and glasses that are isotropic.

Light from the different spectrophotometers is filtered to match the performance of the spectrophotometer. The spectrophotometer is designed to be used with a single spectrophotometer, and it is not recommended for use with a spectrophotometer that is not designed to match the performance of the spectrophotometer.

The technique is applicable to the determination of the optical properties of hydrous minerals and glasses, and it is also applicable to the determination of the optical properties of minerals and glasses that are isotropic. The technique is applicable to the determination of the optical properties of hydrous minerals and glasses, and it is also applicable to the determination of the optical properties of minerals and glasses that are isotropic.

The technique is applicable to the determination of the optical properties of hydrous minerals and glasses, and it is also applicable to the determination of the optical properties of minerals and glasses that are isotropic. The technique is applicable to the determination of the optical properties of hydrous minerals and glasses, and it is also applicable to the determination of the optical properties of minerals and glasses that are isotropic.
Determinations of CO-bearing species in the atmosphere are usually made using an infrared spectrometer, which measures the intensity of infrared radiation absorbed by the sample. The infrared radiation is usually obtained using a thermal detector, such as a photoconductive detector or a pyroelectric detector. The sample is usually passed through a gas chromatograph to separate the individual components before being introduced into the infrared spectrometer. The infrared absorption spectrum of each component is then measured and compared to a reference spectrum to determine the concentration of the component in the sample.

Infrared spectrometry is a valuable tool for the detection and quantification of trace gases in the atmosphere, and is widely used in environmental monitoring and research. It is particularly useful for the detection of greenhouse gases, such as CO2 and CH4, which are important contributors to global warming.

However, infrared spectrometry can be limited by the presence of other gases in the atmosphere, which can interfere with the measurement of the target gas. This is known as spectral interference, and can be minimized by using a high-purity sample, or by using a selective detector.

In conclusion, infrared spectrometry is a powerful tool for the detection and quantification of trace gases in the atmosphere, and is widely used in environmental monitoring and research. It is particularly useful for the detection of greenhouse gases, such as CO2 and CH4, which are important contributors to global warming. However, spectral interference can limit the accuracy of measurements, and care must be taken to minimize its effects.
of extremely low concentrations of dissolved volatile species, possibly down to the ppm range (Meudel et al., 1993).

In selecting small sample areas, the minimum section dimension is generally fixed by the wavenumber range of interest. For example, 1500 cm\(^{-1}\) (for carbonate analysis) corresponds to a light wavelength of 6.7 \(\mu\)m, so that sample dimensions down to approximately twice this value can be studied without fringes from diffraction of the infrared beam by the aperture interfering with the spectrum. In practice, even if interference fringes do begin to appear, these form a regular pattern in frequency space, and so correspond to a single point in the FTIR interferogram. This can be removed by computer subtraction before Fourier transformation of the data. Studies in the near-IR region permit even smaller apertures to be selected, on the order of 1 to 2 \(\mu\)m for the first overtone of O-H stretching near 7000 cm\(^{-1}\). The principal limitation in these experiments becomes the intensity of the source radiation and the sensitivity of the detector used.

For quantitative infrared absorbance measurements, doubly polished sections of the volatile-containing plan are prepared, usually by manual polishing. Sample chips are mounted in epoxy in an orthodontic resin works well, and glued to microscope slides using an adhesive solvable in acetone (e.g., Crystalbond 599, supplied by Arco Products, Inc.). Doubly polished sections are prepared by grinding and polishing with alumina and diamond paste on diamond-impregnated paper (water and curing oil used as lubricants: alcohol tends to soften the resin). It is best to finish with \(9 \mu\)m abrasive: a good surface polish makes it easier to locate features on or within the samples for choice of regions for analysis (a few surface scratches can help in "mapping" the surface). Samples can be stored in air after polishing. Because the volatile system is measured in the bulk sample, traces of adsorbed atmospheric water or CO\(_2\) do not affect the results. However, special care should be taken with samples with a high alkali content (or some germanium), which react substantially with atmospheric water and CO\(_2\). These should be stored in a desiccator or dry box.

The final sample thickness depends on the volatile content and the extinction coefficient of the peaks to be measured. For example, the extinction coefficient for the fundamental O-H stretching vibration lies between 50 and 100 L/cm mol (Newman et al., 1986). For a sample containing 5 wt % water, the sample thickness would be required to be less than 40 \(\mu\)m to have transmission greater than 1% (absorbance less than 2). For this reason, it is not usually convenient to use the fundamental O-H stretching vibration for routine water determination at high concentrations. The molar absorbivities of some overtone bands of hydroxyl species lie in the range between 0.1 and 2 L/cm mol (Table 2).

For water determinations using these bands, samples ranging in thickness from several tens to several thousand \(\mu\)m (1 cm = 1000 \(\mu\)m) are prepared. Concentrations of carbonates are usually on the order of 0.1 wt % or less. The extinction coefficients for C-O stretching vibrations lie in the range between 200 and 1000 L/cm mol (Table 2), and those studied for CO\(_2\) and CO\(_2\) determination have thicknesses on the order of 0.1 to 2 \(\mu\)m (Table 2).
Table 1. Determination of CO\(_2\) and CO\(_3\) concentration in glass.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO(_2) (ppm)</th>
<th>CO(_3) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>25.3</td>
<td>12.4</td>
</tr>
<tr>
<td>Sample 2</td>
<td>30.5</td>
<td>15.7</td>
</tr>
</tbody>
</table>

The infrared spectrum of CO\(_2\) in glass is used to determine its concentration.

For comparison with the CO\(_2\) concentration, a CO\(_3\) value is also determined by the method described above.

The results obtained by this method are in good agreement with the values obtained by the wet chemical method.

Further studies are required to establish the reliability of this method for the determination of CO\(_3\) in glass.
The mid-IR spectrum was measured in the region of 1600 cm\(^{-1}\) to obtain an absorption coefficient for the fundamental H\(_2\)O bending vibration at 1630 cm\(^{-1}\) (6.13 μm). The molar absorptivity for this band was found by subtracting the uncorrected absorbance at 5200 cm\(^{-1}\) (0.19 μm) and the baseline at 5000 cm\(^{-1}\) to obtain the absorbance normalized over 5000 cm\(^{-1}\) (Table 2). Newman et al. (1986) noted that the molar absorptivity of the OH stretching fundamental at 3570 cm\(^{-1}\) decreased with increasing total water content, and suggested that this may be due to the differing proportion of H\(_2\)O molecules and hydroxyl groups contributing to the OH stretch. By modeling the observed absorptions of this band as a sum of contributions from the two species, Newman et al. (1986) obtained different values for both OH-containing species (Table 2). Newman et al. (1986) likewise observed separate molar absorptivities for the OH stretching overtone, and for the band near 4000 cm\(^{-1}\) (Dobson et al. 1989). Dobson et al. (1989) also noted that the extractions of Newman et al. (1986) were incomplete in that small amounts of water remained in glassy run products after extraction. Dobson et al. (1989) succeeded in dissolving their samples by holding the glassy chips at temperatures just below their softening points for durations up to about eight hours. Higgin and Stolper (unpublished results) have shown that additional water molecules can be trapped in bubbles in water-rutile rhodochrosite samples, thus preventing the complete extraction of volatiles for manometric analysis. They have demonstrated that slow cooling reduces the temperature at which reaction between 200 and 400°C will eliminate the formation of "frosty" run products centered at approximately 9500 and 5500 cm\(^{-1}\) (Bell et al., 1976; Goldman and Berg 1980; Rosman, 1988). These provide a broad baseline underneath the vibrational overtones, which must be subtracted for quantitative analysis (Dixon et al. 1994). This can be achieved either by fitting the baseline spectrum with a sum of Gaussian bands (Dixon et al. 1994) or simply by tracing the form of the baseline with a french curve (Ciechlo, 1994; Ciechlo and Holloway, in press). The former method has the advantage that it can be quantified and easily reproduced; however, the second allows for some "artistic impression" in obtaining the best fit. The error introduced by both is likely of the same order; however, unfortunately, these features can not simply be removed by subtracting the spectrum of a water-free sample recorded under the same conditions, because changes occur in the "baseline" spectrum due to removal of the water.

In an extension of the quantitative IR technique to carbon-bearing species, Fine and Stolper (1985) obtained molar absorptivities for the 1530-1430 cm\(^{-1}\) and 1600-1660 cm\(^{-1}\) bands of CO\(_2\) species and the 2350-2300 cm\(^{-1}\) band of molecular CO\(_2\) dissolved in glasses through the SiO\(_2\)-Na\(_2\)O-C\(_2\)O\(_3\) join. The concentration of C in the glass was assumed to correspond to the total concentration loaded into the capsule; the validity of this assumption was verified for four of the samples by analysis via the \[\text{TICl}_2\text{[T}_{2}\text{C}]\text{Cl}_2\] nuclear reaction technique (see earlier). The molar absorptivities obtained for the three characteristic vibrational modes are listed in Table 3. These values have been applied to measurements of the dissolved CO\(_2\) content and precision in natural obsidians (Newman et al., 1988). In analyses of CO\(_2\) and CO\(_2\) species, Equation (15) is used, but the molar mass of water (18.02) is replaced by that for carbon dioxide (44.01 g/mol). This then returns the concentration of the carbon-bearing species in wt %, expressed as dissolved CO\(_2\). Because CO\(_2\) concentrations are very often low, this number is usually multiplied by 10\(^{3}\) to give the CO\(_2\) concentration in ppm.

Fine and Stolper (1986) next calibrated the infrared technique for a suite of natural basaltic glasses, and several synthetic Ca-Mg olivine and Aluminosilicate glasses. These
authors observed a shift in the higher frequency component of the bonding doublet of CO$_2^+$ compared to the sodium aluminate glasses, down to approximately 1515 cm$^{-1}$. None of the glasses, save one with 1.29 wt % total CO$_2$ content, contained any observable molecular CO$_2$, unlike the sodium aluminate series. The molecular absorptivity for the carbonate band was determined to be 375 L/mol/cm. and Fine and Stolper (1986) suggested that this value should be used for total CO$_2$ content of 5-10 wt %, for similar bulk compositions. This extinction coefficient has been used in subsequent studies of CO$_2$ solubility in bauxitic liquids (Stolper and Holloway, 1988; Dixon et al., 1991; Pan et al., 1991; Pawley et al., 1992).

Stolper et al. (1987) undertook a more detailed study of the solubility and speciation of CO$_2$ dissolved in albic melts. The principal 2350 cm$^{-1}$ band is asymmetric and can be divided into two by two gaussian components. These do not change when the sample is frozen to liquid nitrogen temperature, so these correspond to two different environments for molecular CO$_2$ groups dissolved in the glass. The symmetric stretching band of CO$_2$ molecules is clearly visible in their spectrum (Fig. 17), with a molar absorptivity determined to be 17.74 cm$^3$/mol/cm. The band in the 1600-1700 cm$^{-1}$ region clearly contains two unresolved components (Fig. 17). These correspond to carbonate groups in different chemical environments within the glass, with different degrees of structural perturbation through interaction with the silicate framework. Stolper et al. (1987) obtained a molar absorptivity for this composite band which differed only slightly from that of Fine and Stolper (1985). R. Brooker (unpublished results) has recently carried out an extensive series of studies at Arizona State University, which demonstrate that there are indeed two (and for some compositions, more) carbonate components in these glasses, and that the relative intensities of their contributions to the infrared spectrum change with silica content and metal oxide-alumina ratio. This needs to be further explored in future work, as the different types of carbonate sites will have different molar absorptivity values.

Fogel and Rutherford (1990) applied the extinction coefficient determined by Fine and Stolper (1985) for molecular CO$_2$ in sodium aluminate to measure the CO$_2$ content in natural rhyolite. In a similar study, Blank et al. (1993) developed a new value for the extinction coefficients for this band in rhyolite, but this was not published. Thibault and Holloway (1994) have recently examined the solubility of carbon dioxide in a calcium-enriched carbonate composition. They determined an $\alpha$ of 355 L/mol/cm for the carbonate band at 1515 cm$^{-1}$, slightly lower than that obtained by Fine and Stolper (1986) for Ca-Mg glasses.

Quantitative Raman spectroscopy. Although Raman scattering spectroscopy has not yet been applied to the quantitative study of volatile species dissolved in silicate melts, it has been used extensively in structural studies of volatile-containing glasses (Fig. 16). In addition, quantitative Raman studies are now an essential tool in the chemical characterization of fluid inclusions, which may represent fluids coexisting with a volatile-bearing silicate melt phase at depth. Micro-Raman spectroscopy provides a rapid, non-destructive method for quantitative analysis of species present in glasses and liquids of individual fluid inclusions. Usually a rapid scan over characteristic frequency ranges is sufficient to detect the presence or absence of particular molecular species (Dhanelinecout et al., 1979; Bergman and Dubessy, 1984. Pastier et al., 1984). Along with microthermometry, this is often sufficient to characterize the composition of the inclusion (Dubessy et al., 1989). It is often found that the wavelength of the characteristic Raman line of a particular molecular species is shifted from the gas phase value, which gives additional useful information on the density or internal pressure within