

LAMP/89/1

**INTERNATIONAL CENTRE FOR
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**LAMP
SERIES REPORT**

(Laser, Atomic and Molecular Physics)

**CRITICAL ANALYSIS
OF THE OH FUNDAMENTAL VIBRATIONAL SPECTRUM
OF SUPERCOOLED LIQUID WATER**

John Wiafe-Akenten

1989 MIRAMARE - TRIESTE



**INTERNATIONAL
ATOMIC ENERGY
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**UNITED NATIONS
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October 1989

Preface

The ICTP-LAMP internal reports consist of manuscripts relevant to seminars and discussions held at ICTP in the field of Laser, Atomic and Molecular Physics (LAMP).

These reports aim at informing LAMP researchers on the activity carried out at ICTP in their field of interest, with the specific purpose of stimulating scientific contacts and collaboration of physicists from Third World Countries.

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INTRODUCTION:

When liquid water is cooled to a temperature below 0°C at one atmospheric pressure, it freezes or crystallizes and as such it is commonly believed in general that it is impossible for water to exist in the liquid state below 0°C at normal pressures. This is a fallacy. In point of fact, it is possible for water to exist in the liquid state at temperatures below the normal freezing temperature. This is what is known as SUPERCOOLED WATER.

In actuality, crystallization in liquid water has been found not to be solely a property of water per se but that it is a function of the type of solid surfaces and the particulates with which the liquid water comes into contact.

Many transport and thermodynamic properties of water, especially in the SUPRECOOLED STATE OF LIQUID WATER, have given strong indications of tending towards anomalously large values as temperature is lowered below the freezing temperature [Ratcliffe and Irish, 1982]. These indications suggest that some structure ordering in the hydrogen bonded network that exists in water which become even more pronounced in the low temperature region would be taking place. Consequently, detailed spectral information which could provide a clear indication of increased coupling and resulting in enhancement of spectral intensity would be of immense interest and could perhaps give some explanation for the anomalous behaviour of water. It must be pointed out that there have been attempts to experimentally monitor the mechanisms that give rise to the complex spectrum of liquid water and to try and explain the anomalous increase in the changes in the structure of water which gives rise to spectral intensity enhancement under supercooled conditions [Yeh, Bilgram and Kanzig, 1982; Bansil,

ABSTRACT:

The OH stretching vibrations of liquid H₂O have been investigated with Raman Spectroscopic Technique from +65°C down to -20°C. From our experimental results, we suggest in agreement with Yeh et. al., 1932 that in the low temperature region, clusters of tetrabonded water molecules are formed. This will explain the intensity enhancement and the anomalous structure reported by Bosio and coworkers in the supercooled region [Bosio, Teixeira and Stanley, 1981]. Based on our measurements, we propose that the 3200 cm⁻¹ spectral component which is absent from the OH vibrational spectrum of HOD [Murphy and Bernstein, 1972] but which prominently appears in the OH stretching vibrational spectrum of liquid H₂O is a coupling band. The spectral band centers of both the 3200 cm⁻¹ and the 3400 cm⁻¹ components of the OH stretching vibrations in liquid H₂O decrease with decreasing temperature indicating strengthening of hydrogen bonding on the average with decreasing temperature. The rate of decrease of frequency with temperature is greater with the coupling band and this result together with behaviour of the band width leads us to conclude that the coupling band component is the more hydrogen bonded component of the spectrum. The high frequency spectral shoulder at about 3600 cm⁻¹ is found to increase with increasing temperature.

Wiafe-Akenten and Taafe, 1982; D'Arrigo and coworkers, 1981; Bosio Teixeira and Stanley, 1981; Scherer, Go and Kint, 1974). Apparently, the availability of improved Raman techniques with signal averaging facilities which can be obtained in the photon counting mode and the introduction of the laser have led to the observation of more and well-defined structure in the Raman spectrum of H_2O , D_2O and isotopic solutions of HOD.

In an attempt to monitor the structure of water experimentally, Bosio and coworkers, 1981, performed x-ray diffraction measurements. They reported an enhancement of structure with cooling down to a temperature of $-20^\circ C$. With the addition of structure breaking impurities such as hydrogen peroxide or hydrazine, the structure of hydrogen bonded network in the liquid water was broken thus destroying the structure enhancement [Halfpap and Sorensen, 1982; Bosio and coworkers, 1981]. The inference, invariably, is that the enhancement of structure observed in the supercooled region was a hydrogen bonding effect.

Yeh and coworkers, 1982, and D'Arrigo et. al., 1981, have respectively and separately investigated the OH stretching vibrational region of liquid water down to $-20^\circ C$ and $-24^\circ C$. D'Arrigo et. al. have suggested the existence of "iceberg clusters" in the liquid water at very low temperatures to explain the observed anomalous effects. The work of Yeh et. al. includes the low frequency region and they suggest formation of tetrabonded water molecules in the supercooled region. However, in neither of these works was a detailed analysis of the stretching vibrational spectra of liquid H_2O carried out.

We have therefore undertaken a detailed and rather critical analysis of the Raman Spectra of liquid H_2O from $65^\circ C$ down to $-20^\circ C$ in the fundamental stretching vibrational region. Unlike previous interpretation by Scherer et. al., 1974, who consider liquid water to consist of symmetrically and asymmetrically hydrogen bonded water species, to

explain the stretching vibrational spectra, we suggest an interpretation in terms of intermolecular coupling which exists within the water system and which we believe becomes enhanced under supercooled conditions. It must be pointed out however that in doing so, we are in no way necessarily saying that Scherer and coworkers are necessarily wrong in their interpretation. We are, however, suggesting an alternative interpretation which we believe is rather very plausible based on our experimental findings.

EXPERIMENTAL PROCEDURE AND DATA HANDLING

The liquid H_2O used in all the Raman measurements in this work was a doubly distilled and filtered de-ionized liquid water from a millipore purifier. The resistivity at the purifier output was $18M\Omega$ cm. The doubly distilled and filtered de-ionized water was syringed into glass capillary tubes of 1.5 mm inside diameter which had previously been thoroughly cleaned in chromic acid and rinsed several times with de-ionized water. This was necessary because the degree of supercooling of liquid water is a function of the impurities in the water and the surface of the walls of the glass capillary. The tubes were sealed at both ends by using a propane gas torch.

Raman spectra of the liquid H_2O were obtained with a Spex 1401 double grating spectrometer. A 514.5 nm exciting line was used provided by a 4 watt Argon ion laser. The power of the exciting line at the sample was 150 mw. Spectral resolution was 5 cm^{-1} and all the spectra were obtained by respectively signal averaging 20 scans each at a speed of 3 cm^{-1} per sec. on a Nicolet 1180 minicomputer which had been interfaced to the spectrometer. A scrambler device placed behind a polarizing analyzer was used positioned directly in front of the

entrance slit of the spectrometer. This device ensures that the experimentally measured intensity would be independent of the direction of the polarization of the scattered light. Spectra of the scattered light polarized parallel (I_{para}) and perpendicular (I_{perp}) to the polarization vector of the incident light were respectively measured by using a polarizing analyzer.

To control the temperature of the sample, the glass capillary tube containing the liquid H_2O was placed in a Harney-Miller cell through which cold nitrogen gas was circulated. The double walled vacuum-jacketed glass construction of the Harney-Miller cell helps to prevent any condensation of atmospheric moisture on the outside of the cell which, apparently, would perturb the measured spectra in the low temperature region. The sample temperature was measured with a copper-constantan thermocouple with the "hot" end of the thermocouple placed on the outer surface of the glass capillary tube very close to the point of laser illumination and the "cold" end was connected to an Ice-Point Reference Standard Unit. Sample temperatures were maintained to an accuracy of $\pm 0.2^\circ\text{C}$ for all the temperatures at which spectra were recorded. Spectra were recorded for temperatures from $+5^\circ\text{C}$ to -20°C .

Spectral band decomposition was obtained by fitting the experimentally obtained I_{para} spectrum to three overlapping Lorentzian-Gaussian product band components. This empirical choice of band fitting was first introduced by Scherer et. al. Prior to least-squares fitting, the digitized experimental data were normalized for the Boltzmann population factor and the intrinsic Raman intensity which is proportional to the square of the polarizability derivative was obtained by multiplying

the observed Boltzmann corrected intensity by the factor $\frac{\nu}{(\nu_L - \nu)^4}$ where ν_L is the incident laser frequency and ν is the frequency of the scattered signal. We also subtracted a quadratic background from the experimental data. Spectra deconvolution was obtained using the experimentally obtained polarized spectrum, I_{para} , after the necessary corrections had been made without using the isotropic spectrum. The reason for doing this will be given below under discussion of results.

RESULTS AND DISCUSSION:

Figure 1 shows uncorrected experimentally obtained Raman spectra of the relative intensity as a function of the wavenumber shift (Raman Shift) for three temperatures in the supercooled region. All the three spectra are parallel polarized spectra, I_{para} . Each spectrum clearly shows two prominent peaks located around 3200 cm^{-1} and 3400 cm^{-1} in addition to a high frequency spectral shoulder around 3600 cm^{-1} each with a rather broad band width.

In their spectral interpretation, Scherer, Go and Kint, 1974, interpreted their OH stretching vibrational spectrum in terms of four band components. They attributed these four band components to the symmetric and antisymmetric OH stretching vibrations of a symmetrically and asymmetric hydrogen-bonded complexes. According to their model, (the two species model), liquid water should have two types of species, symmetrically hydrogen-bonded water and asymmetrically hydrogen-bonded water.

Walrafen and Monosmith, 1984, in their overtone work on water in the normal temperature region, also interpreted their water spectra in terms of four overlapping bands by fitting the experimentally observed polarized spectrum to four overlapping Gaussian band components. Like

Scherer et. al., they did not use the visually observed features of their experimental spectra. Their band component assignment is however different in interpretation from that of Scherer et. al. Monosmith and Walrafen would assign the 3200 cm^{-1} band component to intermolecular coupling effects which is in agreement with our interpretation. However, they would essentially assign the 3400 cm^{-1} band component to tetrabonded H_2O molecules and 3420 cm^{-1} component supposed to be overlapping with the 3400 cm^{-1} band component would be assigned to tri-bonded H_2O molecule. The 3600 cm^{-1} band component is assigned to the non-hydrogen bonded water molecule.

In view of the results obtained in our previous work on intermolecular coupling effects in HOD solutions [Wiafe-Akenten and Bansil, 1983] we suggest that there is no need to invoke the symmetric and antisymmetric vibrations of water molecules in interpreting the OH stretching vibrational spectra of liquid water as was done by Scherer et. al., 1974. Spectra measurements on decoupled OH oscillators in HOD solutions [Ratcliffe et. al., 1974; Murphy et. al., 1972; Wall and Hornig, 1965] show only the 3400 cm^{-1} with a high frequency spectral shoulder located at about 3600 cm^{-1} . The peak at about 3200 cm^{-1} is clearly not present. In the spectral measurements of OH oscillators in liquid H_2O , however, two prominent peaks respectively located around 3200 cm^{-1} and 3400 cm^{-1} including the high frequency spectral shoulder around 3600 cm^{-1} are clearly observed (see figure 1). Comparatively, the 3200 cm^{-1} spectral band component is clearly absent from the decoupled OH spectra [Ratcliffe et. al. 1982; Scherer et. al. 1974; Murphy et. al. 1972; Wall and Hornig, 1965].

We are therefore proposing what might be called a "single species model" of water. By comparing the spectrum of decoupled OH oscillators

of HOD solution with that of coupled OH oscillators of H_2O , we suggest that one can get an alternative but very plausible explanation for the presence of the 3200 cm^{-1} band component which shows prominently in the H_2O spectrum especially in the low temperature region where it becomes even more pronounced. As we proposed in our previous work [Wiafe-Akenten and Bansil, 1983], the decoupled OH (OD) oscillators in HOD, to a first approximation, can be considered to consist of a large number of one dimensional oscillators which form a continuous hydrogen bonded network with large distribution of hydrogen-bond lengths and angular dependence having in the liquid state, short range order persisting throughout. Suppose these oscillators have negligible vibrational coupling as is the case in very dilute solutions of HOD, then their spectrum would essentially be similar to that of isotopically decoupled OH oscillators of HOD as obtained respectively and separately by Scherer et. al., 1974 and by Murphy and Bernstein, 1972. The large width of the spectrum will be mainly due to the inhomogeneous broadening due to the wide distribution of hydrogen bond geometries. Now, the effects of strong INTERMOLECULAR COUPLING (like those which exist in liquid H_2O) will result in a resolvable peak around 3200 cm^{-1} . The 3200 cm^{-1} band component in liquid H_2O which is not present in HOD is therefore a coupling band. We suggest then that the 3200 cm^{-1} band component does not correspond to any distinct water species but that it is due to coupling effects. Similar models have been used by Rice and Sceats, 1981 and by Bergren and Rice, 1982, for interpreting the OH stretching vibrational spectrum of ice Ih and amorphous solid water, H_2O (as). We essentially assign the 3400 cm^{-1} band component to all OH oscillators that are hydrogen bonded to neighbouring oxygen atoms and the high frequency shoulder band component at about 3600 cm^{-1} is assigned to those OH oscillators

that are so weakly bonded to neighbouring oxygen atoms as to be essentially considered as freely bonded.

In this our interpretation of the Raman spectra of liquid H_2O where we fit the spectrum to the visual features of the experimentally obtained spectrum, the physical reason for analyzing the isotropic and anisotropic spectra of water (that the antisymmetric stretching vibrations are absent from the isotropic spectrum and that they occur only in the anisotropic spectrum) becomes unimportant and therefore one can simply analyze the experimentally observed polarized Raman spectrum itself. It should be pointed out that the effect of Fermi interaction (Fermi resonance) on the coupling band is assumed here to be small. In fact, the Fermi resonance component, per se, has not actually been isolated yet in liquid water. There will be some effects on the band from combination bands which contribute to the width of the band.

Our experimental results show that in the normal temperature region ($0 - 65^\circ C$), the spectral intensity of the 3400 cm^{-1} component is higher than that of the 3200 cm^{-1} component. As temperature decreases below $0^\circ C$, however, we observe a growth in the intensity of the 3200 cm^{-1} spectral component at the expense of the 3400 cm^{-1} component. This observation is in complete agreement with the results of Yeh et. al. 1982 and with D'Arrigo et. al. 1981. In fact, the intensity ratio I_{3200}/I_{3400} increases by a factor of about 2 from $0^\circ C$ to $-20^\circ C$ which agrees with the results of Yeh et. al., 1982. Figure 2(b) shows that the relative integrated intensity of the 3400 cm^{-1} component decreases with decreasing temperature. It decreases at a faster rate in the supercooled region than in the normal temperature region where it seems to be saturating beyond $65^\circ C$. The behaviour of the relative integrated

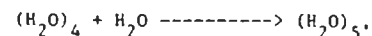
intensity of the 3200 cm^{-1} component, however, is different. Figure 2(a) shows that the relative integrated intensity increases very rapidly as temperature decreases below the equilibrium melting temperature ($0^\circ C$) with a faster rate of increase in the supercooled region.

We suggest that the enhancement of the spectral intensity of the 3200 cm^{-1} component in the low temperature region is due to the cluster formation of tetrabonded water molecules. This result would tend to give support to similar interpretation by D'Arrigo et. al., 1981, and by Yeh et. al., 1982. Besides, Bosio et. al., 1981 observed intensity enhancement in their small angle x-ray measurements which they attributed to density fluctuation that becomes enhanced with supercooling. Their explanation therefore suggests cluster formation of water molecules in the supercooled region. We therefore suggest that in the supercooled region, clusters of tetrabonded water molecules are formed and that they result in an increase or enhancement in the intensity of the 3200 cm^{-1} spectral component; (small angle x-ray scattering has showed that the structure factor increases anomalously in the low temperature region [Bosio et. al. 1981]). This suggestion also coincides with a proposal by Stillinger, 1980. He proposed that the type of structure which is responsible for anomalous supercooled properties in water is one where hydrogen bonded cages or polyhedra, each containing several water molecules, form spontaneously in water. We must state, however, that we do not think that small quantities of true ice exist as heterophase fluctuation in liquid water at low temperatures as has been reported by D'Arrigo et. al., 1981. We also did not detect any band component at 3150 cm^{-1} in the supercooled water spectra as they reported. Besides, the data of Bosio et. al. rule out the claim that "iceberg clusters" appear in the liquid water at low

temperatures. We are inclined to agree with them. We do however observe that the overall intensity of the OH stretching band increases with decreasing temperature in agreement with the results of D'Arrigo et. al.

We show in figure 3(a) an Arrhenius plot of the ratios of intensities at I_{3200}/I_{3400} against $1/T$ from $+65^\circ$ to -20°C . It is quite evident from the graph that in the whole temperature range, the Arrhenius plot is not linear. Shown in figure 3(b), we have also plotted an Arrhenius graph but only for the low temperature region between 0°C and -20°C as was done by Yeh et. al. This turns out to be very linear. Yeh et. al., 1982 obtained an Arrhenius plot in the temperature range from 0°C to -20°C and got a linear graph from which they calculated the activation energy or the change in enthalpy $\Delta H^\circ = 3.1 \pm 0.5$ Kcal./mole.

ΔH° was interpreted by Yeh and coworkers to be the average energy for breaking a hydrogen bond [Yeh et. al., 1982]. Our results plotted over a wider range of temperature to include both the normal and the supercooled temperature regions (Figure 3a) do not seem to give support to this interpretation. From the Arrhenius equation computation, the slope of our confined low temperature Arrhenius plot (as was done by Yeh et. al.) yields an enthalpy change of $\Delta H^\circ = 3.98 \pm 0.17$ Kcal./mole (see figure 3b). We suggest a different interpretation for this enthalpy change in the low temperature region as follows. As was postulated by Yeh. et. al., 1982, we also suggest that in the supercooled region, the reaction that we measured by the spectral signature is



which is the formation of tetrabonded water molecules as mentioned above. If this is the case, then we suggest that ΔH° which we

obtained in the low temperature region, is reflecting the average energy required to form a tetrabonded water molecule.

Table 1 and figure 4 summarize the results obtained for deconvoluting the Raman spectra into three component bands. Figures 4(a) and (b) show that the frequencies of both the 3200 cm^{-1} the 3400 cm^{-1} band centers decrease with decreasing temperature. The 3200 cm^{-1} component band (the coupling band), however, decreases with a greater value for each degree decrease in temperature than the 3400 cm^{-1} component. This result can be rationalised in terms of our proposal that the 3200 cm^{-1} band arises due to strong intermolecular coupling. The width of the 3400 cm^{-1} band represents largely the distribution of the hydrogen bond geometries and coupling constants in strongly coupled (or clusters of) water molecules. As temperature decreases, the overall hydrogen-bond distribution becomes narrower and leads to a decrease in the width of the 3200 cm^{-1} band. It is very likely that the geometrical distribution of hydrogen-bond lengths and angles in clusters of water molecules becomes even more restrictive at lower temperatures than the overall hydrogen-bond distribution. This would lead to a faster decrease in the width of the 3200 cm^{-1} band as compared to the 3400 cm^{-1} band. A linear least-squares fit to the data gives

$$\nu_{3200} = 3222 + (0.62 \pm 0.02)\theta, \text{-----} (1)$$

$$\nu_{3400} = 3430 + (0.3(\pm 0.01)\theta), \text{-----} (2)$$

where θ is the temperature in $^\circ\text{C}$ and both ν_{3200} and ν_{3400} are expressed in cm^{-1} . Notice that the slope of ν_{3200} graph is about twice that of the ν_{3400} graph. The decreasing frequency with respect to temperature implies that hydrogen bonds in the liquid water become

stronger on the average as temperature is decreased [Bansil, Wiafe-Akenten and Taaffe, 1982]. It has been established that in hydrogen-bonded systems, a correlation between the OH stretching vibrational frequency and the average donor-acceptor distance exists [Falk et. al., 1972]. It indicates that, on the average, the oxygen-oxygen separation (R_{OO}) in the liquid water decreases with decreasing temperature. As such, the distribution of OO bond lengths and the wide distribution of OOO angles which is the biggest contributing factor of the spectral width decreases. The spectral deconvoluted results shown in table 1 show that the band width of the coupling band decreases with decreasing temperature compared to the 3400 cm^{-1} spectral component. This result, together with the decreasing ν_{3200} with decreasing temperature, indicates that the coupling band is the more hydrogen bonded component.

In their room temperature work on water, Schultz and Hornig, 1961, measured the depolarization ratio of the Raman spectrum and found that in the OH stretching vibrational region, the value of the depolarization ratio changes across the band. Their results show that the depolarization ratio for the 3200 cm^{-1} component is much lower than that for the 3400 cm^{-1} component. Murphy and Bernstein, 1972 have also measured the depolarization ratio of water in the same vibrational region at room temperature. They found the value of the depolarization ratio for the 3200 cm^{-1} spectral component to be 0.04 and that for the 3400 cm^{-1} band was given to be 0.14. In view of the results of these two independent investigators, we see that the coupling band is more highly polarized than the 3400 cm^{-1} spectral component. We therefore infer that coupling tends to perhaps polarize vibrational modes. This inference is also confirmed by our previous work [Wiafe-Akenten and Bansil, 1983] in which such an observation was noted based on the measured depolarization ratio in that work.

The position of the high frequency spectral shoulder at about 3600 cm^{-1} does not seem to change with temperature. Its intensity, however, increases quite markedly with increasing temperature. As pointed out before, its band width was held fixed at 132 cm^{-1} in the band fitting. This band is identified to be due to those water molecules with very badly bent hydrogen bonds.

CONCLUSIONS:

We have obtained spectral data in the OH fundamental stretching vibrational region from 65°C to -20°C . From the experimental results, we conclude that the 3200 cm^{-1} spectral component is a coupling band and that it is quite adequate to analyze the Raman spectra obtained experimentally without resorting to isotropic and anisotropic spectra. The behavior of the band centers and the band width leads us to conclude that the coupling band is largely related to the vibrations of more strongly hydrogen bonded spectral component. The increase in intensity in the low temperature region and the behaviour of the Arrhenius plot in the temperature range between 0°C and -20°C gives support to the idea that, in the supercooled region, clusters of tetrabonded water molecules are formed.

ACKNOWLEDGEMENT:

I would like to acknowledge and express my sincere thanks to Professor Rama Bansil for her immense help and support in this work. I also greatly appreciate the support and encouragement from the International Centre for Theoretical Physics (ICTP), Trieste, Italy for the opportunities and exposure they continue to give to me to interact with many international scientists and to contribute to science. Lastly, I am very grateful to Mrs. J.W. Nuhia for patiently typing this manuscript for me. I am truly indebted to her.

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TABLE I

T/P °C	ν_{3200} cm ⁻¹	ν_{3400} cm ⁻¹	ν_{3600} cm ⁻¹	ν_{3200} cm ⁻¹	ν_{3400} cm ⁻¹	ν_{3200} cm ⁻¹	ν_{3400} cm ⁻¹	$\Delta\nu_{3200}^{1/2}$ cm ⁻¹	$\Delta\nu_{3400}^{1/2}$ cm ⁻¹
-20	3208.6	3421.8	3609.2	416.5	348.7	296.0	314.1	231.5	223.2
-18	3209.3	3421.8	3605.0	414.2	344.0	296.0	313.2	231.1	221.5
-16	3211.7	3424.1	3604.2	388.4	319.6	315.1	335.9	234.2	221.4
-14	3212.9	3424.0	3606.5	392.1	330.5	313.1	330.4	234.3	223.4
-10	3215.3	3425.2	3602.5	375.5	316.1	322.5	339.7	234.0	221.3
7.8	3215.7	3425.3	3603.2	372.3	320.2	320.0	339.7	232.1	222.8
-6	3216.7	3426.2	3603.7	368.3	320.7	324.8	347.2	232.9	225.3
0	3223.5	3430.9	3603.8	362.0	317.3	348.8	329.0	240.1	218.4
5	3225.3	3431.9	3604.1	366.7	324.3	339.3	325.5	238.1	219.7
0.1	3232.5	3436.4	3603.4	357.0	323.8	361.5	312.8	242.8	215.1
25	3239.3	3440.3	3602.6	357.5	322.9	363.2	310.0	244.3	213.8
45	3250.7	3448.0	3603.5	362.6	317.7	367.4	312.9	246.7	213.0
65	3259.3	3451.8	3598.4	401.8	340.2	336.5	287.8	246.8	210.2

TABLE CAPTION.

Parameters obtained by deconvoluting the spectra into three Lorentzian - Gaussian bands.

$\Delta\nu_{\frac{1}{2}}^{3200}$ and $\Delta\nu_{\frac{1}{2}}^{3400}$ are respectively the full width at half maximum of the 3200 cm^{-1} and the 3400 cm^{-1} spectral components. The parameters ν_{3200} , ν_{3400} and ν_{3600} are as defined in the text.

L and G are parameters that respectively characterize the widths of the Lorentzian and Gaussian components of the band so that L_{3200} and G_{3200} are respectively the Lorentzian and Gaussian parameters for the 3200 cm^{-1} band and L_{3400} and G_{3400} are respectively the parameters that characterize the width of the Lorentzian and Gaussian components of the 3400 cm^{-1} band.

The spectral function used in the least - squares fitting program may be found in the paper by Bansil, Wiafe-Akenten and Taaffe, 1982.

FIGURE CAPTIONS

FIGURE 1: Raman spectra as a function of wavenumber shift for three temperatures in the supercooled region. The spectral range corresponds to the OH stretching vibration.

FIGURE 2: Figures (a) and (b) are respectively the temperature dependence of the relative integrated intensity of the 3200 cm^{-1} and the 3400 cm^{-1} spectral components.

FIGURE 3: An Arrhenius plot of the ratio of the integrated intensities I_{3200}/I_{3400} of the two spectral component bands at 3200 cm^{-1} and 3400 cm^{-1} as a function of $1/T$. (a) covers the temperature range from 65°C to -20°C and (b) covers the low temperature range from 0°C to -20°C .

FIGURE 4: Figures (a) and (b) are respectively the temperature dependence of the peak frequencies ν_{3200} and ν_{3400} of the OH stretching vibrational band.

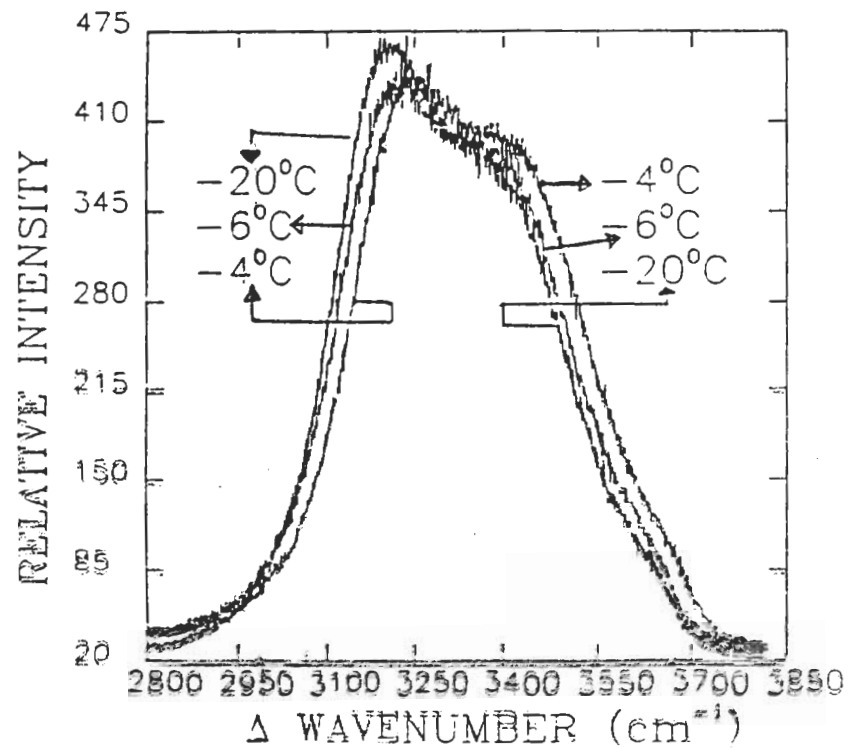
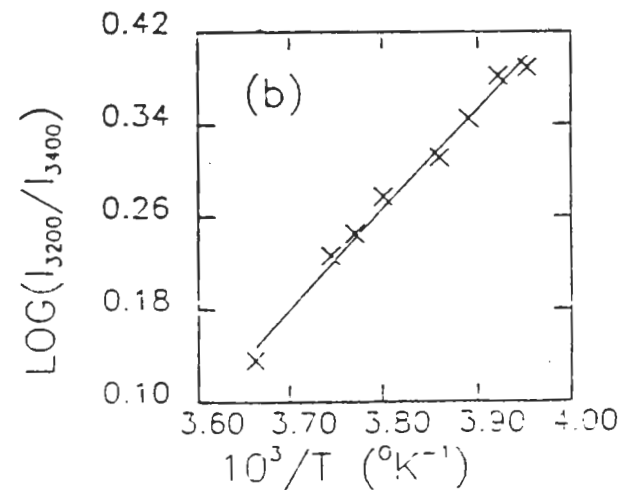
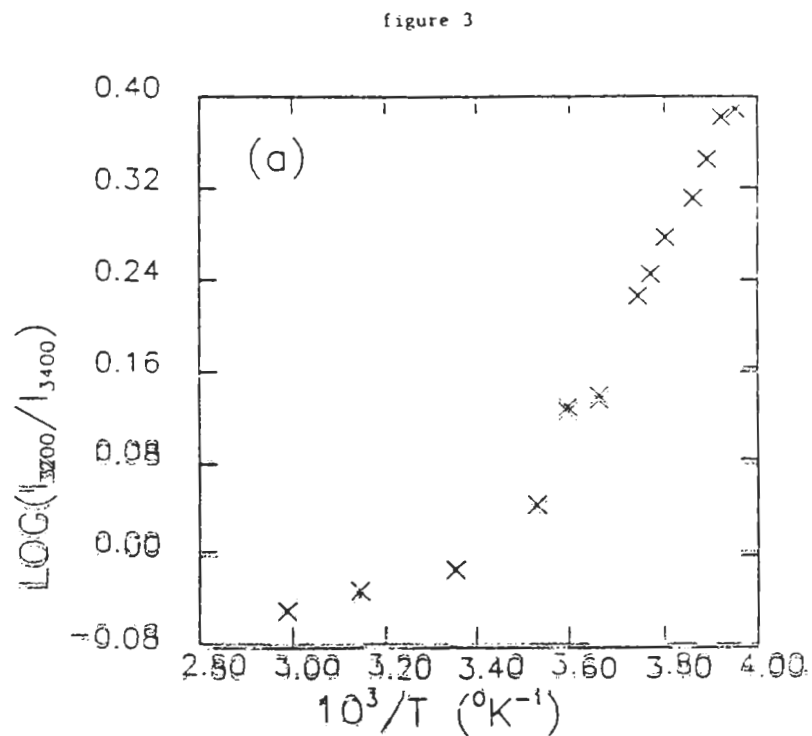


Figure 1



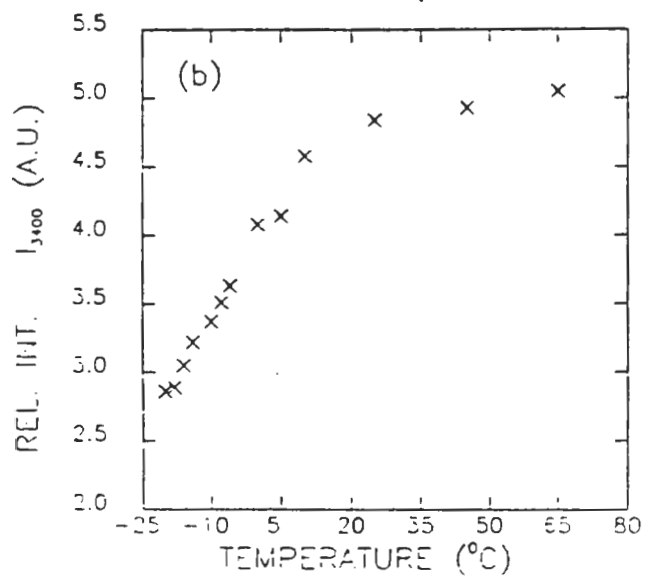
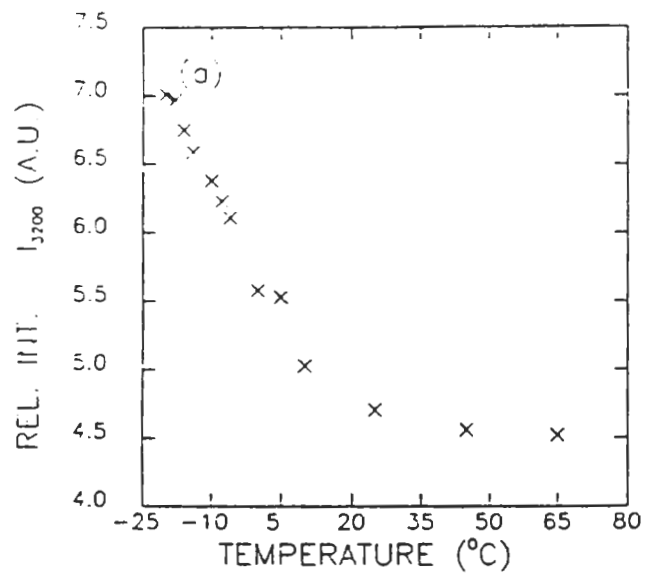


figure 2

figure 4

