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Far-infrared properties of dilute hydroxyl groups in an amorphous silica matrix

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Abstract. The far-infrared absorption coefficient for absorption due to the presence of OH groups in amorphous silica has been investigated at room temperature, 200 K and 80 K, using a far-infrared laser. The observed absorption is interpreted in terms of an asymmetric double well, for which the theory has recently been derived by Hutt and Butcher. This interpretation is discussed in relation to previously published far-infrared, dielectric loss and heat capacity measurements.

In a recent publication (Hutt and Butcher 1988), the far-infrared (FIR) absorption spectra of phenol and thiophenol molecules within a polyethylene matrix were discussed. In these systems a proton exists with a rotational degree of freedom. The rotational energies generally correspond to a FIR quantum. Analysis was based on transitions within double-well systems which are not, in general, symmetric, because of the local environment. Inferences about the matrix could then be made from the features associated with proton tunnelling transitions. We report here the results of applying the same procedure to hydroxyl groups present as an impurity in silica.

We have obtained two types of synthetic silica containing different concentrations of residual water so that the OH contribution can be assessed. In silica, water molecules are preferentially trapped at defect sites, resulting in two hydroxyl groups (Stolen and Walrafen 1976), and there is no evidence for significant interaction between the two hydrogen atoms. Interactions between OH and the SiO₂ environment appear to be dominant. Phillips (1981) reached the same conclusion by considering the OH fundamental stretching vibration. Each OH can therefore be treated independently of the others, with hydrogen moving by hindered rotation about the Si–O bond.

The details of the FIR laser transmission spectrometer have been described elsewhere (Ahmad *et al* 1986, Hutt 1986). Two types of silica were obtained commercially‡: Spectrosil B contains $8 \times 10^{25} \text{ m}^{-3}$ OH⁻ ions and Spectrosil WF around 10^{23} m^{-3} OH⁻ ions (a few ppm of OH by weight). Samples of each type of silica were prepared that approximated Fabry–Perot etalons. The transmission of several etalons of different lengths permits a FIR refractive index to be derived (Hutt and Butcher 1988). In this way the refractive index, n , for Spectrosil WF was found to be 1.950 ± 0.002 at 30 cm^{-1} and

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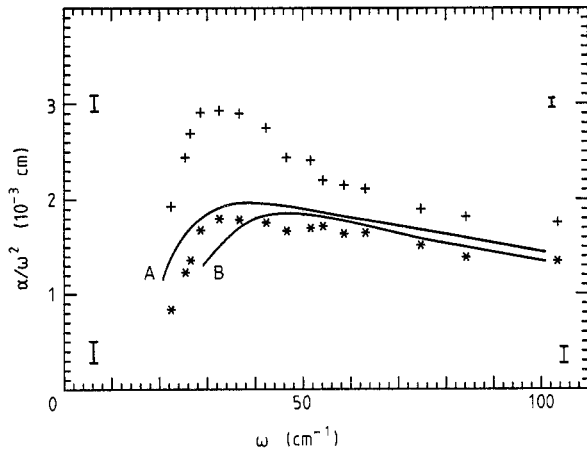


Figure 1. Room-temperature α/ω^2 against ω for Spectrosil B, +, and Spectrosil WF, *. Earlier work on samples of GE101 by Wong and Whalley (1970), curve A, and Stolen (1970), curve B, are also shown.

the frequency dependence, within our errors, followed the Sellmier relation defined by Parker *et al* (1978):

$$n(\omega)^2 = n_\infty^2 + A/[1 - (\Omega/\Omega_0)^2] \quad (1)$$

with $\Omega_0 = 608 \text{ cm}^{-1}$, $n_\infty = 1.45$ and $A = 1.7042$, implying that $n(0) = 1.951$ and $\epsilon_r = 3.807 \pm 0.004$.

The refractive index of Spectrosil B was found to be 1.959 ± 0.002 at 25 cm^{-1} and, in the absence of experimental information, a Sellmier relation could be defined by assuming n_∞ and Ω_0 to be unchanged but $A = 1.732$. This predicted $n(0) = 1.958$ and $\epsilon_r = 3.835 \pm 0.004$. Andeen (1974) has measured ϵ_r for a silica with a similar OH content (Suprasil) and found $\epsilon_r = 3.83$.

The room-temperature (300 K) FIR absorption, $\alpha(\omega)$, is shown in figure 1, plotted as α/ω^2 for Spectrosil WF and Spectrosil B. Also shown are published data of Wong and Whalley (1970) and Stolen (1970) on GE101, which is directly comparable to Spectrosil WF. It is clear that the presence of OH increases the room-temperature absorption of Spectrosil B in the range $20\text{--}100 \text{ cm}^{-1}$. An indication of this effect was previously observed by Stolen and Walrafen (1976).

As the temperature is decreased the absorption also decreases (figure 2) until at 80 K and below (Ghivelder 1988) the two glasses have identical absorptions to within the accuracy of the experiment. The implication is clear; the presence of OH produces a temperature-dependent absorption, centred near 30 cm^{-1} , but covering the range 20 to 100 cm^{-1} . This temperature dependence has not previously been observed.

Independent of any specific model, a number of general conclusions can be drawn from the decrease of absorption with decreasing temperature. The effect of OH groups cannot be simply to increase the coupling between radiation and the bulk phonons, thereby enhancing the usual one-phonon absorption, since the one-phonon process is independent of temperature, as follows from the underlying ω^2 behaviour which is common to all glasses. At the other extreme the absorption cannot arise from OH groups that are entirely free to rotate because the resulting spectrum would include a sharp peak at 23 cm^{-1} increasing in intensity with decreasing temperature. Quite generally, the absorption must involve transitions from an excited state of the OH group moving in an effective potential. The activation energy inferred from our observations suggests an excited state lying approximately 450 cm^{-1} above the ground state.

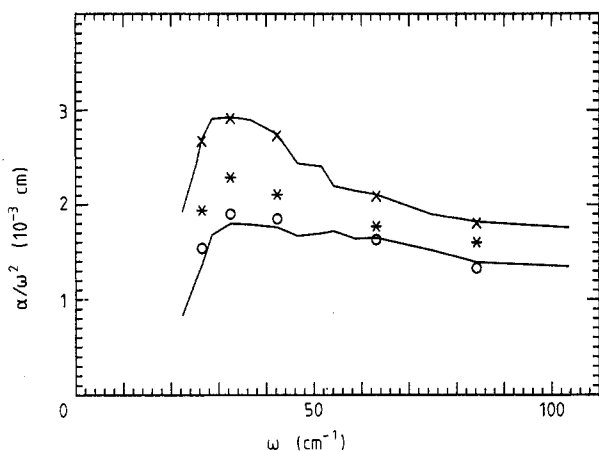


Figure 2. The temperature dependence of α/ω^2 for Spectrosil B and Spectrosil WF was monitored at 26.5, 32.5, 42.3, 63.1 and 84.2 cm^{-1} . Shown are the α/ω^2 values for Spectrosil B at 300 K (x), 200 K (*) and 80 K (O). The behaviour of Spectrosil WF was found to be independent of temperature. The full lines link the room-temperature points shown in figure 1.

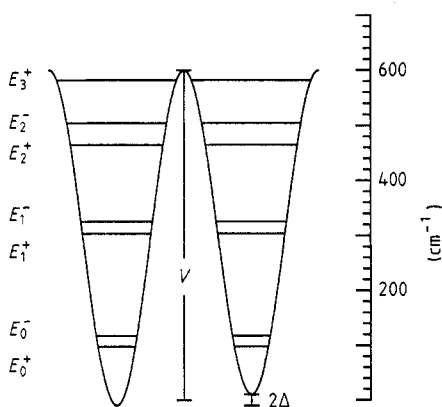


Figure 3. An asymmetric double well with V , Δ and energy level nomenclature defined. The example shown is for $V = 600 \text{ cm}^{-1}$ and $\Delta = 10 \text{ cm}^{-1}$.

Further analysis requires more detailed consideration of the form of the effective potential. The tetrahedral coordination of the Si suggests that the potential should have three minima. If the potential is threefold symmetric, however, direct tunnelling transitions cannot occur (Gordy and Cook 1970), so it is difficult to see how one can ascribe the FIR absorption to OH. This is a direct symmetry argument and, therefore, particularly powerful; the threefold potential must be broken to give any absorption. In general, this symmetry breaking is expected in a glass because of the random structure. In a typical local potential the three minima will then have different energies, so if the wells have substantially different energies a localised description of the states is appropriate. Infrared-active tunnelling transitions become possible only if two wells have energy differences not much greater than the tunnel splitting, so that there can be a good overlap between the localised states. The chance of all three wells having similar energies is small, so the FIR absorption can be discussed entirely in terms of a slightly asymmetric double well as shown schematically in figure 3, which also introduces the notation used to describe the states.

Solutions of the Mathieu equation provide energy levels for all symmetric twofold potential well systems (Gordy and Cook 1970). When asymmetry is added as a perturbation the energy levels can still be derived, and Isnard and Gilchrist (1981a, b) have

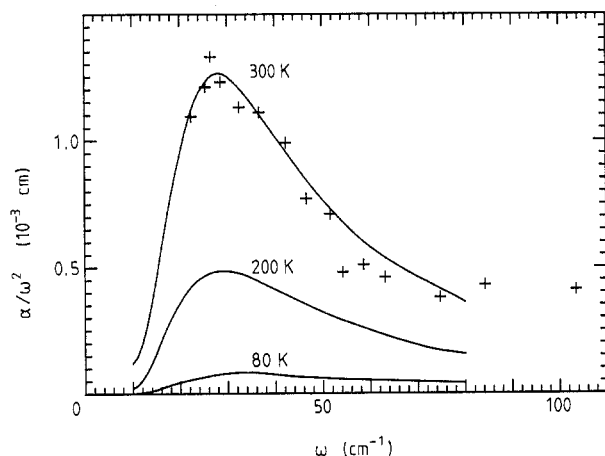


Figure 4. α/ω^2 (Spectrosil B, 300 K) – α/ω^2 (Spectrosil WF, 300–80 K) against ω . The full curves show the predicted frequency dependence of α/ω^2 , for an OH rotor at 300, 200 and 80 K, found using the functions specified in the text.

shown that the equation can easily be adapted to the threefold case by measuring barrier height in terms of $9\hbar^2/8I_r$ in place of $\hbar^2/2I_r$, where I_r is the reduced moment of inertia. Calculations parametrised in this way are independent of the precise details of the potential, which must be introduced only when deriving absolute values for the barrier height.

Consideration of the matrix elements for the states of the double potential well (Hutt and Butcher 1988) shows that the strongest transitions are those of the form $\Psi_n^+ \leftrightarrow \Psi_n^-$ in the notation of figure 3. Examination of the solutions of the Mathieu equation in the symmetric case, for which the matrix elements are largest, shows that the transition $\Psi_2^+ \rightarrow \Psi_2^-$ is compatible with the constraints that the energy splitting should fall in the range 20 to 200 cm^{-1} , and that the energy above the ground state is consistent with the estimated activation energy.

The frequency- and temperature-dependent absorption for the $\Psi_2^+ \rightarrow \Psi_2^-$ transition was therefore calculated, using the procedure of Hutt and Butcher (1988). Energy splittings between the symmetric states can be related to the reduced barrier coordinates using the results given by Abramowitz and Stegun (1965). The effect of asymmetry on energies and matrix elements is included explicitly, and the final result obtained by averaging over the distribution function for the barrier parameter and the asymmetry. A barrier distribution of the form $\text{sech}[(V - V_0)/V_1]$, giving an exponential decrease for large V , was used for the reduced barrier, and a Gaussian distribution centred at zero for the asymmetry.

Calculated values of α/ω^2 at 300, 200 and 80 K are shown in figure 4, together with experimental results for the OH-related absorption at 300 K. The peak in α/ω^2 arises because of a combination of the $1/\omega^2$ factor at high frequencies and the barrier distribution at low frequencies; that is, progressively higher barriers decrease the energy splitting of the Ψ_2 states, and also lead to an increased energy difference $E_2 - E_0$. The peak at 30 cm^{-1} imposes severe restrictions on possible values of $q_0 = V_0/4(\hbar^2/2I_r) = 7.0 \pm 5\%$ and $q_1 = V_1/4(\hbar^2/2I_r) = 0.8 \pm 10\%$. The results are much less sensitive to the width of the asymmetry distribution except when it is reduced to below q_1 , and the results shown in the figure are calculated for an essentially uniform distribution.

The calculated values shown in figure 4 are in excellent agreement with experiment, and it must be emphasised that there are no free parameters in the fit to the temperature dependence. q_0 and q_1 are chosen to fit $\alpha(\omega)$ at 300 K, while the change from 300 to

200 K is determined entirely by the variation in the energy of the state Ψ_2^+ over the range of q . The OH-related absorption at 80 K and below is small, both from $\Psi_2^+ \rightarrow \Psi_2^-$ and from any other possible transition.

Related information on OH in silica is provided by heat capacity and dielectric measurements at low temperatures, both of which are sensitive to the ground state of the system. The heat capacities of Suprasil and Suprasil W (similar OH content to Spectrosil B and Spectrosil WF respectively) have been measured down to 50 mK by Lasjaunias *et al* (1975) who derive a density of states of around $2 \times 10^{45} \text{ J}^{-1} \text{ m}^{-3}$ from the *difference* between the two heat capacities. In our picture, we associate this with transitions between the split ground state Ψ_0 and for consistency must show that the tunnel splitting is less than $k_B T$ down to 50 mK. Approximate solution of the Mathieu equation shows that for $q_0 = 7$, which corresponds to the most likely barrier, the tunnel splitting is about 0.18 K, and calculation shows that the resulting density of states is almost constant above an energy equivalent to 100 mK. In general terms, therefore, our results are consistent with the heat capacity measurements. The FIR results, however, do not give a well defined upper limit to the asymmetry distribution and consequently the density of states cannot be directly related to the concentration of OH groups.

The dielectric data of Mahle and McGammon (1969) and of Frossati *et al* (1977) show a broad spread of relaxation times. Relaxation involves transitions between states Ψ_0^+ and Ψ_0^- which, because of the asymmetry, are equivalent to transitions between states localised in separate wells. At low temperatures transitions occur by direct one-phonon processes, but at higher temperatures they occur by thermal excitation from Ψ_0^+ to higher levels, which are delocalised over both wells, followed by subsequent decay to Ψ_0^- . States important in dielectric loss have asymmetries of $k_B T$ or less (Phillips 1987). In the temperature range 10–100 K, where activation is important, the tunnel splitting of the states Ψ_0^+ to Ψ_0^- is smaller than $k_B T$ but obviously that of Ψ_1^+ to Ψ_1^- is not. Activation does not, therefore, involve the same energy as that appearing in the temperature dependence of the FIR absorption.

Given the distribution of barrier parameter, the range of relaxation times can be estimated using the known parameters for OH (Philips 1981), and seen to be in general agreement with experiment. A precise calculation is difficult in the absence of information on the importance of the Raman processes, and a more complete description of the prefactors occurring in activated processes involving Ψ_0^+ , Ψ_0^- and Ψ_1^+ , Ψ_1^- . It is apparent, however, that obtaining a consistent picture of OH in silica is possible without establishing whether the potential is asymmetric twofold or threefold. The threefold barrier would have a most probable height of 1654 cm^{-1} (equivalent to 2400 K). The most probable twofold barrier height is 735 cm^{-1} (equivalent to 1066 K), and a definitive choice between two- and threefold is impossible at present.

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