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Dielectric and ^{13}C NMR Studies of Sulfur Dioxide-Hydroquinone Clathrates*

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Abstract. Dielectric measurements of SO_2 quinol clathrates show that the reorientation of encaged SO_2 molecules is very rapid and depends greatly on the degree of cage occupancy. For a β-quinol sample of cage occupancy $\theta = 0.57$, the reorientation rate was ~ 1 MHz at 6 K, with a reorientational activation energy of 673 J/mol. For a sample identified by ^{13}C NMR as α-quinol, and for a β-quinol sample with most cages filled with Xe, SO_2 reorientation rates are even greater, with activation energies of only some tens of J/mol. The low temperature dielectric studies show that some ethanol may be enclathrated in β-quinol recrystallized from this solvent. The ^{13}C NMR spectra confirm the X-ray results that the lattice becomes distorted with increased SO_2 content.

Key words. SO_2–Hydroquinone clathrate, SO_2–β-quinol clathrate, dielectric, solid state ^{13}C NMR.

1. Introduction

Several previous dielectric studies [1–7] have attempted to define the reorientational motions of dipolar molecules enclathrated in the β form of quinol (hydroquinone, *p*-dihydroxybenzene). Most of these studies were also concerned with establishing the presence of an orientational ordering at low temperatures in which nearest-neighbour guest molecules with large components of electric dipole moment lying along the crystallographic *c* axis tend to align themselves in the same direction along the axis if the degree of cage occupancy is sufficiently large. Such ordering appears to occur for enclathrated HCN [4], CH_3F [8] and CH_3CN [1], whose geometries promote coincidence of the dipolar axis with the *c* axis of the crystal. For CH_3OH, the dielectric behaviour [7] is complicated by reorientation of the dipole moment component about the *c* axis at a faster rate than reversal of the direction of the component along the *c* axis.

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In contrast, the early X-ray studies by Powell [9] suggested that enclathrated SO_2 molecules were oriented with their symmetry (dipolar) axis perpendicular to the c axis of the $R\bar{3}$ crystal and that the SO_2 molecules were undergoing rapid reorientation about this axis at room temperature. Both of these conclusions agree with the expectations from the size and shape of the SO_2 molecule with respect to the cage which it occupies [10].

Three limited dielectric studies of SO_2-β-quinol have been reported. Dryden obtained [1] a static permittivity of 4.4. at room temperature for a sample with a cage occupancy factor $\theta = 0.94$. Buss [11] measured 10 kHz permittivities between 4 and 300 K for $\theta = 0.75$. From the smallness of the dielectric loss measured at GHz frequencies at temperatures down to 88 K, Davies and Williams concluded [2] that SO_2 reorientation was rapid and that the activation energy was less than 4 kJ/mol.

There is considerable evidence that a variety of molecules, including Ar [12, 13], Xe [14], CH_4 [15], CO_2 [16], and N_2 [17], may also be absorbed in α-quinol. The incorporation of SO_2 in α-quinol was shown by the composition and X-ray studies of Chekhova *et al.* [18] who found that α-quinol of composition $0.021\ SO_2 \cdot C_6H_4(OH)_2$ had unit cell dimensions which were slightly different from those of 'empty' α-quinol. The structure recently published by Wallwork and Powell [19] shows that α-quinol contains cages of roughly the same size as those found in β-quinol but in only one-sixth the number.

The α- and β-quinol lattices may be distinguished by differences in their IR and Raman spectra [20]. The ^{13}C NMR spectra recorded with proton enchancement and decoupling and magic angle spinning have found [21] to differ greatly for the two polymorphs.

We report here the results of (i) dielectric measurements of a number of β- and α-quinol samples containing SO_2 at temperatures down to 2 K and frequencies up to 1 MHz and (ii) room-temperature ^{13}C NMR studies of the quinol lattices with magic angle spinning.

2. Experimental Methods

2.1. DIELECTRIC MEASUREMENTS

Six samples were prepared as outlined in Table I. In most cases SO_2 was bubbled through a saturated solution of hydroquinone in absolute ethanol, the crystals obtained by cooling were dried, ground, and pressed into discs 1.9 cm in diameter and 1.3–1.9 mm thick. Sample D was obtained from sample B, which had lost much of its SO_2 during storage. Sample E was a mixed β-quinol clathrate in which most of the cages were occupied by xenon. Sample F was (metastable) β-quinol crystallized from ethanol in the presence of air. Samples were analyzed for SO_2 content by iodometric titration and loss of weight on heating or dissolution of the sample, with concordant results.

Sample discs were mounted between the parallel-plate electrodes of a dielectric cell [22] equipped with a bellows to maintain contact with the sample. Temperature control and measurement were performed as described previously [23]. Capacitance and loss measurements were made with General Radio models 1615-A and 1682

Table I. Description of dielectric samples

Sample	Crystallization medium	SO_2 cage occupancy
A	Absolute EtOH, 0°C	0.57
B	Absolute EtOH, −13°C	0.78
C	Liquid SO_2, −20°C	0.53
Buss (11)	*n*-propanol, 25°C	0.75
D	Sample B, stored at −13°C	0.04
E	EtOH, 1 atm Xe, 0.26 atm SO_2, 25°C	0.053
F	Absolute EtOH, −13°C	0.0

(1 MHz) capacitance bridges and a Hewlett-Packard 427A self-balancing bridge. The dielectric relaxation of encaged SO_2 proved too broad to be adequately defined by Cole–Cole plots at our temperatures (down to 1.8 K) and frequencies (up to 1 MHz) and the results are reported as temperature-dependent permittivity and loss values at a number of fixed frequencies.

Cell constants were determined from sample and electrode dimensions and are accurate to about 5%. More serious uncertainties appear to have arisen from sample inhomogeneity and irregular crystal packing in some sample discs since the permittivities measured at relatively high temperatures (especially for sample B) did not show the expected linearity with SO_2 content. Similar problems associated with the low plasticity of quinol have been reported by others [1, 2, 11]. In general, the permittivities plotted are probably lower than the true permittivities.

2.2. NMR MEASUREMENTS

^{13}C NMR spectra were recorded at 45.28 MHz with a Bruker CXP-180 spectrometer equipped with a Doty Scientific probe. Single cross-polarization contacts of 5 ms duration were used, with spin temperature alternation and flip back of the magnetization. 2 K datum points were collected at a sweep width setting of 20 kHz; 32–100 decays were co-added with a repetition time of 5 s before zero filling to 8 K and Fourier transformation.

3. Results

Figure 1 shows the temperature dependence of the apparent permittivities measured at 2 kHz for samples of relatively high SO_2 content, along with the 10 kHz values measured by Buss [11]. Samples A and C showed behaviour similar to that found by Buss: a rise in permittivity with decreasing temperature becomes less pronounced below 50 K; ε' rises again below 25 K and then falls abruptly below 10 K. Only the permittivity below 10 K depends significantly on frequency; this dispersion is accompanied by the low-temperature dielectric absorption shown in Figure 2. This region of dielectric relaxation, which must be attributed to reorientation of encaged SO_2 molecules, is extremely broad, sample-dependent and, at our frequencies, extends well beyond the low temperature limit of our measurements.

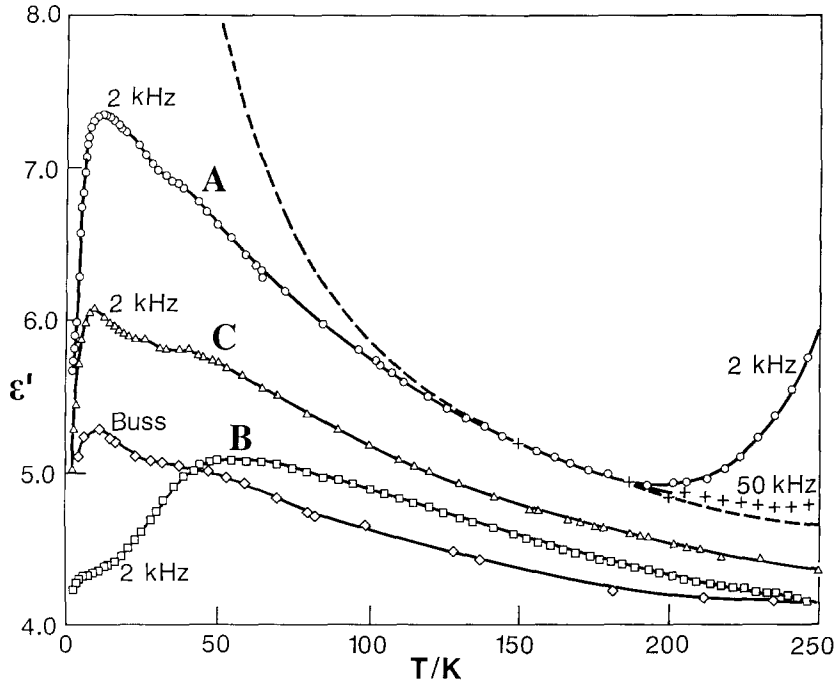

Fig. 1. Permittivity curves at 2 kHz for various relatively high occupancy samples of SO_2–β-quinol. Data of Buss at 10 kHz are also given.

Sample A, the only sample which was not ground and vacuum-dried to remove excess ethanol, showed increasing permittivity and loss effects associated with the presence of space charge with rising temperature above 200 K; the rise in permittivity reported by Buss above ~ 250 K probably had a similar origin.

For low SO_2-content samples the permittivities (Figure 3) tend to rise as $1/T$ down to ~ 10 K and the dielectric loss (Figure 4) is much narrower and apparently peaks well below 2 K.

Small additional loss peaks were observed for all samples prepared in the presence of ethanol but not for the sample (C) prepared without ethanol. Figure 5 shows these loss regions on an expanded scale for some samples. In the best defined cases peaks are observed at 2 kHz near 37 K, 57 K, 69 K and 90 K and all peaks shift to higher temperatures at higher frequencies. The relative amplitudes generally vary with the sample but the ratio between the 69 K and 90 K peak heights is always about 1 : 5. These two peaks occur in the temperature range where dielectric absorption is expected for supercooled liquid ethanol [24] and may arise from the presence of occluded ethanol. The 37 K peak dominates in the samples (A and E) crystallized at the highest temperatures and may result from the incorporation of ethanol molecules in a few per cent of the β-quinol cages. Evans and Richards [25] found that air-free β-quinol crystallized from ethanol, even after prolonged pumping, retained about 0.8% ethanol. A few of the ^{13}C NMR spectra obtained are

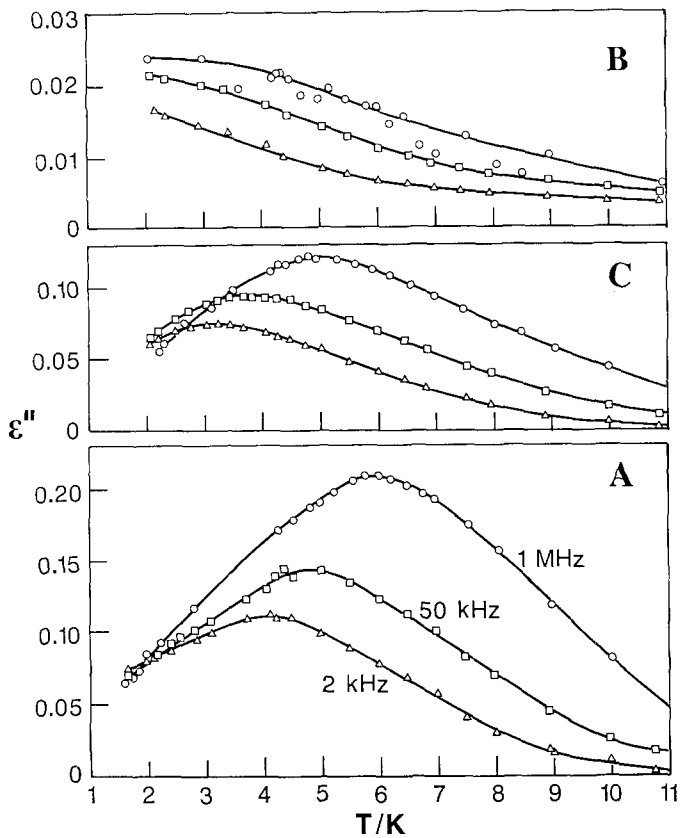

Fig. 2. Low temperature dielectric absorption by SO_2 in SO_2–β-quinol samples.

reproduced in Figure 5. In both β-quinol and α-quinol the isotropic shielding at the C_1 carbon nuclei attached to OH groups is some 32 ppm less than at the C_2 and C_3 nuclei but, in contrast with the single line observed for each of these carbon atoms in β-quinol, a number of lines are resolved in α-quinol [21]. In β-quinol with a centrosymmetric $R\bar{3}$ structure there are only three structurally inequivalent carbon atoms. In α-quinol, on the other hand, the asymmetric unit contains 18 carbon atoms [19] and there are six inequivalent atoms of each of the C_1, C_2, and C_3 types. The chemical shifts are not sufficiently different to enable all 18 lines to be resolved but it is significant that the relative intensities of the three resolved C_1 lines (2:3:1) are only consistent with the presence of six (or some multiple of six) such carbon atoms.

The separation between the C_2 and C_3 lines of β-quinol is found to depend somewhat on the nature of the guest molecules and on the degree of occupancy of the cages. For SO_2 guest molecules and values of θ of 0.55 and 0.73, the separation Δ was 2.05 and 2.16 ppm, respectively. A separation of 1.95 ppm is observed for a metastable

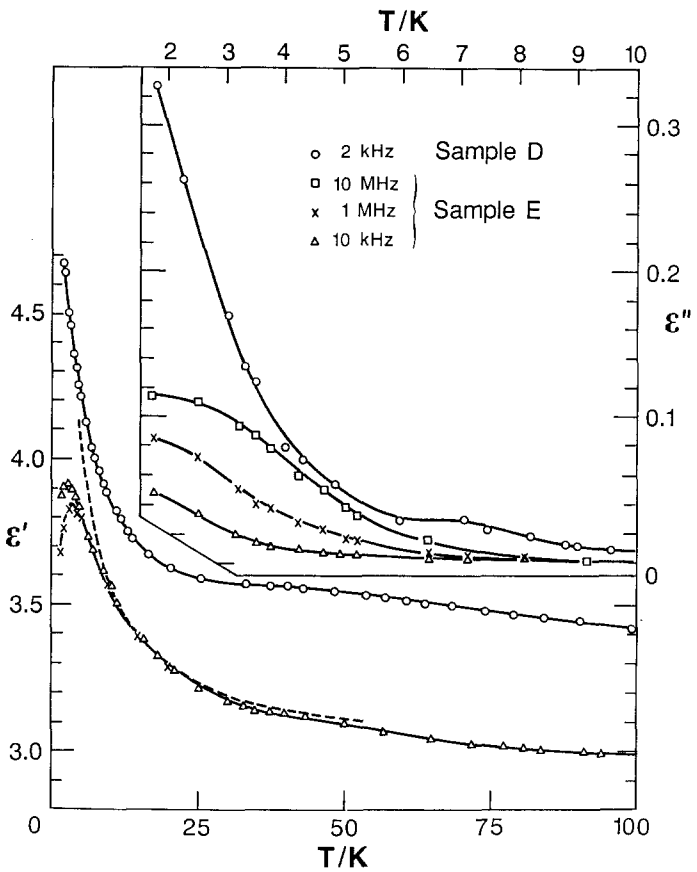

Fig. 3. Permittivity and low temperature dielectric absorption for low occupancy samples.

β-quinol sample prepared from ethanol alone in the presence of air. This evidence of increasing distortion of the lattice with increasing SO_2 content may be correlated with Palin and Powell's observation [26] that the hexagonal unit cell dimensions changed from $a = 16.52$, $c = 5.61$ Å for $\theta = 0.34$ to $a = 16.32$, $c = 5.82$ Å for $\theta = 0.91$. Distortion in the opposite sense appears to occur with H_2S for which $\Delta = 1.62$ ppm (Mak *et al.* [27] found $a = 16.67$, $c = 5.518$ Å for θ (H_2S) = 0.77) and especially for Xe for which $\Delta = 1.29$ ppm ($\theta \sim 0.3$). Another feature of note is the ^{13}C line width of samples with different guest occupancies. It can be seen that for the lower occupancy sample the line width is about twice that of the higher occupancy sample (Figures 5a,b). This can be attributed to a decrease in local order and greater chemical shift dispersion as the number of possible disorder configurations increase.

The NMR spectrum of dielectric sample D (Figure 5d) clearly shows that the sample consists of SO_2 α-quinol, which is a fainter yellow than the SO_2 β-quinol clathrate, and was almost identical with that of empty α-quinol (Figure 5c).

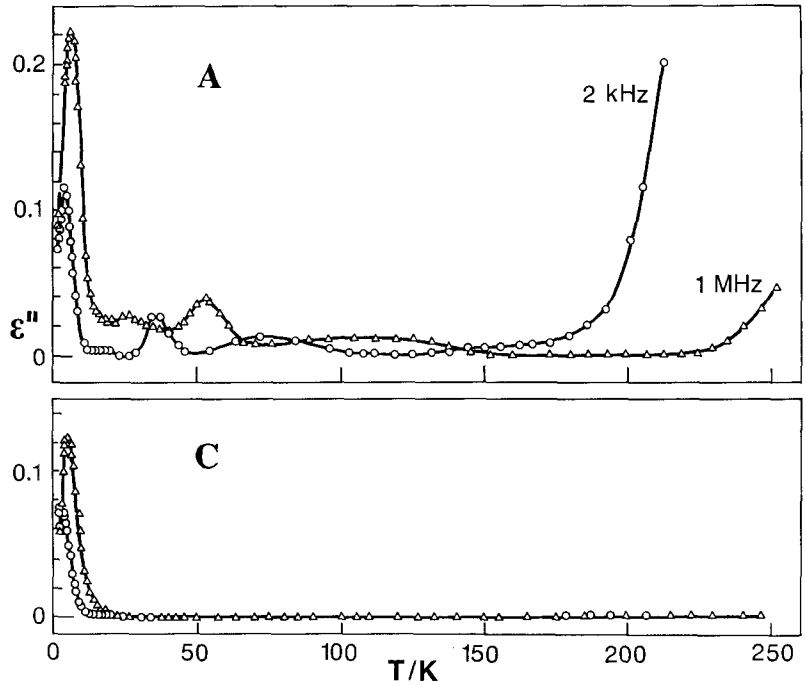

Fig. 4. Expanded dielectric loss curves for various samples.

4. Discussion

Reorientation of the dipole moment of enclathrated SO_2 about the c axis is clearly very rapid since it gives rise to dielectric absorption which for all samples is practically confined to temperatures below 10 K in our frequency range. For medium and high occupancy samples the large absorption breadth reflects the effects of the degree of occupancy of neighboring cages on dipolar interactions between guest molecules and on the local lattice geometry. Inhomogeneity in composition from one part of the sample to another probably also contributes. In the ideal β-quinol lattice the cage centre is a site of $\bar{3}$ symmetry. With partial occupancy of the cages with SO_2 molecules in disordered orientations this symmetry is maintained only over a space and (except at the lowest temperatures) time average. Thus a cage-centred SO_2 molecule aligned with its long axis in the c direction has six symmetrically disposed orientations of equal energy when surrounded by empty cages and a single reorientational relaxation time should result. There may, however, be as many as six orientations of different energy and five distinct relaxation times are to be expected when the molecule is surrounded unsymmetrically by occupied and empty cages. Since there is a distribution of such environments, broad absorption and dispersion is to be expected if, as is shown by the estimates below, the differences in energy are comparable to the average barrier to reorientation.

For an SO_2 dipole moment of 1.63 D the pairwise dipole interaction energies between nearest neighbours along the c direction, in the absence of shielding, are

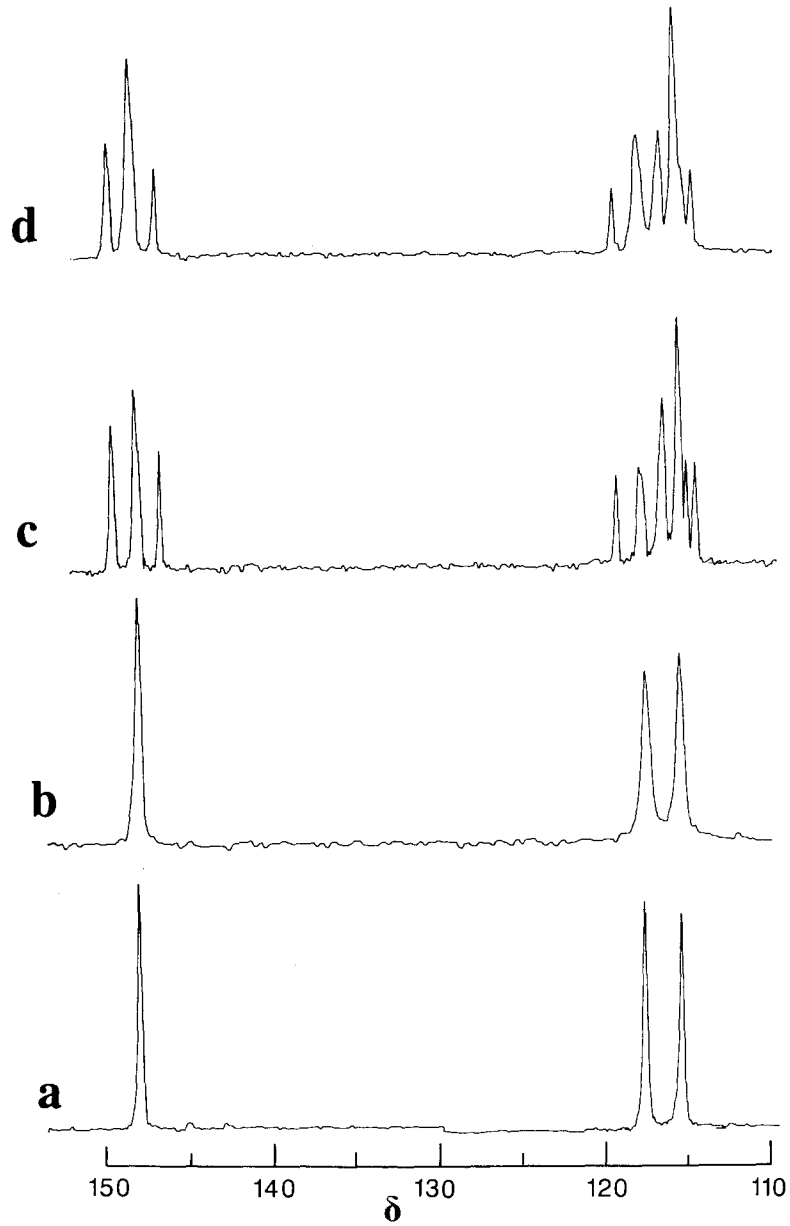

Fig. 5. ^{13}C NMR spectra for β and α-quinols at 300 K. (a) $SO_2-\beta$-quinol, $\theta = 0.73$. (b) $SO_2-\beta$-quinol, $\theta = 0.55$. (c) α-quinol. (d) $SO_2-\alpha$-quinol.

easily shown to be ± 861 and ± 430 J/mol, depending on the relative orientations within the planes perpendicular to c. For the six second nearest neighbours located $(a^{2/3} + c^{2/9})^{1/2}$ away the pair interaction energies are ± 334 and ± 167 J/mol. These energies will be somewhat reduced by the shielding effect of the lattice, but by no more than a factor of two.

An average of unperturbed barrier height cannot in general be accurately defined from the dielectric absorption data since these tend to be biased in favour of the faster reorientation processes. Moreover, the substantial change in lattice dimensions with the extent of cage occupancy means that there is no unique average barrier to reorientation. A rough value may be estimated for sample A in which the absorption is best defined. The temperature dependence of the frequency of maximum absorption gives an activation energy of 648 J/mol. From the approximation that $f(\text{max. abs.}) = \nu_0 \exp(-E_A/kT)$ where $\nu_0 = 30\ \text{cm}^{-1}$, the frequency of the low-temperature far IR band identified with rotational oscillation of SO_2 [28, 29], and $f = 1$ MHz at 5.9 K, one finds $E_A = 673$ J/mol.

Another effect of the energy inequivalence of preferred orientations is the failure of the static permittivity to rise (nearly) as $1/T$ as the temperature falls. This is shown for sample A, for example, by the departure of the experimental permittivity curve from the broken curve below 100 K (Figure 1). This curve was calculated from the relationship

$$\frac{[\varepsilon_0 - 1][2\varepsilon_0 + 1]}{\varepsilon_0} = \frac{[\varepsilon_\infty - 1][2\varepsilon_\infty + 1]}{\varepsilon_\infty} + \frac{4\pi N\mu^2}{kT(1 - f\alpha)^2}, \qquad f = \frac{2\varepsilon_0 - 2}{2\varepsilon_0 + 1}\frac{1}{a^3}$$

which has been found to account for the static permittivities of clathrate hydrates at relatively high temperatures [31]. The values of the parameters employed were $\mu = 1.63$ D, $\alpha = 4.2 \times 10^{-24}\ \text{cm}^3$, $a = 2.9$ Å (the mean free radius of the cage) and $N = 1.28 \times 10^{21}$ SO_2 molecules/cm^3 (for $\theta = 0.57$). A value of $\varepsilon_\infty = 3.86$ was chosen to give good agreement with the experimental ε values at high temperatures; ε_∞ must be considerably larger than 3.2, the value expected for a non-dipolar guest molecule with the same polarizability as SO_2, due to a substantial contribution from the rotational oscillations of the SO_2 dipole which occur at far infrared frequencies. This departure is very pronounced at low temperatures for all the samples shown in Figure 1; for the high occupancy sample B the static permittivity steeply declines with decrease of temperature below 50 K. Such behaviour is common in the clathrate hydrates [30, 31] and other solids where there is an increasing tendency for polar molecules to assume a single most preferred orientation at low temperatures. In general the preferred orientations in different cages are probably not correlated in a regular manner, but for very high cage occupancies most SO_2 dipoles may assume antiparallel alternating orientations (perpendicular to the c axis) with respect to nearest neighbour dipoles a distance c apart.

For samples with low SO_2 content it is to be expected that interaction between dipoles in adjacent cages will be less important in determining motional parameters. For sample D, which was found to be α-quinol, nearest neighbour cages are 5.65 Å away and second nearest neighbours are 11.3 Å distant. Sample E was a β-quinol sample with most cages filled with Xe ($\theta = 0.73$) and relatively few cages with SO_2 ($\theta = 0.05$). In both these cases reorientational barriers may be expected to be determined largely by the interaction between a SO_2 guest and its individual cage. This is also evident from the temperature dependence of ε' as it follows $1/T$ behaviour down to ~ 10 K (Figure 3). As is also shown in Figure 3, the dielectric absorption maxima at our frequencies occur at temperatures $\leqslant 2$ K, indicating reorientational barriers no greater than some tens of J/mol.

5. Conclusions

1. The reorientational rates of SO_2 guest molecules depend greatly on the degree to which β-quinol cages are occupied. For a sample with 57% of the cages filled the reorientational activation energy is 673 J/mol with a dipole reorientational correlation time of 1.0 μsec at 5 K. For low occupancy samples the reorientational activation energy is only some tens of J/mol.
2. ^{13}C NMR spectra confirm that the β-quinol lattice distorts with increasing SO_2 content. The ^{13}C NMR spectrum of α-quinol and SO_2–α-quinol are essentially identical.
3. There is dielectric evidence that a small number of cages are filled with ethanol molecules when β-quinols are recrystallized from this solvent.
4. The results presented in this paper emphasize the need for well-characterized, uniform samples if meaningful results are to be obtained and interpreted.

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