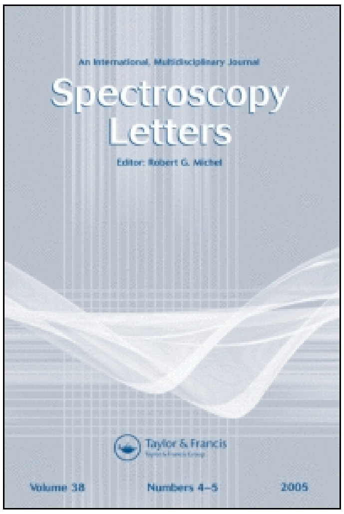

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INFRARED SPECTRA OF LIQUID AND CRYSTALLINE ETHANOL AT HIGH PRESSURES

Key Words: Infrared spectra; ethanol; high pressures; molecular crystals; hydrogen bonding

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ABSTRACT

Mid-infrared spectra in the ranges 400-1800 and 2700-4600 cm^{-1} of ethanol samples in diamond anvil cells at ambient temperature and pressures up to 11 GPa are reported. The freezing pressure is confirmed to be 1.8 GPa, and, unlike methanol, the resulting solid is crystalline rather than glassy. No further phase transitions are observed in this pressure range. The wavenumber shifts of 30 selected peaks with pressure are deduced, and their small magnitudes indicate that only minor distortions of the molecules occur. The effects of the strengthening of the intermolecular hydrogen bonds with pressure on the internal modes are briefly discussed.

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INTRODUCTION

In a recent paper, the mid-infrared spectra of crystalline, glassy and liquid methanol in the pressure range 0-11 GPa have been reported.[1] Unlike methanol, which usually forms a metastable glass when the liquid is subjected to external pressure, ethanol always crystallizes, the freezing pressure at ambient temperature being 1.78 GPa.[2] However, there is some evidence from specific heat[3] and spectroscopic[4] experiments of one or two glassy phases existing at low temperatures. Only one crystalline phase is known, and its structure has been determined by Jonsson using X-ray diffraction techniques.[5] The unit cell is monoclinic, space group Pc $\left(C_s^2\right)$, with four molecules on two sets of general $\left(C_1\right)$ sites.

Methanol and ethanol both form hydrogen-bonded molecular crystals. Recent far-infrared investigations of the lattice spectra of these crystals have provided information on how these hydrogen bonds are affected by external pressure.[6,7] For ethanol, an approximate doubling in strength was estimated over the pressure range 1.8 to 13 GPa. In the present communication, the effects of high pressures on some internal modes of ethanol in the liquid and crystalline states are investigated using mid-infrared absorption spectroscopy. Some relevant properties of ethanol are summarized in Table 1.[8-10]

EXPERIMENTAL TECHNIQUES

Ethanol was supplied by BDH Chemicals and had a minimum assay of 99.7%. Samples were loaded into a diamond anvil cell (DAC) of the piston-cylinder type, together with several ruby chips for in situ pressure measurements using the fluorescent technique.[11] The DAC was equipped with type 2a diamonds and an Inconel gasket, which

TABLE 1

Properties of Ethanol

Property	Value	Unit	Reference
Molecular Mass	46.07	u	8
Dipole Moment	1.70	D	9
Normal Boiling Point	351.7	K	8
Normal Melting Point	155.9	K	8
Freezing Pressure at 295 K	1.78	GPa	2
Molecular Point Group	C_s	---	10
Crystal Space Group	Pc (C_s^2)	---	5
Molecules per unit cell	4	---	5
Site Symmetry	C_1 (2 sets)	---	5
Number of Normal Modes	21	---	--
Symmetry Species	$13a' + 8a''$	---	--

was indented by the diamonds to an initial thickness of about 0.025 mm and drilled to produce a 0.25 mm diameter hole for the sample. Fluorescence spectra of the ruby were excited by the 514.5 nm line of an argon ion laser, operating at powers up to 100 mW, and recorded with a double monochromator equipped with a cooled photomultiplier detector, coupled to photon counting electronics.

A rapid scan FTIR spectrophotometer (Nicolet, model IR42) was used to record the mid-infrared spectra. This was equipped with a water-cooled globar source, potassium bromide beam divider, air-bearing mirror movement and pyro-electric (DTGS) detector and purged with dry, CO_2-free air. Transmission through the small area samples was enhanced by the use of polished brass coned light pipes on both sides of the DAC. Transmittance spectra at 2 cm^{-1} resolution were obtained by ratioing transformed interferograms from sample and background, derived from 2000 and 500 co-added scans, respectively. The spectra of polystyrene film were used to check wavenumber accuracy and resolution performance of the spectrometer.

If necessary, the screws of the DAC were adjusted asymmetrically to produce a slight non-parallelism between the diamond faces and hence reduce interference fringing effects. To minimize hysteresis effects, spectra were recorded after increasing the pressure by a small increment, usually about 0.5 GPa, and waiting for about one hour to allow equilibrium to be established. Widths of the two ruby fluorescent peaks were monitored and these indicated that pressure gradients in the sample were insignificant except at the highest pressures investigated.

RESULTS

Mid-infrared spectra of liquid and crystalline ethanol at four selected pressures are shown in Figure 1 (wavenumber range 400-1700 cm^{-1}) and Figure 2 (2700-3400 cm^{-1}). The intermediate range is not accessible because of strong absorption by the diamonds. From the rich spectra, 30 peaks which could be unambiguously tracked as a function of pressure were selected, and their wavenumbers are plotted in Figure 3. These plots have been fitted to linear functions of the form $\nu = \nu_0 + AP$. Values of the coefficients ν_0 and A are listed in Table 2, together with assignments of the observed modes, comparison with earlier work,[12] and estimates of the percentage changes of mode wavenumbers over the

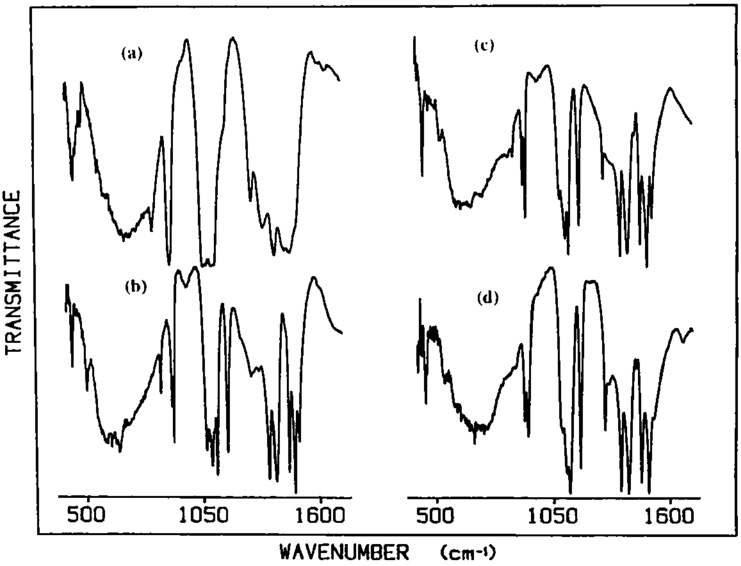

FIG. 1 Infrared Spectra of Ethanol at Selected Pressures. Range: 400-1700 cm^{-1}. Resolution: 2.0 cm^{-1}.
(a) Liquid at 0.4 GPa. (c) Crystal at 5.8 GPa.
(b) Crystal at 2.8 GPa. (d) Crystal at 9.7 GPa.

pressure range 1.78 to 11.0 GPa. Wavenumbers are estimated to be accurate to ±1 cm^{-1} except for broad or saturated peaks or shoulders where the uncertainty could approach ± 3 cm^{-1}, and pressure measurements have a precision of ± 0.1 GPa except for values > 10.0 GPa where gradients degrade this to ± 0.3 GPa.

DISCUSSION

The observed mid-infrared spectra of ethanol at high pressures confirm several results from earlier Raman[2] and far-infrared[6] studies:

(a) the freezing pressure at ambient temperature is 1.8 ± 0.1 GPa;

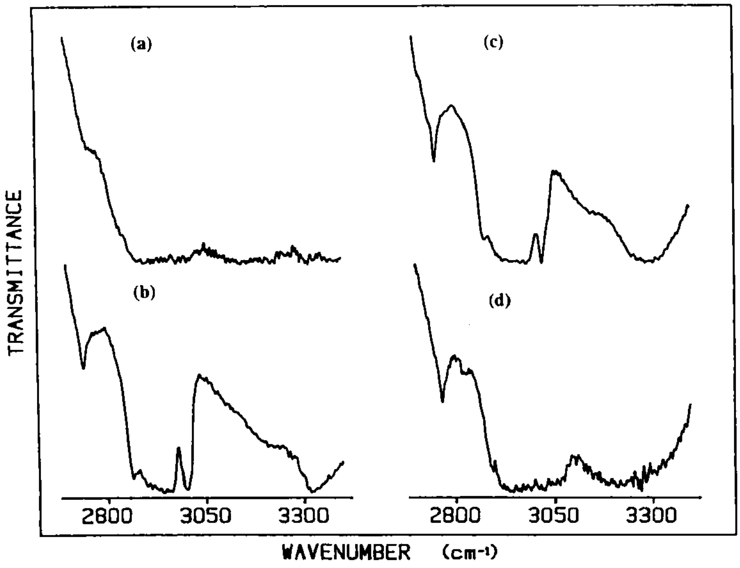

FIG. 2 Infrared Spectra of Ethanol at Selected Pressures. Range: 2700-3400 cm^{-1} Resolution: 2.0 cm^{-1}. Pressures as for Figure 1.

(b) a crystalline rather than a glassy phase is always formed on applying pressure to the liquid;

(c) there are no further phase transitions over the pressure range investigated, 0-11 GPa.

Our results are in good agreement with an earlier mid-infrared study of ethanol in a DAC by Mikawa et al.[12] However, in this work, sample pressures were not measured, and so the dependence of peak wavenumbers on pressure could not be determined.

The ethanol molecule contains nine atoms and hence there are 21 normal vibrational modes. In the crystal, each of these modes splits into four components, as a result of coupling of the four molecules in the unit cell. Because of the low symmetry, all

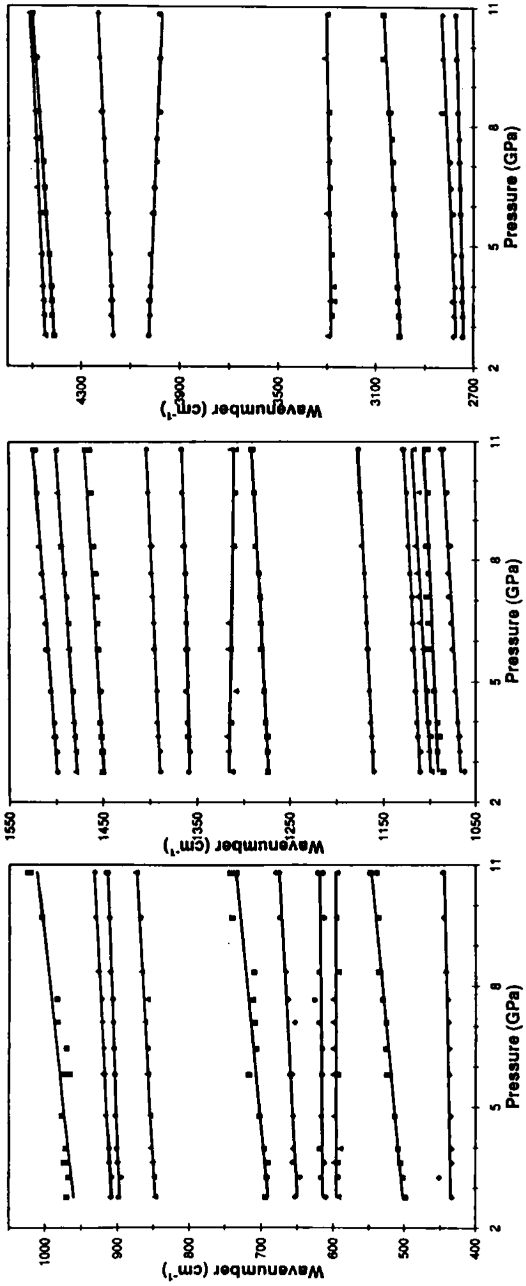

FIG. 3 Plots of Peak Wavenumbers versus Pressure for Crystalline Ethanol. Lines represent fits to the equation $\nu = \nu_0 + AP$, and the coefficients ν_0 and A for the 30 selected peaks are listed in Table 2.

TABLE 2

Infrared Spectra of Crystalline Ethanol
Dependence of Peak Wavenumbers on Pressure

Linear Fits: $\nu = \nu_0 + AP$

				Previous Values[x]		
PEAK[*] #	ν_0 (cm^{-1})	A (cm^{-1} GPa^{-1})	$\Delta\nu / \nu$[†] (%)	Liquid (cm^{-1})	Crystal (cm^{-1})	Assignment[□]
1	431.7	1.18	2.23	433	425	Torsion
2	486.6	5.57	9.22	--	492	Torsion
3	595.1	0.149	0.21	--	570	C-C-O bend
4	613.4	0.543	0.73	---	---	C-C-O bend
5	641.4	3.09	3.93	657	660	C-O-H bend (o/p)
6	675.0	5.54	6.65	---	---	C-O-H bend (o/p)
7	837.9	3.23	3.15	802	840	CH_2 rock
8	891.2	2.11	1.94	880	894	C-C stretch
9	899.5	3.03	2.76	---	902	C-C stretch
10	942.9	6.37	5.49	---	---	Combination
11	1059.4	2.49	1.93	1050	1059	C-O stretch
12	1085.9	1.87	1.41	1089	1080	CH_3 rock
13	1092.8	2.35	1.76	---	1095	CH_3 rock
14	1104.4	2.12	1.58	---	1108	CH_3 rock
15	1155.7	1.91	1.36	1149	1158	CH_3 rock
16	1267.4	2.13	1.37	1273	1280	CH_2 twist
17	1317.4	-0.748	-0.47	1328	1358	C-O-H bend (i/p)
18	1355.7	0.883	0.53	---	1378	CH_3 bend (s)
19	1384.7	1.69	1.00	1381	1390	CH_3 bend (s)
20	1442.5	2.46	1.40	1422	1430, 1449	CH_2 way
21	1470.1	2.77	1.54	1450	1474, 1480	CH_3 bend (as)
22	1490.6	3.12	1.71	1481	1493, 1498	CH_2 bend (s)
23	2732.0	3.58	1.08	2880	2879, 2915	CH stretch (s)
24	2752.3	7.21	2.14	2920	2950	CH_2 stretch (as)
25	2975.0	8.28	2.28	2975	3000	CH_3 stretch (as)
26	3276.6	2.30	0.58	3336	3230, 3335	O-H stretch
27	4041.4	-6.55	-1.34	---	---	Combination
28	4187.7	7.83	1.55	---	---	Combination
29	4381.3	11.3	2.10	---	---	Combination
30	4428.8	7.82	1.45	---	---	Combination

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[*] Peaks may be identified from Fig. 3 (numbered from low to high wavenumber)

[†] Percentage change in wavenumber over pressure range 1.78 - 10 GPa

[x] From Ref. 12. Liquid at ambient pressure; crystal at unknown pressure

[□] Based on Ref. 12. [(o/p), out of plane; (i/p), in plane; (s) symmetric; (as) anti-symmetric] modes are both Raman and infrared active. Hence, a very complex vibrational spectrum is expected, and this is confirmed experimentally, for both the liquid and crystal, as indicated in Figures 1 and 2. Peaks for the liquid are generally broader and stronger, with several showing saturation effects. For the crystal, the peaks are sharper and many modes show multiple components and shoulders, characteristic of an ordered structure. Even so, in this room temperature study, the intrinsic widths and proximity of many peaks result in many components not being fully resolved.

As seen in Figure 3, nearly all modes show small increases in wavenumber as the pressure is increased. The magnitudes of these changes indicate that no major distortions of the molecules occur over this pressure range. One of the exceptions is a torsional mode (#2) which increases by about 9%; another is an out-of-plane C-O-H bending mode (#6) which increases by over 6%. These low frequency vibrations are more affected by the strengthening intermolecular hydrogen bonds, but the changes are much less than those of the lattice modes,[6] directly involving these bonds, where the average wavenumber increase is about 40%. Peak #10, observed in this study, is believed to be a combination mode involving one of these lattice modes; its wavenumber increase is about 5.5%.

Two peaks (#17 and #27) show modest decreases in wavenumber with increasing pressure. The first is the C-O-H in-plane bend. It is thought that the strengthening of the intermolecular hydrogen bonding is accompanied by charge transfer from the O-H molecular bond, which thereby becomes weaker. A similar effect was observed in crystalline methanol.[1] The second is believed to be a combination involving the O-H stretching mode. Rather surprisingly, the peak wavenumber corresponding to this fundamental (#26) is almost independent of pressure, but since this absorption is probably saturated, its evolution with pressure is difficult to measure accurately. A corresponding

Raman peak did show the expected decrease with increasing pressure.[2] Future work on the deuterated species, C_2H_5OD and C_2D_5OD, is planned, which will provide a check on these interpretations and mode assignments.

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