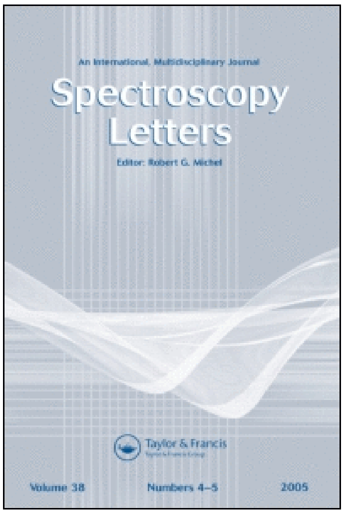

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Anderson, A. , Benson, James , Eaton, Robert A. and Smith, W.(1997) 'Infrared Spectra of Crystalline, Glassy and Liquid Methanol at High Pressures', Spectroscopy Letters, 30: 6, 1125 — 1133
To link to this Article: DOI: 10.1080/00387019708006711
URL: http://dx.doi.org/10.1080/00387019708006711

SPECTROSCOPY LETTERS, 30(6), 1125-1133 (1997)

INFRARED SPECTRA OF CRYSTALLINE, GLASSY AND LIQUID METHANOL AT HIGH PRESSURES

Key Words: Infrared spectra; methanol; high pressures; molecular crystals; hydrogen bonding; glass-crystal transition

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ABSTRACT

Mid-infrared spectra in the range 400-1800 cm^{-1} of methanol samples in diamond anvil cells at ambient temperature and pressures up to 11 GPa are reported. The freezing pressure is confirmed to be 3.6 GPa, and the spectra of the resulting metastable glass are very similar to those of the liquid. When maintained at high pressure, the glass spontaneously transforms to an ordered crystalline phase which is stable over the range 3.6 to 11 GPa. Small changes in peak wavenumbers for 14 internal modes as a function of pressure are observed, indicating that distortion of the molecules is minimal. A slight decrease for the C-O-H bending mode is attributed to charge transfer from the molecular O-H bond to the strengthening intermolecular hydrogen bond.

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INTRODUCTION

Liquid methanol when subjected to external pressure forms a metastable glass or superpressed liquid at around 3.6 GPa[1]. This glass often transforms spontaneously, after an unpredictable time, to an ordered crystal when maintained at high pressures. The competition between vitrification and crystallization has been discussed in a recent paper[2]. Far-infrared spectra of methanol in diamond anvil cells at pressures up to 11 GPa have been reported in an earlier publication[3]. The evolution of five lattice modes as a function of pressure was traced, and no further phase transitions were observed. An increase in hydrogen bond strength by a factor of about 1.5 over this pressure range was estimated from the spectra. In the present communication, we investigate the effects of high pressures on some internal modes of methanol in the liquid, glassy and crystalline states by means of mid-infrared spectroscopy.

EXPERIMENTAL TECHNIQUES

Liquid methanol was supplied by J.T. Baker Co. with a stated purity of 99.5% and was used without further purification. Samples were loaded into a diamond anvil cell (DAC) of the piston-cylinder type, equipped with type IIa diamonds and an Inconel gasket. The latter was pre-indented by the diamonds to a thickness of about 0.025 mm and a hole of diameter 0.250 mm was then drilled, to give an initial sample volume of about 10^{-3} mm^3. Several ruby chips were included in the sample chamber to allow in situ pressure measurements using the ruby fluorescence technique[4]. Fluorescent spectra were excited by the 514.5 nm line of an argon ion laser and recorded on a double monochromator with a cooled photomultiplier as detector, coupled to photon-counting electronics.

Mid-infrared spectra were recorded on a rapid scan FTIR spectrometer (Nicolet, model IR 42), equipped with a water-cooled globar source, potassium bromide beam divider, air-bearing mirror movement and pyroelectric (DTGS) detector. Polished brass coned light pipes were used to reduce the beam size and increase the signal transmitted through the diamond anvil cells. Transmittance spectra at 2 cm^{-1} resolution were obtained by ratioing transformed interferograms from sample and background (typically 2000 and 500 co-added scans respectively). Wavenumber accuracy and resolution performance were checked periodically by recording the absorption spectrum of polystyrene film.

To minimize interference effects, the screws of the DAC were adjusted asymmetrically to introduce a slight non-parallelism between the diamond faces. For consistency and avoidance of hysteresis effects, spectra were always recorded after increasing the pressure by a small increment (typically around 0.5 GPa) and waiting for about one hour to allow equilibrium to be established. From widths of the ruby fluorescent peaks, it appeared that pressure gradients in the sample were minimal except at the highest pressures investigated.

RESULTS

Infrared spectra in the wavenumber range 400-1800 cm^{-1} of liquid and glassy methanol are shown in Fig. 1. Corresponding spectra of the crystal at three selected pressures are displayed in Fig. 2. The range 1800-2700 cm^{-1} is obscured by strong absorption of the diamond anvils. That above 2700 cm^{-1} contains modes associated with C-H and O-H stretches, but, unfortunately, we were unable to load samples in the DAC which were thin enough to allow these peaks to be observed without saturation effects. Wavenumbers of the peaks shown in Fig. 2 have been plotted against pressure in Fig. 3. These plots have been fitted to linear functions of the form $\nu = \nu_0 + AP$. The coefficients ν_0 and A are listed in Table 1 together with assignments of the observed modes, based on those for the liquid[5] and low temperature crystal[6]. For a given scan, pressures are believed to be accurate to ± 0.1 GPa and wavenumbers to ± 1 cm^{-1} (except for broad features or shoulders where the uncertainty could approach ± 3 cm^{-1}). In addition, a slight dependence on sample thickness and history contributes to the scatter evident in the plots of Fig. 3.

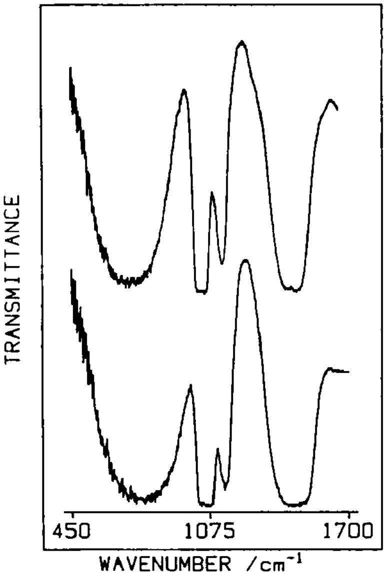

Fig. 1. Infrared spectra of methanol. Upper curve: liquid at 2.83 GPa. Lower curve: glass at 7.36 GPa. Resolution: 2.0 cm^{-1}.

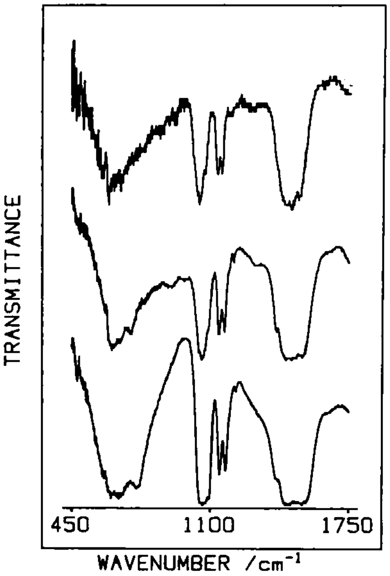

Fig. 2. Infrared spectra of crystalline methanol. Upper curve: P = 4.66 GPa. Middle curve: P = 7.39 GPa. Lower curve: P = 11.0 GPa. Resolution: 2.0 cm^{-1}.

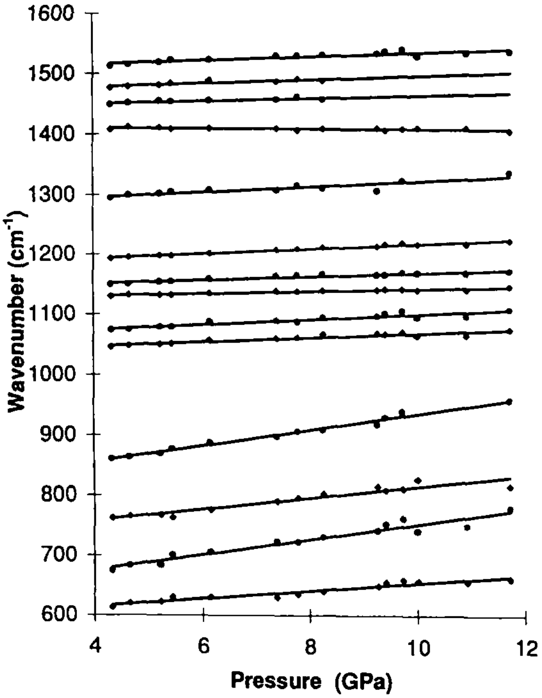

Fig. 3. Plots of peak wavenumbers versus pressure for crystalline methanol. Lines represent fits to the equation $\nu = \nu_0 + AP$, and the coefficients ν_0 and A for the 14 observed features are listed in Table 1.

DISCUSSION

The mid-infrared spectra presented here confirm several conclusions from earlier Raman[7] and far-infrared[3] work:

(a) the freezing pressure is 3.6 ± 0.1 GPa.

(b) a glass or superpressed liquid is always initially formed, and this transforms spontaneously but after an unpredictable time to a crystalline phase.

(c) once formed, the crystal is never observed to revert back to the glass, showing that the latter is a metastable state.

Table 1

INFRARED SPECTRA OF CRYSTALLINE METHANOL
DEPENDENCE OF PEAK WAVENUMBERS ON PRESSURE
Linear Fits: $\nu = \nu_0 + AP$

Peak* #	ν_0 (cm^{-1})	A (cm^{-1} GPa^{-1})	$\Delta\nu/\nu^{\circ}$ (%)	Previous Values (cm^{-1}) Liquid^{x}	Crystal^{+}	Mode (Species)	Description
1	589	6.495	7.85				torsion (TO)
2	623	12.92	14.3	655		$\nu_{12}(a'')$	torsion (TO)
3	722	9.175	8.99		685		torsion (TO)
4	802	13.27	11.6		790		torsion (LO)
5	1033	3.444	2.44	1030	1029	$\nu_8(a')$	C-O stretch
6	1056	4.266	2.95		1046		
7	1123	1.847	1.21	1115	1142	$\nu_7(a')$	CH_3 rock
8	1139	2.878	1.85	1165	1162	$\nu_{11}(a'')$	CH_3 rock
9	1177	3.937	2.45		1256		
10	1278	4.378	2.71		1345	$2\nu_{12}(a')$	overtone
11	1411	-0.354	-0.187	1418	1470 1514	$\nu_6(a')$	C-O-H bend
12	1441	2.214	1.13	1450	1445	$\nu_5(a')$	CH_3 sym.bend
13	1465	3.036	1.52	1480	1426	$\nu_{10}(a'')$	CH_3 asym.bend
14	1503	3.082	1.51	1480	1458	$\nu_4(a')$	CH_3 asym.bend

* Peaks are numbered from Fig. 3 (bottom to top)
° Percentage change from 3.6 to 11.0 GPa
x At 290 K (Ref. 5)
\+ At 93 K (Ref. 6)

It is clear from the similarity of the mid-infrared spectra of the liquid and glass (Fig. 1), that there is no major distortion of the methanol molecules over the pressure range studied and no pronounced discontinuity at the liquid-glass transition. The peaks for both phases show no fine structure, and those for the glass are somewhat broader than those for the liquid. There is a minor shift to higher wavenumbers for most modes as the pressure is increased.

In contrast, the spectra for the crystal (Fig. 2) are considerably more complex, with several peaks splitting and many shoulders appearing. Crystalline methanol in its ordered α-phase has an orthorhombic unit cell, space group $P2_1 2_1 2_1$, containing four molecules on general sites[8]. A group theoretical analysis[9] predicts that all twelve normal modes have four components, as a result of coupling of molecules in the unit cell, of which three are infrared active. In the present room temperature study, the intrinsic widths and proximity of these components will result in many not being fully resolved.

The low frequency torsional mode, ν_{12}, appears as a very broad single peak for the liquid and glass but splits into four components for the crystal in the 500 - 800 cm^{-1} range. The additional peak may result from an LO - TO splitting effect or from a combination with a lattice mode. The C - O stretching mode, ν_8, near 1040 cm^{-1}, a saturated singlet in the liquid and glass, sharpens and develops a shoulder in the crystal. In the Raman spectra of the crystal at low temperatures, a doublet was observed by Pace[10], who used this as an indicator of the transition from the disordered β-phase to the ordered α-phase. The biggest change is in the 1100 - 1200 cm^{-1} range where the CH_3 rocking modes $\nu_7(a')$ and $\nu_{11}(a'')$ appear. These modes overlap and merge in the liquid and glass but separate in the crystal, with a weak third component at higher frequency also visible. A weak shoulder near 1300 cm^{-1} probably originates from an overtone of the strongly absorbing torsional mode, ν_{12}. Four internal modes overlap in the 1400 - 1500 cm^{-1} region. In order of increasing wavenumber, these probably correspond to the C-O-H bend, ν_6; the CH_3 symmetric bend, ν_5; and the CH_3 asymmetric bends $\nu_{10}(a'')$ and ν_4 (a'). They are barely resolved in this work, and at higher pressures two of them (ν_5 and ν_{10}) merge.

All the modes except one show modest increases of wavenumber with pressure as shown in Fig. 3. The percentage changes from the freezing pressure to the maximum investigated, 11.0 GPa, are listed in the right hand column of Table 1. The four torsional modes are affected the most (average about 11%), as might be expected, but even here the change is much less than for the lattice modes (average about 24%)[3]. For the other ten modes observed here, the fractional shifts over this pressure range are all less than 3%, confirming that no major distortions of the molecules occur. The only mode which exhibits a decrease in wavenumber with increase of pressure is, significantly, the C-O-H bending mode. It is known from the far-infrared spectra[3] that the hydrogen bonding between methanol molecules increases significantly with pressure. This strengthening is accompanied by charge transfer from the O-H molecular bond which consequently weakens. This conclusion corroborates that from a Raman study of the O-H stretching region[7], in which a decrease in wavenumber of the ν_1 mode with increasing pressure was observed. The effect is less for the bending mode because the primary motion is almost perpendicular to the O-H and H..O bonds.

Work is in progress on the mid-infrared spectra at high pressures of a related compound, crystalline ethanol, and will be reported in a later paper. Attempts will also be made to develop techniques for loading ultra-thin samples of these interesting hydrogen-bonded systems, so that the strongly absorbing modes at higher frequencies may be investigated.

ACKNOWLEDGEMENTS

This research was supported by grants from the University of Waterloo and the Natural Sciences and Engineering Research Council of Canada.

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Date Received: February 26, 1997
Date Accepted: April 17, 1997