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THE RAMAN SPECTRA OF ICE V AND ICE VI AND EVIDENCE OF PARTIAL PROTON ORDERING AT LOW TEMPERATURES

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ABSTRACT

We present the Raman spectra of ice V at a pressure of 0.54 GPa and ice VI at 0.68 GPa in the temperature range 250 to 83 K. Features in the lattice vibration regions in particular show evidence of proton ordering or a space symmetry transformation at low temperatures. This is in agreement with crystallographic data obtained from X-ray, neutron scattering and dielectric measurements which suggest a very slow ordering transformation below about 123 K. Previous Raman studies of reclaimed samples of ice V and ice VI at 77 K and atmospheric pressure, have not show evidence of proton ordering.

INTRODUCTION

Ice V is stable at pressures of about 0.35 to 0.65 GPa and temperatures below about 250 K. It is regarded as an intermediate high pressure polymorph of ice which comes between the rather open, tetrahedrally linked structures of ices, I_h, I_c, II and III(IX) and the "self clathrate" structure of ices VI, VII and VIII, in which two independent tetrahedrally linked frameworks are incorporated into one another. Ice V can be cooled under pressure and, once it is below about 110 K, the pressure can be removed and a metastable form of this structure recovered at zero pressure.

The unit cell of ice V is monoclinic, space group $A2/a \equiv C_{2h}^6$, containing 28 molecules (ref.1). A neutron diffraction study of quenched D_2O samples of ice V at 110 K (ref.2) indicated a significant proton ordering (in the same space group - $A2/a$) with the population factor ranging from 0.06 to 0.94 found at various sites in the structure. The above space symmetry is consistent with a fully or partially disordered crystal, but is inconsistent with a fully ordered crystal.

Ice VI is stable over a wider range of pressures and temperatures than ice V, 0.62 to 2.1 GPa and temperatures below the melting curve. There is less direct experimental evidence about its structure, but it is believed that the space group of ice VI at high temperatures (ref.3) is $P4_2/nmc \equiv D_{4h}^{15}$ (tetragonal cell with 10 molecules per unit cell). This space symmetry of ice VI requires the protons within the structure to be completely disordered. The low temperature equivalent of ice VI, in which a partial proton ordering was observed by neutron diffraction measurements at 110 K (ref.4) and by dielectric measurements below about 123 K (ref.5) was named ice VI'.

Our high pressure, low temperature Raman cell (ref.6) has been modified to allow the spectra of ice V and ice VI to be recorded in their regions of true thermodynamic stability down to liquid nitrogen temperatures. We present evidence of partial proton ordering at low temperatures; previously published infrared and Raman spectra of reclaimed samples of ice V (refs.7,8,9) and ice VI (refs.9,10) showed no evidence of proton ordering.

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DISCUSSION

ICE V: The Raman spectra of ice V(D_2O) at high (251 K) and low (83 K) temperature in the region of the O–D stretching vibrations and in the region of rotational and translational vibrations are shown in Fig. 1.

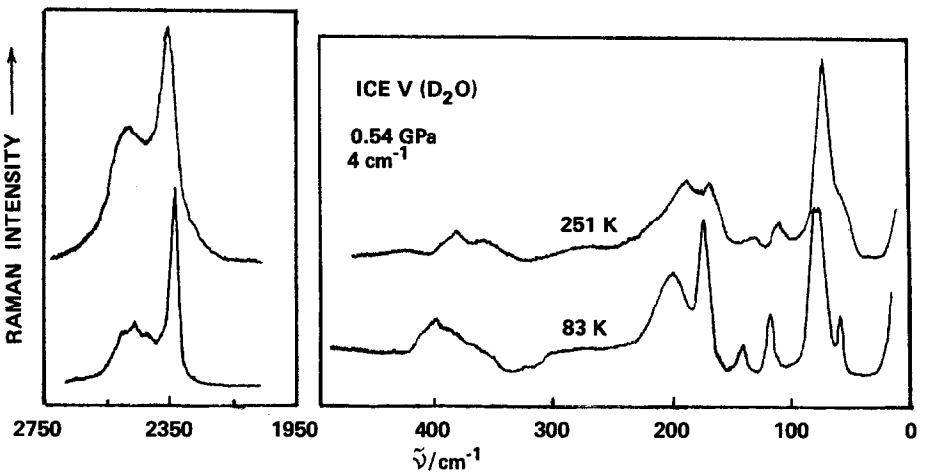

Fig. 1. The Raman spectra of ice V(D_2O) at pressure, temperatures and resolution as indicated.

(NB: There was no evidence of the ice V in our cell wishing to transform into ice II when cooled at 0.54 GPa, although the phase diagrams and previous reports (ref.5) suggest that this should be expected.)

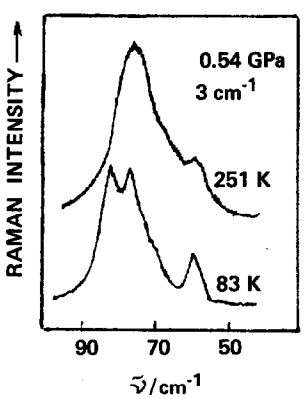

Fig. 2. Some details of the temperature induced changes in the Raman spectrum of ice V(D_2O).(Pressure, temperatures and resolution as indicated.)

The band at 76 cm^{-1} increases its half width on cooling and splits into three components which are separetad by about 5 cm^{-1} at 83 K (Fig. 2). The other bands in the lattice vibration region sharpen considerably and the shoulder at 59 cm^{-1} becomes a sharp band. These changes closely parallel those in the ice III–ice IX transition (Fig. 2 from ref.11). The space symmetry of ice III(IX) allows any state from full order to full disorder and a neutron diffraction experiment detected about 4% disorder in a single crystal of ice IX (ref.12). The sharpening of the bands (with the possible exception of the band at 76 cm^{-1}) and the appearance of new bands in ice V indicates a degree of proton ordering at low temperature which may approach that in ice IX although there is no suggestion of the change in the symmetry (from $A2/a$ to Aa) that would have to accompany a complete proton ordering of this ice form.

ICE VI. The Raman spectra of ice VI(D_2O) at high and low temperatures in the translational, rotational and O–D stretching regions are shown in Fig. 3.

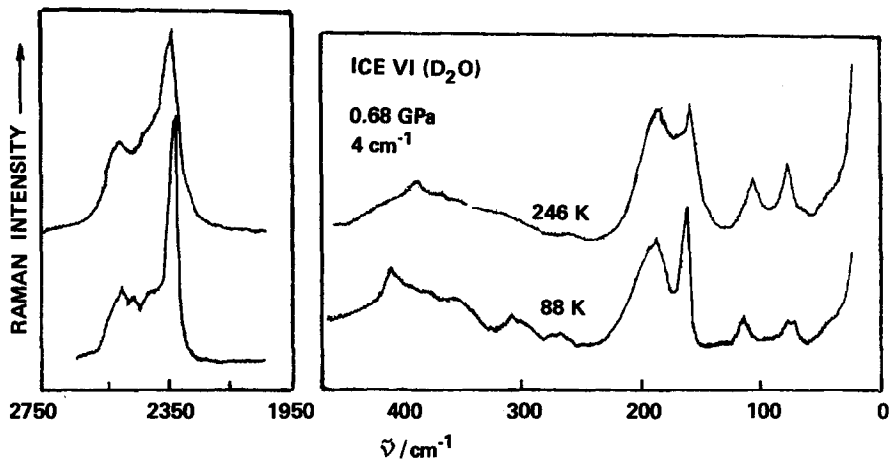

Fig. 3. The Raman spectra of ice VI(D_2O) at pressure, temperature and resolution as indicated.

In contrast to ice V the bands in the lattice vibration region do not show any considerable sharpening on cooling. In this spectral region the Raman spectra of ice VI at high and low temperature differ mainly in two respects: (i) The band at about 80 cm^{-1} (at 246 K) does not show any shift to high frequencies on cooling, although it splits into two components which are about 4 cm^{-1} appart at 88 K (Fig. 4). We have not obsereved this behaviour in lattice vibration bands in other ice forms. (ii) The band at about 160 cm^{-1} is the only band in the Raman spectrum of ice VI in the lattice vibration region which shows appreciable sharpening on cooling (see Table 1, last column).

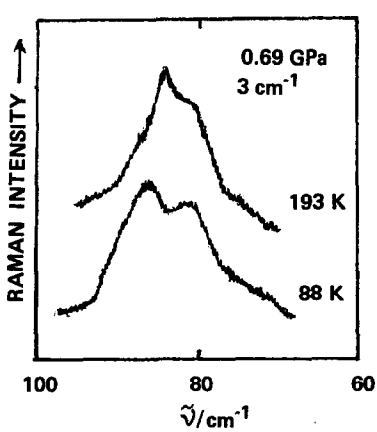

Fig. 4. Some details of the temperature induced changes in the Raman spectrum of ice VI(H_2O).(Pressure, temperatures and resolution as indicated.)

The Raman spectrum of ice VI therefore shows no significant indications of proton ordering on cooling to 88 K (at least not of the kind obsereved in the ice III–ice IX transition or in ice V at low temperaures). The obsereved behaviour may be an indication of a change of the space symmerty of ice VI on cooling.

The fact that we could not detect with certainty any kind of partial ordering in ice VI on cooling, as was done in the dielectric measurements (ref.5), may be due to the different cooling rates. In the dielectric experiments the measurements were made on ice VI samples held for several months at low temperature, while in our Raman experiments the ice VI samples were cooled from 246 K to 88 K in five to six hours. Experimental limitations prevented us from cooling the ice VI more slowly than this.

CONCLUSION

There is no doubt that the Raman spectra of ice V (Figs. 1,2) show evidence of proton ordering at low temperatures. Spectra of both ice V and ice VI suggest possible phase changes at temperatures below 130 K. However, in order to establish this more precisely, more carefully conducted experiments are needed in which the Raman spectra will be recorded by very slow cooling of ice V and ice VI. The isolated O–D or O–H stretching frequencies in HDO molecules in these ices at very low temperatures will also provide useful information. Finally, it will be helpful to have the Raman and far infrared spectra of the disordered phases VII and IV in order to compare them with the corresponding ordered phase. (The table summerises the frequencies and their temperature and pressure dependances, in the lattice mode region of ice V and ice VI.)

TABLE 1

$\nu_{appx.}$ / cm^{-1}	$(\partial\nu/\partial T)_P$ / $cm^{-1}\cdot K^{-1}$	$(\partial\nu/\partial P)_T$ / cm^{-1}/GPa	$1/\nu_{1/2}(\partial\nu_{1/2}/\partial T)_P$ / $10^{-3}\cdot K^{-1}$
ICE V (H_2O)			
80	two components		
	-0.014;-0.068	5.4; 14.2	≃1.6
120	-0.045	14.6	2.5
150	-0.058	23.6	2.3
180	-0.059	25.0	3.0
210	-0.078	44.7	<0.1
error:	(±0.01)	(±1.0)	(±0.5)
	P=0.68 GPa	T=88 K	
ICE VI (H_2O)			
80	two components		
	-0.012;-0.025	15.7; 11.4	≃0.2
120	-0.042	22.8	1.2
170	-0.055	60.0	4.3
200	-0.053	82.8	<0.1
error:	(±0.01)	(±1.0)	(±0.5)
	P=0.74 GPa	T=88 K	

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