

THE RAMAN SPECTRA OF THE KOH-DOPED ICE POLYMORPHS: V AND VI

B. MINČEVA-ŠUKAROVA*, G. SLARK** and W. F. SHERMAN**

* Institute of Chemistry, Faculty of Science, University "Cyril and Methodius", Arhimedova 5, 91000 Skopje, Yugoslavia

** Department of Physics, King's College, Strand, London WC2R 2LS, U.K.

ABSTRACT

The effect on the Raman spectra of the proton ordering induced by KOH in the high pressure phases of ice, ice V and VI has been studied. Our previous Raman studies of ice V and ice VI (ref.1) showed spectroscopic evidence of partial proton ordering at low temperatures (below about 130 K) in ice V and a possible phase change in ice VI. These conclusions were made on the measurements of the lattice vibration region. The present results, based on the observation of the bands due to the uncoupled O-D stretching vibrations of KOH-doped ice V and, in particular, ice VI, show that some kind of proton ordering or partial proton ordering may be induced by the presence of KOH dopant in these two ices.

A Lorentzian curve fit has been used to separate the main band from the side bands in the relatively complex structured band due to the uncoupled O-D stretching vibration in ice V and ice VI.

INTRODUCTION

Over the years, one of our interests in the various phases of ice has been to find spectroscopic evidence of proton ordering. Of ten known ice phases, only ice II is ordered over its whole region of thermodynamic stability. The other two known ordered ice phases, ice IX and ice VIII are ordered forms of their high temperature, disordered forms, ice III and ice VII respectively. Only the naturally occurring ice I_h has not been formed as a proton ordered phase, not even at temperature as low as 15 K. However, recent calorimetric (ref. 2) and dielectric (ref. 3) measurements on KOH doped ice I_h showed that a first order phase transition at 72 K removed about 70% of the residual entropy.

The idea of doping ice crystals with small amounts of salts is not new. It has been known that the presence of certain salts (KOH, NaOH and KSCN for example) in low concentrations in water solution can reduce the dielectric relaxation time of ice crystals. This fact prompted us to study ice V and ice VI doped with a small concentration of KOH in order to corroborate spectroscopically the crystallographic and dielectric indications of partial proton ordering at low temperatures. In fact, in our previous studies of ice V and ice VI (ref. 1), we had been trying to detect signs of proton ordering by looking at the lattice region of the vibrational spectrum. An indication of partial proton ordering in ice V and a possible phase transformation in ice VI has been suggested.

In this paper we report our attempt to detect proton ordering at low temperatures (below 130 K) in ice V and ice VI by observing changes in the bandshapes, intensities and half-widths of the bands due to the uncoupled O-D stretching vibrations in these two ices.

EXPERIMENTAL

Ice V and ice VI were formed in a purpose built high pressure, low temperature liquid cell described in ref. 4. The Raman spectra were excited with a Spectra Physics Ar⁺ ion laser on the 488 nm line and recorded with a Spex Ramalog 5M System.

The KOH doped ices were prepared from redistilled, deionized water with a concentration of 0.08 mol/dm³ with 5% D₂O. [Note: Different concentrations of KOH solution have been tried but, as mentioned in ref. 3, there are no significant changes if the KOH solution is varied from 0.01 to 0.1 mol/dm³]. The samples of ice V and ice VI were held at about 130 K (the temperature at which the proton ordering was reported to occur) for up to two hours.

All the frequencies were calibrated against standard Ne emission lines.

RESULTS AND DISCUSSION

Ice V.

The Raman (ref. 4) and infrared (ref. 5) spectra of the bands due to uncoupled O-D stretching vibrations have already been reported. The shape and half-widths of the bands are similar in both the

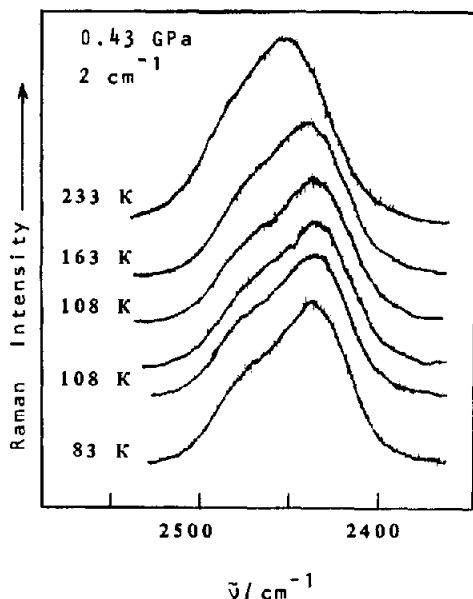


Fig. 1. The Raman spectra of the bands due to the uncoupled O-D stretching vibrations in KOH doped ice V at pressure, temperatures and resolution as indicated.

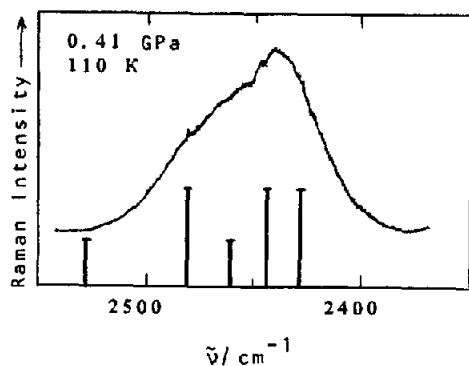


Fig. 2. The Raman spectra of the bands due to the uncoupled O-D stretching vibrations in KOH doped ice V (0.08 mol/dm^3 KOH). The bar graphs indicate the distribution of the $\nu_{\text{OD}}(\text{HDO})$ frequencies as estimated in Table 1.

Raman and infrared spectra. A broad band of about 70 cm^{-1} half-width at 240 K does not sharpen appreciably upon cooling to 83 K but a broad shoulder (about 35 cm^{-1} higher than the maximum) does appear (Fig. 1). At first sight, a comparison of the half-widths of the bands due to uncoupled O-D stretching vibrations at high and low temperature in ice V cannot give any reasonable information about the extent of proton ordering. This is to be expected since there are eight crystallographically different O...O separations (ref. 6) with 10.1 pm between the shortest and longest (see Table 1). This separation requires a half width of the bands due to uncoupled O-D stretching vibrations of at least 100 cm^{-1} , if $d\nu_{\text{OD}}(\text{HDO})/dR_{\text{O}\cdots\text{O}} = +9.8 \text{ cm}^{-1}/\text{pm}$ is used from ref. 7). This may not be enough for a separation of the bands even if full proton ordering occurs.

We have recorded the Raman spectrum of 0.08 mol/dm^3 KOH doped ice V with 5% D_2O at four different temperatures including 110 K at which the sample was held for about two hours as suggested in ref. 8 (see Fig. 1).

Although there is some sign of fine structure in the shape of the bands due to uncoupled O-D stretching vibrations of KOH doped ice V (Fig. 1) it is not easy to decide the extent of proton ordering, if any. We were only able to estimate the positions of the bands due to uncoupled O-D stretching vibrations for the eight different O...O distances (five of which are appreciably different). These are presented in Table 1 and represented schematically in Fig. 2.

The estimated frequencies correspond rather well to the shape and position of the bands due to uncoupled O-D stretching vibrations in ice V. The fact that the components of this band are not clearly resolved at low temperatures shows that there is still an appreciable amount of disorder and that the KOH doping has not induced any ordering, at least none that can be detected spectroscopically.

TABLE 1

Estimated frequencies of the bands due to uncoupled O-D stretching vibrations in ice V*

$R_{O\cdots O}/\text{pm}^{**}$	Estimated $\tilde{\nu}_{OD(HDO)}/\text{cm}^{-1}\dagger$
276.6	2429.0
276.6	2429.0
278.1	2444.0
278.2	2445.0
279.8	2461.0
281.9	2481.0
282.0	2482.0
286.7 \dagger	2528.0

*Estimated using the data from ref. 7: $d\tilde{\nu}_{OD(HDO)}/dR_{O\cdots O} = +9.8 \text{ cm}^{-1}/\text{pm}$ and $\tilde{\nu}_{OD} = 2448.3 + 9.8 (R_{O\cdots O} - 276.9)$

**From ref. 6 at atmospheric pressure and 110 K

 \dagger Corrected for pressure shift, from 0.4 GPa to 0.1 MPa, using the data from ref. 4. \dagger This O...O distance seems to be rather long compared to the others and to the actual band shape (see Fig. 2).**Ice VI.**

Infrared spectra of the bands due to the uncoupled O-D stretching vibrations in ice VI have been reported previously (ref. 9) and the Raman spectra have been obtained by our group (ref. 4). The Raman and infrared spectra look very much alike although the shapes of the bands in the infrared spectra (ref. 9) are not so clear.

The band due to uncoupled O-D stretching vibration in ice VI is quite similar to that in ice V with a half-width of about 80 cm^{-1} and a more pronounced shoulder on the high frequency side, about 42 cm^{-1} from the main maximum. The half-width of this band is about 10 cm^{-1} larger than in ice V which is somewhat unusual, because ice V has eight crystallographically different O...O distances, while ice VI has only three (refs. 10,11). If the crystallographic data are correct (which is still questionable), then the relatively large half-width in ice VI is almost certainly due to the orientational disorder, probably greater than in ice III or ice V.

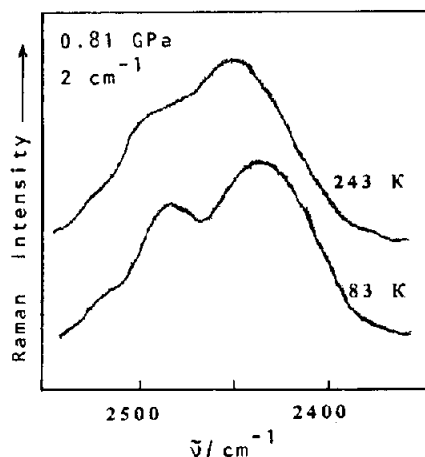


Fig. 3. The Raman spectra of the bands due to uncoupled O-D stretching vibrations in KOH doped ice VI at pressure, temperatures and resolution as indicated.

According to some reports (ref. 12), there may be partial proton ordering in ice VI at low temperatures. This is supported by dielectric measurements (ref. 13), which suggest a slow ordering transition below 123 K.

As in the case of ice V, we have used a KOH dopant in order to attempt to induce ordering, hopefully faster than reported in dielectric measurements. The Raman spectra are shown in Fig. 3.

We have measured the frequencies, half-widths and intensities of the main band and side bands in both KOH doped and undoped ice VI. In order to arrive at a consistent determination of these parameters, we employed a band fitting program (ref. 14) to fit the observed features to Lorentzian bandshapes. An example of this is shown in Fig. 4.

The only difference between the KOH doped and undoped ice VI seems to be the relative ratio of intensities of the main band and side band. The high frequency side band

appears as a well pronounced maximum in KOH doped ice, but remains a shoulder in the undoped sample (Fig. 4. a. and 4. b.) although better resolved than at high temperatures.

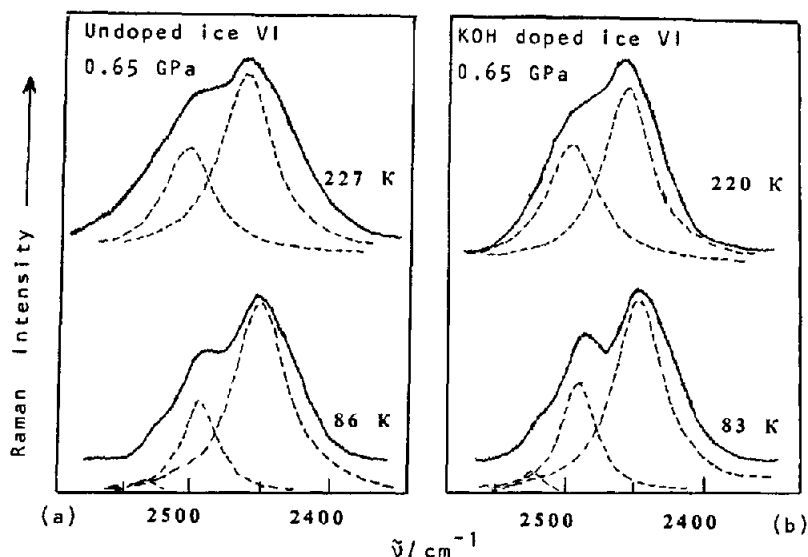


Fig. 4. The Raman spectra of the bands due to uncoupled O-D stretching vibrations in: (a) undoped ice VI and (b) KOH doped ice VI, showing the features of the Lorentzian bandshapes.

It is difficult to arrive at an explanation for this band, particularly when the crystallographic data for ice VI are not yet settled. Neither the main maximum nor the high frequency shoulder sharpen much upon cooling, KOH doped or not, but a small shoulder, about $76\text{--}80\text{ cm}^{-1}$ above the main maximum, does appear upon cooling. The origin of this side band is not clear.

The first high frequency side band, which, in the case of KOH doped ice VI, is a well pronounced maximum is about 42 cm^{-1} higher in frequency than the main maximum. A rough estimate of the position of the band due to uncoupled O-D stretching vibration based on the relation from ref. 7 and the crystallographic data from ref. 10, gives about the same frequencies for the main maximum and the high frequency side band as found in our Raman experiment.

However, there is another explanation for the existence of this side band. It has been suggested (ref. 9), on the basis of the infrared spectra of the bands due to uncoupled O-D stretching vibrations in ice VI, that the high frequency side band is due to the coupling of the O-D...O-D groups. On the other hand, separation of about 42 cm^{-1} of these two bands is rather large and would suggest a strong coupling (if one accepts the explanation from ref. 9). However, this seems quite improbable, bearing in mind a small percentage of HDO in H_2O (5% D_2O in H_2O). There is another high frequency side band with a low intensity, which appears below 200 K, which could be assigned to the antisymmetric stretching vibration of the isolated D_2O molecules.

Neither of these two proposed explanations for the existence of the side bands can be proven or disproven until more reliable crystal data are obtained. More Raman experiments, using different dopants are also needed to give a correct assignment of the bands due to uncoupled O-D stretching vibrations in ice VI and to allow more definite conclusions about the extent of proton ordering.

CONCLUSION

The results presented in this paper do not give as convincing an argument about the extent of proton ordering in KOH doped ice V and ice VI as we had wished. It is quite possible that ordering could occur if cooling were done slowly enough, but it is unlikely to happen above 130 K, which is close to the temperature at which the relaxation time (extrapolated from measurements at higher

temperatures (ref. 15)) becomes about 1 s.

Future attempts to detect induced ordering will use different dopants such as KSCN or LiF in different concentrations.

Infrared and Raman spectroscopy is not as sensitive as other techniques in detecting ordering, but is relatively easy to perform and can provide useful indications of how other experiments may be done.

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