

THE RAMAN SPECTRA OF TETRAHYDROFURAN CLATHRATE HYDRATE AS A
FUNCTION OF PRESSURE AND TEMPERATURE

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Over the years, we have used Raman spectroscopy for studies on ice and its high pressure polymorphs [1]. Recently, we have extended our studies to clathrate hydrates using the same high pressure, low temperature liquid Raman cell as we used for ice work.

Clathrate hydrates are icelike crystalline solids in which small "guest" molecules occupy almost spherical holes in the three dimensional network of tetrahedrally H-bonded water molecules [2].

Among the many clathrate hydrates, tetrahydrofuran clathrate (THF) is one of the most frequently studied. Its infrared [3] and Raman [4] spectra have been reported in somewhat limited regions of pressures and temperatures. In the present work, we report the Raman spectra of THF clathrate hydrate in the temperature range between 250 and 80 K and pressures up to 0.5 GPa. Although we have recorded the Raman spectra of THF clathrate hydrate in the whole spectral region, we will concentrate our attention on the spectral region due to uncoupled O-D stretching vibrations and in some extent on the lattice region. A comparison with the corresponding Raman spectra of ice I_h will be made.

The frequency of the Raman band due to uncoupled O-D stretching vibration in THF clathrate at 230 K is the same as that in ice I_h (Fig. 1). It is noticeable that this band is much broader in THF clathrate hydrate than in ice I_h (its FWH in THF clathrate is 58 cm⁻¹ at 230 K, while in ice I_h it is 33 cm⁻¹, Fig 1a). Although this band sharpens on cooling, it still stays twice as broad as in ice I_h (its FWH at 82 K in THF clathrate is 47 cm⁻¹, while in ice I_h it is 20 cm⁻¹, Fig. 1b). This difference in the halfwidths is to be expected since the unit cell of THF clathrate hydrate contains 136 molecules [5] with four crystallographically distinct O...O distances (276.7, 277.6, 279.6 and 281.2 pm) which are represented in the structure with different multiplicities. The hydrogen atoms are disordered. The broadness of this band in THF clathrate is most probably due to these two effects: (1) the spread of O...O distances of ~4.5 pm and (2) the disordered arrangement of the protons.

The coincidence of the main maximum of the band due to uncoupled O-D stretching vibrations in THF clathrate hydrate and in ice I_h at high (230 K) and at low (82 K) temperature is somewhat surprising in view of the fact that the average O...O distance in THF clathrate hydrate is ~3 pm longer than in ice I_h. This will require ~30 cm⁻¹ higher frequency of $\nu_{OD(H_2O)}$ in THF clathrate compared to ice I_h (estimated using $d\nu_{OD(H_2O)}/dR_{O-O} = +9.8 \text{ cm}^{-1}/\text{pm}$ [6]).

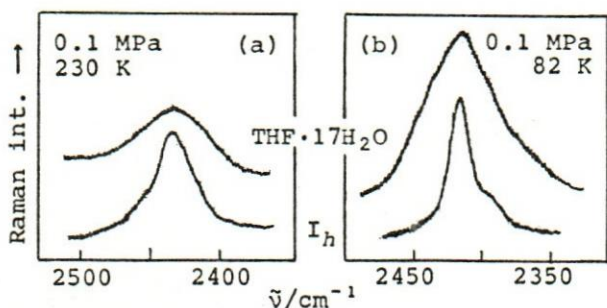


Fig. 1 The Raman spectra of $\nu_{OD}(H_2O)$ in THF clathrate and ice I_h doped with 6% D_2O at (a) 230 K and (b) 82 K

It has been suggested, on the basis of the Raman spectra of O-H and O-D stretching vibrations in THF clathrate [4] that the decrease in ν_{OH} and ν_{OD} is due to the strong coupling between the O-H stretching and O-H...O bending motion which arises from the great deviation from linearity of the O-H...O linkage. There are at least two reasons why this explanation should be reconsidered: (i) it is generally believed that non-linearity of the O-H...O bond leads to weaker, not stronger hydrogen bonds. (ii) the estimated 30 cm^{-1} higher frequency of THF clathrate compared to ice I_h [6] suggests that the crystallographic data on THF clathrate hydrate [5] could be insufficiently precise.

The temperature dependence of the frequency of $\nu_{OD}(H_2O)$ in THF clathrate hydrate at 0.1 MPa is $+0.182 cm^{-1}/K$. Although there is considerable uncertainty in the measurement of this value, it is close to the $d\nu/dT$ values obtained for ice I_h and the other high pressure forms of ice [1].

The increase of pressure, decreases $\nu_{OD}(H_2O)$ by a rate of $-38.5 cm^{-1}/GPa$ (at 240 K), which is again close to the value obtained for ice I_h and other high pressure forms of ice [1]. The effect of pressure on $\nu_{OD}(H_2O)$ in THF clathrate have been measured up to 0.26 GPa. Above this pressure, bands characteristic of ice II appear. Further increase of pressure, at about 240 K, "pushed" the guest molecule out of the clathrate cage and ice V appeared. The FWH of $\nu_{OD}(H_2O)$ bands increases with increasing pressure (from 58 cm^{-1} at 0.1 MPa to 76 cm^{-1} at 0.26 GPa and 230 K). This broadening of the band suggests that a contribution from ice II at higher pressure appears.

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