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INELASTIC NEUTRON SCATTERING OF WATER AND ICE IN POROUS SOLIDS

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Résumé - L'arrangement intermoléculaire de l'eau à 80 K dans les gels de titane, les zéolites et le chlorhydrate d'alumine a été étudié par la diffusion inélastique des neutrons. Les mesures effectuées de 35 jusqu'à 250 meV, comprennent les fréquences des libration et déformation des molécules. Les spectres ont mis en évidence des différences avec la glace qui augmentent quand la taille des pores de l'adsorbat diminue. Ces effets sont attribués à une structure de l'eau moins organisée que celle de la glace et dans laquelle les liaisons hydrogène sont moins nombreuses.

Abstract - The intermolecular structure of sorbed water and its dependence on the surface and porous properties of the adsorbent has been studied by incoherent inelastic neutron scattering measurements of water at 80K in titania gels, Zeolite-A and aluminium chlorohydrate. An energy transfer range from ~35 to ~250 meV was covered which included the frequencies of molecular librations and deformation mode. Spectra showed an increasing departure from that of bulk ice as the pore size and water uptake was reduced. These changes can be tentatively ascribed to a less ordered water structure where hydrogen bonding is restricted compared to that in bulk ice.

1 - INTRODUCTION

There is considerable evidence which suggests that the properties of water close to solid interfaces are significantly different from those in the bulk /1,2/. However the range of influence of interfaces on water structure still remains controversial. Structural studies of water within porous materials may provide an important insight into this problem, as has been demonstrated by recent neutron diffraction measurements of D₂O within porous silicas /3/. From these it was concluded that there was no appreciable structural modification in the liquid but at low temperature there was evidence of structural disorder and the formation of cubic ice, rather than the normal hexagonal ice. Changes in the structure of water are also reflected in the intermolecular vibrational spectra, particularly the librational bands which are very sensitive to variations in hydrogen bonding. This has been demonstrated by several investigations /4,5,6/ of bulk ice and water, using mainly infra red and Raman spectroscopy, which have been related to structural predictions based on computer simulation /7,8/. For the study of water in porous materials however, inelastic neutron scattering (INS) has a particular advantage, because apart from the absence of selection rules, the incoherent cross-section of the H-atom is considerably larger than that of other atoms. This feature is demonstrated in the present INS investigation of ice and water adsorbed at low temperature in well characterised porous titania gels and zeolites.

2 - VIBRATIONAL SPECTRA OF LIQUID WATER AND ICE

Vibrational spectra of water and ice have been determined extensively by infra red /4,9/ and Raman spectroscopy /6,10,11/, although neutron scattering measurements

have been much less numerous. The frequencies of the three intramolecular modes corresponding to the ν_1 symmetric vibration-active in the Raman and inactive in the infra red, the deformation mode (scissors vibration), ν_2 , and the ν_3 antisymmetric vibration - active in the infra red and inactive in the Raman are shown in Table 1. Only one of these, the ν_2 vibration, falls within the range of energy transfer covered in the present study. Bands of lower frequency arise from intermolecular vibrations corresponding to librational and translational motions. The frequencies of these, which are sensitive to hydrogen bonding and the structure of ice and liquid water (they are absent in the vapour), are less well defined and the approximate ranges as determined by Raman spectroscopy /6,11/ are shown in Table 1.

Table 1

Spectral frequencies (meV) of ice and water determined from
i.r. and Raman Spectroscopy

	ν_3	ν_1	ν_2	$2\nu_L$	ν_L	ν_T
water	433	407	204		92-89, 68, 56-53	22-7
ice I	399	384	205	179, 136, 128 *	113, 93, 75 *	~35 - 5

* Values from Raman measurements at 269K /6/; at 123K $2\nu_L$ and ν_L increased by ~8 and 4 meV respectively. N.B. 100 meV $\approx$ 806 cm^{-1}

Fig. 1 - Librational modes of water about the three principal axes of the molecule.

The librational motions of water about the three principal axes of an isolated molecule are shown in Fig. 1. These are referred to as the wagging, twisting and rocking vibrations respectively, and only two of these (about the A and C axes) are active in the i.r. and Raman. All three librations should be observed by neutron scattering and should increase in frequency in the same order as the reciprocal of the respective moments of inertia about the axes: $I_C^{-1} < I_B^{-1} < I_A^{-1}$. In bulk water and ice there is strong molecular coupling due to H-bonding forces, and the 3 librations of one uncoupled molecule will tend to give a broad band of frequencies. These will have a higher frequency in ice compared to water because of the more extensive hydrogen bonding, as has been observed (Table 1). Moreover in ice, which has a structure with four H-bonds per molecule (c.f. ice I_h), compared to the disordered H-bonded structure of liquid water, there will be more possibility that the frequencies of the separate librations will be resolvable.

3 - EXPERIMENTAL

3.1 Materials

Titanias having different surface and porous properties (Table 2) were prepared as follows: hydrous titanium oxide (HTO) was precipitated from a solution of titanium chloride with sodium hydroxide. The wet sample was filtered as a paste (containing exchangeable Na^+ ions; this was dried slowly (at $\sim 295\text{K}$ and eventually at $\sim 350\text{K}$) samples containing different water contents being removed progressively. A similar procedure was used to prepare deuterated samples and also those containing Cs^+ and Li^+ as exchangeable cations. Mesoporous titanias I and II were prepared /12/ by drying two different sols (containing primary particles of anatase having different sizes) to give hard glassy gels. Properties - table 2 were determined from measurements of N_2 adsorption isotherms at 77K made on samples outgassed at $\sim 295\text{K}$.

Table 2

Properties of porous titanias

Titania	Specific surface * area, $S_{\text{BET}}/\text{m}^2\text{g}^{-1}$	Total pore * volume, $V_p, \text{cm}^3\text{g}^{-1}$	Mean pore * diameter, d_p/nm	Structure (XRD)
Hydrous titanium oxide (HTO) - microporous	262 ⁺	0.15 ⁺	< 2	amorphous
Mesoporous titania I	221	0.33	6.5	poorly crystalline anatase
Mesoporous titania II	54	0.43	34	anatase

* per g of hydrated titania - after slow drying in air at $\sim 295\text{K}$

⁺ Results for typical sample washed free of Na^+ ions and dried in air.

Samples of Zeolite 5A (containing exchangeable Ca^{2+}) were obtained from the Linde Corp; these were saturated with water ($\sim 0.3\text{g g}^{-1}$) by exposing at the SVP in a dessicator. Ca^{2+} was enchanged for Li^+ and Cs^+ by immersing the zeolite several times in solutions of LiNO_3 and CsNO_3 (2 mol dm^{-3}).

Aluminium chlorohydrate (ACH) was prepared as a transparent glassy solid by partially drying a commercial (Hoechst) ACH solution which has been studied previously /13/. The amorphous glassy hydrate has the probable constitution - $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]\text{Cl}_7$.

3.2 Neutron scattering

Inelastic neutron scattering measurements were made with the IN1B beryllium filter spectrometer /14/ installed on the hot source of the HFR at ILL, Grenoble. Differential incoherent cross sections were determined by scanning the incident neutron energy; a range from 35 to $\sim 250 \text{ meV}$ was covered using successively the (111), (002) and (220) Bragg reflections of the copper monochromator. The resolution function (FWHM) increased from ~ 3 to 10 and 8 to 35 meV over the ranges covered by the (002) and (220) planes respectively /15/. Samples, contained in thin rectangular aluminium sachets, had a thickness which was calculated to give a total scattering cross section of approximately 10%. The scattering angle at the sample was 40° . Measurements were made at $\sim 80\text{K}$ (liquid nitrogen cryostat), although in one experiment the sample was varied between 10K and 300K using a Displex cryostat.

4 - RESULTS AND DISCUSSION

4.1 Ice, Zeolite A and ACH

The INS spectrum of ice (Fig. 2a) at ~80K shows a librational band, extending from ~65 meV to ~130 meV, with peaks at 81 meV and ~102 meV. There is also evidence (220 plane) of a shoulder at ~110 meV. A broad weaker band extends from ~150 to 240 meV with a maximum ~200 meV. The librational band can be synthesised by convoluting three Gaussians (centred at 78, 96 and 116 meV) as shown. The synthesis showing bands of low intensity in the range 150 - 180 meV, followed by a maximum at 207 meV may tentatively be ascribed to librational overtones and the ν_2 deformation respectively. These frequencies are in very good accord with similar assignments derived from recent Raman measurements (Table 1) /6/.

The spectrum of sorbed water in Zeolite 5A at 80K (Fig. 2b) shows several different features compared to bulk ice: the librational band now has no well defined maxima, and has broadened by shifting to lower frequency, extending from 45 to ~120 meV. The broad librational overtone band has now almost disappeared and the ν_2 band at ~210 meV, has a reduced intensity. Measurements made on the Li^+ and Cs^+ exchanged forms of Zeolite A containing water saturating the intracrystalline pore volume, showed very similar features.

The changes in the libration band suggest that the water in the zeolite cavities has a more disordered structure compared to that of bulk ice, in which the number of H-bonds may be variable with an average somewhat less than the four per molecule in hexagonal ice. Thus, molecular dynamics simulations of the structure of liquid water made by Stillinger /16/, indicate that the number of H-bonds per molecule has a broad distribution with a mean of 2.3; this would likewise accord with the broader libration band observed at even lower frequency for the liquid (Table 1). Disorder may arise in the zeolite cavities because of the effect of interactions between the water molecules and the aluminosilicate framework. Since at saturation there are only ~27 molecules per cavity in CaA, the development of the long range order found in ice would be prevented.

In solid aluminium chlorhydrate (ACH) the librational band (Fig. 2c) occurs at a slightly lower frequency than observed for CaA, but again shows more distinct features (maxima at 70, 76 meV and shoulders at 104, 120, 141 meV) as observed in bulk ice. This would suggest that the hydrogen bonding and co-ordination of water in the hydrate was sufficiently regular although less extensive than in ice, to give rise to discrete librational modes. Although a detailed interpretation is not possible here the present results are consistent with several studies of librational modes in simpler salt crystals /17,18/ from which details of the environment and potential field of water molecules has been derived.

4.2 Porous titanias

Spectra of sorbed water (at 80K) in titanias (Fig. 3a,3b and 3c) containing pores of different sizes (Table 2) clearly illustrate the effect of the cluster size on the intermolecular structure of water, which has been referred to with Zeolite A. Thus the sorbed water (0.24 g g^{-1}) within the titania having the largest pores has a librational spectrum (3a) which is very similar to bulk ice. The additional shoulder at ~58 meV however suggests the presence of some disordered water which may arise close to the titania surface.

Within the smaller pores of the mesoporous titania I, the water (0.26 g g^{-1}) has a less ordered structure, as evidenced by the broad librational band (3b), having similar features to that observed with Zeolite A. Since the pores in the gel are formed by a packing of the approximately spherical particles of anatase /12/, thus giving a structure containing interconnected cavities, it is possible to make a crude estimate of the number of water molecules which would saturate an "individual" pore. (N.B. Fig. 3b corresponds to ~75% of total saturation). Assuming these pores are spheroidal, with a diameter of 6.5 nm, this would correspond to a cluster containing $\sim 4 \times 10^3$ molecules.

Fig. 2 - Inelastic neutron scattering spectra of water at 80K (a) ice (b) in zeolite-A (c) in aluminium chlorohydrate. Broken lines are Gaussians which when synthesised give the experimentally determined spectrum of ice in (a). Open and closed symbols denote measurements with the Cu (002) and (220) monochromator planes respectively.

The pores within the microporous titania are considerably smaller and are of the order of molecular size as is evident from the type I adsorption isotherm obtained with N_2 at 77K. Although further discussion is not appropriate here, it is probable that N_2 is only partially accessible to the structure due to the small size of the pores, and strong retention of water even after pumping. For this reason the values of S_{BET} and V_p quoted in Table 2 are likely to be underestimates; furthermore the value of d_p , although small, cannot be determined precisely from a type I isotherm /19/. Fig. 3c shows the librational band of a gel sample containing a typically high water content (35% weight loss on ignition). Although it is evident that the librational band is broadened and shifted to lower frequency (~ 45 meV), there is a distinct maximum at 70 meV (lower than in ice). The latter may indicate that the water molecules are less hydrogen bonded, but nevertheless have a more ordered structure than in mesoporous titania I and zeolite A, which is perhaps more akin to the co-ordinated water in ACH. Such a structure might arise from the extensive co-ordination of water molecules with the hydroxylated titania surface, which could occur in micropores.

The possible influence of the titania surface on the water structure can also be seen in Fig. 4, which shows librational bands of HTO at progressive stages of dehydration. For a thick paste (26% w/w as TiO_2) the band (4a) is very similar to that of ice although there is an additional shoulder at ~ 65 meV - possibly due to water near the surface of the small (< 4 nm) amorphous particles. In the almost

Fig. 3 - INS spectra of water at 80K in porous titanial gels; (a) and (b), mesoporous titanias I and II, (c) microporous HTO.

solid gel, containing a lower water content (55% w/w as TiO_2), this band is much more evident (4b) until on further dehydration (76% w/w as TiO_2) a broader band shifted to lower energy, is observed (4c).

Samples containing Cs^+ and Li^+ ions, had similar librational spectra to that described for the HTO containing exchangeable Na^+ ions, which would suggest that the pore size and titania surface have a more dominant effect on the intermolecular structure of water than the charge density of the cation. The effects of deuterium substitution on the librational band in one HTO preparation (65% w/w TiO_2) were also investigated. The band was shifted to lower energy, with a maximum at ~ 55 meV, and extended down to ~ 35 meV; a small maximum, at ~ 154 meV, corresponded to the ν_2 vibration. These shifts have a ratio very close to $2^{1/2}$, as is expected for modes involving mainly motions of hydrogen atoms.

In one experiment librational bands of water in HTO (65% w/w TiO_2) were measured at increasing temperatures (10, 45, 200 and 300K) extending above the melting point of bulk ice. Although band broadening occurred with increases in temperature, the position of the peak maximum remained almost unchanged, indicating an absence of a distinct phase transition. This would suggest that the effects of the force fields within the HTO micropores dominate the structure of water, and result in a more extensive H-bonded arrangement of the molecules above 273K, possibly by restricting librational and translation motion.

5 - CONCLUSION

Measurements of librational spectra of water adsorbed at 80K in porous titanias and zeolite A indicate the structure is more disordered and less extensively hydrogen bonded than in bulk ice at similar temperature. These effects become more marked as the pore size is decreased and the water uptake is reduced. Tentative estimates of the adsorbed layer thickness in small mesopores show that disorder may extend out to beyond ~ 1.2 nm from the titania surface but such effects are minimal in larger mesopores where the thickness is ≥ 4 nm.

Fig. 4 - INS spectra of water at 80K in HTO preparations at progressive stages of dehydration. Percentages, w/w of TiO_2 , are (a) 26 (b) 55 and (c) 76 respectively.

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