

## INFRARED SPECTRA OF THE ICES AT $\approx 4$ K AND THE INTERPRETATION OF THE $\nu_{OD}(\text{D}_2\text{O})$ BANDS OF ICES II AND IX

By F. E. BATES, S. M. JACOBS and J. E. BERTIE

(Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada)

**ABSTRACT.** We have studied the infrared absorption by the OD stretching,  $\nu_{OD}(\text{D}_2\text{O})$ , and  $\text{D}_2\text{O}$  rotational,  $\nu_R(\text{D}_2\text{O})$ , vibrations of fully deuterated ice II and ice IX at 10 K, and the absorption by OD stretching vibrations,  $\nu_{OD}(\text{HDO})$ , of HDO molecules isolated in ices Ih, II, and IX at 10 K. Calculations of the frequencies and relative intensities of the zero-wave-vector normal  $\nu_{OD}(\text{D}_2\text{O})$  vibrations of ices II and IX have allowed the  $\nu_{OD}(\text{D}_2\text{O})$  absorption to be assigned. Each component of the band is broad, even at 10 K, most probably because of Fermi resonance between the fundamental OD stretching vibrational states and the isoenergetic continuum of high-order overtone and combination states of the lattice modes. This work has yielded the most complete interpretation yet achieved of an infrared band due to the OH or OD stretching vibrations of a phase of ice.

The far-infrared absorption by the translational vibrations of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  ices Ih and Ic at 4.3 K has been measured, and has revealed differences between the spectra of ices Ih and Ic for the first time.

Papers describing this work in full have been published in *Journal of Chemical Physics*, Vol. 67, No. 4, 1977, p. 1511-18, and Vol. 67, No. 6, 1977, p. 2445-48.

### DISCUSSION

W. B. KAMB: What effect should 4% of proton disorder have on the width of the O-D stretching bands in ice IX?

J. E. BERTIE: The 4% of proton disorder that you showed to exist in ice IX apparently does not affect the width of the O-D stretching bands significantly. I say this because the band of ice IX is just as well resolved as that of ice II, which you showed to be fully ordered. It is hard to give a precise answer which is based on theory, but I would not expect 4% of disorder to broaden vibrational bands very much. We did, of course, neglect the proton disorder in our treatment.

## INFRARED SPECTRA OF THE CLATHRATE HYDRATES

By D. A. OTHEN, P. G. WRIGHT, F. E. BATES, D. K. HENDRICKSEN,  
S. M. JACOBS and J. E. BERTIE

(Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada)

**ABSTRACT.** Detailed mid- and far-infrared spectra have been recorded for authenticated samples of several clathrate hydrates with the two main structures, I and II, at temperatures between 150 and 4 K. The systems are complicated, yet a detailed analysis of the many interesting spectral features is required before reliable, detailed information can be obtained. Consequently only rather general conclusions can be drawn at present.

The mid-infrared spectra have been recorded for the structure I hydrates and deuterates of ethylene oxide, trimethylene oxide, and cyclopropane, and the structure II hydrate and deuterate of trimethylene oxide, all at 100 K. The OD stretching vibrations of isolated HDO molecules,  $\nu_{\text{OD}}(\text{HDO})$ , and of the fully deuterated forms,  $\nu_{\text{OD}}(\text{D}_2\text{O})$ , have also been recorded for cyclopropane and trimethylene oxide structure I hydrates at 40 K, and the absorption by the guest molecules has been studied for all of the structure I hydrates at temperatures down to 40 K.

The absorption by the water molecules at 100 K is similar to that in ice, with frequencies that vary in the expected way with the lattice parameter and, hence, the hydrogen bond lengths. The shapes of the  $\nu_{\text{OH}}(\text{H}_2\text{O})$ ,  $\nu_{\text{R}}(\text{H}_2\text{O})$ , and  $\nu_{\text{R}}(\text{D}_2\text{O})$  bands are essentially the same for structures I and II, while the  $\nu_{\text{OD}}(\text{D}_2\text{O})$  band varies only slightly and depends more on the guest molecule than on the structure. The water absorption changed only slightly when the samples were cooled from 100 to 40 K.

The  $\nu_{\text{OD}}(\text{HDO})$  bands provide clear evidence that the distribution of hydrogen bond lengths in cyclopropane hydrate differs from those in ethylene oxide and trimethylene oxide structure I hydrates, even though powder X-ray methods indicate that the three hydrates are isostructural. The difference is attributed to an interaction between the hydrogen bonds and the dipole moment of the guest which is too irregular to be sensed by powder X-ray methods.

Some absorption bands of the guest molecules are visible in the spectra of structure I hydrates and, as expected, fewer are visible in the spectra of structure II hydrates, which have a higher water-to-guest ratio. For both structures more guest bands are visible in the spectra of deuterates since the  $\text{D}_2\text{O}$  absorption is weaker than that of  $\text{H}_2\text{O}$ . The guest bands are single in most cases, with half-widths of 1 to 5  $\text{cm}^{-1}$  for ethylene oxide and cyclopropane and 5 to 15  $\text{cm}^{-1}$  for trimethylene oxide in its deuterates of both structures. One band of ethylene oxide at 100 K and below is a doublet, and one degenerate and one non-degenerate vibration of cyclopropane yields a doublet at 40 K. This must mean that there are two non-equivalent positions for the guest molecule in the tetrakaidecahedral cage of the structure I hydrate at these temperatures.

Far infrared spectra have been recorded of the structure I hydrates of ethylene oxide, cyclopropane, trimethylene oxide, and xenon, and of the structure II hydrates of trimethylene oxide, cyclopropane, tetrahydrofuran, cyclobutanone, and 1,3-dioxolane, all at 4.3 K. The spectra of the hydrates and corresponding deuterates have enabled the absorption by the rotational vibrations of the guest molecules in the cage to be identified. The absorption above 100  $\text{cm}^{-1}$  by the translational vibrations of the water molecules is significantly different for the two structures, but is rather insensitive to the guest molecule within one structure.

A careful search was made for evidence of the transition in trimethylene oxide structure I hydrate at which the guest molecules partly order, that was detected by Davidson from dielectric studies. No spectral changes due to the transition were detected.

Papers describing this work have been published in *Canadian Journal of Chemistry*, Vol. 51, No. 8, 1973, p. 1159–68; Vol. 53, No. 1, 1975, p. 71–75; Vol. 55, No. 10, 1977, p. 1777–85. A further paper is accepted for publication in *Journal of Chemical Physics* and others are in preparation.

## DISCUSSION

W. B. KAMB: Do you have an interpretation of the splitting, for ice Ih, of the spectral peak at 160  $\text{cm}^{-1}$ , which is not split for ice Ic?

J. E. BERTIE: The general answer is that, because the structures differ, there are twice as many branches of dispersion curves for ice Ih as for ice Ic, so differences between the spectra of the two phases are to be expected. A more specific answer depends on the model you assume for the force field appropriate to the translational vibration. If you use the force field for ice Ih that Klug, Wong, and Whalley presented at Ottawa in 1972, the splitting is explained by two branches of dispersion curves which are fairly flat across the Brillouin zone near  $160\text{ cm}^{-1}$ , and which yield two peaks in the density of vibrational states according to the histogram that Klug and others reported. With other force fields the explanation may differ in detail but must be the same in principle.

J. W. GLEN: Is there any evidence that the differences found for the hydrate of cyclopropane as compared to ethylene oxide and trimethylene oxide correspond to any ordering of protons in the cage or to modifications of the cage electrical properties (presumably caused by electrical interaction with the guest molecule)?

BERTIE: There is no evidence at all to suggest that the protons in the water lattice order at any temperature for any clathrate hydrate of structure I or II. Hexamethylene tetramine hydrate does contain partially ordered protons, but it has a quite different structure, in which the nitrogen atoms are hydrogen-bonded to the water molecules. The dielectric relaxation of the water molecules is much faster, at a given temperature, for the hydrates of the dipolar guest molecules than for those of cyclopropane. This may well be due to the interaction of the dipole moment of the guest molecule with the water molecules, in which case it has the same origin, we believe, as has the difference between the  $\nu_{\text{OD}}(\text{HDO})$  bands of cyclopropane hydrate and those of the dipolar guest molecules.

## DIELECTRIC BEHAVIOUR OF ICE MICROCRYSTALS: A STUDY VERSUS TEMPERATURE

By CHRISTIAN BONED, BERNARD LAGOURETTE and MARC CLAUSSE

(Université de Pau et des Pays de l'Adour, Institut Universitaire de Recherche Scientifique,  
Laboratoire de Thermodynamique, Avenue Philippon, F-64000 Pau, France)

**ABSTRACT.** Dispersions of ice microcrystals were obtained from the breakdown of supercooling of water-in-oil type emulsions whose disperse phase was either resin-exchanged water or aqueous solutions of  $\text{NH}_4\text{Cl}$ . Their complex permittivity  $\epsilon^* = \epsilon' - j\epsilon''$  was studied versus their temperature  $T$ , up to the melting point of the ice microcrystals, by means of an automatically balancing admittance bridge (General Radio 1680A) working at 400 Hz and 1 kHz. The plots  $\epsilon'(T)$ ,  $\epsilon''(T)$ , and  $\epsilon''(\epsilon')$  reveal that these systems exhibit two distinct dielectric relaxations located on both sides of a temperature  $T_m$  which was found to be equal to about  $-20^\circ\text{C}$  in the case of water and lower than  $-20^\circ\text{C}$  in the case of aqueous solutions of  $\text{NH}_4\text{Cl}$ . The relaxation located in the lower temperature range arises from the Debye dipolar absorption of ice while the other one could be related to structural changes occurring within the