

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

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ABSTRACT. We have studied the infrared absorption by the OD stretching, $\nu_{OD}(\text{D}_2\text{O})$, and D_2O 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 H_2O and D_2O 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

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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.