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FT-IR SPECTRA OF VACUUM DEPOSITED CLATHRATE HYDRATES OF OXIRANE, H₂S, THF, ETHANE AND CYCLOPROPANE

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Abstract: An ability to prepare clathrate hydrates using low temperature-high vacuum techniques, originally demonstrated for the hydrate of oxirane (Bertie and Devlin), has been extended to include the structure I hydrate of cyclopropane and H₂S, mixed structure I hydrate of oxirane and ethane as well as the structure II simple hydrate of THF and the double hydrates of THF with oxirane and cyclopropane. The crystalline clathrate films ($\sim 6 \mu$) have been formed either by annealing amorphous host-guest deposits at ~ 130 K, epitaxial growth at 110 K (oxirane and mixed ethane-oxirane or direct deposition at 150 K (THF and its double clathrates). Use of the epitaxial approach at 100 K has permitted the formation of the oxirane clathrate hydrate containing intact isolated D₂O molecules. This has permitted the FT-IR observation of the ν_3 - ν_1 doublet in the O-D stretching region (2455 cm^{-1} and 2380 cm^{-1} at 100 K) with the values, after correction for Fermi resonance, suggesting a splitting from intramolecular coupling of $\sim 56 \text{ cm}^{-1}$ (2455 cm^{-1} vs. 2399 cm^{-1}), which compares closely with the 52 cm^{-1} deduced for cubic ice. Spectra for the structure I hydrates of oxirane and H₂S contain adsorption bands produced by guest molecules confined to both small and large clathrate cages. Use of the structure II double hydrates has permitted the firm identification of the structure I infrared bands with oxirane and H₂S molecules in cages of one size or the other. Thus, the weaker ν_3 and (ν_{11} , ν_{14}) bands of oxirane at 1281 and 1152 cm^{-1} have been assigned to molecules in the small cages since only these oxirane features remain in the structure II double hydrate with THF. In this case the smaller oxirane molecules occupy the small cages while the THF molecules enter the larger cages, exclusively. In a similar manner, the H-S stretching vibrations of H₂S in the structure I small cages have been assigned to a band complex near 2610 cm^{-1} , some 50 cm^{-1} above the band system for H₂S in the large structure I clathrate cages. Such a result suggests that the net H₂S perturbation, relative to the gas phase, is greater for the large than for the small cages and may be interpreted as evidence for a "double well" large cage potential or as further evidence that the cage model of Pimentel and Charles for guest molecule stretching modes is valid.