

active. If the O-hydrogen atoms are not midway between the oxygen atoms then the symmetry is C_2 and all the vibrations represented in Fig. 9 and their first overtones are infrared-active.

The isotope shifts for both observed bands are roughly those expected for a translational mode, and it would be difficult to reconcile them with vibrations 4 and 5 of Fig. 9. It seems likely that they are due to the translational modes 1 and 2. If this is so, then whether they are due to overtones or fundamentals the symmetry of the chain cannot be C_{2h} , and the O-hydrogen atom must be off the midpoint of the O-O line. This is not unexpected, the O-O distance being much longer than usually required for symmetrical hydrogen bonds.

4.4 Bands Due to Dilute Isotopic Molecules

Bands that we ascribe to CH_3OH and CD_3OH occur in crystalline CH_3OD and CD_3OD , respectively; they are included in Tables I-IV. The OH stretching, in-plane bending, and out-of-plane bending are observed for CD_3OH in CD_3OD . The OH stretching and out-of-plane bending bands are observed for CH_3OH in CH_3OD , the OH in-plane bending being hidden by CH_3OD absorption. Unlike the corresponding bands in the pure crystals, the bands of the isotopically diluted species show no splitting. This is to be expected, since no coupling can occur with vibrations of neighboring molecules, which now have too different frequencies.

The uncoupled frequency should fall between the two observed frequencies of the coupled molecules for the following reason. During a vibration the lone-pair electrons that take part in hydrogen-bonding will move in

phase with the nuclei. The two observed bands correspond to motion of adjacent molecules in phase and out of phase. In one of these vibrations the lone-pair electrons will move in step with the hydrogen atom of the adjacent molecule and in the other vibration they will move π radians out of step. Consequently, the coupling will cause one frequency to be higher than in a molecule whose neighbors do not move and will cause the other frequency to be lower. The frequencies of dilute CH_3OH in CH_3OD and of dilute CD_3OH in CD_3OD are probably close to the values they would have if the neighboring molecules did not vibrate. It follows therefore, that the frequency, of a dilute molecule should fall between the two observed frequencies of the coupled molecules. This is indeed observed.

In all the other vibrations of a crystal that correspond to a given vibration of the isolated molecule, adjacent unit cells vibrate out of phase. It follows that the lone-pair electrons of one molecule will be out of step by between 0 and π radians with the O-hydrogen atom of the neighboring molecule. It seems likely that these frequencies will be between those corresponding to a phase difference of 0 and π radians and so that the two observed frequencies are the extremes of the set of crystal frequencies corresponding to a given mode of the isolated molecule.

ACKNOWLEDGMENTS

We should like to thank Dr. R. N. Jones for the use of his Raman spectrophotometer, Dr. K. Noack for the assistance in recording the Raman spectra, and M. E. Bednas for the gas-chromatographic analysis of our methanol samples.