The Deuterium Bond Stretching Vibration

By S. G. W. GINN and J. L. WOOD
(*Department of Chemistry, Imperial College, London, S.W.7*)

THE question of the relative strengths of the hydrogen and deuterium bonds has always attracted a great amount of interest. Comparisons based on equilibrium constants indicate a slightly greater ΔH_f for the deuterium bond,[1-3] a result which can be ascribed to the effect of the mass change on the zero-point energy. Infrared and neutron-diffraction studies of crystalline alkali-metal acid fluorides indicate that the hydrogen-bond potential function is not changed on deuteration.[4-6] However, infrared investigations of crystalline $HCrO_2$[7,8] and $HCoO_2$[8] in KBr discs imply that the potential function in this case changes on deuteration.

One of the most direct ways of investigating a possible difference in the potential curves lies in observing ν_σ, the H- or D-bond stretching vibration of the complex. We have accordingly repeated our examination of the far-infrared spectra of phenol–amine complexes,[9] using [*O*–^{2}H]-phenol in place of [*O*–^{1}H]phenol. The experimental conditions were as previously described. The near-infrared spectra of the deuterated complexes were also recorded to confirm their isotopic composition. This was necessary because the spectra of the complexes in the far-infrared region closely resembled those of the corresponding H-bonded complexes. The band assigned to ν_σ was found to shift on deuteration from 143 to 141 cm.$^{-1}$ for phenol–NMe_3, 123 to 120 cm.$^{-1}$ for phenol–NEt_3, and 134 to 130 cm.$^{-1}$ for phenol–pyridine. For solutions of phenol alone in carbon tetrachloride, the band shifts from 150 to 143 cm.$^{-1}$ The frequency shifts are probably accurate to

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about ±1 $cm.^{-1}$ The band contours do not change appreciably, and, in particular, the pronounced shoulder at 143 $cm.^{-1}$ in the spectrum of phenol–pyridine does not disappear on deuteration but shifts to 139 $cm.^{-1}$ This splitting, then, is not due to proton tunnelling in the H-bond. The shoulder disappears on dilution of the solution with carbon tetrachloride but it would be premature, until present work is completed, to ascribe the higher band of the doublet to the phenol–pyridine complex, and the lower band to the phenate–pyridinium complex. The small frequency shifts observed are comparable to those reported for the H- and D-bond vibration frequencies of phenol polymer suspended in a polythene matrix[10] and of the carboxylic acid dimers.[11]

These results are consistent with no change in the potential energy function on deuteration.

(*Received, November 25th,* 1965; *Com.* 738.)

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