The Absorption Spectrum of Hydrated Hydrogen Atoms

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Summary A simple model is suggested to explain the intense absorption band in the 200 nm region assigned to hydrogen atoms in water.

ALTHOUGH the first absorption band for hydrogen atoms is at 121.57 nm, a strong absorption, reasonably assigned to hydrogen atoms, has been found in the 200 nm region for atoms in aqueous media.[1] This has been interpreted in terms of a shift of the first absorption band for water, normally found in the 180 nm region, for those molecules adjacent to the atoms.[1] It was stressed that e.s.r. spectra for hydrogen atoms in water show that these are quite free.[1]

However, hydrogen atoms trapped in certain solids, especially if these contain basic centres, are remarkably stable.[2] It was suggested that this stability arose because of relatively strong σ-bonding which was depicted in terms of an initial protonation of the base followed by electron-trapping in the resulting σ^* orbital.[2] The net result could be pictured as a hydrogen atom bonded to the oxygen of the water molecule with the same characteristics as a hydrogen bond. The expected fall in the hyperfine coupling, caused by delocalisation is, we believe, almost exactly balanced by an increase caused by other factors,[3,4] so that the e.s.r. spectra remain apparently characteristic of unperturbed atoms. The bonding scheme envisaged is given in Figure 1.

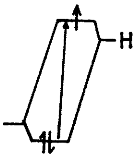

FIGURE 1. *Bonding scheme for a hydrogen atom weakly bonded to a water molecule.*

Two approximations were used for computation: (i) the extra hydrogen atom was constrained to approach along the C_2 axis of a water molecule remote from the other protons, and (ii) the line of approach was along an axis making an angle of 60° with the C_2 axis in a symmetry plane perpendicular to the molecule.

The extended Hückel method[5] was used to give some measure of the interactions assumed to explain the observations. We take the view that the details of the system are so incomplete that more sophisticated theoretical calculations are not worthwhile at the present time.

The results for configuration (i) are given in Figure 2. The results for configuration (ii) are almost identical, the major differences being confined to slight perturbation of the $2pz$ and $2py + (1s_1 - 1s_2)$ molecular orbitals. The $\sigma \rightarrow \sigma^*$ transition ought to be allowed, and is thought to be responsible for the observed absorption. A distance of approach of about 1·5 Å would give a transition energy in the 50,000 cm.$^{-1}$ region, as required. This corresponds closely to normal hydrogen-bond distances, as expected for the model. Furthermore, the σ-level is lowered by about 12 kcal. mole^{-1} which is again close to expectation for a hydrogen-bond to water.[6]

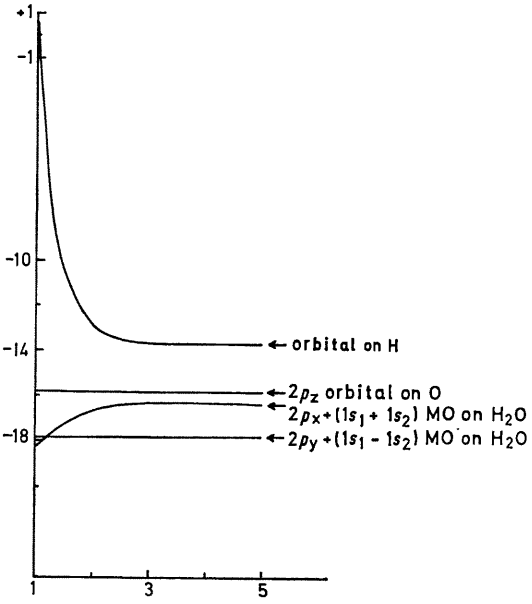

FIGURE 2. *Orbital energies as a function of the* O · · · H *distance using configuration* (*i*) *of the text.*

The inequivalence of the three protons would be expected in liquid water, because most water molecules will be bonded to neighbouring molecules by three or four hydrogen-bonds. This differentiates between the three O–H bonds, and suggests that the angular model is the more appropriate. Both models in fact give similar results. A second lower-energy transition is also predicted, which is formally forbidden in the planar case, but becomes allowed for the pyramidal one. The energy of this transition would be strongly dependent upon the extent to which the "lone-pair" of electrons is involved in hydrogen-bonding to neighbouring molecules, and the overall result is likely to be a broad single band.

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