# The Nature of "A,B,C"-type Infrared Spectra of Strongly Hydrogen-bonded Systems; Pseudo-maxima in Vibrational Spectra

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*Summary* The multiple maxima in "A,B,C"-type i.r. spectra of hydrogen-bonded systems are caused by Fermi resonance of $\nu_{OH}$ (broad band) with $2\delta_{OH}$ and $2\gamma_{OH}$ such that the *minima* correspond to the overtone frequencies.

As the strength of hydrogen bonding increases in an X–H · · · Y system, the $\nu_{XH}$ i.r. absorption band is well known to move increasingly to low frequency, to become greatly enhanced in integrated intensity, and to be increasingly broadened.[1,2] Hadži[3,4] has shown that an extreme of very strong (symmetrical or quasi-symmetrical) hydrogen bonding, as can readily be observed with OHO systems, can lead to exceedingly broad and strong bands centred approximately in the region of 1000—800 cm.$^{-1}$. These low-frequency hydrogen-bonded bands are sometimes referred to as 'D' bands,[4] and their frequencies are to be compared with sharp $\nu_{OH}$ bands in the 3500—3600 cm.$^{-1}$ region normally expected when hydrogen bonding is absent.[1] These are remarkable spectroscopic phenomena by any standards.

In between, say, dimeric carboxylic acids with medium-strength hydrogen bonding which have broad bands[5] in the region of 3000 cm.$^{-1}$ (with sharp sub-maxima near 2700 cm.$^{-1}$ associated with Fermi resonance phenomena involving lower-frequency fundamentals[5]) and the $[RCO_2HO_2CR]^-$ species which have the very broad and low-frequency 'D' bands mentioned above,[4] there is quite commonly obtained a type of i.r. spectrum which has multiple broad maxima associated with the $\nu_{OH}$ region ('A, B, and C' type bands) usually between 2700 and 1600 cm.$^{-1}$.[4,6,9] The relative intensities of these bands vary from A and B strong with C weak, up to A and B weak with C strong. Much attention and discussion has been given to the possible origin of these bands, and particularly of the lowest frequency one, band C,[4,6–8] but there is experimental evidence against, or theoretical difficulty with, all explanations so far offered.[4,9]

Hadži[10] has shown, by examining the i.r. spectra of a given carboxylic acid with a series of bases of increasing strength, that there is a continuity of phenomena between 'A,B,C' type and 'D' type spectra in that the one passes over into the other with increasing base strength. We have also shown,[11] by using the independent parameter of the n.m.r. chemical shift of the hydrogen bonded OH groups in solution, that the sequence {A–B strong, C weak ($Ph\cdot PO(OH)_2$ in dimethyl sulphoxide) → A,B, and C all strong [$Ph\cdot PO(H)OH$ in acetone] → B weak, C medium, D strong [$Ph\cdot PO(H)OH$ in pyridine]} is parallelled by increasing low-field shift of the proton resonance, *i.e.* $\tau = -1\cdot35$, $-3\cdot30$, and $-7\cdot31$ respectively, as expected for gradually increasing hydrogen-bond strength.[12]

We have therefore searched for an explanation of the A,B,C i.r. bands on the assumption that the greatest intensity region within the band system as a whole represents approximately the mean frequency of $\nu_{OH}$. In particular we have examined the possible role of Fermi resonance in this type of spectrum by using deuteriation

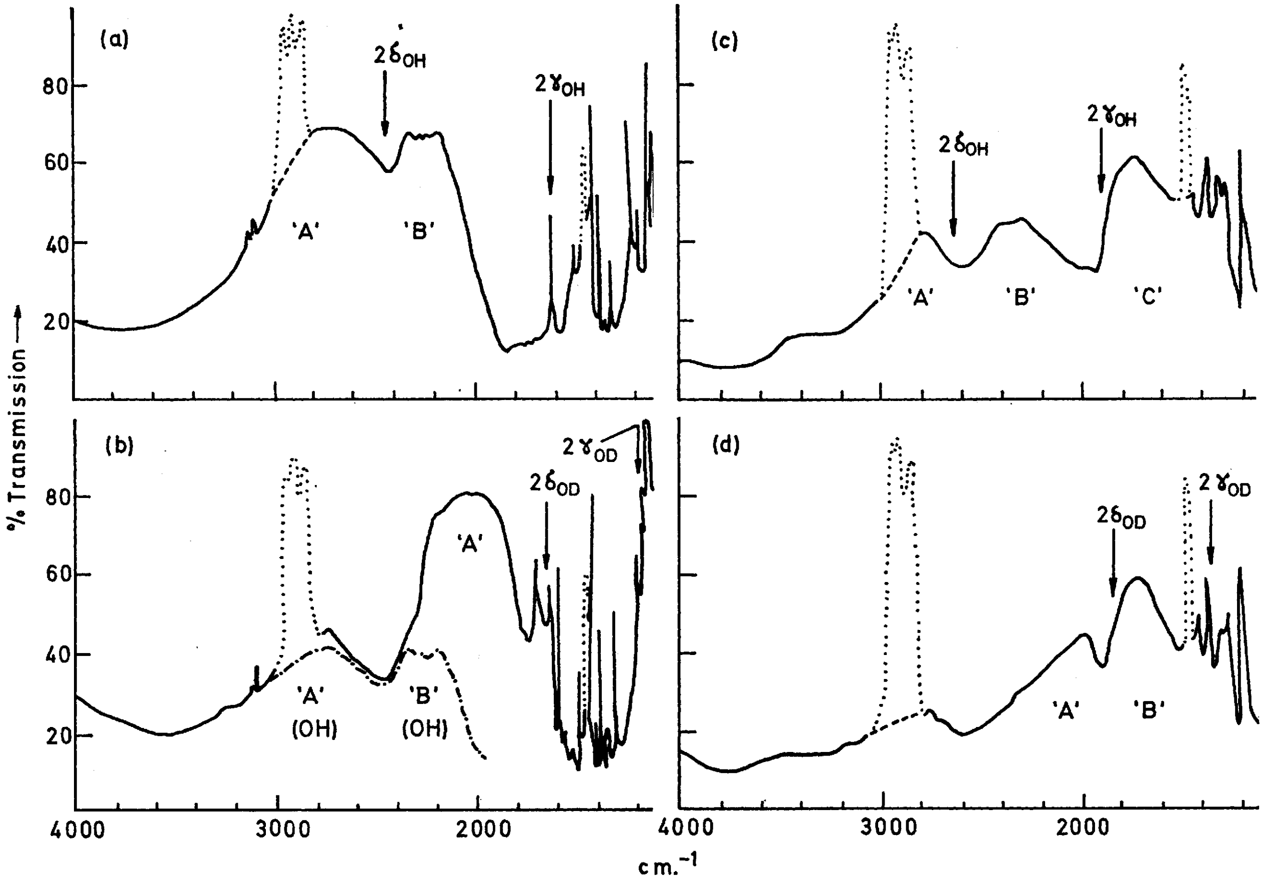

FIGURE 1. *Relationship of overtone frequencies of the* OH (OD) *in-plane and out-of plane deformation frequencies* ($2\delta_{OH}$, $2\gamma_{OH}$) *to the broad absorption region associated with the* OH *stretching vibration* ($\nu_{OH}$) *in the i.r. spectra of some hydrogen-bonded molecules.* A, B, *and* C *denote sub-bands of the* $\nu_{OH(OD)}$ *region.*
(a) *phenylphosphonic acid at* −140°; (b) *partially deuteriated phenylphosphonic acid at* −140°; (c) *dibutylarsinic acid at* 20°; (d) *deuteriated dibutylarsinic acid at* 20°;
----- *background* ..... *Nujol absorptions* -·-·- *residual* 'OH' *bands.*

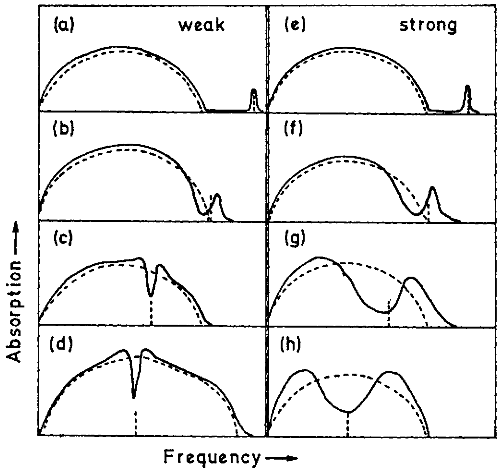

FIGURE 2. *Schematic diagram showing the possible effect of increasing Fermi resonance as the frequency of a sharp overtone approaches that of a very broad fundamental.*
(a)—(d) *moderate-to-weak Fermi resonance*; (e)—(h) *strong Fermi resonance.*
----- *spectrum in absence of Fermi resonance*;
—— *resultant vibrational spectrum when Fermi resonance occurs.*

combined with low-temperature i.r. techniques in order to locate accurately the $\delta_{OH}$ in-plane and $\gamma_{OH}$ out-of-plane fundamentals.[11] These bands are often weak, but sharpen markedly at low temperatures and shift on deuteriation. The $\delta_{OH}$ frequency, as Hadži has shown,[4] does not vary greatly, but we find that $\gamma_{OH}$ increases with increasing hydrogen-bond strength.

We found, at first unexpectedly, that $2\delta_{OH}$ and $2\gamma_{OH}$ corresponded approximately not with maxima in the A,B,C system *but with minima*;[11,13] also that these minima tend to be sharper for OD systems. This is illustrated in Figure 1, which includes spectra for $\nu_{OH}$ and $\nu_{OD}$ examples.

Evans and Wright[14] have previously shown that when a fundamental vibration which gives rise to a broad i.r. band overlaps a sharp fundamental band of the same symmetry, this can lead to a 'transmission window' in the broad band at the frequency of the sharp fundamental. Evans has also given a theoretical interpretation of this phenomenon,[15] the 'missing' intensity being redistributed into the absorption region on either side of the window by resonance repulsion. Furthermore, Hadži[4] has previously shown that such sharp transmission windows are common features within the very broad $\nu_{OH}$ bands of D-type spectra. These latter presumably arise from relatively weak interaction between the $\nu_{OH}$ continuum and other skeletal fundamentals *etc.* of the same symmetry class that are associated with vibrations of substituents.

We therefore postulate that A,B,C type of spectra of hydrogen-bonded systems result analogously from the subdivision of what would otherwise be a single broad $\nu_{OH}$ continuum, into maxima and minima as a result of strong Fermi resonance of $\nu_{OH}$ with $2\delta_{OH}$ and $2\gamma_{OH}$. The minima are considered to be relatively broad for $\nu_{OH}$ because of the strength of the interaction of the fundamental and overtone which involve the same vibrating hydrogen atoms. They are presumably sharper in the OD spectra because of the lower amplitudes and anharmonicities in these cases. A schematic diagram of the type of phenomena to be expected for different degrees of interaction and frequency overlap between a broad continuum and a sharp fundamental or overtone of the same symmetry is shown in Figure 2. Others have postulated in a general way that A,B,C spectra are caused by Fermi resonance between $\nu_{OH}$ and $2\delta_{OH}$ or $2\gamma_{OH}$[4,9] but no satisfactory explanation seems previously to have been given for the frequencies of the absorption maxima.

These phenomena are not, of course, confined to hydrogen-bonded systems;[14] it is just that such systems provide many of the examples of broad fundamental absorption bands. Such pseudo-maxima which do *not* correspond to fundamental vibration frequencies can be expected in many i.r. or Raman spectra where broad continua are present.

The origin of the breadth of hydrogen bonded $\nu_{XH}$ vibrations is also of considerable interest. One of us postulated some years ago[2] that the main operative factors were probably the interaction of $\nu_{XH}$ with the hydrogen bond stretching vibration itself giving rise to sub-bands of the type $\nu_{XH} \pm n\nu_{XH \cdots X}$ (a modified Stepanov hypothesis[2,16]) and that additional structure would be associated with Fermi resonance phenomena.[2,5] Considerable support for this view has recently come from i.r. studies of hydrogen-bonded complexes of different strengths in the gas[17] and low-temperature crystalline solid phases.[18]

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