An Alternative Explanation for the Anomalous Infrared Spectra of $HCrO_2$ and $DCrO_2$

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Summary Fermi resonance between a broad v (OD) fundamental and a sharp 2δ(ODO) overtone is postulated to be the cause of the very different appearance of the v(OH) and v(OD) i.r. absorption bands of $HCrO_2$ and $DCrO_2$.

ONE of the more remarkable phenomena in the i.r. spectra of strongly hydrogen-bonded molecules is the difference between the spectra of both polycrystalline α-chromous acid, $HCrO_2$ and cobaltous acid, $HCoO_2$ and their deuterium-containing analogues.[1,2] These compounds contain OHO and ODO units in the crystalline lattice. Neutron diffraction studies have established that the ODO unit exhibits an unsymmetrical hydrogen bond O–D · · · O, but no firm conclusion was reached about the symmetry or otherwise of the OHO unit.

The remarkable nature of these i.r. spectra concerns the relationship between the absorption bands attributable to the hydrogen (deuterium) stretching vibrations of the OHO and ODO units. The former gives rise to a broad band centred at 1650 cm^{-1}, and the latter to a pair of bands centred near 1750 cm^{-1}. The positive frequency shift in passing from OH to OD, and the double absorption band of the latter spectrum, have been interpreted by Snyder and Ibers[1] as requiring exceptionally different potential energy curves for the OH and OD stretching motions; see also the discussion in ref. 4. For OHO it was postulated that a double minimum curve occurs with a very low central maximum (*ca.* 200 cm^{-1} in height) whereas for ODO the central maximum was thought to amount to about 1950 cm^{-1}.

We suggest an alternative explanation for the i.r. spectral results which, if correct, would imply a difference of a much less extreme kind between the potential functions of the OHO and ODO species. Two of us (M.F.C. and N.S.) have suggested[5] that, in certain circumstances, Fermi-resonance between broad continua associated with ν(OH) bond-stretching vibrations and sharper overtones of angle-bending modes such as δ(OH) can give rise to minima in the broad ν(OH) absorption region close to the position of the 2ν(OH) frequency; the third (B.C.S.) in conjunction with Stratford[6] has made a general theoretical study of such spectral phenomena and with J.A.U.[7] considered specifically chromous acid. If the ODO system has an unsymmetrical deuterium bond O–D · · · · O on the time-scale of the i.r. experiment, *i.e.* effective overall symmetry $C_{\infty v}$, then one component of the overtone of δ(ODO) has the same symmetry as ν(OD) and Fermi resonance can occur between these two. [The latter is equally true if the symmetry of the ODO ion is taken to be $D_{\infty h}$ with a double potential minimum for the D atom, except that in this case Fermi resonance is with a combination of the two components of the inversion-doubled δ(ODO) fundamental]. For $DCrO_2$ the angle bending frequency is near 830 cm^{-1} and the position of its overtone (see arrow on the Figure) corresponds approximately to the minimum between the two absorption bands in the ν(OD) region. We therefore postulate that in the absence of this Fermi resonance the ν(OD) band would, like that of ν(OH), consist of a single broad band centred near 1750 cm^{-1}. On the other hand the overtone of δ(OHO) falls well clear of the maximum of the ν(OH) band (see arrow in Figure, a) although there is some sign of a very weak minimum at about this frequency in the spectrum of $HCrO_2$.

This revised interpretation of the spectrum of $DCrO_2$ in no way reduces the significance of the anomalous value, less even than unity, of the ν(OH)/ν(OD) frequency ratio.[1] Snyder and Ibers[1] have pointed to the reverse type of anomaly for the angle bending frequency, *i.e.* δ(OH)/δ(OD) somewhat greater than $\sqrt{2}$, and indeed our postulated reinterpretation of the ν(OH) and ν(OD) bands in the i.r. spectra depends on the juxtaposition of these two opposite anharmonic phenomena. Diffraction studies[3,8] have shown a contraction of the O · · · O distance in OHO relative to ODO, with the implication that the hydrogen bonding is stronger for the OHO compound. This in itself implies that the potential function for motion of the hydrogen and deuterium atoms will not be identical. However, such differences relate to these atoms moving in potential energy curves which are different 2-dimensional cross-sections of the same 3-dimensional surface describing the variation of the potential energy with respect to both O · · · O and O–H distances.[9,10] The observed H to D isotopic effect on the

O · · · O distance in $HCrO_2$ is in the direction expected for a double-minimum type of potential function controlling the motion of the H or D atoms.[10]

It has been shown that abnormal anharmonicity relationships can lead to values of $\nu(OH)/\nu(OD)$ of considerably less than $\sqrt{2}$ in situations where the potential function broadens out above a certain level of energy;[11–14] for double-minimum potential energy curves this corresponds to the height of the intervening maximum. In all such cases the first excited level of the $\nu(OH)$ vibration falls a short distance above, and that of the $\nu(OD)$ vibration a short distance below the level at which the potential energy function broadens out. Calculations based on mathematical models for the potential functions have indicated that values for $\nu(OH)/\nu(OD)$ down to $<1{\cdot}1$ could be obtained for asymmetrical potential energy curves.[11] For symmetrical double-minimum situations it has been claimed that reasonable potential functions are unlikely to lead to values of $\nu(OH)/\nu(OD)$ of less than 1·2[14] despite earlier suggestions of values considerably nearer unity.[15] The approximate value for chromous acid, based on a single broad maximum replacing the observed doublet in the absence of Fermi resonance with the overtone of $\delta(ODO)$, is 0·95 and is very low in comparison with the theoretical expectations cited above. However, this may be possible in view of the substantial observed increase in the O · · · O distance in passing from $HCrO_2$ to $DCrO_2$; this in turn would correspond to an increased distance between the pair of potential minima and further enhance the $\nu(OD)$ frequency. If this is the correct explanation for the spectrum, then for $HCrO_2$ the central maximum must be somewhat less than 1500 cm^{-1} above the vibrational ground state, corresponding to <2300 cm^{-1} above the potential energy minima when allowance is made for zero-point energy.

Our interpretation of the $DCrO_2$ spectrum leaves single broad $\nu(OH)$ and $\nu(OD)$ bands to be interpreted in terms of what is likely to be a symmetrical double-minimum potential for the motion of the proton or deuteron. However, in these highly ionic systems the motion of the proton from one side of the well to the other will lead to strong changes in electrical asymmetry of the OHO^{3-} ion and therefore to strong coupling of the proton motion to interionic lattice modes. It has been suggested by Fischer *et al.*[16] that this type of strong coupling will lead to a complex situation in which a simple two-maximum absorption band, such as is normally expected of a symmetrical double-minimum situation, may become blurred out into a broad region of absorption. These ideas are similar to ones used by Zundel and others[17] in their discussion of the origin of broad continua in solution spectra of strongly hydrogen-bonded species. Conversely, several double-band phenomena in the i.r. absorption spectra of hydrogen-bonded systems, which have previously been interpreted in terms of double-minimum potential functions, have later found preferable alternative explanations.[18,19]

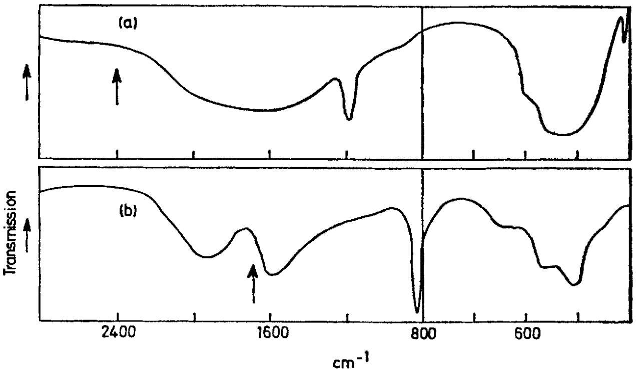

FIGURE. I.r. spectra of (a) $HCrO_2$, and (b) $DCrO_2$.

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