InfraRed Dichroism Involving Hydrogen Bonds

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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and expecially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($4.00 per page) will not be made and no reprints will be furnished free.

Halogen-Halogen Distances in Halogen-Polymer Complexes

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October 31, 1947

RECENTLY West has found that many polymers form complexes with iodine, iodine bromide, and bromine.[1] Stretched fibers of these complexes give x-ray spacings characteristic of one-dimensional lattices with periods of 3.10, 2.90, and 2.70A, respectively, characteristic of the halogen but essentially independent of the polymer. West has interpreted the one-dimensional spacings as interatomic distances in linear, polyhalogen chains.

The single, covalent bond distances in I_2, I-Br, and Br_2 are 2.67, 2.47, and 2.28A, respectively,[2] far shorter than the spacings observed by West. If the above spacings are halogen-halogen interatomic distances, their bond numbers are only about 0.17 for all three cases.[3]

While it is easy to visualize a polyhalogen chain with links of bond order $\frac{1}{2}$ (see below), it is hard to understand the virtual elimination of halogen-halogen bonds in the complexes as West's suggestion demands. One possible explanation involves bonding of the halogen atoms to the polymer, but since the polymer fiber spacings are unrelated to that of the halogen separation,[1] this is hardly possible. Moreover, polymer-halogen bonds are undesirable chemically, and will not explain many of the effects observed in the amylose (starch)-iodine complex.[4]

Since, at best, only three orders of the lattice spacing have been observed,[1] it is by no means certain that the halogen atoms in the one-dimensional array are equally spaced. Hence, it is possible that halogen molecules I_2, I-Br, and Br_2 exist in the array, but with somewhat shortened van der Waals separations between molecules.

It has been suggested that a dipole field of a polymer acting on a highly polarizable, linear array of halogen molecules might account for the stability of the halogen-polymer complexes.[4] Recently Mr. R. S. Stein and the author have examined this proposal more quantitatively,[5] and find that very reasonable fields due to the polymer will lead to very materially reduced van der Waals distances between iodine molecules in the iodine complex. A period of 6.2A (twice the observed period) is quite acceptable for an iodine-iodine bonded distance plus a

non-bonded van der Waals distance. The proposal also accounts for the very low fugacity of iodine over the complex and the other unusual physical properties of these complexes.

Though polyhalogen chains with equally spaced halogens are allowed by our proposal, they result from resonance of the bond between bonded and non-bonded neighbors as the van der Waals and bonded distances approach each other under the influence of the polymer field. A bond number of $\frac{1}{2}$ would result for each bond, and halogen-halogen distances of 2.85, 2.65 and 2.46A are then expected for the three complexes above. These distances are so far below observed spacings it is unlikely that the limiting case is approached in any known complexes.

Our calculations allow variation in the halogen-halogen distance with dipole field of the polymer. West has noted variations in spacing of 0.15A. This variation is difficult to understand in terms of the polyhalogen suggestion.

In summary, West's observed lattice constants appear too long for polyhalogen chains, but are in excellent agreement with expectations based on the dipole interaction suggestion. Consequently, they tend to substantiate the latter proposal rather than otherwise.

[1] C. D. West, J. Chem. Phys. 15, 689 (1947).
[2] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945) second edition, p. 164.
[3] Calculations made in accordance with the rule $R(n)=R(l)-0.3 \log n$, as given by L. Pauling, J. Am. Chem. Soc. 69, 542 (1947).
[4] Rundle, Foster, and Baldwin, J. Am. Chem. Soc. 66, 2116 (1944).
[5] R. S. Stein and R. E. Rundle, "The nature of the interaction between starch and iodine" (to be published in J. Chem. Phys.).

Infra-Red Dichroism Involving Hydrogen Bonds

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October 28, 1947

IT is well known that the vibration bands of $O-H$ units which take part in hydrogen bonds are broadened and shifted toward longer wave-lengths. Most spectroscopic investigations of hydrogen bonding have been upon liquids, which can show no orientation effects. This laboratory, in line with its interest in near infra-red dichroism, has in past years made polarized infra-red studies of solid specimens containing oriented hydrogen bonds.[1-3] Such studies are again being undertaken, now with the dicarboxylic acids.

A striking example of dichroism was found in β-succinic acid. Cleavage sections parallel to the crystallographic c axis and approximately 0.2 mm thick were used. The first spectrograms with polarized light, the E-vector vibrating, respectively, parallel and perpendicular to the c axis, were taken in March 1947. No absorption in the 1.4μ unperturbed $O-H$ region (second harmonic) was observed in either run. The run made with the E-vector parallel to the c axis was quite unique; strong absorption started at roughly 1.57μ, increased to opacity at 1.87μ, and remained completely opaque to beyond 2.7μ, the limit of our recording quartz spectrograph.[4] The perpendicular run showed, in contrast, general transparency save for regions of CH_2 overtone and combination band absorption. These latter were of normal intensity for

specimens of the thickness used, the second harmonic CH_2 stretching vibrations, for example, showing about 40 percent absorption.

A similar investigation in the fundamental vibration region for a high temperature modification of succinic acid has recently been reported by D. A. Crooks.[5] He found a great increase in the absorption of the broad band extending from 3250 to 2300 cm^{-1} as the E-vector was rotated from the perpendicular to the parallel direction. His conclusion, like ours, is that intermolecular hydrogen bonds are responsible for this broad unidirectional absorption.

The intensity of Crooks' broad hydrogen bond absorption in the fundamental region is, if we interpret correctly, less than $\frac{1}{3}$ that of the fundamental CH_2 valence stretching vibrations at 2900 cm^{-1}. A contrast of these findings with our broad region of complete opacity indicates an anomalous ratio of overtone (and combination) to fundamental mode intensities for the hydrogen bond vibrations.

Data from x-ray diffraction[6] indicate that both the chain axis of the succinic acid molecule and the direction of the intermolecular $O-H\cdots O$ bonds are very nearly parallel to the crystallographic c axis. As was remarked by Crooks, the polarized infra-red story bears this out.

X-ray diffraction does not locate definitely the light hydrogen nuclei, their positions on the line connecting the oxygen nuclei of neighboring molecules being the reasonable inference. This inference is strongly supported by the unidirectional nature of the hydrogen bond absorption. It is of interest that no such clear-cut confirmation was found earlier at this laboratory for the looser hydrogen bonds in pentaerythritol.[2]

Adipic acid crystals were also examined with results similar to but not so marked as those of succinic acid. Since the c axis of adipic acid crystals, to which the hydrogen bonds are again parallel, is inclined to the surface[7] rather than in it as for succinic acid, conditions are not so favorable.

We have been attempting, up to now with small success, to grow good crystals of anhydrous α- and β-oxalic acid. These, particularly the β-form, should also show the intense hydrogen bonding dichroism. Since there would be no CH_2 absorption in the perpendicular vibration direction, a suitable crystal might be useful as a near infra-red polarizer.

We attempted to make spectrograms of oxalic acid dihydrate specimens but were frustrated by a curious phenomenon. Clear sections became very quickly opaque in the volume through which the converging beam had passed. Presumably water molecules or perhaps ionized portions of these were knocked out of the crystal by the beam in a sort of photo-molecular effect.

A detailed account will be published in the future when observations and the working out of selection rules from the theory of group representations will have been completed. A discussion of CH_2 as well as $O-H$ vibrations will be included.

[1] J. W. Ellis and J. Bath, J. Chem. Phys. **6**, 221 (1938).
[2] J. W. Ellis and J. Bath, J. Chem. Phys. **7**, 862 (1938).
[3] J. W. Ellis and J. Bath, J. Am. Chem. Soc. **62**, 2859 (1940).
[4] J. W. Ellis, Rev. Sci. Inst. **4**, 123 (1933).
[5] D. A. Crooks, Nature **160**, No. 4053, 17 (1947).
[6] Llewellyn, Cox, and Goodwin, J. Chem. Soc., p. 883 (1937).
[7] W. A. Caspari, J. Chem. Soc., p. 3235 (1928).

A Spectroscopic Evidence for Activation of Fluorescence by High Valency Manganese Ions

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WE have measured the emission spectra of manganese activated zinc beryllium silicate and zinc silicate phosphors. The spectrum represented by the number of emitted photons as a function of the frequency was found to be a sum of several gaussian distribution curves, the maxima of each gaussian being at the same frequency for both materials ($h\nu = 2.35$, 2.27, 2.17, and 2.05 electron volts), the relative intensities of the individual components being, however, different. The main band of zinc silicate was found at $h\nu = 2.35$ and that of zinc beryllium silicate at $h\nu = 2.05$ electron volts.

Similarly analyzing the absorption spectra of different manganese compounds in solution, we have found the remarkable fact that the extinction coefficient of K_2MnO_4 in a strong alkaline solution gives rise to the same curves as the emission spectrum of zinc beryllium silicates (see Fig. 1).

The analysis of the absorption spectrum of the aqueous solution of $KMnO_4$ and $Zn/MnO_4/2$ shows the same bands as zinc silicate, but in this case the intensity ratio of the individual bands is different. The position of the bands was found independent of the cation, being determined only by the anion.

These data led us to the conclusion that the emission centers of the fluorescence are associated with the $(MnO_4)^{--}$ and $(MnO_4)^{-}$ ions imbedded in the silicate lattice. This means that in the divalent manganese compound added for activation there is the necessary quantity of the permanganate resp. manganate ions present, or it will be formed during the applied treatment. The number of the negative ions necessary for fluorescence can be estimated
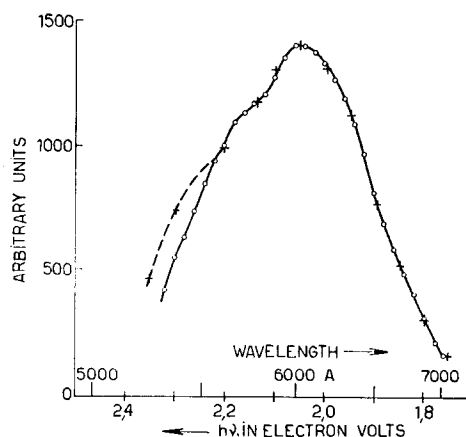

FIG. 1. The $\bigcirc$ denote measured points for the extinction coefficient of K_2MnO_4; the $+$ denote measured points for the emission spectrum of zinc beryllium silicate; ordinate scale for both curves gives the same maximum.