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

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specimens of the thickness used, the second harmonic CH₂ 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 CH₂ 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 CH₂ 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 CH₂ 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).

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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
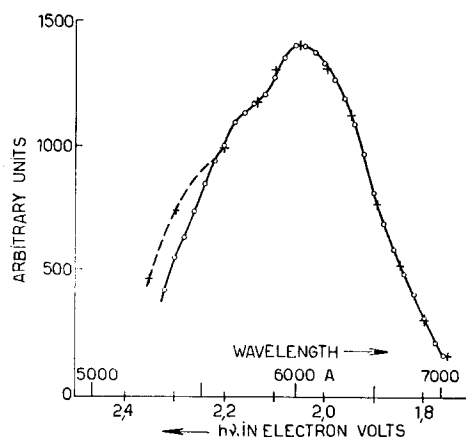

Fig. 1. The ○ denote measured points for the extinction coefficient of K_2MnO_4; the + denote measured points for the emission spectrum of zinc beryllium silicate; ordinate scale for both curves gives the same maximum.

from the saturation value of the emitted fluorescence and by assuming the time of the elementary processes.

For both of these there can be found in the literature only very feeble and uncertain data, but they can still be relied upon for an approximate calculation that the necessary number of centers should lie between 10^{14}–10^{17} centers per gram of fluorescent material.

This means that if the 10^{-4}th part of the present manganese atoms has a valency of six resp. seven, a sufficiently great number of manganate resp. permanganate ions is present to give rise to the measured fluorescence. It is to be noted that the estimated number of these colored anions per unit surface does not cause any perceptible discoloration even in aqueous solutions. Therefore these quantities of the activator anions cannot be detected in the powders by absorption measurements.

Raman Effect of Dichlorohexafluorocyclobutane

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L ATELY the question of the planarity of the ring in simple cyclic hydrocarbons has been of considerable interest. Recent work[1] indicates that the cyclopentane ring is puckered. On the other hand, Raman and infra-red spectroscopy[2] indicates that the cyclobutane ring is planar while the same seems to be true of the ring in perfluorocyclobutane.[3] This study of dichlorohexafluorocyclobutane was undertaken in connection with this laboratory's interest in this problem.

Dichlorohexafluorocyclobutane is a colorless liquid boiling at 60°C. The material used was furnished by the E. I. DuPont de Nemours and Company. It was further purified by vacuum distillation, dried over $CaCl_2$ for twenty-four hours, and made optically clear by shaking with activated charcoal and filtration through a very fine sintered glass filter. The Raman tube, having a volume of 15 ml, was filled by vacuum distillation.

Exposures were made on Eastman spectrographic plates type 103–0 and type 103a–0, using an Adam Hilger E–2 spectrograph. The Raman tube was suspended in a vertical position with the scattered light being directed into the

spectrograph by a right-angle prism. Eight upright mercury arcs arranged in a circle about the Raman tube provided the exciting radiation. Each of these mercury arcs were mounted in front of an individual elliptical reflector which was focused upon the Raman tube. The 4358A line was used as the exciting intensity. Inasmuch as fluorocarbons are notoriously poor light scatterers, exposure times varied from 48 to 172 hours by use of slit widths from 25 to 60 microns. A continuously circulating filter solution of 0.2 percent paranitrotoluene and 0.03 gram of DuPont Rhodamine 5 GDN Extra per liter, dissolved in alcohol, was used[4] to reduce general scattering in the region of 4358A and to eliminate the Raman shifts excited by the 4047A mercury line. The average temperature of the sample was 38°C during the exposures.

We have observed nineteen Raman shifts in dichlorohexafluorocyclobutane. The results are shown in Table I.

We wish to thank Dr. J. D. Park of the Jackson Laboratories of the E. I. DuPont de Nemours and Company for this substance. Further consideration of these results will be published later.

[1] J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, J. Am. Chem. Soc 69, 2483 (1947); J. G. Aston, S. C. Schumann, H. L. Fink, and P. M. Doty, J. Am. Chem. Soc. 63, 2029 (1941); J. G. Aston, H. L. Fink, and S. C. Schumann, J. Am. Chem. Soc. 65, 341 (1943); E. J. Rosenbaum and H. F. Jacobson, J. Am. Chem. Soc. 63, 2841 (1941).
[2] T. P. Wilson, J. Chem. Phys. 11, 369 (1943).
[3] W. F. Edgell, J. Am. Chem. Soc. 69, 660 (1947).
[4] J. T. Edsall and H. Scheinberg, J. Chem. Phys. 8, 520 (1940).

Phases of Fourier Coefficients Directly from Crystal Diffraction Data

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T HE intensity of an x-ray beam diffracted from a crystal can be used to find the absolute value of the "crystal-structure factor" $|F_{hkl}|$, but not its phase. However, it appears to be possible to place limits on the phase or, if F_{hkl} is real, to determine the sign, by combining the intensity data from *several* diffracted beams. The general methods for doing this are outlined in the following paragraphs; a detailed article on the subject will appear later.

Although not necessary, it is helpful in strengthening the method to assume that the "atomic-structure factors," f_j, of the atoms in a crystal are related to one another by the relation $f_j = Z_j f$, where Z_j is the atomic number of the jth atom and f is a function of $(\sin \theta)/\lambda$ called "the unitary atomic-structure factor." If there are N atoms in the unit cell of a crystal and

$$Z = \sum_{j=1}^{N} Z_j$$

is the total number of electrons in a unit cell, then

$$\sum_{j=1}^{N} f_j = Zf.$$

TABLE I. Raman lines of dichlorohexafluorocyclobutane.

$\Delta\nu$ cm^{-1}	Estimated relative intensity	$\Delta\nu$ cm^{-1}	Estimated relative intensity
162	S	863	W
216	VW	910	W
270(b)	S	966	S
334(b)	S	1074	W
396(d)	VS	1111	W
465	S	1190	W
490	S	1243	M
561	W	1287	W
640(b)	VS	1392	M
810	VW		

S = strong; M = medium; W = weak; V = very; b = broad; d = diffuse.