Raman Spectrum of Oxalic Acid

W. Rogie Angus and Alan H. Leckie

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TABLE I.

C_6H_6	C_6D_6	C_6H_6	C_6D_6
605	581	2947	2266
849	662	3042	2293
991	945	3062	
1178	873	3157	
1584 / 1606	1548	3176	
C_6D_6 or C_6D_5H: 1000, 2031, 2575, 2617(?), 2663(?).			
C_6D_5H: 3052, 3108			

hydrogen was determined by the ultraviolet absorption bands of the material, and they set the upper limit to the hydrogen present at one mole percent. If we assume that a negligible portion of this hydrogen is present in molecules containing two or more H atoms, then the amount of C_6D_6H in the C_6D_6 has an upper limit of roughly six mole percent. The high vibration frequencies in benzene and its derivatives are responsible for some of the strongest Raman lines, and accordingly if C_6D_5H were present in the C_6D_6, even to so slight an extent as one mole percent, there should unquestionably appear in the Raman spectrum of this solution traces of lines characteristic of the aromatic C—H linkage. It is therefore suggested that the faint lines 3052 and 3108 found by Wood are due to C_6D_5H and not to C_6D_6. In $C_6D_2H_4$ and C_6DH_5 the 3052 frequency has been found by Redlich and Stricks[5] and this appears almost certainly to be the strong 3062 line of C_6H_6 shifted to the slightly lower value by the lower symmetry and heavier mass of the deuterobenzenes.

One further question must be answered. The presence of the 3052 and 3108 lines in the C_6D_6 spectrum obtained by Wood led him to search for corresponding high lines in C_6H_6. He set a tentative and rough lower limit for the expected lines at 3500 cm^{-1}, although a closer figure would have been 4000 cm^{-1} or higher (i.e., approximately $3100\sqrt{2}$). In the paper on C_6D_6, Wood reported that by long exposure with a green sensitive plate, he was able to obtain a spectrum of C_6H_6 which showed shifts of 3573 and 3627 cm^{-1} from the exciting line, Hg-4358. Since these shifts did not seem very reasonable either on the basis of the customary force constants of C_6H_6 or on the basis of new force constants required to give shifts of 3052 and 3108 in C_6D_6, I obtained Professor Wood's consent to reanalyze his plate. The plate showed the lines in question quite definitely, but because of their very low intensity they were impossible to measure with the usual degree of accuracy. The wave numbers of the lines were found to be 19,341 and 19,296 cm^{-1}. Instead of assigning the lines to excitation by Hg-4358, however, I found that an alternative assignment could be made. If one assigns the line at 19,341 cm^{-1} to Hg-4916, there is observed shift of approximately 990 cm^{-1}, which is the frequency of the strongest line in C_6H_6. Hg-4916 appears on the plate with ample intensity to excite an intense Raman line. If one assigns the 19,296 cm^{-1} line to an anti-Stokes excitation by Hg-5461, again a shift of approximately 990 cm^{-1} is obtained. It is true that one would ordinarily scarcely expect to find an anti-Stokes line of so large a shift as 1000 cm^{-1}. However the 990 line is a very intense one, and Hg-5461 is of extreme intensity on the plate. As a corroboration of this assignment, the 990 anti-Stokes line excited by Hg-4358 was sought and found very definitely at 23,928 cm^{-1}. In consequence it is necessary to reject the 3573 and 3627 vibrations in benzene.

A table of frequencies for C_6H_6 and C_6D_6 revised in accordance with the above appears in Table I. At the foot of the table are included lines either assigned to C_6D_5H or of indefinite assignment. Further investigation of the Raman spectra of solutions containing higher percentages of C_6D_5H will be necessary to remove the ambiguity.

R. C. LORD, JR.

Department of Chemistry,
The Johns Hopkins University,
Baltimore, Maryland,
December 13, 1935.

[1] R. W. Wood, J. Chem. Phys. **3**, 444 (1935).
[2] E. B. Wilson, Jr., Phys. Rev. **45**, 706 (1934); Phys. Rev. **46**, 146 (1934).
[3] D. E. Teets and D. H. Andrews, J. Chem. Phys. **3**, 175 (1935).
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[5] Redlich and Stricks, J. Chem. Phys. **3**, 834 (1935); see also Kohlrausch, *Der Smekal-Raman Effekt*, p. 329 ff.

Raman Spectrum of Oxalic Acid

Recently we published preliminary results on an investigation of the Raman spectra of light and heavy acetic acids.[1] In an extension of this investigation we have examined the Raman spectra of oxalic acid, both in the hydrated crystalline state and as a saturated aqueous solution. The results which we have obtained are sufficiently different from those given by Hibben[2] in a recent paper in this journal as to prompt us to publish our values immediately.

In Table I our values are compared with those previously recorded.

The lack of agreement between the independent values of the different investigators arises doubtless from the difficulty of obtaining clear and distinct Raman spectra on account of a continuous background. This is a difficulty which we have experienced in agreement with the observations of previous workers. Thus an unusually large divergence in the values of a particular frequency is to be expected.

We have included in the table Rao's data for the solid as data on the hydrated crystals since he does not state specifically in his paper that they were anhydrous; and we have therefore inferred that they were the usual dihydrate crystals. On the other hand Hibben has cited Rao's values for the solid as data for anhydrous oxalic acid and finds that Rao's values are in good agreement with his own for the anhydrous acid.

The main point of dissimilarity between Hibben's results

TABLE I.

	Krishnamurti[4]	Rao[3]	Hibben[2]	Authors
$H_2C_2O_4 \cdot 2H_2O$		473		495
(Solid)	855	851	847	854
			1365	
		1506	1470	1471
		1640±20		1661(Broad)
		1758		1759
Aqueous		248(?)		
Solution			395	
		480	453	493
		673(?)		
		845	842	
				1375
		1430±30	1460	
		1656	1645	1647
				1684
		1744	1740	1749

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and ours is the fact that from microphotometer records we obtain definite proof that the frequencies 1661 and 1759 cm^{-1} in the spectrum of the crystals have real existence and are as strong as the corresponding frequencies in the aqueous solution. Hibben found that these frequencies were absent in the dihydrate crystals but present in the anhydrous solid. Our results, obtained from crystals which were definitely dihydrate crystals, agree with those of Rao and support our inference regarding the crystals examined by him.

Since Hibben's conclusions that the two carboxyl groups behave differently depend to a large extent on the difference in the spectra of the anhydrous and hydrated crystals we submit that such conclusions may be invalidated by his comparing the spectrum he obtained for his anhydrous crystals with Rao's spectrum for the solid.

To enter into a full discussion of the results is beyond the scope of this letter in which we merely wish to indicate our observations that the Raman spectra obtained from saturated aqueous solutions of oxalic acid and from dihydrated oxalic acid crystals are substantially the same.

W. Rogie Angus
Alan H. Leckie

University College,
London, W.C. 1,
December 5, 1935.

[1] Angus, Leckie and Wilson, Nature **135**, 913 (1935).
[2] Hibben, J. Chem. Phys. **3**, 675 (1935).
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[4] Krishnamurti, Ind. J. Phys. **6**, 309 (1931).

Infrared Evidence for the Existence of an Isomeric Form of HCN

Hydrogen cyanide has been shown by the experiments of Badger and Binder[1] and of Choi and Barker[2] to be a rectilinear molecule with a simple structure of the vibration-rotation lines. In their work on hydrocyanic gas these investigators found an absorption band with a maximum at 4.76μ.

In recent studies of the effects of isomerism on infrared absorption spectra the writer finds that all organic cyanides have an intense absorption band near 4.5μ, while the isomeric forms of these compounds in which the carbon is divalent give rise to more intense bands at slightly longer wave-lengths. The shift in band position due to isomerism is found to be approximately 0.2μ in every case studied.

The work of Nef[3] and his co-workers seems to indicate the existence of a small amount of the isomer HNC in all hydrocyanic gas. A study of the absorption of a saturated solution of hydrocyanic gas in the region between 4.5μ and 5μ reveals a strong band at 4.76μ and a much weaker band at 4.95μ. The absorption at 4.95μ is attributed to the presence of a small amount of the isomer HNC in the solution. From a comparison of intensities it would seem that the isomer HNC makes up about two percent of the gas in aqueous solution.

Dudley Williams

University of North Carolina,
Chapel Hill,
December 5, 1935.

[1] R. M. Badger and J. L. Binder, Phys. Rev. **37**, 800 (1931).
[2] K. N. Choi and E. F. Barker, Phys. Rev. **42**, 777 (1932).
[3] J. V. Nef, J. Am. Chem. Soc. **26**, 1549 (1904).

An X-Ray Study of Symmetrical Trinitrotoluene and Cyclo Trimethylenetrinitramine

An x-ray study of the above crystals was undertaken with the hope of finding the crystal structure of these powerful explosives and thus contribute toward an understanding of why they decompose violently to shocks of a definite frequency while being unaffected by much stronger shocks of a different frequency. Although the crystal structures proved to be too complicated to be readily found, the symmetries of the crystals and their unit cells were determined.

Professor Tenney L. Davis of the Massachusetts Institute of Technology kindly furnished the crystals.

The trinitrotoluene crystals had been obtained by precipitation in benzene. They were amber in color and flattened along the b axis with (210), (110), (011) and (010) prominent.

There are two reports* as to the crystallographic symmetry of symmetrical trinitrotoluene. Friedländer reports it to be orthorhombic with $a:b:c=0.7586:1:0.5970$. Artini later reported that he had detected a slight inclination of the c axis and that the crystals were therefore monoclinic.

Our Laue photographs clearly show two planes of symmetry parallel to the b axis. Since the intensity of Laue spots is very sensitive to the symmetry, it may be regarded as established that TNT is really orthorhombic. Complete rotation photographs give $a=14.85$A, $b=39.5$A, and $c=5.96$A in agreement with the crystallographic ratios. If there are 16 molecules in the unit cell, the calculated density is 1.710, compared with 1.654 given in the literature.

Reflections $hk0$ are missing for either h or k odd and $0kl$ for k odd. However, the latter is a special case of the non-space group vanishing hkl for h even and k odd, which occurs. This can be accounted for by special positions of the molecules, but the intensity calculations are very complicated and were not carried further.

The cyclo trimethylenetrinitramine crystals were transparent with beautifully developed faces and a brilliant luster. Mr. Harry Berman, mineralogist at Harvard, kindly examined them crystallographically for us. He reported them to be orthorhombic with $a:b:c=0.878:1:0.819$.

X-ray photographs confirm this. We obtain $a=11.5$A, $b=13.2$A, and $c=10.6$A. With eight molecules in the unit cell, the calculated density is 1.82. Reflections $0kl$ with l odd, $h0l$ with h odd and $hk0$ with k odd are missing. All space groups are eliminated except V_h', V_h^5, V_h^{11}, and V_h^{15} with the last most probable since it accounts for all the extinctions.

I am indebted to the Massachusetts Institute of Technology which furnished the facilities for this research and to the National Research Council for the National Research Fellowship under which this work was done.

Ralph Hultgren

Graduate School of Engineering,
Harvard University,
November 21, 1935.

* Groth, Chem. Krist. **4**, 364,766.

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