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The Infra-Red and Raman Spectra of Heavy Cyclooctatetraene

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WE wish to give a preliminary report of the vibrational spectra of completely deuterated cyclooctatetraene (C_8D_8), which we have prepared by the polymerization of heavy acetylene. The purification of our C_8D_8 has been followed spectroscopically. We feel confident that with respect to light hydrogen and the by-products of the polymerization, such as heavy styrene, its purity is more than adequate for the determination of the molecule's structure from its spectra.

The more prominent frequencies in the infra-red and Raman spectra of both C_8H_8 and C_8D_8 are given in Tables I and II. Further study of the Raman spectrum of C_8H_8 has confirmed our earlier results,[1] with the addition of two rather strong lines found by Hg-5770 and -5791 excitation. Although we have not previously published the infra-red data, we have been using infra-red spectra[2] since the fall of 1946 as a guide in the purification of C_8H_8 and, more recently, of C_8D_8. The spectra of C_8H_8 published by others[3,4] agree almost completely, so far as they go, with those listed here. We have received a private communication from Professor Langseth which indicates that he has prepared C_8D_8 and taken its Raman spectrum.

In the interpretation of the vibrational spectra of C_8H_8 and C_8D_8 certain general features are of importance:

(1) The number of Raman lines and infra-red bands in both compounds strong enough to be called fundamentals is small, as is the number of polarized Raman lines;

(2) There are a number of definite coincidences in both compounds between relatively strong infra-red bands in the vapor and relatively strong Raman lines;

(3) There are several very strong infra-red bands at frequencies where no Raman lines are found, and several very strong Raman lines at frequencies where no infra-red bands occur. In particular the polarized Raman frequencies are not found in the infra-red, with one, presumably accidental, exception in C_8D_8.

For a molecule with 42 vibrational degrees of freedom, (1) bespeaks considerable symmetry. A symmetry center is, however, incompatible with (2). A detailed consideration of possible symmetries for C_8H_8 on the basis of (1) and (2) enables almost all of the plausible structures to be ruled out. It is our belief that (3) enables the remaining structures to be excluded with the exception of the D_4 model* suggested in our earlier discussions of the problem.[1,5,6]

A more detailed interpretation, as well as an account of the preparation and purification of C_8H_8 and C_8D_8, will be published later. At present we wish to point out some

TABLE I. Infra-red absorption spectra of liquid C_8H_8 and C_8D_8.

C_8H_8		C_8D_8	
ν in cm^{-1}	Intensity	ν in cm^{-1}	Intensity
584	W	527	VS
630	VS	551	W
670	VS	592	W
800	VS	720	S
873	W	822	M
890	W	838	W
942	S	879	S
966	M	889	W
988	W	899	S
1202	S	928	M
1221	S	1286	M
1399	M	1554	VW
1439	W	1582	W
1573	W	1614	S
1605	M	2220	S
1635	S	2236	VS
1706	W	2252	VS
1725	W		
1750	M		
1781	W		
1845	W		
1922	W		
2004	W		
2425	W		
2745	W		
2781	W		
2826	W		
2950	M		
3004	VS		

TABLE II. Raman spectra of C_8H_8 and C_8D_8.

C_8H_8			C_8D_8		
$\Delta\nu$ in cm^{-1}	I	Approximate depolarization	$\Delta\nu$ in cm^{-1}	I	Approximate depolarization
194	10	1/2	172	10	1/2
249	9	6/7	238	8	6/7?
292	9	6/7	265	9	6/7?
366	10	6/7	312	10	6/7
655	5		565	1	
728	1		576	8	
758	2		591	3	
873	10	1/10	745	1	
908	3		761	8	6/7
948	9	6/7	812	4	1/3
967	7?		822	10	1/6
976	4?		838	3	6/7
994	6?		872	4	6/7
1202	9	6/7	881	8	6/7
1221	4		890	2	
1399	2		930	2	
1417	2		1287	2	
1439	9	6/7	1297	8	6/7
1461	1		1355	2	
1570	1		1542	3	
1601	7	6/7?	1554	2	
1631	8	6/7?	1579	6	
1651	10	1/5	1597	2	
1743	4		1615	6	
2793	2		1636	9	1/6
2832	2		1653	10	1/10
2853	2		1675	2	
2954	9	6/7	2225	9	6/7?
3003	10	6/7	2250	10	<1/10
3013	10	<6/7	2245 to 2263	8	
3048	4				

specific results for C_8D_8 which appear to confirm the D_4 structure. If C_8H_8 and C_8D_8 have this structure, these molecules have a species of vibration A_2 (see Herzberg, "Infra-red and Raman Spectra," D. Van Nostrand Company, New York, 1945, p. 252), which is infra-red active and Raman inactive. There are four vibrations of this species in both C_8H_8 and C_8D_8. We have located unequivocally three strong bands, presumably of this species, at 670, 800, and 3004 cm^{-1} in C_8H_8 and at 527, 720, and 2236 in C_8D_8. The location of a fourth vibration will be discussed when this work is published in detail. Here we wish only to make the point that prolonged exposure of the Raman spectrum has failed to reveal any sign of the 670 and 800 frequencies in C_8H_8 or of 527 and 720 in C_8D_8, although these over-exposed spectra have produced a total of some forty Raman overtones in C_8H_8.

In the symmetry D_{2d}, which has been suggested on the basis of x-ray and electron diffraction studies,[7] all infra-red-active species are Raman-active also. The spectroscopic data accordingly appear to favor strongly the D_4 over the D_{2d} structure.

One of the striking features of the Raman spectra of both C_8H_8 and C_8D_8 is the collection of four strong lines of low frequency. These are presumably to be assigned to ring-puckering vibrations analogous to the non-planar benzene ring vibrations. There should be four such frequencies in both the D_4 and D_{2d} structures. In the D_{2d} structure, however, one of the four is forbidden in both Raman and infra-red spectra, whereas four are Raman-active in D_4. While the assignment of these four lines to the puckering vibrations is not an absolute necessity, the large gap of more than 250 cm^{-1} between the highest of these and the next lowest Raman line in both C_8H_8 and C_8D_8 is convincing support for such assignment and for the D_4 structure.

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[1] Lippincott and Lord, J. Am. Chem. Soc. 68, 1868 (1946).
[2] Cf. Cope and Overberger, J. Am. Chem. Soc. 69, 976 (1947).
[3] Flett, Cave, Vago, and Thompson, Nature 159, 739 (1947).
[4] Bastiansen, Hassel, and Langseth, Nature 160, 128 (1947).
* The D_4 structure, which has been called the "crown structure" by some, consists of a puckered eight-membered ring with alternate single and double bonds. The puckering occurs in such a way that a four-fold axis (C_4) is present, so that the ring has a saw-toothed appearance when viewed edgewise. Even-numbered carbon atoms lie in the same plane, which is parallel to the plane in which the odd-numbered carbon atoms lie. An analogous statement holds for the hydrogen atoms. By symmetry all carbon atoms are equivalent as are all hydrogen atoms. It should be noted that the D_4 structure implies optical isomerism.
[5] R. C. Lord, Jr., Proceedings of the Colloquium on Molecular Structure, Paris, May 27, 1947 (to be published in J. de Chim. physique).
[6] Lippincott and Lord, Symposium on Molecular Spectra, Ohio State University, June 1947.
[7] Kaufman, Fankuchen, and Mark, Nature 161, 165 (1947); J. Chem. Phys. 15, 414 (1947). Personal communication from Professor V. Schomaker.

Hysteresis of the Contact Angle

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THE angle of contact θ of a liquid against a solid is profoundly influenced by the presence of an adsorbed film on the unimmersed portion of the solid (and formed by spreading from the liquid, or by adsorption from the vapor phase, or both). This is implicit in Harkins and Dahlstrom's treatment[1] of the subject in 1930, but was first explicitly and quantitatively discussed by Bangham and Razouk[2] in 1937; they arrived at the expression

$$F_L - F_V = \gamma_L \cos\theta, \qquad (1)$$

where F_L and F_V are the diminutions in free energy when 1 cm^2 of the *clean* solid (i.e., free from film) is immersed in the liquid and exposed to the vapor, respectively; γ_L is the free surface energy of the liquid. In effect, almost all other workers had taken $F_L = \gamma_L \cos\theta$.

For a mobile film, Bangham[3] has shown that F_V may be equated with π, the surface pressure of the film; consequently, Eq. (1) may be written

$$F_L - \pi = \gamma_L \cos\theta. \qquad (2)$$

This form of the Bangham-Razouk relationship possesses the merit of expressing the dependence of θ on the adsorbed film in terms of a simple property of the latter, its surface pressure; and this is calculable, in principle[3,4] and often in practice, from the adsorption isotherm of the vapor on the solid by means of the integrated Gibbs adsorption equation: $\pi = RT \int_0^p \Gamma d \ln p$ (Γ moles = adsorption per unit area of the solid and p = pressure of the vapor). In particular it suggests an immediate connection between hysteresis of the contact angle and hysteresis in adsorption;[4] in this latter phenomenon the pressure P (and with it the surface pressure π) is greater on the "adsorption-increasing" run than on the "adsorption-decreasing" one, for a given adsorption Γ. It should be noted that hysteresis can occur with non-porous adsorbents[5] and is not confined to porous bodies, as is often supposed.

Now in measurements of the advancing contact angle, θ_a, the adsorbed film (surface pressure $= \pi_a$) is in the process of formation by spreading or by adsorption from the vapor phase; it corresponds to the "adsorption-increasing" run of a vapor adsorption experiment. But in measurements of the receding angle, θ_r, the film ($\pi = \pi_r$) adjacent to the line of contact has recently been covered with the bulk liquid, and it corresponds to the "adsorption-decreasing" run. If adsorption hysteresis occurs, $\pi_a > \pi_r$, consequently $\theta_a > \theta_r$, i.e., there is hysteresis of the contact angle.

To eliminate any difference between θ_a and θ_r it is necessary that $\pi_a = \pi_r$, and this requires (i) that adsorption hysteresis be eliminated, and (ii) that the pressure p over the film shall be the same during both measurements. To achieve (ii) is difficult in practice unless p be chosen as p_0, the saturated vapor pressure. Attainment of (i) calls for a number of precautions, notably that ample time be allowed for attainment of adsorption equilibrium, and that impurities be absent. Both these points are implicitly, though not explicitly, taken into account in the procedure adopted by Harkins and Fowkes,[6] whereby they have been able to eliminate hysteresis of the contact angle in a large number of cases.

Nevertheless, Harkins' assertion[7] that the "advancing and receding angles obtained by nearly all investigators other than those in this laboratory is due to improper preparation of the surface and poor techniques in making the measurements," is, in view of the known characteristics