515. *Spectroscopic Studies. Part III.*[1] *Analysis of the Acetaldehyde Vibration–Rotation Band near* 764 cm.$^{-1}$.

By J. A. Ladd and W. J. Orville-Thomas.

The rotational structure of the 764 cm.$^{-1}$ band of acetaldehyde has been measured. This band has been analysed in order to correlate the observed rotational fine structure with the molecular dimensions.

The advent of modern commercial grating spectrometers enables spectroscopic studies of moderately high resolution to be carried out as a routine operation.

In an investigation of the vapour-phase spectra of CH_3·CO·X molecules it was observed that the acetaldehyde band near 764 cm.$^{-1}$ had rotational fine structure. This structure has been measured and analysed.

Experimental

Acetaldehyde (AnalaR grade) was fractionally distilled before use.

A cell of path-length 8 cm. and a multiple reflection cell with an effective path-length of 120 cm. were used to record the spectrum with a Grubb–Parsons G.S.2 spectrometer. A cell temperature of 22° was maintained.

The observed spectrum is shown in Fig. 1; the Table gives the positions of the peaks measured.

Band Analysis and Discussion

The vapour-phase infrared spectrum of acetaldehyde has been studied by a number of workers,[2-4] but band contours alone have been obtained, and there has been no previous report of the observation of rotational fine structure.

[1] Part II, Jones and Orville-Thomas, *J.*, 1964, 692.
[2] Thompson and Harris, *Trans. Faraday Soc.*, 1942, **38**, 37.
[3] Morris, *J. Chem. Phys.*, 1943, **11**, 230.
[4] Evans and Bernstein, *Canad. J. Chem.*, 1956, **34**, 1083.

Rotational structure of the bop(CH) band.

K	pQ-branch ν (cm.$^{-1}$)	$\Delta\nu$ (cm.$^{-1}$)	rQ-branch ν (cm.$^{-1}$)	$\Delta\nu$ (cm.$^{-1}$)	ν_0 (cm.$^{-1}$)
3	$756{\cdot}3_3$				
4	$753{\cdot}3_6$	2·97			
5	$750{\cdot}2_4$	3·12	$781{\cdot}1_0$	3·08	$764{\cdot}1_1$
6	$747{\cdot}2_0$	3·04	$784{\cdot}1_8$	3·16	$764{\cdot}1_3$
7	$743{\cdot}8_6$	3·34	$787{\cdot}3_4$	3·01	$764{\cdot}0_4$
8	$740{\cdot}5_5$	3·31	$790{\cdot}3_5$	2·96	$763{\cdot}8_9$
9	$737{\cdot}5_1$	3·04	$793{\cdot}3_1$	3·24	$763{\cdot}8_5$
10	$734{\cdot}0_4$	3·47	$796{\cdot}5_5$	2·79	$763{\cdot}7_4$
11	$731{\cdot}6_1$	2·43	$799{\cdot}3_4$	3·22	$763{\cdot}9_2$
12	$727{\cdot}7_8$	3·83	$802{\cdot}5_6$	2·55	$763{\cdot}6_1$
13			$805{\cdot}1_1$	2·88	
14			$807{\cdot}9_9$	3·43	
15			$811{\cdot}4_2$	2·93	
16			$814{\cdot}3_5$	3·21	
17			$817{\cdot}5_6$		

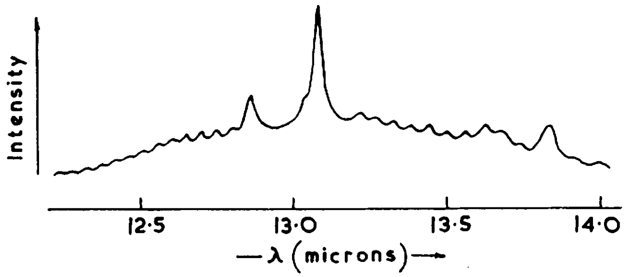

FIG. 1. Fine structure in the 764 cm.$^{-1}$ band.

The analysis of fine structure can be applied (i) as a powerful aid in frequency assignment, and (ii) to obtain moments of inertia. If these are already available, the analysis affords a sensitive check of their correctness, or otherwise.

Frequency Assignment of the 764 cm.$^{-1}$ *Band.*—The assignment of frequencies to bond-stretching modes is nowadays a relatively straightforward matter. This is not the case with the various deformation modes since they may vary over large spectral regions. For example, the CH_2 rocking frequency, which occurs at 1176 cm.$^{-1}$ in CH_2F_2, is found at 714 cm.$^{-1}$ in CH_2I_2, a displacement of 462 cm.$^{-1}$. Two bending modes are associated with the aldehyde CH group. One can be described as a bending-in-plane vibration, bip(CH), the other as a bending-out-of-plane mode, bop(CH). In a number of molecules [5] of the type H•CX:O, where the carbon atom is $\sim$ sp^2-hybridised, these vibrations have the frequencies bip(CH) ~1360 and bop(CH) ~1050 cm.$^{-1}$. In acetaldehyde the bip(CH) band is found near to its expected value but no band occurs [4] between 920 and 1110 cm.$^{-1}$. Evans and Bernstein [4] assigned a sharp peak at 764 cm.$^{-1}$ to the bop(CH) vibration. This is so far from its expected value that additional evidence is needed. If the assignment is correct then the change in dipole moment should occur principally in a direction parallel to the C-axis giving rise to a perpendicular (or C-type) band. The actual band structures to be expected for asymmetric rotors have not been evaluated for the general case. Nielsen,[6] however, has given diagrams of band structures for a number of values of a parameter $\rho = I_A/I_B$. For small ρ values both B-type and C-type bands approximate to the structure of a perpendicular band of a symmetric rotor. That is, no central Q branch is expected. For larger values of ρ, the B and C bands become increasingly different. This happens because, for $\rho = 1$, the C band goes over into a parallel band of a symmetric top whilst both A and B bands become perpendicular. Since parallel bands have a central maximum one would not expect a central qQ-band for very

[5] Orville-Thomas, *Research*, 1956, 9.
[6] Nielsen, *Phys. Rev.*, 1931, **38**, 1432.

small ρ (no parallel component) but only for larger ρ. In fact (Fig. 1), the spectrum is essentially that of a perpendicular band consisting of $pQ(K)$ and $rQ(K)$ branches. For $K > 3$, the sub-bands are fairly well resolved. For smaller K values the structure disappears, owing to the slight asymmetry of the molecule. The band, however, posseses a comparatively strong qQ branch, which indicates that during the vibration the change in dipole moment has a component parallel to the A-axis. The band structure, then, is in accord with that assigned by Evans and Bernstein on the grounds that the band shifts to 668 cm.$^{-1}$ in $CH_3{\cdot}CDO$.

Correlation of Microwave and Infrared Data.—The microwave spectrum [7] of acetaldehyde leads to the following values for the moments of inertia $I_A = 14{\cdot}826$, $I_B = 82{\cdot}556$, and

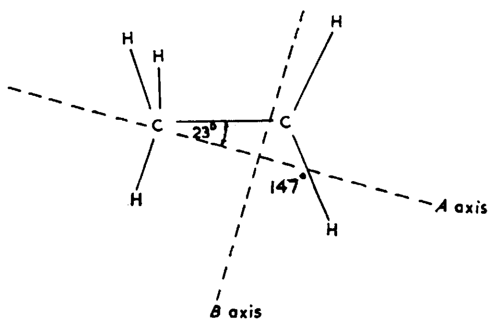

FIG. 2. Major axes in acetaldehyde.

$I_C = 92{\cdot}202 \times 10^{-40}$ g. cm.^{2}. The directions of the axes of inertia are indicated in Fig. 2 (the C-axis is perpendicular to the plane of the paper).

Since $I_A \neq I_B \neq I_C$, the molecule is an asymmetric rotor.*

However, since $I_B \approx I_C \gg I_A$, acetaldehyde will behave almost like a prolate symmetric top, and on this basis an approximate analysis is possible.

The theory of the slightly asymmetric top has been dealt with by Dieke and Kistiakovsky.[8] The molecular parameters derived from the perpendicular bands are

$$\gamma' - \delta' \text{ and } \gamma' - \delta'',$$

where

$$\gamma = h/8\pi^2 cI_A$$

$$\delta = h/8\pi^2 cI_D$$

and

$$1/I_D = (1/I_B + 1/I_C)/2 \qquad (1)$$

These parameters can be obtained from the difference equations,

$$\gamma' - \delta' = [rQ(K) - pQ(K)]/4K$$

and

$$\gamma'' - \delta'' = [rQ(K-1) - pQ(K+1)]/4K \qquad (2)$$

The single prime refers to the upper vibrational state of the transition and the double prime to the lower; within experimental error the δ values are the same for each state. In equations (2), $rQ(K)$ and $pQ(K)$ represent the frequencies of the rotational bands of the r-branch and p-branch, respectively, arising from the Kth energy level of the lower state.

The rotational sub-bands have been assigned K values as shown in the Table, and

* Dieke and Kistiakovsky [8] have defined an assymetry parameter:

$$\beta = \left(\frac{1}{I_B} - \frac{1}{I_C}\right) \Big/ 2\left(\frac{1}{I_A} - \frac{1}{I_D}\right)$$

For a symmetric top $\beta = 0$. Acetaldehyde has the value $\beta = 0{\cdot}0113$. This is quite small and hence as claimed, the molecule can be treated as a slightly asymmetric rotor.

[7] Kilb, Lin, and Bright Wilson, jun., *J. Chem. Phys.*, 1957, **26**, 1695.
[8] Dieke and Kistiakovsky, *Phys. Rev.*, 1934, **45**, 4.

a Fortrat diagram indicates that the band centre lies at 765·8 cm.$^{-1}$. In Fig. 3 K is plotted against the functions $rQ(K) - pQ(K)$ and $rQ(K-1) - pQ(K+1)$, respectively. Straight lines are obtained whose gradients (determined by the method of least squares), used in conjunction with equations (2), lead to the values $\gamma' - \delta' = \gamma'' - \delta'' =$ 1·56 cm.$^{-1}$. These values are in excellent agreement with that (1·565 cm.$^{-1}$) obtained by substituting the microwave data [7] in equations 1.

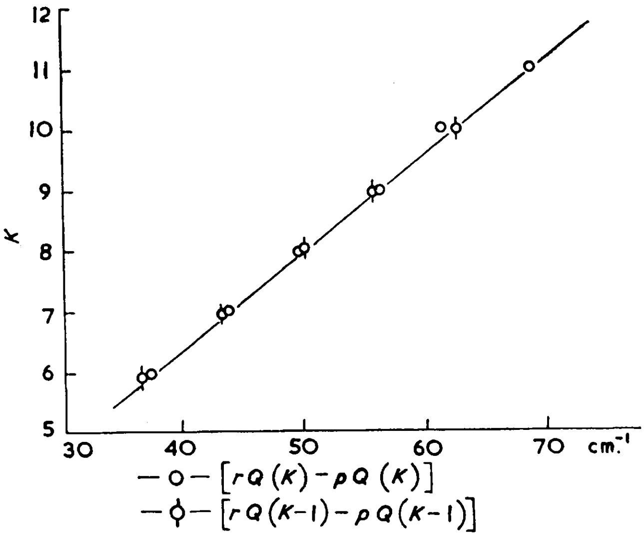

FIG. 3. Determination of the parameters γ and δ.

The band centre is given by the relation,

$$\nu_0 = rQ(K) + pQ(K)/2 + K^2(\gamma'' - \gamma') - (\gamma' - \delta)$$
$$= rQ(K) + pQ(K)/2 + K^2(\gamma'' - \delta) - (K+1)(\gamma' - \delta)$$

Substitution of the value 1·56 cm.$^{-1}$ for $\gamma'' - \delta$ and $\gamma' - \delta$, together with sub-band values for various K's, leads to an average value of $\nu_0 = 763{\cdot}9$ cm.$^{-1}$.

One further test of the compatibility of the infrared and microwave data can be made. Acetaldehyde approximates to a prolate symmetric top, and for such a rotor the separation between sub-bands differing in their K values by unity is

$$\Delta\nu = 2\boldsymbol{h}(1/I_A - 1/I_D)/8\pi^2c \qquad (3)$$

The observed $\Delta\nu$ values are given in Table 1. The overall average value of 3·10 cm.$^{-1}$ is in good agreement with the microwave value of 3·12 cm.$^{-1}$ obtained from equation (3).

We thank the D.S.I.R. for equipment grants and for a Research Studentship (J. A. L.). This research has been sponsored in part by the Air Force Cambridge Research Laboratories, O.A.R., through the European Office, Aerospace Research, U.S.A.F.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

[Present address (J. A. L.): NOYES LABORATORY, UNIVERSITY OF ILLINOIS,
URBANA, ILL., U.S.A.]
[*Received, October* 23*rd*, 1963.]