

472. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part VII.* A Note on the Near-ultra-violet Spectrum of Acetaldehyde.*

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The near-ultra-violet spectrum of acetaldehyde, like that of formaldehyde, consists of at least two electronic transitions. This makes analysis difficult, but the following definite points emerge. Ground-state fundamental frequencies of *ca.* 630 and 779 cm^{-1} suggested by Thompson and Harris are confirmed. A further probable ground-state fundamental frequency is *ca.* 475 cm^{-1} . The long-wave-length end of the spectrum involves an excited state frequency of *ca.* 320 cm^{-1} which plausibly represents an out-of-plane bending of the $\begin{array}{c} \text{H} \\ \diagup \\ \text{C} \end{array} \text{C}=\text{O}$ group. The first electronic transition of formaldehyde is shifted to *short* wave-lengths by methyl substitution; but the second electronic transition probably to long wave-lengths.

IN view of the analysis of the fluorescence and long-wave-length absorption bands of formaldehyde* it is of interest to consider the corresponding absorption system of acetaldehyde.

The near-ultra-violet absorption bands of acetaldehyde vapour have been measured by Schou (*J. Chim. phys.*, 1929, **26**, 27). Apart from his arrangement of the bands, which appears not to have any fundamental meaning, there seems to have been no previous attempt at analysis. The stronger bands begin with a band labelled *A* at *ca.* 3390 Å. The measurements and labels, according to Schou, of the eight longest-wave-length stronger bands are tabulated below. The measurements of bands *A*, *B*, and *a* represent origins taken from Schou's rotational analysis of these bands; those for bands *b* to *f* are approximate positions of the band centres. To the red side of band *A* occur four weak bands here labelled α , β , γ , δ . The Table shows the positions of the band centres. The separations of these from *A* are, respectively, 275, 475, 630, and 779 cm^{-1} . There is no doubt that these bands represent transitions from vibrational levels of the ground state. The fundamental frequencies of the $\text{CH}_3\text{-CHO}$ molecule have been discussed by Thompson and Harris (*Trans. Faraday Soc.*, 1942, **38**, 37) and Morris (*J. Chem. Phys.*, 1943, **11**, 230). The list of fundamentals suggested by the former authors includes a frequency (ν_3) of 780 cm^{-1} (in the Raman spectrum of the liquid; 764 cm^{-1} in the infra-red spectrum) and another (ν_2) of 650 cm^{-1} (in the Raman spectrum of the liquid; 625 cm^{-1} in the infra-red spectrum). The correspondence of these to the *A*- δ and *A*- γ separations makes it practically certain that *A* is a vibrationless band and δ , γ represent transitions from the $n_3'' = 1$ and $n_2'' = 1$ levels, respectively, of the ground state to the vibrationless upper state. It also makes it practically certain that 780 and 630 cm^{-1} represent fundamental frequencies of the ground state. This is in agreement with the suggestions of Thompson and Harris, but not with those of Morris who failed to observe the 625- cm^{-1} infra-red frequency.†

There seems no doubt‡ that the 475- cm^{-1} separation of *A* and β also represents a ground-state fundamental frequency. Not only does the separation occur in the near-ultra-violet absorption of acetaldehyde, but also weak bands lying *ca.* 475 cm^{-1} to the red of the first strong bands of the 1818- and 1660-Å absorption systems are clearly visible on photographs of the far-ultra-violet spectrum of acetaldehyde taken by the author (Walsh, *Proc. Roy. Soc.*, 1946, *A*, **185**, 176). The actual measurements are

1818-Å System	1660-Å System
54,515 cm^{-1} > 481	59,689 cm^{-1} > 481
54,996 " "	60,170 " "

Since the separation is independent of the precise upper state being considered, it apparently represents a ground state frequency only. We shall call the vibration involved ν_x . β is

* Part VI, preceding paper.

† Pitzer and Weltner (*J. Amer. Chem. Soc.*, 1949, **71**, 2842), because of Morris's work, also discarded the 625- cm^{-1} frequency as a fundamental.

‡ Except that it might be possible to interpret β as a transition from the $n_2'' = 1$ level to the same upper level as that of *B*. The separation of β and *B* is 640 cm^{-1} .

thus a transition from the $n_x'' = 1$ level of the ground state to the vibrationless upper state. Thompson and Harris's list does not include any frequency less than 520 cm^{-1} . Morris records the " 520-cm^{-1} " fundamental at 509 cm^{-1} in the infra-red spectrum. He also gives another fundamental frequency at $421\text{--}431 \text{ cm}^{-1}$, finding a strong band here in the infra-red spectrum, but Pitzer and Weltner (*loc. cit.*) cite evidence against *ca.* 426 cm^{-1} being a fundamental frequency. Probably the 475-cm^{-1} separation represents the *ca.* 520-cm^{-1} frequency of the infra-red spectrum. The agreement is not very good, but the measurements of the infra-red and the Raman spectrum do not agree very well. Thus Morris records the " 780-cm^{-1} " fundamental at $733\text{--}765 \text{ cm}^{-1}$, the measurement in the Raman spectrum being $779\text{--}780 \text{ cm}^{-1}$. ν_x , ν_2 , and ν_3 undoubtedly represent deformation vibrations of some kind. The most probable interpretation is that they represent (not necessarily respectively) in-plane C-C-O bending, out-of-plane rocking of the H attached to the carbonyl group, and out-of-plane rocking of the CH_3 group (compare the discussion given by Morris, *loc. cit.*). These are all vibrations which, from our discussion of the corresponding formaldehyde transition, we might expect to occur in the spectrum. It is significant for the interpretation of the formaldehyde spectrum that bands should be associated with *A* of the acetaldehyde spectrum which form a progression in a frequency other than that of C=O stretching.

The interpretation of band α is less certain. There is no obvious band at *ca.* 275 cm^{-1} to the red side of the first strong bands of the shorter-wave-length transitions. It seems therefore that 275 cm^{-1} is not to be interpreted as a ground-state fundamental frequency, but as a difference between an upper-state frequency and a ground-state frequency. We shall return to this point below.

Frequencies and assignments of the long-wave-length absorption bands of acetaldehyde.

Intensity	Label	Band centre, cm. ⁻¹	Assignment					$\nu_{\text{calc.}}$, cm. ⁻¹
			n_y'	n_x'	n_x''	n_2''	n_3''	
1	δ	28,711	0	0	0	0	1	—
1	γ	28,860	0	0	0	1	0	—
1	β	29,015	0	0	1	0	0	—
1	α	29,215	—	—	—	—	—	—
3	<i>A</i>	29,490	0	0	0	0	0	—
2	<i>B</i>	29,655	0	1	0	0	0	—
4	<i>a</i>	29,800	1	0	0	0	0	29,808
3	<i>b</i>	29,974	1	1	0	0	0	29,973
6	<i>c</i>	30,136	2	0	0	0	0	30,122
4	<i>d</i>	30,272	2	1	0	0	0	30,287
6	<i>e</i>	30,358	3	0	0	0	0	30,432
5	<i>f</i>	30,499	3	1	0	0	0	30,597

The diagram of the spectrum given by Schou makes it very probable that bands *A*, *a*, *c*, and, probably, *e* form a progression in some upper-state frequency, while bands *B*, *b*, *d*, and *f* form another progression in the same upper-state frequency. We shall call this frequency ν_y . Except for the *e* and the *f* band the positions of the members of these progressions can be reproduced reasonably well (see Table) by adding the term $(320n_y' - 2n_y'^2)$ to the frequencies of the *A* and the *B* band. 320 cm^{-1} is thus an upper-state frequency. There is a steady increase in intensity in each progression. It therefore appears that the frequency is aroused by an appreciable change of shape of the molecule in the upper state. By analogy with formaldehyde the biggest change involving such a low frequency is likely to be an out-of-plane bending into a pyramidal form. It is plausible therefore to suggest that ν_y' represents an out-of-plane bending vibration of the $\begin{matrix} \text{H} \\ \text{C} \end{matrix} > \text{C}=\text{O}$ group. The separation of the *A* and the *B* band is 165 cm^{-1} . This is shown in the Table as another upper-state frequency, ν_x' , but its interpretation is quite uncertain.* It becomes possible that α represents a transition either from $n_2'' = 1$ to $n_y' = 1$ or from $n_x'' = 1$ to $n_x' = 1$. In either case however its separation from *A* is calculated to be 310 cm^{-1} ($630 -$

* It might represent the separation of two electronic states. In that case what is here called the "second" electronic transition would have to be re-labelled the "third" electronic transition.

320 = 475 - 165 = 310) which is not sufficiently close to the observed 275 cm^{-1} for the assignment, although possible, to be certain.

The observed frequencies of bands *e* and *f* do not agree at all well with the calculated frequencies, although from Schou's diagram they look as though they might well belong to the *A* and the *B* progression respectively. However, it is clear from at least two considerations that, starting around band *d*, the spectrum suffers considerable disturbance. First, the spacing and intensity succession of the bands thenceforward becomes quite different; secondly, the bands from *d* onwards begin to be diffuse whereas bands *A* to *C* have sharp fine structure. It seems very probable that a second electronic transition is concerned from somewhere around band *d* onwards. This is strongly supported by curves given by Schou (*J. Chim. phys.*, 1929, **26**, 77) for the absorption of acetaldehyde in solution in hexane or water. The absorption in hexane is shifted very little relatively to the vapour-phase absorption, although all vibrational structure is blotted out. In these solution curves, the absorption bands discussed here appear as a shoulder ($\log \epsilon_{\text{max.}} \sim 0.1-0.2$) on the long-wave-length side of the main absorption ($\log \epsilon_{\text{max.}} \sim 1.1-1.2$ at 2900 Å in hexane), being overtaken by the second (main) transition at *ca.* 3300 Å in the hexane solution, *i.e.*, just about where the vapour-phase band *d* lies. The occurrence of a second transition affecting the short-wave-length end of the first absorption system is also strongly to be expected from our knowledge of the formaldehyde absorption spectrum (cf. the discussion of the formaldehyde *A, B, C . . .* progression in Part VI). The acetaldehyde bands become completely diffuse at *ca.* 3190 Å (compare 2750 Å for formaldehyde), while eventually continuous absorption sets in. The absorption as a whole thus involves several electronic transitions. This is in accord with expectations from Part VI, but it makes analysis of the whole system difficult. It does not appear profitable at present to carry the vibrational analysis beyond band *f*.

Two further interesting points emerge, however. The positions of the bands β, γ, δ in relation to band *A* leave no doubt that *A* is the origin of the first electronic transition. *A* is at 29,490 cm^{-1} . The frequency of the origin of the corresponding transition in formaldehyde was not greater than 28,313 cm^{-1} . Methyl substitution thus causes this first transition to move to *short* wave-lengths.* On the other hand, the second transition becomes noticeable at *ca.* 30,287 cm^{-1} (band *d*) in acetaldehyde compared with *ca.* 34,032 cm^{-1} (band *F*) in formaldehyde. The position of the onset of complete diffuseness shows a shift in the same direction. Methyl substitution thus appears to cause the second electronic transition to move to long wave-lengths. It is for this reason that the wave-length range in which the first transition can be readily studied in acetaldehyde is so small, with the result that it is not possible to fix the unperturbed magnitude of the larger frequencies (*e.g.*, the C=O valency vibration) that would be expected to occur in the upper state.

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* The shift of the first transition, but not of the second, is in accord with general statements by Burawoy (*Discuss. Faraday Soc.*, 1950, **9**, 70).