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The O-H Band in the Vapors of Some Organic Acids and of Tertiary Amyl Alcohol in the Region $\lambda 9700^*$

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Absorption bands corresponding to the third harmonic of the O-H vibration have been observed in the vapors of formic, acetic, propionic and trichloroacetic acids, with centers at about 10202.8, 10242, 10235 and 10250 cm^{-1} , respectively. Formic acid alone gave a band with resolvable fine structure, but this has unusual features and may be described as a hybrid. The simultaneous presence of characteristics similar to those of both "perpendicular" and "parallel" type bands of symmetrical molecules is due to the fact that the change in electric moment produced by the O-H vibration has components along two of the principal axes of the molecule. Rotational constants for the formic acid molecule have been evaluated and the moments of inertia were found to be 85.2, 74.4 and 10.81×10^{-40} g cm^2 . The structures of the organic acid molecules are discussed and a comparison is made with nitric acid. In *tert*-amyl alcohol a band with single broad maximum at about 10414 cm^{-1} was found.

EXPERIMENTAL

THE absorption cell used in the experiments here described consisted of a Pyrex cell 304.8 cm long, which was confined in a resistance furnace of somewhat greater length. The pressure of vapor in the cell was controlled by regulating the temperature of a side arm which contained an excess of liquid acid (or alcohol) and was provided with an auxiliary heater. The pressures and temperatures used were such that the vapors of the acids were largely dissociated and the spectra obtained are those characteristic of the single molecules as we have previously shown in the case of acetic acid.¹

The spectrograms were taken in the first order of a 21 ft. grating using Eastman 144 Q plates which had been sensitized with ammonia. The iron lines in the second and third orders were used as calibration standards and a few weak water lines, due to traces of water vapor in the spectrograph, were also useful. In the case of formic acid two entirely independent sets of measurements were made which were found to agree very well. In one set the measurements were made directly on two plates with a comparator. In the other case microphotometer curves with a fivefold linear enlargement were used.

* This investigation is a part of a program of research made possible by a grant-in-aid from the National Research Council to one of us (R. M. B.) for which it is desired to express appreciation.

¹ Badger and Bauer, *J. Chem. Phys.* **5**, 605 (1937).

FORMIC ACID

The formic acid band at 10202.83 cm^{-1} has previously been observed by Herzberg and Verleger.² These workers have described the more prominent features of the band but apparently their resolving power was not quite adequate to bring out certain unusual and interesting details. Except for a small region near the center the structure at first sight appears to resemble that of the "perpendicular" type bands of a symmetrical rotator, and consists of a series of very well-defined *pQ* and *rQ* branches³ between which a number of weaker and sometimes incompletely resolved lines are visible. See Fig. 1. Closer inspection shows that the features of a "parallel" type band are also present, though considerably less intense. This is immediately evident only in the series of *qQ* branches which starts from the band origin, though the presence of the "parallel" band appears to be responsible for a very considerable asymmetry in intensity distribution. The "hybrid" character of the formic acid band is evidently due to the fact that the change in electric moment produced by the O-H vibration is not parallel to any of the principal axes of the molecule but has components in the direction of two of them. Such composite bands are generally to be expected in molecules without true elements

² Herzberg and Verleger, *Physik. Zeits.* **12**, 444 (1936).

³ In describing the formic acid band and in designating the rotational constants we shall use the nomenclature of Dieke and Kistiakowsky, *Phys. Rev.* **45**, 4 (1934).

of symmetry even though they may be nearly symmetrical rotators, but we know of no other case so far investigated in which the situation is as clear as in the one under discussion.

From the simplicity of the spectrum it is evident that the formic acid molecule is only slightly asymmetric and indeed the greater part of the band may be represented very accurately by equations of the same form as those applicable to the symmetric rotator. In the region where $K > 3$ we find that the energy levels are fitted within experimental error by the equation: $W/hc = J(J+1)\delta + K^2(\gamma - \delta) + K^4\mu$. The rotational constants ($\gamma' - \delta'$), ($\gamma'' - \delta''$) and μ (which is the same for both upper and lower vibrational states) can be evaluated with satisfactory accuracy from the combinations between the maxima of the pQ and rQ branches which are presented in Table I. It seems permissible to make combinations between the maxima of the branches since they are very narrow and the lines composing them are almost perfectly superposed. The agreement between the observed qQ branches and those calculated from the rotational constants obtained from the other branches is remarkably satisfactory.

The accuracy of the constant δ is probably somewhat less since for its evaluation we were obliged to use the weak lines on either side of the band which we have mentioned above. These lines, in the regions in which they can be resolved, appear to form series with a constant spacing which is a submultiple of that of the pQ and rQ branches between which they lie. On one side of the band the series can be followed for 42 lines, and on the other for 38 lines. The average spacings are 0.700 and 0.693 cm^{-1} , respectively.

TABLE I. Principal maxima in the formic acid band at 10202.83 cm^{-1} .

K	$pQ(K)$	$rQ(K)$	$qQ(K)$	$rQ(K) - pQ(K)$ 4K	$rQ(K-1) - pQ(K+1)$ 4K
3	—	10217.53	—	—	—
4	10187.06	21.59	10202.00	215.81	220.00
5	82.33	25.55	01.76	216.10	219.90
6	77.60	29.47	01.27	216.12	220.29
7	72.68	33.35	00.76	216.67	220.10
8	67.84	37.08	00.15	216.37	220.21
9	62.88	40.70	10199.45	216.16	220.11
10	57.84	44.15	98.65	215.77	220.08
11	52.67	47.50	98.78	215.84	219.81
12	47.43	50.76	96.88	215.27	219.56
13	42.11	54.10	95.84	215.36	219.17
14	36.79	57.18	94.74	214.98	219.07
15	31.42	60.25	93.57	214.71	218.51
16	26.07	63.18	92.18	214.23	218.42
17	20.46	65.89	91.26	213.86	218.00
18	14.94	—	89.55	—	217.51
19	09.28	—	88.03	—	—
20	03.66	—	—	—	—

Band origin is at 10202.83 cm^{-1} .
 $(\gamma' - \delta) = 2.1697 \text{ cm}^{-1}$; $\mu = -5.25 \times 10^{-6} \text{ cm}^{-1}$.
 $(\gamma'' - \delta) = 2.2106 \text{ cm}^{-1}$; $\delta = 0.348 \text{ cm}^{-1}$.
 $A_0 = 85.2 \times 10^{-40}$; $B_0 = 74.4 \times 10^{-40}$; $C_0 = 10.81 \times 10^{-40} \text{ g cm}^2$.

These lines appear to result from the near superposition of several pP and pR or rP and rR branches. That they are moderately sharp and well resolved must be due to two more or less fortuitous circumstances. In the first place it is clear that the constant δ is practically the same in both initial and final vibrational levels. From the sharpness of the pQ , qQ and rQ branches we estimate that its change cannot exceed about 0.5 percent. This being the case the line spacing must be nearly constant throughout all P and R branches. In the second place this spacing happens to be a submultiple of the distance between pQ and rQ branches in the regions of the band where the weak lines are sufficiently intense to observe. We have taken the constant δ as half the average of the mean spacings mentioned above and believe that it is in error by not more than one percent.

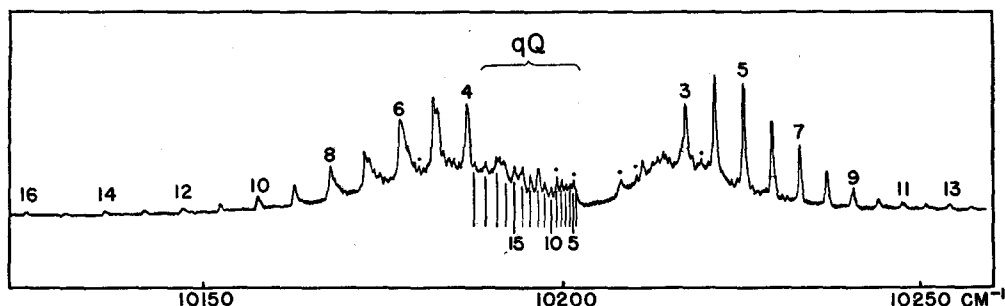


FIG. 1. Microphotometer curve of the O-H absorption band at 10202.83 cm^{-1} characteristic of the single molecules of formic acid in the vapor state. A few lines which may have slightly anomalous intensity due to a coincidence with weak water lines are indicated by dots.

In order to evaluate the moments of inertia of the formic acid molecule from the rotational constants it is necessary to have some knowledge regarding its shape. There seems to be no reason to doubt that the hydrogen attached to the carbon atom lies in the plane of the three heavy atoms, and the nature of the band observed makes it evident that the other hydrogen also lies in this plane. The appearance of the different bands which are possible in the case of a slightly asymmetric rotator has never been adequately discussed in the literature, but a consideration of an energy level diagram such as is given by Dieke and Kistiakowsky,³ and of the selection rules, leads to the conclusion that in the formic acid band we are concerned with a case in which the change in electric moment has components in the direction of both *intermediate* and *minor* axes of inertia. The component in the direction of the minor axis must be comparatively small because of the relative weakness of the "parallel" type features of the band. That the principal component is in the direction of the intermediate rather than the major axis is evident from the considerable lack of intensity near the center of the band, as compared with the "perpendicular" bands of a symmetrical rotator, and from the absence of the rudimentary *Q* branch such as is present in the 10.5μ band of ethylene.

Since the direction of change of electric moment produced by the O—H vibration must be nearly parallel to the O—H bond the facts mentioned above are sufficient to locate the hydroxyl hydrogen in the plane of the other atoms and on the side of the molecule nearest to the oxygen atom to which it is not attached. If it were on the other side of the molecule the "parallel" type features of the band would predominate. Other convincing arguments lead to the same conclusion. The low frequency of the O—H vibration in formic acid as compared with methyl alcohol indicates a large interaction between the hydroxyl hydrogen and the oxygen to which it is not bonded. This interaction may very possibly be of the nature of that found in the hydrogen bond. No strong bond can be formed in this case because of the great distance between the atoms, but the plane configuration of the molecule must nevertheless correspond to a rather deep energy minimum since the torsional vibration of the

hydroxyl hydrogen is evidently not excited to an appreciable extent. If this vibration were excited we should expect a number of overlapping bands arising from absorption by excited molecules, but there is absolutely no evidence of this.

Since the formic acid molecule is plane the moments of inertia *A*, *B* and *C* may be calculated from the relations $A = B + C$; $8\pi^2cd/h = (1/2)(1/A + 1/B)$; $8\pi^2c\gamma/h = 1/C$. Values are given in Table I. Unfortunately it is not possible to draw any very definite conclusions from these moments of inertia regarding the internuclear distances and bond angles of the molecule since there are seven parameters to be determined. It seems reasonable to assume that the C—H and O—H distances are approximately 1.07 and 0.96Å, respectively, that the C—H bond makes nearly equal angles with the two C—O bonds, and that the angle between C—O and O—H bonds is in the neighborhood of 105° . Bonner and Hofstadter⁴ have recently made a vibrational analysis of the formic acid spectrum and have evaluated approximate force constants for the two C—O bonds from which we may conclude that the respective internuclear distances cannot be greatly different from 1.43 and 1.24Å. With any distances in the neighborhood of these the angle between the two C—O bonds must be close to 123° to obtain agreement with our moments of inertia. We find good agreement when the distance from the carbon atom to the hydroxyl oxygen is taken as 1.40Å and the other C—O distance as about 1.25Å.

It should be possible to make a definite statement regarding the orientation of the O—H bond if the ratio of intensity of the "parallel" and "perpendicular" features of the 10202.8 cm^{-1} could be estimated at all accurately. Unfortunately we have not been able to devise any satisfactory way to do this and though our estimate that the intensity ratio is around 1 : 16 suggests that the angle between C—O and O—H bonds may be a trifle less than 105° the probable error is far too great to warrant any definite conclusion being drawn.

ACETIC, PROPIONIC AND TRICHLORACETIC ACIDS

The O—H bands of these substances are represented in the microphotometer curves of

⁴ Bonner and Hofstadter, *Phys. Rev.* **51**, 1017 (1937).

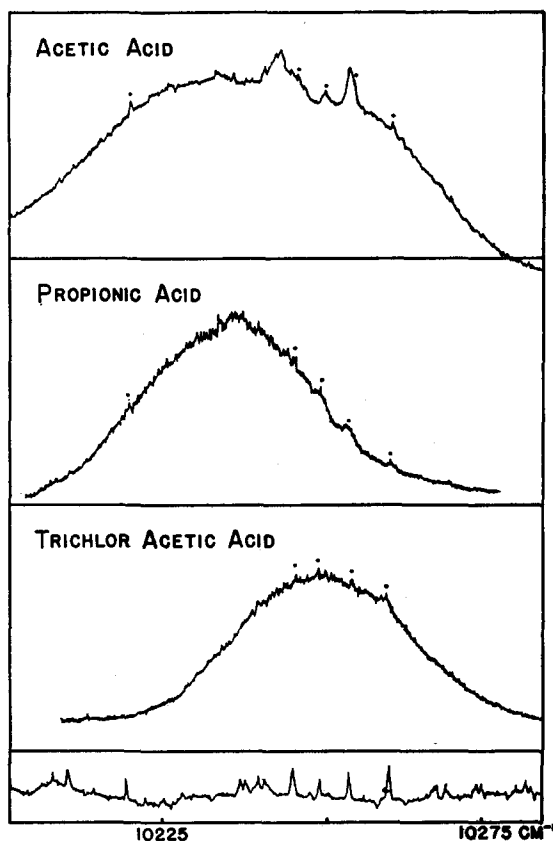


FIG. 2. The O-H absorption bands of three organic acid molecules in the vapor state. Some weak water lines are indicated by dots and the water spectrum is given for comparison at the foot of the figure.

Fig. 2. No fine structure was resolvable in any case and the bands of propionic acid and trichloroacetic acid have smooth envelopes with a single maximum. In acetic acid there is a weak and somewhat broad *Q* branch near the center of the band and another similar peak on the high frequency side. The cause of this secondary peak is doubtful. From the fact that the O-H frequency is nearly the same in the four organic acids which we have studied we conclude that the configuration of the carboxyl group is similar in all of them.

REMARKS ON NITRIC ACID

It is interesting to compare nitric acid with the organic acids. The O-H band of this substance at 10170.2 cm^{-1} , which we have previously described,⁵ has a quite different appearance from those of the other substances and is quite unique in our experience in the narrowness and intensity of its *Q* branch. The presence of this feature makes it necessary to conclude that the nitric acid molecule is nearly a symmetrical rotator and furthermore that the change in electric moment produced by the O-H vibration is nearly perpendicular to both of the principal axes corresponding to the nearly equal moments of inertia. No reasonable model in which all the atoms lie in a plane will meet these requirements. The condition that the molecule be nearly a symmetrical rotator can be met by reasonable arrangements of the four heavy atoms in a plane but the requirement regarding the direction of the electric moment makes it necessary to assume that the O-H bond is inclined nearly normal to this plane. This seems a somewhat surprising situation but we see no way at the moment of escaping from the conclusion.

TERTIARY AMYL ALCOHOL

The O-H band of this substance was found to have a smooth symmetrical envelope with a single broad maximum at about $\lambda 9600$ (10414 cm^{-1}). From our previous study of the vapors of the alcohols⁵ we had concluded that the O-H frequency depends very little on the mass of the molecule but is determined almost entirely by the type of alcohol (primary, secondary or tertiary). Our new observation lends support to this conclusion.

⁵ Badger and Bauer, *J. Chem. Phys.* **4**, 711 (1936).