

in connection with the entropy of solution in two component systems. Thus two normal paraffins may, at least within a certain range, mix without destroying their probably parallel orientation. However, a branched chain hydrocarbon might be expected to diminish the orientation of a straight chain hydrocarbon, with a corresponding increase in the entropy of mixing in excess of $-R(N_1 \ln N_1 + N_2 \ln N_2)$.

There are already several systems that invite this type of treatment. One of the most puzzling, heretofore, has been the solutions of iodine in ethylene bromide which, although violet in color, give solubility curves which are not parallel to those for the other violet solutions, but which deviate in the direction shown by the brown

solutions. It would seem, however, that the combination of moment of the C-Br bond with the rotation about the C-C bond, which has been shown to cause variations in the moment of the whole molecule depending on temperature and solvent,¹² offers possibilities of alterations of structure due to changing temperature and iodine content of the solution sufficient to account for the irregular entropy of this solution. Chloroform, on the other hand, which, although having nearly as large a dipole moment as ethylene bromide, has a buried dipole and little possibility of orientation, dissolves iodine to give a solubility curve parallel with those for other violet solutions.

¹² Cf. L. Meyer, *Zeits. f. physik. Chemie* **B8**, 27 (1930).

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An Absorption Band of Formaldoxime at $\lambda 9572^*$

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The third harmonic of the O-H band in formaldoxime vapor has been found to lie at $\lambda 9572$ ($10,444.1 \text{ cm}^{-1}$) and under high dispersion has been resolved and found to resemble a parallel band of a symmetric rotator. Owing to the weakness of the lines near the center of the band a definitely unique rotational analysis could not be made but the harmonic mean of the two larger moments of inertia appears to lie between the limits 73.3 and $76.6 \times 10^{-40} \text{ g cm}^2$. The hydroxyl hydrogen does not rotate freely and indeed its torsional oscillation appears not to have a very low frequency. It is not possible to locate this hydrogen uniquely until other parameters of the molecule have been determined by electron diffraction. The possible effect of resonance on the O-H frequency is discussed.

EXPERIMENTAL

THE trimer of formaldoxime was prepared in the manner recommended by Scholl.¹ On heating the substance to around 100° it yielded the monomer in the vapor state. The formaldoxime vapor was confined in a ten-foot Pyrex absorption tube at about 100° and one atmosphere. Exploratory spectrograms were first taken with a glass spectrograph of moderate dispersion to locate the O-H band. In the resolution of the rotational structure a 21-ft. grating was employed

which has a dispersion of about 2.5A per mm in the first order. Eastman 144Q plates sensitized with ammonia were used and the wave-length calibration was made by means of iron lines in the third order.

EXPERIMENTAL RESULTS

As may be seen in Fig. 1, a single O-H band was found at $\lambda 9572$ ($10,444.1 \text{ cm}^{-1}$) with a simple structure apparently identical with that of a parallel band of a symmetrical molecule. In Table I are given the frequencies of the observed lines. These are the average of two independent sets of measurements. In the case of some of the

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¹ R. Scholl, *Berichte* **24**, 573 (1891).

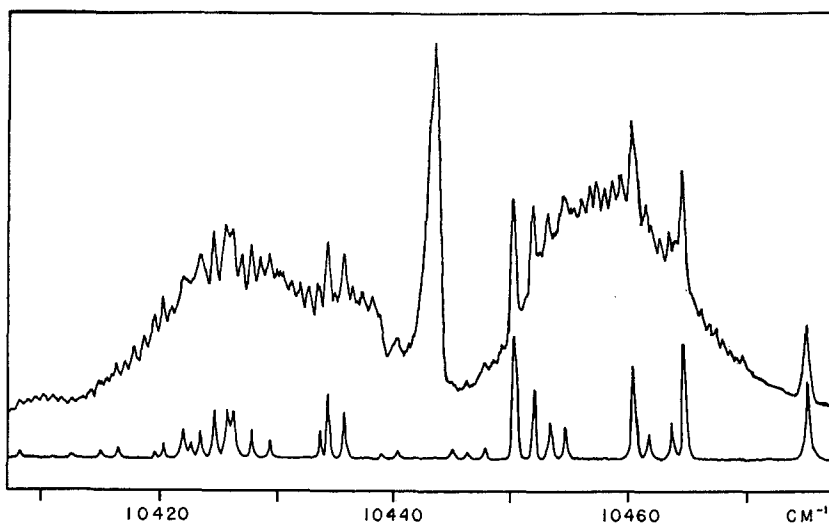


FIG. 1. Microphotometer curve of the O-H band at $\lambda 9572$ in formaldoxime vapor. The water vapor spectrum in the same region is shown below.

weaker lines the error may be as large as 0.1 cm^{-1} . The separation of the maxima of the *P* and *R* branches is 31.0 cm^{-1} .

DISCUSSION OF THE RESULTS

Formaldoxime (H_2CNOH) appears to deviate rather little from being a symmetrical rotator both from considerations regarding its structure and from the appearance of the band here described. Consequently the spacing in this band will, for all practical purposes, be determined by the harmonic mean of the two nearly equal and larger moments of inertia. It should be possible then to evaluate this mean moment of inertia for both upper and lower vibrational states by making the same combinations which would be appropriate for a parallel band.

With the help of a Fortrat diagram *J* values were assigned to the lines. It was not possible to do this uniquely and in both *P* and *R* branches there are two assignments which appear to be equally plausible as shown in Table I. The combinations can consequently be made in four different ways. In obtaining the rotational constants from the combinations $\Delta_2 F'(J) = R(J) - P(J)$ and $\Delta_2 F(J) = R(J-1) - P(J+1)$, it was found convenient to plot $\Delta_2 F''(J)/2(2J+1)$ against $(J+\frac{1}{2})^2$ since the effect of the stretching of the molecule with rotation is quite appreciable, and the extrapolation to the rotationless state would otherwise have been difficult.

The extreme values of the means of the two larger moments of inertia are those given by assignments 1 and 2 of Table I. They are, respectively, as follows: $D'' = 73.3 \times 10^{-40}$ and 76.6×10^{-40} , and $D' = 73.6 \times 10^{-40}$ and 76.8×10^{-40} . There is a slight uncertainty in making the extrapolations but it appears very unlikely that the actual values of the moments of inertia should lie much outside the limits given.

TABLE I. Frequencies of lines in the formaldoxime band at $\lambda 9572$.

ν (cm^{-1})	ALTERNATIVE <i>J</i> ASSIGNMENTS		ν (cm^{-1})	ALTERNATIVE <i>J</i> ASSIGNMENTS	
	No. 1	No. 2		No. 1	No. 2
<i>P</i> branch					
10,411.12	42	43	10,435.66	11	11
11.75	41	42	36.44	10	10
12.49	40	41	37.21	9	9
13.33	39	40	—	—	—
14.13	38	39	<i>Q</i> branch		
14.91	37	38	44.13		
15.58	36	37	<i>R</i> branch		
16.32	35	36	55.31	15	16
17.10	34	35	56.00	16	17
17.83	33	34	56.64	17	18
18.59	32	33	57.27	18	19
19.35	31	32	57.92	19	20
20.13	30	31	58.58	20	21
20.88	29	30	59.18	21	22
—	—	—	—	—	—
26.88	22	22	61.41	25	26
27.67	21	21	62.01	26	27
28.46	20	20	62.65	27	28
29.23	19	19	63.28	28	29
—	—	—	63.88	29	30
31.15	17	17	—	—	—
31.86	16	16	66.12	33	34
32.61	15	15	66.67	34	35
33.42	14	14	67.28	35	36
34.21	13	13	67.91	36	37
—	—	—	68.50	37	38
—	—	—	69.07	38	39

THE STRUCTURE OF FORMALDOXIME

Although it is not possible to determine the structure of formaldoxime from the data at present available, some interesting conclusions can be drawn. One of these is quite certain; the others may be somewhat in doubt and await further investigation for their confirmation. The appearance of the band at $\lambda 9572$ seems to exclude completely the possibility of the free rotation of the hydroxyl hydrogen. The band appears to be simple in structure, and if there are any superposed bands arising from absorption from excited levels they are certainly quite weak. It appears reasonable to conclude that the O-H torsional vibration is not extremely low.

When hydroxyl hydrogen, though not free to rotate, may be found in more than one position of potential minimum, the O-H frequency appears to be considerably different in the different positions unless they correspond to equivalent or very similar configurations of the molecule. The fact that only one O-H band is observed at $\lambda 9572$ may be taken as indicating that in the great majority of molecules at least the hydroxyl hydrogen is to be found in only one definite position, which one would consequently expect to correspond to a rather deep potential minimum. Since the molecule is most probably planar, it is of interest to speculate as to which of the two geometrically possible plane configurations is the more probable.

In both models the O-H bond makes a considerable angle with the minor axis of the molecule and if the change in electric moment is more or less parallel to this bond it is a little difficult to see how either can give rise to hydroxyl bands so predominantly "parallel" in character as the one observed. However, the one represented in Fig. 2 in which the hydroxyl hydrogen is farthest removed from the carbon atom seems definitely to be more probable.

The moments of inertia of the molecule would be of assistance in locating the hydroxyl hydrogen if the other parameters were known. Some of them can be estimated with sufficient accuracy but since there seems to be some possibility of resonance in formaldoxime one hesitates to make

a guess as to the C-N and N-O distances. The latter is particularly uncertain, and the assistance of electron diffraction measurements must be awaited.

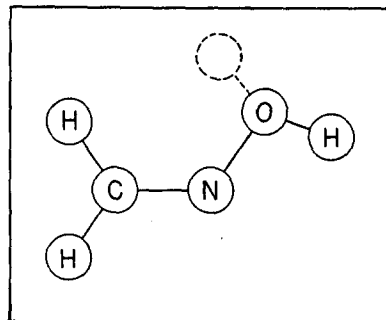


FIG. 2. Possible configurations of the formaldoxime molecule. The less probable location of the hydroxyl hydrogen is shown by dotted lines.

If the N-O bond does have appreciable double bond character, one should expect the O-H frequency to be somewhat affected, probably lowered. An effect of this sort may well be responsible for at least a part of the lowering of the O-H frequency in the carboxylic acids and in nitric acid. Indeed it is possible that the frequency lowering might serve as some measure of the importance of the resonance and it is unfortunate that internuclear distances are not available in any cases which might serve for calibration. However, it is doubtful whether any simple relation exists owing to the presence of numerous other complicating factors.

The third harmonic O-H band of formaldoxime has nearly the same frequency as the analogous one of phenol. In the latter molecule the importance of resonance has already been suggested.² In both cases the frequency is indeed slightly lower than in the primary alcohols but may still be regarded as well within the normal range. Consequently it appears unlikely that the N-O and C-O distances in the two molecules, respectively, will be found to be much shorter than the normal single bond distances. Electron diffraction measurements will, however, be awaited with interest.

² L. Pauling, *J. Am. Chem. Soc.* **58**, 94 (1936).