The Infrared Absorption Spectrum of Formaldehyde. Part I

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The infrared absorption spectrum of formaldehyde has been further investigated to beyond 11.0μ and bands were located at wave-lengths 5.7μ, 6.7μ, 7.5μ, 8.6μ and 9.6μ in addition to the regions originally reported by Salant and West and Patty and Nielsen near wave-lengths 3.5μ, 1.8μ, 1.4μ and 1.25μ. These regions of absorption were all studied under higher resolution and resolved into rotational components. *The 3.5μ region.* This region, originally studied by Patty and Nielsen, was remeasured and found to consist of two parallel type bands with an average spacing between lines equal to about 2.4 cm^{-1}, and a perpendicular type band with an average spacing of about 16.2 cm^{-1}. *The 5.7μ region.* This band was of the parallel type with its center at 5.73μ and with an average line spacing of about 2.4 cm^{-1}. *The 6.7μ region.* This band was also of the parallel type with its center at 6.65μ. Due to the bad overlapping of this region with the atmospheric water vapor bands, it was not attempted to resolve it into rotational structure. *The 7.5μ region.* The absorption near 7.5μ is due to a perpendicular vibration of the CH_2O molecule. The band shows considerable convergence, but when the spacings are averaged over an equal number of lines on either side of the center, it appears to be about 16.1 cm^{-1}. *The 8.6μ region.* The 8.6μ band is of the parallel type with its center at 8.58μ and shows an average separation between lines of about 2.4 cm^{-1}. It was possible also to measure this band as an emission band by heating the cell to somewhat higher temperatures. *The 9.6μ region.* This region was not thoroughly investigated, but a preliminary curve over this region made in emission indicates it to be of the perpendicular type with its center near 9.6μ.

I. INTRODUCTION

THE absorption by formaldehyde vapor was first investigated in the ultraviolet region by Henri and Schou.[1] This work has recently been repeated by Dieke and Kistiakowsky,[2] working under much improved experimental conditions. These investigators report complete resolution of a number of ultraviolet bands from which it is possible to determine values of the moments of inertia of the molecule in the ground state. The absorption by formaldehyde vapor in the infrared was first begun by Salant and West[3] who measured bands at 3.5μ, 1.8μ, 1.4μ and 1.25μ by means of a prism spectrograph. The region lying near 3.5μ was later investigated under higher resolving power by Patty and Nielsen,[4] with an echellette grating ruled with 3600 lines to the inch. This region revealed a complex absorption pattern which was interpreted to consist of three overlapping bands, two of which were of the parallel type and one of the perpendicular type. In addition to these a band of the parallel type, but much weaker, was found near 4.8μ. It also was partially resolved.

In all cases the parallel type bands were incompletely resolved, the lines appearing much like saw teeth. The spacings between lines were not uniform, however, ranging from 2.4 cm^{-1} to 4.0 cm^{-1}, the average being about 3.4 cm^{-1}. The perpendicular type band was identified by a series of broad prominent lines against an unresolved background. The spacings between these was estimated to be about 16 cm^{-1}, but due to the very bad overlapping with the parallel bands lying on both sides, this value could only be taken to be approximate. These two types of spacings should be sufficient to determine the molecular moments of inertia, but it was found that no good agreement was to be had with the values obtainable from Dieke and Kistiakowsky's work. This fact, in addition to the evidence of a non-uniformity of spacing of lines in the parallel type bands much too large to be accounted for by the asymmetry of the molecule, led one to suspect that the spacings observed by Patty and Nielsen were only apparent spacings arising out of incomplete resolution. It was therefore thought desirable, when an opportunity to continue the experiment presented itself, to remeasure these bands, if possible under still higher resolving power. A leave of absence presented this opportunity, and the spectrum has been measured on the spectrographs in the physics department at

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[1] V. Henri and A. Schou, Zeits. f. Physik **49**, 774 (1928).

[2] G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. **45**, 4 (1934).

[3] E. O. Salant and W. West, Phys. Rev. **33**, 640A (1929).

[4] J. R. Patty and H. H. Nielsen, Phys. Rev. **39**, 957 (1932).

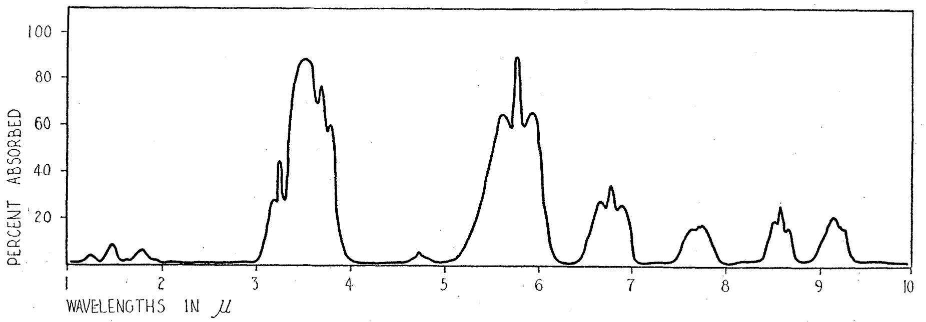

FIG. 1. Survey of absorption of formaldehyde with prism spectrograph in region from 1 to 11μ.

the University of Michigan, which were put at the writer's disposal.

In order that the spectrum might be studied much more extensively than before, an absorption cell was made, fitted with windows of rocksalt. The cell was made of a brass tube six inches long and could be heated by means of a coil extending the entire length of the cell. The inside of the tube contained flanges at some distance from the ends, to which the windows might be clamped by means of rings threaded to the inside of the tube. The windows were made air-tight at the joints by rubber gaskets. The formaldehyde vapor was generated by heating chemically pure trioxymethylene (paroformaldehyde). A container of brass attached to the side of the cell, heated by conduction from the cell itself, served as a reservoir for the paraformaldehyde. The cell and reservoir were thermally insulated by coatings of asbestos. It was found advantageous to operate the cell at a temperature of about 150°C.

Before beginning the measurements with the diffraction gratings, a preliminary prism exploration curve was made. This was done on a prism spectrograph of the Wadsworth type, designed by Sleator. The curve extends from 1.0μ to 11.0μ. This curve is reproduced in Fig. 1.

The grating spectrograph was one designed by Meyer and used by him and Barker and their collaborators in a great many investigations. It was equipped with three echellette gratings to diffract the various parts of the infrared spectrum. At 3.5μ, a grating ruled with 7200 lines per inch was available; from 5.0μ to 7.0μ, one with 4800 lines to the inch, and from 7.0μ to 11.0μ, one with 1200 rulings per inch was used in second order.

II. THE ABSORPTION REGION FROM 3.3μ TO 3.6μ

This is the region principally studied in the work of Patty and Nielsen, and has been remeasured with twice the dispersion and nearly four times the resolving power. In the major details it resembles quite accurately the absorption pattern reported in that work, there being three badly overlapping bands, two of which are of the parallel type, and a third of the perpendicular type.

The essential differences between these measurements and the earlier ones are details revealed by higher dispersion and resolution. The lines in the non-overlapping branches of the parallel type bands have been separated and the spacings near the center are now about 2.4 cm^{-1} instead of about 3.5 cm^{-1} as reported earlier. A certain irregularity in the short wave-length end of the 3.5μ band suggested that perhaps still another weak band was to be found near 3.2μ. This was borne out by a set of explorations in this region, but the cell was too short to obtain any definite results.

The perpendicular type band is identified as before by a group of rather prominent lines standing out against an unresolved background. Near the center of the band, where the overlapping with other bands is least, an alternation of intensities is evident; their ratios cannot, however, be determined exactly. An estimate of about 3 : 1 seems not implausible.

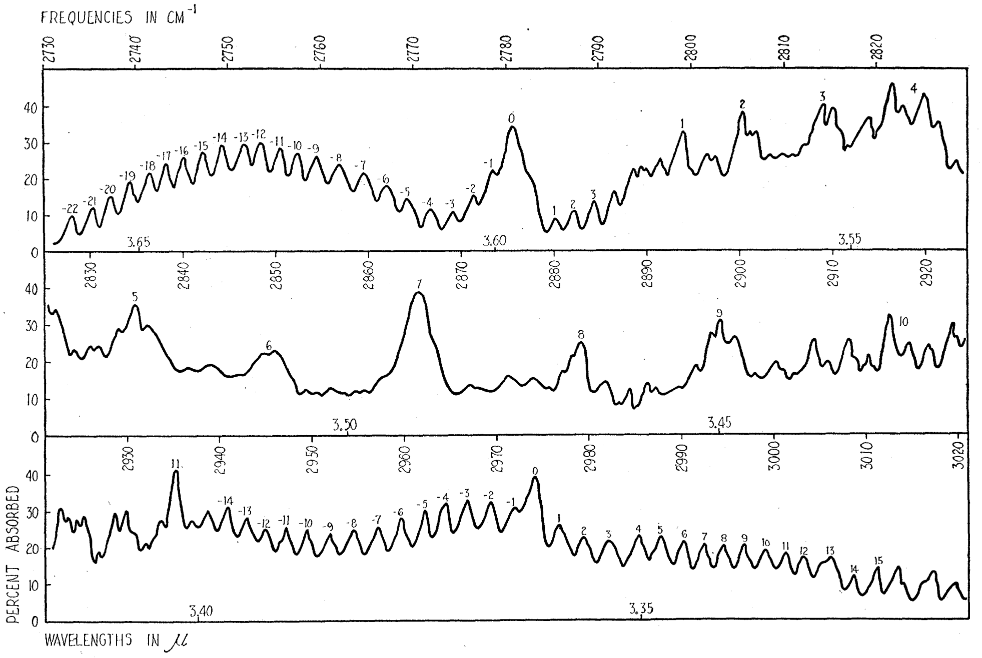

FIG. 2. Absorption of formaldehyde in region from 3.3 to 3.6μ.

In Fig. 2 is shown the new absorption curve for this region. The wave-lengths and frequency positions of lines in the parallel type bands and principal peaks in the perpendicular type band are tabulated in Table I.

TABLE I. *Wave-lengths and frequencies of principal absorption lines of formaldehyde in region 3.3 to 3.65μ.*

Line No.	Wave-length (μ)	Fre-quency (cm^{-1})	$\Delta\nu$ (cm^{-1})	Line No.	Wave-length (μ)	Fre-quency (cm^{-1})	$\Delta\nu$ (cm^{-1})
−21	3.6566	2734.8		−14	3.4002	2941.0	
−20	3.6539	2736.8	2.0	−13	3.3978	2943.0	2.0
−19	3.6512	2738.8	2.0	−12	3.3956	2945.0	2.0
−18	3.6486	2740.8	2.0	−11	3.3929	2947.3	2.3
−17	3.6459	2742.8	2.0	−10	3.3901	2949.8	2.5
−16	3.6433	2744.8	2.0	− 9	3.3873	2952.2	2.4
−15	3.7406	2746.8	2.0	− 8	3.3844	2954.7	2.5
−14	3.6380	2748.8	2.0	− 7	3.3817	2957.1	2.4
−13	3.6352	2750.9	2.1	− 6	3.3789	2959.5	2.4
−12	3.6324	2753.0	2.1	− 5	3.3761	2962.0	2.5
−11	3.6294	2755.3	2.3	− 4	3.3736	2964.2	2.2
−10	3.6265	2757.5	2.2	− 3	3.3713	2966.2	2.0
− 9	3.6236	2759.7	2.2	− 2	3.3679	2969.2	3.0
− 8	3.6206	2762.0	2.3	− 1	3.3652	2971.6	2.4
− 7	3.6176	2764.3	2.3	0	3.3625	2974.0	2.4
− 6	3.6145	2766.6	2.3	+ 1	3.3599	2976.3	2.3
− 5	3.6115	2768.9	2.3	2	3.3568	2979.0	2.7
− 4	3.6085	2771.2	2.3	3	3.3541	2981.4	2.4
− 3	3.6054	2773.6	2.4	4	3.3512	2984.0	2.6
− 2	3.6023	2776.0	2.4	5	3.3483	2986.6	2.6
− 1	3.5992	2778.4	2.4	6	3.3455	2989.1	2.5
0	3.5961	2780.8	2.4	7	3.3426	2991.7	2.6
+ 1	3.5907	2785.0	4.2	8	3.3400	2994.0	2.3
2	3.5881	2787.0	2.0	9	3.3374	2996.3	2.3
				10	3.3347	2998.8	2.5
+ 1	3.5727	2799.0		11	3.3322	3001.0	2.2
2	3.5638	2806.0	7.0	12	3.3296	3003.4	2.4
3	3.5524	2815.0	9.0	13	3.3267	3006.0	2.6
4	3.5411	2824.0	9.0	14	3.3240	3008.4	2.4
5	3.5280	2834.5	9.5	15	3.3213	3011.0	2.4
6	3.5100	2849.0	14.5				
7	3.4904	2865.0	16.0				
8	3.4692	2882.5	17.5				
9	3.4508	2897.9	15.4				
10	3.4290	2916.3	18.4				
11	3.4072	2935.0	18.7				

III. THE 5.7μ REGION

The absorption region near 5.7μ is a region of intense absorption and is a single band of the parallel type. As shown in Fig. 3, the P and R branches have been partially resolved showing a quite regular fine structure with some convergence toward higher frequencies. The average spacing of these lines is about 2.4 cm^{-1}. The positions of the lines seem well represented by the formula

$$\nu = 1744.1 + 2.44n - 0.0072n^2 + 0.000088n^3$$

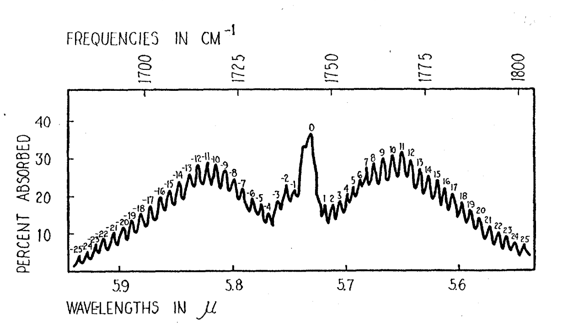

FIG. 3. Absorption of formaldehyde in the region near 5.7μ.

TABLE II. *Absorption lines in formaldehyde in the region near 5.7μ.*

Line No.	Wave-length (μ)	Fre-quency (cm⁻¹)	Δν (cm⁻¹)	Line No.	Wave-length (μ)	Fre-quency (cm⁻¹)	Δν (cm⁻¹)
−17	5.8820	1700.1	..	+ 3	5.7104	1751.2	2.4
−16	5.8723	1702.9	2.8	+ 4	5.7026	1753.6	2.4
−15	5.8630	1705.6	2.7	+ 5	5.6948	1756.0	2.4
−14	5.8538	1708.3	2.7	+ 6	5.6870	1758.4	2.4
−13	5.8445	1711.0	2.7	+ 7	5.6792	1760.8	2.4
−12	5.8353	1713.7	2.7	+ 8	5.6715	1763.2	2.4
−11	5.8261	1716.4	2.7	+ 9	5.6641	1765.5	2.3
−10	5.8173	1719.0	2.6	+10	5.6567	1767.8	2.3
− 9	5.8086	1721.6	2.6	+11	5.6494	1770.1	2.3
− 8	5.7998	1724.2	2.6	+12	5.6421	1772.4	2.3
− 7	5.7911	1726.8	2.6	+13	5.6348	1774.7	2.3
− 6	5.7824	1729.4	2.6	+14	5.6275	1777.0	2.3
− 5	5.7740	1731.9	2.5	+15	5.6202	1779.3	2.3
− 4	5.7657	1734.4	2.5	+16	5.6129	1781.6	2.3
− 3	5.7574	1736.9	2.5	+17	5.6057	1783.9	2.3
− 2	5.7494	1739.3	2.4	+18	5.5988	1786.1	2.2
− 1	5.7415	1741.7	2.4	+19	5.5922	1788.2	2.1
0	5.7336	1744.1	2.4	+20	5.5857	1790.3	2.1
+ 1		....	..	+21	5.5782	1792.7	2.4
+ 2	5.7182	1748.8	..	+22	5.5713	1794.9	2.2

where n is the number of the line from the center of the band. The actual measured positions of the lines in frequency units and wave-lengths is given in Table II.

IV. THE 6.7μ REGION

This region of absorption coincides almost exactly with the intense absorption by water vapor near 6.27μ. The falsification arising from this background was so great that it seemed impractical really to attempt to resolve the band into fine structure. Hence, the spectrometer slits were widened, and only an envelope of the band was made. This envelope is shown in Fig. 4 and reveals it also to be of the parallel type with its center at 6.65μ. The maxima of the P and Q branches lie, respectively, near the frequency positions 1472 cm⁻¹ and 1535 cm⁻¹.

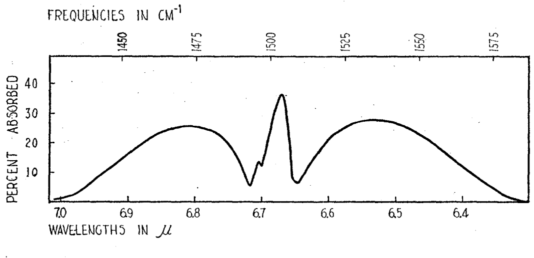

FIG. 4. Envelope of the 6.7μ band of formaldehyde.

V. THE 7.5μ REGION

This band is of the perpendicular type and consists of a series of prominent lines with an unresolved background. In the essential details it resembles the band lying near 3.5μ, but as is readily discernible from Fig. 5, there is a strong convergence of the lines toward higher frequencies. The two maxima with stars fell in a region of intense water vapor absorption. To determine their positions and their relative intensities in the spectrum, it was necessary very carefully to compare the transmission curve for the cell when empty of formaldehyde vapor with that for the cell when containing vapor. The two curves must be run immediately after each other before the background could change appreciably in intensity. In spite of this precaution, only estimates of the exact positions as well as their relative intensity could be made. In this band the alternation of intensities of the prominent lines is a prominent feature, their ratios being roughly 3 : 1. The positions of the lines in the band seem to be well expressed by the equation:

$$\nu = 1338.1 + 13.6n - 2.5n^2,$$

where n is a number arbitrarily assigned to the lines.

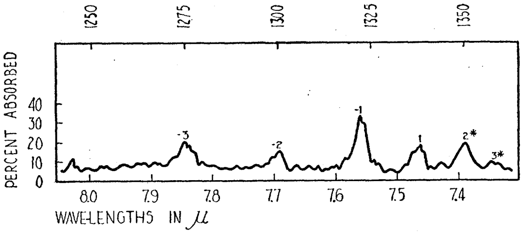

FIG. 5. Absorption of formaldehyde in the region near 7.5μ.

Table III gives the actually measured positions of the lines in terms of wave-lengths and frequencies.

TABLE III. *Wave-lengths of absorption lines in formaldehyde near 7.5μ.*

Line No.	Wave-length (μ)	Frequency in cm⁻¹	Δν(cm⁻¹)
−4	8.0405	1243.7	
−3	7.8444	1274.8	31.1
−2	7.6870	1300.9	26.1
−1	7.5643	1322.0	21.1
0	7.4733	1338.1	16.1
1	7.4118	1349.2	11.1
+2	7.3784	1355.3	6.1
+3			

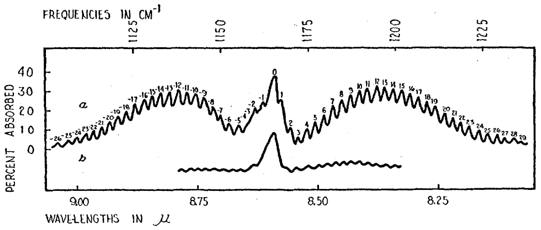

FIG. 6. Absorption of formaldehyde in the region near 8.6μ.

VI. THE 8.6μ REGION

This region has been examined and found to be of the parallel type band. It was measured in absorption in second order with a grating with 1200 lines ruled to the inch. This band also was resolved at least partially into a fine structure pattern (Fig. 6a) very similar to that at 5.8μ, there being here also some convergence toward higher frequencies, of the lines in the P and R branches. The average spacing between lines in frequencies found here agrees well with that in the 5.8μ region and is about 2.4 cm^{-1}. The lines are found to fit quite well to the equation:

$$\nu = 1165.64 + 2.403n - 0.00215n^2 - 0.00001n^3,$$

where as before n is the number of the line measured from the center.

It was found, also that with a somewhat hotter cell, this spectrum could be measured in emission (Fig. 6b). It was measured in first order with the same grating as before, but in spite of the much more incomplete resolution, it is still possible to correlate emission peaks with lines in absorption.

The data obtained are summarized in Table IV where the positions of the lines in terms of wave-lengths and frequencies are tabulated.

TABLE IV. *Wave-lengths of absorption lines of formaldehyde in the region near 8.6μ.*

Line No.	Wave-length (μ)	Frequency (cm^{-1})	Δν (cm^{-1})	Line No.	Wave-length (μ)	Frequency (cm^{-1})	Δν (cm^{-1})
−20	8.9542	1116.8		1	....	....	..
−19	8.9342	1119.3	2.5	2	8.5441	1170.4	..
−18	8.9142	1121.8	2.5	3	8.5266	1172.8	2.4
−17	8.8952	1124.2	2.4	4	8.5092	1175.2	2.4
−16	8.8755	1126.7	2.5	5	8.4918	1177.6	2.4
−15	8.8558	1129.2	2.5	6	8.4746	1180.0	2.4
−14	8.8370	1131.6	2.4	7	8.4581	1182.3	2.3
−13	8.8176	1134.1	2.5	8	8.4410	1184.7	2.4
−12	8.7982	1136.6	2.5	9	8.4239	1187.1	2.4
−11	8.7796	1139.0	2.3	10	8.4069	1189.5	2.4
−10	8.7604	1141.5	2.5	11	8.3907	1191.8	2.3
− 9	8.7420	1143.9	2.4	12	8.3738	1194.2	2.4
− 8	8.7237	1146.3	2.4	13	8.3570	1196.6	2.4
− 7	8.7055	1148.7	2.4	14	8.3410	1198.9	2.3
− 6	8.6873	1151.1	2.4	15	8.3250	1201.2	2.3
− 5	8.6685	1153.6	2.5	16	8.3091	1203.5	2.3
− 4	8.6505	1156.0	2.4	17	8.2932	1205.8	2.3
− 3	8.6326	1158.4	2.4	18	8.2775	1208.1	2.3
− 2	8.6147	1160.8	2.4	19	8.2617	1210.4	2.3
− 1	8.5955	1163.4	2.6	20	8.2461	1212.7	2.3
0	8.5793	1165.6	2.2				

VII. THE 9.6μ REGION

Lack of time prevented the measurement of this band in absorption. A set of emission measurements was, however, obtained extending from about 9.4μ to 9.7μ or covering what appears to be about two-thirds of the band. The measurements revealed about four or five quite prominent maxima against an unresolved background with apparently some convergence toward higher frequencies. This emission curve is not reproduced here since it is believed that the measurements extended over too narrow a region to give a picture complete enough not to be subject to misinterpretation. One can from its general character say, however, that his band appears to be of the perpendicular type with what apparently is its center at 9.6μ, having none of the characteristics of a parallel type. It is hoped to remeasure this band both in absorption and in emission in the very near future in order to ascertain its character definitely.

VIII. CONCLUSION

A discussion of the data herein obtained will be given in Part II by Nordsieck and the writer. It will suffice to point out that with the much more extensive and self-consistent data obtained in this experiment, the apparent discrepancy, which earlier obscured the agreement of the information derived from infrared bands with that obtained from ultraviolet bands, have now been corrected and shown to have been due to incomplete resolution. The results of this investigation thus offer an excellent confirmation of the results of Dieke and Kistiakowsky.

The writer wishes to acknowledge his indebtedness to all his friends in the Michigan laboratory where these measurements were made. He wishes especially to express his gratefulness to Professor H. M. Randall who so kindly placed spectrographs and gratings at his disposal and who in every respect made him feel as one of the Michigan group.