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THE ABSORPTION BY FORMALDEHYDE VAPOR IN THE INFRARED

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ABSTRACT

The absorption spectrum of formaldehyde vapor in the infrared has been investigated with a prism spectrometer to 7.0μ. In addition to confirming the bands reported by Salant and West at 3.5μ, 1.8μ, 1.4μ, and 1.25μ, a fifth band at 4.8μ was located. The two regions at 3.5μ and 4.8μ have been investigated under higher dispersion using an echellette grating ruled with 3600 lines per inch, and resolved into a fine structure. Polymerization of the gas into paraformaldehyde was avoided by using a cell that could be heated.

The 3.5 region. The region at 3.5μ was found to be one of intense absorption and apparently consisting of three partially overlapping bands with centers lying near 3.4μ, 3.5μ and 3.6μ. Of these two appear to have P, Q, and R branches, where the average spacings between lines is about 3.5 cm^{-1}. The third band consists of only one branch where the spacing is about 28 cm^{-1}.

The 4.8μ region. This region is a band showing P, Q, and R branches and very similar in structure to those at 3.4μ. The average spacing between lines in the P and R branches is here found to be about 3.1 cm^{-1}.

THE infrared absorption spectra of asymmetric molecules which have heretofore been investigated have shown themselves to be of a rather complex structure. They have in fact been so complex that they have been given only somewhat qualitative interpretations. The desirability of investigating the spectra of molecules which are only slightly asymmetric, and where one might consequently expect a rather simple structure, immediately suggests itself. It seems particularly desirable since such a spectrum might perhaps be rigorously interpreted, and in so doing methods of attack on more complex spectra might suggest themselves. From chemical considerations, the formaldehyde molecule appears to be just such a one. It seems probable that all the atoms lie in one plane, the carbon and the oxygen being connected by a double bond. Such a molecule would then have one relatively small moment of inertia and two relatively large moments of inertia of about the same magnitude. With this in mind, the investigation of the absorption by formaldehyde vapor in the infrared was begun.

Salant and West[1] have investigated this spectrum with a prism spectrometer and have reported the existence of bands at 3.5μ, 1.8μ, 1.4μ and 1.25μ enumerated in the order of decreasing intensities. We have repeated these measurements and extended the explorations to 7.0μ, confirming the results of Salant and West in addition locating a band at 4.8μ.

As is well-known, formaldehyde forms polymers at room temperatures and in order to maintain it in the vapor state, an absorption cell must be used which can be heated. The vapor is made from paraformaldehyde and the reaction is a reversible one,

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

$$(CH_2O)_x \rightleftarrows xCH_2O$$

the equilibrium of reaction being pushed toward the vapor state with increase of temperature. The temperature was maintained in the neighborhood of 200°C. The cell was of brass and surrounded by a heating coil of nichrome wire. To keep the inside windows at the same temperature as the cell, double windows made of mica were used. The cell was thermally insulated with thick coatings of asbestos. In order to assure a nearly constant concentration of gas in the cell, a continual flow was maintained through it; the vapor being generated in a large test tube which also was electrically heated, and after passing through the cell, the vapor was condensed in a cooled flask. The cell and generator were heated several hours before measurements were taken in order that thermal equilibrium might be reached. It was found that measurements were most effectively made in the regions investigated if the actual path of the cell was made about two millimeters long.

For a study of the spectrum of formaldehyde under higher dispersion, a spectrometer of the Sleator type, originally built by Lowry[2] and later rebuilt by one of the writers, was available. In the usual manner, radiant energy from a Nernst glower passing through the absorption cell is focussed upon the slit of a rock salt spectrometer which serves the purpose of a monochromator. From this, the energy is focussed upon the slit of the grating spectrometer. This slit is at the principal focus of a collimating mirror which reflects the light as a parallel beam on to a grating. After diffraction the radiation is reflected back to the collimating mirror and finally concentrated on the junctions of a thermopile. Dr. J. D. Hardy, National Research Fellow at the University of Michigan, very kindly presented us with a vacuum thermopile of his own construction to be used in this work. The collimating mirror in this case had a focal length of one meter. The thermopile was used in conjunction with a Moll thermal relay and a Leeds and Northrup high sensitivity moving coil galvanometer. The sensitivity was such that the slits could be narrowed to about 17 angstroms and maintained so throughout the experiment.

The grating used was an echellette ruled by Wood on a copper-chromium surface with a spacing of about 3600 lines per inch, and concentrating the energy at about 3.5μ in the first order. The calibration of the spectrometer was obtained from measurements made upon the positions of the 1, 2, -1, -2 lines of HCl as given by Colby, Meyer and Bronk.[3]

The region reported by Salant and West at 3.5μ and that found by us at 4.8μ were found to be regions of intense absorptions; these have been carefully examined under high dispersion and resolved at least partially into a fine structure. A preliminary run was first made over each band with widened slits and readings were taken at intervals of one minute of arc on the circle. This extended on both sides of the band until the absorption fell to zero. The slits were then narrowed and readings were taken at intervals of twenty seconds of arc on the circle. Readings were taken at each setting with the cell in

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[2] E. F. Lowry, J. Opt. Soc. Am. **8**, 647 (1924).

[3] W. F. Colby, C. F. Meyer, and D. W. Bronk, Astrophys. J. **57**, 7 (1924).

and out of the beam, their ratios giving the percentage of transmission. Compensating windows were not used, since the amount absorbed by the windows of the cell could satisfactorily be accounted for by making a run with the cell empty, and moreover since no atmospheric bands occur in these regions.

TABLE I.

Line No.	Wave-length in μ	Frequency in cm^{-1}	$\Delta\nu$ cm^{-1}
0	3.3604	2975.8	
			3.5
1	3.3565	2979.3	
			3.0
2	3.3531	2982.3	
			3.4
3	3.3493	2985.7	
			2.7
4	3.3463	2988.4	
			3.4
5	3.3425	2991.8	
			3.1
6	3.3390	2994.9	
			2.5
7	3.3362	2997.4	
			3.1
8	3.3328	3000.5	
			3.2
9	3.3292	3003.7	
			3.3
10	3.3256	3007.0	
			2.8
11	3.3225	3009.8	
			3.1
12	3.3191	3012.9	
			3.6
13	3.3151	3016.5	
			4.0
14	3.3107	3020.5	
			4.4
15	3.3059	3024.0	
			3.2
16	3.3025	3028.1	
			3.3
17	3.2988	3031.4	
			5.2
18	3.2932	3036.6	
			4.6
19	3.2882	3041.2	
			4.8
20	3.2830	3046.0	
			3.9
21	3.2788	3049.9	

THE REGION AT 3.5μ

This region which was reported by Salant and West as a triplet was found to consist of what is believed to be three overlapping bands of two different kinds. The centers of these lie near 3.4μ, 3.5μ and 3.6μ. The two respectively at 3.4μ and 3.6μ appear similar in structure, showing P, Q and R branches of which the Q branch is relatively weak. The spacing between the lines in the P and R branches is about 3.4 cm^{-1} at 3.6μ and 3.5 cm^{-1} for that lying at 3.4μ.

The band whose center lies near 3.5μ is of entirely different structure. It consists of one very prominent line (much resembling a *Q* branch) near the center and groups of closely spaced lines nearly equally spaced on both sides of it. Between these more prominent lines are other groups of rather closely spaced lines of lesser intensity. These can only imperfectly be resolved and form a more or less continuous background. On the low frequency side the overlapping with the band at 3.6μ is so bad that only the approximate loca-

TABLE II.

Line No.	Wave-length in μ	Frequency in cm^{-1}	$\Delta\nu$ cm^{-1}
1	3.5628	2806.8	
			2.3
2	3.5598	2809.1	
			6.1
3	3.5522	2815.2	
			3.3
	3.5480	2818.5	
			4.0
	3.5430	2822.5	
			3.2
	3.5390	2825.7	
			2.0
	3.5364	2827.7	
			5.9
4	3.5291	2833.6	
			8.0
5	3.5192	2841.6	
			3.2
	3.5152	2844.8	
			3.1
	3.5113	2847.9	
			7.2
	3.5025	2855.1	
			10.1
6	3.4902	2865.2	
			30.2
7	3.4538	2895.4	
			1.6
	3.4518	2897.0	
			27.7
8	3.4191	2924.7	
			2.3
	3.4165	2927.0	
			5.6
9	3.4099	2932.6	
			2.7
	3.4068	2935.3	
			3.4
	3.4029	2938.7	
			2.5
	3.4000	2941.2	
			3.2
	3.3963	2944.4	
			1.7
	3.3943	2946.1	
			4.1
10	3.3896	2950.2	
			2.4
	3.3869	2952.6	

tions of these more prominent lines can be distinguished, but on the high frequency side, while there too is some overlapping, one can distinguish the first three of these more intense line groups at least, as well as determine to a fair degree of approximation what are their intensities. The spacings between the more prominent groups are about 28 cm^{-1}. Fig. 1 shows the percentage absorption due to formaldehyde vapor in this region. It represents the points which have been repeated from several runs over this region. For convenience the original circle settings have been replaced by a wave-length scale in μ and a frequency scale in waves per centimeter. A compilation of the lines of the bands at 3.4μ, 3.5μ and 3.6μ is given in Tables I, II, and III respectively.

TABLE III.

Line No.	Wave-length in μ	Frequency in cm^{-1}	$\Delta\nu$ cm^{-1}
3	3.5838	2790.3	
			3.9
2	3.5889	2786.4	
			2.8
1	3.5925	2783.6	
			4.0
0	3.5977	2779.6	
			4.3
−1	3.6032	2775.3	
			3.5
−2	3.6077	2771.8	
			3.2
−3	3.6119	2768.6	
			3.0
−4	3.6158	2765.6	
			2.9
−5	3.6198	2762.7	
			3.7
−6	3.6245	2759.0	
			2.9
−7	3.6283	2756.1	
			3.1
−8	3.6326	2752.8	
			4.6
−9	3.6388	2748.2	
			3.7
−10	3.6436	2744.5	
			3.0
−11	3.6477	2741.5	
			2.6
−12	3.6511	2738.9	
			2.5
−13	3.6545	2736.4	
			3.3
−14	3.6588	2733.1	
			3.1
−15	3.6629	2730.0	
			3.6
−16	3.6678	2726.4	
			3.8
−17	3.6730	2722.6	
			3.4
−18	3.6775	2719.2	

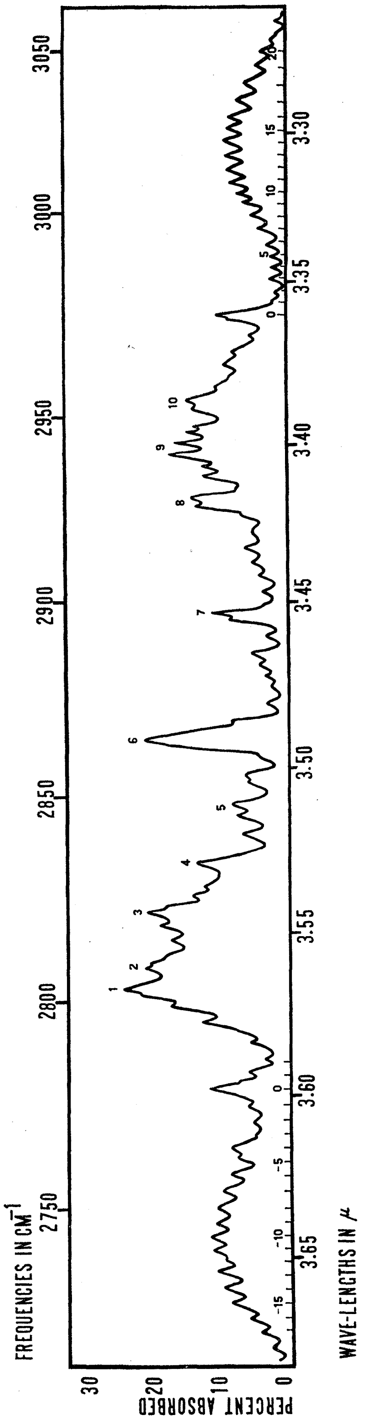
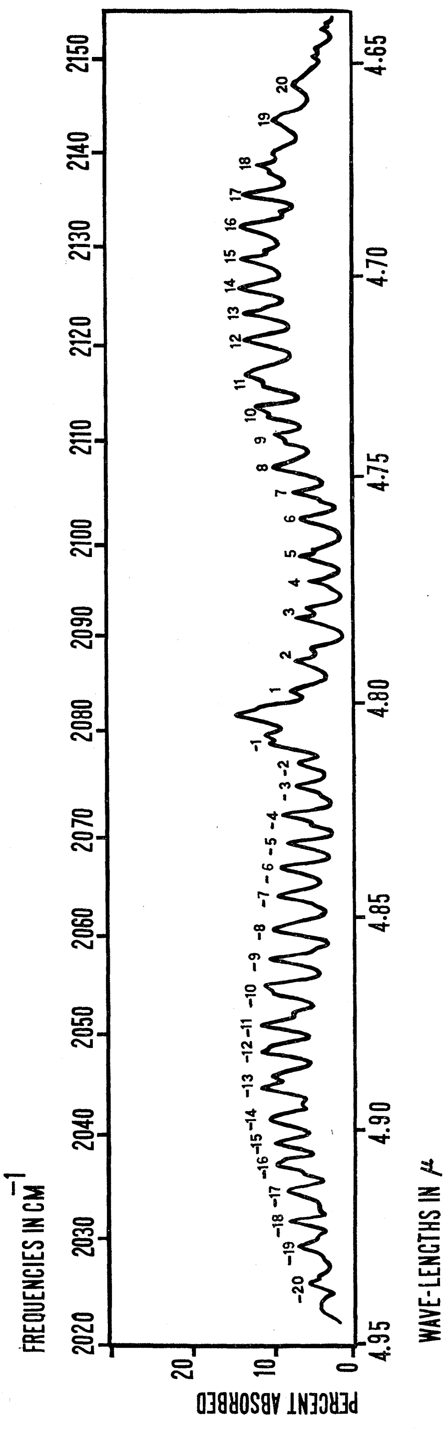

FREQUENCIES IN CM⁻¹
2750
2800
2850
2900
2950
3000
3050
PERCENT ABSORBED
0
10
20
30
WAVE-LENGTHS IN μ
3.65
3.60
3.55
3.50
3.45
3.40
3.35
3.30
1
2
3
4
5
6
7
8
9
10
-15
-10
-5
0
5
10
15
20

Fig. 1.


FREQUENCIES IN CM⁻¹
2020
2030
2040
2050
2060
2070
2080
2090
2100
2110
2120
2130
2140
2150
PERCENT ABSORBED
0
10
20
WAVE-LENGTHS IN μ
4.95
4.90
4.85
4.80
4.75
4.70
4.65
-20
-19
-18
-17
-16
-15
-14
-13
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
1
2
3
4
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16
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19
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Fig. 2.

THE REGION AT 4.8μ

The absorption band at 4.8μ is similar to those at 3.4μ and 3.6μ, showing distinct P, Q, and R branches. As in the two earlier cases, the Q branch is relatively weak. Moreover it appears to be broadened unsymmetrically toward higher frequencies. The higher resolution in this region shows that what appeared as single lines in the P and R branches of the bands at 3.4μ and 3.6μ is actually several lines lying so close together that they cannot be resolved. In this region what appeared as single lines before occurs as quite broad lines with indications of a finer structure. The spacing between the maxima of these groups is somewhat less than in the other two bands of this kind, and is about 3.1 cm^{-1}. Fig. 2 shows the percentage absorption in the 4.8μ region. As before, it is a composite curve showing the characteristics which recur in all runs. As in Fig. 1, wave-length scales and frequency scales have been substituted for the original circle settings. In Table IV is given a compilation of the wave-lengths and frequencies of the observed lines of this band.

TABLE IV.

Line No.	Wave-length in μ	Frequency in cm^{-1}	$\Delta\nu$ cm^{-1}
−20	4.9364	2025.7	
			3.5
−19	4.9280	2029.2	
			2.4
−18	4.9222	2031.6	
			2.9
−17	4.9153	2034.5	
			2.7
−16	4.9088	2037.2	
			2.1
−15	4.9037	2039.3	
			2.4
−14	4.8980	2041.7	
			3.3
−13	4.8899	2045.0	
			3.4
−12	4.8818	2048.4	
			2.9
−11	4.8749	2051.3	
			3.2
−10	4.8674	2054.5	
			2.9
−9	4.8604	2057.4	
			3.0
−8	4.8535	2060.4	
			3.3
−7	4.8457	2063.7	
			2.8
−6	4.8392	2066.5	
			2.6
−5	4.8331	2069.1	
			2.5
−4	4.8272	2071.6	
			3.1
−3	4.8199	2074.7	
			2.2
−2	4.8149	2076.9	
			2.6
−1	4.8088	2079.5	

TABLE IV. (*Continued*).

Line No.	Wave-length in μ	Frequency in cm^{-1}	$\Delta\nu$ cm^{-1}
			2.5
0	4.8030	2082.0	
			2.4
1	4.7976	2084.4	
			3.6
2	4.7892	2088.0	
			4.0
3	4.7800	2092.0	
			3.6
4	4.7719	2095.6	
			2.8
5	4.7654	2098.4	
			3.5
6	4.7577	2101.9	
			2.9
7	4.7511	2104.8	
			2.7
8	4.7449	2107.5	
			2.9
9	4.7384	2110.4	
			3.0
10	4.7318	2113.4	
			3.0
11	4.7249	2116.4	
			4.0
12	4.7162	2120.4	
			3.0
13	4.7095	2123.4	
			2.5
14	4.7038	2125.9	
			3.3
15	4.6955	2129.2	
			3.4
16	4.6890	2132.6	
			3.2
17	4.6821	2135.8	
			3.5
18	4.6743	2139.3	
			4.6
19	4.6643	2143.9	
			4.4
20	4.6548	2148.3	

INTERPRETATION OF THE OBSERVED BANDS

While the rigorous interpretation of these bands is left for a later communication, it seems not wholly amiss here to point out some of the details of the observed bands which are characteristic of molecules of this kind.

The theory of the asymmetric rotator predicts that for a molecule like CH_2O, where the atoms are assumed to be coplanar, three different types of bands may occur.[4] These shall be designated, where the electric moment changes along the least axis of inertia, as type A, where the electric moment changes along the intermediate axis, as type B, and where the vibration is along the largest axis of inertia, as type C.[5] Types B and C will be very nearly

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[4] H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **53,** 553 (1929); S. C. Wang, Phys. Rev. **58,** 730 (1929); O. Klein, Zeits. f. Physik **58,** 125 (1929).

[5] H. H. Nielsen, Phys. Rev. **38,** 1432 (1931).

alike since the two larger moments of inertia are nearly equivalent, the relation being: $A_x = A_y + A_z$, where A_x, A_y, and A_z are chosen the three principal moments of inertia and where $A_x > A_y > A_z$. Of these three types, only two have been observed; namely, type *A* and either type *B* or type *C*. The type *A* bands arise when the electric moment vibrates along the least axis of inertia and consist of *P*, *Q*, and *R* branches. As we have seen, three such bands have been observed, namely, those at 3.4μ, 3.6μ, and 4.8μ. Whether the band occurring at 3.5μ is of type *B* or type *C* can only definitely be determined by an analysis of the normal modes of vibration or by a detailed study of the rotations of the molecule. The rather high frequency position of the band in the spectrum, however, indicates that the interatomic forces involved are relatively large. This suggests that the band observed is due to a vibration of CH_2 configuration along the intermediate axis of inertia, and hence it would be of type *B*. Moreover, a type *C* band would in our molecule arise from a vibration perpendicular to the plane of the molecule, and it seems likely that the forces that would here enter into play would be much smaller, and that consequently the band would lie at longer wave-lengths than those we were able to explore because of the increasing opacity of mica in this region.

Let us first consider the type *A* bands. In the case of the symmetric rotator, this type arises from transitions where $J \rightarrow J$, $K \rightarrow K$; $J \rightarrow J \pm 1$, $K \rightarrow K$, the first giving the *Q* branch and the other the *P* and *R* branches. In the nearly linear slightly asymmetric rotator the levels resemble those of the nearly linear symmetric rotator a great deal except that each level save one ($K=0$) is split up into two, say K' and K''.* Complete discussions of the transition rules for the asymmetric rotator have been given by several writers,[6] but the ones of importance to us may be given as follows: The transition rule in our case corresponding to that above for the symmetric case becomes $J \rightarrow J$ and $K' \rightarrow K''$ or $K'' \rightarrow K'$. Consequently, no sharp *Q* branch can be expected but, as is observed, one that is somewhat broadened. The other transition rule from above becomes $J \rightarrow J \pm 1$, $K' \rightarrow K'$ or $K'' \rightarrow K''$. This gives rise moreover to a fine structure of each of the lines in *P* and *R* branches since the splitting up of the levels is different for different values of *J*. This fine structure is here observed as a broadening of each line in the *P* and *R* branches with occasional evidence of complex structure. It is well-known that this type of vibration in the linear molecule gives a band with a missing line at the center. It was shown by Bennett and Meyer[7] in the case of the methylhalides that as the largest moment of inertia increased from one halide to another while the small one remained approximately the same (i.e., as this series

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* It has seemed in the case of asymmetric rotators of only very slight asymmetry to retain a nomenclature analogous to that used in symmetric rotators would be an advantage. Hence the *K* used for the symmetric case has been replaced by K' and K'' instead of using the τ's introduced by Dennison. This may be done because the actual splitting up of the symmetric levels is small and because the transitions permitted in such rotators which may not occur in the symmetric case occur with only very small intensities.

[6] H. A. Kramers and G. P. Ittmann, Zeits. f. Physik **60**, 663 (1930); D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[7] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).

of molecules effectively more and more approached the linear case) the Q branch diminished in intensity. In the case of formaldehyde which does not depart radically from the linear model we might expect to find exactly this same effect, and this is just one of the details which we have observed at 3.4μ, 3.6μ and 4.8μ.

Type B bands occur in the symmetric rotator when transitions of the kind: $J \rightarrow J$, $K \rightarrow K \pm 1$; $J \rightarrow J \pm 1$, $K \rightarrow K \pm 1$ take place. An analogous set of rules may be formulated for the asymmetric rotator and in our case they may be summarized so: $J \rightarrow J$, $K' \rightarrow K' \pm 1$; $K'' \rightarrow K'' \pm 1$; $J \rightarrow J \pm 1$, $K' \rightarrow K'' \pm 1$, $K'' \rightarrow K' \pm 1$. In the symmetric top the envelope of this kind of band shows only one maximum, each line being made up of several exactly superposed lines arising from several quantum transitions. Here one would not expect them exactly to coincide and consequently a rather complex structure would result. The tendency would be to give a rather intense line group where before there occurred a single line, and now with weaker lines in between. This is precisely what one observes at 3.5μ. A further complication which is encountered is the existence of the identical hydrogen atoms in the molecule. Under these circumstances the levels must be classified as symmetric and antisymmetric, of which the latter are populated three times as densely as the others. In the case of our molecule this would lead to an unsymmetry of the appearance of the lines about the center, a detail which is not exceedingly apparent here because of the strong overlapping. It is, however, clearly evident between the extremely strong line at the center and its mate which is only roughly one third as intense. It is another observed fact that the spacing of the intense line groups of the type B band is about eight times that in the type A bands. This too is in agreement with theory, for as is well-known, as one approaches the linear model the spacings of this type of band becomes ever larger with respect to the spacing of the other type until finally in the limiting case, this type of band disappears completely—the lines being separated by infinite spacings.

Summarizing, we may say that an investigation of the formaldehyde spectrum in the infrared has shown it to consist of at least two different kinds of bands with different spacings. The one type, type A, shows P, Q, and R branches of which the Q branch is relatively weak and the spacings between lines in the P and R branches are quite fine; type B consists only of one branch with a maximum at the center and with spacings between the line groups about eight times as great as in Type A. Finally a qualitative discussion has been given accounting for the more obvious details of this spectrum on the basis of the theory of an asymmetric rotator model not departing radically from the linear type.

The writers wish to express their appreciation to Dr. J. D. Hardy who very kindly presented them with a vacuum thermopile of his own construction for use in this investigation. Also the kind cooperation of Professor Alpheus W. Smith in making available departmental funds for the purchase of gratings and other equipment is acknowledged with gratitude.