The Far Infrared Spectrum of H_2O

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The absorption of atmospheric water vapor is mapped between 38μ and 170μ. The results are shown to be in good agreement with Mecke's analysis of the vibration-rotation bands, and permit an extension of his results.

IN all investigations in the far infrared ($>20\mu$), the energy spectrum shows great irregularities. These, it is well known, are due to the absorption of the atmospheric water vapor. In fact, in order to obtain sufficient energy to work satisfactorily in this region, it is necessary to remove most of the water vapor by drying the interior of the spectrometer with trays of P_2O_5. The H_2O molecule possesses a large permanent dipole moment, is an asymmetric rotator, and hence shows this very strong and irregular absorption, due to "pure rotation." In the course of various investigations in this region, with the apparatus already described[1] we have obtained detailed energy curves throughout the region $38-170\mu$. In this paper we will present these, and discuss them in the light of our present knowledge of the H_2O molecule.

The very excellent work of Mecke and his collaborators[2] has solved the fundamental problems concerning the term-structure of H_2O. From the vibration-rotation bands in the near and photographic infrared, they have obtained the energy term values of 32 of the lowest rotational levels of the ground vibrational state, and correlated these with the predicted levels for an asymmetric top with moments of inertia $A=0.996$, $B=1.908$, $C=2.981$. This corresponds to an $H-O$ distance of 0.97A and an $H-O-H$ angle of 105°. To apply these results to the interpretation of the pure rotation spectrum, it is necessary only to take the differences between these terms, using the correct selection rules. There are two limitations to this, however. In the first place, Mecke's levels, although they account for most of the strong lines, are far from complete. Secondly, even with the good

TABLE I. *Term values for the H_2O molecule.* Values marked a and b are taken from Mecke's measurements in the photographic infrared. Values marked c are assumed in order to explain the experimental results of this paper.

J_τ	cm^{-1}	Class	J_τ	cm^{-1}	Class	J_τ	cm^{-1}	Class	J_τ	cm^{-1}	Class
0_0	0	a	3_3	286.93	a	5_{-1}	446.59	b	7_{-6}	586.6	a
1_{-1}	23.78	a	4_{-4}	222.07	a	5_0	505.54	b	7_{-5}	699.6	c
1_0	37.09	a	4_{-3}	224.81	a	5_1	510.33	b	7_{-4}	705.0	c
1_1	42.31	a	4_{-2}	275.50	a	5_2	611.8	c	7_{-3}	780.5	c
2_{-2}	70.09	a	4_{-1}	300.44	a	5_3	612.1	c	7_{-2}	813.0	c
2_{-1}	79.43	a	4_0	315.83	a	6_{-6}	446.7	a	7_{-1}	840.0	c
2_0	95.15	a	4_1	384.03	a	6_{-5}	447.2	a	8_{-8}	744.1	a
2_1	134.98	a	4_2	385.44	a	6_{-4}	540.5	c	8_{-7}	744.2	a
2_2	136.24	a	4_3	490.64	b	6_{-3}	548.7	b	8_{-6}	871.5	c
3_{-3}	136.76	a	4_4	490.79	b	6_{-2}	601.5	c	8_{-5}	876.8	c
3_{-2}	142.23	a	5_{-5}	325.37	a	6_{-1}	648.0	c	9_{-8}	920.8	b
3_{-1}	173.31	a	5_{-4}	326.56	a	6_0	665.0	c	9_{-8}	920.8	b
3_0	206.35	a	5_{-3}	399.42	a	6_1	761.1	c	10_{-10}	1116.0	b
3_1	212.24	a	5_{-2}	416.21	b	6_2	762.5	c	10_{-9}	1116.0	b
3_2	286.80	a				7_{-7}	586.3	a	11_{-11}	1329.7	c

resolving power obtained with our instrument or the somewhat better resolving power applied in a more limited frequency range by Wright and Randall,[3] there is often an overlapping of lines. This latter fact makes an exact agreement with the calculated spectrum impossible, until the technique in this region is still further improved. Approximate agreement has however been achieved, as Fig. 1 and Tables I and II demonstrate.

Fig. 1 shows the energy curves obtained. The curve is a smoothed idealization of all the points measured. The accuracy varies from region to region, as most of the points were taken with absorption measurements as the primary aim, the energy spectrum being of secondary importance at the time. In some regions, for example, the energy curve has been gone over 7 or 8 times with the narrowest possible slits; in others, only two or three times. The concentration of water vapor in the optical path also varied from time to time. In smoothing the curve for publication, however, no hump that can be construed as an absorption line has been included unless its presence is definitely indicated by two

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[1] R. Bowling Barnes, Rev. Sci. Inst. 5, 237 (1934).

[2] Mecke, Baumann and Freudenberg, Zeits. f. Physik 81, 313, 445, 465 (1933).

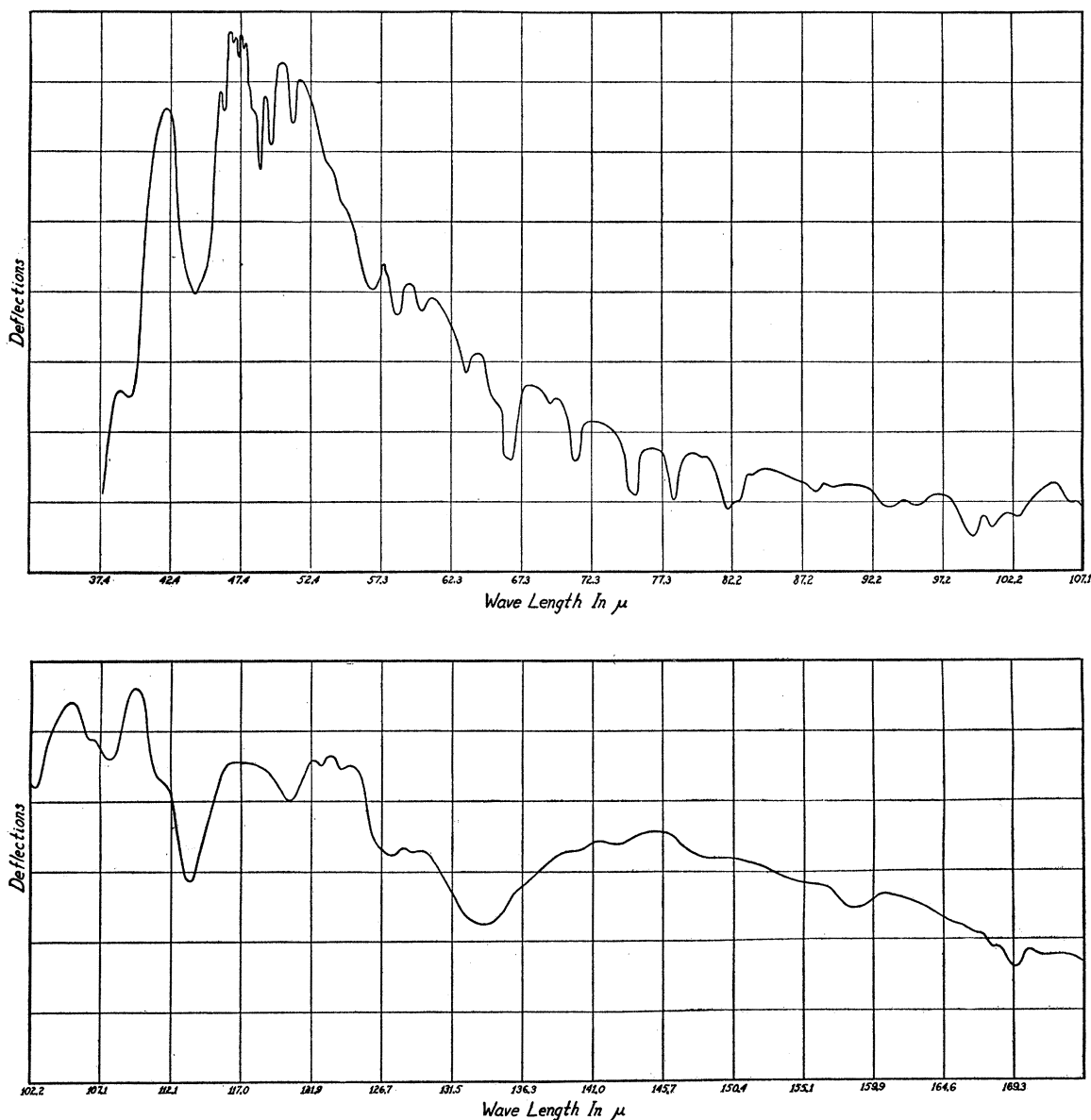[3] Wright and Randall, Phys. Rev. 44, 391 (1933).

FIG. 1. Far infrared spectrum of water vapor, as obtained by using about 3 meters of vapor which had been dried with P$_2$O$_5$. The slit-widths used varied considerably in the various parts of the spectrum.

or more separate groups of points. The agreement with the results of Wright and Randall, in the region reported by them (65–130μ), is satisfactory, as reference to their curves will show. The wavelengths of the various minima in the curve are calculated by the method described in an earlier paper on the absorption spectrum of ammonia,[4] and are tabulated, together with the

approximate relative intensity, in Table II.

Table I gives the term values used in correlating the observed results. Most of the lower levels are taken from Mecke's tables. These are marked a, and should be accurate to 0.02 cm^{-1}. The levels marked b have been obtained by extending Mecke's methods to the same body of photographic infrared data. The details will be published later by one of us. The accuracy is

4 R. Bowling Barnes, Phys. Rev. 47, 658 (1935).

TABLE II. *The far infrared of water vapor.*

ALLOWED TRANS. $J_\tau-J_\tau$	CALC. ν	OBS. ν	INTEN-SITY	OBS. BY OTHERS	OBS. μ	ALLOWED TRANS. $J_\tau-J_\tau$	CALC. ν	OBS. ν	INTEN-SITY	OBS. BY OTHERS	OBS. μ
5_0-6_2	257.0					$7_{-7}-7_{-5}$	113.3	113.3	2	112.97	88.26
5_1-6_1	250.8	250.8	4	247	39.87	2_0-3_0	111.20	111.9	1	111.21	89.4
$5_{-2}-6_0$	248.8					$7_{-4}-7_{-2}$	107.8			107.92	
$3_{-3}-4_1$	247.27					4_1-4_3	106.61	107.0	3w	107.30	93.43
4_1-5_3	228.1					5_0-5_2	106.3				
4_2-5_2	226.4	227.6	7	228	43.94	4_2-4_4	105.35			105.78	
$4_{-3}-5_{-1}$	221.78					$4_{-4}-5_{-4}$	104.49	104.52	2	104.59	95.7
$2_{-2}-3_2$	216.71	216.4	3		46.22	$6_{-5}-6_{-3}$	101.4			101.46	
$10_{-9}-11_{-11}$	213.7	213.7	0		46.80	5_1-5_3	100.7				
$6_{-2}-7_{-2}$	211.5	211.5	2	211	47.28	$4_{-3}-5_{-5}$	100.56	100.78	8w	100.59	99.23
$4_{-1}-5_1$	209.89	210.2	0		47.57	1_0-2_2	99.15	99.20	5	99.04	100.80
		206.7	0		48.17	$6_{-3}-6_{-1}$	99.0				
3_2-4_4	202.99	205.0	5		48.79	$4_{-1}-5_{-3}$	98.98				
3_3-4_3	202.71					6_0-6_2	97.5	97.4	2		102.7
$5_{-1}-6_{-1}$	201.4	201.3	4	201	49.68	5_0-6_{-2}	96.0			96.12	
$9_{-9}-10_{-9}$	195.2	195.3	3	192	51.20	$6_{-6}-6_{-4}$	93.8	93.8	1		106.6
4_0-5_0	189.71	186.9	0?		53.51						
		182.7	0?		54.73	1_1-2_1	92.67	92.9	2	92.51	108.1
3_0-4_2	179.09					$5_{-3}-4_{-3}$	91.22				
$7_{-5}-8_{-5}$	177.2					$5_{-4}-5_{-2}$	89.65	90.3	0?	89.53	110.7
$8_{-7}-9_{-9}$	176.7	176.9	5	177	56.53	$5_{-2}-5_0$	89.33	88.41	6w	88.42	113.1
$8_{-8}-9_{-8}$						$3_{-3}-4_{-3}$	88.05			87.44	
$3_{-2}-4_0$	173.60	174.4	0?	172	57.53	$4_{-1}-4_1$	83.59	83.20	2		120.1
3_1-4_1	171.79	170.8	5		58.53			81.83	0		122.2
$6_{-4}-7_{-4}$	166.5	166.4	3	166.6	60.09	3_0-3_2	80.45	80.94	1		123.5
$7_{-4}-8_{-6}$	166.3					$3_{-2}-4_{-4}$	79.84			79.59	
$7_{-7}-8_{-7}$	157.8	157.8	4	157.9	63.38	$6_{-3}-7_{-1}$	78.9	78.78	4	79.02	126.9
$7_{-6}-8_{-8}$	157.5							77.50	1?	78.26	129.0
2_1-3_3	151.95	152.7	2	153.5	65.49	$4_{-3}-4_{-1}$	75.63			75.59	
$6_{-3}-7_{-5}$	150.9	151.2	6		66.13	3_1-3_3	74.69	75.10	6w		133.2
2_2-3_2	150.56					$3_{-2}-3_0$	74.12			74.22	
$5_{-3}-6_{-3}$	149.3	150.2	6	150.1	66.58	$5_{-5}-5_{-3}$	74.05	73.47	0?		136.1
		143.99	1		69.45	$2_{-2}-3_{-2}$	72.14				
$4_{-2}-5_{-2}$	140.71			140.9		3_0-4_{-2}	71.15	71.37	1		140.1
$6_{-6}-7_{-6}$	139.9	139.74	6	139.3	71.56	4_0-4_2	69.61	70.00	1		142.9
$6_{-5}-7_{-7}$	139.1					$201.3/3=$	67.1	67.41	1		148.4
					73.1	$5_{-1}-5_1$	63.74				
$2_{-1}-3_1$	132.81					$6_{-2}-6_0$	63.5				
$8_{-7}-8_{-5}$	132.6	132.62	7w	132.8	75.41	$6_{-4}-6_{-2}$	63.0	63.02	3		158.7
$6_{-1}-7_{-3}$	132.5			128.8		4_1-5_{-1}	62.56				
$3_{-1}-4_{-1}$	127.13	127.32	6	127.2	78.55			60.76	0?		164.5
$5_{-2}-6_{-4}$	124.3	124.25	0?		80.49			60.08	0?		166.4
$5_{-5}-6_{-5}$	121.95	121.87	6	12.197	82.06	$7_{-3}-7_{-1}$	59.5	59.69	1?		167.5
$5_{-4}-6_{-6}$	120.11	120.3	2	120.20	83.16	$176.91/3=$	58.97	58.57	3		169.6
$7_{-6}-7_{-4}$	118.4	119.0	1?	118.08	84.04	$174.44/3=$	58.14	58.47	0		171.0
		114.9	0?	116.74	87.0						

somewhat less, as fewer combinations involving these levels have been found, but is probably better than 0.2 cm^{-1}. Finally the levels marked $\bar{c}$ have no other experimental backing than that they give agreement with the experimental results of the present paper; they lie, however, close to the positions calculated from the theory of the asymmetrical rotator. Pending an exact treatment of the corrections due to centrifugal stretching of such a rotator, it has not seemed worth while to give the calculated values of these terms. The accuracy of levels c may not exceed ±1 cm^{-1}.

Table II gives the correlation between experiment and theory. The first column gives all the combinations allowed between the terms of Table I, that would lie in the observed region. The "allowed" combinations comprise the strong lines of the types $J_\tau \to J_{\tau+2}$, $J_\tau \to (J+1)_\tau$ (J and τ both odd or both even) or $J_\tau \to (J+1)_{\tau\pm 2}$ (J odd, τ even and *vice versa*). Of these, the lines

involving odd values of τ will be the stronger, by virtue of the "alternating intensities." In addition, transitions to states differing from these levels by $\tau=4$ will appear, but much more weakly. The tables should therefore account for all the possible lines in this region except the very weakest. An exact calculation of the intensities is possible but laborious; in view of the wholesale overlappings of the observed lines it was not attempted.

The second column of Table II gives the frequency of these transitions, calculated from the term values of Table I. The next column gives the frequencies, and the next the intensities, of the nearest observed line. It is seen that the correlation with column 2 is good throughout, considering the overlappings. The next column shows the agreement between our results and those of previous workers in the field. The comparison for frequencies above 167 is with

the results, of low accuracy, of Kühne,[5] and from 167 to 74 with those of Wright and Randall. The latter agree with the calculated values somewhat more closely than do our measurements, showing that as resolving power increases, still closer agreement may be expected.

Our results extend to 170μ. However, in the longest wave region, beyond 138μ, our energy is not pure, but contains some of the third order radiation. Accordingly, lines appear in the spectrum which are really third order lines, not lines

of H_2O. That at least 40 percent of the energy detected remains first order is, however, certain; and the absence of any strong H_2O lines in this region other than at 63 cm^{-1}, in agreement with calculation, is proved experimentally.

We may thus conclude that the pure rotation spectrum of water, as at present observed, is in complete agreement with the results of the rotation-vibration spectrum; and that further progress in locating the higher rotational levels must depend on more complete experimental results in either region.

[5] Kühne, Zeits. f. Physik **84**, 722 (1933).

Vibrational Raman Scattering in Liquids

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A quantitative investigation reveals that the distribution of intensity within the wings accompanying the vibrational Raman line 656 cm^{-1} in liquid carbon disulphide is very similar to that obtained in the wings accompanying the Rayleigh lines. The intensity starts from being a maximum at or very near the center, rapidly falls off till a distance of 20 cm^{-1} is reached after which it gradually diminishes till it fades away altogether. These features are in marked contrast to the predictions of the existing theories of the rotational Raman effect.

INTRODUCTION

IT is well known that practically all the vibrational Raman lines in liquids exhibit the phenomenon of depolarization. It follows as a natural consequence that, as in the case of depolarized Rayleigh scattering, they should in general be accompanied by unresolved wings arising from the rotation of the molecules. Recent investigations by Weiler,[1] Trumpy,[2] Ranganadham[3] and more extensively by the authors[4-7] have shown that in liquids the so-called rotation wings accompanying the Rayleigh scattering are

characterized by a very large concentration of intensity in the close neighborhood of the Rayleigh line and a relatively feeble but a definite extension of the wing to an unexpected distance from the center. The authors have pointed out that such complex patterns are not wholly explicable in terms of the simple theory of rotational Raman scattering by gaseous molecules but are to be attributed partly to internal oscillations in liquids similar to those that exist in a solid. Such conclusions have also been drawn by Gross and Vuks[8] from their investigations on diphenyl ether. These results obviously give rise to the important question whether the wings accompaning the depolarized vibrational Raman lines in liquids behave in a similar manner. This paper describes the experimental results obtained by us in this direction by using liquid carbon disulphide.

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