of the disintegration curve as well as to the average value of the lifetime.

A comparison between the present results and those obtained from the absorption anomaly in air involves knowledge of the mesotron mass  $\mu$ because the latter method gives essentially the ratio  $\tau_0/\mu$ . According to the most reliable measurements,  $\mu$  seems to be between 160 and 240 electron masses.<sup>5</sup> The present value of  $\tau_0$  together

<sup>5</sup> See T. A. Wheeler and R. Ladenburg, Phys. Rev. 60, 754 (1941).

with the value of  $\tau_0/\mu$  determined by Rossi and his collaborators<sup>6</sup> gives  $\mu = 160$  electron masses which is within the above limits, while the value of  $\tau_0/\mu$  determined by Nielsen and his collaborators<sup>7</sup> would give  $\mu = 360$  which seems definitely too large.

<sup>6</sup> B. Rossi and D. B. Hall, Phys. Rev. 59, 223 (1941). B. Rossi, K. Greisen, J. C. Stearns, D. K. Froman, and P. G. Koontz, Phys. Rev. 61, 675 (1942).

<sup>7</sup> W. M. Nielsen, C. M. Ryerson, L. W. Nordheim, and K. Z. Morgan, Phys. Rev. 59, 547 (1941).

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# The Near Infra-Red Spectrum of Water Vapor

Part II. The Parallel Bands  $v_3$ ,  $v_1 + v_3 \cdot v_2 + v_3$  and the Perpendicular Band  $v_1$ 

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An analysis of the rotational structure of the three "parallel" type bands,  $\nu_3$ ,  $\nu_1 + \nu_3$ , and  $\nu_2 + \nu_3$  and the "perpendicular" type band  $\nu_1$  has been carried out. The data lead to the following effective values of A, B, and C:  $(A = h/8\pi^2 I_a, B = h/8\pi^2 I_b, C = h/8\pi^2 I_c)$ ;  $A(\nu_1) = 27.26 \text{ cm}^{-1}$ ,  $B(v_1) = 14.28 \text{ cm}^{-1}, C(v_1) = 9.17 \text{ cm}^{-1}; A(v_3) = 26.50 \text{ cm}^{-1}, B(v_3) = 14.40 \text{ cm}^{-1}, C(v_3) = 9.10 \text{ cm}^{-1};$  $A(\nu_1+\nu_3) = 26.04 \text{ cm}^{-1}, B(\nu_1+\nu_3) = 14.16 \text{ cm}^{-1}, C(\nu_1+\nu_3) = 8.95 \text{ cm}^{-1}; A(\nu_2+\nu_3) = 29.32 \text{ cm}^{-1}, B(\nu_2+\nu_3) = 14.56 \text{ cm}^{-1}, C(\nu_2+\nu_3) = 9.06 \text{ cm}^{-1}.$  These data permit a redetermination of the vibrational constants  $\omega_i$ ,  $x_i$ ,  $x_{ik}$ , and  $\gamma$ . The new values obtained for the  $\omega_i$  are the following:  $\omega_1 = 3829.4, \omega_2 = 1654.5, \text{ and } \omega_3 = 3940.1.$ 

### INTRODUCTION

 $\mathbf{I}^{\mathrm{N}}_{\mathrm{reported new and much improved data on the}}$ vibration-rotation bands  $\nu_2$  and  $2\nu_2$  which arise out of variations of the electric moment parallel to the axis of the intermediate moment of inertia. From an analysis of these data certain of the vibration-rotation constants, already evaluated by Darling and Dennison,<sup>2</sup> have been verified. In this communication a set of improved data is presented on the bands  $\nu_3$ ,  $\nu_1 + \nu_3$ , and  $\nu_2 + \nu_3$  which originate with variations of the electric moment parallel to the axis of the smallest moment of inertia and the band  $\nu_1$ which is of the perpendicular type. The former oscillations are sometimes spoken of as parallel oscillations because they are parallel to the axis of the smallest moment of inertia which in a limiting case may be thought of as an approximate symmetry axis. The band  $\nu_1$  is of the type discussed in Part I. The analysis of these bands permits one to make somewhat improved determinations of a considerable number of the vibration-rotation constants of the water vapor molecule.

#### **EXPERIMENTAL**

The experimental procedure was here entirely the same as for the work reported in Part I, the water vapor in the optical path of the spectrometer acting as the absorbing layer. In order to obtain any resolution whatever in the region of intense absorption near  $2.7\mu$  it was necessary

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<sup>&</sup>lt;sup>1</sup> H. H. Nielsen, Phys. Rev. **59**, 565 (1941). <sup>2</sup> B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940). Cited as D and D later.



Fig. 3.

ν obs.	v calc.	Transition	ν obs.	ν calc.	Transition	ν obs.	ν calc.	Transition
3525.3			3618.5	3618.2	$4_3 - 5_1^*$		( 3702.3	$1_1 - 2_0$
3528.3			3620.1	∫ 3620.3	$4_0 - 5_{-1}$	3702.3	3702.8	$4_{-3} - 4_{-2}$
3529.6	3529.3	$5_0 - 6_{-2}^*$	26220.1	(3619.8	$1_0 - 2_{-2}^*$	0.0200	3702.5	$2_{-1} - 1_{-1}^*$
3531.4	3531.2	$5_1 - 5_3^{*}$	3622.4	3622.5	$2_{-2} - 2_0^{+}$		3702.4	$0_{-1} - 7_{-7}$
3537.0	(3543 5	6 -6 *	3624.6	3023.2	$4_4 - 3_0$	3705.5	3705.6	$6_{1} - 6_{2}$
3543.2	3543.5	$3_{-1} - 4_2$	3627.2			3707.1	3706.9	$5_1 - 6_{-4}$
	3544.6	$4_{-4} - 5_{-4}^*$	3629.2	3628.7	$4_2 - 5_{-3}^*$		3707.1	$3_{-3} - 2_{-1}^*$
3544.6	{ 3544.4	$6_4 - 7_3$	3630.8				(3709.8	$1_{-1} - 2_{-2}$
	3544.6	$0_3 - 7_2$	3631.8	(		3709.9	3709.9	$3_2 - 4_{-4}^*$
2518 1	3548.0	$2_{-1} - 5_{2}$		3635.2	$4_{-1} - 5_{-2}$		3710.1	$5_0 - 5_{-2}$
3340.4	3548.0	$6_1 - 7_1^*$	3635 1	3634 2	$5_{-4} - 0_{-5}$ 5_4 - 0_5		3712.7	$1_{0} - 2_{1}$
3549.3	3549.0		5055.1	3634.7	$4_0 - 5_4^*$	3712.7	3712.5	$\hat{4}_2 - \hat{4}_0^*$
	3552.5	$6_0 - 7_{-1}$		3634.7	$1_{-1} - 1_{1}^{*}$		3715.6	$4_{-2} - 3_{0}^{*}$
	3552.7	$6_{-3} - 6_{-1}^*$	3638.6	3638.4	$2_2 - 3_{-2}^*$	3715.6	3716.1	$5_0 - 5_{-2}^*$
3552.5	3552.0	$4_{-1} - 5_{-3}$		3643.7	$1_{-1} - 2_2$		3715.0	$0_4 - 0_3$
	3552.6	$6_1 - 7_0$	3643.5	3043.2	$5_3 - 4_2$ 5 4.*	3718.0	(3713.0	$0_3 - 0_4$
3554.0	3553.7	$6_{-6} - 6_{-4}^*$		3643.2	$5_0 - 4_4$	0710.0	(3719.4	$5_{-2} - 5_{-1}$
3556.0	3556.1	$6_{-2} - 7_{-3}$	2640.0	3648.1	$3_1 - 4_0$	3719.9	3719.9	$3_{-2} - 2_{-2}^*$
3560.7	3560.7	$6_2 - 7_1$	3648.2	3648.3	$6_{-4} - 6_{-1}$		3721.1	$5_5 - 5_4$
3564.5	3504.7	$2_0 - 3_3$	3650.1	∫ 3650.3	$4_{-4} - 5_{-5}$	3721.1	{ 3721.1	$5_4 - 5_5$
3500.2	(3566.9	$3_0 - 3_{2}^{*}$	0000.1	3650.0	$6_{-5} - 5_{-1}^*$		3721.3	$3_3 - 3_1^*$
3566.8	3567.0	$5_{-5} - 5_{-3}^*$		3651 5	$5_{-1} - 4_{-2}$ 4 5	3722.8	3722.8	$4_1 - 4_1^*$
	3566.6	$5_{-1} - 5_{1}^{*}$	3652.1	3652.9	$6_0 - 5_5$	0122.0	3722.7	$\hat{6}_1 - \hat{6}_2$
3568.7	{ 3568.0	$3_{-2} - 4_{-4}^*$		3652.2	$6_2 - 5_4^*$	3725.3	3725.5	$3_2 - 3_0^*$
000011	3508.9	$0_{-1} - 1_{-2}$ 2 3 - *		3653.8	$3_{-2} - 2_2^*$	3726.2	3726.2	$5_0 - 5_1$
	3576.0	$3_{-3} - 4_{0}$	3653.8	3653.4	$5_1 - 4_3^*$		3727.2	$4_4 - 4_3$
3575.7	3576.2	$5_{-1} - 5_2$		3054.0	$0_{-5} - 0_{-4}$	3727.3	3727.6	$4_3 - 4_4$ $4_2 - 5_3^*$
	3574.5(?)	$5_4 - 6_3$		3656.9	$3_0 - 4_1$		3727.4	$4_{-1} - 4_{-3}^{*}$
	3574.5(?)	$5_5 - 6_4$	3656.8	3656.8	$4_1 - 5_0$	3729.0	3728.9	$4_{-4} - 3_{-2}^{*}$
3577.2	3577.1	$3_0 - 4_{-2}$	3669.6	3669.8	$3_{-3} - 4_{-4}$	3730.6	3730.6	$4_2 - 4_1$
3581.3	(0011.0	10 12	3670.7	{ 3670.7	$1_1 - 1_{-1}^*$	3733.0	3733.0	$0_0 - 1_{-1}$
3584.1	3584.0	$5_{-5} - 4_1^*$	3671 7	3671.4	$3_{-2} - 4_{2}$		3735.5	$0_2 = 0_0$ 4 1 - 4 0
3585.6	3585.8	$4_{-4} - 3_2^*$	5071.7	(3675.1	$2_{2}^{2} - 3_{1}^{2}$		3735.7	$5_{3}^{-1} - 5_{2}^{-1}$
3587.7	3588 1	$5_3 = 0_2$ $5_1 = 6_2$	3675.2	3675.2	$4_{-4} - 4_{-1}$		3735.5	$5_2 - 5_3$
	3588.7	$5_{-3} - 5_{-1}^{*}$		3675.9	$4_0 - 3_2^*$	3735.7	$\frac{3734.9(?)}{2725.5}$	$5_{-3} - 4_{-1}^{*}$
2500.2	3589.0	$5_2 - 6_1$	2677.0	3676.9	$2_0 - 3_{-1}$		3735.5	$4_{-1} - 4_0$
3389.3	3589.6	$2_{-1} - 3_{-3}^*$	3011.2	3676 0(2)	$5_{-2} - 4_3$ 5_5 - 5_*		3735.7	$6_1 - 6_2^*$
	3589.3	$6_{-4} - 6_{-2}^{*}$		(3679.9	$2_1 - 3_0$	2727 1	3737.1	$2_1 - 1_1^*$
3501.8	3501.0	$2_{-1} - 2_1$	3680.1	3680.4	$2_{-2} - 1_{0}^{*}$	3/3/.1	<b>\ 3736.5</b>	$4_{-3} - 3_{-3}^*$
3371.0	3592.0	$6_3 - 7_1^*$		3682.9	$5_{-4} - 5_{-3}$	3738.8	3738.8	$2_{-1} - 2_0$
2502 7	3594.1	$4_{-3} - 4_{2}$	3683.4	{ 3683.5	$3_{-1} - 3_{-3}^{*}$		3741.8	$3_3 - 3_2$
3393.1	3593.0	$6_{-4} - 7_{-5}$		3083.0	$0_0 - 5_2^{*}$		3741.0	$3_{1}^{2} - 3_{3}^{3}$
3596.5	3596.9	$4_{-4} - 4_{-2}^{*}$		3685.6	$3_{-3} - 3_0$ $2_0 - 2_0^*$	3741.8	3741.6	$4_0^1 - 5_{-5}^{-5}$
3507 3	3597.6	$1_1 - 2_1^*$	2605 0	3685.0	$3_1^2 - 3_{-1}^*$		3741.8	$5_{-5} - 4_{-3}^*$
3599.2	007110		3085.8	3685.4	$3_{-1} - 2_1^*$		3741.6	$6_1 - 6_{-1}^*$
3600.8				3685.4	$5_0 - 6_{-6}^*$		3742.9	$4_{-2} - 3_{3}$
3602.9	(			3686.0	$4_0 - 4_{-2}$	3743.0	3743.1	$3_3 - 0_{-2}$ $2_8 - 1_{0}^*$
2601 9	3605.0	$4_4 - 5_3$	3689.5	3689.8	$2_{-2} - 3_{-3}$ $1_{0} - 0_{0}^{*}$		3743.2	$\frac{5}{4_4} - \frac{1}{4_2}^*$
3004.8	3604.8	$4_2 - 5_1$		3691.6	$2_{-1} - 3_{-2}$	2745 1	3745.1	$3_0 - 3_1$
3606.0	3606.2	$4_{-2} - 4_0^*$	3601 5	3691.4	$2_{-2} - 2_{1}$	5745.1	3744.6	$4_3 - 4_1^*$
3608 1	{ 3607.9	5-3-6-4	0071.5	3692.7(?)	$4_{-3} - 3_{2}$		3745.8	$5_1 - 5_0$ 5 - 4 *
5000.1	3608.1	$3_{-1} - 3_1^*$	3604.0	3605 1	$0_0 - 0_{-2}^{-1}$ 5 5 .*	3745.9	3746.1	$5_4 - 4_4$
3610.4	3610.3	$5_{-2} - 5_{3}$ $6_{5} - 7_{6}$	3696.9	3696.7	$6_{-2} - 6_{-4}^{+*}$		3745.4	6_4-6_6*
3010.4	3610.3	$6_{-6} - 7_{-5}$		( 3698.2	$5_{-1} - 4_4$	3747.9	,	-
	3614.1	$2_{-2} - 3_{1}$	3698.6	{ 3697.9	$4_1 - 5_{-5}^*$		3750.1	$2_1 - 2_2$
3613.3	3612.9	$5_{-2} - 6_{-3}$		3698.6	$6_{-3} - 6_{-2}$	2740.0	3749.8	$1_0 - 1_1$ $2_1 - 3_1$
	3013.2	$3_{-3} - 3_{-1}^{-1}$	3700.0	3700 0	$3_{-4} - 4_1$ 2, -2,*	5149.0	3750.1	$2_{2} = 3_{-3}$ $2_{1} = 2_{2}$
3615.6	3616.1	$3_2 - 4_0^*$	0100.0	3700.0	$\tilde{4}_{-2} - \tilde{4}_{-4}^{-1} *$		3749.7	$6_{-6} - 5_{-1}$
			1					

TABLE I. Frequency positions and identifications of water vapor lines near  $2.7\mu$ .

ν obs.	$\nu$ calc.	Transition	ν obs.	$\nu$ calc.	Transition	ν obs.	ν calc.	Transition
3752.5	{ 3752.4 { 3751.9(?) 3752.3	$2_2 - 2_1$ $3_3 - 4_{-2}$ $6_3 - 7_7$	3819.6	{ 3819.4 3820.5 3819.0	$6_6 - 7_1$ $3_0 - 3_{-3}$ $4_0 - 3_{-3}$	3870.5	{ 3870.7 3870.3 3871.0	$5_{-1} - 4_0$ $6_{-5} - 5_{-4}$ $6_{-6} - 5_{-5}$
3757.3	{ 3757.5 { 3757.3	$3_1^2 - 3_0^3 - 2_0^*$	3821.8	3821.9	$4_{2} - 3_{0}^{*}$ $3_{-3} - 2_{-2}$	3872.0 3872.8	(	
3760.2	3760.2	$1_1 - 1_0 \\ 4_0 - 4_{-1}$	3822.5	3822.4 3823.0	$ \begin{array}{r} 3_0 -2_1 \\ 6_5 -7_0 \end{array} $	3875.3	3875.5 ∫ 3881.8	$5_{-3} - 4_{-2} \\ 6_2 - 5_3$
3766.8	3766.8	$5_{-3} - 4_2 \\ 6_4 - 6_2^*$	3824.0	3824.2 (3826.7(?)	$5_{-3} - 5_{-4}$ $4_1 - 3_2$	3881.6	{ 3881.8 3881.8	$6_{-1} - 5_0 \\ 6_1 - 5_1^*$
	3766.6	$     \begin{array}{r}       6_3 - 6_1^* \\       2_0 - 2_{-1}     \end{array} $	3827.0	(3827.7 (3832.4	$3_1 - 2_2 \\ 3_{-1} - 2_0$	3883.7 3886.8	3886.4	$4_1 - 3_{-3}^*$
3770.9	3770.4 3771.0	$5_{-1} - 5_{-2}$ $6_1 - 7_{-4}$	3832.4	(3832.2 (3835.8	$6_5 - 7_{-1}^*$ $4_{-3} - 3_{-2}^*$	3892.2 3894.6	3892.1	$6_{-2} - 5_{-1}$
	3770.0(?)	$6_{-6} - 5_{-4}^*$ $6_{-5} - 5_{-5}^*$	3835.7	3835.6	$5_0 - 5_{-3}$ 4 4 - 3 3	3899.5	3899.2	$5_3 - 6_{-6}$ $5_2 - 5_{-1}$
3778.9	$\left\{\begin{array}{c} 3778.9\\ 3779.0\\ 2770.0\end{array}\right.$	$3_1 - 2_{-1}^*$ $5_{-2} - 4_{-2}^*$	3840.8	{ 3840.7 3841.3	$5_{-2} - 5_{-5}$ $5_1 - 4_{-1}^*$	3902.5 3905.1	3902.4	$4_3 - 4_{-3}^*$
3780.1	3779.8	$4_{-1} - 3_{-1}^{T}$ $1_{-1} - 0_{0}$	3841.9	$\left\{ \begin{array}{c} 3841.6 \\ 3841.8 \end{array} \right.$	$4_3 - 3_3^*  4_4 - 3_2^*$	3900.7 3912.9	3913.0	6-2-5-4*
2795 6	3785.6	$5_{-1} - 5_{-2}$ $6_{-2} - 6_{-3}$	3844.7	(3842.2 3844.9	$6_{-1} - 5_{-1}^*$ $4_{-1} - 3_0$	3918.8	( 3020 6	56
3783.0	3786.0	$4_1 - 5_{-4}$ $6_6 - 6_4^*$	3849.0	( 3850.8	5-1-4-3*	3921.1 3025.0	3921.5	$5_{4} - 6_{-2}^{*}$
3797.0	3796.7	$2_{-1} - 1_0$ $3_{-1} - 3_{-1} *$	3850.2 3852.8	( 3850.2 3852.6	$6_{-4} - 6_{-5}$ $5_0 - 4_1$	3926.2	( 3030 1	4a - 3a
3708 7	3799.0	$3_3 - 5_{-3}$ $4_3 - 5_{-2}$ $3_2 - 2_{-3}$	2054 (	( 3853.8   3854.7	$3_2 - 3_{-1}  4_0 - 3_1$	3930.0 3932.0	3929.9	$5_3 - 5_{-2}$
5190.1	3799.2	$6_{-1} - 7_{-6}$	3854.0	3855.1 3854.7	$4_{-2} - 3_{-1}$ $6_{-3} - 6_{-6}$	3933.1 3935.3	0702.1	03 20
3802.4	3802.4	$3_2^{-2} - 4_{-3}^{-1}$ $5_5 - 6_0^{-1}$		3857.7 3857.7	$5_3 - 4_4 \\ 5_2 - 4_3$	3944.1 3945.8		
3803.8 3807 9	3803.7	$4_{-2} - 4_{-3}$ $2_0 - 1_1$	3858.0	{ 3857.7   3859.0(?)	$5_{-4} - 4_{-3}$ $5_{-5} - 4_{-4}$	3948.3 3949.9	3947.7(?)	$3_2 - 2_{-1}$
2016.4	3816.2 3816.7	$\frac{1}{2_{1}}$ $-\frac{1}{2_{-2}}$ $3_{-2}$ $-2_{-1}$	3863.0	( 3858.1 3863.4	$     \begin{array}{r}       6_6 & -7_{-2}^* \\       2_2 & -1_{-1}     \end{array} $	3951.6		
3810.4	3816.4 3816.4	$5_0 - 4_0^*$ $5_1 - 5_{-5}^*$	3865.5	$\left\{ \begin{array}{c} 3865.6 \\ 3865.8 \end{array} \right.$	$5_{-2} - 4_{-1} \\ 5_1 - 4_2$			

TABLE I. Frequency positions and identifications of water vapor lines near 2.7µ.—Continued.

to dry the air in the spectrometer thoroughly. This was accomplished by placing large glass trays containing  $P_2O_5$  in the bottom of the airtight box which surrounds the optical parts of the spectrometer. It was found profitable to allow the spectrometer to stand for a period of from 15 to 20 hours before beginning observations. In the case of the regions  $\nu_1 + \nu_3(1.4\mu)$  and  $\nu_2 + \nu_3(1.9\mu)$  it was unnecessary to dry the air in the spectrometer.

For the measurements on the regions  $\nu_1$  and  $\nu_3$ ,  $\nu_1 + \nu_3$  and  $\nu_2 + \nu_3$ , an echelette diffraction grating ruled with 4800 lines to the inch by R. W. Wood was used, respectively, in the first, second, and third orders. The sensitivity was sufficient to permit operation of the spectrometer with slits subtending arcs of from 0.2 cm<sup>-1</sup> to 0.5 cm<sup>-1</sup>. The data were recorded in terms of galvanometer deflections, the foreprism being set before observing was begun so that the deflections between the peaks near the beginning and the end of the band were the same. It was believed that a fairly accurate representation of the relative intensities could be obtained in this manner. Composite pictures of the data obtained are shown in the upper curves shown in Figs. 1, 2, and 3, and the frequency positions of the lines and their identifications are shown in Tables I, II, and III.

In each case far better resolution of the lines has been achieved and much more detail has been observed than in the earlier measurements made on these regions by Plyler and Sleator<sup>3</sup> and by Plyler.<sup>4</sup>

### IDENTIFICATION OF THE OBSERVED LINES

In an effort to identify as many as possible of the lines in the bands herein referred to we have <sup>3</sup> E. K. Plyler and W. W. Sleator, Phys. Rev. 37, 1433 (1931). <sup>4</sup> E. K. Plyler, Phys. Rev. 39, 77 (1932).

ν obs.	$\nu$ calc.	Transition	v obs.	ν calc.	Transition	ν obs.	ν calc.	Transition
5143.5	5143.8	$6_{-6} - 7_{-7}$	5282.1	5282.0	$1_1 - 2_0$	5388.0	5387.9	$2_{0} - 1_{1}$
F146 2	5145.6	$6_{-5} - 7_{-6}$	5286.8	5286.7	$1_{-1} - 2_{-2}$	5395.8	5305.8	3 2 .
5140.5	5146.7	$5_{-4} - 5_{1}$	5288.9			0070.0	(53070/2)	5 5
5152.0	\$152.2	$6_{-4} - 7_{-5}$	5292.0	5292.0	$1_0 - 2_{-1}$		5300 5	$3_{-3} - 3_{-4}$
5157.1	5156.8	$6_{-3} - 7_{-4}$	5297.0			5399.6	5300 6	$\frac{21}{3} - \frac{2}{2}$
5158.0			5302.0	5301.9	$3_{-2} - 3_{-1}$		5400.0	$5_{-3} - 2_{-2}$
5159.0			5305.4	5305.7	$5_{-2} - 5_{-1}$		(5405.0	$3_0 - 0_{-5}$
5161.5			5309.7	5309.7	$0_0 - 1_{-1}$	5406.0	5405.0	$3_2 - 4_{-3}$ $3_2 - 2_1$
5165.5	5165.7	$5_{-5} - 4_{4}$	5313.1			5400.0	5406 8(2)	$5_0 - 2_1$ 5 6.
5172.0	(		5318.0	∫ 5318.1	$2_{-1} - 2_0$	5400.6	5400.0(1)	52 - 0-3
5177.3	5177.1	0_6-0_3	3010.0	5318.3	$6_2 - 7_{-3}$	5409.0	(5411.0	$0_{-4} - 0_{-5}$
5177.0	(5177.2	$5_{-1} - 6_{-2}$	5325.8	5326.0	$3_1 - 4_{-4}$	5411.9	5411.8	$3_1 - 2_2$
5180.0	5101 C			5328.4	$4_2 - 5_{-3}$		(5412.2	$3_{-1} - 2_0$
5181.9	5181.0	$5_{-3} - 0_{-4}$	5329.0	{ 5328.6	$3_0 - 3_1$	5413.7	5413.5	$4_{-4} - 3_{-3}$
5180.4	( 5100 0	5 6		(5329.1	$1_0 - 1_1$		(5414.2	$4_{-1} - 4_{-4}$
5189.0	5188.8	$5_1 - 0_0$		5329.5	$6_0 - 6_{-1}$	5416.7		
5109.1	5109.5	0_5-0_4	5333.4	5333.3	$5_{-1} - 6_{-6}$	5419.6	5419.6	6-3-6-6
5198.1	5198.1	$5_0 - 0_{-1}$		5337.0	$2_2 - 2_1$	5424.8	5424.6	$6_{-1} - 5_0$
5199.0	5199.2	$5_{-2} - 0_{-3}$	5338.0	5338.1	$4_{-4} - 3_1$	5426.8	5427.0	$5_{-2} - 5_{-5}$
5204.4	5207.2	5 6	0000.0	5338.2	$5_{-5} - 4_0$	5429.6	5429.8	$4 - 3_{0}$
5207.5	( 5208.4	5	5220.0	(5338.3	$5_0 - 5_1$	5431.0	5430.9	5,-4
5208.5	5208.7	45	5339.9	5339.9	$1_1 - 1_0$	5432.2	5432.0	5 _ 4
5210.6	5210.6	$4^{\circ} - 5^{\circ}$	5340.8	5340.8	$0_1 - 0_2$	5425 7	5452.0	J_5- <b>1</b> _4
5219.0	5219.0	$4_{2}^{-5_{1}}$	5341.7	5341.0	$3_1 - 3_0$	5433.1	F 4 2 6 0	4 2
0217.0	(5219.7	$5_{4} - 6_{3}$	5344.0	5343.9	$0_2 - 0_1$	5457.5	5430.8	$4_{-2} - 3_{-1}$
	5219.8	$5_{5} - 6_{4}$		5344.0	$4_1 - 4_2$	5443.2	5443.1	$4_0 - 3_1$
5220.3	5220.1	$4_{-1} - 5_{-2}$	5245 0	5345.1	$3_2 - 3_3$	5445.1		
022000	5220.5	$5_{-3} - 5_{0}$	5545.2	5345.4	$4_2 - 4_1$	5448 0	∫ 5447.7	$5_0 - 5_{-3}$
	5220.6	$1_{-1} - 2_2$	5246 4	5345.5	$3_3 - 3_2$	5110.0	<b>\ 5448.0</b>	$2_2 - 1_{-1}$
5223.9			5540.4	5340.5	$5_1 - 5_0$	5452.6	∫ 5451.9(?)	$5_{-2} - 4_{-1}$
5224 8	∫ 5224.0	$4_{1} - 5_{0}$	5349.5	5349.4	$5_2 - 5_3$	5452.0	5452.7	$4_1 - 4_{-2}$
5224.0	5225.0	$4_{-4} - 5_{-5}$	5350.8	5350 8	$3_3 - 3_2$	5459.3	5459.5	$5_4 - 6_{-1}$
5227.5	5227.6	$4_{-2} - 4_{1}$	5352 5	5550.0	20 - 2-1	5464.1	5464.3	$5_{-1} - 4_0$
5232.2	5232.2	$3_1 - 4_0$	5354 0	5354 0	11	5466.7		
020202	5232.0	$3_{-1} - 4_{-2}$	0001.7	(5355 /	$\frac{1}{3}$ $-\frac{1}{3}$	5470.0	5469.7	$6_0 - 5_1$
5233.6	5233.5	$4_4 - 5_3$		5355.6	$4_{3} - 4_{-2}$		(5471.6	$5_2 - 4_3$
5025 2	( 5233.7	$4_3 - 5_2$	5355.7	5355 7	$4_{1} - 4_{2}$	5472.0	{ 5471.7	$5_3 - 4_4$
5235.5	5240 4	2 4	000011	5355.7	$6_{1} - 6_{2}$		5472.3	$6_{-2} - 5_{-1}$
5239.9	5240.4	$3_0 - 4_{-1}$		5355.7	$6_3 - 6_4$	5488 4	∫ 5488.4	$3_3 - 3_{-2}$
5240.0	(5240.7	$3_3 - 4_2$	F3F( 7	5356.7	$1_{-1} - 0_0$	0100.1	\ 5488.4	$6_1 - 5_2$
5248.0	5248 1	$3_{-3} - 4_{-4}$	5350.7	5357.1	$5_3 - 6_2$	5490.6	5490.4	$6_2 - 5_3$
	5240.0	$4^{-4}$	5364.0	5364.0	$5_{-1} - 5_{-2}$	5492.9		
5250.1	5250.5	3 - 4	5365.2	5365.0	3_1-3_	5495.1		
5252.4	( 020010	0-20		(5365.9	$6_{-2} - 6_{-3}$	5495.8	5495.8	$6_1 - 6_{-2}$
5056.6	(5256.1	$5_{-4} - 5_{-3}$	5366.1	{ 5366.3	$5_4 - 5_5$		(5502.3	$6_3 - 5_4$
5250.0	5256.9	$2_0 - 3_{-1}$		5366.4	$5_5 - 5_4$	5502.3	{ 5502.3	$6_4 - 5_{b}$
	( 5263.2	$2_1 - 3_0$	5376.3	5376.0	$2_{-1} - 1_0$		5502.9	$6_5 - 7_0$
5263.3	{ 5263.3	$3_{-3} - 3_0$	5378.7	5378.7	$2_{-2} - 1_{-1}$	5510.7		
	5264.0	$5_{-2}-4_{3}$		5385.4	$4_{-2} - 4_{-3}$	5519.9		
5265.9	5265.9	$2_{-2} - 3_{-3}$	5385 5	5385.5	$6_6 - 6_5$	5525.4		
5267.9	5267.8	$2_{-2} - 2_{1}$	0000.0	5385.5	$6_5 - 6_6$	5527.2		
5270.9	5270.9	$2_{-1} - 3_{-2}$		5385.7	6_1-6_4			

TABLE II. Frequency positions and identifications of water vapor absorption lines near 1.87µ.

proceeded after the manner discussed in Part I, where also was given a summary of the theory of the non-linear triatomic molecule as developed by Shaffer and Nielsen.<sup>5</sup> Each line in one of the bands  $\nu_i$  is due to the molecules making a transition from a rotation level in the normal vibration state to a rotation level in the vibration

state  $\nu_i$  and the frequency of such a line will be the difference between a term value in  $\nu_i$  and one in the normal state. The selection rules governing what transitions may take place have been stated very conveniently by Dennison<sup>6</sup> and we shall not repeat them here. By trial and error enough lines are identified so that the

<sup>&</sup>lt;sup>6</sup> W. H. Shaffer and H. H. Nielsen, Phys. Rev. 56, 188 (1939).

<sup>&</sup>lt;sup>6</sup> D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).

ν obs.	ν calc.	Transition	v obs.	ν calc.	Transition	ν obs.	ν calc.	Transition
6995.8			7165.3	7164.8	3_3-4_4	7276.8	7276.8	1_1-00
6999.6			7166 7	∫ 7166.7	$3_{-2} - 4_{-3}$	7279 7	<i>{</i> 7280.0	$3_{-1} - 3_{-2}$
7004.2			/100.7	7166.3	$5_{-2} - 4_3$		(7279.0	$5_0 - 0_{-5}$
7007.7	( <b></b>		7169.5	{ 7169.5	$2_2 - 3_1$	7285.0	7284.0	$4_1 - 5_{-4}$
	7010.7	$6_5 - 7_4$	7171 4	(7169.7	$4_{-4} - 4_{-1}$	7288.0	7201.5	$5_5 - 0_0$
7010.7	{ 7010.7	$6_5 - 7_5$	7171.4	/1/1.3	$2_0 - 3_{-1}$	7291.4	1291.5	$2_{-1} - 1_0$
70161	(7010.9	$4_{-2} - 5_1$	7174.1	7174.0	$\frac{2_1}{5} - \frac{3_0}{5}$	1292.0	(7205.8	34 .
7010.1	7032 5	4 E	7177 0	(7174.5	5_4-5_3	7205 3	7205 1	4 - 4
7025.7	1023.5	4_4-3_1	1111.2	(7182.0	66.	1290.0	7295 8	$6_{e} - 7_{1}$
7023.4			7182.0	7182.0	$6_{1} - 6_{2}$	7297 2	7297.0	$4_{2} - 5_{2}$
1021.5	(70383(?))	3 - 4	/102.0	7182.9	6, -6,		(7299.4	$6_5 - 7_0$
7037.3	7037.0	$6_0 - 7_{-1}$	7184.0	(*****	0.00 0-2	7299.3	{ 7299.4	$2_{-2} - 1_{-1}$
7040.4	(		7106 2	∫ 7186.4	$2_{-1} - 3_{-2}$		(7300.5(?)	$5_4 - 6_{-1}$
7042.7			/180.5	<b>\ 7186.3</b>	$2_{-2} - 3_{-3}$	7304.8	7302.3(?)	$2_0 - 1_1$
7043.5	7043.3	$2_{-1} - 3_2$		(7188.4	$2_{-2} - 2_{1}$	7311 9	{ 7312.0	$3_0 - 3_{-3}$
7045.8			7188.3	{ 7188.4	$4_{-3} - 3_{2}$	7011.2	(7312.0	$3_{-2} - 2_{-1}$
7049.5	7049.1	$6_2 - 7_1$	<b>5</b> 400 C	(7188.8	$5_{-1} - 4_4$	7313.7	7313.9	$3_0 - 2_1$
7052.0	7052.2	$0_{-1} - 7_{-2}$	7192.6	(7109.0	1 2	7310.3	7310,7	$3_{-5} - 2_{-2}$
7054.6	7054.5	$4_{-1} - 4_{4}$	7109 7	7198.9	$1_1 - 2_0$	1311.4	(7321 7	32-
1050.0	( 7050 1	2 2	1190.1	7198.5	$4_{-3} - 4_{-2}$	7321.6	7320.8	4 - 4
7050.0	7060 7(2)	$2_0 - 3_3$ 5 6.		7202 6	$6_{1} - 6_{2}$	7324 6	(1020.0	T-1 - T-4
7039.0	7060.7(2)	$5_{5} - 0_{4}$	7202.7	7202.6	$6_{1} - 6_{1}$	7021.0	(7325.8	$4_1 - 3_2$
7067.0	7066.8	$5_{1} - 5_{2}$	7206.8	7206.8	$1_{-1} - 2_{-2}$	7326.2	7326.7	$5_0 - 5_{-3}$
7001.0	(7069.8	$4_0 - 4_3$		(7207.3	$5_5 - 5_4$	7227 4	<i>}</i> 7327.2	$3_{-1} - 2_0$
7069.9	7070.1	$6_{-4} - 7_{-5}$	7207.4	{ 7207.3	$5_4 - 5_5$	1521.4	7327.3	6-4-6-5
7071.1	7071.0	$3_{-3} - 4_0$		7207.4	6-1-6v	7329.2	7329.3	$5_{-2} - 5_{-5}$
7073 1	{ 7072.9	$5_3 - 6_2$	7209.0	7209.0	$1_0 - 2_{-1}$	7331.5	7331.7	$4_2 - 3_3$
101011	7073.6	$5_2 - 6_1$	7217.7	7218.1	$3_{-2} - 3_{-1}$	72224	(1331.5	$4_{-3} - 5_{-2}$
7075.8	7074.9	$5_1 - 0_0$		7220.5	$0_1 - 0_2$ 5 5.	1333.4	(7335.0	$4_{-4} - 5_{-3}$
7070 7	(1010.2	$0_{-3} - 7_{-4}$	7220.3	7220.3	$5_3 - 5_2$	7336.0	7336.4	$4_1 - 3_0$
7082.9			7223.3	7223.7	$6_{1}^{2} - 6_{1}^{3}$	7339.6	7339.0	6_3-6_6
7088.0			7004.9	7224.8	$4_4 - 4_3$		(7342.5(?))	$5_3 - 4_4$
7089.9	7089.8	$4_{-3} - 4_{2}$	1224.8	7224.8	$4_3 - 4_4$	7343.6	{7342.5(?)	$5_2 - 4_3$
7094.3	7094.0	$5_{-3} - 6_{-4}$		(7227.2	$4_1 - 4_2$		7343.7	$5_0 - 4_1$
7097.8	<b>5</b> 400.0	, <b>-</b>	7227.2	{ 7227.0	$4_{-1} - 4_0$	7345.7	7345.9	$4_0 - 3_1$
7099.6	7100.0	$0_{-6} - 7_{-7}$		7227.9	$5_3 - 0_{-2}$	7247 0	(7340.5	$4_{-2} - 3_{-1}$
	7101.5	$5_{-2} - 0_{-3}$		7230 3	5 - 6	1341.0	(7340)	$5_2 - 5_{-1}$
7101.5	7102.0(1)	$4_{4} - 5_{3}$	7230.3	7230.4	6 - 7	7349.1	7349.2	$6_{4} - 5_{5}$
	7101.5	$6_{5} - 7_{-6}$		7230.6	$6_0 - 6_1$		7349.1	$5_{-4} - 4_{-3}$
7104.5	(	010 100		7235.0	$3_2 - 3_3$	7350.1	7350.3	$5_{-5} - 4_{-4}$
7107.3	7107.2	$4_1 - 5_0$	7235.0	7235.9	$3_1 - 4_{-4}$	7352.8	7352.6	$5_1 - 4_2$
7108.5	7108.3	$4_2 - 5_1$	1233.0	7234.7	$4_2 - 4_1$	7354.1	7354.2	$5_{-2} - 4_{-1}$
7111 2	{ 7111.1	$2_{-2} - 3_{1}$		7234.3	$4_{-2} - 3_{3}$	7357.6	7357.8	$2_2 - 1_{-1}$
7111	(7111.5	$4_0 - 5_{-1}$	7237.0	7237.0	$3_3 - 3_2$		7301.3	$5_{-1} - 4_0$
7114.4	7120.2	4 5	7220.0	(7230.0	$3_0 - 3_1$	7361.2	7361.5	$5_{-3} - 4_{-2}$
7120.3	7120.5	$4_{-2} - 3_{-3}$	7240 4				7361.1	6 -5 5
7124.3			7210.1	(7244.9	$2_{2} - 3_{-3}$	7265 2	7365.1	$6_{-1} - 5_0$
7125.7	7125.5	5-5-6-6	7244.4	7244.2	$2_{1}^{2} - 2_{2}^{2}$	1305.5	7365.2	$6_1 - 5_2$
7126 7	∫ 7126.7	$4_{-1} - 5_{-2}$	7246.3	7246.1	$1_0 - 1_1$		(7370.8	$6_{0} - 5_{1}$
1120.1	<b>\ 7126.6</b>	5-4-6-5	7247 5	<i>{</i> 7246.8	$2_2 - 2_1$	7370.4	7370.2	$6_2 - 5_3$
7129.5			7217.5	17247.1	$3_{2} - 4_{-2}$		7370.2	$6_{-2} - 5_{-1}$
7131.0	(7120.0		1251.7	1251.5	$3_1 - 3_0$	7274 5	1309.1	$0_{-3} - 5_{-2}$
7133.3	7132.9	$5_{-3} - 5_{0}$	7253.4	1232.9	$5_{-3} - 4_{2}$	7370 0	1313.0	$0_{-4} - 3_{-3}$
	(7137 3	$4_{-6} - 4_{-3}$	7256.9	7256.8	$1_{1} - 1_{0}$	7381.4		
7137.5	7137.4	6, -5,		(7258.1	5-4-40	7385.5		
7129 2	7138.4	$3_3 - 4_2$	7258.1	7257.7	$4_0 - 4_{-1}$	7387 6	{ 7387.8	$3_1 - 2_{-2}$
1130.3	7138.0	$3_2 - 4_1$		7257.9	$4_{-4} - 3_{1}$	1001.0	<b>\ 7387.8</b>	$4_4 - 5_{-5}$
7141.9	7142.1	$3_1 - 4_0$	7261.0	7261.0	$5_{-1} - 5_{-2}$	7389.7	7200 F	A 4
7144.0	7144.8	4_4-5_5	1202.1	7762 7	6 6	7393.0	1392.5	$4_2 - 4_{-3}$
7143.4 7148 6	/145.2 7149 /	$0_{-5} - 0_{-4}$	7203.5	1203.1	$0_{-2} - 0_{-3}$	7300.2		
7153.5	/140.4	$J_01$	7266.7	7266.5	$4_{4} - 5_{1}$	7404.4		
7155.5	7156.2	$5_{-5} - 5_{-2}$	7270.6	0 0 00		7411.3		
7159.9			7272.2					
			1			1		

TABLE III. Frequency positions and identifications of water vapor absorption lines near  $1.39\mu$ .

term values for the quantum numbers J=0, J=1, and J=2 can be established. In evaluating these term values it has been assumed that the energy levels of the water vapor molecule inferred from the data on the pure rotation spectrum reported by Randall, Dennison, Ginsburg, and Weber<sup>7</sup> can be relied upon with considerable certainty. As a verification that the lines have been correctly identified, combination relations are employed. For example, take two lines from the band  $\nu_1 + \nu_3$  which have been identified in the following manner:  $1_{-1} - 0_0$ =7276.8 cm<sup>-1</sup> and  $1_{-1}-2_{-2}=7206.8$  cm<sup>-1</sup>. Adding to these the term values  $0_0$ , which is zero, and  $2_{-2}$ , which is 70.0 cm<sup>-1</sup>, respectively (taken from the data of RDGW), we obtain for the term value  $1_{-1}$  in the state  $\nu_1 + \nu_3$ , 7276.8 cm<sup>-1</sup>. By identifying the experimentally determined values for J=0, J=1, and J=2with the corresponding ones of Eq. (1) of Part I,8 and by using for the coefficients of centrifugal stretching the values determined in that work, we may obtain values for  $R_1$ ,  $R_2$ , and  $R_4$ , with the notation of Shaffer and Nielsen, which will be effective for the state  $v_i$ . With the values  $R_s(v_i)$  so determined, values for the rotational energies for a higher value of J, say J=5, are computed and from these additional lines are predicted. These lines are then hunted for in the spectrum and when they are located their experimental values can be used to improve upon the values of the  $R_s(\nu_i)$ . One may then proceed to predict more lines in the spectrum and perhaps further improve the values of the  $R_s(v_i)$ . To guard against incorrect assignment of lines combination relations have been used consistently and in most cases the agreement has been satisfactory. The lines in the spectrum have been identified for levels up to and including J=6 and it is found that most of the important lines on either side of the center of the bands to a distance of about  $100 \text{ cm}^{-1}$  have been accounted for. The identification of the

J	$\nu_1$	ν3	$\nu_1 + \nu_3$	$\nu_2 + \nu_3$
00	3652.7 cm <sup>-1</sup>	3756.8 cm <sup>-1</sup>	7253.6 cm <sup>-1</sup>	5333.5 cm <sup>-1</sup>
1.	3694 5	3797 3	7203 0	5377 0
1.	3680.8	3702 1	7288 4	5371 4
10	2677.0	2770.0	7276.9	5371.4
1_1	3077.0	3779.8	1210.8	5350.7
22	3780.6	3887.2	7381.6	5471.8
21	3779.4	3886.2	7380.3	5469.5
20	3740.7	3850.2	7344.6	5430.2
2 1	3726.3	3833.8	7328.6	5413 1
2_2	3717.5	3826.2	7323.2	5402.6
3.	3033 1	4027 1	7577 3	5630 6
2	2021 9	4027.1	7522.5	5050.0
22	3931.0	4027.1	7520.5	5050.0
31	3030.3	3903.8	7457.8	5547.9
30	3852.3	3957.2	7448.7	5540.7
$3_{-1}$	3820.2	3927.4	7422.2	5507.2
$3_{-2}$	3789.9	3896.1	7391.4	5475.2
3_3	3786.5	3891.7	7386.7	5469.6
4.	4127.1	4215.4	7713.0	5843.9
4.	4127 1	4215.0	7713.0	5843.8
4	4028.2	4113.2	7617 2	5727 0
12	4023.1	4112.0	7611 1	5727.0
4	2061 0	4046.0	7011.1	5121.9
40	3901.2	4000.8	1558.0	5055.2
4_1	3932.1	4051.2	1542.1	5030.1
4_2	3921.9	4028.4	7519.8	5610.1
43	3873.2	3978.0	7473.7	
4_4	3871.1	3975.5	7470.0	5550.2
55		4463.4	7949.6	6108.7
5₄		4463.4	7949.6	6108.6
53		4345.9	7830.7	5959.9
5.	4242.4	4345.9	7830.5	5959.8
Š.	4141.6	4240 7	7736 5	5850.4
5	4132.1	4235 1	7726.2	5847 2
5	4075 5	4196 4	7677 0	5047.2
5-1	4054 2	4165 0	7677.0	5760.0
5_2	4034.2	4103.9	7034.5	5752.2
5-3	4035.2	4150.7	7030.8	5724.4
3_4	3908.2	4082.4	1513.8	5055.0
$5_{-5}$	3966.5	4080.9	7572.2	5653.9
66	4674.9	4750.9	8227.3	6430.8
65	4674.9	4750.9	8227.3	6430.8
6.	4524.3	4604.5	8091.5	6244.6
6.	4523.5	4604.5	8091.5	6244.6
6.	4394.5	4492.2	7980.6	6100.8
6.	4300 7	4480 5	7075 4	6008 6
6.	4203.8	1305.2	7870 7	5078 6
6	1100 7	1295.4	1019.1	J910.0
0_1 6	1200.1	4303.1	1009.0	3940.3
0_2	4239.3	4338.0	/010./	3918.8
0_3	4201.8	4501.4	1185.7	5866.3
6_4	4192.1	4297.4	7774.5	5856.6
6_5	4096.5	4196.8	7688.0	5732.1
6_6	4096.5	4196.2	7686.3	5730.1

TABLE IV. Vibration-rotation term values for the frequencies,  $\nu_1$ ,  $\nu_3$ ,  $\nu_1 + \nu_3$ ,  $\nu_2 + \nu_3$ .

lines is set down in the third column of Tables I, II, and III. In Table IV are set down the energy levels deduced from the identification of the lines and for comparison the positions of the lines in the bands as computed from these deduced energies are set down in the second column of Tables I, II, and III.

As a further test that the correct identification

<sup>&</sup>lt;sup>7</sup> H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, Phys. Rev. 52, 160 (1937). Cited as RDGW later.

<sup>&</sup>lt;sup>8</sup> In Eq. (5) of Part I which determines what the values  $\epsilon$  to be used in the relation I are, it has been noted that in the case of J=5 the second member of the term linear in  $\epsilon$  should be  $(34R_2+706R_3)(R_2+R_3\mp(R_4+2R_5)f)$  and that the term  $(R_2+2S_3)$  occurring as a factor in the first and second members of the constant term should be  $(R_2+35R_3)$ .

of the lines has been made the intensities of the lines were computed for comparison with the observed values. As was pointed out in Part I, to calculate the intensities rigorously becomes a prohibitive task and some approximation method must be resorted to. The argument for the method used here is analogous to the one of RDGW<sup>7</sup> and is somewhat as follows. In the classical theory of the asymmetric rotator, rotation about the axis of the largest moment of inertia and rotation about the axis of the smallest moment of inertia represent stable types of motion. In the quantum theory the energies are, of course, discrete and each discrete energy level has associated with it two symbols J and  $\tau$ . The symbol J is the quantum number of total angular momentum and is always a positive integer. The symbol  $\tau$  is not a quantum number but is merely an index taking all integral values from  $\tau = +J$  to  $\tau = -J$ . For a given J value the largest rotation term value is associated with  $\tau = +J$  and the lowest rotation term value with  $\tau = -J.$ 

For a given value of J the rotational energies associated with a value of  $\tau \approx -J$  correspond to the classical case of the rotator, rotating about the axis of the largest moment of inertia. If we take this axis as the approximately unique axis of the rotator the energies are found to be fairly accurately represented by the relation

$$E = J(J+1)\frac{h^2}{8\pi^2} \left[ \frac{1}{2} \left( \frac{1}{I_A} + \frac{1}{I_B} \right) \right] + \frac{K^2 h^2}{8\pi^2} \left[ \frac{1}{I_C} - \frac{1}{2} \left( \frac{1}{I_A} + \frac{1}{I_B} \right) \right], \text{ where } K \approx J. \quad (1)$$

For a given J value, however, those rotational energies identified with  $\tau \approx +J$  correspond to the limiting case where the molecule rotates almost entirely about the axis of the smallest moment of inertia. If we take this axis as the approximately unique axis of the rotator we find the energies are fairly well approximated by the equation:

$$E = J(J+1)\frac{h^2}{8\pi^2} \left[ \frac{1}{2} \left( \frac{1}{I_B} + \frac{1}{I_C} \right) \right] + \frac{K^2 h^2}{8\pi^2} \left[ \frac{1}{I_A} - \frac{1}{2} \left( \frac{1}{I_B} + \frac{1}{I_C} \right) \right], \text{ where } K \approx J. \quad (2)$$

Levels which are associated with values of  $\tau$  quite different from  $|\tau| = J$  correspond in a very rough manner to the classical motion of the asymmetric rotator about its third axis of inertia and the energies in these cases will be badly represented by either Eqs. (1) or (2).

The pure rotation bands and the type of vibration-rotation band discussed in Part I arise when the electric moment lies along the axis of the intermediate moment of inertia. In such cases the electric moment is therefore normal to both the axis of the smallest and the axis of the largest moment of inertia about which rotation is a stable type of motion in the classical treatment of the asymmetric rotator. Such oscillations must therefore in both of the limiting cases represented by Eqs. (1) and (2) behave as those vibrations termed "perpendicular" in the theory of the symmetric rotator. RDGW have indicated how the intensities may be approximated by using the intensity relations valid for the perpendicular bands in symmetric molecules.

In the case we wish to consider here the oscillation induces a variation of the electric moment in a direction parallel to the axis of the smallest moment of inertia. Hence the electric moment is parallel to one of the axes (the smallest) but normal to the other axis (the largest) about which rotation represents a stable type of motion in the classical theory of the asymmetric rotator.

In the case where the rotator is spinning almost entirely about the axis of the largest moment of inertia; i.e., where  $\tau \approx -J$ , the energy levels are approximated by Eq. (1). When this condition prevails the oscillations must again behave very much like a perpendicular vibration and again we may expect the intensities to be approximated by the relations set down by RDGW, namely:

$$(J-1, K-1|I|J, K) = F \exp(-(W_{J-1, K-1})/kT) \times \frac{(J+K)(J+K-1)}{J}; \quad (3a)$$
$$(J-1, K+1|I|J, K) = F \exp(-(W_{J-1, K+1})/kT) \times \frac{(J-K)(J-K-1)}{J}; \quad (3b)$$

$$(J, K-1|I|J, K) = F \exp(-(W_{J, K-1})/kT) \times \frac{(2J+1)(J+K)(J-K+1)}{J(J+1)}.$$
 (3c)

The quantity F takes the values  $\frac{1}{4}$  and  $\frac{3}{4}$ , respectively, as the value of  $\tau$  in the initial state is even or odd. The two values of F come about because of the division into a symmetric and an antisymmetric classification of the levels arising out of the presence of the two identical hydrogen atoms in the molecule.

When, however, the rotator is spinning mainly about the axis of the smallest moment of inertia, i.e.,  $\tau \approx +J$ , the energy levels are given approximately by Eq. (2). Under these conditions the oscillation must behave very much like that which in the theory of the symmetric molecule is called a parallel vibration. We should therefore expect the intensities this time to be approximately those given by the intensity relations valid for the parallel band in symmetric molecules, namely:

$$(J-1, K | I | J, K) = F \frac{2(J^2 - K^2)}{J} \exp\left(-(W_{J-1, K})/kT\right); \quad (4a)$$

(J, K | I | J, K)

$$=F\frac{2K^{2}(2J+1)}{J(J+1)}\exp\left(-(W_{J,K})/kT\right);\quad (4b)$$

$$(J, K | I | J - 1, K)$$
  
=  $(J - 1, K | I | J, K) \exp (Jh^2/4\pi^2 IkT);$  (4c)

where F takes the values  $\frac{1}{4}$  and  $\frac{3}{4}$ , respectively, depending upon whether  $\tau$  in the initial state is even or odd.

For example, we take the transition  $5_{-4}-5_{-3}$ . The  $\tau$  values are both of the order -5. The levels  $5_{-5}$  and  $5_{-4}$  are nearly coincident and are approximately given by Eq. (1) by setting J=5and K=5. The levels  $5_{-3}$  and  $5_{-2}$  are also fairly nearly coincident and are approximately given by the same equation with K=4. When the above levels are regarded in this manner the transition  $5_{-4} - 5_{-3}$  is of the type  $\Delta J = 0$ ,  $\Delta K = 1$ , and its intensity will be given by Eq. (3b) in which J=5 and K=5. These same two levels might also be thought of as fitting into the scheme of levels given by (2) (although numerically there will be no agreement whatever). where J = 5 and K = 1. In this light the transition is of the type  $\Delta J=0$ ,  $\Delta K=0$  and its intensity would accordingly be given by Eq. (4b). The actual intensity of the transition  $5_{-4} - 5_{-3}$  should therefore be some value interpolated between the two values given by (3b) and (4b); in this case the transition is between levels so nearly approximated by Eq. (1) that the intensity may be computed from (3b) alone. Consider now also the transition  $5_5 - 5_4$ . The levels  $5_5$  and  $5_4$ are very nearly coincident and their values are given very nearly by the relation (2) by setting J = K = 5. The transition is clearly, from this point of view, of the kind  $\Delta J = \Delta K = 0$  and its intensity will be given by the relation (4b). Again we may here regard these two levels as fitting into the scheme of Eq. (1) where J=5, K=0, and K=1. In this sense the transition is of the type  $\Delta J = 0$ ,  $\Delta K = 1$  and the intensity of the transition must accordingly be obtained from (3b). Actually, as before, the intensity will be some value intermediate between these two; in this case the value given by (4b) is probably good enough.

For values of  $\tau$  not at all nearly equal to J the energy levels are badly approximated by both (1) and (2). So also one may expect the intensities of the transitions between such levels to be badly estimated by both (3) and (4). In such cases one must interpolate between the values given for the transition by Eqs. (3) and Eqs. (4), but just how this interpolation is to be effected is not very clear. RDGW have suggested how one might proceed in making such interpolations and here we have followed somewhat their scheme. The validity of the intensities calculated in this manner is open to considerable speculation. It seems quite evident, however, that they will be at least qualitatively right and will serve to aid materially in the analysis of the bands, i.e., if a certain transition should in the actual case occur with a very small intensity our

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TABLE V. Values of the reciprocals of inertia, A, B, and C for  $\nu_1$ ,  $\nu_3$ ,  $\nu_1+\nu_3$ , and  $\nu_2+\nu_3$ .

	$\nu_1$	¥3	V1 + V3	v2+v3
A	27.26 cm <sup>-1</sup>	26.50 cm <sup>-1</sup>	26.04 cm <sup>-1</sup>	29.32 cm <sup>-1</sup>
B	14.28 cm <sup>-1</sup>	14.40 cm <sup>-1</sup>	14.16 cm <sup>-1</sup>	14.56 cm <sup>-1</sup>
С	9.17 cm <sup>-1</sup>	9.10 cm <sup>-1</sup>	8.95 cm <sup>-1</sup>	9.06 cm <sup>−1</sup>

calculated value will not be very large; similarly, if the actual intensity is great our calculated value will also be large. For the sake of comparison the lines have been plotted below the experimental curves in Figs. 1, 2, and 3 with their intensities computed on the above basis. In several instances where several lines have fallen at the same place the composite line has been drawn in. In a few cases the most intense lines have not been drawn quite as intense as their computed value because an awkward scale would have been required. As we have suggested, no great accuracy for the computed line intensities is claimed, but it is of interest to note that in most cases the agreement between the computed and the experimentally observed lines is surprisingly good. Not all of the lines have been identified, but it is believed that those remaining must be due to quantum transitions involving quantum numbers greater than J=6.

In the region near 2.7 $\mu$ , especially on the low frequency side, a considerable number of lines of some intensity could not be accounted for on the basis that this region was due to  $\nu_3$  alone. It seemed not unreasonable to suppose that many of these lines were due to the third fundamental vibration  $\nu_1$  of the water vapor molecule, particularly since the concentration of these unidentified lines seems to center more or less about the frequency position observed in the Raman spectrum of  $H_2O$  for  $\nu_1$ . It has been possible on this basis to identify a great many more of the remaining lines and these are indicated in the figure as "black" lines. The frequency positions of the lines will be found in the first column and their identifications occur in the third column of Table I. To the identifications of the transitions attributed to  $\nu_1$  are affixed asterisks, in order at once to distinguish them from the identifications of lines attributed to  $\nu_3$ . The energy levels deduced from the identification of the lines attributed to  $\nu_1$  are also given in Table IV.

The vibration  $\nu_1$  is one where the induced electric moment lies along the axis of the intermediate moment of inertia and the intensities must be computed by the method employed by RDGW and by us in Part I. Best agreement seems to prevail if the intensities computed in this manner are multiplied by a factor of about  $\frac{3}{4}$ , which is equivalent to saying that the vibration  $\nu_1$  occurs with an intensity of about  $\frac{3}{4}$  of that of  $\nu_3$ . This value must, however, be regarded as very rough.

## DISCUSSION OF THE RESULTS

From the energy level values obtained from the analysis of the preceding bands the values of the quantities  $R_i$  which occur in Eq. (2), Part I, and which are defined in the earlier paper by Shaffer and Nielsen are evaluated. From these the values of the moments of inertia are computed by making use of the theoretically computed centrifugal stretching coefficients. Most weight is given to the levels where J=0, J=1, J=2, and J=3 because of the fact that in these the centrifugal stretching will be small. As the value of J increases it has been shown by RDGW that the centrifugal stretching cannot be adequately corrected for in the above manner.

In Table V are gathered the reciprocals of the moment of inertia  $A, B, \text{and } C, \text{defined as } h/(8\pi^2 I_A), h/(8\pi^2 I_B), \text{ and } h/(8\pi^2 I_C), \text{ respectively, for the vibration states } \nu_1, \nu_3, \nu_1+\nu_3, \text{ and } \nu_2+\nu_3.$  In Table VI are given the observed values of  $I_A$ ,  $I_B$ , and  $I_C$  effective in these vibration states. In addition the values of these, calculated from the semi-theoretical relations of D and D, are set down as well as the observed and theoretical values of the quantity  $\Delta$  defined by them. It will be seen that the agreement between the observed and the predicted values is uniformly better than in the paper by D and D.

The rotation level  $0_0$  in any vibration state is identical with the value of the vibration term value itself. From Table IV we may then obtain the vibration term values of the vibration  $\nu_1$ ,  $\nu_3$ ,  $\nu_1 + \nu_3$ , and  $\nu_2 + \nu_3$ . These are set down in Table VII. The vibration term values for the triatomic molecule may be written :

$$W(v_1, v_2, v_3)/hc = \sum_{i=1}^{3} (v_i + \frac{1}{2})\omega_i + \sum_{i \ge k=1}^{3} (v_i + \frac{1}{2})(v_k + \frac{1}{2})x_{ik}, \quad (5)$$

where the  $\omega_i$  are the normal frequencies  $(\omega_i = x_i - x_{ii} - \frac{1}{2}(x_{ij} + x_{ik}))$  and the  $x_{ik}$  are the anharmonic constants which depend in an

TABLE VI. Theoretical and observed values of  $I_A$ ,  $I_B$ ,  $I_C$ , and  $\Delta$ .

V1, V2, V3	<i>I<sub>A</sub></i> (obs.)	I <sub>A</sub> (calc.)	I <sub>B</sub> (obs.)	IB (calc.)	I <sub>C</sub> (obs.)	I <sub>C</sub> (calc.)	Δ (obs.)	$\Delta$ (calc.)
(1, 0, 0)	1.028	1.029	1.959	1.972	3.050	3.076	.063	.076
(0, 0, 1)	1.055	1.056	1.942	1.939	3.073	3.059	.076	.064
(1, 0, 1)	1.074	1.076	1.975	1.979	3.125	3.120	.076	.064
(0, 1, 1)	.954	.955	1.920	1.915	3.086	3.099	.212	.228

involved manner on the potential energy constants. The constants  $\omega_i$ ,  $x_i$ , and  $x_{ik}$  were evaluated by D and D on the basis of the data available to them. They have pointed out, moreover, that many of the combination bands in the very near infra-red occur in pairs and actually even in multiplets. The positions of these combination bands are badly reproduced by Eq. (5); in fact the levels which occur in pairs or multiplets are predicted to be almost degenerate. This fact is attributed by D and D in an ingenious way to a term  $q_1^2 q_3^2$  which occurs in the second-order transformed<sup>9</sup> Hamiltonian. This term will have the following matrix components  $(v_1, v_2, v_3 | q_1^2 q_3^2 | v_1, v_2, v_3)$  and  $(v_1, v_2, v_3 | q_1^2 q_3^2 | v_1 \pm 2, v_2, v_3 \pm 2)$ . In arriving at Eq. (5) only the diagonal components have been taken into account, the second kind contributing in general only in higher orders of approximation. Since  $\omega_1$  and  $\omega_3$  are so nearly degenerate, however, frequencies of the kind  $\nu(v_1, v_2, v_3)$  and  $v(v_1\pm 2, v_2, v_3\mp 2)$  will also be nearly degenerate. In such cases the off diagonal components  $(v_1, v_2, v_3 | q_1^2 q_3^2 | v_1 \pm 2, v_2, v_3 \mp 2)$  may yield

contributions which are significant to the energy and for the frequency positions of the doublet components D and D obtain:

$$\nu = \left(\frac{\nu_a + \nu_b}{2}\right) \pm \left[\left(\frac{\nu_a - \nu_b}{2}\right)^2 + a\gamma^2\right]^{\frac{1}{2}}, \quad (6)$$

where  $a = \frac{1}{2}\gamma [v_1(v_1-1)(v_3+1)(v_3+2)]^{\frac{1}{2}}$  and  $\gamma$  is a constant depending only on the potential energy constants.  $\nu_a$  and  $\nu_b$  are the values of the two component frequencies when evaluated by Eq. (5). With the aid of ten of the observed vibration frequencies, some of them single levels, some of the doublet levels and in one case the average value of a doublet level D and D have evaluated the  $\omega_i$ ,  $x_i$ ,  $x_{ik}$ , and  $\gamma$ .

Having now available the new data discussed in this paper it becomes of interest to reinvestigate the values of these constants. To do this we have proceeded in a manner slightly different from that of D and D. As our data for evaluating  $x_i$  and  $x_{ik}$  we have used  $\nu_1, \nu_2, \nu_3, 2\nu_2, \nu_2 + \nu_3$ ,  $\nu_1 + \nu_3$ , and the average value of all the doublet levels, i.e.,  $(\nu_a + \nu_b)/2$ . This is more than enough to evaluate the  $x_i$  and the  $x_{ik}$  and the values taken to be the best are values which when put back into (5) will reproduce these data again to within 1 cm<sup>-1</sup>. By proceeding in this manner the determination of the  $x_i$  and  $x_{ik}$  is independent of the value of  $\gamma$ . The constant  $\gamma$  is then evaluated from the separations between the doublet levels, i.e.,  $\Delta \nu = 2\{[(\nu_a - \nu_b)/2]^2 + a\gamma^2\}^{\frac{1}{2}}$  and the value of  $\gamma$  which seems most satisfactory for the doublet levels on the whole is actually just that obtained by D and D.

TABLE VII. Vibrational term values.

$\nu_1 = 3652.7 \text{ cm}^{-1}, \ \nu_3 = 3756.8 \text{ cm}^{-1},$	$\nu_1 + \nu_3 = 7253.6 \text{ cm}^{-1}, \nu_2 + \nu_3 = 5333.5 \text{ cm}^{-1}$

Whether our scheme for the determination of these constants is better than the method used by D and D may certainly be brought into question. The opinion is, however, here advanced that the positions of the centers of gravity of the doublet levels are probably more significant than the values of the component levels themselves. This opinion is based on the fact that  $(\nu_a + \nu_b)/2$ can be determined directly experimentally. No direct experimental method is, however, avail-

<sup>&</sup>lt;sup>9</sup> The first-order Hamiltonian  $H_1$  will contribute nothing in first order of approximation. It is therefore possible to carry out a contact transformation on the Hamiltonian Hso that  $H_0=H_0', H_1'=0$ , and  $H_2'=H_2-(i/2)[SH_1-H_1S]$ , S being the transformation function. [See Shaffer, Nielsen, and Thomas, Phys. Rev. **56**, 895 (1939).] While  $H_1$  does contain terms which contribute to the above-mentioned perturbation, after the contact transformation they are of the form  $q_1^2q_2^2$ .

able to determine how much of the separation  $\Delta \nu$  is actually due to the interaction. The theory of D and D affords, to be sure, a method of calculating this theoretically, and it is indeed found that the  $\gamma$ 's computed in this manner from the several doublet levels agree among themselves to within one or two percent, but it is not inconceivable that the splitting is further influenced to a small extent by still higher order terms.

The values of  $\omega_i$ ,  $x_i$ ,  $x_{ik}$ , and  $\gamma$  obtained from our data are the following:

$x_1 = 3696.5$	$x_{11} = -43.8$	$x_{12} = -22.2$
$x_2 = 1614.7$	$x_{22} = -19.3$	$x_{13} = -155.9$
$x_3 = 3804.8$	$x_{33} = -48.0$	$x_{23} = -18.7$

 $\omega_1 = 3829.4, \ \omega_2 = 1654.5, \ \omega_3 = 3940.1, \ |\gamma| = 74.46.$ 

In the first column of Table VIII are given the known vibrational term values for the water vapor spectrum. In the second column are given the computed values with the above values of  $\omega_i, x_i, x_{ik}$ , and  $\gamma$ . In the third column will be found the actual data used to make our determinations of  $\omega_i$ ,  $x_i$ , and  $x_{ik}$ , i.e., the frequency positions of the single levels and the average values of the doublet levels  $(\nu_a + \nu_b)/2$ . In the fourth column are set down the values of these data recomputed from Eq. (5). As a final check the two observed component levels of the triplet set of levels (4, 0, 1), (2, 0, 3), and (0, 0, 5) have been computed theoretically for comparison with the experimental values. The fact that the calculated values of these levels agree almost

V1, V2, V3	<i>W/hc</i> (obs.)	W/hc (calc.)	$\frac{1}{2}(W_a+W_b)/hc$ (obs.)	$\frac{1}{2}(W_a + W_b)/hc$ (calc.)	
(0, 1, 0)	1595.4	1595.4			
(0, 2, 0)	3152.3	3152.3			
(1, 0, 0)	3652.7	3652.7			
(0, 0, 1)	3756.8	3756.8			
(0, 1, 1)	5333.5	5333.5			
(1, 0, 1)	7253.6	7253.6			
(1, 1, 1)	8807.1	8808.1			
(2, 0, 1)	10613.1	10617.1	10822 7	10822.6	
(0, 0, 3)	11032.4	11028.0	10022.7	10022.0	
(2, 1, 1)	12151.2	12150.3	12358 1	12358 /	
(0, 1, 3)	12565.0	12566.5	12556.1	12550.4	
(3, 0, 1)	13830.9	13834.4	14074 8	14075 8	
(1, 0, 3)	14318.8	14317.2	11071.0	14075.8	
(3, 1, 1)	15347.9	15346.8	15500.2	15580 5	
(1, 1, 3)	15832.5	15832.2	15590.2	10007.0	
(3, 2, 1)	16821.6	16820.4		17064 5	
(1, 2, 3)		17308.6		17004.0	
(4, 0, 1)	16899.0	16899.0			
(2, 0, 3)	17495.8	17495.6			
(0, 0, 5)		1. 1, 0.0			

TABLE VIII. Observed and calculated values of W/hc.

exactly with the measured values is no doubt somewhat accidental, but it serves as another verification that the values  $\omega_i$ ,  $x_i$ ,  $x_{ik}$ , and  $\gamma$ given above are quite good. As a matter of fact the new values of  $\omega_i$ ,  $x_i$ ,  $x_{ik}$ , and  $\gamma$  given here are in general in very good agreement with those given by D and D.