The Microwave Spectrum of Oxazole
The DRM-Spectrum of the ^{15}N-Species in its Natural Abundance

Otto L. Stiefvater

School of Physical and Molecular Sciences, University College of North Wales,
Bangor LL57 2UW, Gwynedd, U.K.

Z. Naturforsch. **33a**, 153—155 (1978); received December 8, 1977

In view of a discrepancy between the rotational constants of the ^{15}N-species of oxazole reported in an earlier study on a pure ^{15}N-sample and those found in a recent study on a sample containing the ^{15}N-species only in its natural abundance, the experimental results of the latter study are reported in detail, and they are compared with predictions based on the results of the earlier work.

After the completion of our earlier structure study on isoxazole [1] by double resonance modulation (DRM) microwave spectroscopy [2] we were very pleased to find that the rotational constants which we had obtained for the ^{15}N-species of that molecule agreed extremely well with those determined at the same time in the Zeeman work on isoxazole and oxazole by Davidson, Burnham, Siegel, Beak and Flygare [3]. In contrast to that, the rotational constants which we have now obtained by the same techniques for the ^{15}N-species of oxazole (preceeding paper) differ noticeably (+1.260 MHz, +1.265 MHz and −0.432 MHz in A, B, and C, respectively) from the values reported in the aforementioned study and, as the nitrogen-atom lies close to a principal inertial axis (*b*-axis, see Fig. 1 of the preceeding paper), the values of the bond distances and angles in oxazole are affected significantly if one or the other set of rotational constants for the ^{15}N-species are adopted in the structure calculation.

In an attempt to clarify this situation, we considered it desirable to perform an additional DRM check in order to establish unequivocally that the numerous *Q*-branch signals (see Table 1) which we had ascribed to the ^{15}N-species of oxazole are not due to an excited vibration state, but belong indeed to the same spectrum as the R-branch transitions which include four DRM pump transitions ($J = 1 \to 2$, marked with an asterisk in Section I of Table 1) identified and measured in the Zeeman study by Flygare and collaborators. To this end we have verified (see Fig. 1) that each of the R-branch transitions $2_{02} \to 3_{03} = 33997.58$ MHz and $2_{12} \to 3_{13} = 33937.28$ MHz can be DR-modulated not only via the pair of pump transitions $1_{01} \to 2_{02} = 24532.1$ MHz or $1_{11} \to 2_{02} = 23885.2$ MHz and $1_{11} \to 2_{12} = 23949.4$ MHz or $1_{01} \to 2_{12} = 24596.3$ MHz, respectively, which had been identified in the Zeeman study [3], but also via the DRM-predicted Q-branch transitions $3_{03} \to 3_{22} = 24379.3$ MHz (in the case of the $2_{02} \to 3_{03}$) or $3_{13} \to 3_{12} = 24058.0$ MHz (in the case of the $2_{12} \to 3_{13}$) which according to the Zeeman work should occur at 24370.8 MHz and at 24049.5 MHz, respectively.

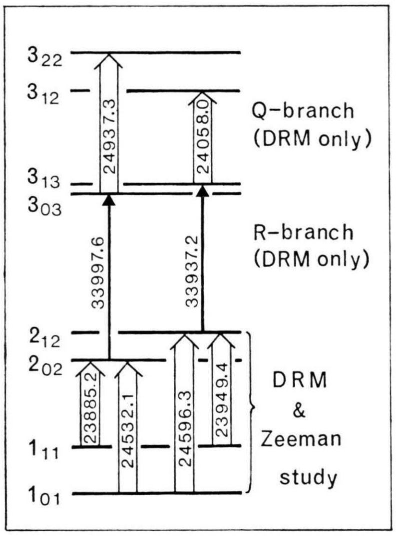

Fig. 1. DRM experiment to link the four $J = 1 \to 2$ R-branch transitions of the Zeeman study with R- and Q-branch transitions (see Table 1) of the DRM study. ("Fat" arrows indicate pump transitions. Separation between energy levels not drawn to scale.)

In conjunction with, *firstly*, the absence of an observable hyperfine splitting from all transitions listed in column I of Table 1, *secondly*, the perfect agreement of the value of the inertial defect resulting from the DRM work on the ^{15}N-species with the other eight isotopic forms (preceeding paper, row 17

Reprint requests to Dr. O. L. Stiefvater, School of Physical and Molecular Sciences, University College of N.-Wales, Bangor LL57 2UW-Gwynedd, Großbritannien.

Table 1. Comparison between the spectrum of the ^{15}N-species of oxazole as deduced from recent DRM (I)- and earlier Zeeman-work (II).

Transition	I DRM-study Frequency (in MHz)	 Obs.-calc.	II Zeeman-study Frequency (in MHz)	 Obs.-calc.	I−II
$0_{0,0} - 1_{0,1}$	14246.72	....	14245.96	− 0.08	0.84
$0_{0,0} - 1_{1,1}$	14893.63	....	14892.90	+ 0.10	0.83
$1_{0,1} - 2_{0,2}$	24532.09 *	P	24532.08	− 0.02	− 0.01
$1_{1,1} - 2_{1,2}$	23949.45 *	P	23949.44	− 0.04	− 0.03
$1_{1,0} - 2_{1,1}$	33037.33	....	33033.95	− 0.01	3.37
$1_{0,1} - 2_{1,2}$	24596.36 *	P	24596.40	+ 0.01	− 0.03
$1_{1,1} - 2_{0,2}$	23885.18 *	P	23885.15	− 0.03	0.00
$2_{1,2} - 2_{1,1}$	13631.84	....	13626.76	+ 0.01	5.09
$2_{0,2} - 2_{2,1}$	15636.84	....	15631.76	− 0.03	5.05
$2_{0,2} - 3_{0,3}$	33997.58	+ 0.06	33998.42	....	− 0.90
$2_{1,2} - 3_{1,3}$	33937.20	− 0.06	33938.15	....	− 0.89
$3_{0,3} - 3_{2,2}$	24379.30	P	24370.83	....	8.47
$3_{1,3} - 3_{1,2}$	24058.03	P	24049.46	....	8.57
$5_{3,3} - 5_{3,2}$	22813.71	P	22804.77	....	8.94
$5_{1,4} - 5_{3,3}$	33928.24	− 0.02	33916.34	....	11.92
$5_{2,3} - 5_{4,2}$	24977.37	P	24969.12	....	8.25
$5_{2,4} - 5_{2,3}$	33815.97	+ 0.13	33803.85	....	11.99
$6_{4,3} - 6_{4,2}$	21586.21	P	21577.02	....	9.19
$6_{2,4} - 6_{4,3}$	33899.19	− 0.04	33887.31	....	11.92
$6_{3,3} - 6_{5,2}$	25731.05	P	25732.09	....	7.96
$6_{3,4} - 6_{3,3}$	33564.83	+ 0.03	33552.66	....	12.14
$7_{5,3} - 7_{5,2}$	19941.49	P	19932.08	....	9.41
$7_{3,4} - 7_{5,3}$	33918.02	+ 0.02	33906.14	....	11.86
$8_{5,3} - 8_{6,2}$	19583.88	P	19575.34	....	8.54
$8_{5,4} - 8_{5,3}$	32304.89	+ 0.07	32292.02	....	12.80
$8_{5,3} - 8_{7,2}$	28977.71	+ 0.02	28971.02	....	6.67
$9_{6,3} - 9_{7,2}$	18724.82	P	18717.01	....	7.81
$9_{5,4} - 9_{6,3}$	31332.52	+ 0.05	31319.34	....	13.13
$9_{6,4} - 9_{6,3}$	31080.25	− 0.08	31066.97	....	13.36
$9_{6,3} - 9_{8,2}$	31853.95	− 0.04	31848.38	....	5.61
$10_{7,3} - 10_{8,2}$	18384.38	P	18377.66	....	6.72
$10_{6,4} - 10_{7,3}$	29926.10	+ 0.04	29912.59	....	13.47
$10_{7,4} - 10_{7,3}$	29356.82	+ 0.12	29342.71	....	15.99
$10_{7,3} - 10_{9,2}$	35768.42	− 0.03	35764.14	....	4.31
$11_{8,3} - 11_{9,2}$	18747.66	P	18742.35	....	5.31
$11_{7,4} - 11_{8,3}$	28297.72	+ 0.03	28284.21	....	13.54
$12_{9,4} - 12_{9,3}$	24470.28	P	24455.27	....	15.01
$12_{9,4} - 12_{10,3}$	36055.81	+ 0.11	36045.32	....	10.49
$13_{9,4} - 13_{10,3}$	25278.24	P	25266.14	....	12.10
$13_{8,5} - 13_{9,4}$	39586.44	+ 0.04	39568.58	....	17.82
$13_{9,5} - 13_{9,4}$	39206.87	+ 0.04	39188.56	....	18.27
$13_{10,4} - 13_{10,3}$	21477.68	P	21462.50	....	15.18
$13_{10,4} - 13_{11,3}$	37305.41	− 0.08	37295.62	....	9.87
$13_{10,3} - 13_{11,2}$	22041.32	P	22039.45	....	1.87
$13_{11,2} - 13_{12,1}$	32495.25	0.00	32495.70	....	− 0.44
$14_{10,4} - 14_{11,3}$	24426.22	P	24415.75	....	10.47
$14_{9,5} - 14_{10,4}$	37850.52	− 0.10	37832.12	....	18.50
$14_{10,5} - 14_{10,4}$	37082.59	+ 0.01	37063.20	....	19.39
$14_{11,4} - 14_{11,3}$	18287.50	P	18272.48	....	15.02
$14_{11,4} - 14_{12,3}$	38913.78	+ 0.10	38904.60	....	9.18
$14_{11,3} - 14_{12,2}$	25039.71	P	25039.62	....	0.09
$14_{12,2} - 14_{13,1}$	37078.52	− 0.03	37078.52	....	0.00
$15_{11,4} - 15_{12,3}$	24328.66	P	24320.36	....	8.30
$15_{10,5} - 15_{11,4}$	35838.24	+ 0.02	35819.40	....	18.82
$15_{11,4} - 15_{11,5}$	34384.46	− 0.04	34364.01	....	20.49
$15_{12,3} - 15_{13,2}$	28842.54	+ 0.08	28843.87	....	− 1.41
$16_{12,4} - 16_{13,3}$	25145.54	P	25139.82	....	5.72
$16_{11,5} - 16_{12,4}$	33753.92	+ 0.03	33735.38	....	18.51
$16_{12,5} - 16_{12,4}$	31169.23	− 0.04	31147.90	....	21.37
$16_{13,3} - 16_{14,2}$	33261.02	− 0.12	33263.42	....	− 2.40
$18_{14,5} - 18_{14,4}$	23682.59	P	23660.69	....	21.90
$18_{13,5} - 18_{14,4}$	30510.78	+ 0.16	30495.70	....	15.24
$18_{14,4} - 18_{15,3}$	29802.45	− 0.08	29802.46	....	0.07
$19_{15,5} - 19_{15,4}$	19723.95	P	19711.61	....	21.90
$19_{14,5} - 19_{15,4}$	29919.04	+ 0.04	29906.69	....	12.32
$19_{15,4} - 19_{16,3}$	33569.37	− 0.07	33571.89	....	− 2.45
$23_{18,6} - 23_{18,5}$	24784.96	P	24755.44	....	29.52
$23_{17,6} - 23_{18,5}$	35583.75	+ 0.11	35566.10	....	17.54
$23_{18,5} - 23_{19,4}$	38015.94	+ 0.01	38018.99	....	− 3.06
$24_{19,6} - 24_{19,5}$	20236.66	P	20208.44	....	28.22
$24_{18,6} - 24_{19,5}$	35480.52	+ 0.03	35467.50	....	12.99

Rotational parameters:

		I		II		I−II
A	in MHz	10042.256	(0.007)	10040.996	(0.016)	1.260
B		9395.346	(0.007)	9394.081	(0.013)	1.265
C		4851.376	(0.006)	4851.808	(0.008)	− 0.432
τ_{aaaa}	in kHz	− 15.081	(0.069)	− 14.922	(ass'd)	....
τ_{bbbb}		− 15.300	(0.051)	− 15.728	(ass'd)	....
τ_{aabb}		0.0	(ass'd)	0.0	(ass'd)	....
τ_{abab}		− 7.400	(0.020)	− 7.489	(ass'd)	....

of Table 1) and, *finally*, in view of the fact that for the intermediate J-values ($5 < J < 12$) we were unable to detect Q-branch signals at the freqencies predicted from the rotational constants given in the Zeeman study [3], while for higher J-values only six out of 33 transitions were found within ±2 MHz of those predictions, the described experiment leaves us little room for doubting the correctness of the DRM analysis, which suggests that only four out of the nine transitions given in Table 1 of Ref. [3] are correctly assigned and measured. At the same time we are aware — especially in view of the good LSQ-fit of those nine transitions —, that the odds are very much against the DRM work as this was done at room temperature with the ^{15}N-species in its natural abundance of 0.36%, whereas the Zeeman study [3] was conducted at a temperature of −60 °C on a purified ^{15}N-sample, so that the intensity of transitions would have been about 10^3 times larger if instrumental features were ignored. We therefore consider it appropriate to publish the list of DRM identified transitions of what we have interpreted as the spectrum of the ^{15}N-species of oxazole, along with the transition frequencies observed in, or predicted on the basis of the Zeeman study. This may aid the work of future investigators interested in resolving the stated discrepancy between the DRM and Zeeman studies of the ^{15}N-species of oxazole.

To arrive at the transition frequencies given in Sect. II of Table 1, we have re-fitted the nine transitions of Ref. [3] (Table 1) with inclusion of the three distortion constants of the parent species (see Sect. III c of the preceeding paper). From the results of this fit, transitions were predicted for the same range of J-values as covered in the DRM work. In the last column of Table 1 the transitions thus predicted are compared with the calculated (rather than with the observed) transition frequencies identified in the DRM investigation. Transitions marked with P in column I of Table 1 were used as DRM pump transitions and, with the exception of the four R-branch lines measured in the Zeeman study, these transitions have not been "observed" in the strict sense of this term. For reasons given previously [2] we feel that we cannot determine the frequencies of such transitions to better than ±0.5 MHz and, accordingly, we do not include the pump transitions in the LSQ-fits of the spectra. Their obvious occurrence at the predicted frequencies adds, of course, significantly to our confidence in the assignments.

[1] a) O. L. Stiefvater, P. Nösberger, and J. Sheridan, Chem. Phys. **9**, 435 (1975). b) O. L. Stiefvater, J. Chem. Phys. **63**, 2569 (1975).

[2] O. L. Stiefvater, Z. Naturforsch. **30a**, 1742 (1975).

[3] J. R. Davidson, A. K. Burnham, B. Siegel, P. Beak, and W. H. Flygare, J. Amer. Chem. Soc. **96**, 7394 (1974).