Microwave Spectra of Furazan.
IV. Rotation Spectra of Vibrationally Excited States of Perdeuterated Furazan

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The pure rotation spectra of molecules in 25 vibrationally excited states of perdeuterated furazan, $C_2D_2N_2O$, have been studied by double resonance modulation (DRM) microwave spectroscopy. Twelve of these spectra have been correlated, – on the basis of relative intensity measurements under DRM –, with fundamental vibrations as previously established by IR spectroscopy. Rotational parameters for these 12 fundamental levels are reported, and the contributions to the effective rotational constants and to the inertia defect of the ground state of d_2-furazan have been determined for 10 modes of vibration.

I. Introduction

In the preceding paper [1 a] we have reported the pure rotational spectra of twelve vibrationally excited states of the heterocyclic compound furazan, $C_2H_2N_2O$. These spectra were shown to arise from molecules in the first excited levels of the twelve lowest fundamental vibrations of this molecule. The experimental work for that study had been carried out concurrently with the study by DRM microwave spectroscopy of the rotation spectra of isotopic forms, which was necessary for the determination of the complete substitution structure of this compound [1 b].

While the sensitivity and, more importantly, the molecular *selectivity* provided by the double resonance modulation (DRM) technique [1 d, e], [2] readily allowed the otherwise expensive isotopomers with ^{13}C, ^{15}N and ^{18}O to be studied in their natural abundances, the comparatively inexpensive isotopic forms d_1-furazan [1 c] and d_2-furazan, $C_2D_2N_2O$, were synthesised to facilitate their spectroscopic investigation. The resulting availability of a sample of d_2-furazan ($\sim 80\%$ enriched) allowed not only a second independent and complete determination of the ring structure of furazan [1 b], but it also invited a repetition of the rotational study of vibrationally excited states of this isotopomer.

In view of the fact that the satellites in the rotational spectrum due to excitation of each of the 12 lowest fundamental vibrations of normal furazan had been identified and analysed before [1 a], such a duplication of earlier work was considered as little more than a routine exercise in DRM spectroscopy which, nevertheless, would help the isotopic work then in hand. However, it soon became apparent that this lightheartedly begun study was to reveal a number of unexpected deviations from the previous data on excited states of normal furazan which, in turn, demanded a little bit more perseverance than had been expected initially. These differences between the present results and the previous data seem to justify the publication of this work. This appears also warranted by the fact that relatively little information exists in the literature concerning the variation of rotational parameters of vibrationally excited states upon deuteration of a compound of this size.

II. Experimental

The preparation of d_2-furazan has been described earlier [1 b]. The instrumental aspects of the present work were essentially identical with those described in the preceding paper [1 a]. A few DRM experiments however, which involved pump frequencies below the cut-off frequency of *K*-band waveguide (14.1 GHz), were conducted with a waveguide absorption cell of the next larger standard cross-section (*J*-band), and this resulted in the expected reduction of available pump power density by a factor 4. Additionally, the range of signal frequencies was slightly extended to just over 40 GHz.

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III. Spectroscopic Results

a) Rotational Assignments

Efficient DR-double search techniques for the assignment of vibrational satellite transitions in the pure rotation spectra of molecules have been described earlier [1 d, e], and details of the application of these techniques in the case of normal furazan are described in the preceding paper [1 a]. Those same DRM procedures were also applied in the present study of perdeuterated furazan, and they resulted in the rotational assignment of transitions from twelve fundamental, ten combination and three overtone levels of vibration. A DR-map [1 d] showing frequency displacements of satellites for the DR-connected transitions $4_{04} \rightarrow 4_{13} \twoheadrightarrow 4_{22}$ is given as Figure 1. Rotational parameters for the G.S. and the 12 lowest fundamentals of d_2-furazan, together with statistical information on each spectrum, is collected in Table 1. Measured frequencies of rotational transitions of molecules in the G.S. and in those 12 fundamental levels are given as an Appendix.

b) Correlation of Satellite Spectra with Particular Modes of Vibration

It was expected at the outset of this study that the rotation-vibration constants α_i for perdeuterated furazan would closely resemble those found for corresponding modes in normal furazan. On that basis, the rotation spectra of particular excited states seemed qualitatively predictable, and the displacement of satellite transitions from the G.S. lines was anticipated to resemble the pattern found in normal furazan. An extensive study of relative intensities for the purpose of ascertaining vibrational symmetries and, ultimately, for the correlation of assigned spectra with the excitation of particular modes of vibration and with the known IR data [3] for d_2-furazan, was expected to be unnecessary.

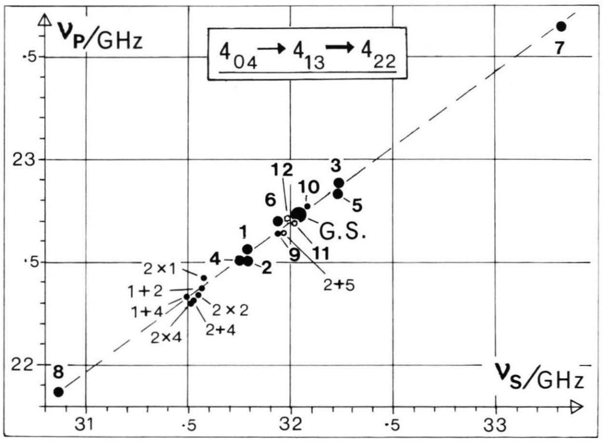

Fig. 1. DR-map of the connection $4_{04} \rightarrow 4_{13} \twoheadrightarrow 4_{22}$ in d_2-furazan, illustrating the displacements of vibrational satellites from the G.S. (The numbering 1 through 12 of satellites has been chosen so as to coincide with the labelling of modes in normal furazan [1 a].)

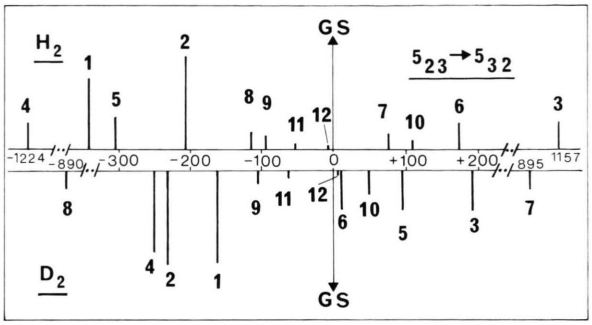

Fig. 2. Displacements (in MHz) of satellite transitions from the G.S. in normal (H_2) and perdeuterated (D_2) furazan.

However, these obviously too naive expectations were not fulfilled (see Fig. 2), and a consideration of the influence of symmetry and spin weights on the relative intensities of transitions, as well as the associated experiments, became necessary again (see [1 a], Sect. III c).

b.1. Symmetry, Spin Weights and Intensities [4]

The replacement of the two protons (fermions) of normal furazan by deuterium nuclei ($I_D = 1$, bosons) requires the total wavefunction, Ψ_{total}, of d_2-furazan to be even under the symmetry operation C_2 which simultaneously exchanges two equivalent nitrogens ($I_N = 1$, bosons) and two equivalent deuterium nuclei. This requires the product of rotational and spin parts of Ψ_{total} to be even when the vibrational factor is even under C_2, and to be odd when the vibrational function is odd. Of the 81 spin functions, which can be formed as products of 9 nitrogen with 9 deuterium spin states, 45 are even under C_2 and the remainder of 36 spin functions is odd. It follows from this that rotational transitions between levels of even symmetry ($K_- + K_+ =$ even) have to be assigned a weight factor of 5, those of odd rotational symmetry a weight factor of 4, when the vibrational function is even (A-species). The reverse weighting applies when the vibrational function is odd (B-species). These considerations are

Table 1. Rotational parameters of the G.S. and 12 vibrationally excited states of d_2-furazan.

1	Satellite spectrum		G.S.	1	2	3	4	5	6
2	Observed transitions		5 R & 94 Q	5 R & 86 Q	5 R & 90 Q	5 R & 95 Q	5 R & 100 Q	5 R & 96 Q	5 R & 101 Q
3	Range of J-values		1-3 & 2-24	1-3 & 3-31	1-3 & 3-29	1-3 & 4-29	1-3 & 3-29	1-3 & 2-29	1-3 & 3-32
4	St'd dev'n (MHz), (N_f)[a]		0.042 (99)	0.053 (79)	0.051 (95)	0.053 (99)	0.057 (74)	0.071 (89)	0.068 (79)
5	A	in MHz	9302.63(2)[b]	9268.03(2)	9282.72(2)	9295.51(3)	9278.48(3)	9334.63(3)	9280.23(3)
6	B		8997.27(2)	8968.75(2)	8953.08(2)	9014.32(3)	8947.52(3)	9010.67(3)	9002.43(3)
7	C		4570.73(2)	4573.50(2)	4572.26(2)	4548.55(2)	4570.75(2)	4565.77(3)	4572.84(3)
8	τ_{aaaa}	in kHz	- 14.9(30)	- 15.8(37)	- 18.6(33)	- 9.8(36)	- 6.7(41)	- 19.1(50)	+ 1.2(51)
9	τ_{bbbb}		- 18.7(30)	- 16.3(34)	- 21.0(33)	- 15.1(34)	- 14.0(39)	- 25.6(48)	- 0.7(50)
10	τ_{aabb}		- 8.7(90)	- 18.3(108)	- 21.3(97)	+ 12.7(120)	+ 13.0(120)	- 52.4(150)	+ 73.1(153)
11	τ_{abab}		- 4.2(30)	+ 1.1(36)	- 0.1(32)	- 11.4(36)	- 11.3(40)	+ 12.6(50)	- 35.8(50)
12	$\alpha_A = A_{G.S.} - A_V$		-	+ 34.60(2)[c]	+ 19.91(2)	+ 7.12(3)	+ 24.15(3)	- 32.00(3)	+ 22.40(3)
13	$\alpha_B = B_{G.S.} - B_V$		-	+ 28.52(2)	+ 44.19(2)	- 17.05(3)	+ 49.75(3)	- 13.40(3)	- 5.16(3)
14	$\alpha_C = C_{G.S.} - C_V$		-	- 2.77(2)	- 1.53(2)	+ 22.18(2)	- 0.02(2)	+ 4.96(3)	- 2.11(3)
15	I_a	in uÅ^2 [d]	54.3261(1)	54.5289(1)	54.4427(1)	54.3678(2)	54.4675(2)	54.1399(2)	54.4573(2)
16	I_b		56.1699(1)	56.3485(1)	56.4471(1)	56.0637(2)	56.4822(2)	56.0864(2)	56.1377(2)
17	I_c		110.5678(3)	110.5009(4)	110.5310(4)	111.1070(5)	110.5674(5)	110.6880(6)	110.5168(6)
18	$I.D. = I_c - I_a - I_b$		+ 0.0717(3)	- 0.3766(5)	- 0.3588(5)	+ 0.6756(5)	- 0.3824(5)	+ 0.4617(6)	- 0.0782(7)
19	$\delta(ID) = ID_V - ID_{G.S.}$		-	- 0.4483(5)	- 0.4305(5)	+ 0.6039(5)	- 0.4541(5)	+ 0.3900(6)	- 0.1499(7)
20	Species/frequ'y (in cm^{-1})			B_2 / 631	A_2 / 555	B_1 / 808	B_2 / 641	A_1 / 744	A_2 / 757
21	in-plane/out-of-plane			out	out	in	out	in	out
22	I.R. mode , level			$\nu_{15} = 1$	$\nu_8 = 1$	$\nu_{13} = 1$	$\nu_{14} = 1$	$\nu_6 = 1$	$\nu_7 = 1$

1	Satellite spectrum			7	8	9	10	11	12
2	Observed transitions			8 R & 75 Q	6 R & 108 Q	5 R & 89 Q	5 R & 111 Q	4 R & 80 Q	4 R & 66 Q
3	Range of J-values			1-4 & 3-29	1-3 & 3-30	1-3 & 4-30	1-3 & 3-34	2-3 & 3-29	2-3 & 3-31
4	St'd dev'n (MHz), (N_f) [a]			0.46 (64)	0.36 (92)	0.052 (94)	0.055 (99)	0.053 (84)	0.082 (65)
5	A	in MHz		*9301.1(3)*[b]	*9308.0(2)*	9304.92(3)	9308.15(3)	9303.04(3)	9279.96(4)
6	B			*8973.8(3)*	*8988.2(2)*	8984.86(3)	9006.47(3)	8972.99(3)	8990.33(4)
7	C			*4367.4(3)*	*4739.4(2)*	4579.30(2)	4570.16(2)	4559.25(2)	4562.02(3)
8	τ_{aaaa}	in kHz		-	-	- 10.9(34)	- 12.2(36)	- 13.4(39)	+ 4.1(74)
9	τ_{bbbb}			-	-	- 14.7(33)	- 16.3(36)	- 17.1(36)	- 0.8(69)
10	τ_{aabb}			-	-	+ 3.1(99)	- 0.4(114)	- 3.6(115)	+ 50.5(220)
11	τ_{abab}			-	-	- 7.9(33)	- 6.9(38)	- 6.0(38)	- 24.0(72)
12	$\alpha_A = A_{G.S.} - A_V$			*+ 1.4(3)*	*- 5.4(2)*	- 2.29(3)	- 5.52(3)	- 0.41(3)	+ 22.67(4)
13	$\alpha_B = B_{G.S.} - B_V$			*+ 23.5(3)*	*+ 9.1(2)*	+ 12.41(3)	- 9.20(3)	+ 24.28(3)	+ 6.94(4)
14	$\alpha_C = C_{G.S.} - C_V$			*+203.3(3)*	*-168.7(2)*	- 8.57(2)	+ 0.57(2)	+ 11.48(2)	+ 8.71(3)
15	I_a	in uÅ^2 [d]		*54.335(2)*	*54.295(1)*	54.3128(2)	54.2939(2)	54.3237(2)	54.4588(3)
16	I_b			*56.317(2)*	*56.227(2)*	56.2475(2)	56.1126(2)	56.3219(2)	56.2133(3)
17	I_c			*115.717(6)*	*106.633(4)*	110.3609(5)	110.5816(5)	110.8462(5)	110.7789(7)
18	$I.D. = I_c - I_a - I_b$			*+ 5.064(7)*	*- 3.889(4)*	- 0.1994(5)	+ 0.1751(5)	+ 0.2006(5)	+ 0.1068(7)
19	$\delta(ID) = ID_V - ID_{G.S.}$			*+ 4.992(7)*	*- 3.961(4)*	- 0.2711(5)	+ 0.1034(5)	+ 0.1289(5)	+ 0.0351(7)
20	Species/frequ'y (in cm^{-1})			B_1 / 914 ?	A_1 / 895 ?	A_1 / 1004	B_1 / 939	A_1 / 1222	A_1 / 1401
21	in-plane / out-of-plane			in ?	in ?	in	in	in	in
22	I.R. mode , level			$\nu_{12} = 1$?	$\nu_5 = 1$?	$_4 = 1$	$\nu_{11} = 1$	$\nu_3 = 1$	$\nu_2 = 1$

[a] N_f is the number of transitions in the LSQ fit. – [b] All uncertainties are 3σ-values, and given in units of the last digit. – [c] Uncertainties in the G.S. parameters have been ignored when differences were taken. – [d] Conversion factor: 505 376 uÅ^2 MHz.

Table 2. Nuclear spin weights for even and odd rotational transitions in dependence of the symmetry of the excited vibrational levels in d_2-furazan. $\Psi_{\text{total}} = \text{even}$ (exchange of two pairs of equivalent bosons).

Symmetry of vibrational wavefunction	Rotational symmetry $K_- + K_+$	Nuclear spin weight
$\Psi_{\text{vib.}} = \text{even}$	even	5
	odd	4
$\Psi_{\text{vib.}} = \text{odd}$	even	4
	odd	5

summarised in Table 2. As in the case of normal furazan, relative intensity comparisons [5] between rotationally even and odd transitions *within* a particular satellite spectrum will therefore allow the determination of the symmetric or antisymmetric nature of the vibrational mode excited. As before [1a], the sign of the inertia defect contribution δ(ID) permits a tentative subdivision of the excited states into "in-plane" (A_1, B_1) and "out-of-plane" (A_2, B_2) vibrations.

b.2. Experimental Results

2.1. Intensity Measurements under SEM

Relative intensity comparisons between rotationally even and odd transitions were arried out under Stark effect modulation (SEM) [6] *within* each of the four most intense satellite spectra. The procedure for extracting the vibrational symmetry of states from such experiments has been detailed in the previous paper ([1a], Sect. III.c.2). From 3, 3, 4 and 3 pairs of transitions in the case of the satellite spectra now labelled '1', '2', '4', and '6' for consistency with the numbering in normal furazan, unequivocal results were obtained. These indicated that satellites '1' and '4' arise from excitation of antisymmetric modes (B-species), while satellites '2' and '6' stem from symmetric vibrations (A-species). Since the inertia defect contribution, δ(ID) (see Table 1), of all four states had emerged as negative from the rotational analysis, the correlation of '1' and '4' with excitation of the two B_2 modes, and that of '2' and '6' with the two A_2 vibrations (IR inactive) was evident. Subsequent intensity comparisons between these four states and with the G.S. spectrum confirmed this conclusion. The results are included in Table 4. (The reader may recall that satellite '4', which arises from the state $v_{14} = 1$, was found strongly perturbed in normal furazan [1a]. No corresponding anomalies were observed in the d_2-form).

Due to the presence in the d_2-sample of normal furazan (~5%), but particularly of d_1-furazan (~15%) with their associated rotational spectra, the selection of pairs of rotationally even and odd transitions which were suitable for the determination of vibrational symmetries from relative intensity measurements under SEM became increasingly difficult. This spectral complexity prompted us to consider the feasibility of relative intensity measurements under double resonance modulation.

2.2. Relative Intensity Studies under DRM

The basic condition for relative intensity work in microwave spectroscopy is that of a "flat" (unchanging) response of the instrument over the frequency range of interest. This condition is generally better satisfied when the absorption cell consists of an "empty" section of waveguide (as in DRM) than when the cell contains a Stark septum (as in SEM instruments). Moreover, the probability of either of the signals to be compared being overlapped by a third signal due to a different rotational transition is generally very small under DRM. This is a consequence of the *selectivity* of the molecular modulation process employed in this technique.

These quite obvious advantages of DRM over SEM spectroscopy (in the latter all signals from all molecular forms, including vibration states and isotopomers, are modulated simultaneously) seem to be counterbalanced by the consideration that a quantitative comparison of DRM signal amplitudes appears meaningful only if both DRM signals are either fully modulated, so that no overlap between the DR lobes and the zero-pump line occurs (which, strictly, is impossible), or if the two signals are modulated to the "*same degree*". (This term is meant to denote an *equal* proportion of overlap between the DR lobes and the zero-pump line.) Since the degree of modulation of a DRM signal depends on both the matrix element of the pump transition as well as on the strength of the radiation field available at the pump frequency (for details, see [1d] and references quoted there), an equal degree of modulation can normally *not* be assumed for different DRM signals. This, presumably, is the reason why relative intensity comparisons under DRM have not been considered in the past.

In the present study, in which we were interested in the correlation of a set of vibrational satellites (consisting in the main of the same rotational transitions) with data from IR spectroscopy, the above reservations concerning differing degrees of modulation of DRM signals can be largely cast aside: In comparing the intensity (amplitude) of a particular rotational transition of one satellite spectrum with that of the *same* rotational transition in another satellite spectrum, the variation of the transition moments of the two (rotationally identical) pump transitions is so minute that it may be disregarded. Consequently, the two DRM signal transitions will be modulated to the same degree, provided the respective pump transitions lie close enough to each other to justify the assumption of equal pump power density at the two pump frequencies. If this latter condition is met, the corresponding DRM signals will provide intensity ratios which are equally meaningful and reliable as those obtained from SEM measurements.

This conclusion has been tested experimentally on six transitions with successive J-values of the sequence of DRM signals arising from the connection $J_{J-3,4} \rightarrow J_{J-2,3} \twoheadrightarrow J_{J-1,2}$ of the satellites now labelled '3' and '5'. The relevant information is gathered in Table 3. The experiment yielded both the vibrational symmetries of these two states as well as their vibrational energy separation on account of the following considerations: If the satellites '3' and '5' had the same vibrational symmetries, pairs of equal rotational transitions in the two states would show a constant intensity ratio for all six J-values. This would immediately yield the vibrational energy separation between '3' and '5' via the Boltzmann law. If, on the other hand, states '3' and '5' have opposite vibrational symmetry (and therefore different spin weights in the pairs with even and odd rotational symmetry), the intensity ratios must alternate for successive J-values. As a little reflection shows, the assumption that state '5' is even and state '3' is odd requires pairs with even J-values (odd rotational symmetry) to give intensity ratios (R_0), which are 25/16 times *larger* than those of pairs with odd J-values. The reverse assumption ('5' = odd, '3' = even) requires pairs of even J-values to yield intensity ratios which are 16/25 times *smaller* than those of odd J-values.

Inspection of the experimental results in Table 3 shows, firstly, that the intensity ratios alternate with J. This proves that state '3' and '5' have opposite vibrational symmetry. Secondly, since the pairs of odd rotational symmetry (even J-values) have larger intensity ratios than those of even rotational symmetry (odd J-values), it follows that satellite '3' belongs to an antisymmetric excited vibration state (B-species), and that '5' arises from a symmetric vibrational mode (A-species). The intensity ratios, R_o and R_e for rotationally odd and even transitions, averaged over three J-values in both cases, are seen to conform quite closely with the expectation of $25/16 = 1.56$ (observed: 1.52). – After the effects of symmetry and spin weights on the measured intensity ratios were properly taken into account, the Boltzmann factor was obtained from even and odd rotational transitions to give an average of 0.747 ± 0.010. This indicated that the antisymmetric vibration '3' lies 61 ± 4 cm^{-1} higher in energy than the symmetric mode '5'. Since the inertia defect contribution δ(ID) from both vibrations had been ascertained as positive, suggesting "in-plane" modes, it had to be concluded that '3' arises from excitation of a B_1 vibration, whereas '5' stems from an A_1 mode. (The same conclusion had been drawn earlier from one intensity comparison in satellite '5' under SEM.) – Comparison with the IR data [3] left no choice but to correlate '5' with excitation of the mode ν_6 at 744 cm^{-1} and satellite '3' with the mode ν_{13} at 808 cm^{-1}. Subsequent intensity comparisons under DRM with the G.S. spectrum and with the four previously correlated satellites were in full agreement with this interpretation. (The reader may recall that the rotation spectrum of the state $\nu_{13} = 1$ was found perturbed in normal furazan [1a]. No rotational anomalies were observed in the corresponding satellite spectrum in d_2-furazan.)

Analogous experiments under DRM as described above were carried out on transitions of the satellite spectra now labelled '9', '10' and '11' with equally conclusive results concerning their vibrational symmetries and their mutual energy separations. The most intense ('10') of these three satellites was compared with the G.S. spectrum, as were the satellites '7' and '8', which could be correlated with excitation of the modes ν_{12} and ν_5, respectively. The weakest satellite ('12') was correlatable with excitation of the mode ν_2 at 1401 cm^{-1} on account of qualitatively similar rotation-vibration constants as those found for that mode in normal furazan and on account of the appropriately small intensity of its rotational transitions.

Table 4 summarizes the results of intensity comparisons by SEM and DRM techniques and correlates the findings with the IR data [3] for d_2-furazan.

c) Rotational Anomalies in the Satellite Spectra

As in the case of normal furazan, deviations of transition frequencies from the rigid rotor pattern were

Table 3. Relative intensity comparison between satellites ‘3’ and ‘5’ under double resonance modulation.

State	PUMP TRANSITION			SPIN STATISTICS			SIGNAL TRANSITION			MEASURED INTENSITY RATIO		
	$(J,K_-,K_+)_3 \leftarrow (J,K_-,K_+)_2$	Frequ'y in MHz	Δν	Rot'l symm'y $K_- + K_+$	Nucl. spin weight for '3' = o '5' = e	for '3' = e '5' = o	$(J,K_-,K_+)_2 \leftarrow (J,K_-,K_+)_1$	Frequ'y in MHz	Δν	D R M signal amp'de	$I_{'3'} / I_{'5'}$ R_o	R_e
'3'	4 3 2 4 2 3	23074.0	16.2	odd	5	4	4 2 3 4 1 4	32221.6	3.6	55	0.917	
'5'		23090.2			4	5		32218.0		60		
'3'	5 4 2 5 3 3	23142.8	38.2	even	4	5	5 3 3 5 2 4	32209.3	6.5	37		0.617
'5'		23181.0			5	4		32202.8		60		
'3'	6 5 2 6 4 3	23261.1	75.2	odd	5	4	6 4 3 6 3 4	32191.6	9.9	60	0.909	
'5'		23336.3			4	5		32181.5		66		
'3'	7 6 2 7 5 3	23445.5	131.5	even	4	5	7 5 3 7 4 4	32169.7	13.0	35		0.583
'5'		23577.0			5	4		32156.7		60		
'3'	8 7 2 8 6 3	23712.8	211.0	odd	5	4	8 6 3 8 5 4	32146.8	12.6	60	0.938	
'5'		23923.8			4	5		32134.2		64		
'3'	9 8 2 9 7 3	24079.5	316.7	even	4	5	9 7 3 9 6 4	32128.9	6.0	60		0.612
'5'		24396.2			5	4		32122.9		98		
											$\overline{R_o} = \frac{175}{190} = 0.921$	$\overline{R_e} = \frac{132}{218} = 0.605$

$$\left.\begin{aligned} B_{'3'/'5',\,o} &= 0.921 \times (4/5) = 0.737 \\ B_{'3'/'5',\,e} &= 0.605 \times (5/4) = 0.756 \end{aligned}\right\} \quad \overline{B_{'3'/'5'}} = 0.747 \pm 0.010$$

$$\underline{\underline{\Delta\nu_{'3'/'5'} = (61 \pm 4)\ \mathrm{cm}^{-1}}}$$

Table 4. Summary of results from intensity comparison between the satellite spectra of d_2-furazan, and correlation with IR data.

MICROWAVE				INFRARED		
Designation	Symmetry of $\Psi_{vib.}$	Vibrat'l energy (in cm^{-1})	δ(ID) (in $u\AA^2$)	Designation	Energy (in cm^{-1})	Symmetry species
1	odd	∿ 630	− 0.4483(5)	ν_{15}	631	B_2
2	even	∿ 560	− 0.4305(5)	ν_8	555	A_2
3	odd*	∿ 810*	+ 0.6039(5)	ν_{13}	808	B_1
4	odd	∿ 640	− 0.4541(5)	ν_{14}	641	B_2
5	even*	∿ 750*	+ 0.3900(6)	ν_6	744	A_1
6	even	∿ 760	− 0.1499(7)	ν_7	757	A_2
7	?	∿ 900	+ *4.992 ?*	ν_{12}	914	B_1
8	?		− *3.961 ?*	ν_5	895	A_1
9	even*	∿ 1000*	− 0.2711(5)	ν_4	1004	A_1
10	odd*	∿ 940*	+ 0.1034(5)	ν_{11}	939	B_1
11	even*	∿ 1230*	+ 0.1289(5)	ν_3	1222	A_1
12	even**	∿ 1400**	+ 0.0351(7)	ν_2	1401	A_1

* Vibrational symmetry and energy separations from intensity comparisons under DRM.
** Estimated.

noted in several satellite spectra of d_2-furazan. Thus, transitions with J-values above $J = 20$ deviate increasingly from expectation to reach discrepancies of up to 20 MHz at the highest observed J-values in the satellite spectra '1' and '4'. Similar effects were noted in the satellite spectra '5' and '6', where the observed transitions with the highest J-values deviate by up to 13 MHz from expectations based on rigid rotor behaviour. In deriving rotational and distortion constants from these four spectra the apparently perturbed high-J transitions were omitted from the least-squares fits to yield the data of Table 1. The noticeable variation from G.S. values of the distortion constants (which are relatively poorly determined) may be taken as a further manifestation of these small perturbations within the mentioned four satellites.

Persistent deviations from rigid rotor frequencies throughout the entire range of J-values were encountered in the satellites '7' and '8'. However, in contrast to the findings with the Coriolis dyad '3', '4' in normal furazan [1 a], the deviations from rigid-rotor behaviour in states '7' and '8' of d_2-furazan range generally around 10 MHz or less (up to 10 GHz in states '3' and '4' of normal furazan). The small magnitude of these deviations allowed these satellite spectra to be investigated up to J-values of 29 and 30 by the usual DRM techniques without excessive effort. – Initial LSQ-fits of all identified transitions of both these spectra resulted in standard deviations of the fits of ∼2.5 MHz, with the most prominent incompatibilities occurring not amongst the high J-values, but within the few low-J R-branch transitions of each satellite. The parameters given in Table 1 were obtained by omission from the LSQ-fits of the transitions with the largest frequency deviations and the simultaneous restriction to the $J = 1 \rightarrow 2$ R-branch transitions. In consideration of these manipulations we feel that the uncertainties quoted for the rotational constants in Table 1 for these states should, realistically, be increased by a factor of at least 10. The distortion constants which resulted from these fits were unacceptably large (1.1–4.2 MHz), of approximately equal magnitude, but of opposite signs in state '7' and '8'.

As is apparent from the quoted constants, the coupling between states '7' and '8' manifests itself in anomalously large changes in opposite directions of the rotational constants C. This indicates, in keeping with Jahn's rule [7], that the interaction between states '7' and '8' (ν_{12} and ν_5) in d_2-furazan is to be ascribed to Coriolis forces.

d) Summary and Appraisal of Results

In analogy and for comparison with the preceding study on normal furazan [1 a], an illustration of the rotationally investigated excited vibration states of d_2-furazan is presented as Figure 3. An explanation of the entries in this diagram may be found in the previous paper ([1 a], Sect. III d). As is made obvious through the higher "sails" in Fig. 3, all satellite spectra of d_2-furazan, including the perturbed pair $\nu_5 = 1$ and $\nu_{12} = 1$ (satellites '7' and '8'), could be investigated up to higher J-values than in normal furazan.

The prediction and subsequent experimental examination of the pure rotation spectra of vibrational overtone and combination levels in d_2-furazan, as indicated in Fig. 3, followed the same principles as described previously ([1 a], Sect. III e). In duplication of the thoughts outlined there, the contributions from individual modes of vibration to the effective rotational constants and to the inertia defect of d_2-furazan are presented as Table 5. Under omission of the uncertain contributions from states '7' and '8' (modes ν_{12} and ν_5) Table 5 indicates that the 10 vibrations for which definite results have been obtained lead to an

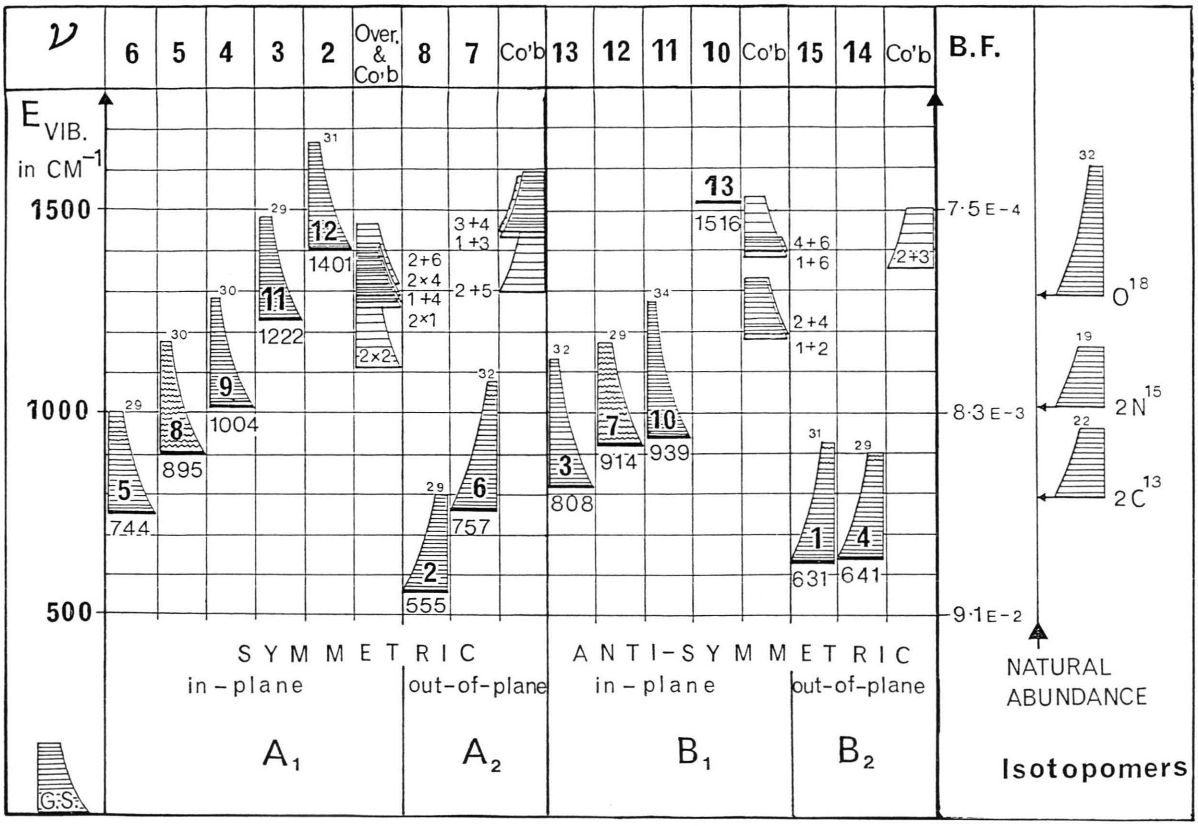

Fig. 3. Illustration of the excited vibration states of d_2-furazan investigated in this study.

Table 5. Contributions from individual modes to the effective rotational constants (in MHz) and to the inertia defect (in uÅ^2) in d_2-furazan.

Mode i	$\alpha_{A,i}/2$	$\alpha_{B,i}/2$	$\alpha_{C,i}/2$	$\delta(ID)_i/2$
1	+ 17.30	+ 14.26	− 1.39	− 0.2242
2	+ 9.96	+ 22.10	− 0.76	− 0.2152
3	+ 3.56	− 8.53	+ 11.09	+ 0.3020
4	+ 12.07	+ 24.87	− 0.01	− 0.2270
5	− 16.00	− 6.70	+ 2.48	+ 0.1950
6	+ 11.20	− 2.58	− 1.06	− 0.0750
(7)	*(+ 0.7)*	*(+ 11.8)*	*(+101.7)*	*(+ 2.532)*
(8)	*(− 2.7)*	*(+ 4.5)*	*(− 84.4)*	*(− 1.981)*
9	− 1.15	+ 6.21	− 4.28	− 0.1355
10	− 2.76	− 4.60	+ 0.29	+ 0.0517
11	− 0.20	+ 12.14	+ 5.74	+ 0.0644
12	+ 11.34	+ 3.47	+ 4.35	+ 0.0175
$\Sigma^{(10)}$	+ 45.32	+ 60.64	+ 16.45	− 0.2463
$R_e^{(10)}$	9347.95	9057.91	4587.18	
$I_e^{(10)}$	54.0628	55.7939	110.1714	
$(ID)^{(10)}$		+ 0.3147		

overall reduction of the rotational constants of the (hypothetical) equilibrium geometry of the molecule. If these reductions, $\sum \alpha_i/2$, are added to the effective G.S. constants, a set of rotational constants, $R_e^{(10)}$, is obtained which corresponds to d_2-furazan molecules in which 10 of the 15 normal modes are "frozen". Conversion of these constants to moments of inertia leads to the conclusion that the five remaining modes (i.e. ν_{12}, ν_5, ν_{10}, ν_9, and ν_1, for which no data are presently available) contribute $+0.315$ uÅ^2 to the inertia defect of d_2-furazan. This is approximately twice as much as in normal furazan. Consideration of the intertia defect contributions, δ(ID), from the ten modes leads to the same conclusion: While the inertia defect of d_2-furazan was found as $+0.072$ uÅ^2 in the G.S. (see Table 1), the ten modes studied here lead to a total contribution of -0.246 uÅ^2, which implies that the unstudied vibrations must jointly contribute $+0.318$ uÅ^2 to the inertia of d_2-furazan.

This rather large contribution re-emphasises the necessity of determining experimentally (i.e. by IR spectroscopy) the inertia defect contributions from the three unstudied vibrations, in particular from the C–D stretching modes at ~2300 cm^{-1}.

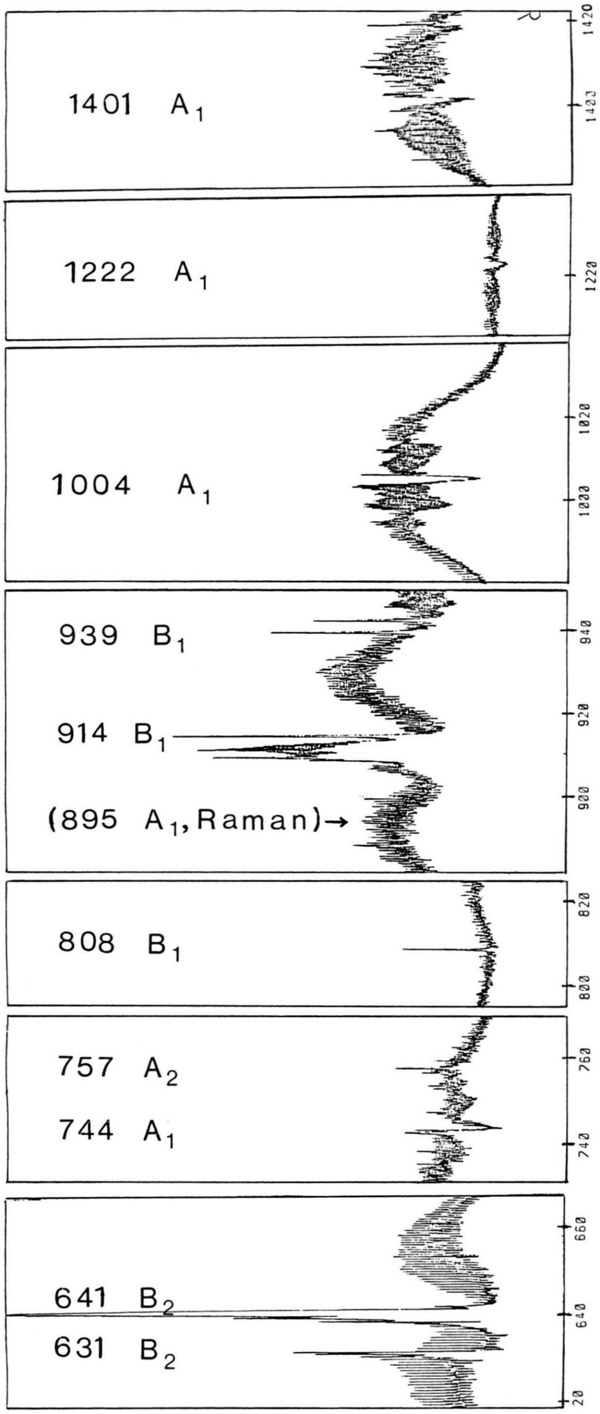

Fig. 4. High-resolution IR spectrum of d$_2$-furazan, showing the vibrational bands to to level studied in this work.

IV. Discussion

The results reported in this paper vindicate the view that the DRM technique allows more molecular information to be extracted from rotational spectroscopy than was considered possible in the past. The data of Table 1, together with those of Table 2 of the preceding paper, are expected to be of considerable assistance in culling complementary information from the analysis of the high-resolution IR bands of furazan.

Figure 4 shows the here relevant sections of the vibrational spectrum of d$_2$-furazan vapour, taken on a Bruker IFS 113 v interferometer with a resolution of 0.03 cm^{-1} at a sample pressure of 15 Torr. It shows 10 of the 12 vibrational bands which are the subject of the present investigation by rotational spectroscopy. The trace justifies the hope that the majority of the vibrational bands of furazan can be sufficiently resolved and appropriately analysed to yield vibration frequencies to ±0.001 cm^{-1} or better under the 10 times higher resolution of at least 0.003 cm^{-1} which is nowadays available on commercial IR instruments (e.g. Bruker IFS 120 HR). This task should be greatly facilitated through the use of the rotational information accumulated in this and the preceding study. We are optimistic that the modern, high-resolution IR techniques will allow the presently missing information on the remaining three vibrations of normal and d$_2$-furazan to be obtained. This will allow the vibrational effects from C–H and C–D stretching motions to be ascertained quantitatively. In conjunction with the proper analysis of the two different Coriolis dyads in normal and d$_2$-furazan, and together with the refined vibration frequencies expected from high-resolution IR spectroscopy, detailed knowledge of all vibrational effects and of the force field in furazan will no doubt emerge.

Acknowledgements

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Appendix

Measured transition frequencies (in MHz) of the G.S. and the first twelve fundamental levels in d$_2$-furazan.

Transition J KA KC → J KA KC	G.S.	1 $\nu_{15}=1$	2 $\nu_8=1$	3 $\nu_{13}=1$	4 $\nu_{14}=1$	5 $\nu_6=1$	6 $\nu_7=1$	7 $\nu_{12}=1$	8 $\nu_5=1$	9 $\nu_4=1$	10 $\nu_{11}=1$	11 $\nu_3=1$	12 $\nu_2=1$
R - branch													
0 0 0 1 1 1	13873.42	13841.5 P	13855.0 P	13844.1 P	13849.2 P	13900.3 P	13853.1 P	*13664.2 P*	*14053.4 P*	13884.2 P	13878.3 P		
1 0 1 2 1 2	23014.84	22988.48	22999.40	22941.2 P	22990.70	23013.78	22998.90	*22395.4 P*	*23536.4 P*	23042.8 P	23018.57	22980.8 P	22966.1 P
1 1 1 2 0 2	22694.15	22674.48	22651.90	22647.14	22641.72	22690.77	22708.43	*22050.90*	*23199.30*	22705.92	22702.10	22632.9 P	22662.7 P
1 0 1 2 2 1						32569.46			*32676.6*				
2 0 2 3 1 3	32009.42	31991.50	31985.96	31902.69	31973.87	32007.88	32010.82	*30977.35*	*32858.90*	32047.95	32013.84	31941.19	31950.85
2 1 2 3 0 3	31993.73	31976.27	31967.48	31889.42	31955.16	31990.25	31997.83	*30960.00*	*32840.90*	32030.57	31998.50	31922.72	31936.73
2 2 1 3 1 2								*39927.34*					
3 0 3 4 1 4								*39718.64*					
3 1 3 4 0 4								*39718.09*					
Q - branch													
3 0 3 3 1 2	22829.57		22650.28	22975.7 P	22632.72	22960.1 P	22787.3 P	*23766.9 P*	*21979.2 P*	22754.8 P	22870.92	22816.3 P	22805.8 P
3 1 3 3 2 2	22905.20	22733.20	22738.9 P	23039.5 P	22722.1 P	23044.6 P	22850.01	*23850.1 P*	*22065.2 P*	22838.0 P	22944.6 P	22904.5 P	22873.9 P
4 0 4 4 1 3	32024.09	31784.95	31783.84	32219.04	31759.88	32214.02	31954.52	*33327.59*	*30857.61*	31925.68	32080.51		
4 1 3 4 2 2	22722.91	22556.86	22525.73	22885.3 P	22507.1 P	22841.3 P	22698.10	*23648.0 P*	*21859.0 P*	22637.6 P	22766.90		
4 1 4 4 2 3	32027.54	31788.04	31787.88	32221.66	31764.14	32218.00	31957.04	*33331.57*	*30861.49*	31929.51	32083.66		
4 2 3 4 3 2	22946.04	22772.90	22786.84	23074.0 P	22770.22	23090.2 P	22883.90	*23894.0 P*	*22112.3 P*	22882.9 P	22984.3 P		
5 0 5 5 1 4									*39707.03*				
5 1 4 5 2 3	32000.34	31761.96	31755.32	32199.14	31731.05	32187.22	31934.82	*33299.97*	*30831.06*	31899.18	32057.18	31987.40	31963.54
5 2 3 5 3 2	22519.95	22360.18	22290.30	22712.18	22269.68	22616.0 P	22527.69	*23425.00*	*21630.8 P*	22415.5 P	22568.77	22457.7 P	22525.3 P
5 1 5 5 2 4									*39706.98*				
5 2 4 5 3 3	32013.36	31774.45	31771.95	32209.31	31748.10	32202.77	31944.67	*33314.96*	*30847.29*	31914.39	32069.92	32004.03	
5 3 3 5 4 2	23027.21	22851.60	22881.60	23142.8 P	22866.06	23181.0 P	22951.28	*23982.00*	*22205.3 P*	22972.2 P	23063.6 P	23046.6 P	
6 1 5 6 2 4									*39692.05*				
6 2 4 6 3 3	31954.37	31717.92	31700.13	32161.19	31675.33	32135.42	31897.28	*33247.59*	*30778.78*	31847.90	32012.68	31932.64	31922.65
6 3 3 6 4 2	22189.46	22039.52	21911.2 P	22427.86	21887.5 P	22251.6 P	22247.56	*23062.1 P*	*21264.0 P*	22056.2 P	22245.75	22079.6 P	22223.9 P
6 2 5 6 3 4									*39692.81*				
6 3 4 6 4 3	31993.57	31755.28	31750.01	32191.62	31725.90	32181.53	31926.96	*33292.66*	*30827.24*	31893.18	32050.32	31982.07	31956.20
6 4 3 6 5 2	23166.67	22986.64	23044.10	23261.1 P	23029.90	23336.30	23067.6 P	*24135.4 P*	*22364.0 P*	23125.1 P	23199.61	23208.3 P	23110.2 P
7 2 5 7 3 4									*39667.38*				
7 3 4 7 4 3	31873.19	31639.68	31602.18	32094.74	31576.28	32043.36	31831.63	*33155.71*	*30685.32*	31756.96	31934.09	31835.44	31850.89
7 4 3 7 5 2	21713.53	21576.7 P	21373.3 P	22012.34	21345.8 P	21731.5 P	21838.1 P	*22542.86*	*20742.6 P*	21543.1 P	21779.25	21542.6 P	21786.1 P
7 3 5 7 4 4									*39670.31*				
7 4 4 7 5 3	31969.81	31732.15	31724.78	32169.70	31700.62	32156.67	31905.08	*33265.04*	*30804.42*	31868.58	32026.90	31956.83	31933.68
7 5 3 7 6 2	23383.12	23196.60	23295.34	23445.5 P	23283.34	23577.07	23248.74	*24372.1 P*	*22609.1 P*	23362.1 P	23410.81	23458.6 P	23306.3 P
8 3 5 8 4 4									*39628.77*				
8 4 4 8 5 3	31738.52	31510.21	31438.90	31984.71	31410.96	31889.79	31723.35	*33003.66*	*30528.58*	31605.65	31803.33	31673.13	31731.70
8 5 3 8 6 2	21095.63	20974.1 P	20689.3 P	21462.40	20657.9 P	21064.7 P	21295.9 P	*21872.7 P*	*20080.6 P*	20885.0 P	21171.65	20858.7 P	21211.1 P
8 4 5 8 5 4									*39636.83*				
8 5 4 8 6 3	31946.85	31709.47	31702.80	32146.82	31678.49	32134.21	31882.00	*33239.50*	*30784.64*	31845.92	32003.87	31934.29	31910.74
8 6 3 8 7 2	23695.58	23499.80	23656.90	23712.9 P	23647.89	23923.86	23511.47	*24713.0 P*	*22961.42*	23703.6 P	23716.11	23818.9 P	23590.3 P

J KA KC → J KA KC	G.S.	1	2	3	4	5	6	7	8	9	10	11	12
9 4 5 → 9 5 4									*39570.45*				
9 5 4 → 9 6 3	31526.42	31306.24	31181.85	31811.74	31150.89	31647.91	31553.29	*32765.09*	*30381.03*	31397.44	31597.89	31417.86	31544.52
9 6 3 → 9 7 2	20365.65	20259.42	19902.6 P	20796.4 P	19868.0 P	20289.9 P	20638.6 P	*21088.3* P	*19318.6* P	20119.5 P	20450.90	20070.5 P	20521.6 P
9 5 5 → 9 6 4									*39591.02*				
9 6 4 → 9 7 3	31932.37	31694.82	31693.53	32128.95	31669.67	32122.88	31863.75	*33223.99*	*30777.74*	31834.26	31988.74	31924.70	31894.05
9 7 3 → 9 8 2	24122.59	23914.10	24148.60	24079.50	24143.83	24396.25	23871.84	*25180.1* P	*23440.3* P	24168.81	24133.34	24309.1 P	23979.0 P
10 5 5 → 10 6 4									*39484.56*				
10 6 4 → 10 7 3	31209.28	31001.25	30799.06	31552.68	30763.54	31286.85	31298.79	*32409.51*	*29911.60*	31011.94	31290.43	31037.30	31263.85
10 7 3 → 10 8 2	19577.97	19484.7 P	19083.6 P	20054.6 P	19047.5 P	19471.85	19905.5 P	*20251.8* P	*18525.2* P	19310.5 P	19669.36	19247.7 P	19763.1 P
10 6 5 → 10 7 4									*39532.00*				
10 7 4 → 10 8 3	31937.52	31698.60	31711.28	32124.66	31688.33	32136.02	31858.53	*33231.27*	*30797.23*	31846.52	31992.21	31941.58	31893.39
10 8 3 → 10 9 2	24680.29	24455.58	24788.10	24560.61	24788.6 P	25011.72	24344.80	*25788.8*	*24062.5*	24775.08	24678.8 P	24946.7 P	24488.3 P
10 9 2 → 10 10 1	22492.38	22212.45	23092.73	21873.3 P	23122.67	23118.07	21658.3 P	*23678.1*		22875.9 P			
11 6 5 → 11 7 4									*39360.27*				
11 7 4 → 11 8 3	30758.97	30567.36	30260.16	31182.18	30218.38	30776.46	30934.89	*31906.26*		30509.44	30853.09	30501.32	30864.03
11 8 3 → 11 9 2	18805.71	18720.0 P	18320.1 P	19295.2 P	18285.3 P	18694.1 P	19153.7 P			18539.8 P	18897.25	18477.7 P	19000.0 P
11 7 5 → 11 8 4									*39460.04*				
11 8 4 → 11 9 3	31976.69	31734.73	31773.60	32145.54	31752.38	32189.94	31877.83	*33277.23*	*30860.13*	31899.01	32028.14	32002.44	31920.91
11 9 3 → 11 10 2	25382.79	25137.90	25589.44	25169.51	25596.56	25784.62	24943.40	*26555* P	*24842.22*	25536.24	25366.52	25746.23	25131.5 P
11 10 2 → 11 11 1	24231.18		24958.88	23481.80	24996.32	24958.77	23246.29	*25545.6*		24692.20	24128.88		
12 7 5 → 12 8 4									*39182.69*				
12 8 5 → 12 9 3	30151.93	29981.46		30676.82		30094.94	30438.56	*31232.09*			30262.50		30321.00
12 9 3 → 12 10 2	18131.64	18045.45		18588.4 P		18047.7 P	18451.9 P				18215.49		18306.7 P
12 11 1 → 12 12 0	22070.14					23164.30		*23506.81*			21867.40		
12 8 5 → 12 9 4									*39377.61*				
12 9 4 → 12 10 3	32066.83	31819.49	31900.59	32205.40	31882.14	32303.97	31935.27	*33381.14*	*30986.02*	32010.21		32127.44	31991.85
12 10 3 → 12 11 2	26240.65	25971.78	26563.0 P	25917.0 P	26577.8 P	26725.7 P	25678.42		*25788.76*	26463.1 P		26717.8 P	25919.4 P
12 11 2 → 12 12 1	26097.96	25747.62		25214.22			24956.66				25975.63		
13 9 4 → 13 10 3				30020.78					*30379.61*				
13 12 1 → 13 13 0	24870.30	24439.02		23364.80		26068.76	23089.67				24649.98		
13 10 4 → 13 11 3	32226.92	31971.20	32114.24	32320.34	32099.75	32499.20	32046.23	*33563.45*		32201.32	32265.52	32338.49	32123.70
13 11 3 → 13 12 2	27261.0 P	26964.1 P	27714.3 P	26811.1 P	27780.3 P	27841.2 P	26557.5 P	*28597.3* P		27561.7 P	27207.4 P	27867.3 P	26859.7 P
14 9 5 → 14 10 4		39946.49	39691.35		39644.08				*38584.97*	39963.73			
14 10 4 → 14 11 3		28330.9 P	27613.9 P		27549.0 P			*29366.47*	*26831*	27996.5 P			
14 12 2 → 14 13 1	18197.34				19545.0 P	19192.6 P		*18092* P	*18891.1* P	18960.5 P	18013.8 P	19499.7 P	
14 13 1 → 14 14 0	27671.82		29192.54	26062.50	29279.42	28960.12	25756.98	*29422.32*	*28334.17*	28613.21	27438.13	29279.03	
14 11 4 → 14 12 3		32209.00	32436.72	32507.35	32427.68	32797.15	32227.56	*33845.86*		32493.19	32504.63	32657.67	32333.87
14 12 3 → 14 13 2		28118.4 P	29044.4 P	27856.3 P	29078.1 P	29133.2 P	27585.4 P	*29884* P		28834.1 P	28371.3 P	29196.0 P	27956.3 P
15 10 5 → 15 11 4		39567.58	39199.48		39144.39	39860.68			*38112.00*	39512.05	39934.66	39509.43	39934.16
15 11 4 → 15 12 3		27308.9 P	26484.9 P		26414.9 P	27112.7 P		*28238.32*	*25738.81*	26896.5 P	27566.0 P	26728.8 P	27786.8 P
15 13 2 → 15 14 1	20551.50	20150.50	22089.42	19072.6 P	22191.98	21751.7 P	18829.0 P	*21984.4* P	*21442.4* P	21482.0 P	20323.86	22126.6 P	19568.8 P
15 14 1 → 15 15 0	30440.24	29933.28	32028.69	28747.02	32119.63	31807.85	28412.14	*32334.81*	*31088.55*	31426.08	30196.16	32129.22	29306.31
15 12 4 → 15 13 3		32551.60	32889.01	32783.92	32887.21	33218.64	32496.48	*34249.37*	*31953.78*	32906.71	32849.69	33106.05	32640.73
15 14 2 → 15 15 1		31850.38	33556.83		33625.62	33474.02		*34159.44*	*32573.30*	33091.35	32133.56	33690.46	
16 11 5 → 16 12 4	39290.99	39063.01	38547.34	39910.53	38482.12	39250.36	39596.74		*37483.81*	38912.00	39425.53	38862.07	
16 12 4 → 16 13 3	26301.12	26224.90	25350.79	27240.6 P	25279.76	25972.24	27056.1 P	*27068.10*	*24640.9* P	25768.6 P	26471.5 P	25587.80	
16 14 2 → 16 15 1	23183.56	22718.87	24968.84	21429.7 P	25088.74	24577.32	21147.3 P	*24822.48*	*24238.6* P	24267.8 P	22915.48	25009.1 P	22028.3 P
16 15 1 → 16 16 0	33157.53	32615.96	34805.40	31393.59	34899.77	34599.00	31030.06	*35189.68*	*33785.51*	34182.19	32904.60	34920.02	31970.15
16 13 4 → 16 14 3		33017.23		33166.82			32869.24		*32540.23*		33318.61		33061.76
16 15 2 → 16 16 1		34037.81		33123.03			*32765.66*		*34853.33*		34341.61		33543.66

J KA KC → J KA KC	G.S.	1	2	3	4	5	6	7	8	9	10	11	12
17 12 5 17 13 4	38606.41	38704.05	37709.85	39362.28	37632.19	38462.51	39060.63	*39904.06*	*35676.37*	38137.40	38763.77	38029.77	38876.97
17 13 4 17 14 3	25223.72	25156.64	24312.39	26177.5 P	24245.79	24900.7 P	26004.94	*25948. P*	*23625.0 P*	24706.2 P	25392.31	24537.7 P	25657.6 P
17 14 3 17 15 2	18791.04				19602.6 P	19449.1 P	18043.7 P	*19845. P*	*18977.5 P*	19238.1 P	18701.46		
17 15 2 17 16 1	26023.28	25497.68	28014.24	24024.8 P	28148.70	27588.50	23701.78	*27682.54*	*27196.25*	27237.72	25720.32	28061.92	24713.6 P
17 16 1 17 17 0	35819.17	35243.81	37524.04	33990.36	37622.28	37332.80	33598.07	*37985.07*	*36426.50*		35558.09	37652.12	34581.84
18 13 5 18 14 4	37745.10	37579.89	36675.62	38663.44	36583.98	37481.79	38376.96	*38937.66*	*35678.23*	37172.69	37928.70	37000.33	
18 14 4 18 15 3	24263.68	24192.63	23474.74	25159.00	23419.55	24000.16	24994.06	*24981.0 P*	*22823.6 P*	23810.1 P	24417.9 P	23683.9 P	
18 15 3 18 16 2	20072.77	19748.76	21207.0 P	19152.1 P	21298.0 P	20990.02	18932.7 P	*21318.9 P*	*20592.6 P*	20747.5 P	19924.71	21265.5 P	19401.1 P
18 16 2 18 17 1	28993.16	28412.21	31141.01	26793.12	*31286.82*	30701.33	26429.49	*31021.16*	*30233.66*	30309.54	28662.9 P	31200.09	27554.88
18 17 1 18 18 0		37819.66		36535.73			36116.58		*39019.35*	39527.52	38159.27		37141.68
19 14 5 19 15 4	36701.56	*36574.22*	35546.26	37798.73	*35350.68*	*36312.72*	*37531.15*	*37777.85*	*34500.65*	36021.85	36913.27	35784.07	37186.12
19 15 4 19 16 3	23513.87	23424.08	22936.18	24267.7 P	22899.82	23369.00	24104.1 P	*24265.4 P*	*22301.22*	23177.1 P	23640.38	23125.3 P	23822.2 P
19 16 3 19 17 2	21785.24	21383.25	23324.40	20467.7 P	23447.98	22983.38	20210.0 P	*23252.6 P*	*22847.6 P*	22703.0 P	21537.83	23369.8 P	20868.3 P
19 17 2 19 18 1	32020.07	31390.16	34276.75	29666.16	*34430.80*	33841.95	29262.76	*34220.47*	*33280.63*	33409.30		34350.47	30481.36
20 15 5 20 16 4	35492.00	*35403.07*	34093.26	36766.89	*33375.95*	*34986.89*	*36520.75*	*36450.26*	*33183.23*	34715.27	35730.24	34420.78	36086.35
20 16 4 20 17 3	23059.68	22934.28	22780.40	23585.1 P	22770.26	23093.08	*23414.79*	*23891.9 P*	*22148.84*	22892.1 P	23144.48	22946.2 P	23226.3 P
20 17 3 20 18 2	23911.80	*23426.22*	25854.21	22179.6 P	*26010.44*	25397.91	21876.8 P	*25620.6 P*	*25102.70*	25074.9 P	23635.67	25890.2 P	22738.7 P
20 18 2 20 19 1	35043.33	34370.92	37369.55	32580.65	*37529.40*	36953.56	32139.56	*37400.15*		36481.12	34680.96	37460.06	33430.30
21 16 5 21 17 4	34158.64	*34103.81*	32658.49	35585.57	*32534.47*	*33565.20*	*35361.94*	*35009.55*	*31795.37*	33312.22	34417.58	32980.78	34845.22
21 17 4 21 18 3	22972.26	*22794.76*	23071.80	23185.0 P	23095.48	23241.0 P	*22999.14*	*23931.8 P*	*22429.36*	23023.2 P	23002.30	23212.6 P	22945.5 P
21 18 3 21 19 2		*25840.69*	28729.51	24270.0 P	*28916.60*	28176.84	23916.53	*28371.06*	*27893.78*	27807.21	26073.78	28761.58	
21 19 2 21 20 1		37310.47		35485.50			35008.85		*39223.17*	39489.38	37650.62		
22 17 5 22 18 4	32769.57	*32739.22*	31249.01	34294.78	*31126.05*	*32136.08*	*34092.53*	*33539.89*	*30430.64*	31898.67	33038.57		33513.56
22 18 4 22 19 3	23306.88	23060.4 P	23855.70	23129.2 P	23920.23	*23863.49*	*22917.66*	*24439.0 P*	*23186.5 P*	23620.3 P	23270.32		23038.9 P
22 19 3 22 20 2	29222.98	*28568.44*	31863.54	26700.94	*32077.44*	31240.18		*31428.88*	*30937.11*	30822.10	28829.20		27563.12
22 20 2 22 21 1				38344.71			37834.14						39221.32
23 19 4 23 18 5	31413.54	*31393.38*	29976.96	32956.32	*29864.86*	*30805.02*	*32771.45*	*32134.00*	*29196.76*	30758.10	31678.06	30270.56	32163.47
23 18 5 23 19 4	24101.70	*23772.18*	25157.30	23465.5 P	25268.66	24990.61	*23218.00*	*25458.2 P*	*24445.3 P*	24714.3 P	23988.80	25247.0 P	23550.7 P
23 19 4 23 20 3	32265.92	*31534.72*	35159.85	29415.48	*35394.84*	34496.38	*28951.82*	*34704.16*	*34139.76*	34029.39	31826.37	35202.17	30403.88
24 19 5 24 20 4	30190.80	*30162.14*		31649.28			*31475.24*				30433.32		
24 20 4 24 21 3	25377.88	*24951.70*	26978.3 P	24227.6 P		26633.4 P	23933.80		*26206.6 P*	26315.8 P	25180.88	27045.1 P	24509.6 P
24 21 3 24 22 2	35454.63	*34656.41*	38525.82	32343.25	*38775.79*	37852.68	*31824.51*		*37411.98*	37337.65	34981.04	38581.93	33431.11
25 20 5 25 21 4				30462.96			*30289.95*				29405.21		
25 22 3 25 23 2		*37852.01*		35408.18			*34836.86*				38211.09		36565.55
26 21 5 26 22 4			28074.2 P		*28065.0 P*				*27336.2 P*		28687.70	28282.7 P	
26 22 4 26 23 3			32052.02	27087.7 P	*32321.48*		*26671.2 P*				28982.57	32086.52	27799.7 P
26 23 3 26 24 2				38536.48			*37916.69*						39734.47
27 21 6 27 22 5			38516.88		*38326.61*	*39736.41*			*37588.00*	39450.28		38916.86	
27 22 5 27 23 4			28366.2 P		*28413.0 P*	*28571.3 P*		*29396.8 P*	*27609.3 P*	28350.7 P	28361.75	28540.4 P	
27 23 4 27 24 3			35171.17		*35489.54*	*34373.56*		*34502.90*	*34147.52*	33901.08	31533.10	35199.72	
28 22 6 28 23 5		*39095.17*	36863.65			*38045.16*		*39725.01*	*35984.33*	37775.98	39434.86	37247.22	
28 23 5 28 24 4		*28234.6 P*	29212.7 P	28498.1 P	*29327.4 P*	*29192.0 P*		*29859.2 P*	*28418.2 P*	28893.1 P	28490.33	29352.4 P	28280.0 P
28 24 4 28 25 3		*34102.57*	38552.91	31644.77	*38912.72*	*37662.75*		*37775.75*	*37430.74*	37139.29	34438.51	38583.65	32367.64
29 23 6 29 24 5		*37473.06*	35390.62	39673.80	*35227.02*	*36481.45*	*39500.46*	*38070.17*	*34551.08*	36222.45	37811.78	35749.92	38570.83
29 24 5 29 25 4		*28851.0 P*	30633.6 P	28612.8 P	*30823.0 P*	30376.3 P	*28310.4 P*	*30884.0 P*	*29782.4 P*	30034.0 P	29118.49	30740.3 P	28628.3 P
29 25 4 29 26 3		*37242.54*		34451.25			*38806.77*				37615.98		35743.73
30 24 6 30 25 5		*36008.20*					*37939.18*		*33406.06*	34908.26			37023.26
30 25 5 30 26 4		*29985.5 P*		29193.8 P			*28822.2 P*		*31698.2 P*	31734.4 P	30270.59		29469.2 P
30 26 4 30 27 3				37516.11			*36795.65*						38941.28

Transitions in *italics* do not conform with the rigid-rotor Hamiltonian.

'P' indicates that a transition was used as DRM pump line without being subsequently remeasured under SEM (Estimated uncertainty: ± 0.3 MHz).

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