Microwave Spectra of Furazan.
III. Rotation Spectra of Vibrationally Excited States

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Dedicated to Professor E. Bright Wilson, Jr. on the occasion of his 82. birthday

The pure rotational spectra of molecules in 21 vibrationally excited states of the heterocyclic compound furazan ($C_2H_2N_2O$) have been detected and studied by DRM microwave spectroscopy. Rotational parameters are reported for the 12 fundamental levels below 1500 cm^{-1}, and the contributions from 10 vibrational modes to the effective rotational constants and to the inertia defect of furazan are calculated.

I. Introduction

In two previous papers [1 a, b] we have reported the doubly determined substitution structure [1 a] of the five-membered ring molecule furazan (1,2,5-oxadiazole, $C_2H_2N_2O$). That structural information was needed before the electric field gradients around the quadrupolar nitrogen nuclei could be extracted from the hyperfine splittings of rotational transitions of the 3-d$_1$ form of this compound [1 b]. During the experimental work which was required for that structure determination, and which was carried out predominantly by double resonance modulation (DRM) microwave spectroscopy [1 c, d], [2], we could not avoid the detection of numerous vibrational satellite transitions in the pure rotation spectrum of furazan. Since the ^{18}O-forms of normal and d$_2$-furazan, with a natural isotopic abundance of only 0.2% of their parent forms, could be detected without much difficulty, we had to conclude that spectra of excited states with populations as small as 0.1% of the vibrational ground state (G.S.) would be detectable on the basis of the sensitivity of the DRM instrument. According to the Boltzmann law, this implied that the pure rotation spectra of all excited states up to vibrational energies of about 1500 cm^{-1} should be detectable.

Our decision to investigate these vibrational satellite spectra as fully as possible had several reasons of different weight:

Firstly, there is probably no safer way of preventing a weak satellite spectrum from being mistaken as the ground state spectrum of a rare isotopomer than to assign that spectrum completely and then to examine the inertia defect for compatibility with that of the parent molecular form. Secondly, for the (then) planned quadrupole analysis on the 3-d$_1$ form [1 b] of furazan it seemed desirable to establish beforehand which hyperfine patterns would be falsified through overlap with vibrational satellite transitions of the normal or of the d$_2$-form of furazan, which were both present ($\sim 10\%$ and $\sim 30\%$, respectively) in the 3-d$_1$ sample. However, the prime reason for the present investigation was seen in the fact that the analysis of the spectra of vibrationally excited states has become a rather central theme of molecular spectroscopy during the past two decades. This field of research was first "ploughed" with the help of laser techniques, which yield the precise vibration frequencies and the molecular parameters of those excited states which happen to be accessible from the G.S. by use of a particular laser, and it has become a topic of high-resolution FT-IR spectroscopy during the past five years. In comparison with those approaches, the present study by DRM microwave techniques has the serious disadvantage of not being capable of yielding precise infrared frequencies. On the other hand, it promises the advantage of providing the rotational parameters not merely of one or two, but of all excited states up to the sensitivity limit of the DRM instrument. With only the Boltzmann population as the decisive factor, vibrational energy levels which cannot be reached from the G.S. by infrared techniques as a consequence of selection rules, are equally accessible to investigation by purely rotational spectroscopy as those levels which can be studied by infrared techniques.

II. Instrumental

Experiments were carried out predominantly by DRM microwave spectroscopy, but measurements under Stark effect modulation (SEM) [3] were added when this appeared profitable. The DRM spectrometer [1 c] employed frequency modulation of the pump radiation. The modulation depth was variable from about 2 MHz to 100 MHz (upper limit dependent on klystron), and was usually kept near 30 MHz. For high sensitivity work the pump power emitted at the two frequencies was levelled through manual adjustment of the klystron supply voltages. The absorption cell of the instrument consisted of 20 m of "empty" K-band waveguide. For the present work the range of pump frequencies was taken from 14.1 GHz (cut-off frequency of K-band waveguide) up to 34 GHz, and the frequency of the signal radiation varied from 16 GHz to 40 GHz. Both pump and signal klystrons were operated unstabilised. The latter was frequency-swept at rates of minimally 1 MHz/sec over ranges of, typically, 10 MHz at a time. All frequency adjustments were carried out manually. Absorption signals were displayed on the oscilloscope, where their frequencies were measured to an estimated accuracy of ± 0.05 MHz. The SEM spectrometer was operated in an analogous fashion. All experiments were carried out at room temperature ($T \sim 300$ K) and at sample pressures near 10 mTorr.

III. Spectroscopic Results

a) Rotational Assignments

The identification of satellite spectra due to states with vibrational energies up to 1300 cm^{-1} was based on the observation, via double resonance (DR) techniques [1 c, d], of the pairs of Q-branch lines $4_{04} \rightarrow 4_{13} \twoheadrightarrow 4_{22}$. The signal transitions $4_{04} \rightarrow 4_{13}$ occur near 35 GHz, and the pump transitions $4_{13} \twoheadrightarrow 4_{22}$ fall into upper K-band (23–25 GHz). The result of a systematic examination of transitions in the vicinity of the G.S. pump line for DR signals near 35 GHz is summarised in the double resonance map [1 c] of Figure 1. Similar maps result for the $J = 5$ connections of the same series of transitions, and for many other sequences of satellite DRs between two Q-branch transitions of low J-value.

In progressing to states with vibrational energies above 1300 cm^{-1}, and hence with still smaller Boltz-

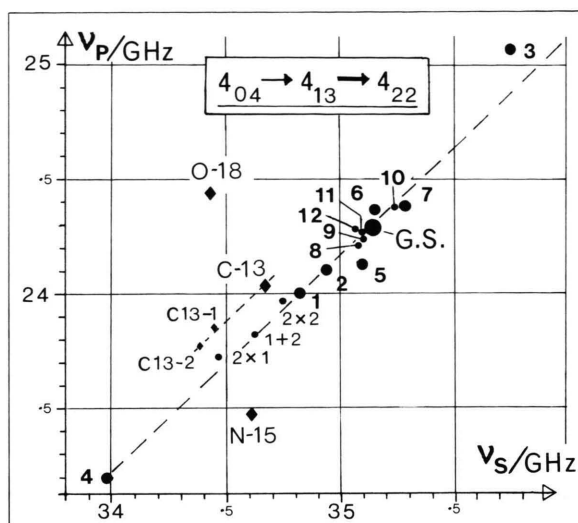Fig. 1. DR-map of the connection $4_{04} \rightarrow 4_{13} \twoheadrightarrow 4_{22}$, illustrating the displacement from the G.S. of transitions due to excited vibration states and isotopomers of furazan. (The numbering 1 through 12 indicates the decreasing intensity of satellites. Accurate frequencies of transitions are given in the Appendix.)

mann populations, the decreasing intensity of rotational lines of low J-value demanded a switch from the $J = 4$ connection to a DR scheme that consisted of more intense rotational transitions. Accordingly, the $J = 14$ connections were chosen which consist of the *three* transitions $14_{9,5} \rightarrow 14_{10,4} \twoheadrightarrow 14_{11,3} \rightarrow 14_{12,2}$ at ~ 37 GHz, ~ 25 GHz and ~ 30 GHz, respectively, with the K-band line near 25 GHz as common pump transitions for the *two* signals. While the pump transitions lie at the band head of the series $J_{J-4,4} \rightarrow J_{J-3,3}$, with the consequence that their frequencies vary relatively little from the G.S. for different excited states, the signal frequencies for that scheme vary by considerably larger displacements from the G.S. than those of the $J = 4$ connections of Fig. 1. The identified DR-connections are presented as Table 1. The various vibrationally excited states which give rise to these rotational transitions are designated in that table by numbers '1' through '12' in order of decreasing intensity of the signals (increasing vibrational energy). The transitions of the isotopomers are included in that table since their intensity (due to natural abundance) provided a first clue on the vibrational energy of identified states. The notation "2×1" in the table and in Fig. 1 indicates that state '1' is excited by two quanta (overtone level), while "$2 + 1$" designates the state in

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Table 1. Frequencies (in MHz) of DR-connected transitions between $J=14$ levels in furazan.

State	$14_{9,5}$ — S1 →	$14_{10,4}$ — P →	$14_{11,3}$ — S2 → $14_{12,2}$
G.S.	36957.1	25194.4	30207.5
1	35889.5	25154.3	31445.7
2	36351.6	25130.4	30814.0
C13-GS	37185.3	24784.4	28393.0
3	?	?	?
4	?	?	?
5	35321.0	25758.2	33647.7
6	37391.2	25112.3	28259.7
7	36980.3	25328.5	30610.0
8	36442.8	25264.7	31110.2
N15-GS	32207.7	27911.9	39970.7
9	36507.7	25263.0	31025.1
10	37255.5	25248.2	29950.5
2 X 1	34873.3	25214.3	32665.1
1 + 2	35295.6	25132.6	32090.6
2 X 2	35879.3	25093.9	31275.9
O18-GS	–	31147.0 (S)	18810.6 (P)
11	36745.7	25206.9	30540.1
12	37075.5	25122.7	29795.1
C13-1	36180.6	24653.2	29538.8
C13-2	36614.1	24648.6	28860.3
1 + 5	34066.9	26089.2	35418.2
2 + 5	34864.1	25762.8	34046.5
1 + 6	37216.9	24952.5	28936.1
2 + 6	37223.8	24969.0	28994.4
1 + 7	35894.3	25319.8	31918.0
2 + 7	(36388.5)	25272.7	31199.8

which mode '1' and mode '2' are simultaneously excited by one quantum each (combination level). The correlation with IR-designations is given at the bottom of Table 2 and across the top of Figure 2.

Upon inspection of Fig. 1 or Table 1 the informed reader will realise that every DR connection (marked by a circle in Fig. 1), and even more so the identification of *two* signal transitions which arise from the *same* pump transition (i.e. every row in Table 1), establishes the entire Q-branch of one vibrational satellite spectrum. – With the Q-branches of satellite spectra established by these experiments and further refined through the measurements of more, but predictable DRs within each Q-branch, the $J=2$ and $J=3$ members of each satellite (which had either been measured or which were precisely predictable) were chosen as

the pump transitions for the $J=1 \rightarrow 2$ and $J=2 \rightarrow 3$ R-branch transitions. The successful completion of these DR experiments yielded the rotational constants of satellites up to 1600 cm^{-1} of vibrational energy.

Fairly precise rotational constants were derived from least-squares fits of the spectra after all accessible transitions (between 80 and 95 lines for each of the fundamentals) had been measured by either DRM or SEM techniques along with the work on the isotopic forms [1 a]. The overall results, together with statistical information on each spectrum, are collected in Table 2. – Although a total of 21 vibrational satellite spectra has been observed and assigned (see Fig. 2), Table 2 lists the rotational parameters of the G.S. and the 12 fundamentals only. The identified transitions of each of those 13 spectra are given as Appendix.

b) Perturbations in the Rotational Satellite Spectra

The rotational spectrum of the G.S. was readily fitted up to $J=24$ to a Hamiltonian with four quartic distortion constants [1 a], and the same behaviour was expected for the vibrational satellite spectra. For six spectra, labelled '7'–'12' in figures and tables, this was indeed the case, and the distortion constants for these six spectra are qualitatively similar to those determined for the G.S.

For the satellites arising from states with vibrational energies between 600 cm^{-1} and 900 cm^{-1} several incompatibilities with the simple quartic Hamiltonian were observed: In the most intense spectrum (labelled '1') it was found that some transitions above $J=13$ showed deviations from rigid behaviour which increased to ~ 26 MHz at $J=23$. These DR-identified perturbed transitions (given in italics in the Appendix) were *not included* in the final LSQ-fit which from 80 well-behaved transitions yielded rotational constants with 3σ-uncertainties of 0.03 MHz. Similar, though smaller, deviations occur for transitions with $J=18-22$ in the second most intense satellite spectrum '2'. Deviations from rigid rotor behaviour occur also in the spectra labelled '5' and '6'. They set in at $J=15$ to reach about 16 MHz in the case of satellite '5', and at $J=11$ to reach about 13 MHz in satellite spectrum '6'. The fitted transitions of those two satellites also lead to abnormally large values of opposite signs for the distortion constants τ_{aabb} and τ_{abab} (see rows 10 and 11 in Table 2).

Much larger deviations from the rigid rotor pattern than in those four spectra are encountered in the spec-

Table 2. Rotational parameters of the G.S. and 12 vibrationally excited states of furazan.

1	Satellite spectrum	G.S.	1	2	3	4	5	6
2	Observed transitions	12 R & 82 Q	6 R & 86 Q	6 R & 85 Q	6 R & 70 Q	6 R & 46 Q	6 R & 81 Q	5 R & 88 Q
3	Range of J-values	1-8 & 2-24	1-3 & 2-23	1-3 & 2-23	1-3 & 2-13	1-3 & 2-10	1-3 & 2-23	1-3 & 2-24
4	St'd dev'n (MHz), (N_f)[a]	0.055 (94)	0.051 (80)	0.052 (86)	7.5 (9)	4.5 (9)	0.072 (73)	0.071 (76)
5	A ⎫	10457.21(2)[b]	10427.54(3)	10436.27(3)	10395.8(16)	10410.1(10)	10476.46(3)	10431.52(3)
6	B ⎬ in MHz	9681.65(2)	9624.04(3)	9647.14(3)	9919.1(18)	9407.8(10)	9621.18(3)	9703.98(3)
7	C ⎭	5023.70(2)	5023.69(2)	5025.11(2)	5044.4(8)	4996.6(5)	5001.55(3)	5024.56(3)
8	τ_{aaaa} ⎫	- 17.1(6)	- 20.0(48)	- 17.5(48)	-	-	- 46.3(70)	+ 7.3(68)
9	τ_{bbbb} ⎬ in kHz	- 20.5(6)	- 23.0(46)	- 20.8(45)	-	-	- 23.4(70)	- 18.7(63)
10	τ_{aabb} ⎪	- 4.4(20)	- 16.3(141)	- 5.7(141)	-	-	-133.3(213)	+128.0(204)
11	τ_{abab} ⎭	- 7.8(7)	- 4.6(48)	- 6.4(48)	-	-	+ 44.4(72)	- 56.4(69)
12	$\alpha_A = A_{G.S.} - A_V$	-	+ 29.67(3)[c]	+ 20.94(3)	+ 61.4	+ 47.1	- 19.25(3)	+ 25.69(3)
13	$\alpha_B = B_{G.S.} - B_V$	-	+ 57.61(3)	+ 34.51(3)	-237.5	+273.8	+ 60.47(3)	- 22.33(3)
14	$\alpha_C = C_{G.S.} - C_V$	-	+ 0.01(2)	- 1.41(2)	- 20.7	+ 27.1	+ 22.15(3)	- 0.86(2)
15	I_a ⎫	48.3280(1)	48.4655(1)	48.4250(1)	48.613(7)	48.547(5)	48.2392(2)	48.4470(2)
16	I_b ⎬ in u$Å^2$ [d]	52.1994(1)	52.5118(2)	52.3861(2)	50.950(9)	53.719(6)	52.5274(2)	52.0792(2)
17	I_c ⎭	100.5983(3)	100.5985(4)	100.5702(4)	100.185(15)	101.145(9)	101.0439(5)	100.5812(5)
18	$I.D. = I_c - I_a - I_b$	+ 0.0709(3)	- 0.3788(4)	- 0.2408(4)	+ 0.622(19)	- 1.121(12)	+ 0.2772(6)	+ 0.0550(6)
19	$\delta(ID) = ID_V - ID_{G.S.}$	-	- 0.4497(4)[c]	- 0.3117(4)	+ 0.551(19)	- 1.192(12)	+ 0.2063(6)	- 0.0159(6)
20	Species/frequ'y (cm⁻¹)		B_2 / 631	A_2 / 635	B_1 / 820 ?	B_2 / 838 ?	A_1 / 872	A_2 / 888
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	6 R & 85 Q	6 R & 83 Q	6 R & 83 Q	5 R & 82 Q	5 R & 81 Q	5 R & 73 Q
3	Range of J-values	1-3 & 2-23	1-3 & 2-23	1-3 & 2-23	2-3 & 3-24	2-3 & 3-24	2-3 & 3-24
4	St'd dev'n (MHz), (N_f)[a]	0.050 (91)	0.056 (89)	0.058 (89)	0.059 (87)	0.056 (86)	0.056 (78)
5	A ⎫	10471.51(2)	10465.43(3)	10468.79(3)	10465.88(3)	10447.68(3)	10433.55(3)
6	B ⎬ in MHz	9686.22(2)	9669.03(3)	9674.32(3)	9696.14(3)	9664.37(3)	9667.85(3)
7	C ⎭	5011.15(2)	5027.39(2)	5029.51(2)	5019.19(2)	5014.52(2)	5013.81(2)
8	τ_{aaaa} ⎫	- 18.1(43)	- 22.5(49)	- 25.6(51)	- 16.3(52)	- 27.4(50)	- 22.2(51)
9	τ_{bbbb} ⎬ in kHz	- 20.9(40)	- 25.1(47)	- 28.7(48)	- 19.7(49)	- 28.7(48)	- 27.2(48)
10	τ_{aabb} ⎪	- 4.8(130)	- 19.2(149)	- 31.6(153)	- 1.2(156)	- 36.8(150)	- 22.0(153)
11	τ_{abab} ⎭	- 8.1(45)	- 3.0(49)	+ 1.0(51)	- 8.8(52)	+ 3.6(50)	- 2.2(51)
12	$\alpha_A = A_{G.S.} - A_V$	- 14.30(2)	- 8.22(3)	- 11.58(3)	- 8.67(3)	+ 9.53(3)	+ 23.66(3)
13	$\alpha_B = B_{G.S.} - B_V$	- 4.57(2)	+ 12.62(3)	+ 7.33(3)	- 14.49(3)	+ 17.28(3)	+ 13.80(3)
14	$\alpha_C = C_{G.S.} - C_V$	+ 12.55(2)	- 3.69(2)	- 5.81(2)	+ 4.51(2)	+ 9.18(2)	+ 9.89(2)
15	I_a ⎫	48.2620(1)	48.9201(1)	48.2745(2)	48.2879(2)	48.3721(2)	48.4376(2)
16	I_b ⎬ in u$Å^2$ [d]	52.1747(1)	52.2675(2)	52.2389(2)	52.1214(2)	52.2927(2)	52.2739(2)
17	I_c ⎭	100.8502(3)	100.5246(4)	100.4821(4)	100.6888(4)	100.7825(4)	100.7969(4)
18	$I.D. = I_c - I_a - I_b$	+ 0.4135(4)	- 0.0330(5)	- 0.0314(5)	+ 0.2795(5)	+ 0.1177(5)	+ 0.0854(5)
19	$\delta(ID) = ID_V - ID_{G.S.}$	+ 0.3426(4)	- 0.1039(5)	- 0.1023(5)	+ 0.2086(5)	+ 0.0468(5)	+ 0.0145(5)
20	Species/frequ'y (cm⁻¹)	B_1 / 952	A_1 / 1005	A_1 / 1036	B_1 / 1175	A_1 / 1316	A_1 / 1418
21	in-plane/out-of-plane	in	in	in	in	in	in
22	I.R. mode , level	$\nu_{12} = 1$	$\nu_5 = 1$	$\nu_4 = 1$	$\nu_{11} = 1$	$\nu_3 = 1$	$\nu_2 = 1$

[a] N_f is the nmber 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 u$Å^2$ MHz.

tra labelled '3' and '4'. In these two satellite spectra even the transitions with the lowest J-value do *not conform* with rigid rotor expectation. A selection of 9 transitions with $J \leq 3$ allowed these deviations to be kept below 10 MHz in both cases and permitted the rotational constants to be determined to ± 2 MHz. These constants, together with the strongly perturbed positions of absorption lines in those two spectra, point to the presence of Coriolis coupling [4] between these two vibrational modes. This throws the rotational constants B some ± 250 MHz off the otherwise expected values. The effect of this coupling on the rotational transition frequencies is such that it necessitated the identification of every transition through DR-double-search [1 c] experiments or, in the absence of a common energy level between a pair of transitions, through the observation of collisional relaxation effects under DRM [1 e]. Despite the time-consuming nature of such work, we have carried out such experiments up to transitions with $J = 13$ in the case of satellite '3', and up to $J = 10$ for satellite '4'. At these J-values, the deviations of transition frequencies from expectations based on a rigid rotor prediction reach up to 10 GHz, with the consequence that it became impossible to predict with any confidence whether transitions with higher J-values would still fall within the frequency range of the DRM instrument. For this reason we have not tried to investigate these two spectra any further. We would suggest that the data in columns 3 and 4 of Table 2 be taken as merely qualitative, with little weight attachable to the error limits quoted there.

c) Correlation of Satellite Spectra with Excitation of Normal Modes of Vibration

As far as we are aware, there exists *no* theory which, in the absence of detailed knowledge about the molecular force field, would allow a correlation of the observed changes in the effective moments of inertia (or rotational constants) with the excitation of a specific normal mode of vibration in a molecule. One is therefore restricted to forging the link between rotational and vibrational spectroscopy almost exclusively on the basis of a comparison of the vibrational *exitation energies* which are obtained in both these two fields of molecular spectroscopy.

The vibrational spectrum of furazan has been the subject of several investigations [5–8] by infrared spectroscopy. A complete assignment of the funda-

mental frequencies of normal modes of vibration has been given by Christensen et al. [8] for normal and deuterated furazan. These researchers quote an accuracy of ± 1 cm^{-1} for their frequency determinations, that is: for the energy of vibrational excitation from the G.S. The following correlation of satellites in the pure rotational spectrum with vibrationally excited fundamenal, overtone and combination levels rests entirely on their work.

As is generally known, the determination of vibrational energies (expressed in wavenumber units) by microwave techniques is accomplished through measurements of the *intensity* of a satellite spectrum relative to the intensity of rotational transitions associated with molecules in the vibrational G.S. From such intensity ratios the vibrational energy separation between a satellite and the G.S. may be deduced via the Boltzmann law. The accuracy which can be achieved in such microwave experiments is significantly *inferior* to that of corresponding data from IR spectroscopy. It ranges generally from about $\pm 3\%$ (optimally) to $\pm 20\%$.

In furazan such vibrational energy determinations via "relative intensity measurements" [9] are, – initially –, hindered by the fact that the C_{2v} symmetry of the molecule, together with the occurrence of a pair of equivalent nitrogen nuclei ($I_N = 1$, bosons) and a pair of equivalent protons ($I_H = 1/2$, fermions), has a pronounced influence on the intensity of all rotational transitions. However, if these "nuclear spin statistical weight" effects *within* each satellite spectrum are analysed first, they offer the possibility of ascertaining whether a particular spectrum arises from molecules in an excited state of a symmetric (A-species) or an antisymmetric (B-species) mode of vibration. Furthermore, if that information is combined with the value of the inertia defects (I.D.), which emerge from the rotational analysis and which usually provide a strong hint on whether a particular satellite arises from excitation of an "in-plane" or of an "out-of-plane" vibration, it becomes possible to distinguish between the four symmetry species A_1, A_2, B_1 and B_2 of the C_{2v} group, into which the various excited vibration states of furazan must fall. Subsequent intensity measurements on satellite transitions relative to the G.S. and other satellites under proper consideration of spin weights will then allow a complete correlation of excited state energies with known IR frequencies.

As detailed in the following two subsections, the experimental procedures resulting from these con-

siderations were successfully applied to the satellite spectra of furazan, and produced a satisfactory correlation of the present rotational data with information from the IR-study of Christensen et al. [8] (see Table 5).

c.1. Symmetry, Nuclear Spin Weights and Intensities [10, 11]

Consider the total wavefunction of the molecule which, under omission of the electronic factor, may be written as

$$\Psi_{total} = \Psi_{vib.} \times \Psi_{rot.} \times \Psi_{spin},$$

where $\Psi_{vib.} = \prod_i \psi_{n_i}^{(i)}(Q_i)$ is the vibrational wavefunction for a state in which the modes i, described by normal coordinates Q_i, are excited by n_i quanta. Under the symmetry operation C_2 this part of Ψ_{total} transforms like the normal coordinate Q_i [10], while the rotational factor $\Psi_{rot.}(J, K_-, K_+)$ is even or odd under C_2 in accordance with even or odd values of $(K_- + K_+)$ [11]. As the interchange of the two protons of furazan requires Ψ_{total} to be antisymmetric (odd) under C_2, it follows that antisymmetric spin functions have to be combined with even rotational functions when the vibrational factor, $\Psi_{vib.}$, is even (A-species). Conversely, if the normal mode i (and its wavefunction) is antisymmetric (odd) under the C_2 operation, the product $\Psi_{rot.} \times \Psi_{spin}$ must be even. This requires the rotational part and the spin factor to have the same symmetry.

The nuclear spin function, Ψ_{spin}, itself may be any one of the $(2I_N+1)^2 \times (2I_H+1)^2 = 9 \times 4 = 36$ products of the form

$$\Psi_{spin} = \psi_s(2N) \times \psi_s(2H),$$

where $\psi_s(2N)$ and $\psi_s(2H)$ represent the degenerate spin states resulting from the combination of two nitrogen spins or two proton spins, respectively. Of the 36 spin functions above,

$$\{(2I_N+1)^2 \times (2I_H+1)^2 + (2I_N+1) \times (2I_H+1)\}/2 = 21$$

are symmetric (even) under the operation C_2, the remainder of 15 being antisymmetric (odd) [11].

If these nuclear spin weights are introduced into the symmetry consideration above, one obtains the relative weights as given in Table 3 for even and odd rotational transitions depending on the symmetry of the vibrational mode excited. Hence, the symmetry of $\Psi_{vib.}$ and of $\psi_{n_i}^{(i)}(Q_i)$ can be determined experimen-

Table 3. Nuclear spin weights for rotational transitions associated with even or odd excited vibrational levels in furazan.

Symmetry of vibrational wavefunction	Rotational symmetry $(K_- + K_+)$	Spin weight
$\Psi_{vib.}$ = even	even	5
	odd	7
$\Psi_{vib.}$ = odd	even	7
	odd	5

tally from a comparison of the intensity of an even rotational transition with that of an odd one *within* the satellite spectrum associated with excitation of the mode i.

c.2. Experimental Results

Relative intensity measurements for the determination of the vibrational symmetries were carried out on most excited vibration state spectra of furazan. One example, reproduced as Table 4, may suffice to illustrate the details:

Three pairs of even and odd rotational transitions of the satellite '2' with rotational frequency separations of about 20 MHz were selected to ensure a flat response of the SEM spectrometer. Each transition was cross-checked against coincidence with a transition from the other 26 spectra associated with the sample, since overlap would, clearly, falsify the apparent intensity. The intensity ratio between the rotationally even and odd component of each pair was then determined experimentally (last column of Table 4). The theoretical intensity of each transition, which had been pre-calculated *without* consideration of the spin weights (column V of the table), was then multiplied with the spin weights that would apply if state '2' corresponded with a symmetric (even) or antisymmetric (odd) vibration, and the expected intensity ratios (columns VI b, VII b) were formed for both possibilities. – As may be verified from the experimental results in column VIII, there could not remain any doubt that state '2' arises from excitation of a symmetric vibration. The inertia defect contribution $\delta(ID) = -0.3117(4)$ uÅ^2 (see Table 2 or 5) suggests that state '2' arises from an "out-of-plane" vibration, which together with the later determined energy separation of ~ 650 cm^{-1} from the G.S. left little choice but to identify state '2' with excitation of the IR-inactive fundamental ν_8 at 635 cm^{-1}.

Table 4. Symmetry determination of satellite '2'.

I	II	III	VI	V	VIa VIb	VIIa VIIb	VIII
Pair	Transition frequency (in MHz)	Rotational assignment	Rotational symmetry $(K_+ + K_-)$	Intensity without weights	Weights & intensity ratio for $\psi^{(2)}_{1,vib.}$ = even	$\psi^{(2)}_{1,vib.}$ = odd	Observed intensity ratio
1	21251.6	$5_{4,2} - 5_{5,1}$	even	22.54	5 0.569 7	7 1.115 5	0.58
	21258.2	$7_{6,1} - 7_{7,0}$	odd	28.30			
2	28833.3	$11_{9,2} - 11_{10,1}$	odd	50.44	7 0.774 5	5 0.395 7	0.74
	28851.8	$16_{12,4} - 16_{13,3}$	even	91.23			
3	30795.1	$9_{8,1} - 9_{9,0}$	odd	25.63	7 0.510 5	5 0.260 7	0.50
	30814.0	$14_{11,3} - 14_{12,2}$	even	70.28			

Table 5. Summary of results of intensity measurements on satellite spectra of furazan and correlation with IR data [8].

MICROWAVE				INFRARED		
Desig-nation	Symmetry of $\Psi_{vib.}$	Vibrat'l energy (in cm^{-1})	δ(ID) (in $u\text{Å}^2$)	Desig-nation	Energy (in cm^{-1})	Symmetry species
1	odd	~ 650	$-0.4497(4)$	ν_{15}	631	B_2
2	even		$-0.3117(4)$	ν_8	634	A_2
3	?	?	$+0.551$?	ν_{13}	820	B_1
4	?	?	-1.192 ?	ν_{14}	838	B_2
5	even	~ 880	$+0.2063(6)$	ν_6	872	A_1
6	even		$-0.0159(6)$	ν_7	888	A_2
7	odd	~ 950	$+0.3426(4)$	ν_{12}	953	B_1
8	even	~ 1000	$-0.1039(5)$	ν_5	1005	A_1
9	even	~ 1040	$-0.1023(5)$	ν_4	1036	A_1
10	odd	~ 1190	$+0.2086(5)$	ν_{11}	1175	B_1
11	even	~ 1310	$+0.0468(5)$	ν_3	1316	A_1
12	even	~ 1420	$+0.0145(5)$	ν_2	1418	A_1

Note: The negative inertia defect contribution of the "in-plane" vibrations 8 and 9 (ν_5 and ν_4) should be noted.

Naturally, it became more difficult with increasing vibrational energy to find suitable pairs of odd and even transitions for intensity comparison within each satellite spectrum. However, at least two such pairs were examined for every fundamental level, and the fact that the relative intensity ratios would have to be in error by a factor $49/25 \sim 2$ to result in an incorrect

vibrational symmetry greatly enhances our confidence in this part of the work.

No such symmetry determinations were attempted on states '3' and '4' as it was obvious that a great deal of "intensity borrowing" was occurring within their mutually perturbed spectra.

Following the determination of vibrational symmetries of satellites, their energy separations from the G.S. and from each other were obtained from further relative intensity measurements, in which the now known weight factors were properly taken into account. While intensity ratios involving G.S. transitions had not sufficient accuracy for distinguishing with certainty between two states that lie within less than 30 cm^{-1} of each other, intensity comparisons between such states allowed a definite conclusion as to which one was higher in energy, including a qualitative determination of the vibrational energy gap between them.

The overall results of relative intensity measurements on vibrational satellite spectra in furazan are collected in Table 5. The left half of this table gives the findings from the present microwave work for comparison and correlation with the IR data [8], which are given in the right half of the table.

d) Summary of Microwave Results

A comprehensive illustration of the present work on the pure rotation spectra of vibrationally excited states of furazan is attempted in Figure 2. In this dia-
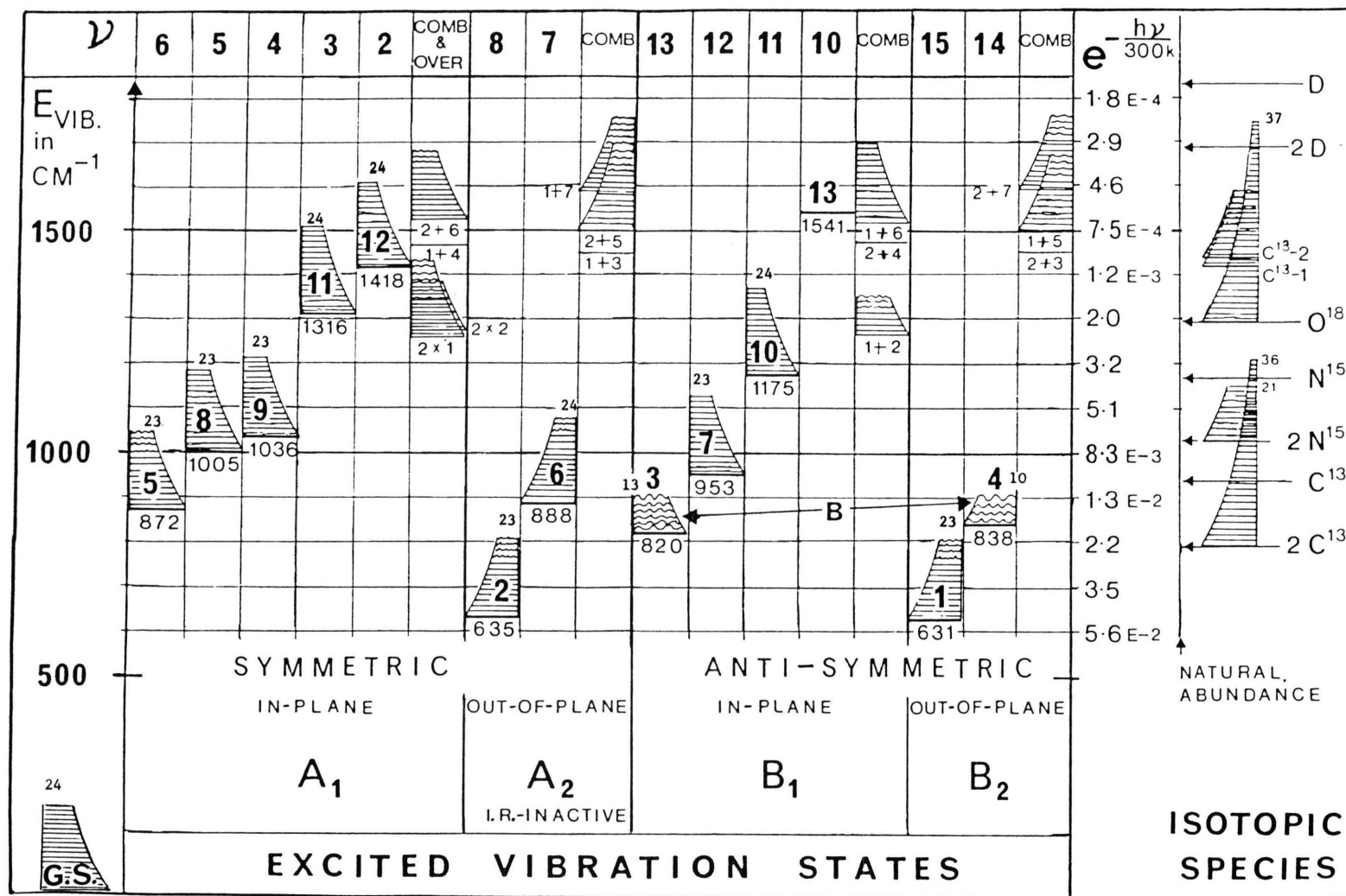
Fig. 2. Illustration of vibrationally excited states of furazan studied by DRM microwave spectroscopy. It should be noted that only the two CH-stretches v_1 and v_9 at ~3100 cm^{-1} are omitted from this diagram. (The notations $2C^{13}$, $2N^{15}$ and 2 D refer to molecular forms with the isotopes in either of the two equivalent positions.)

gram a scale of vibrational energy (in cm^{-1}) is drawn on the left hand side, and the population of states according to the Boltzmann law is given on the right hand side for a temperature of $T = 300$ K. Along that same scale are indicated the natural abundances of the isotopomers involving ^{13}C, ^{15}N, ^{18}O and deuterium (D). This suggests that when the sensitivity of a (DRM) spectrometer is sufficient to allow the detection [12] of a deuterium form of a molecule in its natural abundance of 0.015%, it should also be possible – at least in principle – to detect the pure rotation spectra of vibrationally excited states with comparably small populations, i.e. with vibrational energies in the range of 1800 cm^{-1}. – The manifolds of purely rotational energy levels of excited states are symbolised in Fig. 2 as "sails", drawn at the appropriate position of vibrational energy and with a height that represents the rotational energy of levels. They are labelled by the microwave designation of the rotation spectra. The small numbers at the top of the "sails" give the highest J-value of observed transitions. The horizontal shading of the sails is meant to indicate rotational levels, and is replaced by "wavy" lines where perturbations have been noticed. The curved edge of the sails is intended to indicate the decreasing Boltzmann population of levels on account of their rotational energy. Unfortunately, neither the Boltzmann function nor the density and position of rotational levels can be drawn to scale. – Across the top of the diagram, finally, the IR designations of vibrational modes are given, with separate columns inserted for overtone and combination levels. The designation '1 + 7', for example, is thus readily recognised as denoting the combination state ($v_{15} = 1$, $v_{12} = 1$).

e) Appraisal of Quantitative Results

In the absence of degeneracies the dependence of effective rotational constants on vibrational excitation is commonly approximated [13] as

$$R_{\text{effective}} = R_e - \sum \alpha_i (n_i + 1/2),$$

where R_e is the (hypothetical) rotational constant of the molecule "frozen" in its equilibrium configuration, and the α_i are the so-called rotation-vibration constants for the modes i.

Extensive use of this approximation has been made during the experimental stage of this study. It allowed the prediction of the rotational constants (and hence of the spectra) of vibrational overtone and combina-

tion levels, whenever the α-constants were known for the fundamentals in question. The experimental examination of such predictions (analysis of spectra) was essential not only for the continual assessment of the sensitivity of the spectrometer, but also for the identification of the states '10', '11' and '12' and their correlation with the IR data. These three satellites could be ascribed unequivocally to excitation of the modes v_{11}, v_3 and v_2 only after the overtone and combination spectra (see Fig. 2) had been eliminated. Although details from that work are omitted from the present paper for the sake of brevity, satisfactory agreement of experimental findings with the above approximation was noted throughout. This justifies the extraction of the α_i-constants in Table 2 as differences between corresponding constants of each fundamental level and the G.S. rotational constants:

$$\alpha_{R,i} = R_{\text{G.S.}} - R_{i, n_i = 1} \quad (R = A, B, C).$$

Zero-point vibration contributes for each mode i half that amount to the equilibrium constants R_e to give rise to the effective rotational constants of the G.S. – Hence, if the α_i-values were available for *all* 15 normal modes of furazan, the equilibrium rotational constants R_e could be calculated from the effective constants $R_{\text{G.S.}}$ of the ground state.

While the pure rotation spectra associated with excitation of the two C–H stretching vibrations v_1 and v_9 at ~ 3150 cm^{-1} cannot be considered for investigation by DRM spectroscopy on account to the present limitation in sensitivity, a satellite spectrum '13', assignable to excitation of the mode v_{10} at ~ 1541 cm^{-1} (approximate description: antisymmetric C=N stretch) has not been identified in this study. Furthermore, the rotation-vibration constants $\alpha_{R,3}$ and $\alpha_{R,4}$, calculated in Table 2 from the approximate and perturbed rotational constants for the Coriolis dyad (v_{13}, v_{14}) appear too inaccurate and may be principally inadequate for the task in hand. Hence, vibrational contributions from only 10 normal modes can be extracted from the effective G.S. constants to yield an approximation, $R_e^{(10)}$, to the equilibrium constants of furazan. – This calculation is presented in Table 6.

This table shows that all three constants $R_e^{(10)} = R_{\text{G.S.}} + \sum \alpha_{R,i}/2$ (which correspond to a furazan molecule with only five normal modes (i.e. $v_{13}, v_{14}, v_{10}, v_9$, and v_1) with 10 modes "frozen") are larger than the observed $R_{\text{G.S.}}$. The corresponding moments, $I_e^{(10)}$, lead to a *larger* inertia defect than has been observed

Table 6. Contributions from individual modes to the effective rotational constants (in MHz) and to the inertia defect (in $u\text{Å}^2$) in furazan.

Mode i	$\alpha_{A,i}/2$	$\alpha_{B,i}/2$	$\alpha_{C,i}/2$	$\delta(\text{ID})_i/2$
1	+ 14.84	+ 28.80	0.00	− 0.2249
2	+ 10.47	+ 17.26	− 0.71	− 0.1558
(3)	(+ 30.7)	(−118.7)	(− 10.3)	(+ 0.275)
(4)	(+ 23.5)	(+136.9)	(+ 13.6)	(− 0.596)
5	− 9.62	+ 30.24	+ 11.08	+ 0.1031
6	+ 12.85	− 11.16	− 0.43	− 0.0079
7	− 7.15	− 2.29	+ 6.27	+ 0.1713
8	− 4.11	+ 6.31	− 1.85	− 0.0519
9	− 5.79	+ 3.66	− 2.90	− 0.0511
10	− 4.34	− 7.25	+ 2.25	+ 0.1043
11	+ 4.76	+ 8.64	+ 4.59	+ 0.0234
12	+ 11.83	+ 6.90	+ 4.95	+ 0.0073
$\Sigma^{(10)}$	+ 23.74	+ 81.11	+ 23.25	− 0.0823
$R_e^{(10)}$	10480.95	9762.76	5046.95	
$I_e^{(10)}$	48.2185	51.7657	100.1349	
$(\text{ID})^{(10)}$		+ 0.1507		

for the G.S. Those five modes, for which no information is available, must therefore be judged to contribute rather significantly ($+0.151\ u\text{Å}^2$) to the inertia defect, which has to be zero for the equilibrium configuration. This result is confirmed by consideration of the inertia defect contributions from individual modes (right hand column of Table 6): The ten modes analysed are seen to contribute $-0.082\ u\text{Å}^2$ together, while the G.S. was observed to have an inertia defect of $+0.071\ u\text{Å}^2$. It follows again that the five modes, for which no or no reliable data are presently available, must contribute $+0.153\ u\text{Å}^2$ to the inertia defect of furazan. This unexpectedly large contribution makes a future experimental examination of the three unstudied vibrations v_{10}, v_9, and v_1 highly desirable. Such work (by FT-IR spectroscopy) would be expected to resolve the present question whether the large residual inertia defect arises primarily from the comparatively low vibrational modes '3' and '4' (Coriolis dyad v_{13}, v_{14}) or from the C−H stretching modes v_1 and v_9 at about 3100 cm^{-1}.

IV. Discussion

The present microwave study establishes molecular information which could not have been obtained with the techniques of either rotational or vibrational spectroscopy of the early 1960s. Both fields however have progressed significantly since then.
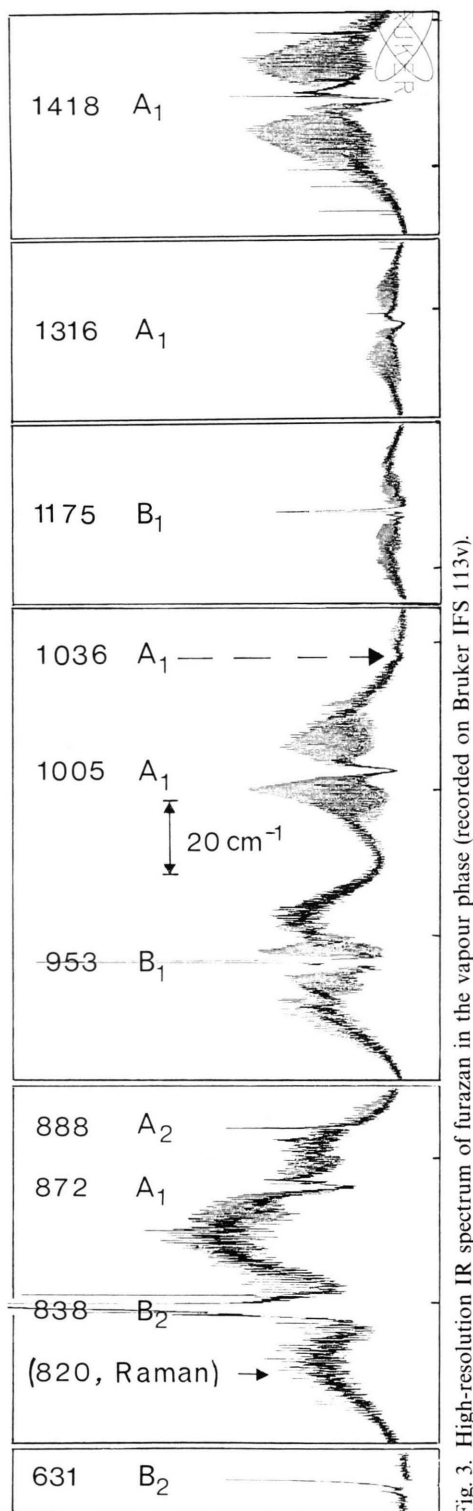

Fig. 3. High-resolution IR spectrum of furazan in the vapour phase (recorded on Bruker IFS 113v).

One experimental advance since that time, which we have been exploiting during the past two decades, is that of Double Resonance Modulation, which was introduced into microwave spectroscopy by E. Bright Wilson, Jr. and collaborators in 1966 [2]. We see the paramount advantage of this modulation technique over Stark effect modulation, introduced also by E. Bright Wilson, Jr. some 30 years earlier [3], in its extreme molecular *selectivity*. As has been demonstrated on a number of examples (see [1 a] or [12] for further references), this selectivity, when coupled with good spectroscopic sensitivity, allows the spectra of quite rare isotopomers to be studied in their natural abundances. As shown in the present paper, it also permits the detection and analysis of the pure rotation spectra of molecules in vibrationally excited states up to vibrational energies of ~ 1500 cm^{-1}. Hence it allows the identification and interpretation of nearly *all* absorptions detected in microwave spectroscopy and the exploitation of the major portion of molecular information commonly on offer.

Developments in vibrational spectroscopy during the same two decades have resulted in the replacement of low-resolution instruments by the high-resolution interferometers (with subsequent Fourier transformation of the interferogram) of today. As a result, molecular vibration spectra can now be recorded under resolutions of 10^{-3} cm^{-1} and, provided the rotational fine structure of such (resolved) IR bands can be unravelled, vibrational frequencies may be determined with the same degree of accuracy.

Figure 3 shows the vibrational spectrum of furazan in the range from 600 cm^{-1} to 1440 cm^{-1}, taken on a commercial, modern IR instrument (Bruker, IFS 113v) with a resolution of 0.03 cm^{-1} at a sample pressure of 15 Torr. Inspection shows that 10 of the 12 fundamentals rotationally analysed in the present study are readily detectable and most likely well resolvable in the IR spectrum. The A_1 mode at 1036 cm^{-1} (arrow) is, admittedly, very weak and the A_2 mode at 636 cm^{-1} is duely missing (IR inactive). The A_2 mode

at 888 cm^{-1}, on the other hand, is detectable presumably as a result of perturbations. No indication of the B_1 mode at 820 cm^{-1} is discernable in the vapour phase spectrum of Fig. 3, but the frequency of that vibration has been determined in the spectrum of the liquid and by Raman spectroscopy [6].

The improvement of IR resolution justifies the hope that all these bands can be satisfactorily resolved and analysed in the near future and that their centre frequencies can be determined to ± 0.001 cm^{-1} or better. This task should be greatly facilitated through the rotational information established here. – It does not seem too optimistic an outlook that FT-IR spectroscopy will permit the mode at 1541 cm^{-1} (B_1, antisymmetric $C=N$ stretch) and the two $C-H$ stretches at 3150 cm^{-1} to be rotationally analysed and to have their inertia defect contributions and their vibration frequencies determined accurately. This information would allow the contribution from vibrational motion to the G.S. moments of inertia to be determined for all modes. At the same time, accurate knowledge of all 15 fundamental frequencies would allow an improved determination of the force field within this molecule.

Such internal potentials, if established for a sufficient number of substances, might in the long run provide a more detailed understanding of chemical reactivity than has been available in the past.

Appendix

Measured transition frequencies (in MHz) of the G.S. and the first twelve fundamental levels in 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	15480.94	15451.26	15461.46	15434.75	15411.29	15477.99	15456.04	15482.70	15492.92	15498.26	-	-	-
1 0 1 → 2 1 2	25528.28	25498.64	25511.58	25523.42	25402.24	25480.73	25505.46	25504.86	25547.43	25557.20	25523.42	25491.12	25474.84
1 1 1 → 2 0 2	24663.70	24598.68	24629.70	25010.24	24250.07	24517.37	24699.53	24628.83	24657.14	24669.34	24666.20	24616.94	24622.31
1 1 0 → 2 2 1	36395.25	36306.09	36333.84	36229.39	36228.14	36430.54	36319.27	36425.64	36423.56	36435.72	36416.80	36357.36	36314.35
2 0 2 → 3 1 3	35224.13	35183.41	35204.89	35401.63	34949.43	35100.12	-	35171.54	35242.32	35257.03	35212.42	35165.40	35154.87
2 1 2 → 3 0 3	35128.60	35079.81	35105.37	35361.98	34786.44	34983.42	35139.12	35074.03	35141.35	35156.54	35118.77	35067.86	35061.72
Q - branch													
2 0 2 → 2 1 1	14062.69	13897.22	13958.66	14663.12	13390.36	13967.02	14116.46	14115.96	14018.68	14027.73	-	-	-
2 1 2 → 2 2 1	16300.47	16211.55	16233.34	16060.02	16239.60	16424.65	16220.80	16381.0 P	16314.0 P	-	-	-	-
3 0 3 → 3 1 2	24850.12	24601.58	24689.24	25416.90	23922.24	24778.90	24881.46	24952.26	24800.2	24813.10	24937.14	24821.25	24814.48
3 1 2 → 3 2 1	13307.01	13132.68	13199.04	14069.16	12627.7 ?	13177.90	13384.70	13354.00	13253.99	13263.73	-	13281.30	-
3 1 3 → 3 2 2	25281.23	25067.13	25137.66	25606.10	24625.7	25299.72	25262.46	25392.08	25254.54	25265.24	25360.66	25261.04	25235.78
3 2 2 → 3 3 1	17516.45	17473.56	17472.00	16769.88	17865.64	17771.27	17358.57	17612.62	17564.25	-	17546.40	17528.1 P	17459.2 P
4 0 4 → 4 1 3	35131.55	34809.48	34919.41	35742.94	33967.56	35098.82	35137.73	35281.36	35079.13	35095.50	35247.87	35097.55	35074.39
4 1 3 → 4 2 2	24290.76	24002.98	24110.28	25084.02	23202.0	24117.14	24380.92	24382.48	24213.74	24229.43	24386.54	24251.68	24266.92
4 2 2 → 4 3 1	12712.06	12555.93	12614.12	13452.84	12229.1 ?	-	-	-	-	-	-	-	-
4 1 4 → 4 2 3	35175.89	34859.62	34966.53	35751.75	34058.55	35157.91	35174.50	35326.94	35127.2	35143.20	35290.96	35143.48	35117.26
4 2 3 → 4 3 2	25510.69	25314.87	25376.22	25645.04	25109.30	25576.94	25465.27	25626.36	25496.28	25505.70	25586.24	25495.26	25460.00
4 3 2 → 4 4 1	19158.32	19178.10	19144.22	17738.99	20030.49	19589.90	18894.43	19275.71	19252.29	19248.40	19175.0 P	19187.2 P	19079.4 P
5 1 4 → 5 2 3	34955.93	34616.41	34735.02	35532.09	33912.41	34878.66	34985.66	35101.58	34891.93	34909.53	35076.18	34917.69	34903.57
5 2 3 → 5 3 2	23357.18	23016.46	23150.32	24514.38	22083.16	23045.24	23531.26	23433.67	23243.04	23262.26	23464.74	23304.18	23349.95
5 4 1 → 5 5 0	12919.55	13223.62	13061.18	-	-	-	-	13051.82	13165.16	13143.60	-	-	-
5 2 4 → 5 3 3	35128.71	34811.27	34918.93	35562.55	34252.73	35108.36	35129.44	35279.25	35079.08	35095.29	35244.02	35096.01	35070.46
5 3 3 → 5 4 2	25952.22	25790.00	25834.62	25786.76	25924.12	26106.68	25857.14	26076.50	25960.66	25967.90	26020.50	25945.32	25891.83
5 4 2 → 5 5 1	21227.84	21325.50	21251.66	18978.47	22680.38	21879.60	20831.16	21371.61	21379.31	21370.33	21228.3 P	21278.08	21121.7 P
6 2 4 → 6 3 3	34598.54	34222.96	34359.64	35241.36	33556.87	34429.03	34677.34	34735.62	34510.68	34530.83	34726.71	34551.48	34555.97
6 3 3 → 6 4 2	22117.79	21732.27	21888.60	23664.70	20959.82	21684.76	22373.60	22178.40	21969.80	21992.14	22235.14	22052.18	22126.96
6 4 2 → 6 5 1	13015.38	13023.06	13001.46	12766.0 ?	13421.36	13314.01	-	13092.98	13074.21	13071.82	13030.00	13032.41	-
6 5 1 → 6 6 0	16671.89	17120.93	16884.70	-	20119.80	18033.65	15850.50	16853.18	17024.57	16993.18	16583.15	16801.50	-
6 3 4 → 6 4 3	35096.20	34782.19	34888.13	35325.99	34488.81	35085.19	35092.91	35247.16	35048.48	35064.43	35210.72	35064.05	35037.31
6 4 3 → 6 5 2	-	26569.82	26588.06	26084.36	27177.76	26972.00	26505.52	26817.28	26723.70	26727.35	26735.96	26685.90	26603.24
6 5 2 → 6 6 1	23711.84	23900.27	23779.69	20495.50	25698.72	24620.50	23159.32	23887.08	23930.88	23915.53	23693.28	23787.14	23573.80
7 3 4 → 7 4 3	33953.04	33514.83	33682.64	34822.33	32773.66	33624.17	34118.67	34075.06	33823.38	33847.80	34094.93	33890.35	33927.79
7 4 3 → 7 5 2	20784.50	20391.0 P	20551.96	22558.68	18889.42	20319.43	21079.68	20835.16	20624.81	20647.90	20903.38	20714.48	20801.90
7 5 2 → 7 6 1	14297.34	14459.21	14361.56	13020.20	16442.16	14980.90	13930.78	14410.37	14457.86	14445.07	14277.24	14352.91	14204.90
7 6 1 → 7 7 0	21009.39	21590.62	21286.17	-	25285.26	22749.87	19943.75	21241.05	21464.22	21423.67	20892.92	21176.94	20784.90
7 4 4 → 7 5 3	-	34821.74	34920.95	35015.71	34837.06	35146.00	35102.18	35275.58	35083.05	35097.95	35233.82	35093.26	35060.13
7 5 3 → 7 6 2	-	27720.36	27701.48	26592.36	28998.52	28242.50	27470.70	27913.44	27850.92	27489.58	27795.94	27781.48	27657.50
7 6 2 → 7 7 1	-	26867.20	26695.42	22288.24	28873.72	27770.68	25853.88	26790.08	26873.08	26851.10	26540.36	-	26406.35

12	11	10	9	8	7	6	5	4	3	2	1	G.S.	J	KA	KC
–	32834.60	33081.33	32760.74	32730.38	33019.50	33213.29	32367.20	*31524.97*	*34205.54*	*32604.74*	32392.86	32919.88	8	4	4
19669.96	19600.40	19766.20	19547.31	19527.88	19712.63	19913.35	19312.72	*18237.51*	*21307.35*	*19455.39*	19320.26	19659.76	8	5	3
25411.68	16605.54	16434.32	16768.32	16794.30	16661.82	15480.64	17687.41	*19568.17*	*13867.83*	*16664.78*	16861.22	16499.28	8	6	2
35199.31	25878.34	25543.34	26171.20	26218.60	25958.26	24404.90	27730.02	*30592.86*	*18166.29*	*26003.94*	26361.66	25679.94	8	7	1
29102.30	35247.31	35373.96	35261.88	35248.70	35428.43	35210.42	35368.88	*35453.95*	*34553.95*	*35083.05*	34998.34	34998.34	8	5	4
	29279.41	29248.48	29382.42	29390.05	29412.86	28799.36	29965.14	*31526.57*	*27363.49*	*29222.42*	29288.86	29288.86	8	6	3
	29915.82	29723.64	30126.69	30155.56	30032.32	28874.84	31270.01	*24342.78*	*24342.78*	*29949.20*	30174.24	30174.24	8	7	2
31497.20	31357.16	31651.11	31247.97	31211.21	31540.80	31911.54	30674.34	*29977.90*	*33313.98*	*31103.71*	30844.54	31467.67	9	5	3
19040.80	19027.65	19134.73	19013.58	19002.45	19129.68	19165.81	19010.21	*18093.50*	*20099.52*	*18919.77*	18846.62	19057.80	9	6	4
19437.50	19820.17	19538.64	20065.85	20106.65	19877.83	18647.89	21422.04	*23830.86*	*15428.91*	*19935.54*	20244.95	19654.68	9	7	1
30138.60	30662.95	30294.12	30991.17	31043.16	30761.32	29004.64	32725.30	*35817.05*	*21809.46*	*30795.11*	31189.96	30442.21	9	8	0
35527.71	35601.74	35704.28	35633.57	35624.02	35781.32	35483.48	35841.84	?	*33703.29*	*35450.89*	35391.75	35610.59	9	6	3
	31206.02	33415.97	31350.72	31365.97	31341.58	30520.95	32159.65	?	*28444.00*	*31175.72*	31298.92	31125.20	9	7	2
33017.83	33427.62	33185.84	33681.21	33716.93	33554.50	32171.38	35048.38	?	*26631.64*	*33480.35*	33758.35	33267.04	9	8	1
29749.90	29565.28	29894.52	29428.92	29387.58	29744.75	30267.60	28734.28	*28853.30*	*32099.39*	*29296.95*	29005.00	29695.31	10	6	3
29175.06	29258.45	29271.02	29309.46	29311.87	29349.53	29093.22	29675.10	*29468.42*	*19163.11*	*19206.66*	19232.04	19240.42	10	7	4
23387.40	23901.03	23509.52	24230.00	24286.20	23964.30	22305.48	26016.02	*28702.16*	*17785.31*	*24069.36*	24489.56	23675.37	10	8	2
34802.92	35372.29	34981.46	35728.01	35782.85	35490.30	33572.29	37599.83	?	*25578.05*	*35504.26*	35925.19	35135.37	10	9	1
36120.38	36234.46	36300.52	36292.83	36288.37	36412.33	35991.36	36651.93	?	*31957.45*	*36103.80*	36083.21	36224.20	10	7	3
33247.69	35234.46	33415.97	33754.61	33778.46	33701.50	32643.95	34817.27	?	*29870.18*	*33561.96*	33748.92	33448.75	10	8	3
36679.63	37155.46	36866.32	37450.73	37492.90	37294.07	35687.28	39035.14	?	*29215.42*	*37225.53*	37554.48	36966.66	10	9	2
27908.66	27711.80	28044.30	27570.20	27529.20	27882.46	28466.00	26888.94	?	*30600.94*	*27448.33*	27158.34	–	11	7	4
20258.47	20476.08	20361.35	20616.82	20637.16	20556.99	19886.13	21476.43	?	*18708.06*	*20497.20*	20654.09	20392.55	11	8	3
27994.96	28624.84	28141.04	29026.90	29095.30	28699.15	26650.02	31170.86	?	*20947.25*	*28833.06*	29345.06	28348.34	11	9	2
39336.33	39944.90	39537.12	29026.90		38023.47	38023.47	?	?	*29302.27*			–	11	10	1
37047.43	37216.33	37232.76	37311.15		37392.54	36801.04	37872.82	?	*29029.98*	*37112.79*	37144.05	37179.90	11	9	3
–	36326.66	36115.14	36570.05		36470.63	35155.92	37901.51	?	*31664.07*	*36356.88*	36611.43	36177.43	11	10	2
26301.72	26141.66	26429.94	26028.54	25994.38	26298.96	26793.68	25546.00	?	*29027.90*	*25911.10*	25672.78	26253.52	12	8	4
22399.21	22782.95	22514.76	23033.72	23075.28	22855.56	21666.34	24480.20	?	*18845.51*	*22889.18*	23202.72	22619.57	12	9	3
32980.54	33698.64	33151.65	34154.87	34231.51	33789.35	31432.85	36551.28	?	*24823.15*	*33929.13*	34502.70	33385.32	12	10	2
								?	*32869.73*			–	12	11	1
38363.64	38601.83	38556.18	38742.57	38754.03	38776.69	37968.44	39554.91	?	*25215*	*37112.71*	38627.71	38532.46	12	10	3
38981.25	39456.22	39179.06	39752.10	39793.67	39606.84	38024.60		?	*33832.03*	*36356.88*	39839.14	39270.44	12	11	2
39296.04	39025.13	39487.57	38822.53	38763.34	39265.21		37768.34	?	*34466.68*	*38650.86*	38229.93	39210.86	13	9	4
	25209.16	25399.42	25162.36	25142.74	25349.52	25577.24	25077.84	?	*27968.10*	*25041.86*	24909.53	25272.04	13	10	3
25613.77	26180.88	25746.94	26551.34	26615.62	26249.14	24477.67	28614.61	?	*19360.18*	*26375.66*	26855.12	25930.71	13	11	2
38070.81	38847.21	38267.25	39338.54	39419.16	38958.52	36389.40		?	*29224.04*	*39082.22*	39689.42	38512.09	13	12	1
37075.57	36745.72	37255.57	36507.71	36442.83	36980.35	37931.23	35320.99	?	*26230.65*	*36351.57*	35889.47	36957.05	14	10	4
25122.70	25206.90	25248.20	25262.98	25264.74	25328.52	25112.28	25758.24	?		*25130.40*	25154.32	25194.35	14	11	3
29795.05	30540.10	29950.48	31025.15	31110.17	30610.02	28259.76	35647.67	?		*30813.96*	31445.68	30207.46	14	12	2
34756.80	34426.42	34934.80	34187.66	34124.42	34649.18	35667.94	33075.53	?		*34043.23*	33598.54	34638.35	15	11	4
26051.64	26333.64	26183.84	26523.98	26552.54	26437.02	26621.52	27744.97	?		*26370.28*	26591.06	26223.90	15	12	3
34710.01	35603.52	34890.54	36181.96	36282.63	35682.72	32832.61	39230.24	?		*35934.35*	36682.38	35204.46	15	13	2
32722.83	32443.83	32882.48	32252.33	32200.64	32647.78	33526.18	31475.49	?		*32112.48*	32112.48	32621.67	16	11	5
28173.72	28689.18	28318.18	29035.31	29094.51	28776.10	27243.52	*31068.68*	?		*28851.78*	28851.78	28465.74	16	12	4
31325.03	31184.41	31479.25	31092.25	31062.10	31364.04	31862.34	*30912.06*	?		*30947.43*	30947.43	31290.20	17	12	5
31492.48	32255.12	31655.32	32764.03	32854.38	32331.10	30023.73	*35603.74*	?		*32544.26*	32544.26	31913.50	17	13	4

J KA KC	J KA KC	G.S.	1	2	3	4	5	6	7	8	9	10	11	12
18 13 5	18 14 4	30966.78	30881.36	30862.15			*31661.78*	*31008.92*	31119.80	31022.75	31022.40	31051.37	30967.7	30897.27
18 14 4	18 15 3	36425.40	38139.51	37273.75			–	*33895.80*	36948.10	37650.85	37533.38	36067.02	36875.13	35881.61
19 13 6	19 14 5	–	*37786.06*	–			*38994.85*	–						–
19 14 5	19 15 4	31873.33	32351.60	32064.64			*33867.62*	*31222.67*	32132.33	32285.14	32247.38	31827.68	32007.98	31667.68
19 15 4	19 16 3	–	–	–			*–.*	*38667.79*						–
20 14 6	20 15 5	38828.40	37618.68	38124.95			*37188.06*	–	38824.65	38213.80	38285.88	39187.44	38572.86	38995.98
20 15 5	20 16 4	34118.32	35217.08	34631.25			*37532.34*	*32662.71*	34503.28	34930.42	34851.58	33927.14	34403.66	33755.1
21 15 6	21 16 5	–	36400.41	36685.40			*36580.63*	38060.55	37227.80	36816.20	36858.55	37428.29	37008.31	37243.67
21 16 5	21 17 4	37684.74	39396.03	38520.93			–	35382.88	38204.56	38901.57	38782.50	37346.62	38123.0	–
22 16 6	22 17 5	36605.10	36451.15	36450.37			*37438.17*	36823.76	36770.93	36634.23	36635.42	36728.50	36588.20	36545.63
22 17 5	22 18 4	–	–	–			–	39315.37	–	–	–	–	–	–
23 17 6	23 18 5	–	37951.97	37616.58			*39883.91*	36733.96	37687.9	37879.54	37831.92	37339.03	37542.45	37152.12
24 18 6	24 19 5	39623.22	–	–			–	37975.56	–	–	–	39388.44	39971.20	39190.80

Transition frequencies 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 (uncertainty ±0.3 MHz).

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