High-Resolution Vibrational Spectra of Furazan

II. The B_1 Fundamental ν_{11} at $\sim 1175\ \text{cm}^{-1}$ from Fourier-Transform Infrared Spectroscopy

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The high-resolution FT-IR spectrum of the A-type fundamental ν_{11} of furazan ($C_2H_2N_2O$) has been recorded and analysed against the background of rotational information from DRM microwave spectroscopy to yield the band origin as $\nu_{11}^0 = 1175.3377 \pm 0.0001\ \text{cm}^{-1}$.

The combined use of microwave (MW) and FT-IR data gives this band origin with a statistical uncertainty of $\sigma = 10^{-6}\ \text{cm}^{-1}$ and leads to a refinement of the rotational constants of the state $\nu_{11} = 1$ over those derivable from either MW or FT-IR data alone.

I. Introduction

In an earlier paper [1 a] we reported the pure rotational spectra of molecules in the first excited levels of twelve of the fifteen fundamental vibrations of the heterocyclic compound furazan ($C_2H_2N_2O$). The observation and analysis of those spectra had become possible as a result of the good spectral sensitivity and the extreme molecular selectivity of the technique of double resonance modulation (DRM) microwave spectroscopy [1 b]. Since the associated fundamental vibration frequencies themselves could not be determined with the desirable precision from this microwave work alone, we subsequently derived such information at least for the fundamentals $\nu_{12} \sim 953\ \text{cm}^{-1}$ and $\nu_5 \sim 1005\ \text{cm}^{-1}$ from CO_2 laser/microwave double resonance (LMDR) experiments [1 c]. By the end of the 1980s, however, the techniques of vibrational spectroscopy had reached the refinement generally expected of high-resolution methods through the change-over from dispersive to interferometric techniques (with subsequent Fourier transformation (FT) of the accumulated interferogram). As a consequence, the high-resolution infrared (IR) spectrum of furazan could now be recorded over the range from $600\ \text{cm}^{-1}$ to $3400\ \text{cm}^{-1}$ for the purpose of a precise determination of the vibrational band origins (ν_i^0) of the IR active modes.

As reported recently [1 d] for the modes ν_{12} and ν_5, the combination of the rotational information for excited states [1 a] with the rovibrational data from FT-IR spectroscopy greatly facilitates the analysis of the latter and leads to an overall improvement in the precision of the molecular information. The present paper describes corresponding results for the A-type B_1-fundamental ν_{11} at $\sim 1175\ \text{cm}^{-1}$.

II. Systematics of Rotation and Vibrations of Furazan

The planar, five-membered ring molecule furazan belongs to the symmetry point group C_{2v}. Its C_2 axis passes through the oxygen atom and the mid-point of the C–C bond. The permanent dipole ($\mu = 3.38$ D [2]) necessarily coincides with that axis. Its moment of inertia is smallest (I_a) about an axis perpendicular to the C_2 axis in the plane of the ring, and largest (I_c) about the axis perpendicular to the ring. Hence, the moment about the C_2 symmetry axis is of intermediate size (I_b) and the pure rotational spectra of the oblate asymmetric rotor furazan ($\varkappa \sim 0.715$) obey the μ_b dipole selection rule. Such spectra have been observed and reported, in addition to those of the vibrational ground state (GS) of the normal species and of isotopomers [1 e] for all but the three energetically highest fundamental vibrational levels [1 a].

The 15 fundamental vibrations of furazan are illustrated in Fig. 1, which has been constructed from the results of a normal coordinate analysis [3]. In this figure, the approximate wavenumbers of fundamental bands, as determined in the study by Christensen et al. in 1973 [4], have been added, and the illustrations of normal modes are arranged at heights which qualita-

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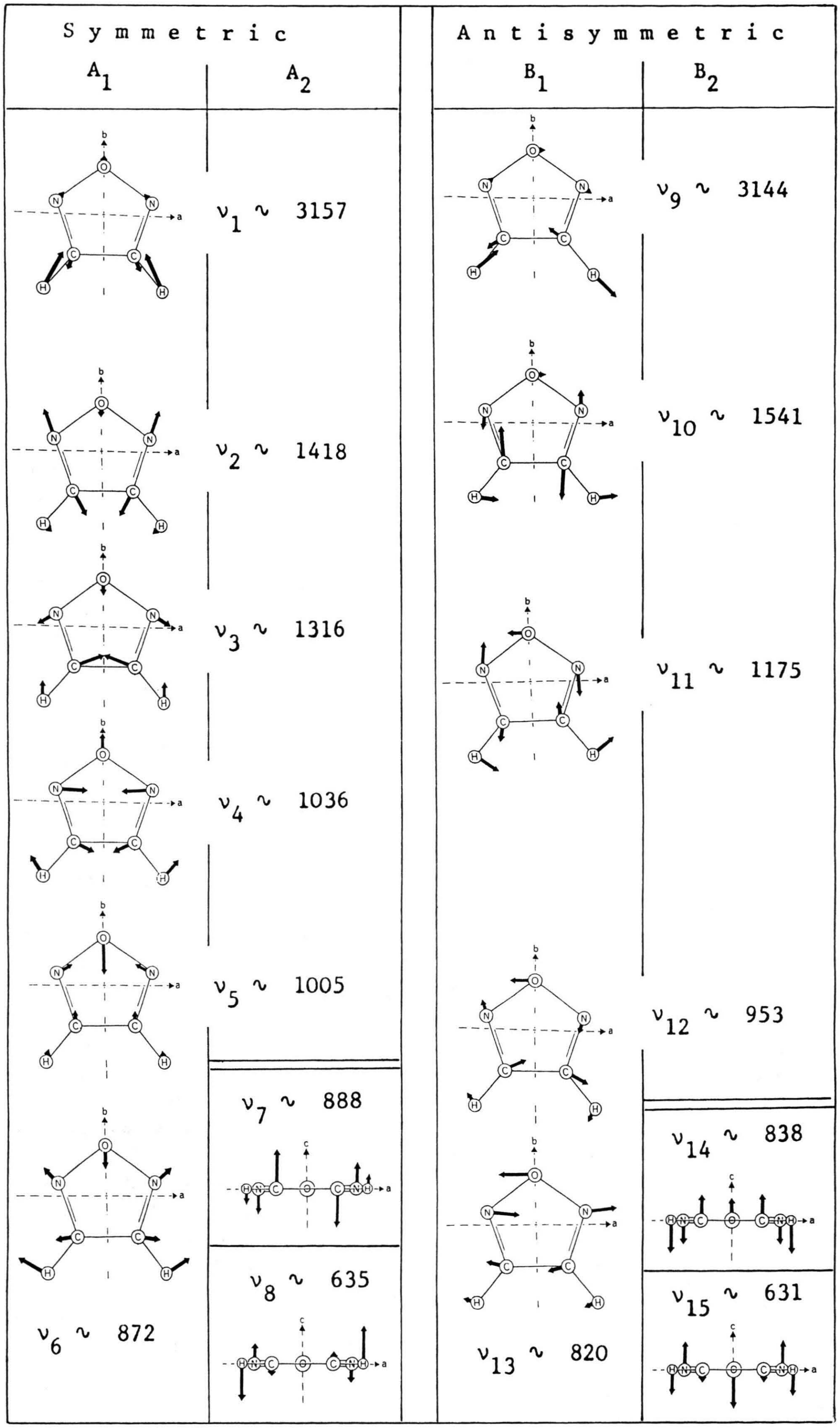


Fig. 1. The fundamental modes of vibration of furazan and their symmetry classification.

tively reflect the energy of vibrations, so as to make the likelihood of interactions between different modes obvious. The 15 modes split into eleven $(2n-3)$ in-plane vibrations and four $(n-3)$ out-of-plane vibrations. The symmetry operation C_2 divides the 15 modes into eight symmetric ones (A-species) and seven antisymmetric ones (B-species). The displacements are given in Figure 1. For the symmetrical planar modes (A_1) the vibrational dipole moment coincides with the C_2 axis, which is the inertial *b*-axis, and the rovibrational transitions in an A_1 fundamental therefore obey the μ_b selection rule (B-type bands). In the two symmetrical out-of-plane modes (A_2) the vibrational bond dipoles on either sides of the C_2 axis mutually cancel, hence the total vibrational moment vanishes, and this renders the A_2 fundamentals IR-inactive. The antisymmetric in-plane vibrations (B_1) produce an oscillating dipole moment along the inertial *a*-direction, and the associated fundamental bands therefore obey the μ_a selection rule (A-type bands). The two antisymmetric out-of-plane modes (B_2), finally, lead to a non-vanishing vibrational moment perpendicular to the furazan ring, and the fundamental bands to these levels are governed by the μ_c selection rule (C-type bands). In the language of group theory [5, 6] all this is condensed into the expression for the irreducible representation Γ_{vib} of the point group in terms of the four vibrational symmetry species:

$$\begin{array}{lcccc} & \Gamma_{\text{vib}} = 6\,A_1 & +\ 2\,A_2 & +\ 5\,B_1 & +\ 2\,B_2 \\ \text{with} & \downarrow & \downarrow & \downarrow & \downarrow \\ \text{band contours:} & \text{B-type} & \text{inactive} & \text{A-type} & \text{C-type.} \end{array}$$

The overall intensity of vibrational bands depends on the magnitude of the oscillating dipole moment. The relative intensity of individual rovibrational transitions, however, is influenced by the nuclear spin degeneracy of rotational levels in the lower vibrational state (here: GS). As has been outlined before ([1 a], Sect. III c) and experimentally exploited for the correlation of observed rotation spectra with symmetric or antisymmetric excited states of vibration, the nuclear spins of the two equivalent nitrogen atoms ($I_N = 1$) and the two hydrogen atoms ($I_H = 1/2$) in furazan impart to the even rotational levels ($K_a + K_c = \text{even}$) of the GS a relative spin statistical weight of 5, and to the odd ones ($K_a + K_c = \text{odd}$) a weight of 7. The dipole selection rules operating in the three band types preserve that weighting.

III. Experimental and Computational

The medium-strong fundamental band ν_{11} was recorded on the Bruker IFS 120 HR commerical FT-IR spectrometer at the Justus-Liebig Universität Giessen (BRD). The sample cell, with wedged KBr windows, was 300 cm long and contained the furazan vapour at a pressure of 2.5 mbar at room temperature (~ 300 K). The IR radiation was provided by a Globar source and was detected with a Ge:Cu crystal cooled to liquid helium temperature (4.2 K). The interferogram was built up from 245 coadded scans and the unapodized resolution was set to 0.0039 cm^{-1}. Immediately after the sample run the instrument was calibrated against accurately known [7] wavenumber values of absorption peaks of N_2O.

The numerical analysis of the experimental data was carried out at the Computing Laboratory of C.P.G.C. with the help of a program developed by Gambi [8] at the Universität Giessen. This computational scheme uses the A-reduced Hamiltonian in the I^r representation, as given by Watson [9], for the calculation of rotational energy levels in the upper and lower state, and it assumes the absence of interactions with other vibrational modes. In view of the previously established [1 a, d] insignificance of sextic distortion constants in the case of furazan, Watson's Hamiltonian was shortened to comprise only the quartic distortion terms:

$$\begin{aligned} \hat{H}_{\text{rot}} = {} & \tfrac{1}{2}(B+C)\,\hat{P}^2 \\ & + (A - \tfrac{1}{2}(B+C))\,\hat{P}_a^2 - \Delta_J \hat{P}^4 - \Delta_{JK} \hat{P}^2 \hat{P}_a^2 - \Delta_K \hat{P}_a^4 \\ & + (\tfrac{1}{2}(B-C) - 2\delta_J \hat{P}^2) \cdot (\hat{P}_b^2 - \hat{P}_c^2) \\ & + [(-\delta_K \hat{P}_a^2), (\hat{P}_b^2 - \hat{P}_c^2)]_+ \,. \end{aligned}$$

Here, *A*, *B*, and *C* are the reduced rotational constants and $\hat{P}$ is the angular momentum operator with components $\hat{P}_a$, $\hat{P}_b$, $\hat{P}_c$ along the inertial axes. Δ and δ are the quartic distortion constants. The third line in this Hamiltonian is the product between the bracketed operators, while the last line denotes the anti-commutator [9] between such terms.

The computer routine consists of two sections, of which the first one (TRANSI) permits the computation of a vibrational band structure (peak wavenumbers and intensities of rovibrational transitions) from the known (or assumed) rotational parameters of the two states and the known (or assumed) wavenumber ν^0 of the band origin (17 parameters altogether). The other part of the program is a least-squares (LSQ) fitting procedure (MINIQ) for the extraction of those 17 parameters of a band from a suitably large set of identified (assigned) rovibrational transitions of the observed spectrum.

Since, in our present application, the eight rotational parameters of the GS were known from preceding MW- and IR-work [1 a, d] the LSQ fitting procedure reduced to the determination of the band origin ν_{11}^0 and of the eight rotational parameters of the excited state $\nu_{11}=1$. However, since the rotational constants of the excited state were also known to good precision [1 a], the assigned rovibrational transitions were used essentially for the determination of the band origin ν_{11}^0, of the quartic distortion constants of the excited state, and for the improvement in accuracy of the three rotational constants for the state $\nu_{11}=1$.

The extent of the available background information will make it plausible to the reader that we saw no need for the additional features of the computer package which are designed for the mutual interconnection of TRANSI and MINIQ with the observed spectrum (see Fig. 4 of [8]).

IV. Results

1. Assignments within the Band ν_{11}

The general similarity between the structure of the ν_{11}-band and that of the previously analysed ν_{12}-band [1 d] of furazan, which are both A-type bands, could hardly be overlooked, and on that basis the origin of the former band was sought near the low wavenumber edge of the central Q-branch. Accordingly, the expected band structure was computed (program TRANSI) with rotational constants for the excited state taken from the DRM microwave study [1 a] and distortion constants taken identical with those of the GS. The rotational parameters of the latter state were taken as given in Table 1 of [1 d], and the assumed band origin was inserted as 1175.3 cm^{-1}. A comparison of the results of this first model calculation with the observd band structure readily allowed th tentative assignment of some 350 observed rovibrational transitions in the range from $J'=20$ to $J'=35$. In this range the $|\Delta J|=1$ clusters [1 d] resolve well into their components. These tentatively assigned lines shared a consistent deviation from their counterparts in the model calculation of $+0.0377 \pm 0.0001$ cm^{-1}. The correctness of all these hand-picked assignments was confirmed in a first LSQ-fit (program MINIQ) which included the 87 known [1 a] pure rotational transitions within the excited state to yield the band origin as $\nu_{11}^0 = 1175.337701(1)$ cm^{-1}. A new calculation of the band with the parameters derived from that first fit served as the basis for all further assignments. It allowed some 700 transitions in both the P- and R-branches between 1150 cm^{-1} and 1200 cm^{-1}, and some 600 Q-branch transitions outside the central range to be identified. To facilitate the assignments within the "cramped" central Q-branch spike, transitions in the wavenumber range 1175.0–1176.5 cm^{-1} were repredicted up to $J_{\max}=70$ from the molecular constants deduced by then from some 2000 assigned and fitted transitions.

2. Qualitative Description of the ν_{11}-Band

The spectral features of the ν_{11}-band neither differ from nor extend what has been reported previously for an A-type band in furazan. A repetition of that earlier description ([1 d], Sect. III,2) is therefore omitted here. However, to allow the reader to assess the similarity between the structures of the ν_{11}- and ν_{12}-band, we produce as Fig. 2 an overview of the ν_{11}-band (in the middle of the figure) with high-resolution sections arranged around it. The style of the figure, including the inserted principal quantum numbers J' of the excited state and the distances of the ranges shown from the band origin, is deliberately kept the same as that of Fig. 1 of [1 d].

3. Molecular Constants and Band Origin

The final molecular parameters for the level $\nu_{11}=1$ and the band origin were derived from 2094 assigned rovibrational transitions together with the 87 rotational (microwave) lines within the excited state. The MW transitions in this fit were given a weight of 10^4 as their frequency accuracy is estimated to be 100 times higher than the accuracy of the IR peak wavenumbers. The rovibrational transitions were all given the same weight. Some 300 tentatively assigned IR transitions with deviations from calculation of $5-10 \times 10^{-4}$ cm^{-1} were eliminated from the final fit in which a compatibility limit of 5×10^{-4} cm^{-1} was imposed for reasons outlined previously ([1 d], Sect. III,3). A number of blended pairs of transitions of comparable intensity with calculated separations of less than the experimental resolution (0.0039 cm^{-1})

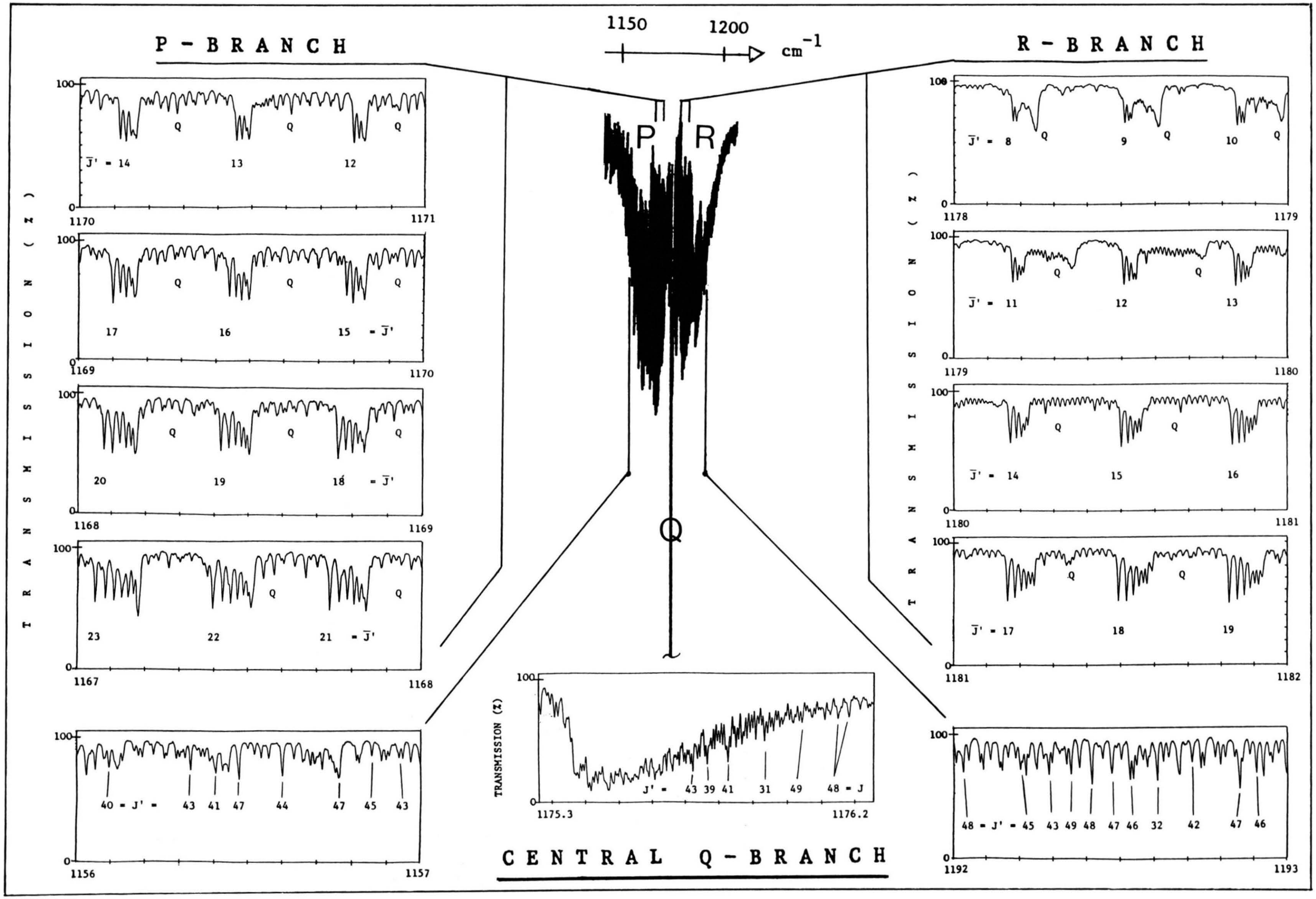
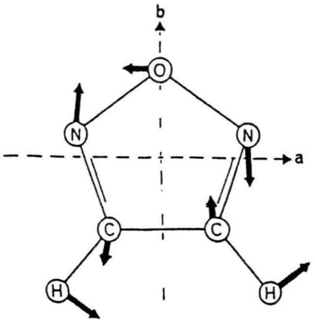


Fig. 2. The A-type band ν_{11} at ~1175 m^{-1} with high-resolution sections.

Table 1. Molecular constants and band origin for the fundamental vibration ν_{11} of furazan.

Mode, level	GS [a]	$\nu_{11}=1$
C_{2v} symmetry species	A_1	B_1
Selection rule/type	(μ_b)	μ_a/A-type
Diagrammatic description		
Fitted transitions		
$N_{\text{P-branch}}$		681
$N_{\text{Q-branch}}$		681
$N_{\text{R-branch}}$	([1 d], Sect. III,4)	732
$N(\text{IR})_{\text{total}}$		2094
Standard deviation of IR fit		2.5 E-4 cm^{-1}
MW transitions		87
$N(\text{IR}+\text{MW})_{\text{Total}}$		2181
Standard deviation (IR + MW)		1.2 E-5 cm^{-1}
Rotational constants (in cm^{-1} and MHz [b])		
A	0.348 814 617 (21) *10 457.1991 (6)*	0.349 104 648 (24) *10 465.8941 (7)*
B	0.322 944 775 (19) *9 681.6408 (6)*	0.323 428 709 (24) *9 696.1488 (7)*
C	0.167 572 473 (19) *5 023.6964 (6)*	0.167 422 520 (28) *5.019.2009 (8)*
Quartic distortion constants (in 10^{-7} cm^{-1})		
Δ_J	0.832 70 (18)	0.837 80 (15)
Δ_{JK}	−0.276 00 (59)	−0.324 37 (73)
Δ_K	0.768 14 (60)	0.835 38 (67)
δ_J	0.332 47 (6)	0.336 42 (8)
δ_K	0.625 57 (27)	0.620 11 (27)
Band origin ν^0_{11} (in cm^{-1})		1175.337 681 (1)

[a] Constants held fixed in the LSQ fit.
[b] Conversion factor $c =$ 29 979.2458 E+6 cm/sec.
[c] Uncertainties are 1 σ limits and given in units of the last quoted digit.

Correlation matrix of the LSQ determination of the molecular constants of the state $\nu_{11}=1$.

1.0000								
−0.3484	1.0000							
−0.3245	0.6785	1.0000						
0.3840	−0.1782	−0.7647	1.0000					
−0.2287	0.1076	0.6548	−0.9555	1.0000				
0.6845	−0.1719	0.0690	−0.0437	0.1276	1.0000			
0.3176	0.0071	0.4551	−0.4659	0.4769	0.7842	1.0000		
0.2127	−0.0449	0.1041	0.0791	−0.1721	0.1083	−0.1000	1.0000	
0.0296	−0.1676	−0.0677	0.0000	0.0046	0.0401	0.0277	0.0030	1.0000

Sequence of variables: $A-B$, B, Δ_J, Δ_{JK}, Δ_K, $B-C$, δ_J, δ_K, ν^0_{11}.

but more than the adopted compatibility limit were included in the fit after the addition and subtraction of half the calculated doublet separation to/from their observed peak wavenumber value. Wavenumbers thus modified are marked with a dot in the list of fitted rovibrational transitions. This list has been deposited with the "Sektion für Spektren und Stukturdokumentation" of the Universität Ulm, Postfach 4066, D-7900 Ulm. It may also be obtained from the author.

The results of the present work are collected in Table 1. This table gives in its top part a diagrammatic description of the normal mode ν_{11}, and this is followed by statistical information concerning the LSQ fit of this IR band. The lower half of the table lists the deduced molecular constants with $1\,\sigma$ uncertainty limits. To facilitate the comparison of the present results with those derived from DRM MW spectroscopy alone [1 a], the values of the rotational constants of the excited state are given in frequency units (in italics) as well as in wavenumber units. The distortion constants, however, are given in wavenumber units only since their frequency equivalents would not be directly comparable with the values quoted in the DRM MW study [1 a]. There, the spectra had been fitted to a Hamiltonian adapted for planar molecules (τ-constants). The molecular constants of the GS of furazan, as deduced previously ([1 d], Sect. III,4), are repeated in Table 1 for the sake of completeness. They were held fixed in the present LSQ fit. Inspection of Table 1 shows the molecular constants of the state $\nu_{11}=1$ to carry uncertainties which are comparable with those of the GS and with those of the states $\nu_{12}=1$ and $\nu_5=1$ [1 d]. The same holds true for the uncertainty of the deduced band origin, which indicates again a statistical uncertainty of 10^{-6} cm^{-1}. Unfortunately, this rather high precision cannot be exploited at present because the calibration of the FT-IR instrument superimposes a 100 times larger absolute error margin on this value. The overall quality of the constants quoted in Table 1 may be assessed by inspection of the correlation matrix of the LSQ fit which is given for that reason.

V. Discussion

The present work shows that the ν_{11}-mode of furazan is not detectably perturbed by vibrational interactions with other modes. This might have been expected since the nearest fundamental and combination levels are at least 100 cm^{-1} removed from the level $\nu_{11}=1$. The absence of Coriolis coupling renders the band suitable for analysis wih he computer package by Gambi.

As may be verified by inspection of Fig. 3 of [1 a] the ν_{11}-band is of significantly smaller intensity than the previously analysed [1 d] ν_{12}-band of furazan. It was necessary therefore to record the ν_{11}-band at a five times higher pressure than the ν_{12}-band and, as a comparison of Fig. 2 with Fig. 1 of [1 d] shows, individual absorptions of the ν_{11}-band were significantly broader than those of the ν_{12}-band. This entailed a reduction of the spectral resolution by approximately a factor 2. The increased line widths and reduced resolution – both consequences of the smaller intensity – manifest themselves in the analysis of the ν_{11}-band in two ways: Firstly, a larger portion ($\sim 15\%$) than before ($\sim 5\%$) of presumably correctly assigned IR transitions had to be discarded from the final LSQ fit because of discrepancies larger than the imposed compatibility limit of 5×10^{-4} cm^{-1} between observed and calculated wavenumber values. Secondly, the broader lines led to an increase in the number of blending transitions which were subsequently split up to preserve them in the final LSQ fit of the ν_{11}-band.

Nevertheless, the present study confirms the previously expressed view that the availability of purely rotational information about the excited vibration states of polar molecules greatly simplifies the analysis of the corresponding vibrational bands in the high-resolution FT-IR spectrum: Although a value for the band origin ν_{11}^0 better than that deduced by dispersive IR techniques in 1973 [4] was not available at the outset of this work, a value comparable in accuracy to those derived for the modes ν_{12} and ν_5 from LMDR experiments [1 c] was quickly deduced from a comparison of the observed high-resolution band structure with that computed on the basis of the earlier microwave data [1 a]. This aspect certainly emphasises the utility of the DRM MW technique. In addition to that, the inclusion in the IR fit of MW transitions with their 100 times higher frequency accuracy than the FT-IR peak wavenumber values reduces the uncertainties of the derived molecular constants by factors of up to three, and that of the band origin by a factor of nearly 20 from their counterparts extractable from a fit of the FT-IR data alone. This also upgrades the utility of DRM MW spectroscopy, which had allowed the acquisition of those purely rotational data in the first place.

Although the rather small standard error ($\sigma = 10^{-6}$ cm^{-1}) of the value of the band origin ν_{11}^0 is "swamped" by the uncertainty which arises from the calibration of the FT-IR spectrometer, we are confident to quote this origin with an absolute uncertainty of 10^{-4} cm^{-1} as $\nu_{11}^0 = 1175.3377 \pm 0.0001$ cm^{-1}.

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