High-Resolution Vibrational Spectra of Furazan

IV. The A_1 Fundamental ν_2 at $\sim 1418\ \mathrm{cm}^{-1}$ from Fourier-Transform Infrared Spectroscopy

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The band origin of the A_1 mode ν_2, which represents the symmetrical stretching vibration of the two C=N bonds of furazan, has been determined from the high-resolution FT-IR band as $\nu_2^0 = 1418.4724 \pm 0.0001\ \mathrm{cm}^{-1}$. The rotational parameters of this excited state, as determined in a preceding DRM microwave study, have been confirmed and their precision was raised through the combined fit of microwave data and of some 2500 rovibrational transitions.

The use of conjugate low-*J* Q-branch lines for the determination of the origin of a B-type IR band of an asymmetric rotor is illustrated.

I. Introduction

In continuation of recent papers [1 a, b, c], which report results of the current study of the high-resolution FT-IR bands of the heterocyclic compound furazan (or: 1,2,5-oxadiazole, $C_2H_2N_2O$), the present contribution deals with the analysis of the symmetrical stretching vibration $\nu_2 \sim 1418\ \mathrm{cm}^{-1}$ of the two C=N bonds of this molecule. This fundamental mode belongs to the fully symmetrical vibrations (C_{2v} symmetry species A_1) and, as noted previously [1 b], the rovibrational transitions of the ν_2-band follow the μ_b selection rule (B-type band). With a Boltzmann factor at room temperature of $\sim 1 \times 10^{-3}$ or less, the state $\nu_2 = 1$ is the energetically highest and therefore the least populated excited vibration state which could still be fully analysed from the purely rotational point of view by double resonance modulation (DRM) microwave spectroscopy [1 e]. As was initially expected [1 d] and has since been confirmed through the rovibrational analyses of five fundamental bands [1 a–c], the earlier rotational information proved very helpful towards the speedy analysis of the ν_2-band as well.

II. Experimental

The wavenumber range from 1100–1900 cm^{-1} was recorded in 1990 under a sample pressure of 2.5 mbar. This relatively high pressure was then chosen for obtaining the best possible data for the study of the medium-strong fundamentals $\nu_{11} \sim 1175\ \mathrm{cm}^{-1}$ and $\nu_3 \sim 1316\ \mathrm{cm}^{-1}$ [1 b, c] and for the weak combination bands in this range (Figure 1). For the strong B-type band $\nu_2 \sim 1418\ \mathrm{cm}^{-1}$ the high sample pressure resulted in an advantage as well as in a disadvantage: The advantage was that the very weak conjugate low-*J* Q-branch transitions nearest to the band origin (Figure 2) could be identified easily to yield the origin with a precision of $\pm 0.001\ \mathrm{cm}^{-1}$ virtually by mere inspection at the outset of the work. The disadvantage lay in the fact that the leading, strongest components of each P- or R-branch cluster of the band remained unresolved up to the highest J'-values as a consequence of pressure broadening, and the lines were totally absorbing (optically thick) in the most intense sections of the P- and R-branch (Figure 3). It was not possible therefore to ascertain the (expected) absence of Coriolis perturbations from the ν_2-band. This necessitated a repeat measurement of this band under a lower sample pressure suitable to reach optimal resolution.

In 1992 the FT-IR spectrum of furazan vapour was re-recorded between 1100 cm^{-1} and 1900 cm^{-1} on the Bruker IFS 120 HR interferometer under a sample pressure of 0.3 mbar at room temperature. This was a nearly ten times lower pressure than that used initially (2.5 mbar). The IR radiation was provided by a Globar source and divided by a KBr beam-splitter coated

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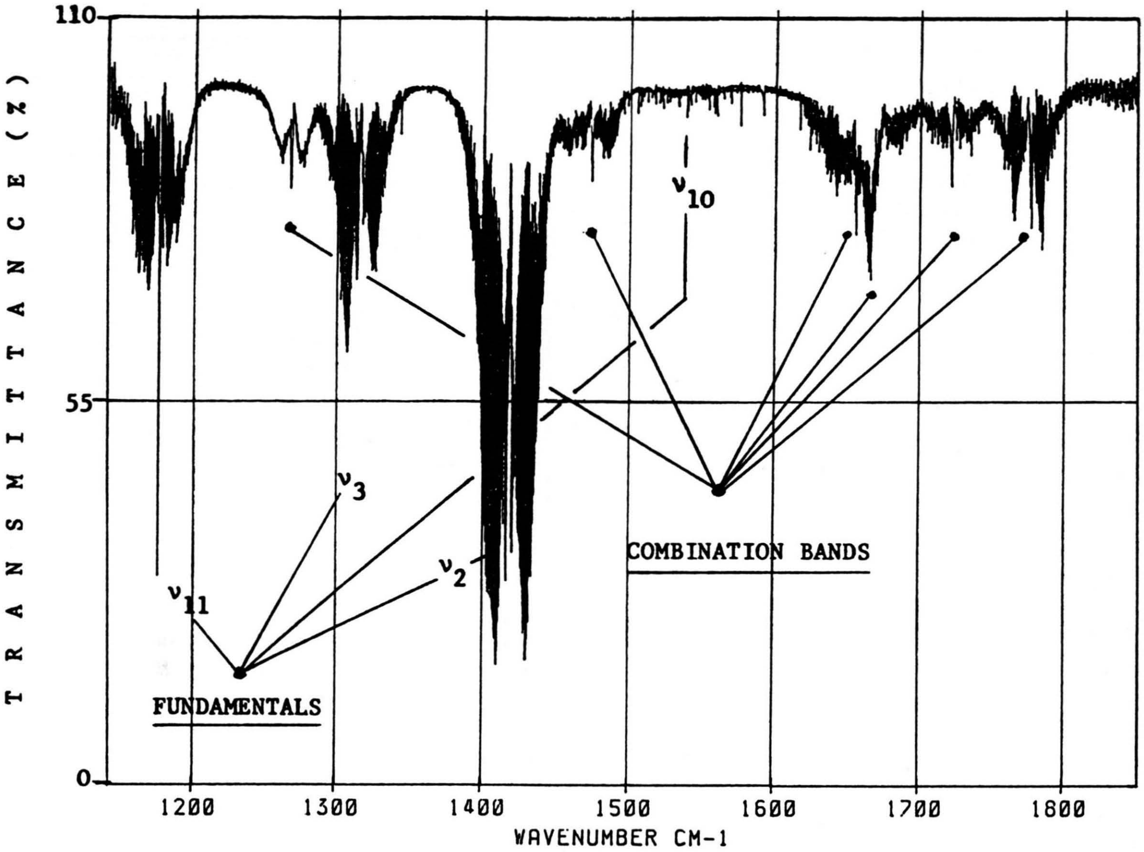


Fig. 1. Survey of the FT-IR spectrum of furazan in the range from 1150 cm^{-1} to 1850 cm^{-1}, showing four fundamentals and several combination bands at a sample pressure of 2.5 mbar.

with Ge. After adequate optical filtering the radiation was detected by an MCT (HgCdTe) detector at 77 K (initially: Ge:Cu detector at 4.2 K). In both experiments the sample cell with wedged CsI windows was an external addition to the commercial instrument providing for an optical path length of 300 cm. The interferogram was built up from 600 co-added scans (initially: 245 scans) and the unapodised spectral resolution was 0.0031 cm^{-1} (0.0039 cm^{-1} in 1990). While the wavenumber scale of the spectrometer had been calibrated in the initial experiment against accurately known [2] absorptions of N_2O, measured immediately after the sample run, precisely known [2] absorptions of H_2O, which was contained in the furazan sample as an impurity, were utilised for calibration in the repeat experiment. This H_2O calibration indicated a standard error of 5.4×10^{-5} cm^{-1} for the wavenumber scale of the instrument.

III. Theory and Computational Aspects

These aspects of the work have been summarised in each of the previous parts [1a–c]. They are re-included here merely for completeness.

Under the assumption that the various vibrational modes of a molecule (for the modes of furazan see Fig. 1 of [1b]) do not interact with each other, the rotational levels of a particular vibration state may be calculated as the eigenvalues of a rotational Hamiltonian which was last revised and formulated under the inclusion of distortion effects by Watson [3]. This Hamiltonian (sometimes endearingly referred to as 'Watsonian') describes the energy of a specific molecule by three reduced rotational constants (A, B, C), five quartic (Δ, δ) and seven sextic (ϕ, φ) distortion constants. These 15 rotational parameters (or combinations thereof) appear in the Hamiltonian as the coefficients of the second, fourth and sixth power of the angular momentum P or of its components $P_{a,b,c}$ along the principal inertial axes of the molecule. Since our previous studies have shown sextic distortion effects in furazan to be unobservably small up to $J \sim 50$, Watson's Hamiltonian may be abbreviated through the omission of the sextic terms and reads then in its A-reduced form in the I^r representation:

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

For practical application, such as the prediction of the rotational fine structure of a high-resolution IR band, Gambi et al. [4] have developed a computer scheme (TRANSI) which sets up the rotational energy matrices for the two vibration states and, after their diagonalisation, computes the frequencies and intensities of the allowed transitions between the levels of the lower and upper vibration state. The results of such a computation, which requires specification of the energy difference between the 0_{00} levels of the two states (band origin) in addition to the rotational parameters of each state, may be used for comparison with an observed IR band to lead to the correlation of observed peaks with calculated transitions between specific pairs of rotational levels of the two vibration states (rovibrational assignment). – The same authors [4] have also provided a least-squares (LSQ) fitting procedure (SMINIQ) for the reverse task of deducing the band origin and the rotational parameters of one (or both) vibration state(s) from a set of assigned peaks of an observed IR band. Further features of this computer package, which are designed to facilitate the usually difficult initial assignments, were not needed in the present work.

IV. Results

1. Assignments within the ν_2-Band

It has been shown previously [1 a] that the rovibrational analysis of an unperturbed high-resolution FT-IR band becomes very simple if, firstly, the sets of rotational parameters of the two connected states and, secondly, the vibrational separation between them are known in advance with sufficient precision. In the present case, the first part of this condition was met on

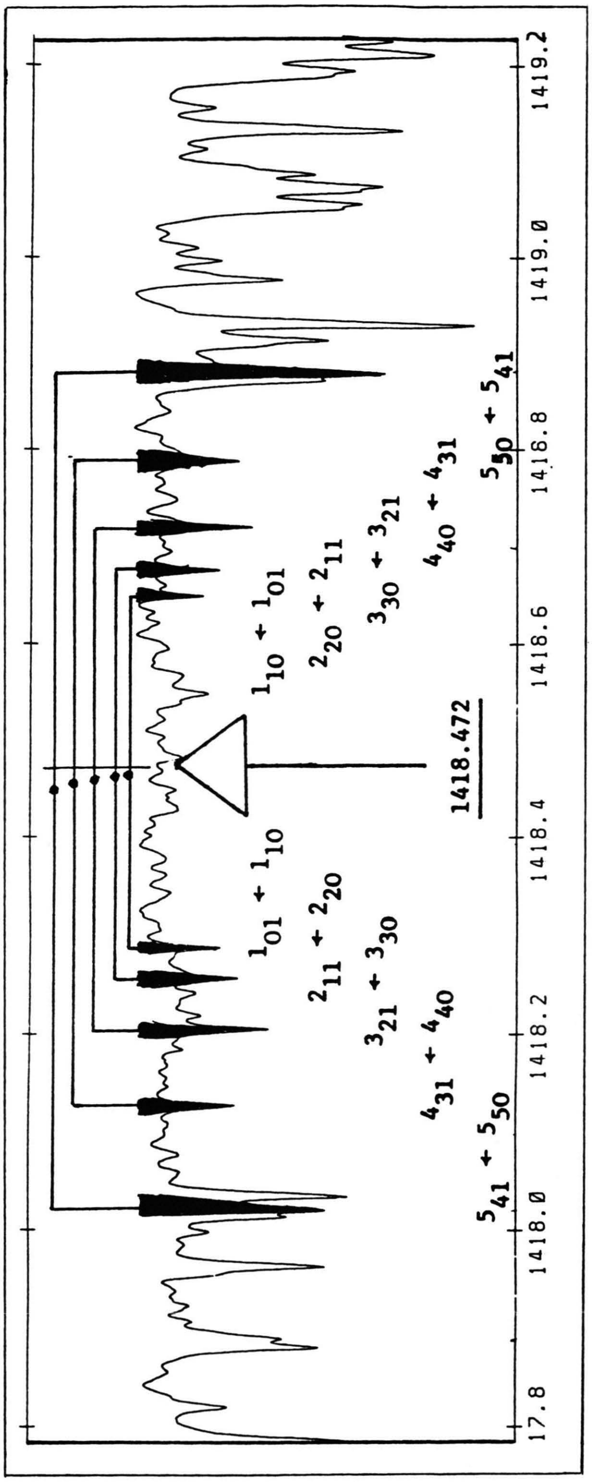


Fig. 2. Pairs of conjugate low-J Q-branch transitions displaced nearly symmetrically around the origin of the B-type band ν_2. (Sample pressure: 2.5 mbar.)

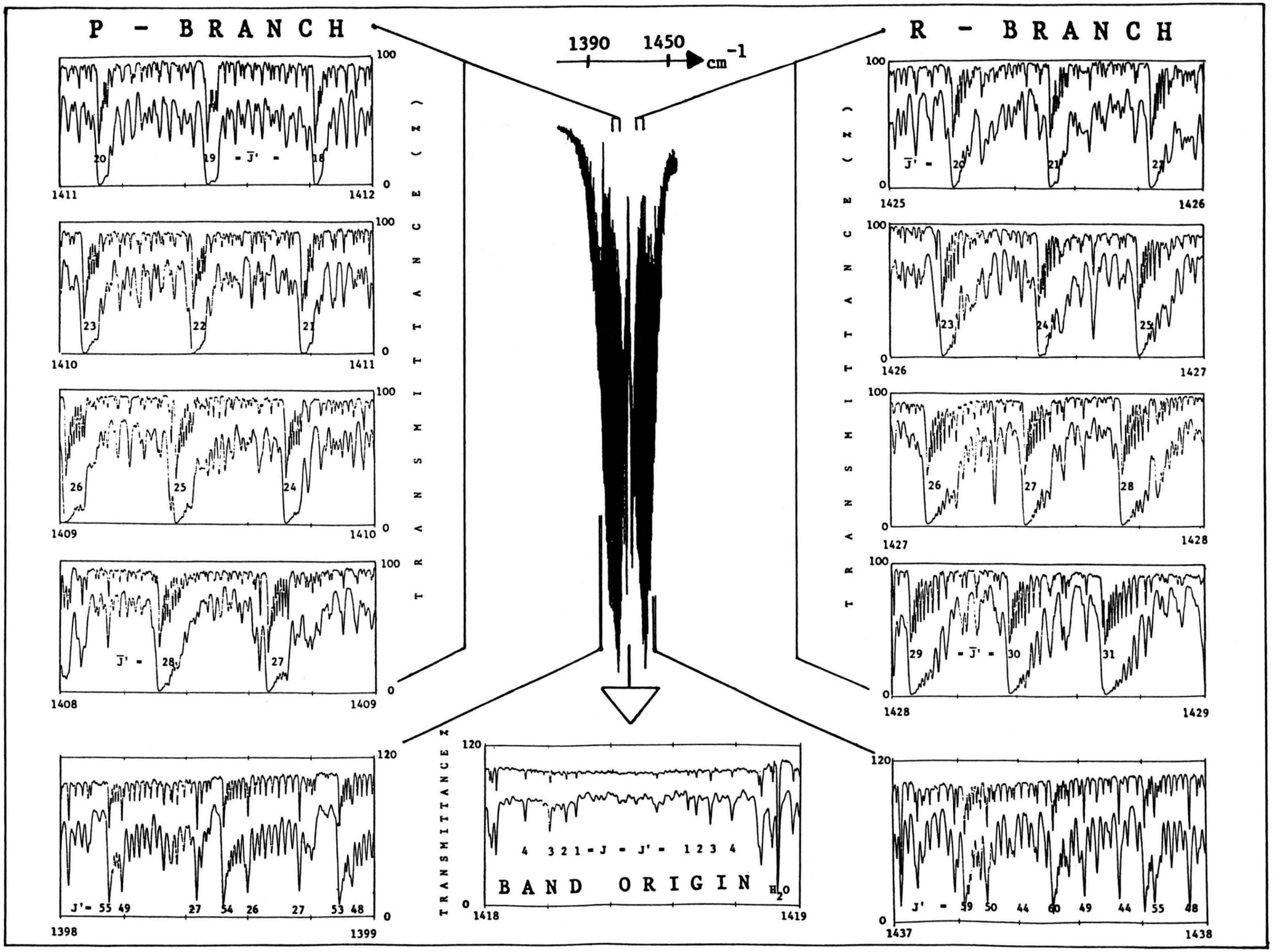


Fig. 3. The B-type band ν_2 with high-resolution sections at sample pressures of 2.5 mbar and of 0.3 mbar.

account of the earlier study [1 d] of the state $v_2=1$ by rotational spectroscopy. The second part requires that the band origin v_2^0 be fixed at the outset with sufficient accuracy (± 0.1 cm^{-1} or, preferably, better) so that ambiguities in the J'-values to be assigned to P- and R-branch clusters and their components can be avoided. – To reach such precision of v_2^0 at the outset, use was made of the previous observation [1 a, c] that pairs of conjugate IR transitions of a B-type band, especially the pair of weak Q-branch transitions $1_{01} \leftarrow 1_{10}$ and $1_{10} \leftarrow 1_{01}$ which is closest to the origin, and the components of similarly conjugate pairs with consecutively higher values of $J=J'$, are displaced almost symmetrically to either side of the origin v^0.

With this fact in mind, the recording of the v_2-band at the (excessively) high pressure of 2.5 mbar was examined in the vicinity of 1418 cm^{-1} [5]. As is emphasised through blackening-in of the relevant peaks in Fig. 2, four pairs of nearly symmetrically displaced transitions could be spotted around an apparent v_2^0-value of 1418.5 cm^{-1}. The assignment of $J=J'$ – values to these transitions was helped by the fact that the separation of the pair with $J=J'=1$, if indeed observed, should be

$$\Delta v_{J=1} = (A-C)_{\mathrm{GS}} + (A'-C')_{v_2=1}\,.$$

From the earlier DRM MW work [1 d] this separation could be calculated as $\Delta v_{\mathrm{calc.}} = 0.362024$ cm^{-1}, and this was compared with the FT-IR measurements which indicated a separation of $\Delta v_{\mathrm{obs.}} = 0.362155$ cm^{-1} for the innermost pair of transitions. On the basis of that result the first four observed pairs could be safely assigned to the conjugate Q-branch transitions with $J=J'=1, 2, 3, 4$ as indicated in Figure 2. The pair for $J=J'=5$ is somewhat obscured due to its blending with other Q-branch transitions, but its identification together with a further dozen pairs of conjugate Q-branch lines followed easily by calculation. The desired band origin emerged from this initial work as $v_2^0 = 1418.4724 \pm 0.0001$ cm^{-1}, and this value was not significantly altered through the later incorporation in the LSQ fit of the band of some 2500 IR transitions measured at the low pressure of 0.3 mbar.

2. *Qualitative Appearance of the v_2-Band*

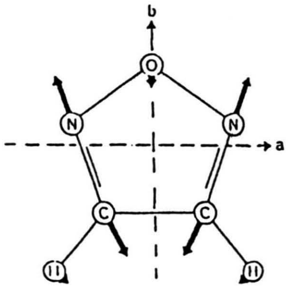
A detailed description of the structures of A- and B-type bands of furazan has been given previously [1 a]. The rotational fine structure of the present B-type band v_2 agrees in all aspects with the characteristic features outlined before: Fig. 3, which shows areas of the band under the high pressure of 2.5 mbar and under the low pressure of 0.3 mbar, illustrates that both the P- and R-branch consist of regularly spaced groups of transitions (clusters) which in each case begin with the strongest component $\bar{J}'_{(0/1),\bar{J}'} \leftarrow (\bar{J}' \pm 1)_{(1/0),(\bar{J}' \pm 1)}$ and continue with transitions with successively lower values of J' and increasing values of K_a. The notation (0/1) for K_a is meant to indicate that the levels are doubly degenerate. Values of the leading quantum number $\bar{J}'$ have been inserted in the high-resolution sections arranged around the compressed band in the middle of Figure 3. At low values of $\bar{J}'$ the clusters are relatively compact and leave room therefore for the observation of Q-branch lines in the wavenumber gaps between successive clusters. From $\bar{J}' \sim 35$ the increasing number of components in each cluster spreads out to fill these gaps and finally, at $\bar{J}' \sim 45$, successive clusters overlap with each other. The readily recognisable rotational structure of the band is then lost (bottom left and right sections of Figure 3).

3. *Molecular Constants and Band Origin*

Following the rovibrational assignment of over 750 P-branch transitions and of an equal number of R-branch lines, more then 1000 Q-branch lines could be identified within about ± 10 cm^{-1} of the band origin. With peak wavenumber values taken from the low-pressure repeat-experiment alone, all these IR transitions were fitted with the LSQ program SMINIQ for the purpose of extracting the best values of the rotational parameters of the state $v_2=1$ and of the band origin v_2^0 from the assigned lines. The rotational parameters of the GS were held fixed at their predetermined values [1 a], which are included in Table 1.

About 40 tentatively assigned absorptions were eliminated from the final LSQ fit of the band on the ground that their peak wavenumbers deviated by more than the adopted compatibility limit of $\pm 5 \times 10^{-4}$ cm^{-1} from the expected (calculated) positions. About 170 observed absorptions of the v_2-band were split into narrow doublets. This 'manipulation' of the experimental data was considered justified whenever the calculated band structure indicated that an observed peak represented two separate rovibrational transitions which could not be resolved experimentally. In the listing of fitted transitions such mod-

Table 1. Molecular constants and band origin for the fundamental vibration $\nu_2$of furazan.

Mode, level	GS[a]	$\nu_2=1$
C_{2v} symmetry species	(A_1)	A_1
Selection rule/ type	(μ_b)	μ_b/B-type
Diagrammatic description		
Fitted transitions		
$N_{\text{P-branch}}$		756
$N_{\text{Q-branch}}$		1038
$N_{\text{R-branch}}$		758
$N(\text{IR})_{\text{Total}}$		2552
St'd dev'n of IR fit		2.0 E-4 cm^{-1}
MW transitions		79
$N(\text{IR}+\text{MW})_{\text{Total}}$		2631
St'd dev'n (IR + MW)		1.2 E-5 cm^{-1}
Rotational constants (in cm^{-1} and MHz)[b]		
A	0.348 814 617 (21)[c] *10 457.1991 (6)*	0.348 026 256 (18) *10 433.5647 (6)*
B	0.322 944 775 (19) *9 681.6408 (6)*	0.322 485 666 (17) *9 667.8770 (5)*
C	0.167 572 473 (19) *5 023.6964 (6)*	0.167 243 834 (22) *5 013.8440 (7)*
Quartic distortion constants (in 10^{-7} cm^{-1})		
Δ_J	0.832 70 (18)	0.908 65 (11)
Δ_{JK}	−0.276 00 (59)	−0.271 25 (66)
Δ_K	0.768 14 (60)	0.676 94 (85)
δ_J	0.332 47 (6)	0.371 50 (6)
δ_K	0.625 57 (27)	0.608 13 (25)
Band origin ν_2^0 (in cm^{-1})		1418.472 356 (1)

[a] GS constants held fixed in final LSQ fit. – [b] Conversion factor $c = 299\,792\,458$ m/sec. – [c] Uncertainties are 1 σ limits and given in units of the last quoted digit.

ified wavenumber values are marked with a dot, although they are readily recognisable from the fact that the separation of these wavenumber values is up to ten times smaller than the spectral resolution of the interferometer (0.0031 cm^{-1}). The list of fitted transitions has been deposited for general access with the "Sektion für Spektren und Strukturdokumentation" of the Universität Ulm (Postfach 4066, D-7900 Ulm/Donau, FRG). It may also be obtained from the authors.

As indicated in Table 1, which includes a diagrammatic description of the mode ν_2 of furazan, the LSQ fit of 2552 IR transitions alone, as determined from the low-pressure repeat experiment, reproduces the peak wavenumber values of absorptions with a standard deviation os 2×10^{-4} cm^{-1}. When the purely rotational transitions within the state $\nu_2=1$ (5 low-J R-branch and 74 Q-branch lines with J-values up to $J'=24$, [1 d]) were included in the fit with a 100 times larger weight than the IR transitions, this deviation reduced by a factor of about 20. Through the inclusion of these DRM MW data the precision of the derived rotational parameters of the excited state was improved by factors of up to 4, and the statistical uncertainty of the band origin was reduced by an order of magnitude to $\pm 10^{-6}$ cm^{-1}. As the bottom half of Table 1 shows, the final uncertainties of the parameters of the state $\nu_2=1$ are essentially the same as those of their counterparts in the GS. The rather high statistical accuracy of the band origin is, unfortunately, lost within the considerably larger uncertainty associated with the calibration of the wavenumber scale of the spectrometer. It seems reasonable in those circumstances to quote the band origin with the absolute uncertainty imposed by the calibration as $\nu_2^0 = 1418.4724 \pm 0.0001$ cm^{-1}.

For an assessment of the LSQ-fit the correlation matrix is reproduced overleaf.

V. Discussion

The successful fit of the rovibrational transitions of the fundamental ν_2 to an unperturbed rotational level scheme of the excited state confirms the expected absence of detectable Coriolis perturbations from this vibration state. In combination with analogous results in the previous studies [1 a–c], all six modes of furazan above 900 cm^{-1} must therefore be judged as free from vibrational interactions. The same conclusion must also be inferred for the seventh fundamental in this wavenumber range, which may be described [1 b] as the antisymmetrical C=N stretching vibration $\nu_{10}(B_1)$ ~1541 cm^{-1} [5]. Unfortunately, we did not succeed in identifying the pure rotational spectrum of

Correlation matrix of the LSQ determination of the molecular constants of the state $\nu_2=1$.

1.0000								
−0.4030	1.0000							
−0.4128	0.5405	1.0000						
0.2166	−0.0120	−0.6577	1.0000					
0.0828	−0.0193	0.3278	−0.8570	1.0000				
0.6012	−0.2671	0.0622	−0.1274	0.1530	1.0000			
0.0904	−0.0092	0.6257	−0.5201	0.2765	0.6776	1.0000		
0.1373	−0.2990	−0.0805	0.2824	−0.4608	0.1463	−0.0645	1.0000	
−0.0106	−0.2033	−0.0594	−0.0195	0.0079	0.0073	0.0096	0.0215	1.0000

Sequence of variables: $A-B$, B, Δ_J, Δ_{JK}, Δ_K, $B-C$, δ_J, δ_K, ν_2^0.

the state $\nu_{10}=1$ (Boltzmann factor at room temperature: $\sim 7\times10^{-4}$) during the earlier DRM MW experiments [1 d], and in the FT-IR experiment the corresponding fundamental is so weak as to be hardly detectable even under the elevated pressure of 2.5 mbar (see Figure 1). On these accounts the provision of experimental data suitable for a rovibrational study of ν_{10}, and hence for the confirmation of the above inference, has to remain a challenge for the future.

The observation and recognition in the present study of the conjugate Q-branch transitions nearest to the band origin, and the subsequent exploitation of these few transitions for the determination of the band origin to an accuracy of $\pm10^{-3}$ cm^{-1}, is equivalent to the previous determination [1 f] of ν_{12}^0 and ν_5^0 through laser/microwave double resonance (LMDR) work prior to the analysis of the corresponding FT-IR bands [1 a]. In both cases, now and previously, a ν^0-value of sufficiently good accuracy was available from the outset of the IR study to render the rovibrational assignments of the IR peaks a rather simple task. Of course, in addition to defining the IR band structure, prior knowledge of the rotational parameters of excited states [1 d] played a significant role for the correct interpretation of the LMDR experiments, and it helped the correct assignment of the conjugate Q-branch transitions in the present case of the ν_2-band. However, even in the absence of such prior knowledge, one might expect that the occurrence and recognition of these conjugate Q-branch lines in the B-type bands of asymmetric rotor molecules will generally aid the determination of the band origins and of the rotational constants A', B', C' of the excited state.

The present work completes the rovibrational studies of the high-resolution fundamentals to the six energetically highest levels which could still be observed by DRM rotational spectroscopy (Table 2 of [1 d]). The previously expressed optimism that these studies would be greatly helped by the rotational information established before, has been vindicated in full. The refinement of rotational and distortion constants of the six excited states and of the GS – through the combination of a large number of vibrational data with a comparatively small number of rotational data with significantly higher precision than the former – was not anticipated at the outset, but is now accepted as an additional bonus appropriate to the combination of two different experimental techniques.

The rovibrational analysis of the fundamentals below 900 cm^{-1} is more troublesome due to the presence of vibrational perturbations between these modes. Their study is in hand and the findings will be communicated in due course.

Acknowledgements

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