Analysis of the FTIR Bands ν_{11} and ν_8 of 1,1-difluoroethylene with Rotational Background Information on Excited States

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Much earlier work on the analysis of the fundamental infrared bands ν_{11} and ν_8 of 1,1-difluoroethylene has been resumed and extended.

The Q-branch of the C-type band $\nu_{11} \sim 802\ \mathrm{cm}^{-1}$ has been analysed, and sextic distortion constants have been obtained for $\nu_8 = 1$ at $\sim 1301\ \mathrm{cm}^{-1}$. The rotational constants of the two states are found to differ noticeably (20–100 standard deviations) from values reported earlier.

The discrepancies are believed to result in part from the availability of purely rotational data on ν_{11} and ν_8 in the present study, but to originate primarily from the adoption of rather poor values of the ground state constants of 1,1-difluoroethylene in the earlier work on these two fundamentals.

I. Introduction

The latest extension [1] of rotational data on 1,1-difluoroethylene (1,1-DFE) into the millimeterwave (MMW) range, but primarily the confirmation and further refinement of the long-known ground state (GS) parameters of this molecule, has prompted us to resume and complete much earlier work [2] on vibrationally excited states of 1,1-DFE. These investigations were suspended when it was learnt in 1990 that other researchers [3–5] had taken up the study of this molecule by the Fourier Transform Infrared (FTIR) technique in the meanwhile. Our offer of all the information which we had established during the preceding seven years, first by double resonance modulation (DRM) microwave spectroscopy [2, 6] and then by the high-resolution FTIR technique, was declined. This left us little choice but to observe the results which could be derived from the analyses of FTIR bands alone.

As it turned out, the molecular parameters deduced from the A-type ν_5-band at $\sim 550\ \mathrm{cm}^{-1}$ [3] were very consistent with our own earlier results. But the results extracted from the C-type ν_{11}-band at $\sim 802\ \mathrm{cm}^{-1}$ [4] and from the B-type ν_8-band at $\sim 1301\ \mathrm{cm}^{-1}$ [5] differed noticeably from our earlier analyses of these bands.

The present contribution therefore deals with these latter two IR-bands, and it describes the molecular parameters which emerge when experimental data from DRM microwave spectroscopy are available for inclusion in the analyses of FTIR bands in addition to optimised molecular constants for the vibrational ground state [1] of a molecule.

II. Experimental and Computational Aspects

a) Experimental

After the initial study of the FTIR spectrum of 1,1-DFE with the Bruker IFS 113v instrument in 1984, the vibrational spectrum of this molecule was observed for a second time, now with the newly developed IFS 120 HR FTIR interferometer of the Bruker company at Rheinstetten in 1988: The IR radiation was supplied by a Globar source, divided by a 'Ge-on-KBr' beamsplitter and, in the case of the ν_{11}-band, detected by a Ge-Cu crystal cooled by liquid He. For the observation of the ν_8-band an MCT detector cooled by liquid N_2 was used. The sample pressure in a conventional gas cell of $\sim$ 30 cm length with wedged KBr windows was around 3 Torr at room temperature. The maximal optical path difference (OPD) available on that instrument was nominally 258 cm and resulted in an unapodized spectral resolution of $0.0035\ \mathrm{cm}^{-1}$. The interferogram was built up from 256 co-added scans and Fourier transformed after apodisation with a trapezoidal function. The wavenumber scale of the instrument was calibrated against known absorptions of CO_2 near $668\ \mathrm{cm}^{-1}$ [7] for the ν_{11}-experiment, while accurately known [7] absorptions of H_2O (which was contained in the sam-

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ple as an impurity) were used for calibration of the ν_8-band.

b) Computational

The numerical analysis of the observed FTIR bands was carried out with the help of a computer routine developed by Gambi, Winnewisser and Christiansen [8]. It consists of a first part (TRANSI) which allows the prediction of the rovibrational structure of a high-resolution IR-band from the rotational parameters (= rotational constants, quartic and sextic distortion constants) of the two states involved and their vibrational separation ν^0 (band origin). The second part of the program (MINIQ) is a least-squares (LSQ) fitting procedure for the extraction of molecular parameters from a suitably large set of identified (assigned) rovibrational transitions of an IR-band. The routines are constructed on the basis of Watson's [9] A-reduced Hamiltonian in I^{r}-representation $((x, y, z) = (b, c, a))$:

$$\begin{aligned}\hat{H}^{(\mathrm{A})}_{\mathrm{rot}} = {} & \tfrac{1}{2}(B+C)\hat{P}^2 \\ & + (A - \tfrac{1}{2}(B+C))\hat{P}_a^2 - \Delta_J\hat{P}_a^4 - \Delta_{JK}\hat{P}^2\hat{P}_a^2 - \Delta_K\hat{P}_a^4 \\ & + \Phi_J\hat{P}^6 + \Phi_{JK}\hat{P}^4\hat{P}_a^2 + \Phi_{KJ}\hat{P}^2\hat{P}_a^4 + \Phi_K\hat{P}_a^6 \\ & + (\tfrac{1}{2}(B-C) - 2\delta_J\hat{P}^2 + 2\phi_J\hat{P}^4)\cdot(\hat{P}_b^2 - \hat{P}_c^2) \\ & + [(-\delta_K\hat{P}_a^2 + \phi_{JK}\hat{P}^2\hat{P}_a^2 + \phi_K\hat{P}_a^2), (\hat{P}_b^2 - \hat{P}_c^2)]_+ .\end{aligned}$$

Here, $\hat{P}$ is the total angular momentum operator and $\hat{P}_{a,b,c}$ are its components along the principal inertial axes of the molecule. A, B, C are the reduced rotational constants and Δ, δ are the quartic distortion constants, while Φ, ϕ denote the sextic distortion constants. The fourth line of this expression is the product of the bracketed quantities. The symbol $[\,,\,]_+$ in the last line denotes the anticommutator [9].

Since the molecular constants of the GS of 1,1-DFE have been known to good accuracy for quite some time, while at least the rotational constants of the excited states $\nu_{11} = 1$ and $\nu_8 = 1$ had been determined through DRM MW work [2], detailed assignments of observed rovibrational transitions of the two FTIR bands were a comparatively simple task. They led to the refinement of the rotational constants and of the previously less well determined quartic distortion constants, as well as to the determination of the elusive sextic distortion constants of the two excited states.

III. Results

1. The C-Type Fundamental ν_{11} at 802 cm^{-1}

a) Analysis

With some fifty μ_a rotational transitions including four R-branch lines, but predominantly Q-branch transitions of the excited state $\nu_{11} = 1$ safely identified by DRM microwave techniques [2, 6] in the early 1980s, the structure of the C-type vibrational band $\nu_{11} = 1 \leftarrow 0$ around 802 cm^{-1} could be precalculated (program TRANSI) with a high degree of confidence. A comparison of that prediction with the FTIR band, as observed in 1988, readily resulted in the assignment of some 450 rovibrational transitions in each the P- and R-branch of the band. J-values ranged from 3 to 40 in both branches and, with the distortion treatment restricted to quartic coefficients for both the GS and the state $\nu_{11} = 1$, a band origin of $\nu^0_{11} = 802.06996\ (20)\ \mathrm{cm}^{-1}$ was indicated.

After the recent confirmation and further refinement of the GS-parameters [1], including sextic distortion constants of 1,1-DFE through the addition of new MMW data, and their combination with the large body of GS data which had been available for quite some time from other researchers [10], we thought it appropriate to resume the earlier analysis of the ν_{11}-band against the background of these latest GS parameters. While this re-examination thoroughly confirmed the much earlier work, it allowed the extension of rovibrational assignments throughout both branches, reaching up to $J' = 46$ at the end of the observed P-branch and up to $J' = 47$ in the observed R-branch. It was noticed during the associated LSQ-fits (program MINIQ) that these $|\Delta J| = 1$ transitions left the rotational constant C about twice as uncertain as the A- and B-constants, and that the emerging sextic distortion constants of the state $\nu_{11} = 1$ showed rather large deviations from their counterparts in the GS. This prompted us to attempt the assignment of FTIR peaks within the Q branch, which in a C-type band is known to be more compact than in A- or B-type IR bands.

While we were initially confident that a reprediction of transitions in this range, which was based on some 1250 fitted $|\Delta J| = 1$ transitions, would suffice to safely assign observed Q-branch peaks, the very high density of expected strong transitions caused substantial uncertainty when this region of the band

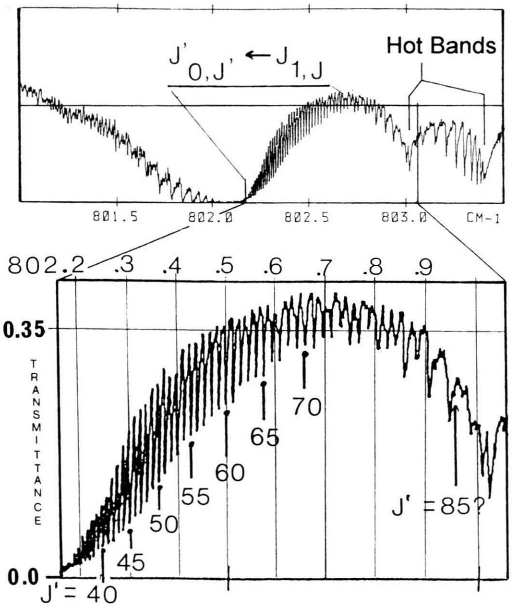

Fig. 1. The Q-branch of the C-type band ν_{11}.

was approached from the low J range at the low wavenumber side of the observed Q-branch. Only when comparing the high wavenumber end of the Q-branch (see Fig. 1) with expectation was it noticed that the observed peaks deviated in a systematic manner from the expected positions of members of the intense series

$$J'_{(0,1),J'} \leftarrow J_{(1,0),J}\,.$$

Here, J' designates the angular momentum quantum number of levels in the excited state and, of course, $J' = J$ for Q-branch transitions. The bracketed indices are the K_a quantum numbers of the doubly degenerate pairs of IR transitions. – In the wavenumber range from 802.24 cm^{-1} to 802.70 cm^{-1} 34 consecutive members of this series with J-values running from 39 to 72 could be identified on the grounds of their intensity and their systematically increasing deviations from expected positions. These 34 observed Q-branch signals were therefore first inserted (initially with increased weights) into the LSQ-fit together with the P- and R-branch lines. They were found to reduce significantly the afore-mentioned uncertainty in the rotational constant C and to rectify the previously 'suspect' values of the sextic distortion constants to closer proximity to their GS counterparts than had been possible through LSQ fitting of P- and R-branch transitions alone. A subsequent reprediction of the Q-branch with the refined parameters permitted the unequivocal assignments of 188 transitions to 125 observed absorptions, with very close coincidence of two or more transitions into one observed peak being the standard situation rather than the exception. The reprediction also allowed the extension of the series $J'_{(0,1),J'} \leftarrow J_{(1,0),J}$ down to $J' = 27$ and up to $J' = 77$, with a weak signal observed at the $J' = 85$ position. The assignment of this latter signal must be considered tentative, however, as its wavenumber value lies well within the range of a hot band centered at ~ 803.0 cm^{-1}.

b) Blending Transitions

In the case of two closely spaced transitions of comparable intensity, the value of the instrumentally available resolution (here: 0.003 cm^{-1}) is incompatible with the simultaneous requirement that a 'fittable' transition should agree with calculation to within the six times smaller margin of 0.0005 cm^{-1}. While some workers prefer to simply ignore the existence of this dilemma by allowing much larger discrepancies between observed and calculated wavenumber values, not withstanding the fact that a considerably higher experimental accuracy than here may be claimed at the same time, we have considered it preferrable for some time now to bridge the gap between the high accuracy of the FTIR technique, on the one hand, and its limited resolution, on the other hand, by splitting up observed blending peaks into the two component transitions which generate them. The procedure is best illustrated by an example: The parameters derived from the LSQ-fit of some 1500 absorptions to within less than 0.0005 cm^{-1} predict the following two transitions:

$$28_{21,8} \leftarrow 27_{20,8} = 821.513424\ \mathrm{cm}^{-1}$$

and

$$28_{23,6} \leftarrow 27_{22,6} = 821.510833\ \mathrm{cm}^{-1}$$

with a separation of

$$\Delta\omega \quad = \quad 0.002591\ \mathrm{cm}^{-1}\,.$$

Under a resolution of 0.003 cm^{-1} (and the sample pressure required for observation of these absorptions in a relatively short [30 cm] absorption cell) the two signals will merge into one which, ideally, should be measured at 821.512128 cm^{-1}. This wavenumber value, however, would deviate by more than twice the imposed compatibility limit (0.0005 cm^{-1}) from either component transition, thus rendering the actually observed wavenumber value of the blending absorption (in this case 821.511926 cm^{-1}) unexploitable in the LSQ-fit of the overall band. To prevent such 'waste' of interpretable experimental information, we consider it justifyable to extract both transition frequencies from the one blending absorption by adding and subtracting half the calculated separation from the one wavenumber value of the observed peak. For the example given above, $\Delta\omega/2 = 0.001296$ cm^{-1} would be added and subtracted to/from the observed value of 821.511926 cm^{-1} to obtain the two component transitions as

$$28_{21,8} \leftarrow 27_{20,8} = 821.513222\ \mathrm{cm}^{-1}$$

and

$$28_{23,6} \leftarrow 27_{22,6} = 821.510630\ \mathrm{cm}^{-1}.$$

As the comparison with the above predictions shows, both these wavenumber values can be included in the LSQ-fit of the band, as they now comply with the adopted compatibility limit of ± 0.0005 cm^{-1}.

The outlined splitting up of blending absorptions *a posteriori* should, in our opinion, not be attempted before all single peaks of a band are satisfactorily accounted for, so that the true separation of two blending transitions can be precalculated to within about 10% or better.

In the case of the ν_{11}-band of 1,1-DFE, the application of the described procedure has led to the incorporation of some 500 fittable transitions, and it has brought the total number of data in the final LSQ-fit of the FTIR-band to ~ 2000.

c) Combination Differences (Co'Dis)

To fully exploit all the information which is provided by a rovibrationally analysed FTIR-band, we have extracted the Co'Dis for the state $\nu_{11} = 1$ from the identified and fitted 2000 transitions of the band. This produced some 550 secondary data. Since the J'-range of the assigned Q-branch transitions is largely above that of the assigned P- and R-branch lines, the great majority of these Co'Dis is of the $\Delta J' = 2$ type. On the basis of the compatibility limit which we had adopted for the observed and fittable transitions, the Co'Dis had to be expected to deviate by up to 0.001 cm^{-1} from calculation, and deviations between 0.0005 cm^{-1} and 0.001 cm^{-1} were indeed found for some 70 Co'Dis. These were therefore removed from the LSQ fit, as were all Co'Dis which involved absorptions that had been split *a posteriori* (Sect. b, above). Furthermore, in view of the fact that the IR-derived Co'Dis for $\nu_{11} = 1$ are in direct competition with the at least 100 times more accurate and observed pure rotational transitions of the excited state, their acceptability limit was narrowed down to ~ 10 MHz (~ 0.00033 cm^{-1}). These restrictions left some 300 Co'Dis in the final LSQ fit of all data. (A reduction in the weight of the Co'Dis by 10^{-4} was also tested and found to produce no significant change in the resulting parameters for $\nu_{11} = 1$.)

d) Rotational Parameters and the Band Origin ν_{11}^0

The constants for the state $\nu_{11} = 1$, as derived from some 2000 observed and interpreted FTIR transitions, and some 300 deduced and fitted Co'Dis, together with 51 purely rotational transitions, are collected in Table 1. The at least 100-fold superiority in precision of the latter over the FTIR data was taken into account by the assignment of a weight factor of 10^4 to those 51 MW and MMW data, while all IR data were given the weight unity. – The correlation matrix between fitted parameters, which emerged from the final LSQ fit of all the data, is reproduced alongside Table 1.

2. The B-Type Fundamental ν_8 at 1301 cm^{-1}

a) Analysis

The rotational constants of the state $\nu_8 = 1$ were known from the early DRM microwave work [2], in which 42 purely rotational transitions within this excited state had been identified. A wavenumber value of $\nu_8^0 = 1301.1 \pm 0.5$ cm^{-1} for the band centre could be readily read off by mere inspection of the FTIR band. From this information, the structure of the *B*-type band ν_8 (C_{2v} symmetry species B_1) was computed, and the comparison of this prediction with the observed FTIR band readily allowed the successive assignment of 1088 rovibrational transitions up to $J' = 45$ in the P- and R-branch, and up to $J' = 33$ in the Q-branch. Together with the 42 purely rotational transitions within the state $\nu_8 = 1$, the LSQ-fit of all these data, but without consideration of sextic distortion effects,

Table 1. Molecular parameters of the state $\nu_{11} = 1$ of 1,1-DFE.

Present study			Previous work [4]
Rotational Constants	in cm^{-1}	in MHz[a]	in cm^{-1}
A	0.366572969 (40)	10989.5811 (12)	0.366575208 (62)
B	0.347155902 (38)	10407.4721 (12)	0.347157965 (73)
C	0.178431438 (26)	5349.2399 (8)	0.178434386 (44)
Quartic Distortion Constants	in $10^{-6}\ \mathrm{cm}^{-1}$	in KHz	in $10^{-6}\ \mathrm{cm}^{-1}$
Δ_J	0.15844 (3)	4.7499 (10)	0.15932 (3)
Δ_{JK}	0.04693 (13)	1.4068 (40)	0.04671 (12)
Δ_K	0.25729 (19)	7.7135 (57)	0.25740 (9)
δ_J	0.06619 (2)	1.9842 (5)	0.06581 (2)
δ_K	0.18405 (8)	5.5177 (25)	0.18242 (3)
Sextic Distortion Constants	in $10^{-12}\ \mathrm{cm}^{-1}$	in 10^{-3} Hz	in $10^{-12}\ \mathrm{cm}^{-1}$
Φ_J	0.066 (15)	1.98 (45)	0.309 (7)
Φ_{JK}	−1.266 (103)	−37.95 (309)	−1.530 (34)
Φ_{KJ}	1.207 (251)	36.18 (735)	2.951 (46)
Φ_K	0.384 (161)	11.51 (483)	−1.186 (26)
ϕ_J	0.076 (8)	2.28 (24)	0.059 (4)
ϕ_{JK}	0.419 (53)	12.56 (159)	0.267 (11)
ϕ_K	3.128 (50)	93.77 (150)	2.306 (11)
Band Origin ν_{11}^0:	802.070119 (2) cm^{-1}		802.070114 (15) cm^{-1}
Stand'd Deviations:			$0.268 \times 10^{-3}\ \mathrm{cm}^{-1}$
$\sigma_{\mathrm{IR+Co'Di}}$	$= 0.229 \times 10^{-3}\ \mathrm{cm}^{-1}$		
$\sigma_{\mathrm{IR+Co'Di+MW/MMW}}$	$= 0.155 \times 10^{-4}\ \mathrm{cm}^{-1}$		
Fitted transitions:			
N_{P}	824	$\delta\nu < 5 \times 10^{-4}\ \mathrm{cm}^{-1}$	
N_{Q}	365		
N_{R}	800		
$N_{\mathrm{Co'Di}}$	319	$\delta\nu < 3.5 \times 10^{-4}\ \mathrm{cm}^{-1}$	
N_{IR}	2308		
$N_{\mathrm{MW/MMW}}$	51	$\delta\nu \leq 5 \times 10^{-6}\ \mathrm{cm}^{-1}$	
N_{Tot}	2359		5254

[a] Conversion factor $c = 299\,792\,458$ m/s.

Correlation matrix of LSQ-fit of $\nu_{11} = 1 \leftarrow 0$ (in A-reduction)

	$A-B$	B	Δ_J	Δ_{JK}	Δ_K	Φ_J	Φ_{JK}	Φ_{KJ}	Φ_K	$B-C$	δ_J	δ_K	ϕ_J	ϕ_{JK}	ϕ_K	ν_{11}^0
$A-B$	1.0000	−0.0328	0.0886	0.2781	0.0101	0.0231	0.3116	−0.2171	0.2176	0.5363	0.2362	0.3815	0.0540	0.3287	0.0798	0.0203
B		1.0000	0.8065	−0.1365	0.0747	0.6539	−0.0462	−0.0848	0.1430	0.3540	0.6403	0.3088	0.6186	0.2346	0.1994	−0.1510
Δ_J			1.0000	−0.2980	0.1373	0.9574	−0.1047	−0.1465	0.2390	0.6713	0.9344	0.5145	0.9394	0.3485	0.3386	−0.0513
Δ_{JK}				1.0000	−0.9026	−0.3606	0.8135	−0.5258	−0.1580	−0.2301	−0.2906	0.5145	−0.3548	0.6033	−0.2052	−0.0033
Δ_K					1.0000	0.1521	−0.7236	0.5266	−0.1253	0.2027	0.1546	−0.5870	0.1535	−0.6181	0.1256	0.0039
Φ_J						1.0000	−0.1609	−0.1357	0.2406	0.6485	0.9379	0.4596	0.9943	0.3140	0.3442	−0.0231
Φ_{JK}							1.0000	−0.9016	0.6729	−0.0758	−0.1096	0.6146	−0.1597	0.8788	−0.4784	0.0013
Φ_{KJ}								1.0000	−0.9028	−0.0937	−0.1471	−0.5958	−0.1378	−0.9190	0.5718	−0.0010
Φ_K									1.0000	0.1908	0.2494	0.3722	0.2462	0.7459	−0.6328	0.0015
$B-C$										1.0000	0.8402	0.4098	0.6850	0.2474	0.2706	0.0128
δ_J											1.0000	0.4833	0.9556	0.3325	0.3329	−0.0150
δ_K												1.0000	0.4446	0.8366	0.1964	−0.0029
ϕ_J													1.0000	0.3080	0.3427	−0.0158
ϕ_{JK}														1.0000	−0.2963	−0.0042
ϕ_K															1.0000	−0.0016
ν_{11}^0																1.0000

indicated the band origin $\nu_8^0 = 1301.27336\ (10)\ \mathrm{cm}^{-1}$ in 1989.

After the further refinement [1] of the GS parameters of 1,1-DFE, the earlier analysis of the ν_8-band was extended to higher J'-values and broadened to cover the observed wavenumber range from 1260 cm^{-1} to 1340 cm^{-1}. The inclusion of sextic distortion constants allowed the identification of rovibrational transitions with quantum numbers up to $J'_{\max} = 75$, $K_{a,\max} = 49$ in the P-branch, $J'_{\max} = 61$, $K_{a,\max} = 49$ in the Q-branch and $J'_{\max} = 75$, $K_{a,\max} = 56$ in the R-branch, with K_c ranging from $J'_{\max}$ down to 0 for J'-values up to 50. This led to the inclusion in the LSQ fit of some 2300 rovibrational transitions with deviations of less than $5 \times 10^{-4}\ \mathrm{cm}^{-1}$. The 42 rotational

Table 2. Molecular parameters of the state $\nu_8 = 1$ of 1,1-DFE.

Present study			Previous work [5]
Rotational Constants			
	in cm^{-1}	in MHz[a]	in cm^{-1}
A	0.366137118 (39)	10976.5147 (12)	0.366137976 (76)
B	0.346956451 (36)	10401.4927 (11)	0.34695777 (12)
C	0.177472630 (28)	5320.4956 (8)	0.177471419 (28)
Quartic Distortion Constants			
	in 10^{-6} cm^{-1}	in KHz	in 10^{-6} cm^{-1}
Δ_J	0.16774 (3)	5.0288 (8)	0.16683 (6)
Δ_{JK}	0.03999 (12)	1.1989 (36)	0.03791 (23)
Δ_K	0.27440 (12)	8.2262 (34)	0.27669 (16)
δ_J	0.06654 (2)	1.9949 (5)	0.06660 (3)
δ_K	0.18670 (5)	5.5971 (14)	0.18648 (3)
Sextic Distortion Constants			
	in 10^{-12} cm^{-1}	in 10^{-3} Hz	in 10^{-12} cm^{-1} [b]
Φ_J	0.465 (10)	13.94 (30)	0.362 (57)
Φ_{JK}	−0.722 (78)	−21.63 (233)	−1.362 (359)
Φ_{KJ}	1.620 (136)	48.58 (409)	2.526 (661)
Φ_K	−0.525 (75)	−15.75 (225)	−0.933 (346)
ϕ_J	0.070 (5)	2.11 (15)	0.068 (29)
ϕ_{JK}	0.002 (27)	0.06 (81)	0.385 (148)
ϕ_K	2.968 (30)	88.97 (89)	2.482 (140)
Band Origin ν_8^0:	1301.273383 (3) cm^{-1}		1301.273596 (15) cm^{-1}
Stand'd Deviations:			
$\sigma_{IR+Co'Di}$	$=0.222 \times 10^{-3}$ cm^{-1}		0.36×10^{-3} cm^{-1}
$\sigma_{IR+Co'Di+MW}$	$=0.401 \times 10^{-4}$ cm^{-1}		
Fitted transitions:			
N_P	1128	$\delta\nu < 5 \times 10^{-4}$ cm^{-1}	
N_Q	901		
N_R	910		
$N_{Co'Di}$	583	$\delta\nu < 3.3 \times 10^{-4}$ cm^{-1}	
N_{IR}	3522		2854
N_{MW}	42	$\delta\nu \leq 5 \times 10^{-6}$ cm^{-1}	
N_{Tot}	3564		

[a] Conversion factor $c = 299792458$ m/s.
[b] Assumed as in GS [4].

absorptions in the state $\nu_8 = 1$, which had been observed initially [2], were included in this fit with weights (2.5×10^3) representing the higher accuracy of purely rotational over FTIR data.

A recomputation of the ν_8-band with the parameters thus derived allowed some further 300 observed peaks to be interpreted as due to blending absorptions of two, occasionally three, separate transitions which occur too close to each other to be resolved instrumentally. As has been outlined in Sect. III.1-b (above), these blending doublets were split *a posteriori* to contribute some 600 assignable transitions, so that the total number of data in the LSQ-fit rose to more than 2900.

Correlation matrix of the LSQ-fit of $\nu_8 = 1 \leftarrow 0$ (in A-reduction).

	$A-B$	B	Δ_J	Δ_{JK}	Δ_K	Φ_J	Φ_{JK}	Φ_{KJ}	Φ_K	B-C	δ_J	δ_K	ϕ_J	ϕ_{JK}	ϕ_K	ν_8
$A-B$	1.0000	−0.5079	−0.4945	0.5981	−0.2376	−0.4469	0.4244	−0.2603	0.1846	0.1055	−0.2104	0.3655	−0.3578	0.3772	−0.1431	−0.0137
B		1.0000	0.8148	−0.3951	0.2181	0.5800	−0.3207	0.2268	−0.1692	0.2586	0.4966	−0.1026	0.4850	−0.2017	0.1801	−0.2677
Δ_J			1.0000	−0.7147	0.4989	0.9099	−0.6514	0.4853	−0.3354	0.5308	0.8222	−0.0337	0.8525	−0.3895	0.4691	−0.1182
Δ_{JK}				1.0000	−0.8778	−0.8061	0.8597	−0.6595	0.3814	−0.3465	−0.6220	0.4183	−0.7713	0.7002	−0.5060	−0.0012
Δ_K					1.0000	0.6080	−0.7647	0.6368	−0.3165	0.3426	0.4987	−0.4903	0.6040	−0.6867	0.4408	−0.0066
Φ_J						1.0000	−0.8563	0.6905	−0.5103	0.4890	0.8233	−0.1572	0.9739	−0.6177	0.6455	−0.0520
Φ_{JK}							1.0000	−0.9298	0.7483	−0.3011	−0.6094	0.4381	−0.8427	0.8952	−0.7335	0.0043
Φ_{KJ}								1.0000	−0.9228	0.2174	0.4689	−0.4111	0.6848	−0.8951	0.7735	−0.0063
Φ_K									1.0000	−0.1120	−0.3171	0.2452	−0.5033	0.7444	−0.7480	0.0040
B-C										1.0000	0.8630	0.1586	0.6047	−0.0738	0.2366	−0.0354
δ_J											1.0000	−0.0243	0.8961	−0.3537	0.4360	−0.0443
δ_K												1.0000	−0.1794	0.7108	−0.0142	−0.0080
ϕ_J													1.0000	−0.6198	0.6369	−0.0316
ϕ_{JK}														1.0000	−0.6635	−0.0025
ϕ_K															1.0000	−0.0067
ν_8																1.0000

b) Combination Differences (Co'Dis)

As described for the state $\nu_{11} = 1$, Co'Dis for the state $\nu_8 = 1$ were extracted from the assigned absorptions of the FTIR band. These secondary data showed the same features as described before and, by application of the same selection criteria as in the case of ν_{11}, 583 Co'Dis (out of a total of 1235) with deviations of less than 0.00033 cm^{-1} (~ 10 MHz) were retained in the final LSQ fit of the ν_8-band.

c) Rotational Parameters and the Band Origin ν_8^0

The molecular constants of the state $\nu_8 = 1$ are collected in Table 2 which, like Table 1, also gives the previously reported constants [5] for comparison. The correlation matrix of the present fit of 3564 data is given alongside the table.

Listings of the fitted IR and MW transitions, including the deduced Co'Dis of both the ν_{11}-band and the ν_8-band have been deposited with the "Zentrum für Struktur-Dokumentation" of the Universität Ulm, Germany. They may also be obtained from the author.

IV. Discussion

The rotational constants derived here for the excited states $\nu_{11} = 1$ and $\nu_8 = 1$ deviate by up to 3×10^{-6} cm^{-1} from their counterparts reported earlier [4, 5]. This amounts to up to 100 times the standard errors in these constants.

For tracing the origins of these discrepancies, one first needs to examine the instrumental features of the IFS 120 HR "demonstration model" at the Bruker company and the IFS 120 HR instrument at the University of Giessen. – The latter spectrometer derives its superiority over the former from the addition of a specifically designed larger and much longer (~ 300 cm) gas absorption cell than the former. This allows sample pressures to be reduced sufficiently to eliminate the pressure broadening of absorptions. Hence, the line width of signals observed with the Giessen instrument is determined by the Doppler width alone. The conventional gas cells (length: ~ 30 cm) used on the "demonstration model" require sample pressure above 1 Torr, with the result that observed signals show the effects of pressure broadening. Furthermore, to exploit the small, Doppler-limited line widths, the interference path length (OPD) of the Giessen instrument is extended over that of the "model" by more than a factor 2 to provide a spectral resolution of 0.0015 cm^{-1}. On both these grounds, the experimental data obtained with the IFS 120 HR at Giessen (in 1989) must be judged significantly superior to our own data, which were obtained in 1988 with the "demonstration model" at the Bruker company itself.

This superiority of the Giessen instrument over the company's "model" is borne out by the fact that the P- and R-branch of the ν_{11}-band could be observed up to $J' = 70$ at Giessen, while our earlier data reach up to $J' = 47$ only. This, however, makes it difficult to understand why the later researchers [4] did not recognise, assign and fit any Q-branch transitions at all. While the low-wavenumber side of the Q-branch (see Fig. 1, above) does not seem to offer any particularly distinctive features, we would expect that under a lower sample pressure, yet higher instrumental sensitivity and higher spectral resolution, the Q-branch series $J'_{0,J'} \leftarrow J_{1,J}$ would present itself as a very striking spectral feature begging for interpretation.

In addition to the analysis of the Q-branch of the ν_{11}-band – despite the instrumental inferiority of the "demonstration model" – the present study differs from the published work [4, 5] in two more aspects:

The rotational constants of the excited states $\nu_{11} = 1$ and $\nu_8 = 1$ were essentially held fixed at the values determined from 47 observed rotational transitions (with 4 MMW transitions added recently [1]) of the state $\nu_{11} = 1$, and 42 rotational transitions of the state $\nu_8 = 1$. We had observed and assigned these transitions more than a decade ago [2] by the DRM technique [6]. – In view of the 100-fold superiority in precision of rotational MW (and MMW) data over FTIR data, these 51 and 42 transitions were given a weight of 10^4 in the present LSQ fits. The ~ 2000 (in the case of $\nu_{11} = 1$) and ~ 3000 FTIR data (for $\nu_8 = 1$) which were found compatible with this rotational information, were all given the weight of unity, and they helped significantly to pin down the distortion constants of the two excited states. As the range of J'-values of observable transitions of an IR band is, generally, much larger than the range of J-values accessible by rotational spectroscopy, the IR analysis seems eminently suited for the determination of distortion constants.

The parameters of the GS of 1,1-DFE, which we have used during the past seven years, are in keeping with the very large number of spectroscopic data provided by many different researchers up to 1987. These

GS constants were recently confirmed and refined through the addition of novel data [1]. The GS constants which were chosen by the previous investigators [4, 5], on the other hand, can hardly be reconciled with the multitude of data established up to 1987 [10]. They were chosen [4] on the basis of an LSQ-fit of 2594 GS Co'Dis extracted from the ν_{11}-band and a further 1914 GS Co'Dis deduced from the A-type ν_5-band [3], together with some 170 rotational data [11]. – We have attempted to gauge the merits of this approach (combination of a huge body of comparatively inaccurate IR-derived Co'Dis with a much smaller number of observed transitions of significantly higher precision than the former) by extracting GS Co'Dis from all six FTIR bands of 1,1-DFE, which we had analysed up to $J' \simeq 45$ by 1989, and their combination with the 440 non-degenerate MW and MMW data on the GS [1]. As was to be expected on the basis of an experimental uncertainty of assigned FTIR peaks of ± 0.0005 cm^{-1}, pairs of identical GS Co'Dis showed discrepancies of up to ± 0.002 cm^{-1} (60 MHz) when derived from different IR bands, and less than 3% of the total number of Co'Dis thus derived were compatible to within at least 2×10^{-4} cm^{-1} (6 MHz) with the wavenumber values that were expected from the known GS parameters. The latter had been derived from much fewer (440), but up to 3000 times more accurate data from rotational spectroscopy [1]. – From that result one has to conclude that the GS constants, which had been adopted by the previous workers [4, 5], are considerably inferior to earlier values for these constants which had been derived by other, but experimental techniques. The very large uncertainties in the adopted GS constants of [4] lend further support to this conclusion. The large discrepancies between the present and the previous rotational parameters for the state $\nu_{11} = 1$ and $\nu_8 = 1$ must therefore be ascribed predominantly to inappropriate GS parameters in the earlier published work.

The close coincidence, finally, of the band origins ν_8^0, and particularly ν_{11}^0, in the present and the previous study should be taken as credit to the Bruker company and the persons who carried out the wavenumber calibrations of the IFS 120 HR instruments at Rheinstetten and at Giessen.

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