# Microwave and Millimeterwave Spectrum of 1,1-Difluoroethylene and the Vibrational Mode $\nu_{10}$ from FT-IR Spectroscopy

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Pure rotational spectra of 1,1-Difluoroethylene (1,1-DFE) in the vibrational ground state (GS) and in excited vibrational states (EVSs) have been investigated by double resonance modulation (DRM) microwave spectroscopy in the range from 12 GHz to 40 GHz, and by millimeterwave spectroscopy in the range from 90 to 260 GHz.

In addition to the GS spectrum, rotational transitions have been observed for the EVSs $\nu_{10}=1$, and 2, $\nu_{12}=1$, $\nu_6=1$, $\nu_{11}=1$, $\nu_4=1$, and $\nu_9=1$. Along with other IR bands up to 1400 cm$^{-1}$, the fundamental vibrational band $\nu_{10}=1\leftarrow 0$ has been observed by FT-IR spectroscopy and has been analysed to yield $\nu_{10}^0=436.8851$ cm$^{-1}$.

Rotational constants and quartic distortion constants were deduced for all observed states. In addition, sextic distortion constants were obtained for the GS and for the EVSs $\nu_{10}=1$, 2, $\nu_6=1$, and $\nu_{12}=1$ by computer fits of combined microwave and millimeterwave data to Watson's A-reduced Hamiltonian in I$^r$ representation. The S-reduced Hamiltonian in III$^r$ representation may be considered more appropriate for the calculation or the fitting of the transitions because 1,1-DFE is a near oblate asymmetric top. Thus, for comparison, results are given for both the A- and the S-reduction.

*Key words:* 1,1-Difluoroethylene, Molecular Spectroscopy, Microwave Spectroscopy, FT-IR Spectroscopy, Excited Vibration States.

## 1. Introduction

1,1-Difluoroethylene, $F_2C=CH_2$ (vinylidene fluoride or 1,1-difluoroethene), here abbreviated as 1,1-DFE, has been the subject of numerous spectroscopic studies. For convenience, these may be grouped into –, firstly, work concerning all vibrational bands by low-resolution infrared (IR) and Raman spectroscopy and of specific bands by the high-resolution techniques of recent years, secondly, studies pertaining to the pure rotational spectrum of the vibrational ground state (GS) by microwave-, millimeterwave- and laser Stark spectroscopy and, thirdly, investigations of the pure rotational spectra due to molecules in excited vibrational states (EVSs) of 1,1-DFE. The present study by double resonance modulation (DRM) microwave spectroscopy (Bangor) and by millimeterwave spectroscopy (Kiel) reports data and results pertaining to the GS spectrum, rotational parameters of EVSs, and it presents the analysis of the lowest normal vibration as observed by FT-IR spectroscopy (at Bruker, Analytische Meßtechnik, Rheinstetten).

Purely vibrational asepcts of 1,1-DFE have attracted the interest of scientists since 1945 [1] and were studied by a number of researchers [2–7] with the low-resolution IR- and Raman-techniques of the period until 1975. By that time, the vibration frequencies and the description of the twelve fundamental modes of 1,1-DFE were conclusively established, and disagreement between different workers was confined to the frequency of the IR-inactive $A_2$ torsional mode $\nu_6$ [2–4]. In 1981 Lafferty et al. [8] reported the investigation of the modes $\nu_4$ and $\nu_6$ by high-resolution diode laser technique, and by heterodyning their diode laser against $CO_2$ laser lines they were able to measure the rovibrational IR transitions to better than ± 6 MHz (± 0.0002 cm$^{-1}$). They derived the GS constants necessary for the analysis of the two bands from 128 known [14–19] rotational transitions and 10 GS combination differences from their own work. The advent of the high-resolution FT-IR technique in the late 1980s prompted detailed investigations of further selected vibrational bands of 1,1-DFE [9–12] in recent years. Unfortunately, the latter workers [9–12] chose to disregard the large body of high-precision data on the GS and on rotationally analysed EVSs, which had been established by techniques other than FT-IR by 1990. – The present work adds to the information on EVSs of 1,1-DFE the rovibrational analysis of the lowest fundamental, $\nu_{10}=1$, carried out un-

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der inclusion of all rotational information on the GS and of the rotational data on $\nu_{10}=1$ itself.

The GS rotational spectrum of 1,1-DFE was first investigated by Edgell et al. [13] in 1957, and Laurie and Pence [14] subsequently reported the GS spectra of four isotopomers and deduced the $r_s$-structure of 1,1-DFE. Their work was extended in several studies by Chauffoureaux [15] in the 1960s. During the same period Thomas [16], in an attempt to clarify centrifugal distortion effects, extended the Q-branch assignments in the GS spectrum to $J=50$ and obtained the first millimeterwave transition frequencies of 1,1-DFE from Cook [16]. Flygare and Lo [17] deduced magnetic parameters of 1,1-DFE from the splitting of GS rotational transitions in an applied magnetic field, and their study added the frequency of seven Q-branch lines in the range 3–6 GHz to the body of rotational data on the GS. A refinement in accuracy of four transition frequencies was reported by Casleton et al. [18] from a molecular beam experiment in 1976. In the same year, Baskakov et al. [19] reported a fresh investigation of the GS spectrum and they fitted 150 transitions (which remain unpublished) with frequencies up to 650 GHz to Watson's Hamiltonian [20] in $\mathrm{III}^1$ representation. The deduced GS constants allowed them to assign a transition of 1,1-DFE, which had earlier been found [21] to coincide closely with the 337 μm HCN laser line and which had subsequently been measured accurately [22] as $890759.60 \pm 0.08$ MHz $=53_{30,23} \leftarrow 52_{30,22}$. The latest extensions of accurate data on the GS of 1,1-DFE arose from a laser Stark study of Johnston et al. [23] in 1987. They examined three high-$J$ R-branch transitions accessible with the HCN laser and they reinvestigated the GS spectrum in the range from 8–80 GHz. – The present work adds to the described body of GS data rotational transitions in the millimeterwave range from 90–260 GHz.

Although Thomas [16] and Chauffoureaux [15c] had identified purely rotational transitions due to molecules in the very lowest EVSs of 1,1-DFE, the systematic study of vibrational satellites in the rotational spectrum first became of importance in connection with the development of laser Stark spectroscopy in the mid-1970s. Thus, Ewart and Cox [24] studied by conventional microwave techniques the EVS spectra of 1,1-DFE up to vibrational energies of 1100 $\mathrm{cm}^{-1}$ in order to help the interpretation of the experimental findings of Duxbury and Herman [25], who then succeeded in deducing the precise ($\pm 0.001$ $\mathrm{cm}^{-1}$) vibrational frequencies and the rotational constants of the IR bands $\nu_4$ and $\nu_9$ by combination of the experimental data from their $CO_2$ laser Stark experiment with the microwave data [24]. –Unaware of details or the extent of the work by Ewart [24], which is not published in the formal literature, one of us (O. L. S.) took up the systematic investigation of vibrational satellites in the microwave spectrum of 1,1-DFE by the double resonance modulation (DRM) technique in 1983. This work [26] readily yielded the complete rotational assignments up to $J=39$ of the spectra of 18 EVSs up to energies of more than 1300 $\mathrm{cm}^{-1}$, and included eight of the twelve fundamental vibrational levels, three first and one second overtone level, and six vibrational combination levels of 1,1-DFE. During the following years (1985–1989) we were able to determine the precise centres of the IR-active bands through the analysis, under inclusion of purely rotational information on the GS and on EVSs, of the FT-IR spectra as obtained initially on the Bruker ISF 113 v instrument and later under higher resolution on the Bruker IFS 120 HR spectrometer.

## 2. Experimental and Computational Aspects

### *a) Experimental*

The sample of 1,1-DFE was supplied by the Aldrich Chemical Company, Inc., with a quoted purity of 99%. It was used without further purification.

Measurements by DRM microwave spectroscopy [27] were carried out between 12.3 GHz and 40.0 GHz on an instrument with a U-shaped, 'empty' K-band absorption cell of 20 m length. OKI klystrons provided the sources for both pump- and signal-radiation. The frequencies of double resonance signals were measured to ±50 kHz in a dual trace oscilloscope presentation. The frequencies of DR pump transitions were measured on the DRM instrument to an accuracy of ±300 kHz, and these transitions were remeasured, if detectable, under Stark effect modulation (SEM) on a conventional SEM spectrometer [28]. The sample pressures in all these experiments ranged from 5–30 mTorr.

For the millimeterwave measurements the sample was contained in a free space glass cell of 250 cm length and at a pressure of 30 mTorr. The fundamental radiation was supplied by Okaya and Varian klystrons and multiplied by Ohl type multipliers [29]. The fundamental frequencies were controlled by a frequency standard (DCF 77, Mainflingen, Germany) and line measurements are estimated to be accurate to ±10 kHz. The recording of spectra and data acquisition was carried out with the computer controlled system described previously [30].

Infrared measurements of fundamentals up to 1350 cm$^{-1}$ were conducted at the Bruker company with the FT-IR instrument IFS 120 HR. For the comparatively weak $\nu_{10}$-band, a multipath absorption cell (White cell) was attached to the instrument. It was set to an effective pathlength of 340 cm and contained the 1,1-DFE vapour at a pressure of 3 mbar. A mercury arc lamp provided the IR radiation, which was detected by a Ge-bolometer. The interferogram was built up from 256 scans and the nominal resolution was 0.0039 cm$^{-1}$. The wavenumber scale of the instrument was calibrated against accurately known [31] absorptions of $H_2O$, which was contained in the sample as an impurity.

### b) *Computational*

The frequencies or wavenumber values of assigned rotational and/or rovibrational transitions were fitted with the help of computer programs [32, 33] to Watson's A-reduced Hamiltonian [20] in $\mathrm{I}^{\mathrm{r}}$ representation $((x, y, z) = (b, c, a))$

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

Here, $A$, $B$, $C$ are the rotational constants, $\Delta$ and $\delta$ are the quartic, and $\Phi$ and $\phi$ are the sextic distortion constants. As usual, $\mathbf{P} = (\mathbf{P}_a, \mathbf{P}_b, \mathbf{P}_c)$ is the angular momentum operator and $\mathbf{P}_\pm = \mathbf{P}_b \pm \mathbf{i}\,\mathbf{P}_c$ are the step operators. The symbol $[\,,]_+$ denotes the anticommutator between the two parts of the square bracket [20].

In view of the near-oblate character of 1,1-DFE, rotational spectra were also fitted [33] to Watson's S-reduced Hamiltonian [20] in the $\mathrm{III}^{\mathrm{r}}$ representation $((x, y, z) = (a, b, c))$

$$\begin{aligned}\mathscr{H}^{(s)} = {} & A\,\mathbf{P}_a^2 + B\,\mathbf{P}_b^2 + C\,\mathbf{P}_c^2 - D_J (\mathbf{P}^2)^2 - D_{JK} \mathbf{P}^2 \mathbf{P}_c^2 \\ & - D_K \mathbf{P}_c^4 + \mathrm{d}_1 \mathbf{P}^2 (\mathbf{P}_+^2 + \mathbf{P}_-^2) + \mathrm{d}_2 (\mathbf{P}_+^4 + \mathbf{P}_-^4) \\ & + H_J (\mathbf{P}^2)^3 + H_{JK} (\mathbf{P}^2)^2 \mathbf{P}_c^2 + H_{KJ} (\mathbf{P}^2) \mathbf{P}_c^4 \\ & + H_K \mathbf{P}_c^6 + h_1 (\mathbf{P}^2)^2 (\mathbf{P}_+^2 + \mathbf{P}_-^2) \\ & + h_2 \mathbf{P}^2 (\mathbf{P}_+^4 + \mathbf{P}_-^4) + h_3 (\mathbf{P}_+^6 + \mathbf{P}_-^6), \\ & \quad (\mathbf{P}_\pm = \mathbf{P}_a \pm \mathbf{i}\,\mathbf{P}_b)\,.\end{aligned}$$

The main effect in the fits to the S-reduced Hamiltonian is a sometimes lower standard error of the parameters and a more acceptable matrix of correlation coefficients.

## 3. Results

1,1-DFE is a small planar molecule and belongs to the symmetry point group $C_{2v}$. Its inertial properties make it a slightly asymmetric oblate top. Ray's asymmetry parameter is $\kappa \simeq 0.797$ in the GS and does not change significantly in EVSs. Its GS dipole moment is $\mu_a = 1.382(3)$ D [23], and on that account absorption lines of the GS can be observed in all frequency ranges. Weak rotational transitions of the higher excited vibrational states in the close vicinity of GS transitions could not always be resolved from the latter, and overlapping transitions from different EVSs sometimes gave rise to erroneous frequency measurements in the MMW-range. As a result, the number of fitted rotational transitions for each EVS is significantly smaller than for the GS. Nevertheless, for the four excited states $\nu_{10} = 1, 2$, $\nu_6 = 1$, and $\nu_{12} = 1$ sufficient data could be established to allow a determination of sextic distortion constants, while for the states $\nu_{11} = 1$, $\nu_4 = 1$, and $\nu_9 = 1$ only rotational and quartic distortion constants could be derived. – Figure 1 attempts to provide an overview of the EVSs which are the topics of the present study.

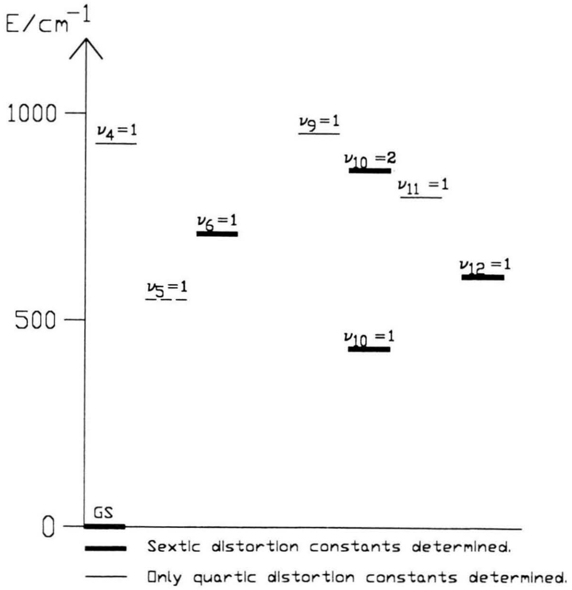

Fig. 1. Vibrational energy levels of 1,1-DFE below 1000 cm$^{-1}$.

### *3.1. The Ground State Parameters*[1]

By combination of the GS transition frequencies first measured by Thomas [16] and those added by other workers [17–19, 22, 23] with our own microwave (MW) and millimeterwave (MMW) data, a satisfactory fit, including the sextic distortion constants, of some 550 GS transitions was obtained. This fit included 430 Q-branch transitions up to $J=58$, of which 87 are $K_a$ degenerate doublets. While the MMW data extended the R-branch assignments up to $J=23 \leftarrow 22$, the frequencies of the three R-branch lines reported in the HCN laser range with $J=47 \leftarrow 46$ [23] and $J=53 \leftarrow 52$ [19, 22] agreed very well indeed with expectations based on the large body of MW and MMW data. Thus, from the three different experimental techniques 125 R-branch transitions were available, of which 28 represented $K_a$ degenerate doublets. After removal of one component of the degenerate pairs, there remained 97 R-branch and 343 Q-branch lines in the LSQ fit.

In an attempt to fill the gap in the R-branch from $J \sim 25$ to $J \sim 50$, for which no rotational data are available, we turned to our earlier FT-IR work and extracted all GS combination differences (Co'Dis) in the range $35 < J < 50$ from the six fundamental IR-bands which we had analysed by 1989. As was to be expected on the basis of an estimated uncertainty of up to ±15 MHz ($\pm 0.0005\ \mathrm{cm}^{-1}$) on rovibrational FT-IR data, particular GS Co'Dis deviated by up to ±30 MHz from each other when derived from different fundamental bands. For that resaon, the overwhelming portion of the IR-derived Co'Dis was considered unsuitable for inclusion with the 100 times more accurate data from rotational spectroscopy, and it was therefore discarded. A small fraction (98 Co'Dis) of IR-derived differences, most of them weighted down by $10^{-4}$, was retained, however, on the ground that these Co'Dis agreed with the data from rotational techniques to better than ±6 MHz ($\pm 0.0002\ \mathrm{cm}^{-1}$).

The final rotational parameters of the GS were derived by a fit of the described data with the computer routine by Gambi et al. [32]. They are collected in Table 1a, where they are given in both wavenumber- and frequency units. The correlation matrix of the fit is included at the bottom of the table.

The program [33] at our disposal (at Kiel) for the S-reduction [20] of the data is designed for the fit of observed rotational transitions only. Accordingly, it is restricted by the well-known dipole selection rules and therefore unsuitable for the fit of the Co'Dis. However, a slight modification of the program permitted the inclusion of 79 Co'Dis with $|\Delta J| = 1, 2$, $\Delta K_a = 0$ and $|\Delta K_c| = 0, 1, 2$ in the final LSQ fit of 519 data. – In Table 1b (S-reduction) the uncertainties of all rotational parameters are seen to be very comparable with those from the A-reduction (Table 1a), while the associated correlation matrix may be considered to indicate a larger degree of interdependence of deduced parameters.

### *3.2. The Vibration State* $v_{10} = 1$

The state $v_{10}=1$ is the lowest EVS of 1,1-DFE and belongs to the $C_{2v}$ symmetry species $B_1$. It is qualitatively described as the in-plane rocking motion of the $CF_2$-group (see Figure 2). With a vibrational frequency of $\sim 437\ \mathrm{cm}^{-1}$ [6] the rotational transitions within this state have a nominal intensity on account of the Boltzmann law of ~ 11.7% of their counterparts in the GS spectrum at room temperature (293 K). Due to the effects of nuclear spin statistics [34] this intensity is modified to ~ 7.0% of the GS lines for satellite transitions with even values of $K_a$, and to ~ 19.5% of the GS counterparts for odd values of $K_a$. In either case, these vibrational satellite transitions in the rotation spectrum are easily detected. Accordingly, ten transitions of this spectrum with very low values of $J$ were identified by Thomas [16] in 1965. His work was extended (by O. L. S.) to 50 transitions in the MW range, comprising the five strongest low $J$-R-branch lines and 45 Q-branch lines up to $J = 38$. The investigation in the MMW range readily added a further 43 R-branch transitions up to $J = 14 \leftarrow 13$ including 10 degenerate transitions and 154 Q-branch lines up to $J = 35$ including 38 degenerate transitions.

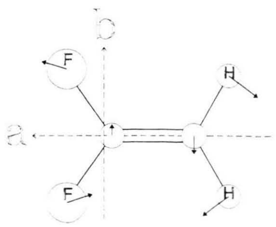

Fig. 2. Displacement vectors in the $B_1$ mode $v_{10} = 1$ (vectors are drawn 10 times larger than calculated).

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[1] A complete list of lines can be obtained from the authors or the Central Library of the University of Kiel under number TNA 34. *Adress*: Universitätsbibliothek Kiel, Zentralbibliothek, Olshausenstr. 40, D-24098 Kiel/Germany.

Table 1 a. Results of the LSQ fit of combined MW, MMW, and IR data for the Ground State of 1,1-DFE with parameters fitted to Watson's A-reduced Hamiltonian in $I^r$-representation. Uncertainties are one standard error and are given in units of the last quoted digit.

Rotational Constants

| | | |
|---|---|---|
| $A$ | 0.367 005 884(7) cm$^{-1}$ | 11 002.5596(3)[1] MHz |
| $B$ | 0.347 873 582(7) cm$^{-1}$ | 10 428.9876(2) MHz |
| $C$ | 0.178 302 611(8) cm$^{-1}$ | 5 345.3778(3) MHz |

Quartic Distortion Constants

| | | |
|---|---|---|
| $\Delta_J$ | 0.160 620(8) $\times 10^{-6}$ cm$^{-1}$ | 4.815 25(26) kHz |
| $\Delta_{JK}$ | 0.050 904(16) $\times 10^{-6}$ cm$^{-1}$ | 1.526 05(56) kHz |
| $\Delta_K$ | 0.259 989(25) $\times 10^{-6}$ cm$^{-1}$ | 7.794 29(73) kHz |
| $\delta_J$ | 0.067 104(3) $\times 10^{-6}$ cm$^{-1}$ | 2.011 74(10) kHz |
| $\delta_K$ | 0.188 181(7) $\times 10^{-6}$ cm$^{-1}$ | 5.641 53(21) kHz |

Sextic Distortion Constants

| | | |
|---|---|---|
| $\Phi_J$ | 0.322(2) $\times 10^{-12}$ cm$^{-1}$ | 9.64(10) $\times 10^{-3}$ Hz |
| $\Phi_{JK}$ | −0.103(16) $\times 10^{-12}$ cm$^{-1}$ | −3.10(40) $\times 10^{-3}$ Hz |
| $\Phi_{KJ}$ | −0.360(59) $\times 10^{-12}$ cm$^{-1}$ | −10.8(18) $\times 10^{-3}$ Hz |
| $\Phi_K$ | 0.938(67) $\times 10^{-12}$ cm$^{-1}$ | 28.1(19) $\times 10^{-3}$ Hz |
| $\phi_J$ | 0.183(1) $\times 10^{-12}$ cm$^{-1}$ | 5.49(3) $\times 10^{-3}$ Hz |
| $\phi_{JK}$ | 0.345(7) $\times 10^{-12}$ cm$^{-1}$ | 10.34(20) $\times 10^{-3}$ Hz |
| $\phi_K$ | 2.573(14) $\times 10^{-12}$ cm$^{-1}$ | 77.14(41) $\times 10^{-3}$ Hz |

Standard Deviations

| | | |
|---|---|---|
| $\sigma$ | 1.10 $\times 10^{-6}$ cm$^{-1}$ | 33 kHz |

Fitted Transitions: $N_{\text{rot}} + N_{\text{Co'Di}} = 440 + 98 = 538 = N_{\text{Total}}$

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[1] Conversion factor $c = 299\,792\,498$ m · s$^{-1}$.

Correlation matrix of LSQ-fit of GS in A-reduction

| | $A$–$B$ | $B$ | $\Delta_J$ | $\Delta_{JK}$ | $\Delta_K$ | $\Phi_J$ | $\Phi_{JK}$ | $\Phi_{KJ}$ | $\Phi_K$ | $B$-$C$ | $\delta_J$ | $\delta_K$ | $\phi_J$ | $\phi_{JK}$ | $\phi_K$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A$–$B$ | 1.0000 | −0.1496 | −0.4089 | 0.3450 | 0.0987 | −0.4217 | −0.3810 | 0.3685 | −0.1952 | 0.8007 | 0.7687 | −0.1462 | 0.7353 | 0.3799 | −0.4315 |
| $B$ | | 1.0000 | 0.7001 | −0.0829 | −0.0404 | 0.5553 | 0.2240 | −0.1967 | 0.1062 | −0.0803 | −0.1694 | 0.1363 | −0.1989 | −0.1508 | 0.2267 |
| $\Delta_J$ | | | 1.0000 | −0.4136 | 0.0964 | 0.9592 | 0.5643 | −0.6043 | 0.4098 | −0.3638 | −0.5994 | 0.4217 | −0.5757 | −0.5239 | 0.6106 |
| $\Delta_{JK}$ | | | | 1.0000 | −0.8537 | −0.5480 | 0.1010 | 0.4762 | −0.6291 | 0.4965 | 0.6096 | −0.3345 | 0.4972 | 0.4234 | −0.1093 |
| $\Delta_K$ | | | | | 1.0000 | 0.2354 | −0.4200 | −0.2393 | 0.5498 | −0.1466 | −0.1794 | 0.0483 | −0.0534 | −0.2482 | −0.2404 |
| $\Phi_J$ | | | | | | 1.0000 | 0.4755 | −0.6605 | 0.5286 | −0.4143 | −0.6042 | 0.4692 | −0.5831 | −0.5348 | 0.5538 |
| $\Phi_{JK}$ | | | | | | | 1.0000 | −0.6678 | 0.2742 | −0.2633 | −0.4051 | 0.2014 | −0.4289 | −0.6665 | 0.8383 |
| $\Phi_{KJ}$ | | | | | | | | 1.0000 | −0.8953 | 0.4249 | 0.5639 | −0.2059 | 0.4483 | 0.8677 | −0.4650 |
| $\Phi_K$ | | | | | | | | | 1.0000 | −0.3473 | −0.4312 | 0.0835 | −0.2631 | −0.7451 | 0.0803 |
| $B$–$C$ | | | | | | | | | | 1.0000 | 0.8998 | −0.1018 | 0.8232 | 0.4563 | −0.3048 |
| $\delta_J$ | | | | | | | | | | | 1.0000 | −0.2844 | 0.9604 | 0.5628 | −0.4683 |
| $\delta_K$ | | | | | | | | | | | | 1.0000 | −0.2903 | 0.1120 | 0.4153 |
| $\phi_J$ | | | | | | | | | | | | | 1.0000 | 0.4724 | −0.5002 |
| $\phi_{JK}$ | | | | | | | | | | | | | | 1.0000 | −0.5225 |
| $\phi_K$ | | | | | | | | | | | | | | | 1.0000 |

Table 1 b. Results of the LSQ fit of combined MW, MMW, and IR data for the Ground State of 1,1-DFE with parameters fitted to Watson's S-reduced Hamiltonian in $III^r$-representation. Uncertainties are one standard error and are given in units of the last quoted digit.

| | | | | | |
|---|---|---|---|---|---|
| $A$ | 11.0025680(3) GHz | $D_J$ | 11.7955(5) kHz | $H_J$ | 0.0283(2) Hz |
| $B$ | 10.4289770(3) GHz | $D_{JK}$ | −20.3423(7) kHz | $H_{JK}$ | −0.1136(8) Hz |
| $C$ | 5.3453792(3) GHz | $D_K$ | 9.3375(4) kHz | $H_{KJ}$ | 0.1394(15) Hz |
| | | $d_J$ | −1.3243(1) kHz | $H_K$ | −0.0558(9) Hz |
| | | $d_K$ | 0.15427(7) kHz | $h_J$ | 0.0030(2) Hz |
| | | | | $h_{JK}$ | −0.0030(2) Hz |
| | | | | $h_K$ | −0.00208(5) Hz |

Standard Deviation: $\sigma$ 39 kHz

Fitted Transitions

$N_{\text{rot}} + N_{\text{Co'Di}} = 440 + 79 = 519 = N_{\text{Total}}$

Correlation matrix of LSQ-fit of GS in S-Reduction.

| | $A$ | $B$ | $C$ | $D_J$ | $D_{JK}$ | $D_K$ | $d_1$ | $d_2$ | $H_J$ | $H_{JK}$ | $H_{KJ}$ | $H_K$ | $h_1$ | $h_2$ | $h_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A$ | 1.000 | | | | | | | | | | | | | | |
| $B$ | 0.944 | 1.000 | | | | | | | | | | | | | |
| $C$ | 0.418 | 0.490 | 1.000 | | | | | | | | | | | | |
| $D_J$ | 0.814 | 0.788 | 0.216 | 1.000 | | | | | | | | | | | |
| $D_{JK}$ | −0.537 | −0.430 | 0.284 | −0.669 | 1.000 | | | | | | | | | | |
| $D_K$ | 0.041 | −0.020 | 0.140 | 0.127 | −0.473 | 1.000 | | | | | | | | | |
| $d_1$ | −0.163 | 0.043 | 0.097 | 0.191 | 0.494 | −0.437 | 1.000 | | | | | | | | |
| $d_2$ | −0.045 | 0.085 | 0.040 | −0.096 | 0.341 | −0.384 | 0.947 | 1.000 | | | | | | | |
| $H_J$ | 0.613 | 0.550 | 0.166 | 0.862 | −0.679 | 0.337 | −0.460 | −0.396 | 1.000 | | | | | | |
| $H_{JK}$ | −0.404 | −0.334 | −0.126 | −0.655 | 0.623 | −0.524 | 0.525 | 0.481 | −0.933 | 1.000 | | | | | |
| $H_{KJ}$ | 0.284 | 0.270 | 0.344 | 0.551 | −0.285 | 0.487 | −0.294 | −0.304 | 0.790 | −0.885 | 1.000 | | | | |
| $H_K$ | −0.247 | −0.258 | −0.391 | −0.509 | 0.132 | −0.373 | 0.157 | 0.185 | −0.691 | 0.770 | −0.975 | 1.000 | | | |
| $h_1$ | 0.208 | 0.092 | 0.079 | 0.354 | −0.422 | 0.432 | −0.748 | −0.747 | 0.752 | −0.858 | 0.712 | −0.584 | 1.000 | | |
| $h_2$ | 0.194 | 0.093 | 0.099 | 0.342 | −0.374 | 0.397 | −0.701 | −0.716 | 0.741 | −0.845 | 0.719 | −0.601 | 0.996 | 1.000 | |
| $h_3$ | 0.241 | 0.161 | 0.151 | 0.414 | −0.346 | 0.358 | −0.564 | −0.574 | 0.780 | −0.872 | 0.790 | −0.691 | 0.960 | 0.977 | 1.000 |

### *3.2a. Rovibrational Analysis of the IR Fundamental $\nu_{10}$*

The rotational parameters derivable from the MW and MMW rotational transitions *within* $\nu_{10} = 1$ together with those of the vibrational GS (Table 1, above) provided an ideal basis for the analysis of the B type IR band $\nu_{10}$, as initially observed on the IFS 113v (Fig. 3) and later on the IFS 120 HR Bruker FT-IR instruments. From the purely rotational information on the GS and on $\nu_{10} = 1$ the rovibrational structure of this IR band could be predicted with confidence, leaving merely the band origin $\nu_{10}^0$ undetermined within $\pm 1$ cm$^{-1}$. As would be expected in such favourable circumstances, detailed assignment of some 1000 rovibrational peaks between 410–470 cm$^{-1}$ and comprising the P-, Q-, and R-branch of the IR band followed readily up to $J' = 60$.

In the final LSQ fit of the IR band, which was carried out with the computer routine of Gambi et al. [32], 961 FT-IR peaks, from which $K_a$-degenerate transitions had been removed, were combined with 92 Co'Dis for $\nu_{10} = 1$. The latter has been extracted from the IR data for the range $30 < J < 53$ and were subjected to the same compatibility limit of $\pm 0.0005$ cm$^{-1}$ ($\pm 15$ MHz) as the wavenumber values of the directly observed IR peaks. The wheightiest contribution to the fit is represented by the rotational data on $\nu_{10} = 1$, as established by MW and MMW spectroscopy. With degenerate pairs of transitions counted only once, the 199 observed frequencies were given a $10^4$ times larger weight than the FT-IR data, since their precision is estimated to be at least 100 times higher than that of the IR data.

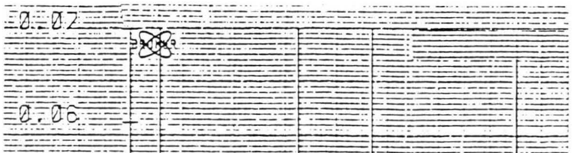

Fig. 3. The IR fundamental band $\nu_{10}$ (observed on Bruker IFS 113v).

The rotational parameters of the EVS $\nu_{10} = 1$, which resulted from the described data, are collected in Table 2a and are given in the same format as adopted for Table 1a. The apparently rather high precision of the results arises from the inclusion in the fit of MW and MMW data. This may be seen from a comparison of the molecular parameters with their counterparts (given in italics in Table 2a) which emerge from a fit of the IR data *alone*. In the latter case, all uncertainties are seen to be about ten times larger than under inclusion of MW and MMW data. The statistical uncertainty in the band origin $\nu_{10}^0$, finally, is in reality completely 'swamped' by the 100 times larger uncertainty associated with the calibration of the wavenumber scale of the IR instrument.

For comparison with the simultaneous fit of rovibrational FT-IR lines, IR combination differences and purely rotational MW and MMW lines for $\nu_{10} = 1$, as given in Table 2a, the 247 rotational transitions in that state were also subjected to LSQ-fits in both the A- and S-reduction. The resulting parameters are collected in Table 2b. The table of correlation coefficients shows for the S-reduction five correlation coefficients larger than 0.9 between: $A$ and $B$, $A$ and $D_J$, $B$ and $D_J$, $D_J$ and $H_J$ and $D_K$ and $H_K$. For the A-reduction we found 36 correlation coefficients $> 0.9$ from the fit of rotational transitions *alone*, while the fit of rotational and vibrational information indicates merely two correlation coefficients of such magnitude.

### *3.3. The Excited Vibration States $\nu_{12} = 1$, $\nu_6 = 1$, and $\nu_{10} = 2$*

Infrared spectroscopy provides relatively little information on these three states: while the $A_2$ mode $\nu_6$ at $\sim 713$ cm$^{-1}$ is IR-inactive, the $B_2$ mode $\nu_{12}$ at $\sim 609$ cm$^{-1}$ produces only a small absorption (presumably the Q-branch of this C-type band) and the $A_1$ overtone band $\nu_{10} = 2 \leftarrow 0$ at $\sim 869$ cm$^{-1}$ is also too

Table 2a. Results of the LSQ fit of combined IR-, MW- and MMW-data and of IR-data *alone* for the state $v_{10}=1$ of 1,1-DFE. Parameters are fitted to Watson's A-reduced Hamiltonian in $\mathrm{I}^r$-representation. Uncertainties are one standard error and are given in units of the last quoted digit ([1] Conversion factor $c=299\,792\,498\ \mathrm{m\cdot s^{-1}}$).

| Rotational Constants | | |
|---|---|---|
| $A$ | 0.367395818(34) $\mathrm{cm^{-1}}$<br>*0.367396380(264)* | 11014.2495(11)[1] MHz |
| $B$ | 0.347583074(31) $\mathrm{cm^{-1}}$<br>*0.347582035(304)* | 10420.2784(9) MHz |
| $C$ | 0.177788990(24) $\mathrm{cm^{-1}}$<br>*0.177789136(88)* | 5329.9798(8) MHz |

| Sextic Distortion Constants | | |
|---|---|---|
| $\Phi_J$ | 0.236(13) · $10^{-12}$ $\mathrm{cm^{-1}}$<br>*0.086(205)* | 7.08(39) · $10^{-3}$ Hz |
| $\Phi_{JK}$ | 0.072(84) · $10^{-12}$ $\mathrm{cm^{-1}}$<br>*0.183(1940)* | 2.2(25) · $10^{-3}$ Hz |
| $\Phi_{KJ}$ | −1.544(220) · $10^{-12}$ $\mathrm{cm^{-1}}$<br>*−0.339(3394)* | −46.3(66) · $10^{-3}$ Hz |
| $\Phi_K$ | 2.102(136) · $10^{-12}$ $\mathrm{cm^{-1}}$<br>*1.261(1722)* | 63.0(41) · $10^{-3}$ Hz |
| $\phi_J$ | 0.147(7) · $10^{-12}$ $\mathrm{cm^{-1}}$<br>*0.056(103)* | 4.41(21) · $10^{-3}$ Hz |
| $\phi_{JK}$ | 0.050(38) · $10^{-12}$ $\mathrm{cm^{-1}}$<br>*0.025(667)* | 1.5(11) · $10^{-3}$ Hz |
| $\phi_K$ | 2.967(53) · $10^{-12}$ $\mathrm{cm^{-1}}$<br>*3.232(539)* | 89.0(17) · $10^{-3}$ Hz |

| Quartic Distortion Constants | | |
|---|---|---|
| $\Delta_J$ | 0.160098(34) · $10^{-6}$ $\mathrm{cm^{-1}}$<br>*0.159709(322)* | 4.7996(10) kHz |
| $\Delta_{JK}$ | 0.038809(111) · $10^{-6}$ $\mathrm{cm^{-1}}$<br>*0.039308(1588)* | 1.1635(33) kHz |
| $\Delta_K$ | 0.277052(165) · $10^{-6}$ $\mathrm{cm^{-1}}$<br>*0.277929(1307)* | 8.3254(46) kHz |
| $\delta_J$ | 0.067343(17) · $10^{-6}$ $\mathrm{cm^{-1}}$<br>*0.067079(165)* | 2.0189(5) kHz |
| $\delta_K$ | 0.190287(49) · $10^{-6}$ $\mathrm{cm^{-1}}$<br>*0.190294(418)* | 5.7047(15) kHz |

| Standard Deciation | | |
|---|---|---|
| $\sigma$ | 5.62 · $10^{-6}$ $\mathrm{cm^{-1}}$<br>*2.36 · $10^{-4}$* | 187 kHz |

| Band Origin $v_{10}^0$ | 436.885147(2) $\mathrm{cm^{-1}}$<br>*436.885141(26)* |
|---|---|

*Fitted Transitions:*

$$N_{\mathrm{IR}}+N_{\mathrm{Co'Di}}+N_{\mathrm{MW+MMW}}=961+92+199=1252=N_{\mathrm{Total}}$$

Correlation matrix (of LSQ-fit of 1252 data for the state $v_{10}=1$ in A-reduction).

| | $A$–$B$ | $B$ | $\Delta_J$ | $\Delta_{JK}$ | $\Delta_K$ | $\Phi_J$ | $\Phi_{JK}$ | $\Phi_{KJ}$ | $\Phi_K$ | $B$-$C$ | $\delta_J$ | $\delta_K$ | $\phi_J$ | $\phi_{JK}$ | $\phi_K$ | $v^0$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A$–$B$ | 1.0000 | −0.0039 | −0.0007 | 0.2130 | 0.2644 | −0.0479 | 0.0718 | 0.0987 | 0.0304 | 0.3283 | 0.2147 | 0.0427 | 0.0974 | −0.0425 | 0.2623 | −0.0361 |
| $B$ | | 1.0000 | 0.8442 | 0.0008 | 0.0039 | 0.5843 | 0.0197 | −0.0947 | 0.1589 | 0.2913 | 0.3101 | 0.0387 | 0.2796 | −0.0003 | 0.1166 | −0.0802 |
| $\Delta_J$ | | | 1.0000 | −0.1235 | 0.0612 | 0.8815 | −0.0033 | −0.1872 | 0.3162 | 0.4942 | 0.5034 | 0.2956 | 0.5333 | 0.1578 | 0.2483 | −0.0280 |
| $\Delta_{JK}$ | | | | 1.0000 | −0.8272 | −0.1906 | 0.7789 | −0.5193 | 0.2232 | 0.0708 | 0.3096 | −0.1047 | 0.1855 | 0.2586 | −0.3049 | 0.0091 |
| $\Delta_K$ | | | | | 1.0000 | 0.0688 | −0.7999 | 0.6881 | −0.2967 | 0.0098 | −0.1793 | −0.1538 | −0.1495 | −0.4766 | 0.3965 | 0.0089 |
| $\Phi_J$ | | | | | | 1.0000 | −0.1288 | −0.0936 | 0.2014 | 0.5623 | 0.6004 | 0.4417 | 0.7201 | 0.3941 | 0.1480 | −0.0095 |
| $\Phi_{JK}$ | | | | | | | 1.0000 | −0.9002 | 0.6418 | 0.0752 | 0.1901 | 0.2901 | 0.1299 | 0.3232 | 0.0420 | 0.0023 |
| $\Phi_{KJ}$ | | | | | | | | 1.0000 | −0.8670 | −0.1806 | −0.2560 | −0.4353 | −0.2432 | −0.3383 | −0.1276 | 0.0028 |
| $\Phi_K$ | | | | | | | | | 1.0000 | 0.2784 | 0.3227 | 0.3339 | 0.3015 | 0.0804 | 0.3065 | 0.0028 |
| $B$–$C$ | | | | | | | | | | 1.0000 | 0.8580 | 0.2525 | 0.7781 | 0.1751 | 0.2152 | 0.0232 |
| $\delta_J$ | | | | | | | | | | | 1.0000 | 0.0824 | 0.9451 | 0.1645 | 0.1097 | 0.0200 |
| $\delta_K$ | | | | | | | | | | | | 1.0000 | 0.2275 | 0.7575 | 0.2797 | 0.0007 |
| $\phi_J$ | | | | | | | | | | | | | 1.0000 | 0.2817 | 0.1298 | 0.0152 |
| $\phi_{JK}$ | | | | | | | | | | | | | | 1.0000 | −0.3193 | −0.0012 |
| $\phi_K$ | | | | | | | | | | | | | | | 1.0000 | 0.0100 |
| $v^0$ | | | | | | | | | | | | | | | | 1.0000 |

Table 2b. Molecular parameters of the state $v_{10}=1$ derived from 247 rotational transitions (including 48 degeneracies) *alone* in both A- and S-reduction. Uncertainties are one standard error and are given in units of last quoted digit.

| A-reduction in $\mathrm{I}^r$ | | | | | | S-reduction in $\mathrm{III}^r$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $A$ | 11.014252(1) | GHz | | | | $A$ | 11.014261(1) | GHz | | | |
| $B$ | 10.420281(1) | GHz | $\Phi_J$ | 0.010(15) | Hz | $B$ | 10.420270(1) | GHz | $H_J$ | 0.041(19) | Hz |
| $C$ | 5.329981(1) | GHz | $\Phi_{JK}$ | 0.073(43) | Hz | $C$ | 5.329983(1) | GHz | $H_{JK}$ | −0.115(2) | Hz |
| $\Delta_J$ | 4.803(1) | kHz | $\Phi_{KJ}$ | −0.133(62) | Hz | $D_J$ | 11.8138(91) | kHz | $H_{KJ}$ | 0.152(5) | Hz |
| $\Delta_{JK}$ | 1.18(1) | kHz | $\Phi_K$ | 0.089(28) | Hz | $D_{JK}$ | −20.6130(22) | kHz | $H_K$ | −0.093(18) | Hz |
| $\Delta_K$ | 8.291(8) | kHz | $\phi_J$ | 0.012(4) | Hz | $D_K$ | 9.5588(67) | kHz | $h_1$ | 0.0031(4) | Hz |
| $\delta_J$ | 2.022(2) | kHz | $\phi_{JK}$ | −0.023(18) | Hz | $d_1$ | −1.3571(5) | kHz | $h_2$ | 0.0026(3) | Hz |
| $\delta_K$ | 5.703(4) | kHz | $\phi_K$ | 0.105(13) | Hz | $d_2$ | 0.1267(2) | kHz | $h_3$ | 0.0019(1) | Hz |
| Standard Deviation: | | | | 34 | kHz | | 34 | kHz | | | |

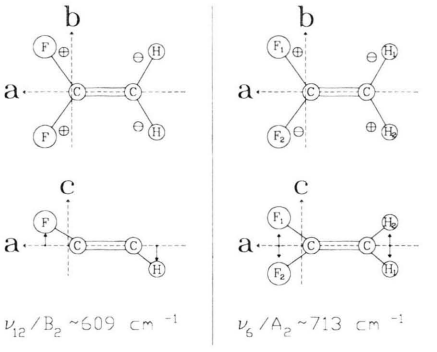

Fig. 4. Displacements in the modes $\nu_{12}$ and $\nu_6$ of 1,1-DFE.

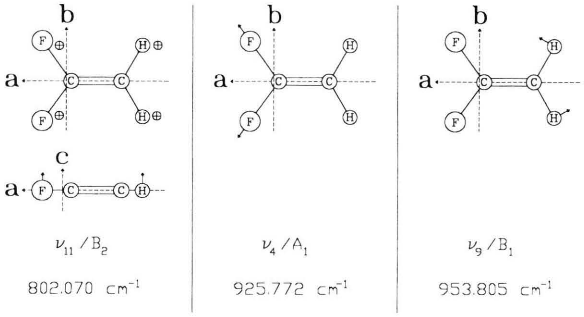

Fig. 5. Displacements in the modes $\nu_{11}$, $\nu_4$ and $\nu_9$ of 1,1-DFE.

Table 3a. Rotational and centrifugal distortion constants from rotational transitions alone of the states $\nu_{12} = 1$, $\nu_6 = 1$ and $\nu_{10} = 2$ using Watson's A-reduction in representation $I^r$. Standard errors are given in units of last quoted digit.

| | $\nu_{12}=1$ ~609 cm$^{-1}$ | $\nu_6=1$ ~713 cm$^{-1}$ | $\nu_{10}=2$ ~869 cm$^{-1}$ | |
|---|---|---|---|---|
| $A$ | 10.997043(1) | 10.999454(1) | 11.025346(2) | GHz |
| $B$ | 10.445253(1) | 10.407325(1) | 10.411696(2) | GHz |
| $C$ | 5.350152(1) | 5.346032(1) | 5.314173(2) | GHz |
| $\Delta_J$ | 4.818(9) | 4.728(13) | 4.809(19) | kHz |
| $\Delta_{JK}$ | 1.835(11) | 1.739(13) | 0.835(20) | kHz |
| $\Delta_K$ | 7.456(9) | 7.661(11) | 8.788(18) | kHz |
| $\delta_J$ | 2.016(2) | 1.972(2) | 2.030(3) | kHz |
| $\delta_K$ | 5.755(4) | 5.612(4) | 5.776(7) | kHz |
| $\Phi_J$ | −0.03(2) | −0.02(4) | 0.07(6) | Hz |
| $\Phi_{JK}$ | −0.01(5) | 0.16(5) | 0.2(1) | Hz |
| $\Phi_{KJ}$ | 0.00(7) | −0.17(8) | −0.6(2) | Hz |
| $\Phi_K$ | 0.02(3) | 0.08(4) | 0.58(9) | Hz |
| $\phi_J$ | 0.005(4) | 0.015(5) | 0.018(9) | Hz |
| $\phi_{JK}$ | 0.00(2) | −0.04(2) | −0.07(4) | Hz |
| $\phi_K$ | −0.08(1) | 0.12(2) | 0.07(4) | Hz |
| Fitted Transitions | | | | |
| | 234 | 190 | 133 | |
| Degenerate Transitions Included | | | | |
| | 55 | 44 | 23 | |
| Standard Deviation | | | | |
| | 35 | 29 | 35 | kHz |

Table 3b. Rotational and centrifugal distortion constants from rotational transitions alone of the states $\nu_{12} = 1$, $\nu_6 = 1$ and $\nu_{10} = 2$ using Watson's S-reduction in representation $III^r$. Standard errors are given in units of last quoted digit.

| | $\nu_{12}=1$ | $\nu_6=1$ | $\nu_{10}=2$ | |
|---|---|---|---|---|
| $A$ | 10.997051(1) | 10.999462(1) | 11.025356(2) | GHz |
| $B$ | 10.445242(1) | 10.407314(1) | 10.411685(2) | GHz |
| $C$ | 5.350154(1) | 5.346034(1) | 5.314175(2) | GHz |
| $D_J$ | 11.864(10) | 11.715(13) | 11.851(19) | kHz |
| $D_{JK}$ | −20.4585(24) | −20.1669(27) | −20.8977(44) | kHz |
| $D_K$ | 9.381(7) | 9.236(8) | 9.795(13) | kHz |
| $d_1$ | −1.3149(6) | −1.3639(8) | −1.3905(11) | kHz |
| $d_2$ | 0.1925(4) | 0.1574(5) | 0.1004(8) | kHz |
| $H_J$ | −0.01(2) | 0.02(4) | 0.12(6) | Hz |
| $H_{JK}$ | −0.116(2) | −0.106(3) | −0.160(8) | Hz |
| $H_{KJ}$ | 0.146(5) | 0.136(8) | 0.27(3) | Hz |
| $H_K$ | −0.06(2) | 0.0(2) | −0.20(5) | Hz |
| $h_1$ | 0.0037(5) | 0.0020(8) | 0.023(2) | Hz |
| $h_2$ | −0.0028(3) | −0.0046(6) | 0.021(2) | Hz |
| $h_3$ | −0.0023(1) | −0.0024(1) | 0.0071(6) | Hz |
| Fitted Transitions | | | | |
| | 234 | 190 | 133 | |
| Degenerate Transitions included | | | | |
| | 55 | 44 | 23 | |
| Standard Deviation | | | | |
| | 35 | 29 | 34 | kHz |

weak for a rovibrational analysis. This situation adds importance to the study of these three vibrational levels by purely rotational spectroscopy.

Following the identification and rotational assignments of the three satellite spectra in the MW range by DRM-techniques in the early 1980s [26], a further pool of 186, 143, and 88 transitions of the spectra of $\nu_{12} = 1$, $\nu_6 = 1$, and $\nu_{10} = 2$, respectively, were added in the MMW range. Thus, for all three states, a sufficiently large number of transition frequencies was available to make the determination of sextic distortion constants at least qualitatively meaningful.

Results of the fits of these three spectra are given in Table 3a for the A-reduction and in Table 3b for the S-reduction. The correlation matrices (not given) from these fits show again marginally smaller coefficients in the case of the S-reduction than for the A-reduction, in keeping with analogous results for the state $\nu_{10} = 1$.

### *3.4. The Excited Vibration States* $\nu_{11} = 1$, $\nu_4 = 1$, *and* $\nu_9 = 1$

The state $\nu_{11} = 1$ represents the $CH_2$ out-of-plane wagging motion of 1,1-DFE (Figure 5). It belongs to the symmetry species $B_2$ and the corresponding IR-fundamental $\nu_{11} = 1 \leftarrow 0$ is a C-type band. It has been analysed [10] in 1992 when its band centre was determined as 802.070 $cm^{-1}$. In the MW range 47 rotational transitions within this EVS were identified by the DRM-technique [26] and MMW spectroscopy allowed 16 further transitions to be observed within that state.

The states $\nu_4 = 1$ and $\nu_9 = 1$ represent the symmetric $CF_2$ stretching motion ($A_1$ symmetry species, A-type IR-band) and the CCH bending motion ($B_1$ symmetry, B-type IR-band), respectively. Rovibrational transitions of these two bands were first studied in 1978 [25] by laser-Stark techniques and by diode laser techniques in 1981 [8]. In the latter work the vibrational frequencies were determined as $\nu_4^0 = 925.77199(4)\ cm^{-1}$ and $\nu_9^0 = 953.80492(4)\ cm^{-1}$.

Purely rotational transitions within these two EVSs were too weak for observation with the MMW spectrometer (Boltzmann factor at room temperature: ~ 0.01). The higher sensitivity in combination with the molecular selectivity of the DRM-instrument, on the other hand, had allowed 49 transitions of the state $\nu_4 = 1$ and 47 transitions of the state $\nu_9 = 1$ to be readily identified, with both sets comprising the same five low-*J* R-branch transitions and Q-branch transitions up to $J = 39$ and $J = 38$, respectively [26].

The purely rotational spectra of these three states were fitted in both the A- and the S-reduction with sextic distortion constants fixed to the GS values of Table 1. The results are collected in Table 4. The correlation matrices of these fits indicate the same slight superiority of the S-reduction over the A-reduction as apparent for the $\nu_{10} = 1$.

Table 4. Rotational and centrifugal distortion constants of the EVSs $\nu_{11}=1$, $\nu_4=1$ and $\nu_9=1$ from Watson's A- and S-reduction with sextic distortion constants held fixed to their GS values. Standard errors are given in units of last quoted digit.

| | $\nu_{11}=1$ 802.070 $cm^{-1}$ | $\nu_4=1$ 925.772 $cm^{-1}$ | $\nu_9=1$ 953.805 $cm^{-1}$ | |
|---|---|---|---|---|
| A-reduction in representation $I^r$ | | | | |
| $A$ | 10.989555(9) | 10.972064(20) | 11.026939(12) | GHz |
| $B$ | 10.407448(8) | 10.415028(20) | 10.436391(12) | GHz |
| $C$ | 5.349223(8) | 5.328531(20) | 5.346144(12) | GHz |
| $\Delta_J$ | 2.670(78) | 7.8(13) | 3.86(79) | kHz |
| $\Delta_{JK}$ | 1.517(50) | 1.11(44) | 0.59(27) | kHz |
| $\Delta_K$ | 7.601(51) | 7.999(73) | 8.73(18) | kHz |
| $\delta_J$ | 1.990(7) | 1.908(72) | 1.950(45) | kHz |
| $\delta_K$ | 5.448(23) | 6.17(16) | 5.59(10) | kHz |
| Standard Deviation | | | | |
| | 95 | 69 | 42 | kHz |
| S-reduction in representation $III^r$ | | | | |
| $A$ | 10.989563(8) | 10.972073(20) | 11.026948(12) | GHz |
| $B$ | 10.407437(8) | 10.415017(20) | 10.436380(12) | GHz |
| $C$ | 5.349225(8) | 5.328533(19) | 5.346145(11) | GHz |
| $D_J$ | 9.50(8) | 14.69(13) | 10.64(74) | kHz |
| $D_{JK}$ | −19.847(19) | −20.774(43) | −20.277(28) | kHz |
| $D_K$ | 9.036(36) | 10.11(28) | 9.61(17) | kHz |
| $d_1$ | −1.2839(44) | −1.3225(31) | −1.3573(22) | kHz |
| $d_2$ | 0.144(4) | 0.207(3) | 0.085(2) | kHz |
| Standard Deviation | | | | |
| | 95 | 67 | 39 | kHz |
| Fitted Transitions | | | | |
| | 63 | 49 | 47 | |
| Degenerate Transitions included | | | | |
| | 6 | – | – | |

## Conclusion

The combination of the new MMW-data for the GS of 1,1-DFE with all the previous MW-data [13–19, 23, 26], with data from laser-Stark- [23] and diode laser [8] spectroscopy, and with selected GS combination differences extracted from six high-resolution FT-IR bands, leads to an optimized set of rotational parameters for this molecule. For comparison with previously published sets, the present are given in both the A-reduction (Table 1 a) and the S-reduction (Table 1 b). These GS parameters are hoped to facilitate future work on the spectra of 1,1-DFE.

The use of the newly determined GS parameters together with the purely rotational data established by MW and MMW techniques on the EVS $\nu_{10} = 1$ allows a satisfactory explanation of the structure of the observed, weak FT-IR band $\nu_{10}$, and it permits the determination of the band centre $\nu_{10}^0$ with a statistical uncertainty ($\pm 2 \times 10^{-6}\ cm^{-1}$) which is considerably smaller then the 'real' uncertainty ($\sim \pm 10^{-4}\ cm^{-1}$) which arises from the wavenumber calibration of modern IR-instruments.

For the three EVSs $\nu_{12} = 1$, $\nu_6 = 1$, and $\nu_{10} = 2$, which are associated with not readily analysable bands in the vibrational spectrum of 1,1-DFE, a sufficient number of purely rotational transitions within each state could be detected in the MW and MMW range to allow the determination of the otherwise elusive rotational parameters of these states. The spectroscopic information concerning the states $v_{11} = 1$, $v_4 = 1$, and $v_9 = 1$, on the other hand, was not extensive enough to allow the determination of sextic distortion constants. Accordingly, these were held fixed to their GS values in an attempt to derive reasonably precise rotational constants and quartic distortion constants for these three states.

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