Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms



The $v_6 = 1$ and $v_6 = 2$ vibrational states of DCF₃

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ARTICLE INFO

Article history: Received 29 December 2007 In revised form 21 April 2008 Available online 1 May 2008

Keywords: Deuterated fluoroform Hot bands Overtone bands 'Lonely' levels Axial ground state constants

ABSTRACT

The high-resolution infrared spectra of DCF₃ were reinvestigated in the v_6 fundamental band region near 500 cm⁻¹ and around 1000 cm⁻¹ with the aim to assign and analyze the overtone level of the asymmetric CF₃ bending vibration $v_6 = 2$. The present paper reports on the first study of both its sublevels (A₁ and E corresponding to l = 0 and ± 2 , respectively) through the high-resolution analysis of the overtone $2v_6^{\pm 2}$ band and the hot $2v_6^{\pm 2} - v_6^{\pm 1}$ and $2v_6^0 - v_6^{\pm 1}$ bands. The well-known "loop method", applied to $v_6, 2v_6^{\pm 2} - v_6^{\pm 1}$ and $2v_6^{\pm 2} - v_6^{\pm 1}$ bands. The well-known "loop method", applied to $v_6, 2v_6^{\pm 2} - v_6^{\pm 1}$ and $2v_6^{\pm 2} - v_6^{\pm 1}$ bands. The well-known "loop method", applied to $v_6, 2v_6^{\pm 2} - v_6^{\pm 1}$ and $2v_6^{\pm 2} - v_6^{\pm 1}$ bands. The well-known "loop method", applied to $v_6, 2v_6^{\pm 2} - v_6^{\pm 1}$ and $2v_6^{\pm 2} - v_6^{\pm 1}$ bands. The well-known "loop method", applied to $v_6, 2v_6^{\pm 2} - v_6^{\pm 1}$ and $2v_6^{\pm 2} - v_6^{\pm 1}$ bands. The well-known "loop method", applied to $v_6, 2v_6^{\pm 2} - v_6^{\pm 1}$ and $2v_6^{\pm 2} - v_6^{\pm 1}$ bands. The well-known "loop method", applied to $v_6, 2v_6^{\pm 2} - v_6^{\pm 1}$ bands. The well-known "loop method", applied to $v_6, 2v_6^{\pm 2} - v_6^{\pm 1}$ bands. The well-known "loop method", applied to $v_6, 2v_6^{\pm 2} - v_6^{\pm 1}$ bands. The well-known "loop method" by the range of K = 6 to 30. In the final fitting of molecular parameters, we used the strategy of fitting all upper state data together with the ground state rotational transitions. This is equivalent to that calculating separately the C_0, D_K^0 and H_K^0 coefficients of the K-dependent part of the ground state energy terms from the combination loops. All rotational constants of the ground state up to sextic order could be refined in the calculation. This led to a very accurate determination of $C_0 = 0.18924413(25) \text{ cm}^{-1}$, $D_K^0 = 2.1789(26) \times 10^{-7} \text{ cm}^{-1}$.

In the course of analyzing simultaneously the overtone $2v_6^{\pm 2}$ band together with the $2v_6^{\pm 2} - v_6^{\pm 1}$ and v_6 bands, the original assignment of the fundamental v_6 band [Bürger et al., J. Mol. Spectrosc. 182 (1997) 34-49] was found to be incompatible with the present one. Assignments of the $(k + 1, l_6 = +1)/(k - 1, l_6 = -1)$ levels had to be interchanged, which changed the value of $C\zeta_6 = -0.14198768(26) \text{ cm}^{-1}$ and the sign of the combination of constants $C - B - C\zeta$ in the $v_6 = 1$ level to a negative value.

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1. Introduction

Much work has already been focused on the rovibrational spectroscopy of trifluoromethane (fluoroform, HCF₃, HFC-23) and of its deuterated species DCF₃. In the main isotopic species HCF₃, all fundamental levels have been investigated by high-resolution IR spectroscopy and the four lowest ones also by microwave and submillimeter wave spectroscopy ([1] and references therein). Studies of several combination and hot bands were also performed: Champion and Graner studied the $v_3 + v_6$ band [2], whereas the $2v_4$ and $v_4 + v_5 + v_6$ bands were analyzed by Pine et al. [3,4]. By analysis of the $v_6 = 2$ level, the coefficients C_0 and D_{K}^{0} of the K-dependent ground-state energy terms have been accurately determined employing the so-called "loop method". This combines transitions belonging to the fundamental, hot and overtone bands [5]. An independent determination of these constants avoids problems concerning accurate determination of C₀ which always occur when D_{κ}^{0} is constrained, usually to a value obtained from the force field.

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The axial rotational constant C_0 of DCF₃ has previously been determined by studying an avoided-crossing in a molecular beam experiment by Meerts and Ozier [6]. They constrained D_K^0 to a force field value 3.07×10^{-7} cm⁻¹. The latter value is considerably larger than that given in the most recent study of Breidung et al. [7], 2.11×10^{-7} cm⁻¹, and also that determined in a previous study by Klatt et al. [8]. It should be noted, however, that this study explored only states with K = 0 and 1, so that the influence of D_K^0 does not exceed the reported uncertainty of $C_0 = 0.1892379(33)$ cm⁻¹.

The rotational constant C_0 of DCF₃ has also been determined by Harada et al. by studying vibrationally induced rotational transitions in the $v_5 = 1$ state [9]. They determined, in addition to $C_0 = 0.1892380(28) \text{ cm}^{-1}$, also $D_K^0 = 1.47(50) \times 10^{-7} \text{ cm}^{-1}$. It is likely that a considerable correlation between these constants persists, because only two transitions with $K = 6 \leftarrow 5$ and $8 \leftarrow 7$ were studied.

It is the main purpose of the present study to remove this inconsistency of the values of the axial ground state constants C_0 and D_K^0 of DCF₃ by determining them independently, using a similar approach like in HCF₃ [5]. The present investigation moreover enlarges the sparse information on overtone and combination levels of the deuterated isotopologue of trifluoromethane since up to now only the combination band $v_2 + v_3$ of DCF₃ has been studied

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with high resolution [10]. Also the fundamental levels of DCF₃ have been studied less thoroughly than those of HCF₃. So far only results for the fundamental bands v_6 [11], v_5 [12], v_2 and v_3 [10] of DCF₃ have been published. The situation is more complicated for the v_4 band, which is in Fermi resonance with the $v_3 + v_6$ combination band. For this dyad, there is only a low-resolution study of Ruoff et al. [13] available.

It is therefore obvious that studies of the overtone level $v_6 = 2$ of DCF₃, accompanied by the analysis of the respective $2v_6 - v_6$ "combination loops" promising the determination of C_0 and D_K^0 , and the study of the v_4 and $v_3 + v_6$ bands, are crucial for the improvement of the experimental force field. This had already been pointed out by Breidung et al. [7].

In the DCF₃ molecule, the study of overtone bands is much more complicated than in HCF₃ for at least the following two reasons:

- The $2v_6$ overtone bands (band centers ~1000 cm⁻¹) fall in the same spectral region as the much stronger v_5 fundamental band (band center ~975 cm⁻¹). Therefore, the spectral features of these overtone bands on the side of the *P*-branches ($\Delta J = -1$) are almost completely hidden by *R*-branches ($\Delta J = 1$) of the v_5 band, whose outside wings reach even the *R*-branch region of the overtones. In fact, in the first attempts of assignment, only some transitions with high *K*-values in the ${}^{p}Q_{K}$ -branches of the $2v_{6}^{\pm 2}$ perpendicular band could be identified in the spectrum above 1000 cm⁻¹.
- In contrast to the case of HCF₃, the $2v_6^0$ parallel component is much weaker than the perpendicular one, and hence no safe assignment could be found for this band. In order to explore the $v_6 = 2$ level the detailed study of v_6 and of all hot bands starting from the $v_6 = 1$ level is therefore necessary.

2. Experimental details

The high-resolution FTIR spectra used in this work were all recorded in Wuppertal with a Bruker IFS 120HR interferometer. The hot bands $v_6 = 2 \leftarrow 1$ were studied from a spectrum recorded in the range 400 to 880 cm^{-1} employing a Globar source, a KBr beam splitter, and a Cu:Ge detector. This spectrum was recorded using a multipass cell, with a 9.6-m optical pathlength, at a pressure of 2.5 mbar and at room temperature. A total of 340 scans were co-added. This spectrum intended for studying weaker hot band transitions had a pressure \times pathlength product about 20 times larger than the spectrum used previously in the analysis of the fundamental v_6 band [11]. On the contrary the latter spectrum had been recorded in a cell cooled to -35 °C to reduce the hot band features. Therefore the present multipass, room temperature spectrum enabled us to extend assignments to the high-*J* ${}^{r}P_{K}(J)$, $K \leq J - 2$, and ${}^{p}P_{K}(J)$, $K \leq J$ sequences of the v_6 band.

The $2v_6$ overtone bands were mainly studied from a spectrum recorded in the range 740 to 1400 cm⁻¹, using a Globar source, a KBr beam splitter, and an MCT 800 detector. The spectrum was recorded employing a multipass cell, with a 9.6-m optical pathlength, at a pressure of 0.2 mbar and at room temperature. A total of 80 scans were co-added. A second spectrum of the $2v_6$ region was furthermore recorded for assigning the high- K^{PQ_K} branches (K = 27-39). For this latter spectrum, the recording was done using the same source, beam splitter and detector as for the former one; the same optical pathlength was chosen, but the pressure increased to 2.5 mbar, which gave rise to some additional pressure broadening of the rovibrational lines. In total 360 scans were co-added. The nominal resolution (1/MOPD, maximum optical path difference) was adjusted to 0.0024 cm⁻¹ for all the spectra used in this work.

The calibration of the spectra in the region 400–880 cm⁻¹ was based on residual CO₂ lines belonging to the v_2 band taken from Ref. [14a] in such a way that the spectrum recorded employing a multipass cell was compared with the less intense spectrum reported in [11]. In this way both spectra were made compatible with each other. The spectra in the range 850–1500 cm⁻¹ were calibrated using residual water lines in the interferometer near 1300 cm⁻¹ as given in Ref. [14a]. Wavenumber precision was better than 2×10^{-4} cm⁻¹.

The accuracy, i.e. the absolute wavenumber scale crucial for the present study, is estimated to be $5 \times 10^{-4} \text{ cm}^{-1}$ or better in the 500-cm⁻¹ region although no respective value is quoted in Ref. [14b]. The H₂O lines used to calibrate the $2\nu_6$ band system were shown to be systematically too high by $2.3 \times 10^{-4} \text{ cm}^{-1}$ at 1000 cm⁻¹ [14b]. The accuracy of these lines, after this systematic error has been corrected, is quoted to be $5 \times 10^{-4} \text{ cm}^{-1}$ [14b]. In our measurements where the sample is contained in a multipass cell, but the calibration reference gas is mostly in the interferometer between the source and the entrance of the multipass cell, the sample and the calibration standard might require a slightly different correction. Taking into account the unconsidered systematic error, the mismatch of the present wavenumber scale spans the interval of -2.7 to $+7.3 \times 10^{-4} \text{ cm}^{-1}$.

In consequence a study that combines as in the present way FTIR spectra from two different regions may reveal a slight inconsistency of their absolute wavenumber calibration. This is indeed the case for the present analysis. When assignments of transitions, which form the combination loops used in the determination of the axial ground state constants, had been established and the corresponding data were put into the global fit, we noticed indeed small but systematic residuals of their reproduction due to the mismatch of the two wavenumber scales. Therefore we applied a post-calibration to the FT spectra in the fundamental/hot band region in order to make the wavenumber scales as coherent as possible. Details of this additional calibration are described in Section 4.

3. Description of the spectra and assignments

3.1. The 500 cm^{-1} region

3.1.1. The v_6 fundamental band

Due to the small value of the combination of constants $C_6 - B_6 - C\zeta_6$, the v_6 band has an appearance of a parallel band, and this small value also explained the congested nature of the Q-branch with a sharp high wavenumber edge at 502.76 cm^{-1} [11]. The smallness of this combination also governs the structure of the *P*- and *R*-branches, which appear as clusters of lines belonging to the same value of *J*, which is again typical feature of a parallel band. A different appearance of the $\Delta K = +1$ and $\Delta K = -1$ transitions was also apparent (cf. Fig. 5 of Ref. [11]). Here the wider branches with K-structures resolved for the lowest values of I were assigned to the $\Delta K = +1$ transitions, i.e. to ^{*r*}X-branches (with X standing for P or R), while the sharp, more congested branches were assigned as $\Delta K = -1$ transitions (^{*p*}X-branches). This distinction followed from the supposed values of $C_6-B_6-C\zeta_6 \approx$ +1.3 \times 10^{-4} cm^{-1} and $(C - B)_6 - (C - B)_0 \approx -4.3 \times 10^{-4} \text{ cm}^{-1}$, which enter as a sum in the expression for wavenumbers of the ^{*p*}*R*-branches and as a difference for the ^{r}R -branches.

In addition to the congestion of the *Q*-branches, the small value of $C_6 - B_6 - C\zeta_6$ further influences the spectral patterns of such a parallel-like band. As can be seen in Fig. 1, clusters of the $\Delta K = +1$ and $\Delta K = -1$ transitions with the same K'' value appear in the spectrum very close to each other. Their assignment can be easily interchanged, unless certain diagnostic transitions are carefully checked. These are the transitions to the so-called 'lonely'



Fig. 1. Scheme of levels and associated transitions in the v_6 band. For a given value of *J*, with J = K, the transitions denoted by arrows belong to *Q*-branches ($\Delta J = 0$). The 'lonely' levels, not affected by the q_{22} *l*-type resonance, are drawn in bold. It is obvious that the level $|v_6 = 1, l_6 = -1, J, K = J$ can be reached only by the ${}^{p}P_{K=J+1}(J + 1)$ transition and has no ground state combination difference partner.

levels, i.e. levels $|v_6 = 1, l_6 = -1, J, K = J\rangle$ and $|v_6 = 1, l_6 = -1, J,$ K=I-1, which are unperturbed by the q_{22} *l*-type resonance. The levels $|v_6 = 1, l_6 = -1, J, K = J - 1\rangle$ can be reached by ${}^{p}P_{K=I}(J+1)$ or ${}^{p}Q_{K=I}(J)$ transitions, while the levels $|v_{6} = 1, l_{6} = -1, J, K = J\rangle$ are reached only by ${}^{p}P_{K=I+1}(J+1)$. In the case of the v_{6} fundamental band of DCF₃, the ${}^{p}P_{K=J}(J)$ transitions coincide in particular for lower values of J systematically with the clusters of the ${}^{r}P_{K}$ transitions. Merely the ${}^{p}P_{K}(J)$ transitions with K = J - 1 are left in the spectrum to distinguish between the $\Delta K = +1$ transitions and the $\Delta K = -1$ ones. These ${}^{p}P_{l-1}(J)$ transitions were probably overlooked in the assignment of Ref. [11]. This may have happened since there were no rotational transitions pertaining to these lonely levels included in the analysis-neither in the set of purely rotational transitions nor among the direct *l*-type resonance transitions, as can be checked in the corresponding line lists. As for the rotational data. the high-K transitions typically have low intensities and are usually not assigned. Direct *l*-type resonance transitions exist only between pairs of levels $|v_6 = 1, l_6 = -1, K - 1\rangle$ and $|v_6 = 1, l_6 = +1$, (K + 1) due to the q_{22} *l*-type resonant coupling between them. Thus the levels in question cannot appear in this type of spectra.

In such a case the interchange of assignments of $\Delta K = +1$ and $\Delta K = -1$ transitions in the IR spectrum corresponds only to an interchange of labels $|v_6 = 1, l_6 = -1, K-1\rangle \leftrightarrow |v_6 = 1, l_6 = +1$, (K+1) of rovibrational levels, accompanied by a slight change of molecular parameters. Such a reassignment, however, has a significant consequence on the sign of $C_6 - B_6 - C\zeta_6$. In Ref. [11] this sign was *positive*, which meant that the (+*l*) levels $|v_6 = 1, l_6 = +1, K + 1\rangle$ lay *above* the (-l) levels $|v_6 = 1, l_6 = -1, K - 1\rangle$. This assignment, however, turned out to be incompatible with assignments in the $v_6 = 2^{\pm 2} \leftarrow 1^{\pm 1}$ hot band, as will be described below. After the ΔK = +1 and ΔK = -1 transitions had been interchanged, putting the (+l) levels now below the (-l) ones, the value of the fitted parameter $C_6 - B_6 - C\zeta_6$ becomes negative ($\approx -1.3 \times 10^{-4} \text{ cm}^{-1}$). One small but important detail in the IR spectrum confirms the correctness of interchanging the assignments of ^{*p*}X- by ^{*r*}Xbranches, as illustrated in Fig. 2. The ${}^{p}P_{K}(12)$ branch (previously labeled as ${}^{r}P_{K}(12)$) has two additional transitions with K'' = J'' - 1 and I'' (11 and 12, respectively), which do not exist in the ${}^{r}P_{K}(12)$ branch. Indeed, the K = 11 transition is clearly visible in the upper part of Fig. 2. In general transitions with K'' = J'' - 1 remained unassigned in Ref. [11]. They fit, however, perfectly to the series of ${}^{p}P_{K=I-1}$ transitions.

The second transition K'' = J'' = 12 coincides with the sharp congested cluster of lines, which is now assigned as the ${}^{r}P_{K}(12)$ branch.

The ${}^{p}P_{K=J}(J)$ are visible only when the ${}^{r}P_{K}$ branches become more and more resolved at J > 25. An example of the clearly resolved ${}^{p}P_{52}(52)$ among the ${}^{r}P_{K}(52)$ transitions is shown in the lower part of Fig. 2.

The two series of levels $|v_6 = 1, l_6 = -1, J, K = J$ and $J - 1\rangle$ are of special importance when the assignment of the $v_6 = 2^{-2} \leftarrow 1^{-1}$ hot band is started. These levels are not affected by q_{22} *l*-type interaction and in principle can only be perturbed by an x,y-Coriolis interaction with a non-degenerate vibrational state. In the present case the nearest such level is $v_3 = 1$ at 694 cm⁻¹, almost 200 cm⁻¹ above $v_6 = 1$. For this reason the latter kind of perturbation can be neglected. Since the q_{22} *l*-type interaction has a resonance character for all other levels of the $v_6 = 1$ vibrational state, these two special transitions appear displaced from their regular position within the clusters of *P*-branches. Assignments of these two special series, however, cannot be checked by ground state combination differences: while the series of ${}^{p}P_{K=I}(J)$ transitions has no counterpart for combination difference checking at all, the second series ${}^{p}P_{K=I-1}(J)$ could be checked in principle against the ${}^{p}Q_{K=I-1}(J-1)$ transition. But this turned out to be impossible due to the strong congestion of the *Q*-branch region of the v_6 band. Furthermore, most importantly transitions of the ${}^{p}P_{K=I}(I)$ and ${}^{p}P_{K=I-1}(I)$ series could not be predicted with the constants from Ref. [11].

The necessity to permute assignments between the +l/-l sublevels of the $v_6 = 1$ vibrational state follows also from the analysis of the combination loops which were used to determine the present axial ground state constants, as described in detail in Section 4.

A set of more than 2000 non-zero weighted reassigned experimental wavenumbers were finally used to least-squares fit the constants of the $v_6 = 1$ vibrational state.

3.1.2. Hot bands in the v_6 region

3.1.2.1. The $2v_6^{\pm 2} - v_6^{\pm 1}$ band. This band, centered at 503.435 cm⁻¹, has at room temperature a relative intensity of 0.18 with respect to the v_6 cold band (Boltzmann factor = 0.090, degeneracy factor = 2). Intensity enhancement due to nuclear spin of identical nuclei¹ occurs for subbands with $K\Delta K = 3p + 1$, $p = 0, \pm 1, \pm 2, ...$ The appearance of the hot band resembles that of the v_6 fundamental, with *J*-clusters of *K*-lines, $0 \le K \le J$. Contrary to the *J*-clusters of ^{*p*}P_K lines of the v₆ band, which are degraded towards low wavenumbers, those of the hot band are degraded towards high wavenumbers (Fig. 3(a)). The $J \le 24$ clusters form band heads, with the ^{*p*}P_{*J*-1}(*J*) lines isolated on the high wavenumbers side and the ^{*p*}P_{*J*}(*J*) at lower wavenumbers. The $\Delta K = +1$ *J*-clusters ^{*r*}R_K(*J*), $0 \le K \le J$, are spread and degraded towards low wavenumbers (Fig. 3(b)).

Assignments span $-26 \le K'' \cdot \Delta K \le 25$ and yield 424 non-zero weighted transitions which were finally used in the least-squares calculation.

3.1.2.2. The $2v_6^0 - v_6^{\pm 1}$ hot band. This band, centered at 502.038 cm⁻¹, has at room temperature a relative intensity of 0.09 with respect to the v_6 cold band (Boltzmann factor = 0.090, degeneracy factor = 1). Intensity enhancement due to nuclear spin occurs for subbands with $K\Delta K = 3p + 2$, p = 0, ± 1 , ± 2 , ... The ${}^{p}P_{K}(J)$, $1 \leq K \leq J$ clusters of this hot band are all rather spread and degraded towards low wavenumbers (Fig. 3(a)). The same structure occurs for the ${}^{p}R_{K}(J)$, $1 \leq K \leq J$ clusters. The ${}^{r}P_{K}(J)$, $K \leq J-2$ clusters,

¹ The spin of identical ¹⁹F nuclei being $I_F = 1/2$, it follows that the spin statistical weights ratio is 4:4:4 for the A_1 , A_2 , and E rovibrational levels. When the A_1-A_2 splitting is not resolved, this ratio becomes 8:4 for the A and E levels. This means intensity enhancement roughly by a factor of two for the transitions reaching A levels (i.e. rovibrational levels having k - l = 3p, p integer). The characteristic intensity pattern which follows is helpful for identifying and assigning the hot band under examination.



Fig. 2. (a) Detail of the infrared spectrum of DCF₃ showing the unresolved ${}^{P}P_{K}(12)$ and the more spread, *K*-resolved ${}^{P}P_{K}(12)$ clusters of the v_{6} fundamental band. Some *K*-assignments are indicated. (b) Detail of the infrared spectrum of DCF₃ in the region of the ${}^{P}P_{K}(52)$ cluster of the v_{6} fundamental band. Some *K*-assignments are indicated; the ${}^{P}P_{51}(52)$ and ${}^{P}P_{52}(52)$ transitions of the same band are also indicated. Pressure 2.5 mbar; pathlength 9.6 m; room temperature.

degraded towards high wavenumbers, are progressively resolved with increasing J (Fig. 3(a)).

Assignments were possible for $-22 \le K'' \times \Delta K \le 14$; altogether, 177 non-zero weighted transitions were used in the final fit.

3.1.2.3. Perturbation-allowed transitions. After assignment of the main features belonging to the $2v_6^{\pm 2} - v_6^{\pm 1}$ and the $2v_6^0 - v_6^{\pm 1}$ hot bands, the spectrum in the 500-cm⁻¹ region still revealed rather intense and regular, not yet assigned patterns. Their closer inspection showed that they can be assigned to $\Delta K = \pm 3$ perturbation-allowed transitions. Their appearance is again due to the accidentally small $C_6 - B_6 - C\zeta_6$ value in the $v_6 = 1$ level. This causes a strong wavefunction mixing between the level pairs $|v_6 = 1, l_6 = -1, J, K-1\rangle$ and $|v_6 = 1, l_6 = +1, J, K+1\rangle$, leading to almost the same inten-

sity of the ΔK = ± 3 perturbation-allowed and of the normally allowed transitions (Fig. 3 (a) and (b)). With the help of the new Loomis–Wood for Windows (LWW) program [15], which uses generalized lower state combination differences and which allows to handle levels with different values of *K*, finally 30 ${}^{t}R_{K}(J)$ and 95 ${}^{n}P_{K}(J)$ perturbation-allowed transitions were assigned and included in the fit.

3.2. The $1000-cm^{-1}$ region

3.2.1. The $2v_6^{\pm 2}$ band

The overtone spectra of CDF₃ are quite different from those observed for the normal isotopologue, for which the $2v_6^6$ parallel component is more intense than the $2v_6^{\pm 2}$ perpendicular one [5]. In the



Fig. 3. (a) Detail of the infrared spectrum of DCF₃ in the region of the ${}^{p}P_{K}(17)$ cluster of the $2v_{6}^{-2} - v_{6}^{-1}$ hot band. The labels are *K*-assignments, indicated also for transitions of the ${}^{p}P_{K}(13)$ branch of the $2v_{6}^{-2} - v_{6}^{-1}$ hot band (\blacklozenge) and the perturbation-allowed branch ${}^{n}P_{K}(17)$ of the $2v_{6}^{-2} - v_{6}^{-1}$ hot band (\bigstar). (b) Detail of the infrared spectrum of DCF₃ in the region of the ${}^{r}R_{K}(10)$ cluster of the $2v_{6}^{-2} - v_{6}^{-1}$ hot band. (\bigstar) and the perturbation-allowed branch ${}^{n}P_{K}(17)$ of the $2v_{6}^{-2} - v_{6}^{-1}$ hot band (\bigstar) branch of the $2v_{6}^{-2} - v_{6}^{-1}$ hot band. The labels are *K*-assignments, indicated also for transitions of the ${}^{p}R_{K}(14)$ branch of the $2v_{6}^{-2} - v_{6}^{-1}$ hot band (\bigstar) and the perturbation-allowed branch ${}^{t}R_{K}(10)$ of the $2v_{6}^{-2} - v_{6}^{-1}$ hot band (\bigstar). Experimental conditions as those for Fig. 1.

present case, the $2v_6^0$ parallel band is so weak that it is invisible in any of the available spectra. Though the $2v_6^{\pm 2}$ perpendicular component, centered at 1006.06 cm⁻¹, has much higher intensity than $2v_6^0$, it is very difficult to identify and assign: it falls into a very congested spectral region being almost completely hidden by the much stronger v_5 band. We were nevertheless able to assign some clear patterns of the ${}^{p}Q_{K}$ branches (9 $\leq K \leq$ 39), although they were overlapped by stronger ^{*p*}R clusters of lines belonging to the v_5 band (see Fig. 4). These Q branches degrade towards high wavenumbers. They are all spread and well resolved into J-lines, which makes their assignments unambiguous. Some ${}^{p}P_{K}$ series (with $30 \le K \le 36$) were then found by means of GSCD. With the help of a preliminary least-squares fit of the already assigned transitions belonging to the $2v_6^{\pm 2} - v_6^{\pm 1}$, $2v_6^0 - v_6^{\pm 1}$ and $2v_6^{\pm 2}$ bands, we were able to predict and identify in the spectrum the ${}^{p}P_{K}$ series, as well as some ${}^{r}R_{K}$ series for $0 \leq K \leq 27$.

A set of 433 non-zero weighted transitions of the $2v_6^{\pm 2}$ band were used in the final least-squares calculations.

4. Results and discussion

The effective vibration–rotation Hamiltonian used in the present analysis is essentially the same as in the previous study of the HCF₃ species [1]. The matrix elements employed in the present work are summarized in Appendix A. In the least-squares fit the experimental data were given weights proportional to the inverse square of their estimated experimental uncertainties. Supplementary material with a list of the data and their reproduction is available online from the Journal of Molecular Spectroscopy Supplementary material Archives, http://msa.lib.ohio-state.edu/ jmsa_hp.htm, and also upon request from the corresponding author. The range of *J/K* values of the data, estimated experimental uncertainties and standard deviations of reproduction are summarized in Table 1.

For the vibrational ground state, we have refined all parameters up to sextic centrifugal distortion constants by fitting rotational data from Ref. [16], together with the A_1 - A_2 splittings from Ref.



Fig. 4. The ${}^{p}Q_{29}$, ${}^{p}Q_{30}$ and ${}^{p}Q_{31}$ branches of the $2\nu_{6}^{\pm 2}$ overtone band, with some *J*-assignments indicated. Some *K*|*J* assignments of ${}^{p}R_{\kappa}(J)$ transitions belonging to the ν_{5} band are also indicated. Pressure 0.2 mbar; pathlength 9.6 m; room temperature.

[17]. The sign of the splitting constant h_3^0 , which cannot be determined from the ground state splittings only, follows from the detailed discussion of the A_1 - A_2 splittings in the excited level $v_5 = 1$ [12]. The J-dependent expansion term h_3^J of this splitting was constrained to the original value from Ref. [16] because of the large statistical uncertainty.

Eventually, all ground state data were fitted together with the combination loops and the whole set of data for the $v_6 = 1$ and 2 levels. We believe that this approach of fitting the ground state constants within a global fit is justified by its excellent consistency with the conventionally done separate fit of the ground state constants. The 'non-axial' constants obtained in the global fit agree within $1-\sigma$ intervals with those of the ground state rotational data from Ref. [16] fitted alone as well as with previous analyses. The standard deviation of reproduction of the microwave data increased only marginally within the estimated experimental uncertainty of 30 kHz, from 9.9 to 14.9 kHz in the global fit and the reproduction of submillimeter wave data from 342 to 360 kHz

Table 1

Summary	v of ex	perimental	data for	the	vibrational	ground	state and	the ve	= 1 and 3	2 levels of D	CF ₂
Summun	y or ch	permitticitui	uutu 101	ci i c	vibiutionui	Siound	state and	a the vb	i unu i		<u> </u>

summary of experimental data for the vibrational ground state and the $v_6 = 1$ and 2 levels of DCF ₃							
	Range of J/K	No. of data ^a	Estimated accuracy ^b	Standard deviation ^b			
v ₆ IR	65/65	2068/2011	2	1.4			
$2v_6^{\pm 2} - v_6^{\pm 1}$ IR	44/26	427/424	2	2.0			
$2v_{6}^{\pm 2} - v_{6}^{\pm 1}$ IR PA ^c	44/34	125/125	2	1.5			
$2v_6^0 - v_6^{\pm 1}$ IR	26/22	179/177	2	2.1			
$2v_6^{\pm 2}$ IR	46/39	443/433	5	2.7			
v = 0 combination loops	37/30	118/118	3 – 7	3.3			
$v_6 = 1 \text{ MMW}$	22/19	134/134	30	20.5			
$v_6 = 1$ direct <i>l</i> -type	24-28/2,4	10/10	30	13.4			
$v_6 = 1$ <i>l</i> -type resonance	35/35	419/419	0.2 – 8	0.32			
v = 0 MW	13/13	36/36	30	14.9			
v = 0 MMW	64/58	302/295	500	360			

Ranges of rotational quantum numbers, accuracies, and standard deviations of reproduction are quoted.

Total number of data/number of data with nonzero weights.

 $^{\rm b}\,$ In units of $10^{-4}\,\text{cm}^{-1}$ for IR data and kHz for MMW data.

^c Perturbation-allowed transitions (see text).

Table 2Molecular parameters of DCF3 (in cm^{-1}) in the vibrational ground state

Parameter	This work	Previous works ^b	
	Global fit	Separate fit ^a	
$B \\ C \\ D_J \times 10^7 \\ D_{JK} \times 10^7 \\ D_K \times 10^7 \\ H_J \times 10^{12} \\ H_{JK} \times 10^{12} \\ H_{KJ} \times 10^{12}$	0.330 933 109 1 (68)	0.330 933 121 1 (105)	0.330 933 114 7 (40)
	0.189 244 13 (25)	0.189 244 1 (10)	0.189 237 9 (33) ^c
	3.198 603 (73)	3.198 290 (136)	3.198 299 (80)
	-4.892 65 (35)	-4.891 81 (79)	-4.891 78 (37)
	2.178 9 (26)	2.170 (11)	2.11 ^d
	0.474 5 (12)	0.469 2 (23)	0.469 2 (14)
	-2.006 5 (58)	-2.003 8 (116)	-2.000 4 (57)
	2.599 4 (98)	2.626 3 (154)	2.622 8 (97)
$H_K imes 10^{12} h_3^{ imes} 10^{14} h_3^J imes 10^{19}$	-1.049 6 (75)	-1.094 ^d	-1.094 ^d
	-7.493 9 (11)	-7.493 9 (19)	-7.496 (17)
	4.77 ^e	4.77 ^e	4.77 (67)

Numbers in parentheses are standard deviations in units of the last digit quoted. ^a Non-axial constants determined in a separate fit of v = 0 rotational data from

^b Constants from Ref. [16]

^c Ref. [6].

^d Ref. [7].

^e Constrained to value from Ref. [16].

with respect to the estimated uncertainty of 500 kHz. Also the axial constants from the global fit agree perfectly with those from a separate fit of combination loop data, as shown in Table 2. In the latter fit, the value of H_{κ}^{0} could not be determined, because its contribution to energies within the range of K of this type of data was still smaller than the experimental accuracy. Therefore we constrained its value in the separate fit to the ab initio prediction -1.094×10^{-12} cm⁻¹ [7]. In the global fit, on the contrary, we were able to determine H^0_{κ} with a low statistical uncertainty of about 1% and in remarkable agreement with the ab initio prediction. The improved statistical errors of axial constants in the global fit are a result of having the data pertaining to the $v_6 = 1$ vibrational level included, which was necessary for analyzing data from hot bands $v_6 = 2 \leftarrow 1$. The $v_6 = 1$ vibrational level has a special character with the already mentioned accidental smallness of $|C_6 - B_6 - C\zeta_6|$, which allowed measurements of several hundred *l*-resonance transitions by extremely accurate Fourier-transform microwave spectroscopy [11]. Their inclusion makes the combination of constants $C_6 - B_6 - C\zeta_6$ determined directly and with high accuracy. This contributes significantly to an accurate determination of all axial constants in the $v_6 = 1$ state and consequently also in the ground state. It should be also noted that inclusion of the $v_6 = 1$ state data into the global fit does not lead to any significant change of its parameters from values determined in its separate fit.

The reassignment in the v_6 band, described in the previous section, had a substantial effect on the value of $\zeta\zeta_6$, which changed by about +7.9 MHz. In consequence the sign of the combination of constants $C_6 - B_6 - C\zeta_6$ became negative. We noted that in the present fit no τ constants (higher order terms of the *z*-Coriolis interaction) were required because they did not improve the fit and were only poorly determined, which is a sign of better convergence of the effective Hamiltonian.

The operator of the q_{22} *l*-type resonance has been taken in the same form as in Ref. [11] and led to very similar values of the parameters. The absolute sign of the leading term (and consequently of all expansion terms) cannot be determined directly due to the unresolved ${}^{r}Q_{0}$ branch, but can be established by simulation of the spectrum in the region of the *Q*-branches. The simulation with $q_{22}^{6} < 0$ and $q_{22}^{6J} > 0$ (Fig. 5, trace (b)) is in perfect agreement with the experimentally observed pattern (Fig. 5, trace (a)). When both signs are changed, the *Q* branches adopt an entirely different shape, with the ${}^{p}Q$ ($\Delta K = -1$) lines dominating (Fig. 5, trace (c)). The intensity perturbation is thus of the same kind as that already observed for HCF₃ [1].

In the least-squares fit we used the same set of purely rotational and direct *l*-type resonance data as in Ref. [11]. The vibration-rotation data were completely reassigned, with the range of transitions considerably extended. Now almost twice as many transitions as before could be used thanks to the longer pathlength spectrum recorded at higher temperature. With 23 upper state parameters refined we achieved a quantitative reproduction of all data pertaining to the $v_6 = 1$ level. The final values of the excited state parameters are presented in Table 3. We used the effective vibration-rotation Hamiltonian in the two reductions Q and D, corresponding to the sets of constants denoted A and B in [11]. The constants of the present study led to excellent consistency of the relations proving unitary equivalence, as shown in Table 4.

In addition to this, the significant change of $C\zeta_6$ due to the interchanged assignments in the v_6 band, has important influence on parameters whose values depend of the reduction of the Hamiltonian. These are the two expansion terms (η_J and η_K) of the diagonal *z*-Coriolis term $C\zeta_t$, the (2, -1) *l*-resonance constant q_{12} , and the parameter d_t of the *l*-dependent $\Delta K = \pm 3$ matrix elements. In Table 10 of Ref. [7], the computed and experimental parameters for the Q ($q_{12} = 0$) and D ($d_t = 0$) reductions for both the HCF₃ and DCF₃ isotopologues were compared. The authors pointed out that the agreement was excellent for HCF₃, thus confirming the accuracy of the cubic force field and indicating that the $v_6 = 1$ state of this molecule is well isolated.

However, the agreement was significantly worse for the $v_6 = 1$ state of DCF₃, with the discrepancies between experimental and *ab initio* values reaching 60% for the η_I and η_K parameters. The authors of Ref. [7] explained this by the inaccuracy of D_{κ}^{0} , to which η_K is fully correlated. However, even after a new fit of the $v_6 = 1$ data with an improved *ab initio* D^0_{κ} value was performed, the discrepancy between experimental and *ab initio* values for η_I and η_K did not disappear. A parameter to which η_K is highly correlated and which was considered to be accurate in Ref. [7] is $F = C_6 - B_6 + 2C\zeta_6$. A careful inspection shows that its value changes from -0.426625 cm⁻¹ in Ref. [7] to -0.426093 cm⁻¹ in the present work. This change of about 5.3×10^{-4} cm⁻¹ alters significantly the values of η_I and η_K . Table 5 proves that now the agreement between experimental and ab initio values of the reduction-dependent parameters for the $v_6 = 1$ state of DCF₃ becomes excellent (within less than 3%). This confirms both the reliability of the ab initio results and the correctness of the present analysis of the experimental spectra.

For the $v_6 = 2$ level the effective Hamiltonian used was truncated to lower order terms because we analyzed only vibrationrotation data with values of *J* and *K* lower than in the $v_6 = 1$ level. The quartic centrifugal distortion constants are remarkably consistent with those of the ground and $v_6 = 1$ states. The sextic centrifugal distortion constants were dynamically constrained to the fitted ground state values, allowing them to depart from these only by less than their statistical errors. Inclusion of these constants was necessary to obtain a good reproduction of the data, although they could not be freely refined in the fitting because this led to large indeterminacies. The q_{22} *l*-type interaction does not have a resonant character in the $v_6 = 2$ state and therefore higher-order expansion terms could be neglected.

The present rovibrational analysis of the $v_6 = 2$ state revealed that the assignment of the early microwave measurements [18] assumed an incorrect relation of rotational constants, i.e. B(l = 0) < B(l = 2). As the *K* structure was not resolved in these spectra, we did not include the data in the fits. The present analysis is therefore a motivation for a detailed rotational study not only of $v_6 = 2$, but also of neighbor levels. The latter comprise $v_4 = 1$ and $v_3 = v_6 = 1$ (at about 1215 and 1193 cm⁻¹, respectively) which together with the $v_2 = 1$ (at 1111 cm⁻¹) and the $v_5 = 1$ (at 975 cm⁻¹) levels form a polyad with complex interactions.

Ref. [16], axial constants in a separate fit of $\Delta K = \pm 3$ combination differences.



Fig. 5. The Q-branch region of the v_6 band of DCF₃. (a) Experimental spectrum: pathlength 235 mm; pressure 6 mbar; $-35 \,^{\circ}$ C. (b) Simulated spectrum, with the parameters given in Table 4. (c) Simulated spectrum, with opposite sign of the l(2,2) resonance parameters (see text).

Although the separations of levels are large enough to justify their independent analysis (obviously except $v_4 = 1$ and $v_3 = v_6 = 1$), there still remain several peculiar anomalies which would recommend a global approach. Such an approach requiring an inclusion of accurate rotational data would represent a stringent test of the correct treatment of the so far neglected interactions.

While the analysis of the A_1 sublevel of $v_6 = 2$ was based only on hot band transitions $v_6 = 2^0 \leftarrow 1^{\pm 1}$, for the $v_6 = 2^{\pm 2}$ (*E*) sublevel we used both hot and overtone band transitions. The spectra pertaining to the $v_6 = 2^{\pm 2}$ sublevel were important for the determination of the axial ground state constants. We began the analysis by using the loop method [5], which provides the intervals of levels $\Delta = E_0(K,J) - E_0(K - 3J)$ by combining a fundamental, a hot and an overtone band transitions (see Fig. 6). It should be mentioned here that the combination loop method needs always at least one *Q*-branch ($\Delta J = 0$) transition, but these were not available from the spectrum, because of the congested *Q*-branch region. Therefore the necessary wavenumbers of transitions ${}^rQ_K(J + 1)$ and ${}^pQ_K(J - 1)$ were calculated from wavenumbers of the ${}^rR_K(J)$ and ${}^pP_K(J)$ transitions and the corresponding ground state combination differences. The latter had been known with sufficient accuracy even before the axial ground state constants were refined, because they correspond to the purely *J*-dependent part of the ground state energy level ladder as determined from ground state rotational spectra.

The differences $\Delta = E_0(K,J) - E_0(K-3J)$ can be written as the sum of two terms, one of which depends only on K and contains C_0 , D_{κ}^0 and H_{κ}^0 . When this was done with the original assignments of the intermediate level $v_6 = 1$ [11], the *K*-dependent term was not constant for a given K value, as would be expected, but contained a residual dependence on J. This discrepancy initiated the search for alternate assignments of the $v_6 = 1$ levels. When this inconsistency was removed, we were still left with small but systematic differences of opposite signs between the two types of combination loops RRP and PPR (cf. Fig. 6). This inconsistency of combination loops indicated a calibration mismatch between the FT spectra from two different regions based upon different calibration standards. When fitting the constants of the $v_6 = 2^{\pm 2}$ level only from hot band transitions while calculating residuals of transitions belonging to the overtone band with given zero weights, the above assumption was found to be confirmed. Therefore a post-calibration of one of the spectral regions is needed-either decreasing the wavenumbers in the overtone region by approximately

Table 3 Molecular parameters of DCF₃ (in cm⁻¹) in the vibrational level $v_6 = 1$

Parameter	Reduction D	Reduction Q
Е	502.623 729 5 (80)	502.623 729 4 (80)
В	0.330 999 162 5 (60)	0.330 999 180 4 (60)
С	0.188 881 73 (25)	0.188 881 71 (25)
$D_J \times 10^7$	3.217 883 0 (838)	3.217 881 5 (836)
$D_{JK} imes 10^7$	-4.946 840 (234)	-4.946 826 (234)
$D_K imes 10^7$	2.211 75 (262)	2.211 84 (261)
$H_J imes 10^{12}$	0.487 08 (210)	0.487 11 (209)
$H_{JK} imes 10^{12}$	-2.058 0 (90)	-2.058 3 (90)
$H_{KJ} \times 10^{12}$	2.648 9 (180)	2.649 9 (180)
$H_K imes 10^{12}$	-1.063 4 (97)	-1.063 8 (97)
Cζ	-0.141 987 684 (256)	$-0.141 \ 987 \ 663 \ (255)$
$\eta_J imes 10^6$	-1.223 016 0 (833)	-1.187 273 6 (833)
$\eta_K imes 10^6$	1.113 73 (105)	1.078 03 (105)
$q_{22}^{\times}10^4$	-2.655 746 028 (57)	-2.655 746 143 (57)
$q_{22}^J imes 10^9$	1.162 510 9 (255)	1.173 647 3 (257)
$q_{22}^{\scriptscriptstyle K} imes 10^9$	-0.972 496 5 (486)	-0.978 049 7 (485)
$q_{22}^{IJ} imes 10^{15}$	-3.966 (28)	-3.905 (28)
$q_{22}^{J\!K} imes 10^{15}$	9.650 (58)	9.624 (58)
$q_{22}^{KK} imes 10^{15}$	-9.567 (48)	-9.568 (48)
$q_{12}^{\times}10^5$	4.362 607 (299)	0.0 ^a
$d_t^{\times} 10^7$	0.0 ^a	-1.088 378 (75)
$f_{42}^{\times}10^{10}$	-5.191 774 (334)	-5.080 446 (333)
$f_{42}^J imes 10^{15}$	2.078 1 (760)	2.148 0 (758)
$h_3^{\times} 10^{14}$	-7.329 7 (311)	-7.331 1 (311)
$h_3^J imes 10^{19}$	4.77 ^a	4.77 ^a

Numbers in parentheses are standard deviations in units of the last digit quoted. ^a Constrained to value from Ref. [16].

Table 4

Demonstration of unitary equivalence between parameters of the Q and D reductions in the vibrational level $v_6 = 1$

Expression	Unit	Verification
$-2q_{12}^D/F$	10 ⁻⁴	2.04773 (14)
$\frac{1}{2}d_t^Q/q_{22}$	10 ⁻⁴	2.04910 (14)
$(\eta_I^D - \eta_I^Q)$	10^{-8} cm^{-1}	-3.5742 (118)
$-(\eta_K^D - \eta_K^Q)$	10^{-8} cm^{-1}	-3.5703 (1484)
$\frac{8(q_{12}^D)^2}{F}$	10^{-8} cm^{-1}	-3.5734 (5)
$\frac{(d_t^Q)^2 F}{2(q_{22})^2}$	10^{-8} cm^{-1}	-3.5782 (5)
$(q_{22}^{I,D} - q_{22}^{I,Q})$	10^{-11} cm^{-1}	-1.1136 (36)
$-2(q_{22}^{K,D}-q_{22}^{K,Q})$	10^{-11} cm^{-1}	-1.1106 (137)
$(f_{42}^D - f_{42}^Q)$	10^{-11} cm^{-1}	-1.1133 (47)
$\left(\frac{2q_{12}^{D}}{F}\right)^{2}q_{22}$	10^{-11} cm^{-1}	-1.1136 (2)

 $F = C - B + 2C\zeta$. Numbers in parentheses are standard deviations in units of the last digit quoted.

Table 5		
Reduction-dependent parameters (in kHz) for the $v_{e} = 1$ s	state of DCF ₂ a	and

 $6 \times 10^{-4} \text{ cm}^{-1}$ or increasing the wavenumbers in the fundamental and hot bands region by approximately $3 \times 10^{-4} \text{ cm}^{-1}$. Since the accuracy of the calibration standard used in the region around 500 cm^{-1} is not quoted [14b] and the needed correction smaller than that in the 1000 cm^{-1} region, we decided to apply the postcalibration to the spectra from the region around 500 cm^{-1} . With this correction, we repeated the final fits as described above in the discussion of fitting the ground state constants. The resulting final constants for both sublevels of $v_6 = 2$ are given in Table 6.

The vibrational parameters ω_6 , x_{66} and g_{66} were derived from the experimental vibrational energies of $v_6 = 1$, ($v_6 = 2$, l = 0) and ($v_6 = 2$, $l = \pm 2$), by using the following relations:

$$\begin{aligned} &(v_6)_0 = \omega_6 + x_{66} + g_{66} \\ &(2v_6^0)_0 = 2\omega_6 + 4x_{66} \\ &(2v_6^{\pm 2})_0 = 2\omega_6 + 4x_{66} + 4g_{66} \end{aligned}$$

The experimental results and the corresponding theoretical values are given in Table 7.

An accurate determination of the rotational constants *B* and *C* in several subsequent degenerate vibrational states also provides the constants describing their vibrational dependence. This can be expressed as

$$X_{\nu} = X_{0} - \alpha_{\nu}^{X} \nu + \gamma_{II}^{X} l^{2}, X = B, C.$$
(2)

The respective values are also included in Table 7.

5. Conclusions

The present study reports on the first high-resolution study of the $(v_6 = 2, l = 0/l = \pm 2)$ levels of DCF₃, through the analysis of the $2v_6^{\pm 2} - v_6^{\pm 1}, 2v_6^0 - v_6^{\pm 1}$ and $2v_6^{\pm 2}$ bands. Hot perturbation-allowed transitions, enhanced by wavefunction mixing of lower levels, were also observed and reported in the present work. To our knowledge, identification of such hot transitions has never been reported before.

The simultaneous analysis of transitions to the $v_6 = 2^{\pm 2}$ level together with those of the fundamental band $v_6 = 1^{\pm 1} \leftarrow 0$, whose assignments had to be corrected, provided an accurate and independent determination of the axial ground state constants C_0, D_K^0 , and H_K^0 . Moreover, we showed that the "loop method" is a powerful tool not only for the determination of C_0, D_K^0 and H_K^0 , but also for checking the ΔK assignments in a v_t perpendicular band, when $(C_t - B_t - C\zeta_t)$ is very small. A corresponding check has still to be done for other similar molecules, e.g. PF₃, NF₃, etc.

In the present study the reproduction of all experimental data is quantitative and the resulting molecular parameters are more accurate than those obtained in previous studies.

Parameter	DCF ₃				HCF ₃	HCF ₃		
	Calc. Breidung et al. ^a	Exp. This work	ExpCalc. (%) This work	Exp. Bürger et al. ^b	ExpCalc. (%) Bürger <i>et al</i> .	Calc. Breidung et al.	Exp. Ceausu <i>et al.</i> c	ExpCalc. (%) Ceausu <i>et al</i> .
η_{I}^{Q}	-35.172	-35.594	1.2	-23.754	48.1	-38.104	-38.393	0.8
ή ^Q κ	31.818	32.319	1.6	19.890	60.0	35.021	35.797	2.2
d ^Q	-3.168	-3.263	2.9	-3.262	2.9	-2.505	-2.570	2.6
η_1^D	-36.212	-36.665	1.2	-24.827	45.9	-38.649	-38.947	0.8
η_K^D	32.857	33.389	1.6	20.963	56.7	35.566	36.351	2.2
q_{12}^{D}	1293	1308	1.2	1310	1.3	972	1088	10.7
$\eta_J + \eta_K^{\mathbf{d}}$	-3.354	-3.276	2.4	-3.864	15.2	-3.084	-2.595	15.8

HCF₂

^a Ref. [7].

^b Ref. [11].

^c Ref. [5].

^d Reduction-independent.





Fig. 6. Schematic diagrams showing possible combinations of transitions in the v_{6} . $2v_{6}^{\pm 2} - v_{6}^{\pm 1}$ (both allowed and perturbation-allowed, the latter in dashed lines), and $2v_{6}^{\pm 2}$ bands, giving the energy difference Δ between two ground state levels *K* and K - 3.

Table 6

Molecular parameters (in cm⁻¹) of DCF₃ in the vibrational level $v_6 = 2$

Parameter	$v_6 = 2^0$	$v_6 = 2^{\pm 2}$
Е	1004.059 819 (67)	1006.060 338 (17)
В	0.331 094 40 (39)	0.331 062 795 (76
С	0.188 523 00 (66)	0.188 546 65 (29)
$D_I \times 10^7$	3.244 9 (54)	3.237 56 (69)
$D_{IK} \times 10^7$	-5.023 (17)	-5.017 2 (19)
$D_K imes 10^7$	2.391 (18)	2.237 4 (33)
$H_{J} \times 10^{12}$	0.474 5 (12) ^a	0.474 5 (12) ^a
$H_{JK} \times 10^{12}$	$-2.006 \ 5 \ (58)^{a}$	-2.006 5 (58) ^a
$H_{KI} \times 10^{12}$	2.599 4 (98) ^a	2.599 4 (98) ^a
$H_{K} \times 10^{12}$	$-1.049 6 (75)^{a}$	$-1.049 \ 6 \ (75)^{a}$
Cζ		-0.141 371 79 (26)
$\eta_J imes 10^6$		-1.149 4 (13)
$\eta_K imes 10^6$		0.882 4 (19)
$q_{22}^{\times}10^4$	-2.	623 63 (32)

Numbers in parentheses are standard deviations in units of the last digit quoted.

^a Constrained dynamically to ground state values.

Table 7

Comparison of some parameters $^{\rm a}$ (in $\rm cm^{-1})$ determined from experiment and force field

	This work	Ab initio
ω ₆	502.217 29	507.3 ^b
x ₆₆	-0.094	0.0 ^b
Z 66	0.500	0.5 ^b
ζ6	-0.750 3	-0.7558
$lpha_6^B imes 10^4$	-0.80	-0.701 ^c
$\gamma_{66}^{B} \times 10^{6}$	-7.9	_
$\alpha_6^C \times 10^4$	3.61	3.53 ^c
$\gamma_{66}^{\breve{C}} imes 10^{6}$	5.9	-

^a All parameters are in cm⁻¹ units, except ζ_6 , which is dimensionless.

^b Ref. [8]. ^c Ref. [7].

Acknowledgments

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Projects IAA400400706 and 1ET400400410) and the Ministry of Education, Youth and Sports of the Czech Republic (Research Program LC06071). H.B. wishes to thank Marion Litz for valuable help.

Appendix A. Definition of matrix elements of the effective vibration-rotation Hamiltonian

The diagonal matrix elements up to sixth order were taken as

$$\begin{split} E^{0}_{\nu r}(J,k,l) &= E_{\nu} + B_{\nu}J(J+1) + (C_{\nu} - B_{\nu})k^{2} - D^{\nu}_{J}J^{2}(J+1)^{2} - D^{\nu}_{JK}J(J+1)k^{2} \\ &- D^{\nu}_{K}k^{4} + H^{\nu}_{J}J^{3}(J+1)^{3} + H^{\nu}_{JK}J^{2}(J+1)^{2}k^{2} + H^{\nu}_{KJ}J(J+1)k^{4} \\ &+ H^{\nu}_{K}k^{6} + [-2C\zeta_{\nu} + \eta^{\nu}_{J}J(J+1) + \eta^{\nu}_{K}k^{2}]kl \end{split} \tag{A1}$$

For the $v_6 = 1$ vibrational level the following *l*-type operators were taken into account

$$\begin{split} \langle v_t^{l\pm 2}; J, k \pm 2 \mid (\mathbf{H}_{22} + \mathbf{H}_{24} + \mathbf{H}_{26}) / hc \mid v_t^l; J, k \rangle \\ &= [(v_t \mp l_t)(v_t \pm l_t + 2)]^{1/2} \Big\{ q_{22} + f_{22}^J J (J+1) + f_{22}^K [k^2 + (k \pm 2)^2] + f_{22}^{JJ} J^2 (J+1)^2 + f_{22}^{JK} J (J+1) [k^2 + (k \pm 2)^2] \\ &+ f_{22}^{KK} [k^4 + (k \pm 2)^4] \Big\} F_2^{\pm} (J, k) \end{split}$$
(A2)

$$\langle \mathbf{v}_{t}^{l_{t}\pm2}; \mathbf{J}, \mathbf{k} \mp 1 \mid \mathbf{H}_{22}/hc \mid \mathbf{v}_{t}^{l}; \mathbf{J}, \mathbf{k} \rangle$$

= $[(\mathbf{v}_{t} \mp l_{t})(\mathbf{v}_{t} \pm l_{t} + 2)]^{1/2} q_{12}(2\mathbf{k} \mp 1)F_{1}^{\mp}(\mathbf{J}, \mathbf{k})$ (A3)

Due to the accidental smallness of $C_6 - B_6 - C\zeta_6$, which is the denominator of the q_{22} *l*-type resonance terms, matrix elements had to be considered up to \mathbf{H}_{26} for these terms, including the *k*-dependent ones, to achieve a quantitative reproduction of experimental data. On the contrary, this was not necessary for the $v_6 = 2$ level where the leading term q_{22} was sufficient. For this level the other two *l*-type interactions (A3-A4) were unnecessary as well.

In the *Q* reduction of the effective Hamiltonian of the $v_6 = 1$ vibrational level the operator of the $\Delta k = \pm 3$ interaction was taken in the form

$$\langle v_t^{l_t}; J, k \pm 3 \mid \mathbf{H}_{23} / hc \mid v_t^{l_t}; J, k \rangle = d_t l_t F_3^{\pm}(J, k)$$
(A5)

The operator of the $\Delta k = \pm 6$ interaction

was included in the vibrational ground state and in the $v_6 = 1$ level. The notation of the matrix elements of rotational shifting oper-

ators was taken conventionally as

$$F_n^{\pm}(J,k) = \prod_{i=1}^n \left[J(J+1) - (k \pm i \mp 1)(k \pm i) \right]^{1/2}$$
(A7)

Appendix B. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohiostate.edu/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.jms.2008.04.011. P. Pracna et al./Journal of Molecular Spectroscopy 250 (2008) 59-69

References

- [12] P. Pracna, K. Sarka, J. Demaison, J. Cosléou, F. Herlemont, M. Khelkhal, H. Fichoux,
- [1] A. Ceausu-Velcescu, J. Cosléou, J. Demaison, G. Graner, G. Duxbury, H. Bürger, J. Mol. Spectrosc. 220 (2003) 291–297.
- [2] J.P. Champion, G. Graner, Mol. Phys. 58 (1986) 475–484.
- [3] A.S. Pine, J.M. Pliva, J. Mol. Spectrosc. 130 (1988) 431–444.
- [4] A.S. Fine, G.T. Fraser, J.M. Piva, J. Chem. Phys. 89 (1988) 2720–2728.
 [5] A. Ceausu-Velcescu, H. Bürger, G. Graner, J. Mol. Spectrosc. 220 (2003) 298– 305.
- [6] W.L. Meerts, I. Ozier, J. Chem. Phys. 75 (1981) 596-603.
- [7] J. Breidung, J. Cosléou, J. Demaison, K. Sarka, W. Thiel, Mol. Phys. 102 (2004) 1827-1841.
- [8] G. Klatt, A. Willetts, N.C. Handy, R. Tarroni, P. Palmieri, J. Mol. Spectrosc. 176 (1996) 64-74.
- [9] K. Harada, K. Tanaka, T. Tanaka, Chem. Phys. Lett. 120 (1985) 276–279.
- [10] P. Pracna, Š. Urban, F. Kolář, J. Cosléou, J. Demaison, P. Paplewski, H. Bürger, J. Mol. Struct. 517-518 (2000) 119-126.
- [11] H. Bürger, J. Cosléou, J. Demaison, C. Gerke, H. Harder, H. Mäder, M. Paplewski, D. Papoušek, K. Sarka, J.K.G. Watson, J. Mol. Spectrosc. 182 (1997) 34-49.

- D. Papoušek, M. Paplewski, H. Bürger, J. Mol. Spectrosc. 184 (1997) 93-105. A. Ruoff, H. Bürger, S. Biedermann, R. Anttila, Spectrochim. Acta A31 (1975) [13]
- 1099-1100. [14] (a) G. Guelachvili, K. Narahari Rao, Handbook of Infrared Standards, Academic
- Press, San Diego, 1986; (b) G. Guelachvili, M. Birk, Ch.J. Bordé, J.W. Brault, L.R. Brown, B. Carli, A.R.H. Cole, K.M. Evenson, A. Fayt, D. Hausamann, J.W.C. Johns, J. Kauppinen, Q. Kou, A.G. Maki, K. Narahari Rao, R.A. Toth, W. Urban, A. Valentin, J. Vergès, G. Wagner, M.H. Wappelhorst, J.S. Wells, B.P. Winnewisser, M. Winnewisser, Pure Appl. Chem. 68 (1996) 193-208; (c) J. Mol. Spectrosc. 177 (1996) 164-179;
- (d) Spectrochim. Acta A52 (1996) 717–732. [15] W. Łodyga, M. Kręglewski, P. Pracna, Š. Urban, J. Mol. Spectrosc. 243 (2007) 218-224.
- [16] R. Bocquet, D. Boucher, W.D. Chen, D. Papoušek, G. Wlodarczak, J. Demaison, J. Mol. Spectrosc. 163 (1994) 291-299.
- [17] J. Sakai, A. Mito, M. Katayama, Chem. Phys. Lett. 118 (1985) 600-603.
- [18] C.C. Costain, J. Mol. Spectrosc. 9 (1962) 317-336.