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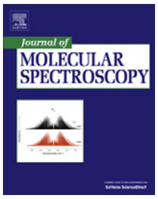

The $\nu_3 + \nu_5$ combination band of DCF_3: Modeling anharmonic and Coriolis interactions in a three-level system near 1700 cm^{-1}

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ABSTRACT

The degenerate combination level $\nu_3 = \nu_5 = 1$ (1669.09 cm^{-1}, E symmetry) was investigated with high-resolution, using a Fourier-transform infrared spectrum recorded in the 1600–1800 cm^{-1} region, at a resolution of 0.0024 cm^{-1}. A second spectrum, recorded in the 900–1100 cm^{-1}, at a resolution of 0.0024 cm^{-1}, was employed to analyze the $\nu_3 + \nu_5 - \nu_3$ hot band. The studied combination level has to be treated as a part of a polyad including two other dark states: ($\nu_3 = 1$, $\nu_6 = 2$, $l_6 = 0, \mp 2$) and ($\nu_4 = \nu_6 = 1$). The important anharmonic, Coriolis, and α-resonance interactions were extrapolated from the previously studied dyads $\nu_5/2\nu_6$ and $\nu_4/\nu_3 + \nu_6$. The reproduction thus achieved is quantitative for all the assigned data and provides spectroscopic parameters which are consistent with those of the system of vibrational levels $\nu_5/2\nu_6$.

1. Introduction

While the high-resolution studies of fluoroform HCF_3 date back to 1970s, the analogous studies for the deuterated species were accomplished (with the exception of the ν_1 CD stretching fundamental band [1]) during the past 15 years [2–5]. There are only very few high-resolution analyses of the overtone and combination bands which are important from the point of view of the anharmonic molecular force field. For HCF_3 there exist only two studies of the system of the $\nu_2/\nu_5/\nu_3 + \nu_6$ bands [6,7] and two other analyses of the $2\nu_4$ overtone band [8] and the $\nu_1/\nu_4 + \nu_5 + \nu_6/\nu_2 + \nu_4 + \nu_6$ polyad [9].

For the DCF_3 species, such studies are more frequent because some of the fundamental levels are coupled to combination or overtone levels by resonance interactions and had to be studied with their explicit inclusion. This was the case of the ν_4 CD rocking fundamental band which exhibits an anharmonic (Fermi) resonance with the $\nu_3 + \nu_6$ combination level [5]. The ν_5 fundamental band (CF_3 asymmetric stretching) has been recently reinvestigated together with the $2\nu_6$ band because of their resonance crossings due to the second-order Coriolis ($\Delta k = \Delta l = \pm 1$) and α-resonances ($\Delta k = \pm 2$, $\Delta l = \mp 1$) [10,11].

The $\nu_3 + \nu_5$ combination level can be thus expected to have analogous couplings with the nearby level $\nu_3 + 2\nu_6$ (see Fig. 1) which have to be taken into account for explanation of most of the anomalies observed previously in the $\nu_3 + \nu_5$ band, when studied as an isolated one [12]. The difference of the current resonance pattern from the situation in the $\nu_5/2\nu_6$ cluster of levels is due to the fact that the $\nu_3 + 2\nu_6$ level is accompanied by the $\nu_4 + \nu_6$ level as a result of adding a quantum of the ν_6 vibration to the $\nu_4/\nu_3 + \nu_6$ dyad. The analysis shows that the Fermi interaction between $\nu_3 + 2\nu_6$ and $\nu_4 + \nu_6$ with a resonant crossing of levels plays an essential role in the studied system. As both these vibrational levels are dark states, the model of their interactions with the $\nu_3 + \nu_5$ level had to be extrapolated from the previous studies of the lower dyads. Their inclusion lead to a substantial improvement of the fit of the $\nu_3 + \nu_5$ band and yielded a set of deperturbed spectroscopic parameters, with their effectivity diminished as much as possible.

2. Experimental details

Two high-resolution FTIR spectra were used in this work: one from the region of the $\nu_3 + \nu_5$ band (spectrum I, already used in Ref. [4], referred as spectrum #1611) and another one from the region of the fundamental band ν_5 (spectrum II, already employed in Ref. [11]). The details of experimental conditions for the two spectra are given in Table 1. Both spectra were recorded in Wuppertal with a Bruker IFS 120HR spectrometer and use the original calibration based on residual water lines taken from Ref. [13a], corrected from systematic errors as indicated in Refs. [13b–d]. Wavenumber precision and accuracy were estimated to 2×10^{-4} and 5×10^{-4} cm^{-1}, respectively.

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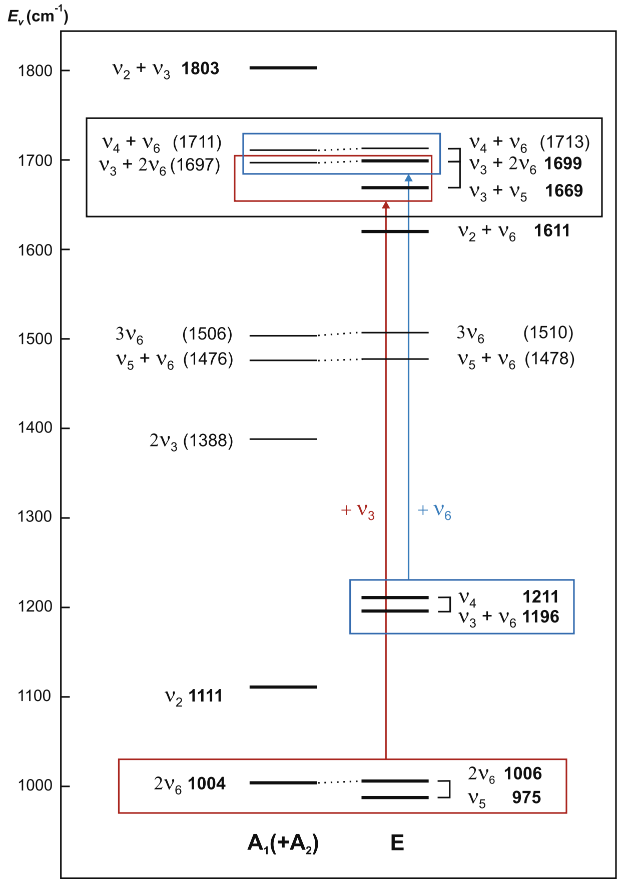

Fig. 1. Diagram of vibrational levels of DCF_3 up to the combination level $v_2 = v_3 = 1$, separated to non-degenerate $(A_1 + A_2)$ and degenerate (E) levels. Overtone and combination levels having sublevels of both symmetries are drawn in both stacks and are connected with dotted lines. The levels analyzed so far are highlighted with bold lines and fonts. The energies of overtone and combination levels given in parentheses are estimated by including anharmonic corrections either from experiment, or from *ab initio* calculations (see text). Those which have to be analyzed as polyads with an explicit account of local resonances are enclosed in rectangles.

Table 1
Experimental details of Fourier transform spectra used in this study.

Spectrum	I	II
Range range (cm^{-1})	1240–2050	740–1400
Detector	MCT800	MCT800
Beamsplitter	KBr	KBr
No. of scans	341	80
Resolution[a](cm^{-1})	0.0024	0.0024
Path length (m)	9.6	9.6
Pressure (Pa)	250	20
Temperature (K)	293	293

[a] The resolution of the Bruker FTS was calculated as 1/MOPD, where MOPD is maximum optical path difference.

3. Description of the spectra and assignments

The $\nu_3 + \nu_5$ combination band, shown in Fig. 2, has a similar structure as the fundamental band ν_5, but does not have such prominent and easily recognizable patterns like the regular clusters of the ^pR lines of the ν_5 band (cf. Fig. 4 of Ref. [11]). The clearest patterns are the series of the ${}^pP_K(J = K)$, ${}^pP_K(J = K + 1)$, ${}^pP_K(J = K + 2), \ldots$ lines shown in Fig. 3a (K spans the values 1, 2, ... within such a series). From these lines the assignments were started, instantly checked by the lower state combination differences (LSCD) using the Loomis–Wood for Windows program [14]. For this the purpose only the lines of the ^pQ could be used, because the ^pR branches have vanishing intensities. With the exception of the ${}^rQ_0$ branch, the lines of the ${}^{p,r}Q$ branches are very frequently overlapped with the lines of the P and R branches and hidden among them. The clusters of the ${}^rR_K(J = K)$, ${}^rR_K(J = K + 1)$, $K(J = K + 2), \ldots ({}^rR_K = 0, 1, \ldots)$ lines, which are clearly visible at lower values of J near the band origin, collapse to overlapped lines around 1672–1673 cm^{-1} and become resolved again for higher values of J as shown in Fig. 3b. The LSCD checking can be performed only against the ^rQ branches because the ^rP branches have again vanishing intensities. A total of 2431 transitions pertaining to the $\nu_3 + \nu_5$ band $(-46 \leqslant K\cdot\Delta K \leqslant 33, J_{max} = 53)$ were assigned from spectrum I and used in the least-squares calculations.

The $\nu_3 + \nu_5 - \nu_3$ hot band, centered at 974.81 cm^{-1}, has a relative intensity of 0.036 at room temperature and is almost completely hidden by the much more intense fundamental ν_5 band. Hence, assignments could be made only for some ${}^pP_K(J)$ transitions, and also for a few high-K ${}^rR_K(J)$ transitions, which occur in less congested windows of the spectrum. From spectrum II, a total of 124 transitions of the $\nu_3 + \nu_5 - \nu_3$ hot band were finally assigned.

4. Theoretical model

The effective vibration–rotation Hamiltonian of the studied system of levels closely follows the models used in the previous studies of the dyads $(v_5 = 1/v_6 = 2)$ [11] and $(v_3 = 1, v_6 = 1/v_4 = 1)$ [5]. Its matrix elements for the individual vibrational levels, expanded up to seventh order, are given in Appendix A, whereas the interaction terms among them, following the notation of Ref. [15], are summarized in Appendix B. The general $\mathbf{H}_{mn}$ notation, where m is the total power of vibrational operators and n the total power of rotational operators, has been used throughout the paper, in the development of the rovibrational Hamiltonian. Recall that such a term is of order $i = m + n - 2$ in the Amat and Nielsen classification [16].

The interaction Hamiltonian between the $(v_3 = v_5 = 1)/(v_3 = 1, v_6 = 2)$ states includes all three major interactions used in the study of the $v_5 = 1/v_6 = 2$ level system, i.e. a Fermi anharmonic interaction, a second-order Coriolis and a second-order α-resonances. The Fermi interaction is nonresonant in both the lower and upper systems, with a crossing estimated to occur around $K'\cdot l = -80$. It was found, however, significant for the data reproduction and possible to be determined in the lower system. Its value in the upper system was thus constrained to that of the lower system. The level

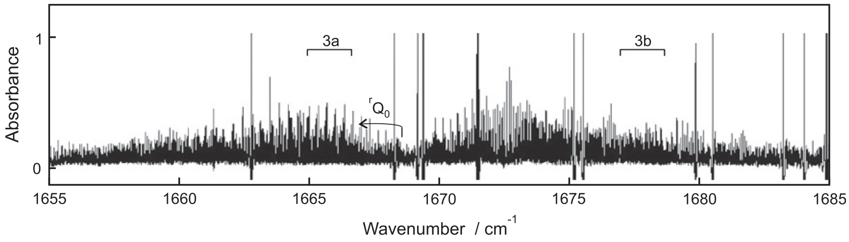

Fig. 2. Overview of the $\nu_3 + \nu_5$ combination band of DCF_3. Intensities of residual water lines dominate over the lines of the very weak $\nu_3 + \nu_5$ band. Experimental conditions: pressure 250 Pa, path length 9.6 m, resolution (1/MOPD) 0.0024 cm^{-1}. The intervals above the spectrum refer to the spectrum sections shown in Fig. 3.