

HIGH-RESOLUTION FOURIER-TRANSFORM INFRARED SPECTRUM OF THE ν_6 FUNDAMENTAL BAND OF $^{13}\text{CH}_3\text{F}^*$

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The ν_6 vibration-rotational band of $^{13}\text{CH}_3\text{F}$ has been measured in the range 1070-1260 cm^{-1} using a Fourier-transform spectrometer with unapodized resolution 0.0027 cm^{-1} . The wavenumbers of 1262 vibration-rotational transitions to the $\nu_6 = 1$ (*E*) vibrational state have been assigned and fitted by least squares with the standard deviation of the fit 1.31×10^{-4} cm^{-1} . This made it possible to determine 19 spectroscopical parameters of the $\nu_6 = 1$ state including parameters of the $\Delta k = \pm 2$, $\Delta l = \mp 2$ and $\Delta k = \pm 4$, $\Delta l = \mp 2$ interactions leading to the $A_1 - A_2$ splittings of many rotational levels with $kl = +1$ and $kl = -2$.

1. Introduction

The accuracy with which the wavenumbers of the vibration-rotational transitions of molecules can be measured with high-resolution Fourier-transform spectrometers is now better than 1×10^{-4} cm^{-1} (see, e.g., [1]). Similarly, frequencies of the rotational transitions in the ground as well as excited vibrational states of polyatomic molecules can also be measured very accurately: using the technique of Fourier-transform microwave spectroscopy, these frequencies can be measured with better than 5 kHz accuracy while rotational transitions in the submillimeterwave spectrum region can be measured with an accuracy better than 30 kHz (see, e.g., [2]). Furthermore, with the increasing sensitivity of these spectroscopical

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techniques, transitions can be measured up to very high values of the rotational quantum numbers.

Having such precise data, the challenge is to fit them quantitatively, i.e. with a standard deviation of the fit approaching the experimental accuracy of the well isolated and symmetric spectrum lines with a good signal to noise ratio. Effective Hamiltonians are widely used in least squares procedures to represent such experimental data by spectroscopical parameters of the vibronic states involved in the rovibronic transitions. Nevertheless, there remain certain problems which require further systematic investigation. From the theoretical point of view, the effective Hamiltonians can be obtained from a vibration-rotational Hamiltonian expanded in normal vibrational coordinates by using a standard perturbation treatment [3, 4]. For light molecules and molecules with large amplitude vibrational motions the resulting power series in terms of the rotational quantum numbers are often poorly convergent (see, e.g., [5] and the references cited therein). As a solution to this problem, other effective Hamiltonian expansions like Pade or Borel approximants have been suggested [5]. Recently, Urban and Yamada [6] discussed a breakdown of the Watson type Hamiltonian for the quasilinear molecule HNCO and rather surprisingly also for other asymmetric top molecules like ketene and diazomethane.

Furthermore, there is an ambiguity in the effective Hamiltonians in the sense that they can be reduced in different ways and the experimental data can be fitted by sets of parameters which are unitary equivalent. This has been for the first time discussed for symmetric top molecules by Lobodenko et al [7], for isolated vibrational levels of symmetry E and two vibrational levels of symmetry A and E coupled by the x , y -Coriolis interaction. Nevertheless, accurate sets of unitary equivalent parameters for an isolated vibrational state of symmetry E have been probably obtained for the first time only recently for CF_3CCH [2]. Besides this, more theoretical work should be done on the reduction of effective Hamiltonians for more than two closely lying interacting vibrational states.

If an effective Hamiltonian does not have a good asymptotic behaviour or if the fit of experimental data is attempted by using a Hamiltonian which is not fully reduced, spectroscopical parameters can be strongly correlated, anomalous values of the parameters can be obtained and the data may not be described quantitatively.

We have recently gathered a considerable amount of experimental data from high-resolution spectroscopy on the vibration-rotational and rotational transition frequencies in the ground vibrational states and the four lowest lying vibrational states of $^{12}\text{CH}_3\text{F}$ and $^{13}\text{CH}_3\text{F}$ (Table I). The analysis of the data for the ground vibrational states of both isotopomers indicated an excellent convergence of the standard polynomial approximation for the ground state energy levels with a quantitative fit of the data up to $J \leq 58$ for $^{12}\text{CH}_3\text{F}$ [12] and $J \leq 50$ for $^{13}\text{CH}_3\text{F}$ [1] (up to sextic centrifugal distortion coefficients). Although standard deviations of the fits of the vibration-rotational transition wavenumbers were of the order of magnitude 10^{-4} cm^{-1} , these fits were not completely quantitative and systematic differences between calculated and experimental wavenumbers were observed especially in the band systems ν_2/ν_5 for certain values of the rotational quantum numbers k and the highest values of J .

Table I
Fundamental vibrational levels in
 $^{12}\text{CH}_3\text{F}$ and $^{13}\text{CH}_3\text{F}$ (in cm^{-1})

Vibrational state	$^{12}\text{CH}_3\text{F}$	$^{13}\text{CH}_3\text{F}$
$\nu_3 = 1 (A_1)$	1048.610701(10) ^a	1027.493201(22) ^b
$\nu_6 = 1 (E)$	1182.674392(17) ^c	1174.890905(12) ^d
$\nu_2 = 1 (A_1)$	1459.39165(80) ^e	1453.658336(60) ^f
$\nu_5 = 1 (E)$	1467.81381(50) ^e	1465.576510(27) ^f

^a Ref. [9]

^b Ref. [8]

^c Ref. [10]

^d Present work

^e Ref. [1]

^f Ref. [11]

The bands ν_3 and ν_6 were analyzed as isolated bands and ν_2/ν_5 as system of bands perturbed by the x, y Coriolis interaction. Thus the question is whether this is a failure of the effective Hamiltonian for excited vibrational states or whether we should introduce vibration-rotational interactions between ν_3 and ν_6 and between ν_6 and ν_2/ν_5 as off-diagonal matrix elements in a variational approach (ν_1 and ν_4 seem to be well isolated from ν_3 , ν_6 , and ν_2/ν_5). The data for such an analysis seem to be complete for $^{12}\text{CH}_3\text{F}$ but for $^{13}\text{CH}_3\text{F}$, the ν_6 band has not yet been measured and analyzed with high resolution.

In this paper, we report the measurement and analysis of the high-resolution Fourier-transform spectra of the ν_6 band of $^{13}\text{CH}_3\text{F}$, recorded at Doppler limited resolution with the Bruker IFS 120 HR spectrometer located at the University of Giessen. This should fill the gap in the data for $^{13}\text{CH}_3\text{F}$. Besides this, we will focus on the problem of different reduction schemes of the effective rotational Hamiltonians in connection with the analysis of the data for an isolated perpendicular band.

2. Experimental details

The spectra were measured in the range 1070–1260 cm^{-1} under the same conditions as described previously [1]. The segment of the spectrum between 1157.0 and 1159.5 cm^{-1} is shown in Fig. 1.

3. Theory

In this paper, we will treat the ν_6 band of $^{13}\text{CH}_3\text{F}$ as an isolated band which corresponds to the $\Delta\nu_6 = 1$, $\Delta J = 0, \pm 1$, $\Delta K = \pm 1$ rovibrational transitions to the doubly degenerate vibrational level of the CH_3 rocking mode. We will therefore use an effective rotational Hamiltonian for the $\nu_6 = 1$ vibrational state which is diagonal

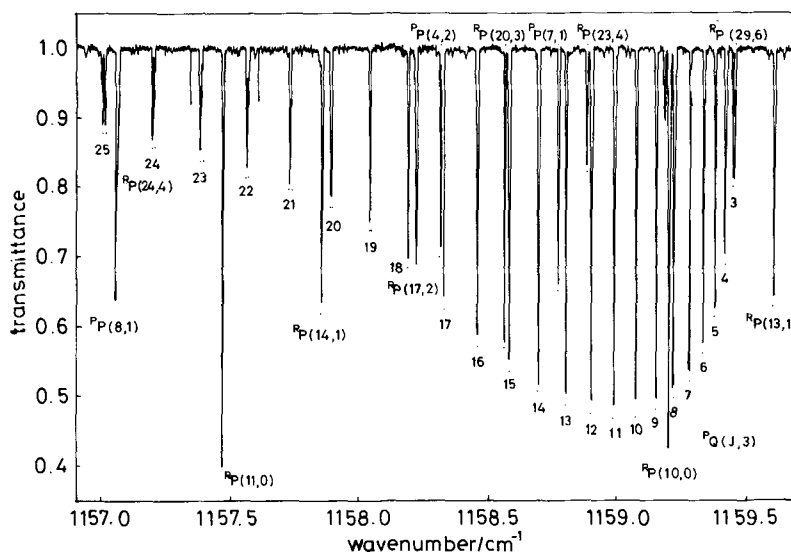


Fig. 1. Part of the high-resolution Fourier-transform spectrum of the ν_6 band of $^{13}\text{CH}_3\text{F}$ showing the J -dependence of the $A_1 - A_2$ splitting of the $^PQ(J, K = 3)$ lines

in all the principal vibrational quantum numbers but contains terms which are off-diagonal in the quantum number l of the vibrational angular momentum and in the rotational quantum number k .

The diagonal matrix element of this Hamiltonian can be written as:

$$\begin{aligned}
 E_{vr}^0(J, k)/hc = & E_v^0/hc + BJ(J+1) + (A-B)k^2 - 2(A\zeta_6^z)kl + \eta_J J(J+1)kl \\
 & + \eta_K k^3 l + \tau_J J^2(J+1)^2 kl + \tau_{JK} J(J+1)k^3 l + \tau_K k^5 l - D_J J^2(J+1)^2 \\
 & - D_{JK} J(J+1)k^2 - D_K k^4 + H_J J^3(J+1)^3 + H_{JK} J^2(J+1)^2 k^2 \\
 & + H_{KJ} J(J+1)k^4 + H_K k^6 + \dots
 \end{aligned} \quad (1)$$

We introduce the "2,2" l -type interaction

$$\begin{aligned}
 \langle 1^{+1}; J, k+2 | (H_{22} + H_{24})/hc | 1^{-1}; J, k \rangle = & 2[q_{22} + f_{22}^J J(J+1) \\
 & + f_{22}^K k(k+2)] F(J, k) F(J, k+1),
 \end{aligned} \quad (2)$$

where

$$F(J, k) = J(J+1) - k(k+1)^{1/2}. \quad (3)$$

We also introduce the "2,-4" interaction,

$$\begin{aligned}
 \langle 1^{-1}; J, k+4 | (H_{24} + H_{26})/hc | 1^{+1}; J, k \rangle = & 2[f_{42} + f_{42}^J J(J+1) + \\
 & f_{42}^K k(k+4)] F(J, k) F(J, k+1) F(J, k+2) F(J, k+3).
 \end{aligned} \quad (4)$$

Table II
Parameters of the $\nu_6 = 1$ vibrational state of $^{13}\text{CH}_3\text{F}$ (in cm^{-1})^a

E_6^0/hc	1174.890905(12) ^a	$q_{22}/10^{-6}$	-16.950(40)
B	0.82553522(10)	$f_{22}^J/10^{-9}$	13.005(43)
A	5.19822031(99)	$f_{42}^J/10^{-9}$	-5.971(39)
Ac_6^z	1.5721831(20)	$f_{42}^J/10^{-12}$	0.348(32)
$D_J/10^{-6}$	1.93679(19)		
$D_{JK}/10^{-6}$	15.1315(36)	Ground state parameters ^c	
$D_K/10^{-6}$	72.3429(132)	B_0	0.8293286629
$H_J/10^{-9}$	0.000465(101)	A_0	5.18242273
$H_{JK}/10^{-9}$	-0.09449(294)	$D_J^0/10^{-6}$	1.925696
$H_{KJ}/10^{-9}$	-1.9982(338)	$D_{JK}^0/10^{-6}$	14.1733
$H_K/10^{-9}$	0.0 ^b	$D_K^0/10^{-6}$	70.9164
$n_J/10^{-6}$	42.182(14)	$H_J^0/10^{-9}$	-0.0009214
$n_K/10^{-6}$	56.073(161)	$H_K^0/10^{-9}$	0.0577
$\tau_J/10^{-9}$	1.8101(127)	$H_{KJ}^0/10^{-9}$	0.67431
$\tau_{JK}/10^{-9}$	48.199(156)	H_K^0	0.0
$\tau_K/10^{-9}$	-18.79(159)		

^a Figures in parentheses are standard errors in units of the last digit quoted

^b Constrained value

^c Constrained to values given in [1]

As discussed by Lobodenko et al [7], a possible reduction of the effective rotational Hamiltonian consists in fitting either the parameter of the so-called "0, ± 3 " interaction or of the "2, -1" l -type interaction (in addition to the interactions described by Eqs (2) and (4)). In our previous paper on the rotational transitions in the $\nu_{10} = 1$ vibrational state of CF_3CCH [2], we called these reductions A and B type reductions and we were able to determine parameters of the "0, ± 3 " as well as of the "2, -1" l -type interactions. For reasons which will be discussed later, these parameters cannot be determined for the $\nu_6 = 1$ vibrational state of $^{13}\text{CH}_3\text{F}$ and we will therefore not give here the expressions for their matrix elements.

4. Analysis of the spectra

The density of lines in the ν_6 band of $^{13}\text{CH}_3\text{F}$ is rather low and their assignments are straightforward. We have fitted the rovibrational line positions of the ν_6 band with the ground state parameters constrained to the extremely precise values which were obtained previously [1]. In each of these least-squares adjustments of the spectroscopic parameters, the results of which are given in Table II, each transition was weighted by the inverse square of its experimental uncertainty. The uncertainty of the isolated and symmetric rovibrational line positions was estimated to be $1 \times 10^{-4} \text{ cm}^{-1}$ (which might be a pessimistic estimate).

We used a fully symmetrized set of basis rovibrational wavefunctions in which the matrix representation of the Hamiltonian was constructed. We used also the

Table III
 $A_1 - A_2$ splittings of the $kl = -2$ energy levels in the vibrational state $v_6 = 1$ of $^{13}\text{CH}_3\text{F}$ (in cm^{-1})^a

J'	Exp. ^b	Calc. ^c	J'	Exp. ^b	Calc. ^c
19	0.00289	0.00335	29	0.01718	0.01713
20	0.00395	0.00409	30	0.01947	0.01950
21	0.00481	0.00494	31	0.02215	0.02211
22	0.00591	0.00591	32	0.02508	0.02496
23	0.00711	0.00702	33	0.02808	0.02806
24	0.00828	0.00828	34	0.03129	0.03143
25	0.00971	0.00968	35	0.03495	0.03508
26	0.01128	0.01126	36	0.03911	0.03903
27	0.01299	0.01302	37	0.04323	0.04330
28	0.01487	0.01497	38	0.04791	0.04786

^a The estimated uncertainty of the experimental value is about $1 \times 10^{-4} \text{ cm}^{-1}$ except for the partially resolved transitions to the $J' = 19$ level where it is about $4 \times 10^{-4} \text{ cm}^{-1}$.

^b Obtained as difference between the higher and lower frequency component of the split line.

^c Obtained as difference between the eigenvalues of the A_- and A_+ matrices (see text)

same definition of phase relations and basis functions as described in [2]. Thus the matrix of the Hamiltonian is actually identical with that which was given explicitly in our previous paper [2].

We assigned 1262 lines and fitted them with the standard deviation of the fit $1.31 \times 10^{-4} \text{ cm}^{-1}$. In both $kl = -1$ and $kl = +1$ levels, the data were fitted up to $J'_{\text{max}}/K'_{\text{max}} = 38/9$.

5. Results and discussion

Both interactions defined by Eqs (2) and (4) have diagonal contributions to the upper state levels $kl = +1$ and $kl = -2$ leading to a measurable splitting of the energy levels into A_1 and A_2 components. The splitting of the $kl = -2$ levels leads to a splitting of the ${}^P X(J, 3)$ ($X = P, Q, R$) lines into doublets. We have been able to resolve this splitting starting with $J' = 19$ and going up to $J' = 38$ (see Fig. 1 and Table III). On the other hand, the $A_1 - A_2$ splitting of the $kl = +1$ levels does not lead to a splitting of the ${}^R X(J, 0)$ lines because the ${}^R P(J + 1, 0)$ and ${}^R R(J - 1, 0)$ transitions go always to the same sublevel of the doublet while the ${}^R Q(J, 0)$ transitions to the other sublevel.

The parameters of both interactions are therefore primarily determined by these splittings (Table II). On the other hand, the interactions "2, -1" and "0, ± 3 " do not have diagonal contributions and unless there is a close coincidence between interacting levels, they are not determinable. In the $v_{10} = 1$ vibrational state of CF_3CCH , such coincidences have made it possible to fit the data by using two unitary equivalent sets of parameters with the parameter of the "0, ± 3 " interaction

fitted in set *A* and parameter of the “2, -1” interaction fitted in set *B*. The $v_6 = 1$ vibrational state of $^{13}\text{CH}_3\text{F}$ is just the opposite example: there are no close coincidences between energy levels connected by the “0, ± 3 ” and “2, -1” *l*-type interactions and their parameters are not determinable.

It should be noted that the signs of the coefficients f_{42} and f_{42}^J are completely arbitrary even for defined phase relations between the corresponding wavefunctions. This is because we cannot decide whether for a given *J* the $^P X(J, 3)$ transition goes to the A_1 or A_2 sublevel of the doublet. If the assignments are interchanged, the signs of the f_{42} parameters change. In the present paper, we assigned the higher frequency component of the doublet arbitrarily to a transition to the A_- block of the symmetry factorized $A_1 - A_2$ matrices, while the lower frequency component to the A_+ block (A_{\pm} notation as defined in [2]).

Parameters of the $v_6 = 1$ vibrational state of $^{13}\text{CH}_3\text{F}$ in Table II correlate well with those found earlier for $v_6 = 1$ state of $^{12}\text{CH}_3\text{F}$ [10]. The q_{22} coefficient for $^{13}\text{CH}_3\text{F}$ is about four times smaller than that found for $^{12}\text{CH}_3\text{F}$ [10]. This parameter absorbs the effect of the *x, y* Coriolis interaction between the $v_3 = 1$ and $v_6 = 1$ vibrational states. Since according to Table I the difference between the corresponding vibrational levels is 47.40 cm^{-1} in $^{13}\text{CH}_3\text{F}$ but only 34.06 cm^{-1} in $^{12}\text{CH}_3\text{F}$, q_{22} can be expected to be much smaller in $^{13}\text{CH}_3\text{F}$ than in $^{12}\text{CH}_3\text{F}$.

Although the standard deviation $1.31 \times 10^{-4}\text{ cm}^{-1}$ of the fit of 1262 lines using 19 parameters indicates a good fit, we feel that it still does not fully correspond to the accuracy of the experimental data. For the highest values of the rotational quantum numbers *k* and *J*, we indeed found systematic differences between calculated and experimental wavenumbers (up to $2 \times 10^{-3}\text{ cm}^{-1}$ for $K' = 9$ and $J' \simeq 30$). We suspect that especially the *x, y* Coriolis interaction between the $v_6 = 1$ state and the $v_2 = 1$ and $v_5 = 1$ states should be taken into account explicitly in a variational approach which might further improve the quality of the fit.

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