

FTIR spectra of the ν_6 and ν_8 bands of ^{13}C formic acid molecule—Assignment of FIR-laser lines

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Abstract

Two interacting vibrational modes ν_6 and ν_8 of ^{13}C species of formic acid have been studied with high resolution FTIR spectroscopy in the range $900\text{--}1300\text{ cm}^{-1}$ with an instrumental resolution of 0.0018 cm^{-1} . More than 10000 lines have been assigned and fitted with a RMS deviation of 0.00024 cm^{-1} . The band centers, as well as the rotational, quartic and sextic centrifugal distortion parameters and 6 interaction parameters have been determined. The obtained parameters have enabled the assignments of 24 FIR laser emissions of this molecule observed previously by Dangoisse and Glorieux [D. Dangoisse, P. Glorieux, *J. Mol. Spectrosc.* 92 (1982) 283–297], Luis et al. [G.M.R.S. Luis, E.M. Telles, A. Scalabrin, D. Pereira, *IEEE J. Quantum. Electron.* QE-34 (1998) 767–769], and Bertolini et al. [A. Bertolini, G. Carelli, C.A. Massa, A. Moretti, F. Strumia, *Infrared Phys. Technol.* 40 (1999) 33–36].
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1. Introduction

The 6^1 and 8^1 vibrational states of the formic acid molecule and its various isotopic species are capable to emit submillimeter laser radiation when pumped by a CO_2 laser [1]. A submillimeter laser transition arises, as a rule, between rotational levels in the excited vibrational state whereas the pumped transition originates from a rotational level of the ground vibrational state and has a common upper level with the laser transition. Most of the laser emissions were observed and measured in the 1970s and the early 1980s, however, not all transitions have yet been assigned.

FIR laser action from the H^{13}COOH isotopic species has been produced and studied in several works. The first one has been performed in 1982 by Dangoisse and Glorieux [2], who have obtained 21 emissions. They measured the frequencies of laser lines with an accuracy of about

1 MHz and gave tentative assignment almost for all transitions. In the second work published in 1998 [3] Luis et al. could observe five new far-infrared lines using a more widely tuned waveguide CO_2 laser. The authors measured the wavelengths of the laser lines with an uncertainty of about $\pm 0.5\text{ }\mu\text{m}$ and also the offset absorption frequencies. However, attempts to assign these lines were not undertaken. The last work related to the FIR laser radiation from H^{13}COOH medium was published in 1999 by A. Bertolini et al. [4]. They used a waveguide CO_2 laser with a tunability of 300 MHz and reported the parameters of 16 new FIR laser lines with wavelengths ranging from 185.3 to 1219.9 μm . The estimated error in the wavelength measurements was of a few parts in 10^{-4} . Seven of the obtained laser transitions were tentatively assigned to the ν_6 band.

It should be noted that two vibrationally excited states 6^1 and 8^1 of H^{13}COOH giving rise to laser action are coupled through a Coriolis interaction and have never been studied in details together neither by microwave nor by high resolution IR spectroscopy. The only work dealing with this subject was that by Ong with coauthors [5]

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published in 1999. They assigned 3004 FTIR transitions in the ν_6 band but were not able to detect the ν_8 band because of its weakness. Processing of the observed data was carried out using the effective Hamiltonian for two interacting vibrational states of an asymmetric top molecule coupled by two terms representing an a- and b-Coriolis interaction and considering the 8^1 state as a dark state. The parameters obtained could reproduce the observed IR transitions in the ν_6 band with a reasonable accuracy up to $K_a = 13$. It is obvious that transitions in the ν_8 band using the parameters derived in Ref. [5] could be calculated with much worse uncertainty. The identification of the laser lines in Refs. [2,4] prior to the work by Ong et al. was carried out using the fact that geometry of the molecule is very little changed when a ^{13}C atom is substituted for a ^{12}C atom, and as a consequence the shape of the spectrum is very similar for these two different species. The authors used the information on the known relative displacement of the most intensive aR -type rotational spectra in the ground and excited states of the main isotopic species and its invariability when coming to the ^{13}C species. This method, according to author's opinion, gives an unambiguous determination for J and low K_a values. Therefore, some assignments especially for transitions in the 8^1 state can only be assumed to be tentative.

A main goal of the present investigation was to study the high resolution IR spectra of the ν_6 and ν_8 bands of the H^{13}COOH molecule to determine their spectroscopic parameters and ultimately to check the assignments given in [2,4] and, when possible, to identify the yet unassigned laser transitions.

2. Experimental details

The infrared measurements of the ν_6 and ν_8 vibrational bands of the isotopically enriched (99%) H^{13}COOH sample obtained from Sigma-Aldrich were carried out using a Bruker IFS 120HR Fourier spectrometer in Oulu. The spectral range from 900 cm^{-1} to 1300 cm^{-1} was recorded at room temperature under two different sets of absorption path length and sample pressure conditions. The first spectrum was obtained using 3.2 m and 4 Pa, and the second using 3.2 m and 84 Pa. The recording time in the both measurements was about 42 h. The lines from both, the low and high path length-pressure spectra, were used in the analysis. A White-type cell [6a,6b] with KBr windows, a Global source at 1400 K, a germanium beam splitter between KBr base plates, and a mercury-cadmium-telluride-detector were employed. The experimental linewidth of small isolated lines is about 0.0022 cm^{-1} at 1100 cm^{-1} resulting from the instrumental and Doppler broadening. The high pressure measurement is first calibrated with lines of the $\text{OCS } 2\nu_2$ band [7]. Then the calibration is transferred to the low pressure measurement with good sample peaks. The uncertainty of this two stage calibration at ν is $\Delta\nu = 1.2 \times 10^{-9}\nu + 3.4 \times 10^{-6}\text{ cm}^{-1}$. The optimized center of gravity method [8] was used to calculate the peak positions. The uncertainty of the peak position for a well-

separated spectral line with this method [8] is $\Delta\nu = \Delta\sigma / (2.8 \cdot S/N)$, where $\Delta\sigma$ is the width of the peak at half height, S/N is the signal to noise ratio of the line. $S/N > 300$ for lines with 100% absorption in these spectra. So, taking into account the calibration accuracy, the uncertainty of a narrow line at 1100 cm^{-1} with 10% absorption is about $3.1 \times 10^{-5}\text{ cm}^{-1}$. A good estimate for the accuracy of a calculated line position and/or the band center is achieved by adding the standard deviation (SD), with reasonable confidence limits, to the calibration accuracy.

3. Details of investigation

Formic acid is a planar molecule belonging to C_s symmetry. The 6^1 and 8^1 vibrational states correspond to in-plane and out-of-plane normal vibrations. These two vibrations are coupled by a relatively strong a- and less strong b-type Coriolis resonances. The fundamental ν_6 band centered at 1095 cm^{-1} is of a/b hybrid type and has a medium intensity, while the ν_8 band with a center at 1020 cm^{-1} is of c type and is a weak band. Using the measured spectra under the low and high path length–pressure conditions, which will be referred to as normal and saturated, respectively, we were able to assign absorption lines in the ν_6 band with J up to 75 and K_a up to 15, and in the ν_8 band up to 60 and 21, respectively. The assignment of the transitions in these two bands was quite straightforward and did not cause any difficulties. The strong transitions with relatively small and medium quantum numbers were taken from the normal spectra while weak lines having large J and K_a were visible only in the saturated spectrum. In Fig. 1 there is shown an overview of the central part of the ν_8 band recorded under the two different conditions. It should be noted that we were able to assign the transitions in the ν_6 band with K_a as high as 22. However, they were perturbed by higher vibrational states just as in the main isotopic species [9] and therefore were not used in the fit.

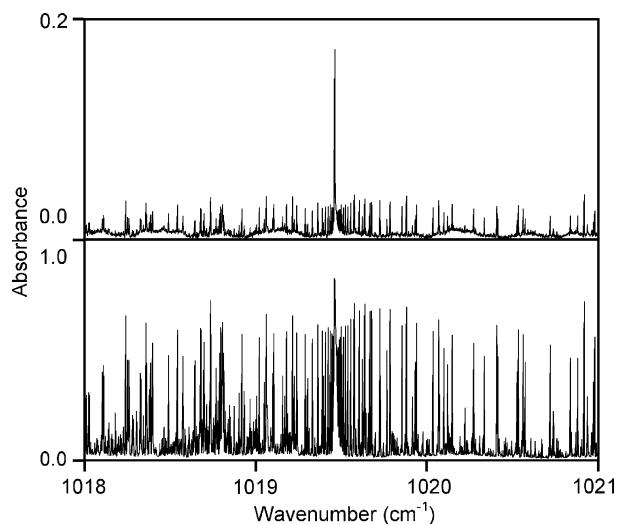


Fig. 1. The central part of the weak ν_8 band of H^{13}COOH measured under the low and high pathlength-pressure conditions.

In order to analyze the infrared bands an effective rovibrational Hamiltonian in the form of a (2×2) operator matrix is required. The rotational Hamiltonians in the diagonal blocks of this matrix determine the energies of the rovibrational levels of the non-interacting vibrational states. The operators in the off-diagonal blocks are responsible for interactions between rotational levels of the two vibrational states. The rotational Hamiltonians in the diagonal blocks have been chosen in the form of Watson's A-reduced Hamiltonian in the I^r representation [10]. The off-diagonal blocks contain rotational operators that are allowed according to the symmetry of the coupled vibrational states. They were taken in the form of sums of terms labeled with the powers of the angular momentum operators:

$$\langle v_i | H | v_j \rangle = \sum_{n,q,r} a_{n,q,r}^{\pm} \hat{h}_{n,q,r}^{\pm},$$

where

$$\hat{h}_{n,q,r}^{\pm} = \hat{J}^{2n} [\hat{J}_a^q, (\hat{J}_+^r \pm \hat{J}_-^r)]_{\pm} \quad \text{when } r \neq 0 \text{ and } q \neq 0,$$

$$\hat{h}_{n,q,0}^{\pm} = \hat{J}^{2n} \hat{J}_a^q \quad \text{when } r = 0,$$

$$\hat{h}_{n,0,r}^{\pm} = \hat{J}^{2n} (\hat{J}_+^r \pm \hat{J}_-^r) \quad \text{when } r \neq 0 \text{ and } q = 0,$$

$\hat{J}_{\pm} = \hat{J}_b \pm \hat{J}_c$ are the angular momentum ladder operators, and $a_{n,q,r}^{\pm}$ are the parameters.

The axes a and b are in the plane of the molecule and the c axis is perpendicular to it. $[\hat{X}, \hat{Y}]_{\pm}$ denotes $\hat{X}\hat{Y} \pm \hat{Y}\hat{X}$. In the present case of vibrational states with different symmetries the sum $q + r$ for $\hat{h}_{n,q,r}^{+}$ operators must be odd, and for $\hat{h}_{n,q,r}^{-}$ operators must be even.

The parameters derived are listed in Tables 1 and 2 together with the spectroscopic constants from Ref. [5] and in addition the interaction parameters for the main isotopic species [11] are given for comparison in Table 2. It should be noted that the ground state parameters were also varied to achieve a better quality of the fit. For this reason we additionally included in the fit known rotational transitions in the ground state used previously for determination of the ground state parameters [12]. Because of relatively large energy gap between two vibrational states under consideration there were not observed any level crossings and local perturbations in the spectra. Nevertheless, to reproduce all the observed features we took into account 6 interaction terms (Table 2), just as for the HCOOH molecule. Total number of assigned IR transitions was 10385 and the RMS deviation of the fit was 0.00024 cm^{-1} .

Table 2
Coriolis interaction parameters of the 6^1 and 8^1 vibrational states of H^{13}COOH

Operator	h operator	HCOOH Ref. [9]	H^{13}COOH Ref. [5]	H^{13}COOH This work
\hat{J}_a	h_{010}^+ /2	MHz 23233.8(4.1)	25647.(100)	24471.6(1.3)
$\hat{J}_+ + \hat{J}_-$	h_{001}^+ /2	MHz 229.3(2.2)	163.(35.)	140.2(4.5)
$\hat{J}_a \hat{J}^2$	h_{110}^+ /2	kHz 308.1(3.7)		281.1(1.3)
\hat{J}_a^3	h_{030}^+ /2	kHz		594.(56.)
$\hat{J}_+^3 + \hat{J}_-^3$	h_{003}^+ /2	kHz 30.89(14)		12.53(37)
$\hat{J}_a \hat{J}^4$	h_{210}^+ /2	Hz $-3.98(75)$		
$(\hat{J}_+^3 + \hat{J}_-^3) \hat{J}^2$	h_{103}^+ /2	Hz $-3.474(91)$		2.48(14)

Table 1
Spectroscopic parameters of the ground vibrational state and diagonal parameters of the 6^1 and 8^1 vibrational states of H^{13}COOH

Parameter ^a		Ground state		6^1 state		8^1 state	
		This work		Ref. [5]	This work	Ref. [5]	This work
E_v	cm^{-1}			1095.403646(30)	1095.403652(11)	1021.539(68)	1019.614990(12)
A	MHz	75580.8778(34)		75621.1(2.2)	75654.569(280)	74533.2(18.9)	75091.267(277)
B	MHz	12053.56852(22)		11995.535(22)	11995.5303(28)	12008.16(1.50)	11999.0964(33)
C	MHz	10378.99938(19)		10311.9435(54)	10311.9650(14)	10378.9987 ^b	10382.0447(25)
Δ_J	kHz	9.92753(25)		10.1303(51)	10.13630(76)	9.2021 ^b	9.71924(97)
Δ_{JK}	kHz	$-84.7562(44)$		$-87.15(18)$	$-82.142(31)$	-84.7993^b	$-76.991(28)$
Δ_K	kHz	1673.021(80)		1647.4(2.8)	1765.39(1.30)	1654.8544 ^b	1547.29(126)
δ_J	kHz	1.98243(12)		2.0455(11)	2.05513(52)	1.9784 ^b	1.8674(12)
δ_K	kHz	41.948(22)		47.76(20)	48.794(68)	42.2887 ^b	25.558(54)
H_J	Hz	0.012313(95)		0.0161(16)	0.01557(20)	0.0093 ^b	0.00623(21)
H_{JK}	Hz	0.098			0.295(19)		0.0603(34)
H_{KJ}	Hz	$-10.266(29)$		$-25.57(60)$	$-30.38(11)$	-10.2889^b	$-7.088(60)$
H_K	Hz	118.70(43)		73.7(3.6)	133.3(1.2)	119.4973 ^b	83.92(31)
h_J	Hz	0.005841(47)		0.0060 ^b	0.00682(11)	0.0060 ^b	0.00429(29)
h_{KJ}	Hz	0.083(10)			$-0.157(21)$		0.083 ^b
h_K	Hz	14.342(71)		12.5613 ^b	19.28(97)	12.5613 ^b	14.342 ^b
L_K	mHz	$-8.65(60)$					
N of lines				3004	5603	0	4782
N of levels					1098		1240
RMS deviation	cm^{-1}			0.00047	0.00027		0.00020

^a Quoted uncertainties of the band centers do not include calibration error.

^b Fixed at the ground state values.

Table 3
Conformation of the assignments of the laser lines from Ref. [2]

CO ₂	CO ₂ emission (cm ⁻¹)	IR absorption observed (cm ⁻¹)	IR absorption calculated (cm ⁻¹)	Emitted frequency measured (MHz)	Emitted frequency calculated (MHz)	Obs. Calc. (MHz)	Pumped transition	Emitted transition	Vib. state	Polarization	Note
9P14	1052.1956	1052.1939	1052.1934	200953.9	200953.6	0.3	9 _{8,1} ← 10 _{9,2}	9 _{8,1} → 8 _{8,1}	6 ^a	II	c
9R30	1084.6352	1084.6331	1084.6330	290953.8	290954.4	-0.6	13 _{3,11} ← 14 _{3,12}	13 _{3,11} → 12 _{3,10}	6	II	c
9R30	Cascade transition			268514.8	268515.1	-0.3	13 _{3,11} ← 14 _{3,12}	12 _{3,10} → 11 _{3,9}	6	II	c
9P12	1053.9235	1053.9240	1053.9239	380004.0	380004.3	-0.3	17 _{6,12} ← 18 _{7,11}	17 _{6,12} → 16 _{6,11}	6 ^a	II	c
9P12	Cascade transition			357589.7	357589.5	0.2	17 _{6,12} ← 18 _{7,11}	16 _{6,11} → 15 _{6,10}	6 ^a	II	c
9R32	1085.7655	1085.7645	1085.7647	523810.4	523810.6	-0.2	24 _{2,23} ← 24 _{2,22}	24 _{2,23} → 23 _{2,22}	6	⊥	c
9P20	1046.8542	—	1046.8537	546225.3	546225.2	0.1	26 _{1,26} ← 27 _{2,25}	26 _{1,26} → 25 _{1,25}	6	II	c
9P24	1043.1632	1043.1612	1043.1611	559214.1	559213.9	0.2	25 _{7,19} ← 26 _{8,18}	25 _{7,19} → 24 _{7,18}	6 ^a	II	c
9R26	1082.2962	1082.2951	1082.2952	668383.6	668383.6	0.0	29 _{3,26} ← 29 _{4,25}	29 _{3,26} → 28 _{3,25}	6	⊥	c
9R26	Cascade transition			645231.8	645232.0	-0.2	29 _{3,26} ← 29 _{4,25}	28 _{3,25} → 27 _{3,24}	6	⊥	c
9P32	1035.4736	1035.4748	1035.4747	761888.8	761889.5	-0.7	34 _{7,28} ← 35 _{8,27}	34 _{7,28} → 33 _{7,27}	6	II	r
9P6	1058.9487	1058.9474	1058.9475	955368.1	955369.0	-0.9	43 _{4,40} ← 44 _{4,41}	43 _{4,40} → 42 _{4,39}	6	II	c
10R32	983.2523	983.2508	983.2507	336434.4	336434.2	0.2	15 _{5,11} ← 16 _{6,11}	15 _{5,10} → 14 _{6,9}	8	II	f
9P30	1037.4341	1037.4345	1037.4344	627229.1	627228.9	0.2	28 _{10,19} ← 27 _{10,17}	28 _{10,19} → 27 _{10,18}	8 ^a	II	f
9P26	1041.2791	1041.2781	1041.2781	784063.1	784063.2	-0.1	35 _{12,23} ← 34 _{12,23}	35 _{12,23} → 34 _{12,22}	8 ^a	II	f
9P24	1043.1632	—	1043.1626	785587.2	785586.8	0.4	35 _{8,28} ← 34 _{8,26}	35 _{8,28} → 34 _{8,27}	8 ^a	II	c

In Tables 3 and 4 the letters in column “Note” mean the following: “c”—confirmation of the previous assignment, “r”—reassignment, “f”—assignment for the first time.

^a Only one component of rotational doublet is given.

Table 4
Assignment of the laser transitions reported in Refs. [3,4]

CO ₂	CO ₂ emission (cm ⁻¹)	IR absorption observed (cm ⁻¹)	IR absorption calculated (cm ⁻¹)	Offset observed (MHz)	Offset calc. (MHz)	Emitted frequency measured (GHz)	Emitted frequency calculated (GHz)	Pumped transition	Emitted transition	Vib. state	Polarization	Note
9R10	1071.8838	1071.8874	1071.8874	115	110	245.8	245.7432	11 _{5,6} ← 11 _{6,5}	11 _{5,6} → 10 _{5,5}	6 ^a	⊥	c
9R30	1084.6351	1084.6331	1084.6330	-30	-65	290.9	290.9544	13 _{3,11} ← 14 _{3,12}	13 _{3,11} → 12 _{3,10}	6	II	f
9R04	1067.5391	1067.5399	1067.5397	-70	20	361.1	361.2792	16 _{3,13} ← 17 _{4,14}	16 _{3,13} → 15 _{3,12}	6	II	f
9P12	1053.9235	1053.9239	1053.9239	-5	10	380.0	380.0045	17 _{6,11} ← 18 _{7,12}	17 _{6,11} → 16 _{6,10}	6 ^a	II	c
9R24	1081.0874	1081.0915	1081.0913	140 (100)	120	402.0	402.2283	18 _{7,11} ← 19 _{7,12}	18 _{7,11} → 17 _{7,10}	6 ^a	II	c
9P10	1055.6251	1055.6205	1055.6204	-135	-140	447.9	447.8861	20 _{5,15} ← 21 _{6,16}	20 _{5,15} → 19 _{5,14}	6	II	c
9R20	1078.5906	1078.5877	1078.5877	-120 (-75)	-90	469.8	469.4503	21 _{7,14} ← 22 _{7,15}	21 _{7,14} → 20 _{7,13}	6 ^a	II	r
9R18	1077.3025	1077.2990	1077.2989	-80 (-90)	-110	488.7	488.9143	22 _{1,21} ← 23 _{1,22}	22 _{1,21} → 21 _{1,20}	6	II	f
9R32	1085.7654	1085.7645	1085.7647	0	-20	523.7	523.8106	24 _{2,23} ← 24 _{2,22}	24 _{2,23} → 23 _{2,22}	6	⊥	f
9R18	1077.3025	—	1077.3005	-80 (-90)	-60	558.6	558.5214	25 _{15,10} ← 26 _{15,11}	25 _{15,10} → 24 _{15,9}	6 ^a	II	r
9P24	1043.1632	1043.1612	1043.1611	0	-65	559.2	559.2139	25 _{7,19} ← 26 _{8,18}	25 _{7,19} → 24 _{7,18}	6 ^a	II	f
9R26	1082.2962	1082.2951	1082.2952	0	-30	668.4	668.3836	29 _{3,26} ← 29 _{4,25}	29 _{3,26} → 28 _{3,25}	6	⊥	f
9R26	Cascade transition					645.0	645.2320	29 _{3,26} ← 29 _{4,25}	28 _{3,25} → 27 _{3,24}	6	⊥	f
9P32	1035.4736	1035.4748	1035.4747	20	35	761.9	761.8895	34 _{7,28} ← 35 _{8,27}	34 _{7,28} → 33 _{7,27}	6	II	f
9P32	1035.4736	1035.4776	1035.4776	20	120	761.9	761.9168	34 _{7,27} ← 35 _{8,28}	34 _{7,27} → 33 _{7,26}	6	II	f
9P16	1050.4413	—	1050.4375	0	-115	1160.2	1159.9723	52 _{5,48} ← 53 _{5,49}	52 _{5,48} → 51 _{5,47}	6	II	f
9P22	1045.0217	—	1045.0220	80 (75)	10	1293.9	1294.2019	57 _{7,50} ← 58 _{7,51}	57 _{7,50} → 56 _{7,49}	6	II	f
10R46	990.6196	990.6210	990.6210	90	40	403.3	403.6630	18 _{6,13} ← 18 _{7,11}	18 _{6,13} → 17 _{6,12}	8 ^a	⊥	f
10R36	985.4883	985.4864	985.4864	-100	-55	405.1	404.9823	18 _{4,14} ← 19 _{5,14}	18 _{4,14} → 17 _{4,13}	8	II	f
9P40	1027.3822	1027.3824	1027.3823	10	5	654.6	654.3924	30 _{1,29} ← 29 _{2,27}	30 _{1,29} → 29 _{1,28}	8	II	f
10P42	922.9143	922.9135	922.9136	-35	-20	717.0	716.7798	32 _{15,18} ← 33 _{16,18}	32 _{15,18} → 31 _{15,17}	8 ^a	II	f
9P48	1018.9007	1018.9024	1018.9025	105	55	818.0	818.1863	38 _{2,37} ← 38 _{1,37}	38 _{2,37} → 37 _{2,36}	8	⊥	f
10R40	987.6202	987.6207	987.6207	0	15	854.1	854.7392	38 _{7,32} ← 39 _{7,32}	38 _{7,32} → 37 _{7,31}	8	II	f
10R28	980.9132	980.9129	980.9127	0	-15	963.7	962.8852	43 _{13,31} ← 44 _{13,31}	43 _{13,31} → 42 _{13,30}	8 ^a	II	f
10P08	954.5451	954.5462	954.5462	20	35	1025.3	1024.4404	48 _{1,47} ← 49 _{2,47}	48 _{1,47} → 47 _{1,46}	8	II	f

The obtained results enabled us to check the assignments of FIR laser emissions observed in [2–4] and also to assign new laser transitions. The action of the optically

pumped laser is based on the creation of a population between rotational levels in the excited vibrational state when pumping IR transition between ground and excited

vibrational states. The ν_6 and ν_8 bands of H^{13}COOH coincide with the CO_2 laser lines. Therefore a CO_2 laser is a suitable source to pump the H^{13}COOH molecule. It was used in [2–4]. The assignments were made by comparing the calculated and observed frequencies of the pumped and emitted transitions together with additional requirement that both transitions possess a common upper level. Moreover the polarization of the FIR radiation relative to that of the pump beam depends upon the selection transition rule of J . All the FIR emissions for the formic acid molecule should be of $^aP_{0,-1}$ type.

Table 3 represents data from [2] while Table 4 is concerned with measurements from Refs. [3,4]. In both tables the column “Note” indicates what laser transition was previously assigned and confirmed, here indicated by letter “c”. Reassigned transitions in the present work are indicated by “r” while transitions assigned for the first time are labeled with “r”. It is worth noting that the molecular parameters in Tables 1 and 2 were obtained solely from the IR transitions which have a measurement uncertainty of 6–10 MHz and no laser line was used in the fit. Nevertheless, the quality of the parameters was high enough to reproduce FIR emissions with accuracy of several hundred kHz (Table 3). Also it should be noted that in Refs. [3,4] an offset of the IR absorption relative to the center frequency of the pump were determined. Measured offset values together with calculated ones are shown in Table 4. A correlation between two sets of offsets, observed and calculated, is equal to 0.83. This also confirms the good quality of the obtained results.

All assigned transitions are listed in the [supplementary material](#).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jms.2008.02.003](https://doi.org/10.1016/j.jms.2008.02.003).

References

- [1] D. Dangoisse, P. Glorieux, in: K.J. Button, M. Inguscio, F. Strumia (Eds.), *Reviews of Infrared and Millimeter Waves, Optically Pumped Far Infrared Lasers*, Vol. 2, Plenum Press, New York, London, 1984, pp. 429–465.
- [2] D. Dangoisse, P. Glorieux, *J. Mol. Spectrosc.* 92 (1982) 283–297.
- [3] G.M.R.S. Luis, E.M. Telles, A. Scalabrin, D. Pereira, *IEEE J. Quantum. Electron.* QE-34 (1998) 767–769.
- [4] A. Bertolini, G. Carelli, C.A. Massa, A. Moretti, F. Strumia, *Infrared Phys. Technol.* 40 (1999) 33–36.
- [5] P.P. Ong, K.L. Goh, H.H. Teo, *J. Mol. Spectrosc.* 194 (1999) 203–205.
- [6] (a) J.M. Flaud, M. Quack, A. Trombetti, G. Duxbury (Eds.), *Proceedings of the Fifteenth Colloquium on High Resolution molecular spectroscopy*, University of Strathclyde, Glasgow, Scotland, 1997, p. 200;
(b) <http://physics.oulu.fi/irspe/sivut/cell40-2002.pdf>.
- [7] V.-M. Horneman, *J. Opt. Soc. Am. B* 21 (2004) 1050–1064.
- [8] V.-M. Horneman. *Instrumental and calculation methods for Fourier transform infrared spectroscopy and accurate standard spectra*. Ph.D. dissertation (University of Oulu, Oulu Finland, 1992) Acta Univ. Oul. A239.
- [9] O.I. Baskakov, I.A. Markov, E.A. Alekseev, R.A. Motiyenko, J. Lohilahti, V.-M. Horneman, B.P. Winnewisser, I.R. Medvedev, F.C. De Lucia, *J. Mol. Struct.* 795 (2006) 54–77.
- [10] J.K.G. Watson, *J. Chem. Phys.* 46 (1967) 1935–1949.
- [11] O.I. Baskakov, J. Demaison, *J. Mol. Spectrosc.* 211 (2002) 262–272.
- [12] M. Winnewisser, B.P. Winnewisser, M. Stein, M. Birk, G. Wagner, G. Winnewisser, K.M.T. Yamada, S. Belov, O.I. Baskakov, *J. Mol. Spectrosc.* 216 (2002) 259–265.