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FTIR and millimeter wave investigation of the 7^1 and 9^1 states of formic acid HCOOH and $H^{13}COOH$

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Abstract

High resolution FTIR spectra of the two overlapping bands ν_7 and ν_9 of the ^{13}C species of formic acid have been measured and analyzed. Rotational transitions in the millimeter wave region were measured and included in the analysis. As in the parent species, there is a strong Coriolis interaction between the 7^1 and 9^1 states. The corresponding IR bands of the parent species have been remeasured and new MMW transitions recorded. The analysis of the spectra for the two species provides an opportunity to consider a reduction of the Hamiltonian employed for the analysis of this type of interacting system of states. Parameters with low correlations could be obtained. Several interstellar features coincide with transitions predicted from these parameters.

Keywords: Formic acid; Vibrational states; Interaction; Perturbation; Reduced Hamiltonian

1. Introduction

The two lowest excited vibrational states of formic acid, 7^1 and 9^1 states, have strong *a*- and *b*-Coriolis coupling and therefore they have been used as a test system for different Hamiltonian models for two interacting vibrational states [1,2]. The coupling is exceptionally strong for HCOOH and DCOOH due to the small separation in vibrational energies compared to the rotational constants. The interaction is somewhat weaker in the case of both HCOOD and DCOOD. The rovibrational energy levels of the 7^1 and 9^1 states have been studied both in the millimeter and submillimeter regions and by means of high resolution FTIR spectroscopy for the parent and all three D substituted isotopomers [2–7]. A comprehensive list of references to spectroscopic studies of formic acid can be found in Ref. [3].

Of the fundamentals of the ^{13}C species only the ν_6 band has previously been investigated with high resolution [8]. Therefore, the primary goal of the present paper was to measure and analyze the high resolution FTIR spectrum of the ν_7/ν_9 fundamental band system of $H^{13}COOH$. For this species the 7^1 and 9^1 states are expected to be as strongly coupled as for the parent species. In addition to the IR transitions, pure rotational transitions in the vibrational states in question were utilized in the analysis.

Although the ν_7 and ν_9 bands of the parent species have been investigated in great detail [3,5], there is still a problem concerning the resulting parameters. Many of the parameters derived in [3] are highly correlated and, consequently, the parameter uncertainties are unusually large. Since the properties of the ν_7 and ν_9 bands in HCOOH and $H^{13}COOH$ are expected to be very similar, the second

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goal of the current work was thus to consider the unsatisfactory correlations determined for HCOOH [3] and to determine a more accurate set of parameters for this species, too. With this object in mind, a new FTIR measurement with higher absorption was carried out for HCOOH and new millimeter wave (MMW) data in the region 115–370 GHz were included. The present measurements provide transitions with higher rotational quantum numbers than those previously available. However, more data did not resolve the problem of correlations.

A reduction scheme has now been defined for the situation presented by the Coriolis interaction, and a corresponding new set of parameters defined for the two interacting states. This reduction scheme and the parameters resulting from the new analysis strategy are presented, together with some interstellar assignments based on the new predictions.

2. Experimental details

The infrared measurements of the ν_9 and ν_7 vibrational bands of HCOOH and isotopically enriched to 99% $H^{13}COOH$ obtained from Sigma–Aldrich were carried out using a Bruker IFS 120HR Fourier spectrometer in Oulu. The spectral range from 400 to 800 cm^{-1} was recorded at room temperature under two different sets of pathlength and sample pressure conditions. The first spectrum for each isotopomers was obtained using 3.2 m and 6.7 Pa, and the second using 38.2 m and 64 Pa. A White-type cell [9] with KBr windows, Globar source at 1400 K, germanium beam splitter between KBr base plates, and liquid-helium-cooled Si-bolometer detector at 1.4 K with a cooled interference filter were employed. The experimental linewidth of small isolated lines is about 0.0015 cm^{-1} resulting from the instrumental and Doppler broadening. The calibration of the $H^{13}COOH$ measurements was performed using water vapor [10] and CO_2 lines [11]. The calibration accuracy, which limits the absolute accuracy, is 48, 55, 62, and 69×10^{-6} cm^{-1} at 500, 600, 700, and 800 cm^{-1}, respectively. For HCOOH, the calibration was performed using only water vapor lines [10], and the values at the same wavenumbers are a little bit worse: 52, 63, 70, and 77×10^{-6} cm^{-1}. A good estimate for the accuracy of a calculated line position or band center is thus the sum of the standard deviation (SD), with reasonable confidence limits, and the calibration accuracy. The optimized center of gravity method [12] was used to calculate the peak positions. For each isotopomer, lines from both the low and high pathlength–pressure spectra were used in the analysis.

The MMW and sub-MMW data in the range 115–370 GHz were obtained from a spectrum obtained using the fast scan sub-MMW spectroscopic technique (FASSST) [13,14] recorded for HCOOH with natural abundance. The sample was heated to 170 °C and the amplification was adjusted to record weak lines. The accuracy of the line positions is estimated to be 50 kHz. Further details may be found in Ref. [14]. In addition several dozen transitions with an accuracy of 10–20 kHz in the range 86–229 GHz were measured individually in Kharkov. A brief description of the spectrometer can be found in Ref. [15].

3. Theory

3.1. Effective Hamiltonian

The effective rotational Hamiltonian for the two Coriolis coupled vibrational states was taken in the form of a 2×2 matrix

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}. \tag{1}$$

Here, the diagonal blocks represent effective rotational Hamiltonians describing unperturbed domains of the rotational levels and the off-diagonal blocks are responsible for the *a*- and *b*-type first order Coriolis interactions and their centrifugal distortion contributions. Diagonal blocks must be Hermitian, invariant to time reversal, i.e. be real, and invariant under operations of C_s symmetry group. Off-diagonal blocks have fewer restrictions. They should be of symmetry $\Gamma^{(i)} = \Gamma^{(A'')}$ which satisfies the relation

$$\Gamma^{(A')} \times \Gamma^{(i)} \times \Gamma^{(A'')} = \Gamma^{(A')},$$

where $\Gamma^{(A')}$ and $\Gamma^{(A'')}$ in the left side are the irreducible representations of the 7^1 and 9^1 vibrational states, respectively. Also, since H is a Hermitian operator, $H_{12} = H_{21}^{\dagger}$. The diagonal and off-diagonal blocks, respectively, can be written in the general forms

$$H_{ii} = \sum_{n,q,r} a^{+}_{ii,nqr} h^{+}_{nqr}, \tag{2}$$

$$H_{ij} = \sum_{n,q,r} a^{+}_{ij,nqr} h^{+}_{nqr} + \sum_{n,q,r} a^{-}_{ij,nqr} h^{-}_{nqr}, \tag{3}$$

where $h^{\pm}_{nqr} = J^{2n}\{J_a^q(J_+^r \pm J_-^r) + (J_+^r \pm J_-^r)J_a^q\}$; J^2, J_a and $J_{\pm} = J_b \pm iJ_c$ are the square and components of angular momentum operators, and $a^{\pm}_{ij,nqr}$ are the parameters. The *a* and *b* axes lie in the plane of molecule. The parameters $a^{+}_{ii,nqr}$ in the diagonal blocks are real and the sum $(q + r)$ can only have even values. In the present case, the interacting vibrational states have different symmetries and therefore the operators h^{+}_{nqr} in the off-diagonal blocks have odd $(q + r)$ and h^{-}_{nqr} operators have even $(q + r)$. Whether the interaction parameters $a^{\pm}_{ij,nqr}$ are real or not depends on the choice of phase factors for vibrational wavefunctions of the states under consideration [2]. If, for example, an A' vibrational function is real and an A'' function is imaginary, then the interaction parameters will be real. Therefore, without loss of generality, the $a^{\pm}_{ij,nqr}$ can be taken to be real.

An effective rotational Hamiltonian in which the interaction between just two states is considered explicitly, taken in the form of an operator matrix (1), is the conventional tool for analysis of the spectra of interacting vibrational states. The diagonal blocks for asymmetric top molecules are conveniently chosen in the form of a Watson-type

Hamiltonian, which is a reduced form of (2). However, the reduced form for the vibrationally off-diagonal blocks is not known, and, as a rule, they are taken as given in Eq. (3), that is, including all leading and higher order terms, as far as they can be determined, in H_{12} of a general form (3). Typically the difficulties encountered when using unreduced Hamiltonians are not important because in most investigations only a few interaction parameters are needed to match the observed transition frequencies, and these are well determined. However, in cases of strong interactions and the availability of precise and extensive measurements over a wide range of J, the number of coupling parameters becomes large, and it becomes necessary to reduce the whole Hamiltonian rather than just the diagonal blocks individually. The Coriolis interaction between the 7^1 and 9^1 states of formic acid, as can be seen from the results of the last paper [3], is obviously such a case. Therefore, in the next subsection the procedure employed in the present work of reducing the Hamiltonian (1) is discussed.

3.2. Reduction of the Hamiltonian

It is well known that in general an effective Hamiltonian (1) is not unique. To eliminate the indeterminacy, some parameters have to be constrained to fixed values. If one knows what parameters are probably not large or physically important, and thus can be fixed, they are chosen, as a rule, to be 0, and in this case it is said that the terms with these zero parameters have been removed. The procedure of removing the “superfluous” parameters or, in other words, of reducing the effective Hamiltonian, was first developed by Watson [16] for the case of an asymmetric top molecule in an unperturbed vibrational state.

In contrast to the case of a single unperturbed vibrational state, the problem of reducing the effective Hamiltonian for several interacting states has to be solved individually for each particular case. The optimum form of the reduced Hamiltonian depends on a variety of properties of the system, such as the symmetry of the molecule and the number and symmetries of the vibrational states involved in the interaction, the kind and magnitude of the interactions, and the energy differences between the states. Also, it is important to know [16] the relations between the magnitudes of the terms in the expansion of the Hamiltonian and the total power of the angular momentum operators of these terms; the rules giving the magnitudes of the terms in off-diagonal blocks can differ from those existing for diagonal blocks.

In the present study, the problem of indeterminacy of the effective Hamiltonian is considered for the particular case of two Coriolis coupled vibrational states of A' and A'' symmetry of a molecule belonging to the C_s point group. The energy difference between the states is ca. 10 cm^{-1}, that is, of the order of the rotational parameters, and therefore the a- and b-type Coriolis interactions are very strong. The problem of constructing the reduced Hamiltonian for two interacting vibrational states of an asymmetric top molecule has been considered previously by Perevalov and Tyuterev [1,17]. However, in these studies there are some shortcomings, making the practical use of the results problematic. In particular, in paper [1] only terms up to the second power of angular momentum in the interaction operator have been considered. In both studies [1,17] the zero order Coriolis coupling parameters in H_{12} are treated as being of the order of $\lambda\bar{B} = (\bar{B}/\bar{\omega})^{1/2}\bar{B}$. In this expression $\lambda = (\bar{B}/\bar{\omega})^{1/2}$ is a small parameter, since $\bar{B}$ and $\bar{\omega}$ are averages of the rotational constants and the vibrational frequencies, respectively. However, for many molecules, and particularly for the 7^1 and 9^1 states of formic acid, the coupling parameters are of the order of $\bar{B}$. Also, in spite of the generality of the procedure in [17], the coordinate representation was chosen inconveniently (z axis is along b axis), so that it is not possible to determine which interaction parameters should remain in the reduced Hamiltonian in the present study. These reasons led us to reconsider the reduction of the effective rovibrational Hamiltonian for the present given case.

As is well known, the reduced and original Hamiltonians are related through a unitary transformation

$$H_{\text{red}} = \text{UHU}^{\dagger} = \mathrm{e}^{\mathrm{i}S} H \mathrm{e}^{-\mathrm{i}S}, \tag{4}$$

where S is a Hermitian operator. In the case of two interacting vibrational states S also has the form of a (2×2)-operator matrix

$$S = \begin{pmatrix} S_{11} & \sigma \\ \sigma^{\dagger} & S_{22} \end{pmatrix},$$

where S_{11}, S_{22} and σ are operators which can be expanded in a power series in the angular momentum operators. To conserve the overall properties of H in H_{red}, S_{11} and S_{22} should be imaginary, totally symmetric and Hermitian. From this we write

$$S_{ii} = \sum_{n,q,r} \mathrm{i} d^{-}_{ii,nqr} h^{-}_{nqr},$$

where $d^{-}_{ii,nqr}$ are real parameters and $(q + r)$ is odd. The properties of σ differ from the properties of the operators in the off-diagonal block H_{12} by a factor of i. One more important property which has to be conserved under transformation (4) is the magnitudes of the terms in the original Hamiltonian. Formal estimations for the orders of magnitudes of the parameters in the effective rotational Hamiltonian are stated to be $\bar{B}\lambda^{2(m-2)}$ [16] where m is the total power of all angular momentum operators, equal to $2n + q + r$ in the $h^{\pm}_{nqr}$ operators.

In practice, the final reduced Hamiltonian H_{red} is obtained through several successive unitary transformations, i.e.

$$\begin{aligned} H^{(1)} &= \mathrm{e}^{\mathrm{i}S^{(1)}} H^{(0)} \mathrm{e}^{-\mathrm{i}S^{(1)}}, \\ H^{(2)} &= \mathrm{e}^{\mathrm{i}S^{(2)}} H^{(1)} \mathrm{e}^{-\mathrm{i}S^{(2)}}, \\ &\;\;\cdots \\ H_{\text{red}} = H^{(m)} &= \mathrm{e}^{\mathrm{i}S^{(m)}} H^{(m-1)} \mathrm{e}^{-\mathrm{i}S^{(m)}}. \end{aligned} \tag{5}$$

Hamiltonian $H^{(0)}$ in the first row of Eq. (5) denotes the original untransformed Hamiltonian H and the aim of each single transformation is to eliminate certain "excessive" terms of the same order of magnitude. To know the explicit expressions for $S^{(k)}$ one has to solve the Eq. (5) with zeros in the transformed Hamiltonians $H^{(k)}$ on the left side in place of those terms which should be removed. The number of omitted terms must be equal to the number of free parameters in $S^{(k)}$, which are the solutions of the Eq. (5). Since the Hamiltonian terms that are to be eliminated are small in magnitude and are of known order of smallness, the operators $S^{(k)}$ should also be small. This fact allows us to linearize the set of Eq. (5): by replacing $\mathrm{e}^{\pm\mathrm{i}S}$ by $(1 \pm \mathrm{i}S)$ in Eq. (5) one obtains

$$\begin{aligned}
H_{11}^{(i)} - H_{11}^{(i-1)} &= \mathrm{i}[S_{11}^{(i)}, H_{\mathrm{R}}] + \mathrm{i}(\sigma^{(i)} H_{\mathrm{G}}^{\dagger} - H_{\mathrm{G}}\sigma^{(i)\dagger}) \\
H_{22}^{(i)} - H_{22}^{(i-1)} &= \mathrm{i}[S_{22}^{(i)}, H_{\mathrm{R}}] + \mathrm{i}(\sigma^{(i)\dagger} H_{\mathrm{G}} - H_{\mathrm{G}}^{\dagger}\sigma^{(i)}) \\
H_{12}^{(i)} - H_{12}^{(i-1)} &= \mathrm{i}[\sigma^{(i)}, H_{\mathrm{R}}] + \mathrm{i}\sigma^{(i)}(E_2 - E_1) \\
&\quad + \mathrm{i}(S_{11}^{(i)} H_{\mathrm{G}} - H_{\mathrm{G}} S_{22}^{(i)}),
\end{aligned} \tag{6}$$

where H_{R} is the rotational Hamiltonian of a rigid asymmetric top,

$$H_{\mathrm{R}} = \frac{B+C}{4} h_{1,0,0}^{+} + \frac{2A-B-C}{4} h_{0,2,0}^{+} + \frac{B-C}{4} h_{0,0,2}^{+}, \tag{7}$$

H_{G} is the first order Coriolis coupling operator, i.e. the main constituent of the off-diagonal block of the effective Hamiltonian,

$$H_{\mathrm{G}} = a_{12,010}^{+} h_{0,1,0}^{+} + a_{12,001}^{+} h_{0,0,1}^{+},$$

and $E_2 - E_1$ is the energy difference between the two vibrational states. All three of these values are assumed in the present case to be of the same order of magnitude as $\bar{B}$. Eq. (6) require that to remove Hamiltonian terms on the order of $\bar{B}\lambda^{m}$, the operators $S_{kk}^{(i)}$ and $\sigma^{(i)}$ should be of the order of λ^{m}.

To analyze and consider the possible solutions of the set of equations defining σ and S_{kk}, Table 1 presents some generalized data concerning a single unitary transformation. The power p in the table is the total power of the angular momentum operators in the generators σ and S_{kk} and the terms in Column "Term in Eq. (6)" have the same order of magnitude. It is worth noticing that both S_{kk} and σ change diagonal as well as off-diagonal blocks of the Hamiltonian. Column "Power of affected term in H" shows only the powers of those terms which should be eliminated and which are used to determine the generators of the transformation in Eq. (6). The powers of these terms are expressed through the power p of the terms in S_{kk} or σ.

It is seen from Table 1 (columns "Power of affected term in H") that the solutions of Eq. (6) can be chosen in two ways: to eliminate the terms in the Hamiltonian with powers $m = p$ or with powers $m = p + 1$. The first case, with power p, proves to be improper since after its implementation some of the remaining terms in the Hamiltonian become of lower order. Indeed, in this case the leading term in Eq. (6) is $\mathrm{i}\sigma^{(i)}(E_2 - E_1)$ and as a consequence the terms in $\sigma^{(i)}$ should be on the order of $\lambda^{2(p-2)}$. However, at the same time $\sigma^{(i)}$ determined in this way, in other terms of Eq. (6) (for instance in $[\sigma^{(i)}, H_{\mathrm{R}}]$), will modify the terms of power $m = p + 1$ (Table 1) and consequently the initial order $\bar{B}\lambda^{2(p-1)}$ of these terms changes to a greater value $\bar{B}\lambda^{2(p-2)}$. On the other hand, if the terms of power p in $\sigma^{(i)}$ are employed to exclude the Hamiltonian terms of power $m = p + 1$, then, all other terms changed will be of the right order. So in Table 1 only the terms with $m = p + 1$ in the columns "Power of affected term in H" need be considered for elimination.

It is not actually necessary to solve Eq. (6) to specify the ultimate form of the reduced Hamiltonian. The final goal of the reduction is to determine how many and what are the terms that are required in the final Hamiltonian. The number of remaining terms of each power is merely calculated as the difference between the number of parameters in the original Hamiltonian and the number of independent parameters in the generators $S_{kk}^{(i)}$ and $\sigma^{(i)}$. The number of remaining terms in each power is given in Table 1 in the corresponding columns.

The operators $S_{kk}^{(i)}$ are used to simplify the diagonal blocks and bring them into the form of Watson's reduced Hamiltonian. In the present case this can be done since, as seen in Table 1, operators $S_{kk}^{(i)}$ used for this purpose

Table 1
Transformation of the Hamiltonian involving operators in $\sigma^{(i)}$ or $S_{kk}^{(i)}$ of power p

Index	Term in Eq. (6) to be employed	Affected block of H	$h_{n,q,r}^{+}$ in $\sigma^{(i)}$ p[a] is odd for $\sigma^{(i)}$			$h_{n,q,r}^{-}$ in $\sigma^{(i)}$ or $S_{kk}^{(i)}$ p is even for σ and odd for $S_{kk}^{(i)}$		
			Affected term in H	Power of affected term in H	Number of remaining terms	Affected term in H	Power of affected term in H	Number of remaining terms
1	$[\sigma^{(i)}, H_{\mathrm{R}}]$	H_{12}	h^{-}	$m = p + 1$	0	h^{+}	$m = p + 1$	$m + 1$
2	$\sigma^{(i)}(E_2 - E_1)$	H_{12}	h^{+}	$m = p$	0	h^{-}	$m = p$	0
3	$(\sigma^{(i)} H_{\mathrm{G}}^{\dagger} - H_{\mathrm{G}}\sigma^{(i)\dagger})$	H_{kk}	h^{+}	$m = p + 1$	$(m + 2)/2$	h^{+}	$m = p$	$(m + 2)/2$
4	$[S_{kk}^{(i)}, H_{\mathrm{R}}]$	H_{kk}	—	—	—	h^{+}	$m = p + 1$	$m + 1$
5	$(S_{11}^{(i)} H_{\mathrm{G}} - H_{\mathrm{G}} S_{22}^{(i)})$	H_{12}	—	—	—	h^{+}	$m = p$[b]	0

[a] $p = 2n + q + r$ in $\sigma^{(i)}$ or $S_{kk}^{(i)}$. m is a power of the terms to be excluded in the Hamiltonian.

[b] Under assumption $S_{11}^{(i)} \sim S_{22}^{(i)}$.

(4th row) do not alter the orders of the terms of the off-diagonal block (5th row). After that, the reduction of the off-diagonal block can be carried out to bring it into a form which will not contain h^- operators at all and in which there will be only $m+1$ operators of the type h^+ for each power m (see the first row of Table 1). The properties of the ultimately transformed interaction block under these considerations are determined only by the commutator $[\sigma^{(i)}, H_\mathrm{R}]$. All other parts of Eq. (6) have a bearing only on the numerical values of the parameters of the remaining terms of the reduced Hamiltonian.

There are two terms in H_R (7) which do not commute with $\sigma^{(i)}$ and so can contribute to $[\sigma^{(i)}, H_\mathrm{R}]$. They contain the operators $h^+_{0,2,0}$ and $h^+_{0,0,2}$. The formulas for the commutators of each term of $\sigma^{(i)}$ with these operators are as follows:

$$
\begin{aligned}
[h^\pm_{n,q,r}, h^+_{0,0,2}] \approx & -4qh^\mp_{n,q-1,r+2} + \quad \text{for any } r \\
& 4qh^\mp_{n+2,q-1,r-2} - 8(q+r)h^\mp_{n+1,q+1,r-2} + \\
& 4(q+2r)h^\mp_{n,q+3,r-2}, \quad \text{if } r >= 2 \\
& qh^\mp_{n+1,q-1,1} - 4(q+r)h^\mp_{n,q+1,1} \quad \text{if } r = 1
\end{aligned}
\tag{8}
$$

$$
[h^\pm_{n,q,r}, h^+_{0,2,0}] \approx 4rh^\mp_{n,q+1,r}. \tag{9}
$$

Table 2
Number of the terms $h^\pm_{nqr}$ of a given power m in the off-diagonal blocks

Term	Parity of $m = 2n+q+r$	Number of the terms
h^+_{nqr}	Odd	$\frac{(m+1)(m+3)}{4}$
h^-_{nqr}	Even	$\frac{m(m+2)}{4}$

In these expressions only the terms with the largest power of angular momentum operators have been kept since they are the ones responsible for the omitted terms in the reduced Hamiltonian.Further terms have only minor effects on the numerical values of the parameters, as described above.From formulas (8) and (9) one can see that h^+ and h^- terms in $\sigma^{(i)}$ have correspondingly an influence on the terms of the form h^- and h^+ in the Hamiltonian and that the powers of those terms of the Hamiltonian which are influenced are greater by one than the powers of the $\sigma^{(i)}$ terms. Table 2 contains expressions for the number of terms of type h^+ and h^- of a given power in the operators $\sigma^{(i)}$ and H_{12}, taking into account the allowed parity of the powers (3).Using the data from this Table it is readily possible to show (the results are in Table 1) that there are $m+1$ operators (and no more) of the type h^+_{nqr} with power $m = 2n+q+r$ that can remain in the off-diagonal blocks of the reduced Hamiltonian and no terms of the type h^-_{nqr}.However, it is interesting to note that during the fitting of the ν_7 and ν_9 data of formic acid the fitting program suggested that in the interaction blocks only the terms with operators $h^+_{n,0,r}$ and $h^+_{n,q,0}$ should be used.At every iteration stage of the fitting, the program written and used in the Kharkov laboratory is able to determine by itself the "best" or "most significant" set of the parameters to be changed, based on their significance and statistical properties.The only explanation for the selection the program makes in the present case is that formic acid is a nearly

Table 3
Parameters of the ground state and diagonal parameters of the 7^1 and 9^1 states of HCOOH

		Ground state		7^1 State		9^1 State	
		Ref. [18]	This work	Ref. [3]	This work	Ref. [3]	This work
E_v	cm^{-1}			626.16561(39)	626.1657424(29)[a]	640.72506(39)	640.7251753(29)[a]
A	MHz	77512.2355(11)	77512.22867(53)	77755.329(920)	77929.1712(43)	77685.036(930)	77511.5582(42)
B	MHz	12055.10645(19)	12055.10525(9)	12034.7345(640)	12048.48592(19)	12006.8924(650)	11993.21926(20)
C	MHz	10416.11512(19)	10416.11449(9)	10394.97265(450)	10394.74866(15)	10405.28011(370)	10405.06463(14)
Δ_J	kHz	9.99603(23)	9.99422(11)	9.92375(220)	9.93946(18)	9.94380(110)	9.92159(21)
Δ_{JK}	kHz	−86.2486(20)	−86.2205(12)	−81.9711(350)	−85.3359(49)	−86.9102(120)	−83.4150(51)
Δ_K	kHz	1702.447(15)	1702.2617(69)	1760.374(730)	1783.57(49)	1700.798(920)	1677.43(48)
δ_J	kHz	1.948815(32)	1.948563(21)	1.92233(110)	1.93266(13)	1.92236(110)	1.90898(13)
δ_K	kHz	42.7318(48)	42.7741(24)	46.653783(130)	46.507(18)	40.576683(120)	39.573(20)
H_J	Hz	0.013143(97)	0.012669(46)	0.013143[b]	0.010595(54)	0.013143[b]	0.012011(64)
H_{JK}	Hz	0.1021(60)	0.1162(22)	0.1021[b]	−0.1715(29)	0.1021[b]	−0.1454(27)
H_{KJ}	Hz	−10.565(23)	−10.6097(89)	−10.565[b]	−10.198(27)	−10.565[b]	−9.287(30)
H_K	Hz	121.195(76)	120.370(37)	147.71(340)	130.17(44)	101.14(470)	116.61(44)
h_J	Hz	0.005763(12)	0.005805(11)	0.005763[b]	0.004981(44)	0.005763[b]	0.005320(42)
h_{KJ}	Hz	0.0975(32)	0.0937(19)	0.0975[b]		0.6012(120)	0.1042(92)
h_K	Hz	14.82(33)	14.95(10)	14.82[b]		14.82[b]	
L_J	mHz	−0.0000719(93)	−0.0000390(21)				
L_{JJK}	mHz		−0.00211(21)				
L_{KJ}	mHz	−0.0397(56)		−0.0397[b]		−0.0397[b]	
L_{KKJ}	mHz	0.875(34)	0.868(12)	0.875[b]		0.875[b]	1.681(28)
L_K	mHz	−11.82(11)	−10.700(44)	−11.82[b]	−10.11(41)	−11.82[b]	−11.68(42)
l_J	mHz		−0.0000160(12)				
l_K	mHz		0.860(70)				

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

[b] Fixed at the value in the ground state.

prolate symmetric top with the coefficients $\frac{2A-B-C}{4} = 33.17$ GHz and $\frac{B-C}{4} = 0.41$ GHz multiplying the operators h^{+}_{020} and h^{+}_{002}, respectively, in H_{R} (7).These numerical values differ by a factor of 80 and therefore, the preferred way to reduce the off-diagonal blocks is to use only the expression (9) since it is based on the operator h^{+}_{020} in H_{R}.This additional restriction leads to the result that it is only the operator types $h^{+}_{n0r} = 2J^{2n}(J^{r}_{+} + J^{r}_{-})$ and $h^{+}_{nq0} = 2J^{2n}J^{q}_{a}$ which can not be deleted from the Hamiltonian. It is also satisfying to note that the number of such operators of power m is precisely equal to the required value, $m + 1$.

4. Results

The ν_7 band of formic acid is a hybrid *a*/*b*-type band, while the ν_9 band is a *c*-type band. Accurate values for the unperturbed band centers are given in Tables 3 and 4. Since the separation in the vibrational energies is less than 20 cm^{-1}, the bands are strongly overlapped. Identification of the FTIR transitions of the ν_7 and ν_9 bands of the parent species HCOOH was performed by straightforward calculation of the transition wavenumbers using parameters of the excited states from Ref. [3] and of the ground state from Ref. [18]. The initial assignment of the transitions

Table 4
Parameters of the ground state and diagonal parameters of the 7^1 and 9^1 states of $H^{13}COOH$

		Ground state		7^1 State	9^1 State
		Ref. [18]	This work	This work	This work
E_v	cm^{-1}			621.5988882(53)[a]	639.0757555(50)[a]
C	MHz	10379.00043(35)	10378.99871(16)	10357.12859(70)	10368.02239(64)
A	MHz	75580.8793(38)	75580.8205(20)	76003.709(24)	75592.241(24)
B	MHz	12053.56994(39)	12053.56907(17)	12047.0957(11)	11991.50788(89)
Δ_J	kHz	9.92824(41)	9.92604(22)	9.87185(41)	9.85198(42)
Δ_{JK}	kHz	−84.7762(74)	−84.7022(22)	−83.713(20)	−82.038(20)
Δ_K	kHz	1673.020(64)	1670.588(24)	1745.77(78)	1652.78(78)
δ_J	kHz	1.98247(12)	1.982587(92)	1.96650(42)	1.94266(32)
δ_K	kHz	41.971(24)	41.996(19)	45.901(35)	38.5756(24)
H_J	Hz	0.001246(11)	0.011898(79)	0.010182(96)	0.010613(98)
H_{JK}	Hz	0.098(15)	0.0978(81)	−0.1941(56)	−0.1616(55)
H_{KJ}	Hz	−10.440(63)	−9.871(28)	−9.086(48)	−8.778(47)
H_K	Hz	116.94(29)	107.90(58)	118.24(55)	105.71(55)
h_J	Hz	0.005834(41)	0.005865(31)	0.00556(11)	0.005372(78)
h_{KJ}	Hz	0.0975[b]	0.0982(64)		
h_K	Hz	14.41(75)	14.10(40)		
L_{JJK}	mHz		−0.00431(37)		
L_K	mHz		2.501(35)		

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

[b] Fixed at the value for the parent specie.

Table 5
Interaction parameters of the 7^1 and 9^1 states of HCOOH and $H^{13}COOH$

Operator	h Operator		HCOOH		$H^{13}COOH$
			Ref. [3]	This work	This work
J_z	$h^{+}_{010}/2$	MHz	31514.52(620)[a]	32695.284(27)	32383.63(19)
$J_+ + J_-$	$h^{+}_{001}/2$	MHz	3937.105(850)[b]	4123.0901(16)	4088.793(11)
$J^2_+ - J^2_-$	$h^{-}_{002}/2$	MHz	5.1659(165)[a]		
$[J_+ - J_-, J_z]_+$	h^{-}_{011}	MHz	−14.5065(1200)[b]		
$[J_+ + J_-, J^2_z]_+$	h^{+}_{021}	kHz	675.315(550)		
J_zJ^2	$h^{+}_{110}/2$	kHz	90.5143(120)	32.692(41)	35.53(15)
J^3_z	$h^{+}_{030}/2$	kHz		−728.2(33)	−745.2(63)
$(J_+ + J_-)J^2$	$h^{+}_{101}/2$	kHz		−18.0392(44)	−17.783(13)
$J^3_+ + J^3_-$	$h^{+}_{003}/2$	kHz		0.3683(20)	0.4633(72)
J_zJ^4	$h^{+}_{210}/2$	Hz		−0.376(11)	−0.411(28)
$(J_+ + J_-)J^4$	$h^{+}_{201}/2$	Hz		−0.0597(27)	−0.0847(42)
$(J^3_+ + J^3_-)J^2$	$h^{+}_{103}/2$	Hz		−0.0267(26)	
J^5_z	$h^{+}_{050}/2$	Hz		175.6(52)	152.9(78)
J^7_z	$h^{+}_{070}/2$	mHz		−28.9(23)	−28.7(28)
$J^7_+ + J^7_-$	$h^{+}_{007}/2$	mHz		−0.00444(34)	

[a,b] Two sets of highly correlated parameters are indicated by a and b, respectively.

for $H^{13}COOH$ was based on the similarity of the bands for the two isotopic species. Prominent $^{R}Q_{K_a}$ or $^{P}Q_{K_a}$ subbranches were assigned, without initially looking for small K_a values, through implementation of the method of combination differences. Ground state parameters for this species were known from [18]. Fig. 1 presents the $^{R}Q_{K_a=9}$ subbranch of the ν_7 band of $H^{13}COOH$ used for primary identifications, indicating the quality of the spectra obtained. However, assigning the low K_a transitions was a problem. It is seen from Fig. 2 that the rotational levels of the 7^1 and 9^1 vibrational states have a highly complex behavior for $K_a \leqslant 4$, where they cross, mix and change vibrational identification, while the higher K_a branches of both vibrational states alternate without crossings or obvious mixing. Fortunately, we were able to find several series of lines with low K_a which simplified the procedure of identification. Two subbranches in the ν_7 band, $^{Q}P_{K_a=0}$ and $^{Q}P_{K_a=1}$, are shown in a Loomis-Wood diagram in Fig. 3.

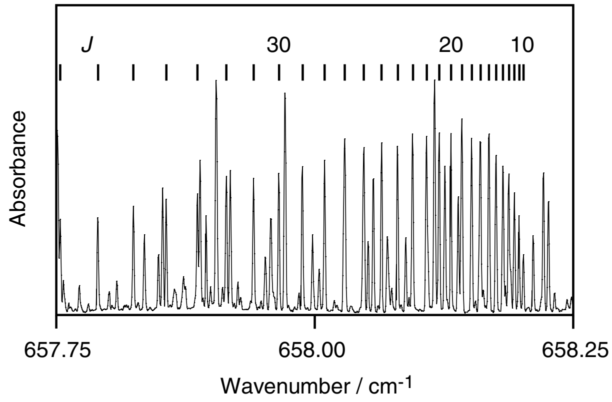

Fig. 1. $^{R}Q_{K_a=9}$ subbranch of the ν_7 band of $H^{13}COOH$.

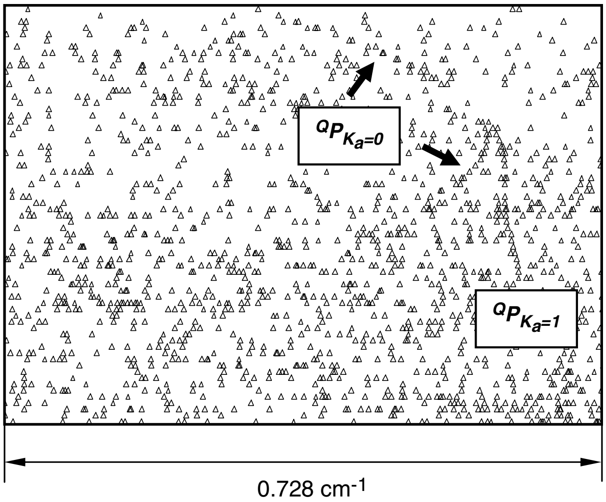

Fig. 3. Loomis–Wood diagram with the observed $^{Q}P_{K_a=0}$ and $^{Q}P_{K_a=1}$ subbranches in the ν_7 band of $H^{13}COOH$. The period of the successive rows of the diagram is $0.728\ cm^{-1}$. The upper left corner corresponds to $586\ cm^{-1}$, and the lower right corner is approximately $630\ cm^{-1}$. The positions of the observed lines are given by triangles, the sizes of which are proportional to intensity. To improve the quality of the figure, the intensity range was limited. For this reason some lines in the various series are missing.

All assigned FTIR transitions and available rotational lines in the excited vibrational states were fitted for both HCOOH and $H^{13}COOH$ using the Hamiltonian (1), where the diagonal blocks were taken in the form of Watson's A-reduced effective Hamiltonian in the I^r coordinate representation and the off-diagonal blocks contained rotational operators only of types $h^{+}_{n,0,r}$ and $h^{+}_{n,q,0}$. IR transitions for each isotopic species have been collected from two different observations. Weak transitions with high J and K_a were compiled from the spectra obtained with a long absorption

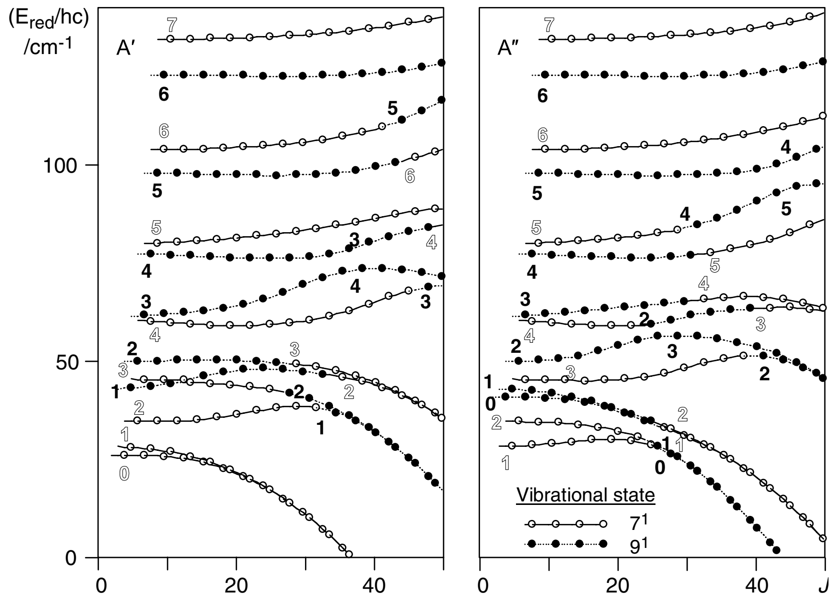

Fig. 2. Reduced energy levels of the 7^1 and 9^1 states of $H^{13}COOH$. $(E_{red}/hc) = (E/hc)$-600-0.374313 $J(J+1)$; the factor is selected for convenience in plotting; it is close to $(B+C)/2$.

Table 6
MMW transitions in the 7^1 state of $H^{13}COOH$

Frequency (MHz)	Upper level			Lower level			O − C (MHz)
	J	K_a	K_c	J	K_a	K_c	
154447.56	7	0	7	6	0	6	−0.02
175981.53	8	0	8	7	0	7	0.07
197333.00	9	0	9	8	0	8	−0.04
218504.68	10	0	10	9	0	9	0.06
239508.78	11	0	11	10	0	10	−0.04
260367.32	12	0	12	11	0	11	0.05
301760.53	14	0	14	13	0	13	−0.01
322354.35	15	0	15	14	0	14	0.03
342913.87	16	0	16	15	0	15	−0.02
363458.40	17	0	17	16	0	16	−0.04
160915.77	7	1	6	6	1	5	−0.01
183732.08	8	1	7	7	1	6	−0.09
206471.40	9	1	8	8	1	7	0.07
229118.07	10	1	9	9	1	8	−0.05
251655.37	11	1	10	10	1	9	−0.06
274064.20	12	1	11	11	1	10	−0.01
296323.29	13	1	12	12	1	11	−0.09
318410.30	14	1	13	13	1	12	−0.02
340301.31	15	1	14	14	1	13	−0.03
361972.89	16	1	15	15	1	14	0.01
157211.57	7	2	5	6	2	4	0.01
180095.95	8	2	6	7	2	5	0.09
203119.54	9	2	7	8	2	6	−0.01
226274.14	10	2	8	9	2	7	0.00
249540.42	11	2	9	10	2	8	−0.07
272889.81	12	2	10	11	2	9	−0.06
296286.64	13	2	11	12	2	10	−0.09
319692.28	14	2	12	13	2	11	−0.04
343068.08	15	2	13	14	2	12	−0.08
366378.59	16	2	14	15	2	13	0.02
222771.22	10	3	7	9	3	6	0.01
268449.33	12	3	9	11	3	8	−0.02
291216.79	13	3	10	12	3	9	0.00
314034.17	14	3	11	13	3	10	−0.05
177500.53	8	4	4	7	4	3	0.01
199812.83	9	4	5	8	4	4	−0.01
222166.46	10	4	6	9	4	5	−0.02
267013.96	12	4	8	11	4	7	0.01
289516.19	13	4	9	12	4	8	0.05
312075.97	14	4	10	13	4	9	−0.03
334697.01	15	4	11	14	4	10	0.01
357381.54	16	4	12	15	4	11	−0.02
197654.84	9	5	4	8	5	3	0.01
242759.32	11	5	6	10	5	5	0.00
265301.91	12	5	7	11	5	6	0.00
287851.70	13	5	8	12	5	7	0.02
310415.06	14	5	9	13	5	8	−0.01
332997.33	15	5	10	14	5	9	0.02
355603.07	16	5	11	15	5	10	0.00
158584.65	7	6	1	6	6	0	−0.02
181176.97	8	6	2	7	6	1	0.04
203756.00	9	6	3	8	6	2	0.03
226324.39	10	6	4	9	6	3	−0.04
248885.18	11	6	5	10	6	4	0.06
180131.89	8	7	1	7	7	0	0.09
202650.22	9	7	2	8	7	1	0.10
225169.57	10	7	3	9	7	2	0.00
247690.54	11	7	4	10	7	3	0.03
292738.56	13	7	6	12	7	5	0.06
315266.57	14	7	7	13	7	6	0.06
337797.93	15	7	8	14	7	7	0.03
360333.25	16	7	9	15	7	8	0.02

(*continued on next page*)

Table 6 (*continued*)

Frequency (MHz)	Upper level			Lower level			O − C (MHz)
	J	K_a	K_c	J	K_a	K_c	
202260.94	9	8	1	8	8	0	0.02
224740.65	10	8	2	9	8	1	0.05
247222.37	11	8	3	10	8	2	0.04
269706.36	12	8	4	11	8	3	0.00
292192.99	13	8	5	12	8	4	0.08
314682.32	14	8	6	13	8	5	0.07
337174.69	15	8	7	14	8	6	0.06
359670.41	16	8	8	15	8	7	0.06
224538.63	10	9	1	9	9	0	0.06
269459.01	12	9	3	11	9	2	0.09
291921.67	13	9	4	12	9	3	0.04
314386.31	14	9	5	13	9	4	0.06
336852.96	15	9	6	14	9	5	0.05
171591.29	8	1	8	7	1	7	0.04
214113.87	10	1	10	9	1	9	0.00
235300.73	11	1	11	10	1	10	−0.04
256437.58	12	1	12	11	1	11	−0.03
298565.47	14	1	14	13	1	13	0.08
319560.36	15	1	15	14	1	14	0.00
361426.71	17	1	17	16	1	16	−0.03
133445.80	6	2	5	5	2	4	0.06
155594.13	7	2	6	6	2	5	−0.05
177699.85	8	2	7	7	2	6	0.09
221757.07	10	2	9	9	2	8	−0.01
243695.79	11	2	10	10	2	9	−0.02
265565.61	12	2	11	11	2	10	−0.01
309069.88	14	2	13	13	2	12	−0.06
330689.31	15	2	14	14	2	13	0.02
352209.18	16	2	15	15	2	14	−0.06
373620.89	17	2	16	16	2	15	−0.01
178039.32	8	3	6	7	3	5	−0.01
200334.68	9	3	7	8	3	6	−0.02
222637.97	10	3	8	9	3	7	0.00
244944.95	11	3	9	10	3	8	−0.02
311828.58	14	3	12	13	3	11	0.01
334085.53	15	3	13	14	3	12	0.00
356308.88	16	3	14	15	3	13	−0.06
132983.61	6	4	3	5	4	2	−0.07
155224.09	7	4	4	6	4	3	−0.08
177497.07	8	4	5	7	4	4	0.04
199805.43	9	4	6	8	4	5	0.04
222152.38	10	4	7	9	4	6	−0.02
244541.64	11	4	8	10	4	7	0.01
266977.67	12	4	9	11	4	8	−0.06
289467.49	13	4	10	12	4	9	−0.06
312021.87	14	4	11	13	4	10	−0.08
334659.02	15	4	12	14	4	11	0.00
197653.70	9	5	5	8	5	4	−0.05
220212.63	10	5	6	9	5	5	0.00
265293.17	12	5	8	11	5	7	0.03
287836.30	13	5	9	12	5	8	0.02
310389.34	14	5	10	13	5	9	−0.03
355539.74	16	5	12	15	5	11	−0.02

path length where the strong lines were totally absorbing. These transitions were merged in the fit with transitions having lower rotational quantum numbers from the spectrum recorded with lower pressure and path length. This gave us about 40% more rotational levels in the 7^1 and 9^1 states than were available in Ref. [3]. The new FTIR data are listed in the supplementary tables in Tables S1–S4. For the parent species, 661 MMW transitions belonging to the 7^1 and 9^1 states were assigned in the FASSST and Kharkov spectra. They are listed in the supplementary data in Table S6. Also, all rotational transitions in the excited states from Ref. [3] which were not superseded by the FASSST measurements were employed in the fit. They are also included in Table S6. For $H^{13}COOH$ we were able to assign 224 FASSST rotational lines in these vibrational states which are given in Tables 6 and 7. A summary of

Table 7
MMW transitions in the 9^1 state of $H^{13}COOH$

Frequency (MHz)	Upper level			Lower level			O – C (MHz)
	J	K_a	K_c	J	K_a	K_c	
111844.16	5	0	5	4	0	4	−0.09
133853.65	6	0	6	5	0	5	−0.01
177290.43	8	0	8	7	0	7	0.02
198696.60	9	0	9	8	0	8	0.02
219905.62	10	0	10	9	0	9	0.02
261849.43	12	0	12	11	0	11	0.02
282658.69	13	0	13	12	0	12	0.02
303407.90	14	0	14	13	0	13	0.00
324128.33	15	0	15	14	0	14	0.00
344847.89	16	0	16	15	0	15	0.00
365593.98	17	0	17	16	0	16	−0.02
163208.74	7	1	6	6	1	5	−0.01
209401.07	9	1	8	8	1	7	−0.01
232356.74	10	1	9	9	1	8	0.02
255196.77	11	1	10	10	1	9	−0.01
277902.97	12	1	11	11	1	10	−0.04
300455.91	13	1	12	12	1	11	0.04
322835.19	14	1	13	13	1	12	−0.05
345021.33	15	1	14	14	1	13	0.02
366996.02	16	1	15	15	1	14	−0.02
159258.50	7	2	5	6	2	4	−0.03
182471.33	8	2	6	7	2	5	−0.01
205825.91	9	2	7	8	2	6	−0.02
229306.83	10	2	8	9	2	7	0.01
252886.05	11	2	9	10	2	8	−0.07
276525.06	12	2	10	11	2	9	0.00
300176.40	13	2	11	12	2	10	−0.03
323786.80	14	2	12	13	2	11	−0.09
347297.27	15	2	13	14	2	12	−0.02
370639.25	16	2	14	15	2	13	−0.03
135957.27	6	3	3	5	3	2	0.04
158642.26	7	3	4	6	3	3	0.01
204079.69	9	3	6	8	3	5	0.00
226849.32	10	3	7	9	3	6	−0.03
249666.82	11	3	8	10	3	7	−0.07
295494.53	13	3	10	12	3	9	−0.04
341666.10	15	3	12	14	3	11	−0.03
364911.17	16	3	13	15	3	12	−0.07
118815.82	5	4	1	4	4	0	−0.04
183505.68	8	4	4	7	4	3	−0.02
205802.85	9	4	5	8	4	4	0.03
228170.39	10	4	6	9	4	5	0.01
250586.31	11	4	7	10	4	6	0.00
295529.35	13	4	9	12	4	8	−0.04
318051.17	14	4	10	13	4	9	0.02
340606.83	15	4	11	14	4	10	−0.02
363198.79	16	4	12	15	4	11	0.01
155042.24	7	5	2	6	5	1	0.04
177289.86	8	5	3	7	5	2	0.04
199565.16	9	5	4	8	5	3	0.09
221867.15	10	5	5	9	5	4	0.01
155994.79	7	6	1	6	6	0	0.01
222938.65	10	6	4	9	6	3	0.01
245271.66	11	6	5	10	6	4	0.03
289969.56	13	6	7	12	6	6	0.03
312335.76	14	6	8	13	6	7	0.02
334714.28	15	6	9	14	6	8	0.03
357105.66	16	6	10	15	6	9	0.02
178645.51	8	7	1	7	7	0	0.04
223337.56	10	7	3	9	7	2	−0.02
245690.94	11	7	4	10	7	3	0.02
290414.62	13	7	6	12	7	5	0.10

(*continued on next page*)

Table 7 (*continued*)

Frequency (MHz)	Upper level			Lower level			O − C (MHz)
	J	K_a	K_c	J	K_a	K_c	
335163.72	15	7	8	14	7	7	0.10
357548.82	16	7	9	15	7	8	0.01
201178.64	9	8	1	8	8	0	0.12
245906.72	11	8	3	10	8	2	0.11
290647.66	13	8	5	12	8	4	0.06
335403.73	15	8	7	14	8	6	0.04
223669.80	10	9	1	9	9	0	0.00
246043.43	11	9	2	10	9	1	−0.02
268419.02	12	9	3	11	9	2	0.04
290796.56	13	9	4	12	9	3	−0.02
313176.52	14	9	5	13	9	4	0.13
335558.58	15	9	6	14	9	5	0.00
357943.24	16	9	7	15	9	6	−0.05
215950.31	10	1	10	9	1	9	−0.03
258116.34	12	1	12	11	1	11	−0.06
279328.13	13	1	13	12	1	12	0.03
300553.31	14	1	14	13	1	13	−0.03
343022.16	16	1	16	15	1	15	−0.08
364268.54	17	1	17	16	1	16	−0.02
157467.70	7	2	6	6	2	5	0.01
179834.24	8	2	7	7	2	6	0.01
202150.87	9	2	8	8	2	7	−0.02
224412.76	10	2	9	9	2	8	−0.01
268756.71	12	2	11	11	2	10	−0.04
290834.12	13	2	12	12	2	11	0.00
312847.98	14	2	13	13	2	12	0.00
334800.82	15	2	14	14	2	13	0.01
158595.00	7	3	5	6	3	4	0.01
181253.92	8	3	6	7	3	5	0.03
203911.37	9	3	7	8	3	6	0.00
226565.53	10	3	8	9	3	7	0.02
249213.74	11	3	9	10	3	8	0.01
271852.80	12	3	10	11	3	9	0.00
294478.85	13	3	11	12	3	10	−0.01
317087.49	14	3	12	13	3	11	−0.01
339673.89	15	3	13	14	3	12	−0.02
362233.04	16	3	14	15	3	13	−0.02
118815.82	5	4	2	4	4	1	−0.02
183504.84	8	4	5	7	4	4	−0.07
205800.96	9	4	6	8	4	5	0.02
228166.37	10	4	7	9	4	6	0.02
250578.32	11	4	8	10	4	7	0.02
273025.74	12	4	9	11	4	8	−0.02
295502.81	13	4	10	12	4	9	−0.03
318006.09	14	4	11	13	4	10	−0.01
340533.25	15	4	12	14	4	11	0.01
363082.49	16	4	13	15	4	12	0.05

the FTIR and FASSST data used in the fit and some important statistical quantities are given in Table 8. In this table the corresponding values for the parent species HCOOH from Ref. [3] are presented for comparison. When almost all transitions were identified it turned out that the previously published ground state parameters for both species were not accurate enough. Therefore, in both cases, all available rotational transitions in the ground state were added to the fit and the ground state parameters were permitted to change. Ground state rotational transitions for HCOOH were those cited in the work dealing with the global analysis of seven higher vibrational states [14]. For $H^{13}COOH$ the ground state data reported in [18], from the same FASSST spectrum which was the source of the excited state transitions, were used.

A few remarks should be made concerning the reduced energy level diagram in Fig. 2. There are two panels: one depicts the lowest levels of A' symmetry and another those of A'' symmetry. The A' rovibrational levels are constructed from E+ and O− Wang basis functions of the 7^1 vibrational state and E− and O+ Wang functions of the 9^1 state; the A'' levels are composed in the opposite way. As usual, for the sake of convenience, the levels with adjacent J values are joined to form level series. For small J, when the interaction between the vibrational states is not very strong, levels

Table 8
Summary of assigned experimental data and quality of the fits

	HCOOH				$H^{13}COOH$	
	This work		Ref. [3]		This work	
Vibrational state	7^1	9^1	7^1	9^1	7^1	9^1
FTIR						
Number of lines[a]	7248	6334	7134	6869	8285	7721
J max	69	70	61	64	75	70
K_a max	30	29	24	22	32	30
Number of levels	1708	1589	1268	1114	1756	1714
Standard deviation (10^{-3} cm^{-1})	0.224		0.31		0.202	
FASSST						
Number of lines	616				224	
Standard deviation (kHz)	40				42	
Kharkov (new measurements)						
Number of lines	45					
Standard deviation (kHz)	12					
Lille + Kharkov						
Number of lines			175			
Standard deviation (kHz)			78			

[a] Unresolved asymmetry doublets were counted in the present study as single transitions.

with the same K_a and the same vibrational state v are included in the same series. For some low K_a values, there are level crossings at higher J due to the strong interaction, and we cannot join in one smooth series the levels for the next J with the same K_a and v identification as for the lower members of the series. In this case, for defining the series connected by lines, the index of the eigenvalues is used to define the series, which therefore form smooth curves. The markers (circles), however, indicate the vibrational identity of each level. In the case of the change of rotational quantum numbers the corresponding transition point in the series is marked with a new value of K_a. Attribution of the vibrational and rotational quantum numbers to the levels was carried out in accordance with the method described in [14], where first the vibrational state was established and after that the rotational quantum numbers. The very strong mixing of states results in "forbidden" transitions in the infrared spectrum and inter-vibrational rotational transitions in the MMW region. Table 9 contains assigned inter-vibrational transitions of HCOOH observed in the FASSST spectrum.

The parameters determined are given in Tables 3–5 and the correlation constants between these parameters are listed in the supplementary material as Tables S9 and S10. It is readily seen that the uncertainties in the present work for the parent species are smaller by nearly two orders of magnitude for many zero-order and first-order parameters than in Ref. [3]. This refers to both diagonal and off-diagonal parameters. The first reason is that in the present work a reduced effective Hamiltonian was used. In Table 5 two pairs of off-diagonal parameters used in [3], namely the coefficients of $J_z = \frac{1}{2}h^{+}_{0,1,0}$ and $J_+^2 - J_-^2 = \frac{1}{2}h^{-}_{0,0,2}$, and on the other hand $J_+ + J_- = \frac{1}{2}h^{+}_{0,0,1}$ and $[J_+ - J_-, J_z]_+ = h^{-}_{0,1,1}$, are strongly correlated, as was already mentioned in [3]. In Table 5 they have been marked with a and b. As was shown in the Section 3 , the rotational operators $h^{-}_{n,q,r}$ in the off-diagonal parts of the Hamiltonian with even $q+r$ are not independent and (see below) can be excluded by an appropriate unitary transformation. The second reason for the smaller uncertainties of the parameters, of course, is the larger extent of the data used in the present work.

To disperse doubts that the parameters obtained are less correlated simply because of using a larger set of experimental data, several test calculations were performed using a limited set of the data very close to that used in Ref. [3]. The input data consisted of all MMW, sub-MMW and FIR rotational transitions in the excited vibrational states from Ref. [3] and the present FTIR measurements corresponding to the range of J and K_a used in Ref. [3] (see Table 8). We have carried out five evaluations of different sets of the parameters: In two cases, the Hamiltonian as formulated in Ref. [3] was used, both with fixed sextic and octic centrifugal distortion parameters as in Ref. [3] (Test 1), and also with all of these parameters adjusted (Test 2). In the three other cases, the present Hamiltonian was used, also both with fixed (Test 3) and varied sextic and octic centrifugal distortion parameters (Tests 4 and 5). In the two last cases two different numbers of coupling parameters were used. All the parameters obtained are listed in Tables S11–S13 of the supplementary data and a comparison of the the most important results is given in Table 10. The correlation matrices for the five test fits are also included in the supplementary information as Tables S14–S18. The ground state parameters in all cases were taken as in Ref. [18]. In Test 1 we did not change the number of interaction parameters from that used in Ref. [3]. Despite the fact that the higher order centrifugal distortion parameters of both states were constrained in Ref. [3] to the ground state values, we tried to vary them in the Test 2 and succeeded in their determination. As can be seen in Table 10, the standard deviation of both FTIR and MMW transitions became significantly better (columns 1 and 2) and is nearly identical to the standard deviation obtained with the present Hamiltonian (columns 3, 4 and 5). This means that the model of interactions from Ref. [3] yields equivalent results, with respect to the eigenvalues, as the model used in the present work. However, the standard errors of the constants obtained, especially for rotational and zero-order Coriolis coupling parameters, differ significantly for the two models (Table 10), just as noted above in Tables 3–5, and are a clear indication of the use of reduced or unreduced Hamiltonians. The total number of adjusted parameters needed to achieve the same results is the same in both models (columns 2 and 5). We performed other test calculations not indicated in Table 10. In every

Table 9
Inter-vibrational MMW transitions assigned in the FASSST spectrum of HCOOH

Frequency (MHz)	Upper level				Lower level				O − C (MHz)
	J	K_a	K_c	V	J	K_a	K_c	V	
134113.39	12	3	10	7	12	0	12	9	−0.03
135936.88	26	3	23	9	25	5	21	7	−0.01
140177.96	13	3	11	7	13	0	13	9	−0.03
146906.23	14	3	12	7	14	0	14	9	0.04
152461.16	11	3	9	7	11	0	11	9	−0.03
154682.46	15	3	13	7	15	0	15	9	0.10
163400.67	11	2	9	9	11	3	9	7	0.01
163643.73	16	3	14	7	16	0	16	9	0.01
163729.00	36	5	31	7	36	4	33	9	0.06
167270.33	37	5	32	7	37	4	34	9	−0.03
171143.60	27	3	24	9	26	5	22	7	−0.01
173652.11	38	5	33	7	38	4	35	9	−0.10
182624.51	39	5	34	7	39	4	36	9	−0.09
194015.26	40	5	35	7	40	4	37	9	0.02
195608.42	12	2	10	9	12	3	10	7	−0.02
206106.01	13	2	11	9	13	3	11	7	0.02
206814.88	28	3	25	9	27	5	23	7	0.04
207734.77	41	5	36	7	41	4	38	9	0.01
223756.98	42	5	37	7	42	4	39	9	0.10
233048.36	15	2	13	9	15	3	13	7	−0.03
236431.84	9	3	7	7	8	1	7	9	−0.04
242617.21	29	3	26	9	28	5	24	7	0.09
248879.05	16	2	14	9	16	3	14	7	−0.03
253498.73	10	3	8	7	9	1	8	9	−0.03
259530.65	13	3	11	7	12	1	11	9	−0.03
266022.77	17	2	15	9	17	3	15	7	−0.04
269666.44	12	3	10	7	11	1	10	9	−0.01
274419.92	11	3	9	7	10	1	9	9	0.01
278129.54	30	3	27	9	29	5	25	7	0.17
327371.36	22	4	19	7	22	1	21	9	−0.01
330555.31	23	4	20	7	23	1	22	9	−0.03
331496.59	20	4	17	7	20	1	19	9	−0.01
337674.74	19	4	16	7	19	1	18	9	0.02
345874.20	18	4	15	7	18	1	17	9	0.09
355630.07	17	4	14	7	17	1	16	9	−0.02
356962.04	11	8	3	7	11	7	5	9	−0.02
358057.05	12	8	4	7	12	7	6	9	0.02
359234.16	13	8	5	7	13	7	7	9	−0.04
360491.41	14	8	6	7	14	7	8	9	−0.07
361826.52	15	8	7	7	15	7	9	9	−0.10
363237.21	16	8	8	7	16	7	10	9	−0.01
364720.76	17	8	9	7	17	7	11	9	−0.06

case, when we tried to include in our model any interaction term of total power 2, i.e. $h^{-}_{0,1,1}$ or $h^{-}_{0,0,2}$, or exceed the allowed number of coupling terms of third power in the reduced Hamiltonian, the standard errors of rotational and zero-order Coriolis parameters turned out to be very large as in columns 1 and 2 of Table 10, while at least one eigenvalue of the correlation matrix proved to be as small as 10^{-7}–10^{-8} whereas its minimal value otherwise was 10^{-4}–10^{-5}. The high correlations between parameters in Ref. [3] can result in less reliable predictions of transitions which were not used in the fit.

As a final note, calculated MMW transitions frequencies in the 7^1 and 9^1 vibrational states were compared with those of observed but unassigned interstellar molecular microwave transitions collected by F.J. Lovas at the NIST Internet site http://physics.nist.gov/PhysRefData/Micro/Html/contents.html. Several coincidences, within 2 MHz, were found for strong ${}^{a}R_{0,1}$ transitions, and are given in Table 11.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the

Table 10
Selected results of diagnostic fits of a limited data set for the 7^1 and 9^1 states of HCOOH

Parameter or term			As in Ref. [3] fixed centrifugal distortion parameters	As in Ref. [3] adjusted centrifugal distortion parameters	Present work fixed centrifugal distortion parameters	Present work 7 coupling parameters	Present work 9 coupling parameters
Test index			1	2	3	4	5
7^1 State	A	MHz	77762.578(1390)	77784.693(1520)	77929.094(4)	77929.304(6)	7792.924(7)
	B	MHz	12034.7686(43)	12034.7989(43)	12048.4984(4)	12048.4882(6)	12048.4861(6)
9^1 State	A	MHz	77677.802(1390)	77655.678(1520)	77511.645(5)	77511.420(8)	77511.481(9)
	B	MHz	12006.8710(37)	12006.8475(36)	11993.2201(2)	11993.2193(4)	11993.2194(4)
Coupling terms	J_z	MHz	31564.86(960)	31717.37(1050)	32694.65(2)	32696.15(4)	32695.76(4)
	$J_+ + J_-$	MHz	3937.407(55)	3937.866(52)	4123.158(2)	4123.114(2)	4123.092(3)
Standard deviation of the FTIR transitions (10^{-3})		cm^{-1}	0.259	0.232	0.255	0.232	0.230
Standard deviation of the 175 MMW transitions		kHz	83	55	82	50	47
Number of adjusted parameters			26	39	27	37	39

Table 11
Possible assignments of the observed interstellar MMW transitions to the 7^1 and 9^1 states of HCOOH

Interstellar	FASSST	Calculated	Upper level			Lower level			Vibrational state	Interstellar-calculated	FASSST-calculated
			J	K_a	K_c	J	K_a	K_c			
135824.60	135823.48	135823.38	6	2	5	5	2	4	9	1.22	0.10
224771.00	224770.95	224770.97	10	9	2	9	9	1	7	0.03	−0.02
242360.00	242359.97	242359.98	11	0	11	10	0	10	9	0.02	−0.01
246170.00	246169.82	246169.84	11	6	5	10	6	4	9	0.16	−0.02
246495.00	246494.45	246494.47	11	8	3	10	8	2	9	0.53	−0.02
348202.60	348201.23	348201.25	15	2	13	14	2	12	9	1.35	−0.02

All frequencies and frequency differences are in MHz.

Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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