

The millimeter wave spectrum of *cis*-HCOOH in the ground state and in the $v_9 = 1$ and $v_7 = 1$ excited vibrational states, and *cis*-H¹³COOH in the ground state

Oleg I. Baskakov^a, Brenda P. Winnewisser^{b,*}, Ivan R. Medvedev^b, Frank C. De Lucia^b

^a Department of Quantum Radi. Physics, The Karazin Kharkov National University, Svobody sq. 4, 61077 Kharkov, Ukraine

^b Department of Physics, The Ohio State University, Columbus, OH 43210, USA

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Abstract

A broadband recording of the millimeter/submillimeter wave spectrum of formic acid heated to 170 °C with the FASSST spectrometer has yielded a multitude of rotational transitions of HCOOH in excited vibrational states. These include transitions of the *cis*-rotamer, the analysis of which is reported here. The data for the ground state could be significantly extended (546 lines), and the first information on rotational structure in vibrationally excited *cis*-HCOOH in the $v_9 = 1$ and $v_7 = 1$ states was obtained. Finally, transitions of *cis*-H¹³COOH in the ground state were also observed. The rotational parameters resulting from the analysis of each of these spectra are reported, together with an initial determination of the Coriolis coupling parameters for the $7^1/9^1$ resonance interaction, an experimental force field calculation and a new structure determination. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The first detection of the *cis* rotamer of formic acid was the measurement of its microwave spectrum [1] 30 years ago. Subsequent work extended the measurements to several isotopic species, allowing the determination of a substitution structure [2], and the dipole moment components were also determined [1]. A full characterization of the ground state rotational spectrum of *cis*-HCOOH, based primarily on FTIR data in the FIR, was published a few years ago [3]. Recently, the FASSST spectrometer at the Ohio State University [4] was used to record the millimeter/submillimeter wave spectrum of formic acid with the intention of identifying transitions in excited vibrational states, taking advantage of recent improvements to the FASSST spectrometer [5]. In addition, the cell was heated to increase the intensity of lines in higher-lying states. The sensitivity was sufficient that in addition to transitions in numerous excited vibrational states of *trans*-HCOOH, which will be reported in a separate publication, a large number of transitions were

observed which could be attributed to *cis*-HCOOH. The present paper is concerned with these transitions and the information that can be derived from them concerning the *cis* rotamer.

The ground state of *cis*-HCOOH lies roughly 1365 cm^{-1} above that of *trans*-HCOOH [1]. At room temperature, its abundance is consequently about 1/730 that of *trans*-HCOOH. Because of this low abundance, and the overlap of bands of the two rotamers, no vibrational bands of *cis*-HCOOH have been detected in the gas phase, although a very skillful study of the matrix isolation spectrum of the *cis* rotamer has been reported in recent years by Pettersen and coworkers [6,7]. However, the rotational spectrum is an easier way to detect *cis*-HCOOH than the vibrational spectrum because the dipole moment components are much larger for *cis*-HCOOH [1], and the larger transition moments of the rotational lines partially compensate for the low abundance.

We report here a revised set of rotational constants and centrifugal distortion constants for the ground state of *cis*-HCOOH, the first analysis including millimeter wave data for *cis*-H¹³COOH, and the very first rotational information for excited vibrational states of *cis*-HCOOH, consisting of data for the weakly interacting states $v_9 = 1$ and $v_7 = 1$. An experimental force field has also been derived from the currently available data.

* Corresponding author.

E-mail address: winnebp@mps.ohio-state.edu (B.P. Winnewisser).

2. Experimental aspects and data reduction

The FASSST spectrometer attains a high sensitivity due to its basic concept, in which a fast (≈ 1 s) scan of a backward wave oscillator (BWO) through roughly 30 GHz, provides an effective modulation of the spectral features [4]. Although the sensitivity of a single scan suffices for many experiments, recent improvements include the facility to average 400 scans, 200 up and 200 down in frequency scan direction, as in the current study. Each scan was checked for consistency and calibrated individually, and between 177 and 200 scans were retained in the various segments. Modifications to the calibration, including accounting for the effect of atmospheric water on the separation between fringes produced by the external etalon used for calibration, are described in recent publications [5,8]. Most important for this study, the current cell is made of aluminum, and can be heated or cooled. For these measurements the cell was heated to 170 °C. The measurements cover 115–186 and 193–370 GHz. The sample pressure was 1–10 mtorr, with 5–15 mtorr of SO₂ in a separate cell for absolute calibration. The lines were thus essentially Doppler limited (FWHM of 820 kHz at 370 GHz and at 170 °C). The instrumental contribution leads to broadening, but the roughly second derivative instrumental line shape peak has a FWHM on the order of 600–800 kHz. With the implementation of up/down averaging and improved calibration, the estimated accuracy of the line positions is 50 kHz, limited primarily by scan sweep variation. Partially split asymmetry doublets were omitted from the fit, and unresolved doublets were represented by one component in the fit.

The rotational data for each state analyzed were fit to a Watson A-reduced Hamiltonian in the I^r reduction.

3. Ground state transitions of *cis*-HCOOH

Since a very complete analysis of pure rotational transitions of the ground state was available [3], it was easy to identify further lines on the basis of predictions. However, the FIR data used in the previous work have a much lower accuracy, so that the 546 lines identified in the FASSST spectrum contributed to an improved accuracy of the constants, and led to the identification of one wrong assignment ($45_{3,43} \leftarrow 44_{3,42}$ was mis-assigned to 974111.760 MHz) in the previous paper, which had led to an erroneously high value of Φ_{JK} . Table 1 gives the previous constants and the new, revised constants and parameters of the fit for the ground state. The new transitions included in the fit are given in Table S1 of the supplementary data. The FIR data which was important in Ref. [3] was not included, since with the great quantity of highly accurate MMW/SMMW data, the less accurate FIR transitions do not noticeably improve the constants.

4. Ground state transitions of *cis*-H¹³COOH

For the isotopic species *cis*-H¹³COOH, the only previously reported data consisted of 28 microwave transitions below 45 GHz [2]. These were sufficient to predict and assign 100

very weak transitions in the FASSST spectrum. Since ¹³C has an abundance of 1.1%, the intensities of these transitions corresponds to those of excitation of 1000 cm⁻¹ relative to the ground state of *cis*-HCOOH, or 2300 cm⁻¹ relative to the ground state of *trans*-HCOOH. The constants obtained from all 128 available rotational transitions are included in Table 1, and the millimeter wave data are listed in Table S2 of the supplementary data.

5. $\nu_9=1$ and $\nu_7=1$ states of *cis*-HCOOH

The term values for the two lowest vibrational states $\nu_9=1$ and $\nu_7=1$, as determined from the matrix isolation spectra and ab initio calculations, are shown in Table 2. The separation between them, ≈ 160 cm⁻¹, is large enough to allow us to assume that these two states do not interact significantly. The intensity of the rotational lines at 170 °C in these two states should be (Fig. 1) about five times less than in the ground state. The strongest rotational lines in the ground state have a S/N of 300. These circumstances indicated that rotational transitions in the 7¹ and 9¹ states could be detected, and that they could be described by an ordinary Watson asymmetric top Hamiltonian.

Since there were no previous rotational data for any excited vibrational states of the *cis* rotamer, the shift of the a-type ^rR transitions from those of the ground state were guessed, and the spectrum was searched for characteristic patterns with the expected intensities. The key was the asymmetry splitting of the $K_a=3$ transitions, which form a simple, close pattern together with the unsplit $K_a=4, 5$ and 6 transitions in each cluster of ^rR lines for successive J values. Fig. 1 shows the group of lines that were first assigned for both the 9¹ and 7¹ states, together with the corresponding lines for the ground state. For the 9¹ state, 427 lines were successively identified and included in the fit, including some $\Delta K_a=3$ transitions. For the higher 7¹ state, 336 lines were obtained.

Relative intensities were used to confirm the assignments and to determine the vibrational term values of the two states and thus the difference between the two states (Fig. 2). Although the line shapes and thus the peak intensities varied considerably, primarily due to sweep rate variations, when 166 widely scattered pairs of intensities can be ratioed, useful values of the vibrational wavenumbers and especially of the wavenumber interval can be obtained. Fig. 2 shows the distribution of ratios found for lines of each of the two excited states ratioed against the corresponding ground state lines; each ratio is between transitions having all rotational quantum numbers in common, and differing only in the vibrational excitation quantum. The upper axis gives the corresponding vibrational term values. The values obtained from the means of these two distributions are included in Table 2. These term values are considerably lower than those cited by Macaos et al. [7], but this difference may represent matrix effects.

Since the 9¹ and 7¹ states are predicted, and found, to lie considerably farther apart in the *cis* than in the *trans* rotamer, where they are only separated by 16 cm⁻¹, the Coriolis interactions observed in the *trans* rotamer were initially assumed to be negligible. The data were, therefore, fitted

Table 1
Rotational and centrifugal distortion constants of *cis*-HCOOH

Parameter	Ground state (Ref. [3])	Ground state (this work)	$\nu_9 = 1^a$	$\nu_7 = 1^a$	<i>cis</i> -H ¹³ COOH
A (MHz)	86461.6235(22) ^b	86461.6124(12)	84790.1785(19)	8775.3411(30)	84201.7544(67)
B (MHz)	11689.18453(44)	11689.18149(16)	11648.04229(22)	11695.76928(47)	11687.51738(73)
C (MHz)	10283.99637(50)	10283.99126(15)	10285.57554(21)	10263.26555(47)	10249.65471(65)
Δ_J (kHz)	8.35515(97)	8.34931(18)	8.29231(37)	8.4343(14)	8.2918(12)
Δ_{JK} (kHz)	−71.4412(43)	−71.4384(28)	−74.4141(62)	−66.785(14)	−69.858(17)
Δ_K (kHz)	2361.672(46)	2361.349(27)	1758.16(13)	2956.32(25)	2311.35(47)
δ_J (kHz)	1.41773(10)	1.419537(34)	1.376327(69)	1.45808(18)	1.44669(52)
δ_K (kHz)	40.747(47)	41.1210(53)	11.002(14)	68.058(34)	40.486(23)
Φ_J (Hz)	0.01064(52)	0.008366(53)	0.00713(20)	0.0228(12)	0.008366 ^c
Φ_{JK} (Hz)	−0.2974(19)	−0.0272(29)	−1.699(22)	0.873(47)	−0.0272 ^c
Φ_{KJ} (Hz)	−9.673(39)	−10.768(19)	−8.77(11)	−11.10(17)	−11.37(47)
Φ_K (Hz)	185.11(49)	181.70(22)	−200.7(32)	602.2(74)	181.70 ^c
ϕ_J (Hz)	0.002317(95)	0.003932(14)	0.003341(66)	0.00474(10)	0.00409(48)
ϕ_{JK} (Hz)	−0.73(11)	0.0633(30)	−0.242(20)	−	0.0633 ^c
ϕ_K (Hz)	−	18.10(17)	−90.9(15)	77.5(25)	18.10 ^c
L_J (mHz)	−	−	−	−0.00444(34)	−
L_{JK} (mHz)	−	0.00166(24)	−	0.302(12)	−
L_{JKK} (mHz)	−	−	−0.901(47)	1.53(12)	−
L_{JKKK} (mHz)	−	0.406(72)	4.11(24)	−4.07(32)	−
L_K (mHz)	−20.2(12)	−	239.(26)	443.(63)	−
l_{JK} (mHz)	0.558(45)	−	−	−	−
l_K (mHz)	−	2.36(21)	−	−	−
Nr. of Mw trans. (SD/kHz)	−	22(28)	−	−	28(26)
Nr. of MMW trans. (SD/kHz)	−	546(37)	427(37)	336(42)	100(57)
Nr. of SMMW trans. (SD/kHz)	−	52(70)	−	−	−
J_{\max}	47 ^d (63 ^e)	69	52	45	29
$K_{a,\max}$	12 ^d (16 ^e)	16	16	16	8

^a Coriolis interactions ignored.

^b Figures in parentheses represent one standard deviation in units of the last digit.

^c Fixed at value for the ground state of the parent species.

^d J_{\max} and $K_{a,\max}$ of the MMW and SMMW transitions.

^e J_{\max} and $K_{a,\max}$ of the FIR transitions.

using effective Hamiltonians for two unperturbed states, resulting in the constants given in Table 1. The data for the 9¹ and 7¹ states, with assignments and deviations in the fits, are listed in Tables S3 and S4, respectively.

The standard deviations are satisfactory, the constants do not indicate any obvious perturbation, but it is noticeable that the A rotational constant and all five of the quartic distortion constants, and especially Δ_K , show deviations from the ground state values which are very nearly equal and opposite, and of a magnitude considerably larger than expected for the purely vibrational dependence of these constants.

These irregularities indicate that the interaction between the two states is significant, even though a fit to experimental accuracy was possible with two independent Watson Hamiltonians. We therefore applied a two-state Hamiltonian. The Coriolis interaction between $\nu_9 = 1$ and $\nu_7 = 1$ was represented with an off-diagonal matrix element between the vibrational states of different symmetry A' and A'' having two terms, namely, for a- and b-type Coriolis coupling

$$\hat{H}_{\text{cor}} = \xi_{7,9}^a \hat{J}_a + \xi_{7,9}^b \hat{J}_b, \quad (1)$$

the former giving nonzero matrix elements between rovibrational levels with $\Delta K_a = 0$ and the latter between levels with $\Delta K_a = 1$. However, the three parameters ($\xi_{7,9}^a$, $\xi_{7,9}^b$ and $\Delta E/hc$) needed to describe the interactions are correlated with the rotational parameters and could not be determined simultaneously with the other parameters indicated in Table 1.

A second fit was then made, in which the primary purpose was to determine the Coriolis coupling constants between the rotational levels of the two states. The data set was limited to 214 transitions with $J \leq 11$, and $K_a \leq 5$, to eliminate the need for higher order centrifugal distortion constants, and the quartic centrifugal distortion constants were held fixed at the ground

Table 2
Band center values for the ν_7 and ν_9 fundamental bands of *cis*-HCOOH

Source	ν_7 (cm ^{−1})	ν_9 (cm ^{−1})	$(\nu_7 - \nu_9)$ cm ^{−1}
Ab initio [7]	647.3	430.8	216.5
Matrix IR [7]	662.3	504.1 ^a	158.2
Relative intensities	560(45)	439(65)	121(60)
Coriolis resonance	−	−	118.97(57)

^a Average of values for two matrix sites.

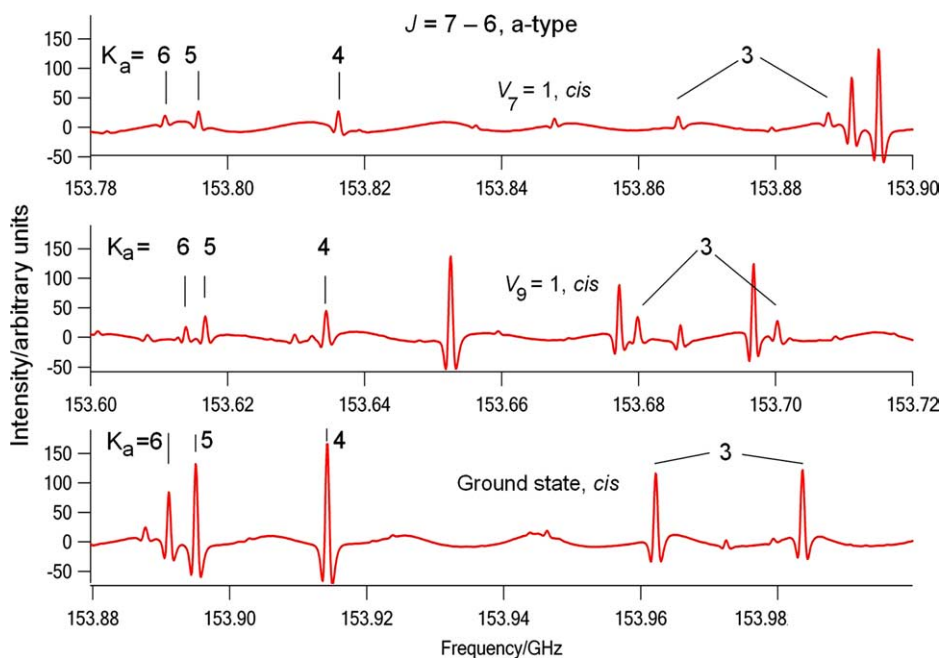


Fig. 1. Key groups of lines in the spectrum of *cis*-HCOOH used for initial identification of transitions in the excited vibrational states 9^1 and 7^1 . The intensity is in arbitrary units.

state values; no higher order distortion constants were included. Only the rotational constants, the interval $\nu_7 - \nu_9$, and the Coriolis coupling parameters in the matrix element given by Eq. (1) were adjusted. Though the resulting rotational parameters, shown in Table 3, are of lower accuracy than those in Table 1, the A rotational constant now differs only moderately from the ground state value for both states, and the term value difference is roughly consistent with the matrix data for the *cis* conformer; it is remarkably close to the value derived from intensity data. A comparison with the *trans* rotamer values is not useful, since the forms of the two normal modes differ substantially in the two rotamers. In Table 3, instead of the parameters $\xi_{7,9}^a$ and $\xi_{7,9}^b$, the true Coriolis coupling parameters $\zeta_{7,9}^a$ are given. The two sets of parameters are connected through the relation

$$\xi_{7,9}^a = A^\alpha \zeta_{7,9}^a \left[\left(\frac{\omega_9}{\omega_7} \right)^{1/2} + \left(\frac{\omega_7}{\omega_9} \right)^{1/2} \right], \alpha = a, b. \quad (2)$$

where $A^\alpha = A, B, C$ for $\alpha = a, b, c$.

6. Force field and structure calculation

With the data presented here, together with the vibrational data of Pettersen et al. [6,7], we have carried out force field calculations similar to those for *trans*-HCOOH made by Davis et al. [9]. The first calculation (I) used as input quartic centrifugal distortion parameters of seven isotopic modifications of *cis*-HCOOH from Ref. [2], eight vibrational fundamentals from Ref. [7] and the two Coriolis parameters from Table 3. The geometric structure was taken from Ref. [2]. The symmetry coordinates are defined identically for both rotamers as follows: $S_1 = \Delta R(\text{O-H})$, $S_2 = \Delta R(\text{C-H})$, $S_3 = \Delta R(\text{O=C})$, $S_4 = \Delta R(\text{O-C})$, $S_5 = \Delta \alpha$,

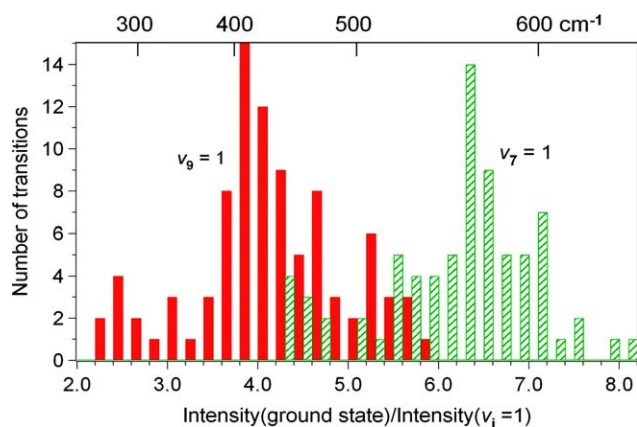


Fig. 2. Distribution of the intensity ratios of ground state lines to those in the excited vibrational states 9^1 and 7^1 , comparing only lines having all of their rotational quantum numbers the same.

Table 3

Parameters of the 9^1 and 7^1 states of *cis*-HCOOH from transitions with $J \leq 11$ and $K_a \leq 5$ determined using a model including Coriolis interactions and fixing the quartic centrifugal distortion parameters to the ground state values

Parameter	$\nu_9=1$	$\nu_7=1$
A (MHz)	86030(20) ^a	86535(20)
B (MHz)	11651.38(57)	11693.47(54)
C (MHz)	10284.965(21)	10262.756(16)
$(\nu_7 - \nu_9)$ (cm^{-1})		118.97(57)
$\zeta_{7,9}^a$		0.382
$\zeta_{7,9}^b$		0.133
Standard dev. (kHz)		197

^a Figures in parentheses represent one standard deviation in units of the last digit.

Table 4
Rotational and centrifugal distortion parameters and residuals for seven isotopomers of *cis*-HCOOH used in obtaining the harmonic force field

	HCOOH			HCOOD			DCOOH			DCOOD		
	Value ^a	I ^b	II	Value	I	II	Value	I	II	Value	I	II
A (MHz)	86462	92	−10	83963	12	8	62653	141	7	61507	94	9
B (MHz)	11689	−21	5	10884	−18	5	11690	−20	6	10885	−17	7
C (MHz)	10284	−28	−9	9625	−25	−6	9838	−24	−10	9237	−21	−6
Δ_J (kHz)	8.349	64	49	6.733	70	72	7.899	109	87	6.267	−5	−10
Δ_{JK} (kHz)	−71.44	−85	−73	−48.11	196	165	−22.94	−16	11	−15.25	22	33
Δ_K (kHz)	2361.	5	1	984.	−3	5	954.4	−90	−154	848.5	−135	−164
δ_J (kHz)	1.420	−5	−1	1.063	−11	−7	1.663	−2	0	1.243	−20	−16
δ_K (kHz)	41.12	18	16	33.191	0	6	37.54	−2	−9	31.32	−16	−14
	H13COOH			HC18OOH			HCO18OH					
	Value	I	II	Value	I	II	Value	I	II			
A (MHz)	84202	115	11	85388	97	−12	85175	90	1			
B (MHz)	11688	−20	7	11059	−19	5	11094	−19	7			
C (MHz)	10250	−27	−8	9779	−25	−8	9803	−26	−7			
Δ_J (kHz)	8.288	50	36	7.428	5	−15	7.682	30	22			
Δ_{JK} (kHz)	−69.69	−113	−99	−72.70	−303	−278	−68.472	−16	−20			
Δ_K (kHz)	2308.	2	0	2345.	15	12	2276.	−3	−3			
δ_J (kHz)	1.447	−5	−2	1.233	−8	−6	1.262	−9	−5			
δ_K (kHz)	40.36	−6	−0	37.55	13	12	37.93	19	17			

^a Estimated errors for determining weights are specified in the text.

^b Columns I and II present differences between observed and calculated values for two calculations (see text), given in units of the last significant figure of the value.

$S_6 = (\Delta\gamma_1 - \Delta\gamma_2)$, $S_7 = \Delta(1/\sqrt{6})(2\beta - \Delta\gamma_1 - \Delta\gamma_2)$, $S_8 = \Delta\omega(\text{HCO}_2)$, $S_9 = \Delta\tau(\text{COH})$, where $\alpha = \angle(\text{COH})$, $\beta = \angle(\text{OCO})$, $\gamma_1 = \angle(\text{O}=\text{CH})$ and $\gamma_2 = \angle(\text{O}-\text{CH})$. The fundamental wavenumbers, averaged over two matrix sites, were corrected for anharmonicity following Dennison [10] and McKean [11], and the error for determining the weights was taken to be 5% plus the site splitting. The estimated errors of the centrifugal distortion constants were taken to be 2% of the values. However, the distortion parameters of *cis*-HC¹⁸OOH were taken to be half as accurate as those of the other species since the planarity relationship is not well fulfilled; it seems that this is because the Δ_{JK} constant is not well determined. The data used are given in Tables 4 and 5, and the residuals from the calculation are shown in column I. The force field resulting from calculation I is given in Table 7.

A second calculation (II) was also carried out, in which the ground state rotational constants were included as input for the same 7 isotopic species, in addition to the data cited above, and the geometric structure parameters were adjusted in addition to the force constants. The errors estimated for the ground state rotational constants A, B, and C were 100, 20 and 20 MHz, respectively. The resulting residuals are included in Tables 4 and 5. The deviations from calculation II are seen to be significantly less than from calculation I. The structural parameters in Ref. [2] are r_s parameters. Several of these parameters rely on small substitution parameters, but the errors quoted in Table 6 considered this fact. The r_s values are, however, within the errors of the values determined in calculation II. The small residuals for the rotational constants

indicate that the structure obtained from this calculation is useful for calculating rotational constants of isotopic species, but may not be a better estimate of the equilibrium structure, since the calculation ignores anharmonic contributions. The force field resulting from calculation II is included in Table 7.

The centrifugal distortion parameters do not depend on the A'' block of the F matrix. There are thus only three input data, ω_9 , $\zeta_{7,9}^a$ and $\zeta_{7,9}^b$, which could be used to determine the three A'' force constants, since the value of ω_8 was not obtained in the work of Petterson et al. [6,7]. These three actually only contribute to the determination of two A'' force field

Table 5
Vibrational parameters of *cis*-HCOOH used in obtaining the harmonic force field

	Value ^a	I ^b	II
ω_1 (cm ^{−1})	3806.9	0.2	0.2
ω_2 (cm ^{−1})	3018.7	−0.1	−0.3
ω_3 (cm ^{−1})	1835.3	−0.7	−0.4
ω_4 (cm ^{−1})	1420.2	−1.0	−1.3
ω_5 (cm ^{−1})	1265.1	−0.4	0.3
ω_6 (cm ^{−1})	1122.8	0.2	−0.4
ω_7 (cm ^{−1})	675.8	9.9	10.9
ω_8 (cm ^{−1})	−	−	−
ω_9 (cm ^{−1})	519.7	0.0	0.0
$\zeta_{7,9}^a$	0.382	0.0	0.0
$\zeta_{7,9}^b$	0.133	0.0	0.0

^a Anharmonic corrections and estimated errors for determining weights are specified in the text.

^b Columns I and II represent differences between observed and calculated values for two calculations (see text).

Table 6
Derived geometrical structure of *cis*-HCOOH

	$r(\text{C}=\text{O})$ (Å)	$r(\text{C}-\text{H})$ (Å)	$r(\text{C}-\text{O})$ (Å)	$r(\text{O}-\text{H})$ (Å)	$\angle(\text{OCH})$ (°)	$\angle(\text{OCO})$ (°)	$\angle(\text{COH})$ (°)
Case I (Ref. [2])	1.1945(31) ^a	1.1050(43)	1.3520(28)	0.9555(53)	123.23(58)	122.12(37)	109.68(44)
Case II (this work)	1.188(11)	1.1045(57)	1.360(11)	0.9624(57)	125.3(32)	122.183(92)	109.30(36)

^a Quoted figures in brackets give one standard deviation in the last significant digits.

Table 7
Experimentally determined harmonic force field of *cis*-HCOOH

		A' block						
		S1	S2	S3	S4	S5	S6	S7
S1	I ^a	8.084(45) ^b						
	II	8.084(41)						
S2	I	0.0	4.46(21)					
	II	0.0	4.58(26)					
S3	I	0.0	4.70(66)	15.0(20)				
	II	0.0	4.35(90)	14.1(22)				
S4	I	0.0	−0.57(21)	1.49(13)	6.54(38)			
	II	0.0	−0.69(26)	1.48(17)	6.60(40)			
S5	I	0.0	0.0	0.0	−0.55(11)	1.507(14)		
	II	0.0	0.0	0.0	−0.59(14)	1.524(18)		
S6	I	0.0	0.0	0.0	−0.667(65)	0.0	0.587(16)	
	II	0.0	0.0	0.0	−0.664(58)	0.0	0.575(20)	
S7	I	0.0	0.0	0.92(16)	0.130(21)	0.0	0.0	1.1905(85)
	II	0.0	0.0	0.85(15)	0.120(21)	0.0	0.0	1.1867(82)
		A'' block						
		S8	S9					
S8	I ^a	0.469 ^c						
	II	0.469						
S9	I	0.168(13)	0.174(11)					
	II	0.178(14)	0.184(12)					

^a Rows I and II represent results from two calculations; see text.

^b Stretching force constants are in $\text{aJ } \text{Å}^{-2}$; stretch-bend and bending force constants are in $\text{aJ } \text{Å}^{-2}$ and aJ , respectively.

^c Fixed at the value found for *trans*-HCOOH [9].

parameters, while f_{88} had to be constrained to the value for *trans*-HCOOH.

7. Conclusions

The present work has extended our knowledge of the rotational spectrum of *cis*-HCOOH to excited vibrational states. It has provided independent information about the relative energy of the vibrational states $v_9=1$ and $v_7=1$ in that species, which is inverted relative to the situation in the *trans* rotamer, and about the Coriolis interaction between these states.

The detection of transitions in such highly excited levels, and finally even of the *cis*-H¹³COOH species, equivalent to the intensity (at 170 °C) for excitation to 1000 cm^{-1} , was possible due to the sensitivity of the recently improved FASSST millimeter/submillimeter wave system. The observation of transitions of *cis*-H¹³COOH implies the possibility of detecting rotational transitions in higher vibrational states than those reported here. The standard deviations achieved in the fits shown in Table 1 now represent the typical line

position accuracy of the current FASSST system for a relatively sparse spectrum with negligible overlapping of transitions.

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Appendix. Supplementary Material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2005.05.057](https://doi.org/10.1016/j.molstruc.2005.05.057)

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