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The far infrared spectrum of trans-formic acid: An extension up to 175 cm^{-1}

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ABSTRACT

The far infrared spectrum of HCOOH was recorded at a high resolution (0.0009 cm^{-1}) and long path length (72 m) at the far-infrared beamline, Canadian Light Source. Spectra were recorded in the region 62–300 cm^{-1}, showing transitions from the *trans*-isomer.

Ground state rotational transitions with K_a up to 30, were identified up to 175 cm^{-1}, extending the observation reported in the literature. A total of 3321 transitions were assigned and fitted together with previous (4149) published data. An improved set of rotational parameters was obtained adopting the symmetric top (A) reduction of the rotational Hamiltonian in the I^r representation. The newly measured far infrared transitions allowed the determination of all diagonal and off diagonal 8th order parameters L and of some of the diagonal 10th order parameters P.

1. Introduction

Formic acid (HCOOH), the simplest organic acid, exists in two rotameric form, *cis* and *trans* with respect to the relative position of the two hydrogen atoms. Both forms are planar and the *cis* form lies about 1365 cm^{-1} [1] above the ground state *trans* form. The *trans* form is a slightly asymmetric top with an asymmetry parameter $k=-0.95$. Formic acid is an important and ubiquitous molecule. It was detected in the interstellar medium by Zuckerman et al. in 1971 [2] and in the upper troposphere by Goldman et al. [3]. The first observation of the pure rotational spectra of this molecule was reported more than 60 years ago. In 1971, Bellet et al. [4] recorded the pure rotational spectrum of formic acid in the 8–300 GHz region. The obtained extensive data set was included in a large compilation containing the ground state rotational spectra of six different isotopologues of this molecule reported by Willemot et al. [5]. The radio-frequency spectrum and the hyperfine structure were studied by Chardon et al. in 1976 [6], while in 1992 Vander Auwera [7] recorded the far infrared (FIR) spectrum in the region 10–100 cm^{-1} at a resolution of 0.005 cm^{-1}. An extensive study of the rotational spectra of the *cis*- and *trans*-formic acid together with the ^{13}C substituted *trans*-form was reported by Winnewisser et al. in 2002 [8]. Microwave, millimeter-wave, and high resolution (0.001 cm^{-1}) FIR measurements were recorded and analyzed simultaneously to obtain accurate sets of spectroscopic parameters for the 3 molecules. Few years later, Baskakov et al. [9], in a study of the ν_7 and ν_9 interacting bands, reported a large number of pure rotational transitions in the ground state, which led to improved sets of molecular constants for this molecule. Further information on the ground state was obtained from theoretical approaches by Flaud and co-workers [10]. Finally, Cazzoli et al. [11] performed a series of high precision and high resolution

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measurements by means of the Lamb-dip technique improving the ground state molecular and hyperfine parameters.

In this paper we report the observation and the analysis of the FIR spectrum of *trans*-HCOOH recorded under high resolution and very long path length. The observation is restricted to the *trans* rotamer, since in the adopted experimental conditions the weak transitions of the *cis* rotamer can be observed only below 40 cm^{-1}, outside the low wavenumber limit of the present recording, 62 cm^{-1}.

2. Experimental details

Three absorption spectra were recorded at a unapodized resolution of 0.00096 cm^{-1} in the 62–300 cm^{-1} range and pressures of 36.4, 66.66, and 266.64 Pa, using the Bruker IFS 125 Fourier transform spectrometer located at the far-infrared beamline, Canadian Light Source. Optimum instrumental performance was achieved using the synchrotron source, 2 mm mylar beamsplitter and Si bolometer detector cooled at 4 K. The spectrometer aperture was set to 2 mm. A scanner velocity of 80 kHz was used with an analog electronic filter set for a low band pass of 5 kHz. No optical filter was used. The boxcar apodisation adopted during the Fourier transform led to an instrumental line width of 0.00096 cm^{-1} (0.61/optical path length difference), full width half maximum. Zero-filling factor of 2, Mertz phase correction, and phase resolution of 1.0 were also used in the Fourier transform. All the spectra were recorded using a multipass coolable absorption cell of 2 m base, with wedged polypropylene windows, set for 72 m path length. The sample was supplied by Sigma-Aldrich with a purity of 98% and used without any further purification. All the spectra were recorded at 298 K. The gas pressure was measured using a 0–1 Torr Baratron gauge, for the spectra recorded at 36.4 and 66.66 Pa, and a 0–10 Torr one, for the spectrum at 266.64 Pa. Rotational water lines [12,13] were used to calibrate the wave number scale, but no correction was applied since the calculated deviation was much smaller than the accuracy of the measurements. Our measurements in the range 62–98 cm^{-1} were also compared to those in Ref. [8], and resulted in a very good agreement, within the relative accuracy. A more detailed description of the synchrotron can be found in Ref. [14]. A portion of the spectrum obtained using the synchrotron source is illustrated in Fig. 1.

3. Description of the spectrum and analysis

The most distinctive feature in the spectrum of the *trans*-HCOOH is a series of ^rQ branches separated by about 4.2 cm^{-1} extending up to 105 cm^{-1}, which correspond to $K_a=25\leftarrow24$. These b-type branches are rather weak as can be seen in Fig. 1. ^rR transitions with $\Delta K_a=+1$ and $\Delta K_c=\pm1$ are present up to about 150 cm^{-1}, corresponding to $K_a=30\leftarrow29$. These lines are those connecting the highest energy levels in the observed spectrum. The ^rP branches are too weak to be seen in the spectrum under the present experimental conditions. The a-type transitions are those at the highest energy. In particular, the $^rR_{Ka,Kc}$ branches with $\Delta K_a=2$ and $\Delta K_c=-1$ dominate the upper part of the spectrum in the region 150–175 cm^{-1}, although the maximum observable value of K_a does not exceed 19. The analogous rather weak $^rQ_{Ka,Kc}$ branches are observed in the region below 110 cm^{-1}, separated by about 8.6 cm^{-1}. Asymmetry doublets separated by more than 30 MHz can be observed only at moderate values of K_a and rather large value of J.

The analysis of the spectrum was straight forward. Below 120 cm^{-1} almost all identified transitions, corresponding to $K_a\approx24$–25, were found at wave numbers very close to the values calculated by means of the ground state parameters in Refs. [9,11]. From 120 to 175 cm^{-1} the deviations between measured and predicted wave numbers increase up to about 25–30 MHz ($7.5–9.0\times10^{-4}$ cm^{-1}), well beyond

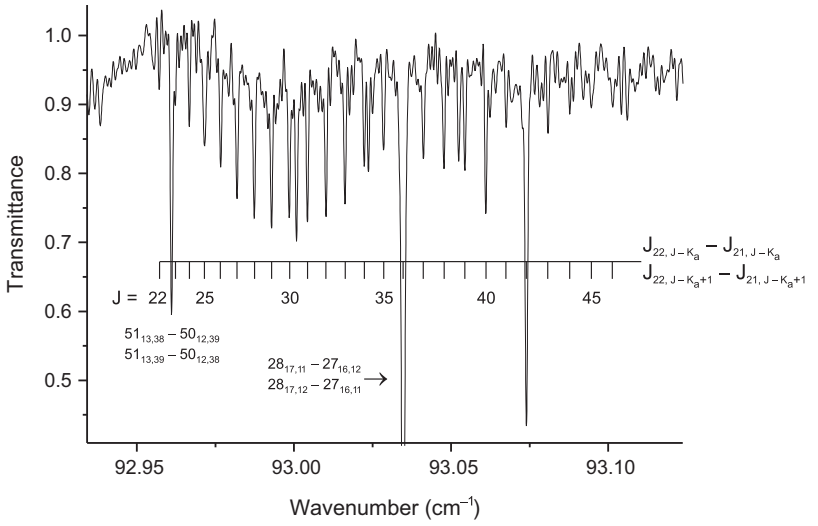

Fig. 1. Detail of the far-infrared spectrum of *trans*-HCOOH in the region 92.94–93.12 cm^{-1} showing the ^rQ branch K_a 22←21. Experimental conditions: pressure 66.66 Pa, and path length 72 m.

the estimated accuracy of our measurements (3.3 MHz). Transitions above 120 cm^{-1} were added to the data set with increasing value of K_a, one at a time, obtaining new parameters, which fitted the new lines which in turn allowed the calculation of transitions with higher values of K_a. This procedure was repeated until transitions with the maximum value of K_a (30), observable under the present experimental conditions, were identified.

Table 1 lists the various data sets taken into account simultaneously in the least-squares analysis, with their accuracies, statistical weights, and the root mean-square (rms) values. Data are identified in the table using the related reference or the research group, which recorded them if the reference merges data from different laboratories. The data sets have a considerable amount of identical transitions, which were all included in the least-squares analysis. In particular, in the region 62–98 cm^{-1}, the present FIR assignments strongly overlap those in Ref. [8]. The same is true, although to a lesser extent, for the microwave and millimeter-wave measurements. All the transitions listed in Table 1 were fitted simultaneously to the symmetric top (A) reduction of the rotational Hamiltonian in the I^r representation by Watson [15], including terms up to the 10th power in the angular momentum. The weights of

Table 1
Ground state rotational transitions of *trans*-HCOOH used in the least-squares analysis.

Spectral region	Number of transitions	Estimated accuracy	Statistical weight	Root mean square	Refs.
1638.805 GHz	1	3.0 kHz	0.11×10^6	0.9 kHz	Zuckerman et al. [2]
0.089–43.15 MHz	27	0.1–1.4 kHz	0.1×10^9–0.5×10^6	0.40 kHz	Chardon et al. [6]
0.83–0.99 THz	126	50–200 kHz	400–25	34.9 kHz	Uni Köln [8]
0.17–0.36 THz	102	30–150 kHz	1111–45	89.8 kHz	Uni.Kharkov [8]
8–300 GHz	234	200–400 kHz	25–6.2	92.1 kHz	Willemot et al. [5]
0.6–3.0 THz	2635	5.0 MHz	0.04	2.46 MHz	DLR [8]
86–225 GHz	48	8.0 kHz	0.156×10^5	7.7 kHz	Uni Kharkov [9]
108–375 GHz	620	33 kHz	920	33.7 kHz	Ohio State Uni [9]
0.089–1.50 THz	356[a]	1–75 kHz	1.0×10^6–178	3.5 kHz	Cazzoli et al. [11]
1.85–5.25 THz	3321	3.3 MHz	0.092	2.04 MHz	This work
Total	7470				

[a] Not considering the hyperfine structure.

Table 2
Spectroscopic parameters for the ground state of *trans*-HCOOH, a reduction I^r representation[a].

parameters		This work	Ref. [9]	Ref. [11]
B_z	MHz	77512.226067(141)	77512.22867(53)	77512.22486(31)
B_x	MHz	12055.1047160(152)	12055.10525(9)	12055.104683(10)
C_y	MHz	10416.1139625(144)	10416.11449(9)	10416.1139857(96)
Δ_J	kHz	9.9940848(253)	9.99422(11)	9.994275(20)
Δ_{JK}	kHz	−86.2211257(315)	−86.2205(12)	−86.22189(19)
Δ_K	kHz	1702.26776(314)	1702.2617(69)	1702.2381(58)
δ_J	kHz	1.94858375(559)	1.948563(21)	1.9485409(48)
δ_K	kHz	42.776279(836)	42.7741(24)	42.78384(53)
Φ_J	Hz	0.0125585(155)	0.012669(46)	0.012703(15)
Φ_{JK}	Hz	0.12809(124)	0.1162(22)	0.13806(93)
Φ_{KJ}	Hz	−10.66818(470)	−10.6097(89)	−10.7008(33)
Φ_K	Hz	120.6862(266)	120.370(37)	120.464(37)
ϕ_J	Hz	0.00587594(454)	0.005805(11)	0.0058700(46)
ϕ_{KJ}	Hz	0.079524(932)	0.0937(19)	0.08105(30)
ϕ_K	Hz	15.8356(647)	14.95(10)	16.087(49)
L_J	mHz	−0.00003914(233)	−0.0000390(21)	0.0000606(23)
L_{JJK}	mHz	0.002073(443)	−0.00211(21)	−0.001981(49)
L_{KJ}	mHz	−0.3921(240)		−0.03264(44)
L_{KKJ}	mHz	2.0342(682)	0.868(12)	1.0198(32)
L_K	mHz	−12.6775(736)	−10.700(44)	−11.077(64)
l_J	mHz	−0.000018472(918)	−0.0000160(12)	−0.00002202(89)
l_{JK}	mHz	−0.001189(226)		
l_{KJ}	mHz	0.1668(210)		
l_K	mHz	−11.498(774)	0.860(70)	
P_{JJJK}	μHz	−0.0001693(220)		
P_{KKJ}	μHz	0.02051(224)		
P_{KKKJ}	μHz	−0.1240(177)		
P_K	μHz	1.2421(405)		
Number of fitted data		7395		
Standard deviation of an observation unit weight		1.08		

[a] Standard uncertainties (1σ) in parentheses refer to the least significant digits.

the experimental data were chosen proportional to the inverse of their squared estimated uncertainties. Transitions that differ from their corresponding calculated values by more than 6.0 MHz, about two times the estimated uncertainty of the present FIR data were excluded from the data set in the final cycle of the analysis. Out of 7470 transitions 7395 were retained in the final fit. All the 75 discarded transitions are FIR data, 46 from Ref. [8], and 19 from our measurements. The latter correspond to unresolved asymmetry doublets whose frequencies differ by less than 6.0 MHz from the center of gravity of the calculated values for the individual components. The newly measured FIR transitions allowed the determination of all the diagonal and off diagonal 8th order parameters L and l, and of some of the diagonal 10th order parameters P. Table 2 lists the parameters obtained in this work together with those reported by Baskakov et al.[9], and by Cazzoli et al. in column 4 of Table 1 [11]. The parameters of the model Hamiltonian, which are not present in Table 2 were nevertheless allowed to vary, but they resulted statistically undetermined and were constrained to zero. All the corresponding constants in the various sets are in good agreement. The quality of the obtained parameters can be verified by considering the rms values for the various data sets. They are all better than or very close to the estimated accuracy of the measurements, see columns 4 and 6 of Table 1.

The 3321 lines identified in the present investigation, together with all the other data present in the literature as described in Table 1, are listed in the depository with the calculated and (observed–calculated) values obtained using the parameters in Table 2.

4. Conclusion

In this paper we reported on the observation and the analysis of the FIR spectrum of *trans*-HCOOH recorded under high resolution and very long path length using the FIR beamline at the Canadian light source. The 3321 identified transitions were fitted together with previous published data from various origins, leading to an improved set of ground state rotational parameters.

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Appendix A. Supplementary materials

Supplementary materials associated with this article can be found in the online version at doi:10.1016/j.jqsrt.2012.01.026.

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