

# FTIR spectra of the $\nu_6$ and $\nu_8$ bands of $^{13}\text{C}$ formic acid molecule—Assignment of FIR-laser lines

O. Baskakov<sup>a,\*</sup>, V.-M. Horneman<sup>b</sup>, S. Alanko<sup>b</sup>, J. Lohilahti<sup>b</sup>

<sup>a</sup> Department of Quantum Radiophysics, The Karazin National University, 4, Svobody square, UA-61077 Kharkiv, Ukraine

<sup>b</sup> Department of Physical Sciences, P.O. Box 3000 90014, University of Oulu, Finland

Received 2 December 2007

Available online 21 February 2008

## Abstract

Two interacting vibrational modes  $\nu_6$  and  $\nu_8$  of  $^{13}\text{C}$  species of formic acid have been studied with high resolution FTIR spectroscopy in the range  $900\text{--}1300\text{ cm}^{-1}$  with an instrumental resolution of  $0.0018\text{ cm}^{-1}$ . More than 10000 lines have been assigned and fitted with a RMS deviation of  $0.00024\text{ cm}^{-1}$ . The band centers, as well as the rotational, quartic and sextic centrifugal distortion parameters and 6 interaction parameters have been determined. The obtained parameters have enabled the assignments of 24 FIR laser emissions of this molecule observed previously by Dangoisse and Glorieux [D. Dangoisse, P. Glorieux, *J. Mol. Spectrosc.* 92 (1982) 283–297], Luis et al. [G.M.R.S. Luis, E.M. Telles, A. Scalabrin, D. Pereira, *IEEE J. Quantum. Electron.* QE-34 (1998) 767–769], and Bertolini et al. [A. Bertolini, G. Carelli, C.A. Massa, A. Moretti, F. Strumia, *Infrared Phys. Technol.* 40 (1999) 33–36].  
© 2008 Elsevier Inc. All rights reserved.

**Keywords:** Formic acid; Vibrational states; Interaction; Laser; Effective Hamiltonian

## 1. Introduction

The  $6^1$  and  $8^1$  vibrational states of the formic acid molecule and its various isotopic species are capable to emit submillimeter laser radiation when pumped by a  $\text{CO}_2$  laser [1]. A submillimeter laser transition arises, as a rule, between rotational levels in the excited vibrational state whereas the pumped transition originates from a rotational level of the ground vibrational state and has a common upper level with the laser transition. Most of the laser emissions were observed and measured in the 1970s and the early 1980s, however, not all transitions have yet been assigned.

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

1 MHz and gave tentative assignment almost for all transitions. In the second work published in 1998 [3] Luis et al. could observe five new far-infrared lines using a more widely tuned waveguide  $\text{CO}_2$  laser. The authors measured the wavelengths of the laser lines with an uncertainty of about  $\pm 0.5\text{ }\mu\text{m}$  and also the offset absorption frequencies. However, attempts to assign these lines were not undertaken. The last work related to the FIR laser radiation from  $\text{H}^{13}\text{COOH}$  medium was published in 1999 by A. Bertolini et al. [4]. They used a waveguide  $\text{CO}_2$  laser with a tunability of 300 MHz and reported the parameters of 16 new FIR laser lines with wavelengths ranging from 185.3 to 1219.9  $\mu\text{m}$ . The estimated error in the wavelength measurements was of a few parts in  $10^{-4}$ . Seven of the obtained laser transitions were tentatively assigned to the  $\nu_6$  band.

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

\* Corresponding author.

E-mail address: [oibas2003@yahoo.com](mailto:oibas2003@yahoo.com) (O. Baskakov).

published in 1999. They assigned 3004 FTIR transitions in the  $\nu_6$  band but were not able to detect the  $\nu_8$  band because of its weakness. Processing of the observed data was carried out using the effective Hamiltonian for two interacting vibrational states of an asymmetric top molecule coupled by two terms representing an a- and b-Coriolis interaction and considering the  $8^1$  state as a dark state. The parameters obtained could reproduce the observed IR transitions in the  $\nu_6$  band with a reasonable accuracy up to  $K_a = 13$ . It is obvious that transitions in the  $\nu_8$  band using the parameters derived in Ref. [5] could be calculated with much worse uncertainty. The identification of the laser lines in Refs. [2,4] prior to the work by Ong et al. was carried out using the fact that geometry of the molecule is very little changed when a  $^{13}\text{C}$  atom is substituted for a  $^{12}\text{C}$  atom, and as a consequence the shape of the spectrum is very similar for these two different species. The authors used the information on the known relative displacement of the most intensive  $^aR$ -type rotational spectra in the ground and excited states of the main isotopic species and its invariability when coming to the  $^{13}\text{C}$  species. This method, according to author's opinion, gives an unambiguous determination for  $J$  and low  $K_a$  values. Therefore, some assignments especially for transitions in the  $8^1$  state can only be assumed to be tentative.

A main goal of the present investigation was to study the high resolution IR spectra of the  $\nu_6$  and  $\nu_8$  bands of the  $\text{H}^{13}\text{COOH}$  molecule to determine their spectroscopic parameters and ultimately to check the assignments given in [2,4] and, when possible, to identify the yet unassigned laser transitions.

## 2. Experimental details

The infrared measurements of the  $\nu_6$  and  $\nu_8$  vibrational bands of the isotopically enriched (99%)  $\text{H}^{13}\text{COOH}$  sample obtained from Sigma-Aldrich were carried out using a Bruker IFS 120HR Fourier spectrometer in Oulu. The spectral range from  $900\text{ cm}^{-1}$  to  $1300\text{ cm}^{-1}$  was recorded at room temperature under two different sets of absorption path length and sample pressure conditions. The first spectrum was obtained using 3.2 m and 4 Pa, and the second using 3.2 m and 84 Pa. The recording time in the both measurements was about 42 h. The lines from both, the low and high path length-pressure spectra, were used in the analysis. A White-type cell [6a,6b] with KBr windows, a Globar source at 1400 K, a germanium beam splitter between KBr base plates, and a mercury-cadmium-telluride-detector were employed. The experimental linewidth of small isolated lines is about  $0.0022\text{ cm}^{-1}$  at  $1100\text{ cm}^{-1}$  resulting from the instrumental and Doppler broadening. The high pressure measurement is first calibrated with lines of the  $\text{OCS } 2\nu_2$  band [7]. Then the calibration is transferred to the low pressure measurement with good sample peaks. The uncertainty of this two stage calibration at  $\nu$  is  $\Delta\nu = 1.2 \times 10^{-9}\nu + 3.4 \times 10^{-6}\text{ cm}^{-1}$ . The optimized center of gravity method [8] was used to calculate the peak positions. The uncertainty of the peak position for a well-

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

## 3. Details of investigation

Formic acid is a planar molecule belonging to  $C_s$  symmetry. The  $6^1$  and  $8^1$  vibrational states correspond to in-plane and out-of-plane normal vibrations. These two vibrations are coupled by a relatively strong a- and less strong b-type Coriolis resonances. The fundamental  $\nu_6$  band centered at  $1095\text{ cm}^{-1}$  is of a/b hybrid type and has a medium intensity, while the  $\nu_8$  band with a center at  $1020\text{ cm}^{-1}$  is of c type and is a weak band. Using the measured spectra under the low and high path length–pressure conditions, which will be referred to as normal and saturated, respectively, we were able to assign absorption lines in the  $\nu_6$  band with  $J$  up to 75 and  $K_a$  up to 15, and in the  $\nu_8$  band up to 60 and 21, respectively. The assignment of the transitions in these two bands was quite straightforward and did not cause any difficulties. The strong transitions with relatively small and medium quantum numbers were taken from the normal spectra while weak lines having large  $J$  and  $K_a$  were visible only in the saturated spectrum. In Fig. 1 there is shown an overview of the central part of the  $\nu_8$  band recorded under the two different conditions. It should be noted that we were able to assign the transitions in the  $\nu_6$  band with  $K_a$  as high as 22. However, they were perturbed by higher vibrational states just as in the main isotopic species [9] and therefore were not used in the fit.

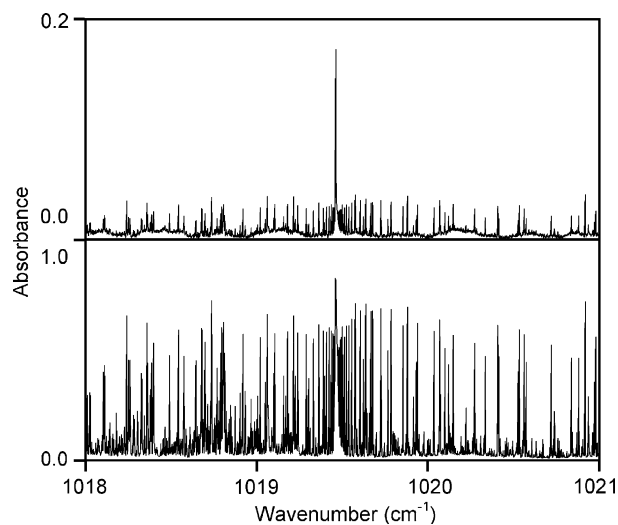


Fig. 1. The central part of the weak  $\nu_8$  band of  $\text{H}^{13}\text{COOH}$  measured under the low and high pathlength-pressure conditions.

Download English Version:

<https://daneshyari.com/en/article/5415819>

Download Persian Version:

<https://daneshyari.com/article/5415819>

[Daneshyari.com](https://daneshyari.com)