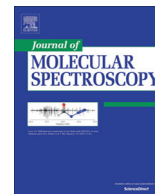




Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

Microwave spectroscopy of $\text{HCOO}^{13}\text{CH}_3$ in the second methyl torsional excited state

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ARTICLE INFO

Article history:

Received 16 May 2017

In revised form 25 July 2017

Accepted 11 August 2017

Available online xxx

Keywords:

Methyl formate

Isotopologue

Internal rotation

Microwave spectroscopy

Pseudo-PAM method

ABSTRACT

The new experimental results and analysis of the microwave spectra of $\text{HCOO}^{13}\text{CH}_3$ in the second methyl torsional excited state are reported. Pseudo-principal axis method (pseudo-PAM) was successfully applied to the normal methyl formate in the second torsional excited state and again applied to this isotopologue. We succeeded to assign 536 A-species transitions up to $J = 33$ and $K_a = 15$ and 417 E-species transitions up to $J = 32$ and $K_a = 14$. Thirty parameters were used to do the least-squares-analysis by using the pseudo-PAM Hamiltonian consisting of rotational, centrifugal distortion, and internal-rotational constants.

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1. Introduction

Methyl formate (HCOOCH_3), which was first identified in Sgr B2 [1], is one of typical complex organic interstellar molecules found in the star-forming regions. This molecule is also a typical example of organic molecules that have an internal rotor, or methyl rotor which is equivalent to the torsional vibration. Torsional vibrations are generally low-lying vibrational motions and interact with the pure rotation. The interaction causes splitting to A and E species in the observed spectrum due to the permutation–inversion group G_6 of the molecule under the present investigation equivalent to the C_{3v} symmetry point group and often the pure rotational transitions in the vibrational excited states are observed at room temperature. For methyl formate, the term values of the first and the second torsional excited state are about 132 [2] and 240 cm^{-1} [3] above the ground state, respectively. Not only in laboratory but also in interstellar space, we identified the rotational transitions of normal species even in the first and second torsional excited states [4,5]. Carbon 13 is relatively abundant isotope in the interstellar space and carbon 13 substituted isotopologues (both $^{13}\text{C}_1$ - and $^{13}\text{C}_2$ -methyl formate) in the ground and first torsional excited

state were also identified in the interstellar spaces based on the laboratory studies [6,7]. A survey study with the APEX telescope was also carried out and tentative detections of $\text{HCOO}^{13}\text{CH}_3$ toward four massive star-forming region was reported [8].

The first laboratory rotational spectroscopic study of methyl formate including many isotopologues was carried out by Curl [9]. There are extensive rotational spectroscopic studies on the normal species including those in the first and second torsional excited states [10–21]. About 200 transitions in the second torsional excited state was first reported by Maeda et al. [21] by using ERHAM model with limited range of K_a for the E sublevel. Our study started independently and succeed to extend the assignment, especially to high K_a for the E level. In the analysis, we adopted the pseudo-principal axis method (pseudo-PAM) and 1951 transitions belonging to the $\nu_t = 2$ state (ν_t denotes the quantum number of the methyl torsion) were satisfactorily least-square fitted with 42 parameters [22]. The second excited state of $\text{H}^{13}\text{COOCH}_3$ was studied by Maeda et al. [21] but there is no study on that of $\text{HCOO}^{13}\text{CH}_3$ so far. Considering low-lying nature of the second torsional excited state and high sensitivity of radio telescopes, it is likely that the rotational transitions in the second torsional excited state will be observed in the near future. We present the analysis based on pseudo-PAM model and provide rest frequencies.

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2. Experiment

All the data were taken by using our conventional Stark/source-modulation spectrometers. The details of the spectrometers were described elsewhere [22,23]. The microwave radiation from a synthesized sweeper was used in combination with an appropriate frequency-multiplier to generate microwave radiation. The signal from a liquid helium cooled InSb bolometer was introduced to a lock-in amplifier detector with a reference signal from the modulator. The frequency region of 50–238.5 GHz was observed at room temperature without gap and part of the 241–321.7 GHz region was also observed. Our experiment was carried out at room temperature and the sample pressure was maintained at about 30–50 mTorr. The conventional 3 m waveguide cell and 1.15 m free-space cell were used below and above 110 GHz, respectively. An example of the observed spectra of A-species is shown in Fig. 1. Estimated frequency measurement errors are 50 kHz.

The $^{13}\text{C}_2$ enriched methyl formate sample was synthesized as follows. Formic acid, phosphoric acid and dimethyl sulfoxide (DMSO) were purchased from Wako Chemical Co. Ltd. Methanol- ^{13}C was purchased from Cambridge Isotope Laboratories, Inc. A 200-mL one-necked round-bottomed flask equipped with a Claisen adapter was filled with argon. Methanol- ^{13}C (5.00 g, 151 mmol), formic acid (58.5 mL, 1.56 mol) and DMSO (50 mL) were added and the flask was cooled to 0 °C. Phosphoric acid (0.5 mL) was added dropwise, keeping the internal temperature below 10 °C. The Claisen adapter was then replaced with a distillation adapter equipped with a Liebig condenser and argon inlet, and the flask was heated gradually to 110 °C (oil bath) over 2 h. Fraction distilling at 32–34 °C was collected. $^{13}\text{C}_2$ methyl formate (2.45 g, 40.1 mmol, 26%) was isolated as a colorless oil.

^1H NMR (CDCl_3 , 300 MHz) δ 8.08 (d, $^3J = 4.2$ Hz); 3.76 (d, $^1J = 147$ Hz).

3. Assignment and analysis

Based on the preceding microwave studies of normal species in the second torsional excited state [22], similar spectral pattern with reasonable intensity was searched for. The characteristic quartet structure shown in Fig. 1 helped our assignment. The assignments were confirmed by the combination loops when possible. To extend the line assignments, we used pseudo-PAM model which was useful to analyze the normal species in $\nu_t = 2$ [22] and the ground state CD_3SH [24]. The detail of this treatment is also described in these papers and we used the energy labeling as the normal species in $\nu_t = 2$ [22]. The pseudo-PAM Hamiltonian used in this work is as follows,

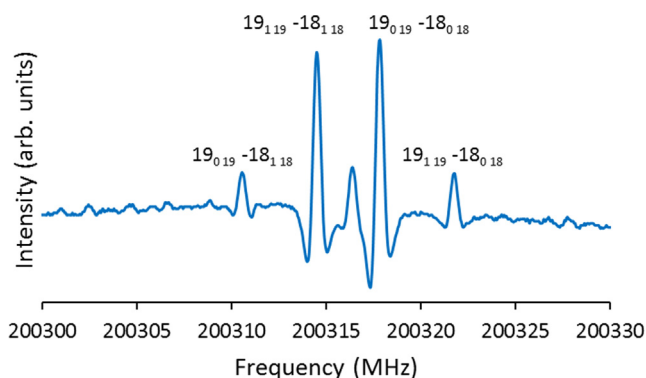


Fig. 1. The A-species $J = 19 - 18$ transitions of $\text{HCOO}^{13}\text{CH}_3$ in $\nu_t = 2$.

$$\begin{aligned}
 H = & A J_z^2 + (B + B_p p^2) J_x^2 + (C + C_p p^2) J_y^2 - \Delta J^4 - \Delta_K J^2 J_z^2 - \Delta_K J_z^4 \\
 & - 2\delta_J J^2 (J_x^2 - J_y^2) - \delta_K J_z^2 (J_x^2 - J_y^2) + F p^2 + F_c [p^2, 1 - \cos 3\theta] \\
 & + \frac{1}{2} V_3 (1 - \cos 3\theta) + \{(q + q_p p^2) + (q_J + q_{Jp} p^2) J^2 \\
 & + (q_K + q_{Kp} p^2) J_z^2\} J_z p + \{(r + r_p p^2) J_x + (r_J + r_{Jp} p^2) J_x J^2 \\
 & + (r_K + r_{Kp} p^2) (1/2) [J_x, J_z^2]\} p + r_{J3} J_x (J_x^2 - J_y^2) p \\
 & + A_c J_z^2 (1 - \cos 3\theta) + B_c J_x^2 (1 - \cos 3\theta) + C_c J_y^2 (1 - \cos 3\theta) \\
 & - \Delta_{Jc} J^4 (1 - \cos 3\theta), \quad (1)
 \end{aligned}$$

where J_x, J_y and J_z are the x -, y - and z -component of the total angular momentum operator, $J^2 = J_x^2 + J_y^2 + J_z^2$, θ represents the CH_3 internal rotation angle, p is the momentum operator associated with the CH_3 internal rotation ($p = -i\hbar \frac{\partial}{\partial \theta}$), and $[X, Y] = XY - YX$.

We briefly summarize the difference between the PAM and pseudo-PAM Hamiltonians by limiting the case up to the second order of J_x, J_y, J_z and p . Then the PAM Hamiltonian is given by

$$\begin{aligned}
 H_{\text{PAM}} = & F(p - \rho_a J_a - \rho_b J_b)^2 + (1/2) V_3 (1 - \cos 3\theta) \\
 & + A_{\text{PAM}} J_a^2 + B_{\text{PAM}} J_b^2 + C_{\text{PAM}} J_c^2, \quad (2)
 \end{aligned}$$

and the pseudo-PAM Hamiltonian is given by

$$\begin{aligned}
 H_{\text{ps-PAM}} = & F p^2 + (1/2) V_3 (1 - \cos 3\theta) \\
 & + A_{\text{ps-PAM}} J_z^2 + B_{\text{ps-PAM}} J_x^2 + C_{\text{ps-PAM}} J_y^2 + q J_z p + r J_x p. \quad (3)
 \end{aligned}$$

By simple manipulation, the relations between the pseudo-PAM and PAM parameters are deduced as follows:

$$\begin{aligned}
 \rho_a = & -\frac{1}{2F} (q \cos \beta + r \sin \beta), \\
 \rho_b = & -\frac{1}{2F} (-q \sin \beta + r \cos \beta), \\
 A_{\text{PAM}} = & A_{\text{ps-PAM}} \cos^2 \beta + B_{\text{ps-PAM}} \sin^2 \beta - F \rho_a^2, \\
 B_{\text{PAM}} = & A \sin^2 \beta + B \cos^2 \beta - F \rho_b^2, \\
 C_{\text{PAM}} = & C_{\text{ps-PAM}}, \\
 \tan 2\beta = & \frac{qr}{2F(B_{\text{ps-PAM}} - A_{\text{ps-PAM}}) + \frac{1}{2}(q^2 - r^2)}. \quad (4)
 \end{aligned}$$

In Eq. (1), p - and θ -dependent terms of effective rotational constants A, B, C , Coriolis-like parameters r, q and their centrifugal analogs in addition to the Watson's A-reduced centrifugal distortion constants are added phenomenologically. The r_{J3} term, which was also used in the previous analysis for the $\nu_t = 2$ state of the normal species [22], is the term that serves to reduce the root mean square (rms) deviation of the fit based on phenomenological consideration.

In the end, 536 A-species transitions up to $J = 33$ and $K_a = 15$ and 417 E-species transitions up to $J = 32$ and $K_a = 14$ were assigned. Some of the transitions include levels above the internal rotation barrier. Complete transition frequencies with transition intensities are given in the supplementary Table S1. The line lists will also be deposited in the Toyama Microwave Atlas (ToyaMA) (<http://www.sci.u-toyama.ac.jp/phys/4ken/atlas/> and <https://toyama.nao.ac.jp>) In the last column of Table S1, the relative intensity factor $S\mu^2$ is given. The new dipole moment components was reported in the recent study on HCOOCH_3 and DCOOCH_3 [25]. The PAM components are $\mu_z = -1.648(8)$ D and $\mu_x = 0.706(12)$ D, respectively [10] and these are transformed to those of $\text{HCOO}^{13}\text{CH}_3$ by the axis rotation caused by the ^{13}C substitution ($\mu_z = -1.638$ D and $\mu_x = 0.730$ D). Then these components are again transformed for the pseudo-PAM axis ($\mu_z = -1.614$ D and $\mu_x = 0.782$ D).

With as little as 30 parameters, 953 transitions in total, 536 A-species and 417 E-species transitions in $\nu_t = 2$ were least-square fitted. The rms was 0.067 MHz which is close to the estimated frequency measurement errors. The molecular constants are summarized in Table 1.

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