



Submillimeter-wave spectra of $\text{H}^{12}\text{COOCH}_3$ and $\text{H}^{13}\text{COOCH}_3$ in excited CH_3 torsional states

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ABSTRACT

Several satellite series of rotational spectra have been observed in addition to the spectral lines arising from the ground torsional state for the normal and $^{13}\text{C}_1$ species of methyl formate in the 110–380 GHz frequency region. They have been assigned to the first and second excited torsional state for both species. Combined least-squares analyses of selected lines from the *A* and *E* substates in each excited torsional state have been undertaken independently from the ground state with the effective rotational Hamiltonian procedure for the internal rotation analysis. Intensity ratios for the same rotational transitions in different torsional states have been compared to estimate relative energies of the excited torsional states and to confirm their assignments.

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1. Introduction

It is an honor to contribute an article to a volume dedicated to the spectroscopic careers of Herb Pickett and Ed Cohen. In this paper, we report some new results on the rotational-torsional spectra of the normal and $^{13}\text{C}_1$ isotopomers of methyl formate. Methyl formate (HCOOCH_3) has been detected ubiquitously in interstellar hot cores and is known as an interstellar “weed” for its dense rotational spectrum. Recently, some previously unidentified spectral lines of the first excited torsional state of the normal isotopomer have been assigned for the first time towards Orion KL [1]. The assignments were based on new laboratory spectral evidence discussed below.

As these new assignments confirm, for unambiguous identifications of interstellar lines, either high resolution laboratory measurements or an accurate prediction of transition frequencies is necessary. Methyl formate has proven to be a challenge for many spectroscopists to analyze because the methyl-top undergoes a large-amplitude internal rotation, or torsional motion. This motion

results in several complications to the normal asymmetric-top rotational motion. First, closely-spaced torsional vibrational levels exist and can be reached at room temperature so that additional rotational spectral lines appear. Secondly, interactions between overall rotation and the internal rotation of the methyl-top split each torsional state into two components with *A* and *E* symmetry.

Because of the difficulty in analyzing the spectra of internal rotors, several methods have been developed to construct different effective Hamiltonians, such as the principal axis method (PAM), the internal axis method (IAM), the *rho* axis method (RAM), and most recently, the effective rotational-torsional Hamiltonian (ErHam) procedure, which has been developed for molecules with single or dual internal rotors [2–4]. Most of the previous studies of methyl formate contained a global analysis of the *A* and *E* substates with the RAM Hamiltonian, in which the molecular reference *z* axis is chosen to be parallel to the *rho* vector, $\vec{\rho}$ [5–11].² Most recently, we have applied the ErHam procedure with the principal axis system (PAS) in a global analysis of the FASSST rotational-torsional spectrum of methyl formate- ^{13}C ($\text{H}^{13}\text{COOCH}_3$) as well as normal methyl formate in the ground *A* and *E* substates [12]. Unitless standard deviations of 0.86 and 1.1 were obtained for the $^{13}\text{C}_1$ and normal species,

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² Although some refer to the RAM Hamiltonian as the IAM Hamiltonian, the two are not the same.

respectively, with 32 parameters for 4921 and 5366 transitions, respectively, through $J'' = 59$ and $K_a'' = 16$. In previous studies of both the normal and $^{13}\text{C}_1$ species [10–12], it was found that transitions with higher J and K_a rotational quantum numbers in the ground torsional state tend to deviate from the fit probably due to perturbation with excited vibrational or torsional states.

Although assignments of rotational transitions of methyl formate in excited torsional states remained unavailable for many years, such assignments were finally made within the last five years in the 7–200 GHz frequency region [9,10]. Odashima et al. measured the rotational spectrum of methyl formate in its first excited CH_3 torsional state ($\nu_t = 1$) for the first time and assigned transitions to the A substate [9], while Ogata et al. extended the assignments to the E substate in $\nu_t = 1$ [10]. Altogether, a total of 785 transitions through $J'' = 18$ and $K_a'' = 7$ in the A and E substates of $\nu_t = 1$ have been analyzed together with the ground state ($\nu_t = 0$). With the RAM Hamiltonian of Ogata et al. [10], a set of 69 molecular parameters was determined from the global analysis of $\nu_t = 0$ and 1 with a unitless standard deviation of 1.96.

To the best of our knowledge, there has until the present been no rotational spectroscopic study of other isotopomers of methyl formate in excited torsional states. In our previous study of methyl formate in $\nu_t = 0$ [12], spectra of both the normal and $^{13}\text{C}_1$ species were observed in the 110–380 GHz frequency region by means of the FASSST (Fast Scan Submillimeter Spectroscopic Technique) apparatus [13]. Among the FASSST spectra of methyl formate in the $\nu_t = 0$ state, several satellite R -branch transitions having two components were found with fairly strong intensity. These transitions occur at frequencies 0.5–2.0 GHz below the corresponding series of transitions of $\nu_t = 0$ for both species. Fig. 1 shows an example of these doublet satellite transitions, subsequently assigned to the $^{13}\text{C}_1$ species in the $\nu_t = 1$ state. The doublet components arise from A and E substates, and much larger torsional splitting between A and E lines can be seen in the $\nu_t = 1$ state compared with those of $\nu_t = 0$.

In this paper, we report rotational assignments of normal methyl formate and methyl formate- $1\text{-}^{13}\text{C}$ in excited torsional states. The torsional assignments will be discussed according to molecular constants obtained from the ErHam procedure and relative energies derived from intensity ratios. The experimental conditions of the FASSST measurements for both the normal and

$^{13}\text{C}_1$ species of methyl formate were reported in our previous paper [12], and are not described here.

2. Assignment and analysis

For the rotational assignments and analysis of the FASSST spectrum of methyl formate in the excited states, we applied the same scheme as done for the ground state in our previous study [12]. In particular, the rotational assignments were undertaken with the CAAARS (Computer Aided Assignment of Asymmetric Rotor Spectra) program, which applies the Loomis-Wood type procedure so that frequencies and intensities between observed and predicted lines are visually compared for a series of transitions. The ErHam program³ was utilized for predictions and the least-squares fitting analysis of methyl formate in the excited torsional states studied. The theoretical background and details of the ErHam procedure are provided elsewhere [2–4] and its application to molecules with a single internal rotor is discussed in previous studies [12,14]. When this approach is used, rotational levels are expressed with a basically conventional effective Hamiltonian for asymmetric rotors with some tunneling terms that arise from interactions between overall rotation and internal rotation. The tunneling terms are given as Fourier series of torsional energy and rotational parameters with the Fourier expansion coefficient $q \neq 0$ and they are functions of ρ and β . The ρ parameter is the magnitude of $\vec{\rho}$ and β is the angle between the principal a -inertial axis and the z molecular reference axis of the ρ axis system (RAS).

2.1. Normal methyl formate in its excited torsional states

Prior to the rotational assignment of the normal species in the first excited state, previous data of the A and E substates in $\nu_t = 1$ [9,10] were re-analyzed with the ErHam procedure for frequency predictions at higher frequency. A unitless standard deviation of 0.87 was obtained from our fit of the previously measured 770 spectral lines in $\nu_t = 1$ with 35 parameters. Note that this fit contains values for the internal rotation parameters ρ and β for $\nu_t = 1$ that are different from those of the ground state. Rotational assignments of the satellite bands were then carried out with the CAAARS procedure, in which newly assigned transitions and previous data are fitted together to produce improved predictions of unassigned transitions. Initial assignments were aided by comparing series of transitions in $\nu_t = 1$ and $\nu_t = 0$ in reduced Fortrat diagrams, where reduced frequencies of transitions in particular series defined by the pseudo quantum numbers K_a and K_c are plotted vs. J'' . For example, Fig. 2 shows a reduced Fortrat diagram for selected a -type, R -branch transitions of normal methyl formate in A substates of the first two torsional states with $K_a = 0\text{--}3$. The series for $\nu_t = 0$ and $\nu_t = 1$ show important similarities in both the shapes of the curves and the J'' values at which degeneracies between two pairs of series break due to asymmetry doubling. The particular pairs of series of transitions shown in Fig. 2 have lower-level quantum numbers for each J of $K_a, K_c = J - K_a$ and $K_a + 1, K_c = J - K_a$; since methyl formate is a quasi-asymmetric top, such pairs of a -type R -branch transitions are split at low J but merge at higher values of J [15]. Indeed, methyl formate has many transitions that are blended or nearly blended despite the additional complication of internal rotation. Although such groups of closely-spaced transitions are included in the dataset, for those transitions either totally blended or nearly blended with separations less than 200 kHz, only one transition is used in the fit with an average weight equal to the total intensity of the line divided by the number of blended transi-

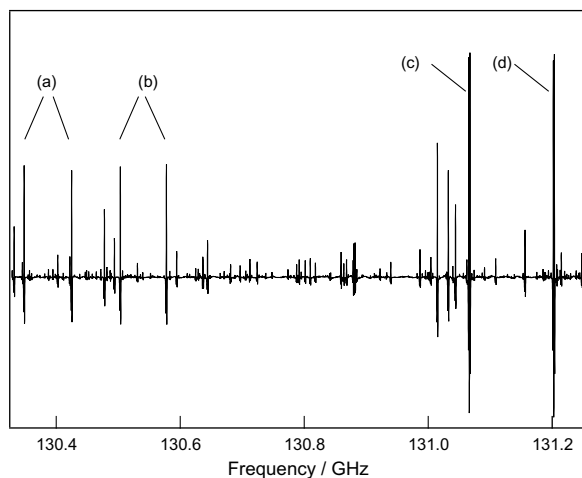


Fig. 1. Rotational transitions of $J = 12 \leftarrow 11$ in the $\nu_t = 0$ and 1 torsional states of the $^{13}\text{C}_1$ isotopomer. The designations (a and b) represent the A and E components of transitions with $K_a = 1$ and $K_a = 0$ in $\nu_t = 1$, respectively, while (c and d) represent the E and A components of transitions with $K_a = 1$ and $K_a = 0$ in $\nu_t = 0$, respectively.

³ Available at: <http://www.ifpan.edu.pl/~kisil/prospe.htm>.

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