

# Identification of a vibrationally excited level in methyl formate through microwave and far-infrared spectroscopy

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Methyl formate ( $\text{HCOOCH}_3$ ) is an important interstellar molecule. More than 1000 rotational transitions including those from the ground state, torsionally excited states and of its isotopologues have been observed towards several astrophysical sources. The laboratory spectra of methyl formate in the microwave spectral region contain many unassigned transitions and many of them are likely to be due to rotational transitions in the low-lying excited states. We report the laboratory identification of new rotational transitions in the COC deformation ( $\nu_{12}$ ) excited state. The identification was made possible by combining the microwave data with rotation-vibration spectra taken in the far-infrared at the Canadian Light Source synchrotron.

## I. INTRODUCTION

The *cis*-methyl formate molecule ( $\text{HCOOCH}_3$ , see Fig. 1) is commonly detected in molecular clouds and other astrophysical sources by using its rest frequencies determined by microwave spectroscopy. It was first observed over 40 years ago in the giant gas molecular cloud Sgr B2 [1], and since then over 1000 transitions attributed to this molecule have been found, many in Sgr B2 and in another cloud Orion KL. It has also been discovered in other star-forming regions [2]. The transitions are assigned to a variety of excited torsional states as well as to the ground vibrational state, so some degree of vibrational excitation is attained in the astrophysical environments where methyl formate is found [3–6]. Therefore,

measurement and characterization of the molecule's low-lying torsions and vibrations is important to facilitate its detection as well as to eliminate its lines in spectra where new species are sought.

The first microwave spectra of methyl formate and its isotopologues were reported by Curl [7]. Subsequent microwave studies of the normal species provided measurements and analyses of the ground state and of the  $\nu_{18}$  and  $2\nu_{18}$  levels arising from excitation of the torsion of the methyl group [8–18]. The energies of the excited torsional levels and of other vibrational levels have been determined in low-resolution infrared studies. [19]. Surprisingly little work has been attempted to rotationally resolve the vibrational spectra, with one study from Synchrotron SOLEIL reporting a high-resolution study of the  $\nu_{18}$  fundamental band near  $132\text{ cm}^{-1}$  [20]. Since the rotational structure of the upper and lower states had already been characterized by microwave spectroscopy, the far-infrared study primarily made a precise measure of the band origin and aided in the determination of the

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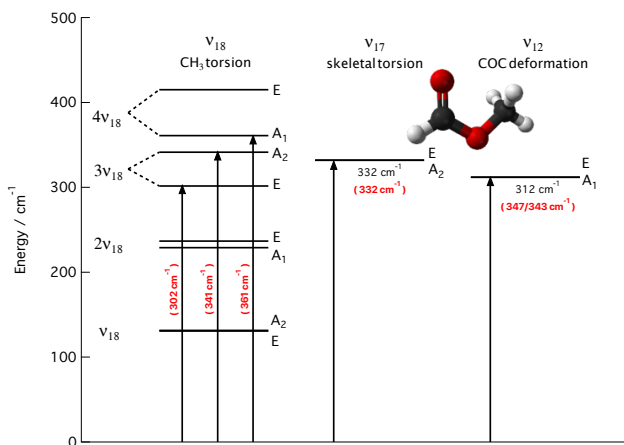


FIG. 1. Low-lying energy states of methyl formate. Energies of the states potentially associated with the new microwave series S are indicated, relative to the A sublevel of the ground state. Numbers printed in red and within parentheses are taken from calculations [22], and where experimental numbers are available (this work, and ref. [19]) they are printed in black without parentheses. In the figure, the A and E sublevels of  $\nu_{12}$ ,  $\nu_{17}$  and  $\nu_{18}$  are not resolved. The A-E energy ordering of  $\nu_{12}$  and  $\nu_{17}$  follows the *ab initio* predictions of ref. [22].

torsional barrier.

In the course of microwave spectroscopy experiments on methyl formate conducted at University of Toyama, a new series of spectral lines which we will label S was observed that appeared to arise from a previously unidentified vibrational level. There are four vibrational levels that have components that are likely candidates (see Fig. 1):  $3\nu_{18}$  ( $302\text{ cm}^{-1}$ , E and  $341\text{ cm}^{-1}$ ,  $A_2$ ) and  $4\nu_{18}$  ( $361\text{ cm}^{-1}$ ,  $A_1$ ), for which energies have been calculated [22], and  $\nu_{12}$  ( $312\text{ cm}^{-1}$ ,  $A_1/E$ ) and  $\nu_{17}$  ( $332\text{ cm}^{-1}$ ,  $A_2/E$ ), which have been observed in low-resolution far-infrared spectra [19]. The intensities of the new series relative to those already assigned did not unambiguously identify the vibration to which they belonged, so we collected high-resolution far-infrared rotation-vibration spectra of methyl formate at the Canadian Light Source synchrotron to help resolve the ambiguity. This paper describes our experiments and the assignment the unidentified series by comparison of the data collected in the microwave and far-infrared experiments.

## II. EXPERIMENT

### A. Microwave spectroscopy

Microwave spectroscopy data up to 268 GHz were taken at the University of Toyama over a number of years [13, 14, 18], and more experiments are in progress. De-

tails of the source-modulation spectrometer have been reported elsewhere [18, 23], and will be described here only briefly. The required frequencies of microwave radiation were generated by a synthesizer whose output was manipulated with frequency multipliers. The radiation produced was detected with a liquid helium-cooled InSb detector and demodulated with a lock-in amplifier. To estimate the energies of the new vibrationally excited state, data below 110 GHz were taken both at room temperature and after cooling the sample cell with dry ice (195 K). The ratio of intensities between analogous transitions within the ground and vibrationally excited state indicate that they are separated by  $292(98)\text{ cm}^{-1}$ . Since the intensities of the observed lines were not calibrated between different frequency ranges, the uncertainty in the energy of the vibrationally excited state is large. Table I lists the assigned observed frequencies below 200 GHz for series S.

### B. Far-infrared spectroscopy

Anhydrous methyl formate (99% pure, from Sigma-Aldrich) was transferred to a small sample cell under a dry nitrogen atmosphere at the Canadian Light Source synchrotron (CLS). The sample was subjected to 5 cycles of freezing with liquid nitrogen, pumping and thawing to remove unwanted gases. A small amount of vapour ( $0.0022\text{ Torr}$ ) was then admitted into a 2-m-long White cell cooled to 198 K, set so that the synchrotron light could traverse a 72 m path through the cell. The beam splitter in the Bruker IFS125HR Fourier transform spectrometer on the beamline was a Mylar film 6 microns thick. The detector was a helium-cooled silicon bolometer, which was sensitive to about  $370\text{ cm}^{-1}$ . In total 752 scans were co-added to produce the final interferogram, which was taken at a resolution of  $0.00096\text{ cm}^{-1}$ .

The far-infrared spectrum from  $295\text{--}365\text{ cm}^{-1}$  is shown in Fig. 2. The COC deformation band,  $\nu_{12}$ , and the  $\nu_{17}$  skeletal torsion band are shown together. A strong Q-branch dominates the  $\nu_{17}$  band. The Doppler width for individual lines of methyl formate at 198 K is about  $0.0005\text{ cm}^{-1}$  at  $350\text{ cm}^{-1}$ , so the resolution of our spectrum is limited by the Fourier transform spectrometer's maximum possible path length. This situation is calculated to persist to about  $770\text{ cm}^{-1}$ , at which point the spectra change from instrument- to Doppler-limited. For unblended lines we estimate the uncertainty in the measured wavenumber to be about  $0.0002\text{ cm}^{-1}$ .

## III. ANALYSIS

### A. Microwave data

Following the same strategy that we used in studying  $\text{HCOO}^{13}\text{CH}_3$  in its second vibrationally excited state, we sought patterns with a characteristic quartet structure

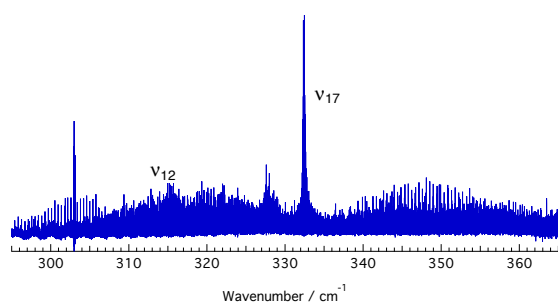


FIG. 2. An overview of the far-infrared spectrum of methyl formate from 295-365  $\text{cm}^{-1}$ . The positions of the  $\nu_{12}$  and  $\nu_{17}$  bands previously observed at low resolution [19] are indicated.

arising from strong  $J + 1_{0,J+1} - J_{0,J}$  and  $J + 1_{1,J+1} - J_{1,J}$  transitions and weaker  $J + 1_{1,J+1} - J_{0,J}$  and  $J + 1_{0,J+1} - J_{1,J}$  transitions (see Fig. 1 in reference [24]). Series S from the new vibrationally excited state was identified in this manner, and assignments were confirmed with combination difference loops when possible. We fit the assigned rotational transitions of series S with Watson's A-reduced Hamiltonian, assuming that they were sublevels of  $A_1$  or  $A_2$  symmetry. However, the number of lines included in the fit was limited, and the possibility that the new transitions arise from sublevels of  $E$  symmetry cannot categorically be ruled out. The molecular constants are shown in Table II. The rms of the fit was 0.037 MHz, which is comparable to our estimated experimental uncertainty, 50 kHz, but the best choice of fit parameters was unusual in that including  $\phi_K$  proved better than including  $\Delta_K$ , and the centrifugal distortion constants are very large compared to those of the ground state. The fit is therefore only effective, reproducing the transition frequencies but unlikely to have predictive power.

The expected pattern of energy states for the  $3\nu_{18}$  methyl torsion level can be predicted from our previous microwave study of the  $2\nu_{18}$  level. Transitions up to 220 GHz with  $J \leq 20$  were calculated, but did not produce the quartet pattern observed in the ground state. This suggests that the new series arises from either the  $\nu_{12}$  COC deformation level or the  $\nu_{17}$  skeletal torsional level.

### B. Far-infrared data

Although the far-infrared spectrum of  $\text{HCOOCH}_3$  between 300-370  $\text{cm}^{-1}$  is reasonably well resolved, it has proven quite resistant to analysis by the usual method of identifying sub-band branches in a Loomis-Wood plot. Figure 2 shows the two main structures, assigned in low-resolution and theoretical work as the  $a/b$ -type  $\nu_{12}$  and  $c$ -type  $\nu_{17}$  bands [21, 25].

The data from the new microwave series allows us to calculate the energies of the  $K_a = 0$  and  $K_a = 1$  levels relative to an arbitrary reference energy. The ground-state

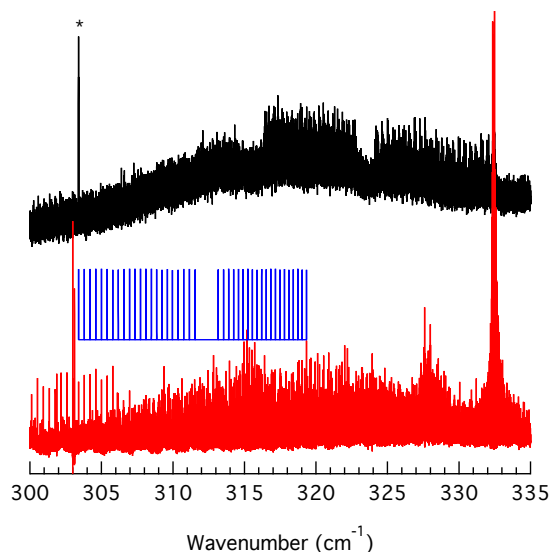


FIG. 3. Illustration of the correlation process. The bottom trace (red) is the far-infrared spectrum, the middle trace (blue) is the 'mask' with the calculated spectrum of the  $a$ -type  $K_a=0$  P and R branches, and the top graph (black) is the correlation between the two lower traces. The correlation spike, which occurs when the lines of the mask coincide with corresponding features in the spectrum, is marked with an asterisk.

energy levels can be obtained from Ref. [20]. (Note that at the resolution afforded by the far-infrared data the  $E$  and  $A_1/A_2$  levels for a given  $J$ ,  $K_a$  and  $K_c$  cannot be distinguished.) This allows  $a$ - and  $b$ -type rotation-vibration transitions to be calculated, and a simulated spectrum (which we call the 'mask', see Fig. 3) for each type to be obtained with the same wavenumber interval between consecutive points as in the far-infrared spectrum. The mask is then correlated with the spectrum: starting from the first point of the spectrum, the two are multiplied together and the result is integrated. The value of the integral is then plotted against wavenumber, and when the mask matches exactly with the corresponding lines in the spectrum the plot exhibits a narrow, sharp spike as seen in the top trace of Fig. 3. This technique has been applied previously to NCNCS with great success [26].

When this was attempted, the only correlations that occurred were with masks of  $a$ -type branches, which correlated with lines in the  $\nu_{12}$  spectrum for both the  $K_a = 0$  and  $K_a = 1$  series. Thus, we conclude that the new transitions seen in the microwave spectrum arise from rotational transitions within the  $\nu_{12}$  band. Some of the lines assigned via correlation are shown in Fig. 4.

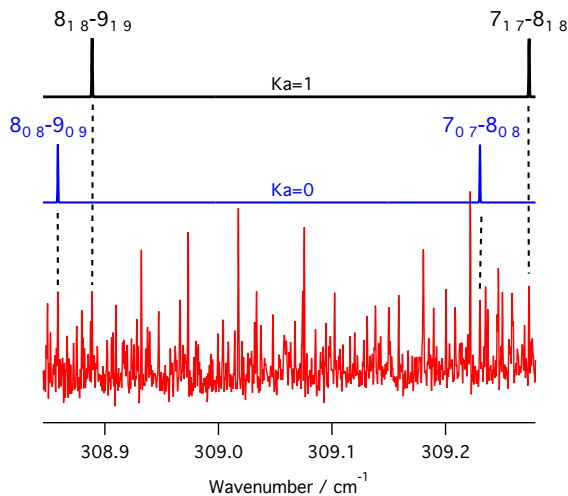


FIG. 4. An expanded view of the infrared spectrum and two correlation masks, with assigned  $a$ -type P-branch lines of the  $\nu_{12}$  spectrum indicated for the  $K_a=0$  and  $K_a=1$  series.

#### IV. DISCUSSION AND CONCLUSIONS

Our data permit us to more precisely measure the energy of the  $\nu_{12}$  COC deformation level of methyl formate. The  $1_{01}-2_{02}$  transition of the  $\nu_{12}$  band is measured at  $311.5498 \text{ cm}^{-1}$ , so by adjusting this value by the ground-state  $2_{02}$  level position of  $1.2181 \text{ cm}^{-1}$  obtained from the SOLEIL data and by the  $\nu_{12}$   $1_{01}-0_{00}$  interval of  $0.4001 \text{ cm}^{-1}$  calculated from the fitting of the new  $K_a = 0$  series we find that the  $\nu_{12}$  level is at  $312.3678 \text{ cm}^{-1}$ , compared to  $318 \text{ cm}^{-1}$  determined from low-resolution spectra[19].

The  $A-E$  sublevel splittings within a vibrational level are due to the methyl torsion, and the splitting increases with higher excitation of this mode. The  $\nu_{12}$  and  $\nu_{17}$  levels involve no torsional excitation, so the splittings in these levels should be small, as it is in the ground state. However, assuming that we have correctly assigned the symmetry of levels in series S as  $A_1$  and  $A_2$ , we have not yet identified the  $E$  sublevels of this state. This is possibly due to interactions with the  $E$  sublevels of nearby states, which will perturb them from their expected positions. Indeed, the calculations of refs. [21] and [22] show that the  $A-E$  splittings in the  $\nu_{12}$  and  $\nu_{17}$  levels are larger than that of the ground state, possibly due to  $E$ -sublevel interactions. In principle, the  $E$  sublevel of the  $\nu_{12}$  level could be identified in the far-infrared spectrum, but given the high density of lines and the overlap with the  $\nu_{17}$  spectrum this has not been possible so far. (All of the above discussion can be equally well applied if in fact we have observed the  $E$  sublevels of  $\nu_{12}$ , in which case mutual perturbations between the levels of  $A_1$  and  $A_2$  symmetry could lead to enhanced  $A-E$  splitting.) We will continue to analyze and assign both the microwave and far-infrared data, exploiting correlations of the type

used here when possible.

#### V. ACKNOWLEDGEMENT

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TABLE I. Assigned microwave transitions of methyl formate in the COC deformation excited state.

symmetry $J' K'_a K'_c$			symmetry $J'' K''_a K''_c$			Observed Frequency(MHz)	Obs.-Calc. (MHz)		
A2	3	0	3	A1	2	0	2	35544.019 <sup>a</sup>	0.624
A1	4	0	4	A2	3	0	3	46895.892 <sup>a</sup>	0.300
A2	5	0	5	A1	4	0	4	57904.424 <sup>a</sup>	0.066
A1	6	0	6	A2	5	0	5	68611.725	0.025
A2	7	0	7	A1	6	0	6	79119.592	-0.021
A1	8	0	8	A2	7	0	7	89538.559	0.007
A2	9	0	9	A1	8	0	8	99945.181	0.025
A1	10	0	10	A2	9	0	9	110374.851	-0.071
A2	11	0	11	A1	10	0	10	120836.082	-0.021
A1	12	0	12	A2	11	0	11	131324.746	-0.040
A2	13	0	13	A1	12	0	12	141833.852	0.029
A1	14	0	14	A2	13	0	13	152356.605	0.014
A2	15	0	15	A1	14	0	14	162888.053	0.018
A1	16	0	16	A2	15	0	15	173424.630	0.010
A2	17	0	17	A1	16	0	16	183963.969	-0.014
A1	18	0	18	A2	17	0	17	194504.623 <sup>a</sup>	0.055
A2	3	1	3	A1	2	1	2	33758.679 <sup>a</sup>	-0.084
A1	4	1	4	A2	3	1	3	44891.488 <sup>a</sup>	-0.180
A2	5	1	5	A1	4	1	4	55937.099 <sup>a</sup>	-0.081
A1	6	1	6	A2	5	1	5	66890.498	-0.086
A2	7	1	7	A1	6	1	6	77754.986	-0.028
A1	8	1	8	A2	7	1	7	88539.776	-0.007
A2	9	1	9	A1	8	1	8	99257.931	0.027
A1	10	1	10	A2	9	1	9	109923.568	0.023
A2	11	1	11	A1	10	1	10	120550.036	0.041
A1	12	1	12	A2	11	1	11	131148.420	-0.055
A2	13	1	13	A1	12	1	12	141727.727	0.013
A1	14	1	14	A2	13	1	13	152294.080	0.007
A2	15	1	15	A1	14	1	14	162851.922	-0.023
A1	16	1	16	A2	15	1	15	173404.236	0.014
A2	17	1	17	A1	16	1	16	183952.747	0.026
A1	18	1	18	A2	17	1	17	194498.657 <sup>a</sup>	0.135
A2	5	1	5	A1	4	0	4	63838.028 <sup>a</sup>	0.118
A1	6	1	6	A2	5	0	5	72824.143	0.008
A2	7	1	7	A1	6	0	6	81967.404	-0.045
A1	8	1	8	A2	7	0	7	91387.751	0.132
A2	9	1	9	A1	8	0	8	101106.955	-0.017
A1	10	1	10	A2	9	0	9	111085.323	-0.037
A2	11	1	11	A1	10	0	10	121260.441	0.008
A1	12	1	12	A2	11	0	11	131572.838	0.033
A2	13	1	13	A1	12	0	12	141975.753	0.020
A1	14	1	14	A2	13	0	13	152435.978	-0.005
A2	15	1	15	A1	14	0	14	162931.302	-0.035
A1	16	1	16	A2	15	0	15	173447.501	-0.023
A2	17	1	17	A1	16	0	16	183975.603	-0.022
A1	18	1	18	A2	17	0	17	194509.940 <sup>a</sup>	-0.224
A1	6	0	6	A2	5	1	5	62678.189	0.041
A2	7	0	7	A1	6	1	6	74907.150	-0.028
A1	8	0	8	A2	7	1	7	86690.742	0.026
A2	9	0	9	A1	8	1	8	98096.118	0.029
A1	10	0	10	A2	9	1	9	109213.137	0.030
A2	11	0	11	A1	10	1	10	120125.662	-0.003
A1	12	0	12	A2	11	1	11	130900.372	-0.084
A2	13	0	13	A1	12	1	12	141585.779	-0.025
A1	14	0	14	A2	13	1	13	152214.732	0.051
A2	15	0	15	A1	14	1	14	162808.670	0.027
A1	16	0	16	A2	15	1	15	173381.558 <sup>a</sup>	0.240
A2	17	0	17	A1	16	1	16	183941.081	0.002
A1	18	0	18	A2	17	1	17	194492.926 <sup>a</sup>	0.000

<sup>a</sup>Not included in the fit.

TABLE II. Molecular constants of methyl formate in the COC deformation excited state.

Parameter	Value (MHz)
$A$	19740.415(728)
$B$	6721.417(227)
$C$	5276.759(100)
$\Delta_J$	0.0913(39)
$\Delta_{JK}$	1.557(35)
$\delta_J$	0.05039(182)
$\delta_K$	1.892(69)
$\phi_K$	0.07426(92)

<sup>a</sup> ( $1\sigma$ )

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