Global assignment and extension of millimeter- and submillimeter-wave spectral database of $^{13}C_1$-methyl formate ($H^{13}COOCH_3$) in the ground and first excited states

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ABSTRACT

A compilation of the available spectroscopic millimeter and submillimeter-wave data of the ground and first excited states of $^{13}C_1$-methyl formate has been carried out. The exhaustive analysis of the available transition lines of $H^{13}COOCH_3$ (Willaert et al. 2006; Maeda et al. 2008a,b; Carvajal et al. 2009) has led to the assignment of 7457 spectral lines by means of a global fit of 45 parameters, using the RAM method and the BELGI-Cs code, with a resulting unitless standard deviation of 0.57. Over 1600 lines are included for the first time in the fit. In addition, the line strengths of spectral lines are also calculated using the most recent experimental measurement of the electric dipole moment (Margulès et al. 2010). In conclusion, the present study represents a notable improvement with respect to previous $H^{13}COOCH_3$ spectral analyses. Therefore the better accuracy of the present analysis may help the future identification of new $^{13}C_1$-methyl formate lines in the interstellar and circumstellar media, and may contribute to decrease some of the spectral confusion due to this species in astronomical surveys.

Subject headings: catalogs - submillimeter - millimeter - techniques: spectroscopic
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1. Introduction

Molecules are used in astronomy as probes of the physical conditions and as probes of the lifetimes of the sources. In this set of molecules, methyl formate is one of the approximately 50 molecular species with more than 6 atoms detected in the interstellar and circumstellar media (Herbst & van Dishoeck 2009). As a consequence of its relatively large abundance observed in different objects (Ikeda et al. 2001; Cazaux et al. 2003; Remijan et al. 2004; Bottinelli et al. 2007), methyl formate is considered as an interstellar Class I weed (Herbst & van Dishoeck 2009; Remijan & Markwick-Kemper 2008; Bergin et al. 2006), given that it is fundamental to discriminate its emission lines in the astronomical surveys in order to identify new molecular species.

In fact, in the interstellar medium, since its first time detection (Brown et al. 1975; Churchwell & Winnewisser 1975), different species of methyl formate ($H^{12}COO^{12}CH_3$, $H^{13}COOCH_3$, $HCOO^{13}CH_3$, and tentatively $DCOOCH_3$) have been identified i.e. in Orion KL and W51 e2 (Kobayashi et al. 2007; Demyk et al. 2008; Carvajal et al. 2009; Margulès et al. 2010). Moreover, spectral transition lines in the first excited torsional state of main isotopologue of methyl formate has also been identified (Kobayashi et al. 2007; Demyk et al. 2008).

Since a few years ago, due to the development of new astronomical observatories which operate in the sub-millimeter wave range, the spectral analysis (Ogata et al. 2004; Willaert et al. 2006; Carvajal et al. 2007; Maeda et al. 2008a,b; Ilyushin et al. 2009; Carvajal et al. 2009; Margulès et al. 2010) and theoretical calculations (Senent et al. 2005; Demaison et al. 2010) of methyl formate and its isotopologues have been intensified.

The first microwave spectral recording of methyl formate and nine of its isotopologues was carried out by Curl (1959). Among them, 16 lines in the spectral range of 12-26 GHz were reported for $^{13}C_1$-methyl formate. In 2006, Willaert et al. (2006) observed the rotational spectrum of this $^{13}C_1$ isotopologue in the frequency range of 7-610 GHz and provided 528 new lines. Two years later Maeda et al. (2008a) recorded around 4400 lines, belonging to the ground torsional state, in the range 110-380 GHz and they fitted a data set of 4921 lines (including almost all lines from Willaert et al. (2006)) with a standard deviation of 86 kHz, floating 33 fitting parameters with the "Effective Rotational-torsional Hamiltonian (ERHAM)" procedure (Groner 1992, 1997). The same year Maeda et al. (2008b) also reported for first time rotational spectral lines in the first two torsional excited states for both the normal species and the $^{13}C_1$ species. They were fitted separately with the ERHAM code. Some 910 transitions belonging to the first excited state $v_t = 1$ were fitted with an unitless standard deviation of 0.77 using 27 floated parameters, plus 7 parameters for which the values were fixed to their ground torsional state $v_t = 0$ value. For the second excited state $v_t = 2$, 231 transitions were fitted with an unitless standard deviations of 0.99 using 18 fitted parameters, plus 9 parameters fixed to their $v_t = 0$ values. However Maeda et al. (2008b) omitted in their fit some 1972 transitions belonging to the first excited state $v_t = 1$ for the $^{13}C_1$-methyl formate species, even though those lines were tentatively assigned.

In 2009, a spectral analysis for the ground torsional state of both $^{13}C_1$ and $^{13}C_2$ methyl formate species was carried out using the RAM ("Rho Axis Method") theoretical approach (Lin & Swalen 1959; Hougen et al. 1994) and the BELGI code (Kleiner 2010) with the aim of identifying new lines in Orion KL interstellar cloud (Carvajal et al. 2009). In the case of $^{13}C_1$ species, 4954 lines were fitted using 24 parameters. From this set of fitted lines, some 24 lines of 3 kHz of accuracy were either new measurements or remeasurements performed with a Fourier Transform Microwave Spectrometer (FTMW) in Lille. All other lines were measurements published by Willaert et al. (2006) and Maeda et al. (2008b). The standard deviation of the fit was 66.9 kHz.

The aim of this manuscript is to provide a conscientious compilation of data for $^{13}C_1$-methyl formate species including transitions belonging to $v_t = 0$ and 1 and using the RAM “global” approach. This so-called global method allows us to deal with the total set of states (to a certain truncation level) associated with the internal rotation of the methyl group, using one Hamiltonian and fitting the data to within experimental accuracy. The global approach used in the BELGI code is therefore quite different from other methods that separate these states into groups (by torsional states like in the ERHAM code mentioned above), and then treat each group of states using its own Hamiltonian. Those latter methods are called here “local” or “effective” methods (Kleiner 2010).

One reason to perform such a global analysis of two torsional states together is to get uncorrelated values for the torsional parameters F, V_3 and V_6. Another reason is to avoid inconsistencies in the data bases originated by the analysis of experimental spectra from different laboratories which can have some unfortunate repercussion in astronomical observations in the interstellar and circumstellar medium.

In the present work, a global fit of 7457 spectral lines for the ground and first excited torsional state of $^{13}C_1$ species was carried out using 45 fitted parameters with an unitless standard deviation of 0.57. To achieve this result we had to change the labeling of 777 lines already included in the fit published by Maeda et al. (2008a) and of two lines from Willaert et al. (2006). Besides, some 1591 transitions belonging to $v_t = 1$ which could not be included in the fit of Maeda et al. (2008b) are now included in our analysis for the first time.

The present paper also presents a line intensity calculation undertaken using more accurate values for the electric dipole moment components determined recently (Margulès et al. 2010) in comparison with the values determined by Curl (1959) for the normal species of methyl formate. For all these reasons, the present calculation represents a notable improvement with respect to previous analyses and we hope that it can help to identify $v_t = 1$ lines for first time, and new $v_t = 0$ lines, for the $^{13}C_1$ methyl formate in interstellar clouds, as realized by Kobayashi et al. (2007) and Demyk et al. (2008) for the normal species of methyl formate.

2. Theoretical assignment method

The theoretical formalism used in the assignment procedure of $^{13}C_1$ isotopologue of methyl formate is the so-called RAM (Rho-Axis Method) (Lin & Swalen 1959; Hougen et al. 1994; Kleiner 2010). This formalism was thought up for dealing with rotational and rovibrational spectra of molecules with one large amplitude motion of the type of internal CH_3 rotor.

The methyl top in a molecule, under internal torsion, is responsible of a splitting of each rotation-torsion state in two, one of A-symmetry (either A_1 or A_2) and another of E-symmetry. The RAM formalism has the ability of taking into account simultaneously both A- and E-species for different torsional states in the fitting procedure of molecular transition lines. The effective RAM Hamiltonian incorporates a number of pure rotational, pure torsional and rotation-torsion terms which are set up after minimizing the rotation-torsion interaction, when rotating the Principal Axis System to Rho-Axis System (Lin & Swalen 1959; Hougen et al. 1994; Kleiner 2010). The RAM Hamiltonian is based on previous works (Kirtman 1962; Lees & Baker 1968; Herbst et al. 1984).

The RAM formalism for the global spectroscopic analysis of molecules with a CH_3 top has been applied for a number of molecules as i.e. acetaldehyde and acetic acid (Kleiner et al. 1996; Ilyushin et al. 2003, 2008) and different isotopologues of methyl formate (Carvajal et al. 2007; Ilyushin et al. 2009; Carvajal et al. 2009; Margulès et al. 2010). The BELGI version of the RAM code used for the authors is available in the web [1] and its details for the application to methyl formate are described in Carvajal et al. (2007).

3. Spectral analysis of the ground and first torsional states

In the present paper, the spectral analysis has been carried out gradually, by including the transition lines from lowest to highest J values. At the beginning of the procedure, we start with initial guess values for the second order RAM rotational constants (A^{RAM}, B^{RAM}, C^{RAM}, D_{ab}), the five centrifugal distortion parameters (D_J, D_{JK}, D_K, δ_J, δ_K), the potential barrier (V_3), the coupling term between the conjugate torsional momentum and the rotational angular momentum (ρ) and the internal rotation constant (F), which was originally fixed to the *ab initio* value calculated in Carvajal et al. (2009). All other interaction parameters were initially fixed to zero.

After fitting the spectral data up to a given J, the analysis of the experimental data from different sources was undertaken with the subsequent prediction of $J + 1$ lines, adding the relevant torsion-rotation interaction parameters corresponding to higher order terms in the Hamiltonian. With this fitting procedure, the ground state lines were first included in the fit. After finishing with the ground state data, we started up again with the same procedure but including data of both states under study, from the ground and first torsional states.

The result of this global fitting procedure is reviewed in Table 1 where the overall

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[1] The source code BELGI for the fit, an example of input data file and a readme file are available at the web site (http://www.ifpan.edu.pl/˜kisiel/introt/introt.htm#belgi) managed by Dr. Zbigniew Kisiel. Extended versions of code are also available with one of the authors (I. Kleiner).

quality of the fit can be checked. The root-mean-square deviations are reported for transitions grouped according to their measurement uncertainties. A total number of 7457 A- and E- symmetry transitions in the ground ($v_t = 0$) and first excited ($v_t = 1$) states were analyzed with the use of 45 fitting parameters. The unitless standard deviation resulted 0.57.

The 4956 $v_t = 0$ lines included in the global fit come from Willaert et al. (2006) and Maeda et al. (2008a) and 24 lines from Lille Fourier Transform Microwave Spectrometer (L-FTMW). Although these last data were used for the ground state data fit of Carvajal et al. (2009) their frequencies have never been reported. The 24 $v_t = 0$ L-FTMW lines newly measured with a 3 kHz uncertainty replaced the Willaert et al. (2006) measurements when those exist.

From the total number of fitted $v_t = 0$ lines, 4429 lines come from Maeda et al. (2008a) although 777 A- and E- lines, mainly E-lines, turned out to have different labeling according to global RAM formalism used in this work, compared to the labeling of the ERHAM code (Groner et al. 2007). Those lines are quoted as "LABEL" in Table 1. In addition, we also pay special attention to the A/E → E/A inversion in the J'=J+1, K'_a=0/1, K'_c=J+1 ← J''=J, K''_a=0/1, K''_c=J series of $v_t = 0$ transitions, as pointed out by Ilyushin et al. (2009) for the normal species of methyl formate, which is also ocurring for the $^{13}C_1$ species. We also included in the present fit 503 $v_t = 0$ lines from Willaert et al. (2006). From them, 312 lines were recorded in the 300-610 GHz range with a 50 kHz uncertainty and the remaining 191 lines turned out to be in fact measured in the 7-62 GHz range. Within this data set in the 7-62 GHz range, 161 were given a weight corresponding to a experimental uncertainty of 100 kHz for isolated transitions, and 30 blended lines were given a slightly higher weight of 150-200 kHz (see Table 1). We also decided to use the frequencies of a number of lines from Willaert et al. (2006) rather than those reported by Maeda et al. (2008a), as the former were measured with a better experimental accuracy (50 kHz).

The 2501 fitted $v_t = 1$ lines in the global fit of this work come from Maeda et al. (2008b) who provided assignments for only 910 of those $v_t = 1$ lines (quoted in Table 1 as "FASSST2" measurements). A set of remaining 1972 transitions were omitted in their final fit and were listed with a tentative assignment. In the course of the present work it was noticed that there were in fact three sets of "omitted" transitions. The first set consisted of 1591 lines which were properly analyzed and we succeeded to fit them for first time in this work. Those transitions are indicated in the present paper as "NEWLY FITTED" even though they were recorded and assigned by Maeda et al. (2008b). The second set contains the "omitted" transitions which are not taken into account in our fit because their frequencies are already used with different tentative assignments, and their residuals are quite large. The third set included 25 lines that need more accurate experimental remeasurements and 68 lines that need, if not a new experimental recording, to find their right assignments. The lines of this third set are not also considered in our fit.

In summary, in this work, we have added 35 more lines for the ground torsional state $v_t = 0$. 1591 belonging to $v_t = 1$ lines are newly fitted with respect to Maeda et al. (2008b).

Table 2 shows the values, and their uncertainties, for the 45 torsion-rotation parameters of RAM model used in our final fit in order to achieve nearly experimental accuracy. It was only needed to include torsion-rotation interactions up to 6th-order.

A sample of the transition lines of $^{13}C_1$ methyl formate included in our fit are compiled in Table 3, which shows the line assignments, the observed frequencies with the measurement uncertainties (in parentheses), the computed frequencies with the estimated theoretical uncertainties (in parentheses), the observed-calculated values, the line strengths, the lower state energies relative to the $J = K_a = 0$ A-species $v_t = 0$ level taken as the zero for energy levels, and the sources of each transition line according to those marks given in Table 1. Table 3 is published in its entirety in the electronic version of the Journal.

During the analysis of the spectral data, we noted the presence of some blended lines: 62 $v_t = 0$ lines from Willaert et al. (2006), 665 $v_t = 0$ lines (11 of them are reassigned) from Maeda et al. (2008a), 86 $v_t = 1$ lines from Maeda et al. (2008b) and 93 $v_t = 1$ lines indicated as NEWLY FITTED. These lines are marked in Table 3 with the symbol "B", which stands for BLENDED. An alternative procedure to deal with blended transitions has been proposed by Ilyushin et al. (2009) for the normal species of methyl formate. It was not used in our work since the blended transitions do not show really bad observed-calculated values.

4. Intensities calculation

For the line strengths calculation, the procedure reported for the RAM formalism was already explained in detail (Hougen et al. 1994; Kleiner 2010). Recently the dipole moment components in the Principal Axis System were remeasured experimentally with an Stark spectrometer (Margulès et al. 2010), with a better accuracy than those given by Curl (1959), for the main species ($H^{12}COO^{12}CH_3$) and the monodeuterated species ($D^{12}COO^{12}CH_3$). The line strengths are assumed to be only driven by the permanent electric dipole components (Hougen et al. 1994), like in previous studies of methyl formate isotopologues (Carvajal et al. 2007, 2009; Margulès et al. 2010).

With the approximation that the dipole moment components of $H^{12}COO^{12}CH_3$ species keep invariable with the isotopic substitution of ^{13}C, we found that the dipole moment components in RAM Axis system are $\mu_a^{RAM} = 1.792$ D and $\mu_b^{RAM} = -0.044$ D for $H^{13}COO^{12}CH_3$. These values are obtained by rotating the dipole moment under the angle $\theta_{RAM} = 24.585°$ between RAM and PAM axis systems (see Table 4).

The line strengths of the assigned transitions are presented in Table 3 for both ground and first excited states. The degenerate transition lines were considered as one line with a line strength which is result of the sum of line strengths of the cluster transition lines (Ilyushin et al. 2009).

5. Discussion

In this work, a careful analysis of the available experimental millimeter and submillimeter-wave spectral data of $H^{13}COOCH_3$ has been carried out to allow us to gather all spectroscopic data recently reported, and to improve the prediction accuracy for this important astrophysical species. This study has resulted in the increase of almost 1600 spectral lines in the $^{13}C_1$-methyl formate database which initially were assigned by Maeda et al. (2008a) but were not included in their fit. A number of lines were rejected in the fit as a consequence of being already assigned, blended or misassigned.

The RAM formalism is used here with a global fit procedure of 7457 A- and E-symmetry species for the ground and first excited states of $H^{13}COOCH_3$. The computational quality for A- and E- symmetry lines is similar because they have, for approximately same number of lines, a comparable standard deviation (see Table 1). In comparison with the ERHAM procedure, which fits each torsional state separately (Maeda et al. 2008a,b), our global fit takes into account a number of extra interactions between different rotation-torsional v_t's states. At the other end, ERHAM is a very efficient and fast procedure which allows to deal with a large dataset at high J values.

The improvement in our present fit is not only perceived through the decrease of the number of parameters used in the Hamiltonian compared to previous works, but also because it was possible, after cleaning up the dataset, to assign a number of experimental lines with the RAM global formalism which were not fitted previously with ERHAM. In this way, increasing the number of experimental spectral data in this analysis gives more accurate and predictive torsion-rotation parameters in the RAM Hamiltonian, which in turn can predict, with higher accuracy, new transition lines which can be observed in the interstellar molecular clouds. Therefore, it is hoped that this work will make feasible the identification of $^{13}C_1$-methyl formate $v_t = 1$ lines in interstellar clouds, as Kobayashi et al. (2007) and Demyk et al. (2008) achieved for the normal species of methyl formate, or at least it will help to clean up future astronomical surveys.

In order to avoid pitfalls, a comparison is undertaken among Hamiltonian parameters of other procedures. In Table 4, the values of rotational constants in the principal axis system (PAM) and internal rotation parameters ρ and F for $H^{13}COOCH_3$ obtained in this work are presented together with the values of Maeda et al. (2008a,b), and Carvajal et al. (2009). Although in general there is a good agreement among the values for these low order parameters, comparisons between RAM and ERHAM values are difficult to make because the ERHAM parameters show a strong dependence on the torsional state (Carvajal et al. 2009). Some of the present fitted parameters seem to be less precise than in the previous fit (Maeda et al. 2008a,b). This is due to the fact that in some cases, the RAM global method followed in the BELGI code induces a high correlation between some parameters, e.g. between the rotational constants A, B, C and the D_{ab} parameter (Demaison et al. 2010). It is however necessary to free them in order to get a good fit.

The value of the internal rotation parameter F determined in this work presents, on one hand, a rather poor agreement with respect to its *ab initio* value used for the analysis of the ground state (Carvajal et al. 2009) and with respect to the ERHAM values obtained separately for the first three torsional states $v_t = 0$, 1, and 2 (Maeda et al. 2008a,b). On the other hand, it presents a very similar value to that obtained with a global RAM fit by

Carvajal et al. (2007), and by Ilyushin et al. (2009) for $\mathrm{v}_t = 0$ and $\mathrm{v}_t = 1$ transition lines of main species of methyl formate.

The discrepancies between the values determined for the torsion or rotation constants by various programs or compared to the equilibrium structure obtained by *ab initio* calculation is a rather complicated question (Demaison et al. 2010). Most programs determine F in a given torsional state v_t interactionless with the others, whereas the BELGI code, taking into account the interactions between different torsion-rotation states, determines the parameter F in a so-called "torsionless" state. The order of magnitude of the lowest-order experimental torsion-rotation interaction constant $\alpha_t^F = F(\mathrm{v}_t{=}0) - F(\mathrm{v}_t{=}1)$ (see Eq. (1) of Demaison et al. (2010)) is about 3-4% of F. For instance, for the parent isotopologue of methyl formate: $F(\mathrm{v}_t{=}0){=}178221(48)$ MHz; $F(\mathrm{v}_t{=}1) = 171706(37)$ MHz (Maeda et al. 2008b) whereas $F(\mathrm{BELGI}){=}164597(39)$ MHz (Ilyushin et al. 2009), a value which is not in agreement with the one obtained using Eq. (20) of Demaison et al. (2010): $F(\mathrm{BELGI}) = F(\mathrm{v}_t = 0) + \frac{\alpha_t^F}{2}$.

The reasons for this discrepancy have already been discussed in Demaison et al. (2010). One of them lies in the relation between I_α and the moments of inertia I_a, I_b and I_c in the principal axis system is

$$I_\alpha = I_a^0 + I_b^0 - I_c^0 + \Delta_{vib} \quad . \tag{1}$$

The problem is given by the pseudo inertial defect Δ_{vib} which is far from negligible (about 0.06 uÅ^2). Therefore, one could not expect a good agreement between the different determinations of I_α, i.e. from either ρ, the direction cosines, λ_a, λ_b, and λ_c, of the internal rotor axis i of the top in the principal axis system, and the moments of inertia $I_{g=a,b,c}$ (see Eq. (4) of Demaison et al. (2010)), or from the experimental derived value F_{exp}, which gives rI_α, or from the equilibrium structure (see Eq. (22) of Demaison et al. (2010)). For this reason, the different methods to determine the parameter F cannot be directly compared. Besides, F is usually highly correlated (especially when treating only one torsional state) with other internal rotation parameters and, therefore, it is rather inaccurate, i.e. small differences in the data or the method used may induce a large variation of F. Hence, F should be considered as an empirical fitting parameter without precise relationship to the structure.

Anyway, one would expect that the fitted value of F is actually better determined in the present work than in previous analyses because it uses a global procedure and takes into account more data in the ground and excited states simultaneously. In particular, in comparison with the study of Carvajal et al. (2009) which included in the fit data belonging only to the ground torsional state, the present work provides a value for F less correlated with the V_3 value. Besides, other torsional parameters as the values for potential V_3 (371.83617(408) cm^{-1}) and V_6 (25.34157(249) cm^{-1}) parameters determined in the present work for the $^{13}C_1$ isotopologue, are in good agreement with their values determined for main species, given by Carvajal et al. (2007) ($V_3 = 370.924(113)$ cm^{-1}, $V_6 = 23.9018(636)$ cm^{-1}), and by Ilyushin et al. (2009) ($V_3 = 372.6720(42)$ and $V_6 = 17.862(15)$ cm^{-1}).

In this paper, we also report the line strength calculation because it is an absolute prerequisite for a correct molecular identification in the interstellar medium. It is expected that the calculated line strengths presented in this work are in better agreement with the experimental ones for two reasons. First the analysis of an increasing number of experimental lines provides a safer prediction of its spectrum and, therefore, more reliable eigenfunctions needed for the line strength calculation. The second reason is that the used dipole moment was recently determined for the normal species of methyl formate (Margulès et al. 2010) with better accuracy than that given by Curl (1959).

Finally, as for the normal species of methyl formate, no lines from $v_t = 2$ were assigned or included in the fit. As perturbations with the other low frequency modes (ν_{12} and ν_{17} are located at 389 cm^{-1} and 403 cm^{-1} respectively for the normal species (Kleiner 2010)) of some of the energy levels from $\mathrm{v}_t = 2$ are probably occurring, the analysis of the third torsional level of methyl formate is still waiting for a global treatment of those perturbations.

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Table 1: Root-mean-square (rms) deviations from the global fit[a] of transitions involving $v_t = 0$ and $v_t = 1$ torsional energy levels of $^{13}C_1$- methyl formate ($H^{13}COOCH_3$).

Number of parameters	45
Number of lines	7457
rms of the 4956 MW v_t=0-0 lines	53.0 kHz
rms of the 2501 MW v_t=1-1 lines	58.4 kHz
rms of the 3700 A symmetry lines	56.5 kHz
rms of the 3757 E symmetry lines	53.2 kHz

Source[b]	Range[c] (GHz)	v_t, J_{max}, K_{max}[d]	Number of lines[e]	σ_{exp}[f] (MHz)	rms[g] (MHz)
L-FTMW	8-20	0,7,3	24	0.003	0.0033
WILLA	300-610[h]	0,58,24	312	0.050	0.0444
WILLA	7-62[i]	0,48,12	161	0.100	0.0538
FASSST	110-380	0,59,27	3652	0.100	
LABEL	110-380	0,32,20	777	0.100	
FASSST2	110-380	1,37, 8	910	0.100	
NEW	110-380	1,41,22	1591	0.100	
WILLA	7-62[i]	0,48,12	27	0.150	
WILLA	7-62[i]	0,13,6	3	0.200	0.2089

[a] Parameter values are given in Table 2. The complete list of observed minus calculated residuals of $v_t = 0$ and $v_t = 1$ lines is given in Supplementary Table.

[b] Sources of data: L-FTMW stands for Lille Fourier Transform Microwave Spectrometer (Carvajal et al. 2009) and they are for first time reported; WILLA data comes from Willaert et al. (2006); FASSST data are reported by Maeda et al. (2008a); LABEL data were reported by Maeda et al. (2008a) but with different assignment, see text; FASSST2 data were reported and fitted by Maeda et al. (2008b); and NEW data are fitted for first time in the present work but recorded and tentatively assigned by Maeda et al. (2008b).

[c] Spectral range of the measurements.

[d] Torsional state (v_t), and maximum J and K_a for each group of measurements.

[e] Number of MW lines in each uncertainty group.

[f] Uncertainty in MHz used in the fit.

[g] Root mean square deviation in MHz for each group.

[h] The spectrometer spectral ranges for these measurements are 300-322 GHz and 570-610 GHz with an accuracy better than 0.050 MHz (Willaert et al. 2006).

[i] The accuracy of spectral measurements of lines in the range 7-62 GHz given by Willaert et al. (2006) were generally better than 0.100 MHz for isolated lines but some lines are either blended or present a bad S/N ratio and therefore their measurement accuracy is taken as either 0.150 MHz or 0.200 MHz according to the broadening of the experimental line.

Table 2. Torsion-rotation parameters needed for the global fit of transitions involving $\mathrm{v}_t = 0$ and $\mathrm{v}_t = 1$ torsional energy levels of ^{13}C$_1$-methyl formate (H^{13}COOCH$_3$).

nlm[a]	operator[b]	parameter	Values[c]	nlm	operator	parameter	Values[c]
220	$(1-\cos 3\alpha)/2$	V_3	371.83617(408)		$-2P^2(P_b^2-P_c^2)$	δ_J	$0.1667(124)\,10^{-7}$
	P_α^2	F	5.5001302(483)		$-\{P_a^2,(P_b^2-P_c^2)\}$	δ_K	$0.71357(395)\,10^{-6}$
211	$P_\alpha P_a$	ρ	0.084131896(592)		$P^2(P_aP_b+P_bP_a)$	D_{abJ}	$-0.10425(502)\,10^{-6}$
202	P_a^2	A^{RAM}	0.58434493(312)		$(P_a^3P_b+P_bP_a^3)$	D_{abK}	$0.203086(339)\,10^{-5}$
	P_b^2	B^{RAM}	0.30424790(350)	642	$(1-\cos 6\alpha)P^2$	N_v	$-0.29087(137)\,10^{-3}$
	P_c^2	C^{RAM}	0.175972092(272)		$(1-\cos 6\alpha)(P_b^2-P_c^2)$	c_{11}	$-0.14218(216)\,10^{-3}$
	$(P_aP_b+P_bP_a)$	D_{ab}	−0.16207328(334)		$P_\alpha^4\,(P_aP_b+P_bP_a)$	$\Delta\Delta_{ab}$	$-0.11349(991)\,10^{-7}$
440	$(1-\cos 6\alpha)/2$	V_6	25.34157(249)		$(1-\cos 6\alpha)P_a^2$	K_2	0.0010357(115)
422	$(1-\cos 3\alpha)P^2$	F_v	−0.00224342(126)		$(1-\cos 6\alpha)\,(P_aP_b+P_bP_a)$	dd_{ab}	$-0.31770(554)\,10^{-3}$
	$P_\alpha^2P_a^2$	k_2	$-0.42493(383)\,10^{-4}$	624	$(1-\cos 3\alpha)P^4$	f_v	$0.108168(133)\,10^{-7}$
	$(1-\cos 3\alpha)P_a^2$	k_5	0.0099145(167)		$2P_\alpha^2\{P_a^2,(P_b^2-P_c^2)\}$	c_{1K}	$0.5233(100)\,10^{-9}$
	$2P_\alpha^2(P_b^2-P_c^2)$	c_1	$-0.11060(357)\,10^{-5}$		$(1-\cos 3\alpha)\{P_a^2,(P_b^2-P_c^2)\}$	c_{2K}	$0.50620(617)\,10^{-7}$
	$(1-\cos 3\alpha)(P_b^2-P_c^2)$	c_2	$0.1888(304)\,10^{-4}$		$(1-\cos 3\alpha)(P_aP_b+P_bP_a)P^2$	d_{abJ}	$0.52179(182)\,10^{-7}$
	$\sin 3\alpha(P_bP_c+P_cP_b)$	D_{bc}	0.0012672(115)		$(1-\cos 3\alpha)(P_a^3P_b+P_bP_a^3)$	d_{abK}	$-0.3108(121)\,10^{-7}$
	$(1-\cos 3\alpha)(P_aP_b+P_bP_a)$	d_{ab}	−0.00586781(586)		$(1-\cos 3\alpha)P_a^2P^2$	k_{5J}	$-0.69760(225)\,10^{-7}$
	$P_\alpha^2\,(P_aP_b+P_bP_a)$	Δ_{ab}	$0.5712(132)\,10^{-5}$	606	P^6	H_J	$-0.3039(33)\,10^{-13}$
413	$P_\alpha P_aP^2$	L_v	$0.33864(193)\,10^{-5}$		$P^4P_a^2$	H_{JK}	$0.62514(192)\,10^{-10}$
	$P_\alpha P_a^3$	k_1	$0.100847(682)\,10^{-4}$		P_a^6	H_K	$-0.115352(373)\,10^{-9}$
	$P_\alpha\{P_a,(P_b^2-P_c^2)\}$	c_4	$0.25224(114)\,10^{-5}$		$P^2\{P_a^2,(P_b^2-P_c^2)\}$	h_{JK}	$0.16321(50)\,10^{-10}$
	$P_\alpha\{P_a^2,P_b\}$	δ_{ab}	$-0.63986(292)\,10^{-5}$		$\{P_a^4,(P_b^2-P_c^2)\}$	h_K	$0.12169(149)\,10^{-10}$
404	$-P^4$	D_J	$0.10787(247)\,10^{-6}$		$P^4\,(P_aP_b+P_bP_a)$	D_{abJJ}	$-0.11932(36)\,10^{-10}$
	$-P^2P_a^2$	D_{JK}	$0.12066(200)\,10^{-5}$		$P^2\,(P_a^3P_b+P_bP_a^3)$	D_{abJK}	$-0.49498(161)\,10^{-10}$
	$-P_a^4$	D_K	$0.6884(276)\,10^{-6}$				

[a] Notation from Ilyushin et al. (2003); n = l+m, where n is the total order of the operator, l is the order of the torsional part and m is the order of the rotational part.

[b] Notation from Ilyushin et al. (2003). $\{A, B\} = AB + BA$. The product of the parameter and operator from a given row yields the term actually used in the vibration-rotation-torsion Hamiltonian, except for F, ρ and A^{RAM}, which occur in the Hamiltonian in the form $F(P_\alpha - \rho P_a)^2 + A^{\mathrm{RAM}} P_a^2$.

[c] Values of the parameters in cm^{-1} given in the present work, except for ρ which is unitless. Statistical uncertainties are given in parentheses in units of the last quoted digit.

Table 3. Assignments, observed frequencies, calculated frequencies, residuals from the RAM fit, line strengths, and lower energy levels for $^{13}C_1$-methyl formate ($H^{13}COOCH_3$) microwave transitions from $v_t = 0$ and $v_t = 1$ torsional states included in the fit with parameters of Table 2.

	Upper state[a]					Lower state[a]									
LNum[b]	v_t'	J'	K_a'	K_c'	P'	v_t''	J''	K_a''	K_c''	P''	Obs. Freq.(Unc)[c]	Calc. Freq.(Cal. Unc.)[d]	Line Str.[e]	Lower energy[f]	Ref.[g]
3228	1	33	1	32	−	1	33	∗(0, 1)	33	+	298945.476(0.100)	298945.573(0.023)	2.391	332.6410	NEW,B
3111	1	25	4	22	−	1	24	3	21	−	298960.207(0.100)	298960.207(0.005)	6.568	259.5370	NEW
123535	0	37	12	26		0	37	11	27		299122.238(0.100)	299122.199(0.007)	7.887	343.2518	FASSST
2240	0	37	12	26	−	0	37	11	27	+	299138.201(0.100)	299138.186(0.005)	10.190	343.2555	FASSST
124609	1	25	−4	22		1	24	3	21		299174.539(0.100)	299174.463(0.006)	6.540	259.4066	NEW
1011	0	42	10	32	+	0	41	11	31	+	299285.100(0.100)	299285.102(0.012)	2.641	408.8008	FASSST
123813	0	37	−12	25		0	37	11	27		299295.135(0.100)	299295.098(0.016)	2.303	343.2518	FASSST
121325	0	28	0	28		0	27	0	27		299319.320(0.050)	299319.332(0.003)	75.583	136.9628	WILLA
19	0	28	0	28	+	0	27	0	27	+	299319.945(0.050)	299319.962(0.003)	75.589	136.9506	WILLA
121494	0	24	−7	17		0	23	−7	16		299416.490(0.050)	299416.474(0.002)	59.650	135.5582	WILLA

Note. — Table 3 is published in its entirety in the electronic edition of the *Astrophysical Journal Supp. Ser.*. A portion is shown here for guidance regarding its form and content.

[a] Upper and lower state quantum numbers are indicated by $'$ and $''$ respectively. Torsion-rotation levels of A species have a “parity” label; levels of E species have a signed K_a value (Herbst et al. 1984). Note that for degenerate transitions, only the sum of line strengths of the degenerate transitions for a given cluster is preserved. Therefore the degenerate clusters of transitions is represented by only one transition frequency accompanied by the sum of line strengths calculated for the cluster components. For those cases, instead of the usual label J, K_a, K_c , the cluster is represented by the rotational state designation J, $*$ where the asterisk stands for the two degenerate levels with the same J, K_c but with different K_a quantum numbers, or with the same J, K_a but with different K_c quantum numbers. In the parentheses,

for the A-species, the two different K_a (or K_c) levels and the parity quantum number + or − are indicated and means that those two levels are degenerate within the selected cutoff (0.005 MHz). For the E-species, the parentheses contains + or $-K_a$ (K_c) and it means that those two levels are degenerate within the same selected cutoff (0.005 MHz).

[b] The first column is a line number, allowing to sort the lines by J and K sub-branches if needed.

[c] Observed $\mathrm{v}_t = 0$ and 1 microwave transitions in MHz, with estimated uncertainties in parentheses (in MHz).

[d] Calculated line frequency in MHz with calculated uncertainty in MHz.

[e] Calculated line strengths in D^2 (for details of the calculation procedure, see text).

[f] ower state energy (cm^{-1}) refered to the $J = K_a = 0$ A-species energy level taken as the zero of the energy (zero point torsional energy : 71.3465 cm^{-1}).

[g] Sources of data are explained in footnote b of Table 1. Blended lines are indicated with a capital letter B. They should be resolved with a spectrometer with a better resolution. Two corrected lines of Willaert et al. (2006) are marked by a capital letter C because of their symmetry are interchanged.

Table 4: Rotational constants in the principal axis system (PAM), angles between the principal axis and the methyl top axis and internal rotation parameters of methyl formate upon isotopic substitution.

	$HCOOCH_3$[a]	$H^{13}COOCH_3$[b]	$H^{13}COOCH_3$[c]	$H^{13}COOCH_3$[d]	$H^{13}COOCH_3$[d]
	Global fit (v_t = 0,1)	Global Fit (v_t = 0)	Global Fit (v_t = 0,1)	v_t = 0	v_t = 1
A(MHz)	19925.58(30)	19709.546(258)	19741.205(110)	19798.73249(43)	19917.3706(78)
B(MHz)	6946.75(21)	6909.555(225)	6898.138(116)	6864.74991(14)	6798.41624(91)
C(MHz)	5318.021(78)	5274.5475(189)	5275.51060(814)	5262.53086(13)	5236.59430(30)
$<(i,a)$[e]	53.06	52.48	52.63		
θ_{RAM}[f]	24.87	24.54	24.58475(38)	21.8604(79)	22.201(11)
ρ	0.0842153(11)	0.08407138(395)	0.084131896(592)	0.084497(20)	0.086209(43)
F (cm^{-1})	5.5053839(22)	5.8039485	5.5001302(483)	5.954(1)	5.7704(3)
σ[g]	0.71	0.67	0.57	0.86	0.99
N° of transitions	10533	4954	7457	4921	910

[a] Rotation-torsion parameters for the normal species $HCOOCH_3$ obtained in Ilyushin et al. (2009) with the RAM-axis system, after transforming the RAM values for the A, B, C rotational parameters into PAM values following the procedure described in Carvajal et al. (2007). Because of blending, 9298 measured lines correspond in their fit to 10533 transitions.

[b] Rotation-torsion parameters for $^{13}C_1$-methyl formate from Carvajal et al. (2009) transformed to the Principal Axis System. F was fixed to its *ab initio* value.

[c] Rotation-torsion parameters for $^{13}C_1$-methyl formate from the present work transformed to the Principal Axis System.

[d] Rotation-torsion parameters for $^{13}C_1$-methyl formate from Maeda et al. (2008b) obtained separately for each torsional state studied, using the ErHam procedure.

[e] Angle in degrees between the a-principal axis and the methyl top axis (i).

[f] The angle θ_{RAM} between the a-principal axis and the a-RAM axis is given in degrees and obtained from Eq. (1) from Carvajal et al. (2007), with the parameters A^{RAM}, B^{RAM}, C^{RAM}, and D_{ab} of Table 2.

[g] Unitless standard deviation.