

Reinvestigation of The Ground and First Torsional State of Methylformate

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ABSTRACT.

We have reinvestigated the laboratory spectrum for the methylformate HCOOCH_3 molecule involving both the ground and first excited torsional states.

We have fitted within almost experimental accuracy a data set for this molecule consisting of 3496 $v_t = 0$ and 774 $v_t = 1$ microwave lines, using the so-called “rho axis method” (RAM) and a model extended to include perturbation terms through eighth order. The previously published $v_t = 0$ and $v_t = 1$ microwave lines covering the J values up to 43 in the ground state and up to 18 in the first excited state have been extended by 434 new measurements from Lille in the 567-669 GHz spectral range, corresponding to transitions with $J_{\max} = 62$, $K_{\max} = 22$ in $v_t = 0$. The final fit requires only 49 parameters to achieve a unitless weighted standard deviation of 1.43 for a total of 4270 lines for the whole fit. This result represents an improvement over the previous fit which achieved a standard deviation of 1.96 for 3862 lines using 69 parameters. A calculation of the line strengths of torsion-rotation transitions up to $J = 60$ needed for the astronomical survey is also provided.

Keywords: methyl formate, radioastronomy, internal rotation, microwave spectrum

I. INTRODUCTION

Methyl formate (HCOOCH_3) is one of the most important molecules in astrophysics and it has been detected in the hot cores of giant molecular clouds such as Orion KL and Sgr B2(N) and in comets [1-4]. The relatively large abundance of methylformate in hot core sources has led to the identification of an important number of interstellar lines (about 500 rotational lines belonging to the ground state were identified in the hot core regions where stars are forming and very recently 20 lines belonging to $v_t = 1$ were identified in Orion KL [3]). Even though methyl formate, HCOOCH_3 , is extremely abundant in numerous interstellar clouds [3-4] its mechanism of formation is not yet understood [5], requiring further studies.

Its rotational spectrum is dense because of a relatively small rotational A constant (almost 0.6 cm^{-1}), leading to the observation of very high J values (up to 70), because of the presence of two non-zero components of the dipole moment, leading to both a-type and b-type transitions (μ_a

= 1.63 Debye and $\mu_b = 0.68$ Debye), and because of the existence of three states at low frequencies (the torsional mode at 130 cm^{-1} , the COC bending mode ν_{12} at 318 cm^{-1} and the out-of-plane bending mode ν_{17} at 332 cm^{-1}), leading to the observation of rotational transitions within those levels populated at room temperature. These three low frequency vibrations can also in principle interact with each other, perturbing the frequency and intensity distribution, but no evidence for such perturbations has been observed in the range of the quantum numbers we study. To give an idea of the density of the spectrum, let us note that for a temperature of 296K and with an arbitrary cutoff for the line strength of $1 \cdot 10^{-4}$, more than 33000 lines are predicted for the ground torsional state $\nu_t = 0$ in the range 0-4000 GHz (with most of the transitions occurring in the range 0-1600 GHz).

The methylformate spectrum is also complicated by the combination of a large amplitude motion, the torsion, with the large asymmetry splittings occurring in this fairly asymmetric near-prolate rotor ($\kappa = -0.78$). In particular, the internal rotation of the methyl group splits each rotational line into a doublet (characterized by the symmetry labels A and E). As the molecule is light and as the barrier to internal rotation is not so high, the internal rotation splittings are relatively large and the transition frequencies are extremely difficult to calculate with accuracy. For this reason, the identification of interstellar methyl formate was made possible only thanks to intense laboratory work, which has led to the assignment of more than 3000 lines up to 608 GHz in the vibrational ground state [6-14]. In the most recent studies, the rotational spectrum of the first excited torsional state was observed in the frequency range 7-200 GHz [14]. Around 530 lines were also recorded up to 620 GHz for the vibrational ground state of $^{13}\text{C}_1$ -methyl formate [15].

For some time the 500-600 GHz spectral range has been of particular interest for astronomers because the radio telescopes which are in development (HERSCHEL, ALMA, SOFIA) will operate in this sub-millimeterwave range. For this reason, it is important to have accurate predictions for methyl formate in this spectral range.

The challenge faced in the present study was to test the performance of the method when applied to the analysis of internal rotation phenomena at the especially high values of J and K quantum numbers one reaches in the 500-600 GHz range. Although the present paper represents some improvement over past millimeter and microwave studies on methyl formate [6-14], the main effort was focused on getting higher J values, which are rather intense and of importance for astrophysical detection.

The global fit achieved in the present work allows us to obtain a better determination of all the parameters compared to previous studies, especially the higher-order terms.

Even though the microwave spectrum of methylformate is rather complex and dense as said above, this eight-atom molecule is rather small and well adapted to perform high level quantum chemical calculations. It can become another “test” model to validate ab initio [16] and Density Functional Theory calculations by comparing them with experimental results, in the same way as acetaldehyde CH_3CHO or methanol CH_3OH [17]. High-level ab initio calculations are now being performed in order to compare the barrier height obtained with the experimentally derived value. The equilibrium structure of methylformate which was never determined with high accuracy will also be determined in this future paper [18].

II. EXPERIMENTAL DETAILS

The submillimeterwave measurements were performed in Lille with a source-modulated spectrometer using phase-stabilized backward wave oscillators working in the frequency range 300-700 GHz. The sources were Russian ISTOK backward-wave oscillators. They were phase-locked on the emission of a harmonic of a 2-20 GHz Hewlett-Packard (HP 83711A) synthesizer whose frequency was first multiplied by six and amplified by a Millitech active frequency multiplier. The intermediate frequency beat near 320 MHz was compared with the 32nd harmonic of the 10 MHz signal from a second HP synthesizer (HP 3325B). The mixer was a new planar Schottky diode optimized for the range 500-650 GHz and provided by the University of Virginia. It was placed in a parabolic structure. The large step frequency tuning of the source was

obtained by changing the frequency of the 2-20 GHz synthesizer. The small step frequency scan is provided by means of a 10 MHz (9.75 – 10.25 MHz) synthesizer. The typical acquisition time was 0.1 s per point. A sine-wave frequency modulation of 5 kHz (modulation depth: 400 kHz) was applied to the 10 MHz and the signal was demodulated at twice this frequency. The circular absorption cell, 6 cm in diameter and 110 cm long, was made of stainless steel. The absorption was detected with a liquid helium cooled InSb bolometer (QMC). The measurements were made at room temperature and the pressure in the absorption cell was from 10 to 30 mTorr. Computer processing was used to improve the signal/noise ratio and to measure the frequency of the lines, whose accuracy is better than 50 kHz in most cases.

III. THEORETICAL MODEL

The Hamiltonian used in the present work is the so-called "RAM" ("Rho Axis Method") internal-rotation Hamiltonian based on the work of Kirtman [19], Lees and Baker [20], and Herbst et al. [21]. Since rather complete descriptions of this method, which takes its name from the choice of axis system, has been presented in the literature [21-23], we will not repeat here such a general description. We also have applied this formalism and our code to a number of internal rotor molecules (see for example [24]). We will only emphasize here the various characteristics that the RAM program had to face for the present study.

The three-fold torsional potential barrier is rather high ($V_3 \approx 371 \text{ cm}^{-1}$) but the value of the reduced height $s = 4V_3/9F$ (with $F \approx 5.49 \text{ cm}^{-1}$ being the internal rotation constant) is about 30, so torsional splittings reach values up to a few MHz in the torsional ground state.

In addition, methyl formate has two small-amplitude vibrations [25], the COC bending mode ν_{12} at 318 cm^{-1} and the out-of-plane COC bending ν_{17} mode at 332 cm^{-1} , which lie near the top of the barrier and therefore could cause some perturbations on the rotational-torsional energy levels under study in the present work.

Third, methylformate is a fairly asymmetric near-prolate internal rotor molecule ($\kappa = -0.78$) leading to a clustering of the transitions with the same K_c quantum number for high J , low

K_a values. This large asymmetry, modeled by the difference between the B and C constants multiplying the term $(P_b^2 - P_c^2)$ in the Hamiltonian, leads to the determination of a rather large number of torsionally dependent contributions to this term of the form $P_\gamma^2(P_b^2 - P_c^2)$, $\cos 3\gamma (P_b^2 - P_c^2)$

Finally, the value of the ρ parameter which represents the coupling term between internal rotation and global rotation in the kinetic energy operator $F(P_\gamma - \rho P_a)^2$ where F is the internal rotation constant, P_γ is the internal angular momentum and P_a is the component of the global rotation angular momentum along the RAM a axis, is only 0.084. The consequence of such a small ρ value is to lengthen the period of the cosine function describing the torsional splittings as described in Eqs. (4) and (6) of Ref. [23]. For the $F(P_\gamma - \rho K)^2$ sign choice of our program, the $+K_a$ E-species levels belonging to even values of v_t lie below the $-K_a$ levels, and the $+K_a$ E species levels belonging to odd values of v_t lie above the $-K_a$ levels for all values of $|K_a|$ from 1 to 18. This is the same labeling scheme as the one adopted for our previous acetic acid study [24]. In this reference, the connection with the more traditional J_{K_a, K_c} labeling scheme was also discussed.

IV. ASSIGNMENTS and FIT.

In the present paper, we present a combined analysis of (i) 2 lines published by Brown et al [7] with a 3 kHz uncertainty, (ii) 51 lines published by Bauder [8] with a 20 kHz uncertainty, (iii) 97 lines published by Plummer et al 1984 [10] with a 50 kHz uncertainty, (iv) 147 lines of the 148 originally fitted by Plummer et al 1986 [11] with a 50 kHz uncertainty, (v) 44 lines from Demaison et al [9] with a 50 kHz uncertainty, (vi) 2591 lines (of 2612) from Ogata et al [14] also with a 50 kHz uncertainty and 7 lines from these authors with a 200 kHz uncertainty, (vii) 897 lines of the 908 originally published by Oesterling et al [12] with a 200 kHz uncertainty and (viii) 434 new lines (of the 438 originally measured) from Lille, measured using broadband recording in various frequency intervals between 567 and 669 GHz with an uncertainty of 50 kHz.

Starting from the same data set as in Ref. [14] which includes 3077 $v_t = 0$ lines and 785 $v_t = 1$ microwave transitions, we refit the data using our program [23-24]¹ starting at low J and going up progressively. Some improvements were made in our program in order to fit transitions with higher J and K than was possible with the previous version of the code.

During this process, we noticed that a number of previously published lines showed observed-calculated values which were much worse than the ones belonging to the rest of the same K sub-branch. Those lines correspond also to transitions which were given a weight of 250 kHz in Table 1 of [14]. We have thus decided to take some of them out of the fit. In addition, based on our fitting residuals, we have allocated an increased weight of 200 kHz, instead of the 100 kHz originally quoted by the authors, to all Oesterling data [12]. A noticeable improvement in our root-mean-square deviation was achieved by this change, since the unitless weighted standard deviation decreased from 1.52 to 1.43. We suggest that some Oesterling lines with observed-calculated deviations higher than exhibited by the other lines in the same series should be checked with a new experimental recording.

The "best" fit allowed 49 parameters (much less than the 69 parameters used in [14]) to vary. The microwave root-mean-square deviations obtained are 94 kHz (for 3496 $v_t = 0$ lines) and 84 kHz (for 774 $v_t = 1$ lines), respectively, involving transitions with $J \leq 62$, $K_a \leq 22$ for the ground torsional state and $J \leq 17$ and $|K_a| \leq 7$ for the $v_t = 1$ state. Separate root-mean-square deviations for the A and E species are 91 and 94 kHz for 2181 and 2089 lines respectively. Since we fit both species simultaneously, this demonstrates the similar quality of the fit for the two symmetry species. All the present standard deviations represent an improvement over those of Ref. [14], especially for the E species where the previous standard deviations were 134 kHz and 163 kHz for $v_t = 0$ and 1 respectively.

¹ The source code 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.K).

The overall quality of the fit is illustrated in Table 1, which gives the root-mean-square deviations for transitions grouped according to their measurement uncertainties (weight in the fit was proportional to reciprocal of squared uncertainty).

Table 2 presents the values for the rotation-torsion parameters used in our model, which includes up to eighth order parameters, i.e. those with $n = l + m = 8$, 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, respectively, following the notation of our previous papers on the RAM method like Ref. [24]. In comparison with the previous work, only 49 parameters are needed to achieve nearly experimental accuracy. However because no direct information on the torsional vibrational frequency $\nu_t = 1-0$ is included in the fit, the correlation between the torsional parameters F , V_3 and V_6 is rather strong, increasing the true uncertainties of those parameters somewhat beyond the standard deviations given in Table 2.

Tables 3 and 4 show some examples of the line assignments, the observed frequencies with the measurement uncertainties (in parentheses), the observed-calculated values, the references of the data sources, the line strengths for the transitions in the $\nu_t = 0$ and 1 torsional states respectively, and the lower and upper state energies. The whole table of the fitted lines is available in the Supplementary Data. Despite our efforts, some lines from the new measurements show somewhat large observed-calculated values, but at the present time it is unclear whether the discrepancies occur because of some missing high order parameters or because some of lines which present large observed-calculated values, are causing the parameters to shift. Indeed some previously measured MW lines show inadequate combination differences, i.e. violate a “closed combination differences loop criterion” similar to that described in Ref. [20]. Indeed, of all the “loops” checked, 12% of them (involving 1747 energy levels) show combination differences exceeding about 0.4 MHz.

As a test of quality of our parameters it is useful to compare the rotational constants among references. Hence a transformation of our rotational constants from the RHO axis system (RAM) to the principal axis system (PAM) was carried out. In Table 5 both the RAM rotational

constants obtained in the fitting (see Table 2) in MHz and their transformed values in the principal axis system are presented. The 3x3 matrix of RAM rotational constants (A^{RAM} , B^{RAM} , C^{RAM} , plus the off-diagonal inertia constant D_{ab}) was diagonalized using the values of those parameters from Table 2. This transformation corresponds to a rotation of the RAM axis system (where the a-axis lies along the direction of the ρ vector) into the PAM axis system. This rotation is about the out-of-plane c axis, which stays the same in the two axis systems. The angle (θ_{RAM}) between the RHO a-axis and the principal a-axis can be obtained from the following expression:

$$\tan(2\theta_{\text{RAM}}) = \frac{2D_{ab}}{(A - B)} \quad (1)$$

From the values of the rotational constants A, B and D_{ab} from Table 2, $\theta_{\text{RAM}} = 24.83$ degrees. In Table 5 we also corroborate our result with an ab initio calculation (MP2/VTZ) of the principal axis rotational constants from the molecular structure. The angles in degrees between the principal axis (a,b,c) and the methyl top axis (i) obtained from our fitting and calculated by means of MP2/VTZ are also compared in Table 5.

V. INTENSITY CALCULATION.

For astrophysical detections, line intensities are of course very important. In the case of the methylformate molecule, we need to take into account the internal rotation splittings. In the same way that the Hamiltonian was used in the calculation and fit of the line positions, the calculation of the line strengths was also carried out in the RHO axis system. For this purpose, the components of the dipole moment must be expressed in this non-principal reference system. The approach and the equations used here are given in detail in Ref. [23].

To obtain the line strengths in the RAM system, the dipole moment components must be transformed by a rotation of the principal-axis dipole moment components :

$$\begin{bmatrix} \mu_a \\ \mu_b \end{bmatrix}_{RAM} = \begin{bmatrix} \cos(\theta_{RAM}) \sin(\theta_{RAM}) \\ -\sin(\theta_{RAM}) \cos(\theta_{RAM}) \end{bmatrix} \begin{bmatrix} \mu_a \\ \mu_b \end{bmatrix}_{PAM} \quad (2)$$

Our intensity calculations will be based on the assumption that the microwave intensities are only driven by the permanent electric dipole moments [23], without any dependence on the torsional angle and other vibrational coordinates. In the case of methyl formate, the permanent electric dipole moment components have the values $\mu_a=+1.63$ D and $\mu_b=+0.68$ D in the principal axis system [8]. The direction in which the dipole moment was found to lie at an angle of $39.4(2)^\circ$ from the C=O bond (Fig. 1, [6]). In the “chemical” convention we have adopted, μ_a and μ_b have positive signs with respect to the chosen principal axes (i.e. the dipole moment is pointing from the positive charges to the negative charges of the molecule), a convention which we also used for acetic acid [24]. The RAM dipole moment components obtained by Eq. (2) are given in Table 6.

The line strengths for all the assigned transitions were obtained and are presented in Tables 3 and 4 for the torsional ground and first excited states, respectively. A comparison between our calculated line strengths and those calculated by Ogata et al [14] shows that they are in general in very good agreement. One cautionary comment should be made on the calculated intensities here. For the A species transitions certain selection rules on the parity (corresponding to $A_1 \leftrightarrow A_2$ overall selection rules) must be obeyed. However as a consequence of carrying out the calculations without factorizing the A block of the Hamiltonian matrix into A_1 and A_2 submatrices, the parity of the numerically generated eigenvector is not well defined when K-type doublets remain degenerate. Intensities for such cases were obtained by calculating both the formally parity-allowed and parity-forbidden components of a given K-type doublet transition, and then ascribing all the calculated intensity to the two allowed transitions.

The transition energies and line strengths have been predicted for a number of lines within the torsional ground state and the first excited state (around 33100 lines for $v_t=0$ and 38280 lines for

$v_t = 1$ at a temperature of 296K and with a cutoff of $1 \cdot 10^{-4}$ for the line strength. The prediction involves transition energies up to 4000 GHz and $J \leq 60$, $K_a \leq 60$, with most of the transitions falling in the range 0-1600 GHz. These lines should be useful for astrophysicists in the identification of new spectral lines in the interstellar space.

VI. CONCLUSION.

A new global analysis of the rotational levels in the torsional ground and first excited states for the parent methyl formate has been carried out by using the RHO Axis Model. In this study around 400 new submillimeter lines provided by the group of Lille were assigned and included in a joint fit with the existing data in the microwave, millimeter and submillimeter spectral region. An analysis of our rotational constants shows that they are in agreement with other spectroscopic parameters of different authors.

Due to the importance of this molecule for the remote sensing of the interstellar medium we have calculated not only the frequencies but also the relative intensities of the available data and we have predicted them for nearly 71380 lines (at 298K and with a cutoff for the line strength of $1 \cdot 10^{-4}$) within $v_t=0$ and $v_t=1$.

In the future, a new recording of some available data lines would be valuable in order to obtain those lines with better accuracy and to refine the rotational parameters. Also a recording of high resolution far infrared data in the 130 cm^{-1} region where the torsional fundamental $v_t = 1-0$ band (and overtones) absorb would be important to refine the torsional parameters and make them uncorrelated.

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Tables Captions.

Table 1. Root-Mean-Square (rms) Deviations From the Global Fit^a of Transitions Involving $\nu_t = 0$ and 1 Torsional Energy Levels of Methylformate ($\text{H}^{12}\text{COOCH}_3$).

Table 2. Torsion-Rotation Parameters Needed for the Global Fit of Transitions Involving $\nu_t = 0$ and $\nu_t = 1$ Torsional Energy Levels of Methylformate ($\text{H}^{12}\text{COOCH}_3$)

Table 3. Assignments^a, Observed Values^b, Residuals from the Fit^c, Line strengths^d, Sources^e, and Energy Levels^f for selected Methylformate Microwave Transitions within the $\nu_t = 0$ State.

Table 4. Assignments^a, Observed Values^b, Residuals from the Fit^c, Line strengths^d, Sources^e, and Energy Levels^f for selected Methylformate within the $\nu_t = 1$ State.

Table 5. Rotational constants in the RHO axis system (RAM) and in the principal axis system (PAM). Angles between the principal axis and the methyl top axis.

Table 6. Dipole moment components in Debye in the principal axis system (PAM) and in the RHO axis system (RAM).

Table 1. Root-Mean-Square (rms) Deviations From the Global Fit^a of Transitions Involving $v_t = 0$ and 1 Torsional Energy Levels of Methylformate ($H^{12}COOCH_3$).

	Number of parameters			49		
	Number of lines			4270		
	rms of the 3496 MW $v_t=0-0$ lines			0.0940 MHz		
	rms of the 774 MW $v_t=1-1$ lines			0.0836 MHz		
	rms of the 2181 A symmetry lines			0.0906 MHz		
	rms of the 2089 E symmetry lines			0.0939 MHz		
Source ^b	Range ^c (GHz)	v_t, J_{max}, K_{max} ^d	Number of lines ^e	Uncertainties ^f (MHz)	rms ^g (MHz)	
Brown	around 1.6	0,1,1	2	0.003	0.0029	
Bauder	8-58	0,40,10	51	0.020	0.0267	
LILLE	567-669	0,62,22	434	0.050 ^h	0.0778	
PluE	200-352	0,30,15	147			
PluA	216-506	0,40,18	97			
DeMa	150-313	0,28,12	44			
TYAM	7-200	0,40,17	2591			
TYAM	7-200	1,18,7	7	0.200 ⁱ	0.1340	
Oest	250-510	0,43,18	897			

^aParameter values are given in Table 2. Some examples of the observed minus calculated residuals are given in Table 3 for $v_t = 0$ lines and in Table 4 of the present paper for $v_t = 1$.

^bSources of data: Brown – Ref. [7]; Bauder – Ref. [8]; LILLE data comes from present work; PluE – Ref. [11]; PluA – Ref. [10]; DeMa – Ref. [9]; TYAM – Ref. [14]; Oest – Ref. [12].

^cRange containing the measurements in a given row.

^d v_t state and maximum J and K_a for each group of measurements.

^eNumber of MW lines in each uncertainty group.

^fOne-sigma standard uncertainty in MHz used in the fit.

^gRoot mean square deviation in MHz for each group.

^hIn reference [9] the experimental uncertainty was assumed to be 30 kHz.

ⁱIn reference [12] the experimental uncertainty was assumed to be 100 kHz and in reference [14] to be 250 kHz.

Table 2. Torsion-Rotation Parameters Needed for the Global Fit of Transitions Involving $v_t = 0$ and $v_t = 1$ Torsional Energy Levels of Methylformate ($H^{12}COOCH_3$)

nlm ^a	Operator ^b	Parameter	Present Work ^c	nlm	Operator	Parameter	Present Work
220	$(1-\cos 3\gamma)/2$	V_3	370.924(113)	404	$-P^4$	D_J	0.00000042854(455)
	P_γ^2	F	5.49038(129)		$-P^2 P_a^2$	D_{JK}	-0.0000019285(527)
211	$P_\gamma P_a$	ρ	0.08427127(723)		$-P_a^4$	D_K	0.0000036534(594)
202	P_a^2	A^{RAM}	0.5884101(188)		$-2 P^2 (P_b^2 - P_c^2)$	δ_J	0.00000017990(227)
	P_b^2	B^{RAM}	0.3082455(179)		$\{-P_a^2, (P_b^2 - P_c^2)\}$	δ_K	0.00000028824(900)
	P_c^2	C^{RAM}	0.17711843(416)		$(P_a^3 P_b + P_b P_a^3)$	D_{abK}	0.0000020747(108)
	$(P_a P_b + P_b P_a)$	D_{ab}	-0.1649794(162)	642	$(1-\cos 6\gamma) P^2$	N_v	-0.0000507(127)
440	P_γ^4	k_4	0.0004368(184)		$(1-\cos 6\gamma)(P_b^2 - P_c^2)$	c_{11}	-0.0014751(202)
	$(1-\cos 6\gamma)/2$	V_6	23.9018(636)		$2 P_\gamma^4 (P_b^2 - P_c^2)$	c_3	0.00000045962(750)
431	$P_{\gamma_b}^3 P_a$	k_3	-0.00012758(711)	624	$(1-\cos 3\gamma) P^4$	f_v	0.00000009957(441)
422	$P_{\gamma_b}^2 P^2$	G_v	0.000002709(432)		$(1-\cos 3\gamma) (P_b^2 - P_c^2) P^2$	c_{2J}	0.00000005483(445)
	$2P_\gamma^2 (P_b^2 - P_c^2)$	c_1	0.000018117(264)		$(1-\cos 3\gamma)\{P_a^2, (P_b^2 - P_c^2)\}$	c_{2K}	0.00000024458(404)
	$\sin 3\gamma (P_a P_c + P_c P_a)$	D_{ac}	-0.0068896(540)		$2P_\gamma^2 (P_b^2 - P_c^2) P^2$	c_{1J}	0.0000000017386(211)
	$(1-\cos 3\gamma) P^2$	F_v	-0.0025827(184)		$(1-\cos 3\gamma) (P_a P_b + P_b P_a) P^2$	d_{abJ}	-0.00000012488(883)
	$(1-\cos 3\gamma) P_a^2$	k_5	0.0112949(386)		$(1-\cos 3\gamma) (P_a^3 P_b + P_b P_a^3)$	d_{abK}	0.00000019649(625)
	$(1-\cos 3\gamma)(P_b^2 - P_c^2)$	c_2	0.0012608(253)		$(1-\cos 3\gamma) P_a^2 P^2$	k_{5J}	-0.0000005853(125)
	$(1-\cos 3\gamma)(P_a P_b + P_b P_a)$	d_{ab}	-0.0063031(176)	633	$P_\gamma^3 P^2 P_a$	k_{3J}	0.00000007061(198)
	$P_{\gamma_b}^2 P_a^2$	k_2	-0.00002837(166)		$P_\gamma^3 P_a^3$	k_{3K}	-0.00000008230(461)
	$P_{\gamma_b}^2 (P_a P_b + P_b P_a)$	Δ_{ab}	-0.000008874(434)		$P_\gamma^3 \{P_a, (P_b^2 - P_c^2)\}$	c_{12}	-0.00000006946(110)
413	$P_\gamma P_a P^2$	L_v	0.000003932(110)		$P_\gamma^3 \{P_a^2, P_b\}$	$\delta\delta_{ab}$	-0.000000061998(808)
	$P_{\gamma_b} P_a^3$	k_1	-0.000000596(279)	606	P^6	H_J	0.000000000000333(35)
	$P_\gamma \{P_a, (P_b^2 - P_c^2)\}$	c_4	0.0000001100(561)		$P^4 P_a^2$	H_{JK}	0.000000000015998(570)
	$P_\gamma \{P_a^2, P_b\}$	δ_{ab}	-0.000010141(145)		$P^2 P_a^4$	H_{KJ}	-0.00000000007620(187)
					P_a^6	H_K	0.00000000009098(281)
				826	$(1-\cos 3\gamma) (P_b^2 - P_c^2) P^4$	c_{2JJ}	0.000000000001746(201)
				844	$2 P_\gamma^4 (P_b^2 - P_c^2) P^2$	c_{3J}	-0.000000000029116(514)

^aNotation of Ref. [24]; $n = l+m$, 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.

^bNotation of Ref. [24]. $\{A,B\}=AB+BA$. 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 , which occur in the Hamiltonian in the form $F(P_\gamma - \rho P_a)^2 + A^{\text{RAM}} P_a^2$.

^cValues of the parameters from the present fit for $v_t = 0$ and 1. All values are in cm^{-1} , except for ρ which is unitless. Statistical uncertainties are given in parentheses in units of the last quoted digit.

Table 5. Rotational constants in the RHO axis system (RAM) and in the principal axis system (PAM). Angles between the principal axis and the methyl top axis.

	RAM ^a	PAM ^b	PAM ^c
A(MHz)	17640.0910	19939.5304	19848.5032
B(MHz)	9240.9676	6954.4483	7006.1251
C(MHz)	5309.8769	5309.8769	5351.3017
D _{ab} (MHz)	-4945.9580	0.0	0.0
<(i,a)		52.989	58.568
<(i,b)		37.011	31.432
<(i,c)		90.000	90.000
θ_{RAM}	24.83 ^d		

^a Rotational constants obtained in our work for RAM-axis system (see Table 2).

^b Rotational constants of our work transformed to the Principal Axis System and angles in degrees between the principal axis (a,b,c) and the methyl top axis (i).

^c Calculation of the principal axis rotational constants from the molecular structure (MP2/VTZ) and of the angles in degrees between the principal axis (a,b,c) and the methyl top axis (i).

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

Table 6. Dipole moment components in Debye in the principal axis system (PAM) and in the RHO axis system (RAM).

	RAM	PAM ^a
μ_a	+1.765	+1.63
μ_b	-0.067	+0.68

^a Experimental dipole moment from Ref. [8].

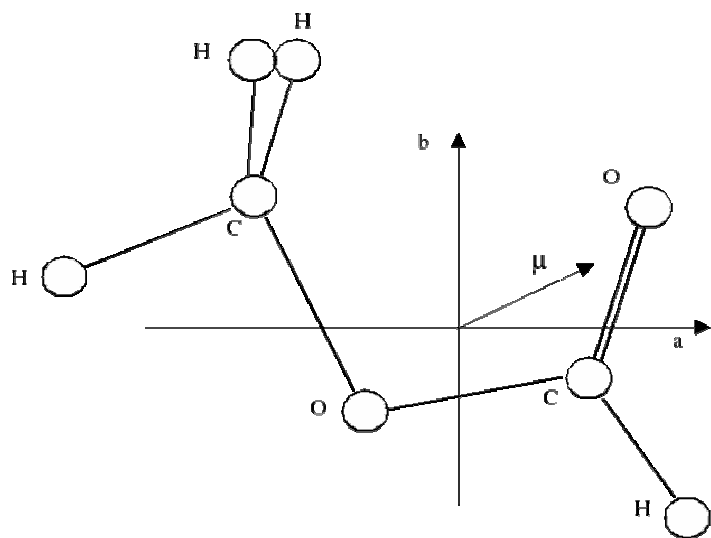


Fig.1. The chemical structure, principal axes and direction of the dipole moment of methyl formate [6]. The **a-b** plane is a plane of symmetry.