

# Program Belgi-Cs.for

This read-me file is organized in the following sections:

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Brief summary of what the code is doing

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## **I. Brief summary of the program**

The code presently posted allows the user to calculate and fit transitions of molecules containing an internal rotor (of  $C_{3v}$  symmetry) which can turn relatively to the rest of the molecule. This internal rotation is hindered by a threefold potential barrier.

The present code can fit one or two different vibrational states (each of them having their own torsional "bath" of levels,  $v_t = 0, 1, \dots$ ). In the input file posted here, it calculates the internal rotation energy levels for the ground vibrational state only.

The theoretical background for the code, i.e. the internal rotation Hamiltonian for a  $C_{3v}$  internal rotor and an asymmetric frame with a plane of symmetry ( $C_s$ ) is based on Kirtman's treatment (1) and also Lees and Baker (2). Eric Herbst published in 1984 a few papers (for ex. 3) where he showed how to diagonalize the Hamiltonian in a two-step efficient way.

In our code, the Hamiltonian is written in the so-called "**rho-axis system**" or **RAM**, which is an axis system turned from the principal axis system by an angle,  $\Theta_{RAM}$  chosen in such a way that the torsional Hamiltonian will only keep the  $-2F \rho_a p_\alpha P_a$  coupling term between the internal rotation angular momentum  $p_\alpha$  and the global rotation angular momentum  $P_a$ .

$F$  is the internal rotation constant related to the inertial moment of the top and  $\rho_a$  is related to the ratio of the inertial moment of the top and the inertial moment of the whole molecule

The torsional Hamiltonian  $H_{tors} = V(\alpha) + F(p_\alpha - \rho P_a)^2$  where  $V(\alpha)$  is the potential function (which is for a  $C_{3v}$  internal rotor:  $V_3/2(1 - \cos 3\alpha) + V_6/2(1 - \cos 6\alpha) + \dots$ )

will therefore only have  $\Delta K = 0$  matrix elements in the basis set:  $|K v_t \sigma\rangle = \exp [i(3k + \sigma)\alpha]$

with  $K$  being the quantum number associated to the projection of the global angular momentum  $P_a$  on the  $a$  axis, but will still take into account much of the internal-rotation-global-rotation Coriolis interaction. The quantity  $v_t$  (called IVTOR or IV in the code) is the principal torsional quantum number (which at the limit of a very high barrier would be the harmonic oscillator quantum number so is a "good" quantum number if the barrier height is high),  $\sigma$  (called ISIG in the code) is a symmetry quantum number = 0 for the A species and  $\pm 1$  for the E species.  $k$  is an integer running from -10 to +10, this range being determined by a truncation parameter (called KTRONC in the code).  $KTRONC = 10$  was shown to be valid for high barrier cases like acetaldehyde but higher values should be checked for especially

high barrier cases. All axis systems (PAM, RAM and IAM) as well as group theory considerations are described in (5).

$H_{\text{tors}}$  is diagonalized in the first step. The rest of the Hamiltonian (rotational terms, centrifugal distortion terms and higher order coupling terms between internal and global rotation angular momenta) are diagonalized in the second step, using the torsional eigenvalues obtained after the first diagonalization and corresponding to the first 9 torsional levels ( $v_t=0,1,2,\dots,8$ ). So the dimension of the matrix for this second step is  $(9)(2J+1) \times (9)(2J+1)$ .

The particularity of this method is that it treats simultaneously A and E species and all the torsional energy levels (truncated at the 10 first as we said) arising from one vibrational state.

## II. Structure of the program

After the subroutine DATA1 and DATA11 (reading of the input file, the parameters and the observed line frequencies), the first subroutine to be called is SETUP which is where all eigenvalues and derivatives needed for the least-squared fitting are stored into ENER and DERIV. The SUBROUTINE ROTTOR essentially coordinates the do-loops for K from  $-N$  to  $+N$  (the rotational quantum numbers) and for  $\sigma$  (symmetry quantum number, called ISIG) = 0 for A species and 1 for E species.

The torsional Hamiltonian is setup in the SUBROUTINE HTORS:

$H_{\text{tors}} = V(\alpha) + F(p_\alpha - \rho P_a)^2$  where  $V(\alpha)$  is the potential function (which is for a  $C_{3v}$  internal rotor:  $V_3/2 (1 - \cos 3\alpha) + V_6/2 (1 - \cos 6\alpha) + \dots$ ) only has  $\Delta K = 0$  matrix elements in the basis set:

$$|K v_t \sigma\rangle = \exp [i(3k+\sigma)\alpha]$$

with K being the quantum number associated with the projection of the global angular momentum  $P_a$  on the a axis,

$v_t$  (called IVTOR or IV in the code) is the principal torsional quantum number  
k is an integer running from -10 to +10, where 10 is the value of a truncation parameter (called KTRONC in the code) which was shown to be valid for high barrier cases like acetaldehyde but which should be checked for higher barrier cases.

The diagonalization of  $H_{\text{tors}}$  gives eigenvalues, which are the torsional energies ( $E_{\text{tors}}$ ), and eigenvectors which can be written as (3)

$$|K v_t \sigma\rangle = \frac{1}{\sqrt{2\pi}} |K\rangle \sum_{k=-10}^{10} A_{3k+\sigma}^{K v_t} \exp(i[3k + \sigma]\alpha).$$

Those eigenvectors (labelled in terms of  $v_t=IVTOR$ , K and  $\sigma$  and stored in SUBROUTINE ASET) are then used after multiplying them by the symmetric rotor functions

$|JKM\rangle = |JKM\rangle |K v_t \sigma\rangle$  to serve as basis set wavenfunctions to diagonalize the rest of the Hamiltonian (rotation, centrifugal distortion and rotation-torsion coupling terms). The matrix elements of this second step diagonalization (with  $\Delta K = 0, \pm 1, \pm 2$ ) are calculated in SUBROUTINE HRTSET and in the different FUNCTION ROUTINES H0, H1, H2, ...

The diagonalization subroutines are TRED2 and TQL2. The labels of the eigenvalues and eigenvectors are found in Subroutine ENCAL and in the functions IPOSA, IPOSA2, IPOSE and IPOSE2.

The derivatives are numerically calculated in VSET (and VTORS, VRTDI1, VRTDI2,...) using the Hellman-Feynman theorem and the eigenvectors found after the two diagonalizations.

Once the energies and derivatives are stored, the least square procedure can begin, which is done in the main part of the code. At each iteration, SETUP is called and the new eigenvalues and derivatives are stored.

LINECA is the subroutine which calculates the frequency associated with each of the observed transitions introduced in the data set.

Weighted standard deviations (unitless) are given taking into account the weights of each line. Unweighted root-mean square deviations in MHz and cm-1 are also given.

### III. Explanations for the input file

The first line is:

EPSI,IBUG1,IBUG2,IBUG3,IBGTME,IBGVTD ,IBUG4

EPSI has no meaning (just put 0.), IBUG1  $\neq$  0 is a debug flag for printing out the matrix for  $H_{\text{tors}}$ , IBUG2 is for printing out the matrix of  $H_{\text{rot}}+H_{\text{R-T}}$  (2<sup>nd</sup> step diag.), IBUG3 is the same, IBGTME serves to print out the observed-calculated values for the transitions, (called TME for “terms minus energies”) with the upper and lower state energies and standard deviation S:  
IF(IBGTME.EQ.1) WRITE(6,300) K,TME(K),EUPPER,ELOWER,S  
IBGVTD: prints out the derivative matrix before and after the inversion of the least-square matrix.

IBUG4 could serve to print out the energy levels.

The second and third lines are:

READ(5,20) KTRONC : the truncation of the torsional matrix (10 for acetaldehyde)

READ(5,20) IRMW : if IRMW=1 then we treat only one vibrational state, if IRMW=2, we treat 2 different vibrational states

Fourth line: cm-1 or MHZ: depending in what units the constants will be. Note that the frequencies in the input and output files will be automatically in cm-1 for the FIR, IR and in MHz for MW.

Then come the values of the parameters for the lower state : the meaning of those parameters are given at the bottom of this file. Please read the relevant papers for other parameters or ask one of the authors.

CM-1

&CSTE

OA = 0.35150076793036794,

B = 0.15346996670417229,

C = 0.10623368397991501,

DAB = -0.03670915325930996,

V3 = 359.14177475235487691,

RHORHO = 0.06376911062071215,

DJ = 0.00000002437284721,

DJK = -0.00000009591481227,

DK = 0.00000050414394189,

ODELN = 0.0000000643746548,

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ODELK = 0.00000005243912659,
FV = -0.00066221961568995,
GV = -0.00000391742705810,
C2 = 0.00035156965648996,
AK5 = -0.00089980123533588,
AK4 = -0.00097847419455220,
ODAB = -0.00327796176492539,
C4 = 0.00000008224168601,
C2J = 0.00000000058765299,
C2K = 0.00000006353966985,
F = 5.64133778441192124,
DABK = -0.00000045221069168,
V6 = -0.58455328933903850,
ANV = 0.00024840261281152,
BK2 = -0.00118848074512593,
ODAB6 = 0.00032906802255014,
AK2 = 0.00002191043963404,
ODABJ = -0.00000001087019176,
DELTA = -0.00001491168567958,
DAC = 0.00317103917591652,
BK1 = -0.00000006237484431,
ODELTA = 0.00000493132583919,&END

```

Then comes the vibrational term value for the lower state (0. for the GS)

After it is asked how many parameters for that state we want to fit and the names of those parameters.

If IRMW =2, then the same input is asked for, but now for the upper state:

Cm-1

Parameter values

Vibrational upper state term

Number of parameters floated

Names of those floated parameters

The line just before the data set is:

0,9,1,20 = FITNU0,ITERATIONS,JKAKC,JMAX

FITNU0 =0 if we do not want to float the upper state vibrational energy (it is the case if we do not have two vibrational states of course), ITERATIONS (NITT in the code) is the number of iterations we want, JKAKC = 1 means we want to have the line assignments in terms of JKaKc in the output. JMAX is the maximum value of J (=N).

The dataset consists of the A species first, then the E species separated by a fake line where the observed frequency is “-900.”

Example: A species

Freq (in MHz)	Upper				Lower				last	Weight (IW)	Source	
	Vt'	J'	Ka'	P'	vt''	J''	Ka''	P''				
15004.81800	0	2	0	+	0	1	0	+	0	1	1003	Lille'02

For the A species the label is JK<sub>a</sub> and a parity (P) quantum number + or –

E species:

10000.00000 0 2 0 0 0 1 -1 0 0 1000

Here the label is J, + or –K (a signed value of K is needed for the E species)

IAST is 1 : line included in the fit

IAST is 0: line not included in the fit but calculated after the fit is over

Weight: IW above 1000: Microwave data (possibilities: 1005, 1010, 1020, etc., see below).

IW below 1000 (1,2 or 3 are the possible values corresponding to vt= 1-0, 2-1 and 3-2 respectively): IR or FIR data

Attention: make sure that the weight of your data corresponds to one of the allowed categories (or otherwise the code has to be modified)!

See below how the weight is actually calculated from the IW (in subroutine DATA1)

C THE WEIGHT (W) IS EQUAL TO THE INVERSE OF THE SQUARE OF

C EXPERIMENTAL UNCERTAINTY

IF(IW(I).EQ.1005) THEN

C this is 5 kHz accuracy

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=3.59502E+13

ELSEIF(IW(I).EQ.1000) THEN

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=8.98755E+12

ELSEIF(IW(I).EQ.1010) THEN

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=8.98755E+12

ELSEIF(IW(I).EQ.1040) THEN

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=5.61722E+11

ELSEIF(IW(I).EQ.1004) THEN

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=5.61722E+13

ELSEIF(IW(I).EQ.1003) THEN

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=9.986168E+13

ELSEIF(IW(I).EQ.1020) THEN

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=2.24688E+12

ELSEIF(IW(I).EQ.1050) THEN

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=3.59502E+11

ELSEIF(IW(I).EQ.1030) THEN

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=9.98617E+11

ELSEIF(IW(I).EQ.1008) THEN

ETTRANS(I)=ETTRANS(I)/29979.2458

W(I)=1.4043E+13

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ELSEIF(IW(I).EQ.1100) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=8.98755E+10
ELSEIF(IW(I).EQ.1990) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=8.98755E+8
ELSEIF(IW(I).EQ.1180) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=2.77393E+10
ELSEIF(IW(I).EQ.1130) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=5.31807E+10
ELSEIF(IW(I).EQ.1150) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=3.51076E+10
ELSEIF(IW(I).EQ.1160) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=3.99446E+10
ELSEIF(IW(I).EQ.1200) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=2.24688E+10
ELSEIF(IW(I).EQ.1080) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=1.4043E+11
ELSEIF(IW(I).EQ.1070) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=1.83419E+11
ELSEIF(IW(I).EQ.2000) THEN
  ETRANS(I)=ETTRANS(I)/29979.2458
  W(I)=2.24688E+8
ELSEIF(IW(I).EQ.1000.AND.IVOBS(1,I).EQ.1) THEN
  W(I)=5.61722E+11
  ETRANS(I)=ETTRANS(I)/29979.2458
ELSE IF(IW(I).EQ.10) THEN
  W(I)=4000000.0
ELSE IF(IW(I).EQ.2.OR.IW(I).EQ.3) THEN
  W(I)=4000000.0

```

Each category of lines contributes to its own weighted standard deviation (see SUBROUTINE LINECA and see also the main code where the number of lines in each category is calculated):

DO NOT USE JUST any number in the input column IW: this will not work. You must use one of the possibilities above.

#### IV. Meaning of the parameters:

See Table 2 of JMS 2006: Torsion-Rotation Parameters from the Global Fit of Transitions Involving  $v_t = 0$  and 1 Torsional Energy Levels of Methyl Carbamate  $H_2NC(O)OCH_3$

The meaning of additional parameters can be found in the file “constants”

$nlm^a$	Operator <sup>b</sup>	Parameter <sup>b</sup>	Value <sup>c</sup>	Name in the code
220	$\frac{1}{2}(1-\cos 3\gamma)$	$V_3$	359.141(24)	V3
	$P_\gamma^2$	F	5.64133(28)	F
211	$P_\gamma P_a$	$\rho$	0.0637691(10)	RHORHO
202	$P_a^2$	A	0.35150076(74)	OA
	$P_b^2$	B	0.15346996(35)	B
	$P_c^2$	C	0.10623368(34)	C
	$(P_a P_b + P_b P_a)$	$D_{ab}$	-0.0367091(10)	DAB
	$(P_a P_c + P_c P_a) \sin 3\gamma$	$D_{ac}$	0.003171(12)	DAC
440	$P_\gamma^4$	$k_4$	$-0.9784(18) \times 10^{-3}$	AK4
	$\frac{1}{2}(1-\cos 6\gamma)$	$V_6$	-0.5845(45)	V6
422	$P_\gamma^2 P^2$	$G_v$	$-0.3917(67) \times 10^{-5}$	GV
	$(1-\cos 3\gamma)P^2$	$F_v$	$-0.6622(28) \times 10^{-3}$	FV
	$(1-\cos 3\gamma)P_a^2$	$k_5$	$-0.8998(57) \times 10^{-3}$	AK5
	$(1-\cos 3\gamma)(P_b^2 - P_c^2)$	$c_2$	$0.35156(47) \times 10^{-3}$	C2
	$(1-\cos 3\gamma)(P_a P_b + P_b P_a)$	$d_{ab}$	-0.0032779(87)	ODAB
	$P_\gamma^2 P_a^2$	$k_2$	$0.2191(22) \times 10^{-4}$	AK2
	$P_\gamma^2 (P_a P_b + P_b P_a)$	$\Delta_{ab}$	$-0.1491(17) \times 10^{-4}$	DELTA
413	$P_\gamma \{P_a^2 (P_b^2 - P_c^2)\}$	$c_4$	$0.822(42) \times 10^{-7}$	C4
	$P_\gamma \{P_a^2 P_b + P_b P_a^2\}$	$\delta_{ab}$	$0.4931(24) \times 10^{-5}$	ODELTA
404	$-P^4$	$D_J$	$0.24372(78) \times 10^{-7}$	DJ
	$-P^2 P_a^2$	$D_{JK}$	$-0.959(47) \times 10^{-7}$	DJK
	$-P_a^4$	$D_K$	$0.5041(72) \times 10^{-6}$	DK
	$-2P^2 (P_b^2 - P_c^2)$	$\delta_J$	$0.6437(38) \times 10^{-8}$	ODELN
	$-\{P_a^2, (P_b^2 - P_c^2)\}$	$\delta_K$	$0.524(16) \times 10^{-7}$	ODELK
	$(P_a^3 P_b + P_b P_a^3)$	$D_{abK}$	$-0.4522(69) \times 10^{-6}$	DABK
642	$(1-\cos 6\gamma)P^2$	$N_v$	$0.2484(21) \times 10^{-3}$	ANV
	$(1-\cos 6\gamma)P_a^2$	$K_2$	$-0.11884(53) \times 10^{-2}$	BK2
	$(1-\cos 6\gamma)(P_a P_b + P_b P_a)$	$dd_{ab}$	$0.3290(57) \times 10^{-3}$	ODAB6
	$P_\gamma^4 P_a^2$	$K_1$	$-0.6237(56) \times 10^{-7}$	BK1
624	$(1-\cos 3\gamma)(P_b^2 - P_c^2)P^2$	$c_{2J}$	$0.587(14) \times 10^{-9}$	C2J
	$(1-\cos 3\gamma)\{P_a^2, (P_b^2 - P_c^2)\}$	$c_{2K}$	$0.6353(35) \times 10^{-7}$	C2K
	$(1-\cos 3\gamma)(P_a P_b + P_b P_a)P^2$	$d_{abJ}$	$-0.1087(14) \times 10^{-7}$	ODAJ

<sup>a</sup>Notation of Ref. [13,14];  $n = l+m$ , 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, respectively.

<sup>b</sup>Notation of Ref. [13,14].  $\{A,B\}=AB+BA$ . 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,  $\rho$  and A, which occur in the Hamiltonian in the form  $F(P_\gamma - \rho P_a)^2 + A P_a^2$ .

<sup>c</sup>Values of the parameters from the present fit. All values are in  $cm^{-1}$ , except for  $\rho$  which is unitless. Statistical uncertainties are shown as one standard uncertainty in the last digits.

## V. History, references, and Geographic description of the authors...

Initially written by **I. Kleiner and M. Godefroid** from the "Laboratoire de Chimie Quantique et Photophysique", Free University of Brussels (Belgium) during Isabelle's thesis in 1985-1989, under Michel Godefroid's direction, the program was modified and updated constantly since then, which explains the many commented-out or changed subroutines. The program was adapted to fit different cases of **internal rotation molecules** (from high barrier cases to low barrier cases, with or without a plane of symmetry in the molecule "frame", for the ground vibrational state or for two different vibrational states) and modified many times. The authors apologized for the "uncleanliness" and somewhat confusing state of the code resulting from this.

The theoretical background for the code, i.e. the internal rotation Hamiltonian for a  $C_{3v}$  internal rotor and an asymmetric frame with a plane of symmetry ( $C_s$ ) is based on Kirtman's treatment (1) and also Lees and Baker (2). Eric Herbst published in 1984 a few papers (for ex. 3) where he showed how to diagonalize the Hamiltonian in a two-step efficient way.

People interested in internal rotation should also read the Lin and Swalen review paper (4).

During Isabelle's post-doc with **Jon Hougen** at the National Institute of Standards and Technology, Gaithersburg, USA (1989-91), we tested the code and we applied to **acetaldehyde  $CH_3CHO$**  in  $vt=0, 1$  and  $2$  involving microwave and far infrared data (6-9).

The code was then successfully applied to higher torsional states of acetaldehyde (up to  $vt=3$  and  $4$ ) of the ground vibrational state, called "bath states" (10).

This caused us to 1) add more torsional-rotational interaction terms in the code and 2) find a better way to label the energy levels. This label problem (arising from the fact that a non-principal axis system is used and also from the fact that levels from different torsional states  $vt$  are interacting) was a recurrent problem in all molecules we tried, keeping us from applying the code "immediately as it is" to any internal molecule.

The next person to use and modify the code on the microwave spectra and infrared spectra of methanol  $CH_3OH$  is **Li-Hong Xu** (now a faculty member at the University of New Brunswick in Canada) who began this project while she was a post-doc at the NIST with Jon Hougen. Anyone who would like to know about this version of the code and methanol data is invited to

contact Li-Hong Xu ([lxu@unbsj.ca](mailto:lxu@unbsj.ca)).

see also the list of references on methanol at the end of this document.

In the 1995, **Juan Ortigoso** (from Instituto de Estructura de la Materia, CSIC, Serrano, Madrid, Spain) came to post-doc with Jon Hougen at NIST and did work on the labelling problem mentioned above. The problem was becoming especially annoying above the barrier height (which is about  $400\text{ cm}^{-1}$  in acetaldehyde) because of the high mixing of wavefunctions. Juan did work on a classical method to solve this problem and consequently he added subroutines in the code to implement his method which helps to solve the labelling problems above the barrier (11).



The next step was to calculate intensities for an internal rotor: together with Frank Lovas and Michel Godefroid we published an astrophysical paper on acetaldehyde (12) (and Li-Hong Xu did the same on methanol)

**The code versions calculating intensities (and line positions) are always separate versions from the ones fitting the line positions.**

**The code can fit infrared transitions** (transitions between **two different vibrational states**) and it was applied to several bands of  $\text{CH}_3\text{CHO}$  (13-16).

Applications to high barrier case involve  **$\text{CD}_3\text{CHO}$  (17) and  $\text{CF}_3\text{CH}_2\text{CH}_3$**  (18-19).

The next molecule we applied the code to was  **$\text{CH}_3\text{COOH}$ , acetic acid** (microwave spectra  $\nu_t=0,1$  and 2, (20-21) which had the particularity to have a much lower barrier height than acetaldehyde (about  $160\text{ cm}^{-1}$ ) and therefore the labeling scheme had to be modified again. This was when **Vadim Ilyushin** from the Radio astronomy Institute of NASU, Kharkov (Ukraine) came in the game in 2000 and developed another method for labelling the eigenvectors for a low barrier case (22). Vadim also rewrote parts of the code and made it available on PC.

This scheme was also applied to **acetamide  $\text{CH}_3\text{CONH}_2$**  (MW,  $\nu_t=0$  and 1 (23-24)), one of the simplest molecules showing a peptide linkage link and a very low barrier ( $25\text{ cm}^{-1}$ ).

With acetamide we were beginning to study "biomimetic" molecules or simple molecules which can play the role of imitating the behavior of small regions in large molecules of biological interest. In acetamide we had to deal first with the hyperfine structure (due to the quadrupole of  $^{14}\text{N}$ ): the strategy was to first "dehyperfine" the measurements to determine hypothetical center frequencies, which we then used in our internal rotation fit.

In **EAA (ethylacetamido acetate) and in the ester of the alanine dipeptide** we compared the results from our code with the results of JB95 (David Plusquellic, NIST) and with the ab initio results (25-26).

One of the EAA conformers (called CII) and the ester have a frame without a symmetry plane. We thus had to derive all non-planar Hamiltonian terms allowed by symmetry in the  $C_1$  group (27).

Let us note also that in the ester, there are in fact TWO  $\text{CH}_3$  groups showing internal rotation splittings in the MW.

However we were able to use our code (written for ONE-internal rotor) because the two tops are relatively far away from each other in the molecule and the coupling between them is therefore negligible.

At this date (October 2006), the latest application is **methyl carbamate** a molecule with a relatively high barrier ( $396\text{ cm}^{-1}$ ), showing hyperfine structure as well and where the frame of the molecule has a plane of symmetry ( $C_s$ ).

**We decided to post here the version of the code (belgi- $C_s$ ) used to treat this molecule together with the input and output file (28).**

The label scheme used for this molecule is the original (1989) one (in subroutines IPOSA and IPOSE for the A and E species respectively).

**We are planning to post Vadim Ilyushin's label scheme code later on:** this label scheme is more complicated to use, since it requires significant operator intervention, but it should be much more exportable to any molecule, whereas the present version will work essentially on

the high to intermediate barrier cases (and on low barrier cases but with some effort being made to label the energy levels).

The users are thus warned to be cautious when applying the code to their molecules since they may have to deal with the label problem for their eigenvalues.

To deal with higher J values necessary for the astrophysical detection of species like methyl formate  $\text{HCOOCH}_3$  and in prevision of the extended spectral range up to 600 GHz (and presumably higher) which will be available in the future with the new observatories (ALMA, Herschel, Sofia) a new version of the code has also been recently extrapolated by **Dr. M. Carvajal-Zaera** from the "Departamento de Física Aplicada", University of Huelva (Spain).

### **We also plan to post the intensity code soon.**

Finally a version which can deal with a **two-state interacting dyad** also exists and we are presently testing it on the GS/ $v_{10}$  dyad system in acetaldehyde.

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