



# Ab initio studies of the FIR spectra of non-rigid molecules of astrophysical interest.

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# OUTLINE

- Prebiotic molecules: relevance for astrochemistry (motivation)
- Non-rigid molecules (theoretical aspects) (tool)
- Our codes ENEDIM and FIT-ESPEC (tool)
- Some examples: ethanol, acetic acid, glycolaldehyde and methyl formate (applications)
- Recent studies: DME and Ethyl-methyl-ether (applications)

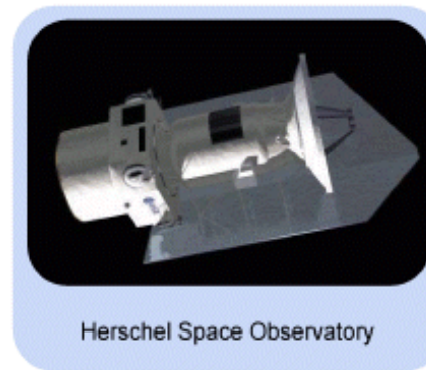
## Astrochemistry (motivation)

# New observatories

**ALMA**  
Radioastronomy  
MW ( > 2012)



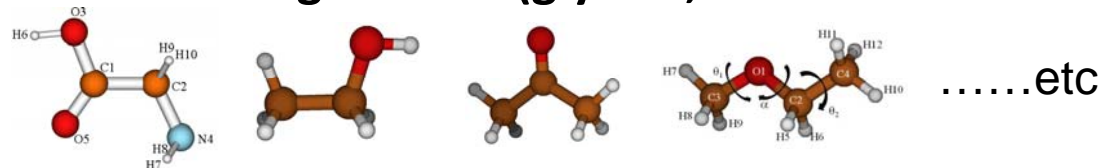
**HERSCHEL**  
FIR (2009)



- 1) “**The Molecular Universe**: an interdisciplinary program on the physics and chemistry of molecules in space”, Commission of the European Communities: Marie Curie research training networks, Contract n° MRTN-CT-2004-512302.
- 2) **COST Action CM0805 “The Chemical Cosmos**; understanding chemistry in astronomical environments”.

# Complex organic molecules: relevance for astrochemistry

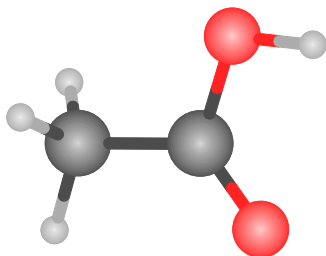
- The molecular gas in our galaxy represents 10% of its mass.
- The dead of stars ejects C, O and other elements (N, S,...) to ISM clouds.
- The consequence is the formation of many species containing H, C, O and N (important rol of gas phase reactions ( $\downarrow E_a$ ) and dust grain chemistry)
- Many organic molecules have been astrophysically detected (ISM and CSM).
- **The detection of certain molecules is really relevant given their connection with the problem of the origin of life (glycine, glycolaldehyde.....)**



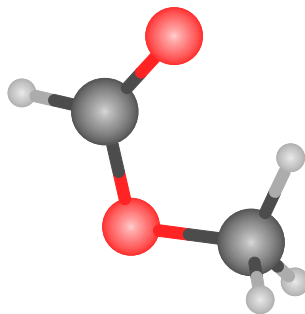
## Our non-rigid molecules (before 2003)

		Torsional barriers (in cm <sup>-1</sup> )			Fundamental frequencies (in cm <sup>-1</sup> )		
		Calc.	Exp.	Ref.	Calc.	Exp.	Ref.
<b>Acetone</b> CH <sub>3</sub> -CO-CH <sub>3</sub>	J.Chem.Phys., 98,2754 (1993) MP2/+31G**	246.9	266.1	Vacherand et al. J.Mol.Spec., 118,355 (1986) (MW) Groner et al. J.Chem.Phys., 86,565 (1987) (FIR)	$\nu_{17}=130.7$ $\nu_{12}=84.1$	$\nu_{17}=96.9$ $\nu_{12}=55.0$	Groner et al. J.Chem.Phys.,86, 565 (1987) (FIR)
<b>Dimethyl-ether</b> CH <sub>3</sub> -O-CH <sub>3</sub>	J.Chem.Phys., 102,3952(1995) MP4/+31G**	950.6	942.6	Groner et al. J.Chem.Phys., 66,1856 (1977) (FIR)	$\nu_{17}=241.2$ $\nu_{12}=193.3$	$\nu_{17}=241.0$ $\nu_{12}=188.6$	Groner et al. J.Chem.Phys.,66, 1856 (1977) (FIR)
<b>Hydroxylamine</b> NH <sub>2</sub> OH	J.Mol.Spec., 186,162 (1997) MP2/+ 311G+G(2pd)				419	386	Taubman et al., J.Mol.Spectrosc. 123,366 (1987)
<b>Methylamine</b> CH <sub>3</sub> -NH <sub>2</sub>	J.Mol.Spec.,191 ,232 (1998) MP2/+ 311G++G(3d3pd)	708.6			602.6	600	Kregevsly, NA TO/ASI pp 29- 43, Kluwer Dordrecht, 1993.
<b>Methanol</b> CH <sub>3</sub> OH	CPL 273, 135 (1997). MP4/AUG-cc- pVT Z	347.7	373.1	Herbst et al., J. Mol Spec.,108, 42 (1984) (MW)	289.1	294.4	Burkhard et al., J.Mol.Spectrosc.329 9 (1959)
<b>Hydrogen Peroxide</b> H-O-O-H	Spect. Acta, 56A, 1457 (2000) MP4/AUG-cc- pVT Z	406.1	387.1	Flaud et al., J.Chem.Phys., 91, 1504 (1989) (FIR)	260.1	254.5	Flaud et al., J.Chem.Phys.,91, 1504 (1989) (FIR)
<b>Ethanol</b> CH <sub>3</sub> -CH <sub>2</sub> OH	J.Chem.Phys. 112,5809 (2000) MP4/cc-pVT Z	$V_3^T=1226.7$ $V_3^G=1296.3$ $V_{CH}^{(12)}=404.1$ $V_{CH}^{(180)}=423.3$	1185 1251 402.8 364.3	Durig et al., J.Mol.Struct., 238,195 (1989) (FIR)	Me=205.5 OH=257.0	202.6 244.4	Durig et al., J.Mol.Struct.,238, 195 (1989) (FIR)
<b>Acetic Acid</b> CH <sub>3</sub> -COOH	Mol.Phys., 15, 1311 (2001) MP4/cc-pVT Z	169.8	168.2	Wlodarczak et al., Astron. Astrophys., 192, 313 (1988) (MW)			

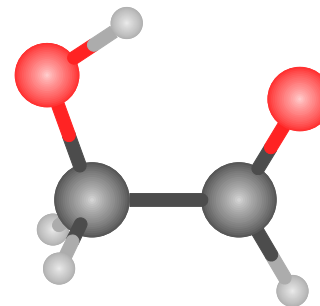
## Recent studies



**Acetic acid**  
Abundance= 1  
E = 0 kJ/mol



**Methyl formate**  
Abundance=26  
E = 72 kJ/mol

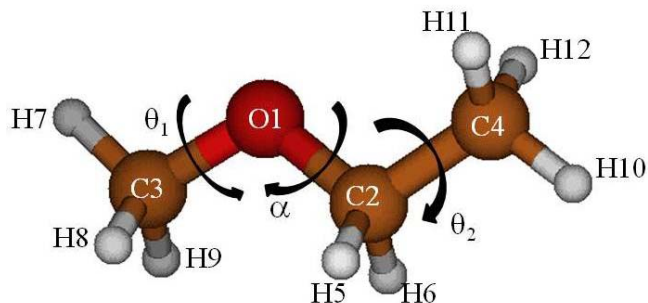


**Glycolaldehyde**  
Abundance = 0.5  
E = 118 kJ/mol

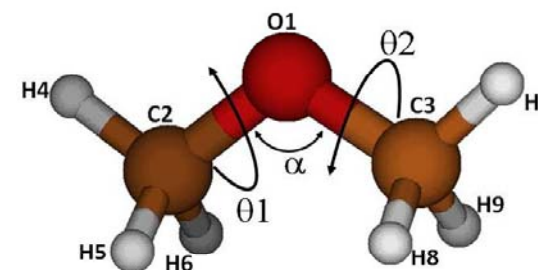
Ab initio determination of the torsional spectra of acetic acid, M.L.Senent, **Mol.Phys** , 2001

Ab initio determination of the torsional spectrum of glycolaldehyde, M.L.Senent, **J.Phys.Chem**, 2004

Ab initio study of the rotational-torsional spectrum of methyl format, M.L.Senent, M.Villa, F.J.Meléndez and R. Domínguez-Gómez, **Astrophys.J.**, 2005.



**Dimethyl-ether**  
and  
**Ethyl-methyl-ether**



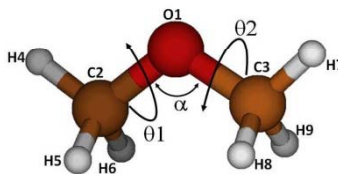
CCSD(T) study of the FIR spectrum of EME, Senent , Ruiz, Dominguez-Gómez, and Villa, **J.Chem.Phys.** 2009

CCSD(T) study of FIR spectrum of EME isotopic varieties, Senent, Ruiz, Villa, and Domínguez-Gómez, **Chem.Phys.**, 2010

CCSD(T) study of the FIR spectrum of DME isotopomers, Villa, Carvajal-Zaera, Alvarez, Domínguez-Gómez and Senent (in preparation)

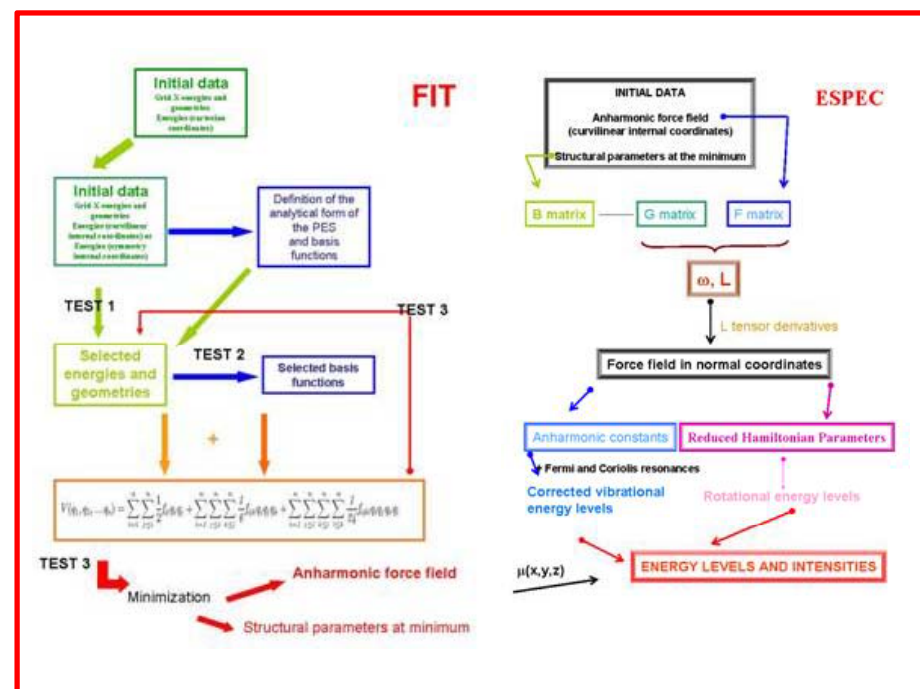
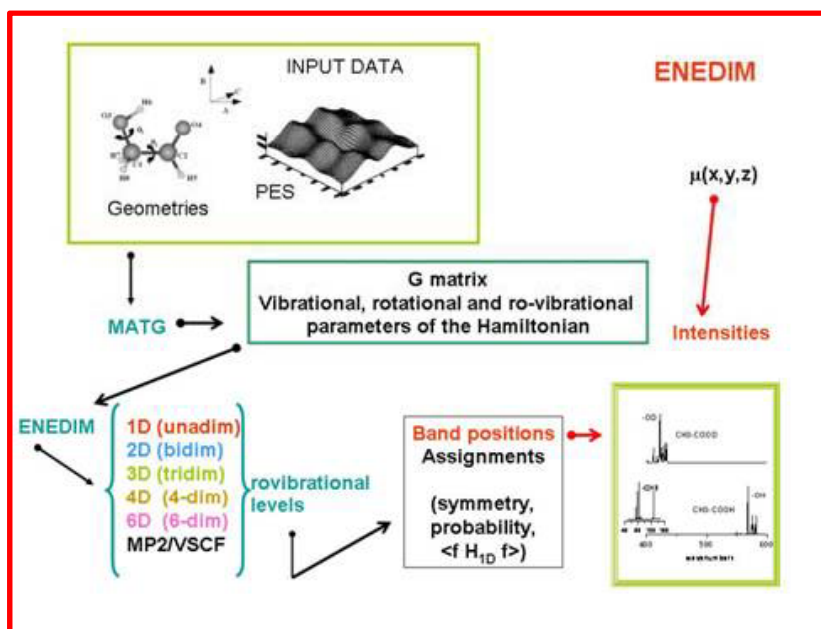
# Non-rigid molecules: theoretical aspects

Many organic molecules of radio-astronomical interest can be classified as non-rigid molecules



- 1) Definition: PES presents various minima (interconvert through “feasible” internal motions).
- 2) Large amplitude vibrations (LAM): inversion and torsional modes interconvert the minima.
- 3) Levels corresponding to the LAM are populated at very low T
- 4) Interesting and complex FIR (tunneling effects; MS groups)
- 5) Important organic molecules for radioastronomy: (ALMA and also Herschel)

# Our codes



Theoretical Chemistry Team: *I. Estructura de la Materia, CSIC, Madrid*

<http://tct1.iem.csic.es/PROGRAMAS.htm>



## Theory (enedim)

**2 reference systems (origin=c.d.m.)**

O(x,y,z) rotating with the molecule  
O'(X,Y,Z) space fixed

**Kinetic energy in internal coordinates (matrizG code):**

$$2T = (P^t, p^t) \begin{pmatrix} I & X \\ X^t & Y \end{pmatrix}^{-1} \begin{pmatrix} P \\ p \end{pmatrix} = (P^t, p^t) G \begin{pmatrix} P \\ p \end{pmatrix}$$

Inertia matrix

$$X_{ij} = \sum_{a=1}^N m_a \left[ \vec{r}_a^T x \left( \frac{\partial \vec{r}_a}{\partial q_j} \right) \right]_i$$

$$Y_{ij} = \sum_{a=1}^N m_a \left( \frac{\partial \vec{r}_a}{\partial q_i} \right) \left( \frac{\partial \vec{r}_a}{\partial q_j} \right)$$

$$g_{ij} = g_{ij}(q_1, q_2, \dots, q_{3N-6})$$

**+ Podolsky “trick”**

$$2T = g^{-1/4} \sum_{\alpha=1}^3 \sum_{\beta=1}^3 P_{\alpha} g^{1/2} g_{(\alpha\beta)} P_{\beta} g^{-1/4}$$

$$+ g^{-1/4} \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} p_i g^{1/2} g_{(i+3,j+3)} p_j g^{-1/4}$$

$$+ g^{-1/4} \sum_{\alpha=1}^3 \sum_{i=1}^{3N-6} (p_i g^{1/2} g_{(i+3,\alpha)} p_{\alpha} + P_{\alpha} g^{1/2} g_{(\alpha,i+3)} p_i) g^{-1/4}$$

Senent M.L. 1998, Chem.Phys.Lett., 296, 299.

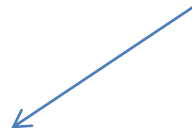
Senent M.L. 1998, J.Mol.Spectrosc., 191, 265.

Senent M.L. 2001, Mol.Phys., 15, 1311.

## Theory (enedim)

**Quantum mechanical operator for J=0:**

$$\hat{H}_{vib} = - \sum_i^{3N-6} \sum_j^{3N-6} \left( \frac{\partial}{\partial q_i} \right) B_{ij} \left( \frac{\partial}{\partial q_j} \right) + V(q_1, q_2, \dots, q_{3N-6}) + V'(q_1, q_2, \dots, q_{3N-6})$$



$$V' = \frac{\hbar^2}{8} \sum_i^{3N-6} \sum_j^{3N-6} \left[ \left( \frac{\partial}{\partial q_k} \right) g_{kl} \left( \frac{\partial Lng}{\partial q_l} \right) - \left( \frac{\partial Lng}{\partial q_k} \right) g_{kl} \left( \frac{\partial}{\partial q_l} \right) \right] + \frac{\hbar^2}{8} \sum_i^{3N-6} \sum_j^{3N-6} \left( \frac{\partial Lng}{\partial q_k} \right) g_{kl} \left( \frac{\partial Lng}{\partial q_l} \right)$$

**Quantum mechanical operator for J > 0:**

$$\hat{H}_R = \sum_{\alpha=1}^3 \sum_{\beta=1}^3 g_{\alpha\beta} P_{\alpha} P_{\beta}$$

$$\hat{H}_{RT} = \frac{i\hbar}{2} \sum_{\alpha=1}^3 \sum_{J=1}^{3N-6} \left( 2g_{\alpha j} P_{\alpha} \frac{\partial}{\partial q_j} - \left( \frac{\partial g_{\alpha j}}{\partial q_j} \right) P_{\alpha} \right)$$

**Intensities:**

$$I = \frac{q}{3ReB} (E_j - E_i)(P_j - P_i) \langle \phi_i | \mu | \phi_j \rangle^2$$

## Theory (enedim):

But .....variational calculations in 3N-6 D are not realistic for complex molecules.  
What do do?

- 1) The  $n$  large amplitude vibrations (LAM') are supposed to be **independent** on the remaining  $3N-6-n$  coordinates.
- 2) The **PES** is determined from the energies of a **grid** of conformations selected for different values of the  $n$  coordinates.
- 3) The remaining  $3N-6-n$  are **optimized** in all the conformations; this is a **partial** way to take into consideration their small interactions with the LAM
- 4) As these  $3N-6-n$  modes are expected “to be at the ZPVE” instead “at the PES minima”, a ZPVE corrections must to be added.

$$\hat{H}_T = - \sum_i^n \sum_j^n \left( \frac{\partial}{\partial q_i} \right) B_{ij} \left( \frac{\partial}{\partial q_j} \right) + V(q_1, q_2, \dots, q_n) + V'(q_1, q_2, \dots, q_n) + V^{ZPVE}(q_1, q_2, \dots, q_n)$$

**That works?.....Yes**, when the interactions among the LAM and the remaining coordinates are **relatively small**. Otherwise:

$$H_{LAM} = H_{LAM'} + H_{mh} + H_{LAM',mh}$$

## Theory (enedim)

### Classification of the vibrational levels

a) Symmetry (Molecular Symmetry Groups)

b) Probability integrals (loca. PES minima)

$$\int_q^q \phi_i^* \phi_i dq_1 dq_2 dq_n$$

c) One dimensional Hamiltonians (assign. modes)

$$\langle H_n \rangle = \langle \phi_i^* H_n \phi_i \rangle$$

$$H_n = -B_i^0 \frac{\partial^2}{\partial q_n^2} + V(q_n)$$

## Theory (enedim)

### Trial wave-functions

**For J=0:** Fourier series, Harmonic Oscillator, Morse, Coon...etc  
Integrals: analytical methods and gaussian quadratures ...

**For J> 0**

$$\Psi(\theta, \Theta, \chi, q_1, q_2, \dots, q_n) = \sum_{n,J,K,m} C_{n,J,K,m} \phi_n^{vib} G_{J,\pm K,m}(\theta, \Theta, \chi)$$

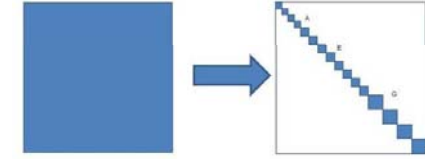
$$G_{J,\pm K,m}(\theta, \Theta, \chi) = B(S_{J,+K,m}(\theta, \Theta, \chi) e^{i(+K)\chi} \pm B(S_{J,-K,m}(\theta, \Theta, \chi) e^{i(-K)\chi}$$

**For large systems:**

- a) Contracted basis sets
- b) Symmetry adapted functions

# Theory (enedim)

## Symmetry eigenvectors of DME ( $G_{36}$ )



$$P_j = \frac{l_j}{36} \sum_R^{36} \chi_j(R) \hat{R}$$

$$\Phi = \sum_I \sum_J (C_{IJ}^{CC} \cos I\theta_1 \cos J\theta_2 + C_{IJ}^{CS} \cos I\theta_1 \sin J\theta_2 + C_{IJ}^{SC} \sin I\theta_1 \cos J\theta_2 + C_{IJ}^{SS} \sin I\theta_1 \sin J\theta_2)$$

$A_1$

$$\begin{aligned} & \cos 3K\theta_1 \cos 3L\theta_2 + \cos 3L\theta_1 \cos 3K\theta_2 \\ & \sin 3K\theta_1 \sin 3L\theta_2 + \sin 3L\theta_1 \sin 3K\theta_2 \\ & L \leq K \end{aligned}$$

$A_2$

$$\begin{aligned} & \cos 3K\theta_1 \sin 3L\theta_2 - \sin 3L\theta_1 \cos 3K\theta_2 \\ & \sin 3K\theta_1 \cos 3L\theta_2 - \cos 3L\theta_1 \sin 3K\theta_2 \\ & L \leq K \end{aligned}$$

$A_3$

$$\begin{aligned} & \cos 3K\theta_1 \sin 3L\theta_2 + \sin 3L\theta_1 \cos 3K\theta_2 \\ & \sin 3K\theta_1 \cos 3L\theta_2 + \cos 3L\theta_1 \sin 3K\theta_2 \\ & L \leq K \end{aligned}$$

$A_4$

$$\begin{aligned} & \cos 3K\theta_1 \cos 3L\theta_2 - \cos 3L\theta_1 \cos 3K\theta_2 \\ & \sin 3K\theta_1 \sin 3L\theta_2 - \sin 3L\theta_1 \sin 3K\theta_2 \\ & L < K \end{aligned}$$

$E_1$

$$\begin{aligned} & \cos(3K \pm \delta)\theta_1 \cos(3L + \delta)\theta_2 \pm \sin(3K \pm \delta)\theta_1 \sin(3L + \delta)\theta_2 \\ & + \cos(3L + \delta)\theta_1 \cos(3K \pm \delta)\theta_2 \pm \sin(3L + \delta)\theta_1 \sin(3K \pm \delta)\theta_2 \\ & \cos(3K \pm \delta)\theta_1 \sin(3L + \delta)\theta_2 \mp \sin(3K \pm \delta)\theta_1 \cos(3L + \delta)\theta_2 \\ & - \sin(3L + \delta)\theta_1 \cos(3K \pm \delta)\theta_2 \mp \cos(3L + \delta)\theta_1 \sin(3K \pm \delta)\theta_2 \\ & L \leq K \end{aligned}$$

$E_2$

$$\begin{aligned} & \cos(3K \pm \delta)\theta_1 \cos(3L + \delta)\theta_2 \pm \sin(3K \pm \delta)\theta_1 \sin(3L + \delta)\theta_2 \\ & - \cos(3L + \delta)\theta_1 \cos(3K \pm \delta)\theta_2 \mp \sin(3L + \delta)\theta_1 \sin(3K \pm \delta)\theta_2 \\ & \cos(3K \pm \delta)\theta_1 \sin(3L + \delta)\theta_2 \mp \sin(3K \pm \delta)\theta_1 \cos(3L + \delta)\theta_2 \\ & + \sin(3L + \delta)\theta_1 \cos(3K \pm \delta)\theta_2 \mp \cos(3L + \delta)\theta_1 \sin(3K \pm \delta)\theta_2 \\ & L \leq K \end{aligned}$$

$E_3$

$$\begin{aligned} & \cos(3K \pm \delta)\theta_1 \cos(3L + \delta)\theta_2 \mp \sin(3K \pm \delta)\theta_1 \sin(3L + \delta)\theta_2 \\ & + \cos(3L + \delta)\theta_1 \cos(3K \pm \delta)\theta_2 \mp \sin(3L + \delta)\theta_1 \sin(3K \pm \delta)\theta_2 \\ & \cos(3K \pm \delta)\theta_1 \sin(3L + \delta)\theta_2 \mp \sin(3K \pm \delta)\theta_1 \cos(3L + \delta)\theta_2 \\ & + \sin(3L + \delta)\theta_1 \cos(3K \pm \delta)\theta_2 \mp \cos(3L + \delta)\theta_1 \sin(3K \pm \delta)\theta_2 \\ & L > K \end{aligned}$$

$E_4$

$$\begin{aligned} & \cos(3K \pm \delta)\theta_1 \cos(3L + \delta)\theta_2 \mp \sin(3K \pm \delta)\theta_1 \sin(3L + \delta)\theta_2 \\ & - \cos(3L + \delta)\theta_1 \cos(3K \pm \delta)\theta_2 \mp \sin(3L + \delta)\theta_1 \sin(3K \pm \delta)\theta_2 \\ & \cos(3K \pm \delta)\theta_1 \sin(3L + \delta)\theta_2 \mp \sin(3K \pm \delta)\theta_1 \cos(3L + \delta)\theta_2 \\ & - \sin(3L + \delta)\theta_1 \cos(3K \pm \delta)\theta_2 \mp \cos(3L + \delta)\theta_1 \sin(3K \pm \delta)\theta_2 \\ & L > K \end{aligned}$$

$G$

$$\begin{aligned} & \cos 3K\theta_1 \cos(3L + \delta)\theta_2 \\ & \sin 3K\theta_1 \sin(3L + \delta)\theta_2 \end{aligned}$$

$$\begin{aligned} & \cos 3K\theta_1 \sin(3L + \delta)\theta_2 \\ & \sin 3K\theta_1 \cos(3L + \delta)\theta_2 \end{aligned}$$

$$\begin{aligned} & \cos(3K + \delta)\theta_1 \cos 3L\theta_2 \\ & \sin(3K + \delta)\theta_1 \sin 3L\theta_2 \end{aligned}$$

$$\begin{aligned} & \cos(3K + \delta)\theta_1 \sin 3L\theta_2 \\ & \sin(3K + \delta)\theta_1 \cos 3L\theta_2 \end{aligned}$$

## Theory (enedim)

### MP4-VSCF Implemented for large systems

Vibrations are classified in  $l$  blocks; each block contains modes that interact strongly

$$H_{LAM} = \sum_j^l T_{l_j} + \sum_j^l \sum_k^l T_{l_j, l_k} + \sum_j^l V_{l_j} + \sum_j^l \sum_k^l V_{l_j, l_k}$$

For each set:

$$H_{l_j} \Phi_{l_j} = [T_{l_j} + V_{l_j}] \Phi_{l_j} = E_{l_j} \Phi_{l_j}$$

$$V_{l_j} = \langle \Phi_{l_j} | V_{m_1 m_2 \dots m_l} | \Phi_{l_j} \rangle \quad \underline{\text{SCF potential}}$$

Zero-order energies:

$$E_i^0 = \sum_{j=1}^l E_{l_j}^{SCF}$$

## Theory (enedim)

### MP4-VSCF Implemented for large systems

“Correlation” is corrected with Perturbation Theory (“MPx”)

$$E_i^1 = \langle \phi_i^0 | H' | \phi_i^0 \rangle$$

$$E_i^2 = \sum_{j \neq i} \frac{|\langle \phi_i^0 | H' | \phi_j^0 \rangle|^2}{E_i^0 - E_j^0}$$

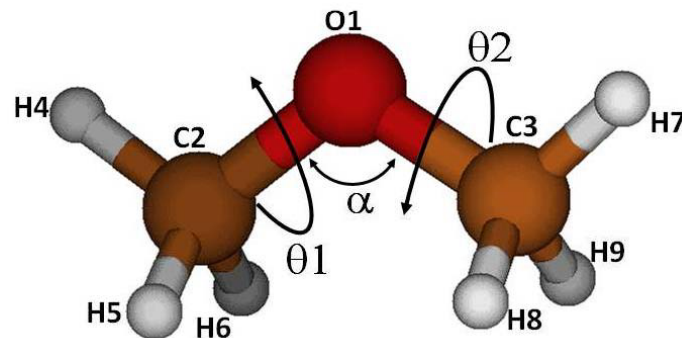
$$E_i^3 = \sum_{j \neq i} \left[ \sum_{j \neq i, k \neq i} \left( \frac{\langle \phi_i^0 | H' | \phi_j^0 \rangle \langle \phi_j^0 | H' | \phi_k^0 \rangle \langle \phi_k^0 | H' | \phi_i^0 \rangle}{(E_i^0 - E_j^0)(E_i^0 - E_k^0)} \right) - E_i^1 \frac{\langle \phi_i^0 | H' | \phi_i^0 \rangle}{E_i^0 - E_j^0} \right]$$

$$E_i^4 = - \sum_{j \neq i} \left[ \frac{E_i^1 \langle \phi_i^0 | H' | \phi_i^0 \rangle}{(E_i^0 - E_j^0)^2} \left( \sum_{k \neq i} \frac{\langle \phi_i^0 | H' | \phi_k^0 \rangle \langle \phi_j^0 | H' | \phi_k^0 \rangle}{E_i^0 - E_k^0} - \frac{E_i^1 \langle \phi_i^0 | H' | \phi_i^0 \rangle}{E_i^0 - E_j^0} \right) \right. \\ \left. - \sum_{k \neq i} \frac{\langle \phi_i^0 | H' | \phi_i^0 \rangle \langle \phi_i^0 | H' | \phi_k^0 \rangle}{(E_i^0 - E_j^0)(E_i^0 - E_k^0)} \left( \sum_{l \neq i} \frac{\langle \phi_j^0 | H' | \phi_l^0 \rangle \langle \phi_k^0 | H' | \phi_l^0 \rangle}{E_i^0 - E_j^0} \right. \right. \\ \left. \left. - \frac{E_i^0 \langle \phi_j^0 | H' | \phi_k^0 \rangle}{E_i^0 - E_k^0} \right) + \frac{E_i^2 (\langle \phi_i^0 | H' | \phi_i^0 \rangle)^2}{(E_i^0 - E_j^0)^2} \right]$$



# Theory (enedim)

## MP4-VSCF Dimethyl-ether



### Blocks of coordinates:

- 1 The two torsion
- 2 The COC bending

Table 1  
The DME energy levels (in  $\text{cm}^{-1}$ ) calculated variationally and with the MP2/SCF approach<sup>a</sup>

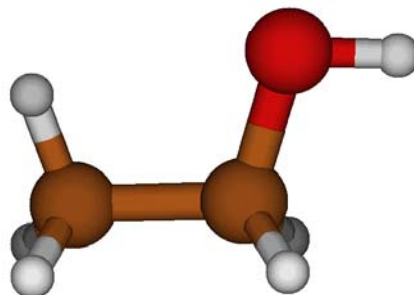
$v \ v' \ v''$		Variational	SCF	MP1	MP2	$\Delta E^b$	$v \ v \ v'$		Variational	SCF	MP1	MP2	$\Delta E$
000	A <sub>1</sub>	446.586	448.649	447.069	446.589	0.003	200	A <sub>1</sub>	839.812	843.954	841.375	839.930	0.118
	G	446.586	448.649	447.069	446.590	0.003		G	839.887	844.010	841.434	840.002	0.115
	E <sub>1</sub>	446.586	448.649	447.069	446.590	0.004		E <sub>1</sub>	839.963	844.066	841.495	840.075	0.112
	E <sub>3</sub>	446.586	448.649	447.069	446.590	0.004		E <sub>3</sub>	839.963	844.066	841.495	840.075	0.112
100	A <sub>3</sub>	646.085	647.262	646.601	646.091	0.003	110	A <sub>4</sub>	872.174	872.167	873.448	872.214	0.040
	G	646.080	648.545	646.635	646.089	0.003		G	872.302	880.188	876.015	872.324	0.022
	E <sub>2</sub>	646.074	647.252	646.591	646.080	0.006		E <sub>2</sub>	872.431	878.747	875.561	872.442	0.011
	E <sub>3</sub>	646.074	648.541	646.630	646.083	0.009		E <sub>4</sub>	872.431	874.322	873.712	872.480	0.049
010	A <sub>2</sub>	687.806	689.304	689.123	687.845	0.039	020	A <sub>1</sub>	927.436	934.784	928.618	926.638	-0.798
	G	687.800	695.057	691.137	687.795	-0.005		G	927.478	934.822	928.658	926.679	-0.799
	E <sub>1</sub>	687.795	695.053	691.132	687.790	-0.005		E <sub>1</sub>	927.519	934.860	928.697	926.720	-0.799
	E <sub>4</sub>	687.795	689.292	689.112	687.834	0.039		E <sub>3</sub>	927.519	934.860	928.697	926.720	-0.799
<i>Hot bands</i>													
001	A <sub>1</sub>	876.019	887.030	885.450	876.535	0.516							
101	A <sub>3</sub>	1070.590	1084.184	1083.522	1069.552	-1.038							
011	A <sub>2</sub>	1101.482	1130.991	1130.809	1089.511	-11.971							

<sup>a</sup>  $t_1 = t_2 = T_1 = T_2 = 37$ ;  $b = B = 13$ .

<sup>b</sup>  $\Delta E = E_{\text{MP2}} - E_{\text{varia}}$ .

# Theory (enedim)

## MP4-VSCF Ethanol



### Sets of coordinates:

1 CH3 torsion

2 OH torsion

Table 3

Comparison of the ethanol torsional energy levels (in  $\text{cm}^{-1}$ ) calculated variationally and with the SCF and Möller Plesset approach<sup>a</sup>

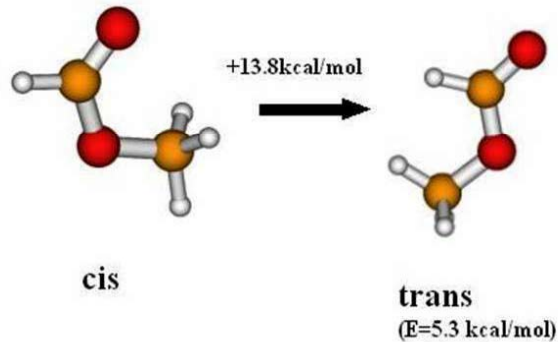
$v$	$v'$	SCF	MP1	MP2	MP3	MP4	Variational	$\Delta E^b$
00	A <sub>1</sub>	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
00 <sup>+</sup>	A <sub>1</sub>	33.8214	34.9757	25.0525	25.4344	25.5049	25.5001	0.0048
00 <sup>-</sup>	A <sub>2</sub>	44.9981	38.3426	27.9404	28.4464	28.4940	28.5084	-0.0144
01	A <sub>2</sub>	214.5376	211.9635	204.9320	204.0188	205.7345	205.5341	0.2004
01 <sup>+</sup>	A <sub>1</sub>	240.1226	241.1271	232.4701	233.1121	232.9270	232.9724	-0.0454
01 <sup>-</sup>	A <sub>2</sub>	293.6587	283.1417	273.9029	275.3452	275.2354	278.3455	-3.1103
02	A <sub>1</sub>	358.4014	359.3760	352.6020	352.7864	352.8353	352.8394	-0.0041
02 <sup>-</sup>	A <sub>2</sub>	484.3653	479.4909	468.9774	470.5565	470.0658	470.1634	-0.0976
02 <sup>+</sup>	A <sub>1</sub>	476.8014	478.0625	475.3766	475.1895	467.8373	473.2384	-5.4011
10	A <sub>2</sub>	257.4744	254.6435	258.4399	258.3313	257.2992	257.0046	0.2946
10 <sup>-</sup>	A <sub>2</sub>	298.4465	304.8703	297.5755	296.6009	297.0632	294.3952	2.6680
10 <sup>+</sup>	A <sub>1</sub>	293.5907	302.9818	294.5630	294.3635	294.6461	294.5989	0.2509
20	A <sub>1</sub>	493.0936	489.9748	501.7906	504.8016	497.6744	499.2496	-2.2335
20 <sup>+</sup>	A <sub>1</sub>	526.9150	545.4955	531.6317	528.4115	530.9249	532.1052	-1.1803
20 <sup>-</sup>	A <sub>2</sub>	538.0658	547.8388	542.7247	541.0883	541.3771	541.8850	-0.5079
11	A <sub>1</sub>	467.8554	468.8441	451.5371	450.0389	462.8540	456.5150	6.3390
11 <sup>-</sup>	A <sub>2</sub>	504.9619	505.8822	497.0355	497.5041	497.9240	497.4524	0.4716
11 <sup>+</sup>	A <sub>1</sub>	543.4039	550.7394	550.9233	553.2161	552.4305	550.7041	1.7264

<sup>a</sup>  $t1 = T1 = 37$  and  $t2 = T2 = 51$ .

<sup>b</sup>  $\Delta E = E_{\text{MP4}} - E_{\text{varia}}$ .

**Some examples (always astrophysical molecules with very complex (“tricky”) FIR spectra )**

# Methyl FORMATE



## Rotational constants (previous works)

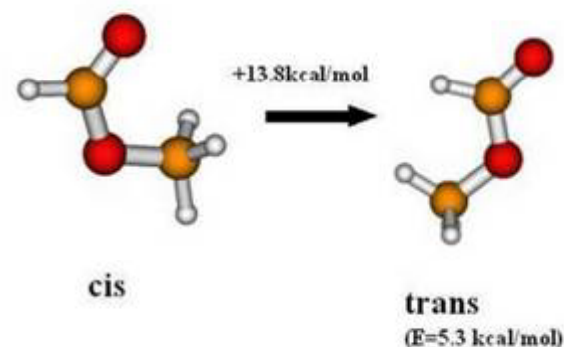
	Ref.[2]	Ref.[3]	Ref.[4]	Ref.[5]	Ref.[6]	Ref.[7]
<b>A(MHz)</b>	<b>19983.05</b>	<b>19985.7623</b>	<b>19983.06</b>	<b>17522.36993</b>	<b>19141.92</b>	<b>19120.151</b>
<b>B(MHz)</b>	<b>6914.4198</b>	<b>6914.757</b>	<b>6914.928</b>	<b>9323.547665</b>	<b>9112.39</b>	<b>9181.7185</b>
<b>C(MHz)</b>	<b>5303.2477</b>	<b>5304.468</b>	<b>5304.236</b>	<b>5312.69996</b>	<b>5264.63</b>	<b>5254.7515</b>

Ab initio study of the rotational-torsional spectrum of methyl-formate, M.L.Senent, M.Villa, F.Meléndez, R.Dominguez-Gómez, *Astrophys. J* (2005)

# Methyl FORMATE

TABLE 1: Potential and kinetic parameters of methyl formate conformers

Conformers	cis	trans
Symmetry	C <sub>s</sub>	C <sub>s</sub>
E <sub>R</sub> (cm <sup>-1</sup> )	0.0 <sup>b</sup>	1823
θ (degrees)	180.0	0.0
α (degrees)	0.0	180.0
μ <sub>a</sub> (debyes)	1.7437	4.0973
μ <sub>b</sub> (debyes)	0.9640	2.3135
<i>Kinetic energy parameters</i>		
A (MHz)	19945.0367	48356.9026
B (MHz)	7017.5506	4702.4032
C (MHz)	5364.7803	4404.2494
κ	-0.77329	-0.98643
B <sub>11</sub> (cm <sup>-1</sup> )	6.9948	7.1831
B <sub>22</sub> (cm <sup>-1</sup> )	5.7788	2.8895
B <sub>12</sub> (cm <sup>-1</sup> )	-2.7498	-0.4040
V <sup>1</sup> (cm <sup>-1</sup> )	0.3412	0.2200
<i>Potential energy barriers (cm<sup>-1</sup>)</i>		
CH <sub>3</sub>	CH <sub>3</sub>	C-O
cis	trans	cis → trans
V <sub>3</sub> = 368	V <sub>3</sub> = 26	V <sup>CO</sup> = 4826
V <sub>3</sub> (ZPVE) = 422	V <sub>3</sub> (ZPVE) = 9	V <sup>CO</sup> (ZPVE) = 4790



a) calculated with MP4(SDTQ)/cc-pVQZ//MP2/cc-pVQZ  
 b) E<sub>a</sub> = -2.28.804898 a.u.

TABLE 5  
TORSIONAL ENERGY LEVELS (IN  $\text{cm}^{-1}$ )

$v v'$	SYMMETRY	Cis				TRANS		
		2D	+ZPVE	Experimental <sup>a</sup>	1D	2D	+ZPVE	1D
0 0	$A_1$	0 <sup>b</sup>	0 <sup>c</sup>	...	0	0 <sup>d</sup>	0 <sup>e</sup>	0
	$E$	0	0	...	0	6.3	7.0	6.1
1 0	$A_2$	123.6	134.8	130	126.1	61.3	61.8	64.6
	$E$	122.8	134.3	...	125.1	29.6	20.8	31.4
2 0	$A_1$	219.9	242.8	...	225.4	65.6	63.0	66.6
	$E$	228.0	248.9	...	233.0	111.1	110.0	115.0
3 0	$A_2$	334.1	358.0	...	339.6	...	...	...
	$E$	293.7	322.4	...	300.8	...	...	...
4 0	$A_1$	349.6	378.8	...	356.8	...	...	...
	$E$	409.3	434.6	...	415.8	...	...	...
0 1	$A_2$	321.7	329.5	332	294.2	181.5	177.1	148.3
	$E$	321.9	330.3	...	...	187.1	184.9	...
0 2	$A_1$	634.8	648.4	...	581.1	...	...	...
	$E$	635.3	649.1	...	...	...	...	...
0 3	$A_2$	939.8	957.2	...	860.8	...	...	...
	$E$	940.4	958.0	...	...	...	...	...
1 1	$A_1$	440.8	457.4	...	...	...	...	...
	$E$	439.9	456.9	...	...	...	...	...
1 2	$A_2$	531.2	608.4	...	...	...	...	...
	$E$	540.8	564.5	...	...	...	...	...
2 1	$A_2$	749.8	770.0	...	...	...	...	...
	$E$	748.6	769.3	...	...	...	...	...

<sup>a</sup> Chao et al. (1986).

<sup>b</sup> 228.8  $\text{cm}^{-1}$ .

<sup>c</sup> 240.2  $\text{cm}^{-1}$ .

<sup>d</sup> 1924.8  $\text{cm}^{-1}$ .

<sup>e</sup> 1969.3  $\text{cm}^{-1}$ .

# Methyl FORMATE

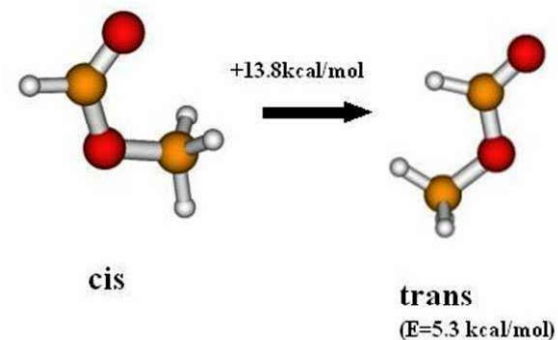


TABLE 7  
ROTATIONAL LEVELS (IN  $\text{cm}^{-1}$ ) FOR THE TWO COMPONENTS  $A$  AND  $E$   
OF THE CIS AND THE TRANS VIBRATIONAL GROUND STATES

$J_{ K_a  K_c }$	Cis		TRANS	
	$A$	$E$	$A$	$E$
0 0 0 $A_1$	0.000	0.012	1729.111	1736.061
1 0 1 $A_2$	0.411	0.424	1729.417	1736.367
1 1 1 $A_2$	0.847	0.859	1730.840	1737.789
1 1 0 $A_1$	0.901	0.913	1730.850	1737.800
2 0 2 $A_1$	1.229	1.241	1730.029	1736.978
2 1 2 $A_1$	1.615	1.627	1731.441	1738.391
2 1 1 $A_2$	1.778	1.790	1731.472	1738.421
2 2 1 $A_2$	3.085	3.096	1735.739	1742.690
2 2 0 $A_1$	3.090	3.102	1735.739	1742.690
3 0 3 $A_2$	2.439	2.453	1730.946	1737.895
3 1 3 $A_2$	2.767	2.777	1732.343	1739.293
3 1 2 $A_1$	3.089	3.101	1732.405	1739.354
3 2 2 $A_1$	4.319	4.330	1736.656	1743.607
3 2 1 $A_2$	4.342	4.354	1736.656	1743.607
3 3 1 $A_2$	6.639	6.645	1743.794	1750.746
3 3 0 $A_1$	6.636	6.651	1734.794	1750.746

# Methyl FORMATE

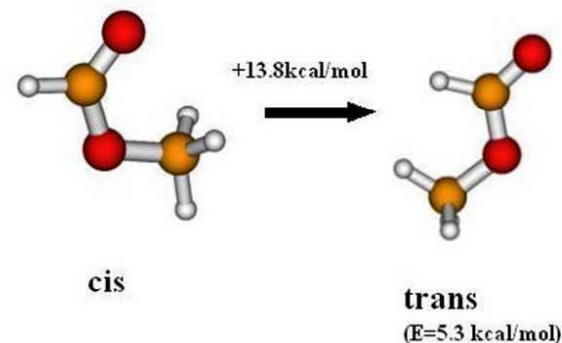


TABLE 8  
COMPUTED ROTATIONAL PARAMETERS OF *Cis*- AND *Trans*-METHYL FORMATE AT THE LOWEST TORSIONAL STATES

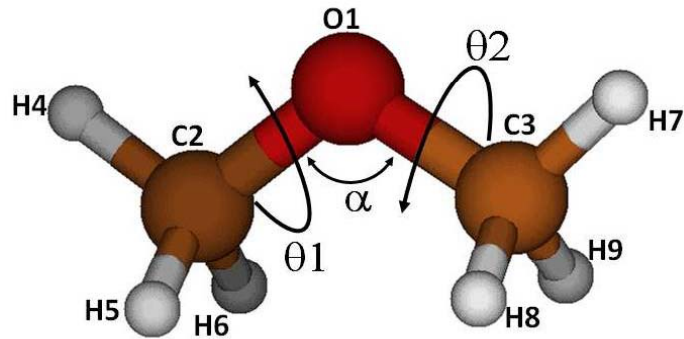
GROUND STATE Cis (0 0)	<i>A</i>		<i>B</i>	
	Calculated	Experimental <sup>a</sup>	Calculated	Experimental <sup>b</sup>
<i>A</i> (MHz).....	20,040.473	19,985.7623	20,040.492	19,980.3907
<i>B</i> (MHz).....	6974.140	6914.7577	6974.399	6913.6822
<i>C</i> (MHz).....	5350.851	5304.4681	5350.851	5304.5114
<i>D<sub>J</sub></i> (kHz).....	-0.510	6.1781	2.070	5.8895
<i>D<sub>JK</sub></i> (kHz).....	1.566	-17.1981	14.712	-23.313
<i>D<sub>K</sub></i> (kHz).....	-0.619	82.3578	5.898	75.4009
$\delta_J$ (kHz).....	-0.237	1.9502	-0.223	1.8571
$\delta_J$ (kHz).....	-0.309	7.6605	-1.554	2.057
EXCITED STATES	Cis (1 0)		TRANS (0 0)	
	<i>A</i>	<i>E</i>	<i>A</i>	<i>E</i>
<i>A</i> (MHz).....	20,164.023	20,167.381	47,380.066	47,389.645
<i>B</i> (MHz).....	6913.492	6911.891	4738.781	4737.653
<i>C</i> (MHz).....	5323.755	5323.043	4430.339	4429.715
<i>D<sub>J</sub></i> (kHz).....	-0.186	1.014	49.831	34.346
<i>D<sub>JK</sub></i> (kHz).....	2.087	-8.374	-252.397	-64.170
<i>D<sub>K</sub></i> (kHz).....	-0.197	18.119	363.661	54.583
$\delta_J$ (kHz).....	-0.499	1.542	-7.278	-47.373
$\delta_J$ (kHz).....	-0.577	2.961	-12.135	-21.751

<sup>a</sup> Plummer et al. (1984).

<sup>b</sup> Plummer et al. (1986).

## 2 non-rigid molecules

### dimethyl-ether = DME



Symmetry= G36 and C2v

PES= 9 minima (2 torsions)

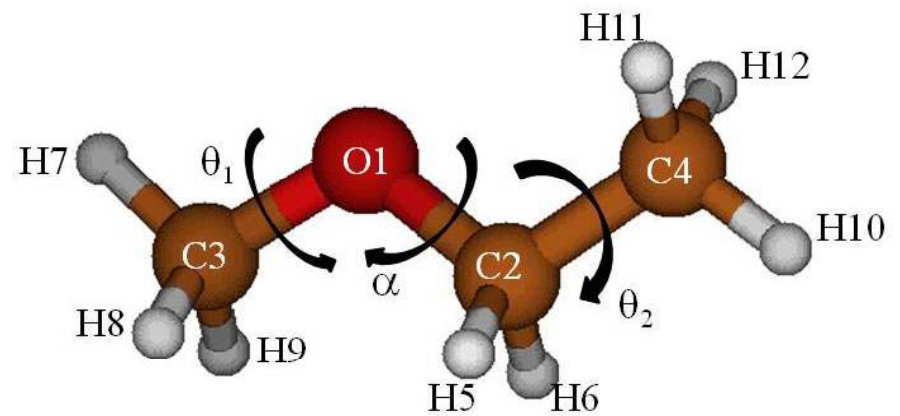
Radio detection (ISM-DME), *ApJ*. 1974

Symmetry= G18 and Cs

PES= 27 minima (3 torsions)

Radio detection (tentat), *A&A*, 2005

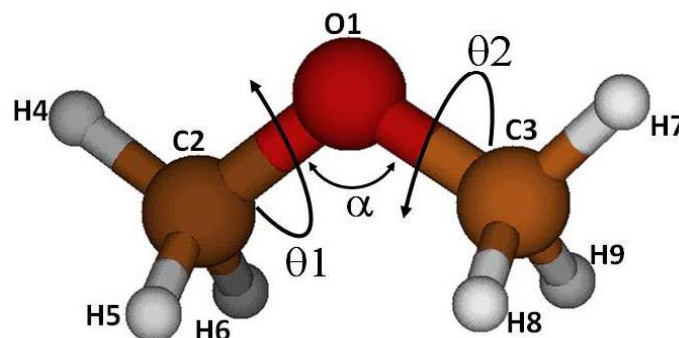
### Ethyl-methyl-ether = EME





# Dimethyl-ether = DME

(preliminary results)



## Previous papers:

1) An ab initio and spectroscopic study of DME. An analysis of the FIR and Raman spectra. Senent, Moule and Smeyers, [Can.J.Phys., \(1995\)](#) → 2 - **Dimensional**

**2)** An ab initio determination of the bending-torsion-torsion spectrum of DME, (CH<sub>3</sub>)<sub>2</sub>O and (CD<sub>3</sub>)<sub>2</sub>O, Senent, Moule and Smeyers, [J.Chem.Phys., \(1995\)](#) → 3 - **Dimensional**

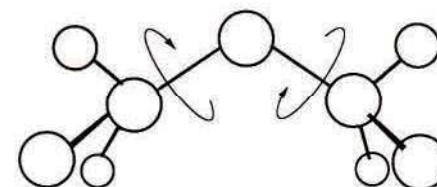
## New:

CCSD(T) study of the FIR spectrum of DME isotopomers, Villa, Carvajal-Zaera, Alvarez, Domínguez-Gómez and Senent (in preparation)

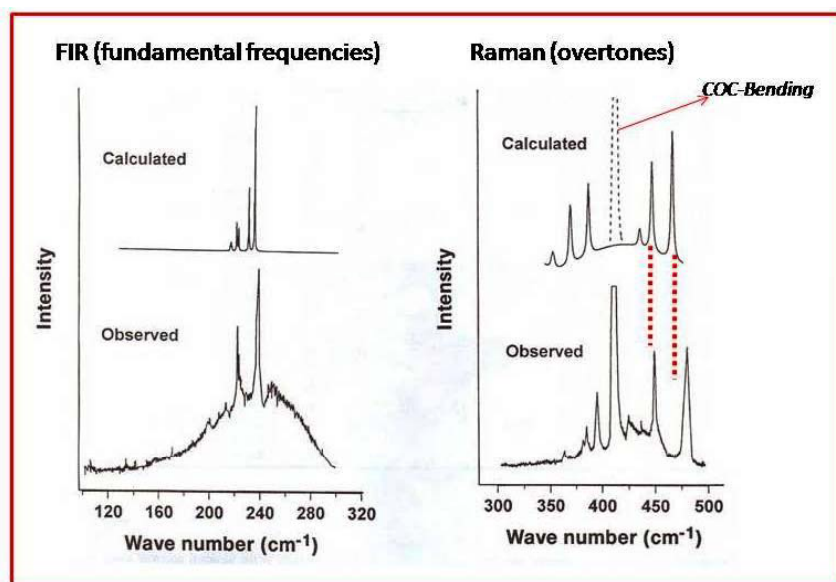
## Why 2 previous papers on DME?

How many independent variables are necessary to simulate the FIR spectrum?  
2D or 3D or more ?

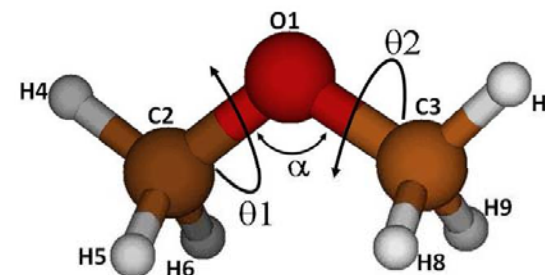
**2D (Can.J.Phys. 1995)**



$$\mathcal{H}(\theta_1, \theta_2) = -\frac{\partial}{\partial \theta_1} B_{11}(\theta_1, \theta_2) \frac{\partial}{\partial \theta_1} - \frac{\partial}{\partial \theta_1} B_{12}(\theta_1, \theta_2) \frac{\partial}{\partial \theta_2} - \frac{\partial}{\partial \theta_2} B_{21}(\theta_1, \theta_2) \frac{\partial}{\partial \theta_1} - \frac{\partial}{\partial \theta_2} B_{22}(\theta_1, \theta_2) \frac{\partial}{\partial \theta_2} + V(\theta_1, \theta_2)$$



**3D (J.Chem.Phys, 1995)**



Exp: Groner, Durig. J. Chem. Phys. (1977).

## Why a new paper on DME?

(the use of actual computational resources allow to improve accuracy)

$$\hat{H}(\alpha, \theta_1, \theta_2) = -B_1(\alpha, \theta_1, \theta_2) \frac{\partial^2}{\partial \theta_1^2} - 2B_{12}(\alpha, \theta_1, \theta_2) \frac{\partial^2}{\partial \theta_1 \partial \theta_2} - B_2(\alpha, \theta_1, \theta_2) \frac{\partial^2}{\partial \theta_2^2} - 2B_{13}(\alpha, \theta_1, \theta_2) \frac{\partial^2}{\partial \alpha \partial \theta_1} \\ - 2B_3(\alpha, \theta_1, \theta_2) \frac{\partial^2}{\partial \alpha^2} - 2B_{23}(\alpha, \theta_1, \theta_2) \frac{\partial^2}{\partial \alpha \partial \theta_2} + V(\alpha, \theta_1, \theta_2),$$

$$V(\alpha, \theta_1, \theta_2) = V^\alpha(\alpha) + V^{cc,ss}(\theta_1, \theta_2) + \sum_M V_M^{\alpha cc, \alpha ss}(\alpha, \theta_1, \theta_2)$$

**1995**

MP4/MP2  
6-31G(d,p)

28 geometries  
3N-9 opt.para.

(approx. definition of the torsional coordinates)

No ZPVE



**2010-2011**

CCSD(T)/CCSD  
Aug-cc-pVTZ

126 geometries  
3N-9 opt.para.

(exact. definition of the torsional coordinates)

+ ZPVE correction

# Dimethyl-ether = DME

(preliminary results)

CCSD/aug-cc-pVTZ structural parameters and dipole moment of DME	
O1C2 = O1C3	1.4090
H4C2 = H7C3	1.0879
H5C2 = H6C2 = H8C3 = H9C3	1.0962
C3O1C2	111.4
H4C2O1 = H7C3O1	107.5
H5C2O1 = H6C2O1 = H8C3O1 = H9C3O1	111.2
H4C2O1C3 = H7C3O1C2	180.0
H5C2O1H4 = H9C3O1H7	119.4
H6C2O1H4 = H8C3O1H7	-119.4
$\mu$ (MP2/aug-cc-pVTZ)	1.4882 Debyes

Torsional barriers (in $\text{cm}^{-1}$ )	CCSD	CCSD +ZPVE
$V_{060}$	863	883
$V_{6060}$	1592	1610

# Dimethyl-ether = DME

(preliminary results with PT2 theory)

Fundamental frequencies (in $\text{cm}^{-1}$ ) DME							
sym.	mode	MP2		CCSD			
		DME-h6		DME-h6		DME-d6	DME-d2
		$\omega$	$\nu$	$\omega$	$\nu$	$\omega$	$\omega$
A <sub>1</sub>	$\nu_1$	3179	<b>3043</b>	3147	3014	<b>2270</b>	2864
	$\nu_2$	3024	<b>2827</b>	3011	<b>2766</b>	<b>2039</b>	<b>2148</b>
	$\nu_3$	1533	1489	1537	1492	1163	1491
	$\nu_4$	1498	1461	1511	1474	1084	1377
	$\nu_5$	1275	1244	1291	1260	1060	1114
	$\nu_6$	958	931	971	946	838	845
	$\nu_7$	417	<b>405</b>	421	<b>401</b>	<b>331</b>	<b>373</b>
A <sub>2</sub>	$\nu_8$	3090	<b>2979</b>	3059	<b>2977</b>	<b>2203</b>	3059
	$\nu_9$	1507	1462	1511	1465	1069	1296
	$\nu_{10}$	1173	1151	1180	1156	880	1108
	$\nu_{11}$	210	202	202	189	138	176
B <sub>1</sub>	$\nu_{12}$	3082	<b>2950</b>	3055	<b>2913</b>	<b>2204</b>	2910
	$\nu_{13}$	1518	1471	1521	1474	1076	1299
	$\nu_{14}$	1201	1173	1212	1183	938	1140
	$\nu_{15}$	260	246	252	235	183	207
B <sub>2</sub>	$\nu_{16}$	3178	3043	3145	<b>3027</b>	<b>2262</b>	<b>2864</b>
	$\nu_{17}$	3019	<b>2898</b>	3002	<b>2936</b>	<b>2051</b>	<b>2160</b>
	$\nu_{18}$	1519	1471	1522	1475	1184	1472
	$\nu_{19}$	1467	1434	1478	1445	1083	1349
	$\nu_{20}$	1211	1176	1231	1198	1070	1166
	$\nu_{21}$	1131	1105	1139	1113	866	926

# Dimethyl-ether = DME

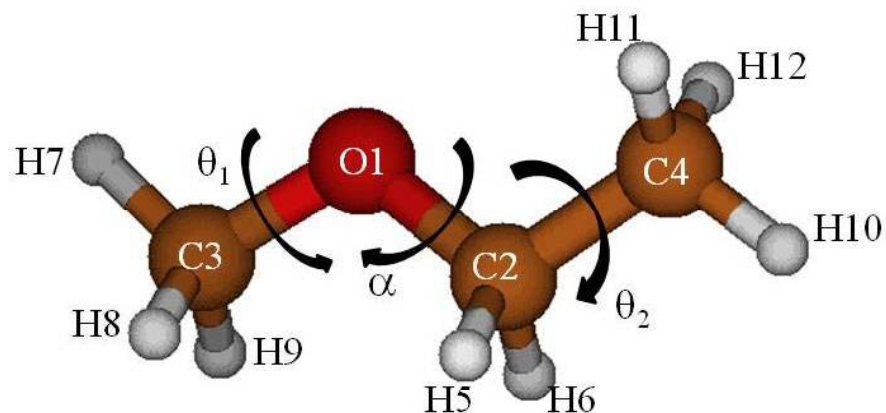
(preliminary results with PT2)

CCSD Strong Fermi displacements of the torsional levels (cm <sup>-1</sup> )		
	DME-h6	DME-d6
$2\nu_{15}$ ( <i>torsion</i> )	467 → 479	471 → 482
$\nu_7$ ( <i>COC bending</i> )	413 → 401	341 → 331

CCSD Rotational parameters (in MHz) (Second order Perturbation Theory)		
	DME-h6	DME-d6
$\Delta_J$	0.0091	0.0048
$\Delta_K$	0.3328	0.0663
$\Delta_{JK}$	-0.0292	0.0018
$A_e$	38973.13	25853.98
$B_e$	10145.29	7533.13
$C_e$	8961.41	6841.78
$A_0$	38764.72	25727.95
$B_0$	10298.74	7630.60
$C_0$	9083.22	6927.51

Fortran Code: *FIT-ESPEC (PT2)* , M. L. Senent,  
<http://tct1.iem.csic.es/senent/PROGRAMAS.htm>.

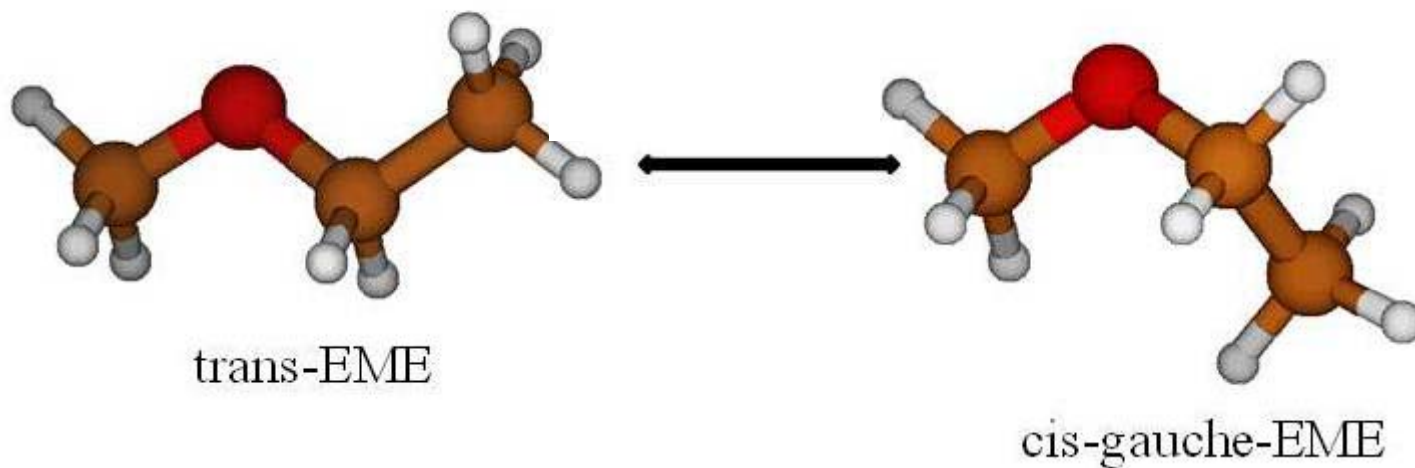
## Ethyl-methyl-ether = EME



CCSD(T) study of the FIR spectrum of EME, Senent, Ruiz, Dominguez-Gómez, and Villa, **J.Chem.Phys. 2009**

CCSD(T) study of FIR spectrum of EME isotopic varieties, Senent, Ruiz, Villa, and Domínguez-Gómez, **Chem.Phys., 2010**

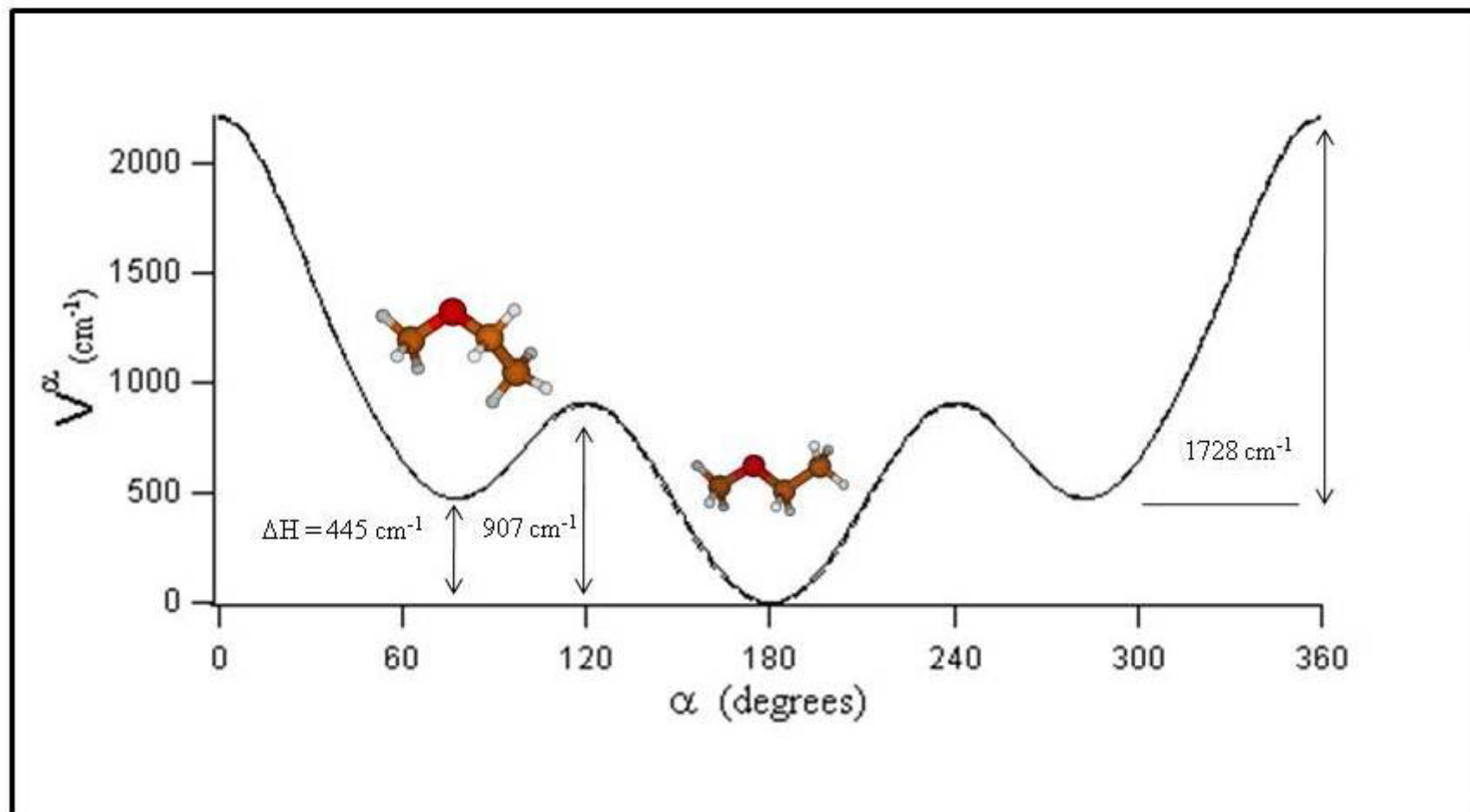
# EME



MHz	A	B	C
trans	28341.5	4193.2	3921.5
cis-gauche	15993.7	5223.6	4546.3



# EME: Torsional energy barriers



# EME: 3D-PES

$$V(\alpha, \theta_1, \theta_2) = \sum_{l=0} \sum_{m=0} \sum_{n=0} [\cos(l\alpha)\cos(3m\theta_1)\cos(3n\theta_2) + \sin(l\alpha)\sin(3m\theta_1)\cos(3n\theta_2) + \sin(l\alpha)\cos(3m\theta_1)\sin(3n\theta_2) + \cos(l\alpha)\sin(3m\theta_1)\sin(3n\theta_2)]$$

CCSD(T)/CCSD

cc-pVTZ

+ZPVE correction

300 geometries (3N-9 opt. coord.)

Exact definition of torsional coordinates from  
Szalay, Császár, Senent, J.Chem.Phys., 2002

**CCSD(T) band positions (in cm<sup>-1</sup>) and intensities of *trans*-EME**

Assign.	Symm.	$\nu$	Intensity (273°K)	exp $\nu$ (intens)	Assign.	Symm.	$\nu$	Intensity (273°K)	exp $\nu$ (intens)
<i>Skeletal torsion</i>									
<b>000 → 100</b>	A <sub>1</sub> →A <sub>2</sub>	<b>115.3</b>	<b>0.41 10<sup>-4</sup></b>	<b>115.40 (vs)</b>	<b>300 → 400</b>	A <sub>2</sub> →A <sub>1</sub>	<b>101.6</b>	<b>0.34 10<sup>-4</sup></b>	<b>103.54</b>
	E <sub>1</sub> →E <sub>1</sub>	<b>115.3</b>	<b>0.81 10<sup>-4</sup></b>		E <sub>1</sub> →E <sub>1</sub>	<b>101.6</b>	<b>0.68 10<sup>-4</sup></b>		
	E <sub>2</sub> →E <sub>2</sub>	<b>115.3</b>	<b>0.81 10<sup>-4</sup></b>		E <sub>2</sub> →E <sub>2</sub>	<b>101.7</b>	<b>0.68 10<sup>-4</sup></b>		
	E <sub>3</sub> →E <sub>3</sub>	<b>115.3</b>	<b>0.41 10<sup>-4</sup></b>		E <sub>3</sub> →E <sub>3</sub>	<b>102.1</b>	<b>0.34 10<sup>-4</sup></b>		
	E <sub>4</sub> →E <sub>4</sub>	<b>115.3</b>	<b>0.41 10<sup>-4</sup></b>		E <sub>4</sub> →E <sub>4</sub>	<b>102.1</b>	<b>0.34 10<sup>-4</sup></b>		
<b>100 → 200</b>	A <sub>2</sub> →A <sub>1</sub>	<b>110.9</b>	<b>0.48 10<sup>-4</sup></b>	<b>111.77</b>	<b>400 → 500</b>	A <sub>1</sub> →A <sub>2</sub>	<b>96.4</b>	<b>0.27 10<sup>-4</sup></b>	<b>99.0</b>
	E <sub>1</sub> →E <sub>1</sub>	<b>111.1</b>	<b>0.96 10<sup>-4</sup></b>		E <sub>1</sub> →E <sub>1</sub>	<b>96.4</b>	<b>0.34 10<sup>-4</sup></b>		
	E <sub>2</sub> →E <sub>2</sub>	<b>111.1</b>	<b>0.96 10<sup>-4</sup></b>		E <sub>2</sub> →E <sub>2</sub>	<b>96.4</b>	<b>0.34 10<sup>-4</sup></b>		
	E <sub>3</sub> →E <sub>3</sub>	<b>111.1</b>	<b>0.48 10<sup>-4</sup></b>		E <sub>3</sub> →E <sub>3</sub>	<b>96.4</b>	<b>0.27 10<sup>-4</sup></b>		
	E <sub>4</sub> →E <sub>4</sub>	<b>111.1</b>	<b>0.48 10<sup>-4</sup></b>		E <sub>4</sub> →E <sub>4</sub>	<b>96.4</b>	<b>0.27 10<sup>-4</sup></b>		
<b>200 → 300</b>	A <sub>1</sub> →A <sub>2</sub>	<b>106.4</b>	<b>0.42 10<sup>-4</sup></b>	<b>107.80</b>					
	E <sub>1</sub> →E <sub>1</sub>	<b>106.4</b>	<b>0.84 10<sup>-4</sup></b>						
	E <sub>2</sub> →E <sub>2</sub>	<b>106.5</b>	<b>0.84 10<sup>-4</sup></b>						
	E <sub>3</sub> →E <sub>3</sub>	<b>106.1</b>	<b>0.42 10<sup>-4</sup></b>						
	E <sub>4</sub> →E <sub>4</sub>	<b>106.1</b>	<b>0.42 10<sup>-4</sup></b>						
<i>Methyl torsions</i>									
<b>000 → 010</b>	A <sub>1</sub> →A <sub>2</sub>	<b>206.6</b>	<b>0.31 10<sup>-4</sup></b>	<b>202 (m)</b>	<b>000 → 001</b>	A <sub>1</sub> →A <sub>2</sub>	<b>255.2</b>	<b>0.24 10<sup>-5</sup></b>	<b>248 (m)</b>
	E <sub>1</sub> →E <sub>1</sub>	<b>206.6</b>	<b>0.61 10<sup>-4</sup></b>		E <sub>1</sub> →E <sub>1</sub>	<b>255.2</b>	<b>0.47 10<sup>-5</sup></b>		
	E <sub>2</sub> →E <sub>2</sub>	<b>206.6</b>	<b>0.61 10<sup>-4</sup></b>		E <sub>2</sub> →E <sub>2</sub>	<b>255.2</b>	<b>0.47 10<sup>-5</sup></b>		
	E <sub>3</sub> →E <sub>3</sub>	<b>206.6</b>	<b>0.31 10<sup>-4</sup></b>		E <sub>3</sub> →E <sub>3</sub>	<b>255.2</b>	<b>0.24 10<sup>-5</sup></b>		
	E <sub>4</sub> →E <sub>4</sub>	<b>206.6</b>	<b>0.31 10<sup>-4</sup></b>		E <sub>4</sub> →E <sub>4</sub>	<b>255.2</b>	<b>0.24 10<sup>-5</sup></b>		
<b>010 → 020</b>	A <sub>2</sub> →A <sub>1</sub>	<b>195.2</b>	<b>0.19 10<sup>-4</sup></b>		<b>001 → 002</b>	A <sub>2</sub> →A <sub>1</sub>	<b>242.3</b>	<b>0.19 10<sup>-5</sup></b>	
	E <sub>1</sub> →E <sub>1</sub>	<b>195.2</b>	<b>0.19 10<sup>-4</sup></b>		E <sub>1</sub> →E <sub>1</sub>	<b>242.3</b>	<b>0.38 10<sup>-5</sup></b>		
	E <sub>2</sub> →E <sub>2</sub>	<b>195.5</b>	<b>0.38 10<sup>-4</sup></b>		E <sub>2</sub> →E <sub>2</sub>	<b>242.3</b>	<b>0.38 10<sup>-5</sup></b>		
	E <sub>3</sub> →E <sub>3</sub>	<b>195.5</b>	<b>0.38 10<sup>-4</sup></b>		E <sub>3</sub> →E <sub>3</sub>	<b>242.3</b>	<b>0.19 10<sup>-5</sup></b>		
	E <sub>4</sub> →E <sub>4</sub>	<b>195.5</b>	<b>0.19 10<sup>-4</sup></b>		E <sub>4</sub> →E <sub>4</sub>	<b>242.3</b>	<b>0.19 10<sup>-5</sup></b>		
<b>020 → 030</b>	A <sub>1</sub> →A <sub>2</sub>	<b>179.3</b>	<b>0.90 10<sup>-5</sup></b>		<b>002 → 003</b>	A <sub>1</sub> →A <sub>2</sub>	<b>230.0</b>	<b>&lt; 10<sup>-5</sup></b>	
	E <sub>1</sub> →E <sub>1</sub>	<b>179.3</b>	<b>0.18 10<sup>-4</sup></b>		E <sub>1</sub> →E <sub>1</sub>	<b>230.0</b>	<b>&lt; 10<sup>-5</sup></b>		
	E <sub>2</sub> →E <sub>2</sub>	<b>179.4</b>	<b>0.18 10<sup>-4</sup></b>		E <sub>2</sub> →E <sub>2</sub>	<b>230.1</b>	<b>&lt; 10<sup>-5</sup></b>		
	E <sub>3</sub> →E <sub>3</sub>	<b>179.4</b>	<b>0.90 10<sup>-5</sup></b>		E <sub>3</sub> →E <sub>3</sub>	<b>230.1</b>	<b>&lt; 10<sup>-5</sup></b>		
	E <sub>4</sub> →E <sub>4</sub>	<b>179.4</b>	<b>0.90 10<sup>-5</sup></b>		E <sub>4</sub> →E <sub>4</sub>	<b>230.1</b>	<b>&lt; 10<sup>-5</sup></b>		
<i>Combination bands</i>									
<b>100 → 110</b>	A <sub>2</sub> →A <sub>1</sub>	<b>206.0</b>	<b>0.15 10<sup>-4</sup></b>		<b>210 → 310</b>	A <sub>2</sub> →A <sub>1</sub>	<b>106.1</b>	<b>0.15 10<sup>-4</sup></b>	
<b>010 → 110</b>	A <sub>2</sub> →A <sub>1</sub>	<b>114.7</b>	<b>0.14 10<sup>-4</sup></b>		<b>101 → 201</b>	A <sub>1</sub> →A <sub>2</sub>	<b>110.1</b>	<b>0.15 10<sup>-4</sup></b>	
<b>001 → 101</b>	A <sub>2</sub> →A <sub>1</sub>	<b>114.0</b>	<b>0.11 10<sup>-4</sup></b>		<b>201 → 301</b>	A <sub>2</sub> →A <sub>1</sub>	<b>105.8</b>	<b>0.11 10<sup>-4</sup></b>	
<b>110 → 210</b>	A <sub>1</sub> →A <sub>2</sub>	<b>116.0</b>	<b>0.16 10<sup>-4</sup></b>		<b>001 → 011</b>	A <sub>2</sub> →A <sub>1</sub>	<b>190.9</b>	<b>0.65 10<sup>-5</sup></b>	

CCSD(T) fundamental band positions (in $\text{cm}^{-1}$ ) of <i>cis-gauche</i> -EME				
Assign.	Symmetry	Band position	Intensity (273°K)	exp $\nu$ (intens)
$0^+00 \rightarrow 1^-00$	$A_1 \rightarrow A_2$	91.0	$0.62 \cdot 10^{-6}$	93.56 (m)
$0^-00 \rightarrow 1^+00$	$A_2 \rightarrow A_1$	91.0	$0.62 \cdot 10^{-6}$	93.56 (m)
$0^+00 \rightarrow 0^-10$	$A_1 \rightarrow A_2$	192.5	$0.82 \cdot 10^{-7}$	
$0^-10 \rightarrow 0^+10$	$A_2 \rightarrow A_1$	192.5	$0.82 \cdot 10^{-7}$	
$0^+00 \rightarrow 0^-01$	$A_1 \rightarrow A_2$	243.8	$0.29 \cdot 10^{-7}$	
$0^-10 \rightarrow 0^+01$	$A_2 \rightarrow A_1$	243.8	$0.29 \cdot 10^{-7}$	

Fortran Code: *ENEDIM* (variational), M. L. Senent,  
<http://tct1.iem.csic.es/PROGRAMAS.htm>.

**Fundamental frequencies in  $\text{cm}^{-1}$   
(intensities)**

We suggest a new assignment for  $\text{CH}_3\text{-O-CH}_2\text{-CH}_3$

Exp. (Durig et al. 2002) OLD assign (Durig et al 2002) NEW assign (this paper)	$\text{CH}_3\text{-O-CH}_2\text{-CH}_3$							
	CCSD(T)	Exp (OLD)	Exp (NEW)	$\Delta$				
<i>trans-EME</i>								
$\nu_{28}$ (C- $\text{CH}_3$ -torsion)	<b>255.2</b>	278	248	7.2				
$\nu_{29}$ (O- $\text{CH}_3$ -torsion)	<b>206.5</b>	248	202	4.5				
$\nu_{30}$ (O- $\text{C}_2\text{H}_5$ -torsion)	<b>115.3</b>	115.4	115.4	-0.1				
<i>cis-gauche-EME</i>								
$\nu_{28}$ (C- $\text{CH}_3$ -torsion)	<b>243.8</b> <b>243.8</b>							
$\nu_{29}$ (O- $\text{CH}_3$ -torsion)	<b>192.5</b> <b>192.5</b>	202						
$\nu_{30}$ (O- $\text{C}_2\text{H}_5$ -torsion)	<b>91.0</b> <b>91.0</b>	93.56	93.56	-2.6				

**Fundamental frequencies in  $\text{cm}^{-1}$   
(intensities)**

**We suggest a new assignment for  $\text{CH}_3\text{-O-CH}_2\text{-CH}_3$**

Exp. (Durig et al. 2002) OLD assign (Durig et al 2002) NEW assign (this paper)	$\text{CH}_3\text{-O-CH}_2\text{-CH}_3$							
	CCSD(T)	Exp (OLD)	Exp (NEW)	$\Delta$				
<i>trans-EME</i>								
$\nu_{28}$ (C- $\text{CH}_3$ -torsion)	<b>255.2</b>	278	248	7.2				
$\nu_{29}$ (O- $\text{CH}_3$ -torsion)	<b>206.5</b>	248	202	4.5				
$\nu_{30}$ (O- $\text{C}_2\text{H}_5$ -torsion)	<b>115.3</b>	115.4	115.4	-0.1				
<i>cis-gauche-EM</i>								
$\nu_{28}$ (C- $\text{CH}_3$ -torsion)	<b>243.8</b> <b>243.8</b>							
$\nu_{29}$ (O- $\text{CH}_3$ -torsion)	<b>192.5</b> <b>192.5</b>	202						
$\nu_{30}$ (O- $\text{C}_2\text{H}_5$ -torsion)	<b>91.0</b> <b>91.0</b>	93.56	93.56	-2.6				

**Fundamental frequencies in  $\text{cm}^{-1}$   
(intensities)**

**We suggest a new assignment for  $\text{CH}_3\text{-O-CH}_2\text{-CH}_3$**

Exp. (Durig et al. 2002) OLD assign (Durig et al 2002) NEW assign (this paper)	<i>CH<sub>3</sub>-O-CH<sub>2</sub>-CH<sub>3</sub></i>							
	<b>CCSD(T)</b>	<b>Exp (OLD)</b>	<b>Exp (NEW)</b>	$\Delta$				
<i>trans-EME</i>								
<b>v<sub>28</sub></b> ( <i>C-CH<sub>3</sub>-torsion</i> )	<b>255.2</b>	<b>278</b>	<b>248</b> (m)	7.2				
<b>v<sub>29</sub></b> ( <i>O-CH<sub>3</sub>-torsion</i> )	<b>206.5</b>	<b>248</b> (m)	<b>202</b> (m)	4.5				
<b>v<sub>30</sub></b> ( <i>O- C<sub>2</sub>H<sub>5</sub>-torsion</i> )	<b>115.3</b>	<b>115.4</b> (vs)	<b>115.4</b> (vs)	-0.1				
<i>cis-gauche-EME</i>								
<b>v<sub>28</sub></b> ( <i>C-CH<sub>3</sub>-torsion</i> )	<b>243.8</b> <b>243.8</b>							
<b>v<sub>29</sub></b> ( <i>O-CH<sub>3</sub>-torsion</i> )	<b>192.5</b> <b>192.5</b>	<b>202</b> (m)						
<b>v<sub>30</sub></b> ( <i>O- C<sub>2</sub>H<sub>5</sub>-torsion</i> )	<b>91.0</b> <b>91.0</b>	<b>93.56</b> (m)	<b>93.56</b> (m)	-2.6				

**Fundamental frequencies in  $\text{cm}^{-1}$   
(intensities)**

We suggest a new assignment for  $\text{CH}_3\text{-O-CH}_2\text{-CH}_3$

Exp. (Durig et al. 2002) OLD assign (Durig et al 2002) NEW assign (this paper)	$\text{CH}_3\text{-O-CH}_2\text{-CH}_3$				$\text{CD}_3\text{-O-CH}_2\text{-CH}_3$			
	CCSD(T)	Exp (OLD)	Exp (NEW)	$\Delta$	CCSD(T)	Exp (OLD)	Exp (NEW)	$\Delta$
<i>trans-EME</i>								
$\nu_{28}$ (C- $\text{CH}_3$ -torsion)	255.2	278	248 (m)	7.2	249.0	241	241	8.0
$\nu_{29}$ (O- $\text{CH}_3$ -torsion)	206.5	248 (m)	202 (m)	4.5	166.6	163	163	3.6
$\nu_{30}$ (O- $\text{C}_2\text{H}_5$ -torsion)	115.3	115.4 (vs)	115.4 (vs)	-0.1	106.2	106	106	0.2
<i>cis-gauche-EME</i>								
$\nu_{28}$ (C- $\text{CH}_3$ -torsion)	243.8 243.8							
$\nu_{29}$ (O- $\text{CH}_3$ -torsion)	192.5 192.5	202 (m)						
$\nu_{30}$ (O- $\text{C}_2\text{H}_5$ -torsion)	91.0 91.0	93.56 (m)	93.56 (m)	-2.6				



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