GOBIERNO DE ESPAÑA

MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES

CSIC

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GIFMAN

Spectroscopy of non-rigid organic species: theory, experiments and application to astrochemistry.

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DYMCOM

Dynamical Methods for COld Molecular collisions, from laboratory to beyond the Earth

University Paris-Saclay, 4-29 Nov 2019

DEFINITIONS

Non-Rigid Molecules: <u>various minima</u> (conformers) in the Potential Energy Surface; large amplitude vibrational motions (such as torsional modes) intertransform the minima.
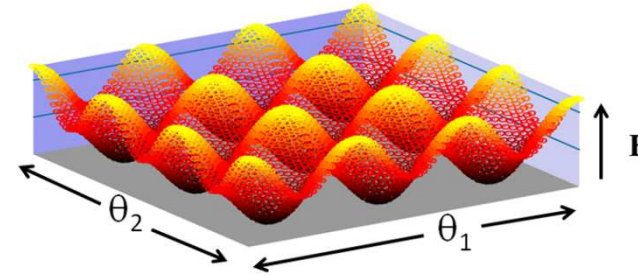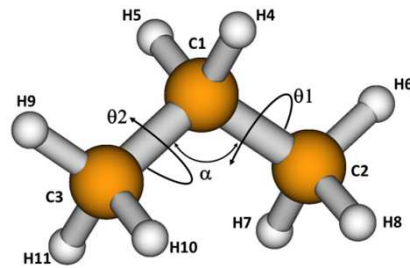
Semi-Rigid Molecules: <u>one minimum</u> in the Potential Energy Surface or various minima (isomers) that intertransform throught chemical reactions.
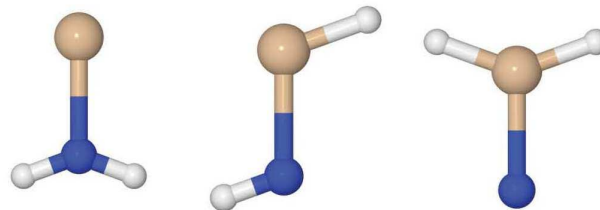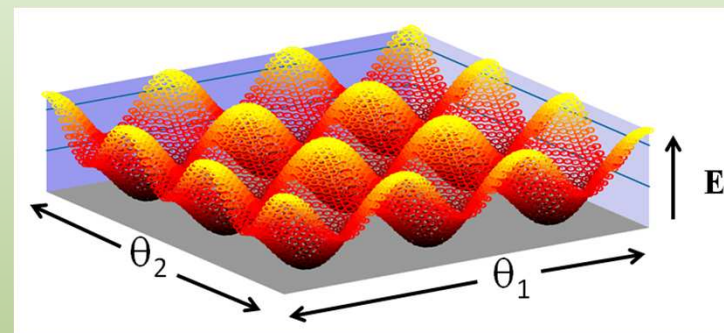
Non-rigid molecules

- $N_m > 1$ minima in the PES separate by relatively low Potential Energy Barriers

- Inter conversion of the minima through "feasible" large amplitude motions (LAMs) (without bond breaking).

- LAMs: usually very anharmonic.
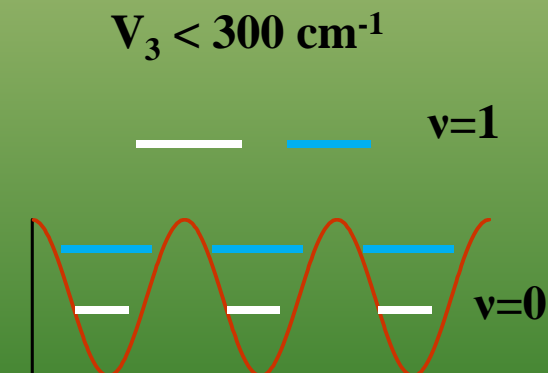
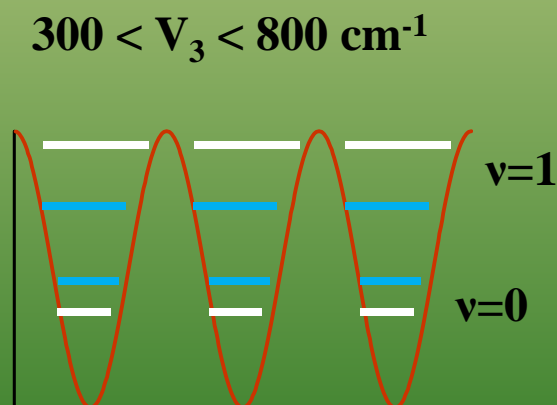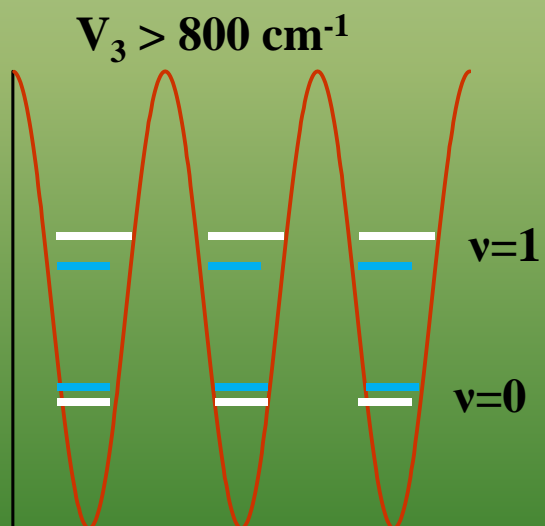- Tunneling effects split the vibrational levels

Methyl-groups tunneling effects
A and E components of the levels

(typical "egg box" of a
two-methyl groups system)

3 different behaviors (v=0, v=1)
A, E components

$V_3 > 800$ cm^{-1}

$300 < V_3 < 800$ cm^{-1}

$V_3 < 300$ cm^{-1}

v=1

v=0

v=1

v=0

v=1

v=0
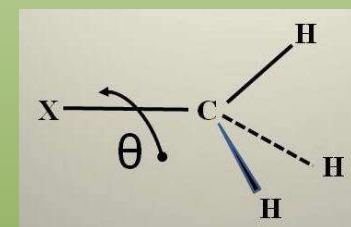
Why these molecules are relevant for astrophysics?

1) Some NRigM are abundant species in the ISM gas phase sources (few species such as propane and methanol exist in planetary atmospheres and planetoids)

1) **Related to the problem of origin of life: PREBIOTIC**

1) **The internal motions responsible for the non-rigid properties display very low energy levels that can be populated at low temperatures.**
(i.e. the torsional levels are separated typically by 100 to 200 cm^{-1})

ISM Detected molecules
(gas phase)

10M (1970-1979)
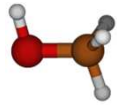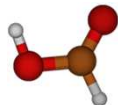
Methanol 1970 · Formic acid 1971 · Formamide 1971 · Acetaldehyde 1973 · **Dimethyl-ether 1974** · Methyl-amine 1974 · **Ethanol 1975** · **Methyl-formate 1975**
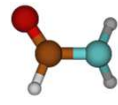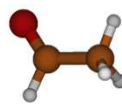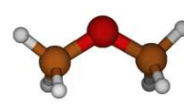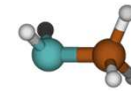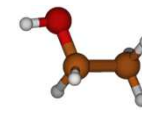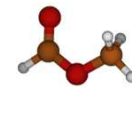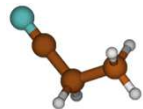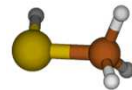
Ethyl-cyanide 1977 · Methyl-Mercaptan 1979

1M (1980-1989)
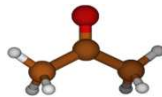
Acetone 1987

1M (1990-1999)
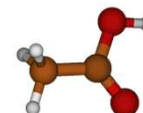
Acetic acid 1997

10+1+1+11+15 = 38 ¡¡¡

11M (2000-2009)

Glycolaldehyde 2000

Vinyl alcohol 2001

Ethylene glycol 2002

Glycine ? 2003-2005

Propanal 2004

Propenal 2004

Dihydroxi acetone 2005

Acetamide 2006

Propylene 2007

Aminoacetonitrile 2008

Ethyl formate 2009

15M (2010-2019)

H2O2 2011

Ethanimine 2013

Cyanomethanimine 2013

Methyl acetate 2013

Phenol 2013

Ethyl mercaptan 2014

Isopropyl cyanide 2014

Methyl isocyanate 2015

Ethyl methyl ether 2015

Propylene oxide 2016

N-methyl formamide 2017

Methyl silane 2017

Methoxi methanol 2017

glyconitrilo 2017

urea 2019

Usual techniques
(FIR, Raman, and rotational spectroscopy;
ab initio calculations)

**FIR and
Raman**

**Rotational
spectroscopy**

**Theory and ab initio
calculations**

MW spectroscopy (0-30 GHz)
Millimeter-wave spectroscopy (30-300 GHz)
Sub-millimeter-wave spectroscopy (300-1000 GHz)

Ab initio calculations
Highly correlated methods (if possible)

1- **Structures**, equilibrium rotational constants, and **dipole moments**

2- **VPT2:** anharmonic analysis (**full-dimensional**)

3-**VARIATIONAL** procedure of **reduced dimensionality** for the **n large amplitude vibrations (LAM)** responsible for the non-rigid properties.

Ground vibrational state rotational parameters
i.e. rotational constants

$$B_0 = B_e \text{ (CCSD(T)-F12)} + \Delta B_e^{core} \text{ (CCSD(T))} + \Delta B^{vib} \text{ (MP2)}$$

1- Structures and equilibrium rotational constants and dipole moments

2- VPT2: full-dimensional anharmonic analysis

3-VARIATIONAL procedure for the n large amplitude vibrations (LAM) responsible for the non-rigid properties

(MOLPRO and GAUSSIAN)
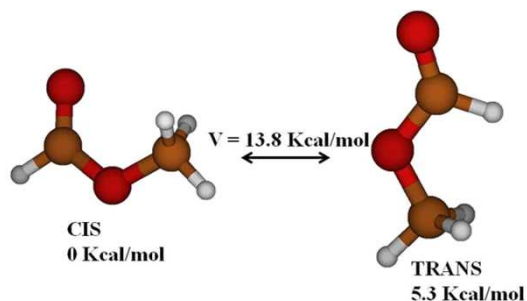
CIS
0 Kcal/mol

V = 13.8 Kcal/mol

TRANS
5.3 Kcal/mol

1) methyl-Format

	Rotational constants (MHz) of cis-methyl-format 7 sets of experimental values					
Exp.	**[1]**	**[2]**	**[3]**	**[4]**	**[5]**	**[6]**
A	**19983.05**	**19985.7623**	**19983.06**	**17522.36993**	**19141.92**	**19120.151**
B	**6914.4198**	**6914.757**	**6914.928**	**9323.547665**	**9112.39**	**9181.7185**
C	5303.2477	5304.468	5304.236	5312.69996	5264.63	5254.7515

A^{calc}=19990.97 MHz; B^{exp}=6907.92 MHz; C^{exp}= 5301.47 MHz

$|A^{calc}-A^{exp}| \sim$ **7 MHz**; $|B^{calc}-B^{exp}| \sim$ **6 MHz**; $|C^{calc}-C^{exp}| \sim$ **2 MHz**

Senent et al. Astrophys. J (2005); Gámez et al. J.Phys.Chem.A (2019)

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2) methyl isocyanate

Methyl Isocyanate(CH_3-NCO)

Calculated		Laboratory rotational spectroscopy		
A_0	76164.32	**73849.2**	**78395(410)**	**128402(13)**
B_0	4411.89	**4392.22**	**4442.982(49)**	**4414.6287(75)**
C_0	4254.58	**4256.66**	**4256.691(31)**	**4256.7452(71)**

J. Koput, J.Mol.Spectrosc, (1986)   (lab rotational spectroscopy)
D. T. Halfen, et al. Astrophys. J. (2015)   (Interstellar detection + lab rotational spectroscopy)
J. Cernicharo et al, Astron & Astrophys (2016)   (Interstellar detection + lab rotational spectroscopy)

Methyl Cyanate(CH_3-OCN)

Calculated		Laboratory rotational spectroscopy	
A_0	**39089.80**	**39042.4(8)**	**38989.07 (20)**
B_0	**5314.78**	**5322.88(3)**	**5322.25(15)**
C_0	**4816.35**	**4821.33(3)**	**4821.31(13)**

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L. Kolesnikova, et al. Astron & Astrophys (2016) (lab rotational spectroscopy)

16

3) isopropyl-cyanide

Kerkeni, Gámez, Senent, Feautrier, PCCP (2019)
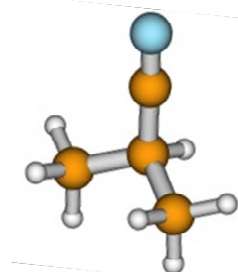
	iso-PrCN			
	Calc.	Exp.[a]	Exp.[b]	Exp.[c]
A_0	7939.497	7940.877174(31)	7940.8746(16)	7940.8723(43)
B_0	3964.2339	3968.087775(27)	3968.08888(52)	3968.087339(56)
C_0	2898.4008	2901.053223(22)	2901.05458(53)	2901.052880(43)
$\Delta J \times 10^6$	612.550	610.2684(153)	612.7(12)	609.971(16)
$\Delta JK \times 10^3$	12.433	12.17725(42)	12.1698(43)	12.176382(65)
$\Delta K \times 10^3$	-5.261	-5.23242(61)	-5.231(27)	-5.2110(11)
$d_1 \times 10^6$	-238.167	-244.0908(69)	-243.93(11)	-244.012(10)
$d_2 \times 10^6$	-187.016	-189.2889(76)	-189.404(63)	-189.3655(54)
$H_J \times 10^{12}$	-1054.181	-584.83(151)		-633.0(22)
$H_K \times 10^9$	12.057	-37.163(248)		
$H_{JK} \times 10^9$	46.861	38.267(140)	34.7(16)	37.319(10)
$H_{KJ} \times 10^9$	-45.824	10.968(281)		11.908(34)
$h_1 \times 10^{12}$	-87.493	68.73(77)		44.0(14)
$h_2 \times 10^{12}$	989.246	884.23(83)	931.0(72)	895.1(13)
$h_3 \times 10^{12}$	303.884	322.39(140)	326.0(33)	318.02(55)
μ_A	4.3609	4.0219 (50)		
μ_B				
μ_C	0.7573	0.6192 (267)		

a) Müller, Coutens, Walters, Grabow, & Schlemmer, *J.Mol.Spectros.* (2011)
b) Arenas, Gruet, Steber, Giuliano, & Schnell, *PCCP* (2017).
c) Kolesniková, Alonso, Mata, Cernicharo, & Alonso, *ApJ* (2017).

Variational procedure (LAMs)

1- Structures and equilibrium rotational constants and dipole moments.

2- VPT2: full-dimensional anharmonic analysis.

3-VARIATIONAL procedure of reduced dimensionality: large amplitude vibrations (LAMs) responsible for the non-rigid properties.

ENEDIM code

ENEDIM
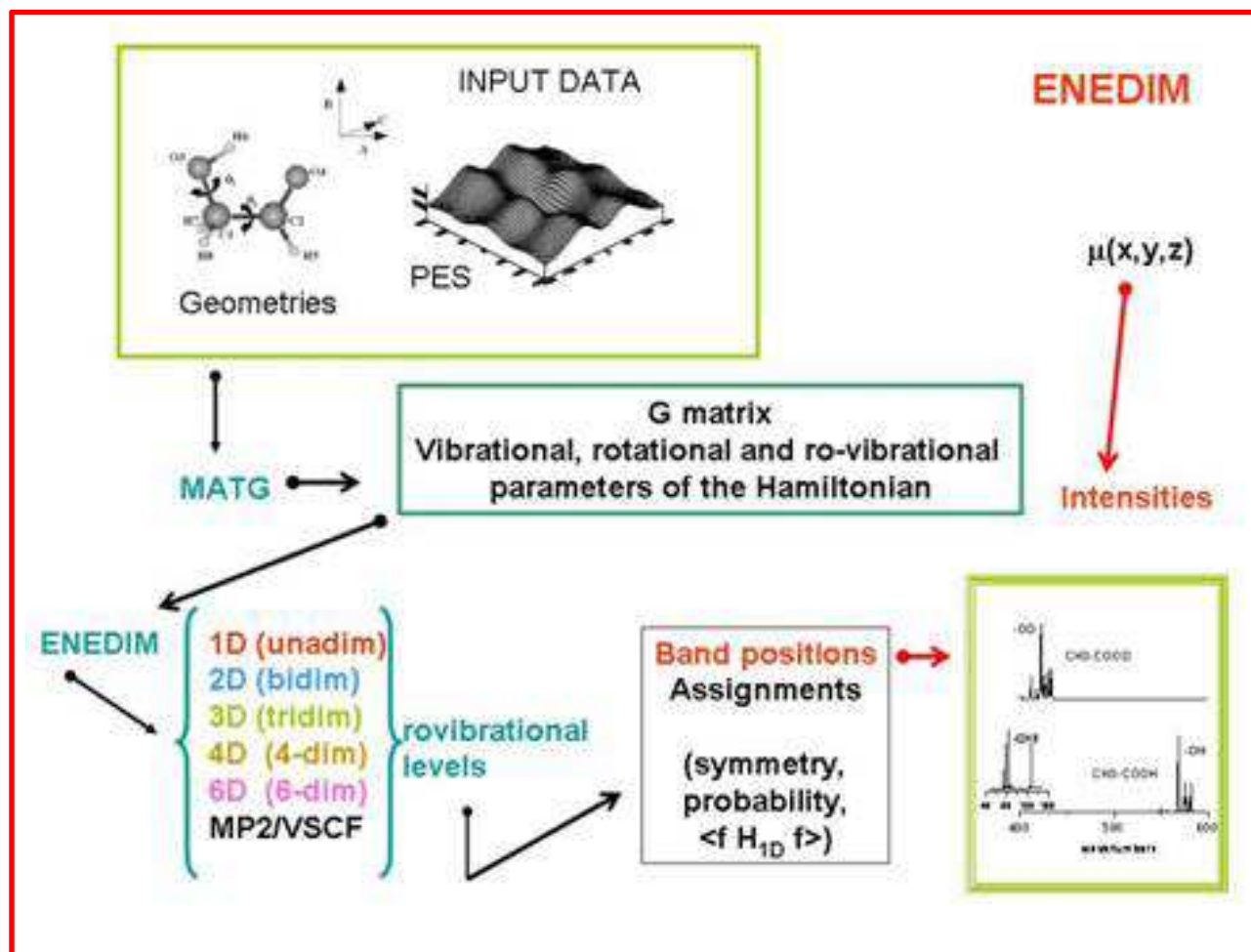
Theoretical Chemistry Team: *I. Estructura de la Materia, CSIC, Madrid*
http://tct1.iem.csic.es/PROGRAMAS.htm

Variational procedure $\boxed{H_{RV} = T_{RV} + PES}$

curvilinear Internal Coordinates $(q_1, q_2, \ldots q_{3N-6})$

(matrizG code)

2 reference systems (origin=c.d.m.)
$\left\{ \begin{array}{l} \text{O(x,y,z) rotating with the molecule} \\ \text{O'(X,Y,Z) space fixed} \end{array} \right.$

Inertia matrix

G matrix

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

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

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

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

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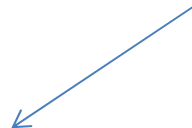
Senent M.L. 2001, Mol.Phys., 15, 1311.

Variational procedure $\boxed{H_{RV} = T_{RV} + PES}$

Quantum mechanical operator for J=0:

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

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

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

Quantum mechanical operator for J> 0:

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

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

Variational procedure

But ....a full-dimensional variational calculation is not realistic for complex molecules. What do do?

1) The n large amplitude vibrations (LAM') are considered 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 represents 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 correction must be added.

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

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

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

Variational procedure

Classification of the vibrational levels

a) **Symmetry (MSGs)**

b) **Probability integrals (PES minima)**

$$\int_q^{q'} \phi_i^* \phi_i \, dq_1 dq_2 dq_n$$

c) **Expectation values of the one-dimensional Hamiltonians (vibrational modes)**

$$< H_n > = < \phi_i^* H_n \, \phi_i > \qquad\qquad H_n = -B_i^0 \frac{\partial^2}{\partial q_n^2} + V(q_n)$$

d) **Intensities (vibrational modes)**

$$I = \frac{q}{3 Re B} (E_j - E_i)(P_j - P_i) < \phi_i | \mu | \phi_j >^2$$

Variational procedure

Trial functions

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

For J> 0

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

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

For large systems:

a) Contracted basis sets
b) Symmetry adapted functions

MSG G$_{36}$

A$_1$	$cos\ I\theta_1\ cos\ J\theta_2 + cos\ J\theta_1\ cos\ I\theta_2$ $sin\ I\theta_1\ sin\ J\theta_2 + sin\ J\theta_1\ sin\ I\theta_2$	L ≤ K	I=3K J=3L
A$_2$	$cos\ I\theta_1\ cos\ J\theta_2 - cos\ J\theta_1\ cos\ I\theta_2$ $sin\ I\theta_1\ sin\ J\theta_2 - sin\ J\theta_1\ sin\ I\theta_2$		
A$_3$	$cos\ I\theta_1\ sin\ J\theta_2 + sin\ J\theta_1\ cos\ I\theta_2$ $sin\ I\theta_1\ cos\ J\theta_2 + cos\ J\theta_1\ sin\ I\theta_2$		
A$_4$	$cos\ I\theta_1\ sin\ J\theta_2 - sin\ J\theta_1\ cos\ I\theta_2$ $sin\ I\theta_1\ cos\ J\theta_2 - cos\ J\theta_1\ sin\ I\theta_2$	L < K	
E$_1$	$cosI\theta_1cosJ\theta_2 \pm sinI\theta_1sinJ\theta_2 + cosJ\theta_1cosI\theta_2 \pm sinJ\theta_1sinI\theta_2$ $cosI\theta_1cosJ\theta_2 \mp sinI\theta_1sinJ\theta_2 - cosJ\theta_1cosI\theta_2 \mp sinJ\theta_1sinI\theta_2$	L ≤ K	I=3K±δ J=3L+δ δ=±1
E$_2$	$cosI\theta_1cosJ\theta_2 \pm sinI\theta_1sinJ\theta_2 - cosJ\theta_1cosI\theta_2 \mp sinJ\theta_1sinI\theta_2$ $cosI\theta_1sinJ\theta_2 \mp sinI\theta_1cosJ\theta_2 + sinJ\theta_1cosI\theta_2 \pm cosJ\theta_1sinI\theta_2$		
E$_3$	$cosI\theta_1cosJ\theta_2 \mp sinI\theta_1sinJ\theta_2 + cosJ\theta_1cosI\theta_2 \mp sinJ\theta_1sinI\theta_2$ $cosI\theta_1sinJ\theta_2 \pm sinI\theta_1cosJ\theta_2 + sinJ\theta_1cosI\theta_2 \pm cosJ\theta_1sinI\theta_2$	L > K	
E$_4$	$cosI\theta_1cosJ\theta_2 \mp sinI\theta_1sinJ\theta_2 - cosJ\theta_1cosI\theta_2 \pm sinJ\theta_1sinI\theta_2$ $cosI\theta_1sinJ\theta_2 \pm sinI\theta_1cosJ\theta_2 - sinJ\theta_1cosI\theta_2 \mp cosJ\theta_1sinI\theta_2$		
G	$cos\ I\theta_1\ cos\ J\theta_2$ $sin\ I\theta_1\ sin\ J\theta_2$ $cos\ I\theta_1\ sin\ J\theta_2$ $sin\ I\theta_1\ cos\ J\theta_2$	L < K	I=3K J=3L+δ δ=±1
	$cos\ I\theta_1\ cos\ J\theta_2$ $sin\ I\theta_1\ sin\ J\theta_2$ $cos\ I\theta_1\ sin\ J\theta_2$ $sin\ I\theta_1\ cos\ J\theta_2$		I=3K+δ J=3L δ=±1

3D-WF of DME (G$_{36}$) $\Psi^{3D} = \Psi^{2D} \sum_i A_i\ \alpha^i$

4) methyl-acetate

cis ($\alpha = 0^o$)

($\alpha = 93^o$)

4457 cm^{-1}

1852 cm^{-1}

trans ($\alpha = 180^o$)

$\Delta H^o = 2604$ cm^{-1}
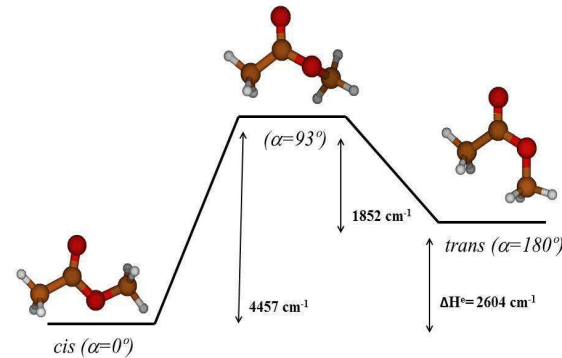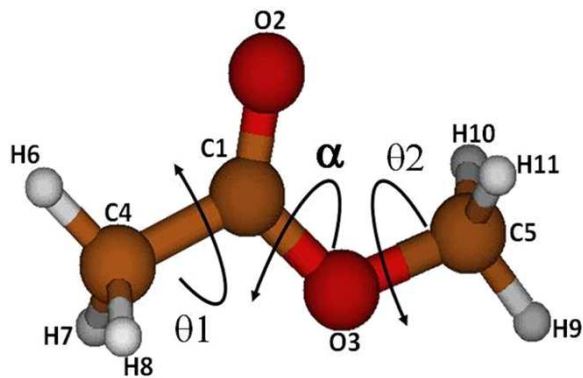
1) 3 internal rotations intertransform 18 inequivalent minima (MSG G$_{18}$)

2) Astrophysical detection: Tercero, Kleiner, Cernicharo, Nguyen, López, & Muñoz Caro, ApJ (2013)

3) Laboratory rotational spectroscopy and assignments in 2D: Tudorie, Kleiner et al. J.Mol.Spectrosc. (2011)

4) 3D ($\rightarrow$ 2D) Ab initio calculations: Senent, Dominguez-Gómez, Carvajal & Kleiner, J.Chem.Phys., 138, 044319 (2013)

4) methyl-acetate

3D-torsional Hamiltonian

$$\mathcal{H}(\alpha, \theta_1, \theta_2) = -\sum_{i=1}^{3} \sum_{j=1}^{3} \frac{\delta}{\delta q_i} B q_i q_j \ (\alpha, \theta_1, \theta_2) \frac{\delta}{\delta q_j} + V(\alpha, \theta_1, \theta_2) + V'(\alpha, \theta_1, \theta_2) + V^{ZPVE}(\alpha, \theta_1, \theta_2)$$

$$q_i, q_j = \alpha, \theta_1, \theta_2$$

3D-Potential energy surface

**148 geometries optimized with CCSD/VTZ; CCSD(T)/VTZ Energies, MP2/VTZ
ZPVE correction:**

$$V(\alpha, \theta_1, \theta_2) = \sum_{N=0}^{9} \sum_{M=0}^{2} \sum_{L=0}^{2} A_{N3M3L} \ \cos(N\alpha) \cos(3M\theta_1) \cos(3L\theta_2) + \sum_{N=0}^{9} A_{N-3-3} \ \cos(N\alpha) \sin(3\theta_1) \sin(3\theta_2)$$

$$+ \sum_{N=1}^{8} \sum_{M=0}^{2} A_{-N3M-3} \ \sin(N\alpha) \cos(3M\theta_1) \sin(3\theta_2) + \sum_{N=1}^{8} \sum_{L=0}^{2} A_{-N-33} \ \sin(N\alpha) \sin(3\theta_1) \cos(3L\theta_2)$$

Hamiltonian matrix size: 5493 (A_1) 5492 (A_2), 10985 (E_1, E_2, E_3, E_4)
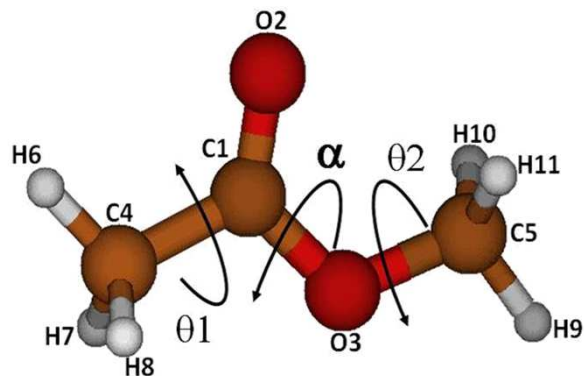
4) methyl-acetate

ZPVE

000	A$_1$	0.00
	E$_1$	1.08
	E$_2$	0.01
	E$_3$	1.09
	E$_4$	1.09

C-CH$_3$ (ν_{27})

010	A$_2$	63.74
	E$_1$	51.93
	E$_2$	63.74
	E$_3$	51.93
	E$_4$	51.93
020	A$_1$	87.35
	E$_1$	113.77
	E$_2$	87.35
	E$_3$	113.77
	E$_4$	113.77

O-CH$_3$ (ν_{26})

001	A$_2$	136.09
	E$_1$	137.98
	E$_2$	135.72
	E$_3$	136.73
	E$_4$	136.73
002	A$_1$	248.0

C-O torsion (ν_{25})

100	A$_2$	175.81
	E$_1$	178.62
	E$_2$	175.75
	E$_3$	178.56
	E$_4$	178.56
200	A$_1$	348.6
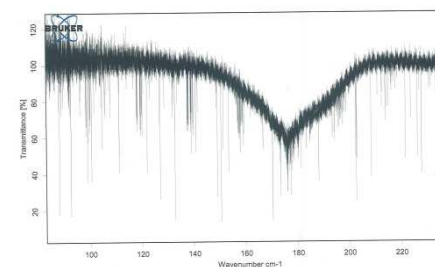
cos $n\theta_1$, cos $m\theta_2$
kinetic parameters 😄👍

(sin $n\theta_1$ sin $m\theta_2$) ? 🤔

2D PES and kinetic parameters

Ab initio CCSD(T)/VTZ
3D→ 2D ($\alpha = 0°$)

Senent, Dominguez-Gómez, Carvajal & Kleiner, J.Chem.Phys., 138, 044319 (2013)

$V(\theta_1,\theta_2)$ = 269.642 **-206.919 cos $3\theta_2$** -13.447 cos $6\theta_2$ **-50.081 cos $3\theta_1$**
+0.707 cos $\theta_1$cos $3\theta_2$ -0.227 cos $3\theta_1$cos $6\theta_2$ +0.548 cos $6\theta_1$ -0.36 cos $6\theta_1$cos $3\theta_2$
+0.112 cos $6\theta_1$cos $6\theta_2$ **-6.489 sin $3\theta_1$sin $3\theta_2$**

$B_{\theta1\theta1}$=5.66 cm^{-1}; $B_{\theta1\theta2}$=0.34 cm^{-1}; $B_{\theta2\theta2}$= 5.64 cm^{-1}

Fitted (effective Hamiltonian)
more than 800 microwave and millimeter-wave transitions
Tudorie, Kleiner, Hougen, Melandri, Sutikdja, & Stahl, J.Mol.Spectrosc. (2011)

$V(\theta_1,\theta_2)$ = 258.418 **-207.548 cos $3\theta_2$ -47.344 cos $3\theta_1$** -3.526 cos $3\theta_1$cos $3\theta_2$
+34.24 sin $3\theta_1$sin $3\theta_2$

$B_{\theta1\theta1}$=5.554669 cm^{-1}; $B_{\theta1\theta2}$=0.332 cm^{-1}; $B_{\theta2\theta2}$= 5.523464 cm^{-1}

4) methyl-acetate

Non-degenerate torsional energy levels (in cm^{-1})			
v v'	Sym.	Ab initio [I]	Fitted [II]
00[a]	A$_1$	0.0	0.0
10	**A$_2$**	**64.9**	**62.6**
20	A$_1$	83.5	83.1
01	**A$_2$**	**141.2**	**133.1**
11	A$_1$	205.4	189.4
30	A$_2$	221.1	205.6
40	A$_1$	223.4	222.5
21	A$_2$	226.2	226.6
ZPVE (a)		107.0	76.0

(I) Senent, Dominguez-Gómez, Carvajal & Kleiner, J.Chem.Phys., 138, 044319 (2013)

(II) Tudorie, Kleiner, Hougen, Melandri, Sutikdja, & Stahl, J.Mol.Spectrosc. (2011)

5. Ethyl-Methyl-Ether
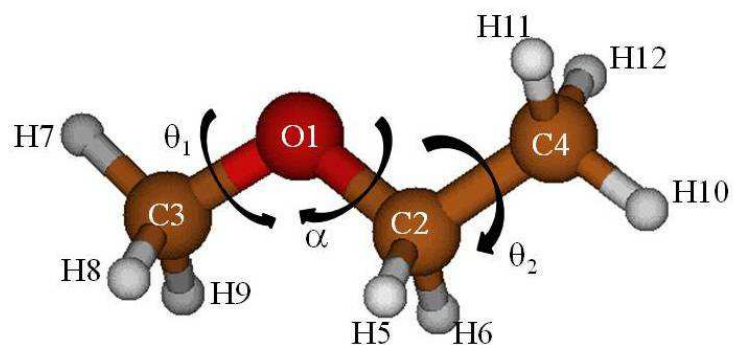
	E	2(456)	2(123)	2(123)(456)	2(123)(465)	9(23)(56)*	$C_3^1 \times C_3^2$
A_1	1	1	1	1	1	1	AA
A_2	1	1	1	1	1	-1	AA
E_1	2	2	-1	-1	-1	0	EA
E_2	2	-1	2	-1	-1	0	AE
E_3	2	-1	-1	2	-1	0	EE
E_4	2	-1	-1	-1	2	0	EE

1) **PES= 27 minima (3 torsions)**

2) **Symmetry= G_{18} and Cs**

3) **Theory:** Senent , Ruiz, Dominguez-Gómez, & Villa, J.Chem.Phys. (2009); Chem.Phys., (2010)
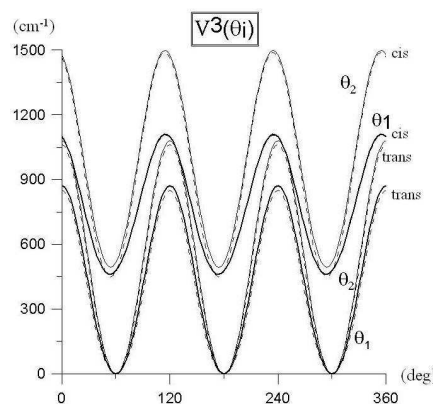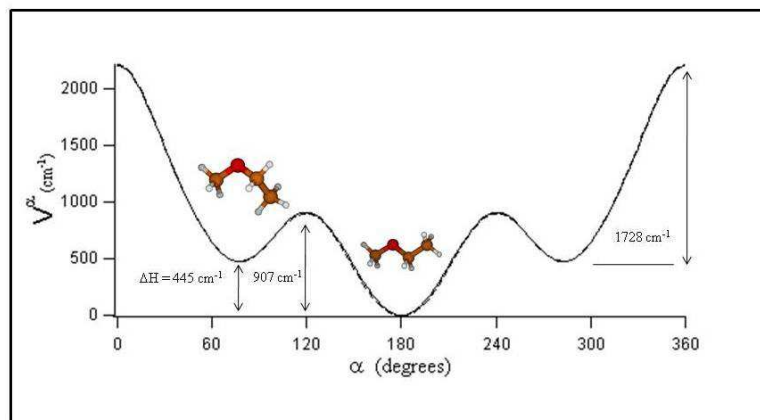
θ_1 (O-CH$_3$)
V$_3$ (trans)=871 cm^{-1}
V$_3$ (trans) =1079 cm^{-1}

θ_2 (C-CH$_3$)
V$_3$ (gauche)=639 cm^{-1}
V$_3$ (gauche) =996 cm^{-1}

5. Ethyl-Methyl-Ether
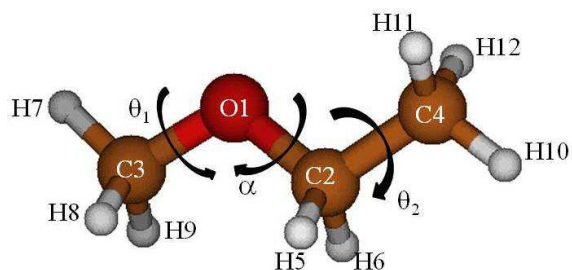
FIR and RAMAN, Durig et al., Struct.Chem., (2002)

ROTATIONAL SPECTROSCOPY

The MW in the ground state

Fuchs et al., ApJ (2002)

Tsunekawa et al., Molecules (2003)

The MW in the first skeletal torsionally excited state ($v_{30}=1$)

Kobayashi et al., *J*.Mol.Spectrosc. (2008)

Analysis of the pure-rotational spectrum in the $v_{28}=1$ excited torsional state

Kobayashi, et al. J.Mol.Spectrosc. (2011)

The MW in the $v_{29}=1$ excited torsional state

Kobayashi, et al. J.Mol.Spectrosc. (2009)

Reanalysis of the ground and three torsional excited states

Kobayashi et al., J.Mol. Spectrosc. (2016)

5. Ethyl-Methyl-Ether

Ab initio
CCCSD(T)/CCSD/VTZ+ZPVE
300 geometries

CCSD(T) band positions (in cm^{-1}) and intensities of *trans*-EME

Assign.	Symm.	ν	Intensity (273°K)	exp ν (intens)	Assign.	Symm.	ν	Intensity (273°K)	exp ν (intens)
					Skeletal torsion				
000→100	$A_1 \to A_2$	115.3	$0.41\ 10^{-4}$	115.40 (vs)	300→400	$A_2 \to A_1$	101.6	$0.34\ 10^{-4}$	103.54
	$E_1 \to E_1$	115.3	$0.81\ 10^{-4}$			$E_1 \to E_1$	101.6	$0.68\ 10^{-4}$	
	$E_2 \to E_2$	115.3	$0.81\ 10^{-4}$			$E_2 \to E_2$	101.7	$0.68\ 10^{-4}$	
	$E_3 \to E_3$	115.3	$0.41\ 10^{-4}$			$E_3 \to E_3$	102.1	$0.34\ 10^{-4}$	
	$E_4 \to E_4$	115.3	$0.41\ 10^{-4}$			$E_4 \to E_4$	102.1	$0.34\ 10^{-4}$	
100→200	$A_2 \to A_1$	110.9	$0.48\ 10^{-4}$	111.77	400→500	$A_1 \to A_2$	96.4	$0.27\ 10^{-4}$	99.0
	$E_1 \to E_1$	111.1	$0.96\ 10^{-4}$			$E_1 \to E_1$	96.4	$0.34\ 10^{-4}$	
	$E_2 \to E_2$	111.1	$0.96\ 10^{-4}$			$E_2 \to E_2$	96.4	$0.34\ 10^{-4}$	
	$E_3 \to E_3$	111.1	$0.48\ 10^{-4}$			$E_3 \to E_3$	96.4	$0.27\ 10^{-4}$	
	$E_4 \to E_4$	111.1	$0.48\ 10^{-4}$			$E_4 \to E_4$	96.4	$0.27\ 10^{-4}$	
200→300	$A_1 \to A_2$	106.4	$0.42\ 10^{-4}$	107.80					
	$E_1 \to E_1$	106.4	$0.84\ 10^{-4}$						
	$E_2 \to E_2$	106.5	$0.84\ 10^{-4}$						
	$E_3 \to E_3$	106.1	$0.42\ 10^{-4}$						
	$E_4 \to E_4$	106.1	$0.42\ 10^{-4}$						
				Methyl torsions					
000→010	$A_1 \to A_2$	206.6	$0.31\ 10^{-4}$	202 (m)	000→001	$A_1 \to A_2$	255.2	$0.24\ 10^{-5}$	248 (m)
	$E_1 \to E_1$	206.6	$0.61\ 10^{-4}$			$E_1 \to E_1$	255.2	$0.47\ 10^{-5}$	
	$E_2 \to E_2$	206.6	$0.61\ 10^{-4}$			$E_2 \to E_2$	255.2	$0.47\ 10^{-5}$	
	$E_3 \to E_3$	206.6	$0.31\ 10^{-4}$			$E_3 \to E_3$	255.2	$0.24\ 10^{-5}$	
	$E_4 \to E_4$	206.6	$0.31\ 10^{-4}$			$E_4 \to E_4$	255.2	$0.24\ 10^{-5}$	
010→020	$A_2 \to A_1$	195.2	$0.19\ 10^{-4}$		001→002	$A_2 \to A_1$	242.3	$0.19\ 10^{-5}$	
	$E_1 \to E_1$	195.2	$0.19\ 10^{-4}$			$E_1 \to E_1$	242.3	$0.38\ 10^{-5}$	
	$E_2 \to E_2$	195.5	$0.38\ 10^{-4}$			$E_2 \to E_2$	242.3	$0.38\ 10^{-5}$	
	$E_3 \to E_3$	195.5	$0.38\ 10^{-4}$			$E_3 \to E_3$	242.3	$0.19\ 10^{-5}$	
	$E_4 \to E_4$	195.5	$0.19\ 10^{-4}$			$E_4 \to E_4$	242.3	$0.19\ 10^{-5}$	
020→030	$A_1 \to A_2$	179.3	$0.90\ 10^{-5}$		002→003	$A_1 \to A_2$	230.0	$< 10^{-5}$	
	$E_1 \to E_1$	179.3	$0.18\ 10^{-4}$			$E_1 \to E_1$	230.0	$< 10^{-5}$	
	$E_2 \to E_2$	179.4	$0.18\ 10^{-4}$			$E_2 \to E_2$	230.1	$< 10^{-5}$	
	$E_3 \to E_3$	179.4	$0.90\ 10^{-5}$			$E_3 \to E_3$	230.1	$< 10^{-5}$	
	$E_4 \to E_4$	179.4	$0.90\ 10^{-5}$			$E_4 \to E_4$	230.1	$< 10^{-5}$	
				Combination bands					
100→110	$A_2 \to A_1$	206.0	$0.15\ 10^{-4}$		210→310	$A_2 \to A_1$	106.1	$0.15\ 10^{-4}$	
010→110	$A_2 \to A_1$	114.7	$0.14\ 10^{-4}$		101→201	$A_1 \to A_2$	110.1	$0.15\ 10^{-4}$	
001→101	$A_2 \to A_1$	114.0	$0.11\ 10^{-4}$		201→301	$A_2 \to A_1$	105.8	$0.11\ 10^{-4}$	
110→210	$A_1 \to A_2$	116.0	$0.16\ 10^{-4}$		001→011	$A_2 \to A_1$	190.9	$0.65\ 10^{-5}$	

Fundamental frequencies in cm^{-1} (intensities)

We suggest a new assignment for $CH_3\text{-}O\text{-}CH_2\text{-}CH_3$

Exp. (Durig et al. 2002) OLD assign (Durig et al 2002) NEW assign (this paper)	$CH_3\text{-}O\text{-}CH_2\text{-}CH_3$							
	CCSD(T)	Exp (OLD)		Δ				
trans-EME								
ν_{28} (*C-CH$_3$-torsion*)	255.2	278						
ν_{29} (*O-CH$_3$-torsion*)	206.5	248						
ν_{30} (*O- C$_2$H$_5$-torsion*)	115.3	115.4						
cis-gauche-EME								
ν_{28} (*C-CH$_3$-torsion*)	243.8 243.8							
ν_{29} (*O-CH$_3$-torsion*)	192.5 192.5	202						
ν_{30} (*O- C$_2$H$_5$-torsion*)	91.0 91.0	93.56						

Exp: FIR and RAMAN, Durig et al., Struct.Chem., (2002)

Fundamental frequencies in cm^{-1} (intensities)

We suggest a new assignment for $CH_3-O-CH_2-CH_3$

Exp. (Durig et al. 2002) OLD assign (Durig et al 2002) NEW assign (this paper)	$CH_3-O-CH_2-CH_3$							
	CCSD(T)	Exp (OLD)	Exp (NEW)	Δ				
trans-EME								
ν_{28} (*C-CH$_3$-torsion*)	255.2	278	248	7.2				
ν_{29} (*O-CH$_3$-torsion*)	206.5	248	202	4.5				
ν_{30} (*O- C$_2$H$_5$-torsion*)	115.3	115.4	115.4	-0.1				
cis-gauche-EME								
ν_{28} (*C-CH$_3$-torsion*)	243.8 243.8							
ν_{29} (*O-CH$_3$-torsion*)	192.5 192.5	202						
ν_{30} (*O- C$_2$H$_5$-torsion*)	91.0 91.0	93.56	93.56	-2.6				

Exp: FIR and RAMAN, Durig et al., Struct.Chem., (2002)

Exp. (Durig et al. 2002) OLD assign (Durig et al 2002) NEW assign (this paper)	CH_3-O-CH_2-CH_3							
	CCSD(T)	Exp (OLD)	Exp (NEW)	Δ				
trans-EME								
ν_{28} (*C-CH$_3$-torsion*)	255.2	278	248 (m)	7.2				
ν_{29} (*O-CH$_3$-torsion*)	206.5	248 (m)	202 (m)	4.5				
ν_{30} (*O- C$_2$H$_5$-torsion*)	115.3	115.4 (vs)	115.4 (vs)	-0.1				
cis-gauche-EME								
ν_{28} (*C-CH$_3$-torsion*)	243.8 243.8							
ν_{29} (*O-CH$_3$-torsion*)	192.5 192.5	202 (m)						
ν_{30} (*O- C$_2$H$_5$-torsion*)	91.0 91.0	93.56 (m)	93.56 (m)	-2.6				

Fundamental frequencies in cm^{-1} (intensities)

We suggest a new assignment for CH$_3$-O-CH$_2$-CH$_3$

Exp: FIR and RAMAN, Durig et al., Struct.Chem., (2002)

Fundamental frequencies in cm^{-1} (intensities)

We suggest a new assignment for CH_3-O-CH_2-CH_3

| Exp. (Durig et al. 2002) OLD assign (Durig et al 2002) NEW assign (this paper)	CH_3-O-CH_2-CH_3				CD_3-O-CH_2-CH_3			
	CCSD(T)	Exp (OLD)	Exp (NEW)	Δ	CCSD(T)	Exp (OLD)	Exp (NEW)	Δ
trans-EME								
ν_{28} (C-CH_3-torsion)	255.2	278	248 (m)	7.2	249.0	241	241	8.0
ν_{29} (O-CH_3-torsion)	206.5	248 (m)	202 (m)	4.5	166.6	163	163	3.6
ν_{30} (O-C_2H_5-torsion)	115.3	115.4 (vs)	115.4 (vs)	-0.1	106.2	106	106	0.2
cis-gauche-EME								
ν_{28} (C-CH_3-torsion)	243.8 243.8							
ν_{29} (O-CH_3-torsion)	192.5 192.5	202 (m)						
ν_{30} (O-C_2H_5-torsion)	91.0 91.0	93.56 (m)	93.56 (m)	-2.6				

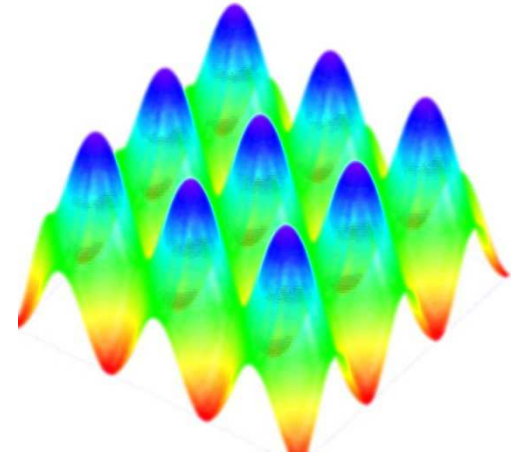**Exp: FIR and RAMAN,** Durig et al., Struct.Chem., (2002)

6-dimethyl-ether

2-torsional modes

$\theta_1 - \theta_2$ **IR active**

ν_{15}
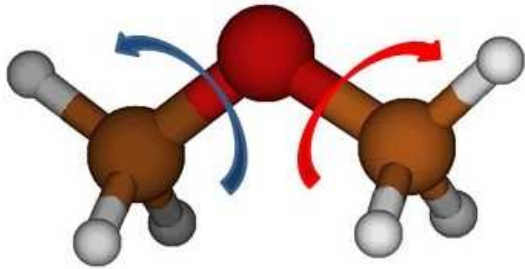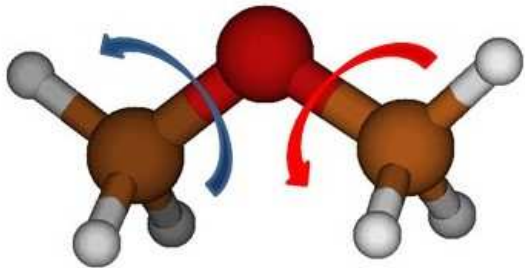
$\theta_1 + \theta_2$ **dark**

ν_{11}

42 years of DME (1977-2019)

Groner & Durig, J. Chem. Phys. (1977) 2D
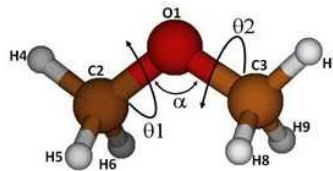
Our old ab initio calculations (Senent et al. 1995)

The COC bending angle varies to minimize the non-bonding interactions between H atoms

First ab initio studies: 2D or 3D ?
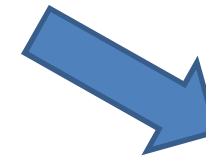
2D (Can.J.Phys. 1995)

3D (J.Chem.Phys. 1995)

$$\mathcal{H}(\theta_1, \theta_2) = -\sum_{i=1}^{2}\sum_{j=1}^{2} \frac{\delta}{\delta i} B_{\theta_1,\theta_2}(\theta_1,\theta_2)\frac{\delta}{\delta j} + V^{MP4}(\theta_1,\theta_2)$$

$$\mathcal{H}(\alpha, \theta_1, \theta_2) = -\sum_{i=1}^{3}\sum_{j=1}^{3} \frac{\delta}{\delta i} B_{\alpha,\theta_1,\theta_2}(\alpha,\theta_1,\theta_2)\frac{\delta}{\delta j} + V^{MP4}(\alpha,\theta_1,\theta_2)$$

Fermi displacements of the CH_3 overtones

Our recent ab initio calculations (2011-2014)...............................3D
1) M.Villa et al. J.Phys.Chem.A (2011) **(main isotopologue)**
2) M.L.Senent et al. J.Phys.Chem.A. (2012) **(DME-d$_6$ and DME-d$_3$)**
3) M. Carvajal et al. J.Mol.Spectrosc. (2012) **(^{13}DME)**
4) M.Carvajal et al. Chem.Phys.Lett. (2014) **(DME-d1)**

New measurements and assignments based on ab initio calculations (ApJS-2019)

NEW 3D studies (motivated by the astrophysical interest of isotopologues)

↑↑↑ level of theory (Objective: 🕊 accuracy)

1995	**2010-2011**
MP4/MP2/6-31G(d,p) 28 geometries (approx. definition of the torsional coordinates) No ZPVE	CCSD(T)/CCSD/AVTZ 126 geometries (proper. definition of the torsional coordinates) + ZPVE correction

1995

$$\mathcal{H}(\alpha, \theta_1, \theta_2) = -\sum_{i=1}^{3}\sum_{j=1}^{3} \frac{\delta}{\delta i} B_{\alpha,\theta_1,\theta_2}(\alpha, \theta_1, \theta_2) \frac{\delta}{\delta j} + V^{MP2}(\alpha, \theta_1, \theta_2)$$

2010-2011

$$\mathcal{H}(\alpha, \theta_1, \theta_2) = -\sum_{i=1}^{3}\sum_{j=1}^{3} \frac{\delta}{\delta i} B_{\alpha,\theta_1,\theta_2}(\alpha, \theta_1, \theta_2) \frac{\delta}{\delta j} + V^{CCSD(T)}(\alpha, \theta_1, \theta_2) + V'_{CCSD(T)}(\alpha, \theta_1, \theta_2) + V^{ZPVE}_{MP2}(\alpha, \theta_1, \theta_2)$$

Mass dependent   **Ab initio**   **Mass dependent**   **Mass dependent**

New Values (CCSD(T)/AVTZ))
Main isotopologue

		3D MP4	3D CCSD(T)	Fitted	Exp. Groner et al. 1977
		IR			
$A_1 \rightarrow A_2$	ν_{15}	241.2	244.7	241.8	241.0
$A_1 \rightarrow A_2$	$2\nu_{15} \leftarrow \nu_{15}$	239.6	242.4	239.1	240.2
$A_1 \rightarrow A_2$	$3\nu_{15} \leftarrow 2\nu_{15}$	237.6	241.1	237.0	238.9
		Raman			
$A_1 \rightarrow A_1$	$2\nu_{15}$	481.2	487.3↑	480.9 ↓	481.2
$A_1 \rightarrow A_1$	$2\nu_{11}$	393.2	388.4↓	391.1 ↓	395.5
		COC bending			
$A_1 \rightarrow A_1$	ν_{15}	429.4	421.6	412.1	412.0

Fitting procedure: refinement of the:
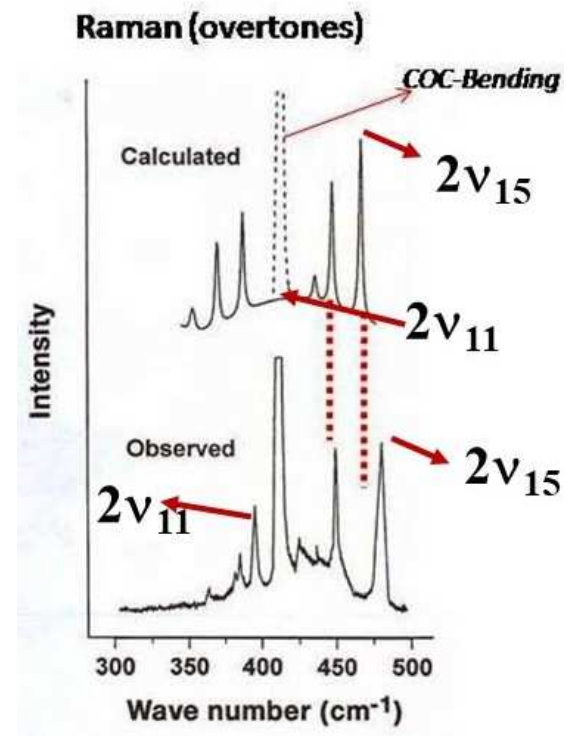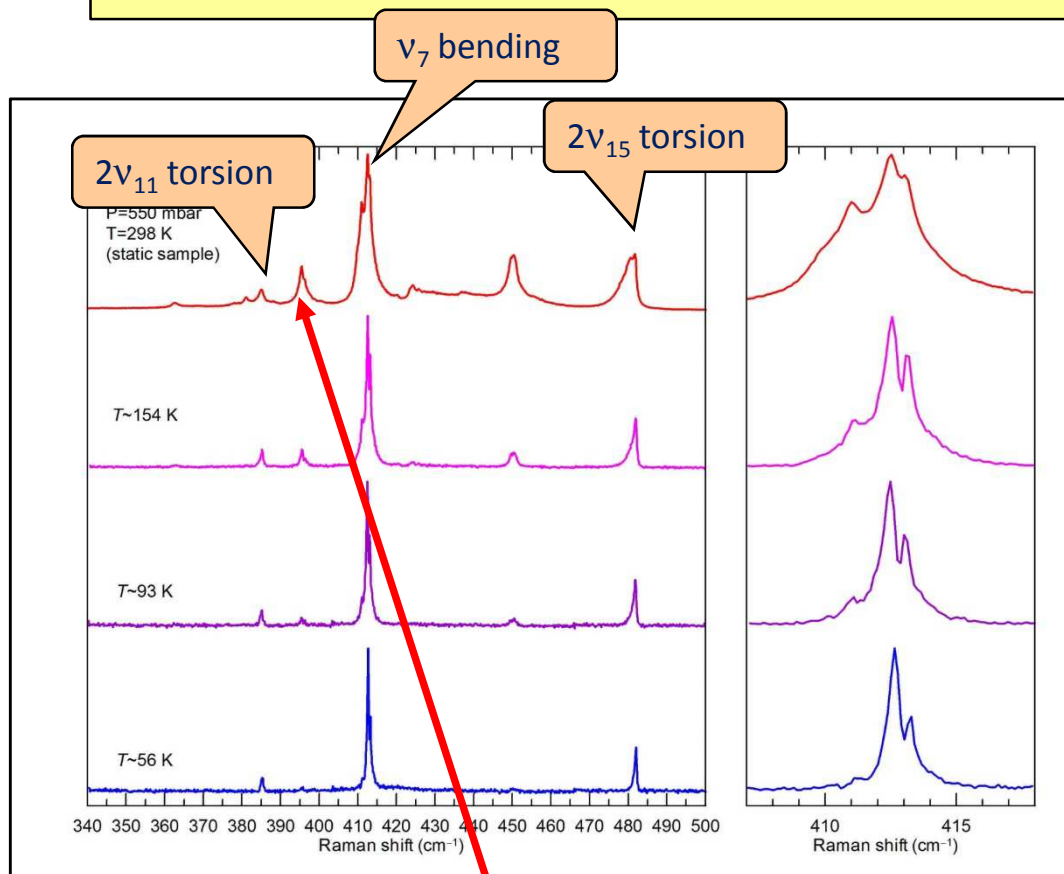
a) The α bending coordinate $\quad \alpha' = \alpha\,(1 + F/100)$

b) The parameters of the $B_{\alpha\alpha}$ kinetic expanssion

$$\text{Accuracy} = \frac{1}{\text{level of theory}}$$

DME. Torsional overtones (Raman)

DME. Torsional overtones (Raman)

ν_7 bending

$2\nu_{15}$ torsion

$2\nu_{11}$ torsion

P=550 mbar
T=298 K
(static sample)

T~154 K

T~93 K

T~56 K

340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500
Raman shift (cm^{-1})

410   415
Raman shift (cm^{-1})

Raman (overtones)

COC-Bending

Calculated

$2\nu_{15}$

$2\nu_{11}$

Observed

$2\nu_{11}$

$2\nu_{15}$

Intensity

300   350   400   450   500
Wave number (cm^{-1})
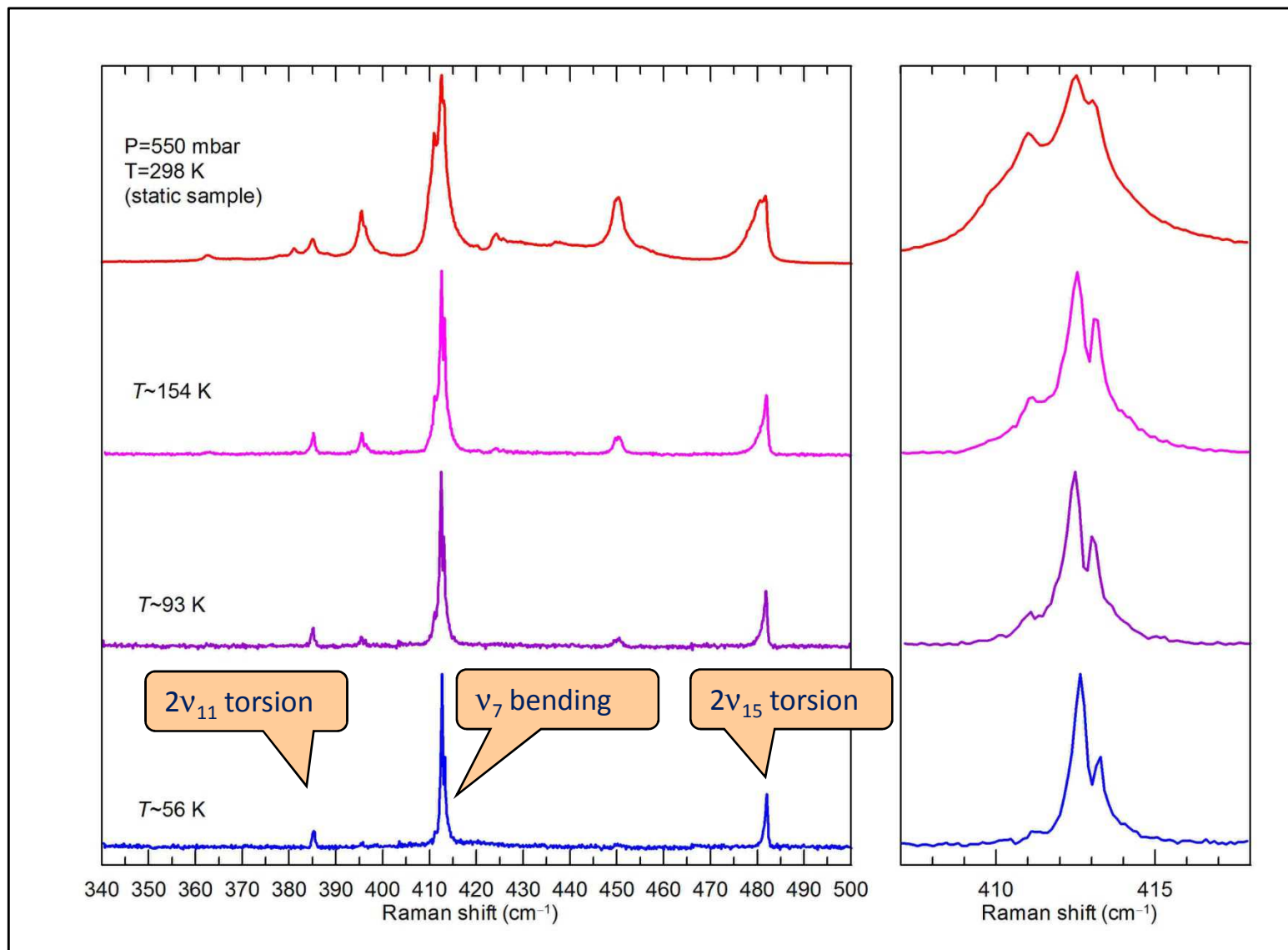
Firts Assignment (1977) of $2\nu_{11}$ (395.5 cm^{-1}) It is a hot band ¡¡¡¡

New Assignment (2019) of $2\nu_{11}$ (385.2 cm^{-1})

	Groner Durig 1977	3D MP4	3D CCSD(T)	FIT 2011	New FIT 2019	New Raman 2019
IR						
ν_{15}	241.0	241.2	244.7	241.8	242.6	
$2\nu_{15} \leftarrow \nu_{15}$	240.2	239.6	242.4	239.1	239.3	
$3\nu_{15} \leftarrow 2\nu_{15}$	238.9	237.6	241.1	237.0	236.0	
RAMAN						
$2\nu_{15}$	481.2	481.2	487.3↑	480.9	481.9	482.0±0.2
$2\nu_{11}$	395.5	393.2	388.4↑	391.1	386.5	385.2±0.2
COC bending						
ν_7	412.0	429.4	421.6 ↑	412.1	413.0	412.5±0.2

Fernández-Tejeda-Carvajal-Senent, ApJS (2019)

7- Ethylene glycol
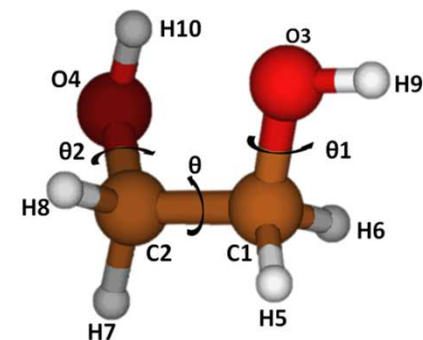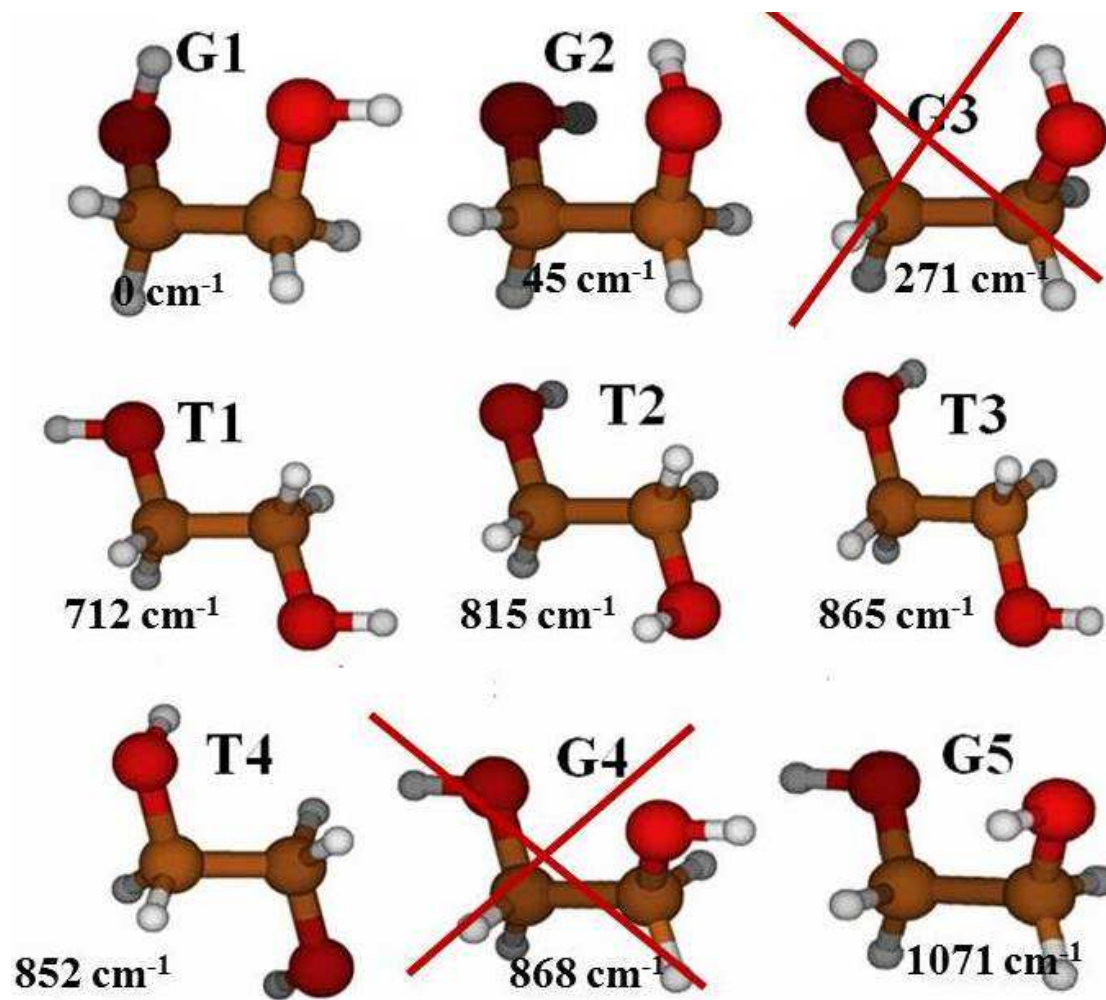
$$V^{Gauche \rightarrow Trans} \sim 1800 \text{ cm}^{-1}$$
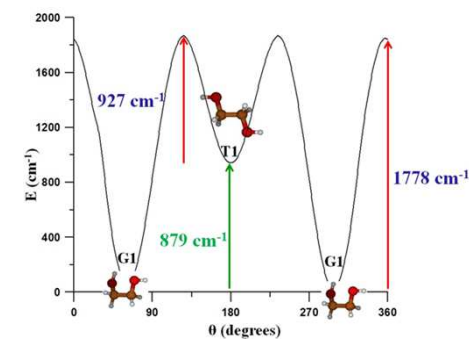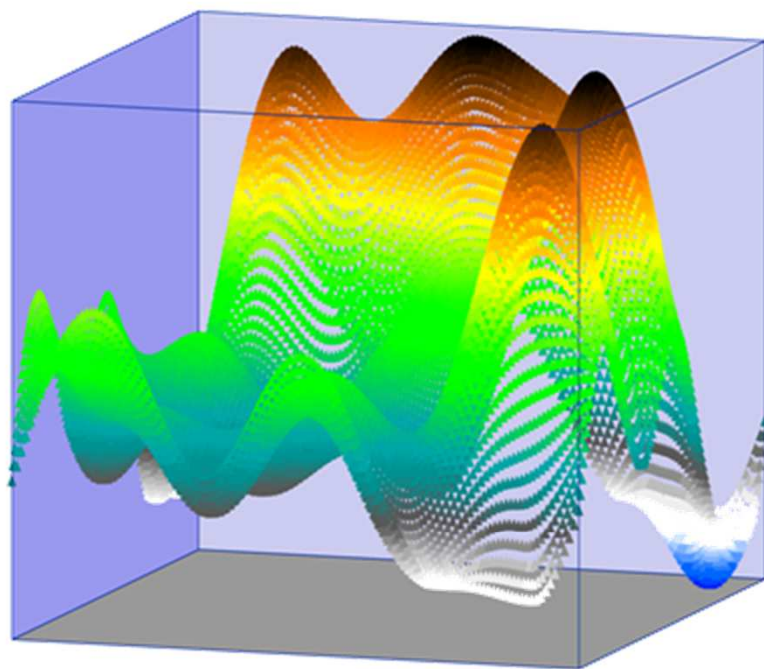
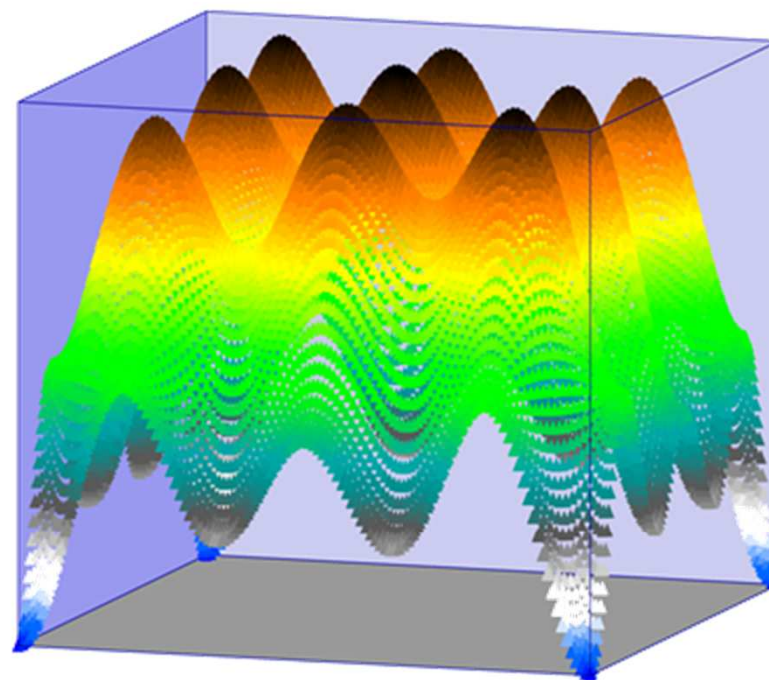**CCSD(T)-F12/AVTZ + ZPVE(MP2/AVTZ)**

Potential energy surface (3D-PES)

- The molecule can be considered a triple rotor system where intramolecular hydrogen bonds govern the relative stabilities of the favoured conformers and their internal dynamics.

- Their intertransformation processes imply the breaking of weak bonds and can occur through more or less relatively high energy barriers which can cause relevant tunnelling effects.

- The main part of the conformers corresponds to double minima.

- Moreover, the C-C bond internal rotation varies de relative orientation of two identical CH_2OH groups. To classify the rovibrational energy levels and their splittings, a double Molecular Symmetry Group (MSG) is required

- Accordingly, all this features produce a potential energy surface (PES) of 50 minima very anisotropic in the *gauche* region and very isotropic in the *trans* region.

7- Ethylene glycol

gauche

trans

7- Ethylene glycol

$$H(2\alpha, \theta_1, \theta_2) = -\sum_{i=1}^{3}\sum_{j=1}^{3}\left(\frac{\partial}{\partial q_i}\right) B_{q_i q_j}(2\alpha, \theta_1, \theta_2)\left(\frac{\partial}{\partial q_j}\right)$$

$$+ V^{eff}(2\alpha, \theta_1, \theta_2)$$

$$V^{eff}(2\alpha, \theta_1, \theta_2) = V(2\alpha, \theta_1, \theta_2) + V'(2\alpha, \theta_1, \theta_2) + V^{ZPVE}(2\alpha, \theta_1, \theta_2)$$

The 3D-PES (see Figure 3) was constructed using a set of 322 energies calculated with CCSD(T)-F12/AVTZ-F12

Grid : $\Delta\theta_1$, $\Delta\theta_2$ = 45, 135, ...
$\Delta\theta$=45, 135, .., in the trans region, and $\Delta\theta$=22.5, 45, 67.5, in the anisotropic gauche region.

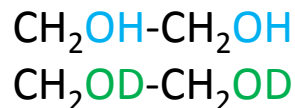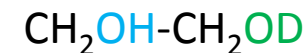# Trial function and Assignment of the calculated energy levels ?????

1-Symmetry:

CH_2OH-CH_2OH
CH_2OD-CH_2OD

TABLE 7: G_8 torsional symmetry eigenvectors				
A_1	J=2M	$\cos J\alpha \,(\cos N\theta_1 \cos L\theta_2 + \cos L\theta_1 \cos N\theta_2)$	N=0,1,2,..	L$\leq$N
		$\cos J\alpha \,(\sin N\theta_1 \sin L\theta_2 + \sin L\theta_1 \sin N\theta_2)$	N=0,1,2,..	L$\leq$N
A_{1d}	J=2M+1	$\sin J\alpha \,(\sin N\theta_1 \cos L\theta_2 + \cos L\theta_1 \sin N\theta_2)$	N=1,2,..	L$\leq$N
		$\sin J\alpha \,(\cos N\theta_1 \sin L\theta_2 + \sin L\theta_1 \cos N\theta_2)$	N=1,2,..	L$<$N
A_2	J=2M	$\cos J\alpha \,(\sin N\theta_1 \cos L\theta_2 - \cos L\theta_1 \sin N\theta_2)$	N=0,1,2,..	L$\leq$N
		$\cos J\alpha \,(\cos N\theta_1 \sin L\theta_2 - \sin L\theta_1 \cos N\theta_2)$	N=0,1,2,..	L$<$N
A_{2d}	J=2M+1	$\sin J\alpha \,(\cos N\theta_1 \cos L\theta_2 - \cos L\theta_1 \cos N\theta_2)$	N=1,2,..	L$<$N
		$\sin J\alpha \,(\sin N\theta_1 \sin L\theta_2 - \sin L\theta_1 \sin N\theta_2)$	N=1,2,..	L$<$N
A_3	J=2M	$\cos J\alpha \,(\sin N\theta_1 \cos L\theta_2 + \cos L\theta_1 \sin N\theta_2)$	N=0,1,2,..	L$\leq$N
		$\cos J\alpha \,(\cos N\theta_1 \sin L\theta_2 + \sin L\theta_1 \cos N\theta_2)$	N=0,1,2,..	L$<$N
A_{3d}	J=2M+1	$\sin J\alpha \,(\cos N\theta_1 \cos L\theta_2 + \cos L\theta_1 \cos N\theta_2)$	N=1,2,..	L$\leq$N
		$\sin J\alpha \,(\sin N\theta_1 \sin L\theta_2 + \sin L\theta_1 \sin N\theta_2)$	N=1,2,..	L$<$N
A_4	J=2M	$\cos J\alpha \,(\cos N\theta_1 \cos L\theta_2 - \cos L\theta_1 \cos N\theta_2)$	N=0,1,2,..	L$<$N
		$\cos J\alpha \,(\sin N\theta_1 \sin L\theta_2 - \sin L\theta_1 \sin N\theta_2)$	N=0,1,2,..	L$<$N
A_{4d}	J=2M+1	$\sin J\alpha \,(\sin N\theta_1 \cos L\theta_2 - \cos L\theta_1 \sin N\theta_2)$	N=1,2,..	L$\leq$N
		$\sin J\alpha \,(\cos N\theta_1 \sin L\theta_2 - \sin L\theta_1 \cos N\theta_2)$	N=1,2,..	L$<$N

CH_2OH-CH_2OD

ONLY:
2 Representations
A1 and A2 ¡¡¡¡¡

Hamitonian matrix dimension (98865 x 98865)

2-Contrated basis functions: (convergence ←13 contrated functions)

$$\varphi_{vNL}(2\alpha,\theta_1,\theta_2) = \sum_M \varphi_M(2M\alpha)\,[\varphi_N(N\theta_1)\varphi_L(L\theta_2) \pm \varphi_L(L\theta_1)\varphi_N(N\theta_2)]$$

Reduction of the Hamitonian matrix dimension (19773 x 19773 ← 98865 x 98865)

3-Probability integrals and expectation values of one-dimensional Hamiltonians

4-Transition dipol moments ← Intensities

Matrix elements

$$\langle \varphi_{M(2\alpha)}\ \phi_{N(\theta1,\theta2)}\ |H\ |\ \varphi_{M'(2\alpha)}\ \phi_{N'(\theta1,\theta2)}\ \rangle$$

M=1 M'=1 L=0	L=1	L=2	L=3	L=4	L=5
	M=2 M'=2 L=0	L=1	L=2	L=3	L=4
		M=3 M'=3 L=0	L=1	L=2	L=3
			M=4 M'=4 L=0	L=1	L=2
				M=5 M'=5 L=0	L=1
					M=6 M'=6 L=0

L=|M-M'| CH$_2$OH-CH$_2$OH

	L=0	L=1	L=2	L=3	L=4
A1 A2 A2-A1	276.2692 276.5530 0.2838	263.7798 264.1072 0.3274	263.9834 264.3094 0.3260	263.9503 264.2764 0.3261	263.9478 264.2739 0.3261
A1 A2	425.0072 425.3583	406.1971 406.3802	405.7074 405.8813	405.6230 405.7963	405.6256 405.7989
A1 A2	444.0069 457.1958	431.5899 440.2541	431.6899 441.0730	431.6407 440.9607	431.6401 440.9468
A1 A2	468.6974 469.0040	440.6974 446.7797	440.9601 446.3267	440.8618 446.2944	440.8463 446.2963
A1 A2	537.9298 589.7966	526.8428 5772747	526.3336 576.8800	526.2930 576.8170	526.2936 576.8204

…etc (convergence ←13 contrated functions)

(CC, OH, OH)		CH_2OH-CH_2OH	CH_2OD-CH_2OD	CH_2OH-CH_2OD
0 0 0	A1	0.000	0.000	0.000
	A2	0.326 (exp=0.2)	0.712	5.089
	A1	141.678	138.393	129.991
	A2	141.851	137.482	139.503
0 1 0	A1	167.692	139.961	150.903
	A2	182.345	142.026	162.695
	A1	262.346	228.633	283.673
	A2	312.873	247.071	300.090
1 0 0	A1	176.899	172.801	171.172
	A2	176.999	175.020	179.029
	A1	324.184	308.578	309.520
	A2	325.928	303.022	321.136

16 components
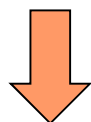
J=0

~200 vibrational levels
below 500 cm^{-1}

7- Ethylene glycol