Weak Intramolecular Interaction Effects on the Structure and The Torsional Spectra of Ethylene Glycol, an Astrophysical Species.

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ETHYLENE GLYCOL

a relevant astrophysical species

EG is an organic compound primarily used as antifreeze. it is an odorless, colorless, and sweet-tasting liquid which melting and boiling points at -12.9º C and 197.3 ºC, respectively.

EG appears (together with glycolaldehyde and ethanol) as a key species in the comparison of interstellar and cometary ices.

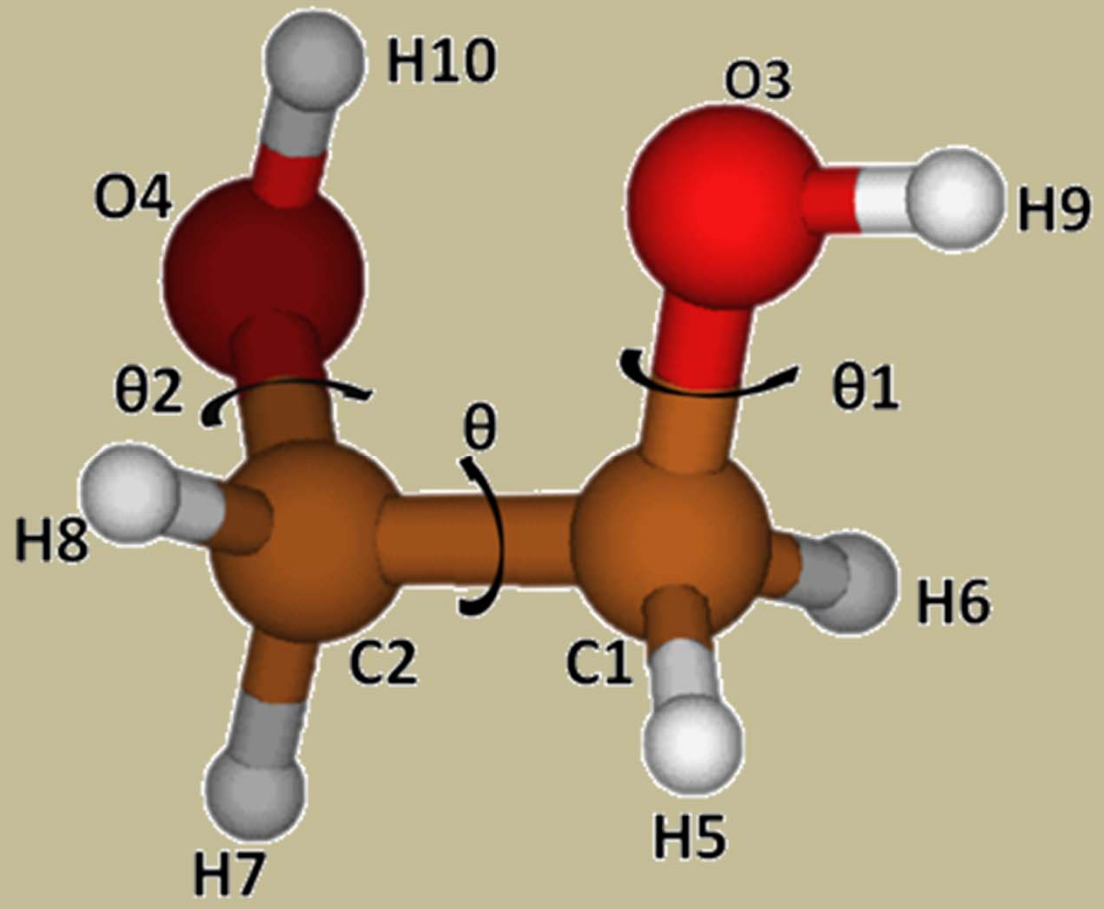
EG was identified in the Murchison and Murray meteorites and very recently, in ices in the hot core of Orion.

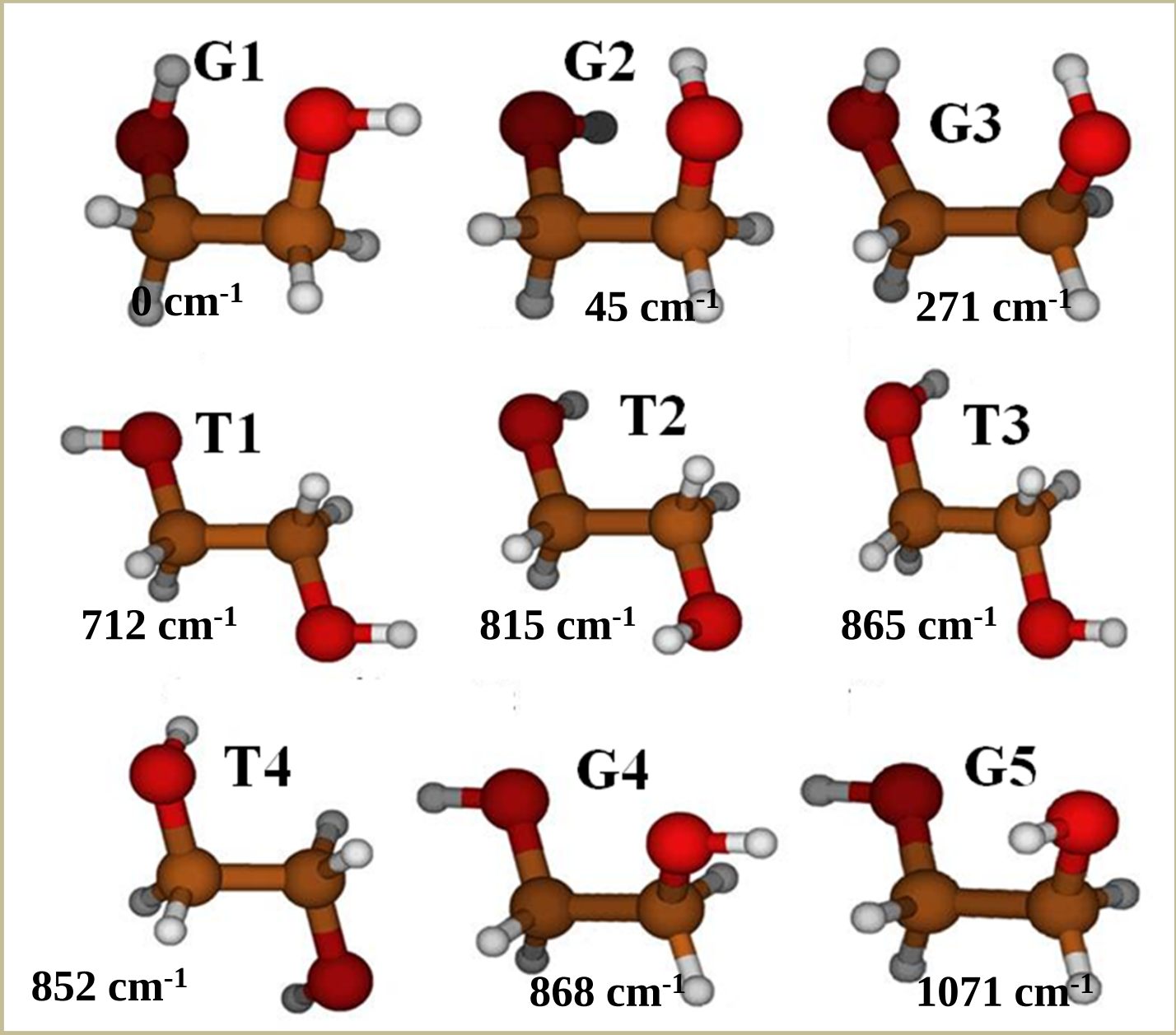
In 2002, EG was detected in emission toward the galactic center source Sagittarius B2(N-LMH) by means of several millimeter-wave rotational torsional transitions of its lowest energy conformer

it is assumed to be low abundant in gas phase interstellar sources.

[1] G. Cooper et al. *Nature*, **414**, 879 (2001).
[2] N. Brouillet et al. , *Astron.Astrophys*., **576**, A129 (2015).
[3] J. M. Hollis et al., *Astrophys.J*, **571**, 59 (2002)

ETHYLENE GLYCOL





E_r+**ZPVE** = E_r (CCSD(T)-F12/AVTZ//MP2/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.

FULL DIMENSIONAL ANHARMONIC ANALYSIS (VPT2)

(mandatory for a full structural characterization)

a) Torsional modes

Torsional modes	G1 tG^+g^-		G2 $g^+G^+g^-$		G3 $g^-G^+g^-$		T1 tTt		T2 g^+Tg^-		T3 tTg^+		T4 g^+Tg^+		G4 tG^+t		G5 tG^+g^+	
	ω	υ	ω	υ	ω	υ	ω	υ	ω	υ	ω	υ	ω	υ	ω	υ	ω	υ
OH	422	**380**	455	**380**	423	**355**	230	**203**	266	**219**	365	**321**	304	**210**	168	**30**	225	**189**
OH	248	**214**	290	**238**	91	-	216	**176**	249	**210**	172	**159**	249	**252**	90	-	239	**185**
C-C	170	**161**	169	**154**	159	**155**	116	**122**	141	**141**	99	**90**	145	**143**	148	**95**	133	**115**

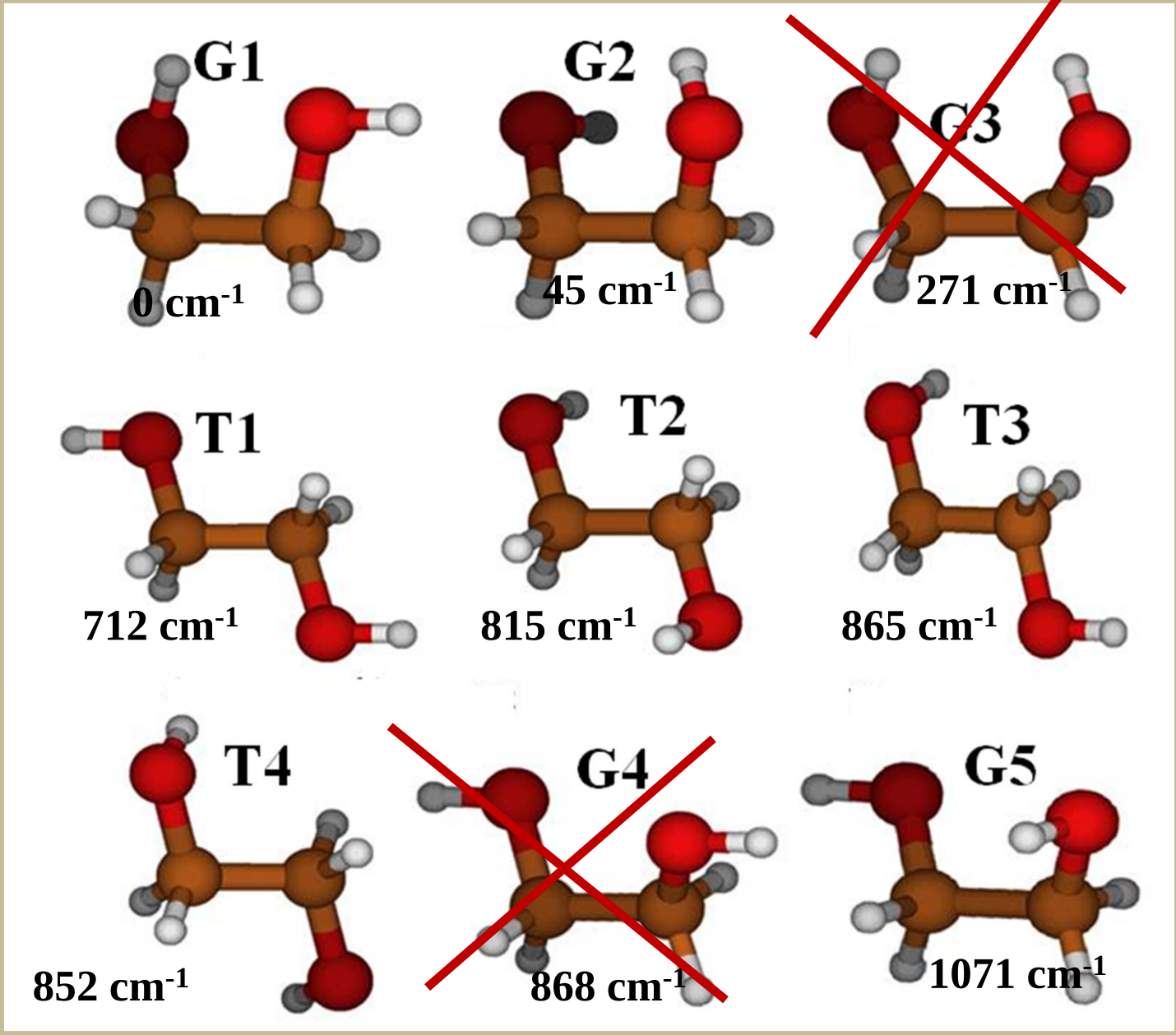
The stability of $g^-G^+g^-$ (G3) and tG^+t (G4) is questionable on the basis of the anharmonic full-dimensional analysis. **The PES shows ONLY 42 MINIMA instead of 50.**

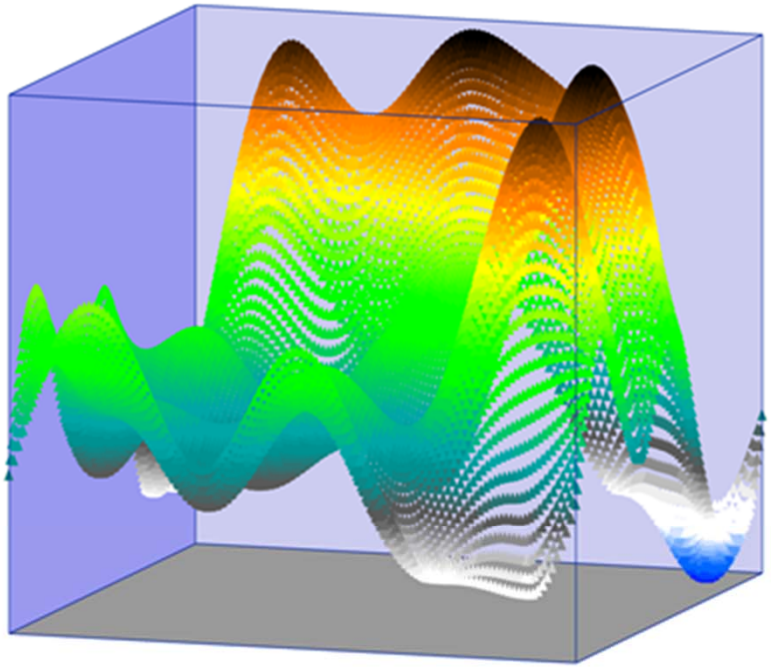
b) **OH stretching**

G1 tG^+g^-	G2 $g^+G^+g^-$	G3 $g^-G^+g^-$	T1 tTt	T2 g^+Tg^-	T3 tTg^+	T4 g^+Tg^+	G4 tG^+t	G5 tG^+g^+
3680	3655	3667	3683	3664	3847	3662	3695	3677
3628	3615	3667	3683	3663	3846	3661	3695	3661

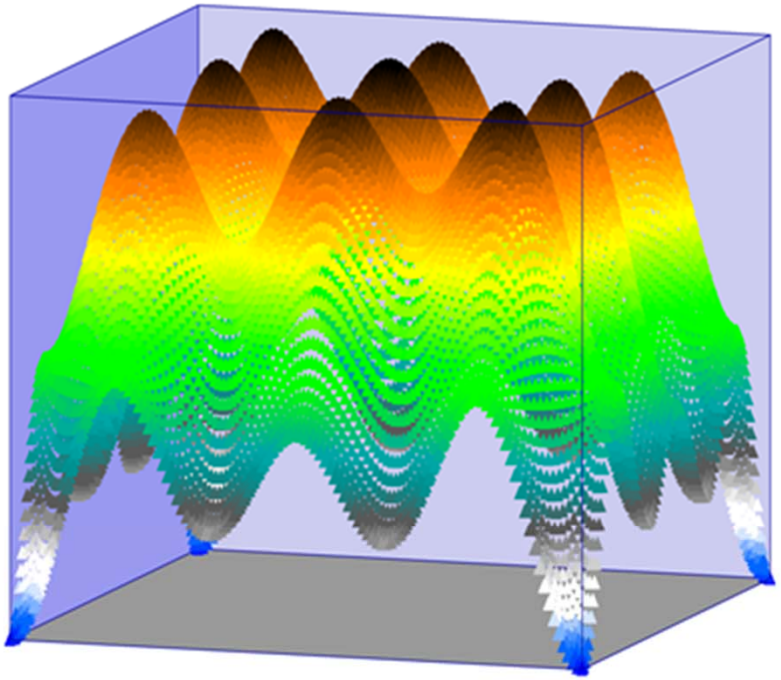
G1 and G2 stabilize by the formation of intramolecular hydrogen bonds

PES very anisotropic in the *gauche* region and very isotropic in the *trans* region.

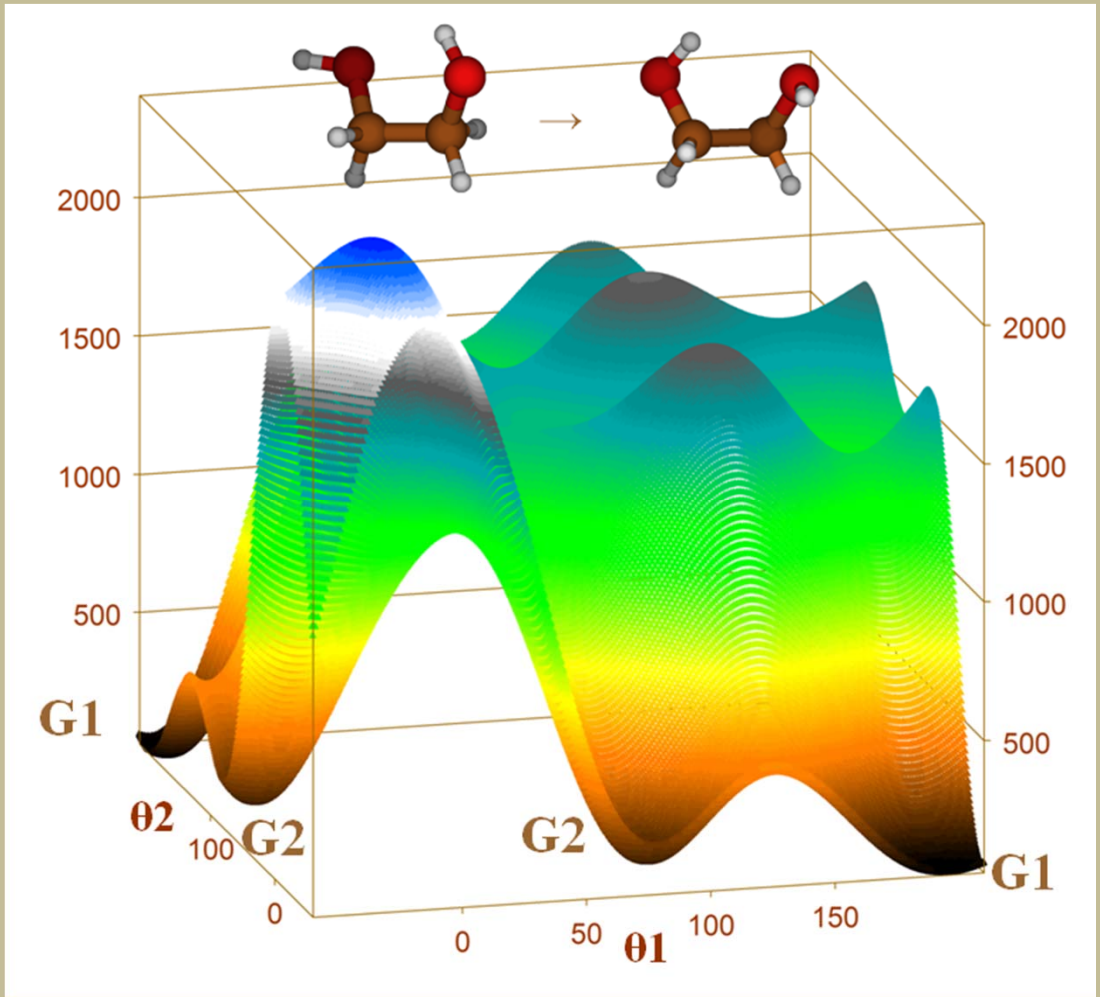

G1
0 cm-1
G2
45 cm-1
G3
271 cm-1
T1
712 cm-1
T2
815 cm-1
T3
865 cm-1
T4
852 cm-1
G4
868 cm-1
G5
1071 cm-1



gauche



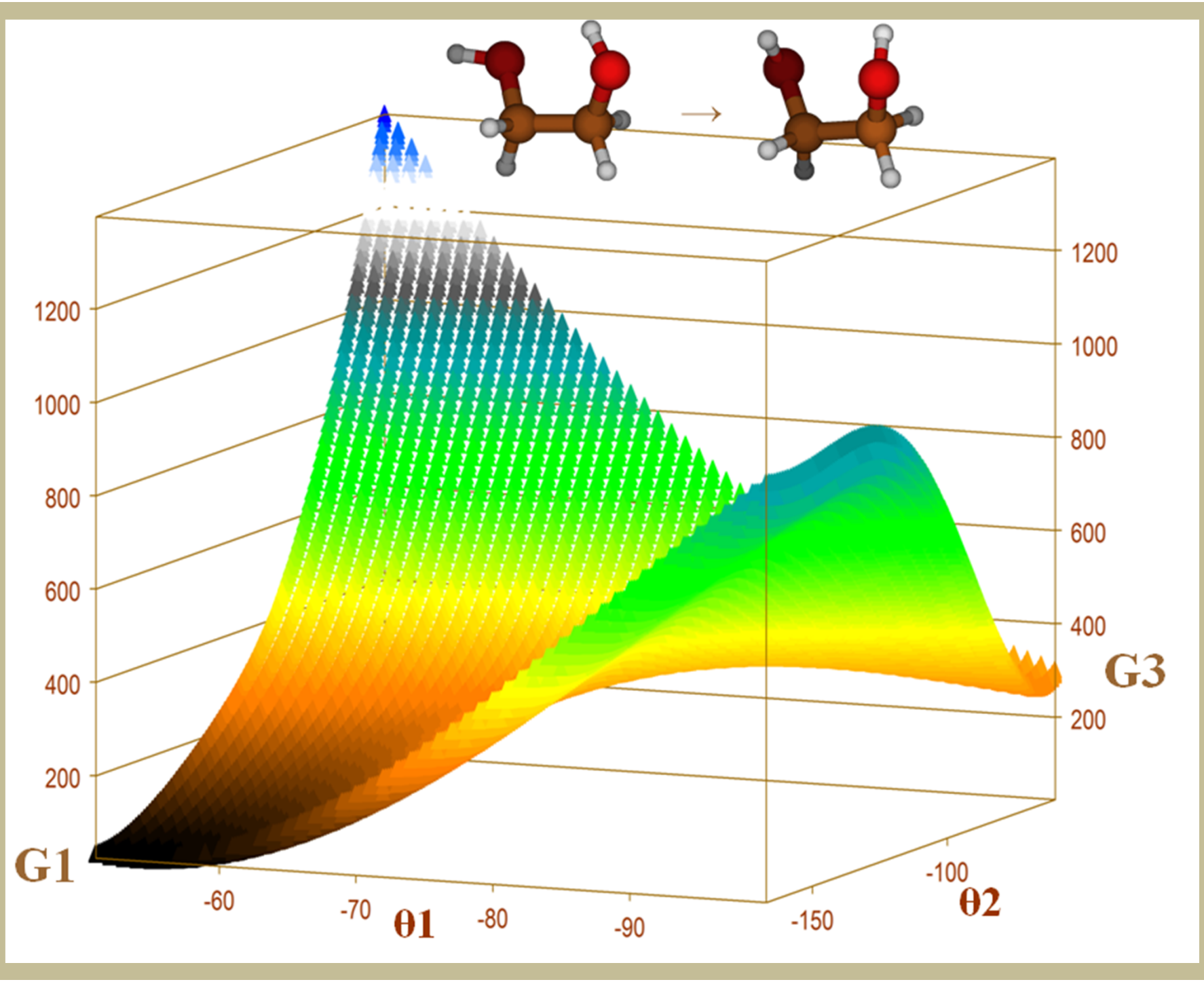
trans

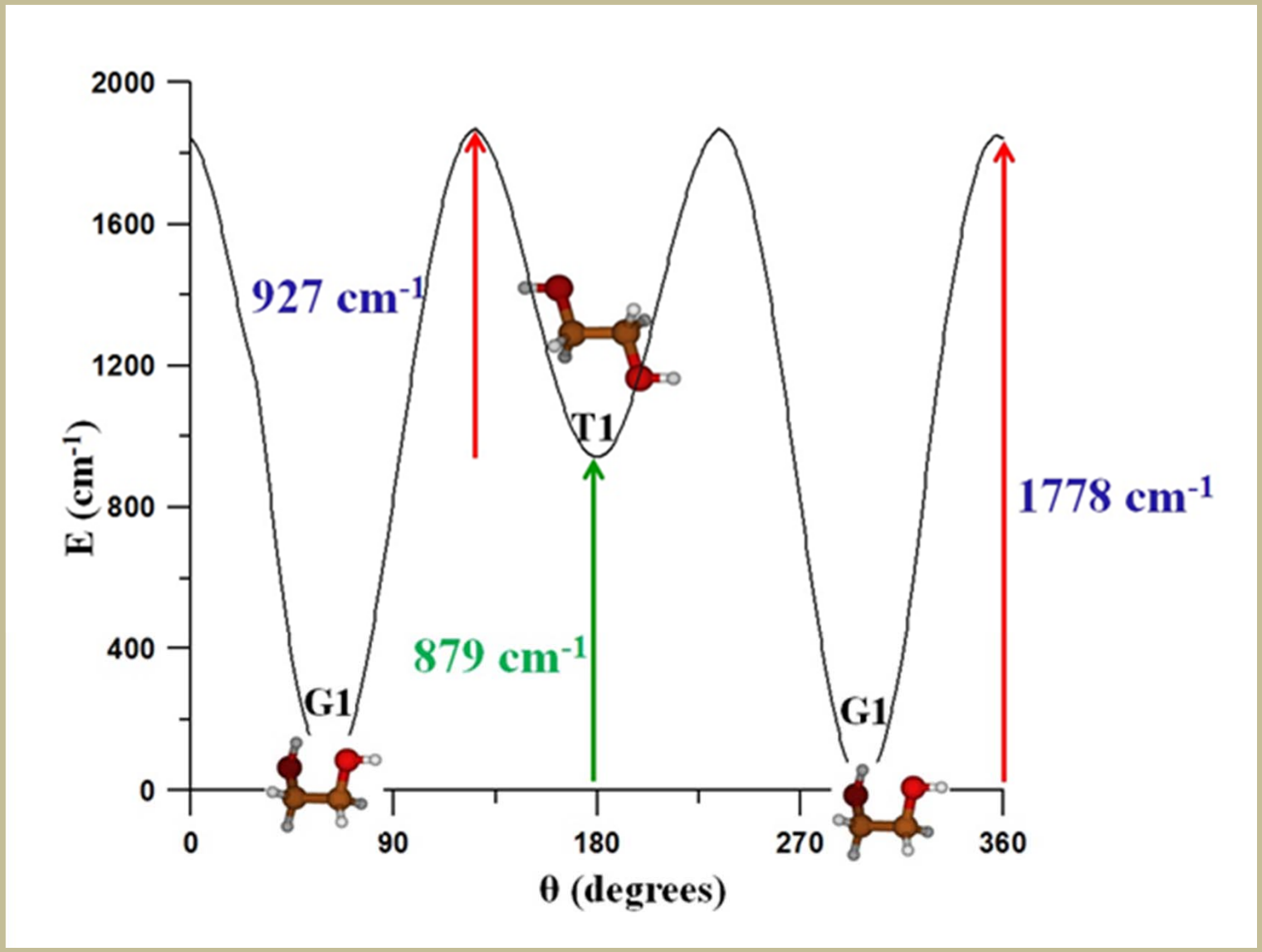


Two “prominent conformers” G1 and G2

V (G1 → G1’) = 315 cm^{-1}
V (G2 → G2’) = 1050 cm^{-1}
V (G2 → G1’) = 410 cm^{-1}

G1 A_0=15369.57 MHz, B_0=5579.87 MHz, C_0=4610.02 MHz
(exp A_0=15363.2798(31) MHz; B_0=5587.0982(13), C_0=4613.5366(14) MHZ) , Christen et al, *J. Mol.Spectrosc.,* **172**, 57 , 1995)
G2 A_0=15129.03 MHz, B_0=5508.57 MHz, C_0=4571.57 MHz
(exp A_0=15214.601(5) MHz; B_0=5538.3316(29), C_0=4595.025(2)MHZ) , Christen et al, J.*Mol.Spectrosc.,* **205**, 185, 2001).


1200
1000
800
600
400
200
G1
-60
-70
θ1
-80
-90
1200
1000
800
600
400
200
G3
-100
θ2
-150


2000
1600
1200
800
400
0
E (cm-1)
927 cm-1
879 cm-1
1778 cm-1
T1
G1
G1
0
90
180
270
360
θ (degrees)

FAR INFRARED SPECTRUM

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

PES

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

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:

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≤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_{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≤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≤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≤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≤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≤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

Hamitonian matrix dimension (51244 (A_1), 49016(A_2), 51221(A_3), 48994(A_4), 51750(A_{1d}), 49500 (A_{2d}), 51750(A_{3d}), 49500(A_{4d})).

2-Contrated basis functions

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

3-Probability integrals

TORSIONAL SPLITTINGS

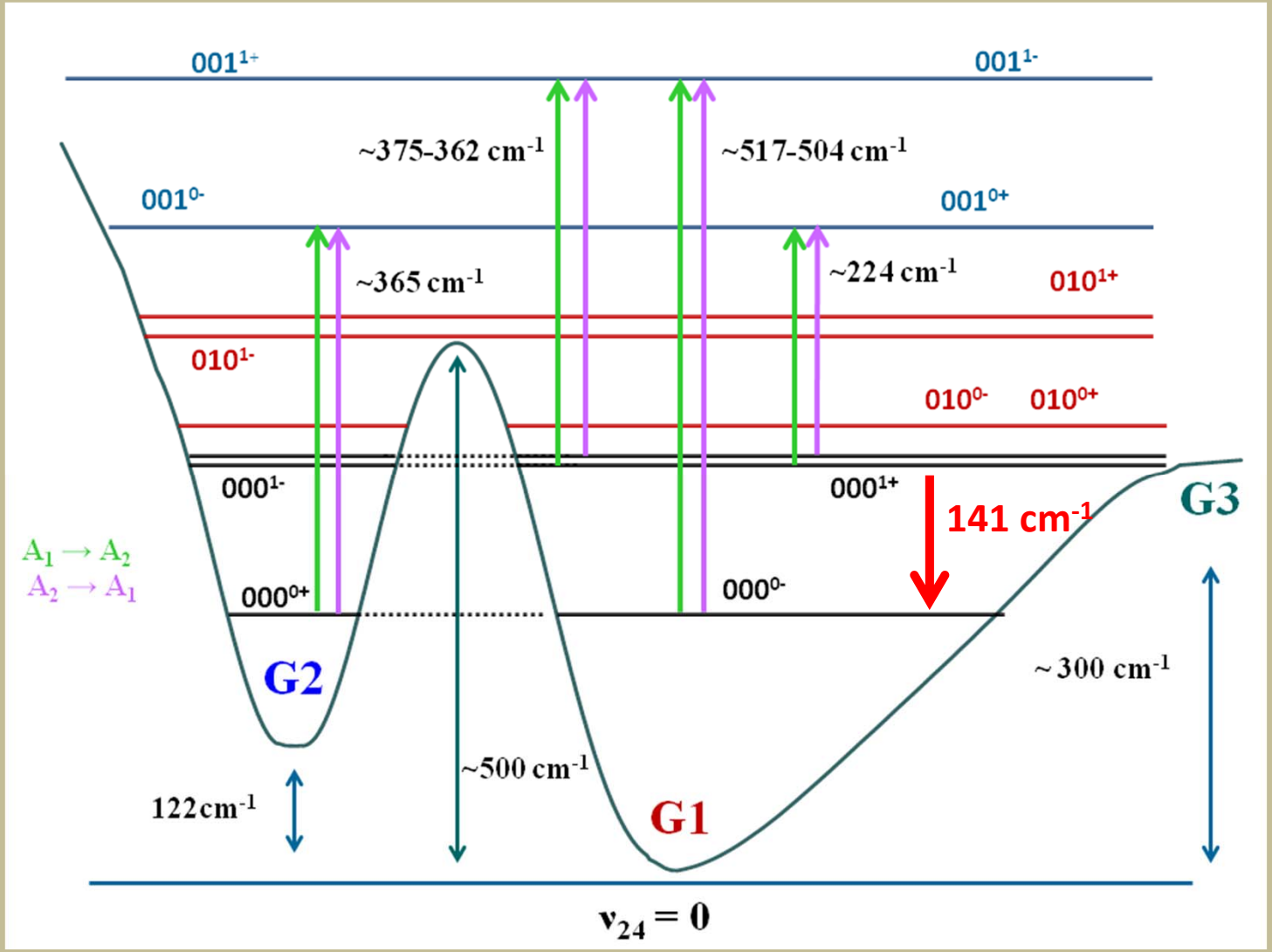
ν_1,ν_2,ν_3 (CC-t, OH-t,OH-t)	Symmetry	E	
0 0 0	A_1,A_{1d}	0.000[a]	141.804
	A_3,A_{3d}	0.000	141.882
	A_2,A_{2d}	0.260	142.029
	A_4,A_{4d}	0.300	141.993
0 1 0	A_1	167.846	262.677
	A_2	182.335	313.111
1 0 0	A_1	177.395	324.901
	A_2	177.493	326.714
2 0 0	A_1	355.189	501.569
	A_2	356.640	509.069
1 1 0	A_1	338.210	428.953
	A_2	354.453	484.688
0 0 1	A_1	365.322	504.265
	A_2	365.876	517.006
0 2 0	A_1	361.167	440.209
	A_2	393.162	491.212
2 1 0	A_1	514.886	
	A_2	529.774	
1 0 1	A_1	537.554	
	A_2	537.412	
0 1 1	A_1	530.729	
	A_2	555.450	
1 2 0	A_1	541.275	
	A_2	572.440	
3 0 0	A_1	572.516	
	A_2	574.566	

a) ZPVE = 414.325 cm^{-1}

LOW FREQUENCY TRANSITIONS

ν_{23}, ν_{24}		ν_{21} (strong Q branches)		
Calc.			Calc	Exp P.Buckley et al. 1967
0 0 0 →0 1 0 (ν_{23})			**0 0 0 →0 0 1** (ν_{21})	
$A_1 \rightarrow A_1$	167.8	**$A_1 \rightarrow A_2$**	365.9	375 s
	120.9		375.2	
	262.7		517.0	522 w
	26.0		224.1	230 w
0 0 0 →1 0 0 (ν_{24})			**1 0 0 →1 0 1**	
$A_1 \rightarrow A_1$	177.4	**$A_1 \rightarrow A_2$**	360.0	
	183.1		212.5	210 w
	324.9			
	35.6			
1 0 0 →2 0 0 ($\nu_{21} \rightarrow 2\nu_{21}$)				
$A_1 \rightarrow A_1$	177.8			
	176.7			
0 1 0 →0 2 0 ($\nu_{23} \rightarrow 2\nu_{23}$)				
$A_1 \rightarrow A_1$	193.4			
	177.5			
0 1 0 →1 1 0				
$A_1 \rightarrow A_1$	170.4			
	171.6			
1 0 0 →1 1 0				
$A_1 \rightarrow A_1$	160.8			
	104.1			

a) s=strong; w=weak


001^1+
001^1-
~375-362 cm-1
~517-504 cm-1
001^0-
001^0+
~365 cm-1
~224 cm-1
010^1+
010^1-
010^0-
010^0+
000^1-
000^1+
141 cm-1
G3
A1 → A2
A2 → A1
000^0+
000^0-
G2
~300 cm-1
~500 cm-1
122cm-1
G1
v24 = 0