Acc. Chem. Res. 2015, 48, 1413−1422

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Quantum Chemistry Meets Spectroscopy for Astrochemistry: Increasing Complexity toward Prebiotic Molecules

Vincenzo Barone,*[,†] Malgorzata Biczysko,*[,‡] and Cristina Puzzarini*[,¶]

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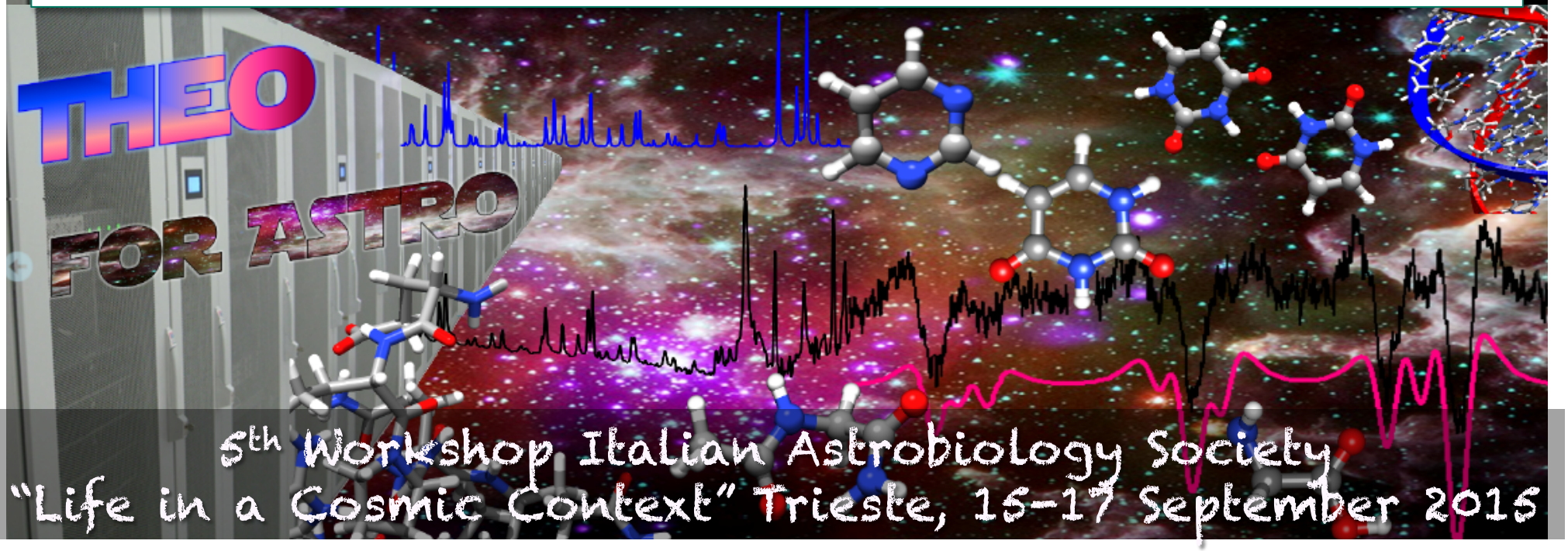
[¶]Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via F. Selmi 2, 40126 Bologna, Italy



5th Workshop Italian Astrobiology Society
"Life in a Cosmic Context" Trieste, 15-17 September 2015

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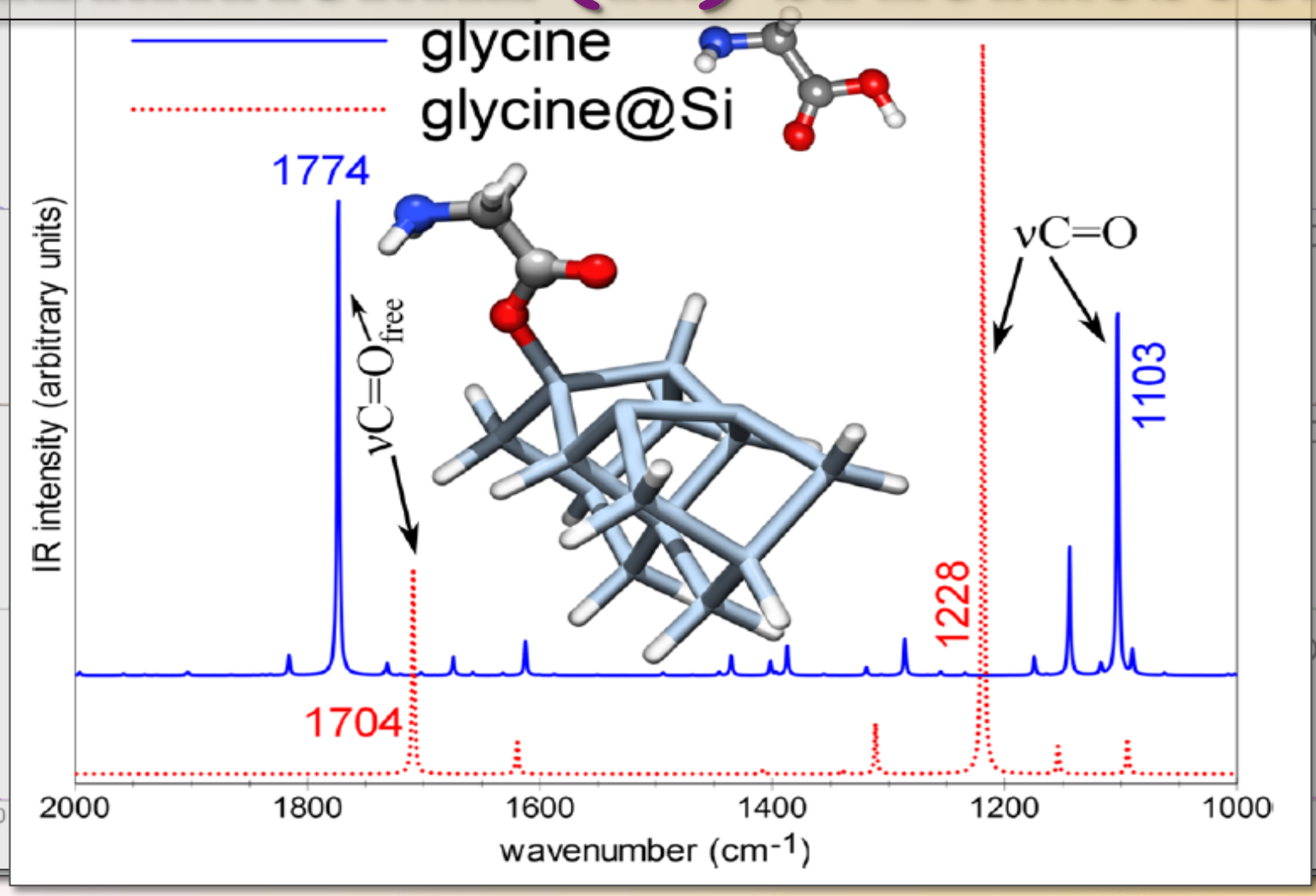
VIBRATIONAL (IR) SPECTROSCOPY



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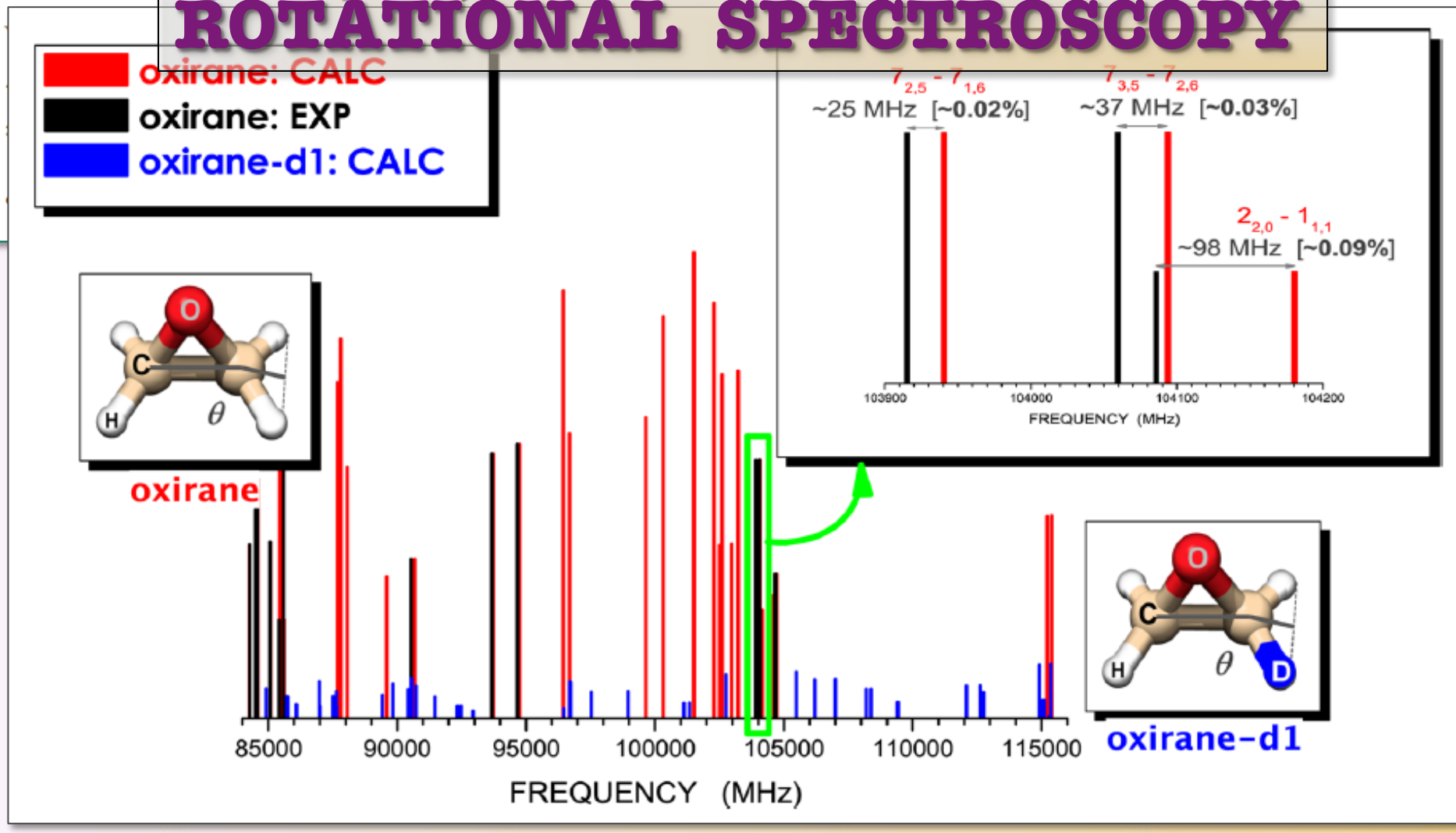
Quantum Chemistry Meets Spectroscopy for Astrochemistry: Increasing Complexity toward Prebiotic Molecules

ROTATIONAL SPECTROSCOPY



Quantum-Chemical Calculation of Rotational Spectroscopy Parameters:

Rotational constants

Centrifugal-distortion constants

Hyperfine parameters

Nuclear quadrupole coupling constants

Spin - rotation constants

Spin - spin constants

C. Puzzarini, J.F. Stanton, J. Gauss *Int. Rev. Phys. Chem.* 29, 273 (2010)
C. Puzzarini *Phys. Chem. Chem. Phys.* 15, 6595 (2010)

Quantum-Chemical Calculation of Spectroscopic Parameters: Rotational (equilibrium) constants

$$B = \frac{\hbar}{4\pi c I_B}$$

INERTIA TENSOR

$$\mathbf{I} = \sum_K m_K \left(\mathbf{1} R_K^2 - \mathbf{R}_K \mathbf{R}_K^T\right)$$

Equilibrium rotational constants only depend on equilibrium structure

Accurate geometry optimization!!

COMPOSITE APPROACH

$$\frac{dE_{tot}}{dx} = \frac{dE^{\infty}(HF-SCF)}{dx} + \frac{d\Delta E^{\infty}(CCSD(T))}{dx} + \frac{d\Delta E(core)}{dx} + \frac{d\Delta E_{CCSDT}}{dx} + \frac{d\Delta E_{CCSDTQ}}{dx} + \ldots$$

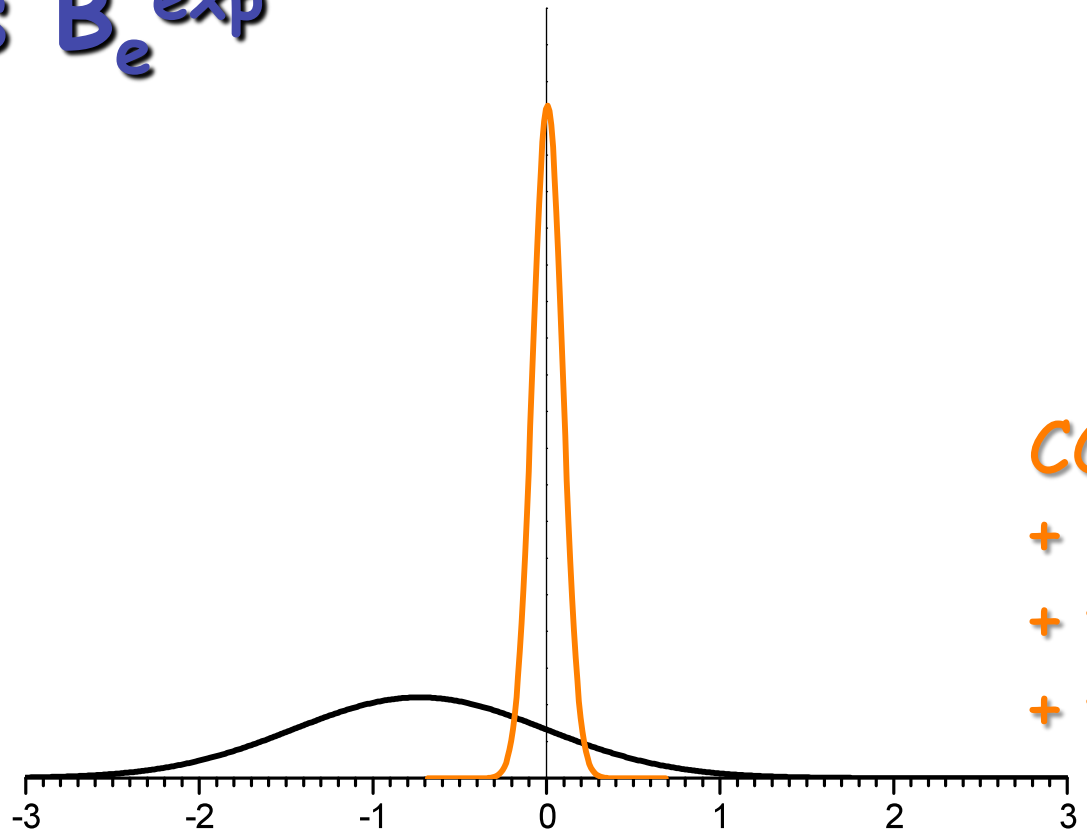
Heckert, Kallay, Gauss, Mol. Phys. 103, 2109 (2005)

Heckert, Kallay, Tew, Klopper, Gauss, JCP 125, 044108 (2006)

CFOUR, Coupled-Cluster techniques for Computational Chemistry:
www.cfour.de

Accuracy of Theoretical Rotational Constants: Statistics

B_e^{calc} vs B_e^{exp}



normal distributions of relative errors

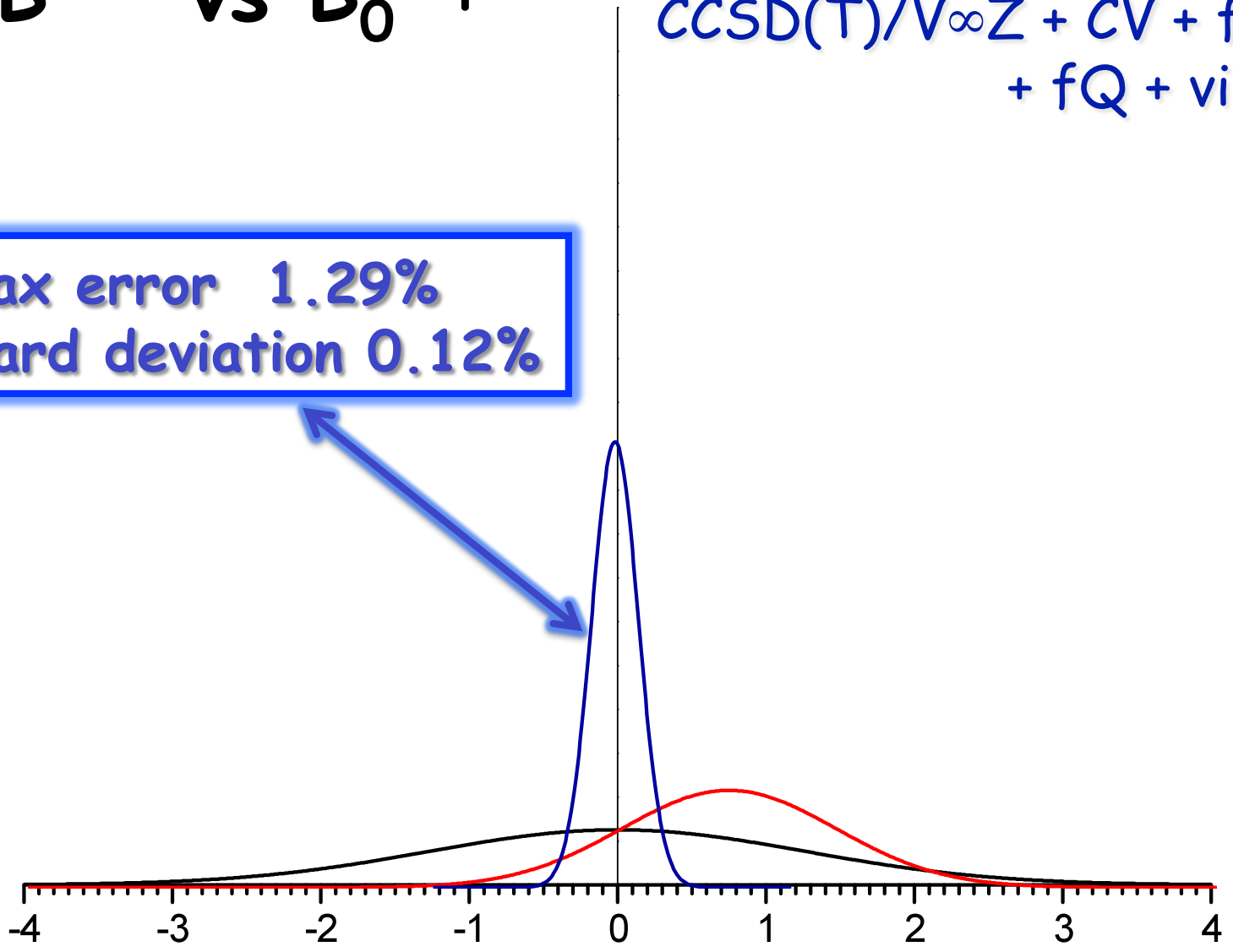
CCSD(T)/∞Z
+ core
+ fT
+ fQ

C. Puzzarini, M. Heckert, J. Gauss *JCP* *128*, 194108 (2008)

B^{calc} vs B_0^{exp}

CCSD(T)/V∞Z + CV + fT
+ fQ + vib

max error 1.29%
standard deviation 0.12%

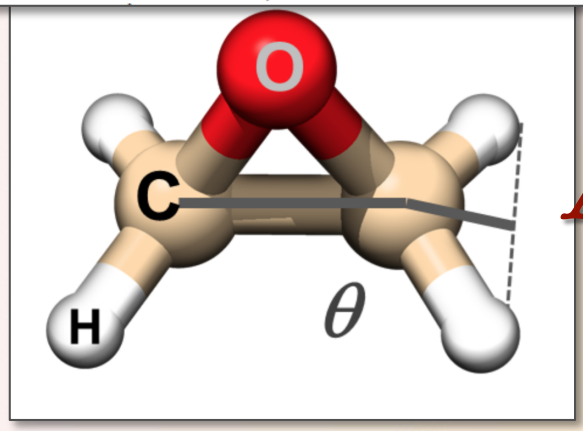


normal distributions of relative errors

C. Puzzarini, M. Heckert, J. Gauss *JCP* *128*, 194108 (2008)

ACCURATE SPECTROSCOPIC CHARACTERIZATION OF OXIRANE: A VALUABLE ROUTE TO ITS IDENTIFICATION IN TITAN'S ATMOSPHERE AND THE ASSIGNMENT OF UNIDENTIFIED INFRARED BANDS

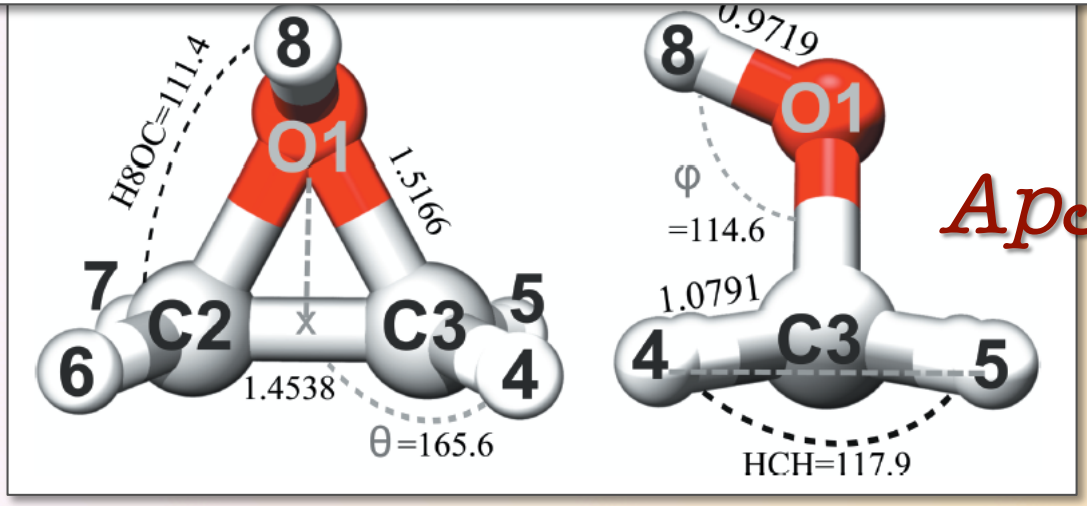
CRISTINA PUZZARINI[1], MALGORZATA BICZYSKO[2,3], JULIEN BLOINO[2,3], AND VINCENZO BARONE[2]



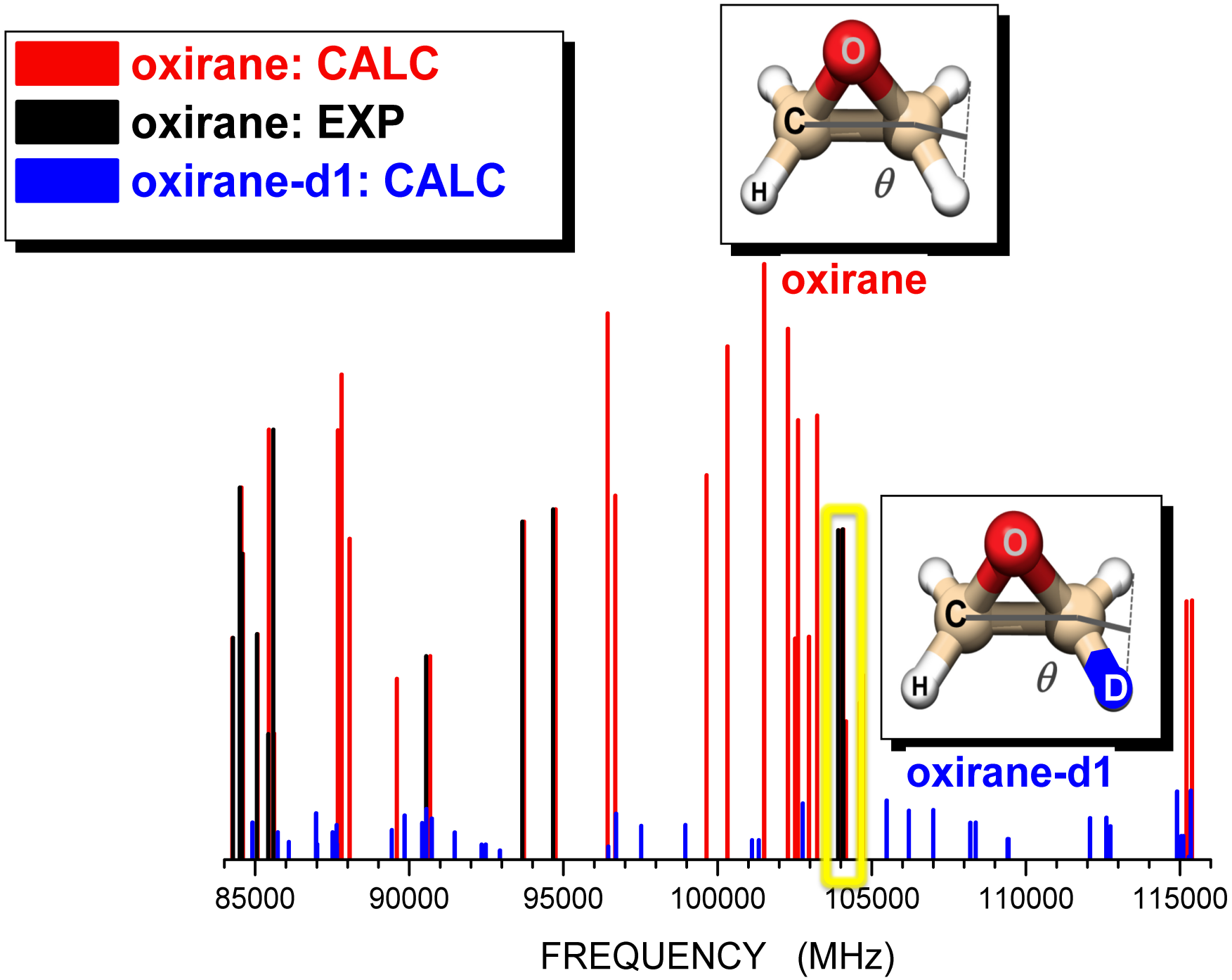
ApJ 785, 107 (2014)

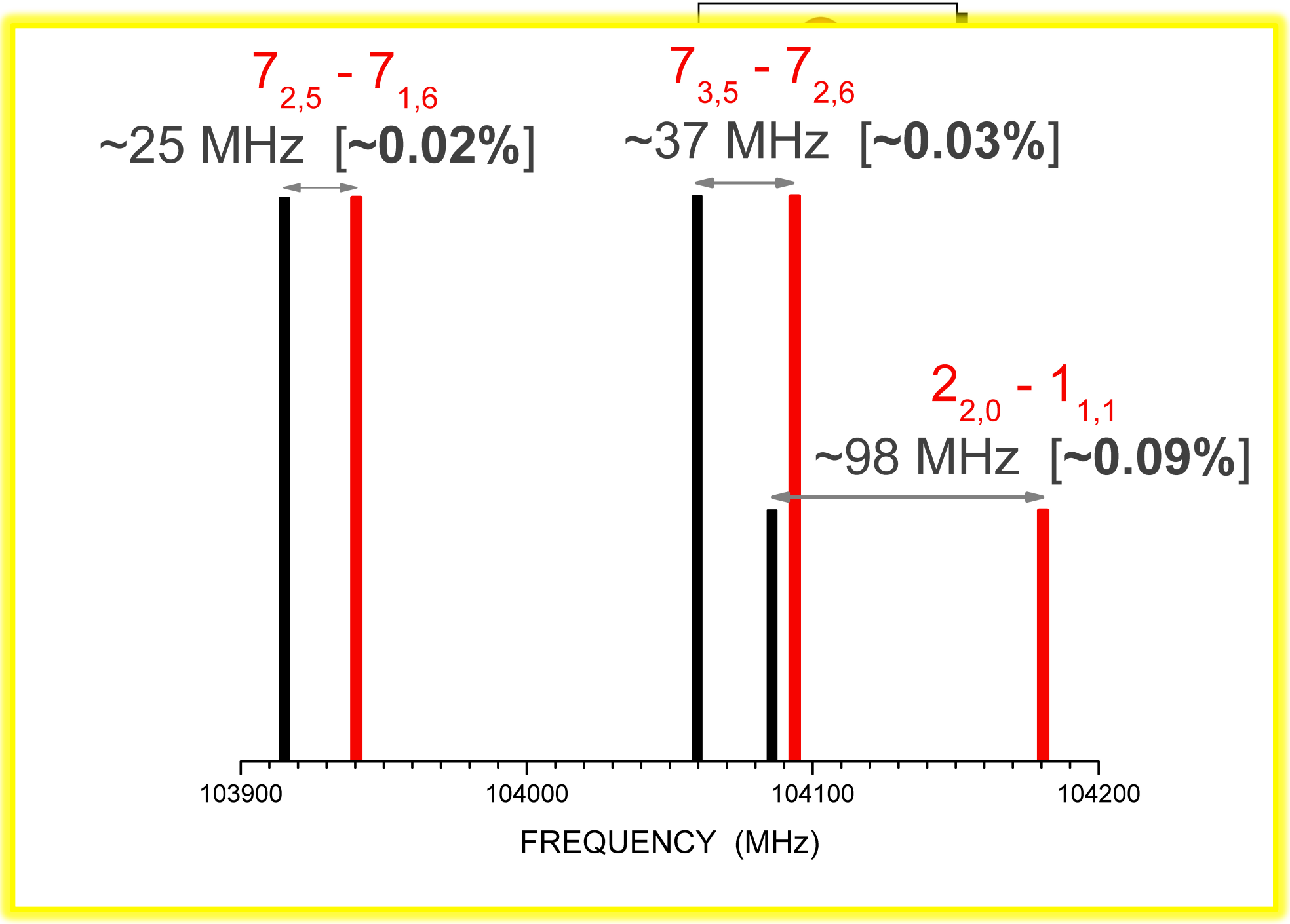
ACCURATE SPECTROSCOPIC CHARACTERIZATION OF PROTONATED OXIRANE: A POTENTIAL PREBIOTIC SPECIES IN TITAN'S ATMOSPHERE

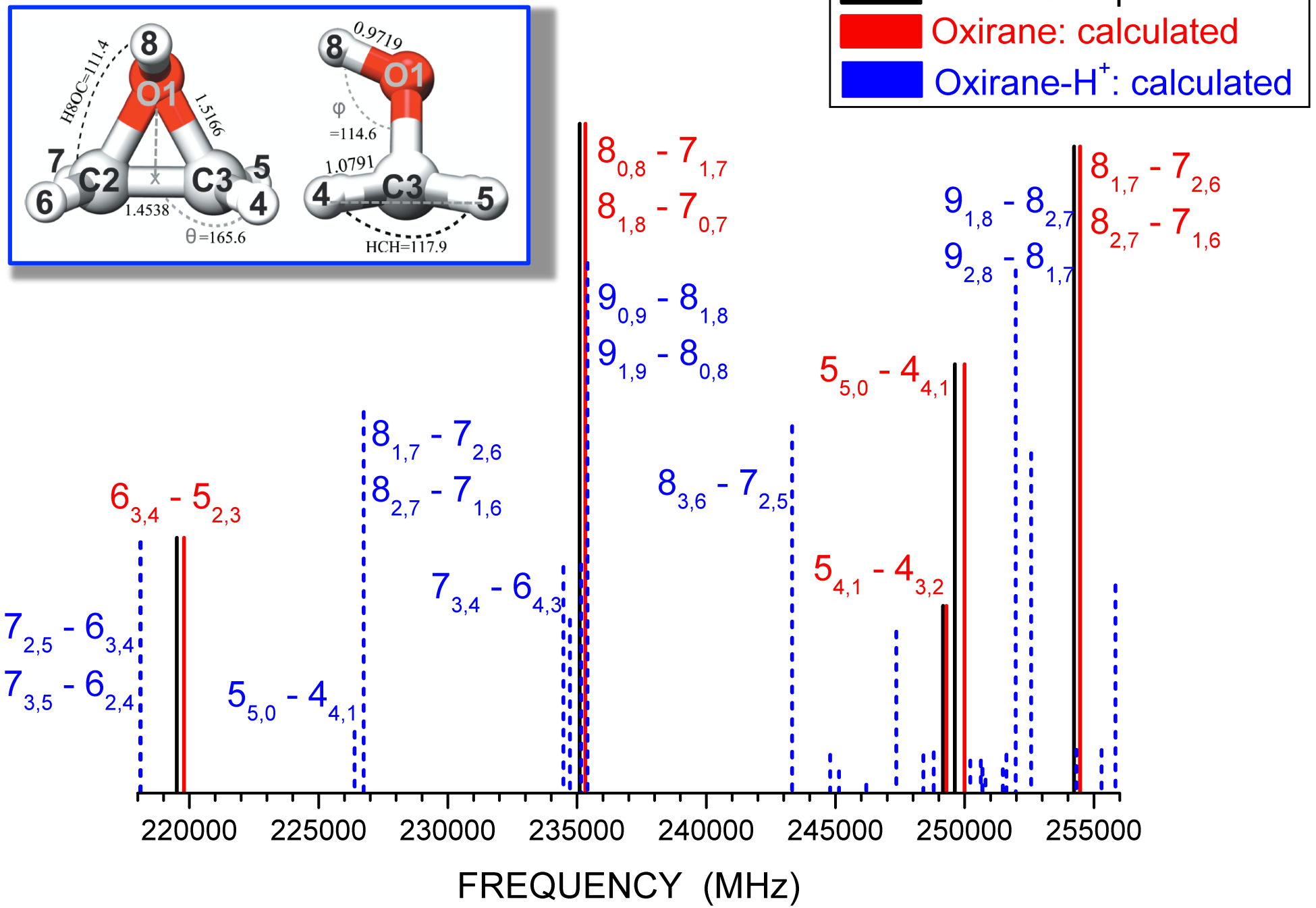
CRISTINA PUZZARINI[1], ASHRAF ALI[2], MALGORZATA BICZYSKO[3,4], AND VINCENZO BARONE[3]



ApJ 792, 118 (2014)


oxirane: CALC
oxirane: EXP
oxirane-d1: CALC
O
C
H
θ
oxirane
O
C
H
θ
D
oxirane-d1
85000
90000
95000
100000
105000
110000
115000
FREQUENCY (MHz)


$7_{2,5} - 7_{1,6}$
~25 MHz [~0.02%]
$7_{3,5} - 7_{2,6}$
~37 MHz [~0.03%]
$2_{2,0} - 1_{1,1}$
~98 MHz [~0.09%]
103900
104000
104100
104200
FREQUENCY (MHz)


Oxirane: experiment
Oxirane: calculated
Oxirane-H+: calculated
H8OC=111.4
1.5166
1.4538
θ=165.6
0.9719
φ
=114.6
1.0791
HCH=117.9
8
O1
7
C2
C3
6
5
4
x
8 0,8 - 7 1,7
8 1,8 - 7 0,7
9 0,9 - 8 1,8
9 1,9 - 8 0,8
8 1,7 - 7 2,6
8 2,7 - 7 1,6
6 3,4 - 5 2,3
7 2,5 - 6 3,4
7 3,5 - 6 2,4
5 5,0 - 4 4,1
7 3,4 - 6 4,3
8 3,6 - 7 2,5
9 1,8 - 8 2,7
9 2,8 - 8 1,7
5 5,0 - 4 4,1
5 4,1 - 4 3,2
8 1,7 - 7 2,6
8 2,7 - 7 1,6
220000
225000
230000
235000
240000
245000
250000
255000
FREQUENCY (MHz)

CASE STUDIES

Semirigid Life Bricks:
DNA bases

Flexible Life Bricks:
Glycine and Its
Peptide Analogue

CASE STUDIES

Semirigid Life Bricks: DNA bases

COMPOSITE APPROACH: the case of larger "bio" molecules

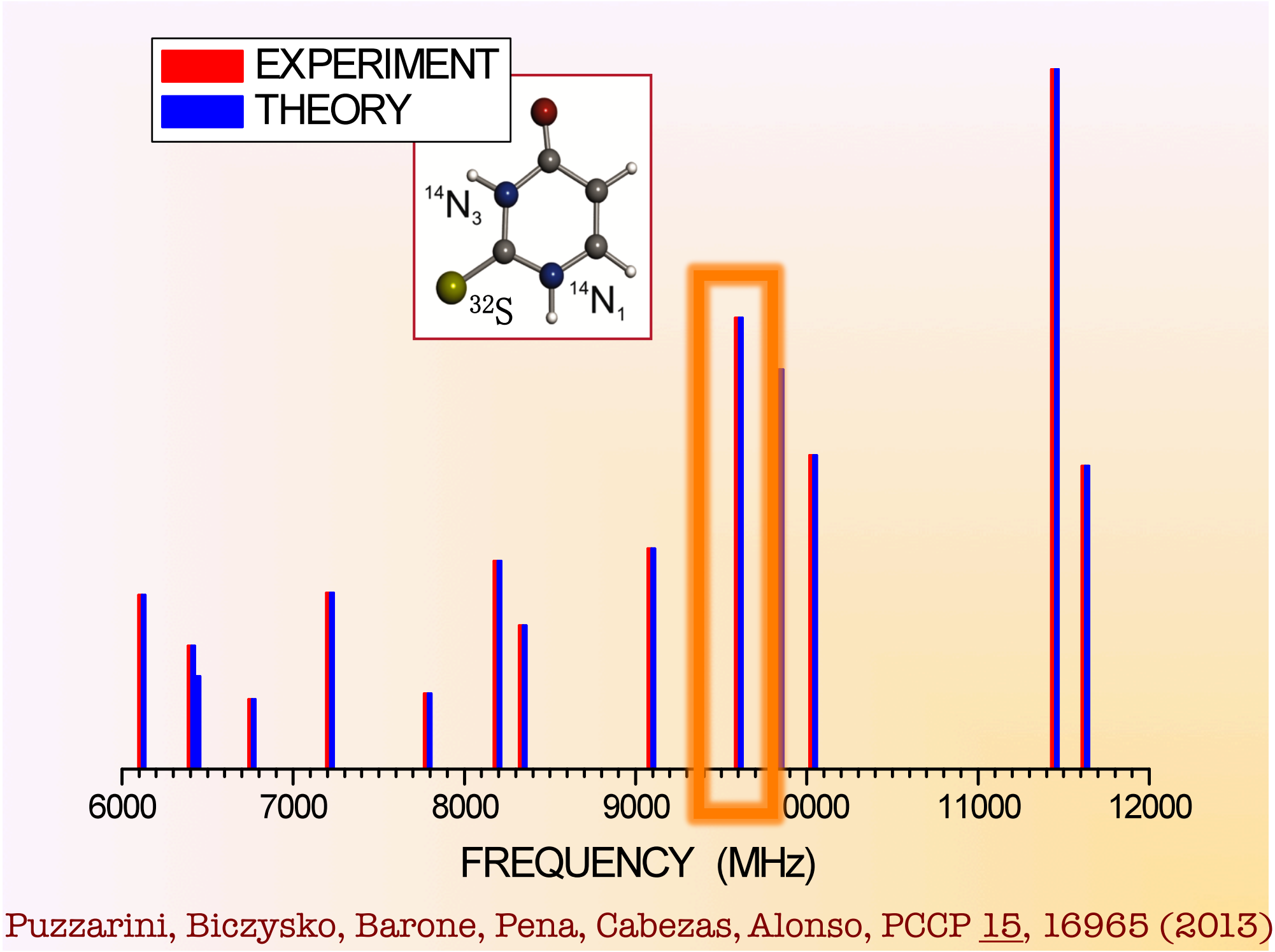
1) r_e (B_e), D's, q's: "cheap" geom scheme

Best = CCSD(T)/VTZ
+ ΔCBS(MP2/TZ-QZ)
+ Δdiff(MP2/AVTZ)
+ ΔCV(MP2/CVTZ)

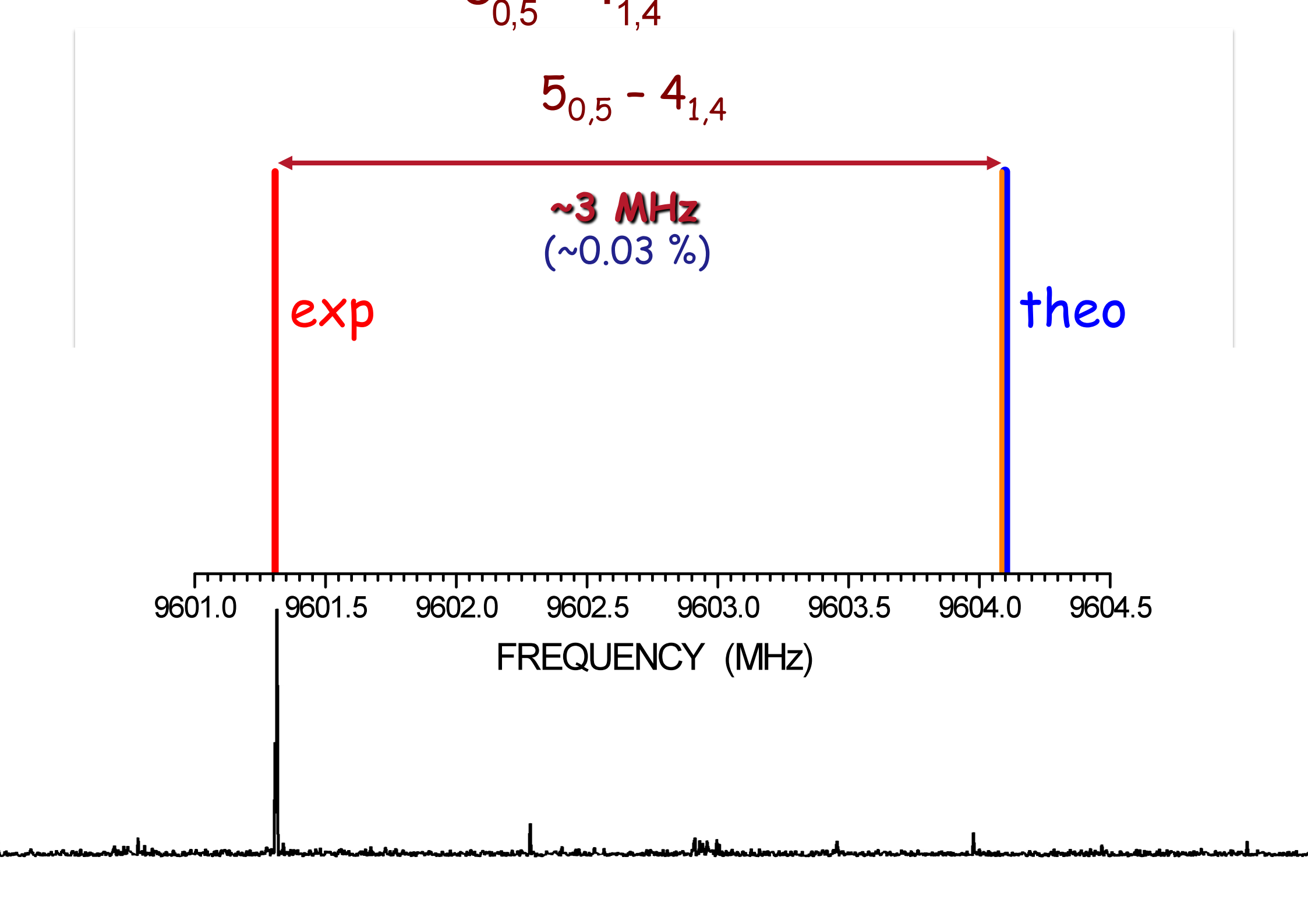
2) alphas: DFT

$$B_0 = B_e - \frac{1}{2}\sum_r \alpha_r^B$$

DFT = B3LYP/SNSD

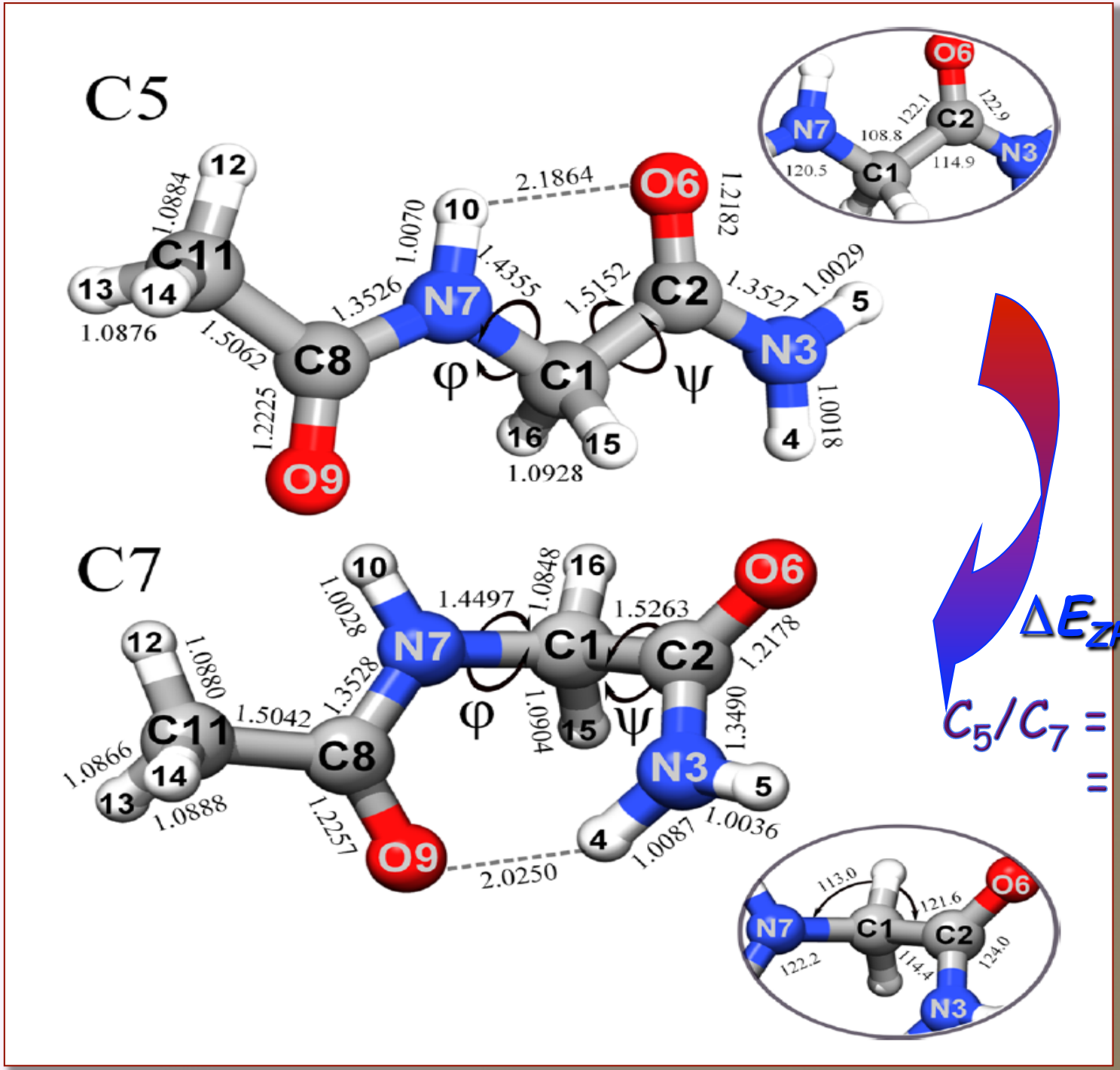


Puzzarini, Biczysko, Barone, Pena, Cabezas, Alonso, PCCP 15, 16965 (2013)


$5_{0,5} - 4_{1,4}$
~3 MHz
(~0.03 %)
exp
theo
9601.0
9601.5
9602.0
9602.5
9603.0
9603.5
9604.0
9604.5
FREQUENCY (MHz)

CASE STUDIES

Flexible Life Bricks: Glycine and Its Peptide Analogue



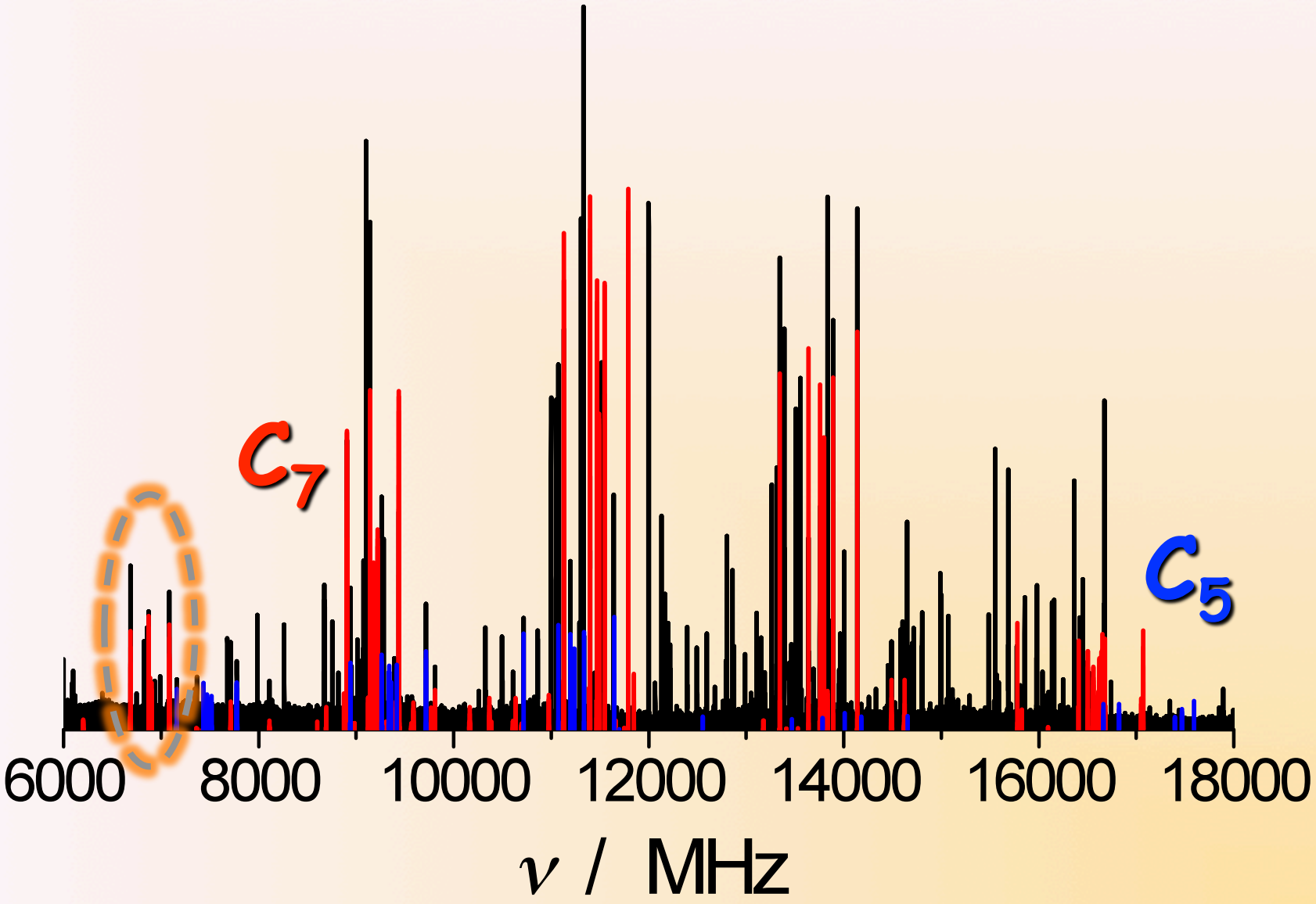
ΔE_{ZPV} = 197 cm^{-1}

C_5/C_7 = 0.32(10) Exp

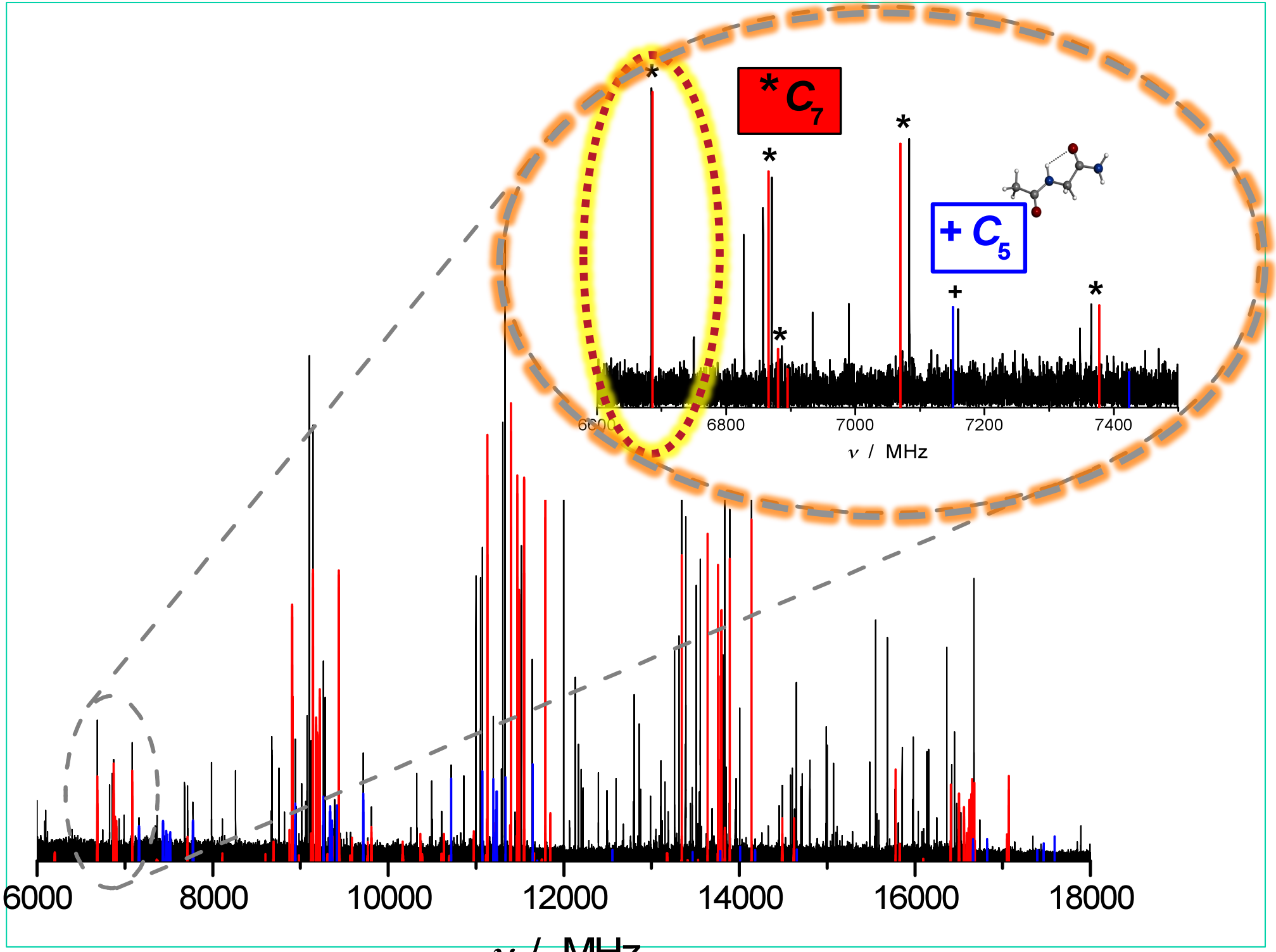
= 0.43 Theo

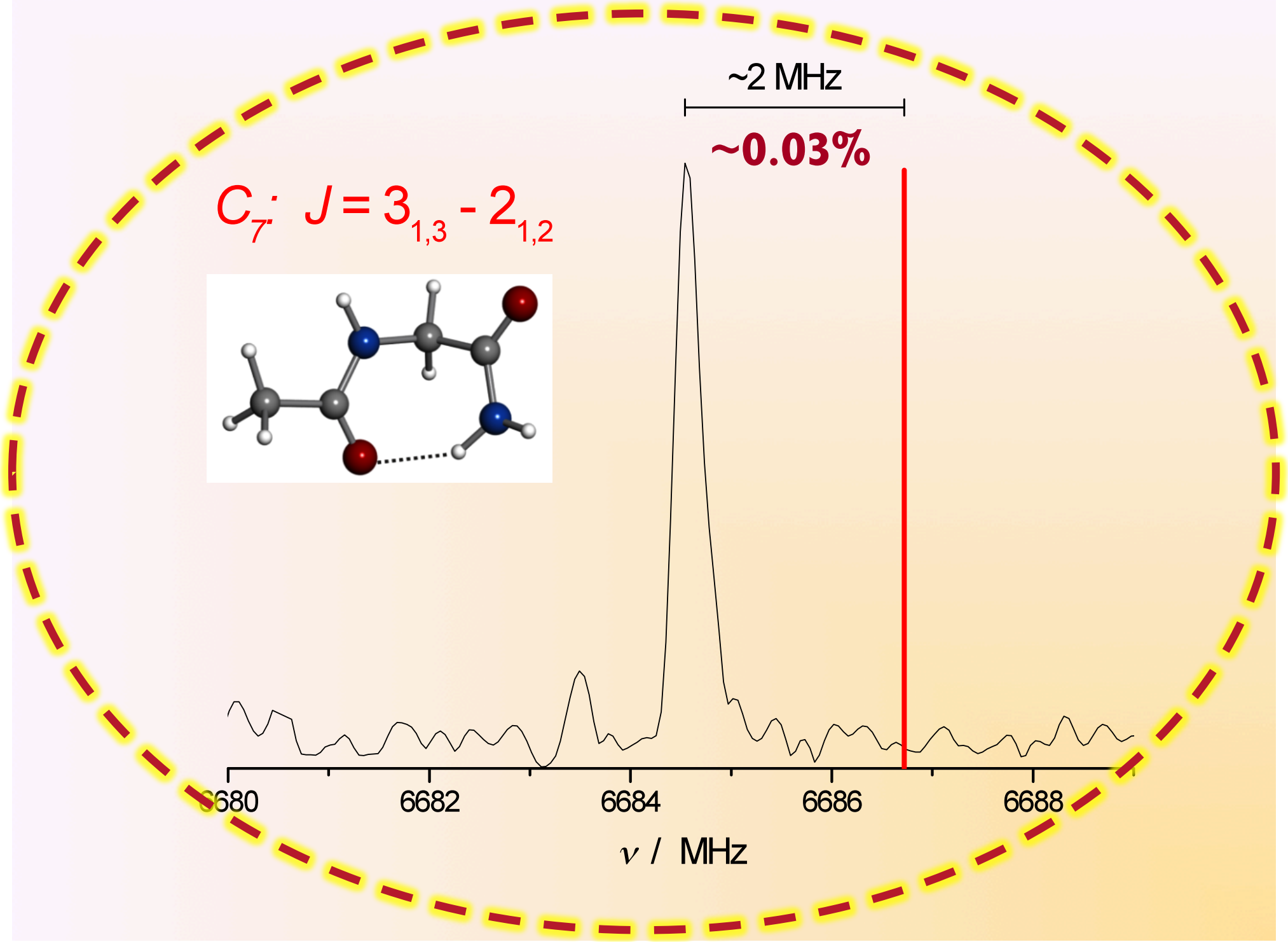
Puzzarini, Biczysko, Barone, Largo, Pena, Cabezas, Alonso, *JPC Lett* 5, 534 (2014)

Rotational spectrum: CALCULATED (A state) vs OBSERVED

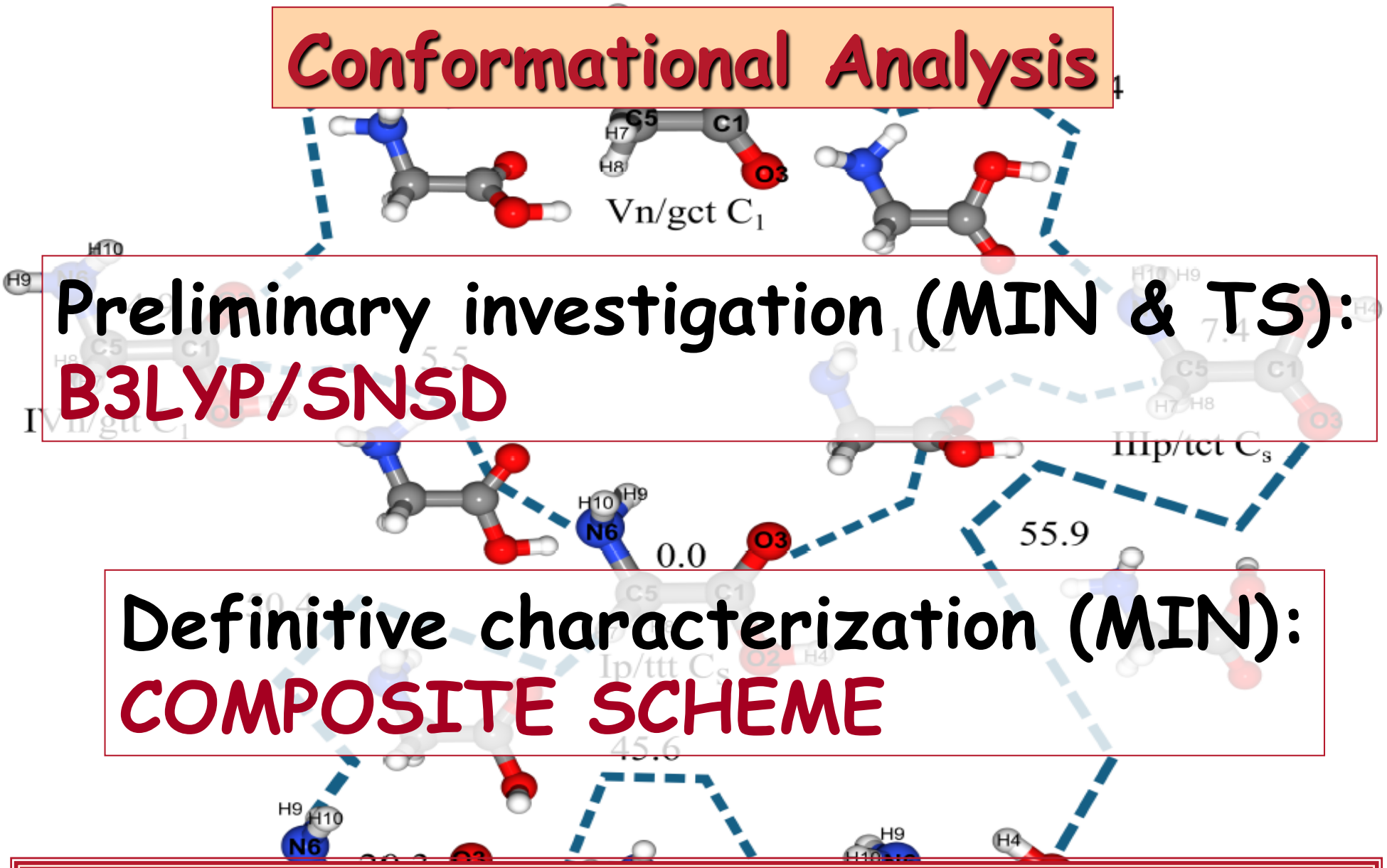


Puzzarini, Biczysko, Barone, Largo, Pena, Cabezas, Alonso, *JPC Lett* 5, 534 (2014)


* C7
+ C5
6800
7000
7200
7400
ν / MHz
6000
8000
10000
12000
14000
16000
18000
ν / MHz


~2 MHz
~0.03%
C_7: $J = 3_{1,3} - 2_{1,2}$
6680
6682
6684
6686
6688
ν / MHz

Conformational Analysis



Preliminary investigation (MIN & TS):
B3LYP/SNSD

Definitive characterization (MIN):
COMPOSITE SCHEME

V. Barone, M. Biczysko, J. Bloino, C. Puzzarini, PCCP 15, 1358 (2013)
V. Barone, M. Biczysko, J. Bloino, C. Puzzarini, JCTC 9, 1533 (2013)
V. Barone, M. Biczysko, J. Bloino, C. Puzzarini, PCCP 15, 10094 (2013)

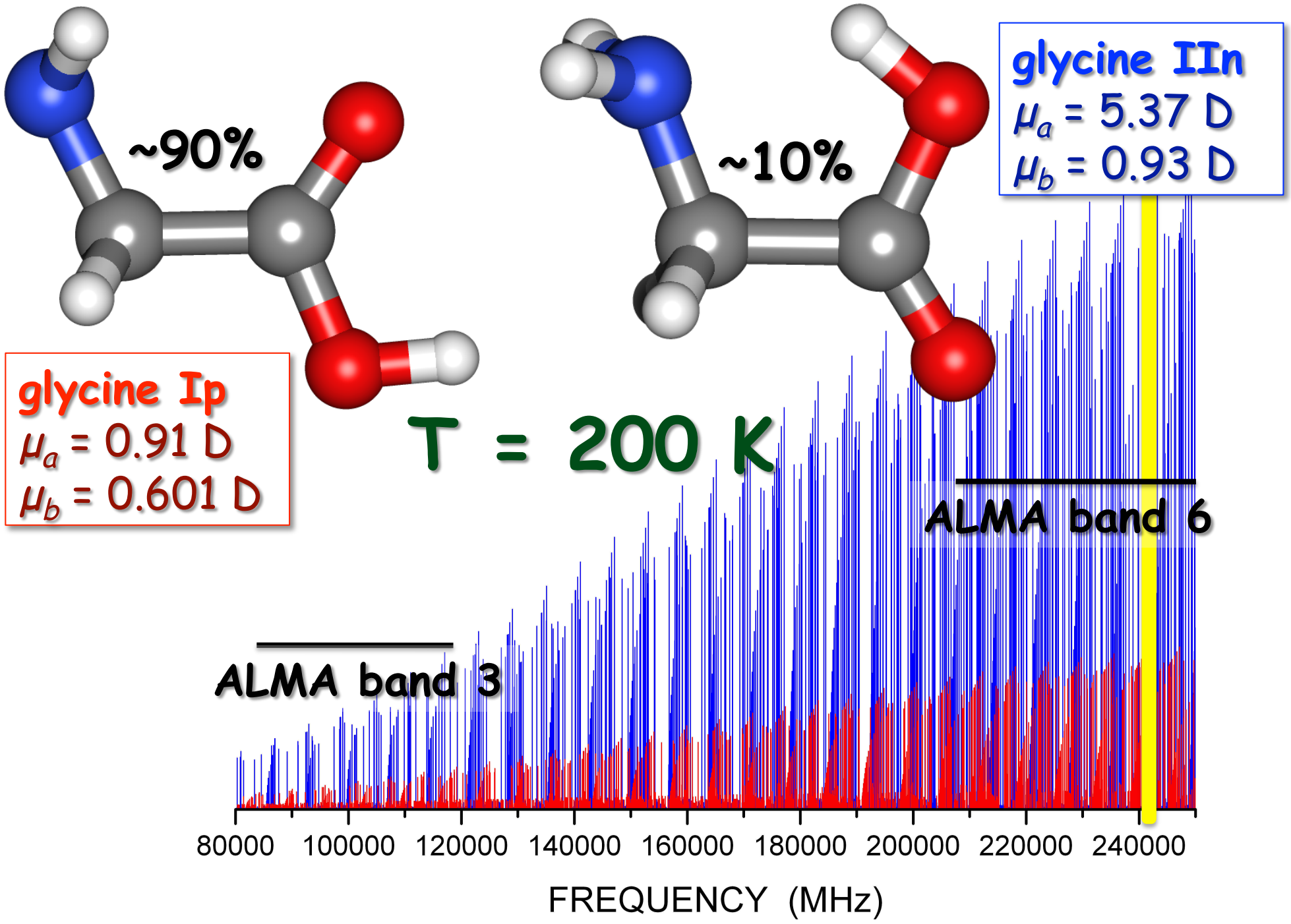
Accuracy: 1 kJ / mol

Values in kJ/mol

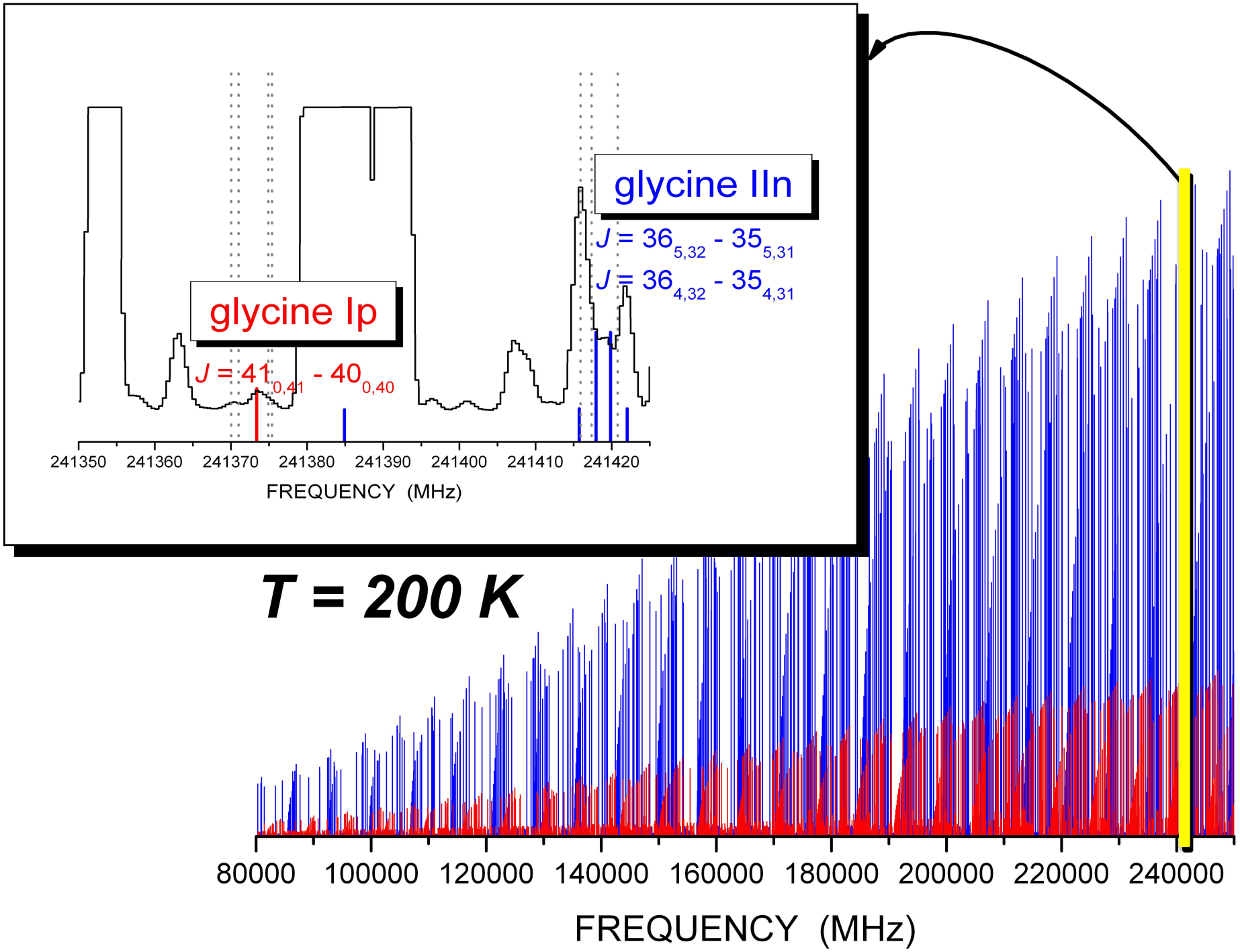
Conformer	Model	T = 0 K ΔE_{ele} best/DFT[b]	ΔE_{ele} best/best[b]	ΔE_{ZPVE}[c]	T = 15 K ΔH	ΔG	T = 410 K ΔH	ΔG
IIn/ccc	HO	2.45	2.29	3.82	3.82	3.82	2.80	5.41
	HO + HR[d]	—	—	—	3.85	3.80	2.50	4.57
	SPT(HRAO)[d,e]	—	—	3.73	3.77	3.72	2.45	4.41
	Exp.[f]						1.38	
IVn/gtt[g]	HO	4.89	4.87	4.81	4.81	4.81	4.59	5.97
	HO + HR[d]	—	—	—	4.82	4.82	4.68	5.99
	SPT(HRAO)[d,e]	—	—	4.74	4.75	4.75	4.62	5.78
	Exp.[f]						4.81	
IIIp/tct[g]	HO	7.42	7.44	7.48	7.59	7.34	7.61	−1.17
	HO + HR[d]	—	—	—	7.55	7.28	6.59	0.04
	SPT(HRAO)[d,e]	—	—	7.94	7.90	7.87	6.62	9.72
	Exp.[h]						5.8	
Vn/gct	HO	10.99	10.88	11.22	11.23	11.23	10.87	12.10
	HO + HR[d]	—	—	—	11.22	11.23	11.21	12.15
	SPT(HRAO)[d,e]	—	—	11.21	11.21	11.22	11.21	12.02
VIp/ttc[i]	HO	20.34	20.32	19.39	19.89	19.89	20.02	20.34
	HO + HR[d]	—	—	—	19.80	19.77	20.08	20.24
	SPT(HRAO)[d,e]	—	—	19.80	19.81	19.80	20.24	20.26
TS IIp/ccc		2.87	2.92					

best = CCSD(T)/CBS + CV

V. Barone, M. Biczysko, J. Bloino, C. Puzzarini, PCCP 15, 10094 (2013)

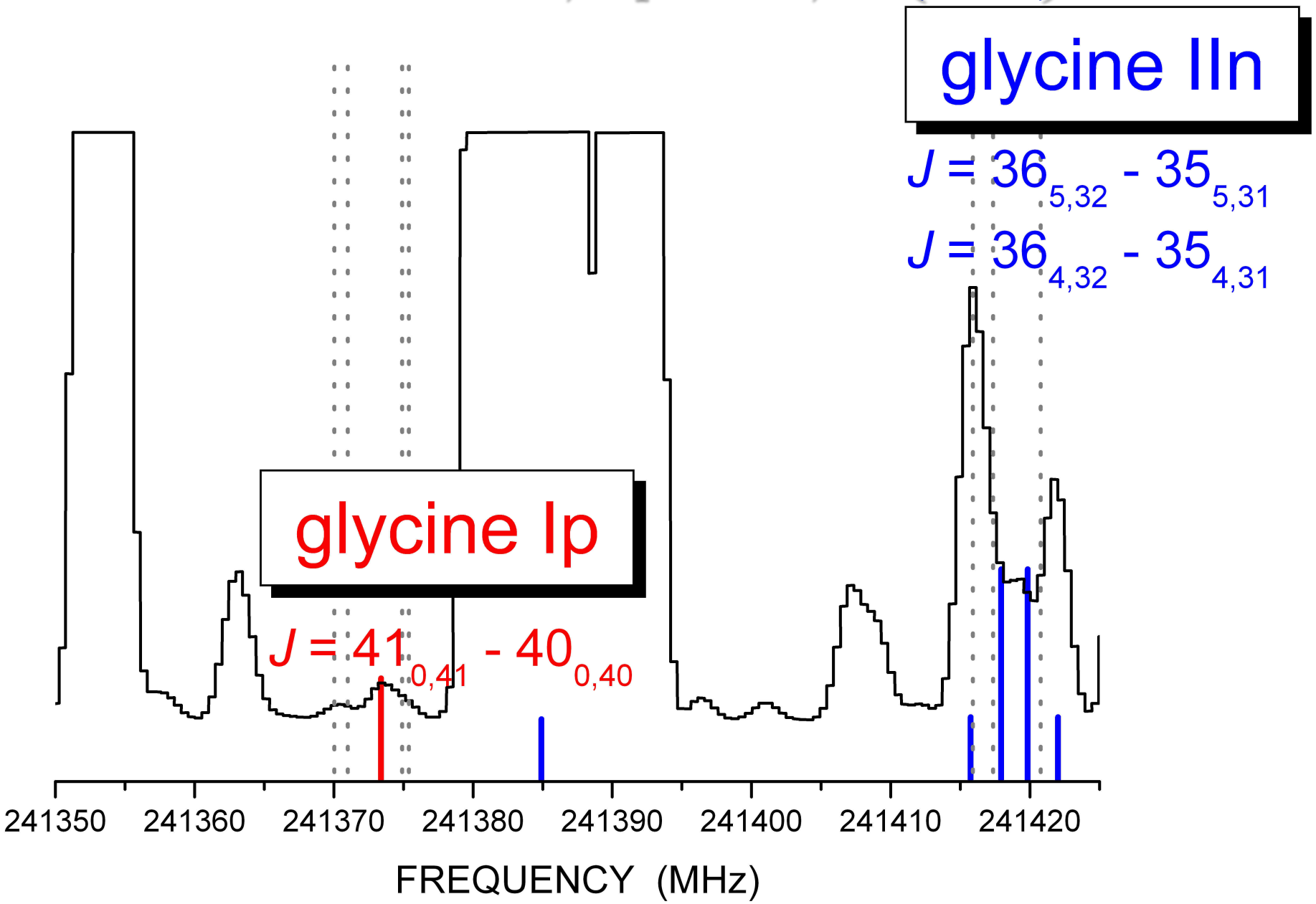


V. Barone, M. Biczysko, C. Puzzarini, Acc. Chem. Res. 48, 1413 (2015)



V. Barone, M. Biczysko, C. Puzzarini, Acc. Chem. Res. 48, 1413 (2015)

Simulated emission spectrum for the hot-core source NGC 6334 IRS1: R.T. Garrod, ApJ **765**, 60 (2013).



V. Barone, M. Biczysko, C. Puzzarini, Acc. Chem. Res. 48, 1413 (2015)

THANK YOU For YOUR ATTENTION

THANKS $$$$$$: MIUR & University of Bologna