Pigment of red coral and African snail Helixia Aspersa. Molecular modeling of polyenes

Teobald Kupka

+

coworkers

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Overview

1. Introduction

2. Theory

3. Results

4. Conclusions

5. Acknowledgments

Aim and scope of work

Theoretical support to analysis of Raman spectra of red coral and African snail

1. **Systematic calculations of structure and ν(C=C) and ν(C-C) in all-trans and all-cis polyenes**
2. **models: ethylene and polyenes with 2 – 14 C=C units**
3. **DFT (B3LYP, BLYP)**
4. **CBS (pc basis sets for ethylene, 6-311-++G** for polyenes**

Tools: Gaussian 09, version D.01

Molecules
(structure, vibrations)

Interpretation
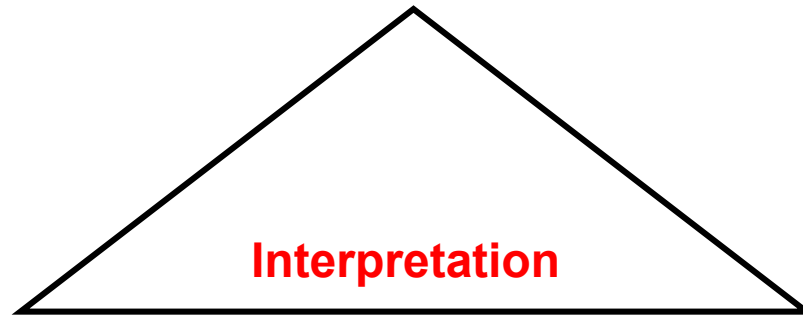
Experimental

Raman (IR) spectrum

Theory
structure/vibrational
parameters

Symbiosis of experiment and theory

Theoretical calculations[a]

1. **Geometry optimization**

2. **C_2H_4: DFT(BLYP, B3LYP)**

3. **Basis sets: Pople type 6-311++G**, 6-311++G(3df,2pd);**

   Jensen's polarization-consistent pc-n, aug-pc-n, pcseg-n, aug-pcseg-n, n = 0, 1, 2, 3 and 4.

   Polyenes: DFT(BLYP, B3LYP); 6-311++G**, 6-311++G(3df,2pd).

4. **Frequency calculations:**

   harmonic,

   anharmonic VPT2 ?

5. **Comparison of theory with experiment**

CBS Estimation of NMR parameters

In thermochemistry series (hierarchies) of basis sets (aug-)cc-pVXZ
(for X = 2, 3, 4, 5 i 6) and three-parameter exponential function are used:
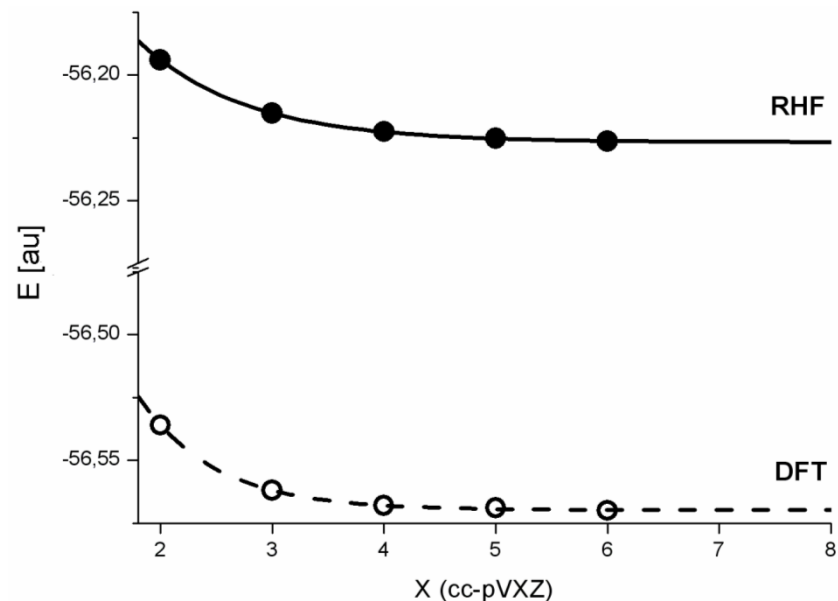
$$Y(X) = Y(\infty) + A*(exp(-B*X).$$

$Y(\infty)$ is estimated value of parameter in infinity (for complete basis set, $X = \infty$), A i B are
fitting parameters. A two-parameter function:

$$Y(X) = Y(\infty) + A/X^3.$$

Estimation of atomic or molecular parameter
in the *complete basis set limit (CBS)*.

**T. H. Dunning, J. Phys. Chem. A, 2000, 104, 7799.**
A. Halkier, W. Klopper, T. Helgaker, J. Chem. Phys., 1999, 111, 4424.

Basis sets:
(aug)-cc-pVXZ   Dunning
(aug)-pc-n   Jensen

(24) Dunning, T. H., Jr. *J. Phys. Chem. A* **2000**, *104*, 9062−9080.
(25) Jensen, F. *J. Chem. Phys.* **1999**, *110*, 6601−6605.
(26) Jensen, F. *J. Chem. Phys.* **2001**, *115*, 9113−9125.
(27) Jensen, F. *J. Chem. Phys.* **2002**, *116*, 7372−7379.
(28) Jensen, F. *J. Chem. Phys.* **2003**, *118*, 2459−2463.
(29) Jensen, F.; Helgaker, T. *J. Chem. Phys.* **2004**, *121*, 3463−3470.
(30) Jensen, F. *Chem. Phys. Lett.* **2005**, *402*, 510−513.
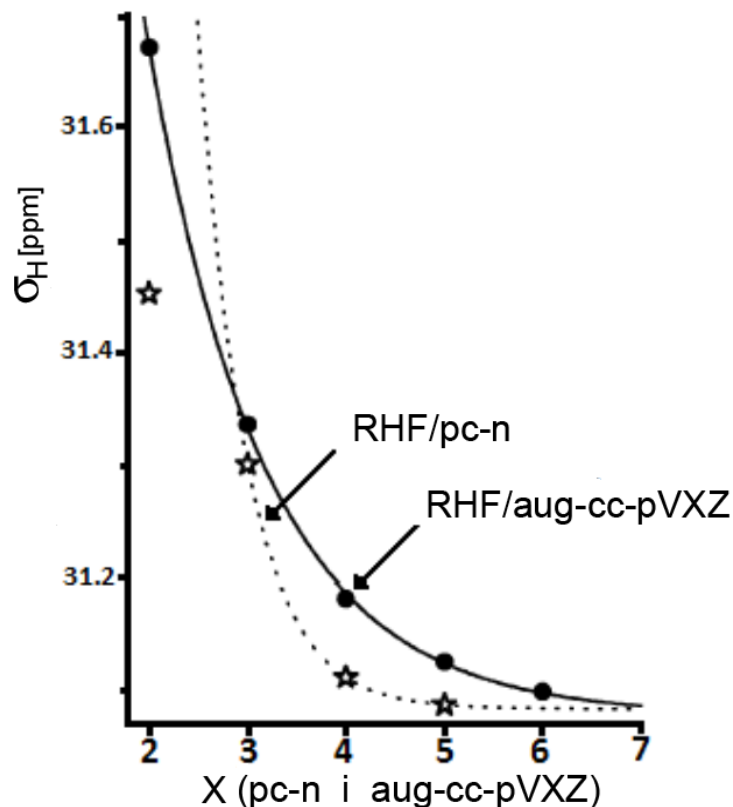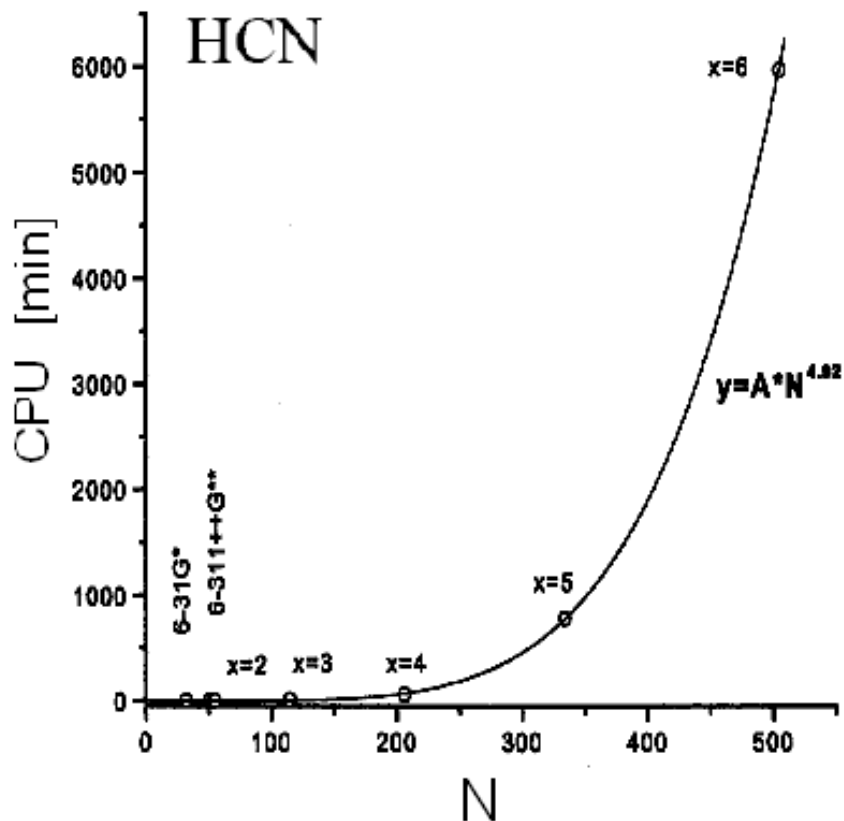
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Table 3. CPU Time (min) of Benzene Calculations

		CPU Time		
basis set	N	opt.	freq.	NMR
		B3LYP (VSXC)		
STO-3G	36	3.8 (7.2)	8.9 (10.4)	1.1 (2.3)
6-31G*	102	7.6 (16.8)	33.5 (55.4)	5.2 (5.7)
STO-3G$_{el}$	126	6.6 (37.5)	80.2 (132.5)	9.2 (11.2)
STO-G$_{mag}$	126	7.3 (36.3)	70.0 (125.5)	7.9 (14.2)
pcS-2	282	29.5 (69.9)	190.3 (301.9)	50.2 (44.1)

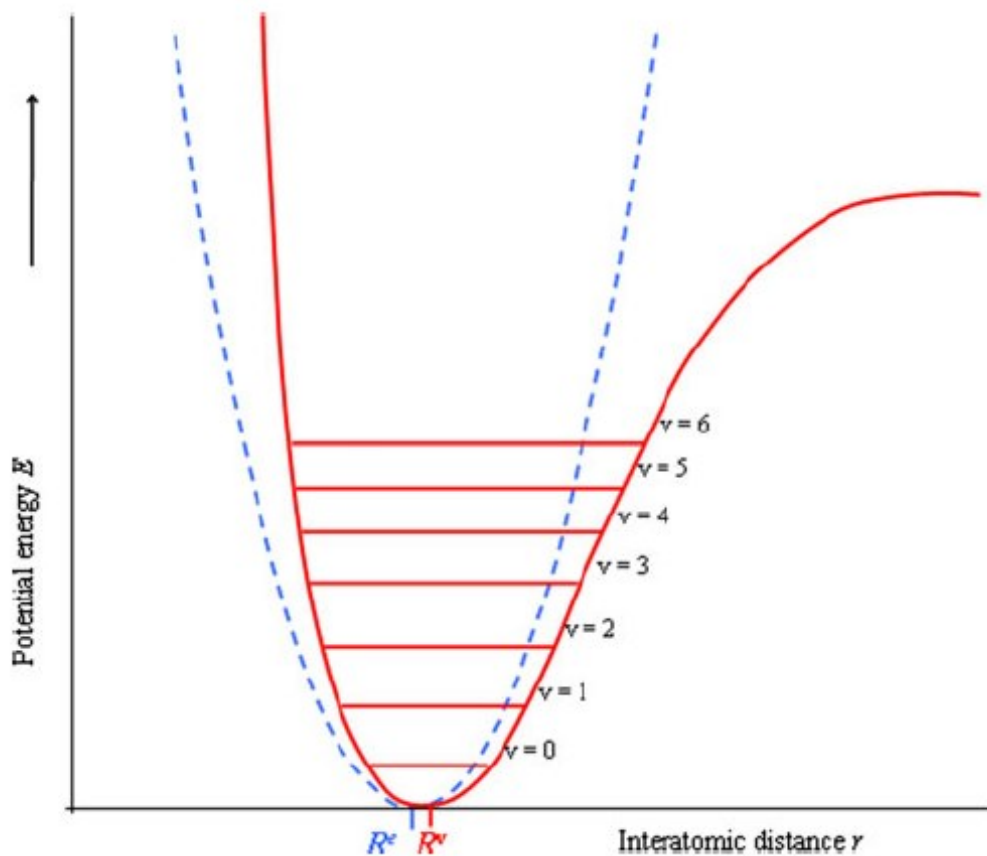# Harmonic vs anharmonic frequencies (modeling IR/Raman spectra)

Fig. 1 Schematic representation of the potential energy surface of two interacting atoms using harmonic (*dashed line*) vs anharmonic (*solid line*) approximations
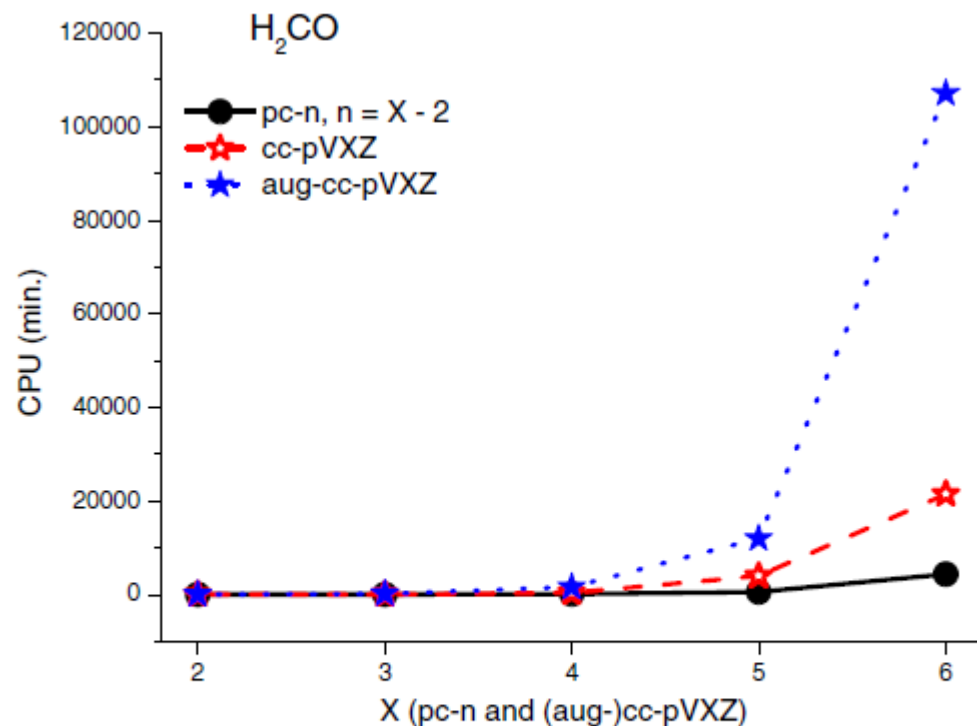

Fig. 3 CPU time (min) dependence on the type and size of basis set for formaldehyde VPT2 calculation with pc-*n*, cc-pVXZ and aug-cc-pVXZ basis sets

VPT2 model

Efficient Modeling of NMR Parameters in Carbon Nanosystems

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S *Supporting Information*

ABSTRACT: Rapid growth of nanoscience and nanotechnology requires new and more powerful modeling tools. Efficient theoretical modeling of large molecular systems at the *ab initio* and Density Functional Theory (DFT) levels of theory depends critically on the size and completeness of the basis set used. The recently designed variants of STO-3G basis set (STO-3G$_{el}$, STO-3G$_{mag}$), modified to correctly predict electronic and magnetic properties were tested on simple models of pristine and functionalized carbon nanotube (CNT) systems and fullerenes using the B3LYP and VSXC density functionals. Predicted geometries, vibrational properties, and HOMO/LUMO gaps of the model systems, calculated with typical 6-31G* and modified STO-3G basis sets, were comparable. The ^{13}C nuclear isotropic shieldings, calculated with STO-3G$_{mag}$ and Jensen's polarization consistent pcS-2 basis sets, were also identical. The STO-3G$_{mag}$ basis sets, being half the size of the latter one, are promising alternative for studying ^{13}C nuclear magnetic shieldings in larger size CNTs and fullerenes.

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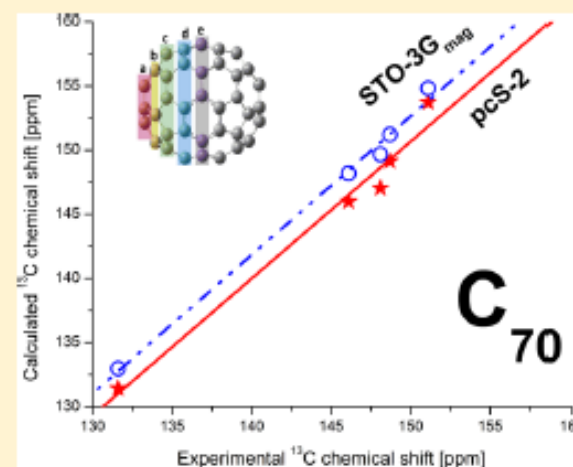
Scheme 1. Bond Labeling in Linearly Conjugated Planar (p) Benzene Rings (acenes, $n = 1-9$)
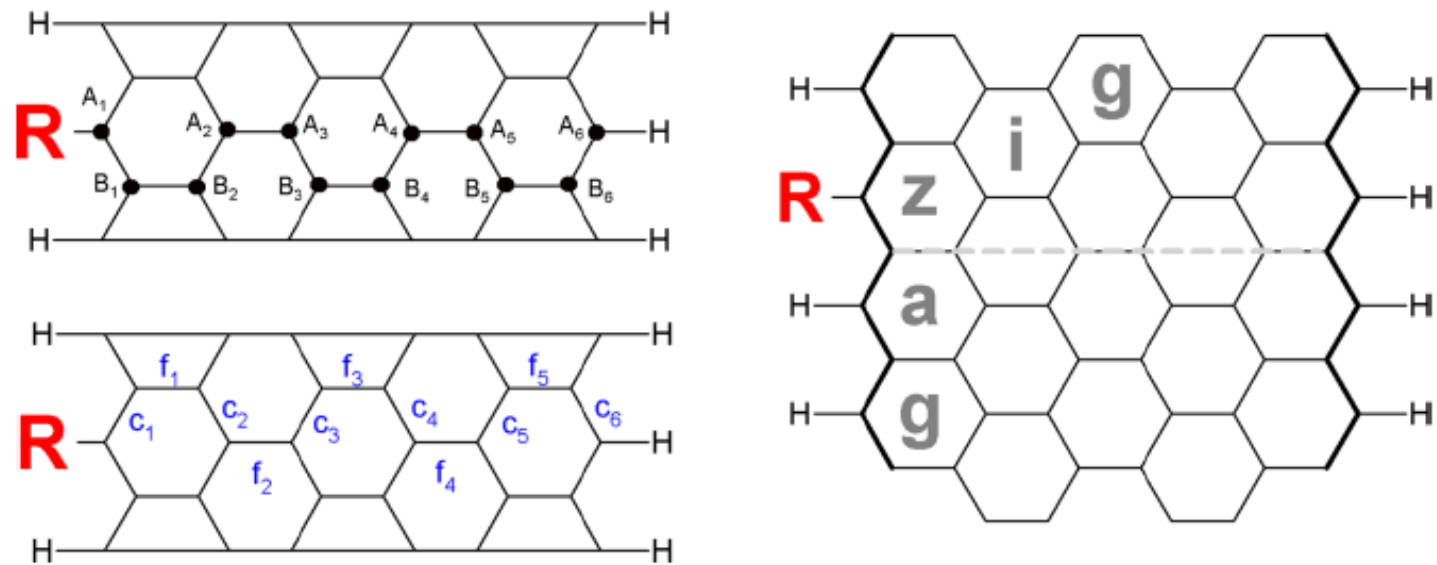

R = OH, COOH, NH$_2$
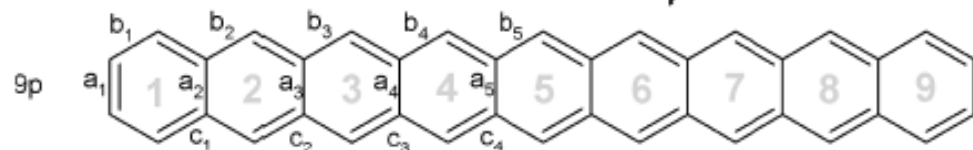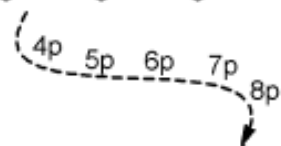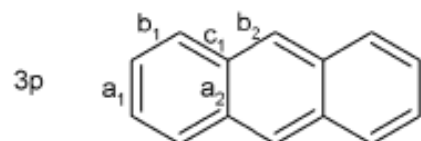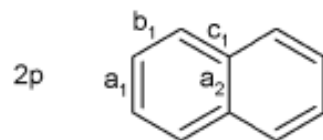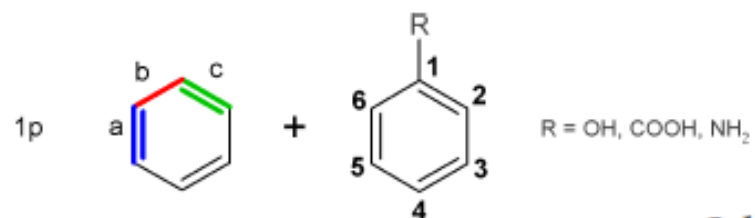
Scheme 2. Bond Labeling in Molecular "Belt" Systems (Cyclacenes, where $n = 4-8$)

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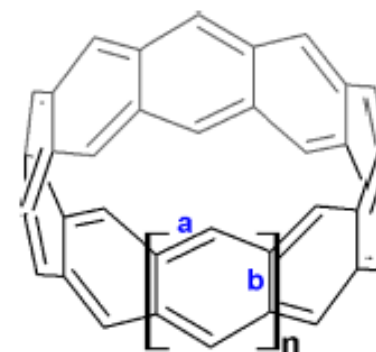
Scheme 3. Bond and Atom Labeling in Short *Zigzag* (4,0) SWCNT Model Consisting of Five "Bamboo" Units[a]

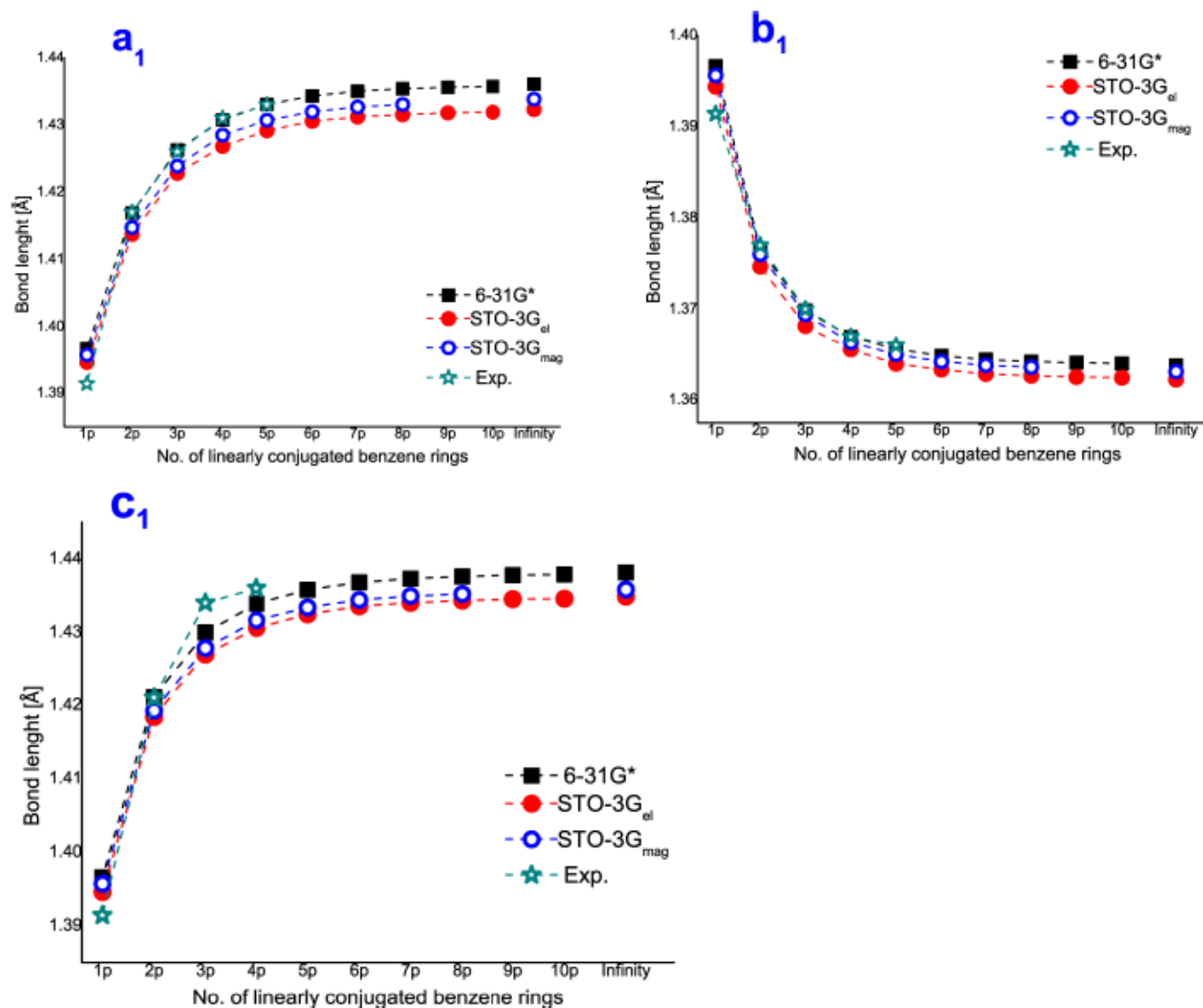[a]A dashed line indicates tube axis and the two *zigzag* type rims are marked by a thicker line.

Figure 1. Regular convergence of three types of C−C bond lengths in polyaromatic hydrocarbons, calculated using B3LYP combined with 6-31G*, STO-3G$_{mag}$, and STO-3G$_{el}$ basis sets, upon increasing the number of linearly conjugated benzene rings (see Scheme 1): (A) a_1 type, (B) b_1 type, (C) c_1 type. Experimental data are from refs 78, 101−103 and individual points are connected for the reader's convenience.

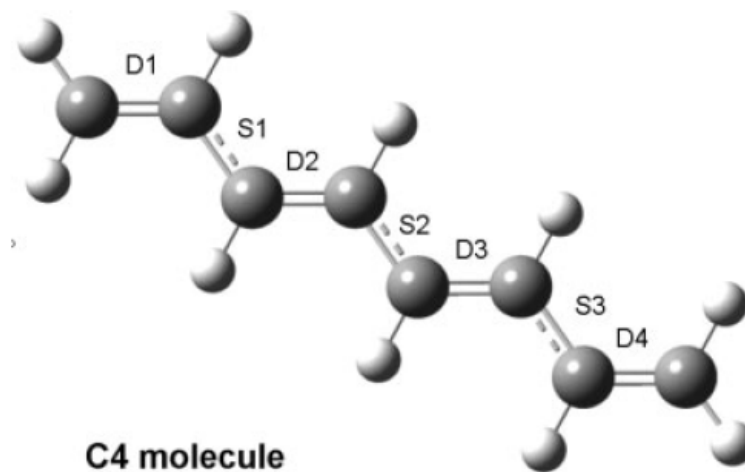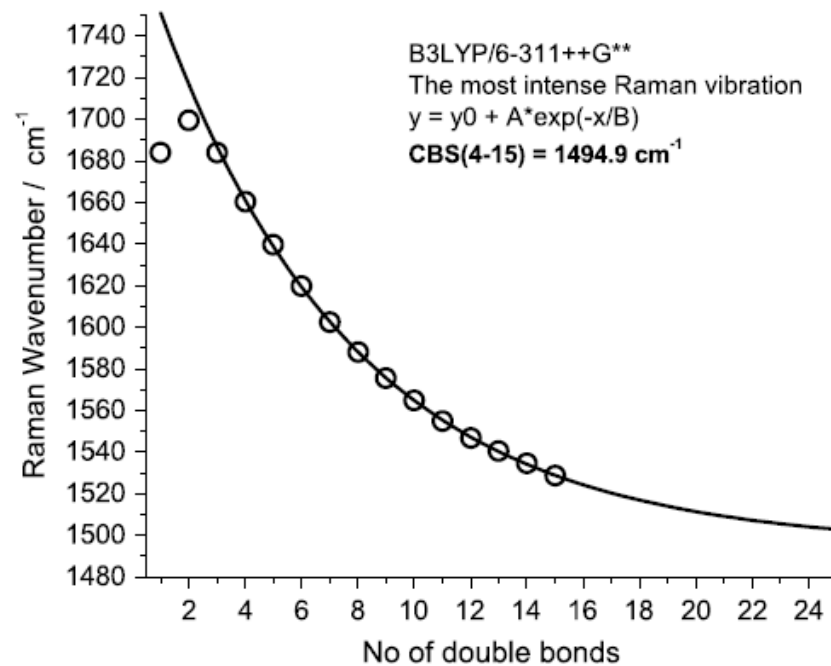# Red coral (an art piece from Asia)
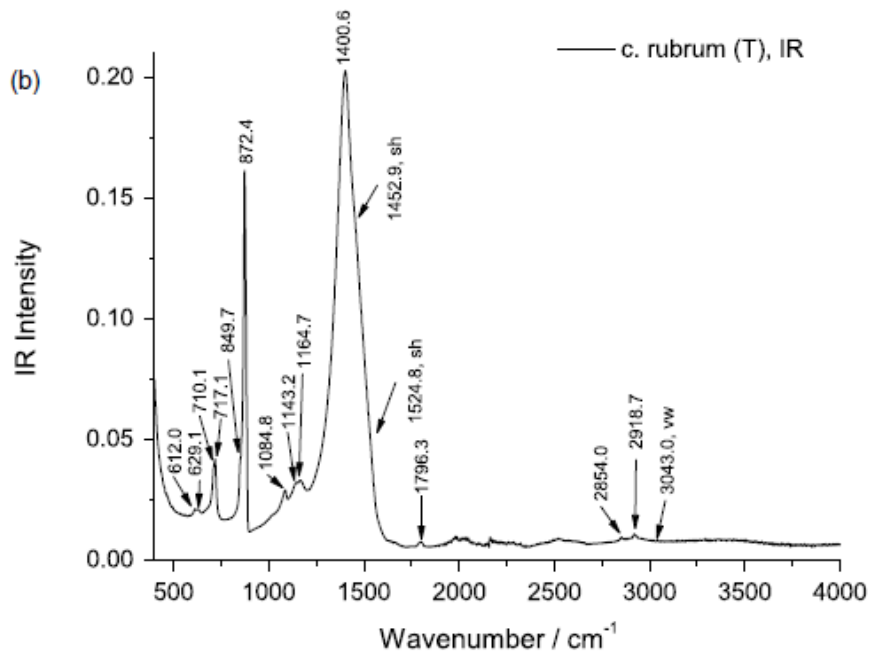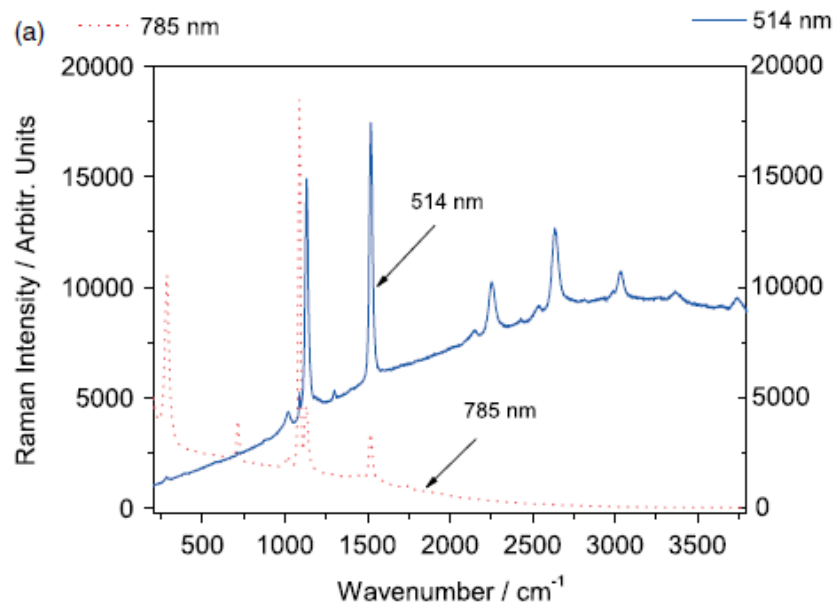
Figure 3. (A) Raman spectrum of red coral (Italy) recorded with 514 and 875 nm laser lines. (B) FT-IR spectrum of red coral (Taiwan).

C4 molecule

Figure 4. Schematic presentation of all-trans linear polyene chain (C4 molecule) containing four double bonds with labeled double and single bonds (due to symmetry D1 = D4, D2 = D4, S1 = S3, S2 ≠ S1, S3).

B3LYP/6-311++G**
The most intense Raman vibration
$y = y_0 + A*\exp(-x/B)$
CBS(4-15) = 1494.9 cm^{-1}

Figure 5. Wavelength of the most intense Raman band as function of the number of double bonds in all-*trans*-polyenes (B3LYP/6-311++G** structure). The continuous line represents a decaying exponential fit.
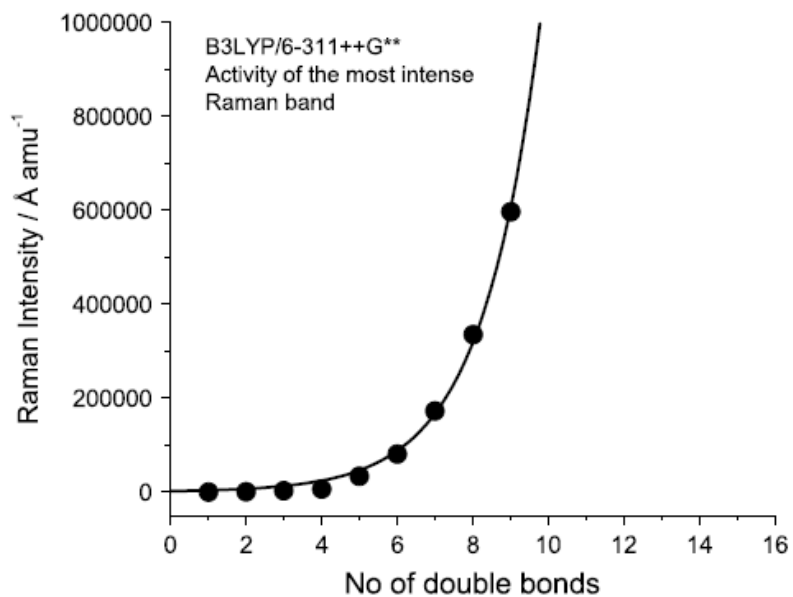
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Figure 6. Raman activity of the most intense Raman band as function of the number of double bonds in all-*trans*-polyenes (B3LYP/6-311++G** structure). The continuous line represents an exponential fit.

Table 2. Comparison of theoretically predicted most intense Raman harmonic vibrations (wavenumbers in cm^{-1}, B3LYP/6-311++G** unscaled and scaled) for selected Cn molecules with the experimental signal from red coral

		Scaled		Experimental	
n	Unscaled	0.96	0.97	514 nm	785 nm
6	1620	1555	1571		
7	1602	1538	1554		
8	**1590**	**1526**	1542		
9	**1577**	**1514**	**1530**		
10	**1565**	**1502**	**1518**		
11	1555	1493	**1508**		
12	1548	1486	**1502**		
13	1540	1478	1494		
14	1533	1472	1487		
15	1529	1468	1483		
16	1524	1463	1478		
Raman (limit)	**1491**	**1431**	**1446**		
Red coral (Italy)				1521.5;	1517.3;
Red coral (Taiwan)				1520.7	1516.1

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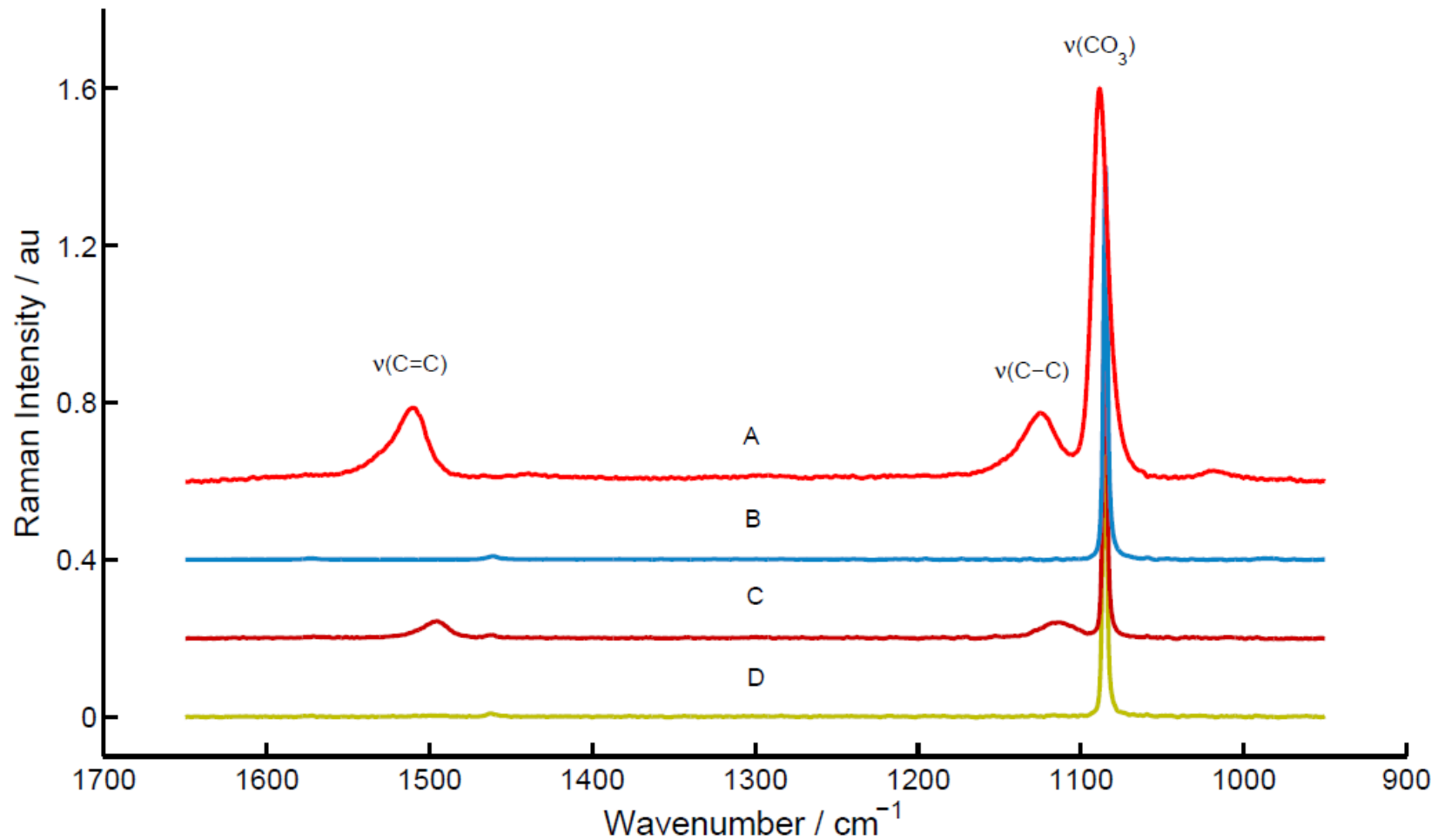**Experimental and theoretical studies on corals. On the nature of pigments in red coral and African snail shell (Helixia Aspersa)**
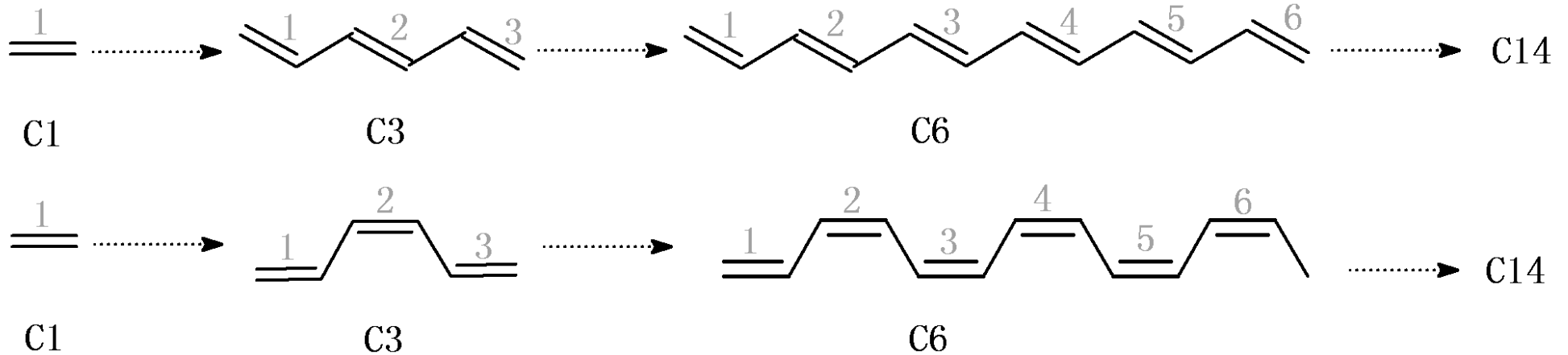
Ethylene and Model all-trans and all-cis polyenes containing 2-14 conjugated C=C units
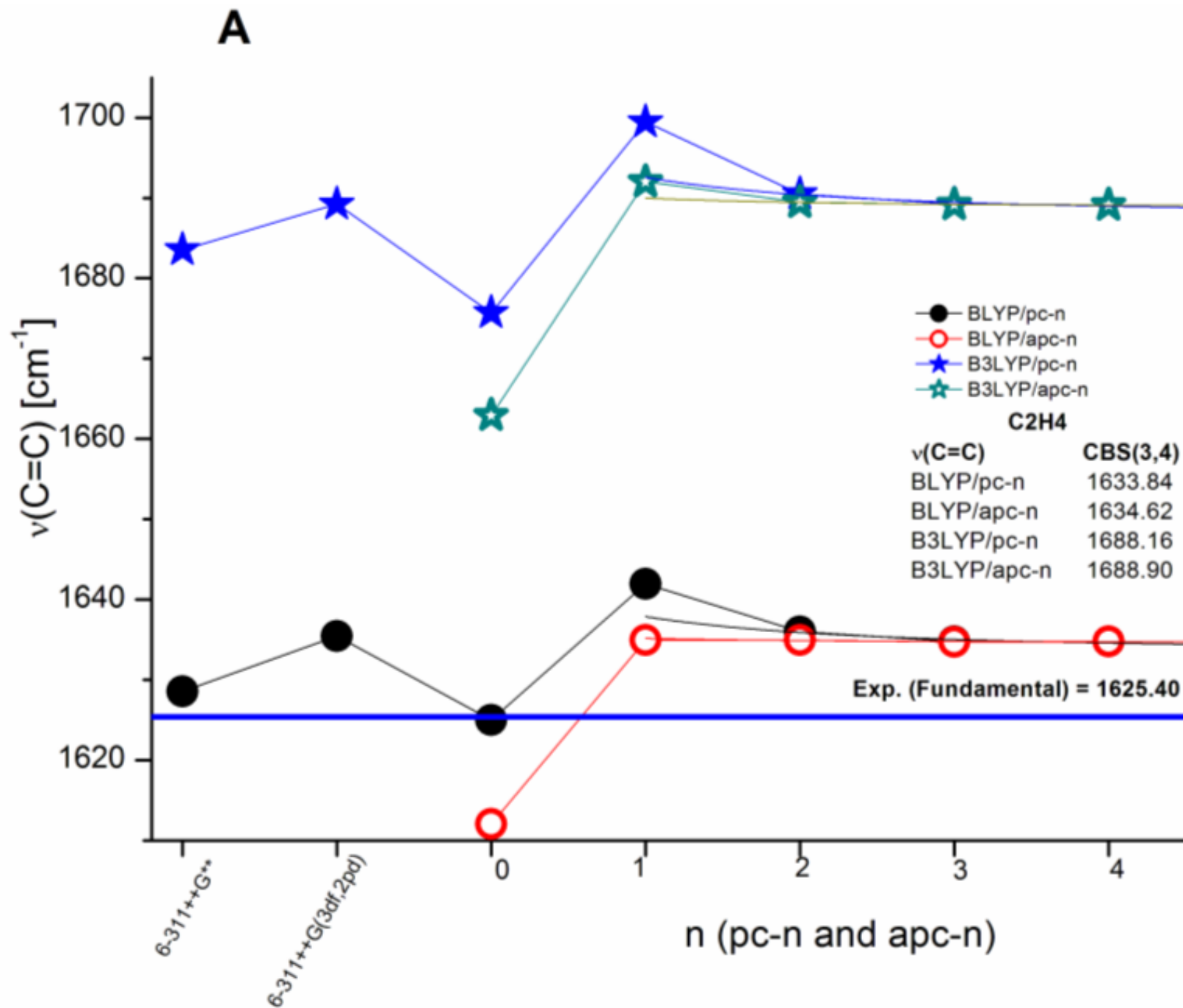
20
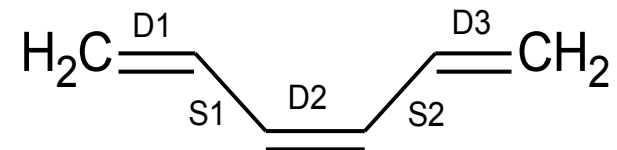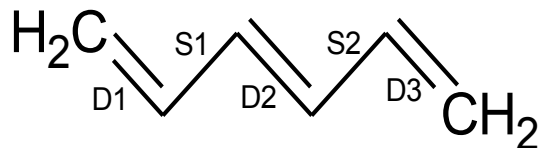
(left) typical shell of Helixia Aspersa snail and (top) selected fragments of Raman spectra (1064 nm laser beam) of (A) red and (B) white coral, (C) dark part and (D) white part of African snail shell
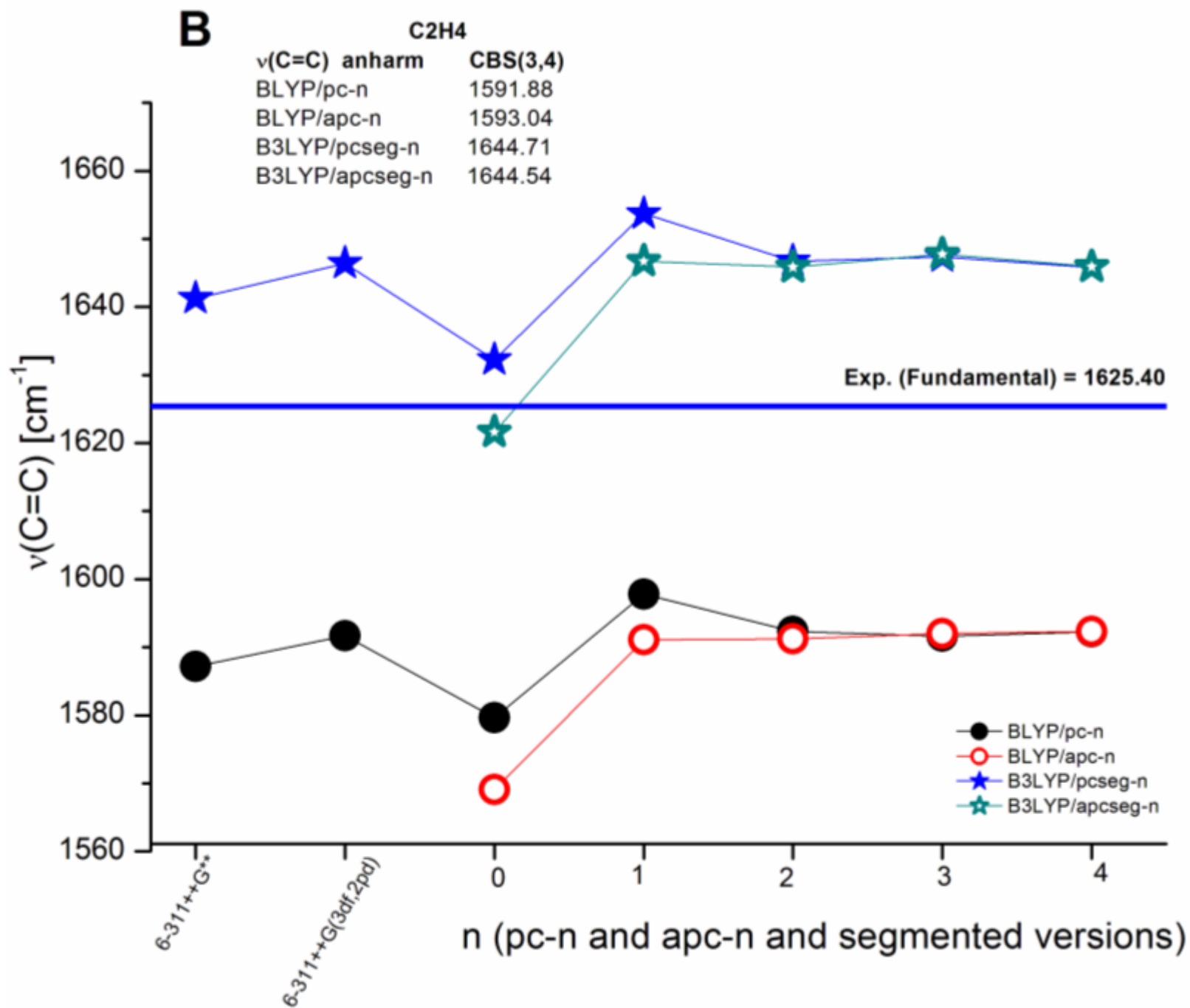
Structural parameters and v(C=C) harmonic and anharmonic frequencies of ethylene calculated using BLYP and B3LYP density functionals and selected basis sets. The CBS values were fitted with two-parameter formula from Eq. 2.

Method/Basis	No. of b. f.	r(CC)	r(CH)	CCH	v(C=C) Harmonic	v(C=C) Fundamental /Anharm
B3LYP						
6-311++G**	72	1.3289	1.0850	121.74	1683.54	1641.27
6-311++G(3df,2pd)	138	1.3247	1.0823	121.74	1689.25	1646.41
pc-n (CBS)	26 – 470	1.3240	1.0815	121.73	1688.16	1644.71[a]
aug-pc-n (CBS)	38 - 642	1.3239	1.0815	121.74	1688.90	1644.54[b]
BLYP						
6-311++G**	72	1.3384	1.0915	121.79	1628.54	1587.18
6-311++G(3df,2pd)	138	1.3341	1.0887	121.79	1635.46	1591.71
pc-n (CBS)	26 – 470	1.3335	1.0877	121.78	1633.84	1591.88
aug-pc-n (CBS)	38 - 642	1.3334	1.0877	121.79	1634.62	1593.04
Lit.						
Best composite theory[c]		1.3307	1.0809	121.44		
Best composite theory[d]		1.3308	1.0803	121.40		
Semi-experimental[e]		**1.3305(10)**	**1.0805(10)**	**121.45(10)**	**1656.4[f]**	**1625.40[g]**

Ethylene: harmonic ν(C=C)

A

ν(C=C) [cm^{-1}]

1700

1680

1660

1640

1620

- BLYP/pc-n
- BLYP/apc-n
- B3LYP/pc-n
- B3LYP/apc-n

C2H4

ν(C=C)	CBS(3,4)
BLYP/pc-n	1633.84
BLYP/apc-n	1634.62
B3LYP/pc-n	1688.16
B3LYP/apc-n	1688.90

Exp. (Fundamental) = 1625.40

6-311++G**

6-311++G(3df,2pd)

0   1   2   3   4
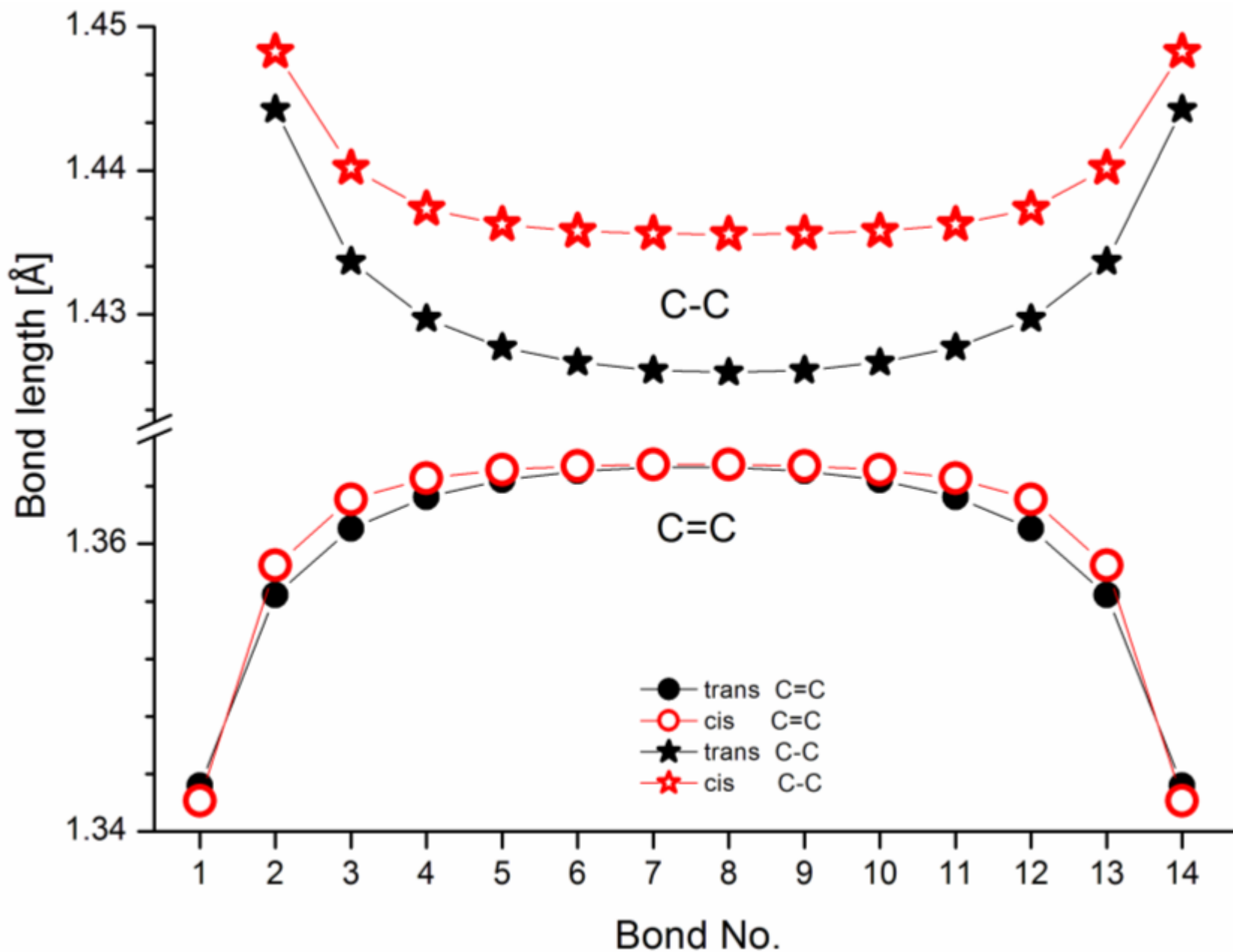
n (pc-n and apc-n)

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Ethylene: anharmonic ν(C=C)

Change of B3LYP/6-311++G** calculated C=C bond length in all-trans polyenes
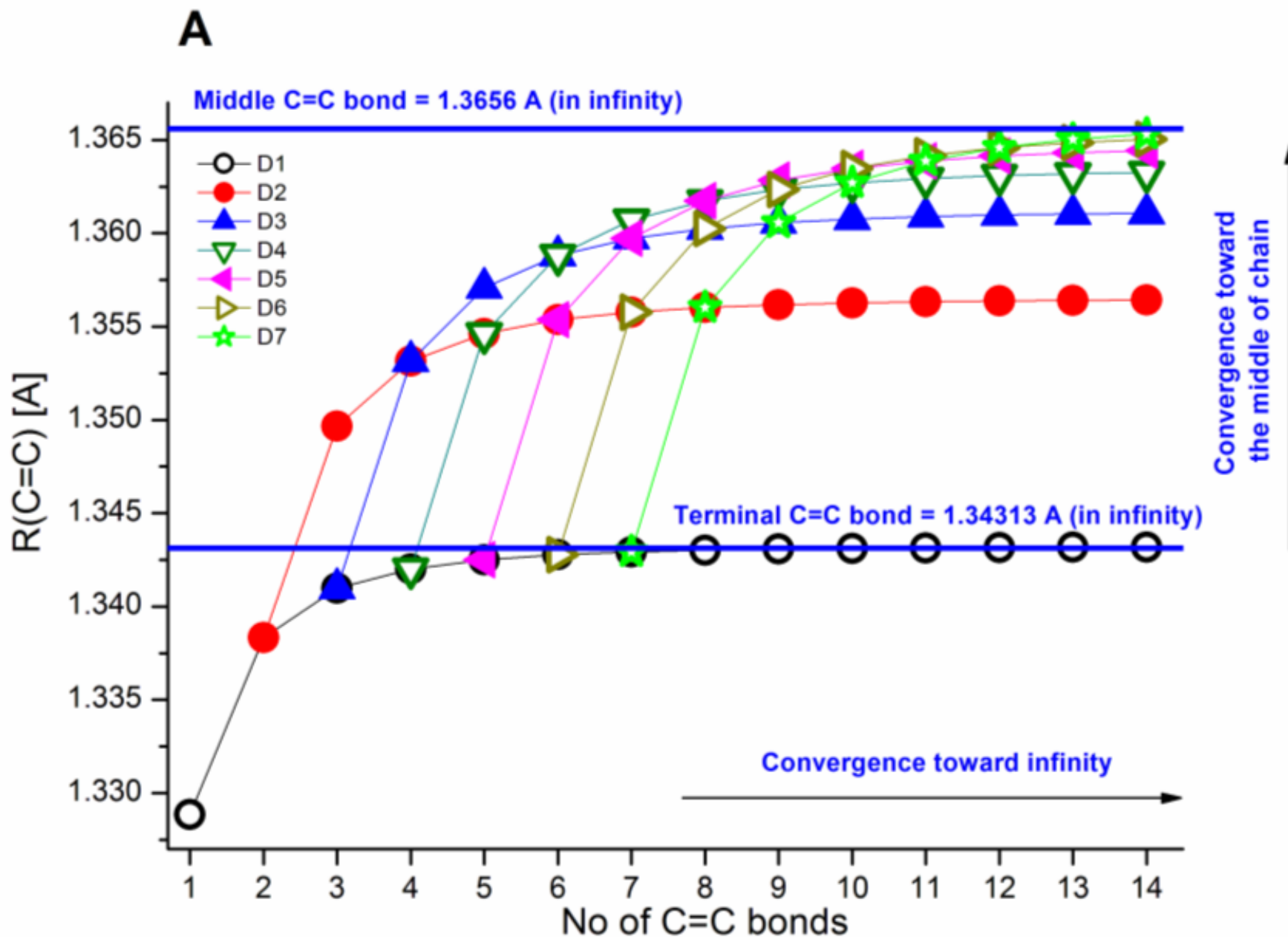
## Change of B3LYP/6-311++G** calculated C=C bond length in all-trans polyenes
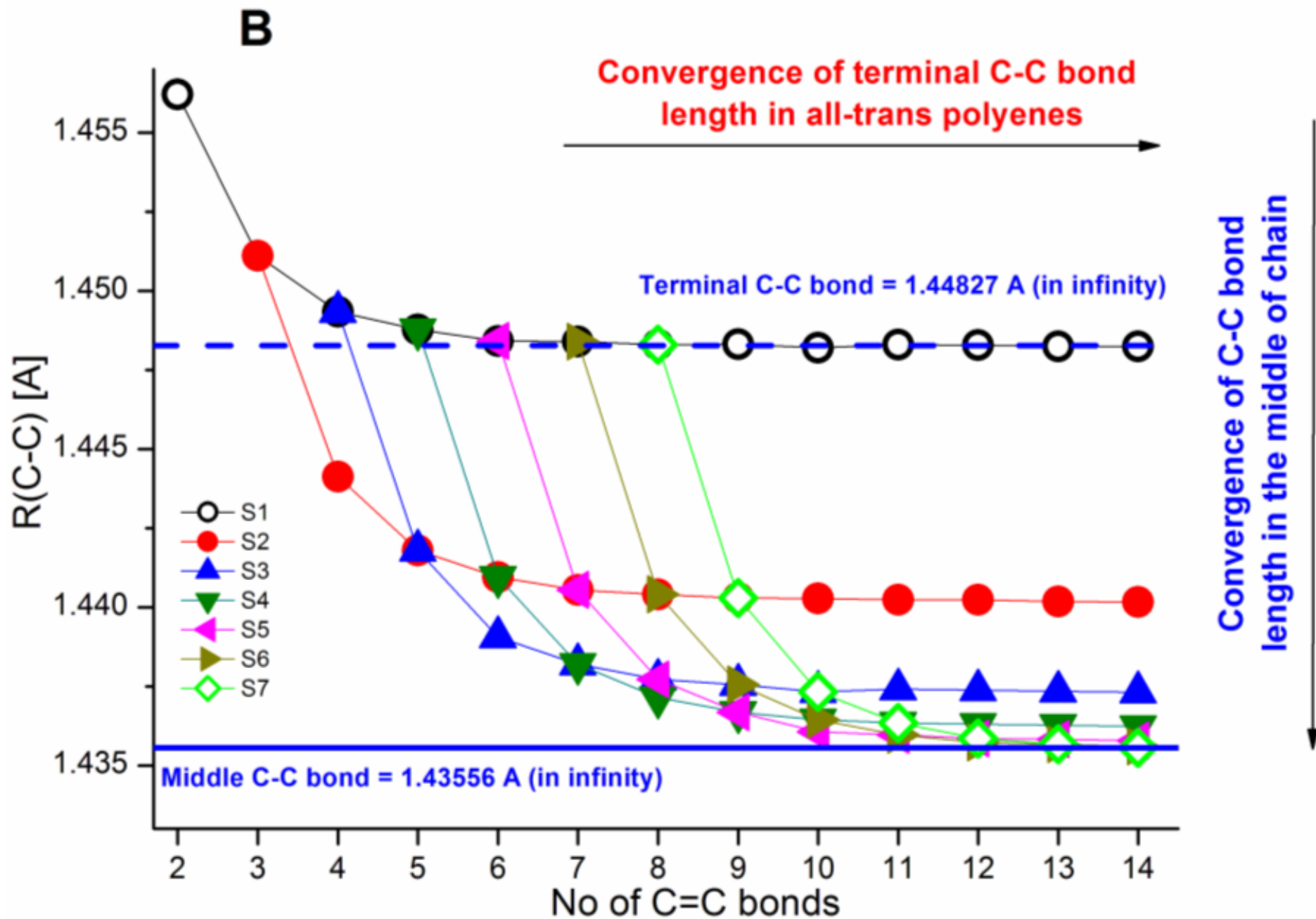
Opposite patterns of C-C and C=C bond lengths change (B3LYP/6-311++G** results) along all-trans and all-cis polyene chains containing 14 conjugated double bonds

Estimated C=C and C-C bond lengths for very long all-trans and all-cis polyene chains (from three-parameter fitting of B3LYP and BLYP values calculated with 6-311++G** basis set) and deviations from the reference C=C and C-C values

Bond	all-trans		all-cis	
	B3LYP	**BLYP**	**B3LYP**	**BLYP**
C=C				
Terminal	1.343	1.357	1.342	1.355
Middle	1.366	1.387	1.365	1.385
C-C				
Terminal	1.444	1.446	1.448	1.450
Middle	1.426	1.422	1.436	1.433
Reference				
C=C in C_2H_4	1.329	1.338	1.329	1.338
"naked" C-C sp^2-sp^2		1.482[a]		
C-C in C_2H_6	1.531	1.542	1.531	1.542
Deviation				
C=C from C_2H_4				
Terminal	0.014	0.018	0.013	0.017
Middle	0.037	0.048	0.037	0.046
C-C from "naked" C-C				
Terminal	-0.037	-0.036	-0.034	-0.032
Middle	-0.056	-0.060	-0.046	-0.048

Sensitivity of Raman active single, and double carbon-carbon stretching frequencies (unscaled BLYP/6-311++G** results) to the length of all-trans and all-cis polyene chains. The observed band positions in Raman spectra of red coral (continuous line) and snail Helixia Aspersa (dashed line) are also shown.
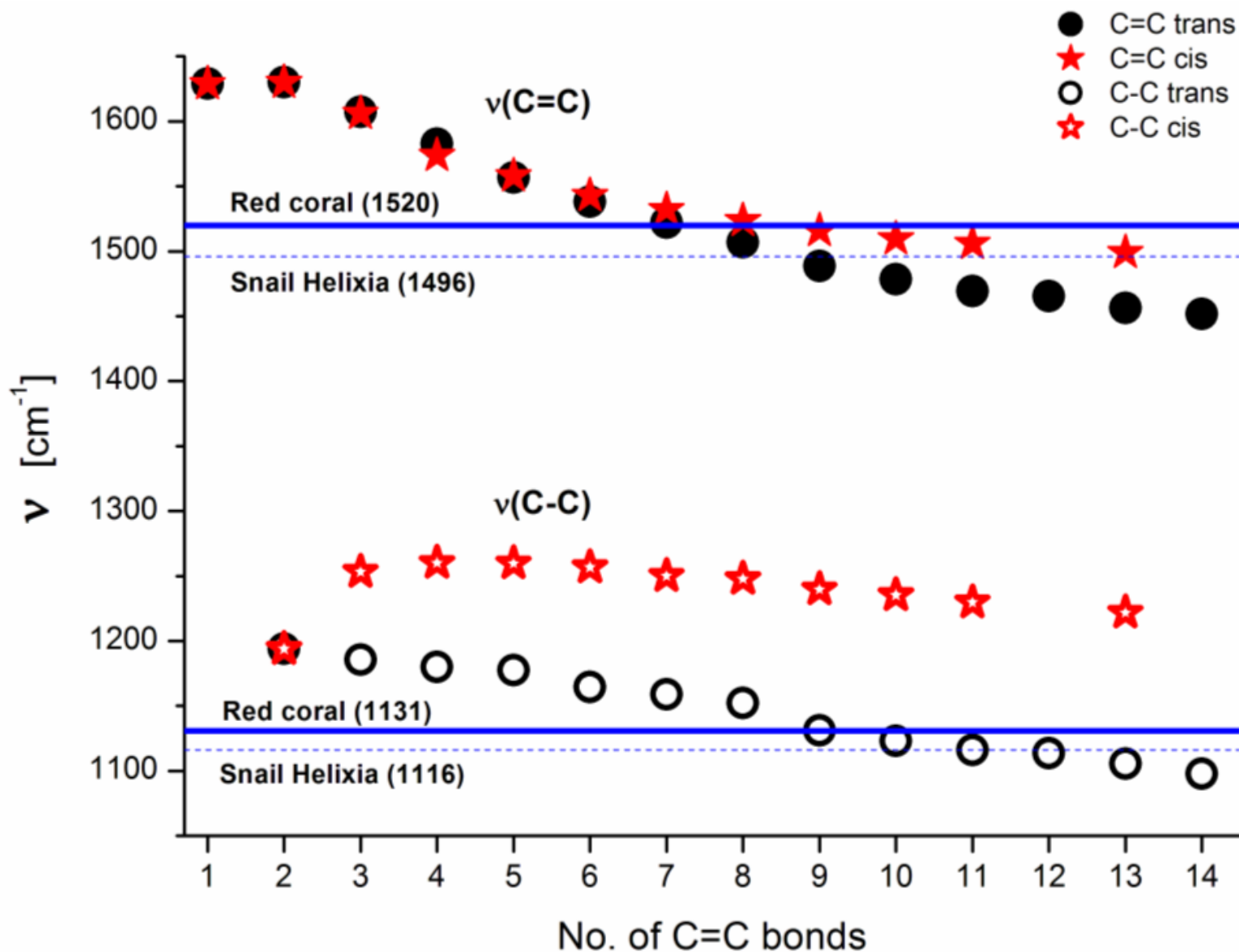
Comparison of BLYP/6-311++G** calculated (unscaled) harmonic ν(C=C) and ν(C-C) frequencies in all-trans tert-buthyl ended polyenes containing 3 to 12 C=C bonds with experiment.
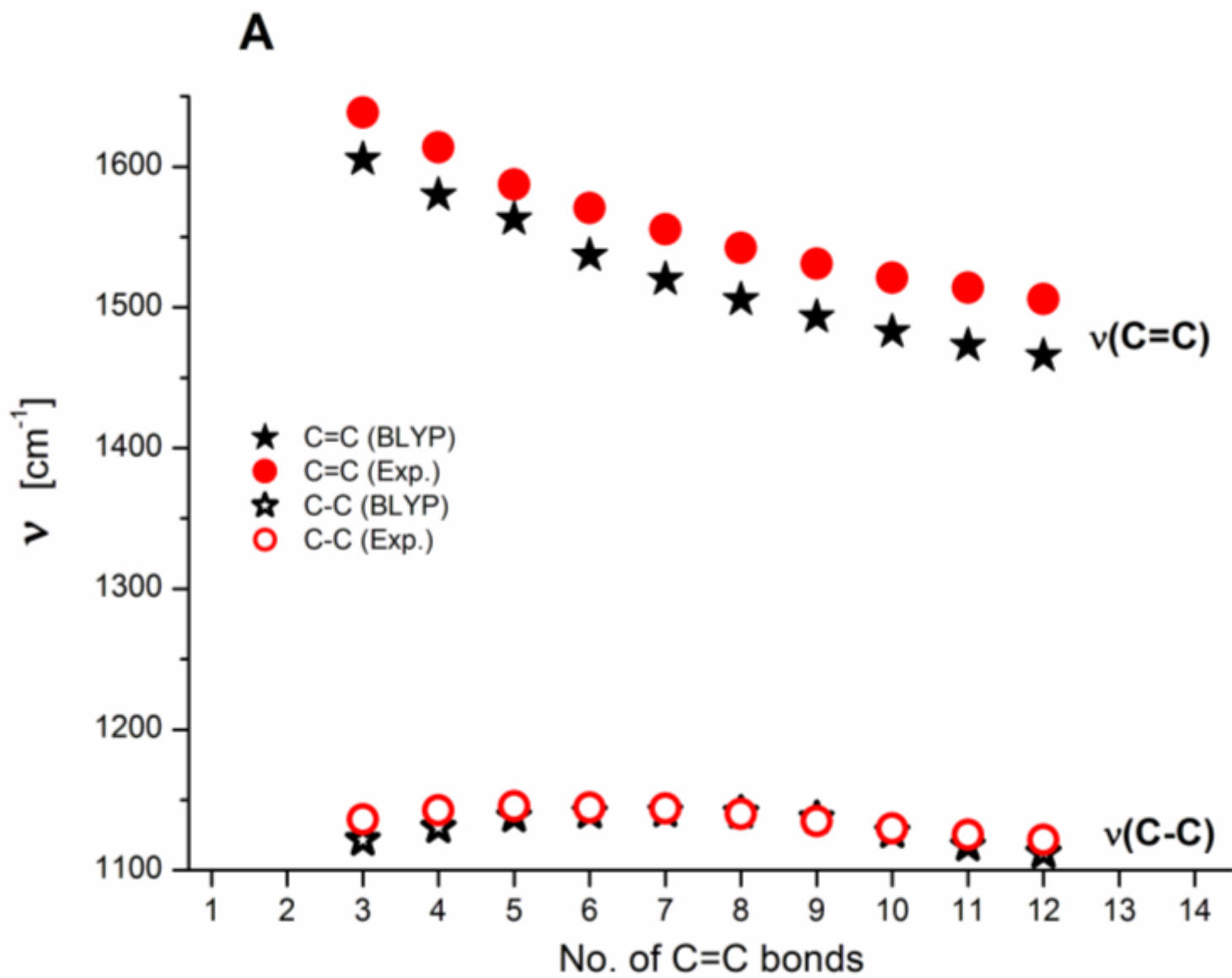
Trends in deviations between B3LYP/6-311++G** calculated harmonic n(C=C) and n(C-C) frequencies in all-trans tert-buthyl ended polyenes vs. chain length. Linear fits of data points and fitting parameters are shown, too.
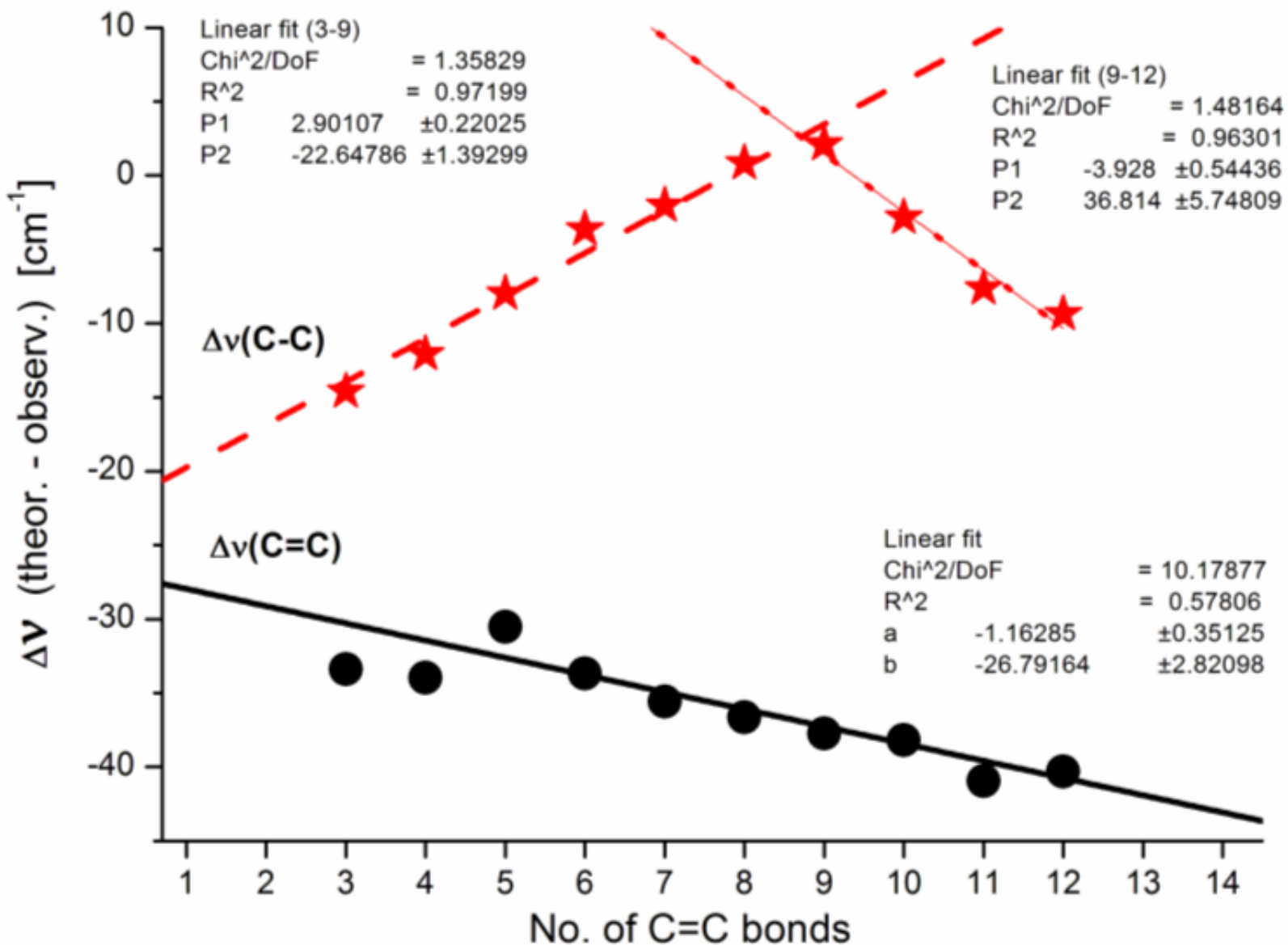
Comparison between raw and **c**orrected B3LYP/6-311++G** calculated harmonic $\nu(C=C)$ and $\nu(C-C)$ frequencies in ethylene and all-trans C2 – C14 polyenes with measured Raman bands positions in red coral and snail shell pigments.
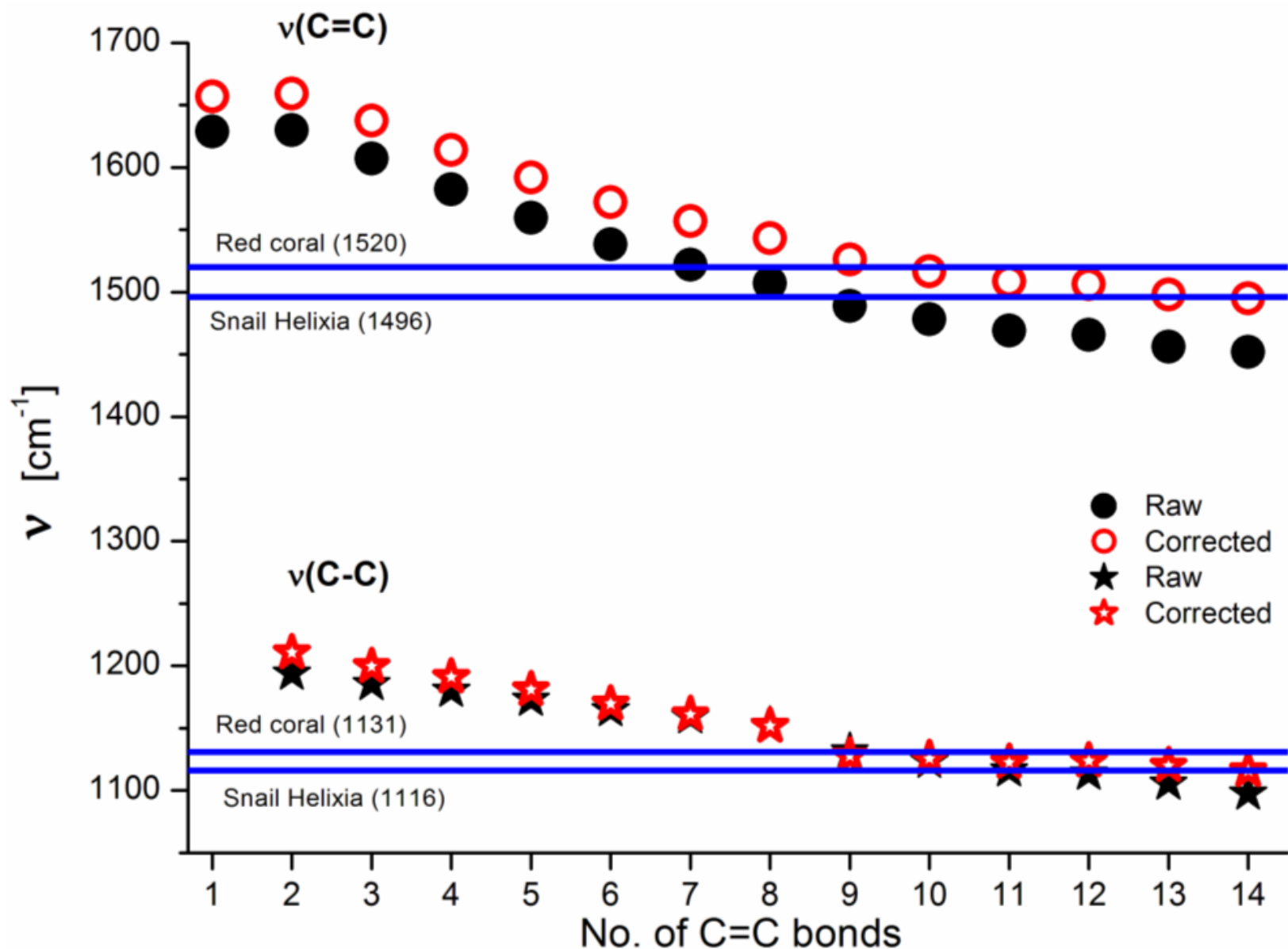
Conclusions:

1. Recommendations for structural, IR/Raman calculations:

Ethylene: CBS and VPT2 with Jensen basis sets (?)

Polyenes:

structure (B3LYP/6-311++G**),

harmonic frequencies (BLYP/6-311++G**).

2. All-trans polyenic pigments contain several C=C units:

9-12 (red coral)

10-14 (dark parts of African snail shell)

ACKNOWLEDGMENT

KAPITAŁ LUDZKI
NARODOWA STRATEGIA SPÓJNOŚCI

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