

Supporting Information

Theoretical investigation and computational evaluation of overtone and combination features in resonance Raman spectra of polyenes and carotenoids

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We present here an additional example: all-trans hexatriene. This molecule has been considered for testing Peticolas-Nafie-Stein (PNS) theory of Raman overtones and combinations and provides opportunity of comparing with alternative approaches based on the evaluation of Franck-Condon (or Huang-Rhys - HR) factors – notably Albrecht's theory (see ref [11] of the main text and [1]). From this point of view it is worth to recall that the calculation of HR factors is not needed in the PNS approach, rather the HR coefficients are implicitly embedded. This is stated explicitly in ref. [7] of the main text.

The evaluated HR factors for the lowest bright singlet excited state of hexatriene are given in **Table 1** below and are sizeable, showing that the geometry difference between the equilibrium structure of the ground and excited states is also remarkable (see **Table 2** for the CC bond length changes upon excitation). For sake of comparison, the corresponding data for β -carotene are given in **Table 3**. β -carotene is more conjugated than all-trans hexatriene and exhibits a smaller bond length change upon excitation.

ν_k (cm^{-1} , unscaled)	S_k
350.1	0.2109
445.4	0.2016
1226.4	0.1831
1321.6	0.1755
1708.4	0.9940

Table 1. Huang Rhys factors of all-trans hexatriene (after TD-B3LYP/6-31G** calculations) relative to the lowest bright singlet excited state.

CC bond # (from head to tail of conjugated backbone)	R_{CC}^e (\AA)	R_{CC}^g (\AA)	$R_{CC}^e - R_{CC}^g$ (\AA)
1	1.388	1.342	0.045
2	1.411	1.450	-0.039
3	1.430	1.352	0.078
4	1.411	1.450	-0.039
5	1.388	1.342	0.045

Table 2. Equilibrium bond length change upon excitation from the ground (g) to the lowest bright singlet excited state (e) of all-trans hexatriene (after TD-B3LYP/6-31G** calculations).

CC bond # (from head to tail of conjugated backbone)	R_{CC}^e (\AA)	R_{CC}^g (\AA)	$R_{CC}^e - R_{CC}^g$ (\AA)
1	1.358	1.367	0.010
2	1.475	1.460	-0.015
3	1.355	1.370	0.016
4	1.454	1.434	-0.020
5	1.368	1.389	0.021
6	1.434	1.412	-0.023
7	1.364	1.389	0.025
8	1.443	1.415	-0.028
9	1.374	1.403	0.029
10	1.428	1.400	-0.028
11	1.368	1.398	0.030
12	1.428	1.400	-0.028
13	1.374	1.403	0.029
14	1.443	1.415	-0.028
15	1.364	1.389	0.025
16	1.434	1.412	-0.023
17	1.368	1.389	0.021
18	1.454	1.434	-0.020
19	1.355	1.370	0.016
20	1.475	1.460	-0.015
21	1.358	1.367	0.010

Table 3. Equilibrium bond length change upon excitation from the ground (g) to the lowest bright singlet excited state (e) of β -carotene (after TD-B3LYP/6-31G** calculations)

At first we evaluated the absorption spectrum of hexatriene following the method described in [2,3] which makes use of HR factors (differently from [2] we have adopted Lorentzian lineshape instead of Gaussian). The result of the simulation of electronic absorption of all-trans hexatriene is reported in **Figure 1** and compared with experimental data available from the literature [4]. Inspection of **Figure 1** reveals that the HR factors determined by the level of theory we have adopted (**Table 1**) are reliable since they produce a good simulation of the vibronic structure of the UV-Vis absorption spectrum.

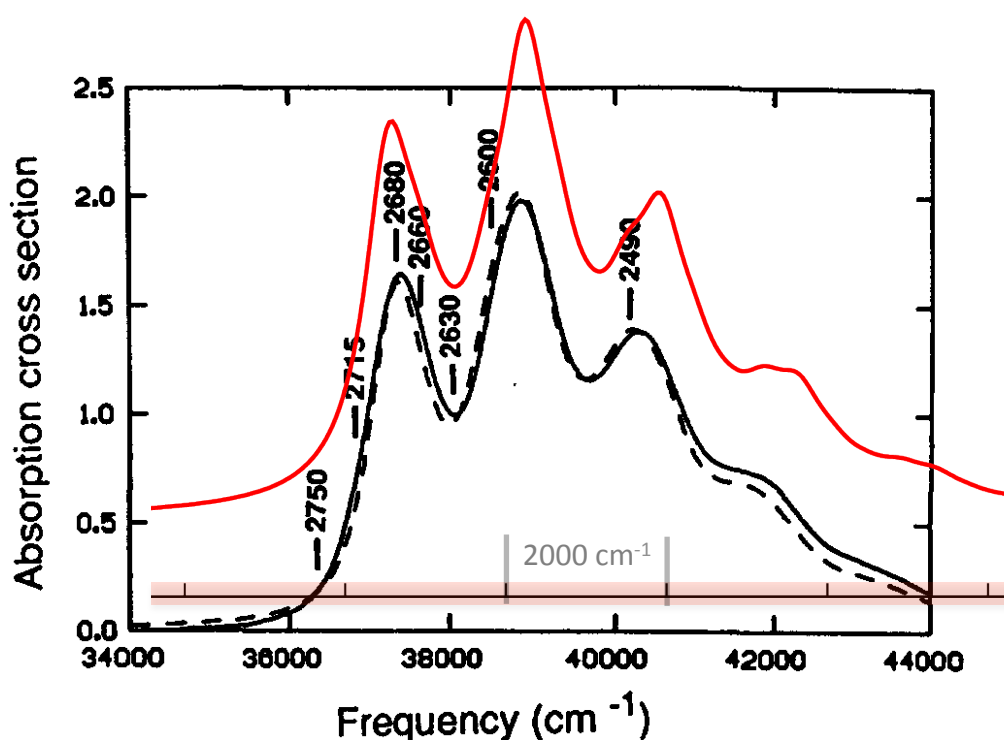


Figure 1. Electronic absorption spectrum of all-trans hexatriene in cyclohexane [4]. The experimental spectrum is reported with a solid black line; the calculated fit (using experimentally deduced parameters) is reported as broken line. The simulated absorption using data from DFT calculations (B3LYP/6-31G**) is given as a red line. The origin of the simulated spectrum has been fixed in such a way to superimpose the 0-0 transition experimentally found at 2680 Å. Then the spacing of 2000 cm⁻¹ between the horizontal axis marks has been matched in the two plots. Scaling factor of 0.965 has been adopted for DFT computed vibrational frequencies, consistently with resonant Raman calculations and the rest of calculations on β -carotene.

Hence we considered the simulation of the Raman response in perfect resonance by means of PNS theory (*i.e.* eqs. 15-19 of the main text). The comparison with experimental data available in literature [4] is pretty good (see **Figure 2**). This is within the rather small and acceptable inaccuracies of the chosen method in determining vibrational structure and the gradient at FC point.

We conclude that the selected quantum chemistry approach and PNS theory is a very good starting point for analyzing resonance Raman overtones/combination spectra in polyenes and presumably also in many other π -conjugated systems.

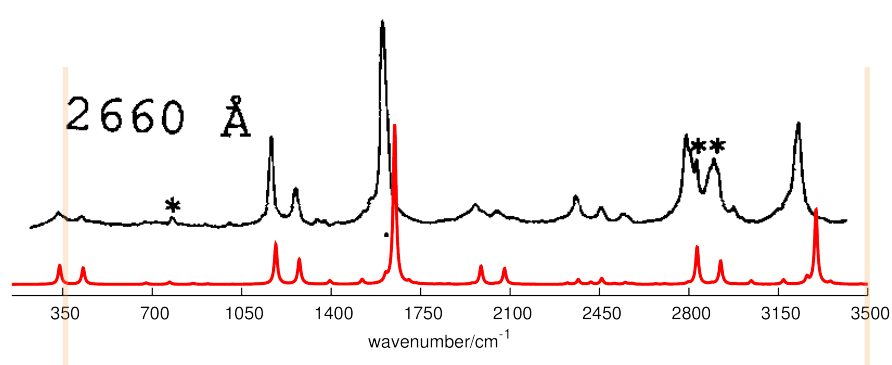


Figure 2. Resonance Raman spectrum of all-trans hexatriene. Comparison between experiments in cyclohexane [4] (solvent peaks marked with *) and present calculations based on DFT (red line). The scaling factor of vibrational frequencies computed with DFT is 0.965. Comparison with literature data recorded on hexatriene in gas phase [5] reveals that the doublet computed in the vicinity of 2800 cm^{-1} is real and partially masked by solvent peaks.

References

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