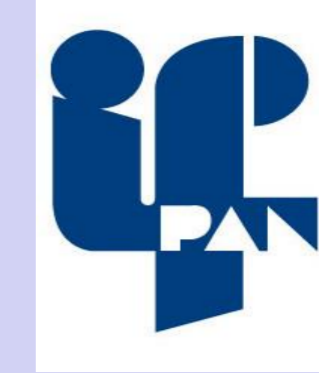


# SOLVING THE PUZZLE OF RED CHROMOPHORE IN ULTRAMARINE PIGMENTS BY ELECTRONIC STRUCTURE METHODS

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## 1. MOTIVATION

Ultramarines (UM) are well known blue pigments, both synthetic & mineral (lazurite). Their blue coloration stems from  $S_3^{\bullet-}$  radicals embedded in the protective matrix of sodalite (SOD) type aluminosilicates. It is possible to produce **red UM** (actually various shades of violet or pink), where red chromophore accompanies the blue one. However, the nature of red chromophore was not resolved experimentally ( $S_4, S_4^{\bullet-}, S_3Cl$  suggested). This work aims to identify this species by means of the density functional theory (DFT) calculations.

## 2. CLUES

- ✓ Species larger than  $S_4$  are unlikely to fit SOD cages.
- ✓ Red UM are obtained by heating blue UM with chlorine, which may imply  $S_xCl_y$  species. Clark *et al. Inorg. Chem.* **1983**, 17, 3169
- ✓ But, the analogues of red UM were obtained in Cl free process. Kowalak & Jankowska *Micropor. Mesopor. Mater.* **2003**, 61, 213; Basnayake & co. *Micropor. Mesopor. Mater.* **2016**, 219, 172
- ✓ Absorption @520 nm observed in sulfur vapors/melts & ascribed to *cis*- $C_{2v}$ - $S_4$  molecule. Hassanzadeh & Andrews *J. Phys. Chem.* **1992**, 96, 6579; Steudel & Wong *Chem. Phys. Lett.* **2003**, 379, 162
- ✓ Red UM reported to be less paramagnetic than blue UM, suggesting non-radical chromophore. Klinowski & co. *Nature* **1987**, 330, 56



## 3. MODELS & METHODS

### (i) Periodic models of tetrasulfides encapsulated in SOD:

several stoichiometries & initial orientations of  $S_4/S_4^{\bullet-}$



DFT/PBE geometry optimization +  $\Gamma$  point phonons

QUANTUM ESPRESSO code: PW cutoff = 40 Ry, ultrasoft pseudo-potentials,  $\Gamma$  point only in Brillouin zone

### (iia) Cluster models cut from above (dangling bonds saturated with H)

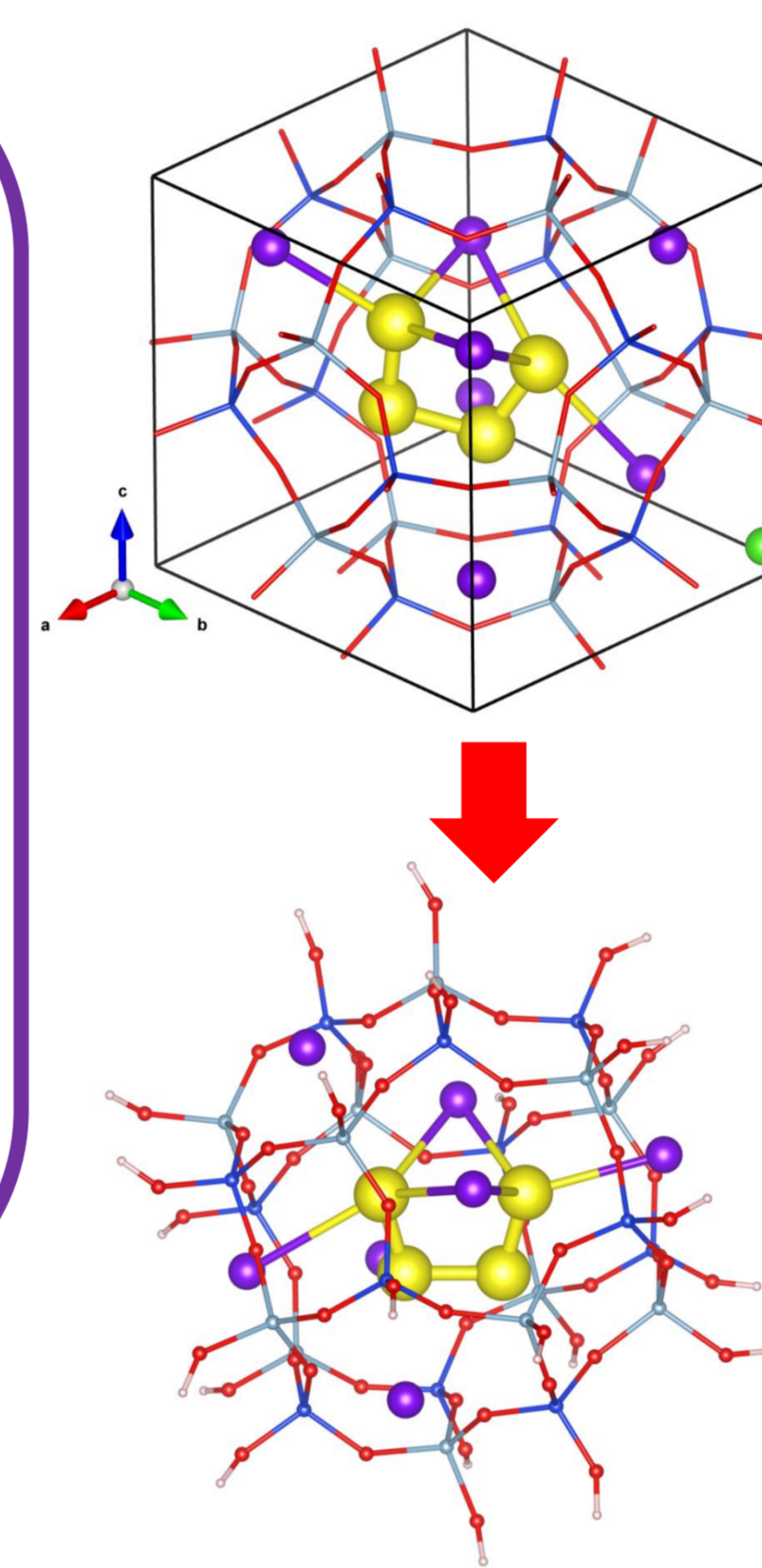


time-dependent DFT /LC-BLYP\* calculations of UV-Vis excitations

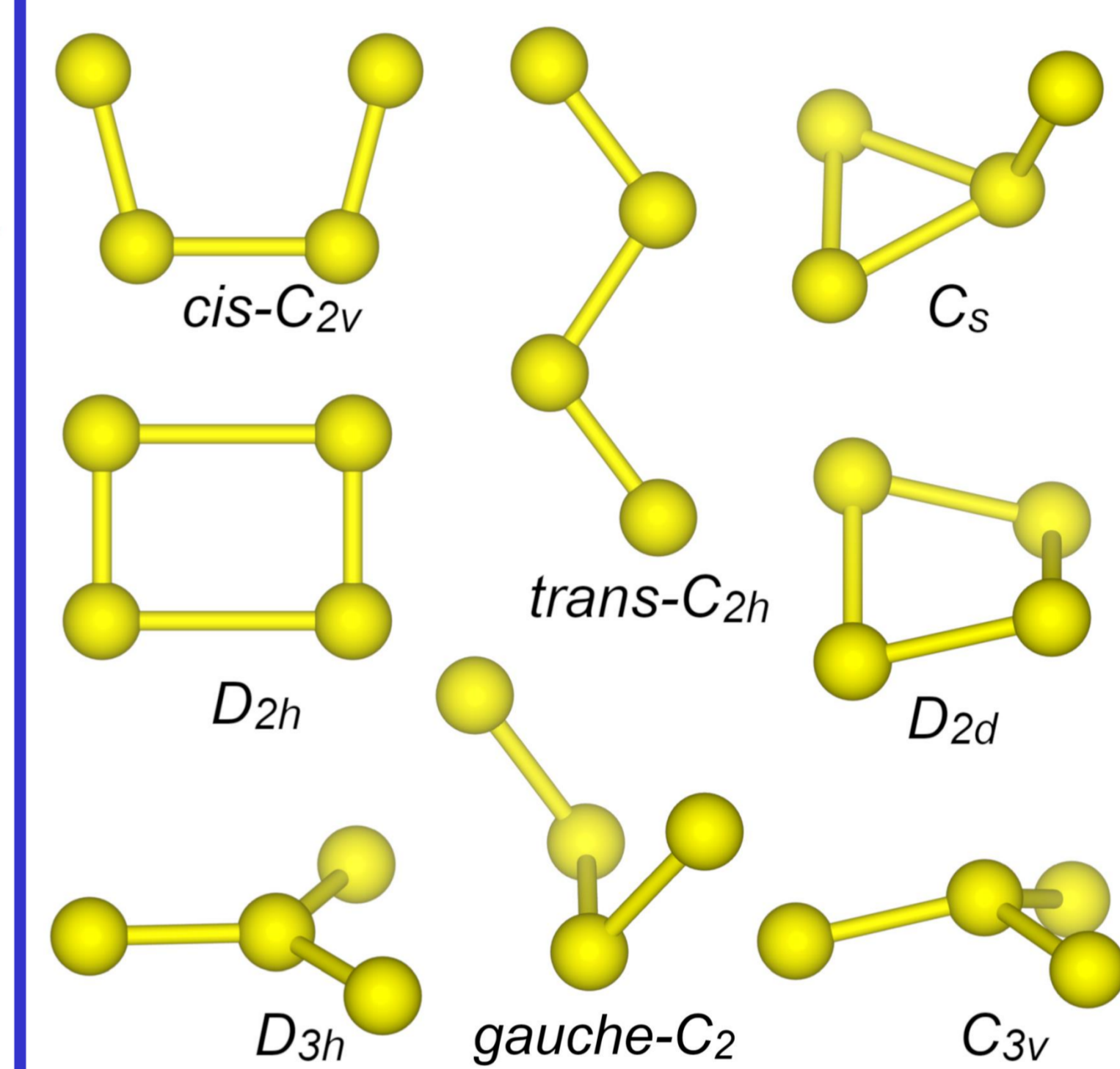
### (iib) Gas phase $S_4/S_4^{\bullet-}$ DFT optimization/vibrational analysis + single point wavefunction method

calculations: CCSD(T), CASSCF+NEVPT2.

ORCA code: polarized triple & quadruple zeta Gaussian basis// \* long range corrected hybrid functional



### Tetrasulfur isomers considered in this work



## 4. RESULTS

### (i) Energetic ordering of isomers

$S_4$

$S_4^{\bullet-}$

Gas *cis*- $C_{2v}$  > *trans*- $C_{2h}$  >>  $C_s$  >>  $D_{3h} \approx D_{2d}$

*cis*- $C_{2v} \approx$  *trans*- $C_{2h}$  >>  $C_{3v}$  >>  $C_s$

SOD *cis*- $C_{2v}$  >>  $C_s$  > *gauche*- $C_2$ , *trans*- $C_{2h}$  >  $D_{3h}$  >  $D_{2d}$

*cis*- $C_{2v}$  >> *gauche*- $C_2$  >  $C_{3v}$  >  $C_s$

$D_{2h}$  transition state, *gauche* unstable in gas phase,  $D_{3h}/C_{3v}$  stable only for  $S_4/S_4^{\bullet-}$

### (ii) UV-Vis excitations

The most intensive optical transitions in gas phase are due to

HOMO  $\rightarrow$  LUMO in  $S_4$  & SOMO-1/-2  $\rightarrow$  SOMO in  $S_4^{\bullet-}$ .

The relevant states preserve their characters upon embedding in SOD (periodic & cluster models), the excitations for cluster models can be interpreted accordingly.

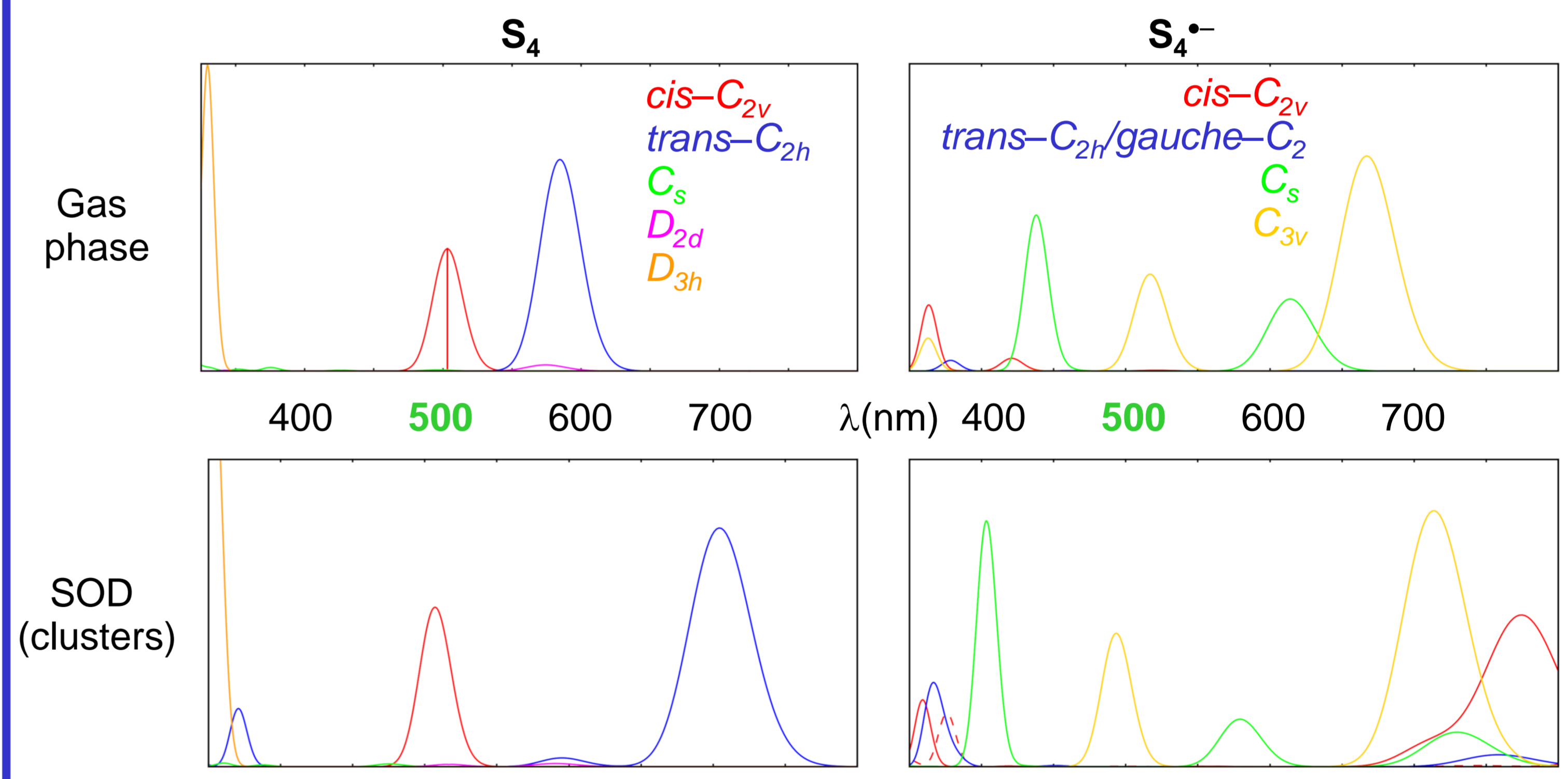
Only *cis*- $C_{2v}$ - $S_4$  &  $C_{3v}$ - $S_4^{\bullet-}$  absorb strongly green light.

(i) & (ii) Credibility of DFT confirmed by CCSD(T) & CASSCF+NEVPT2 calculations for gas phase  $S_4/S_4^{\bullet-}$  (only mild multireference character found for *cis*- & *trans*- $S_4$ ).

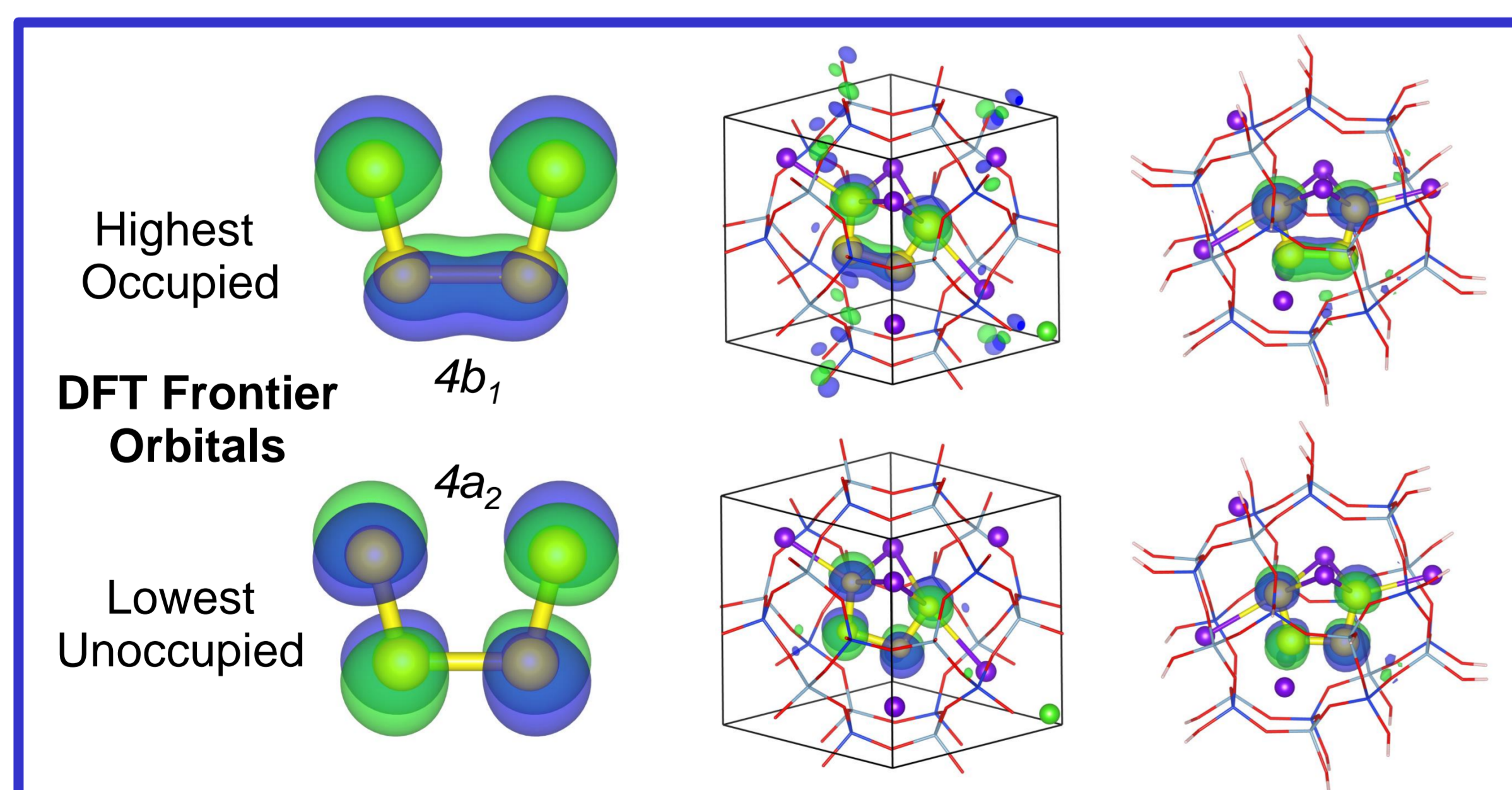
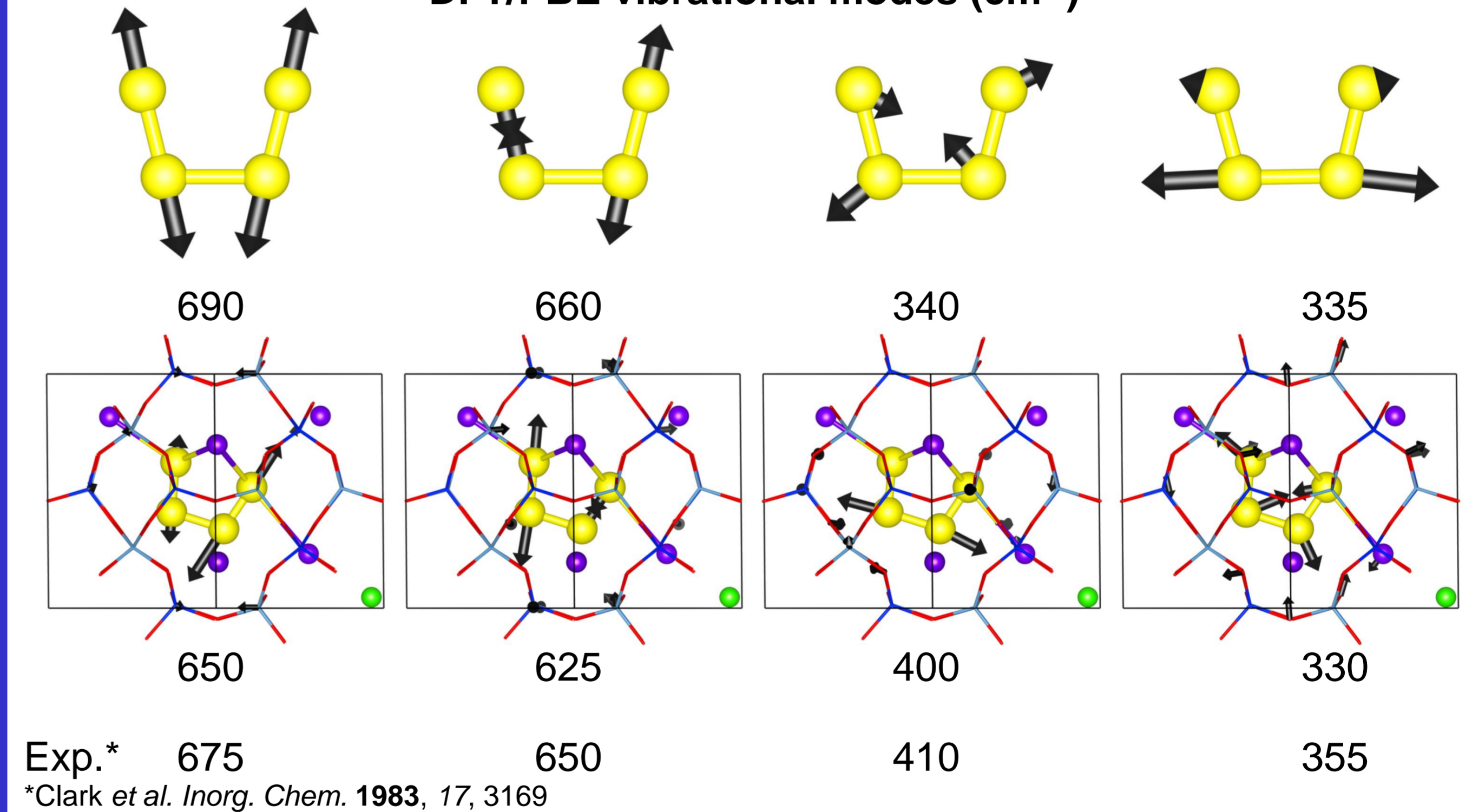
### (iii) Vibrational analysis

Only *cis*- $C_{2v}$ - $S_4$  matches well exp. Raman data: none other tetrasulfide has both bands about 400 & 650  $cm^{-1}$ .

### DFT/LC-BLYP UV-Vis absorption energies



### DFT/PBE vibrational modes ( $cm^{-1}$ )



## 5. CONCLUSIONS

- ✓ *cis*- $C_{2v}$  isomers are the most stable ones for both neutral  $S_4$  molecules & ionic  $S_4^{\bullet-}$  radicals in gas phase & embedded in SOD.
- ✓ *cis*- $C_{2v}$ - $S_4$  is the only plausible candidate for red chromophore: it strongly absorbs green light (~520 nm) & its vibrational modes match exp. Raman spectra.
- ✓ The embedding of tetrasulfides within the aluminosilicate matrices:
  - changes the relative energetic stability of isomers, destabilize/stabilize species present/absent in gas phase
  - shifts the positions & lift accidental degeneracy of certain vibrational modes
  - strongly affects the electron excitation energies for anionic tetrasulfides.



P. Rejmak „Computational refinement of the puzzling red tetrasulfur chromophore in ultramarine pigments” *Phys. Chem. Chem. Phys.* **2020**, 22, 22684-22698