The mysterious near-UV absorber in the Venusian atmosphere

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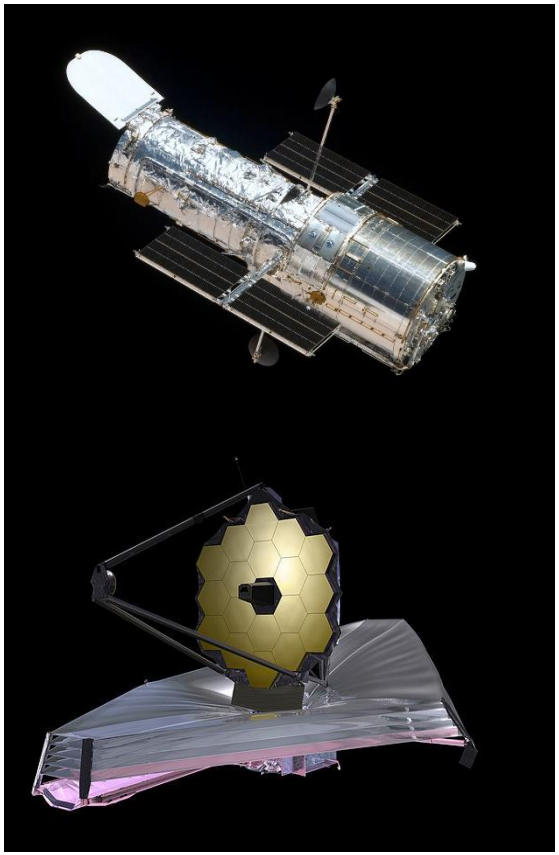
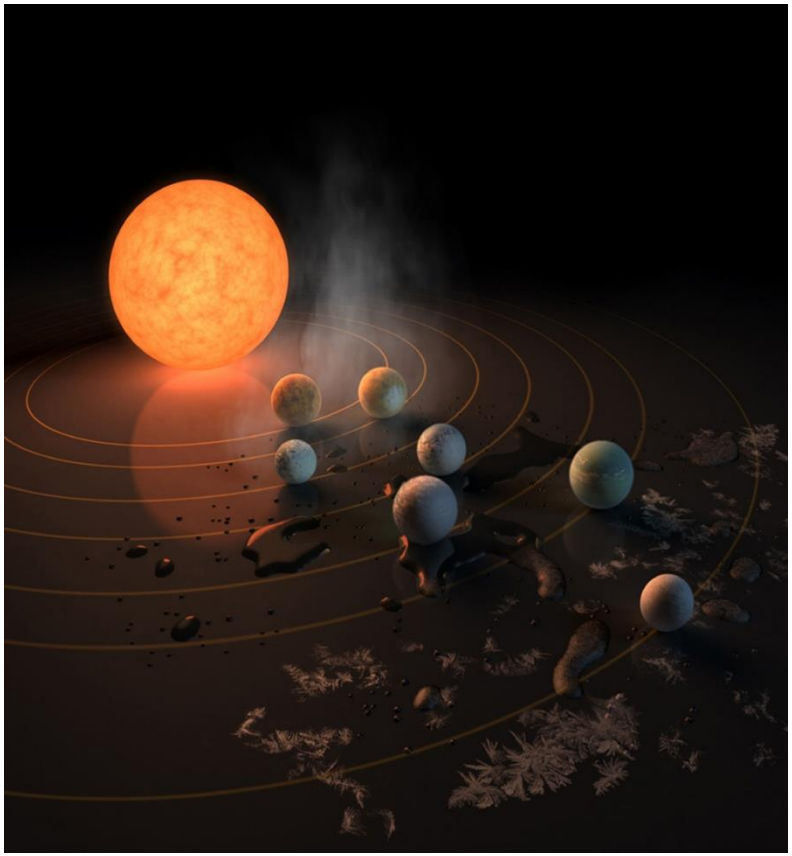
NZIC 2019

Spectroscopy



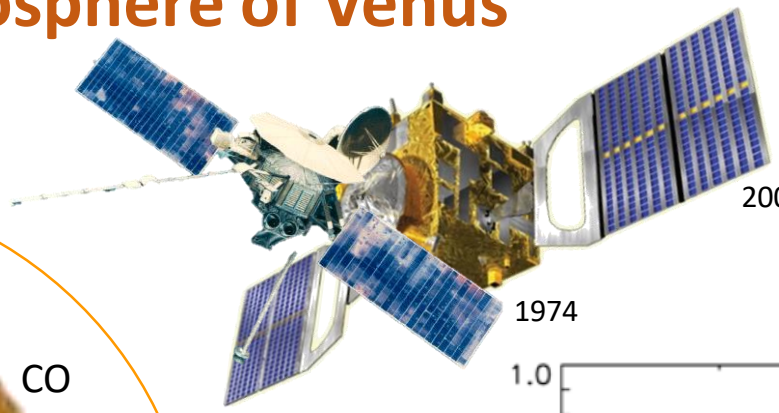
Hubble and James Webb Space Telescopes



TRAPIST-1 System

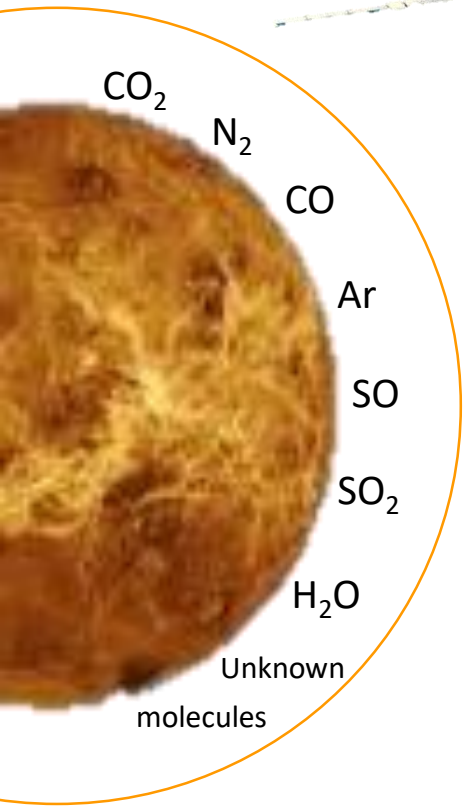
Photos from NASA's image gallery

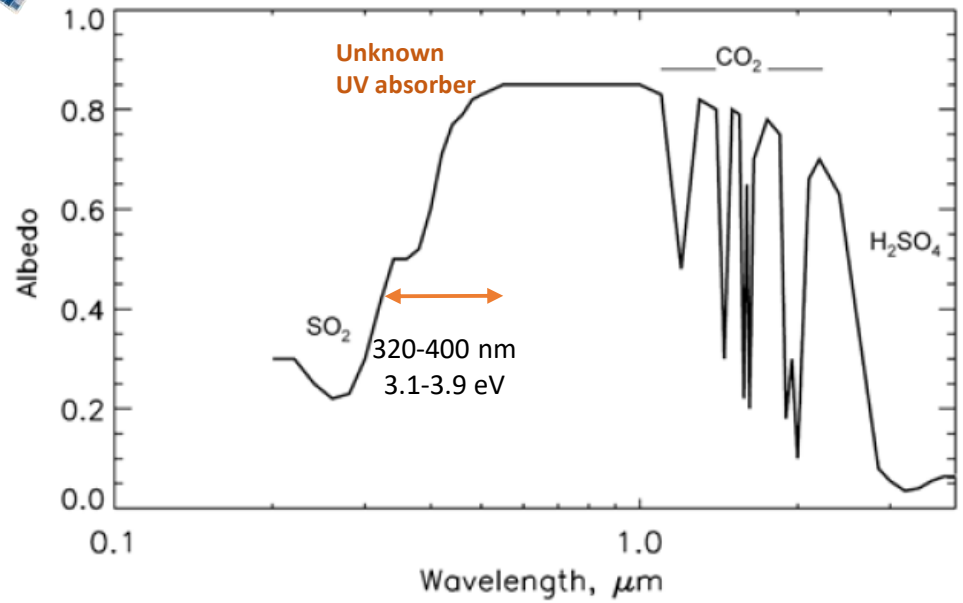
Atmosphere of Venus



2006

1974



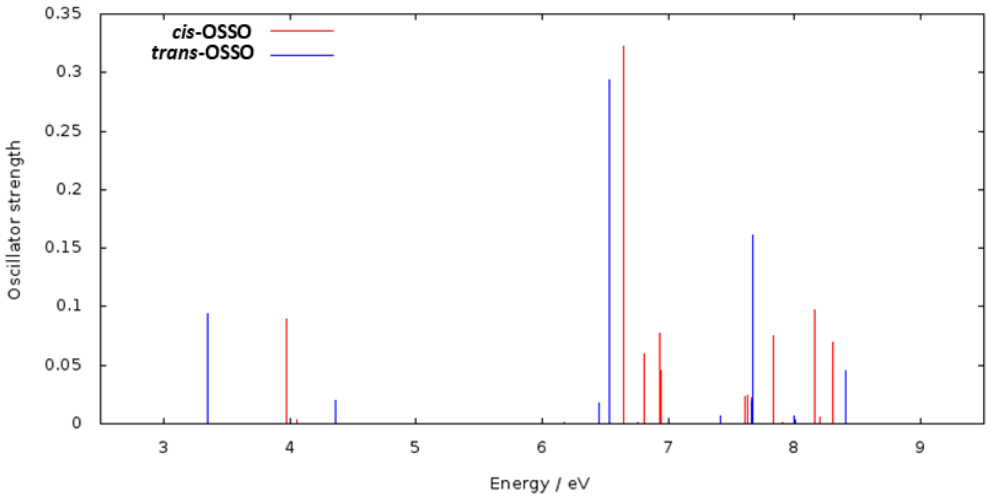


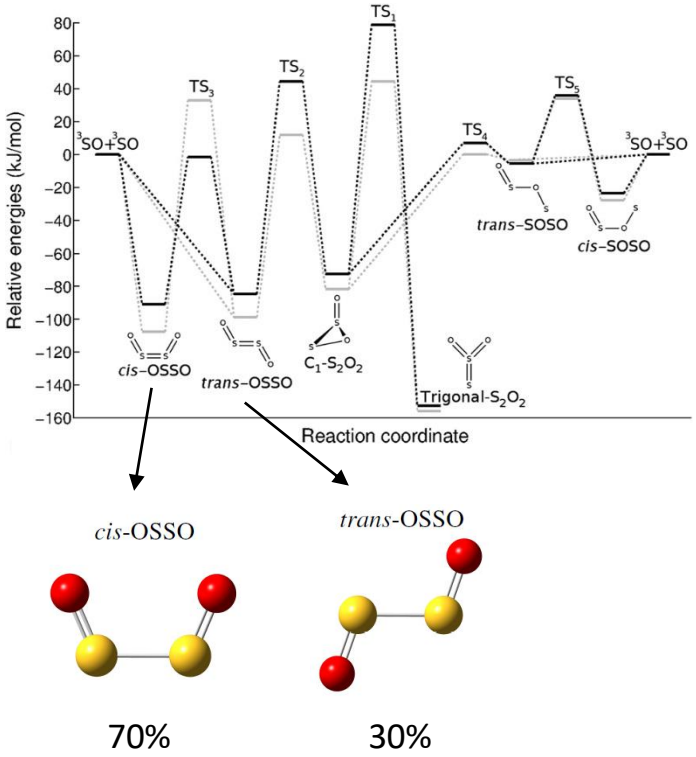
Spherical albedo of atmosphere of Venus

Titov, D. V.; Bullock, M. K.; Crisp, D; Renno, N. O.; Taylor, F. W.; Zasova, L. V. Radiation in the Atmosphere of Venus. In *Exploring Venus as a Terrestrial Plan*et; Esposito, L. W., Stofan, E. R., Cravens, T. E., Eds.; American Geophysical Union: 2013; 121-138.

Previous study on S_2O_2

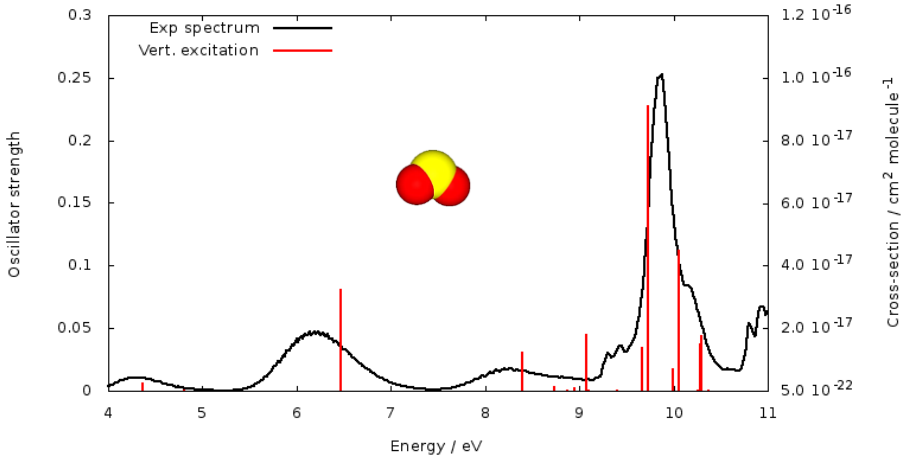
- Identified two cis-OSSO and trans-OSSO conformers
- Calculated the vertical excitations





Frandsen, B. N.; Wennberg, P. O.; Kjaergaard, H. G. Identification of OSSO as a near-UV absorber in the Venusian atmosphere., *Geophys. Res. Lett.* **2016**, *43*, 11146−11155.

Spectrum simulation



Spectrum simulation requires more than simple vertical excitation calculations.

A post Frank-Condon approach is needed to simulate the spectra for dissociative excited states and compare them with experiment.

Simulation approach

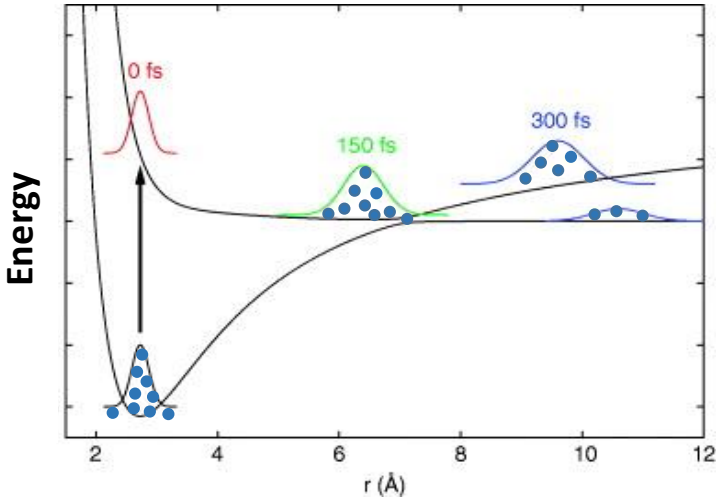
Absorption spectra simulation

Photodissociation dynamics simulation

Newton-X program interfaced with
different electronic structure packages

Electronic structure

ab initio calculations



Nuclei motion

Classical treatment

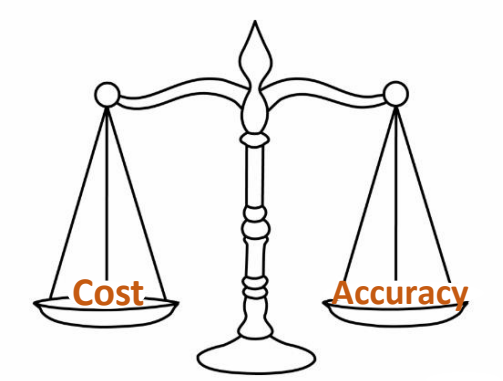
Absorption spectra simulation

Newton-X parameters

- Number of points
- Distribution
- Band shape
- Phenomenological broadening of the spectrum (δ)

Electronic structure parameters

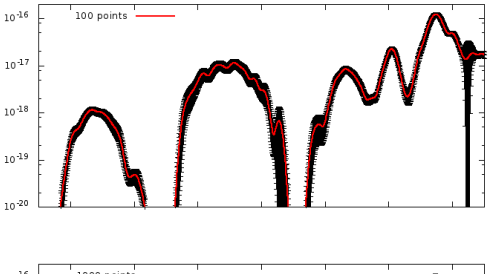
- *Ab initio* method
- Basis set

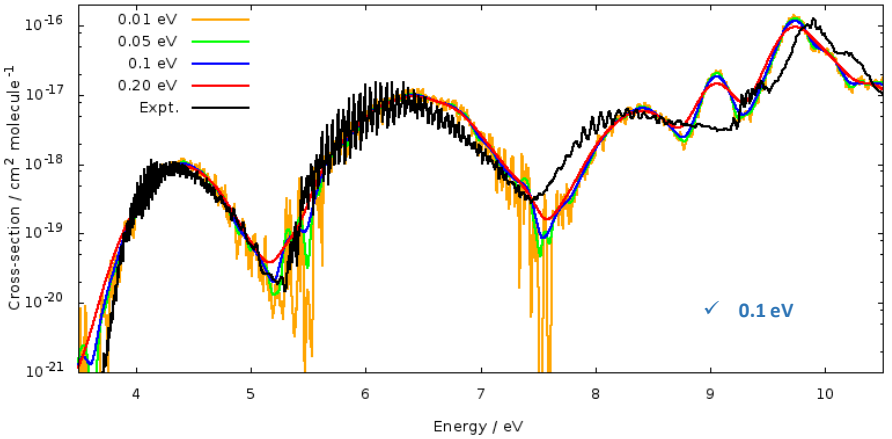


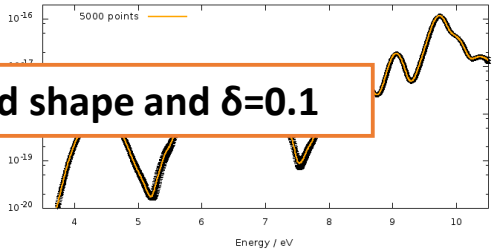
Newton-X parameters

SO_2

- Number of points
- Distribution
- Band shape
- Phenomenological broadening of the spectrum (δ)





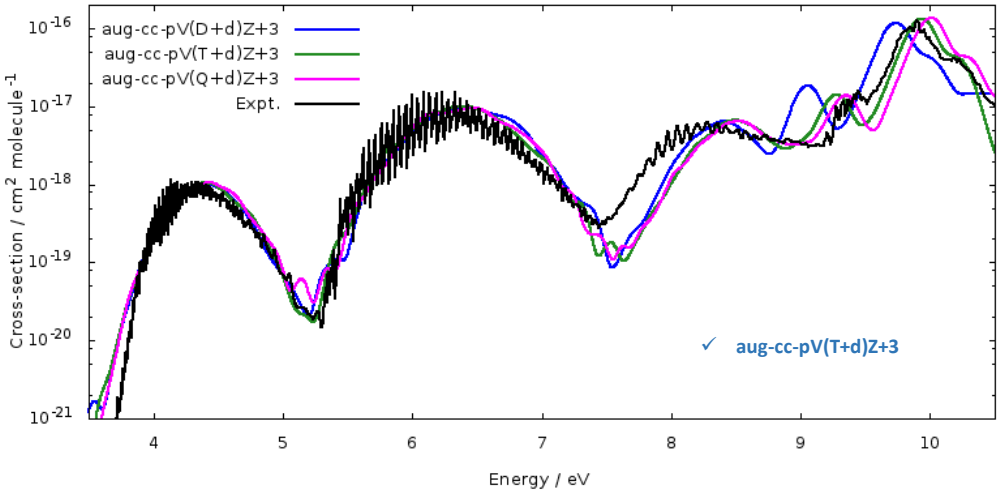


2000 points, Wigner distribution, Guassian band shape and δ=0.1

Electronic structure parameters

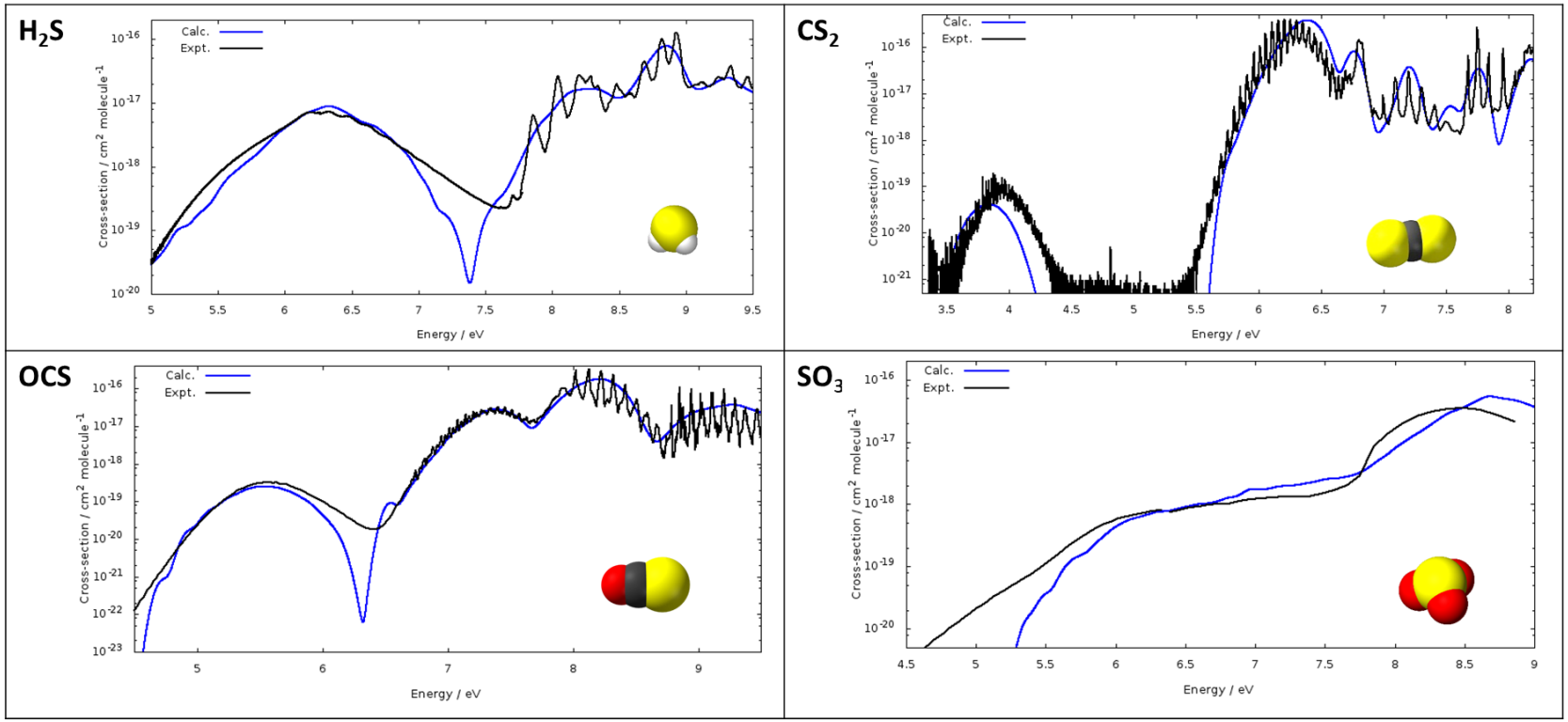
SO_2

- *Ab initio* method
- Basis set



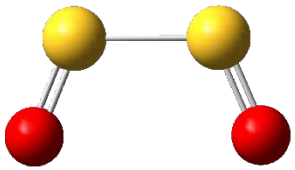
EOM-CCSD and aug-cc-pV(T+d)Z+3

Other benchmarking S-molecules

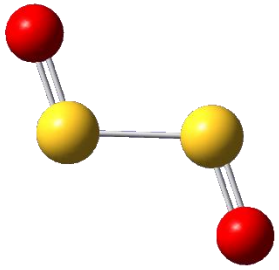


Farahani, S.; Frandsen, B. N.; Kjaergaard, H. G.; Lane, J. R. Simulated Electronic Absorption Spectra of Sulfur-Containing Molecules Present in Earth's Atmosphere. *J. Phys. Chem. A* **2019**, *123*, 6605-6617.

OSSO's simulated spectrum

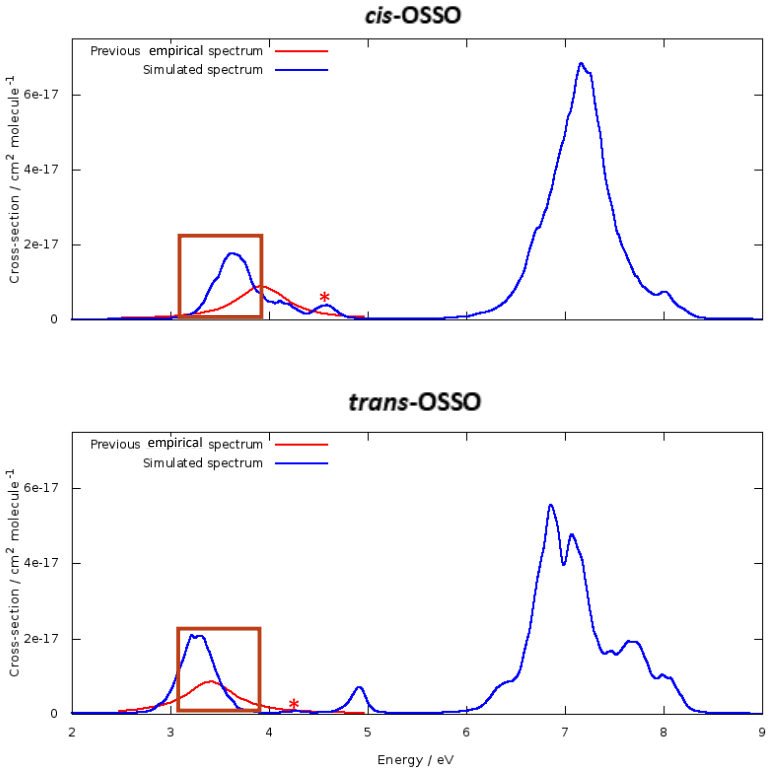


cis-OSSO



trans-OSSO

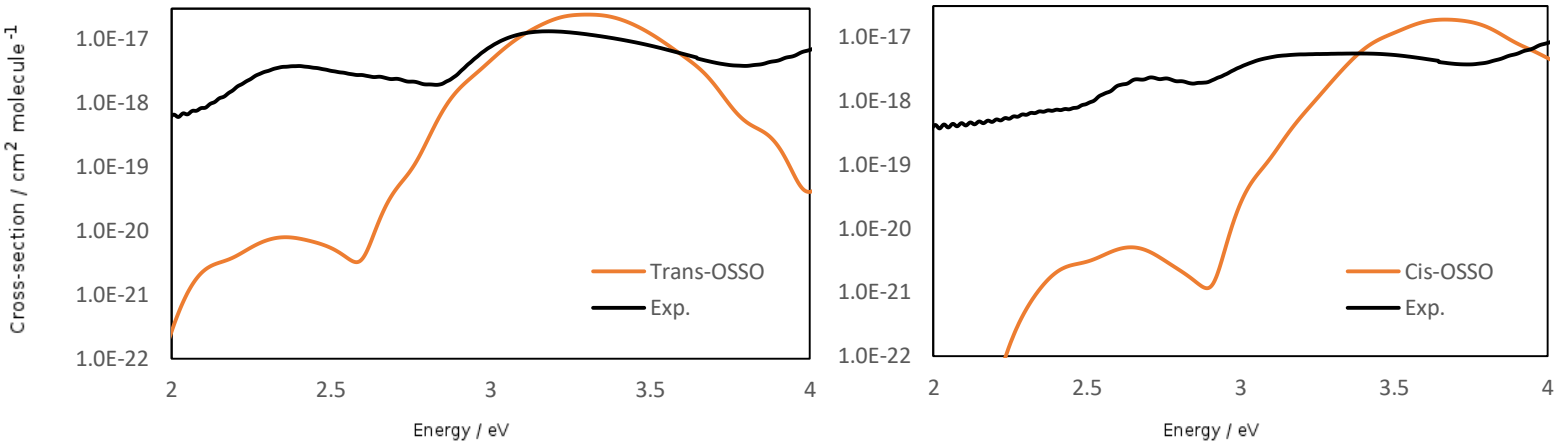
ΔE_{ZPE}= 11.96 kJmol^{-1}



*Empirical spectrum was simulated only up to 5 eV.

Frandsen, B. N.; Wennberg, P. O.; Kjaergaard, H. G. Identification of OSSO as a near-UV absorber in the Venusian atmosphere., *Geophys. Res. Lett.* **2016**, *43*, 11146−11155.

OSSO's simulated spectrum



Wu, Z.; Wan, H.; Xu, J.; Lu, B.; Lu, Y.; Eckhardt, A. K.; Schreiner, P. R.; Xie, C.; Guo, H.; Zeng, X. The near-UV absorber OSSO and its isomers. *Chem. Commun.* **2018**, *54*, 4517−4520

Conclusions

- A method for simulating the atmospherically relevant sulfur molecules was developed and validated.
- Some agreement between the simulated spectra and the first experimental results of OSSO was observed.
- Further experimental investigation on OSSO's absorption spectra is required.

Acknowledgement

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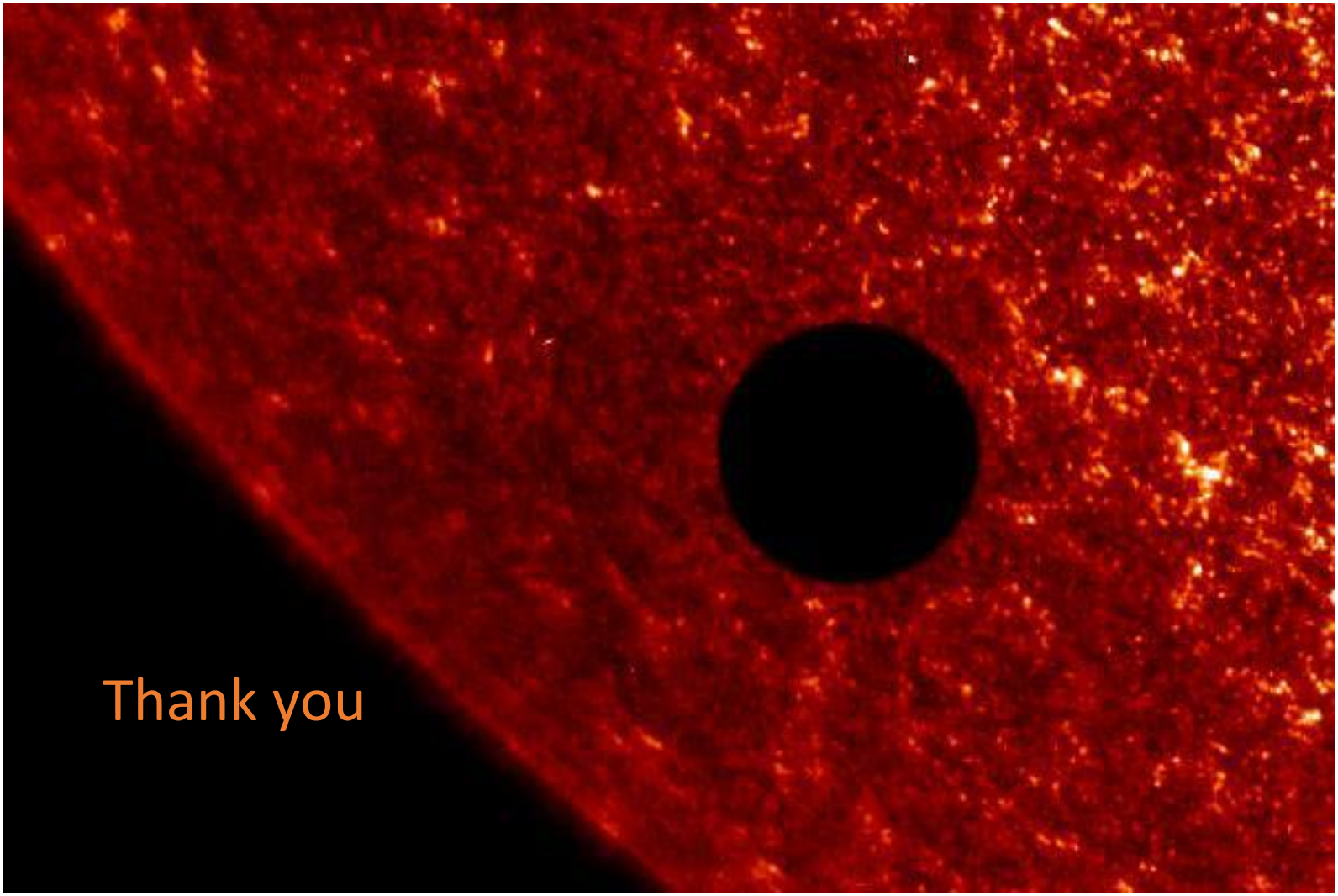
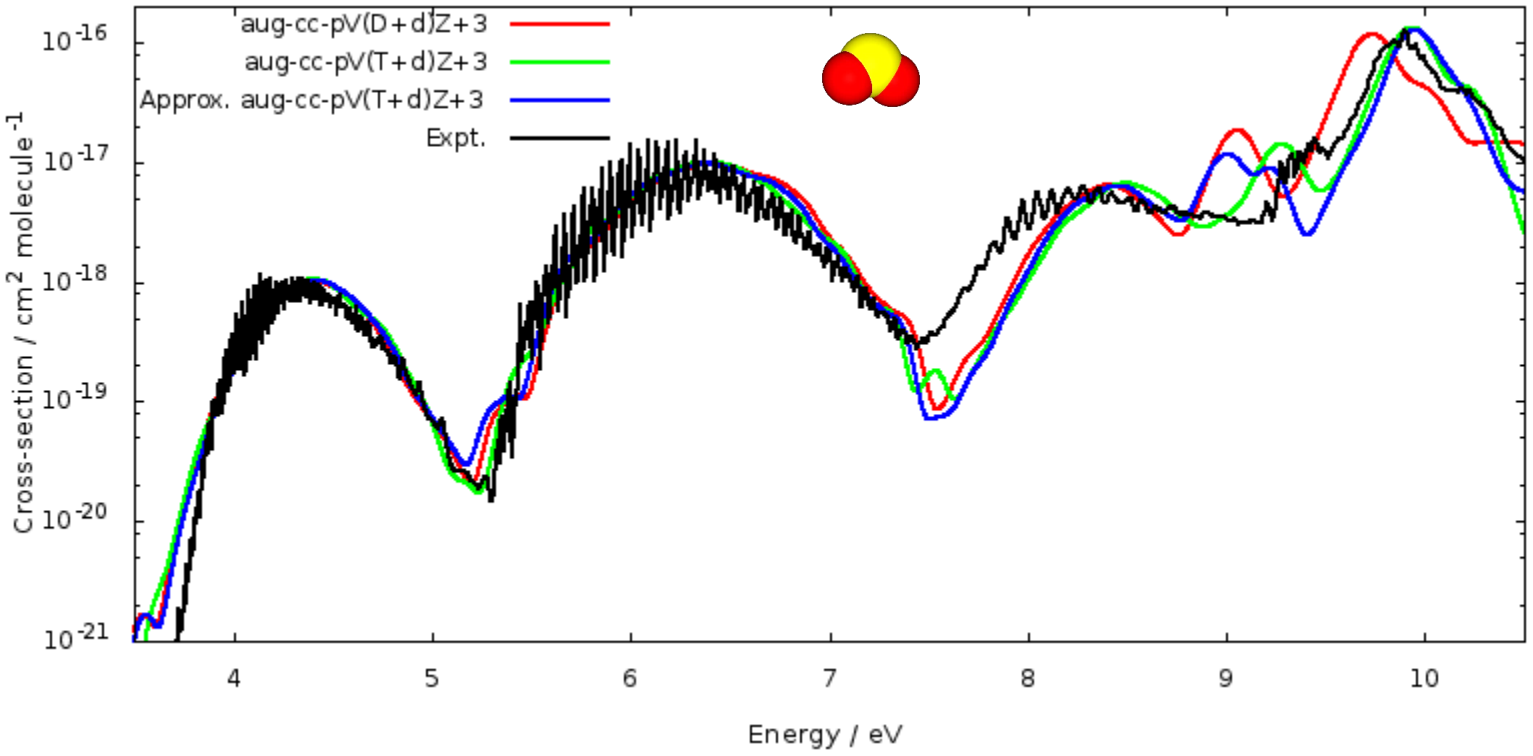
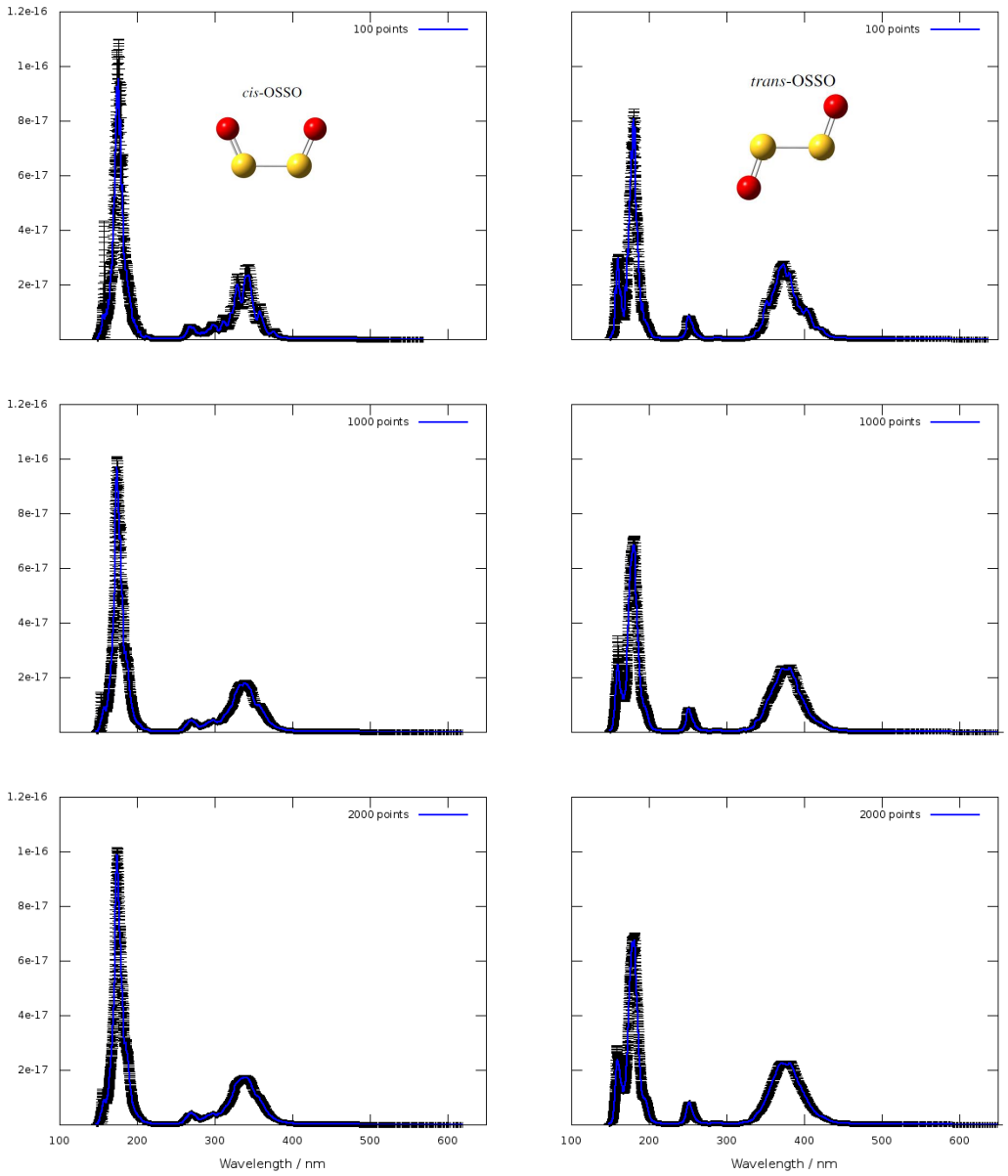


Photo from NASA's image gallery

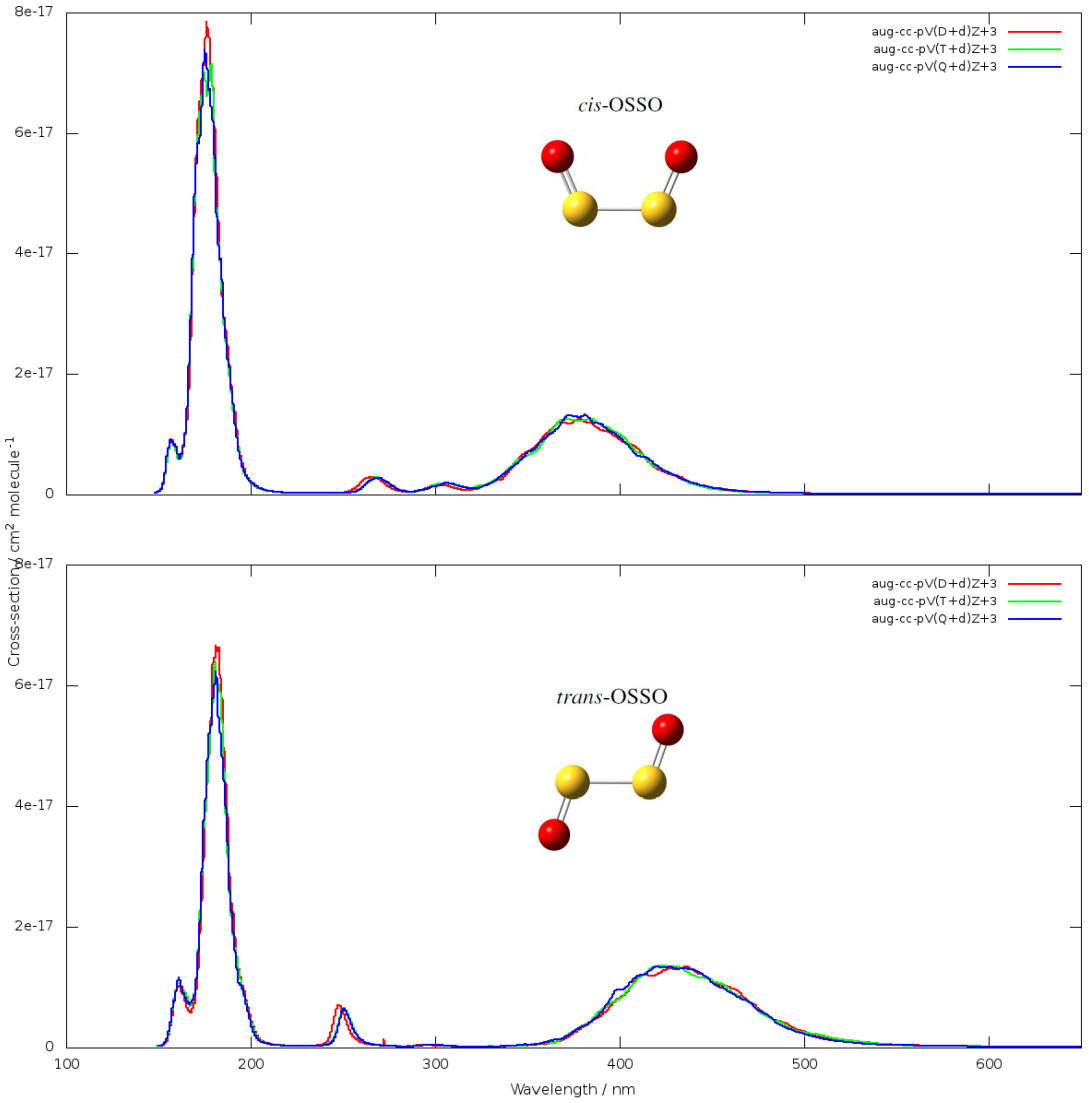
Venus Transit seen by NASA's Sun-observing TRACE spacecraft

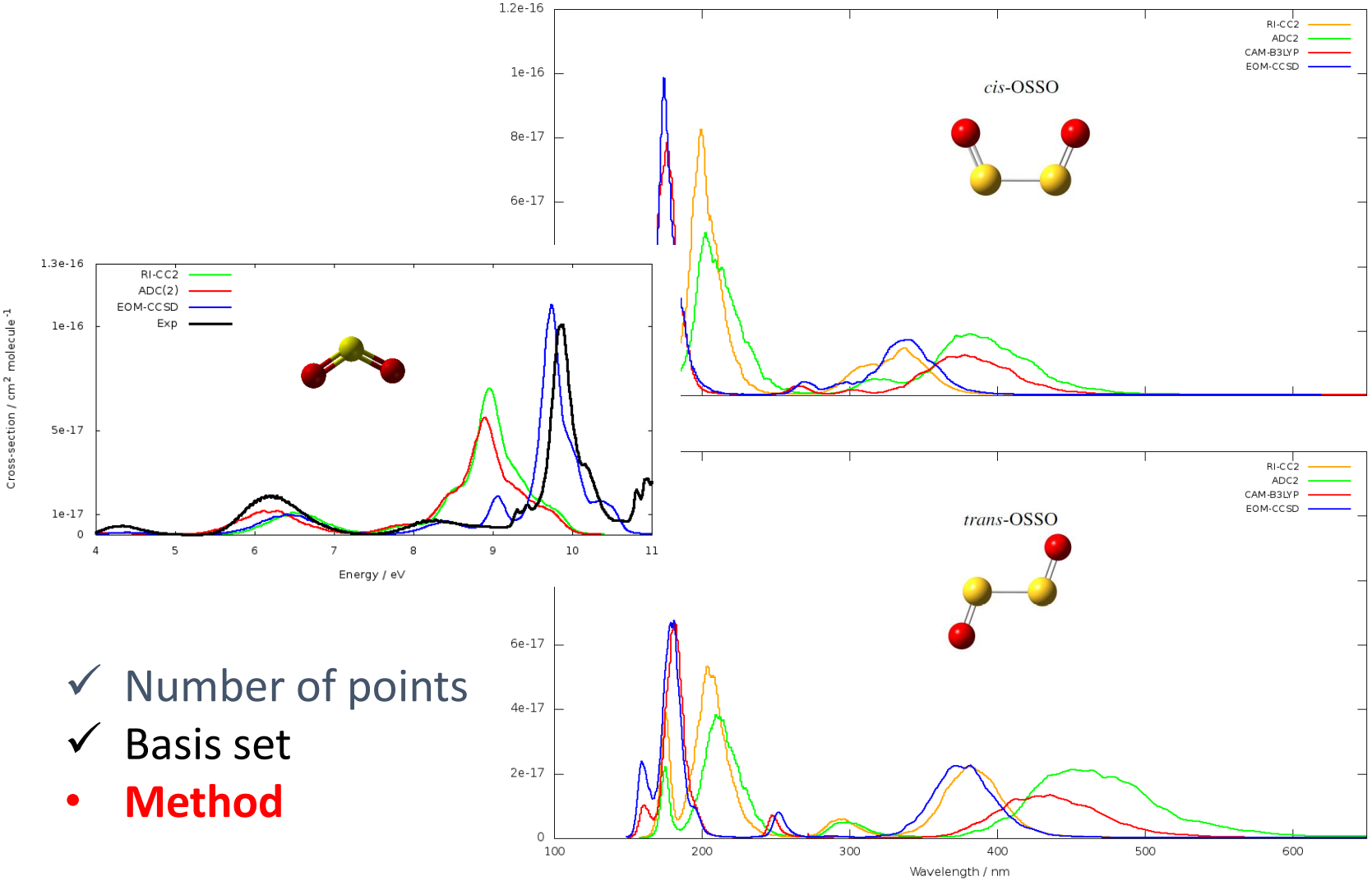

aug-cc-pV(D+d)Z+3
aug-cc-pV(T+d)Z+3
Approx. aug-cc-pV(T+d)Z+3
Expt.
Cross-section / cm^2 molecule^{-1}
10^{-16}
10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
4
5
6
7
8
9
10
Energy / eV

- ✓ **Number of points**
- Basis set
- Method

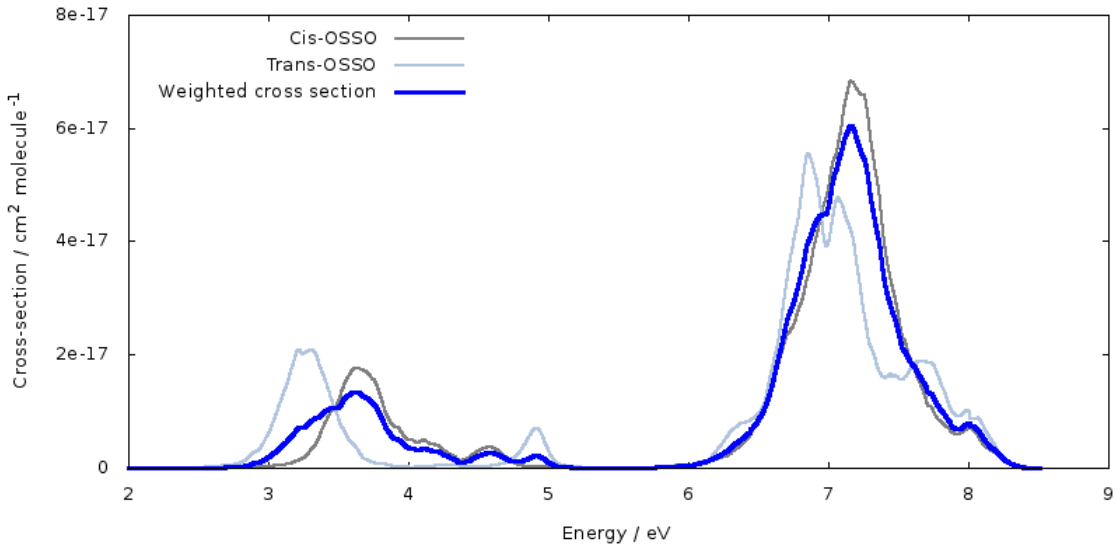


- ✓ Number of points
- ✓ **Basis set**
- Method





- ✓ Number of points
- ✓ Basis set
- • **Method**


Cis-OSSO
Trans-OSSO
Weighted cross section
Cross-section / cm^2 molecule^{-1}
Energy / eV
8e-17
6e-17
4e-17
2e-17
0
2
3
4
5
6
7
8
9