



Accurate approach in simulating the electronic absorption cross section of small to medium molecules

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1- Introduction

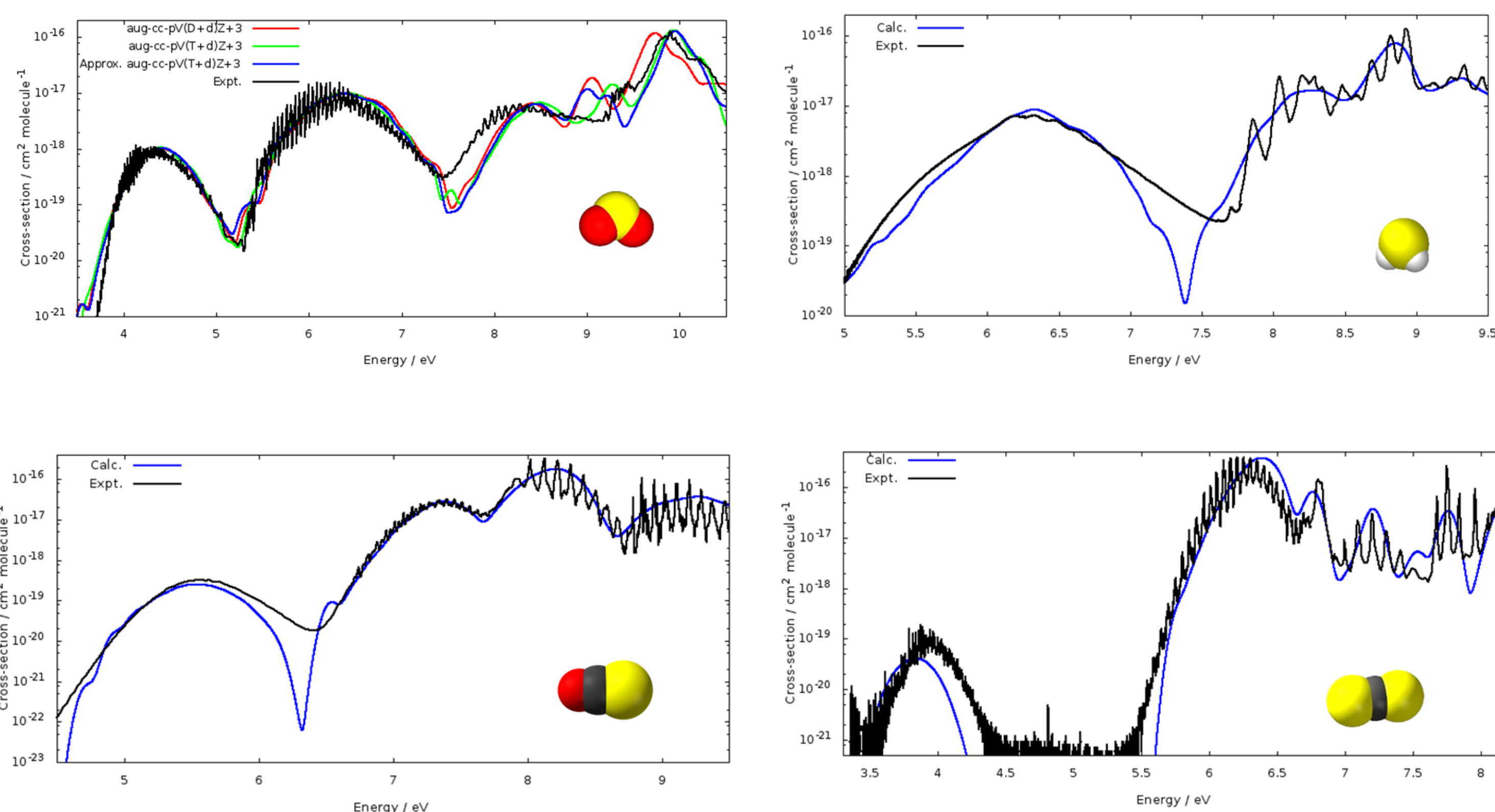
Sulfuric acid (H_2SO_4) is the dominant form of atmospheric sulfur in the stratosphere and plays an important role in terms of aerosol formation¹. In Earth's atmosphere, the aerosol particles provide sites for heterogeneous chemical reactions, some of which lead to depletion of ozone (O_3) in the polar regions and affect the Earth's climate by scattering sunlight². Sulfur compounds are also the main candidates for proposed geoengineering solutions to offset climate change in Earth's atmosphere³. However, despite its atmospheric significance, the experimental spectrum of H_2SO_4 is not yet known, although there have been multiple attempts to record it⁴⁻⁵.

2- Theoretical details

The electronic absorption spectra of some small sulfur-containing molecules of atmospheric importance have been simulated using a nuclear ensemble approach with the Newton-X⁶ package. The ensemble is based on Wigner sampling of vibrational frequencies calculated at the CCSD(T) level of theory with the aug-cc-pV(T+d)Z basis set. The electronic excited state transition energies and oscillator strengths of each geometry in the ensemble are calculated with the EOM-CCSD, RI-CC2 and ADC(2) methods using correlation consistent basis sets with additional diffuse basis functions, denoted aug-cc-pV(X+d)Z+3. We show that computational cost of these simulated spectra can be substantially reduced with negligible loss of accuracy by using a combination of results obtained with the aug-cc-pV(D+d)Z+3 and aug-cc-pV(T+d)Z+3 basis sets.

3- Benchmarking molecules

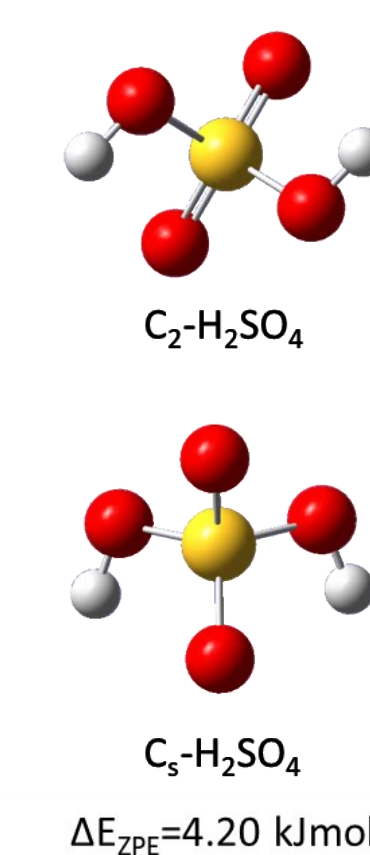
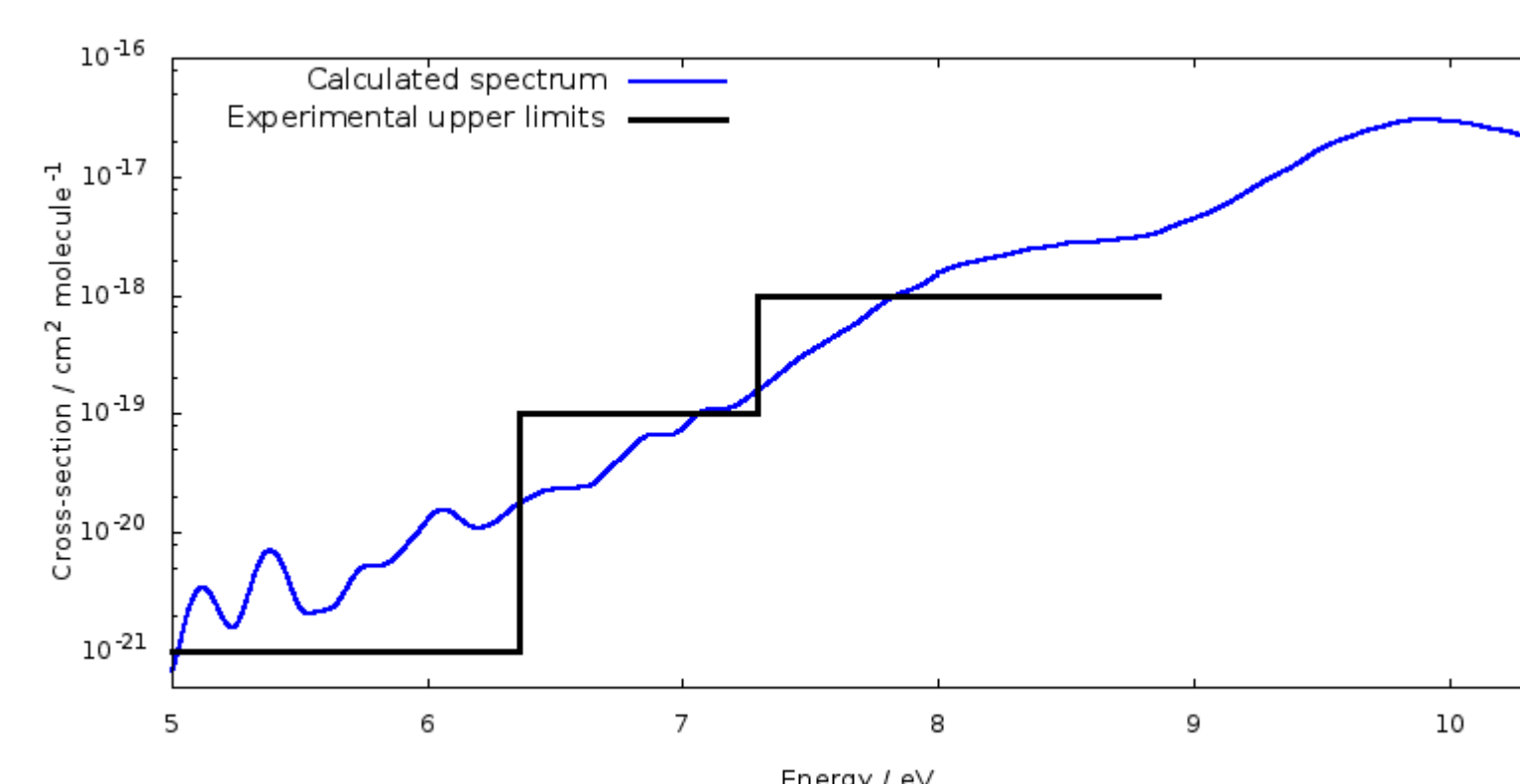
- SO_2 , H_2S , OCS , CS_2 and SO_3 with available experimental spectra and atmospheric relevance were chosen to benchmark the simulation approach.
- The benchmarked Newton-X and electronic structure parameters are number of points in the ensemble, distribution, shape line, phenomenological broadening of the spectrum, the ab initio method, basis set and number of excited states.



- The simulated spectra show very good agreement with the experimental results.
- The computational cost of the simulation is substantially reduced with negligible loss of accuracy by combining the results obtained from aug-cc-pV(T+d)Z+3 and aug-cc-pV(D+d)Z+3 basis sets.

4- H_2SO_4 spectra simulation

- The two low-energy conformers that are abundant under atmospheric conditions are considered.
- Above 6.4 eV, our calculated spectrum is generally in agreement with the experimental upper limits^{4,5} for the absorption cross-section.
- Below 6.4 eV, cross-section is higher than experimental upper limits^{4,5} and suggest that further experimental investigation is needed.

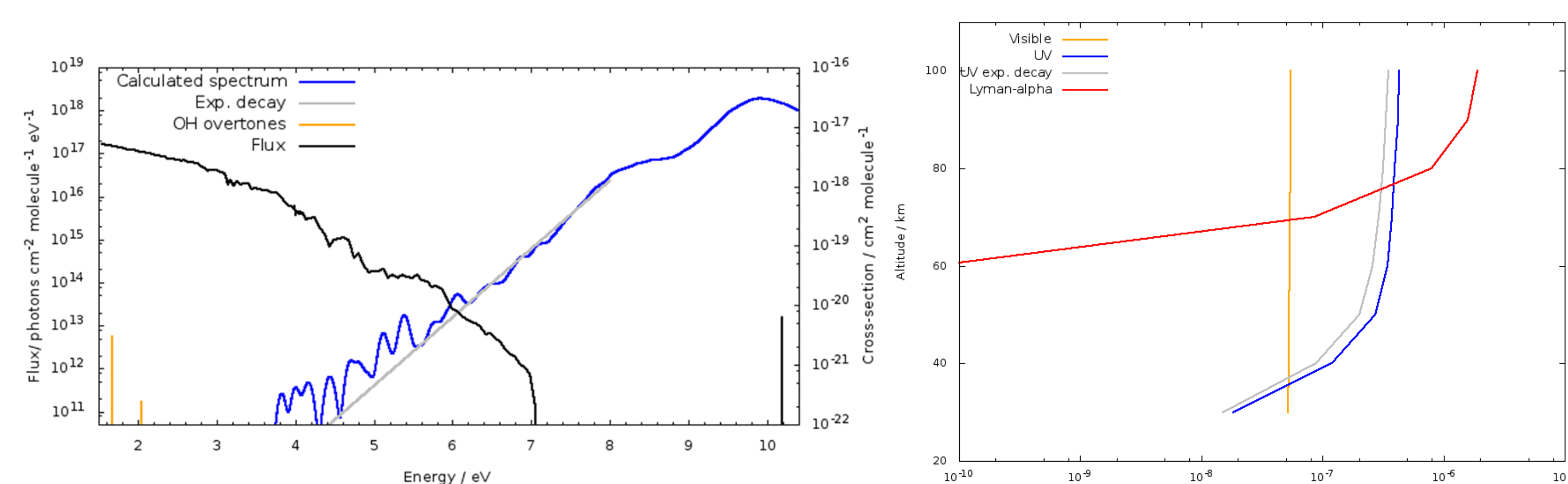


For a given molecule, the rate of photodissociation in Earth's atmosphere depends on its cross-section, the solar flux, and the quantum yield:

$$J = \int I(\lambda) \phi(\lambda) \sigma(\lambda)$$

Poor overlap between the cross-section of H_2SO_4 and solar flux leads to three separate photodissociation mechanisms of UV photodissociation, visible or OH-stretching overtone vibrational photodissociation and Lyman- α photodissociation.

5- Atmospheric implication



- We find that all three mechanisms are significant, and that at certain altitudes each mechanism is dominant.
- Consistent with previous findings⁸, below 35 km the Visible OH-stretching vibrational overtone mechanism is dominant.
- However, above this altitude the UV mechanism dominates and at higher altitudes still the Lyman-alpha mechanism dominates.

6- References

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