

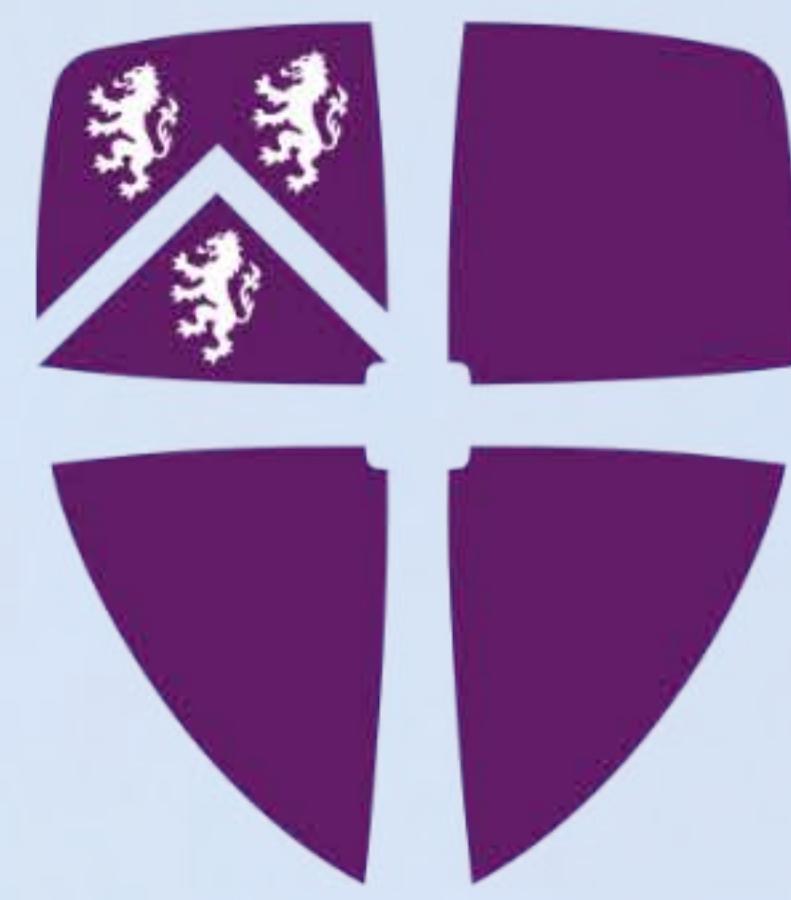
# A Theoretical Perspective on the Actinic Photochemistry of 2-hydroperoxypropanal

Emanuele Marsili

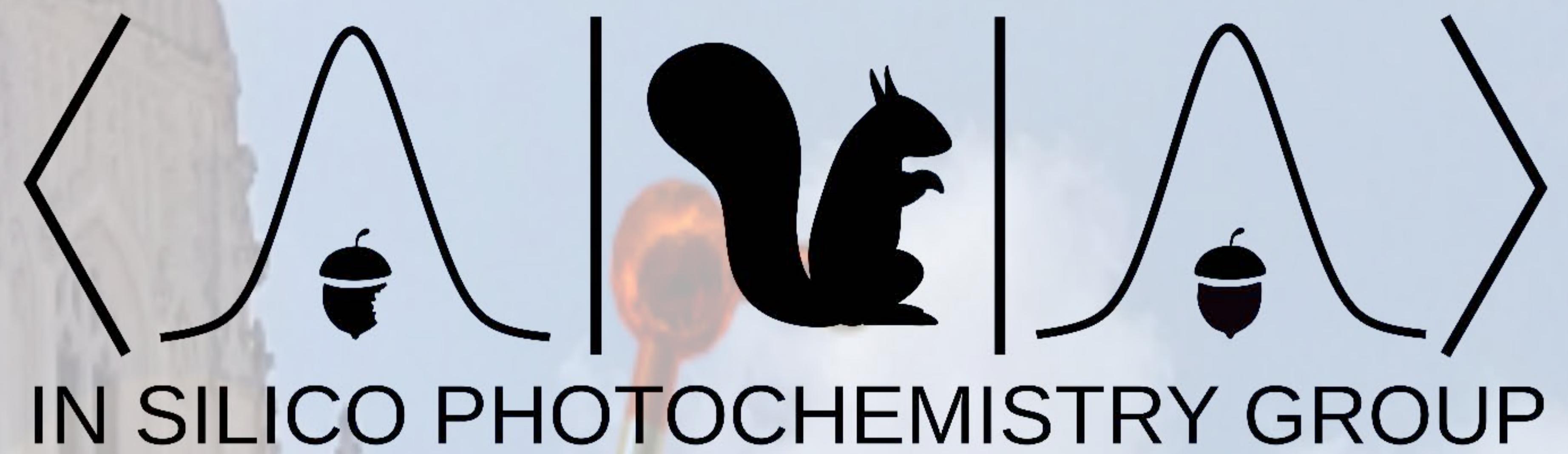
22/06/2022



University of  
BRISTOL



Durham  
University



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# Introduction

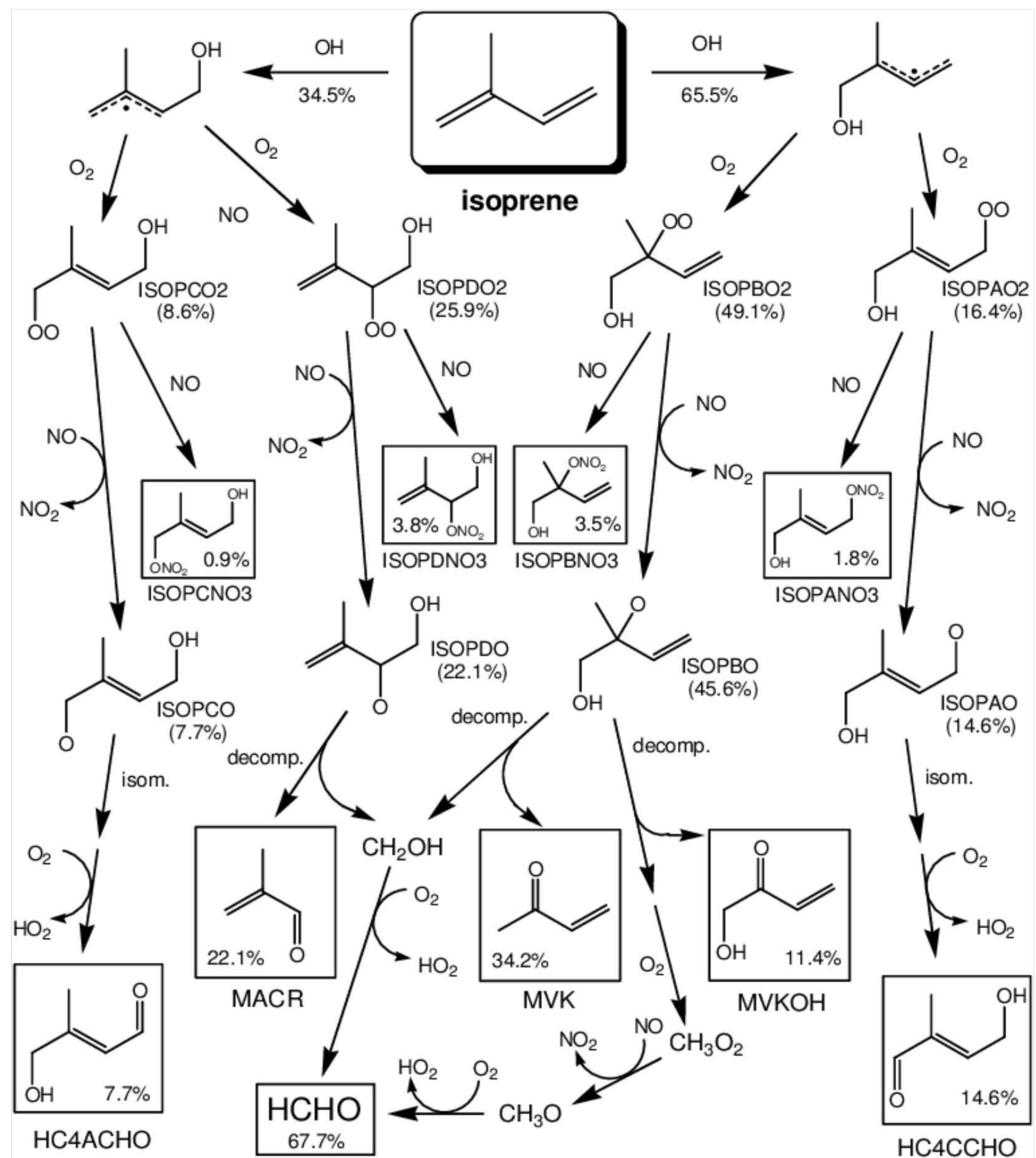
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- Volatile Organic Compounds (**VOCs**) are of particular interest to atmospheric chemistry

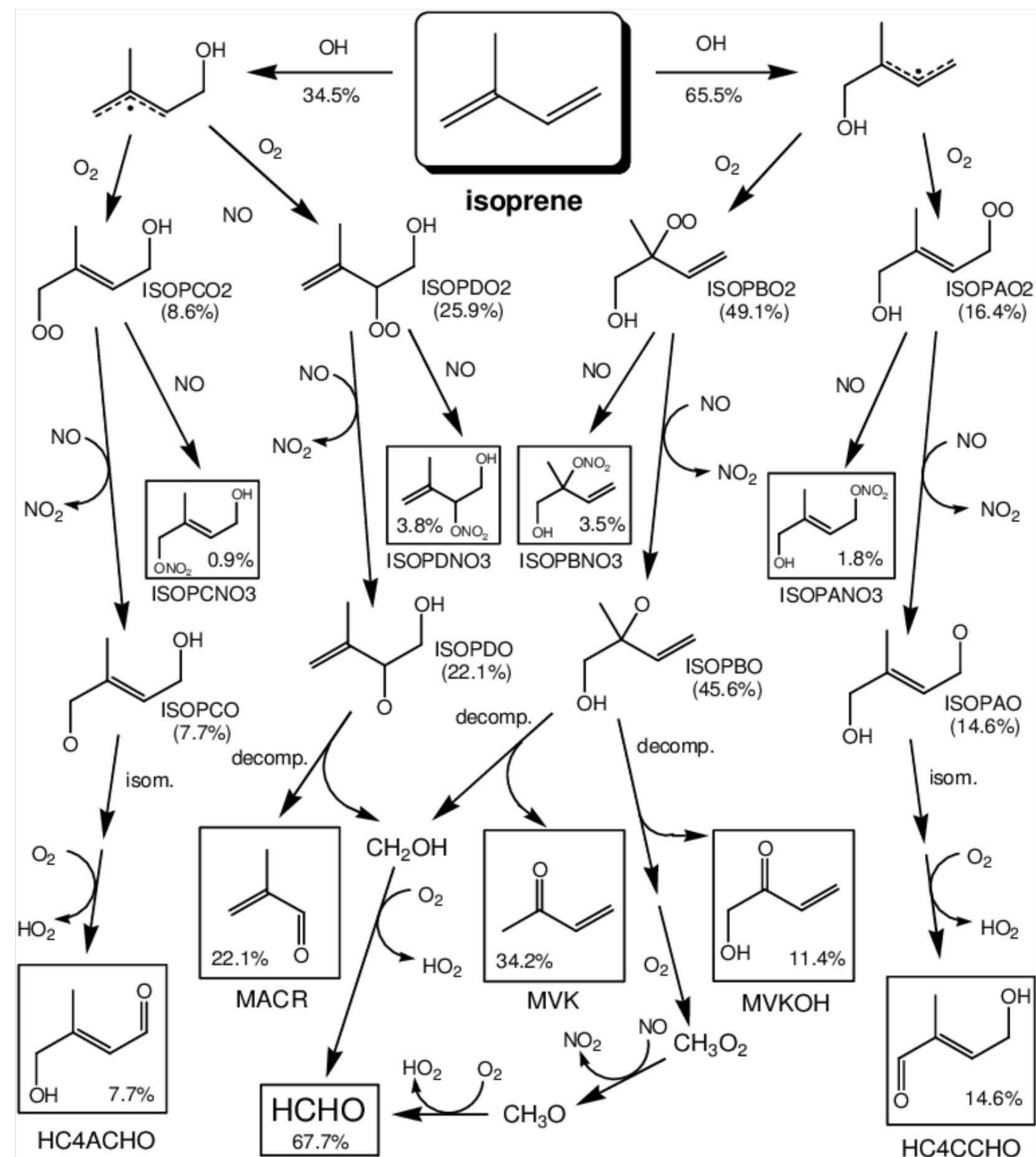
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- Many VOCs are **transient** species that cannot be studied experimentally



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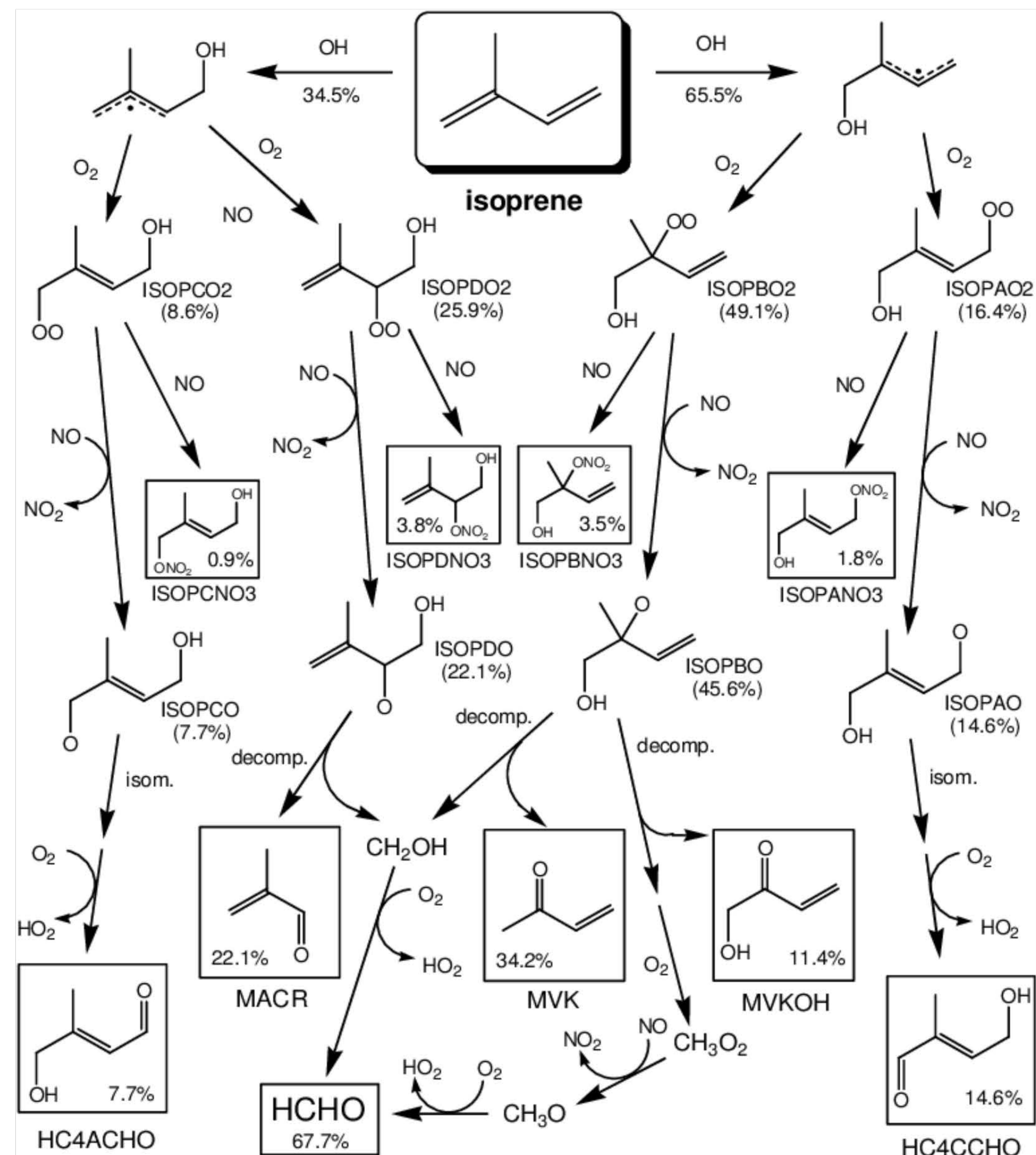
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- Isoprene oxidation triggers a cascade of oxidative reactions

- Many VOCs are **transient** species that cannot be studied experimentally

- The role of **sunlight** in the reactivity of transient VOCs is still largely unexplored



Atmospheric Chem. Phys. 2010, 10 8097-8118

# Photolysis rate constant $J$

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$$J = \int_{\lambda_{min}}^{\lambda_{max}} F(\lambda) \sigma(\lambda) \phi(\lambda) d\lambda$$

In silico photolysis rate constant: *J. Phys. Chem. Lett.* 2020, 11, 14, 5418–5425

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**flux of the light source**

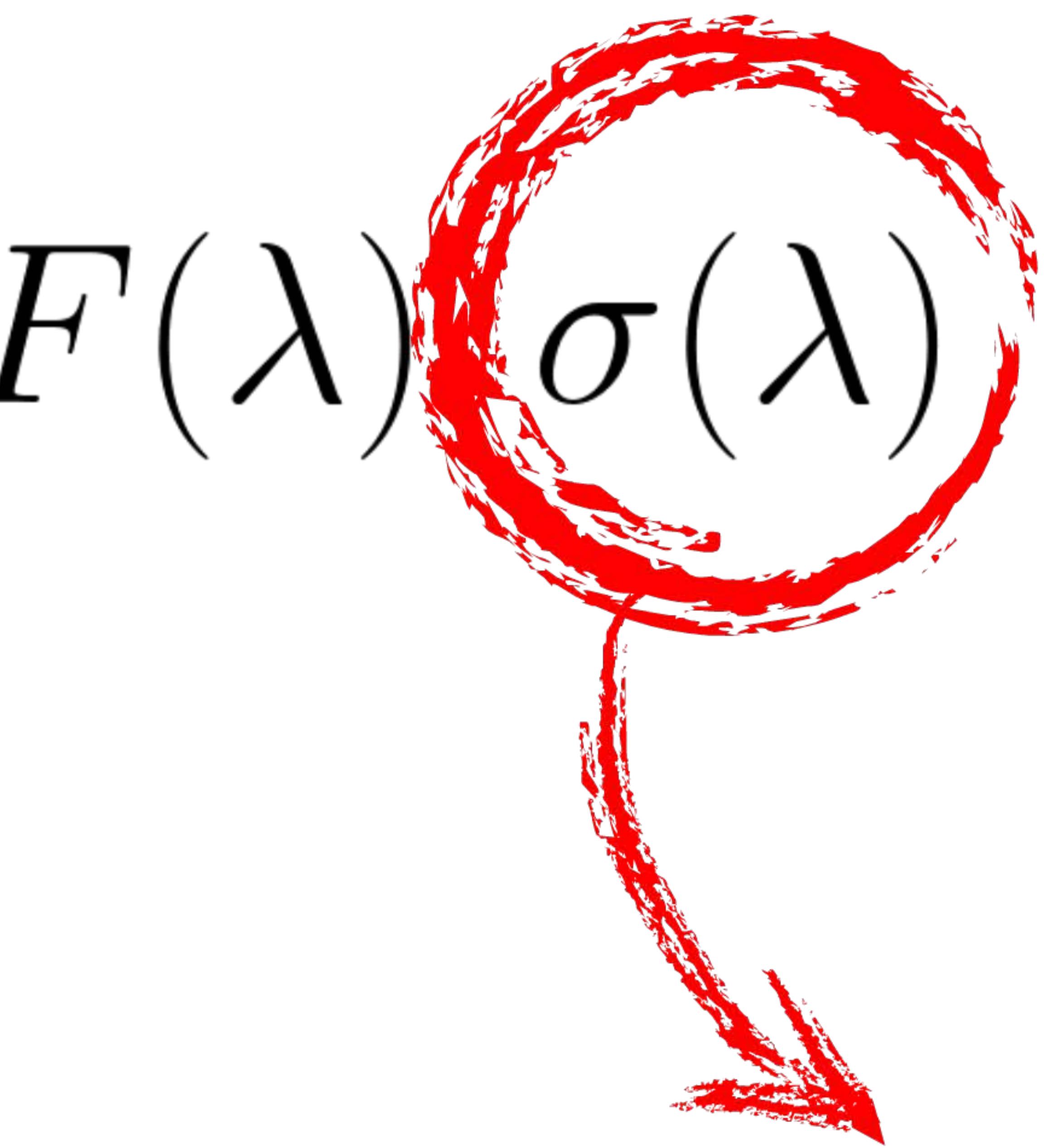
**How many photons are available at the wavelenght  $\lambda$ ?**

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**photoabsorption cross section**

**What is the probability that the molecule will absorb a photon at a given wavelength?**

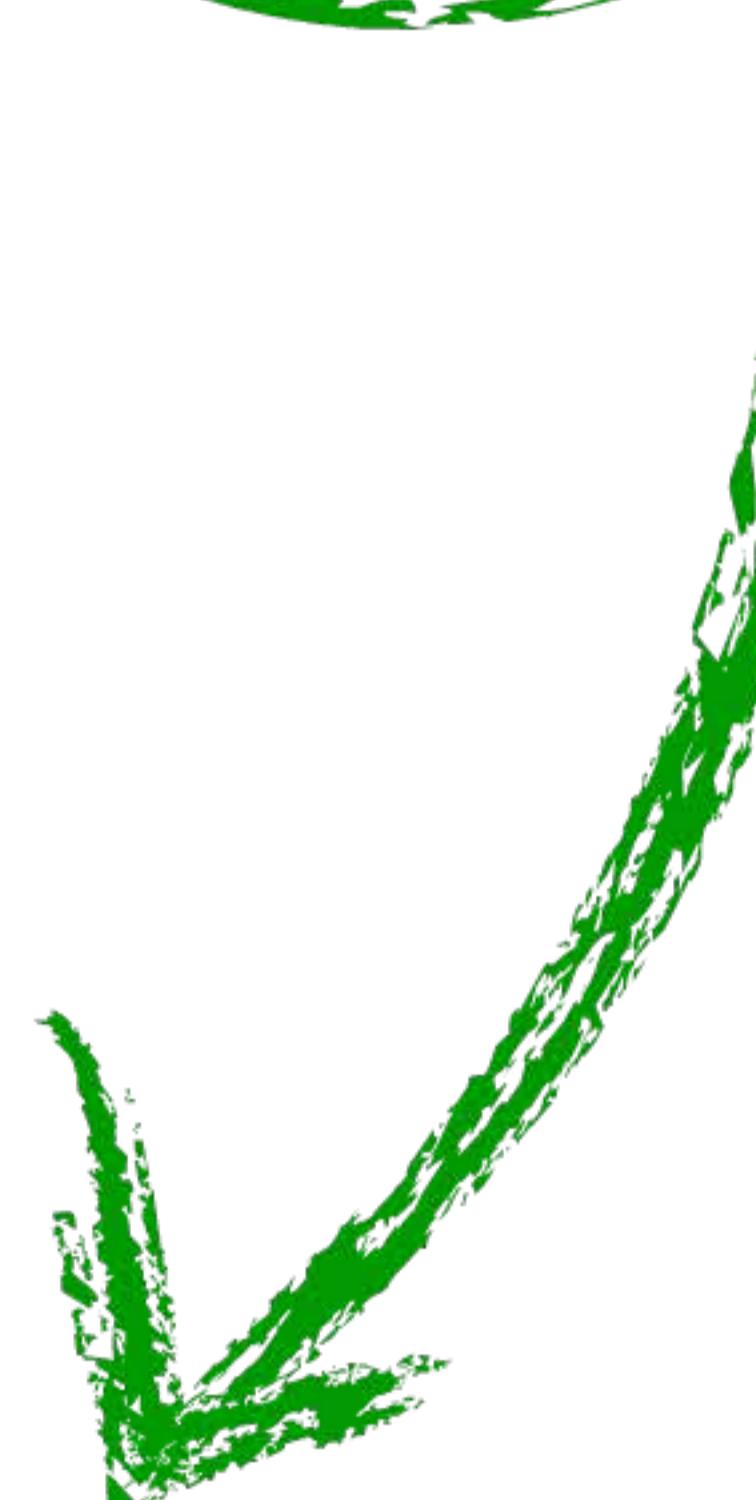
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$\phi(\lambda)$



**photolysis quantum yield**

**What is the yield of a given photolysis process once a photon of wavelength  $\lambda$  is absorbed?**

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"**in silico**" using computational and quantum chemistry methods

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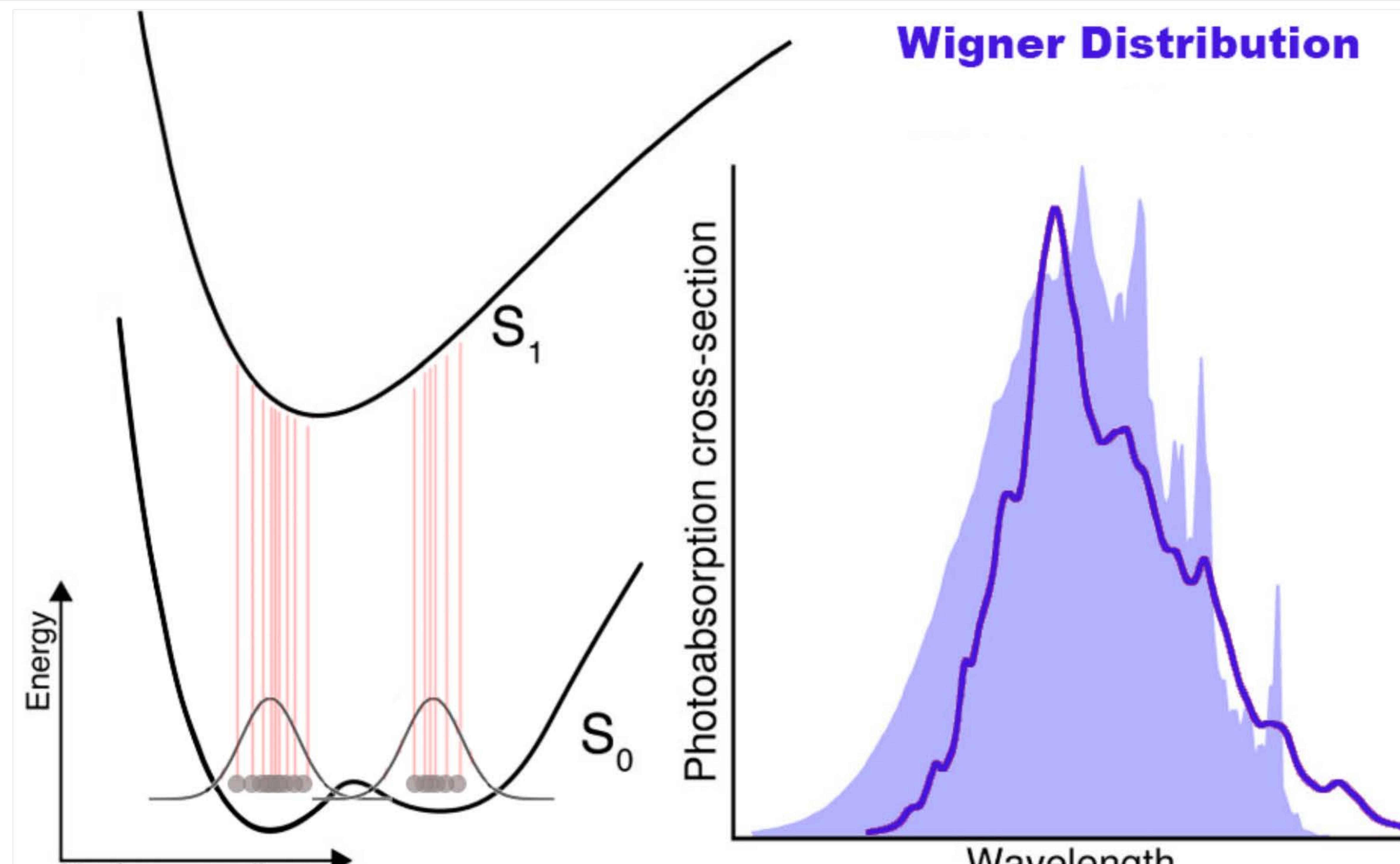
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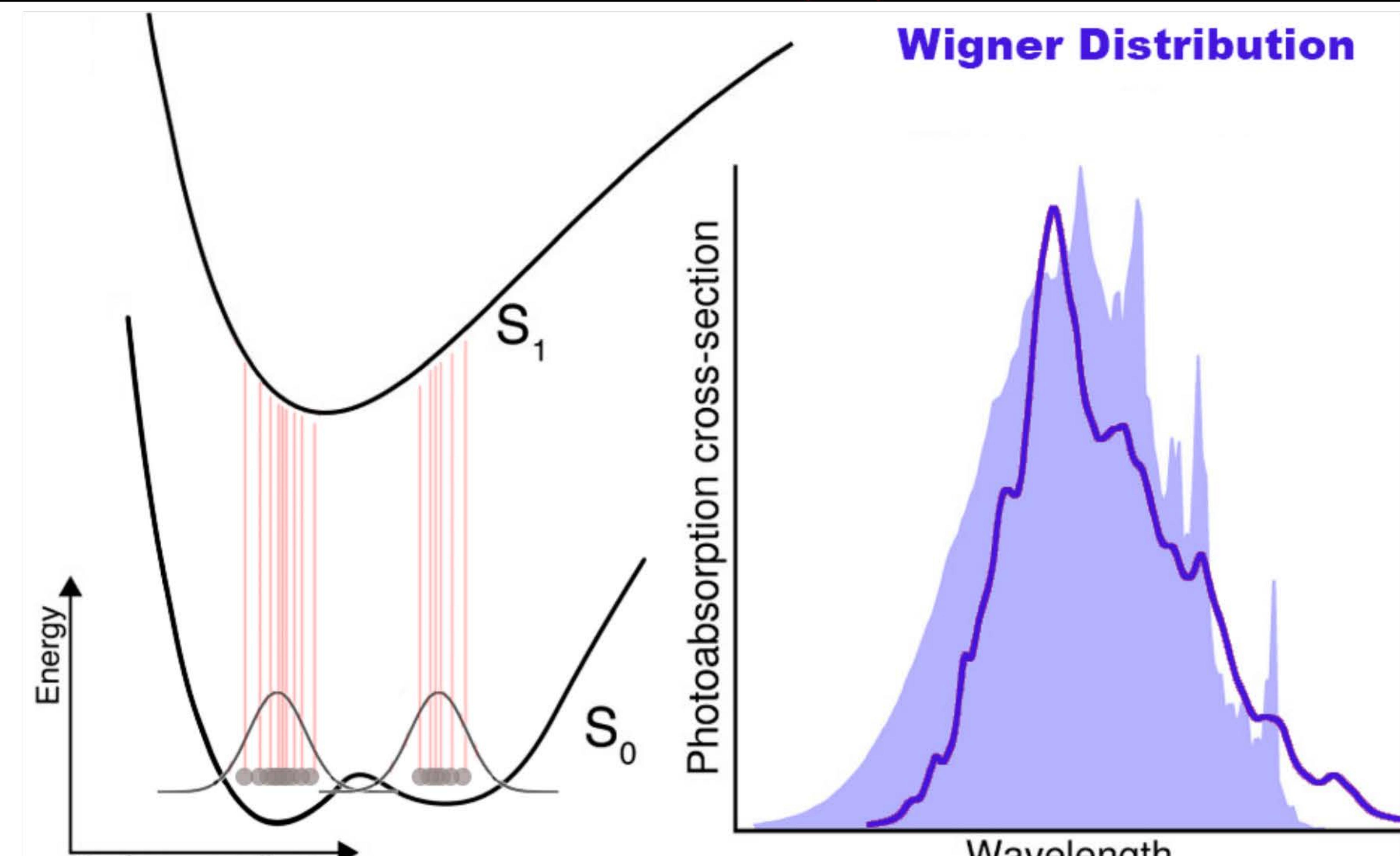
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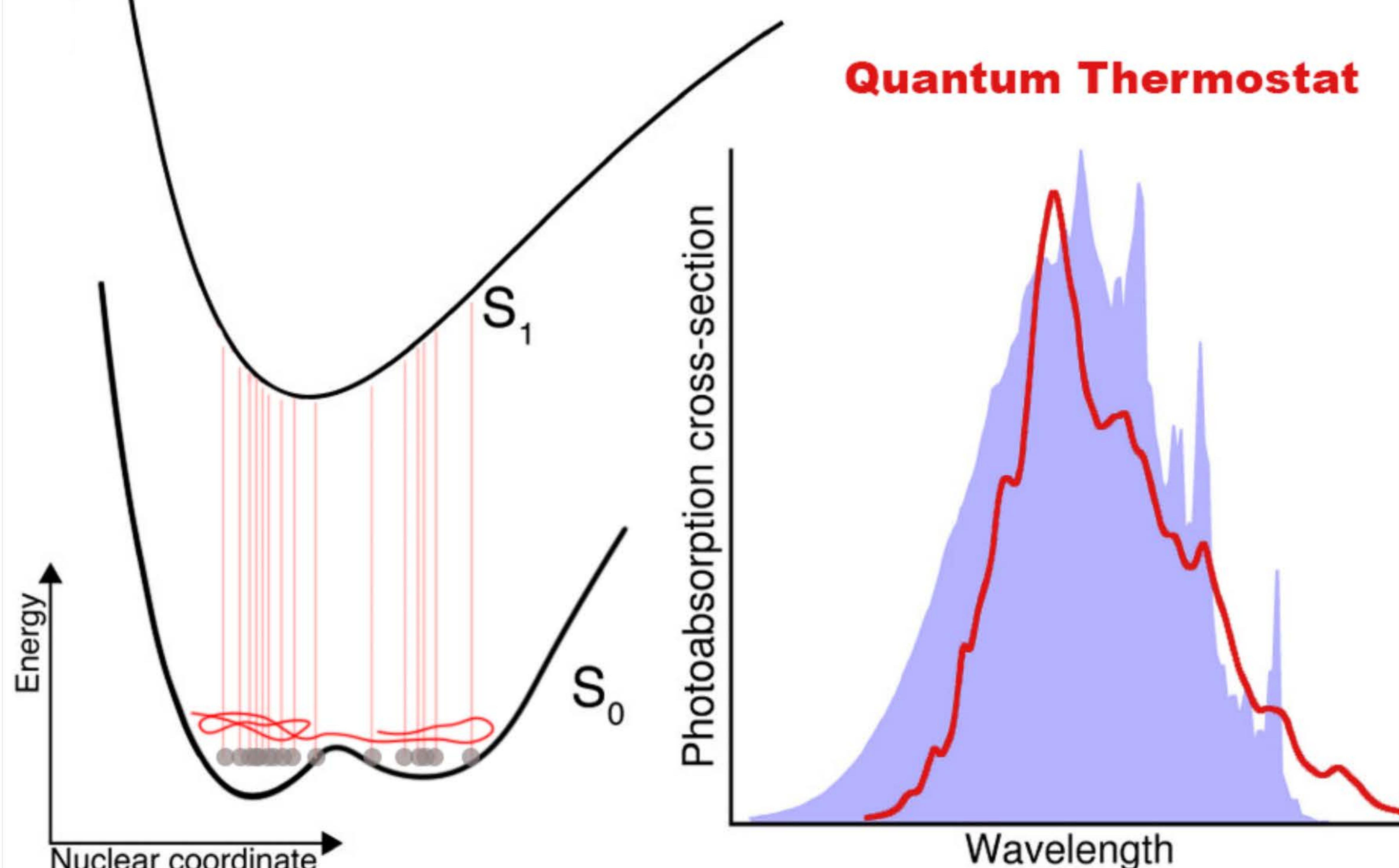
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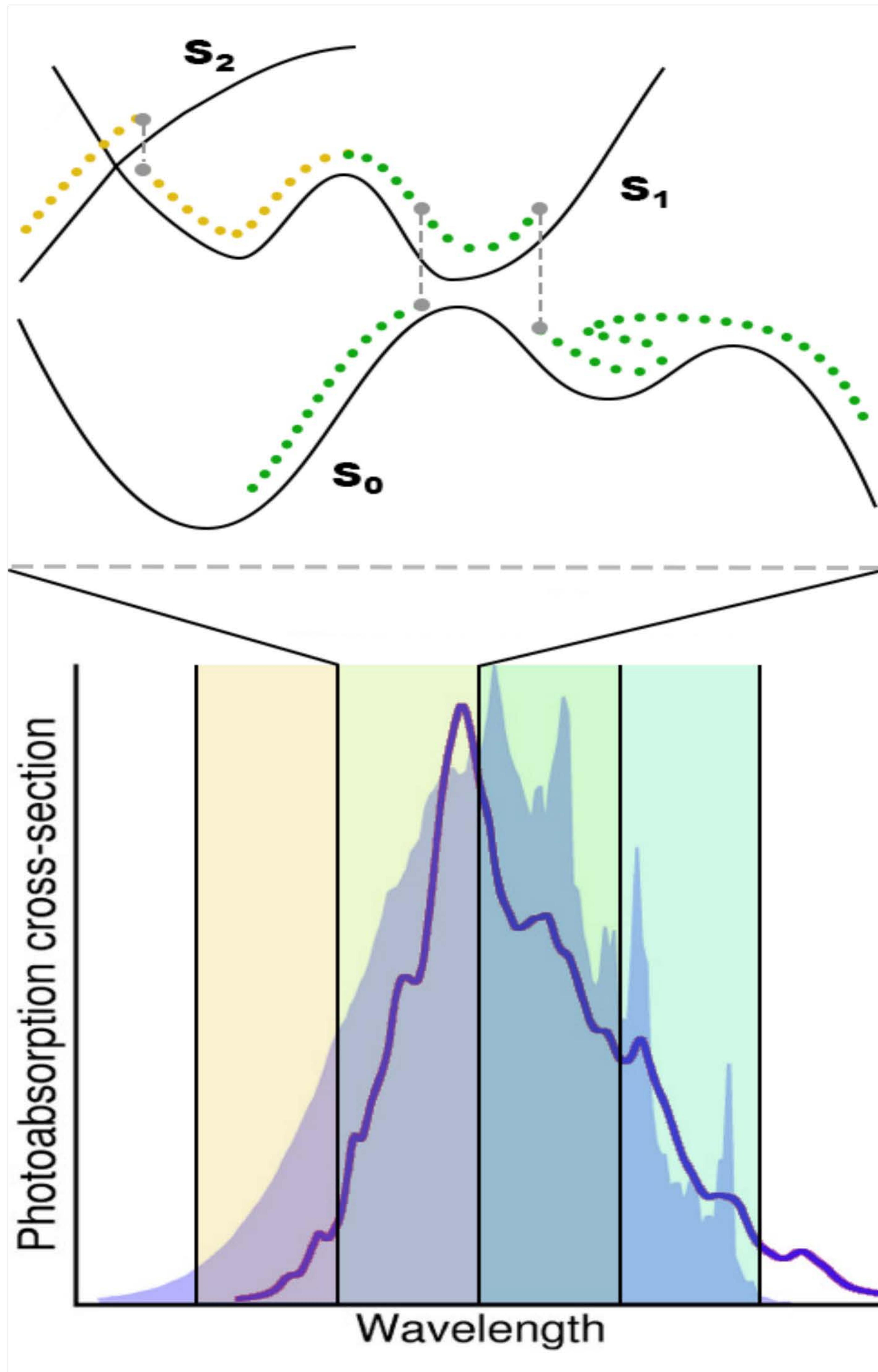
- **Wigner distribution**



- **Quantum Thermostat**

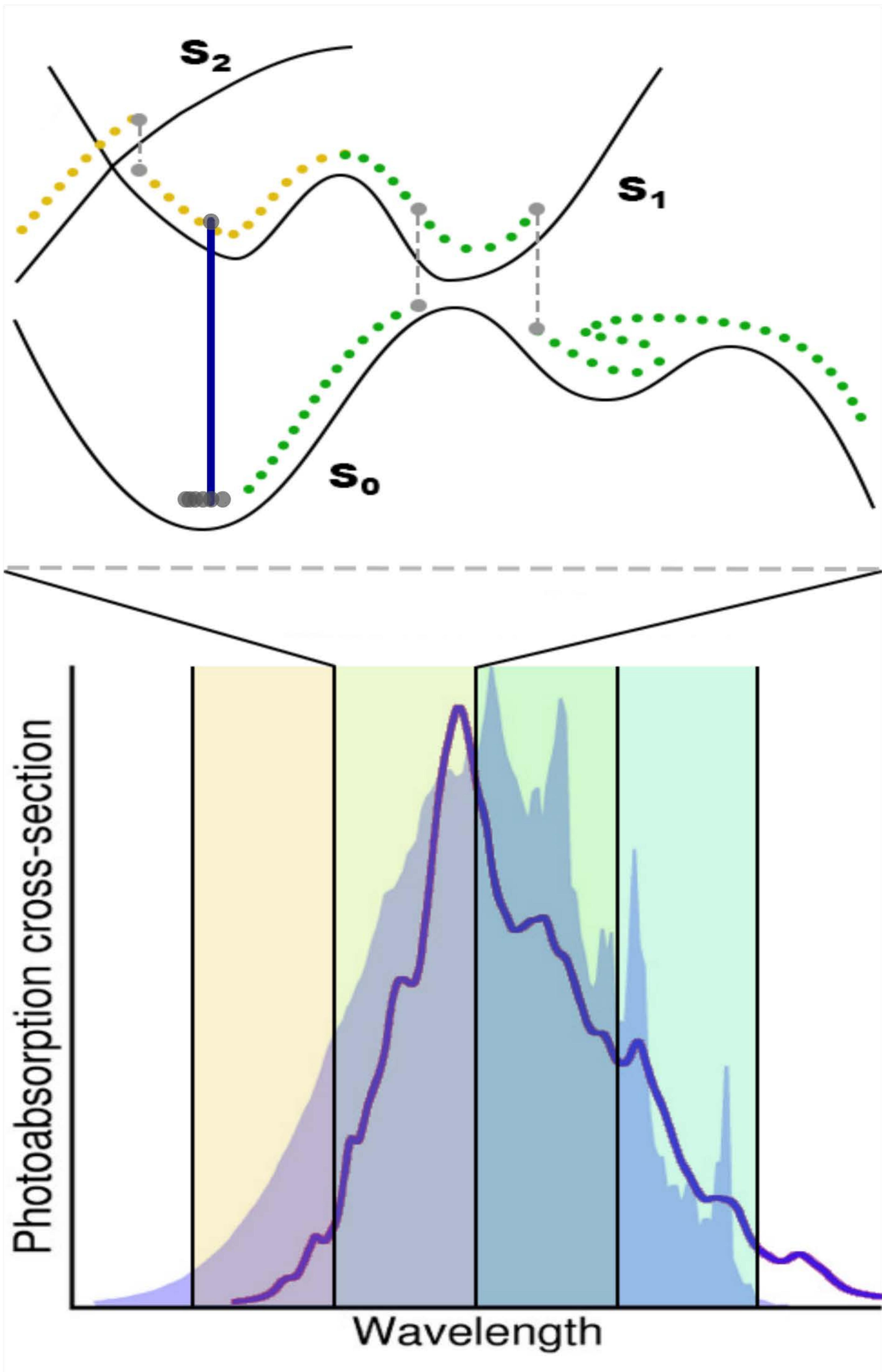


# Wavelength dependent quantum yield $\phi(\lambda)$



- Partitioning the spectra in energy windows

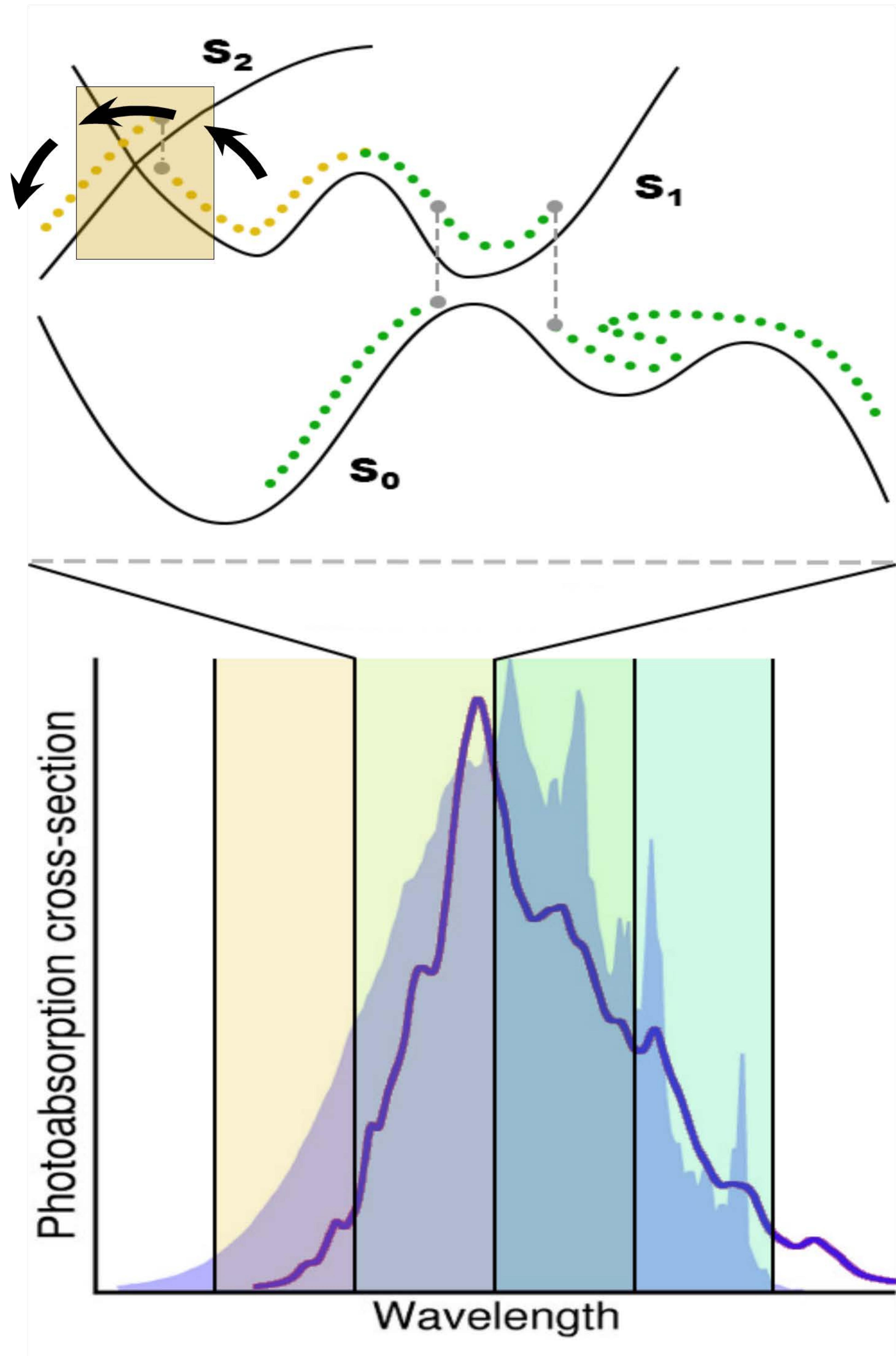
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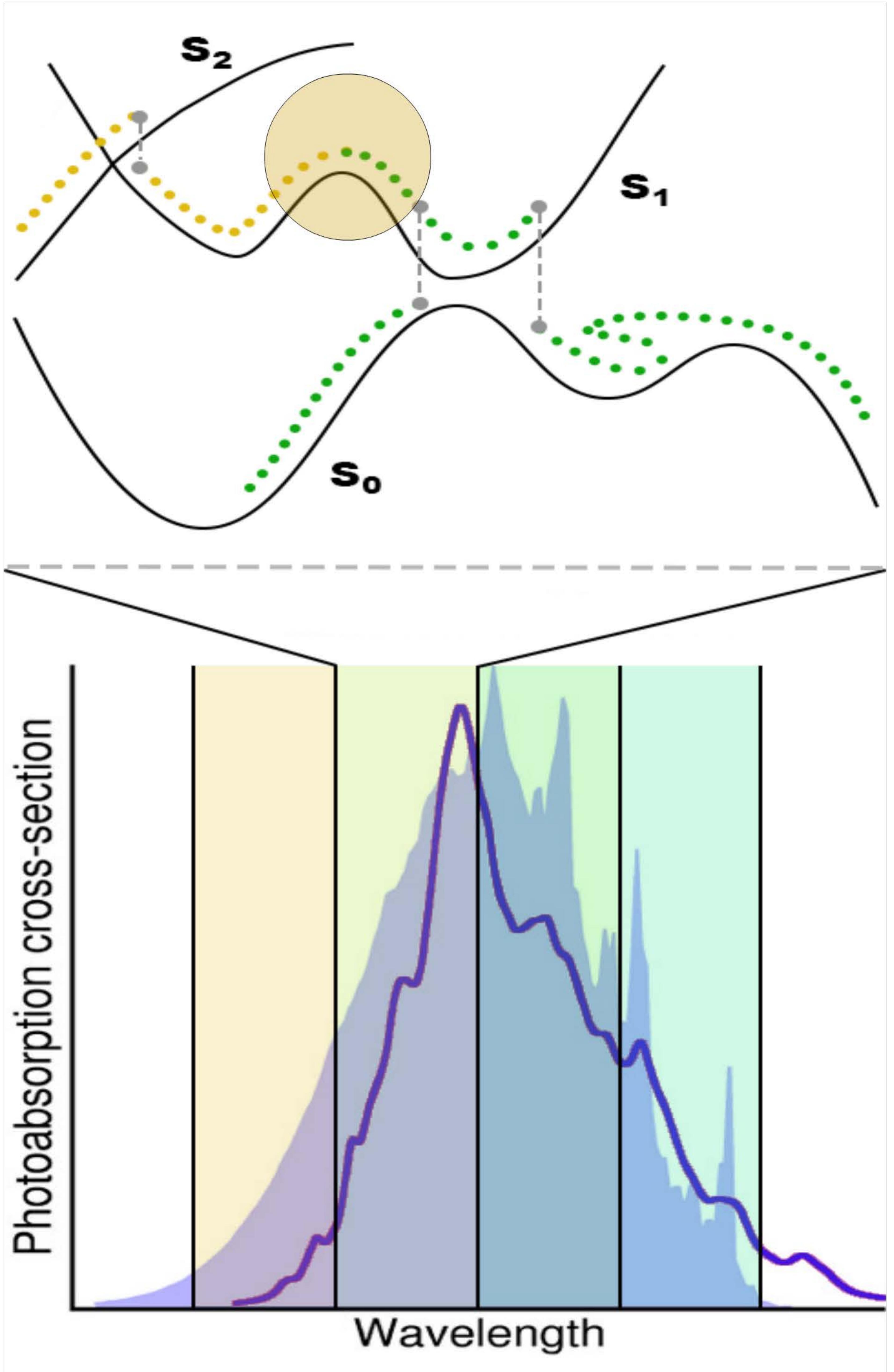
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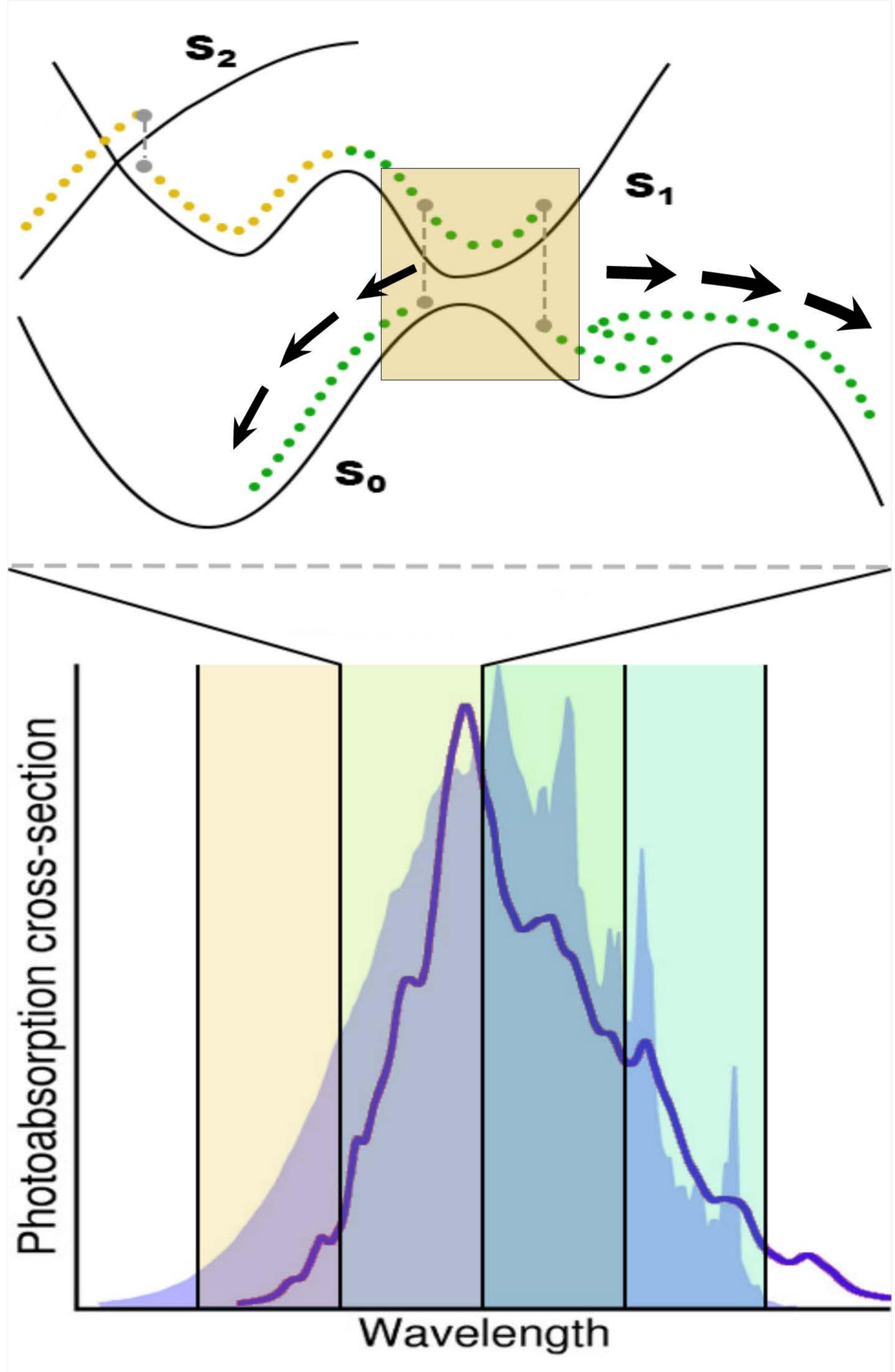
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- Switch** to a more multi-configurational (computationally **expensive**) electronic structure method when the  $S_0$  and  $S_1$  states approach

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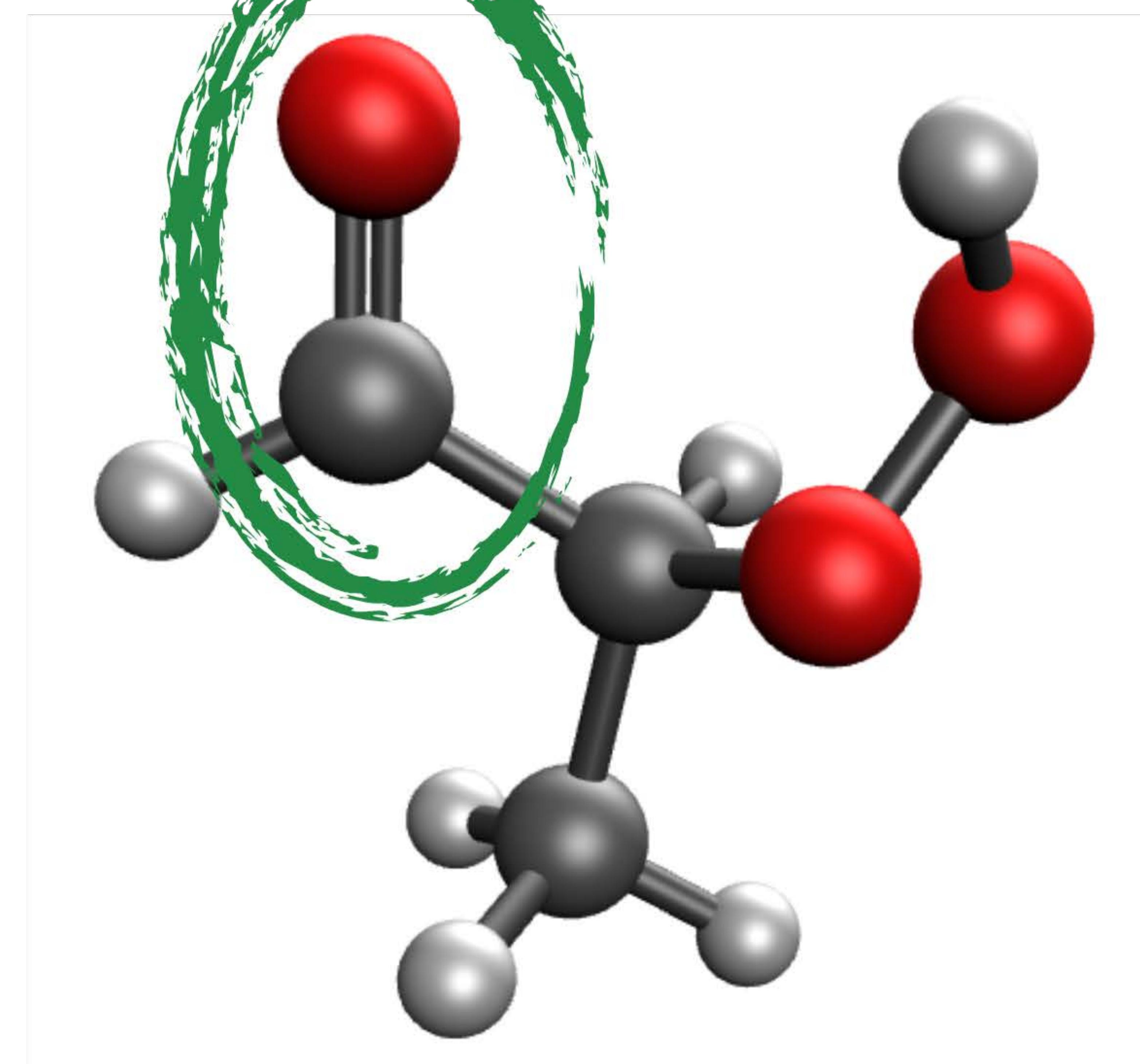
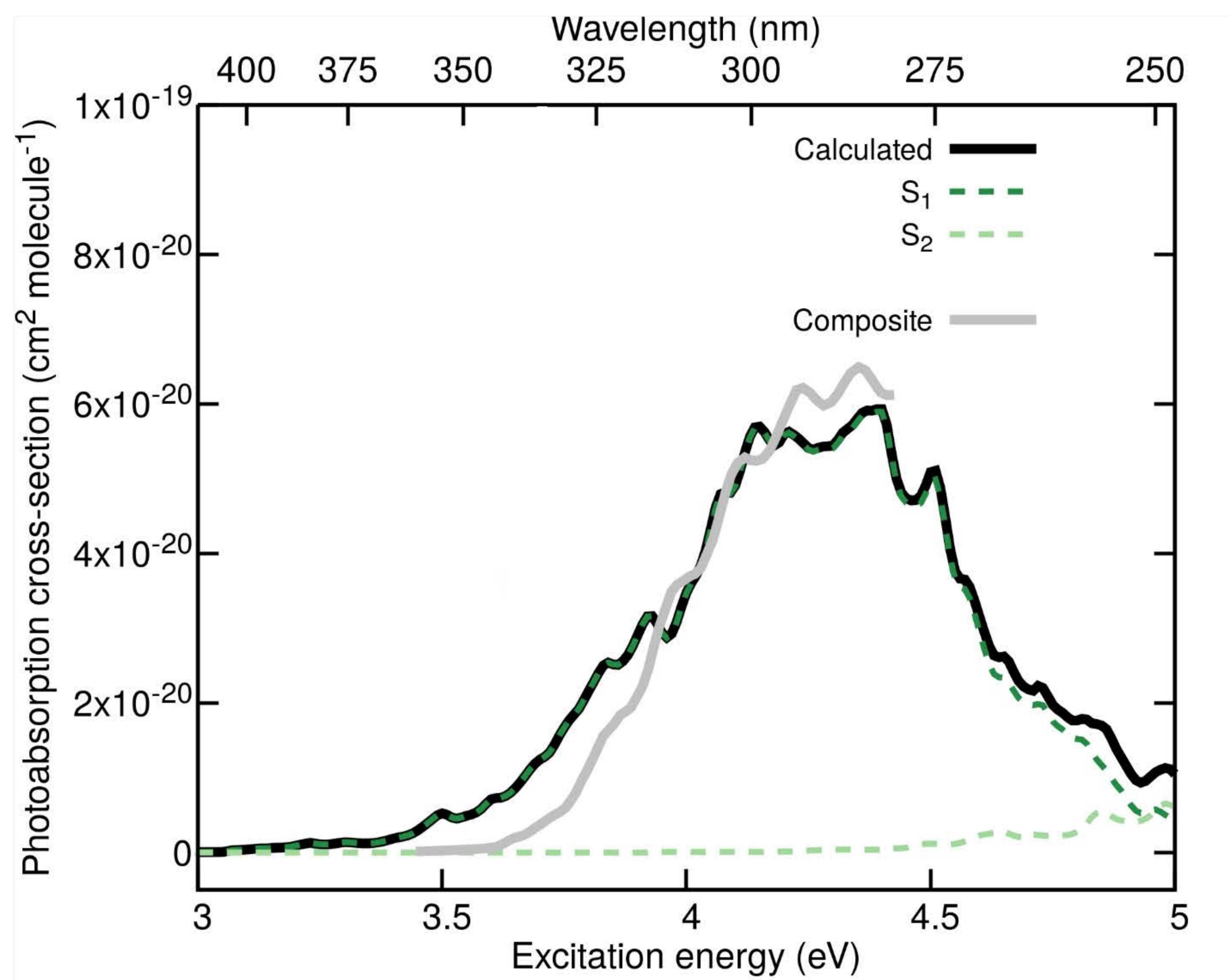
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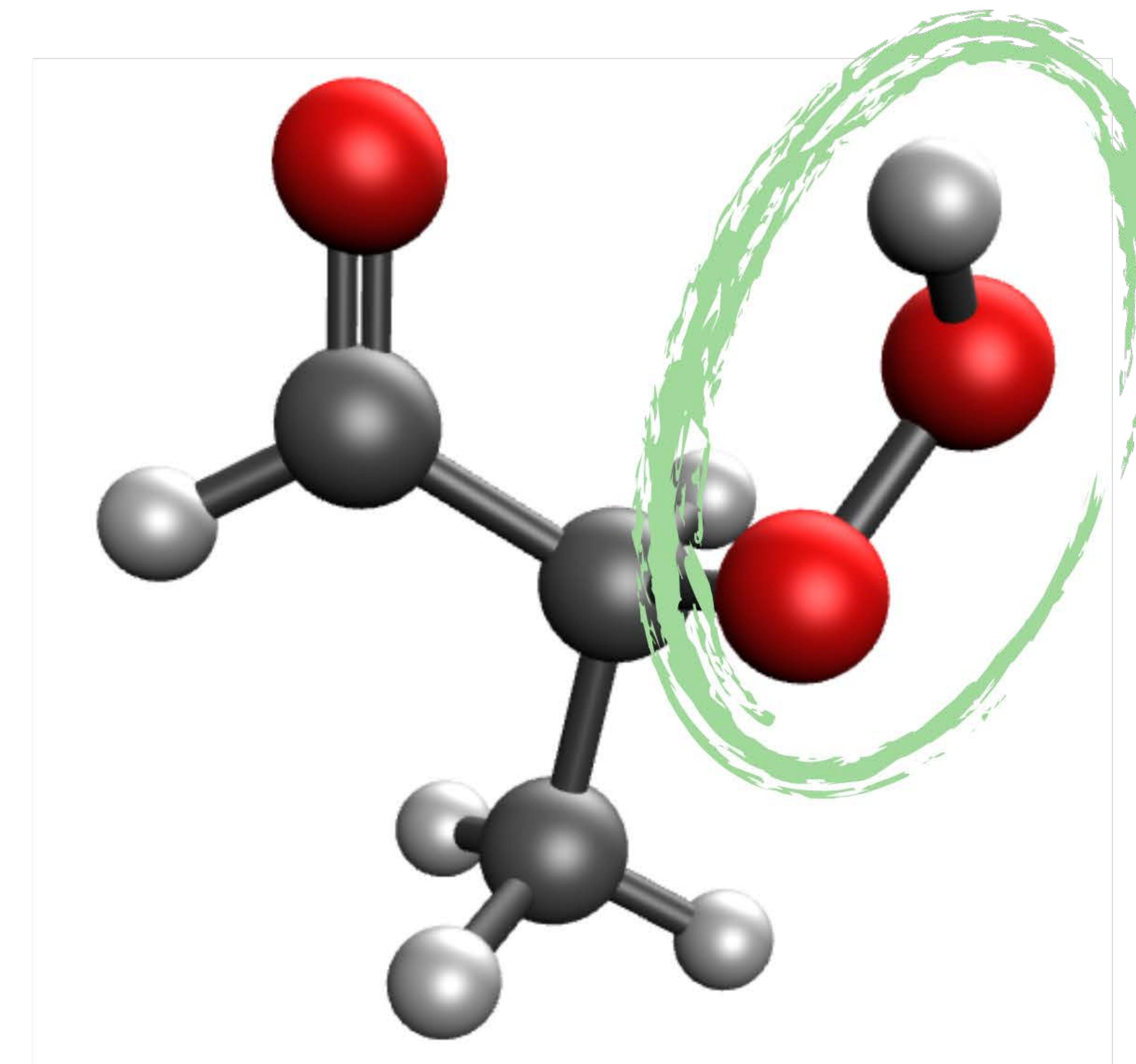
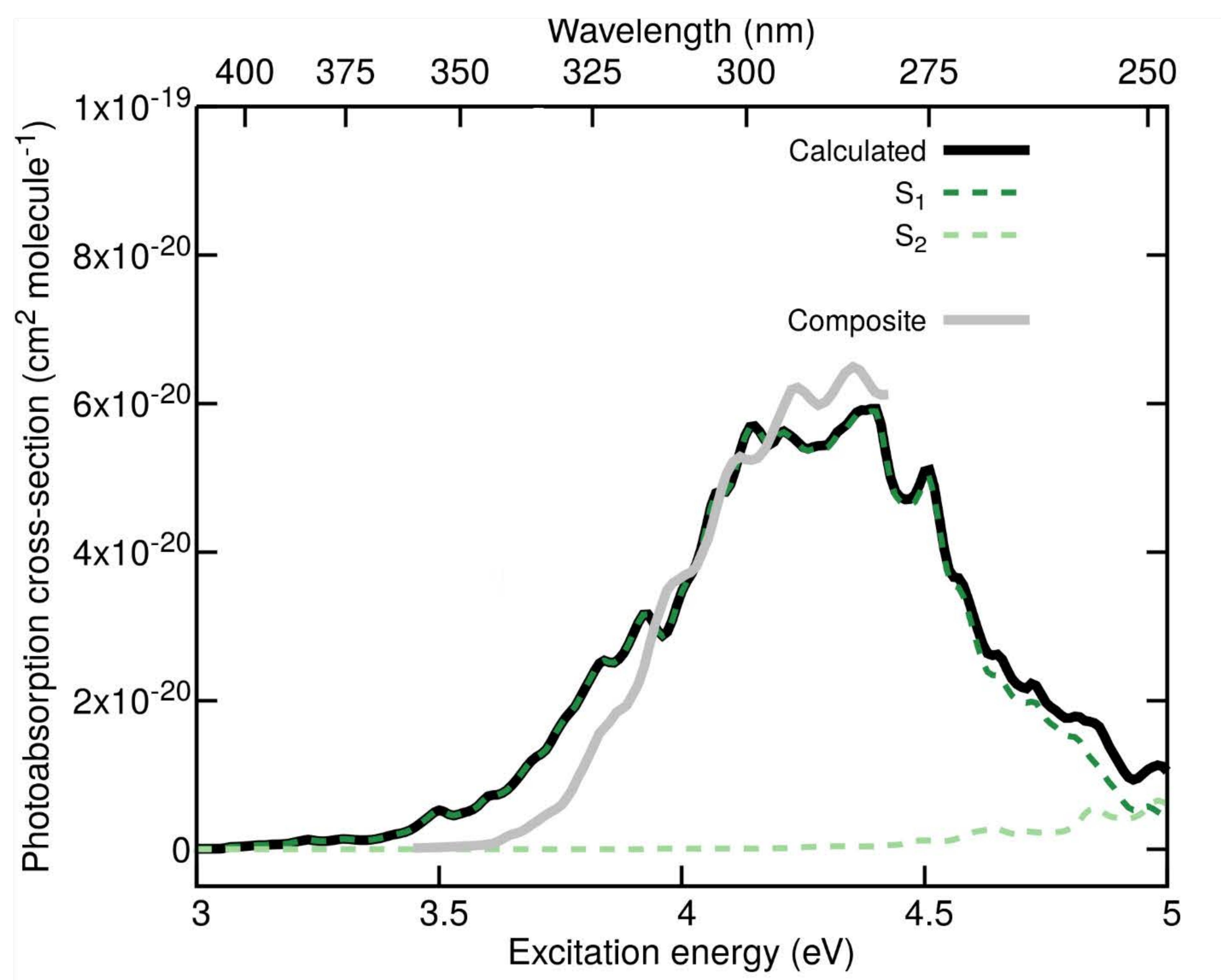
# Photoabsorption cross section $\sigma(\lambda)$



**2-hydroperoxypropanal**


Marsili Emanuele, Antonio Prlj, and Basile FE Curchod. Submitted (2022)

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


## 2-hydroperoxypropanal


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
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
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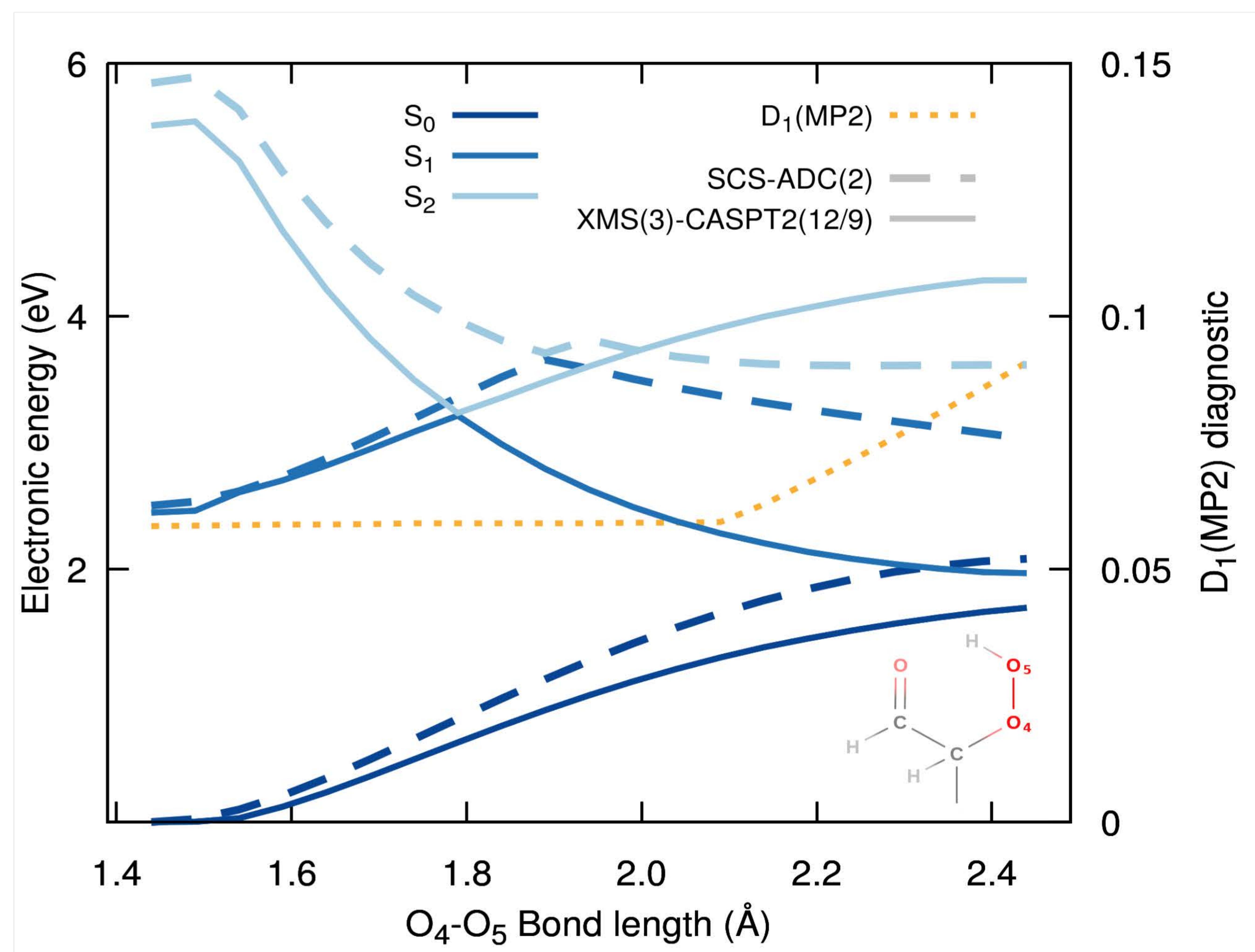
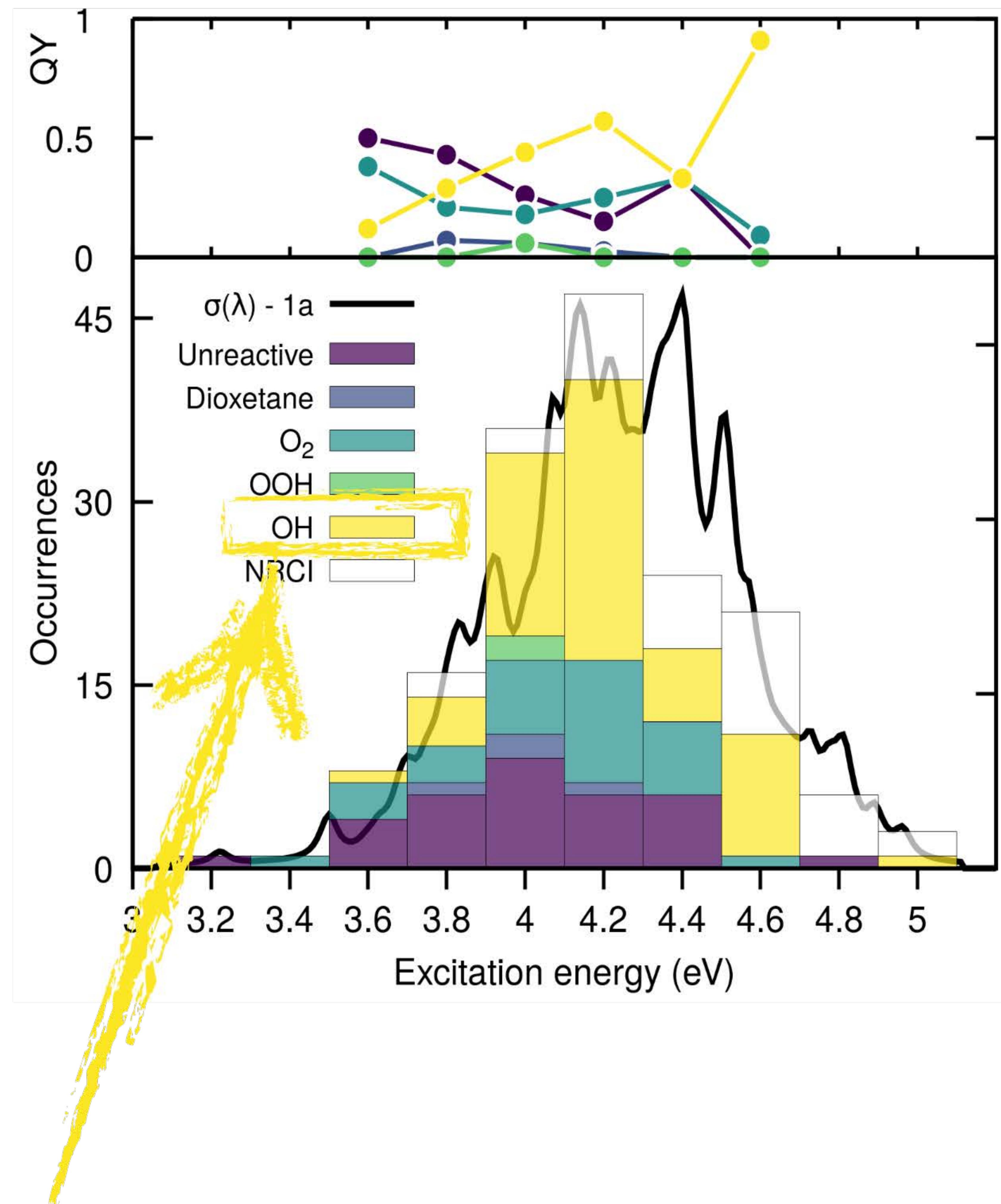


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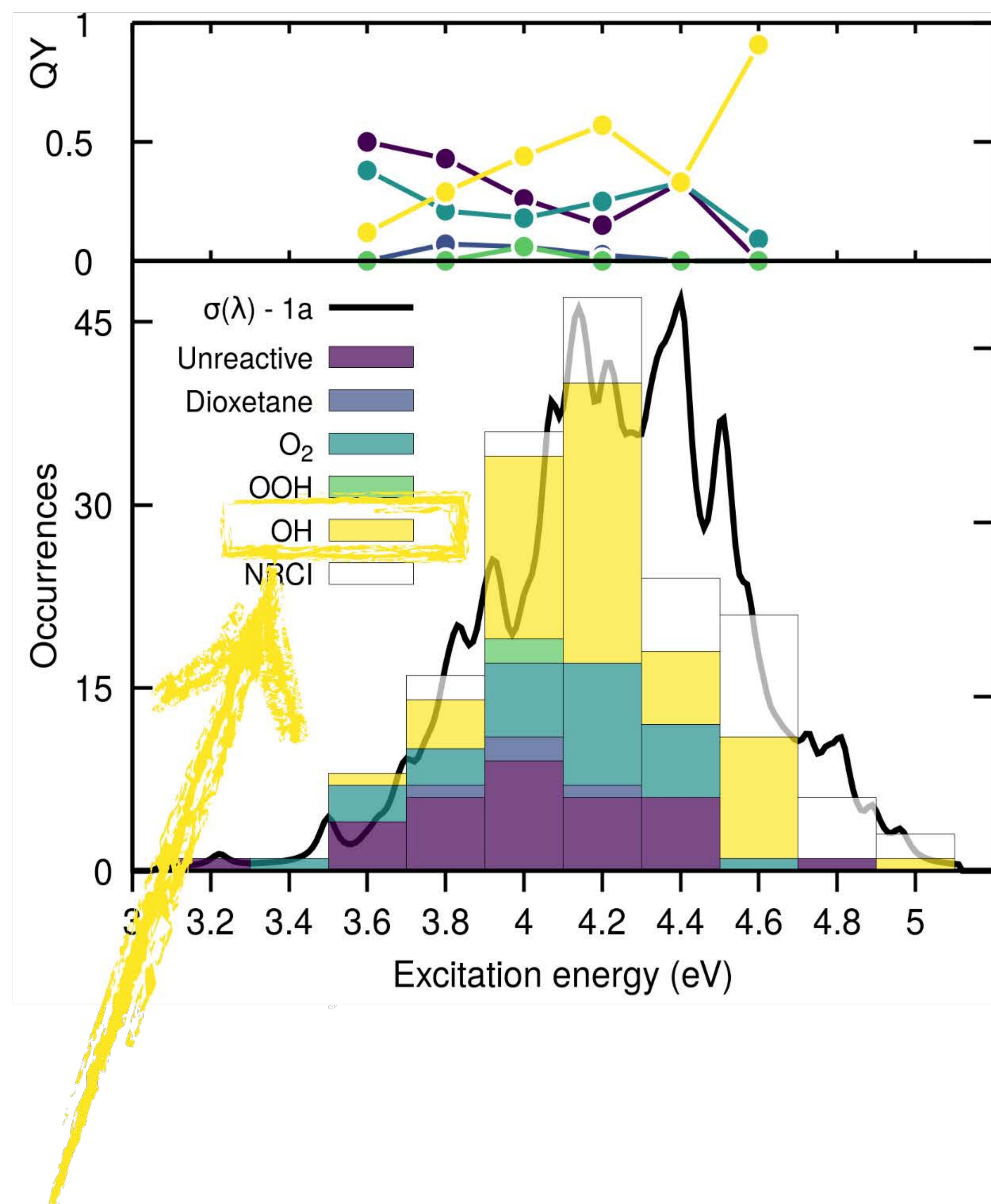


Caveat of ADC(2): *Phys. Chem. Chem. Phys.*, 2021, 23, 12945-1294

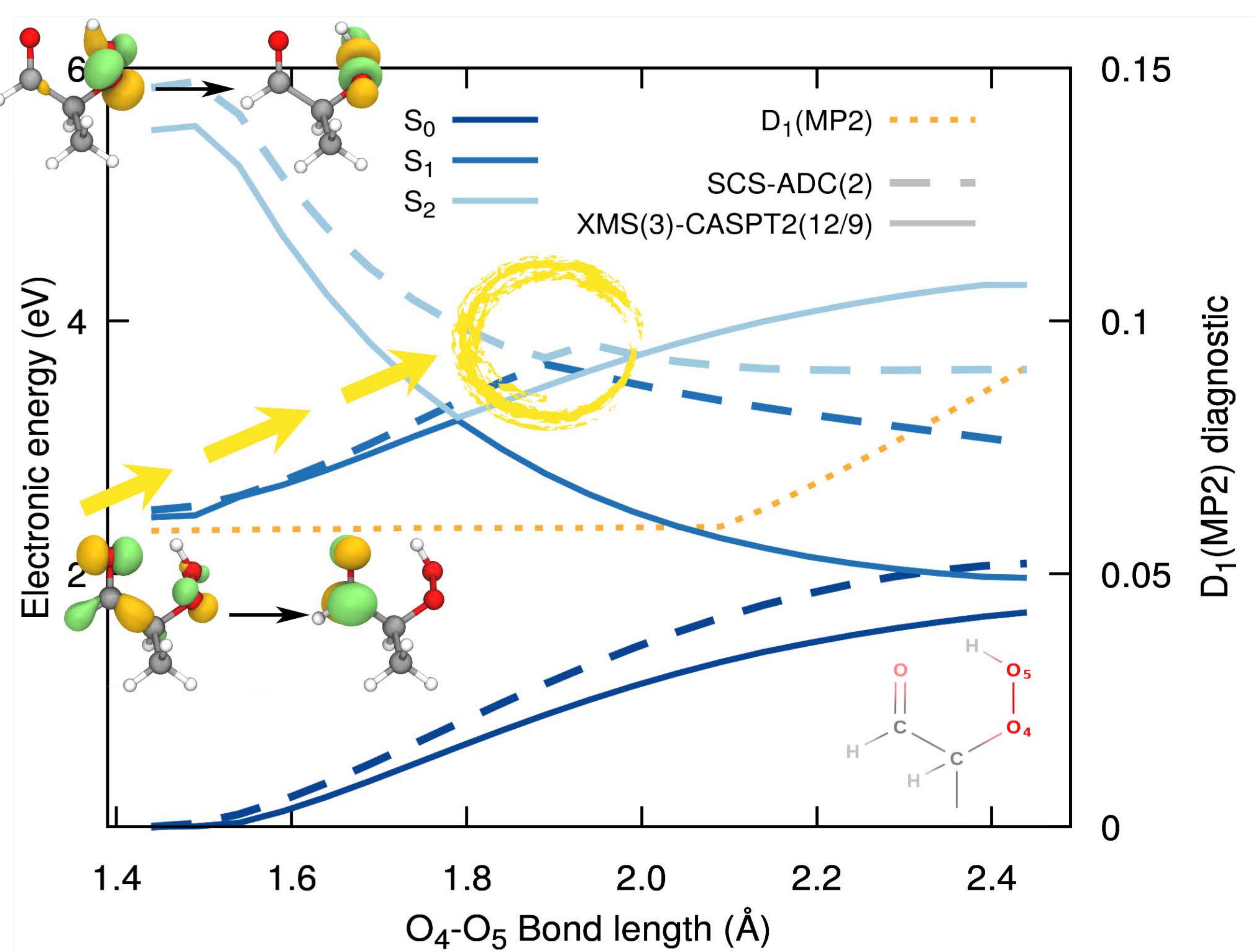
# OH quantum yield



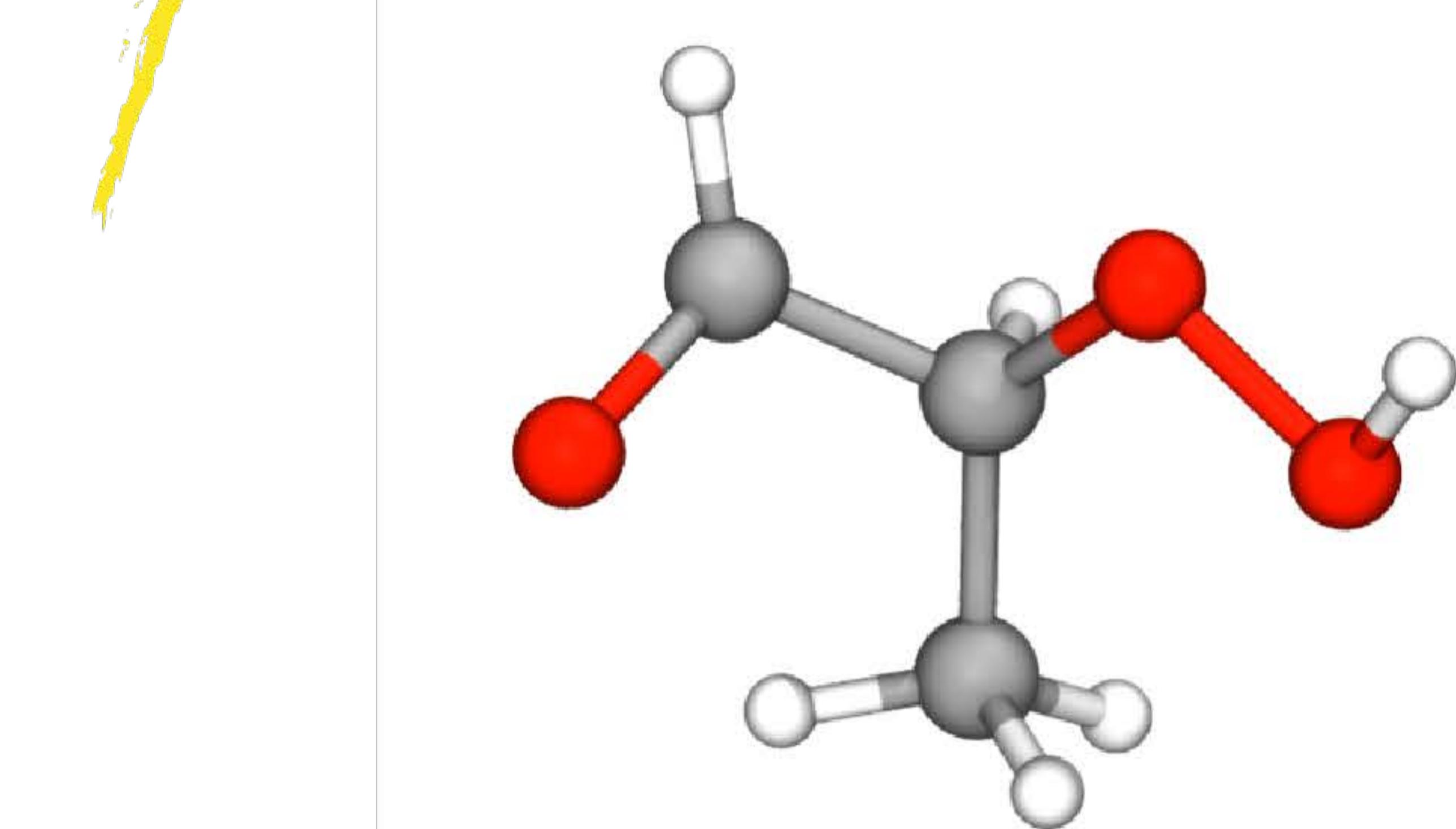
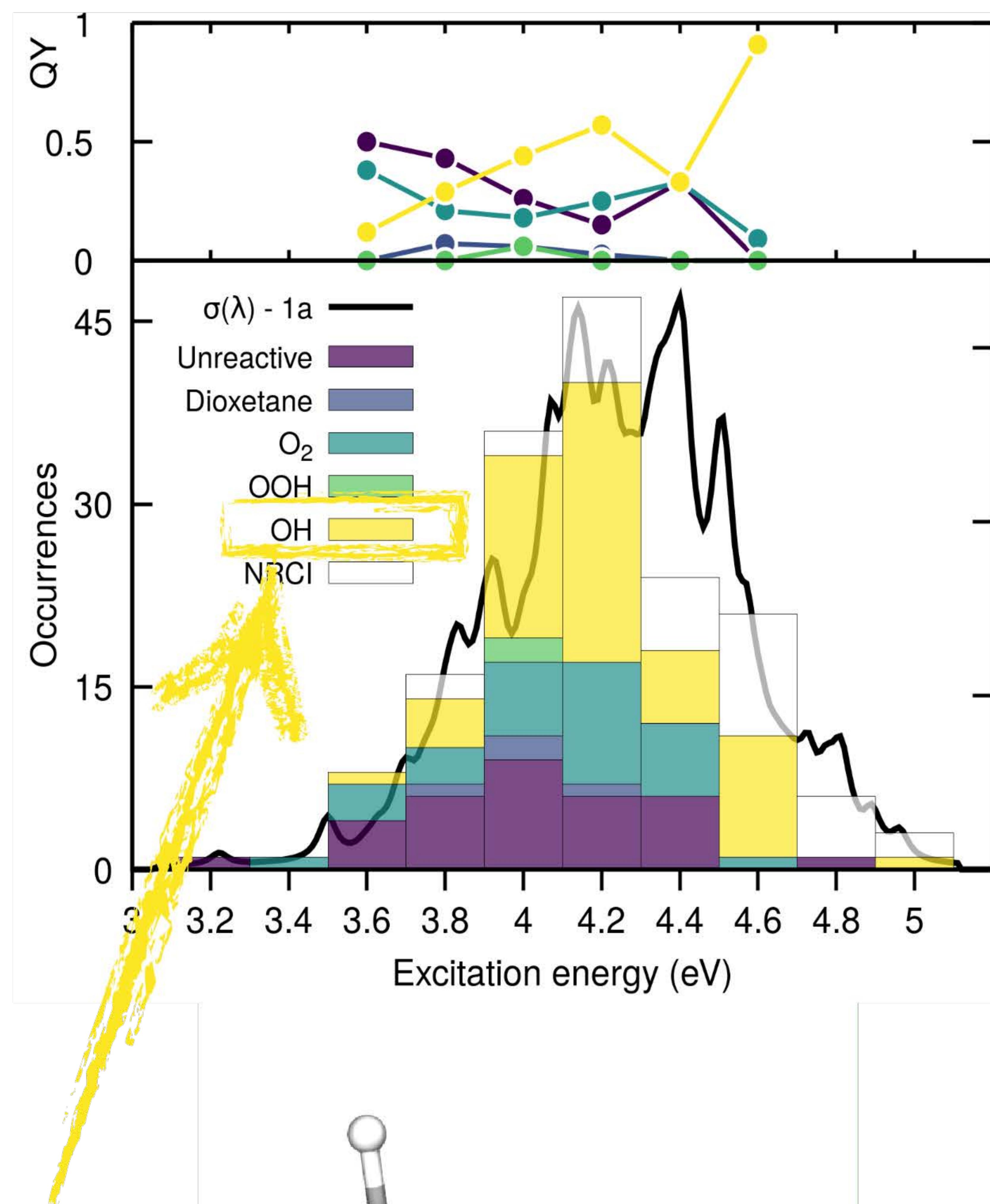
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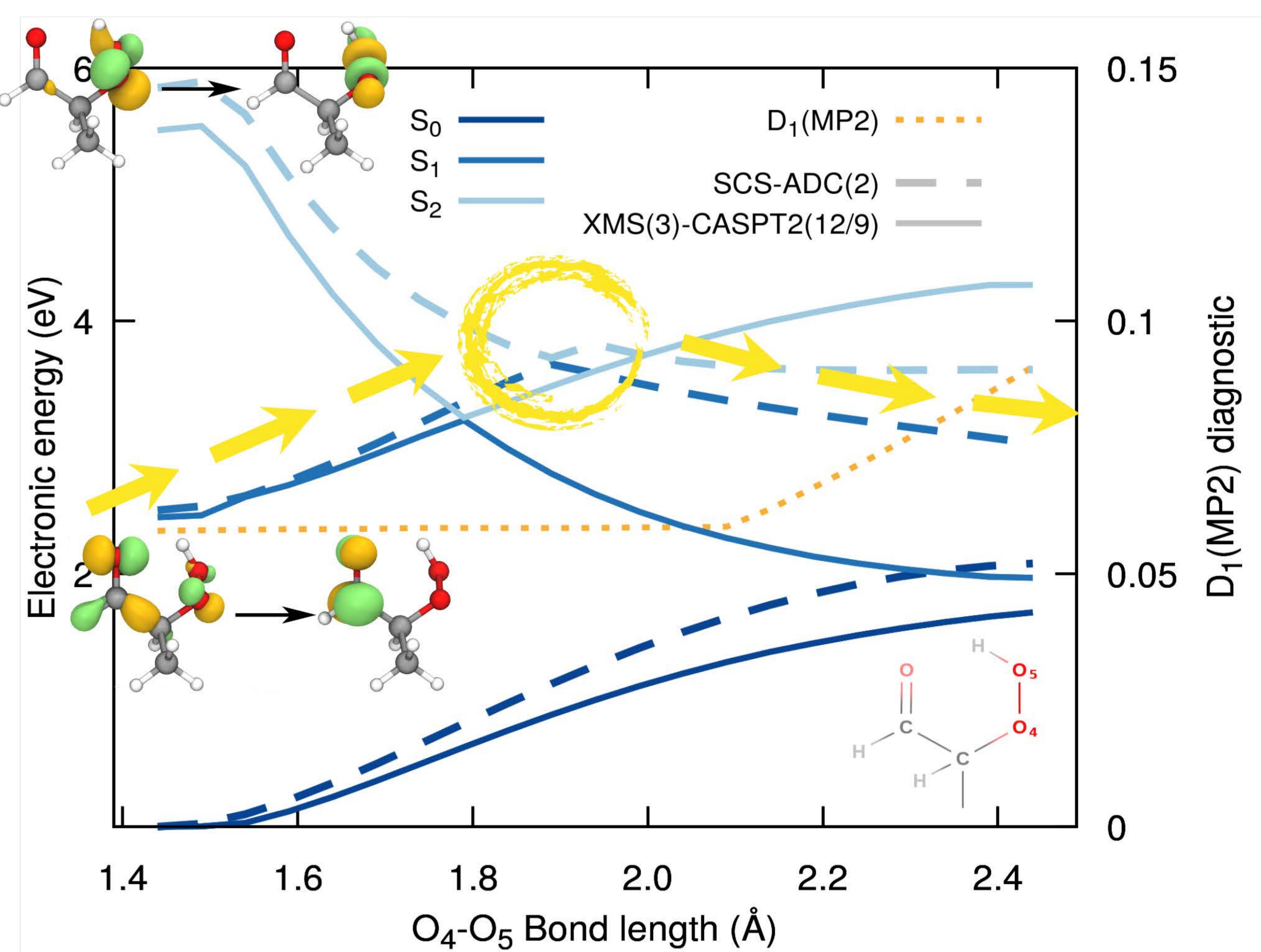
- The  $O_4-O_5$  elongation leads to the  $S_1/S_2$  intersection seam



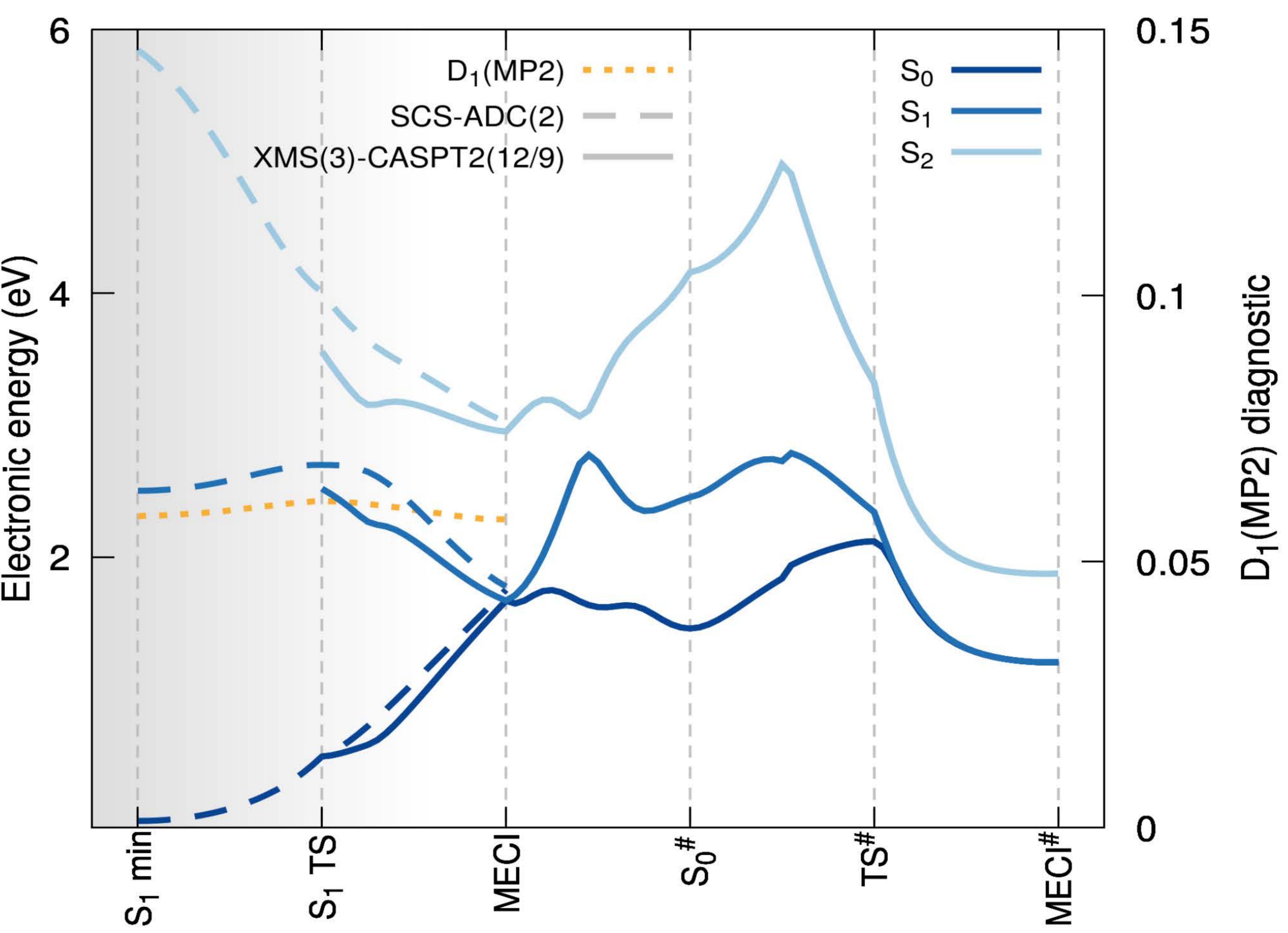
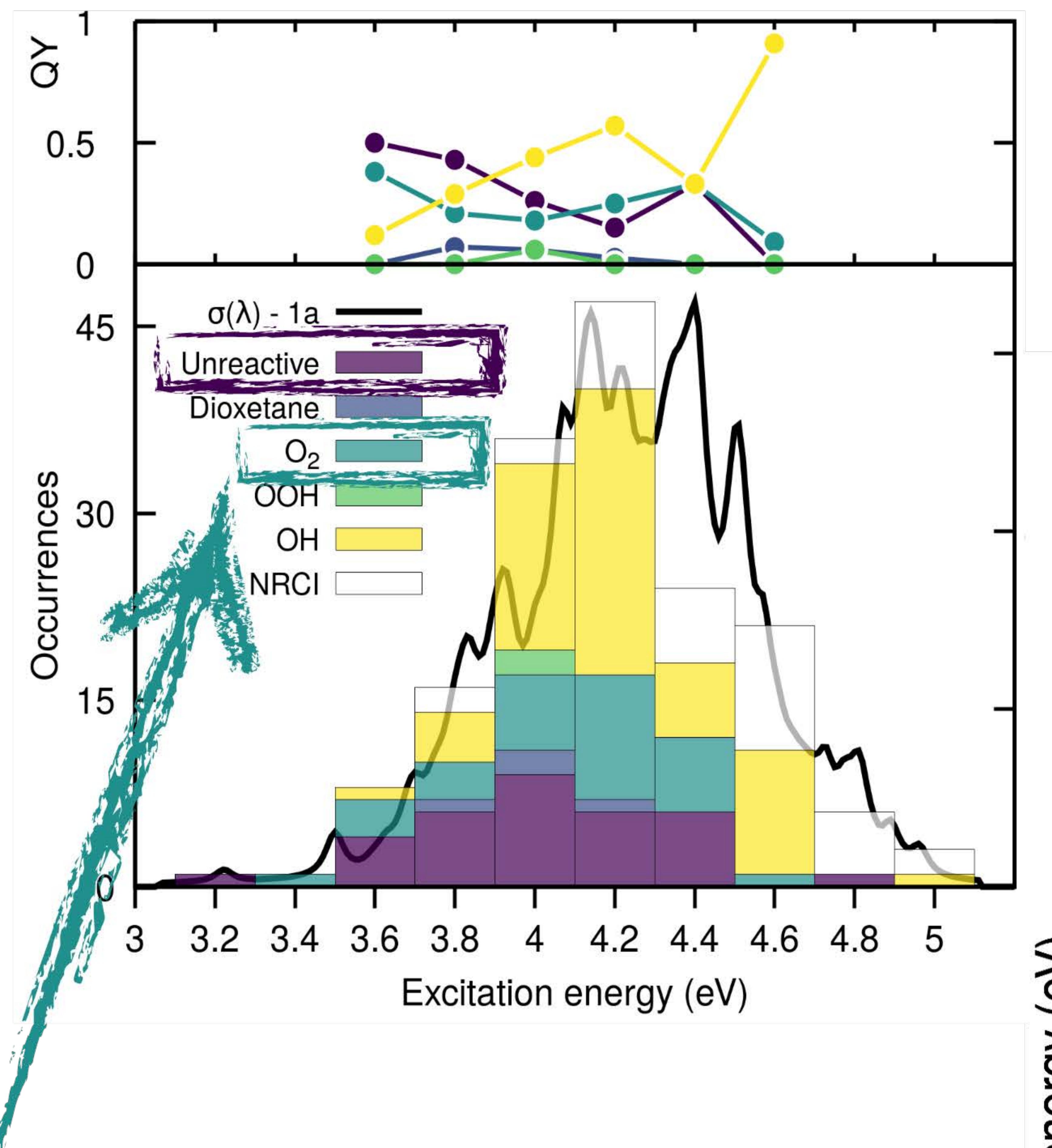
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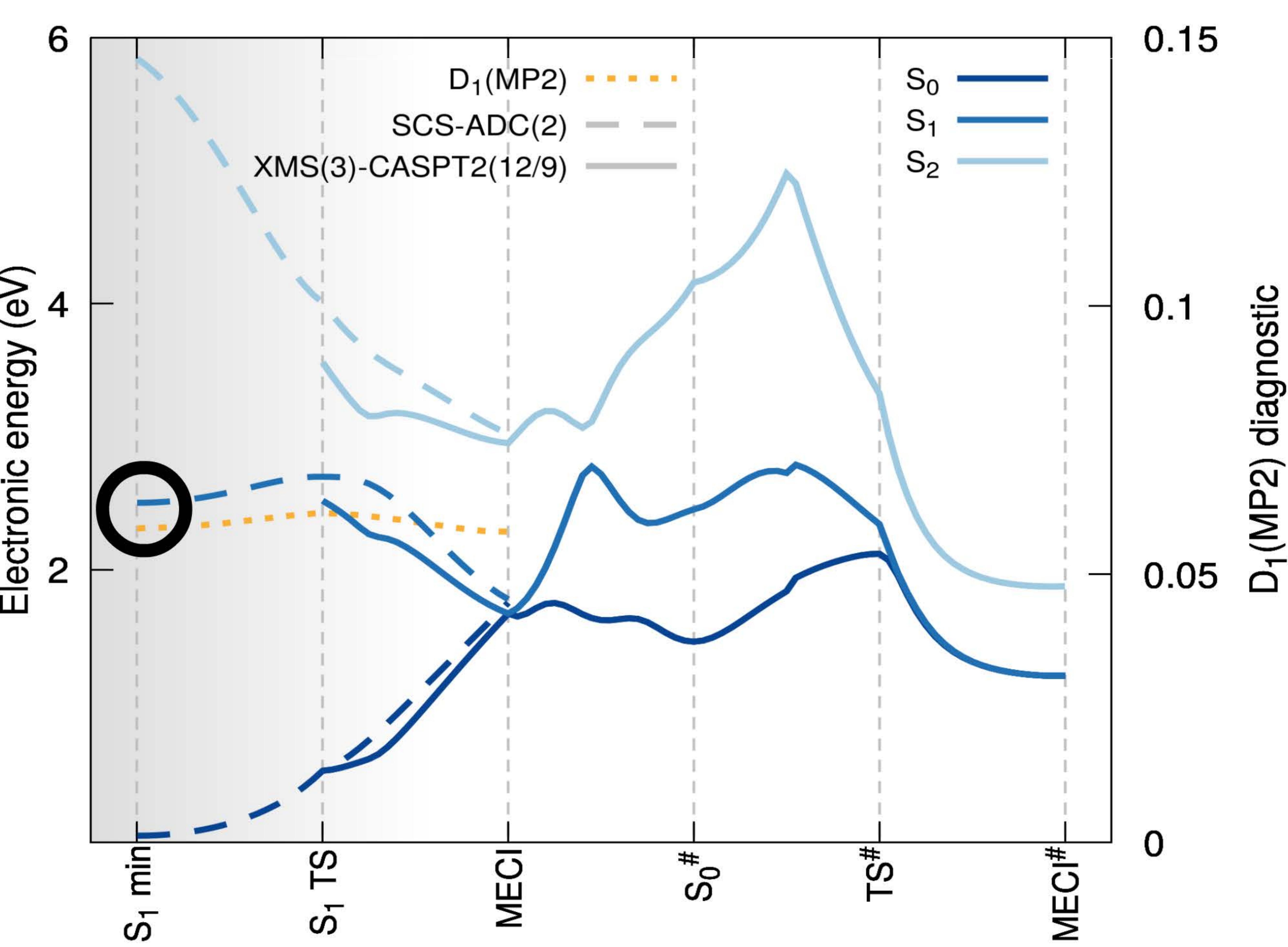
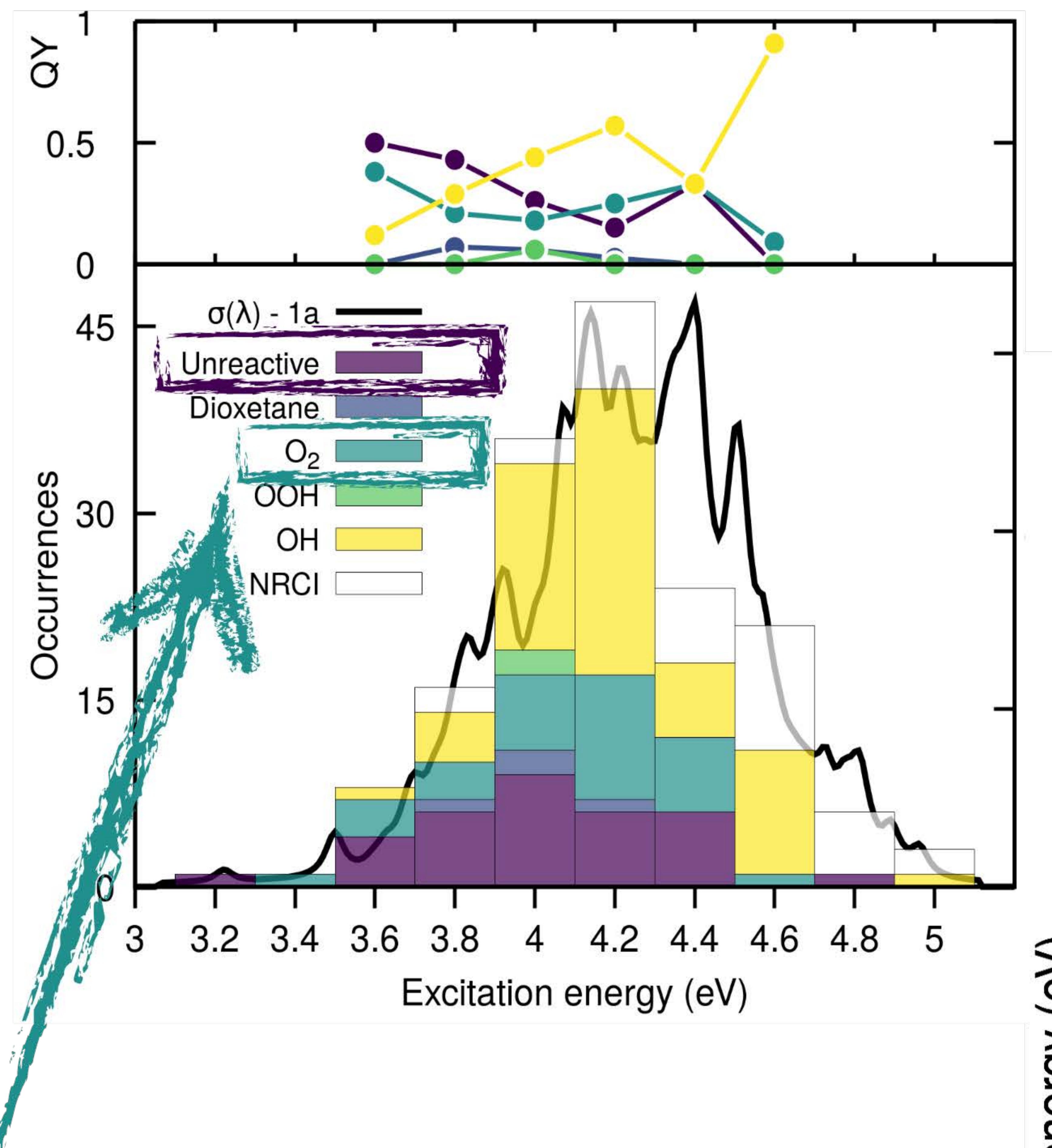
- The  $\text{O}_4\text{-O}_5$  elongation leads to the  $S_1/S_2$  intersection seam
- The change of the electronic character of the "active state" triggers the OH release



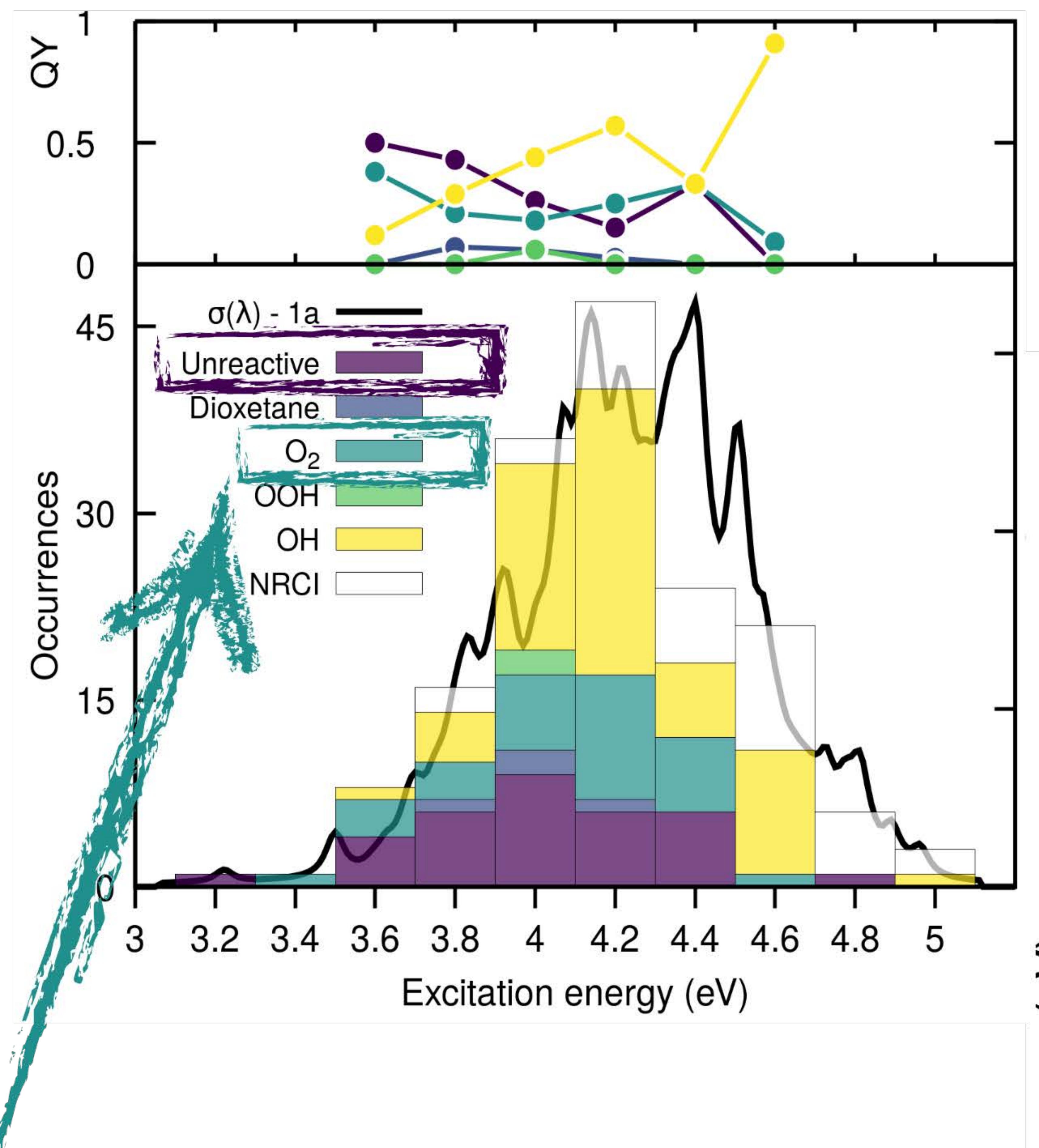
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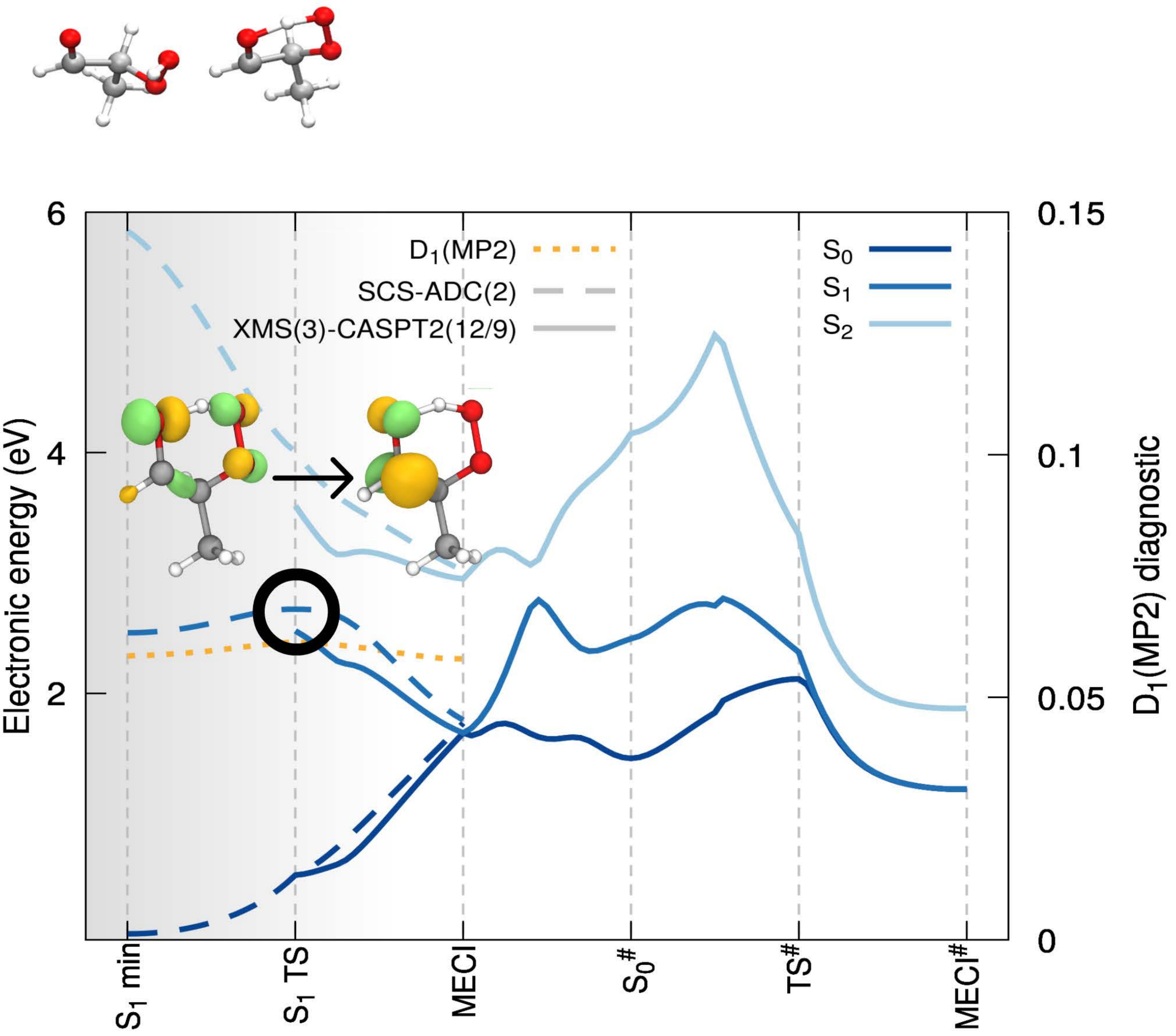
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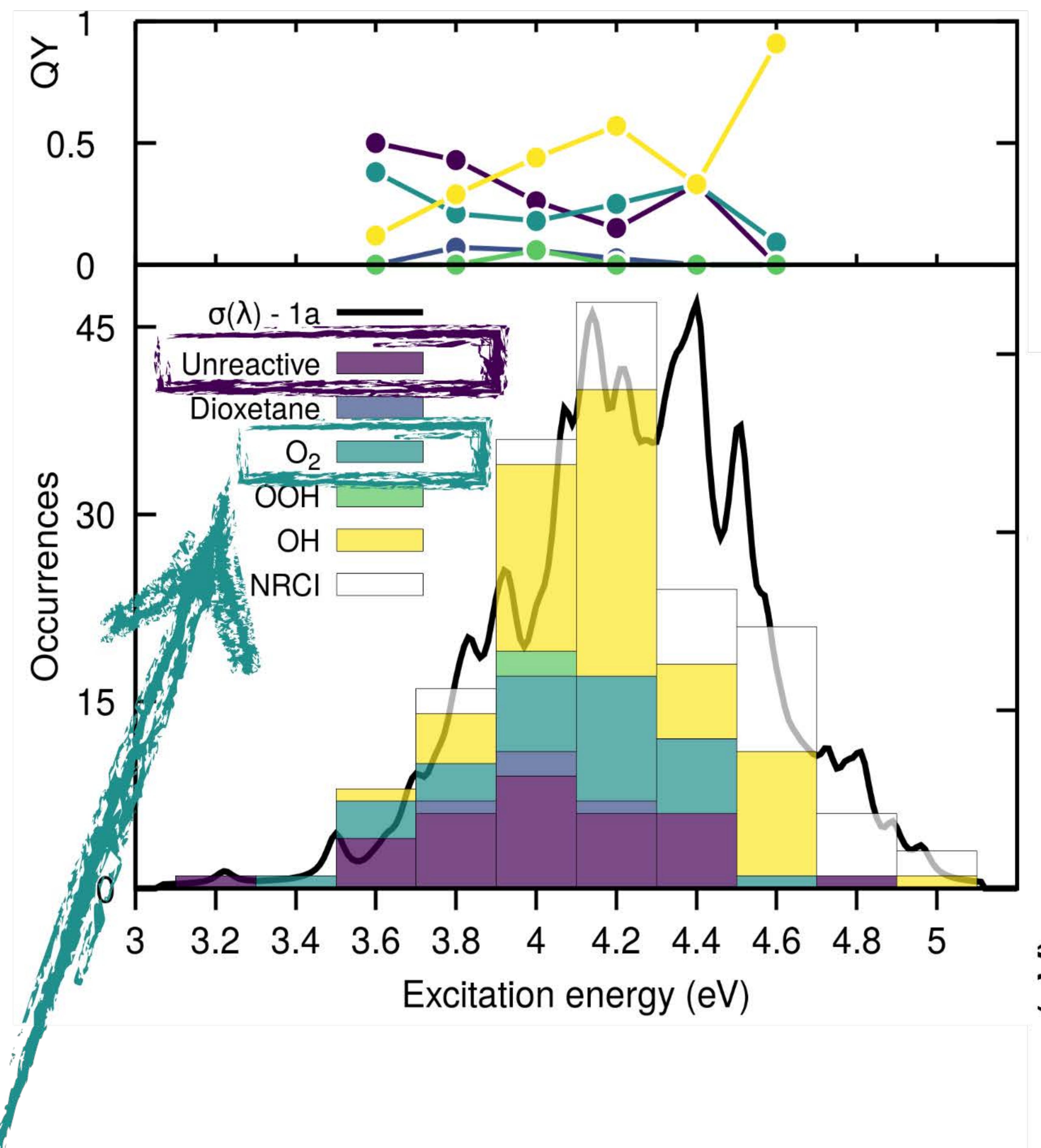
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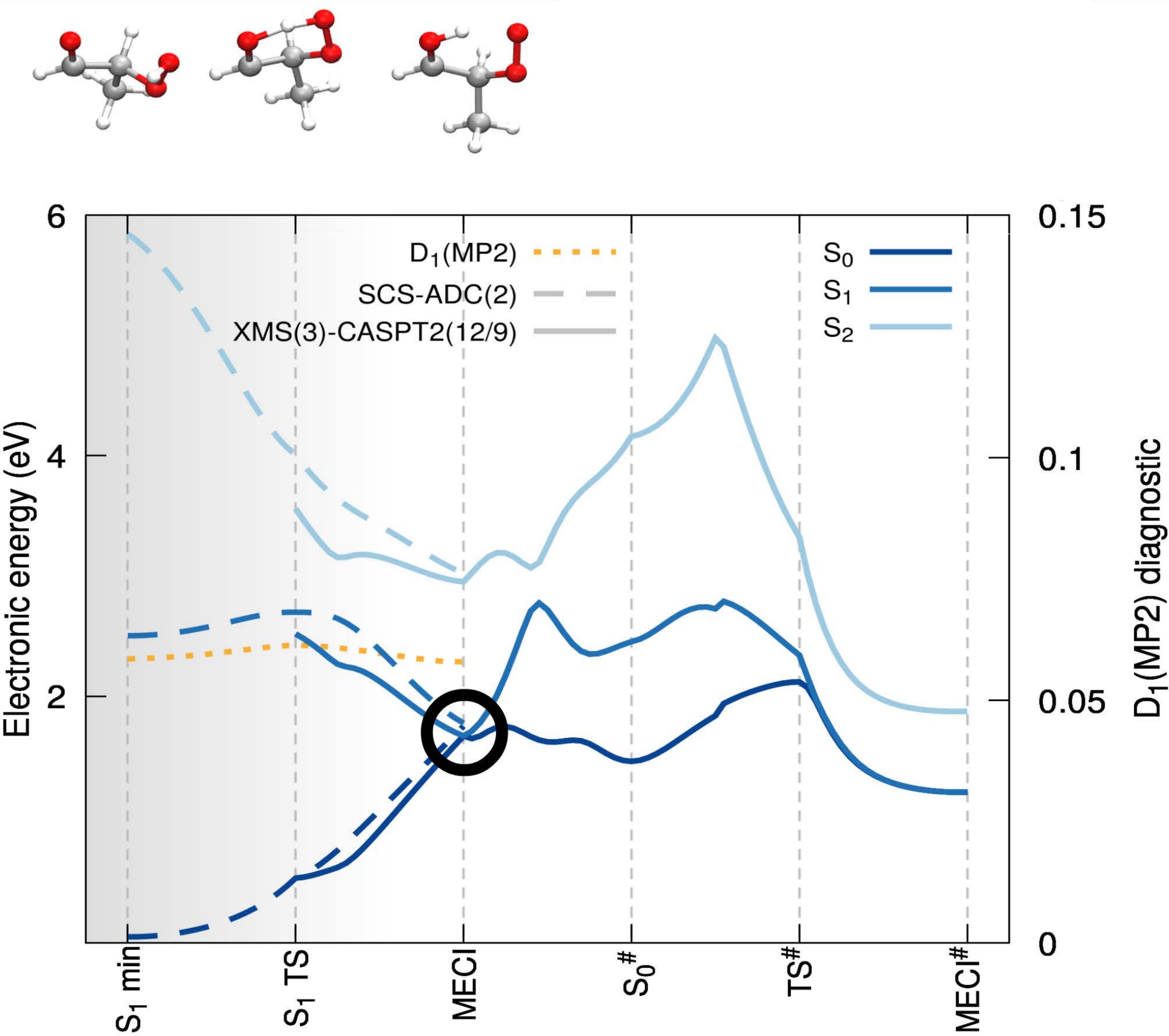
- The proton-coupled electron transfer (PCET) occurs in the excited state




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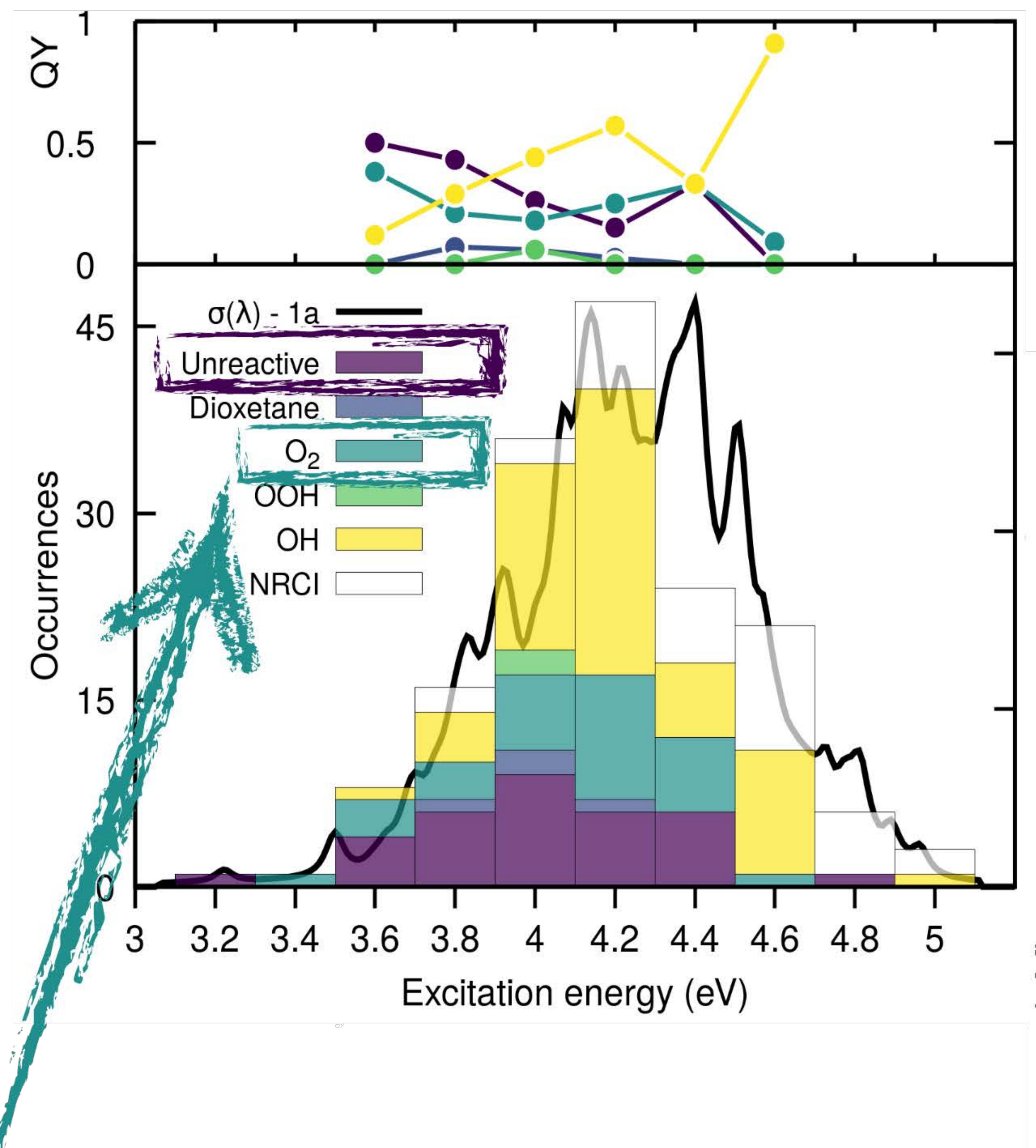
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- When approaching the conical intersection we switch to a multi-reference method



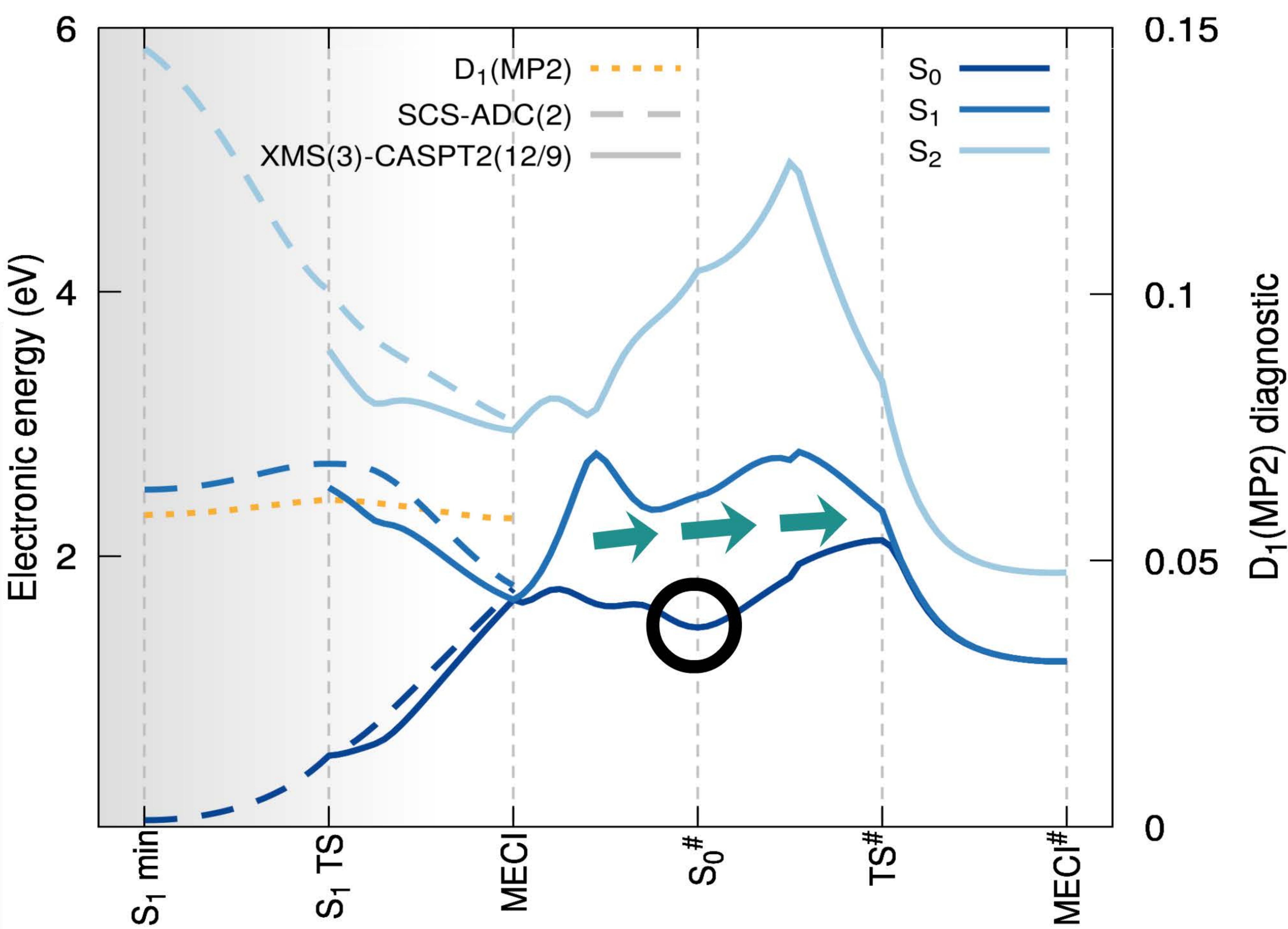
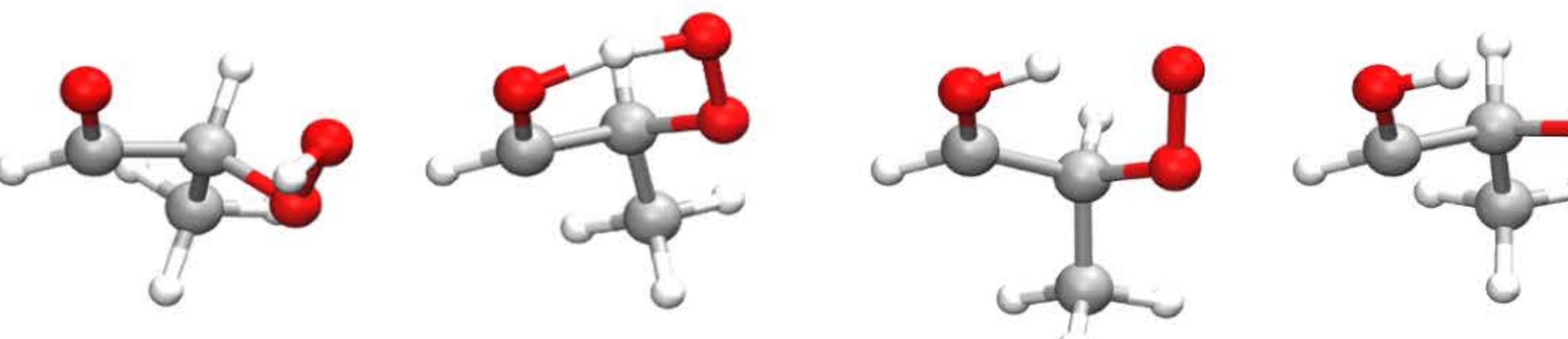
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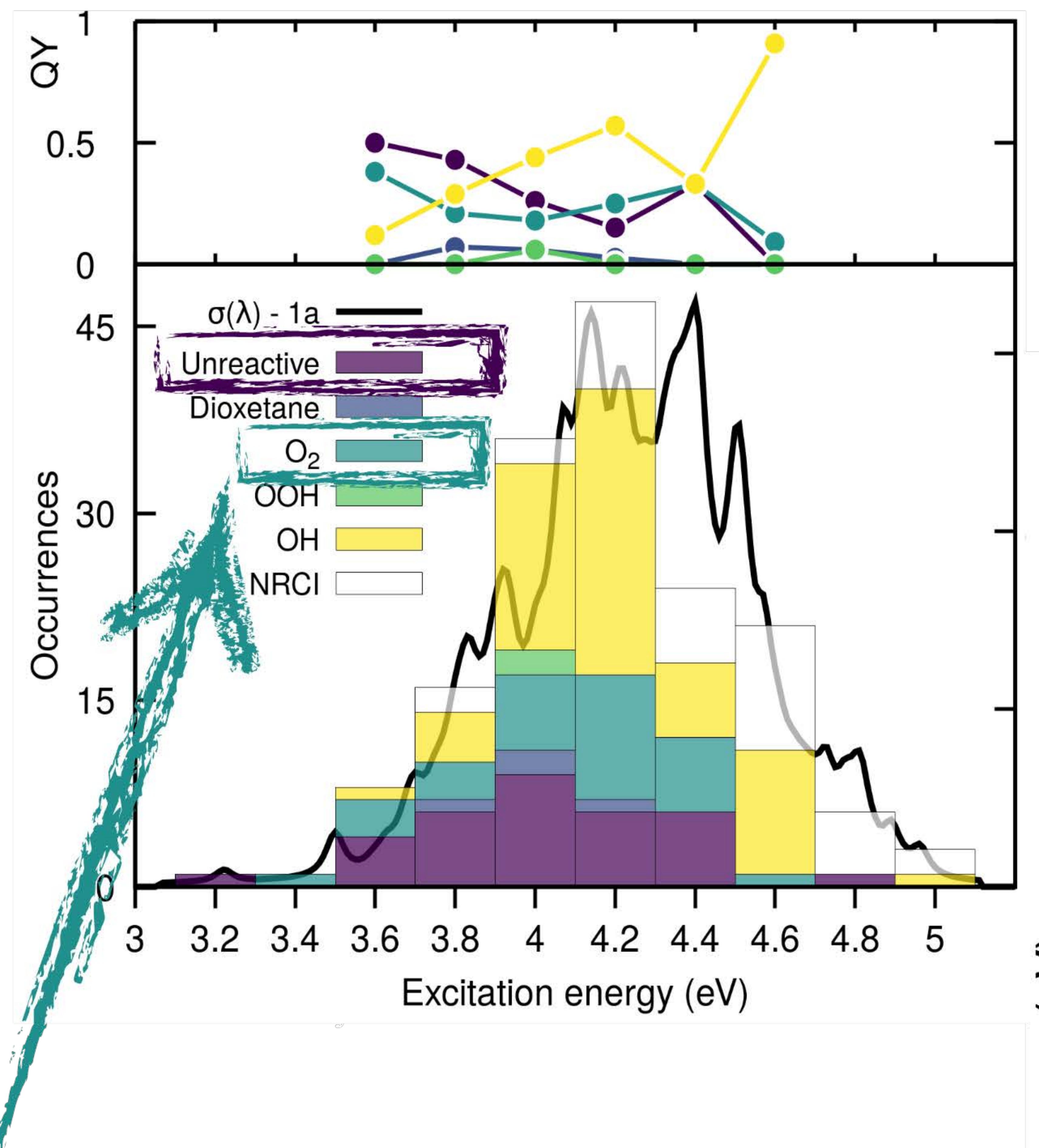
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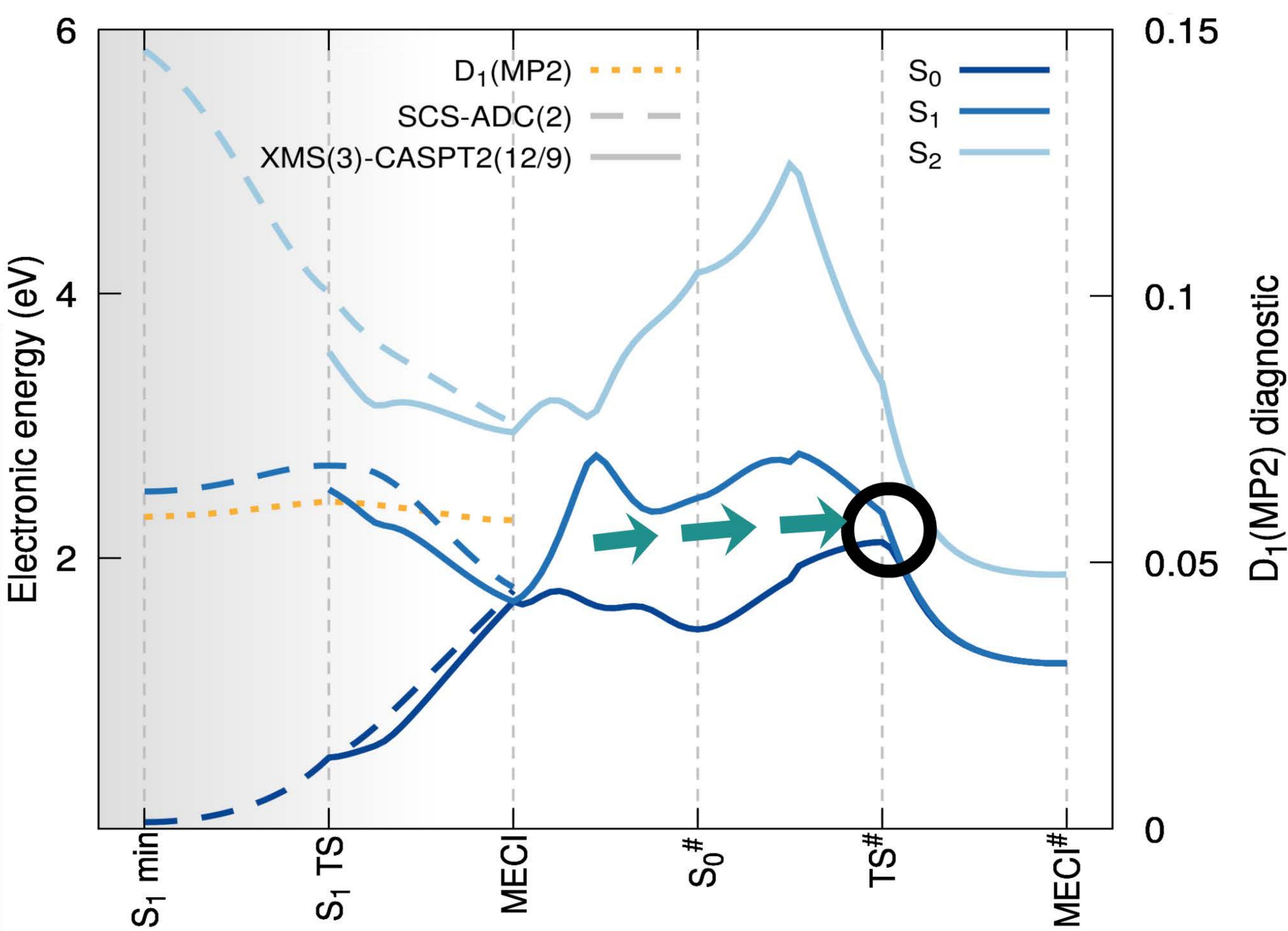
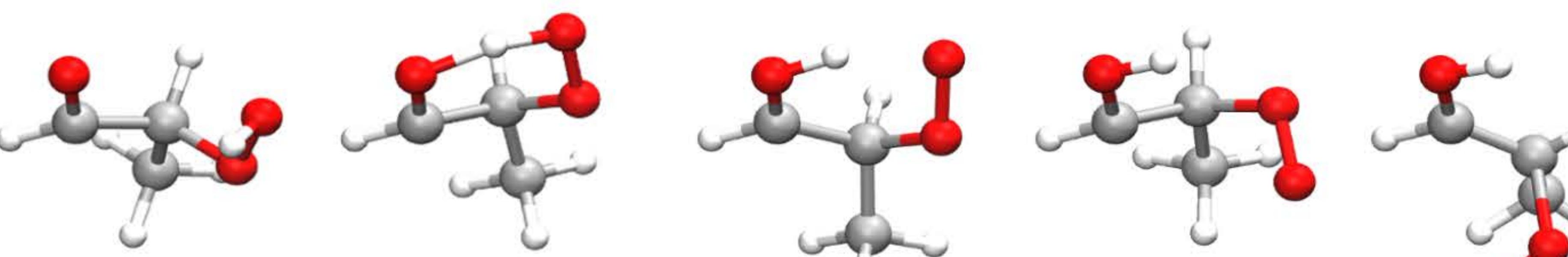
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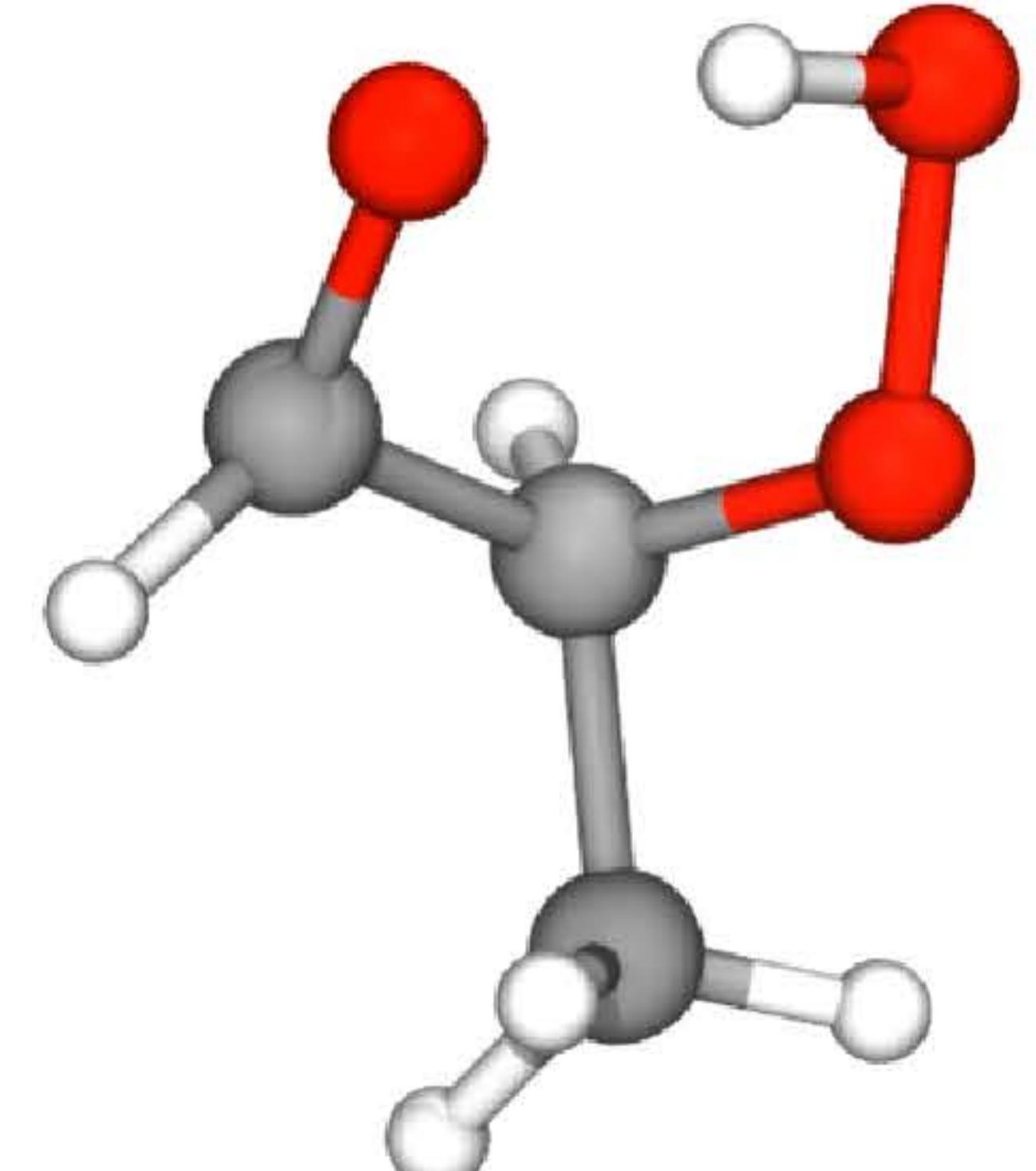
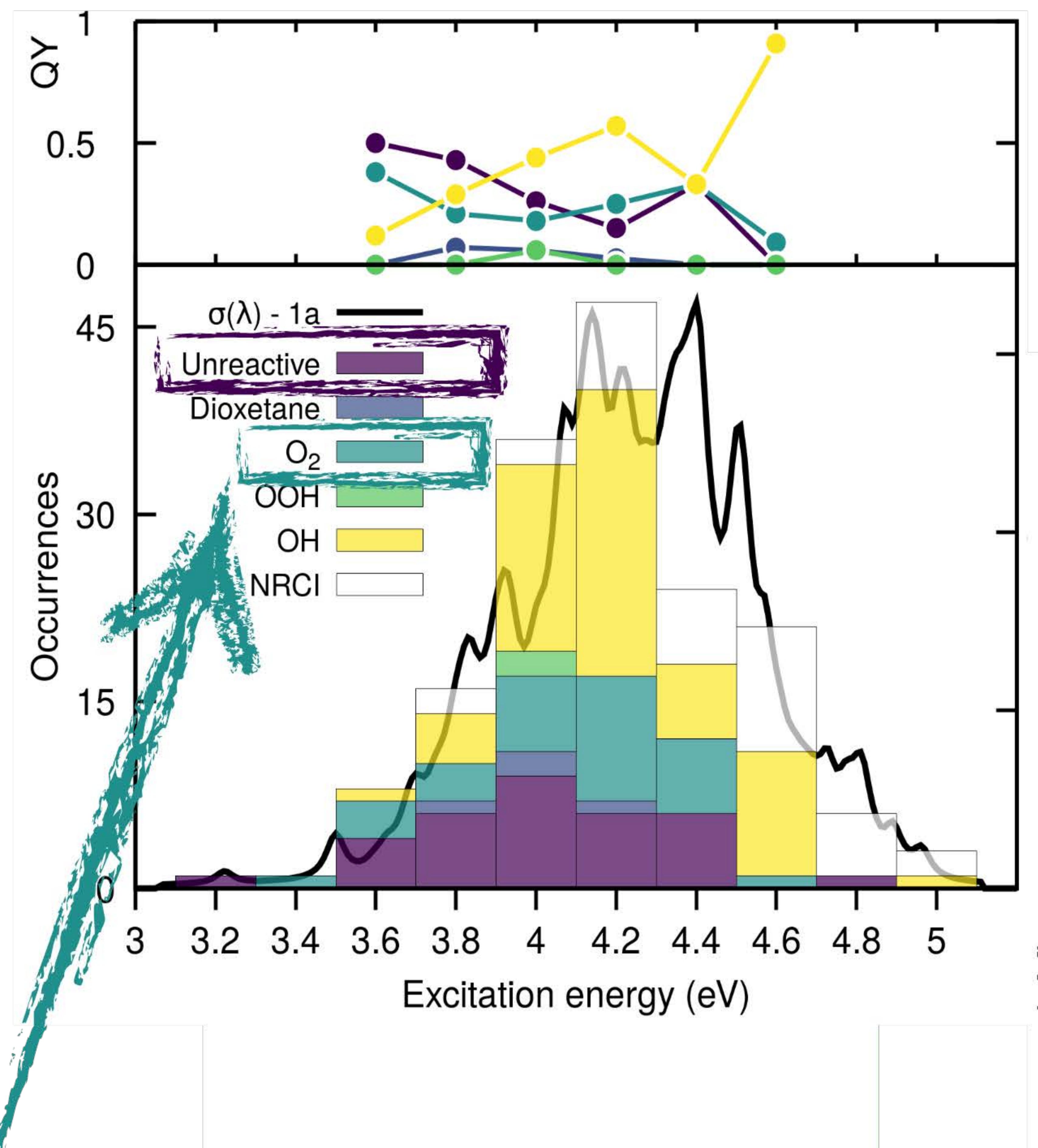
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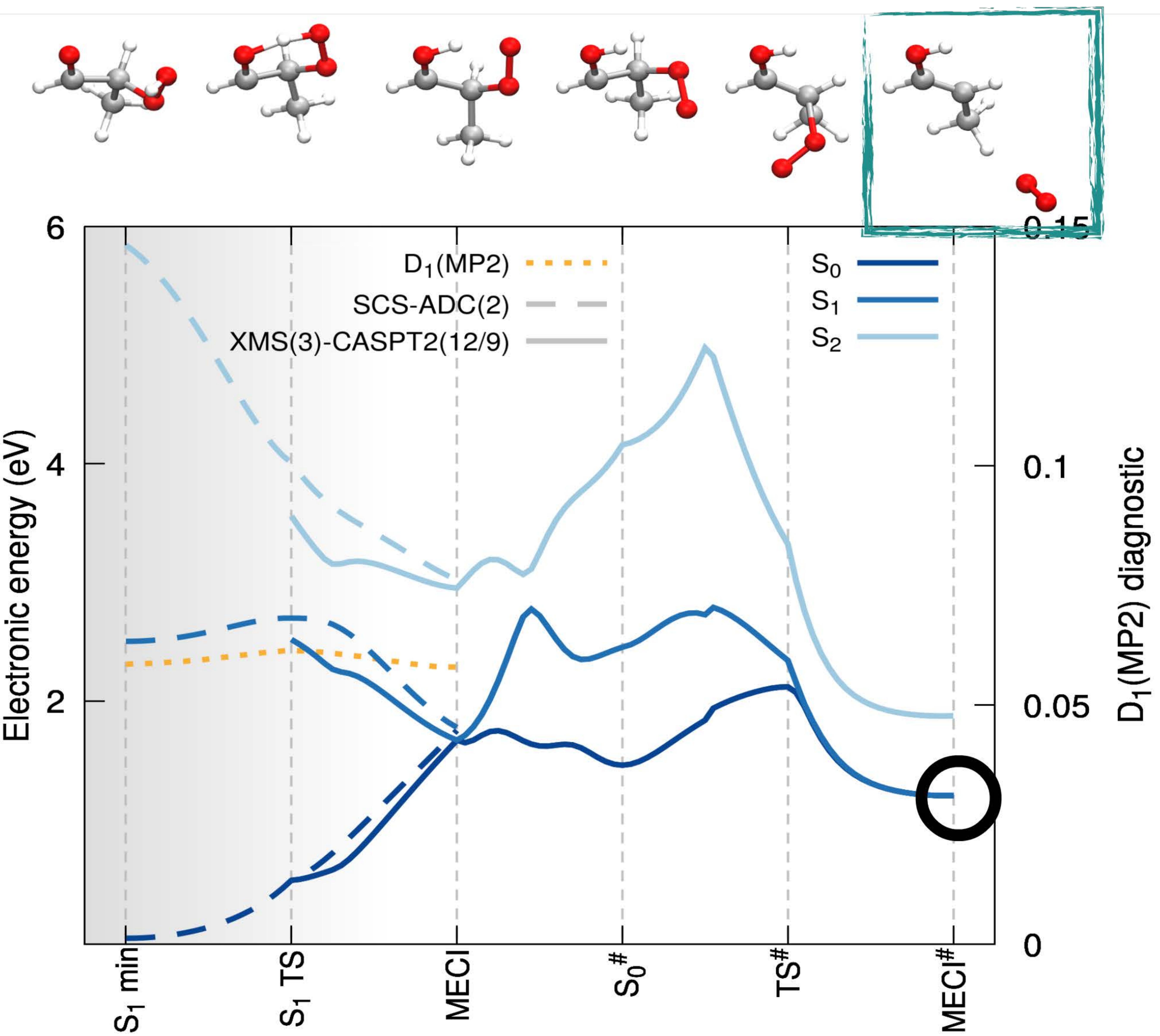
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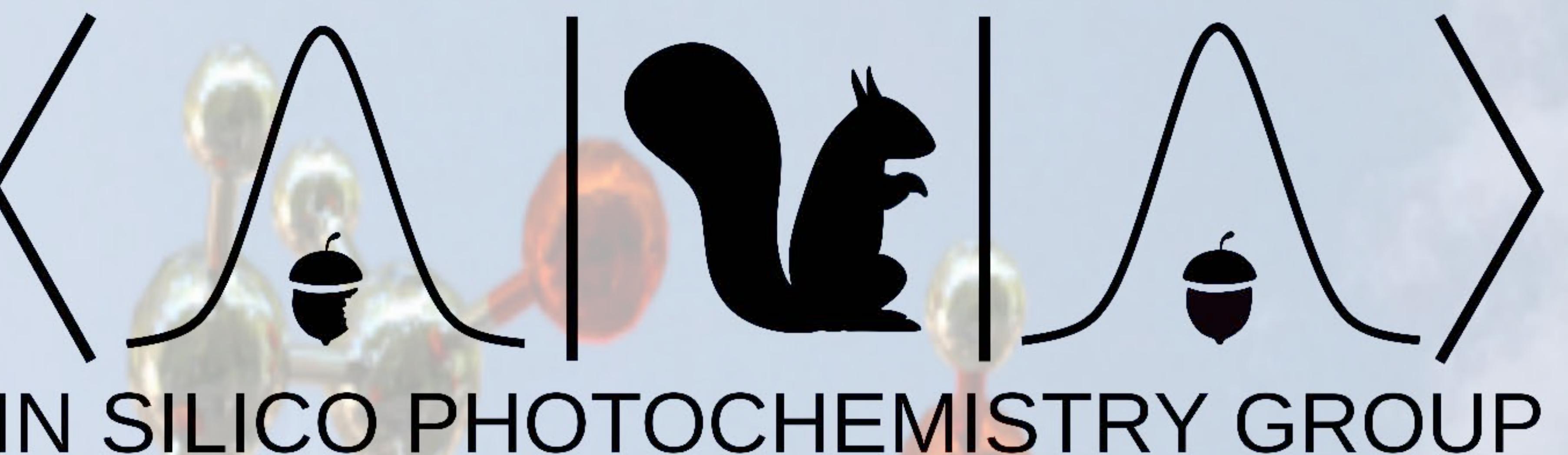
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Using  $\sigma(\lambda)$  and  $\phi(\lambda)$  we have computed the photolysis rate constant ( $J$ ) under atmospheric conditions

***The photochemistry of 2-hydroperoxypropanal is relevant in determining the oxidation balance of the troposphere***

# Acknowledgment



**Prof. BASILE F. E. CURCHOD'S  
RESEARCH GROUP**  
<https://in-silico-photochem.com/>

