Quantum Control of Photoelctron Circular Dichroism on Limonene

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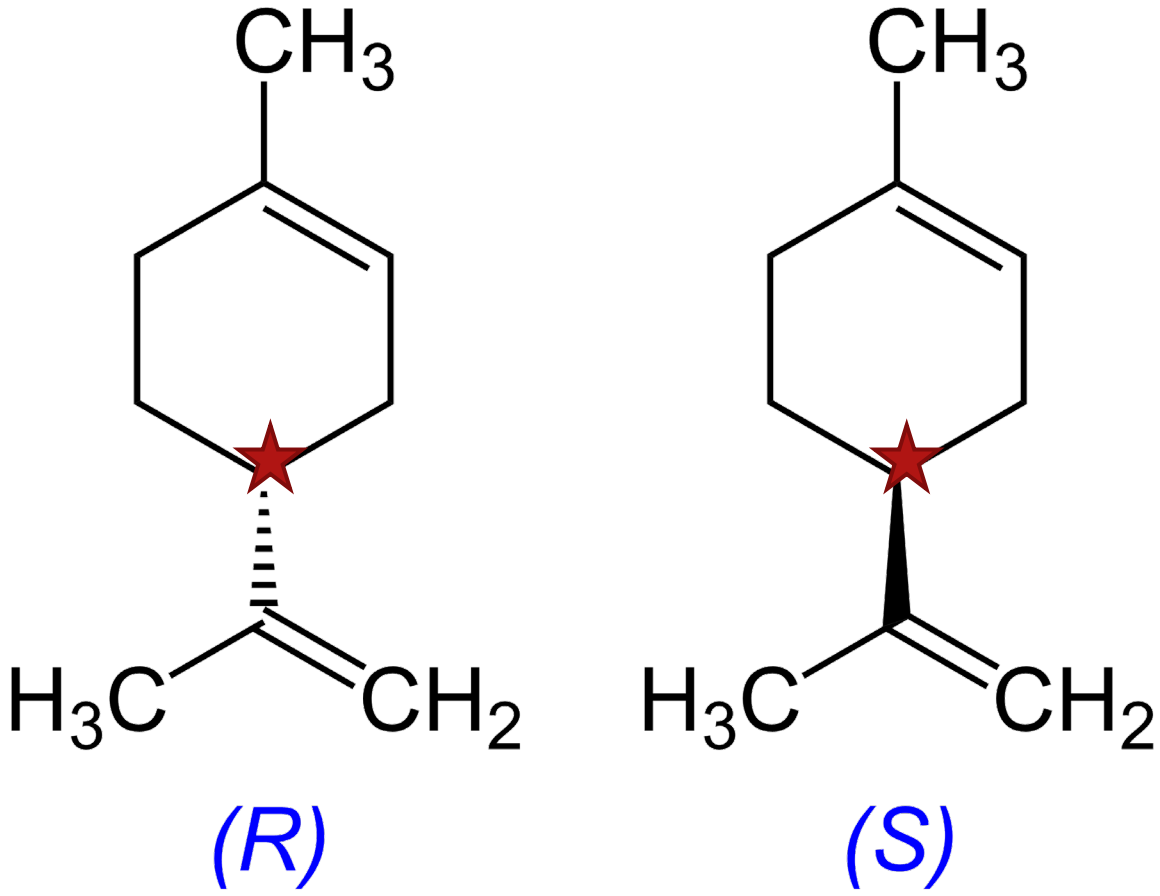
Limonene

- Found as major component of the oil in citrus peels
- It is a Chiral Molecule; non-superimposable with their mirror image
- Interesting due to its size and complexity



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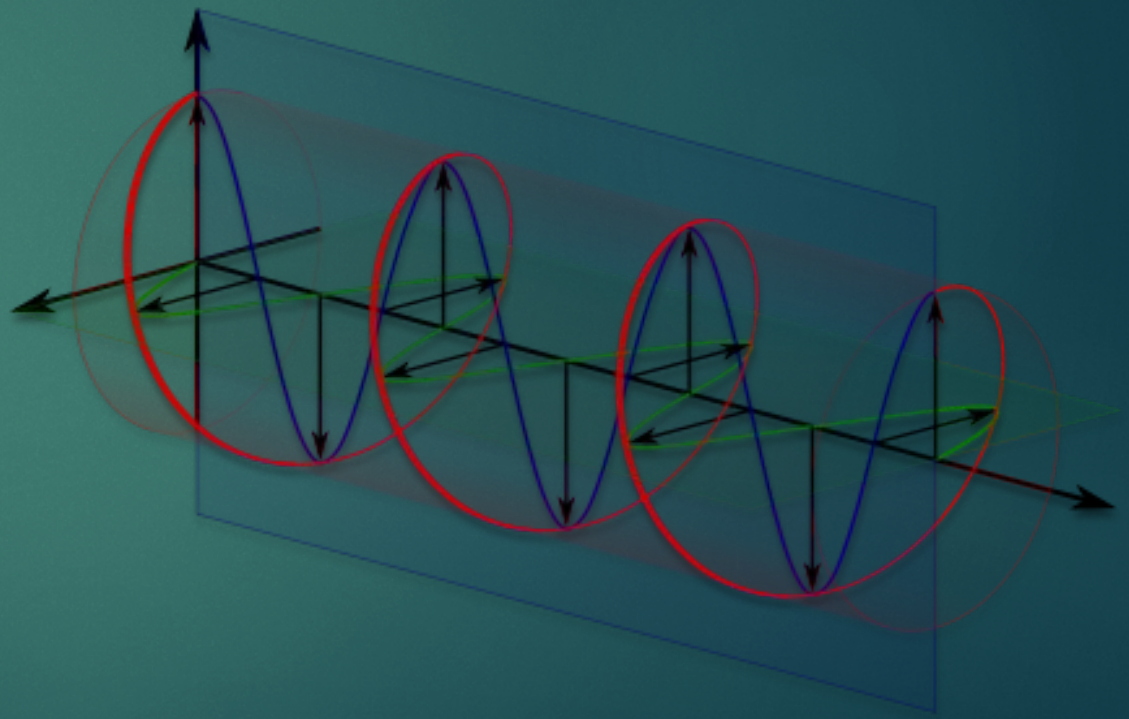
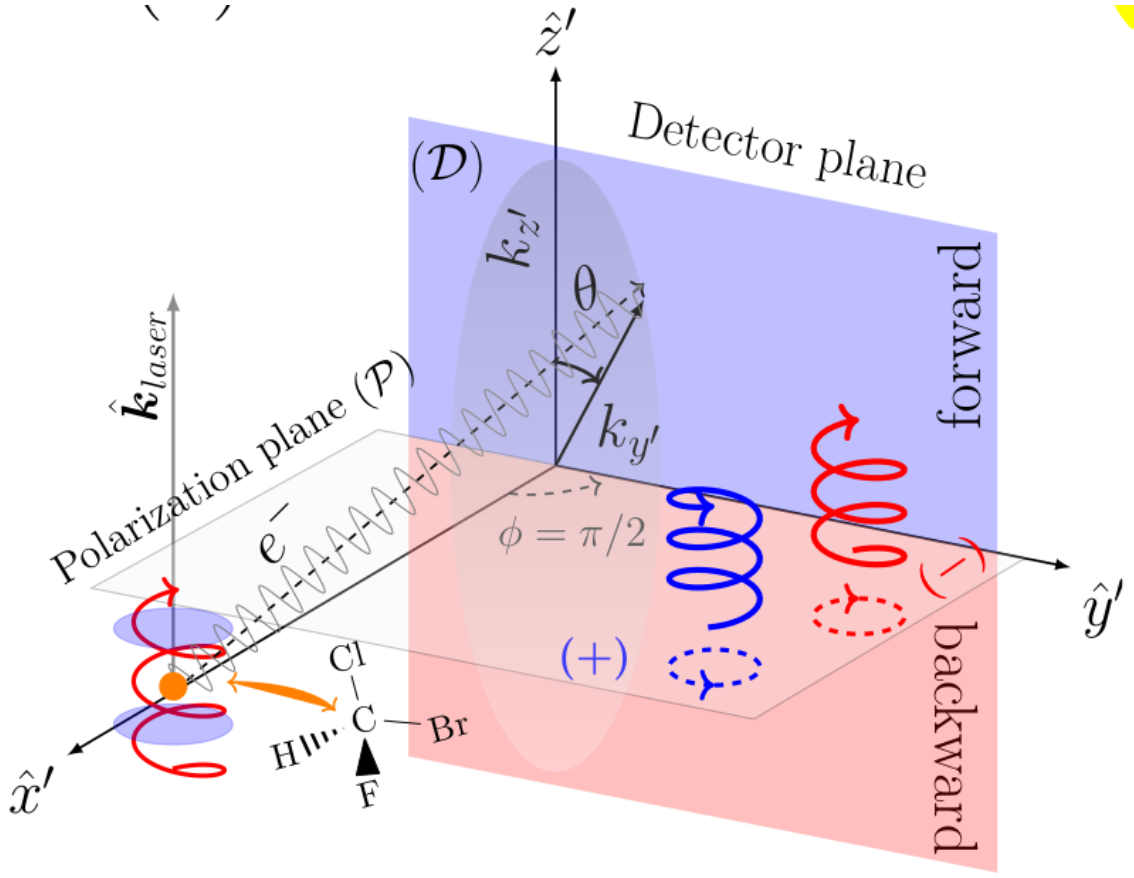
What is Circular Dichroism?

- Chiroptical effect
- Based on the differential absorption of left and right circularly polarized light
- Make use of magnetic dipole moment of the molecule



Photoelectron Circular Dichroism (PECD)

- Make use of Electric dipole moment
- Much stronger signal than CD
- Sensitive to
  - Electronic Structure
  - Vibrational Excitation
  - Molecular Conformation
- Differential in photo-electron angular distribution



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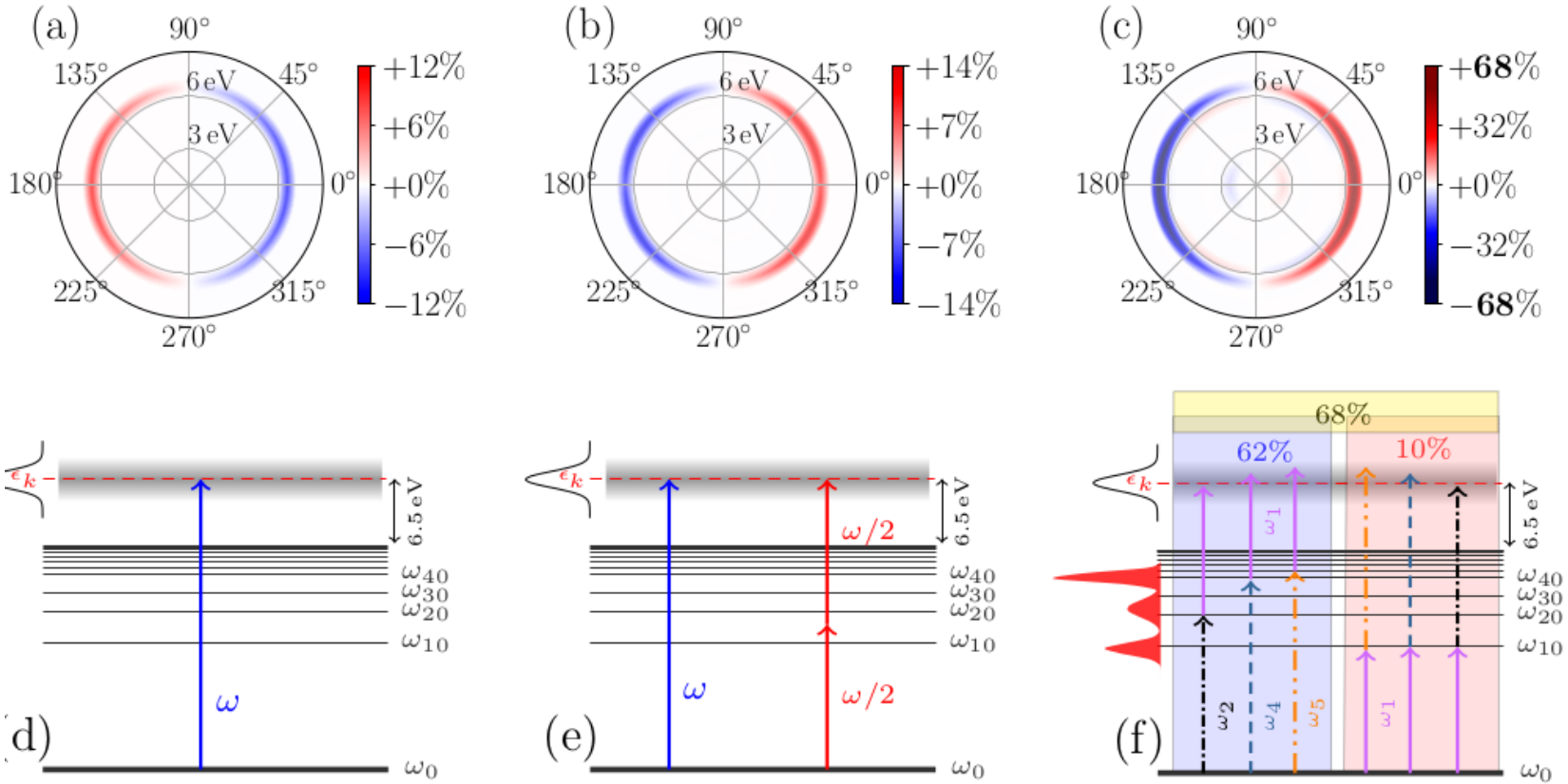
What´s Been Done Before

- Angular resolved PECD
  - One-Photon ionization
  - Bichromatic pulse
  - Two-photon pathway



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Structure of Research

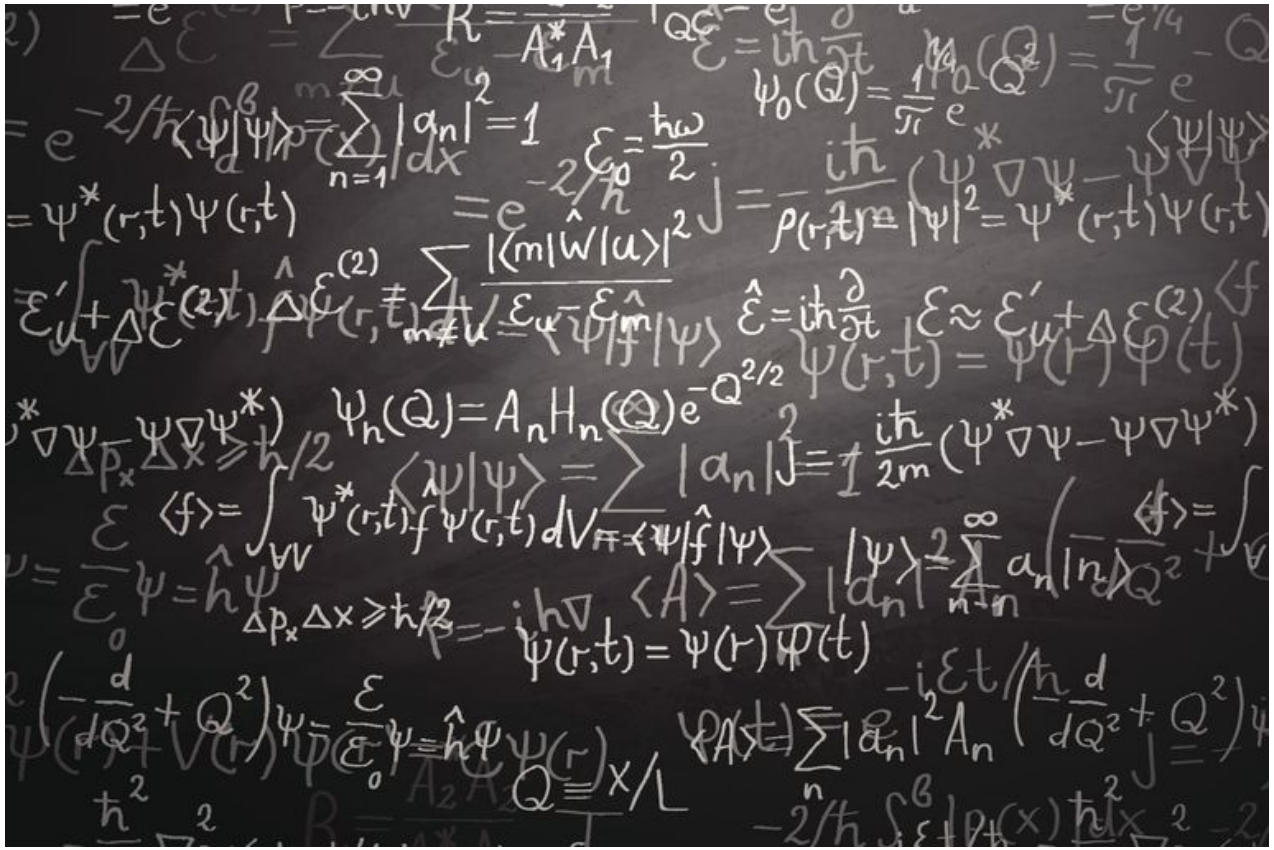
- Time-independent description of Limonene
  - Description of Limonene orbitals
  - Description of photoionization
- Time dependent behavior
  - Interaction with laser pulse

Obtaining Limonene Orbitals

- Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(\boldsymbol{x})\psi = E\psi$$

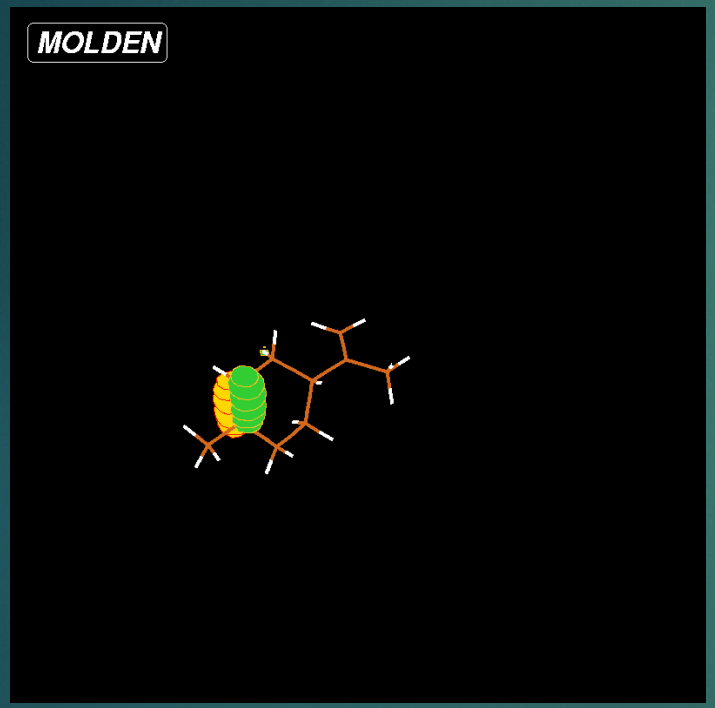
- Hartree-Fock Approximation
  - Make a multi-electron system into a single electron system
- Solved using Molpro in NERSC´s Cori supercomputer



Limonene Orbitals

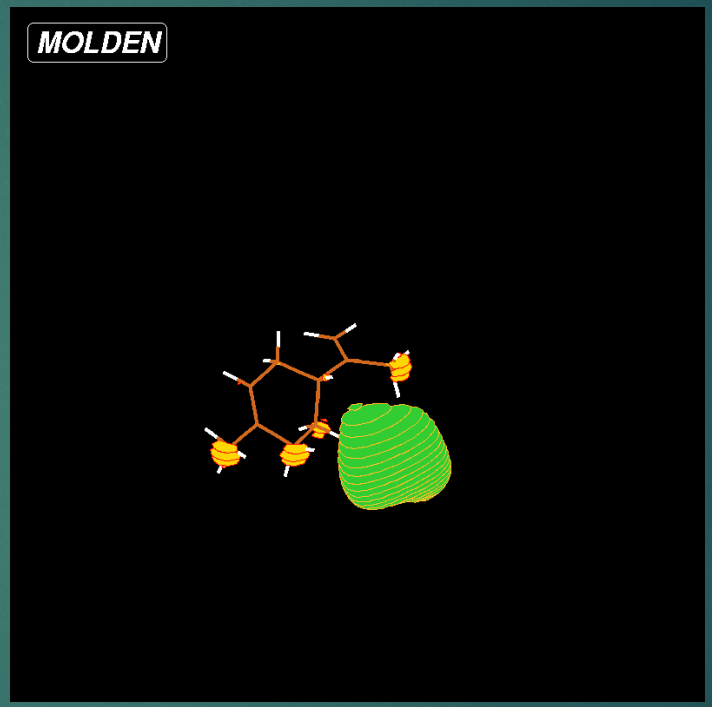
Highest Occupied Molecular Level

ε= -9.0 eV



Lowest Unoccupied Molecular Level

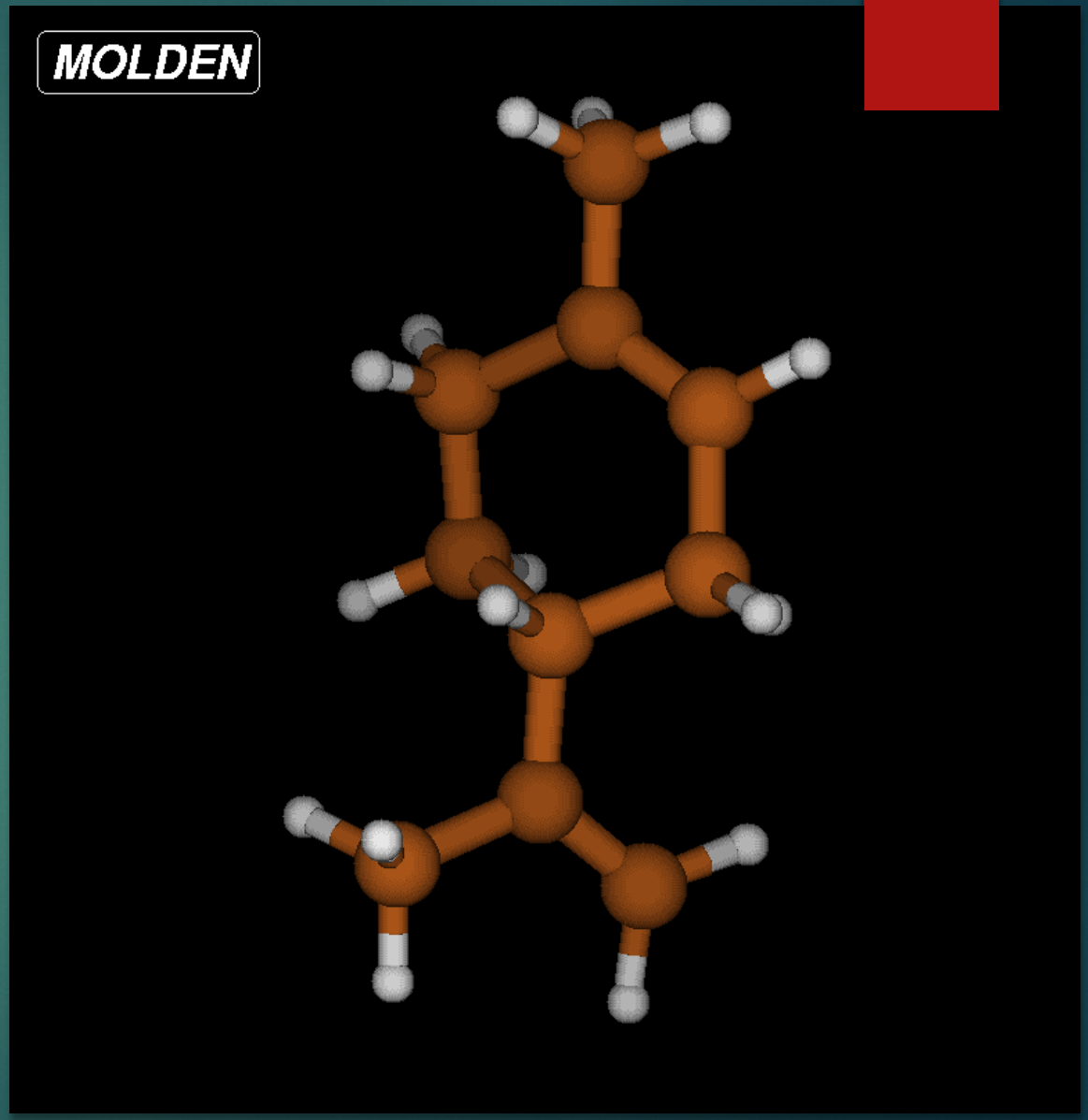
ε= 0.95 eV



Experimental Ionization Energy = 8.3 eV
Calculated Ionization Energy = 9.98 eV

Photoionization

- Simulated using ePolyScat; software used to study photoelectron scattering
- Produces the photoionization dipole matrix elements at a given energy.



Outlook & Conclusion

- Finish time-independent description of Limonene
- Move into quantum control of PECD for Limonene
- Compare to the results found on CHBrClF
- Expand the tools we have for probing chiral molecules

Acknowledgments

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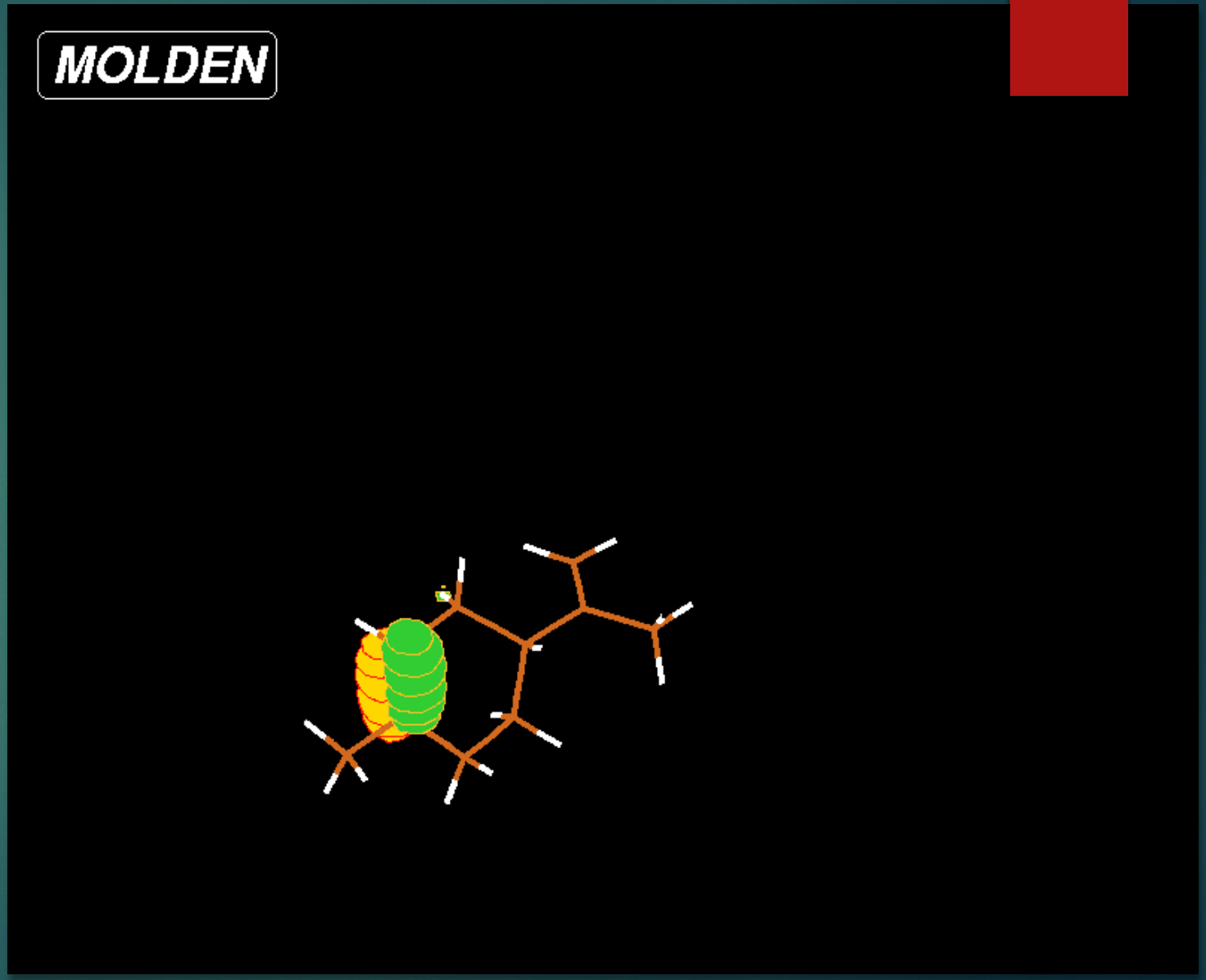
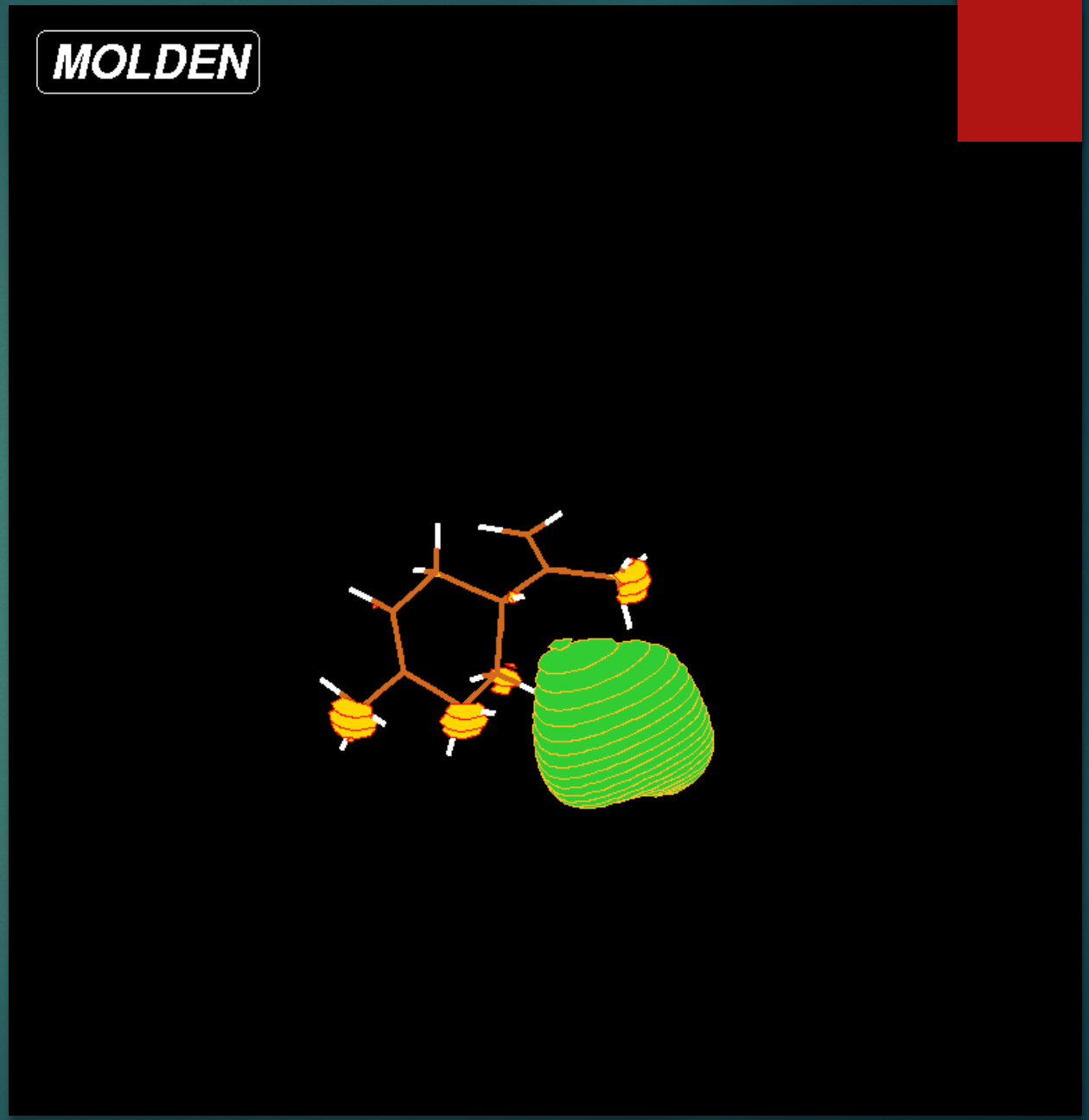
Limonene Orbitals

- Limonene HOMO with aug-cc-pVDZ
- Energy HOMO = -9.0446 eV



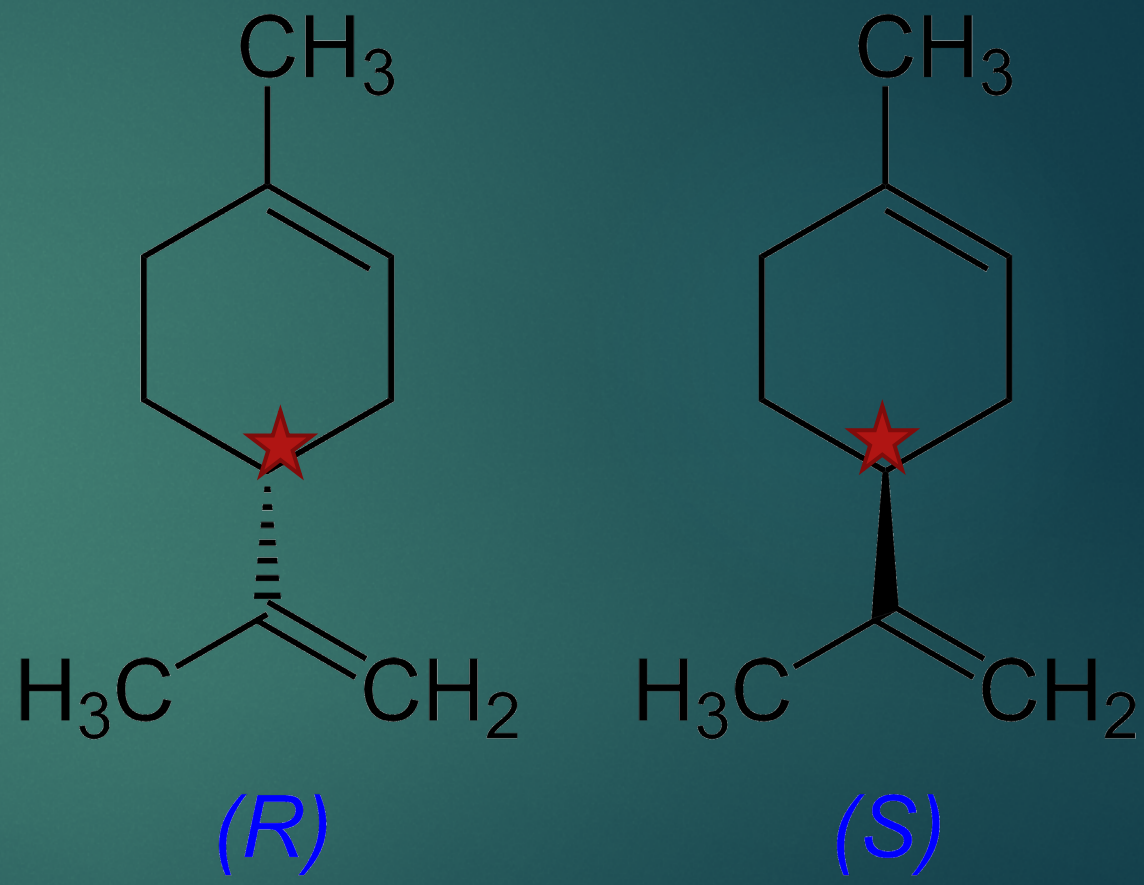
Limonene Orbitals

- Limonene LUMO with aug-cc-pVDZ
- Energy LUMO = 0.7729 eV



Limonene

- Found as major component of the oil in citrus peels
- It is a Chiral Molecule; non-superimposable with their mirror image
- Uses
  - Dietary supplements, Fragrance, Ingredients for cosmetics
  - Solvent for fused filament fabrication-based 3D printing



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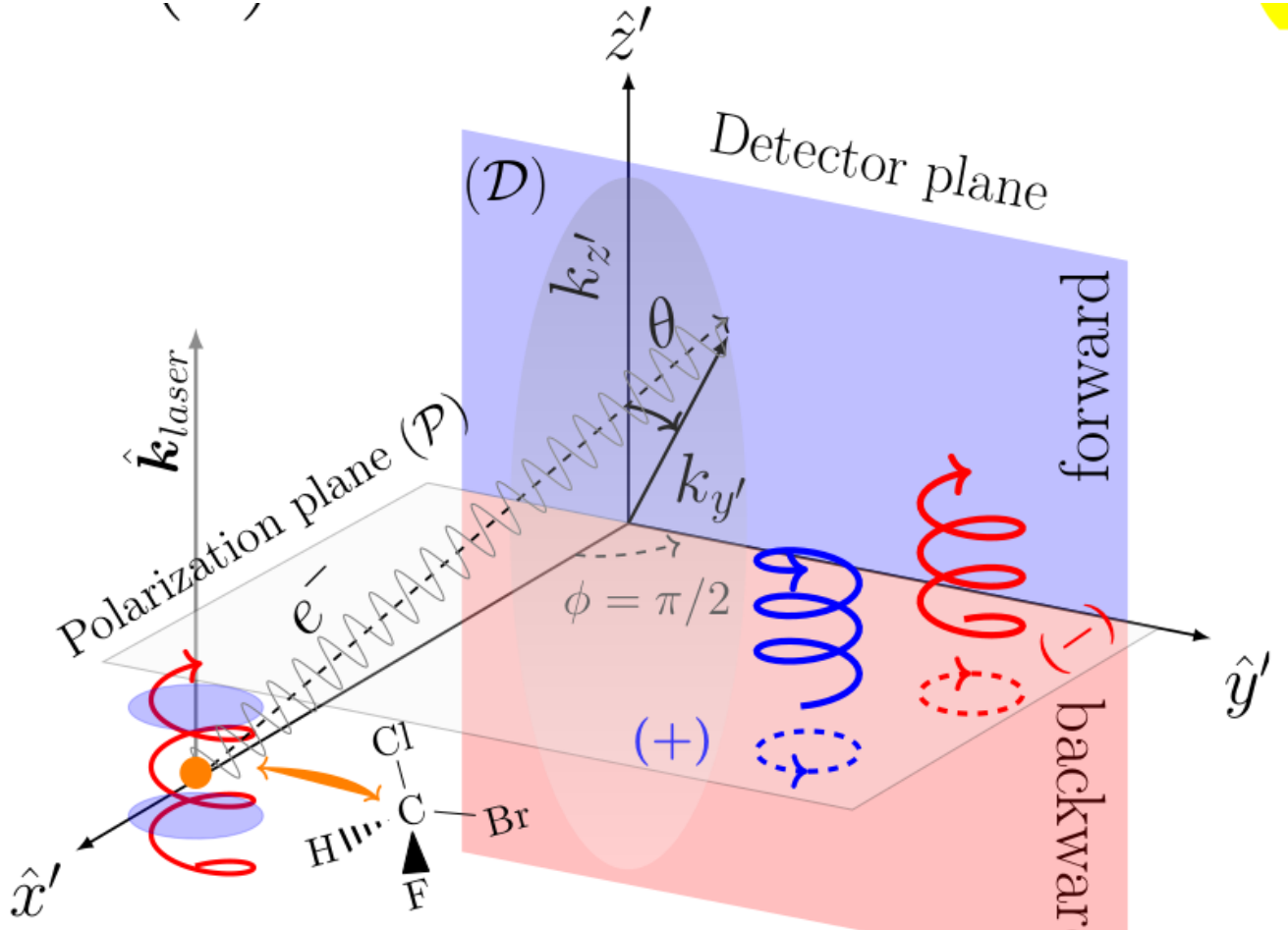
- Worked with CHBrClF



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Case Study