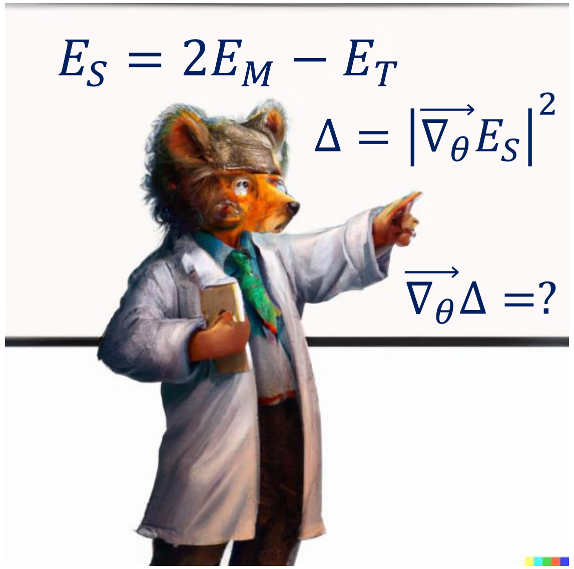
Investigating Jahn-Teller Distortion in CH_4^+ with Time-resolved X-ray Absorption



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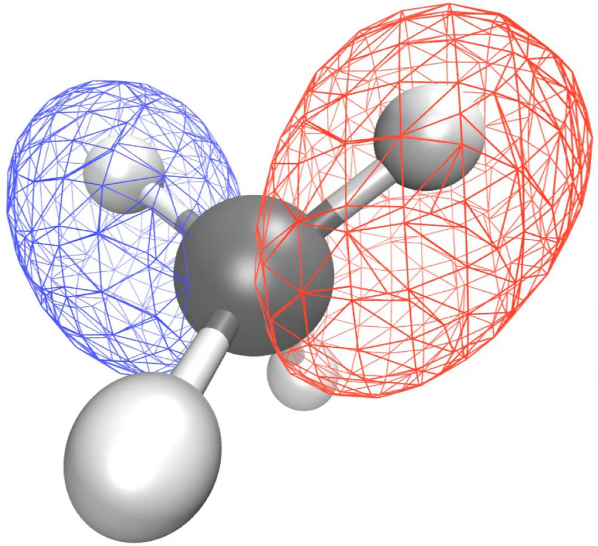


Ground vs Excited states

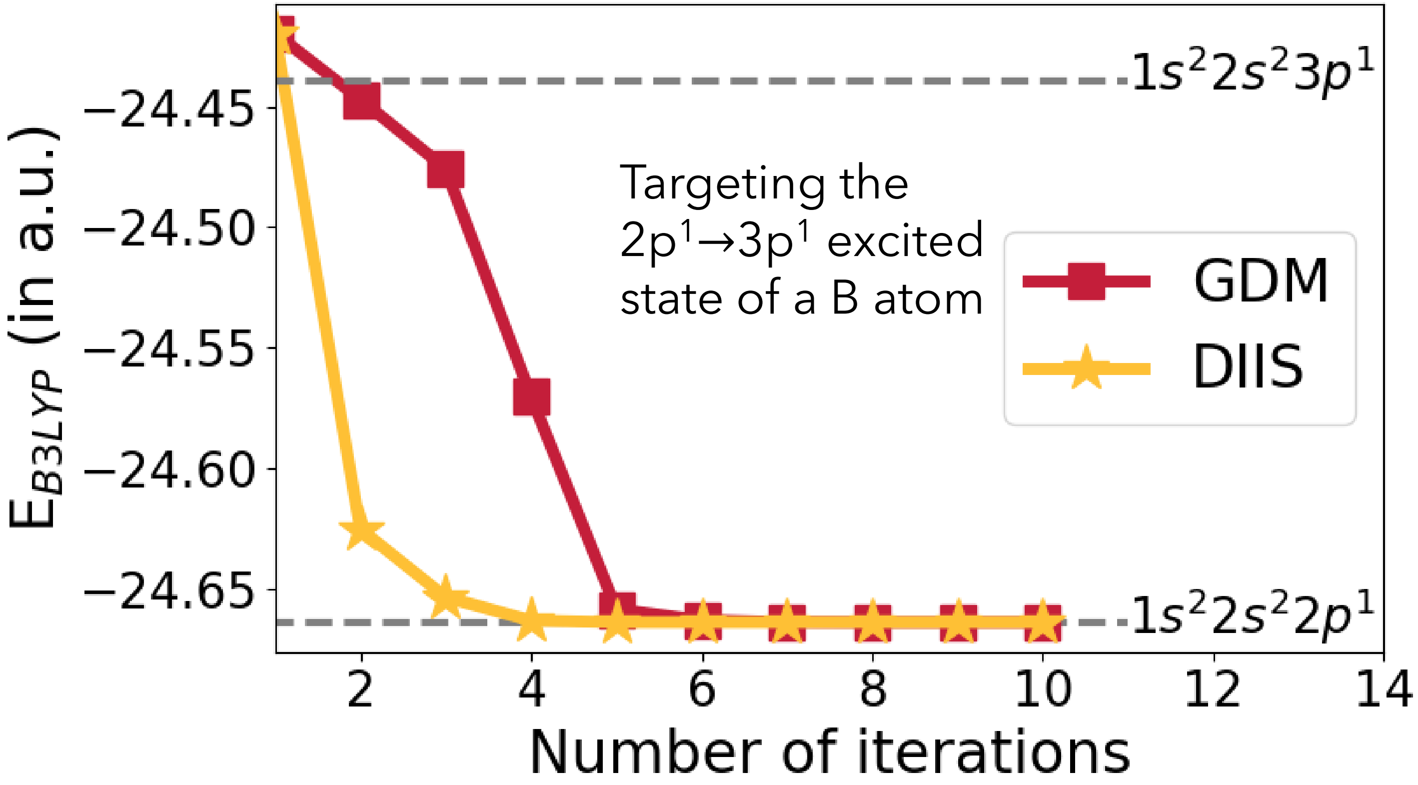
Variational Theorem

The ground state energy is the lowest possible energy that can be obtained from any candidate wavefunction.

- Ground state methods minimize energy.
- Not typical for excited states!
  - Usual path: Linear response on ground state
  - Examples: TD-DFT, EOM-CCSD etc.

Variational collapse

- Excited states are normally saddle points of energy.
- Orbital optimization (OO) often results in collapse to ground state.



Extremization → Minimization

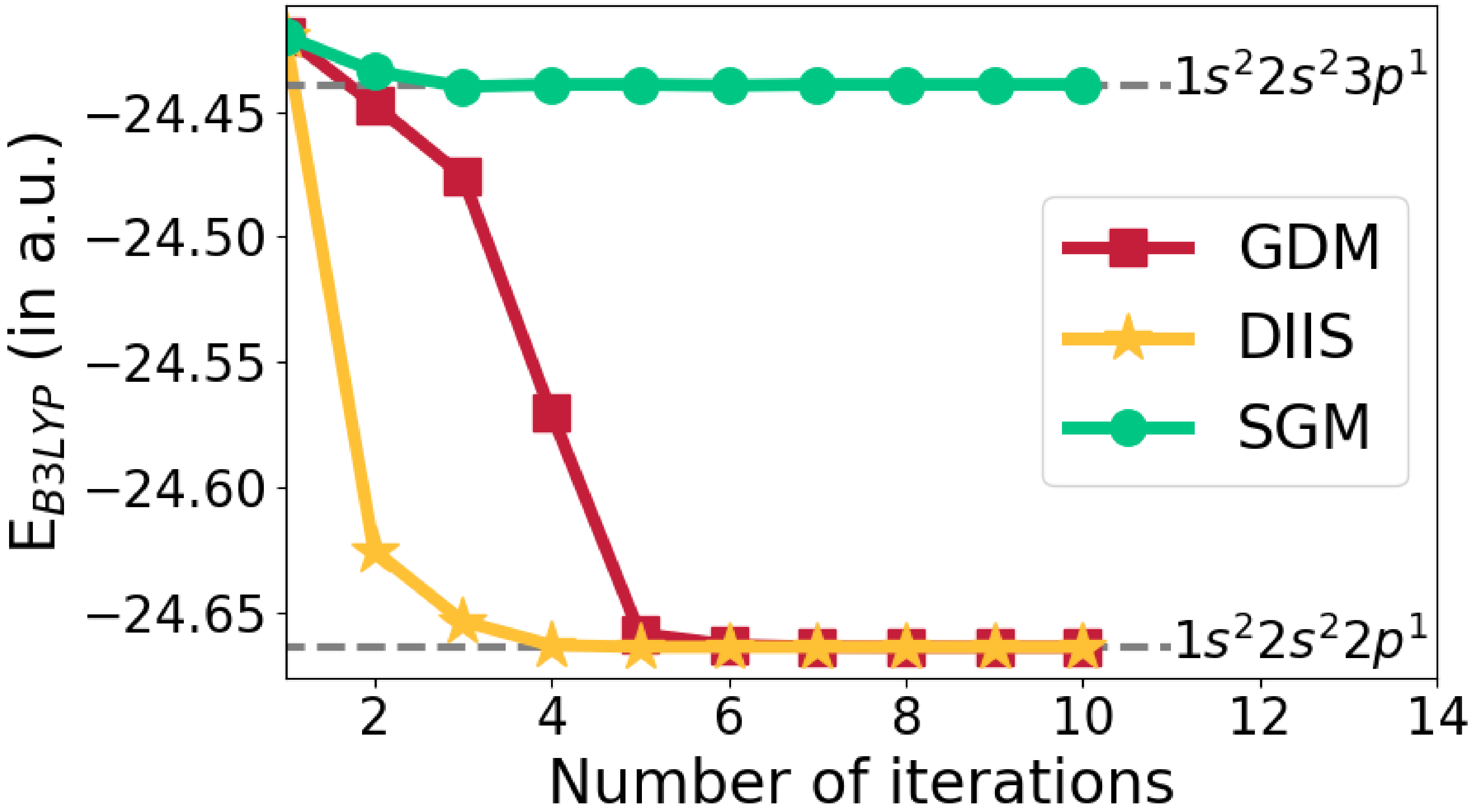
- **Objective:** Find some energy E that is stationary vs orbitals θ and corresponds to an excited state configuration.

- **Solution:** All stationary points are global minima of

$$\Delta = \left|\overrightarrow{\nabla_\theta} E\right|^2$$

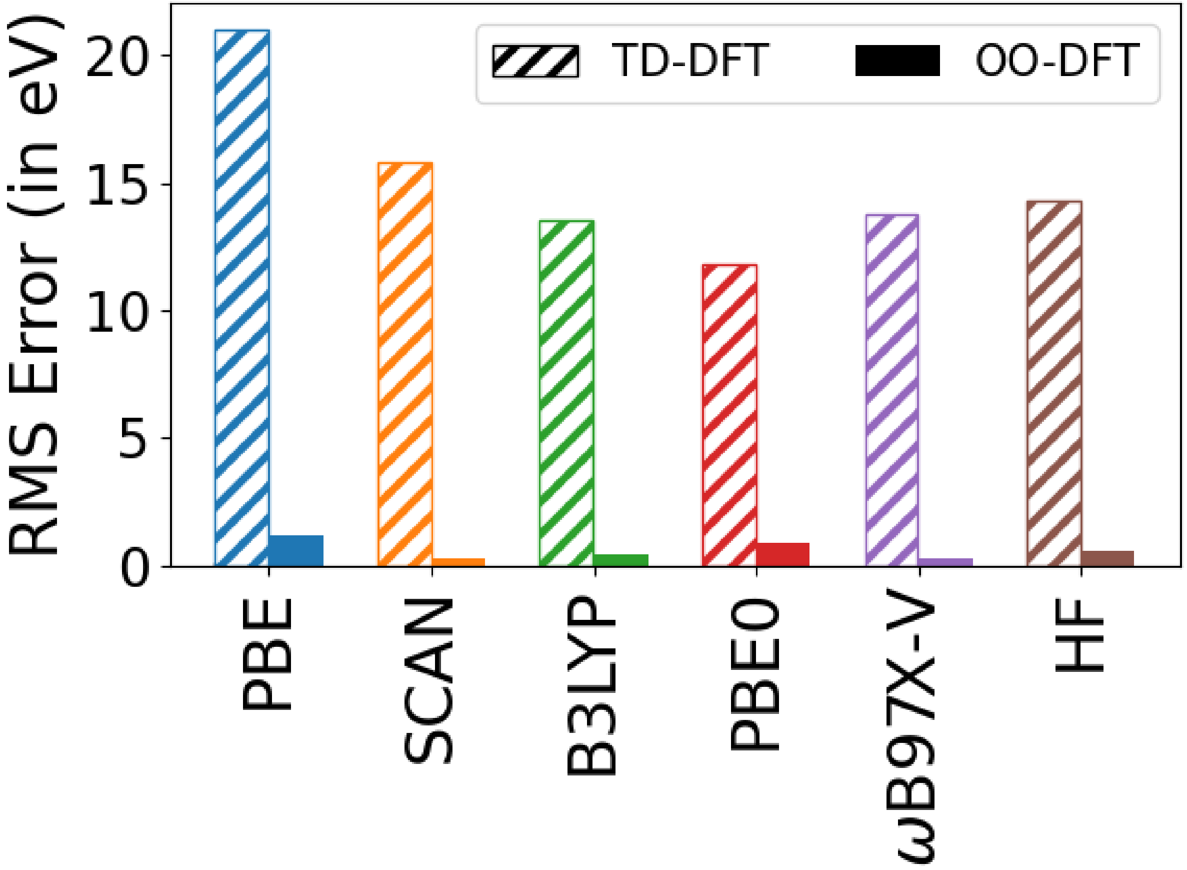
- **Square Gradient Minimization (SGM)** preserves ground state scaling, with a slightly larger prefactor.

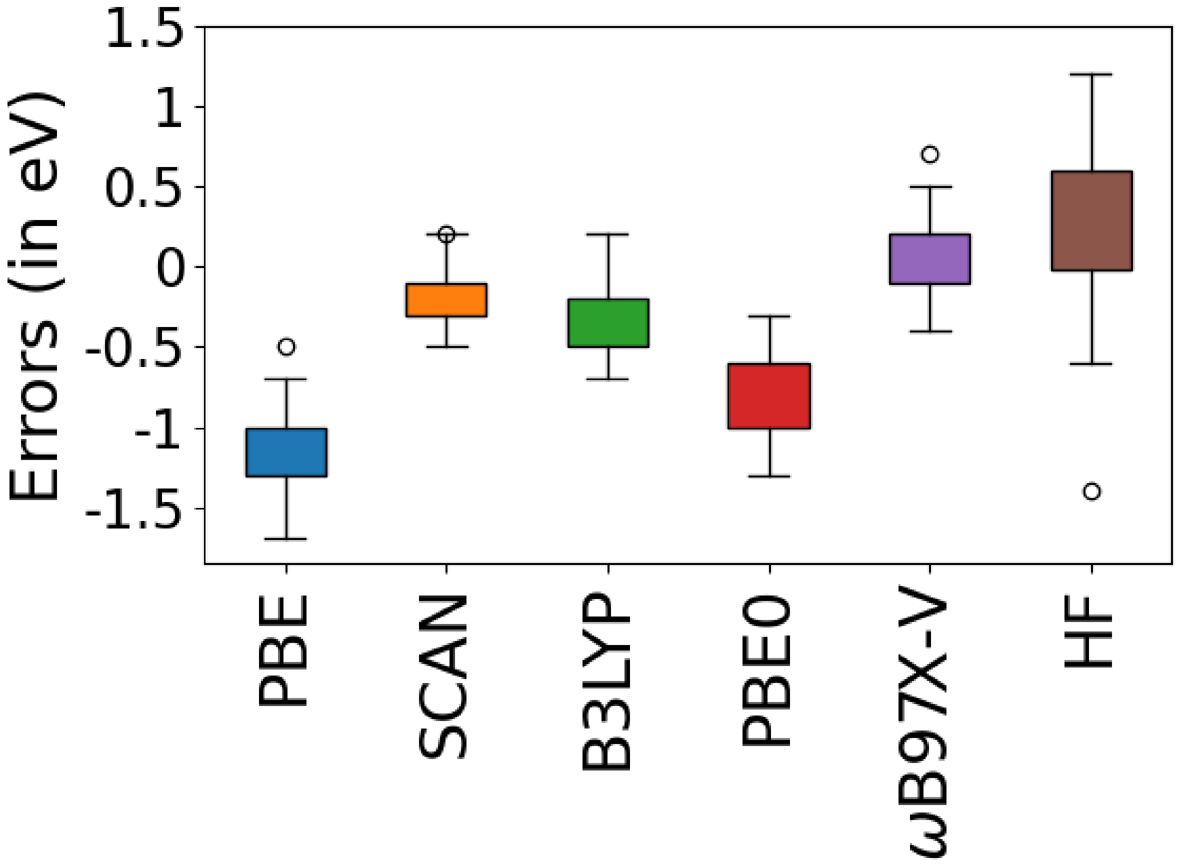
SGM converges to excited states



Also successfully applied to charge-transfer, double excitations, etc.

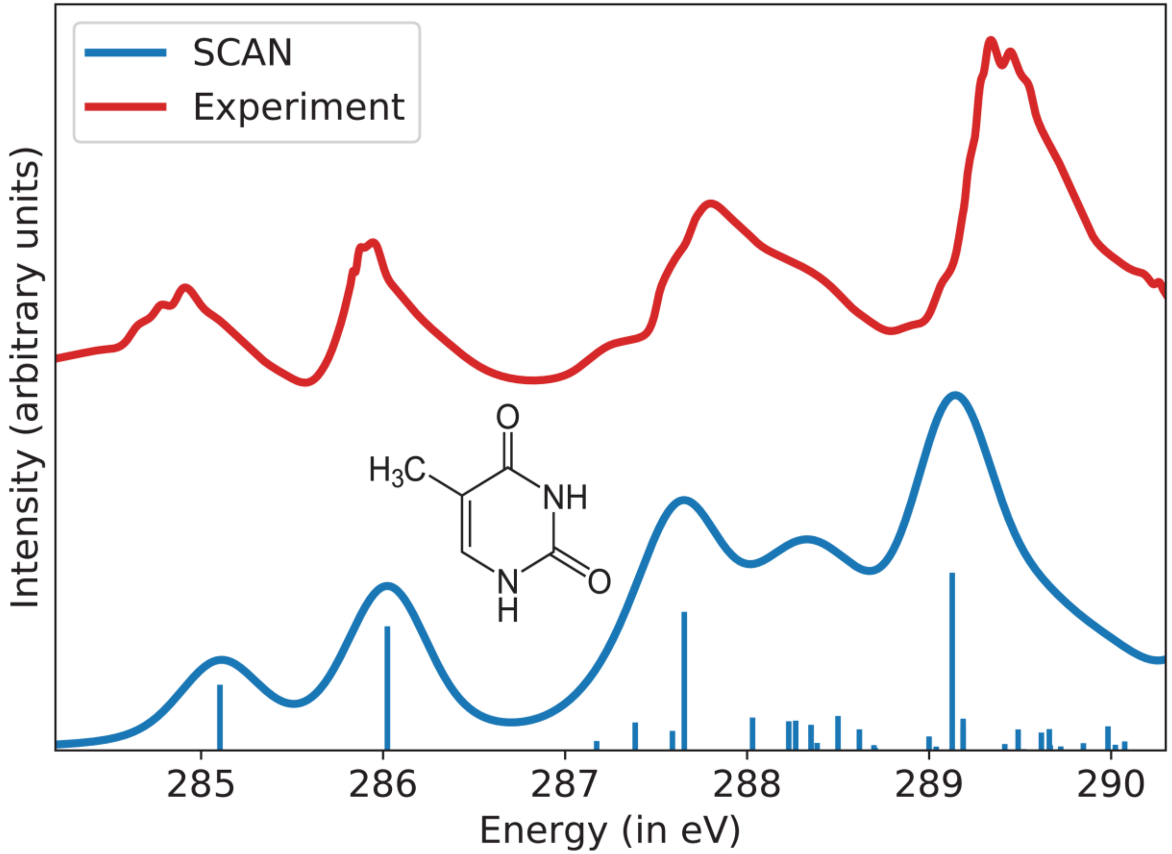
Accurate core-excitations with OO-DFT

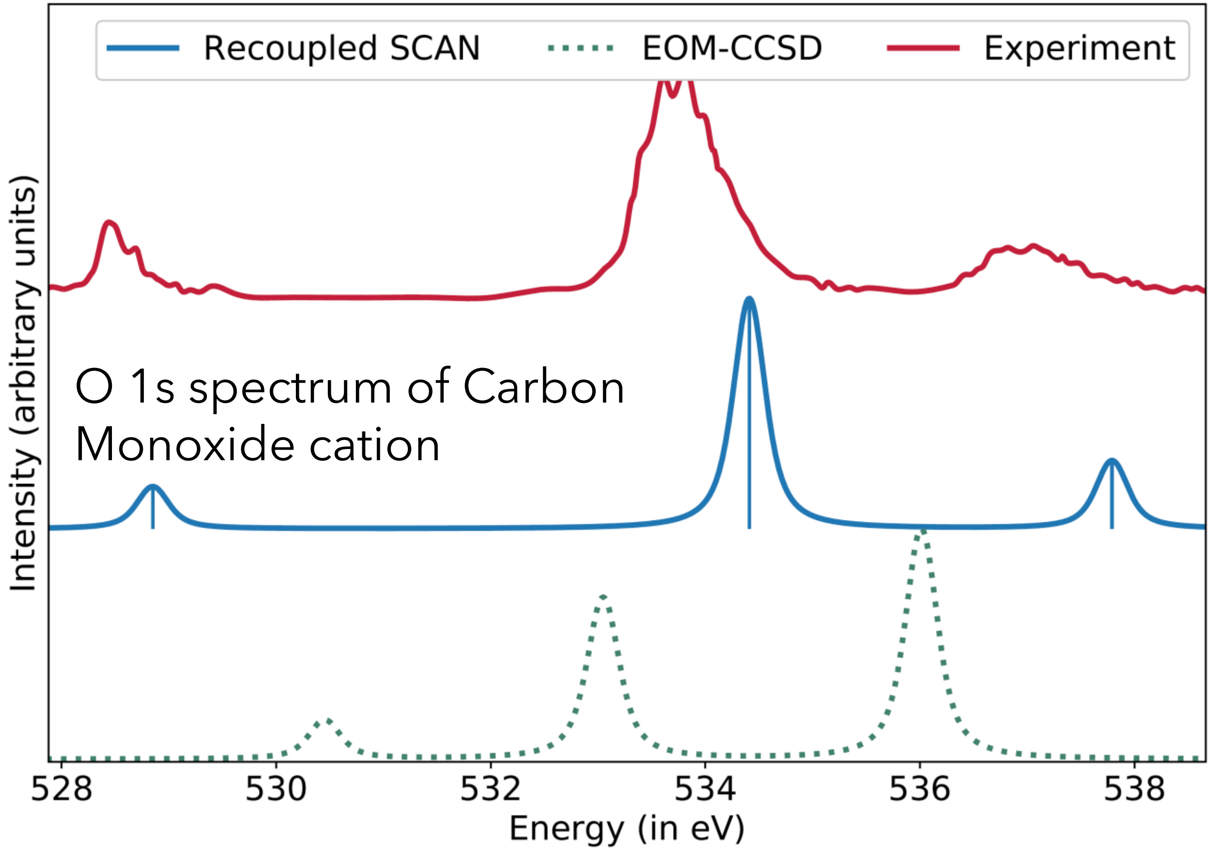




Hait and Head-Gordon, *J. Phys. Chem. Lett.*, 2020.

X-ray absorption without shifts

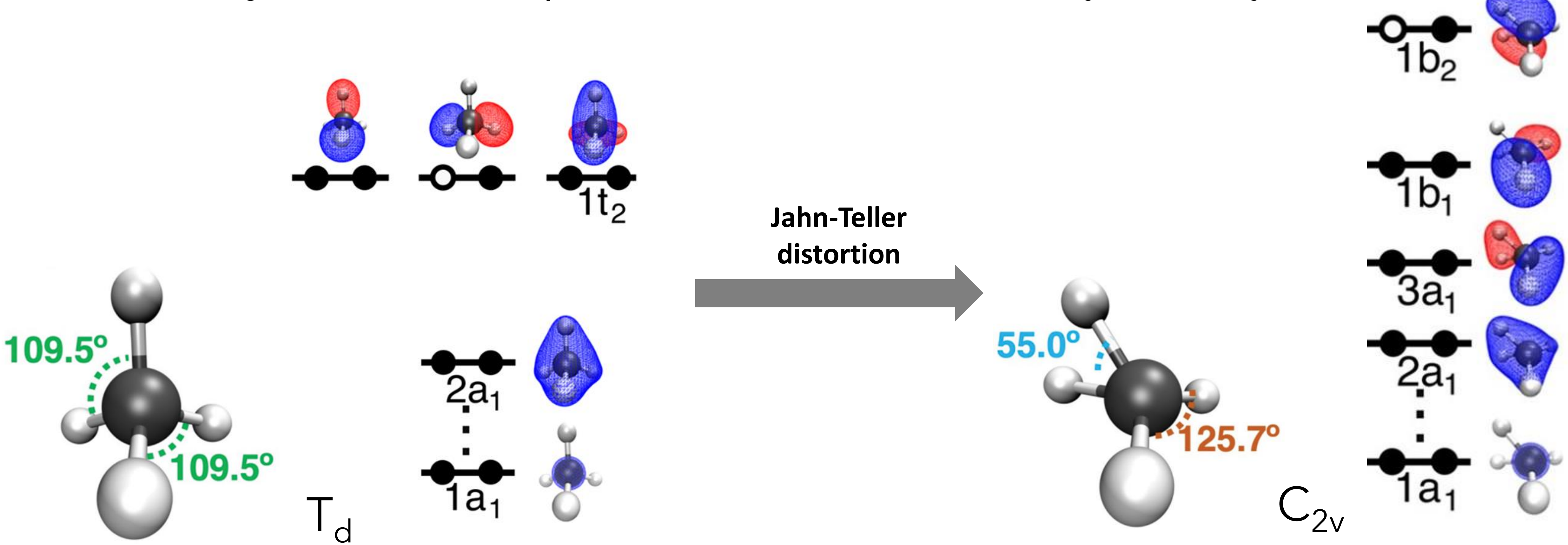




 Hait and Head-Gordon, *J. Phys. Chem. Lett.*, 2021.

Jahn-Teller distortion in methane cation

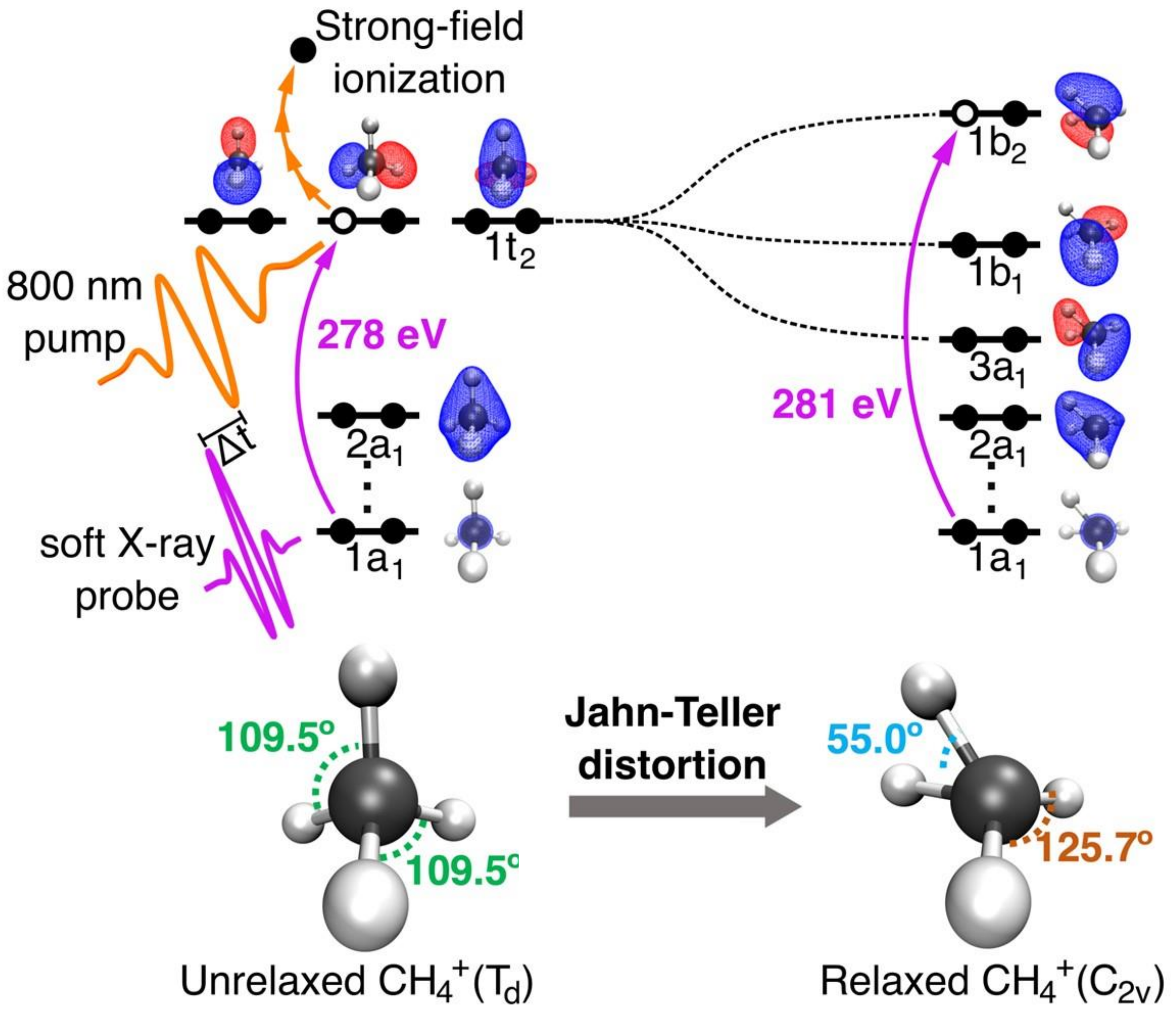
Spatially degenerate electronic states in nonlinear molecules undergo nuclear displacements that reduce symmetry.



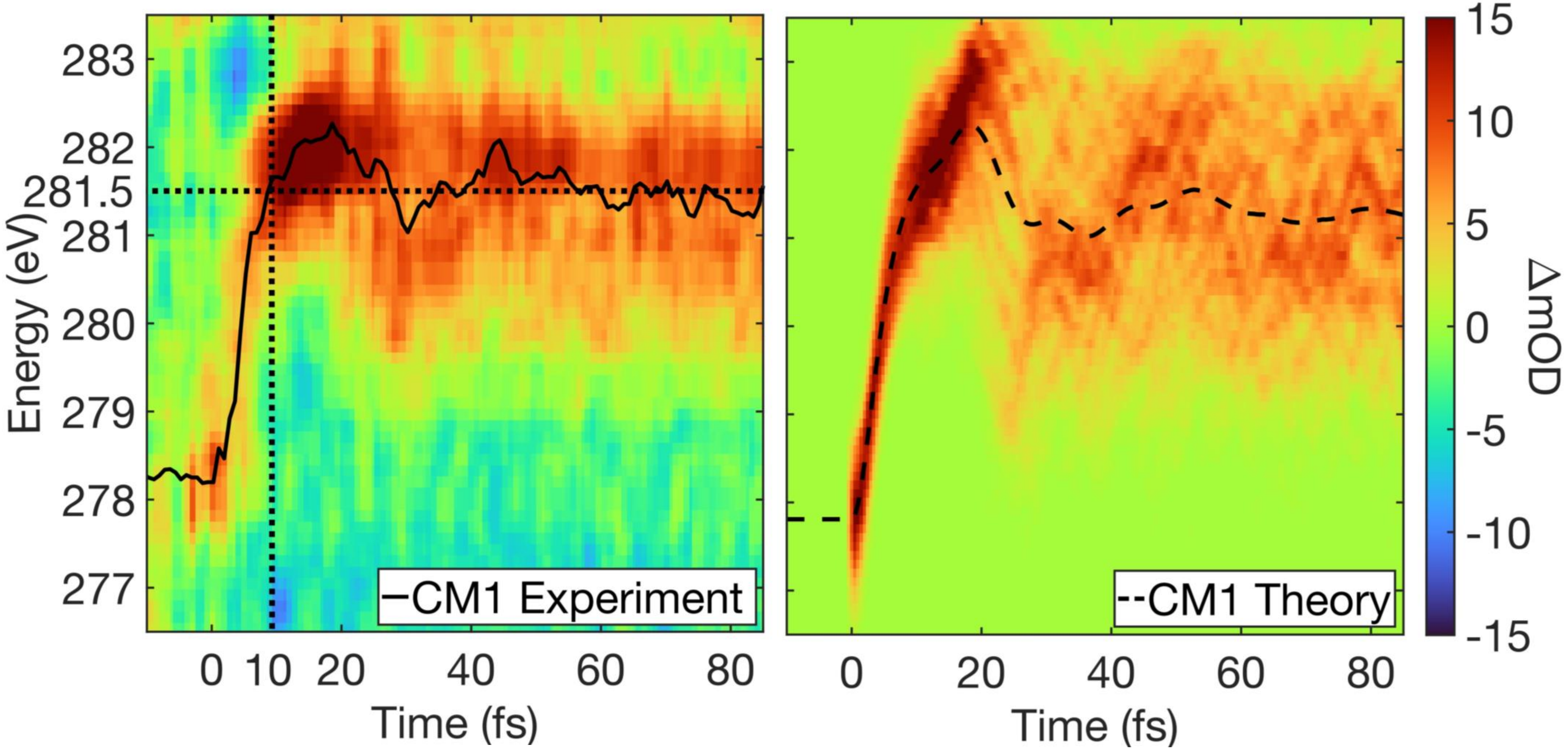
Ridente*, Hait*, et al., *Science*, 2023.

Transient X-ray absorption schematic

- Timescale: ~C-H vibrations
- Distortion destabilizes SOMO
- Bright 1s→SOMO signal can show dynamics



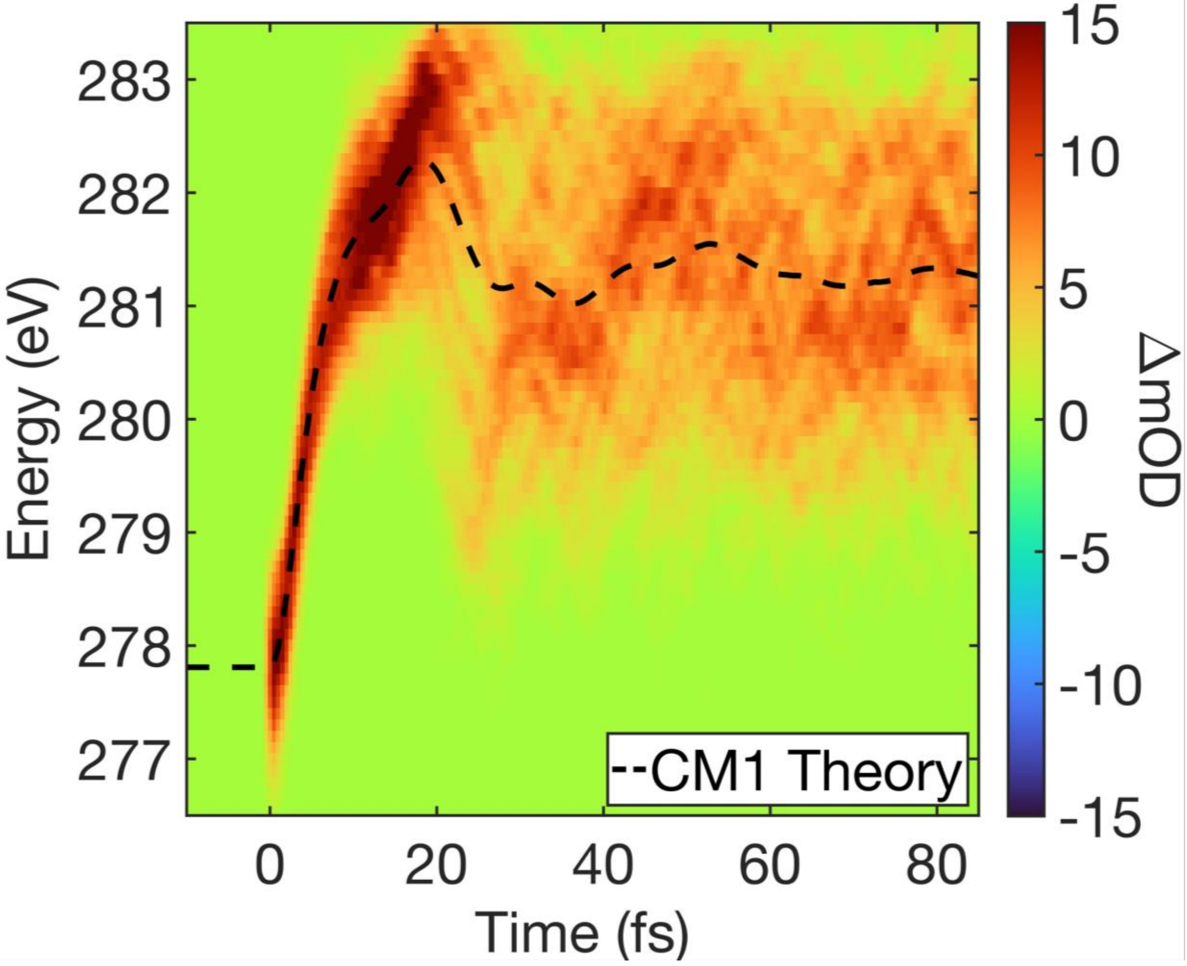
Experiment and Theory agree!

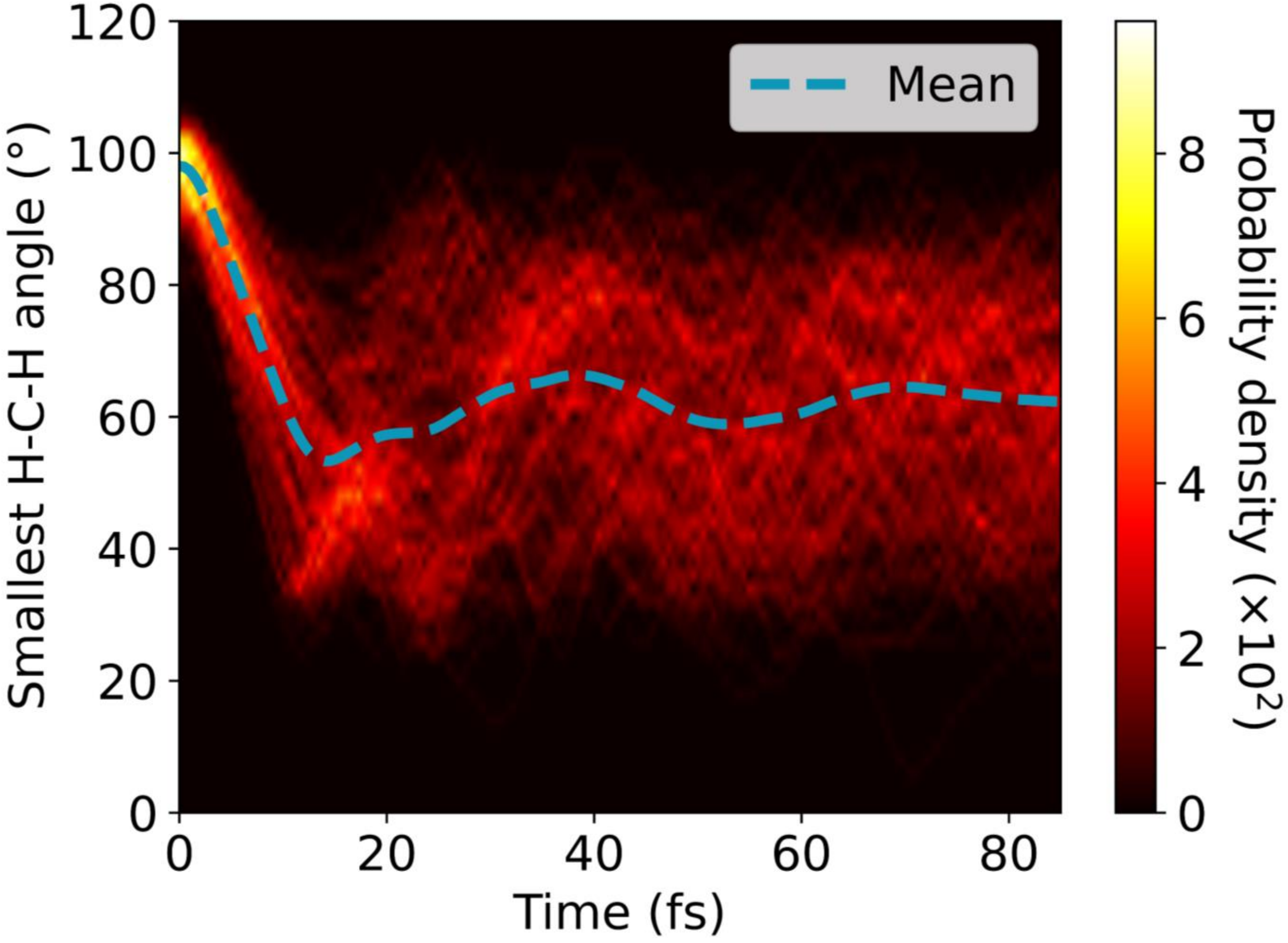


CM1: Signal center of mass

Theory: SCAN/pcX-1 @ spectrum, EOM-IP-CCSD/cc-pVDZ @ dynamics

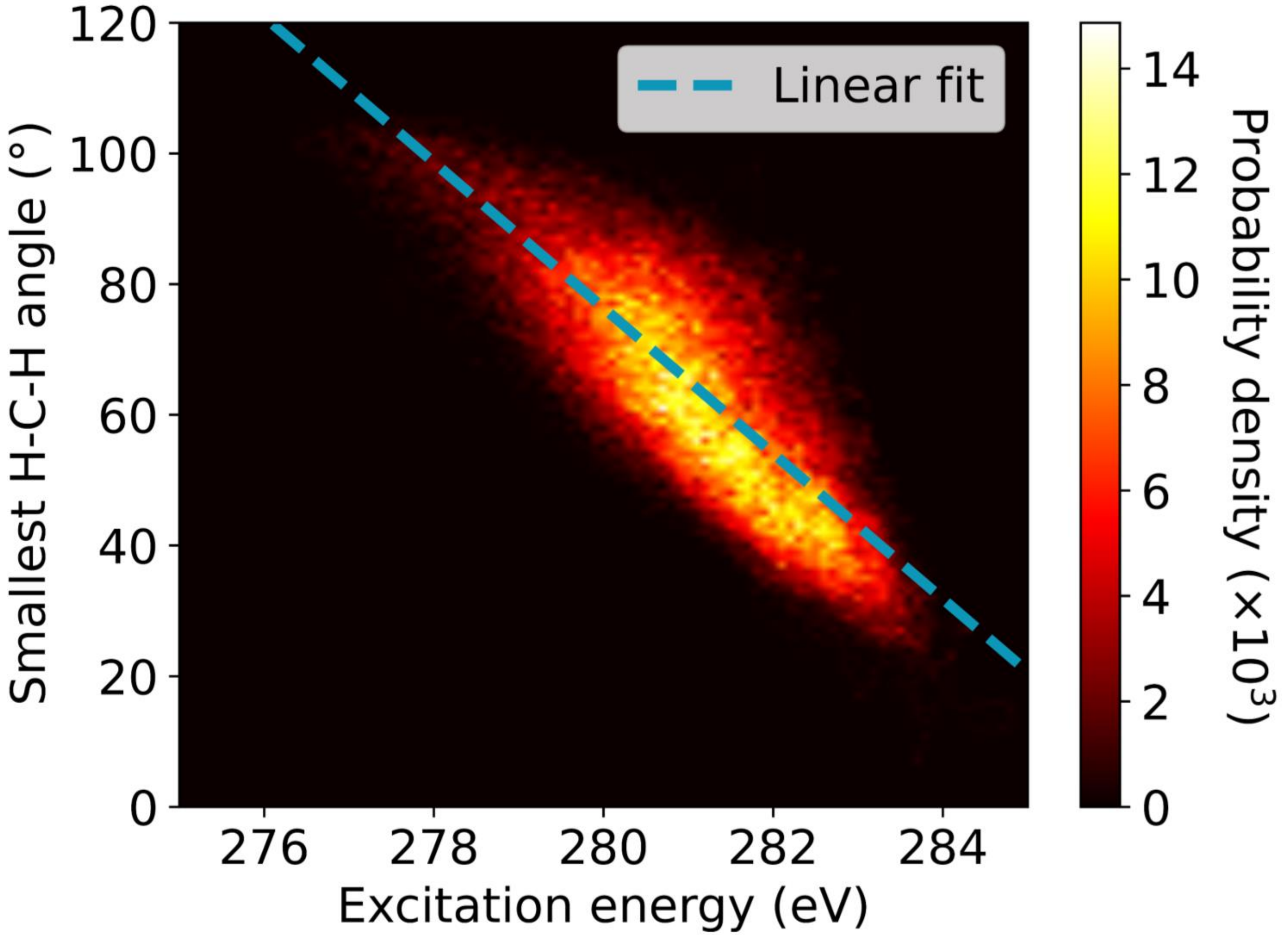
Signal evolves on bending timescales

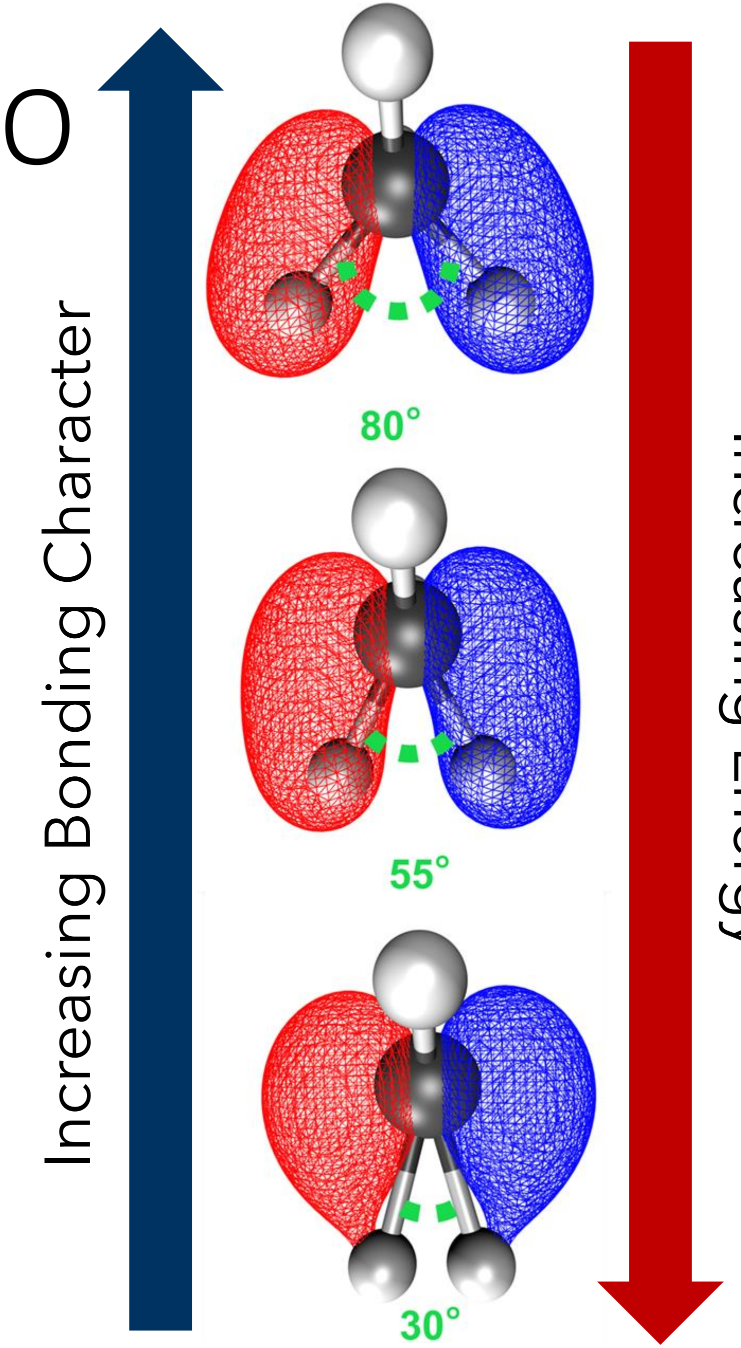




Theory: SCAN/pcX-1 @ spectrum, EOM-IP-CCSD/cc-pVDZ @ dynamics

Tracing the evolution of the SOMO

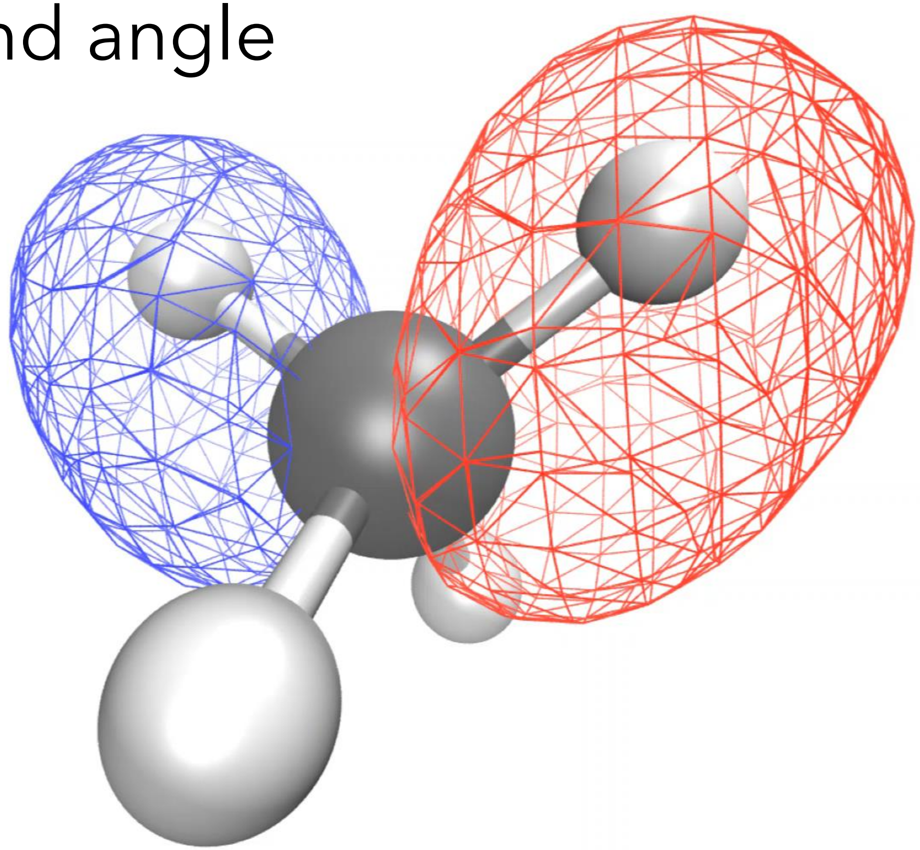




Ridente*, Hait*, et al., *Science*, 2023.

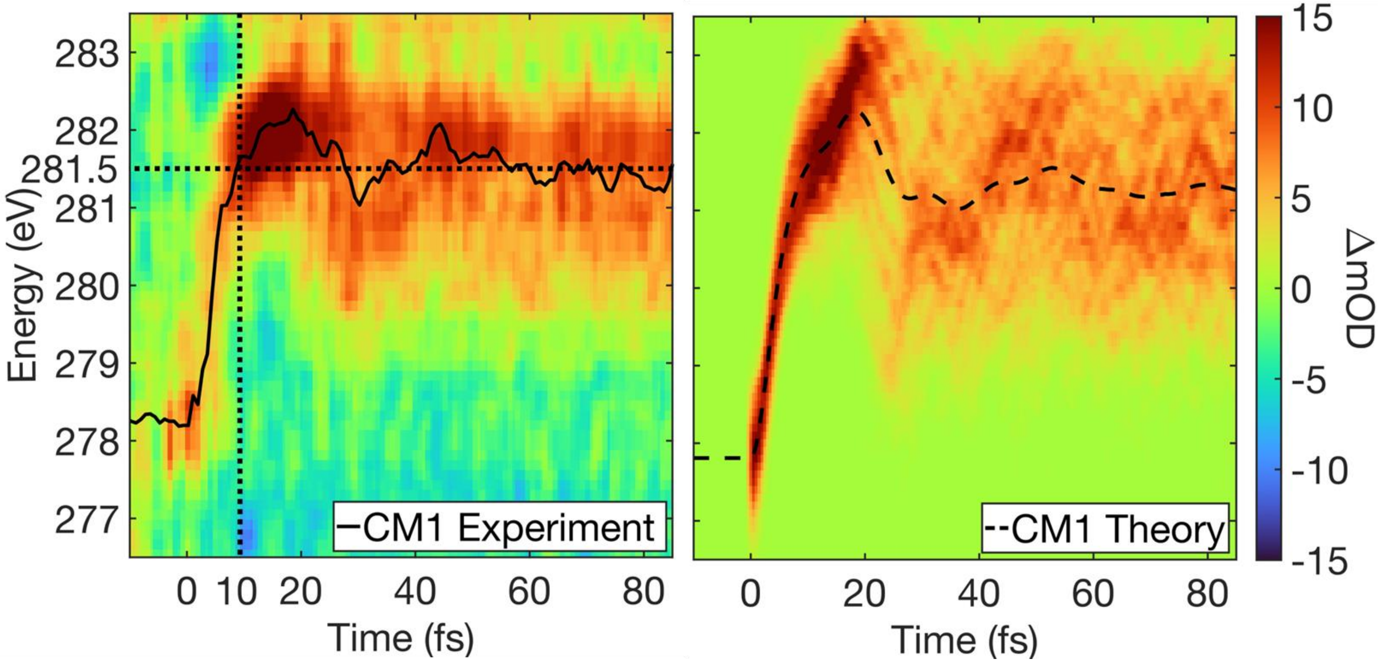
Summary of methane cation dynamics

- Jahn-Teller distortion takes ~10 fs
- Activates scissoring about smallest bond angle
- Scissoring changes bonding character
- Coherence damped in ~60 fs



Conclusions

OO-DFT can cheaply model challenging excitations



Effectively used to model transient X-ray absorption experiments

More comparisons to experiment needed to characterize limitations

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U.S. DEPARTMENT OF ENERGY | Office of Science

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Theory

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Application

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* Authors contributed equally