Supporting Information for:

UV Absorption of Criegee Intermediates:

# Quantitative Cross Sections from High-level *Ab*

Initio Theory

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1. Distributions of important geometric parameters in the PI+GLE MD simulation

The distributions of molecular geometries are eventually more important for the final spectrum than the optimal geometries. Therefore, we compared distributions of the three important geometric parameters for different methods (see Fig. S1) used for the ground state calculations in the PI+GLE simulation. The COO angle and C-O bond length distributions are generally well described by all the electronic structure methods, the O-O bond length distribution is the most problematic part. The BLYP and MP2 O-O bond lengths deviate significantly from the experiment, representing probably the pure biradical and zwitterionic structural limits. The CASPT2(4,4), PBEPBE and B3LYP approaches turned out to be the most promising methods

for the ground state calculations. They all provide structures supporting the zwitterionic character over the biradical.
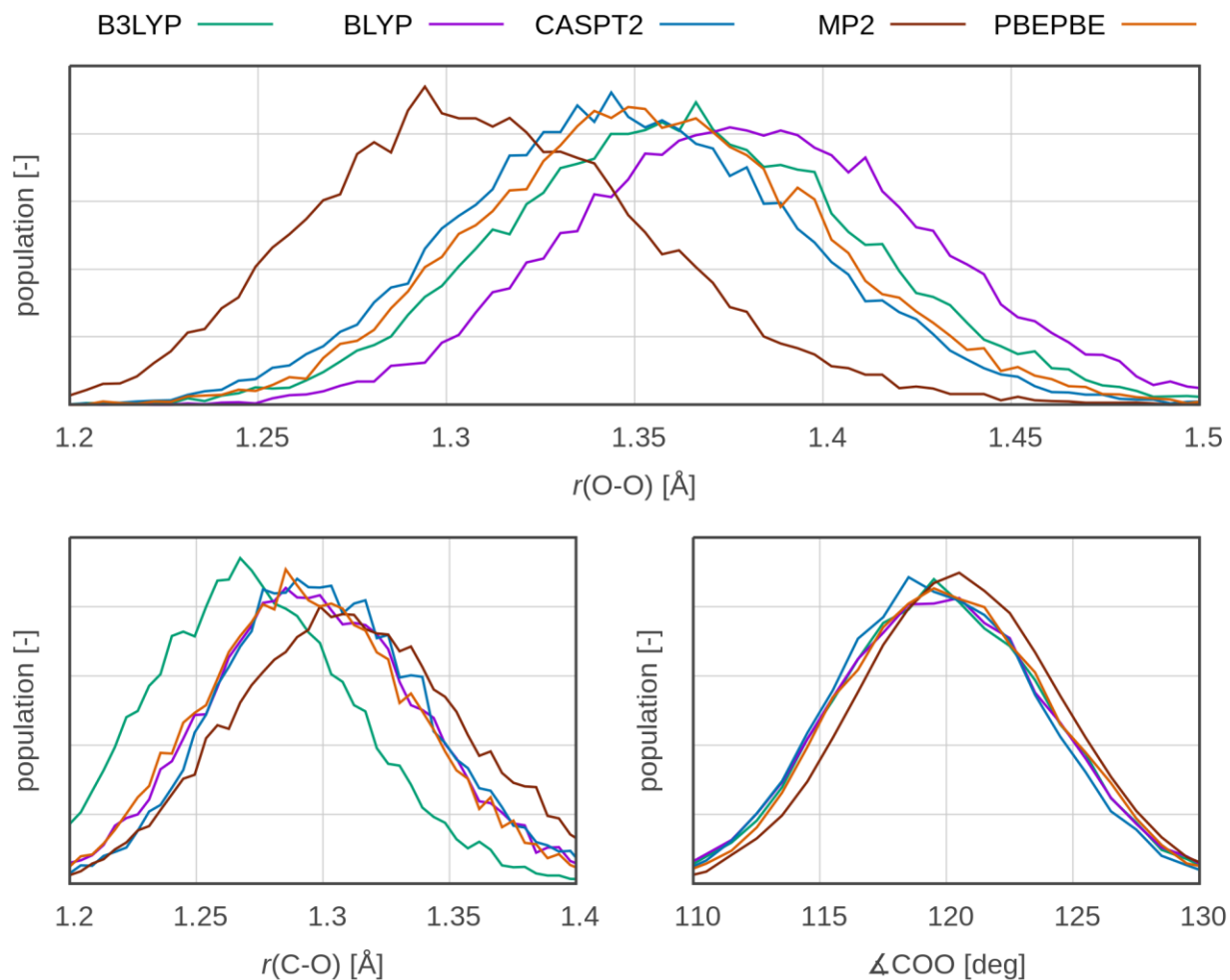

Fig. S1: Distributions of important geometric parameters from PI+GLE MD with different electronic structure methods for ground state calculations. The temperature of the simulation was set to 300 K. The time step was 20 au and the total simulation time was 24 ps.

2. Absorption cross sections for nuclear densities calculated with different ground state methods

To select one method for further calculations, we uniformly calculated final spectra with the MRCI(4,4) method and aug-cc-pVDZ basis set for nuclear densities calculated with different

ground state methods (Fig. S2). Excited state calculations at the MRCI(4,4)/aug-cc-pVDZ level provide fast semi-quantitative results for the simplest Criegee intermediate CH_2OO as discussed in the paper.

Fig. S2 confirms that the BLYP and MP2 methods are not suitable for further calculations while the PBEPBE approach describes the shape of the experimental spectrum by Ting *et al.*[1] well. The CASPT2(4,4) spectrum has a maximum shifted to lower wavelengths compared with the PBEPBE spectrum and the experiment. The B3LYP spectrum is slightly shifted to the longer wavelengths in comparison with the PBEPBE and CASPT(4,4) methods. This corresponds to the longer O-O bond length given by the distribution. It has also the maximum shifted to the left side of the spectrum as in the case of CASPT(4,4) method. Therefore, we have selected the PBEPBE approach for the ground state calculations as it best reproduces the shape of the experimental spectrum and it is fast and easy to utilize even for higher CIs.
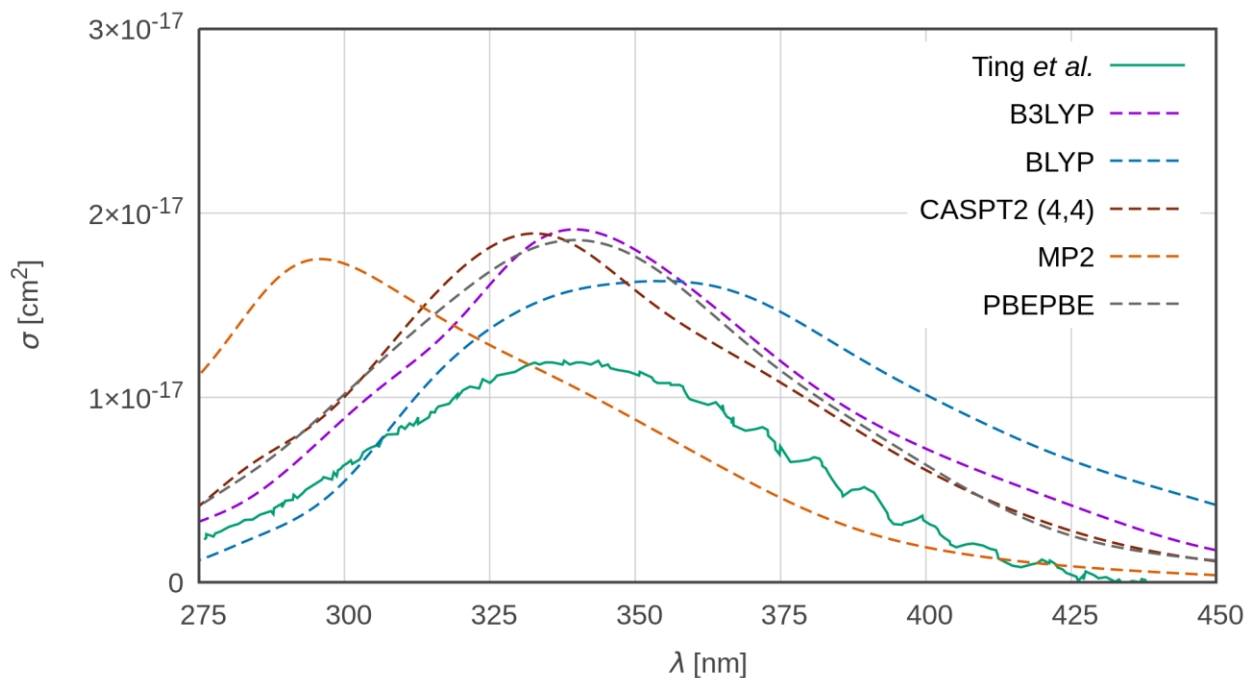
Fig. S2: MRCI(4,4)/aug-cc-pVDZ absorption cross sections for different methods used within the PI+GLE molecular dynamics for ground state calculations with aug-cc-pVDZ basis. The spectra were calculated using

1010 geometries along PI+GLE trajectory for excited state energies and transition dipole moments calculations.

## 3. Sensitivity of the absorption spectrum with respect to geometric parameters

To determine which geometric parameters have the biggest influence on the final spectrum, we utilized Pearson correlation coefficients as discussed in the paper for excited state calculations along the PI+GLE trajectory. Pearson correlation coefficients for geometric parameters and excited state properties are listed in the Table S1. The coefficients for angles and dihedrals which are not listed in the Table S1 are negligible. We identified three important geometric parameters with a significant correlation or anticorrelation with the excitation energy and transition dipole moment: the O-O bond length, the COO angle and the C-O bond length.

Table S1: Pearson correlation coefficients for geometric parameters of the CH$_2$OO molecule with the excitation energy and transition dipole moment.

	C-O	O-O	C-H1	C-H2	∢COO	E	$|\mu|^2$
E	-0.46	-0.64	0.02	0.05	0.60	1.00	0.46
$|\mu|^2$	0.53	-0.87	-0.10	-0.03	0.34	0.46	1.00

4. TDDFT absorption cross sections of the CH$_2$OO molecule

We examined the TDDFT method with different functionals (see Fig. S3). As expected, the TDDFT approach provided spectra shifted to longer wavelengths by approximately 50 nm.
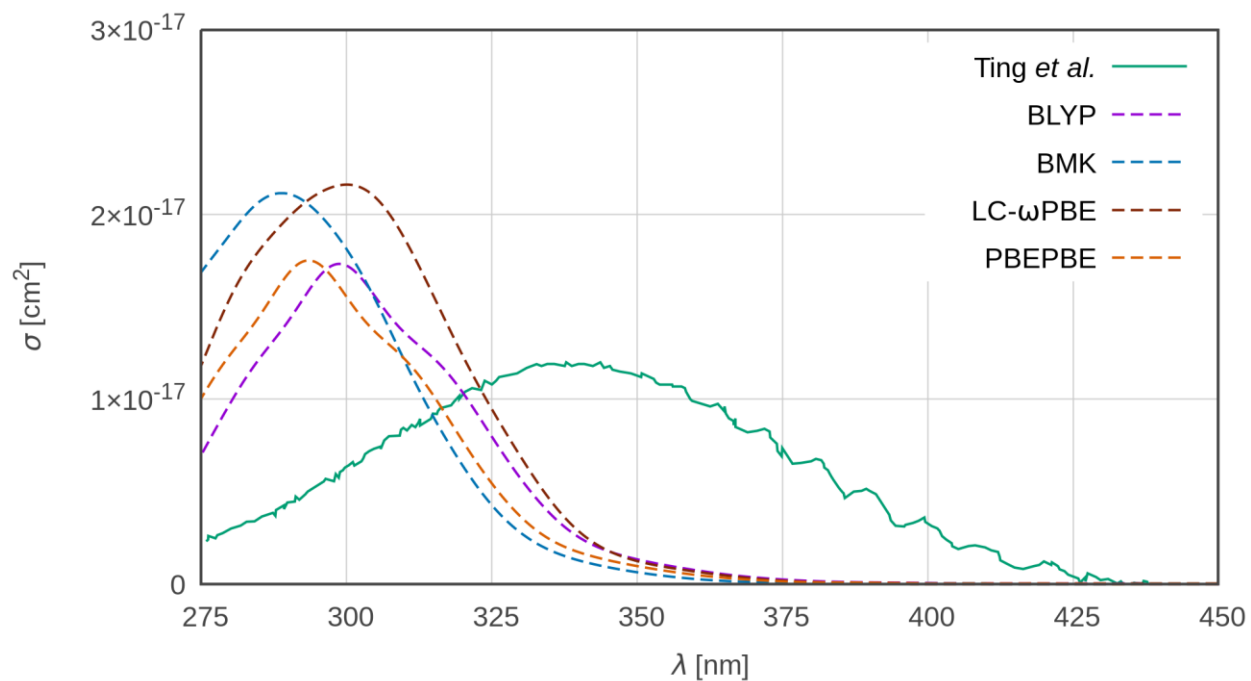
Fig. S3: TDDFT absorption cross sections of the CH$_2$OO molecule obtained with different functionals and the aug-cc-pVDZ basis set. The spectra were calculated using 1010 geometries along PI+GLE trajectory.

REFERENCES

1   W.-L. Ting, Y.-H. Chen, W. Chao, M. C. Smith and J. J.-M. Lin, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10438–10443.