Experimental Evidences for the Elusive Ketohydroperoxide Pathway and the Formation of Glyoxal in Ethylene Ozonolysis

By

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Theoretical method:

Computations were carried out using Gaussian 16[1] and started by optimizing the ground state of neutral and cationic equilibrium structures and frequencies of the species. These computations were done using the density functional theory (DFT) PBE0 exchange–correlation functional, where the atoms are described using the aug-cc-pVDZ basis set.[2] Afterwards, the PBE0/aug-cc-pVDZ geometries and frequencies were used to deduce an accurate adiabatic ionization energy (AIE) of each species. AIE were calculated using the composite CBS-QB3 method[3,4] and the CBS extrapolated coupled cluster CCSD(T)/CBS method. CCSD(T)/CBS energies were extrapolated from CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ and, CCSD(T)/cc-pVQZ energies using the scheme suggested by Martin[5] and Feller and Dixon[6]. Note that the values provided in Table S1 are the one derived from the (TZ, QZ) extrapolation. The calculation of the AIE includes the zero-point energy correction. Then, the simulations of the vibrationally resolved electronic spectra were achieved at 300K by means of the time-independent adiabatic Hessian Franck-Condon (TI-AH|FC) model.[7] The resulting stick spectra were convolved with a 20 meV bandwidth Gaussian profile to match the overall experimental resolution. The computed spectra are then shifted in energy with respect to the AIE uncertainty, so that they match the experimental spectra. This method has already been validated in several studies.[8–12]
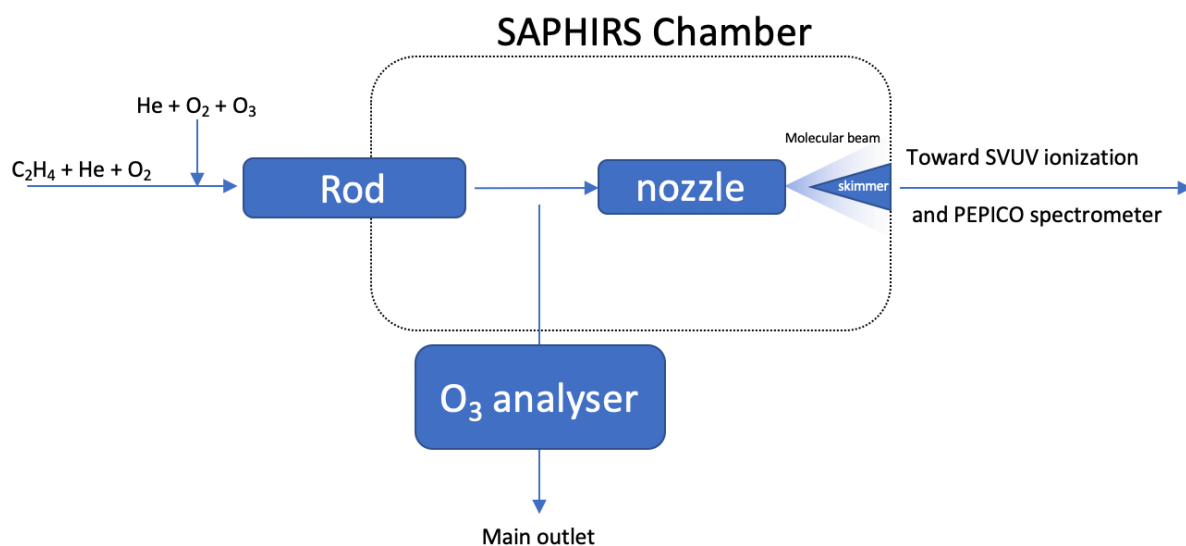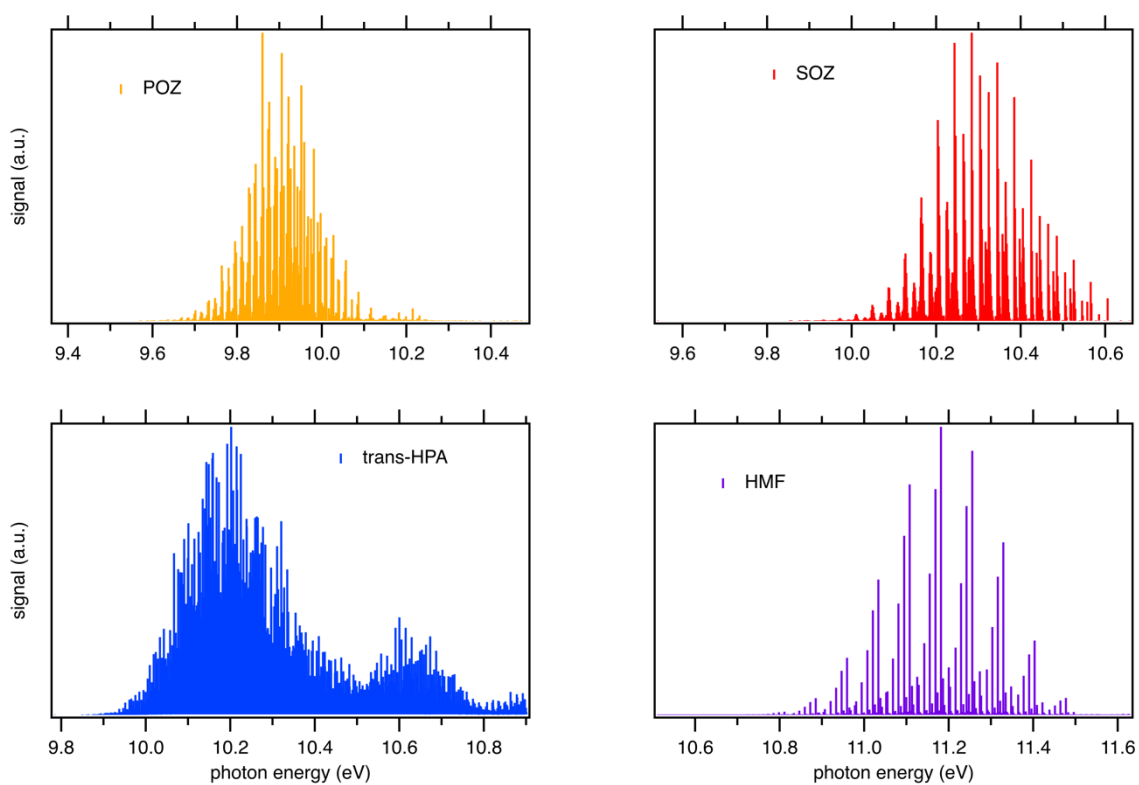
Figure S1. Scheme of the experimental setup.

Figure S2. Computed stick spectra of primary ozonide (top left, orange sticks), secondary ozonide (top right, red sticks), trans 2-hydroperoxyacetaldehyde (bottom left, blue sticks), and hydroxymethyl formate (bottom right, purple sticks).

Table S1. Calculated AIE of the lowest energy conformer of the $C_2H_4O_3$ and $C_2H_2O_2$ isomers considered in this work at different levels of theory.

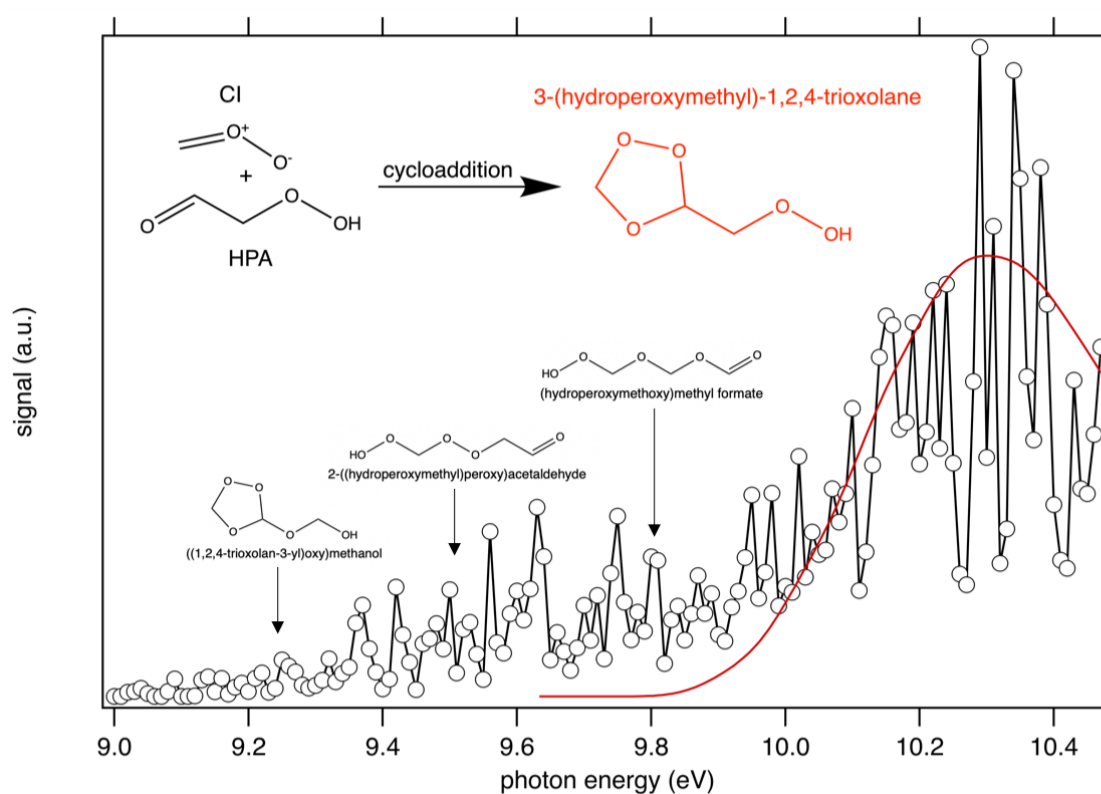| Species	CBS-QB3 (eV)	CCSD(T)/CBS (eV)
cis-HPA	9.65	9.82
trans-HPA	9.68	9.85
POZ	9.57	9.53
SOZ	9.74	9.68
HMF	10.63	10.62
cis-glyoxal	9.94	10.01
trans-glyoxal	10.14	10.21

Figure S3. SPES of m/z 122 (open dots) compared to the simulated spectrum of 3-(hydroperoxymethyl)-1,2,4-trioxolane (red line). The AIE(CBS-QB3) of the lowest-lying conformers of other $C_3H_6O_5$ isomers considered in this work is also indicated
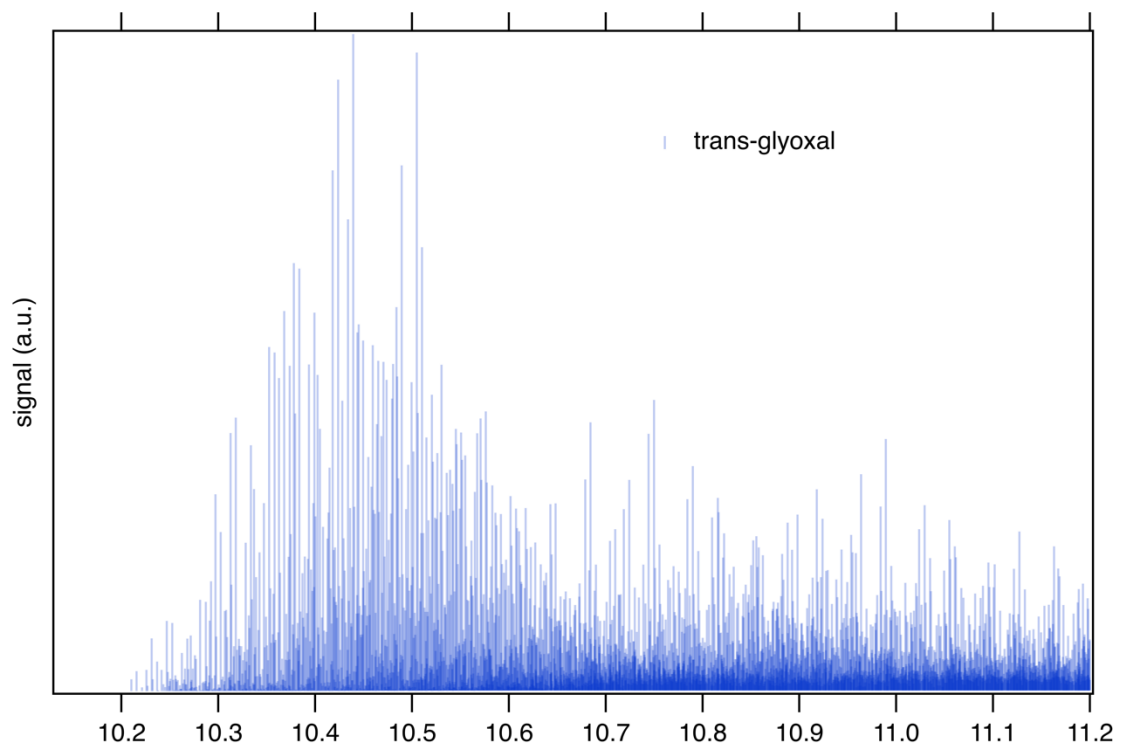
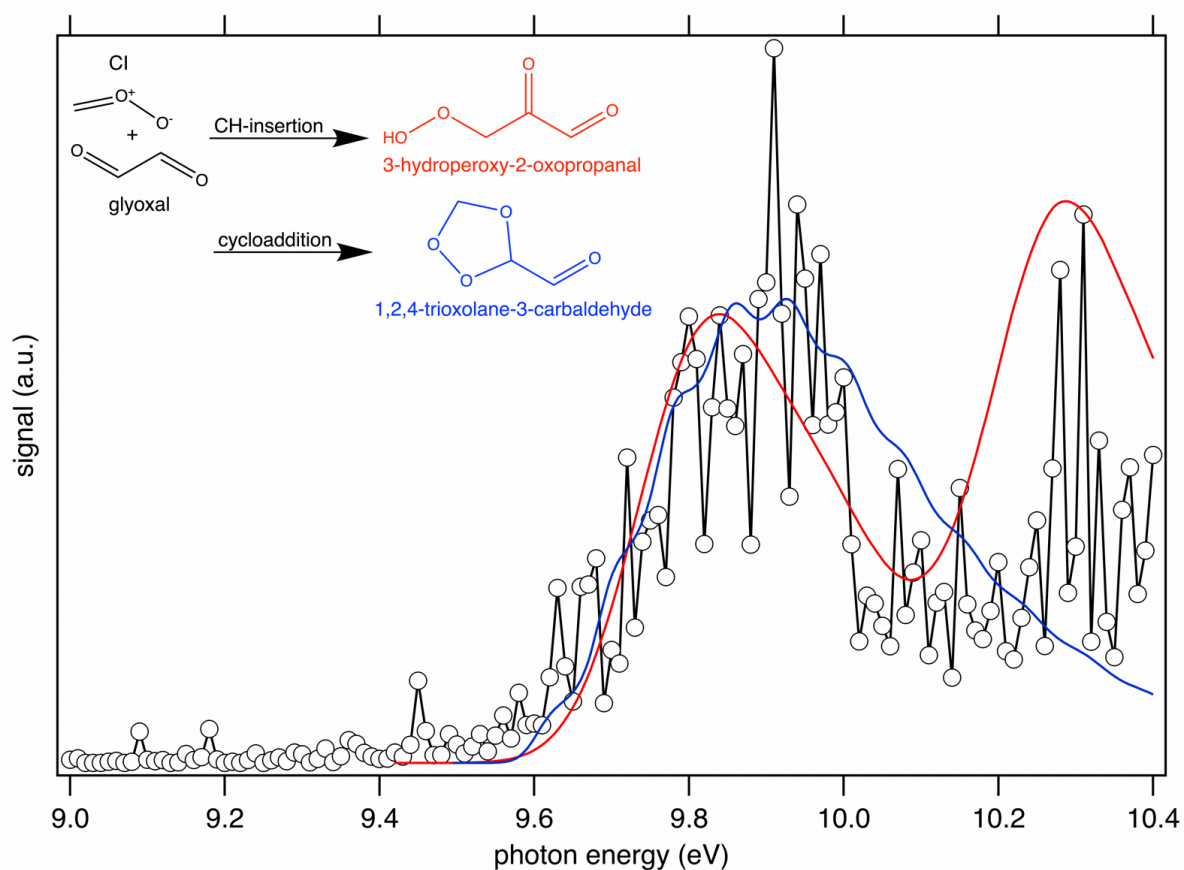Figure S4. Computed stick spectrum of trans-glyoxal (blue sticks).

Figure S5. SPES of m/z 104 (open dots) compared to simulated spectra of 3-hydroperoxy-2-oxopropanal (red line) and 1,2,4-trioxolane-3-carbaldehyde (blue line) that have been shifted by 100 and 50 meV respectively.

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