Threshold photoelectron spectrum of the CH_2OO Criegee intermediate

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Experimental methodology

Experiments have been performed at the DESIRS beamline of the French synchrotron SOLEIL,[1] on the permanent end-station SAPHIRS.[2] The continuous microwave discharge flow-tube reactor used in the present experiments is composed of a one inch internal diameter quartz reactor, and a moveable quartz injector that slides inside the reactor[3]. The distance between the injector and the first skimmer—placed at the end of the reactor—defines the reaction time, which can be adjusted within a range of a few msec.

A 20 sccm (standard cubic centimeters per minute) flow of commercial methyl iodide (CH_3I) from Aldrich was mixed with 600 sccm of pure oxygen (O_2) and 100 sccm of pure He. The resulting mixture was fed into the flow-tube reactor through an injector. A 5% mixture of F_2/Ar was diluted with 1000 sccm of pure He and traversed a continuous 2.5 GHz microwave discharge where 100% of the F_2 is converted into F atoms before entering the reactor through a side arm. The total pressure in the reactor was kept at 1.1 torr. The F atoms abstract a H atom from CH_3I to generate CH_2I, which reacts with O_2 to form CH_2OO. Before injecting O_2, the reaction time and concentrations were adjusted to avoid consecutive H-abstractions and maximise the signal on the CH_2I channel.

The output of the reactor traversed two skimmers before crossing the synchrotron VUV light at the center of the double imaging PEPICO (i^2PEPICO) spectrometer Delicious 3.[4] The momenta of the resulting photoelectrons and photoions are correlated, and for these experiments only the photoelectrons correlated to ions having mass *m/z* 46 and a net translational energy along the reactor axis are measured. The mass resolving power M/ΔM was measured at 1100 at the FWHM, comparable to the resolution needed to separate CH_2O_2 (m/z= 46.0254) and C_2H_6O (m/z=45.0684). The *tagged* photoelectron images are obtained as a function of the photon energy, and they are Abel inverted using the pBasex algorithm[5] to provide the *tagged* electron signal as a function of electron kinetic energy and photon energy. The error bars shown throughout assume an initial Poisson distribution on the image pixel counts, propagated through all subsequent mathematical operations.

The beamline was set to provide a resolution of 5 meV with an estimated photon flux of $5x10^{12}$ photon/s. Spectral purity was ensured by means of a gas filter filled with Kr.[6] The gas filter was further used to calibrate *in-situ* the energy scale with the 5s Kr absorption lines appearing within the energy range shown in this work,[7] along with the known ionization energy of the methyl radical,[8] which is also observed in the reactor, offering an accuracy on the energy scale of ±3 meV. The photon flux was recorded with a dedicated photodiode (AXUV, Optodiode) and used to normalize the data.

Supplementary figures

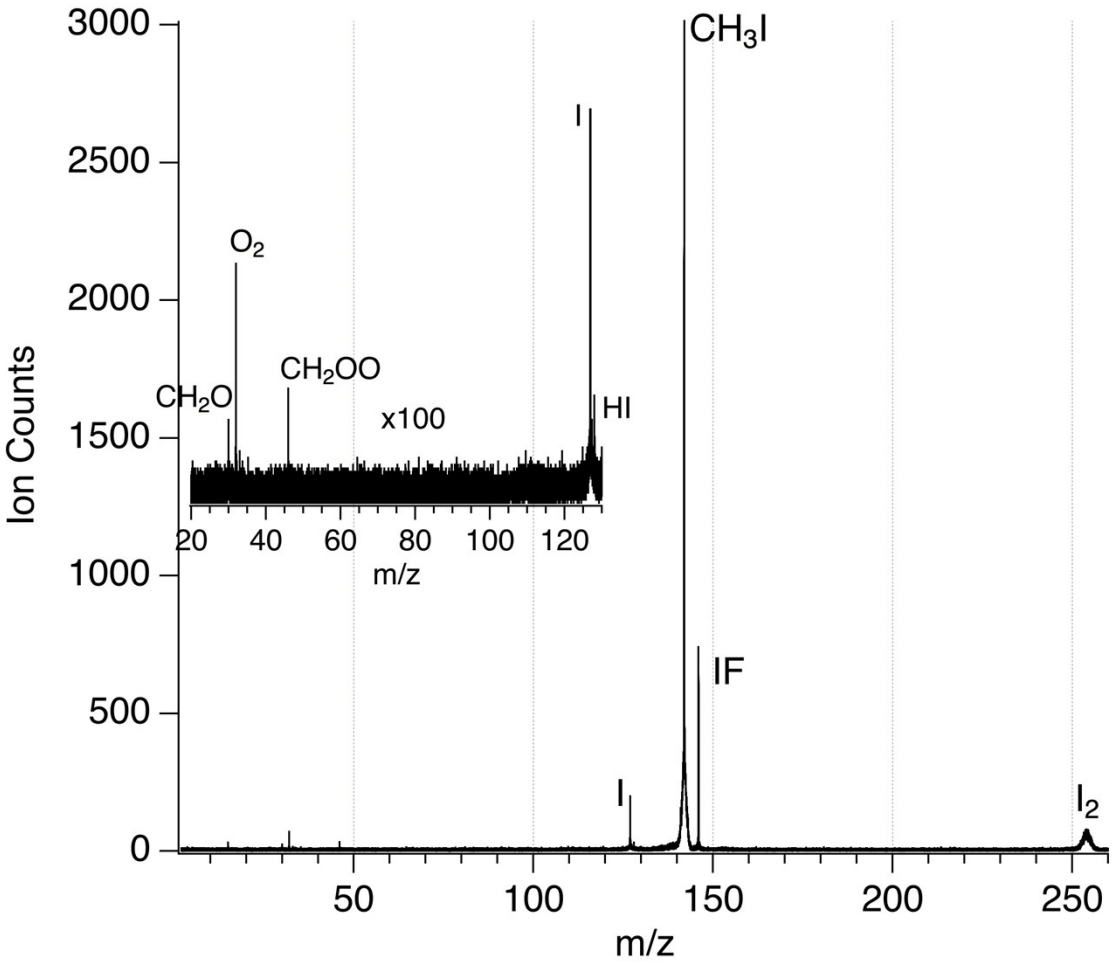

Figure S1: *TOFMS obtained at a photon energy of 12.0 eV. The inset shows a zoom on the region corresponding to the lighter masses.*

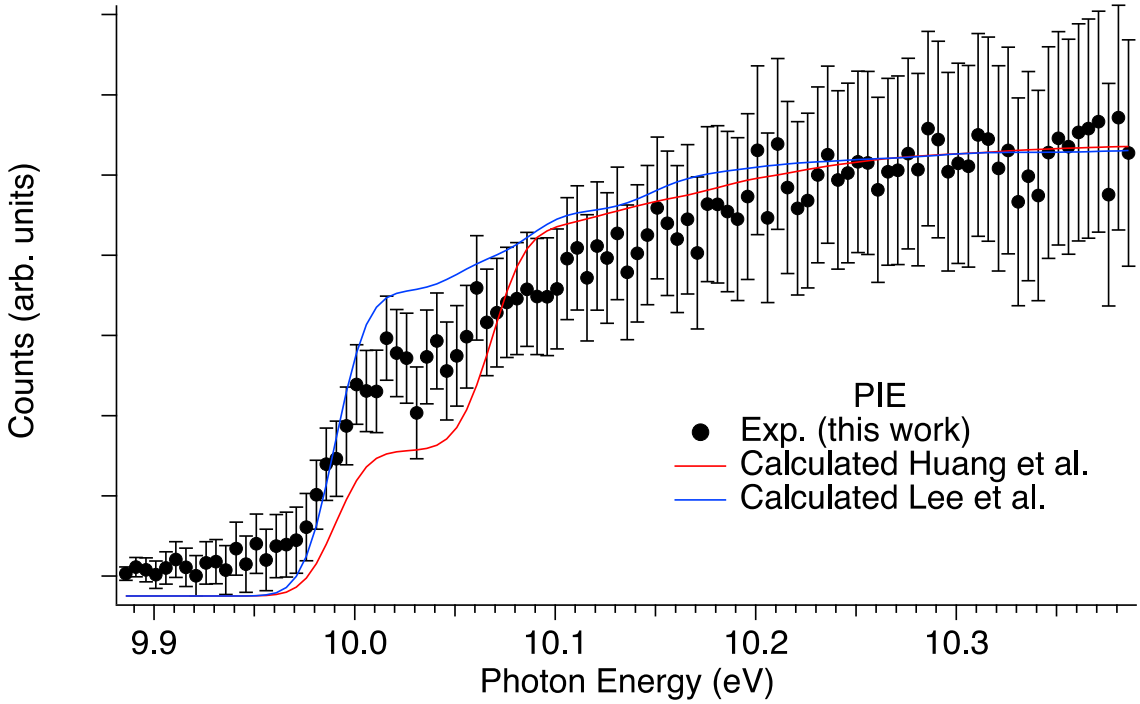

***Figure S2**: Experimental PIE of m/z 46 (black circles) and calculated curves: Blue from Lee et al.*[9] *obtained at the QCISD/6-31G** level of theory; Red from Huang et al.*[10] *obtained at the DLPNO-CCSD(T)/aug-cc-pV(T,Q)Z level. The simulated PIEs have been shifted by +20 meV (blue) and -17 meV (red) as in Figures 3, S3 and S4. A 3:4 ratio for the A':A" transitions has been applied to the Huang et al. data as in the original reference.*

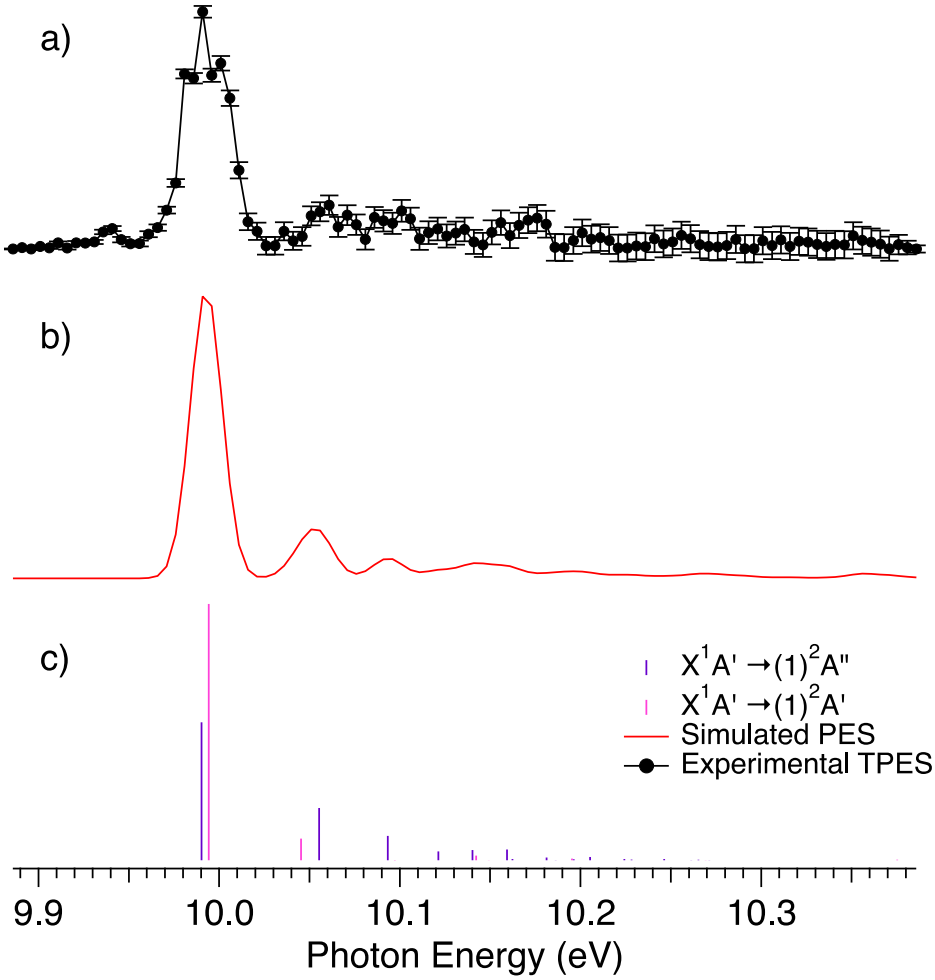

***Figure S3**: a) Experimental TPES. b) simulated PES and c) calculated FC factors at the B3LYP/6-311++G** level of theory by Lee et al.*[9], to be compared with those shown in Figure 3 of the main article performed at a higher level of theory, *QCISD/6-31G**. The simulated PES and calculated FC factors have been shifted by +20 meV from the calculated adiabatic ionization energy of 9.971 eV.*

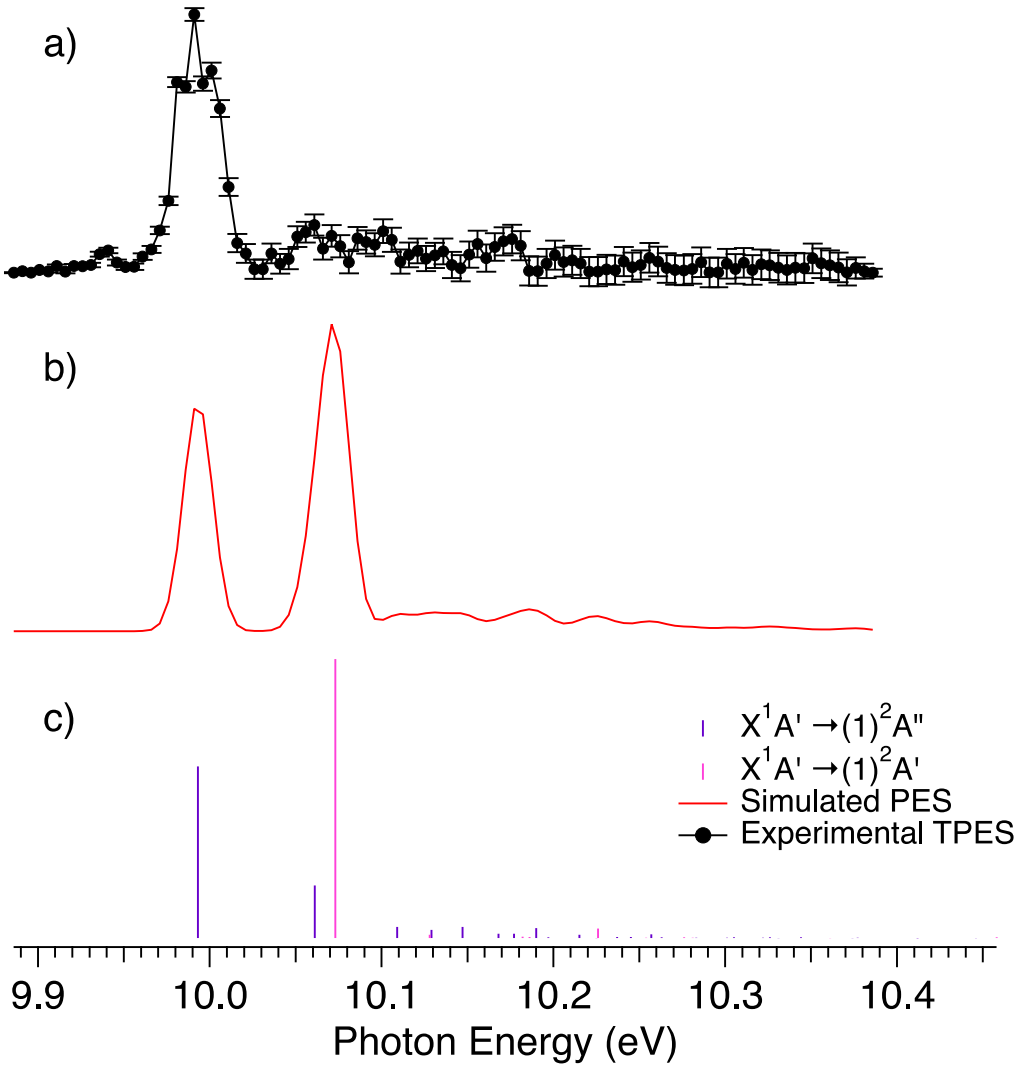

***Figure S4**: a) Experimental TPES. b) simulated PES and c) calculated FC factors at the M06-2X/aug-cc-pVTZ level of theory by Huang et al.[10]. The simulated PES and calculated FC factors have been shifted by +60 meV from the calculated adiabatic ionization energy of 9.931 eV.*

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