Threshold photoelectron spectrum of the CH$_2$OO Criegee intermediate†

David V. Chicharro,$^{a, b}$ Sonia Marggi Poullain,$^{b}$ Luis Bañares,$^{b, *}$ Helgi Ragn Hammarsson,$^{c}$ Gustavo A. García$^{b, c}$ and Jean-Christophe Loison$^{d, *}$

We present the photoelectron spectroscopy of the simplest Criegee intermediate, CH$_2$OO, close to the first ionization energy. Comparison with existing theoretical data yields the experimental adiabatic ionization energy and provides a benchmark for theoretical studies on larger Criegee intermediates, which play an important role in the ozonolysis of alkenes.

Carbonyl oxides were postulated by Criegee in the 1950s to be formed in the ozonolysis of alkenes$^7$ as intermediates in a three-step mechanism that is now generally accepted.$^2$ The detection and study of carbonyl oxides, also known as Criegee intermediates (CIs), are of considerable atmospheric importance considering that alkenes are the second largest anthropogenic and biogenic (CIs), are of considerable atmospheric importance considering that alkenes are the second largest anthropogenic and biogenic organic volatiles after methane.$^3$ Additionally, ozonolysis is an important mechanism for their atmospheric removal, as well as an important pathway to OH formation,4,5 or reacting with water, SO$_2$, NO$_2$, etc. Tangentially, reactions with other organic molecules such as acids or carbonyls lead to other oxidized organics that eventually evolve into secondary organic aerosols, thus enhancing aerosol formation.$^6$ The interested reader will find a more exhaustive review on the reactivity of carbonyl oxides elsewhere.$^7,8$

Although there is a large amount of literature on CIs, the first direct detection was not achieved until 2008,$^9$ where the simplest CI, CH$_2$OO, was identified in a gas phase reactor by photoionization mass spectrometry and its formaldehyde oxide structure was confirmed over all other possible isomers by comparing the experimental photoionization efficiency (PIE) curve at m/z 46 to the calculated one.$^{10}$ The gas phase structure was later corroborated by infrared spectroscopy.$^{11}$ Therein, the CH$_2$OO bond lengths were found to be more comparable with those of a zwitterion rather than a biradical, as already suggested in the pioneering photoionization study. The first direct measurement of its reactivity followed four years later, where the rate constant for the oxidation of SO$_2$ to SO$_3$ by CH$_2$OO was obtained and found to be much larger than originally predicted. This highlights the importance of these challenging experiments.$^{13}$ Recently, the CH$_2$OO intermediate has been directly observed in the gas phase in the ozonolysis of ethylene by microwave spectroscopy.$^{13}$

In spite of the accumulating experimental data on this intermediate, its adiabatic ionization energy is not precisely known. Experiments gave a first estimation of this value at $\sim$9.96 eV,$^9$ while theoretical calculations have provided values ranging from 9.931 to 10.02 eV.$^{9,10,14,15}$ In this work, we have recorded for the first time the photoelectron spectrum of CH$_2$OO close to the first adiabatic ionization energy, yielding an accurate value for the adiabatic ionization energy. Comparison of this value, along with the simulated photoelectron spectrum, provides a more stringent test of the model than the existing PIE curves, which is critical to confidently move towards modelling larger CIs.

Additionally, in the last decade, the mass tagged photoelectron spectrum obtained through photoelectron photoion coincidence (PEPICO) techniques$^{16}$ has been used as a fingerprint for multiplex species identification in complex media, since the obtained vibronic structure provides more specificity and sensitivity than PIE curves, which is advantageous specially when isomer differentiation is necessary.$^{17–20}$

Experiments have been performed at the DESIRS beamline of the French synchrotron SOLEIL,$^{21}$ on the permanent end-station SAPHIRS.$^{22}$ The continuous microwave (MW) discharge flow-tube reactor used in the present experiments has been
described in detail elsewhere and the relevant parameters are discussed at length in the ESL. Briefly, CH₂OO is formed by reaction between CH₂I and O₂, where the iodomethyl radical is produced by H abstraction from the iodomethane precursor:

\[ CH_3I + F \rightarrow CH_2I + HF \]

The chemical species produced in the reactor are ionized by the synchrotron VUV radiation and the electrons and ions are detected in coincidence using a double imaging PEPICO (i²PEPICO) device.†

Fig. 1 shows the time-of-flight mass spectrum (TOFMS) accumulated over the photon energy range 9.8–10.4 eV. Apart from the peak of interest at \( m/z = 46 \) corresponding to CH₂OO, the mass channels \( m/z = 15, 28, 32, 33, 141, 142 \) and 143 are also visible and assigned via their vibronic structure to the CH₃ radical, metastable \( N_2(A^3\Sigma_u^-) \), O₂ (traces from the remaining second order ionization), CH₂F and CH₂I radicals, CH₃I and \(^{13}\text{CH}_3\text{I}, \) respectively.

There are several possible channels for the reaction between CH₂I and O₂: production of CH₂OO + I, production of the CH₂OO adduct and a minor channel leading to formation of formaldehyde and IO. As in previous photoionization mass spectrometry (PIMS) experiments, the CH₂OO channel is not observed since we would expect stabilisation of this species to occur only at high reactor pressures, although it could also be that the parent ion is not stable within the energy range of this work. TOFMS data obtained over the ionization energy (IE) of formaldehyde, at \( h\nu = 12 \) eV (see Fig. S1 of the ESL†), shows a small signal at \( m/z = 30 \) that could correspond to formaldehyde, although its low signal-to-noise precludes an unambiguous identification. Additionally, the counterpart product, IO, is not seen in the \( m/z = 143 \) channel. Only a vibronic structure consistent with \(^{13}\text{CH}_3\text{I} \) is detected in that channel and the ratio between the areas of the \( m/z = 143 \) and \( m/z = 142 \) peaks corresponds to the expected natural abundance of the \(^{13}\text{C} \) isotope within our error bars. We do see atomic iodine in Fig. S1 (ESI†), alongside HI, I₂ and IF.

Fig. 2 shows the electron signal as a function of the electron kinetic energy and photon energy for the \( m/z = 46 \) channel. Energy conservation leads to diagonal lines of constant unity slope (constant ionic state, CIS, lines) for each cationic state \( i: eKE/(h\nu - \text{IE}_i) \), where eKE is the electron kinetic energy and \( \text{IE}_i \) is the ionization energy of the \( i \)th state. From this matrix, several relevant projections can be plotted, such as the well-known PIE curve obtained by integrating over all the electron energies, which is also depicted in Fig. 2 and Fig. S2 of the ESL.†

The curve is in agreement with previous experiments. However, as indicated above, integration greatly reduces the spectroscopic information contained in the curve. Hence other projections such as the photoelectron spectrum (PES) at a given photon energy, or the threshold photoelectron spectrum (TPES) are more desirable. The latter is obtained by integrating over all the electron energies, which is also depicted in Fig. 2 and Fig. S2 of the ESL.†

The white curve with error bars corresponds to the photoionization efficiency (PIE) as a function of photon energy.

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Fig. 1 Time-of-flight mass spectrum (TOFMS) obtained by integrating all mass spectra for photon energies from 9.8 to 10.4 eV. The inset shows a zoom on the region corresponding to the lighter masses.

Fig. 2 Intensity colormap representing the electron signal as a function of electron kinetic energy (eKE) and photon energy for the \( m/z = 46 \) channel. The white curve with error bars corresponds to the photoionization efficiency (PIE) as a function of photon energy.
configuration interaction wave function. The same authors also calculated the first adiabatic ionization energy at the CCSD(T)–CBS level and found a value of 9.98 eV for the $1^3\tilde{A}' \rightarrow X^1\tilde{A}'$ transition, that corresponds mainly to the removal of the electron from the terminal oxygen atom. The accuracy of the calculated adiabatic ionization energy (IE$_{\text{ad}}$) was estimated at 50 meV, mostly due to zero-point energy errors. The authors placed the first neutral triplet state at 1.8 eV above the $1\tilde{A}'$ ground state, but we have not detected ionization transitions from this state, most likely because the internal energy of the nascent CH$_2$OO is lower, the CH$_2$I + O$_2$ → CH$_2$OO + I being only slightly exothermic, between 50 and 130 meV.\textsuperscript{12,14} Taatjes et al. performed a Franck–Condon (FC) harmonic simulation using optimized CBS-QB3 geometries\textsuperscript{7} and found an intense adiabatic transition due to the small geometry change between the neutral $X^1\tilde{A}'$ ground state and the cationic $(1)^3\tilde{A}'$ ground state, which agrees with our experimental spectrum shown in Fig. 3a.

In a more complete theoretical work, Lee et al.\textsuperscript{14} calculated ionization transitions to the cationic ground and first excited states, $(1)^3\tilde{A}'$ and $(1)^3\tilde{A}'$, using a large variety of theoretical methods. These states are very close in energy, so it is not yet conclusive which of them is the “actual” ground state. The calculated adiabatic energies at their highest level of theory for transitions to the $A'$ and $A''$ states are 9.974 eV and 9.971 eV, respectively. Lee et al. simulated the photoelectron spectrum using a harmonic model and an equal weighting for the $A'$ and $A''$ transitions. At the QCISD/6-31G** level of theory, an intense adiabatic peak was obtained with weak excitation in the COO bending and O–O stretching modes, mainly in the $A''$ state, as shown in Fig. 3c.

The agreement between the simulated spectrum in Fig. 3b, obtained by convolving the stick spectrum with a Gaussian having a full-width-half-maximum (FWHM) of 20 meV, and the experimental spectrum of Fig. 3a is remarkably good, including the higher energy vibrational structure seen between 10.02 and 10.2 eV, although the experimental signal-to-noise ratio combined with the weak FC factors is not sufficient to provide reliable vibrational frequencies. A small feature at 9.94 eV, which does not correspond to the IE$_{\text{ad}}$ of any of the aforementioned isomers, is seen in the spectrum and could correspond to a hot band that would be consistent with excitation of one quantum of the COO bending mode in the neutral, calculated by Lee et al. at around 500 cm$^{-1}$. In Fig. S3 of the ESI\textsuperscript{†} we show the comparison between experiment and the simulated spectrum obtained by Lee et al. at the B3LYP/6-311++G** level of theory, where we find a somewhat worse qualitative agreement.

Note that for both simulations, the best agreement between simulated and experimental spectra is obtained by shifting the calculated IE$_{\text{ad}}$ by 20 meV, from 9.971 eV to 9.991 eV. This provides an experimental IE$_{\text{ad}}$ value of 9.991 ± 0.005 eV, where the error bar takes into account the precision of the energy scale and the inability to distinguish between the $A'$ and $A''$ states. This value leads to an enthalpy of formation of the cation of $\Delta H_0(\text{K}(\text{CH}_2\text{OO}^+) = 1076.3 \pm 0.8 \text{ kJ mol}^{-1}$, using the recommended ATr\textsuperscript{28} enthalpy of formation for CH$_2$OO, 112.43 ± 0.61 kJ mol$^{-1}$.

More recent calculations by Huang et al. at the DLPNO-CCSD(T)/aug-cc-pVXZ (X = T, Q) level of theory\textsuperscript{15} suggest a larger separation of the $A'$ and $A''$ transitions, of 70 meV instead of 3 meV. Although their simulated PIE curve reportedly matches the existing experimental ones, and as shown in Fig. S2 (ESI\textsuperscript{†}), the PIE obtained in this work, the simulated PES shown in Fig. S4 of the ESI\textsuperscript{†} does not agree with our experimental spectrum. Perhaps an explanation for the disagreement can be found in the systematic theoretical study of the CH$_2$OO Cl, where Lee et al.\textsuperscript{14} observed that the ordering and energy differences of the $A'$ and $A''$ transitions, as well as the FC factors, were very sensitive to the level of theory. In any case, within the measured 18 meV experimental resolution we do not see two separate adiabatic transitions, which supports the Lee et al. findings and disagrees with the predictions of Huang et al.

In conclusion, the present study reports an accurate measurement of the adiabatic ionization energy (IE$_{\text{ad}}$) of the simplest Cl, CH$_2$OO. Our measured threshold photoelectron spectrum is consistent with the calculations by Lee et al.\textsuperscript{14} but disagrees with the more recent calculations by Huang et al.\textsuperscript{15} While both calculations seem to provide good agreement with existing PIE curves, the simulated photoelectron spectrum is shown to be very sensitive to the level of theory. Therefore, the experimental TPES reported here provides a more rigorous benchmark of the calculations in order to move towards larger Cls. Finally, the spectrum depicted in Fig. 3 not only validates the theoretical methods, but can also serve as a precise fingerprint for the identification of these elusive species in atmospheric or combustion reactions using photoelectron photoion coincidence techniques.\textsuperscript{29}

Conflicts of interest

There are no conflicts to declare.
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Notes and references