

Identification of combustion intermediates via photoionization: Large amplitude motions in alkyl- and ketohydroperoxides

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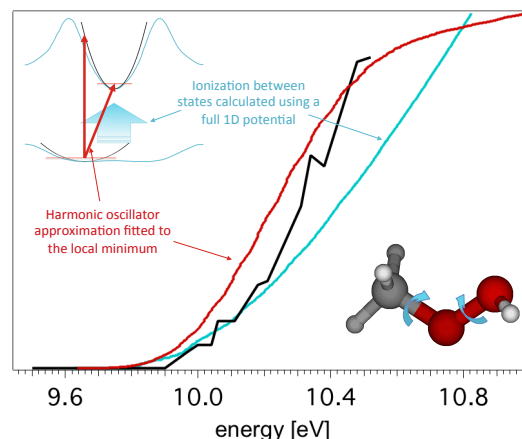
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Experimental investigations of low-temperature oxidation chemistry hinge on the detection of key molecular species.¹⁻⁴ Mass spectrometry coupled to photoionization (PIMS) experiments enable isomer-selective signal identification based on measured photoionization onsets and photoionization efficiency (PIE) curve shapes. Measured in reactive mixtures PIE curves are often compared to pure compound PIE curves; however, pure samples of many important species, such as those of alkyl- and ketohydroperoxides or many reactive intermediates, are not available. In these cases, the identification is done in comparison with calculated adiabatic ionization energies (AIE) calculated as the zero-point-energy-inclusive difference between the lowest energy conformer of the neutral and its adiabatically ionized cation state. The PIE curves are commonly calculated using the photoelectron Franck-Condon spectra using the harmonic oscillator approximation.

However, many structures of interest, such as alkylhydroperoxides (ROOH) and ketohydroperoxides (KHP), feature large amplitude modes and numerous conformers and therefore cannot be described accurately by a single-structure harmonic oscillator approximation even at room temperature. In this work, we show the impact of including the conformational distribution and some of the large amplitude motions on the calculated PIE curve shapes and on the photoionization onset for molecules. Our examples include tetrahydrofuranyl- and cyclohexylhydroperoxides, and butyl- and hexylketohydroperoxides.

We include in these calculations the relevant conformational space of these molecules. We also develop a separable 1-D hindered rotor methodology and show its effect on both the onsets and the shapes of the PIE curves. We compare our results to experimental PIE data and discuss the insight into mechanism we gain in cases where multiple isomers contribute to one m/z signal. We discuss the mechanistic implications of our results for the oxidation reactions.



References

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