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

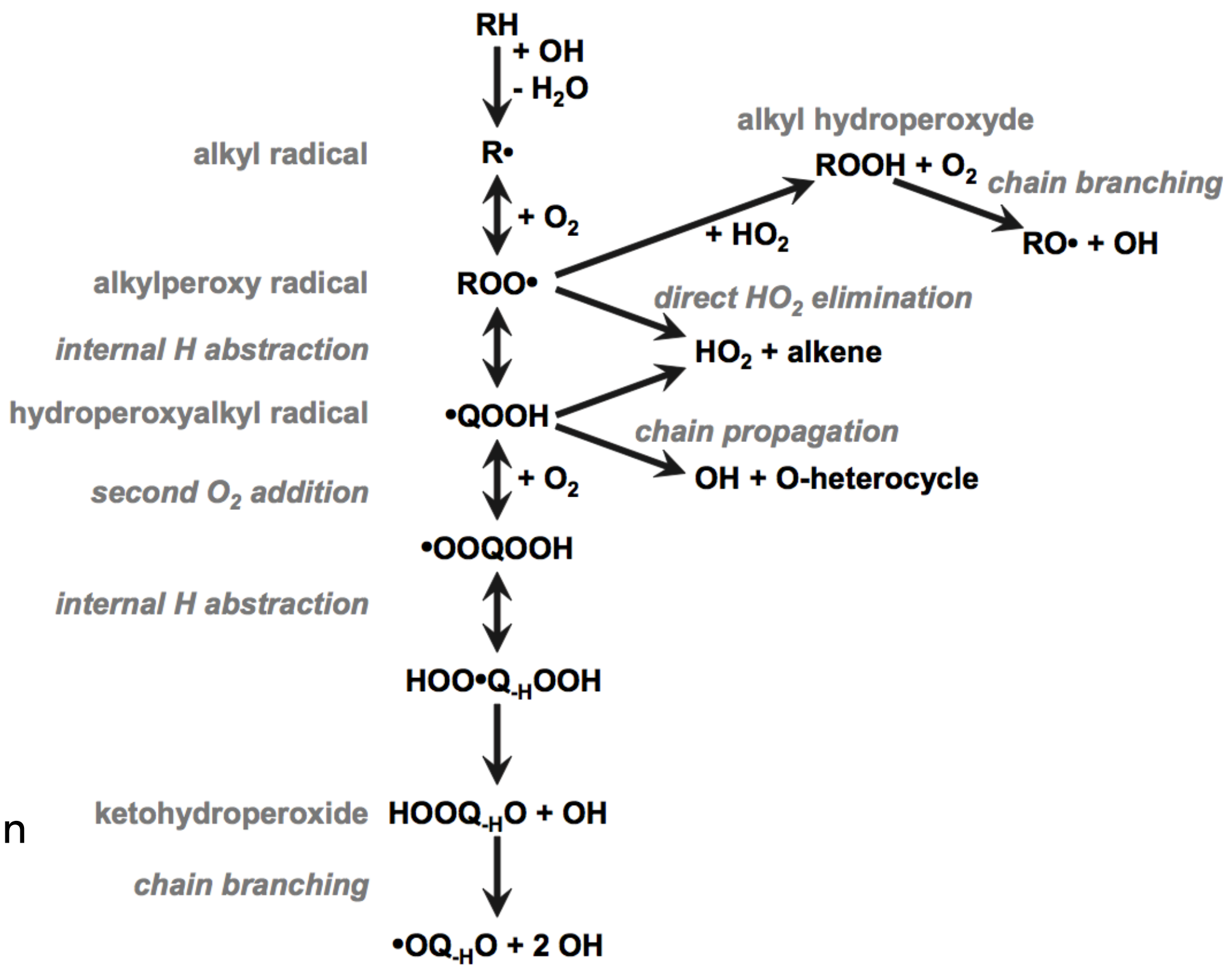
Ewa Papajak, Brandon Rotavera, Leonid Sheps, Craig Taatjes, and Judit Zádor
Sandia National Laboratories, Livermore, CA, USA

Hydroperoxides and keto-hydroperoxides in combustion chemistry

Molecules characterized by rovibrating groups include alkyl chains, -OO, and -OOH groups and appear in the key molecules such as alkylperoxy radicals (ROO), QOOH, and ketohydroperoxides (KHP) are central to low-temperature chain-branching and autoignition. Their detailed modeling is an important objective in the development of chemical kinetics mechanisms for combustion and atmospheric chemistry.

Low-temperature autoignition in combustion system starts by the formation of an initial organic radical (R), which undergoes reaction with molecular oxygen to form the alkylperoxy radical (ROO). Unimolecular hydrogen abstraction within ROO leads to isomerization of ROO to (usually several prossible) QOOH radical isomers. QOOH can abstract OH (chain propagation) or HO$_2$

QOOH can also react with an oxygen molecule forming OOQOOH, chemistry of which is somewhat analogous to that of ROO. Isomerization and decomposition reactions of the OOQOOH adduct can lead to chain-branching by the production of two OH radicals (chain branching) through a sequence of steps involving the formation of ketohydroperoxide. The detailed knowledge of the mechanism of these steps is crutial to modeling of chain branching/propagation, and termination in low-temperature ignition.



Experiment

Experimental investigation of the reaction mechanisms above hinges on the detection of small concentrations of key radical intermediates and determination of their concentration as function of time. In practice signals obtained from mass spectrometry can often be assigned to observed experimentally chemical species based on their photoionization energy onsets. These onsets are commonly approximated as adiabatic harmonic oscillator (HO) ground-state-to-ground-state energy difference (ionization energy) for the relaxed geometries of the lowest energy conformers of the ground and ionized molecules. However, in the case of multiple isomers contributing to a particular m/z signal, the knowledge of the photoionization efficiency curves of all involved species becomes crucial. The whole PIE curves can be calculated by integrating photoelectron/photodetachment Franck-Condon spectra also calculated within the double harmonic approximation.

However, the HO predicts negligible spectral intensities in molecules mentioned above when ionization is acompanied by a large internal rotation. This is especially pronounced in -OOH groups that appear in QOOH, and ketohydroperoxides (KHP).

Photoelectron spectrum

Since in the harmonic approximation vibrational wavefunctio are products of one dimensional harmonic oscillator wavefunctions, the multidimensional Franck-Condon factors (FCFs) are products of one dimensional FCFs.

$$\langle\chi'(Q)|\chi''(Q)\rangle = \langle\chi'_1(Q_1)\cdot\chi'_2(Q_2)\cdot\ldots|\chi''_1(Q_1)\cdot\chi''_2(Q_2)\cdot\ldots\rangle = \langle\chi'_1(Q_1)|\chi''_1(Q_1)\rangle\cdot\langle\chi'_2(Q_2)|\chi''_2(Q_2)\rangle\cdot\ldots$$

In the case of large geometry change along one vibrational mode the small overlap for that mode leads to extremely low calculated intensities for the whole spectrum.

Therefore, we take the anharmonic mode out of the HO FC calculation and the C–OOH and CO–OH rotational modes are treated as a separable 1D problems.

We solve $\hat{H}\psi = E\psi$ where $\hat{H} = -\frac{-\hbar}{2m}\frac{d^2}{d\varphi^2} + V(\varphi)$

and V is the 1D potential from a relaxed geometry scan calculated using electronic structure and fitted to a function:

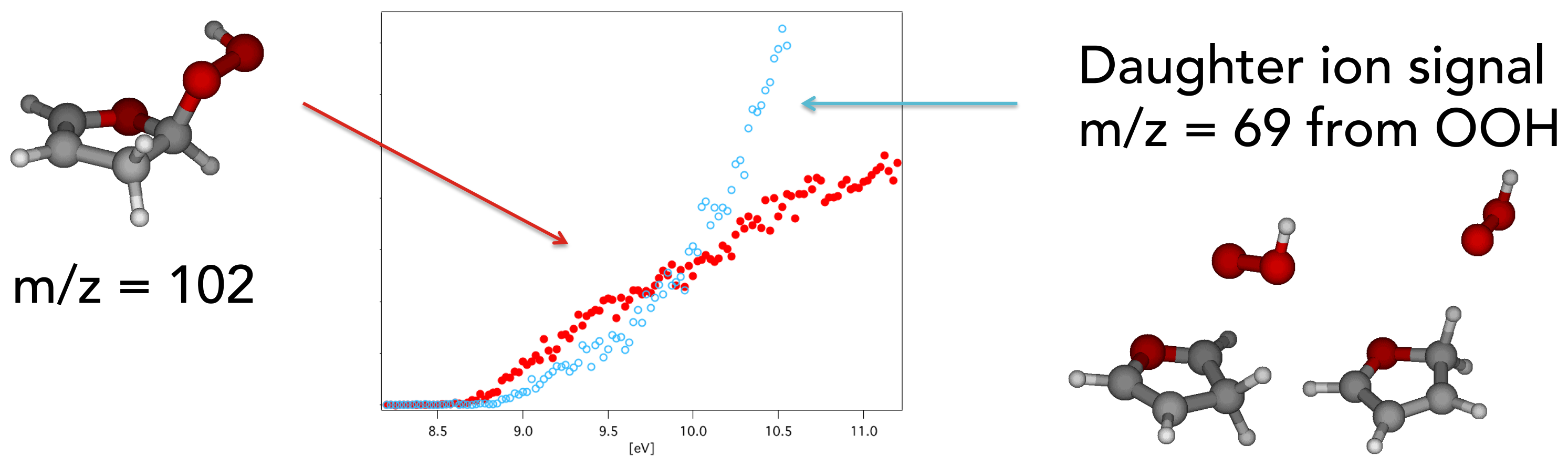
$$V = V_0 + \sum_{n=1}^{6}(c_n(1-\cos(n\varphi)) + s_n(1-\sin(n\varphi)))$$

Ψ is then approximated as a finite linear expansion in the free rotor functions

$$\psi = \sum_k c_k\phi_k(\varphi) = \sum_k c_k\frac{1}{\sqrt{2\pi}}e^{ik\varphi}$$

The 1D spectra of the anharmonic modes can then be convoluted with the HO spectrum of all the remaining modes, which after integration to obtain PIE curve produces a pronounced shift in the original, HO-derived curve.

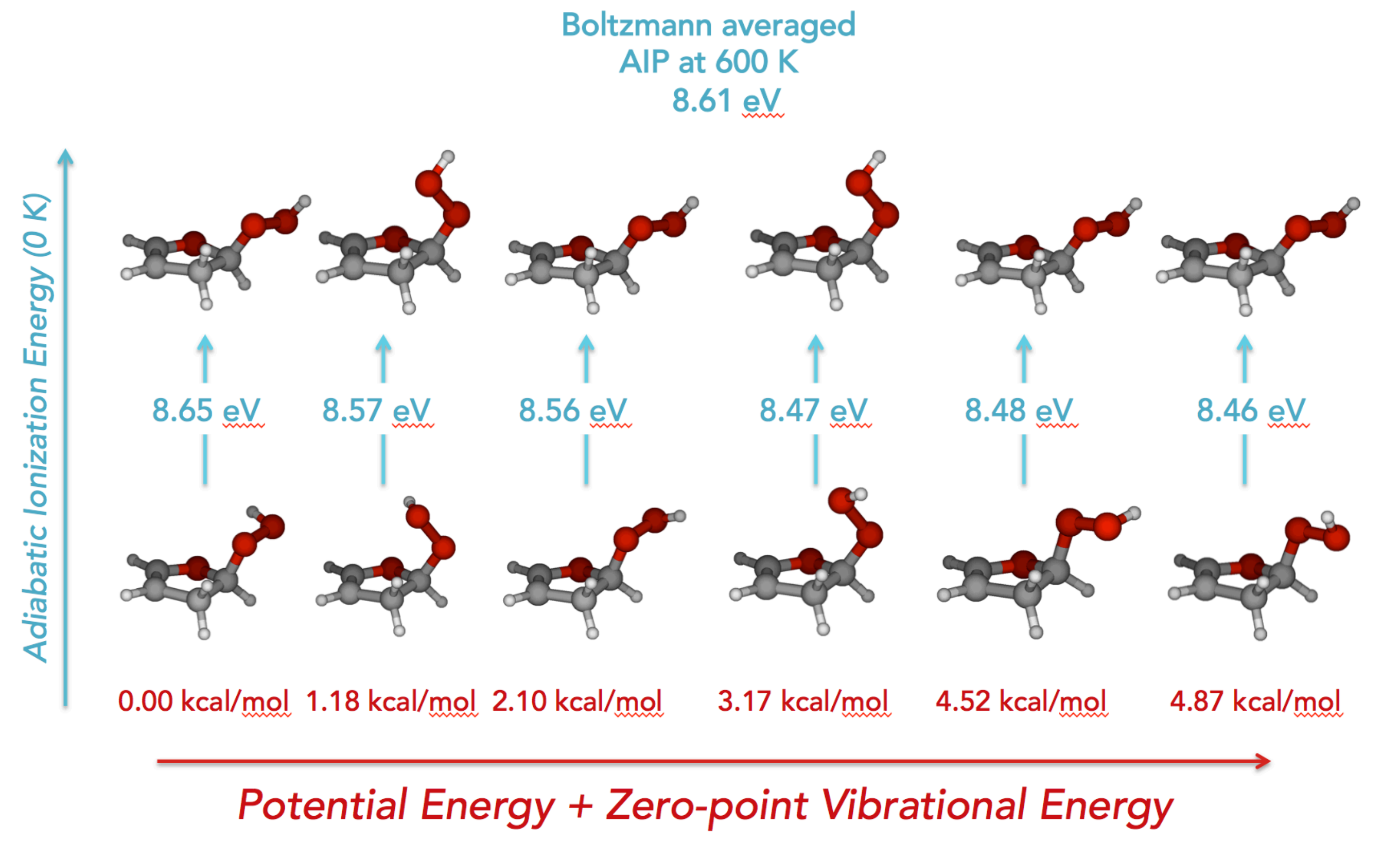
Experimental results



m/z = 102

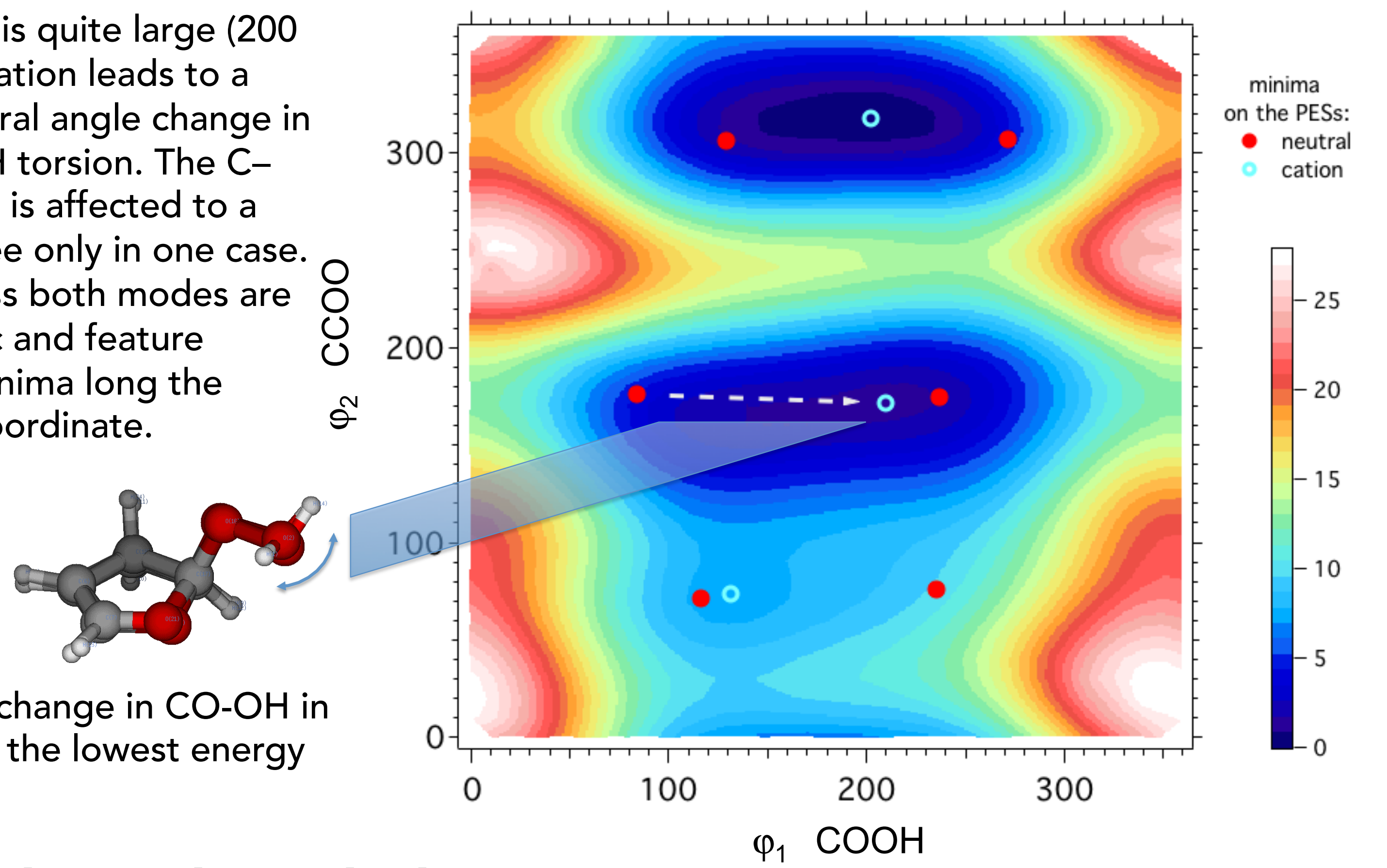
Daughter ion signal
m/z = 69 from OOH loss

The internal complexity of the molecule



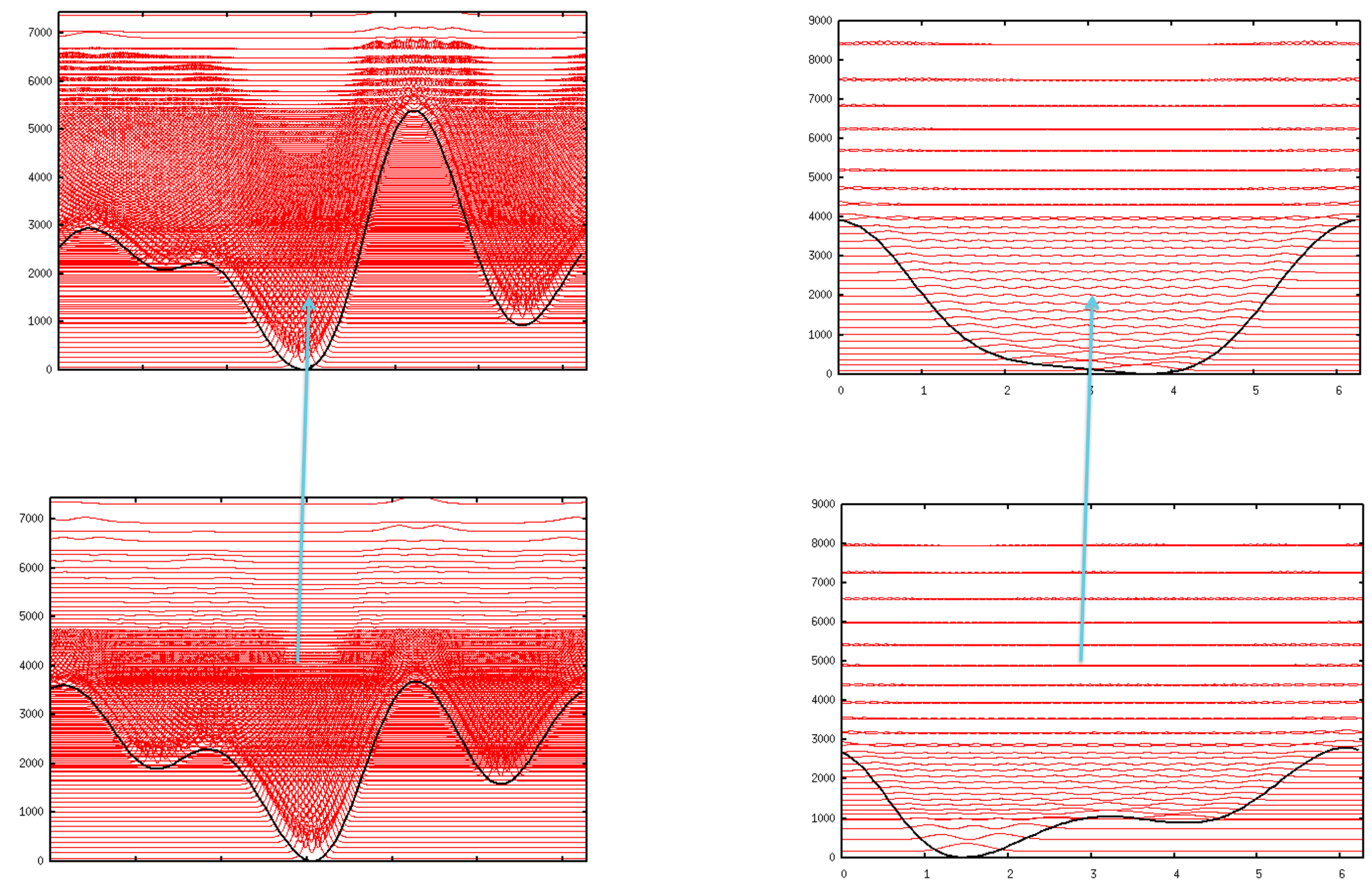
The spread in the calculated AIPs of the 6 conformers of the neutral is quite large (200 meV). Ionization leads to a large dihedral angle change in the CO–OH torsion. The C–OOH angle is affected to a large degree only in one case. Nonetheless both modes are anharmonic and feature multiple minima long the torsional coordinate.

Cation electronic potential energy as a function of the two torsional angles



83 degree change in CO-OH in the case of the lowest energy conformer

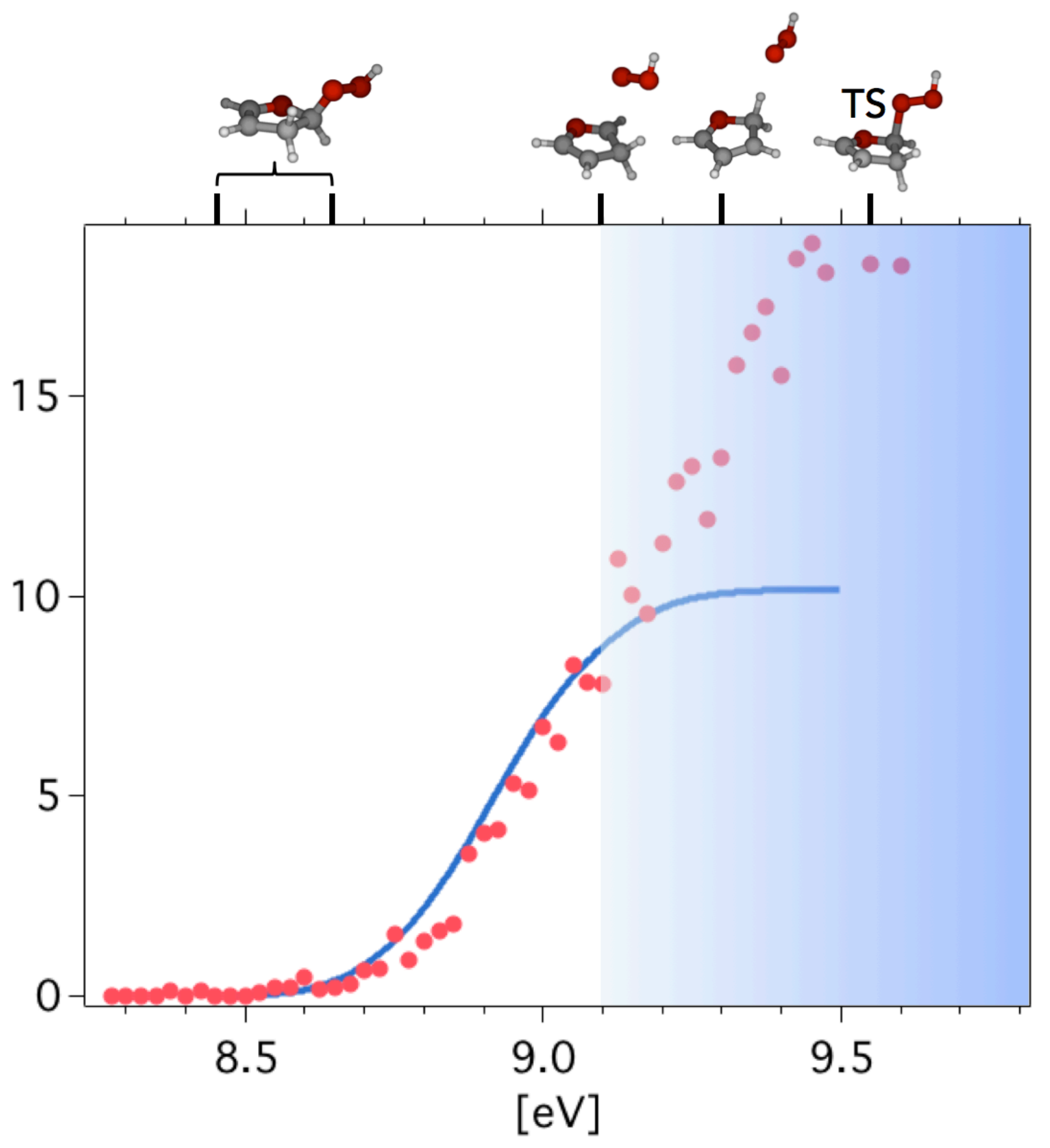
1D Frank-Condon calculation



C–OOH rotation

CO–OH rotation

The possible reactions that take place on the cation potential energy surface complicate the origin of the signal obtained experimentally above 9 eV. However, in the 8.5 – 9.1 eV range both the shape and the onset of the two curves are in agreement. Their onset is slightly higher than the predictions of the single structure AIPs confirming that the separable 1D treatment is useful here.



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