Supplementary Information

Isomer-sensitive characterization of low temperature oxidation reaction products by coupling a jet-stirred reactor to an electron/ion coincidence spectrometer: case of *n*-pentane

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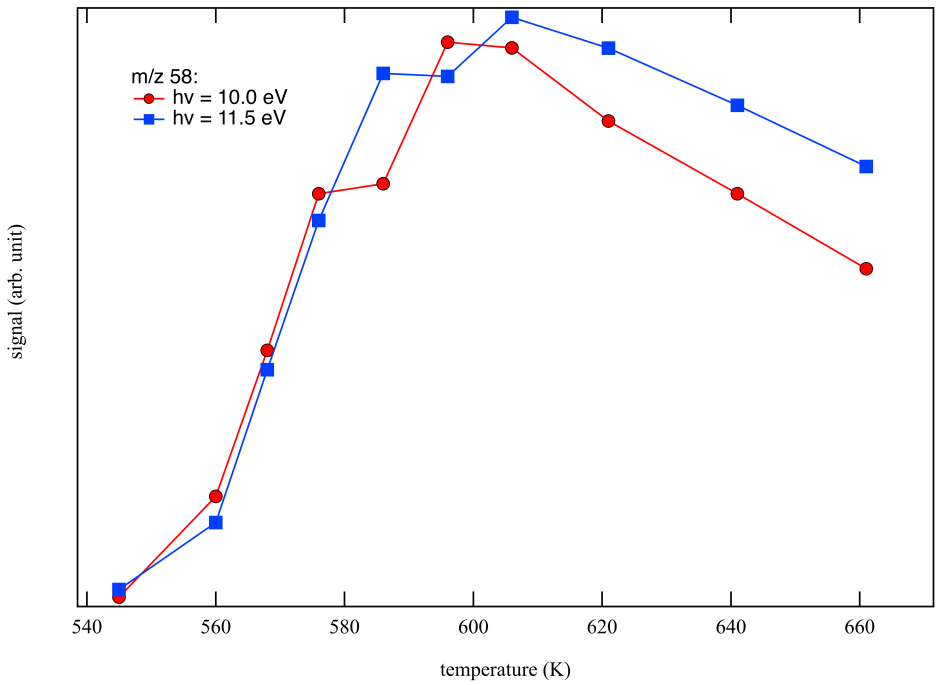

Figure S1. Variation of the ion signal at *m/z* 58 as function of the temperature for two different photon energies (10.0 eV in red and 11.5 eV in blue).

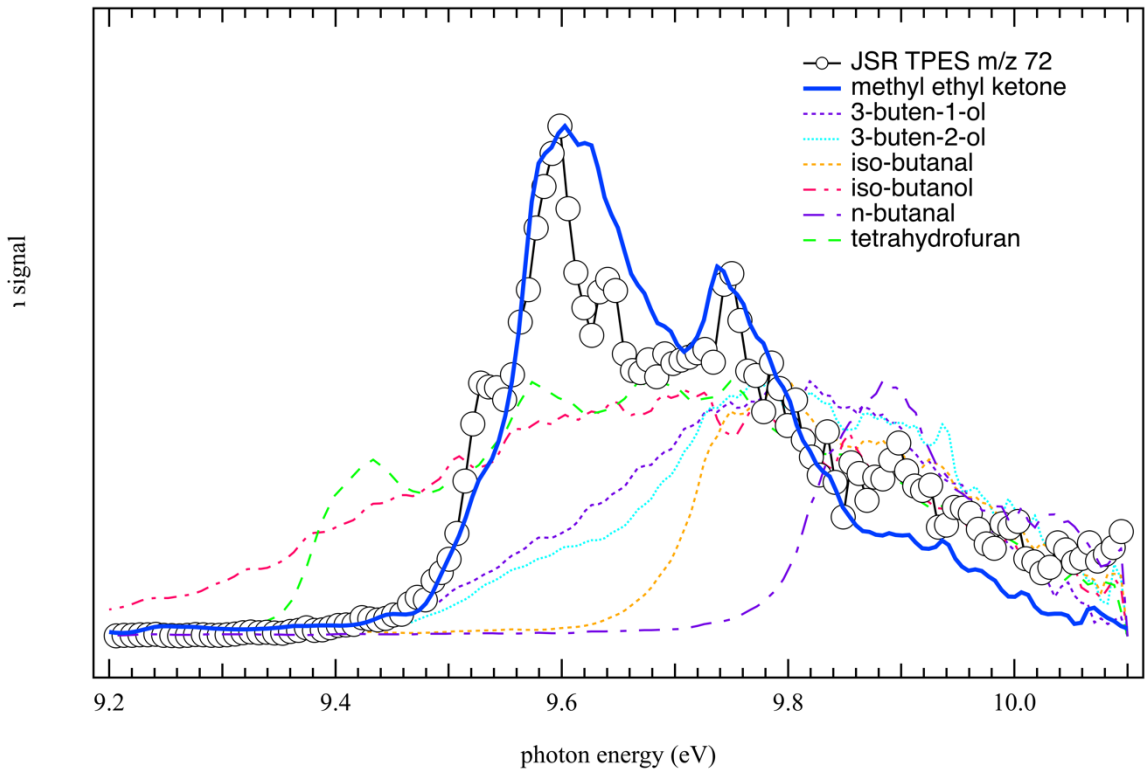

Figure S2. Comparison of the TPES at m/z 72 (open circles) measured during the JSR oxidation of *n*-pentane at a reaction temperature of 585 K with an equivalence ratio of $\phi = 0.5$ to the reference spectra from Pieper et al. [1] of the isomers: *n*-butanal, iso-butanol, tetrahydrofuran, 3-buten-1-ol, 3-buten-2-ol and iso-butanal.

Isomer	Amount detected by GC-MS [2] (ppm)	**Branching ratio in m/z 86 signal**	Predicted value (ppm) using the model of Bugler et al. [2]
2-methyltetrahydrofuran	88	**0.69**	79
2-pentanone	54	**0.82**	40
3-pentanone		**1**	90
2-ethyl-3-methyloxirane	20	**0.82**	27
2,4-dimethyloxetane	32	**0.56**	21
2-ethyloxetane	19	**0.39**	6.6
tetrahydropyran	7	**Not considered in the fitting**	0.2
propyloxirane	5	**Not considered in the fitting**	1.7
pentenol	9	**Not considered in the fitting**	5 *But not obvious ways of formation from n-pentane*
pentanal	9	**Not considered in the fitting**	Not in the model

Table S1. Comparison between the amount detected by GC-MS [3], the predicted value using the model of Bugler et al. [2] (under the conditions of [3]) and the observed signal branching ratio for isomers at m/z 86.

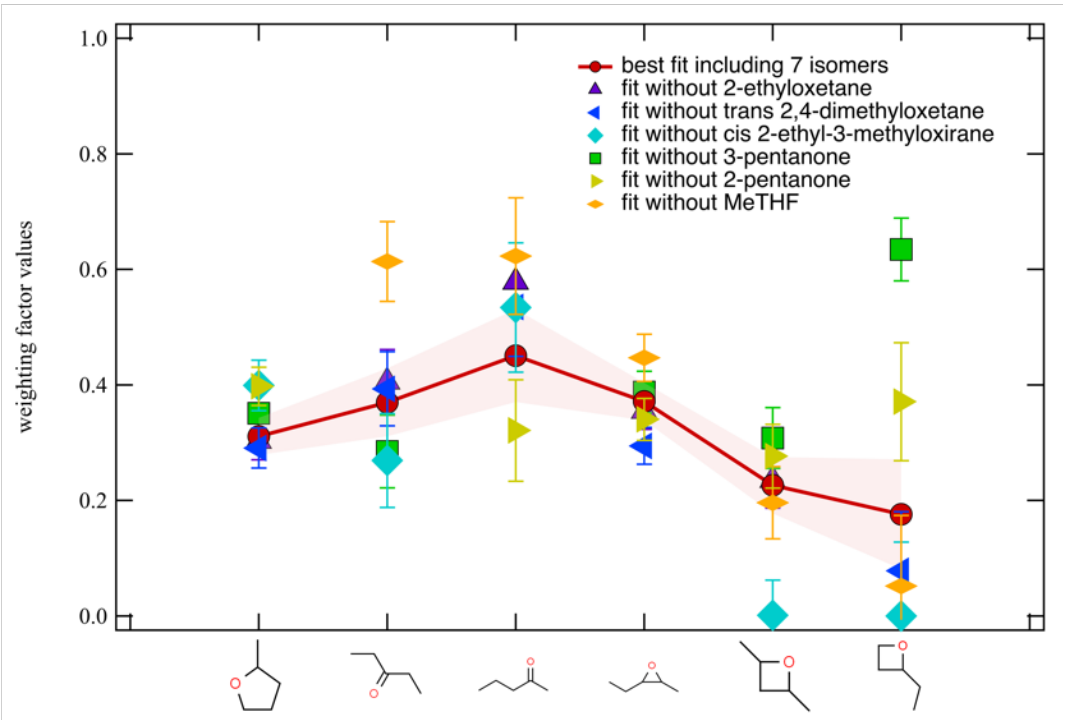

Figure S3. Weighting factor values with their standard deviation (1σ) for each 6 isomers obtained after optimization in the best fit using the calculated TPES of 6 isomers (2-methyltetrahydrofuran, 2-pentanone, 3-pentanone, cis 2-ethyl-3-methyloxirane, trans 2,4-dimethyloxetane and 2-ethyloxetane) and for 6 fits with a different isomer missing: fit without 2-ethyloxetane, fit without trans 2,4-dimethyloxetane, fit without cis 2-ethyl-3-methyloxirane, fit without 3-pentanone, fit without 2-pentanone and fit without 2-methyltetrahydrofuran.

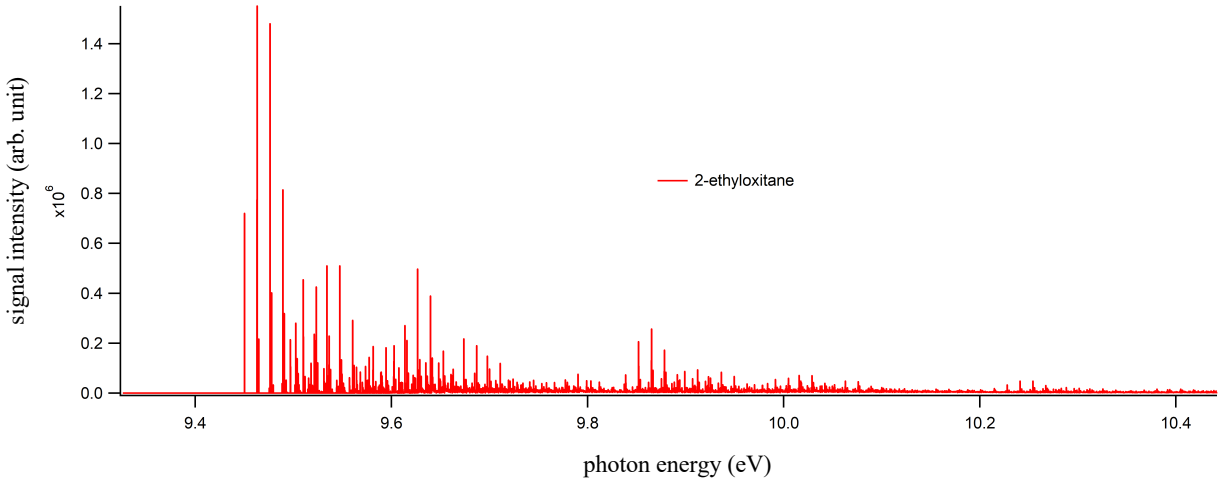

Figure S4. Simulated vibrationally resolved electronic spectrum of 2-ethyloxitane

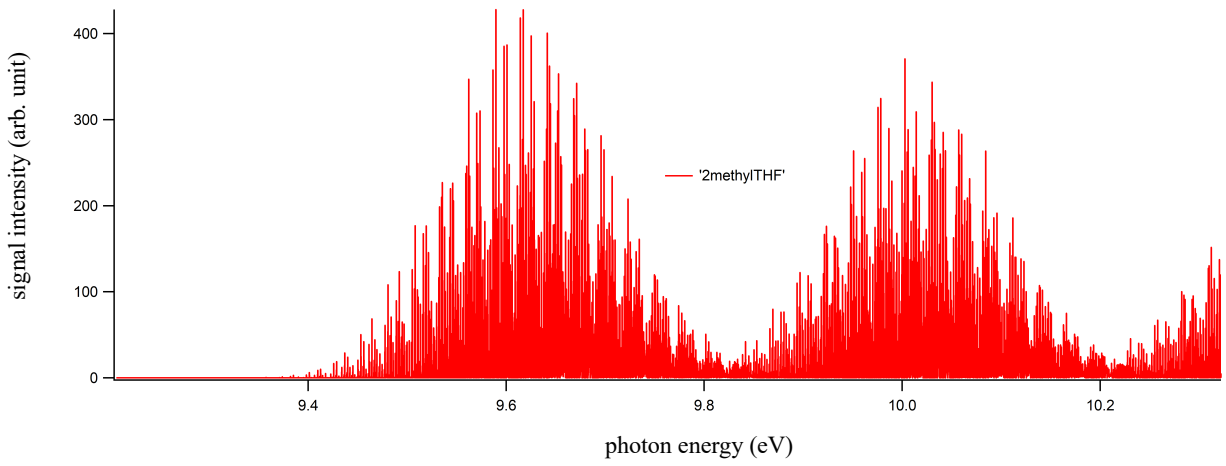

Figure S5. Simulated vibrationally resolved electronic spectrum of 2-MeTHF.

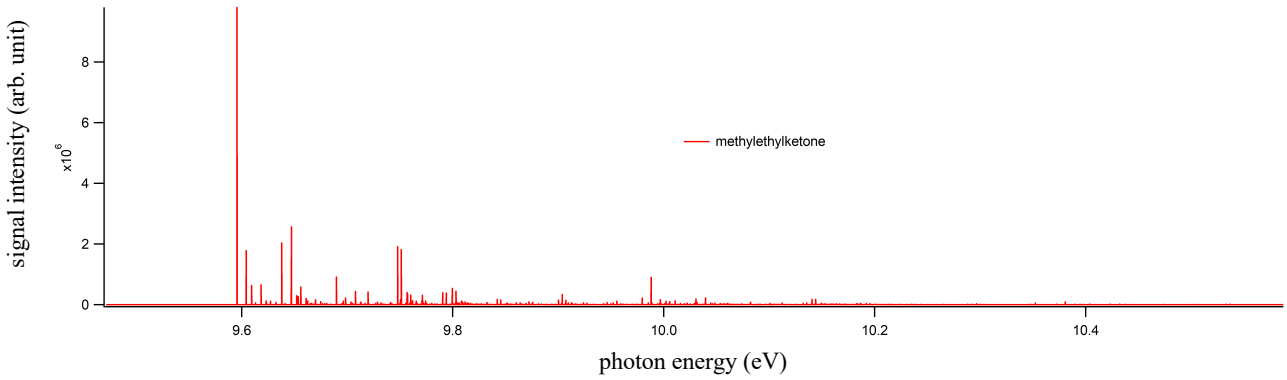

Figure S6. Simulated vibrationally resolved electronic spectrum of methylethylketone.

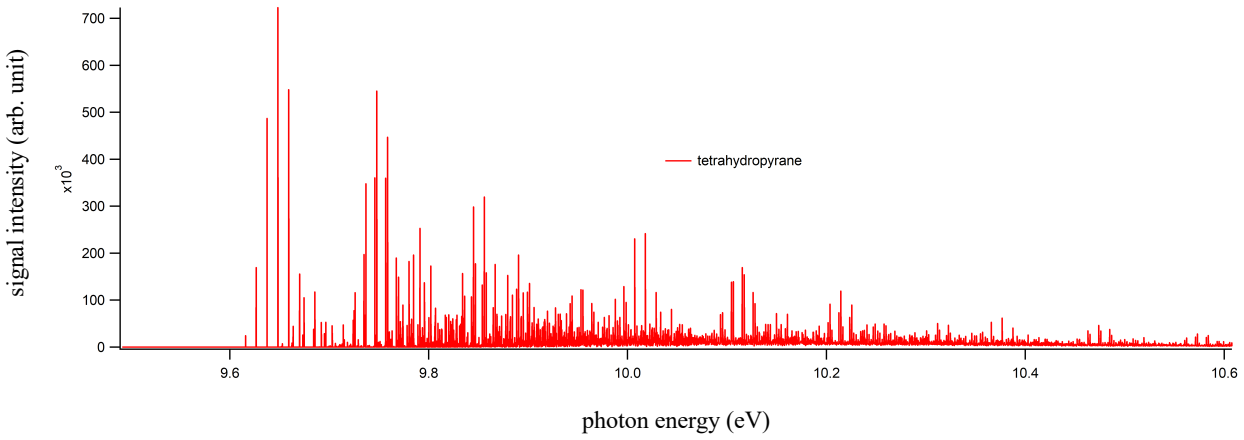

Figure S7. Simulated vibrationally resolved electronic spectrum of tetrahydropyrane.

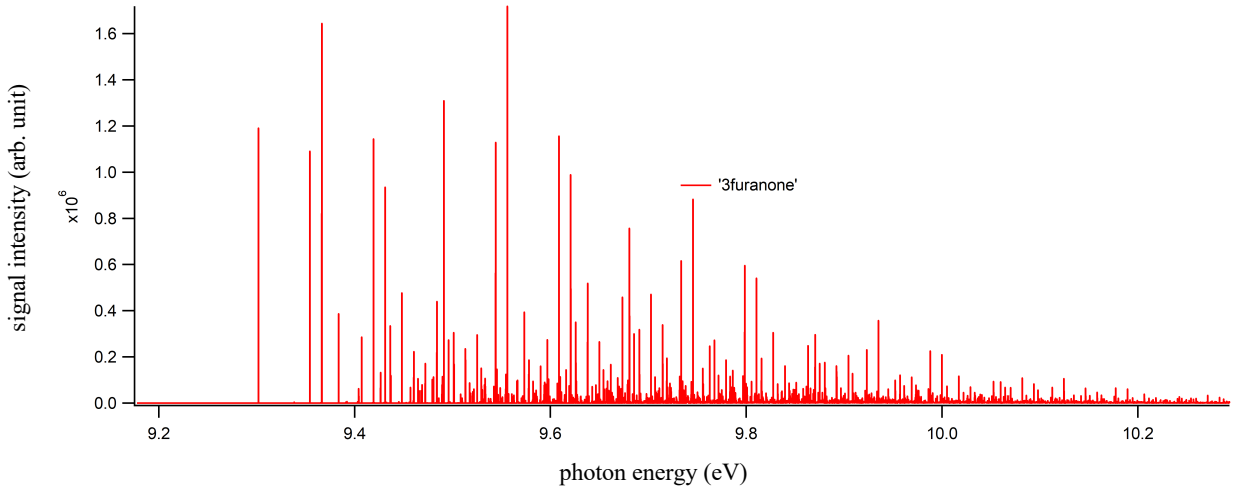

Figure S8. Simulated vibrationally resolved electronic spectrum of 3-furanone.

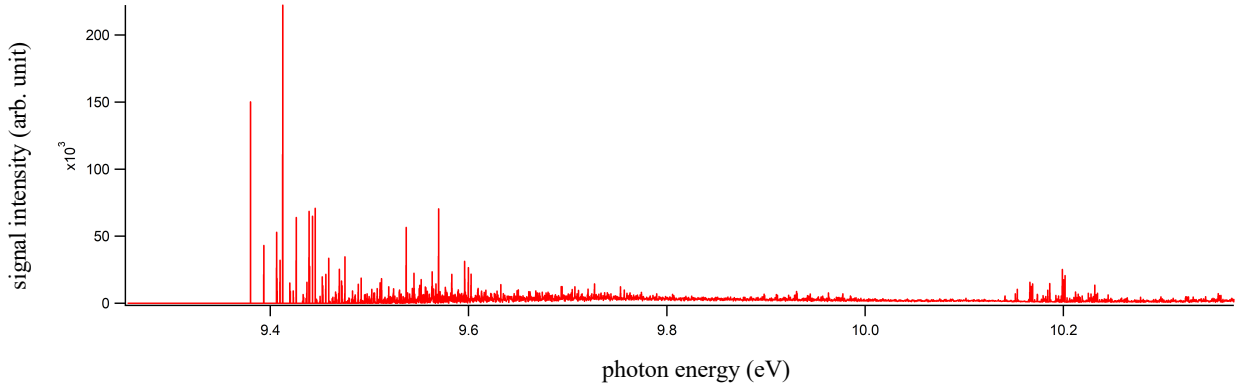

Figure S9. Simulated vibrationally resolved electronic spectrum of trans 2,4-dimethyloxetane.

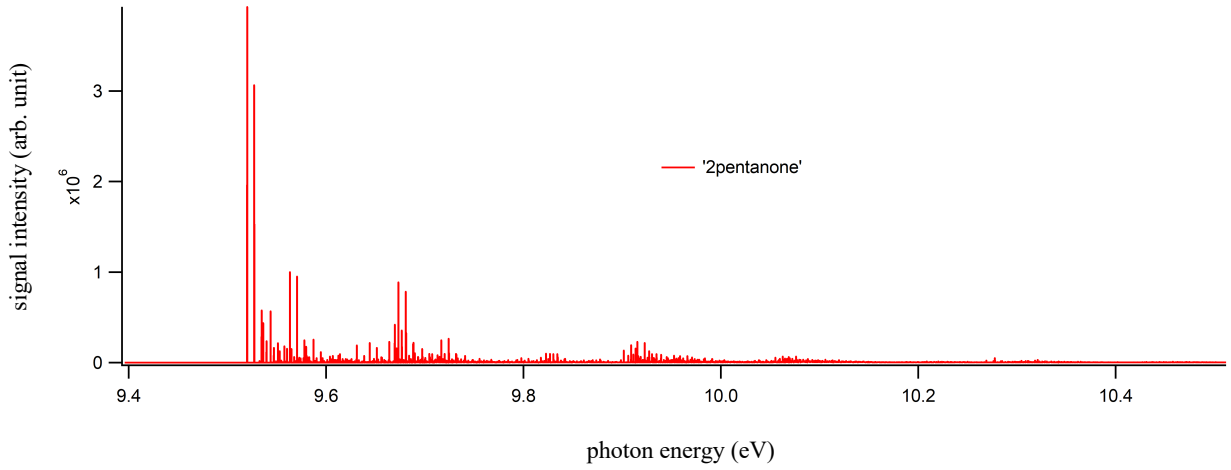

Figure S10. Simulated vibrationally resolved electronic spectrum of trans 2-pentanone.

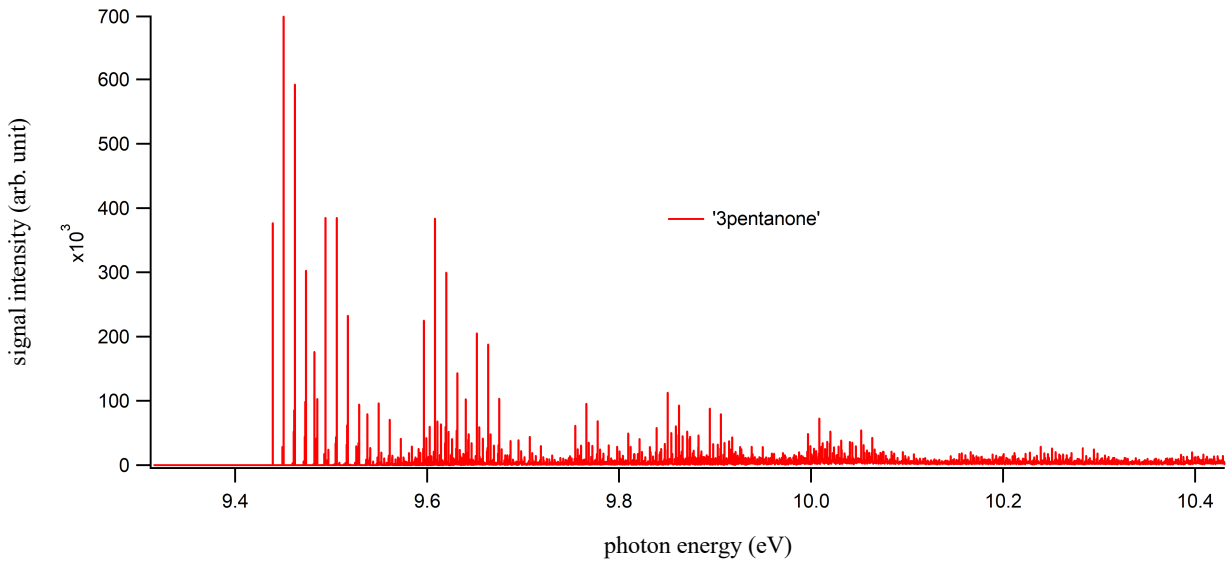

Figure S11. Simulated vibrationally resolved electronic spectrum of 3-pentanone.

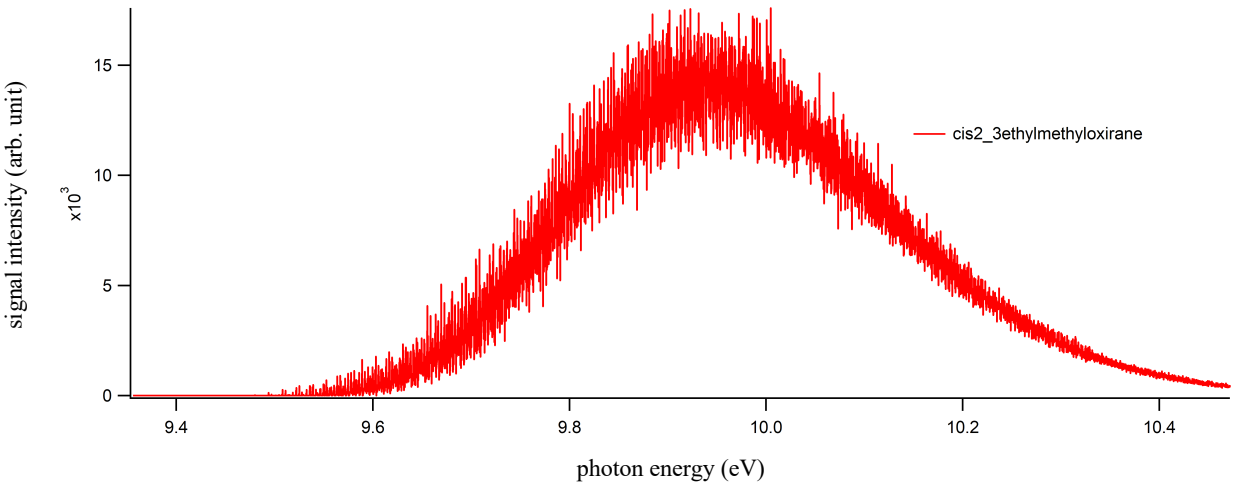

Figure S12. Simulated vibrationally resolved electronic spectrum of cis 2,3-ethylmethyloxirane.

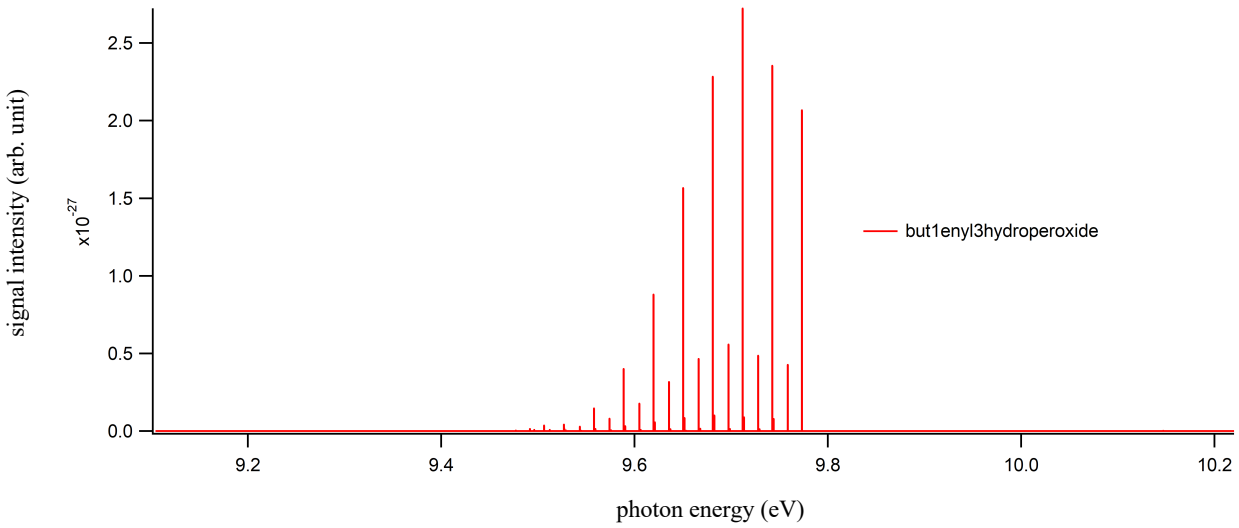

Figure S13. Simulated vibrationally resolved electronic spectrum of but-1-enyl-3-hydroperoxide.

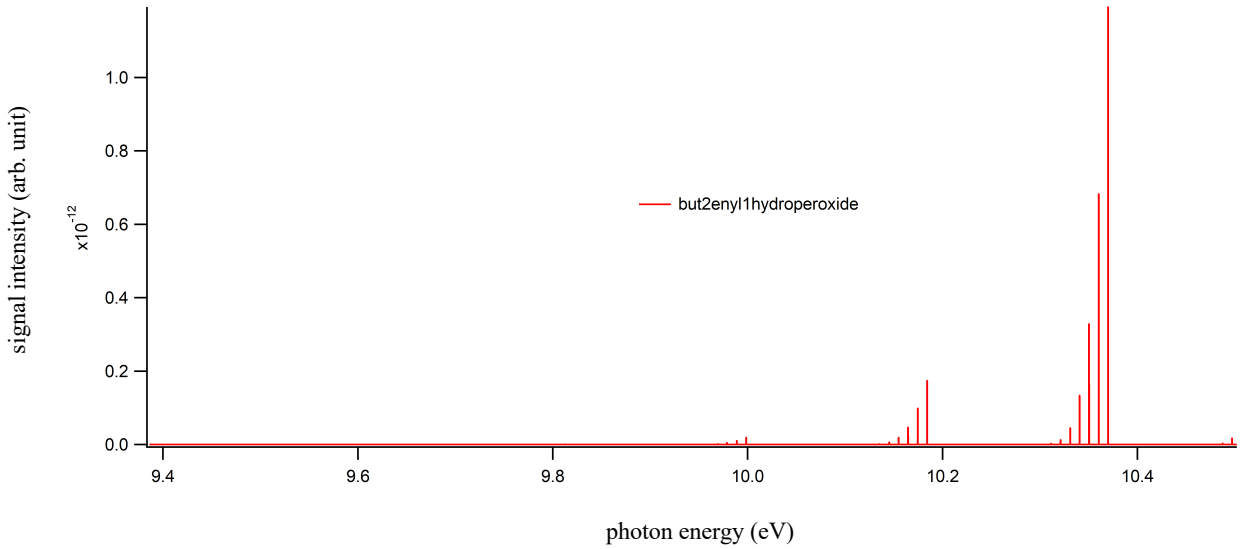

Figure S14. Simulated vibrationally resolved electronic spectrum of but-2-enyl-1-hydroperoxide.

References

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[2] J. Bugler, A. Rodriguez, O. Herbinet, F. Battin-Leclerc, C. Togbé, G. Dayma, P. Dagaut, H.J. Curran, An experimental and modelling study of n-pentane oxidation in two jet-stirred reactors: The importance of pressure-dependent kinetics and new reaction pathways, Proc. Combust. Inst. 36 (2017) 441–448. doi:10.1016/J.PROCI.2016.05.048.

[3] A. Rodriguez, O. Herbinet, Z. Wang, F. Qi, C. Fittschen, P.R. Westmoreland, F. Battin-Leclerc, Measuring hydroperoxide chain-branching agents during n-pentane low-temperature oxidation, Proc. Combust. Inst. 36 (2017) 333–342. doi:10.1016/J.PROCI.2016.05.044.