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Supporting Information for

Photoelectron Spectroscopy and Thermochemistry of o-, m-, and p-Methylenephenoxide Anions

Daniel J. Nelson,[1,†] Wilson K. Gichuhi,[1,‡] Charles M. Nichols,[1,§] Veronica M. Bierbaum,[1,*] W. Carl Lineberger[1,*] and Julia H. Lehman,[1,2,*]

[1]JILA and the Department of Chemistry, University of Colorado, Boulder, CO 80309, United States of America

[2]School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom

*Corresponding Authors e-mails: J.Lehman@leeds.ac.uk (J.H.L), Carl.Lineberger@colorado.edu (W.C.L), Veronica.Bierbaum@colorado.edu (V.M.B.)

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[†] Present address: Leybold, 5700 Mellon Rd, Export, PA 15632, United States of America

[‡] Present address: Department of Chemistry, Tennessee Tech University, Cookeville, TN 38505, United States of America

[§] Present address: Agilent Technologies, Santa Clara, CA 95051, United States of America

I. PHOTOELECTRON SPECTRA ANISOTROPY PARAMETERS

Photoelectron angular distributions with respect to laser polarization were measured for the photoelectron spectra shown in Fig. 3 of the main text. The angular distributions are characterized by the anisotropy parameter (β). The electron in each case is likely detached from what can be described as a hybrid oxygen p-like molecular orbital. It is therefore expected that we should observe a negative β for detachment to the neutral singlet ground state when using a photon energy of 3.494 eV.[1, 2] Photodetachment in region A for ortho and para isomers (Fig. 3 of the main text) displays β ~ – 0.15 using a photon energy of 3.494 eV. This anisotropy parameter stayed approximately constant at ~ – 0.15 for the progression in region B (all three isomers). The photoelectron angular distributions for electrons with binding energies greater than 3 eV (in region C) for all three isomers were isotropic (β ~ 0). However, these transitions are all close in binding energy (< ~ 500 meV) to the photon energy, thus the photoelectrons have low kinetic energies, and so an isotropic angular distribution is expected.[1]

II. ADDITIONAL PHOTOELECTRON SPECTRA

Several additional spectra were collected and are presented here. Fig. S1 displays the spectra of the anion isomers at m/z = 106 studied using the cw PES instrument. These spectra are heavily contaminated with methylphenoxide (m/z = 107), the primary product of the reaction of O^- and methylphenol. This is demonstrated by the spectral progressions found at ~2 eV binding energy and extending to ~2.5 eV. This contamination is verified by comparison to the previously studied deprotonated methylphenols.[3] This contamination is expected considering the mass resolution of the cw PES instrument (m/Δm ~ 60) and the mass of methylphenol, 108 amu. However, this mass contamination is not an issue with the pulsed PES instrument. Fig. S2 shows a comparison between PES of m/z = 106 (black lines) and m/z = 107 (red lines) taken with the pulsed PES instrument. These spectra are quantitatively different, illustrating that the PES of m/z = 107 (methylphenoxide) does not interfere with the work presented here and in the main text on the PES of m/z = 106.

Autodetachment behavior was documented in the cases of o- and m-methylenephenoxide. Although unobserved for the para isomer for the few photon energies used, this does not necessarily mean it is not an issue for all three isomers. Fig. S3 displays the photoelectron spectra of o-methylenephenoxide obtained with several photon energies, and a photon energy dependence of the PES is clear. The spectra measured with photon energies of 1.929 eV and 3.494 eV were collected with the pulsed PES instrument, while the spectrum measured with a photon energy of 3.408 eV was collected with the cw PES instrument. Fig. S4 shows the photoelectron spectra of m-methylenephenoxide using two different photon energies (3.832 eV and 3.494 eV), again displaying signs of photon energy dependent photoelectron signal. This type of photon energy dependence cannot be explained by a variation of resolution and is most likely due to electron autodetachment. This effect has been seen previously in several similar aromatic compounds.[3-6]

The remaining figures (Figs. S5-S8) show PES already reported in the main text, and are repeated here with the addition of the calculated transitions and their corresponding FCFs, which would have been too difficult to clearly indicate in the main text.

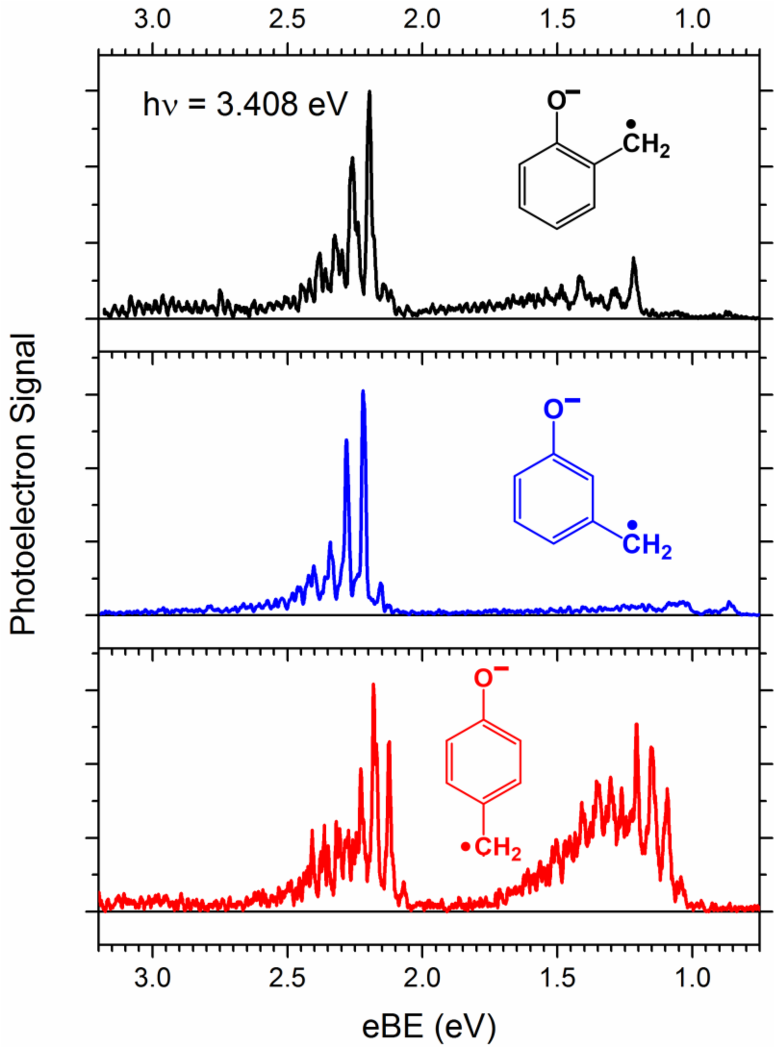


Fig. S1. Photoelectron spectra of m/z = 106 anions resulting from the reaction of O^- with o-, m-, and p-methylphenol collected with the cw PES instrument with a photon energy of 3.408 eV. There is significant contamination from methylphenoxide anions (m/z = 107) in the range of 2 – 2.5 eV due to the poor mass resolution of this instrument. More details found in the text.

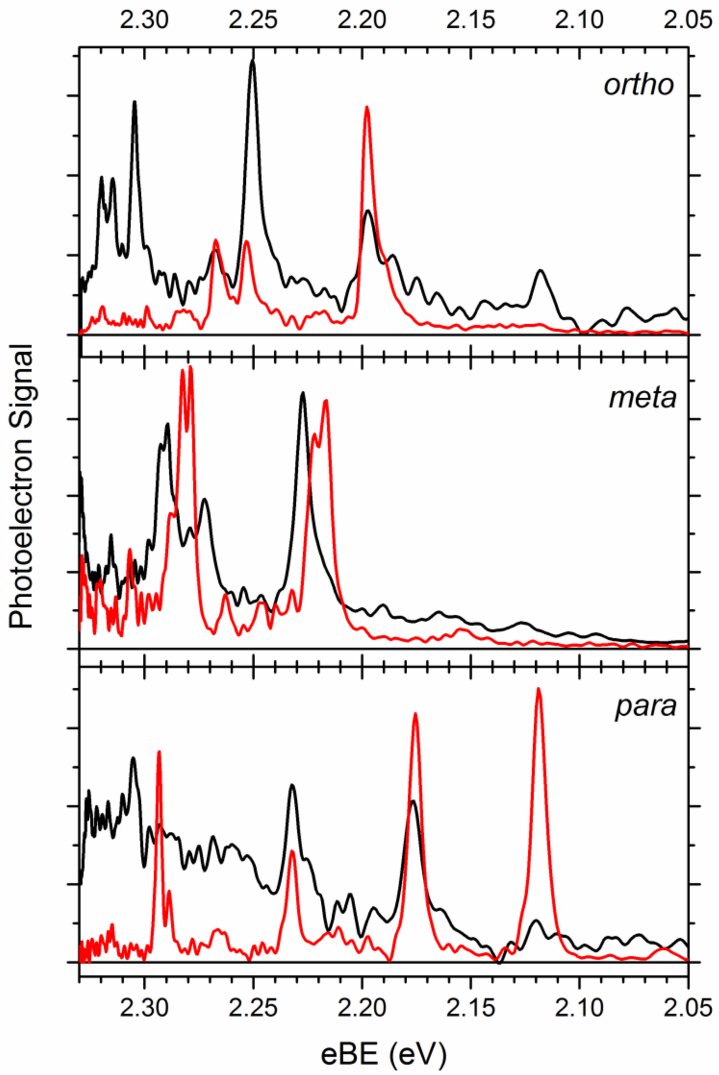


Fig. S2 Photoelectron spectra of m/z = 106 and m/z = 107 obtained with a photon energy of 2.330 eV using the pulsed PES instrument. These spectra were obtained by alternating the laser timing to either intersect m/z = 106 (black curves) or 107 (methylphenoxide, red curves). The red and black spectra share several similarities, such as the approximate spacing between peaks, however they are quantitatively different. This discounts the possibility of mass contamination in region B of the spectrum when the PES were taken with this instrument.

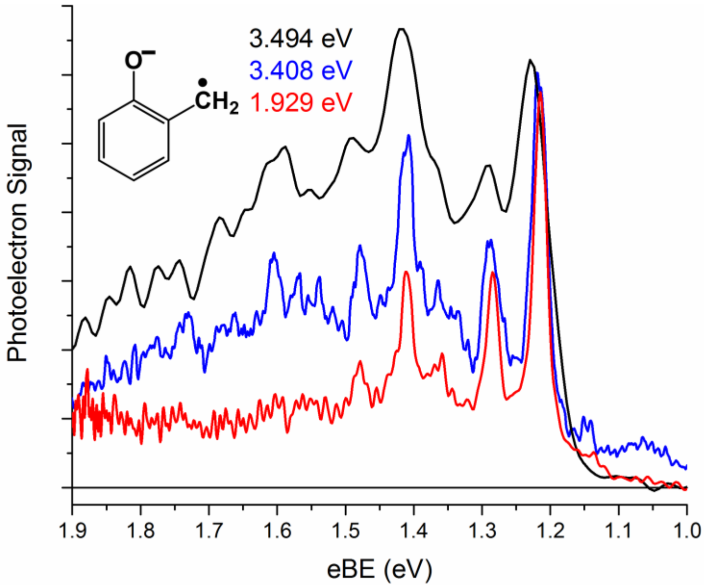


Fig. S3. Photoelectron spectrum of o-methylenephenoxide obtained with three different photon energies, 3.494, 3.408, and 1.929 eV. The spectra collected with photon energies of 3.494 and 1.929 eV were obtained utilizing the pulsed PES instrument, whereas the spectrum collected with a photon energy of 3.408 eV was obtained with the cw PES instrument. These spectra show evidence of photon energy dependence attributed to autodetachment, i.e. an increase in underlying continuum which cannot be explained by experimental resolution, which increases with photon energy. Slight discrepancies in peak positions are due to differences in calibrations.

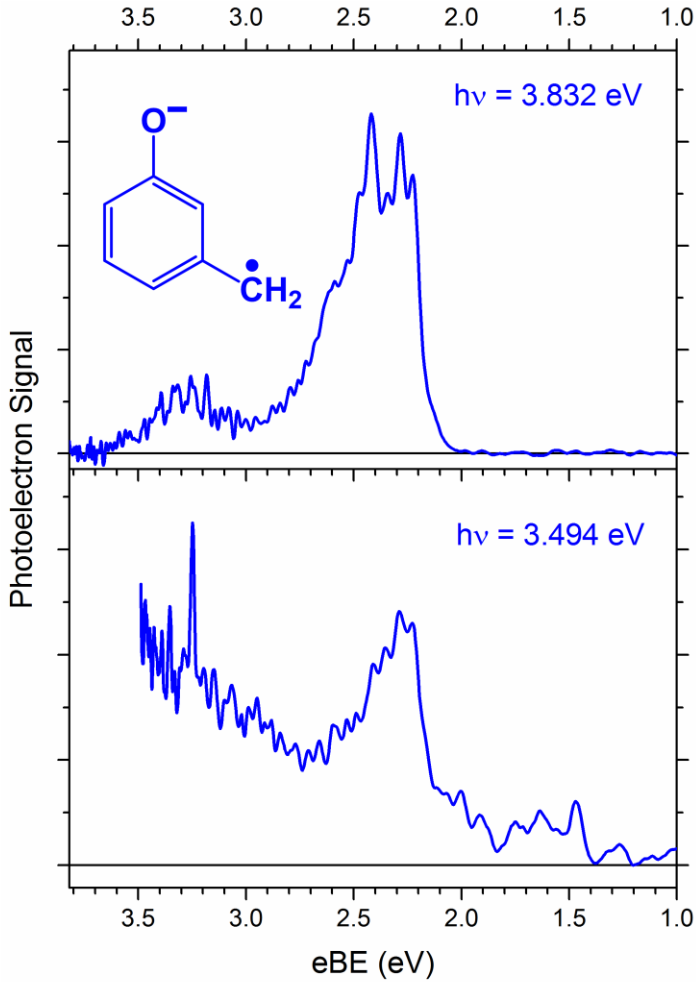


Fig. S4. Photoelectron spectra of m-methylenephenoxide anions obtained with the pulsed PES instrument with two different photon energies, 3.494 eV and 3.832 eV. There is an obvious photon energy dependence displayed between the two spectra. This again likely arises from autodetachment.

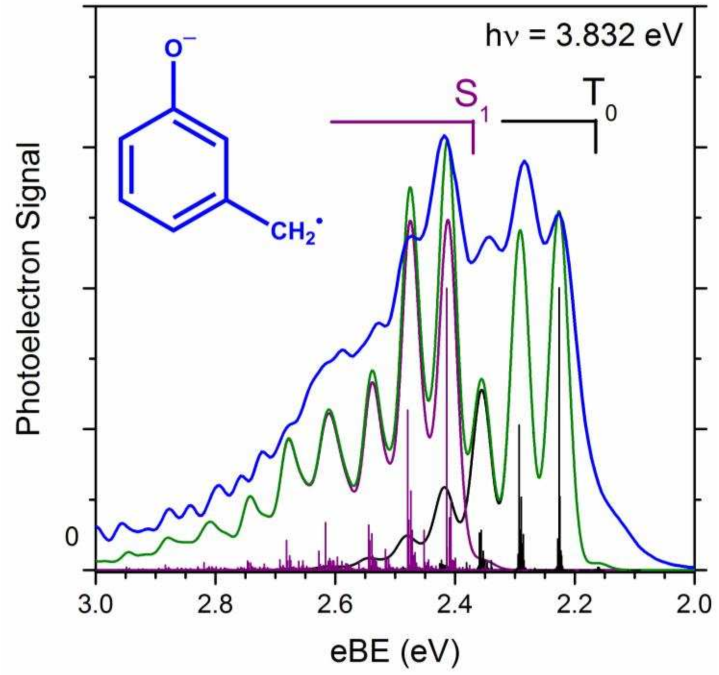


Fig. S5. Photoelectron spectrum of m-methylenephenoxide anion obtained with the pulsed PES instrument using 3.832 eV photon energy. The calculated transitions and their corresponding Franck–Condon intensities are represented by black and purple sticks for transitions to the T_0 and S_1 electronic states, respectively, while their convolutions with experimental resolution are shown as black and purple lines. The sum of the two convolutions is shown as a green line.

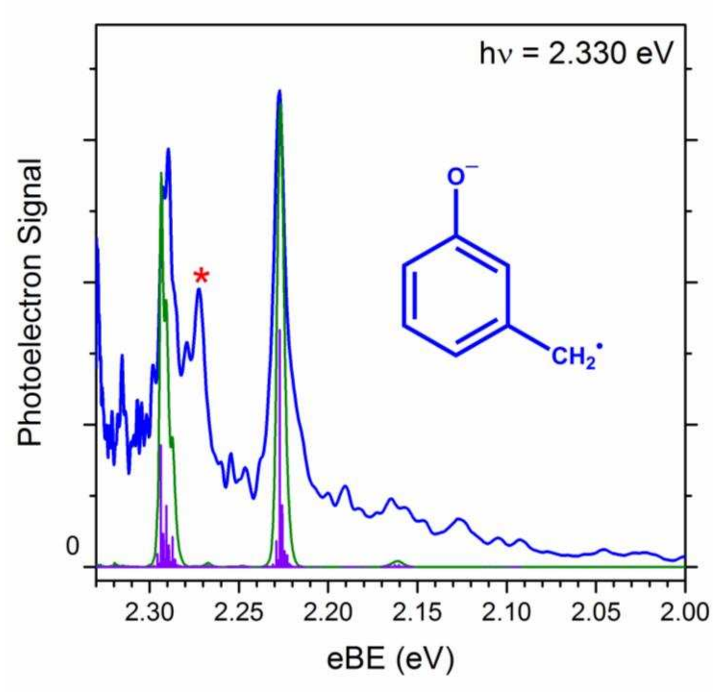


Fig. S6. Photoelectron spectrum of m-methylenephenoxide anion obtained with the pulsed PES instrument using 2.330 eV photon energy. The calculated transitions and their corresponding Franck–Condon intensities are represented by purple sticks for transitions to the T_0 electronic state, while their convolution with experimental resolution is shown as a green line. The peak marked with a red asterisk is likely due to detachment from methylphenyloxide isomers, as discussed in the main text.

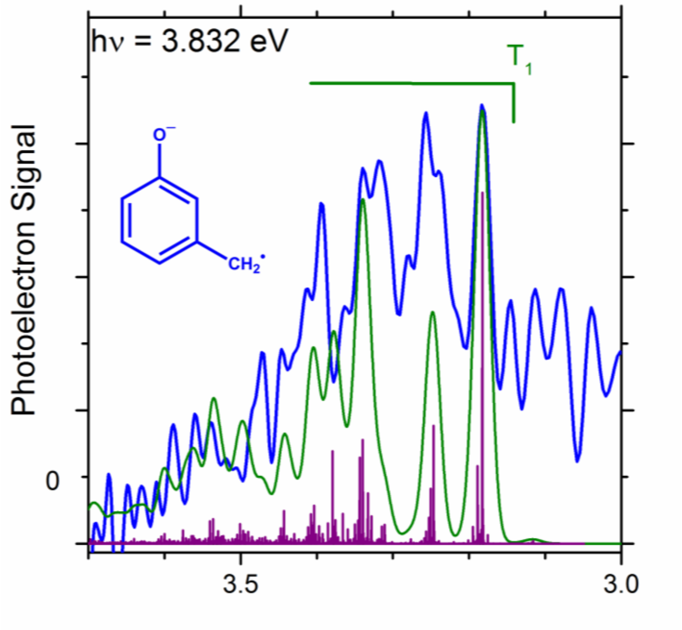


Fig. S7. Photoelectron spectrum of m-methylenephenoxide anion obtained with the pulsed PES instrument using 3.832 eV photon energy. The calculated transitions and their corresponding Franck–Condon intensities are represented by purple sticks for transitions to the T_1 electronic state, while their convolution with experimental resolution is shown as a green line.

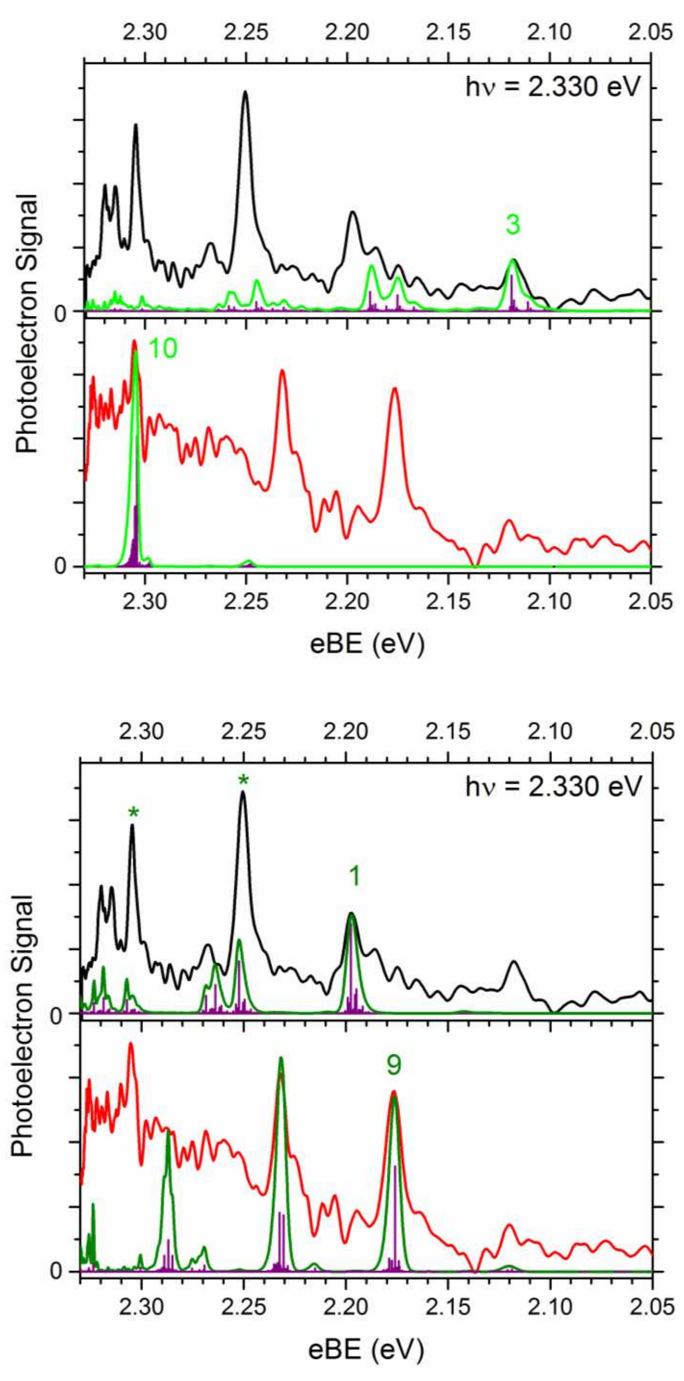
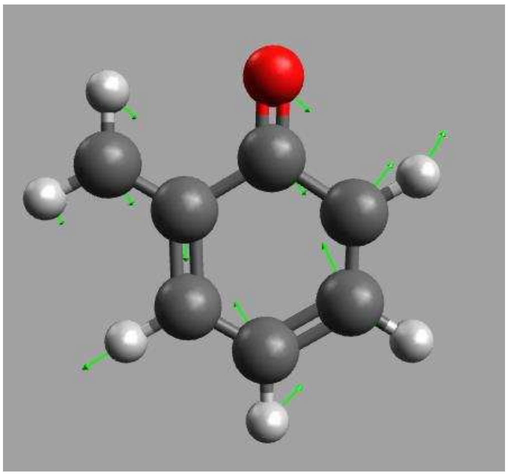


Fig. S8. Photoelectron spectra of m/z = 106 resulting from the reaction of O^- with ortho (black) and para (red) methylphenol, collected with the pulsed PES instrument with a photon energy of 2.330 eV. The numeric labels indicate the methylphenyloxide isomer listed in Fig. 2 of the main text. The simulated PES, following their convolution with the experimental resolution, are shown in dark and light green lines. The calculated transitions and their corresponding FCFs are shown as purple sticks. The asterisks are discussed in the main text.

III. FRANCK-CONDON ACTIVE NORMAL MODE EIGENVECTORS

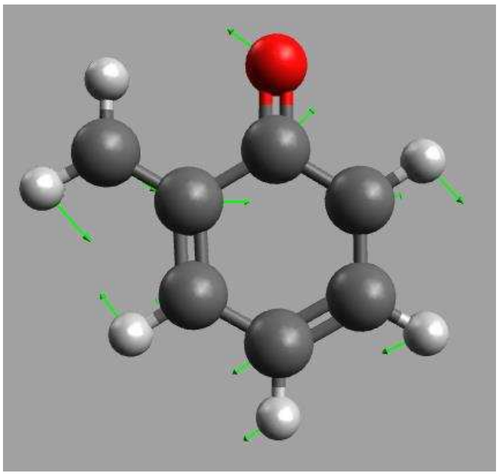
The following diagrams display the eigenvectors for the Franck-Condon active normal modes discussed in the main text for each neutral product studied, calculated at the BMK/6-311+G(3df,2p) level of theory/basis set.

6-methylene-2,4-cyclohexadien-1-one
(S_0 state)

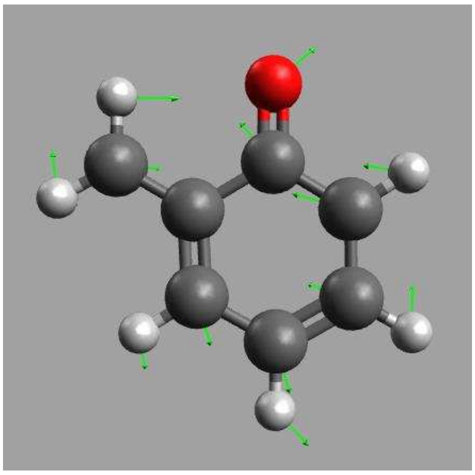


ν_{29} (574 cm^{-1})

Ortho-Methylenephenoxyl (T_1 state)

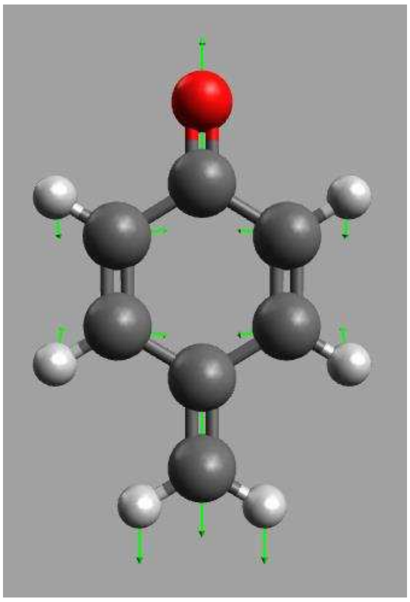


ν_{32} (456 cm^{-1})



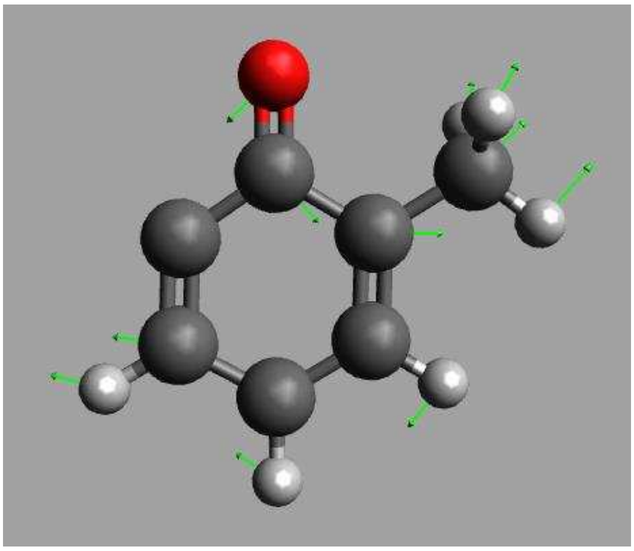
ν_{29} (530 cm^{-1})

4-methylene-2,5-cyclohexadien-1-one
(S_0 state)



ν_{32} (462 cm^{-1})

Methylphenyloxyl Isomer 1
(T_0 state)



ν_{31} (441 cm^{-1})

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