

Supplementary Material for

Anion Photoelectron Spectroscopy of Deprotonated *ortho*-, *meta*-, and *para*-Methylphenol

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Table of Contents

I. ADDITIONAL PHOTOELECTRON SPECTRA.....	1
II. ACIDITY CALCULATIONS	7
III. FRANCK-CONDON ACTIVE NORMAL MODE EIGENVECTORS.....	8

I. ADDITIONAL PHOTOELECTRON SPECTRA

In addition to the photoelectron spectra presented in the main text, several additional spectra were collected and are presented here. Fig. S1 shows ~~survey photoelectron spectra~~ of all four products of the reaction of methylphenol with hydroxide made in the Flowing Afterglow (FA) ion source, and collected with the hemispherical electron energy analyzer, ~~utilizing 3.40814 eV photons~~. Note that due to the method by which hydroxide is generated in the FA source (reaction of O⁻ with methane gas), ~~excess O⁻ still likely going to be present~~ in the ion source region. ~~This excess O⁻ is capable of both dehydrogenating (removal of H₂⁺) and~~ deprotonating the methylphenols, and a trace signal from this product channel is seen in the bottom panel of Fig. S1. Fig. S2 shows the photoelectron (PE) spectrum of *o*-methylphenoxide taken with a photon energy of 2.822 eV on the VMI spectrometer. This data is in agreement with the PE spectra found in the main text, and further confirms the absence of autodetachment in the *ortho* isomer. Fig. S3 displays the photoelectron spectrum of *m*-

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methylphenoxide taken with the VMI spectrometer with a photon energy of 3.832 eV, compared with the spectrum using 3.494 eV (which is also shown in Fig. 1 of the main text). The ratio of the peaks highlighted in Fig. S3 as part of the $\tilde{X}_{\text{neutral}} + e^- \leftarrow \tilde{X}_{\text{anion}}$ transition reveals the autodetachment behavior. Fig. S4 shows the PE spectrum of *m*-methylphenoxide obtained with a photon energy of 2.329 eV. These data were gathered to confirm the lack of photon energy dependence in the PE spectrum of *m*-methylphenoxide at lower photon energies (< 3.494 eV). Fig. S5 shows the photoelectron spectra of *p*-methylphenoxide at two different photon energies, 2.329 and 2.637 eV. These PE spectra further demonstrate the autodetachment found in the *para* isomer.

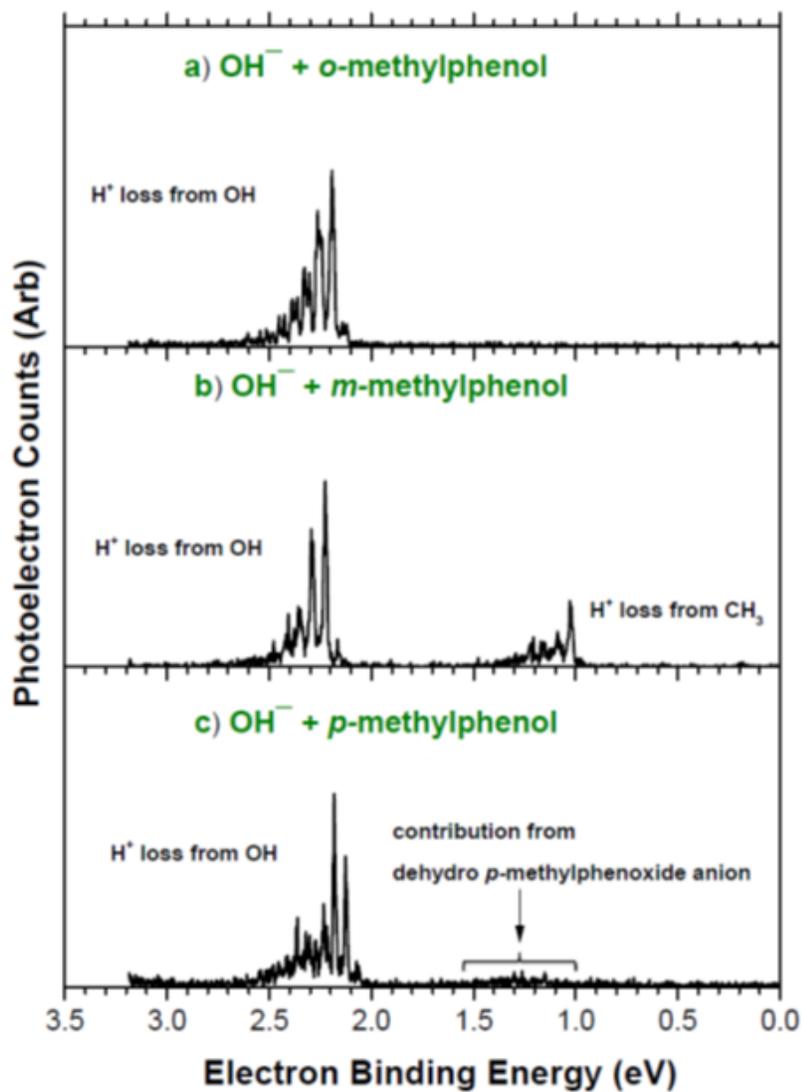


Fig. S1. Photoelectron spectra of the products of methylphenol reacted with hydroxide in a flowing afterglow ion source obtained with a photon energy of 3.40814 eV and collected in a hemispherical energy analyzer. Note that there is a trace of O⁻ in this source which leads to a small signal from a dehydro product in the *para* case.

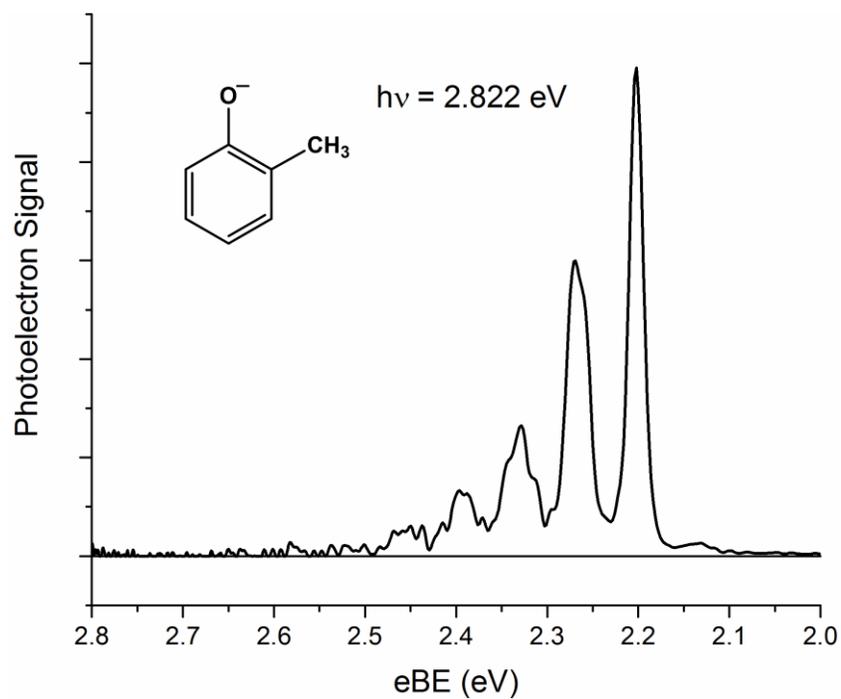


Fig. S2. Photoelectron spectrum of *ortho*-methylphenoxide taken with a photon energy of 2.822 eV, utilizing the VMI photoelectron spectrometer. Only experimental data are shown. The peak intensities in this spectrum are consistent with those shown in the top panel of Fig. 4 of the main text, which were taken using the hemispherical analyzer.

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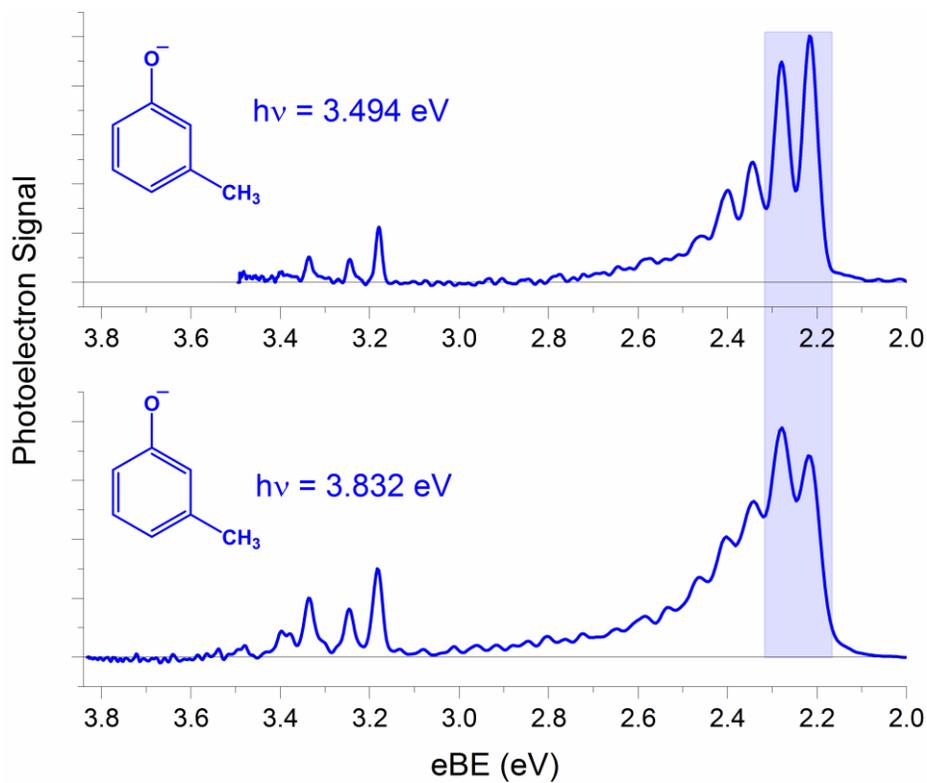


Fig. S3. The photoelectron spectrum of *meta*-methylphenoxide taken on the VMI spectrometer with photon energies of 3.494 eV and 3.832 eV. Only experimental data is shown. The highlighted region demonstrates the photon energy dependence of the peak intensities characteristic of autodetachment.

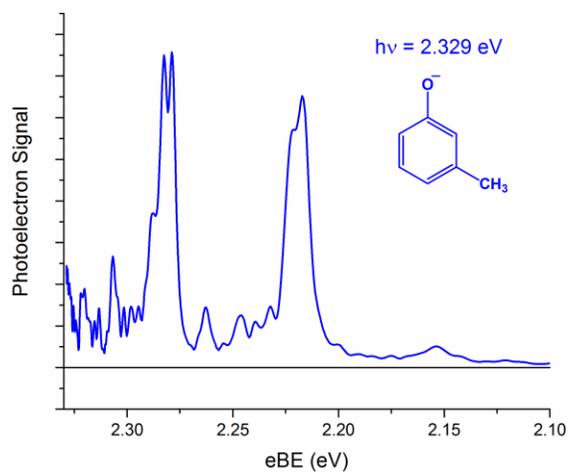


Fig S4. The photoelectron spectrum of *meta*-methylphenoxide taken on the VMI spectrometer with a photon energy of 2.329 eV.

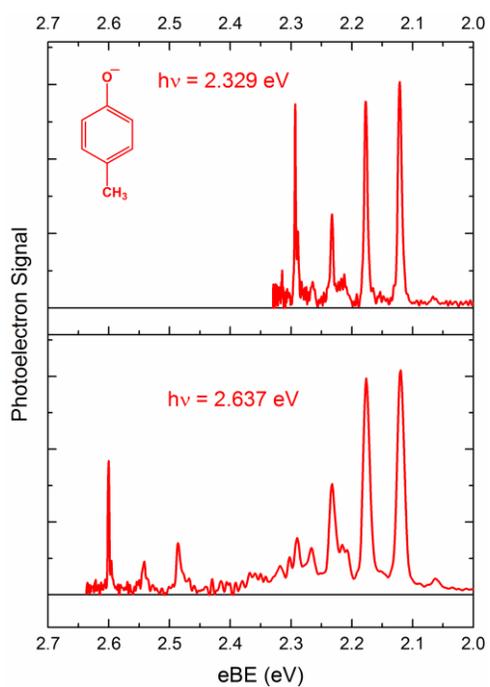
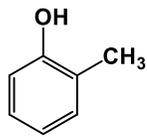
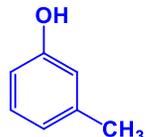


Fig. S5. Photoelectron spectra of *para*-methylphenoxide obtained with the VMI spectrometer with photon energies of 2.329 eV and 2.637 eV for the top and bottom panels respectively. Note how the changing resolution can cause peaks close to the photon energy to appear more dominant due to their narrowing FWHM and corresponding increase in amplitude to conserve the transition integrated intensity.

II. ACIDITY CALCULATIONS

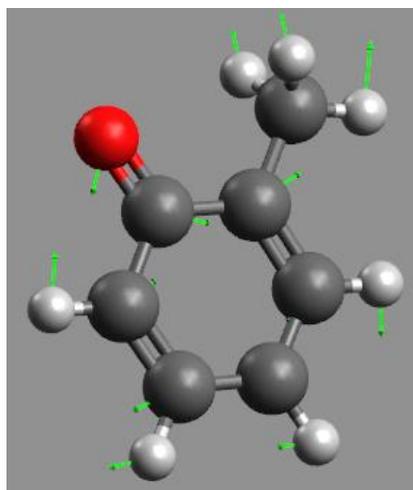
The enthalpies for the reactions removing a proton from either the OH or CH₃ groups on the methylphenols were computed and are presented here. The electron affinity for the corresponding radical of the deprotonated methylphenol is also reported. These were all calculated at the B3LYP/aug-cc-pVQZ level. In all cases the OH site is the most acidic site on the molecule by ~30 kcal/mol, with *m*-methylphenol showing the least acidic OH as compared to the CH₃. Note that the acidities of H₂O and NH₃ are 390 and 403 kcal/mol.¹ Note that experimental enthalpies include a correction using calculated heat capacities.

Methylphenol	Deprotonation Site	$\Delta_{acid}H_{298K}^{\circ}$ (kcal/mol) (Theory)	$\Delta_{acid}H_{298K}^{\circ}$ (kcal/mol) (Experiment)	Calculated EA (eV)	Experimental EA (eV)
<i>o</i> -methylphenol					
	OH	347.6	<i>cis</i> 348.4 ± 0.5 <i>trans</i> 348.1 ± 0.5	2.135	2.1991 ± 0.0014
	CH ₃	372.3	N/A	1.279	N/A
<i>m</i> -methylphenol					
	OH	348.9	348.9 ± 0.5	2.167	2.2177 ± 0.0014
	CH ₃	378.8	N/A	1.013	1.024 ± 0.008
<i>p</i> -methylphenol					
	OH	349.6	349.2 ± 0.5	2.065	2.1199 ± 0.0014
	CH ₃	385.2	N/A	0.710	N/A

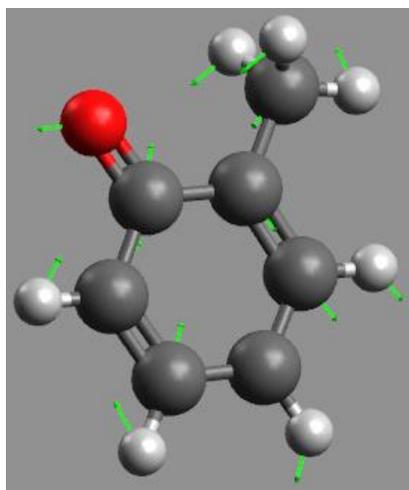
III. FRANCK-CONDON ACTIVE NORMAL MODE EIGENVECTORS

The following diagrams show the primary Franck-Condon active normal modes discussed in the main text for each product studied. Each eigenvector shown here is that of the neutral molecule, and was calculated at the B3LYP/aug-cc-pVQZ level of theory.

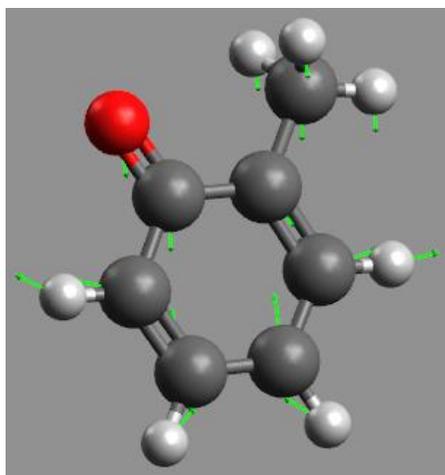
Ortho-methylphenoxy radical (\tilde{X} state)



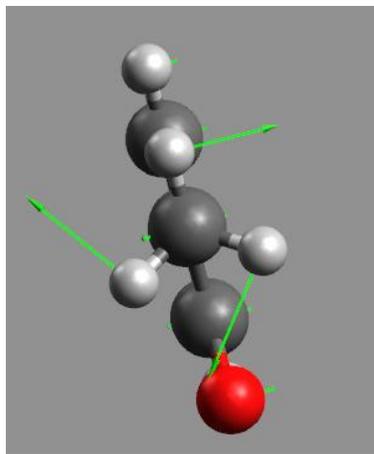
ν_{33} (453 cm^{-1})



ν_{31} (540 cm^{-1})

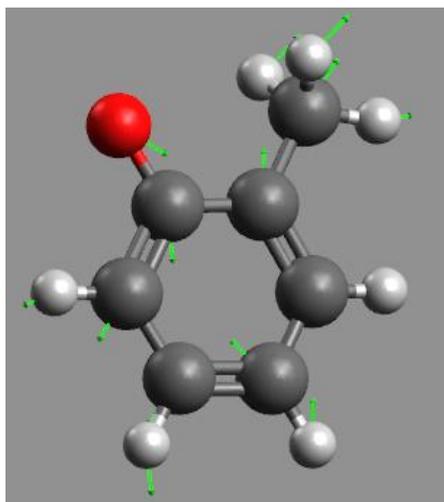


ν_{30} (577 cm^{-1})

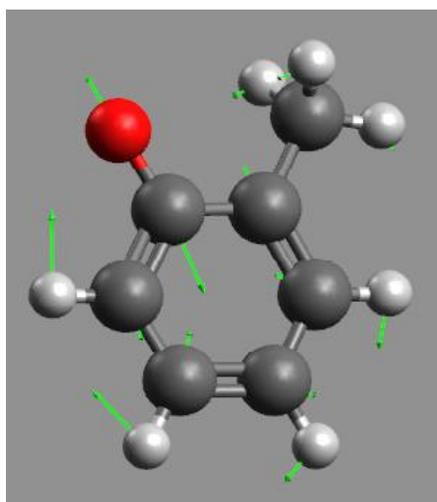


ν_{39} (106 cm^{-1})

Ortho-methylphenoxy radical (\tilde{A} state)

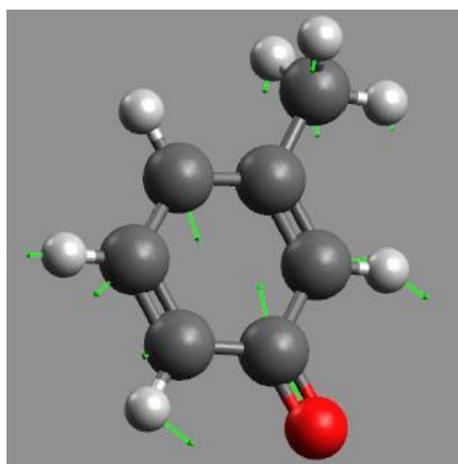


ν_{32} (506 cm^{-1})

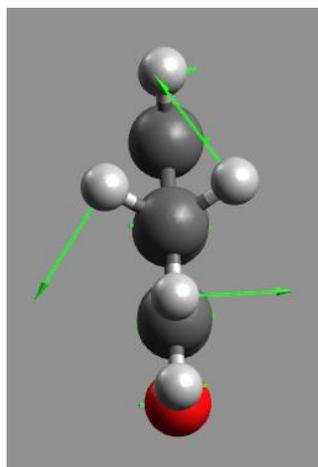


ν_{15} (1312 cm^{-1})

Meta-methylphenoxy radical (\tilde{X} state)

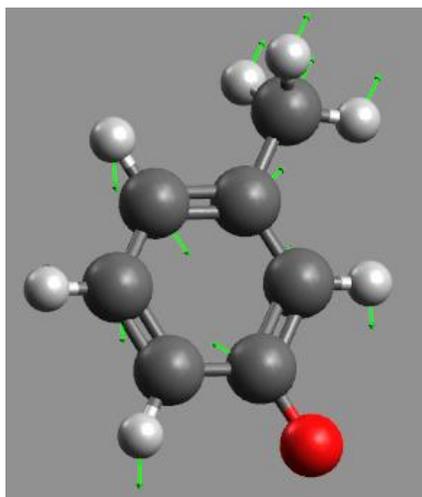


ν_{31} (540 cm^{-1})

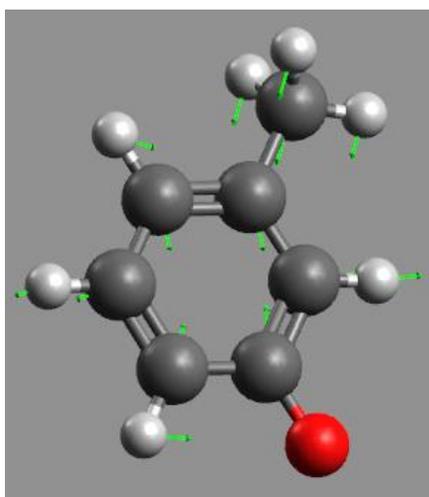


ν_{39} (81 cm^{-1})

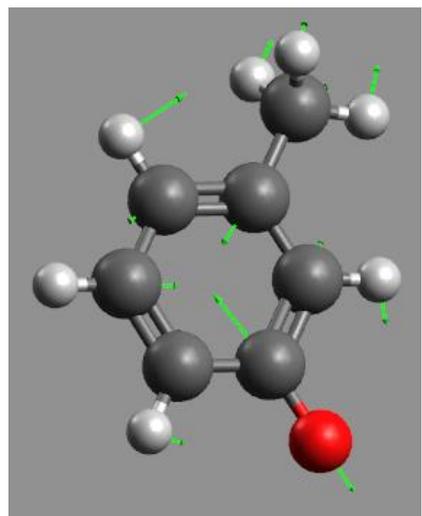
Meta-methylphenoxy radical (\tilde{A} state)



ν_{32} (516 cm^{-1})

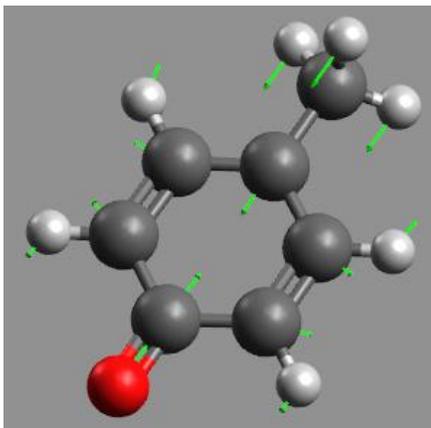


ν_{31} (542 cm^{-1})



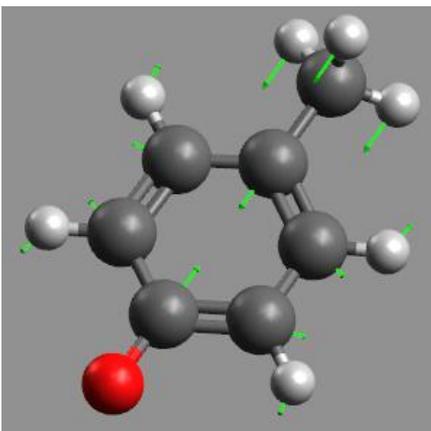
ν_{15} (1330 cm^{-1})

Para-methylphenoxyl radical (\tilde{X} state)

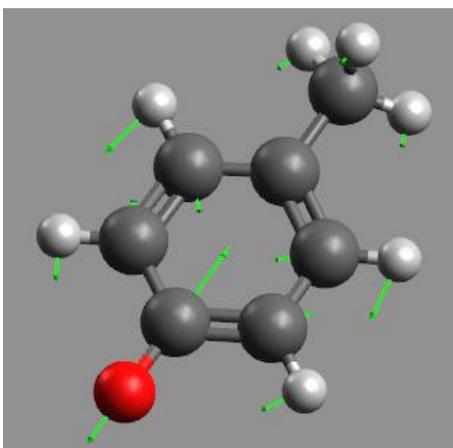


ν_{32} (463 cm⁻¹)

Para-methylphenoxyl radical (\tilde{A} state)

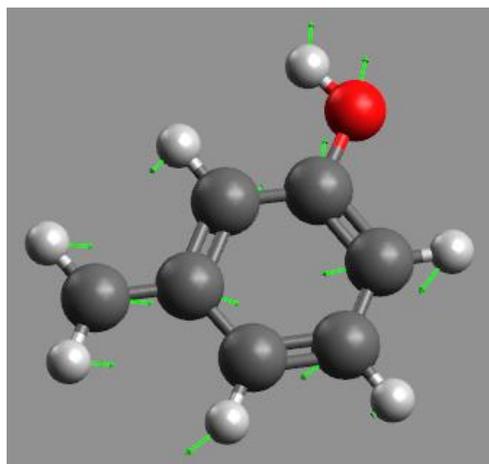


ν_{32} (461 cm⁻¹)

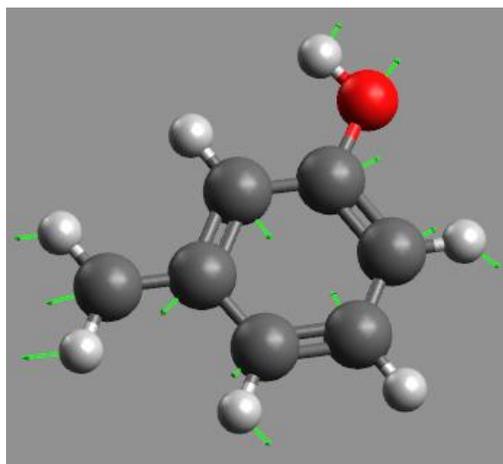


ν_{15} (1320 cm⁻¹)

Meta-methylenephenol (\tilde{X} state)



ν_{31} (525 cm^{-1})



ν_{30} (547 cm^{-1})

References

- ¹ K. M. Ervin and V. F. DeTuri, *J. Phys. Chem. A* **106**, 9947 (2002).