**Photoelectron Spectroscopy Study of Quinonimides**

Ekram Hossain,‡ Shihu M. Deng,‡ Samer Gozem,§ Anna I. Krylov,§ Xue-Bin Wang,§,*‡ and Paul G. Wenthold§,*‡

†The Department of Chemistry Purdue University West Lafayette, Indiana 47906, United States
‡Physical Sciences Division, Pacific Northwest National Laboratory P.O. Box 999, MS k8-88 Richland, Washington 99352, United States
§Department of Chemistry University of Southern California Los Angeles, 90089, United States

* Supporting Information

**ABSTRACT:** Structures and energetics of ortho-, meta-, and para-quinonimide anions (OC₆H₄N⁻) and quinoniminyl radicals have been investigated by using negative ion photoelectron spectroscopy. Modeling of the photoelectron spectrum of the ortho isomer shows that the ground state of the anion is a triplet, while the quinoniminyl radical has a doublet ground state with a doublet-quartet splitting of 35.5 kcal/mol. The para radical has doublet ground state, but a band for a quartet state is missing from the photoelectron spectrum indicating that the anion has a singlet ground state, in contrast to previously reported calculations. The theoretical modeling is revisited here, and it is shown that accurate predictions for the electronic structure of the para-quinonimide anion require both an accurate account of electron correlation and a sufficiently diffuse basis set. Electron affinities of ortho- and para-quinoniminyl radicals are measured to be 1.715 ± 0.010 and 1.675 ± 0.010 eV, respectively. The photoelectron spectrum of the meta-quinonimide anion shows that the ion undergoes several different rearrangements, including a rearrangement to the energetically favorable para isomer. Such rearrangements preclude a meaningful analysis of the experimental spectrum.

**INTRODUCTION**

Benzoquinones (1o, 1m, 1p) are important chemical structures that are found in a large variety of systems with different applications. As convenient electron acceptors, quinones play essential roles in critical biological processes including photosynthesis and respiration. However, quinones are also involved in several harmful processes in biological systems. Ortho- and para-quinones can be easily formed by oxidation of the corresponding catechols, and can even be formed from the oxidation of aromatic molecules, such as benzene. Ortho-quinones formed in this manner have been proposed as the sources of benzene toxicity and carcinogenicity. Similarly, ortho-quinones formed in the oxidation of urushiol cause the contact-dermatitis associated with plants like poison ivy. Benzoquinones are also utilized in various chemical applications, serving as dyestuffs, battery electrodes, and hydrogen storage materials and as oxidizing agents and dienophiles in organic synthesis.

The electronic structures of benzoquinones are highly dependent on their topology. The stable quinones encountered in the situations described above are the ortho- and para-isomers, and the stabilities are readily apparent in their Kekulé valence structures, as shown in 1o and 1p. Consistent with this view, both 1o and 1p have closed-shell singlet ground states, with triplet-states lying 1.68 and 2.32 eV higher in energy, respectively. In contrast, the meta-isomer, 1m, has a non-Kekulé structure and an open-shell, triplet ground-state 9.0 kcal/mol lower in energy than the lowest-energy singlet state. The relative stabilities of the ortho- and para-isomers compared to 1m are reflected in the absolute enthalpies of formation. The measured enthalpies of formation of 1o and 1p are −21.0 ± 3.1 and −29.3 ± 0.9 kcal/mol, respectively, whereas ΔH₂₉₈(1m) = 8.1 ± 3.4 kcal/mol.

The benzoquinones 1o–1p are just one type within the class of molecules with quinoidal structures. As shown in Figure 1, the substituents on the aromatic ring can be varied to create quinone analogs. The most common of these would include the quinomethanes (X = O, Y = CR₂, Figure 1) or the quinodimethanes (xylylenes), where both X and Y are carbon-centered substituents. However, essentially all multi-
valent atoms can be incorporated and in almost any combination. Whereas each variation will have unique properties, the common theme is that the ortho- and para- isomers will have stable,\textsuperscript{55,49} Kekulé structures with closed-shell singlet electronic states, whereas the meta-isomers are higher-energy,\textsuperscript{50} non-Kekulé structures with high-spin electron coupling in the ground state, which is why \textit{meta}-phenylene derivatives are commonly used as the basis for high-spin materials.\textsuperscript{51–54}

We recently reported a flowing afterglow study of quinoidal imides, including quinonimides (2, \(X = O, Y = \text{N}^+\)) and quinomethanimides (3, \(X = \text{CH}_2, \text{N}^+\)).\textsuperscript{55}

Significant differences were observed in the reactions of 2p and 3p with nitric oxide. Whereas 3p reacts with NO merely by addition, 2p reacts by addition and by a novel, N–O exchange reaction to form the semiquinone radical anion, as shown in eq 1. The observed differences in reactivity were attributed to differences in the electronic structures. The addition reaction that occurs with 3p is consistent with what is expected for the closed-shell, imide anion.\textsuperscript{56} In contrast, the N–O exchange reaction has been observed previously with nitrene radical anions\textsuperscript{57} and is interpreted as indicating an open-shell electronic structure.\textsuperscript{58} Consequently, our previous study indicates that while 3p has a robust ground-state singlet, 2p is either a ground-state triplet or a singlet with a thermally accessible triplet state.\textsuperscript{55}

A low-lying triplet state for 2p is somewhat surprising considering that it is isoelectronic with \(p\)-benzoquinone, 1p, which is a singlet with a large (>2 eV) singlet–triplet splitting.\textsuperscript{28} However, it can be rationalized by considering that 2p can alternatively be viewed as an oxo-substituted phenyl nitrene, as shown in Scheme 1. Considering that the energies of closed-shell singlet states in aromatic nitrenes are approximately 30 kcal/mol higher than the triplets,\textsuperscript{59,60} the fact that the singlet is close in energy to the triplet indicates that the singlet quinonimide is highly stabilized, at least for a closed-shell singlet nitrene. Triplet nitrene 2p has also been proposed as an intermediate in the photolysis of \(p\)-azidophenoxide in aprotic conditions,\textsuperscript{61} affirming that the triplet state is chemically accessible.

The conclusions about the electronic structures of 2p and 3p were consistent with reported electronic structure calculations\textsuperscript{55} that predict 3p to be a ground-state singlet with a singlet–triplet splitting of about 5 kcal/mol, with 2p a ground state \textit{triplet}, with a singlet that is 1–2 kcal/mol higher in energy.

In this work, we describe a negative ion photoelectron spectroscopy (NIPES) study of the quinonimides, 2o–p. Negative ion photoelectron spectroscopy provides a means to investigate the electronic properties of ions as well as those of the neutral molecules obtained upon electron detachment.\textsuperscript{62} Therefore, in addition to being a study of the quinonimides, this study also provides new spectroscopic information for quinoniminy radicals, 4.

The quinoniminy radicals are isoelectronic with the benzoquinone radical cations.\textsuperscript{63,64} On the basis of isotropic proton coupling in ESR experiments, Chandra et al.\textsuperscript{63} proposed that ionization of 1p occurs from a \(\sigma\) orbital. By analogy, 4p would be a \(\sigma\)-radical, with a closed-shell \(\pi\) system, leading to a doublet ground state, and the ortho-radical (4o) should be similar. High-spin coupling of the \textit{meta}-phenylene arrangement in 4m, however, should favor a quartet ground state.\textsuperscript{65} The \textit{para}-quinoniminy radical, 4p, has previously been suggested as a possible intermediate in the Gibbs reaction between \(N\)-haloquinominines and phenoxides.\textsuperscript{56}

In this study, we use NIPES to examine the \textit{ortho}-, \textit{meta}-, and \textit{para}-isomers of the quinonimides. In addition to determining electron affinities of the quinoniminy radicals, we also use modeling of the spectroscopic features to show that \textit{ortho}-quinonimide, 2o, has a triplet ground state, consistent with electronic structure calculations. For the \textit{para}-isomer, 2p, the spectroscopy results are best interpreted as indicating a \textit{singlet} ground state, in contrast to previous electronic structure predictions, which have been revisited in this work. The spectra and calculations presented for 2p, combined with the reactivity studies reported previously,\textsuperscript{55} suggest that whereas the isomer has a singlet ground state, it also has a low-lying triplet state that can be accessed during reaction.

### EXPERIMENTAL METHODS

All NIPES experiments were carried out at PNNL using an apparatus consisting of an electrospray ionization source (ESI), a cryogenic ion trap, and a magnetic-bottle time-of-flight (TOF) photoelectron spectrometer.\textsuperscript{67} Azidophenols were synthesized from \(p\)-azido-

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**Scheme 1**

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Figure 1. Some variations of quinoidal molecules.

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guides into an ion trap, where they were accumulated and cooled for 20–100 ms by collisions with cold buffer gas at 20 K, before being transferred into the extraction zone of a TOF mass spectrometer. The cooling of the anions to 20 K eliminated the possibility of the appearance of hot bands in the NIPES spectra.

Each of 2o, 2m, or 2p anions were then mass selected, and maximally decelerated before being photodetached with 266 (4.661 eV), 355 (3.496 eV), and 532 nm (2.331 eV) photons from a Nd:YAG laser. The laser was operated at a 20 Hz repetition rate, with the ion beam off at alternating laser shots to enable shot-to-shot background subtraction to be carried out.

Photoelectrons were collected with ~100% efficiency with the magnetic bottle and analyzed in a 5.2 m long electron flight tube. The recorded TOF photoelectron spectrum was converted into an electron kinetic energy spectrum by calibration with the known NIPES spectra of I− and OsCl6−. The electron binding energy spectrum was obtained by subtracting the electron kinetic energy spectrum from the energy of the detaching photons. The energy resolution was about 2%, that is, ~20 meV for 1 eV kinetic energy electrons.

**Computational Methods**

All geometries and frequencies reported in this work are computed with density functional theory (DFT) with the BS05OLYP functional\textsuperscript{70,71} and 6-311++G(d,p) basis set. BS05OLYP is a hybrid functional that uses 50% Hartree–Fock, 8% Slater and 42% Becke exchange, and 19% VWN+81% LYP correlation, and is used because extensive benchmarks indicate that it yields improved geometries, energies, and vibrational frequencies in combination with the spin-flip (SF)-DFT approach.\textsuperscript{73} We employ SF-DFT for low-spin (singlet or doublet) states in ortho and para isomers (2o, 2p, 2o, 2p), but not for meta (2m, 2m) because in that case SF states were strongly spin-contaminated. For high-spin (triplet and quartet) states and for all meta isomer calculations, standard DFT was used. The DFT or SF-DFT geometries were then used for subsequent energy calculations with coupled-cluster-based methods.

Singlet–triplet and doublet-quartet energy splittings were computed with the spin-flip equation-of-motion coupled-cluster (EOM-SF-CC) method.\textsuperscript{74} The SF approach employs a high-spin reference state and uses a spin-flipping operator that allows description of both the high-spin and low-spin target states on an equal footing.\textsuperscript{74–76} As needed for the systems presented in this study, the SF approach is capable of describing multiconfigurational character encountered in open-shell singlets and doublet radicals, which may not be described correctly in a single-configuration formalism. Previous studies have shown that the SF variant of EOM-CC\textsuperscript{2,73,77} gives accurate singlet–triplet splittings in aromatic nitrenes.

EOM-SF-CC energies are calculated with singles and doubles excitations, denoted EOM-SF-CCSD. In addition, the effect of triple excitations was included by perturbative triples correction, denoted EOM-SF-CCSD(T).\textsuperscript{77,78} Coupled-cluster calculations were carried out using B3LYP orbitals as the reference orbitals, as described previously,\textsuperscript{72,74} to mitigate spin-contamination.\textsuperscript{73} Electron attachment energies were computed between the triplet and quartet states by taking the difference in coupled-cluster energies with single and double excitations and perturbative triples correction, CCSD(T). Electron attachment energies for other states are then derived on the basis of triplet-quartet CCSD(T) energy difference and EOM-SF-CCSD(T) splittings, as described above.\textsuperscript{40} All reported energies are adiabatic (i.e., accounting for geometry relaxation of different states) and are corrected for zero-point energies (ZPE) computed from DFT or SF-DFT unscattered vibrational frequencies at the corresponding geometry. For all coupled-cluster calculations, we employ Dunning’s correlation consistent basis sets.\textsuperscript{81}

Unless stated otherwise, the values for EOM-SF-CCSD(T)/(aug-)cc-pVTZ calculations were estimated by using the additive approach shown in eq 2.

\[
E_{\text{projected}} = E(\text{CCSD}/(\text{aug}-)\text{cc-pVTZ}) - E(\text{CCSD}/(\text{aug}-)\text{cc-pVdz}) + E(\text{CCSD}(T)/(\text{aug}-)\text{cc-pVdz})
\]

(2)

Previous studies,\textsuperscript{60} have found that this approach gives singlet–triplet energy differences within ~0.5 kcal/mol of those obtained by a direct EOM-SF-CCSD(T)/cc-pVdz calculation. In this work, the projected energies will be indicated as p-EOM-SF-CCSD(T)/(aug-)cc-pVdz. All the calculations are performed using QCHEM ab initio package.\textsuperscript{82,83}

Photoelectron spectra, including Franck–Condon vibrational progressions and detachment cross sections, have been calculated using procedures described previously. Franck–Condon factors are calculated from DFT or SF-DFT normal modes and frequencies (depending on the isomer and state; see above). The Franck–Condon factors for detachment are calculated using ezSpectrum.\textsuperscript{84}

Detachment cross sections were calculated using ezDyson.\textsuperscript{85,86} Photoionization and photodetachment cross sections can formally be computed from the photoelectron dipole moment element, D_{nf}^2, eq 3, where \Psi_f and \Psi_{n-1} are the wave functions of the initial (N-electron) and final (N−1-electron) states, respectively, \nu is the dipole operator for the ionizing radiation, and \Psi_{el} is the wave function of the ejected electron.\textsuperscript{87,88}

\[
D_{nf}^2 = \langle \Psi_f^n | \nu | \Psi_{n-1}^1 \rangle
\]

(3)

Owing to electron indistinguishability, D_{nf}^2 can be expressed in terms of a Dyson orbital, \phi,\textsuperscript{4} such that it is now calculated from one-electron functions, as shown in eq 4.\textsuperscript{89,90}

\[
D_{nf}^2 = \langle \phi_{n}^1 | \nu | \phi_{n}^1 \rangle
\]

(4)

The Dyson orbitals are correlated extensions of Koopmans’ theorem. Here Dyson orbitals are calculated by using the ionization potential EOM-CCSD (EOM-IP-CCSD) approach,\textsuperscript{89,90} which accounts for orbital relaxation and electron correlation. The wave function for reference triplet state of the anion was computed at the CCSD/aug-cc-pVdz level of theory, and the neutral state wave functions were calculated by using the EOM-IP-CCSD/aug-cc-pVdz method.

To analyze diradical character, we also compute the Head-Gordon’s index,\textsuperscript{91} using the EOM-CCSD/aug-cc-pVdz wave functions. The Head-Gordon index is computed from state density matrices (or, more precisely, populations of natural orbitals) and therefore does not depend on the choice of molecular orbitals. In this work, we use the nonlinear variant (eq 5).\textsuperscript{92}

\[
N_{el} = \sum_{j=1}^{M} n_j(2 - n_j)^2
\]

(5)

where M is the total number of orbitals and n_j is the occupation number for each natural orbital. The value of N_{el} is a measure of the effective number of unpaired electrons, such that for a closed shell system it is 0, a radical gives 1, and a perfect biradical gives 2, etc.

**Computational Results**

Before reporting the results of the photoelectron measurements, we provide a discussion of the electronic structures of the ions and corresponding neutrals. The electronic structures of the anions, 2o, 2m, and 2p, can be understood from the framework of substituted phenyl nitrenes. The nonbonding molecular orbitals in nitrenes usually include the benzylic-like \pi orbital and the \sigma (p) orbital localized on nitrogen (Scheme 2).

An O− substituent adds an additional benzylic-like \pi orbital that can interact with the \pi orbital of the nitrene. For the O− in the ortho and para positions, the two \pi orbitals have significantly different energies, resulting from quinoidal bonding and antibonding combinations as shown at the top of Figure 2. Consequently, the bonding \pi orbitals are expected to be significantly stabilized with respect to the \sigma orbitals, while
Because the orbitals are all very similar in energy, there are multiple options for orbital occupancy. However, the electronic state with the lowest energy is predicted to have two electrons in a phenoxide benzylic orbital, with the other two electrons occupying the \( \sigma \) orbital and the \( \pi \) benzylic orbital on nitrogen. Therefore, in 2m the \( \pi \) orbitals localize into their benzylic forms (linear combinations of \( \pi_1 \) and \( \pi_2 \)), presumably because it puts the negative charge predominantly on the oxygen. Consequently, 2m is best described as a phenoxide anion orthogonal to a phenyl nitrene. Finally, because it is a phenyl nitrene distinct from the phenoxide, it is not surprising that it has a triplet ground state. Similarly, the lowest energy singlet state of 2m is likely the singlet nitrene. The singlet–triplet energy gap computed with EOM-SF-CCSD/aug-cc-pVTZ is 17.3 kcal/mol.

The difference in the electronic structure of 2m compared to those of 2o and 2p is readily observed in Head-Gordon’s indices for the lowest-lying singlet state of each isomer. While \( N_{zz} \) for both 2o and 2p is 0.04, indicating closed shell character consistent with the \( \pi^2\sigma^0 \) assignment discussed above, the same index is 0.04 for 2m, indicating that even the lowest energy singlet state has significant diradical character.

The neutral quinoniminy radicals, 4, formed upon detachment of 2 are nominally triradicals, in that they have 3 electrons in three nearly degenerate orbitals. However, because of the strong bonding interactions that stabilize the \( \pi \) orbitals in 4o and 4p, these isomers have doublet ground states, with high-energy quartet states (Table 1). In contrast, the ground state of 4m is predicted to be a quartet, with multiple low-lying doublet states. The relevant computed state energies are shown in Table 1, including computed electron affinities and doublet–quartet splittings.

### EXPERIMENTAL RESULTS

In this section, we report the measured negative ion photoelectron spectra for the [M–N\(_2\)H\(^-\)] \(^-\) ions obtained upon electrospray ionization of basic solutions of o-, m-, and p-azidophenol. Survey spectra, measured at 266 nm, are shown in Figure 3. Detailed descriptions of each spectrum are provided in the sections below.

**ortho** (2o). The 266 nm spectrum for the ortho isomer, Figure 3a, shows three identifiable features. The lowest energy feature is a narrow band with an origin at 1.715 ± 0.010 eV. The highest energy feature is dominated by the origin peak at 3.256 ± 0.005 eV, indicating a nearly vertical transition. The center band begins at 2.54 eV. However, the relative intensity of this feature is variable and affected by source conditions. Consequently, the center band results from detachment of a different ion from that giving the other features in the spectrum.

The 532 nm photoelectron spectrum of 2o (vide infra) only contains the lowest energy feature. However, because the photodetached electrons have lower energies, they are better resolved than in the 266 nm spectrum. The identifiable peaks for the ortho isomer are listed at the top of Table 1.

**para** (2p). The 266 nm spectrum of the para-substituted ion, shown in Figure 3c, has only a single intense feature, with an origin at 1.675 ± 0.010 eV. As with the ortho isomer, the 532 nm spectrum (vide infra) shows a well-resolved band. The observed peaks are shown at the bottom of Table 1.

**meta** (2m). The 266 nm spectrum of 2m, shown in Figure 3b, has three features. However, the lowest energy band is identical to the lowest energy feature for the para isomer, in...
Figure 3, indicating that the meta isomer undergoes rearrangement prior to photodetachment. The most intense feature in the spectrum of 2m has an origin at 2.11 eV, with many closely spaced peaks. The identifiable peaks are listed in Table 1. A third, weaker feature is also observed in the spectrum. Although it is unresolved, it has a maximum at a vertical detachment energy of about 3.15 eV.

### DISCUSSION

In this section, we present an analysis of the measured photoelectron spectra of the ions derived from ortho-, meta-, and para-azidophenoxide, with a focus on determining the electronic states of the anions and the radicals.

**ortho.** The spectrum of the ortho isomer contains features attributed to two different ions. The high and low energy features result from a common ion, and are readily assigned to formation of the doublet and quartet states of 4o, respectively, formed upon detachment of 2o. The measured electron affinity, 1.715 eV, agrees reasonably well with the calculated EA for formation of the triplet anion, 1.61 eV (Table 1). More importantly, the energy difference between the bands, 35.5 kcal/mol, is in very good agreement with the predicted doublet-quartet splitting of 36.0 kcal/mol, obtained at the p-EOM-SF-CCSD(T)/aug-cc-pVTZ level of theory (Table 1).

The photoelectron spectrum of 2o shown in Figure 3a also clearly demonstrates that the ion has a triplet electronic state. The most important evidence for the triplet state of 2o is the fact that detachment to both the doublet and quartet states are observed. Given that the selection rule for photodetachment is $\Delta S = \pm 1$, the only way to form both the doublet and quartet states of 4o is to detach from the triplet state of 2o.

To confirm that the experimental peaks indeed are assigned to doublet and quartet states formed from the triplet anion, we refer to quantum chemical calculations. In this way, we have unequivocal evidence that the ground state is a triplet.

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Table 1. Observed Peaks in the Photoelectron Spectra of 2o, 2m, and 2p

<table>
<thead>
<tr>
<th>ion and neutral electronic state</th>
<th>peak eBE (eV)</th>
<th>relative energy (cm⁻¹)</th>
<th>vibrational assignment</th>
<th>calculated energy¹</th>
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<tbody>
<tr>
<td>2o</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>doublet</td>
<td>1.715 ± 0.010</td>
<td>EA</td>
<td>$\nu 8$</td>
<td>1.61 eV⁰</td>
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<td>1.780</td>
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<td>$\nu 8$</td>
<td>532</td>
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<td>1.845</td>
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<td>$\nu 8$</td>
<td>1186</td>
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<td>1530</td>
<td>$\nu 23$</td>
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<td>2160</td>
<td>$\nu 8 + \nu 23$</td>
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</tr>
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<td></td>
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<tr>
<td>quartet</td>
<td>3.256 ± 0.005</td>
<td>+35.5 kcal/mol</td>
<td>$\nu 5$</td>
<td>+36.0 kcal/mol³</td>
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<td>3.430</td>
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<td>3.15 (vertical)</td>
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<tr>
<td>doublet</td>
<td>1.675 ± 0.010</td>
<td>EA</td>
<td>$\nu 5$</td>
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<td>1.730</td>
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<td>1.935</td>
<td>2100</td>
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<td>quartet</td>
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<td>+50.2 kcal/mol</td>
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¹Vibrational energies, in cm⁻¹, calculated at the (SF)-B3LYP/6-311++G(d,p) level of theory, scaled by 0.92; electron affinities and doublet-quartet splittings are adiabatic energy differences and include ZPE correction. ²Calculated from p-CCSD(T)/aug-cc-pVTZ triplet-quartet energy differences and p-EOM-SF-CCSD(dT)/aug-cc-pVTZ splittings. ³p-EOM-SF-CCSD(dT)/aug-cc-pVTZ.

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Figure 3. 266 nm photoelectron spectra of the m/z 106 ions derived from (a) ortho-, (b) meta-, and (c) para-azidophenol. The asterisk (*) in panels a and b indicate bands whose relative intensity depends on source conditions.
particular, structural differences between the triplet and singlet states are manifested in the shapes of the features in the spectrum. The 532 nm photoelectron spectrum of the ion 2o, shown in Figure 4, has a well-resolved vibrational progression for the doublet state. For comparison, we have calculated the expected Franck-Condon profile for formation of the doublet from the triplet (Figure 4a) and singlet (Figure 4b) states of the ion, using geometries and frequencies calculated at the DFT or SF-DFT B5050LYP levels of theory.\(^8\) The calculated spectrum obtained when using the triplet anion is in excellent agreement with the measured spectrum, in both the positions of the peaks and in their intensities. In contrast, the calculated band for detachment from the singlet state has poor resemblance to the measured spectrum. Therefore, the Franck-Condon calculation further confirms that the ion has a triplet ground state.

Using this approach, we have also calculated the shape of the quartet feature, shown in Figure 5. As with the doublet feature, there is outstanding agreement between the predicted relative peak positions and intensities calculated from the triplet anion, and those measured experimentally. The band for the doublet state in Figure 5 is the same as that shown in Figure 4a, but with significantly broader peaks (450 cm\(^{-1}\) vs 150 cm\(^{-1}\) full-width at half-maximum) due to the lower resolution of the band in the 266 nm spectrum. Overall, these results create a consistent picture for the photoelectron spectrum, indicating detachment of the triplet state of the anion forming the doublet and quartet states of the neutral.

The middle band observed in the spectrum has an identifiable origin peak at 2.54 eV, but the band has a relative intensity that is dependent on source conditions, and therefore results from detachment of an isobaric ion. Given the azidophenoxide precursor, the most likely ionic formula is either C\(_6\)H\(_4\)NO\(^-\) or C\(_6\)H\(_4\)N\(_3\)\(^-\). Either would result from more complex dissociation of the precursor. We have not been able to determine the actual structure of the ion leading to the observed signal, but the electron binding energy suggests an oxygen-based anion, such as those shown in Figure 6. Cyanocyclopentadiene has been previously found to be formed by rearrangement of phenylnitrene in the gas-phase.\(^9\) Simple B3LYP calculations predict cyclopentadienyl structures such as those in Figure 6 to be up to 2 eV more lower in energy than 2o.

Figure 4. Comparison of the low-energy feature in the 532 nm photoelectron spectrum of 2o with the band predicted from (SF)-DFT B5050LYP/6-311++G(d,p) geometries and frequencies of the (a) triplet state and (b) singlet state of the anion and the doublet state of the radical, 4o. Calculated harmonic frequencies were scaled by 0.92.

Figure 5. Comparison of measured (266 nm) and calculated spectra for 2o. The calculated spectra correspond to detachment of the triplet state of 2o. Calculated harmonic frequencies were scaled by 0.92.

Figure 6. Possible structures of the second ion in the spectrum of 2o.
5a and 5b are 2.06 and 1.71 eV, respectively, at the B3LYP/6-31+G* level of theory, and so are in the range of the measured band. However, neither structure alone accounts for the observed feature, as the bands for 5a or 5b are predicted to be too narrow to account for the observed spectrum. Therefore, the low-energy feature in the spectrum of the meta isomer is either a mixture of ions such as 5a and 5b or due to some other undetermined rearrangement product. Although the ketenimine structures 5a and 5b are calculated to be slightly higher in energy than triplet 2m, they lower in energy than the singlet state.

**para.** The spectrum of the ion obtained from p-azidophenoxide is the simplest of the three, containing only one identifiable band, with an origin peak at 1.67 ± 0.01 eV. The measured electron affinity is in reasonable agreement with the predicted value for the electron affinity of the doublet state (Table 1). Although there is broad signal at higher binding energy, there is no feature that can be clearly identified as resulting from detachment to form the quartet state, which is predicted to be ∼2.2 eV higher in energy than the doublet (Table 1), and therefore within the energy range of the experiment.

The fact that there is only a single product formed upon detachment of the para anion is significant. As noted in the discussion of the ortho spectrum, detachment of the triplet state of the anion would form both the doublet and quartet state of the neutral product. Therefore, a possible explanation for the absence of a peak for the quartet state is that the ion is in a singlet state. In order to confirm the singlet state, we have carried out an analysis of the Franck-Condon progression similar to what we did for 2o. Figure 7 shows a comparison between the experimental 532 nm photoelectron spectrum of 2p and those predicted for formation of the doublet upon detachment of the triplet (Figure 7a) and singlet (Figure 7b) states of the anion.

Although the agreement between the calculated and predicted spectra is clearly better for the singlet state, there is not a sufficient difference in the quality of the agreement between the spectra for the singlet and triplet states for the para isomer to make an unequivocal assignment of the electronic state, and the differences observed for the triplet state in Figure 7a are not sufficient to rule it out as the electronic state of the anion.

Because the Franck-Condon calculation cannot sufficiently distinguish between the triplet and singlet states of 2p, the assignment of the electronic state depends on the absence of the quartet band. However, this conclusion requires the assumption that the quartet band should be observable to a sufficient extent. Although the spectrum for 2o, for example, suggests that the quartet band should be strong, it is not conclusive. Therefore, we have calculated the expected relative cross sections for formation of the doublet and quartet states using the Dyson orbitals computed for correlated EOM-CCSD wave functions, as described above.

The challenge in this calculation involves the choice for the wave function for the detached electron. For simple atomic systems, the detached electron can be described as a Coulomb wave in the case of photoionization or as a plane wave in the detachment of an atomic anion. To a first approximation, one can treat the detachment of 2p as similar to that of an atomic anion, and describe it as a plane wave. However, for the ortho isomer, it was found that the relative intensity of the quartet feature was underestimated by using a plane wave approximation (see Supporting Information). Alternatively, it has been found previously that, for larger molecular systems, using a Coulomb wave with a partial charge between 0 and 1 often gives the best agreement with experiment. Because we do not have a rigorous procedure to determine the best effective charge, we have computed the cross section at Z values of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0, and used the average values to obtain relative cross sections. This approach has been used successfully to predict the cross sections for ionization of aldehydes and enols and is the approach used to determine the relative intensities for the 2o shown in Figure 5. For the quinonimides, the relative intensities of the quartet states obtained by using a modified Coulomb wave are consistently larger than those obtained by using a plane wave approximation, regardless of the chosen Z value (see Supporting Information).

The average calculated total absolute cross sections for detachment of triplet 2p to form the doublet and quartet states of 4p are 4.7 and 6.2 megabarns, respectively, giving relative cross sections of about 1/1.3 for formation of the doublet and quartet, respectively. Therefore, as expected, detachment of the
triplet anion should lead to abundant formation of the quartet state. Scaling the integrated Franck–Condon profiles by the calculated total cross sections results in the predicted spectra shown in Figure 8, which confirm that the quartet is not being formed as expected if 2p were a triplet anion. Although the predicted relative cross-section for formation of the quartet state is lower when using a plane wave approximation for the detached electron, the band for the quartet state is nonetheless predicted to be prominent in the spectrum (see Supporting Information). Consequently, the photoelectron spectrum is best interpreted as resulting from detachment of the singlet state of 2p.

Vibrational Assignments. The calculation of the Franck–Condon intensities from theoretical structures and frequencies can be used to identify the vibrations active in the photoelectron spectra. For example, as shown in Table 1, the active modes in the doublet feature in the spectrum of 4o include ν8 (525 cm⁻¹), ν20 (1210 cm⁻¹), and ν23 (1530 cm⁻¹). The vibrational motions associated with these modes are shown in Scheme 3. The assigned modes are those predicted to be active in the Franck–Condon calculations. The mode ν8 is a ring-deformation mode, similar to the ν6a mode in benzene, and is commonly active in negative ion photoelectron spectra of aromatic molecules.101–104 The mode ν20 is predominately stretching of the CO and CN carbon atoms, whereas ν23 is the symmetric combination of the CO and CN stretching motions. In contrast, the active modes in the quartet state of 4o, ν24 and ν25, are antisymmetric combinations of the CO and CN stretching motions. The active ring-deformation mode, ν5, involves the CN stretch.

The active modes in the doublet state of 4p consist of the ring-deformation mode, ν5, and a ring breathing mode, ν11.

Comparison to Reactivity and Theoretical Results. As noted in the introduction, the reactivity of 2p has been previously interpreted as indicating that 2p is either a ground-state triplet or a singlet with a thermally accessible triplet state.55 The 20K photoelectron spectrum indicates that the ion has a ground state singlet, and so if reactivity is due to the triplet state, it must be accessed during the reaction. Keittamäa and co-workers have found that singlet diradicals are capable of undergoing reactions involving the triplet state,105,106 and therefore the presence of a singlet ground state for 2p is not inconsistent with the apparent radical reactivity.

The singlet ground state found for 2p is, however, inconsistent with predictions from electronic structure theory reported previously.55 As noted above, all three quinonimide anions were predicted to have triplet ground states. The calculations leading to the prediction of the triplet ground state for 2p reported in the previous work55 were carried out at the BLYP/6-311++G(3df,2p) and EOM-SF-CCSD(T)/cc-pVDZ levels of theory. The former is a DFT method employing a large basis set with both polarization and diffuse functions, while the latter is method that accounts for static (via SF ansatz) and dynamic (up to triple excitations) electron correlation. Nonetheless, both of these approaches failed to predict the correct ground state for 2p. Here we revisit the calculations on the singlet–triplet splitting of 2p, summarized in Table 2.

We find that standard DFT methods give triplet ground states, regardless of the basis set. As for EOM-SF-CC calculations, we find that increasing the size of the basis set leads to preferential stabilization of the singlet state. In particular, augmentation of the basis set with diffuse functions significantly stabilizes the singlet state more than it does the triplet, such that the predicted ground state when using singly augmented functions is the singlet state. At the best level of theory used in this work, p-EOM-SF-CCSD(dt)/aug-cc-pVTZ, 2p is indeed predicted to have a singlet ground state, with a singlet–triplet energy splitting of 0.8–1.0 kcal/mol.

Therefore, accurate prediction of the correct ground state in 2p requires both an accurate account of electron correlation but also a very large basis set that includes diffuse functions. Interestingly, SF-DFT with B5050LYP/6-311++G(d,p) also predicts a singlet ground state, by 1.6 kcal/mol.

The predicted energy difference between the singlet and triplet states is sufficiently small that it is possible that there could be some population of triplet state present at thermal temperatures. The spectra shown above were all measured at a temperature of 20 K, and therefore, where the population of the excited state should not be significant. We have also measured the 355 nm photoelectron spectrum of 2p at a temperature of 299 K. Although there are some differences in the relative peak intensities of the doublet feature, they are not sufficient to be
attributed to triplet anion contribution. It is especially difficult to draw any conclusions due to the similarities of the doublet bands obtained from the singlet and triplet states of the anion (see the calculated spectra in Figure 7).

## CONCLUSIONS

Negative ion photoelectron spectroscopy studies have been used to provide ground state assignments for quinonimide anions. Whereas previous experimental and computational studies\(^5\) suggested that para-quinonimide, \(2p\), either has triplet ground state or a low-lying triplet, the photoelectron spectrum presented in this work is best interpreted as showing a ground state singlet. It is likely the case that the triplet state is relatively low in energy, as very high levels of theory, involving an accurate account of electron correlation and triple-\(\zeta\) basis sets with diffuse functions, are required to predict correctly the singlet ground state, while standard density functional methods are insufficient. However, SF-DFT is able to produce singlet–triplet energy splittings in reasonably good agreement with EOM-SF-CCSD(dT) calculations, and correctly predict a singlet ground state for para.

In contrast, the ortho isomer, \(2o\), is found spectroscopically to have a triplet ground state, which is consistent with destabilization of the singlet state due to electron-pair repulsion, as proposed for ortho-quinone.\(^2\) The effect in \(2o\) is likely more pronounced because of the diffuse nature of the lone pair of electrons on the anionic nitrogen.

Removing an electron to form the radical, \(4o\), reduces the electron repulsion. Any effects of repulsion of the in-plane unpaired electron in \(4o\) appear to be minimal, as the relative electron affinities of \(4o\) and \(4p\) are similar to what has been found previously for o- and p-benzoquinone (\(1o\) and \(1p\)), 1.90 and 1.85 eV, respectively.\(^2\) Similarly, the measured doublet–quartet splitting in \(4o\), 35.5 kcal/mol, is similar to that found for \(1o\), 36.0 kcal/mol. Consequently, the o- and p-quinonimyl radicals resemble the corresponding quinones.

The meta-quinonimide anion, \(4m\), is found to rearrange to the para- and other unidentified isomers. The instability of \(4m\) is not surprising. Attempts to generate this anion under flowing afterglow conditions\(^5\) were unsuccessful, and reactivity studies of the \(m\)-quinomethanide analogs, \(6\), indicated that it also likely undergoes rearrangement.\(^5\)

The \(m\)-quinomethanide anion, \(2m\), and the radical, \(4m\), are both meta-phenylene structures and therefore would be expected to have high-spin ground states, which is supported by calculations.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b05197.

Calculated spectra for \(2o\) and \(2p\) obtained using a plane wave approximation; comparison of 355 nm spectra of \(2p\) taken at 20K and 290 K; and calculated structures, energies, and frequencies used in this work (PDF)

### AUTHOR INFORMATION

Corresponding Authors
*Xuebin.Wang@pnnl.gov
*pgw@purdue.edu

ORCID

Xue-Bin Wang: 0000-0001-8326-1780
Paul G. Wenthold: 0000-0002-8257-3907

Notes

The authors declare no competing financial interest.

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### REFERENCES


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### Table 2. Calculated Values for the Singlet-Triplet Energy Splitting in \(2p\)

<table>
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<th>computational method</th>
<th>(\Delta E_{ST}) (kcal/mol)(^{a,b})</th>
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<td>B3LYP/6-31+G(^*)</td>
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<tr>
<td>B3LYP/6-31+G(3d2p)</td>
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<td>EOM-SF-CCSD(dT)/aug-cc-pVTZ</td>
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\(^{a}\)Singlet-state energies, relative to triplet state. Positive values indicate a triplet ground state. \(^{b}\)DFT energies are for geometries optimized at the respective level of theory; spin-flip energies are for singlet geometries optimized with SF-B3LYP/6-311++G(3dp) and triplet geometries optimized with B3LYP/6-31G(3dp). \(^{c}\)Projected value calculated using the EOM-SF-CCSD/aug-cc-pVTZ energy with the dT component calculated with the aug-cc-pVDZ basis set. \(^{d}\)Projected value calculated using the EOM-SF-CCSD/aug-cc-pVTZ energy with the dT component calculated with the cc-pVTZ basis set. \(^{e}\)Direct (nonprojected) calculation.