**Negative Ion Photoelectron Spectroscopy Confirms the Prediction of the
Relative Energies of the Low-Lying Electronic States of 2,7- Naphthoquinone**

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Abstract

Cryogenic negative ion photoelectron (NIPE) spectra of the radical anion of 2,7-naphthoquinone ($\text{NQ}^{\bullet-}$) have been taken at 20 K, using 193, 240, 266, 300, and 355 nm lasers for electron detachment. The electron affinity of the **NQ** diradical is determined from the first resolved peak in the NIPE spectrum to be 2.880 ± 0.010 eV. CASPT2/aug-cc-pVDZ calculations predict with reasonable accuracy the positions of the 0–0 bands in the three lowest electronic states of **NQ**. In addition, the Franck-Condon factors calculated from the CASPT2/aug-cc-pVDZ optimized geometries, vibrational frequencies, and normal modes, successfully simulate the vibrational structures in these bands. The NIPE spectrum of $\text{NQ}^{\bullet-}$ confirms that, as predicted, $^3\text{B}_2$ is the ground state, and the $^1\text{B}_2$ and $^1\text{A}_1$ states are, respectively, 12.7 and 16.4 kcal/mol higher in energy than the triplet ground state. The experimental value of $\Delta E_{\text{ST}} = 12.7$ kcal/mol in **NQ** and the finding that $^1\text{B}_2$ is the lower energy of the two singlet states confirm the results of the previous calculations on **NQ**. These calculations predicted an *increase* in ΔE_{ST} on the substitution of both methylene groups in 2,7-naphthoquinodimethane (**NQDM**) by oxygens in **NQ**, thus providing a dramatic contrast to the decrease of 17.5 kcal/mol in ΔE_{ST} found for substitution of one methylene group by one oxygen on going from trimethylenemethane (**TMM**) to oxyallyl (**OXA**).

Introduction

The greater strength of the C=O π bond in the oxyallyl (**OXA**) diradical, relative to a C=C π bond in the trimethylenemethane (**TMM**) diradical, and the ability of the C=O π^* orbital in **OXA** to accept an electron pair were predicted to result in a very large reduction in the singlet-triplet energy separation (ΔE_{ST}) on going from **TMM** to **OXA**.^{1,2} Subsequently, Lineberger and coworkers, used negative ion photoelectron spectroscopy (NIPES)^{3,4} to confirm this prediction. As shown in Figure 1, NIPES found a decrease of 17.5 kcal/mol in ΔE_{ST} between **TMM** (ΔE_{ST} = 16.2 kcal/mol, triplet ground state)^{5,6} and **OXA** (ΔE_{ST} = -1.3 kcal/mol, singlet ground state).^{7,8}

Figure 1. Singlet-triplet energy separations (ΔE_{ST}) in trimethylenemethane (**TMM**)^{5,6} and oxyallyl (**OXA**),^{7,8} measured by negative ion photoelectron spectroscopy (NIPES).^{3,4}

Based on these results, it might have been expected that a similarly large decrease in ΔE_{ST} should occur on replacement of the two methylene groups in the *meta*-benzoquinodimethane (**MBQDM**) diradical with the two oxygens in the *meta*-benzoquinone (**MBQ**) diradical. However, electronic structure calculations predicted only a very small decrease in ΔE_{ST} .^{9,10} This prediction was confirmed experimentally, two decades later, when, as shown in Figure 2, NIPES found the value of ΔE_{ST} in **MBQ** (ΔE_{ST} = 9.0 kcal/mol)^{10,11} to be only 0.6 kcal/mol smaller than that in **MBQDM** (ΔE_{ST} = 9.6 kcal/mol).¹²

Figure 2. ΔE_{ST} , measured by NIPES,^{3,4} between the triplet ground state (³B₂) and the lowest singlet state, ¹A₁ in *meta*-benzoquinodimethane (**MBQDM**)¹² and ¹B₂ in *meta*-benzoquinone (**MBQ**).^{10,11}

The reason for the very small change in the size of ΔE_{ST} on going from **MBQDM** to **MBQ** was given in the theoretical paper that predicted this change would, in fact, be found to be small.^{9,10} In **MBQDM** the lowest singlet state is ¹A₁, in which the aromaticity of the benzene ring is largely preserved by localizing the two nonbonding electrons on the exocyclic methylene groups. However, in **MBQ** the lowest singlet state is ¹B₂, due to the strength of π bonds to the carbonyl groups in this state. The ¹B₂ state is stabilized, relative to the ³B₂ ground state, by ≥ 12.5 kcal/mol on going from **MBQDM**¹² to **MBQ**.^{10,11}

However, ΔE_{ST} is measured between the triplet and the lowest singlet state, which changes from ¹A₁ in **MBQDM** to ¹B₂ in **MBQ**. Since ¹B₂ starts off ≥ 11.9 kcal/mol above the lowest singlet state (¹A₁) in **MBQDM**,¹² the ≥ 12.5 kcal/mol stabilization of ¹B₂, relative to ³B₂, in **MBQ** results in a decrease in ΔE_{ST} of only about 0.6 kcal/mol.

Very recently, calculations have predicted a similar change in the nature of the lowest singlet state in going from the 2,7-naphthoquinodimethane (**NQDM**) diradical to the 2,7-naphthoquinone (**NQ**) diradical.¹³ However, in this case the ¹B₂ state is calculated to be 28.3 kcal/mol above the ³B₂ ground state in **NQDM**; whereas, the ¹A₁ state of **NQDM** is computed to

be only 5.5 kcal/mol above the $^3B_2$ ground state. Consequently, although the $^1B_2$ state is calculated to be stabilized, relative to $^3B_2$, by 17.3 kcal/mol on going from **NQDM** to **NQ**, Figure 3 shows that the value of ΔE_{ST} is actually predicted to *increase* from $\Delta E_{ST} = 5.5$ kcal/mol in **NQDM** to $\Delta E_{ST} = 11.0$ kcal/mol in **NQ**.

Figure 3. ΔE_{ST} , calculated between the triplet ground state ($^3B_2$) and the lowest singlet state, $^1A_1$ in 2,7-naphthoquinodimethane (**NQDM**) and $^1B_2$ in 2,7-naphthoquinone (**NQ**).¹³

This predicted increase of 5.5 kcal/mol in ΔE_{ST} on the substitution of both methylene groups in **NQDM** by oxygens in **NQ**, provides a dramatic contrast to the decrease of 17.5 kcal/mol in ΔE_{ST} found experimentally for **TMM** $\rightarrow$ **OXA**. As a first step in testing this prediction for **NQDM** $\rightarrow$ **NQ**, we have obtained the NIPE spectrum of **NQ $\dot{\text{C}}^-$** , a distonic radical anion^{14,15} with potentially important applications in a variety of contexts. A careful analysis of the vibrational structure of the peaks that correspond to the two lowest singlet states of **NQ** confirms that, as predicted,¹³ the energy of the $^1B_2$ state is below that of the $^1A_1$ state. NIPES provides an experimental value of $\Delta E_{ST} = 12.7$ kcal/mol in **NQ**, which is about 2 kcal/mol larger than the calculated value of $\Delta E_{ST} = 11.0$ kcal/mol.¹³

Experimental Methodology

The negative ion photoelectron spectroscopy (NIPES) experiments were carried out at PNNL using an apparatus consisting of an electrospray ionization (ESI) source, a temperature controlled cryogenic ion trap, and a magnetic-bottle time-of-flight (TOF) photoelectron spectrometer.¹⁶ A 0.1 mM acetonitrile solution of 2,7-dihydroxynaphthalene, titrated with a small amount of NaOH dissolved in water, was prepared in a N₂ glovebox, and used to generate $\text{NQ}^{\bullet-}$ by electrospray under an N₂ atmosphere. The inert N₂ environment helps reduce unwanted radical reactions in solution and in the sprayed droplets, thus helping to generate strong and stable ion beams. The ESI conditions were optimized to ensure that the doubly deprotonated species, $\text{NQ}^{\bullet-}$, was a prominent peak in the mass spectrum. The ions generated by ESI were guided by quadrupole ion guides into the ion trap, where they were accumulated and cooled for 20 – 100 ms by collisions with cold buffer gas (20% H₂ balanced in helium) at 20 K, before being transferred into the extraction zone of a TOF mass spectrometer. The cooling of the anions to 20 K improved the spectral energy resolution and minimized the possibility of the appearance of peaks in the NIPE spectra resulting from hot bands (see Supporting Information, as well as Ref.16).

The $\text{NQ}^{\bullet-}$ ions were then mass selected and maximally decelerated before being photodetached. In the current study, photon energies of 193 nm (6.424 eV) from an excimer laser, 266 nm (4.661 eV) and 355 nm (3.496 eV) from a Nd:YAG laser, and 240 nm (5.166 eV) and 300 nm (4.133 eV) from doubling frequency of 480 nm and 600 nm photons from an OPO/OPA laser were used. The lasers were operated at a 20 Hz repetition rate, with the ion beam off at alternating laser shots, in order to enable shot-to-shot background subtraction. Photoelectrons were collected with ca. 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 NIPE spectra of Γ^- ,¹⁷ Au^- ,¹⁸ OsCl_6^{2-} ,¹⁹ and thiophenoxide.²⁰ The electron-binding energy (EBE) was obtained by subtracting the electron kinetic energy from the energy of the detaching photons. The energy resolution was about 2% (i.e., ~ 20 meV for 1 eV kinetic-energy electrons).

Computational Methodology

Geometries were optimized and vibrational analyses were performed with (12/12)CASSCF calculations, in which all twelve of the π electrons were correlated by distributing them among five bonding, two non-bonding, and five antibonding π molecular orbitals (MOs). These calculations were carried out with the aug-cc-pVDZ basis set.^{21,22}

In order to include the effects of dynamic electron correlation,²³ (12/12)CASPT2 calculations²⁴ were performed, and the CASSCF geometries were reoptimized at this level of theory. For these calculations the aug-cc-pVDZ basis set was also used. Additional calculations with the aug-cc-pVTZ showed that basis-set expansion had a negligible effect on the computed, relative energies of the electronic states.¹³

All of the CASSCF and CASPT2 calculations were performed with the MOLCAS (version 8.0) suite of programs.²⁵ The fully optimized CASSCF and CASPT2 geometries and the CASSCF zero-point energies are available in the Supporting Information for this manuscript.

Simulations of the vibrational structures in the NIPE spectra, based on Franck–Condon Factors (FCFs), were performed using the ezSpectrum (version 3.0) program developed by Mozhayskiy and Krylov.²⁶ The necessary equilibrium geometries, harmonic vibrational frequencies, and normal mode vectors for NQ^- and NQ were obtained from the CASPT2/aug-cc-pVDZ calculations.

Results and Discussion

The NIPE Spectra of $\text{NQ}^{\bullet-}$

The NIPE spectra of $\text{NQ}^{\bullet-}$, obtained with 193, 240, 266, 300, and 355 nm photons, are shown in Figures 4(a), (b), (c), (d), and (e), respectively. Spectrum 4a, obtained with 193 nm photons, shows a first band with an electron binding energy (EBE) of 2.8 to 3.3 eV, followed by a series of complex bands, until the detachment threshold at 6.4 eV is reached. The first two bands are marked as X, and A. The intensity of band X is higher than that of band A in the 193 nm spectrum.

Figure 4. The 20 K NIPE spectra of $\text{NQ}^{\bullet-}$ at (a) 193, (b) 240, (c) 266, (d) 300, and (e) 355 nm. The origins of the bands for what appear to be the first two electronic states of NQ are marked X and A. Bands * and # are most likely due to resonant autodetachment (AD) (see text for details).

In the 240 nm spectrum (Figure 4b), the intensity of band A has increased dramatically, making it the highest peak. An additional small peak starts to show up between band X and A, at ~ 3.06 eV, and is marked with an asterisk (*). The spectrum intensity on the higher binding energy side of band * increases with it and fills the gap between the X and A bands. The peak at

~3.63 eV also gains more intensity, and is marked with a hash (#). The EBEs of the origins of band X and A in the 240 nm spectrum are measured to be 2.88 and 3.43 eV, respectively.

At 266 nm, the intensity of band A has increased even more significantly (Figure 4c). The intensities of both peaks at ~3.06 eV and 3.6 eV, however, become lower. The EBE of the first peak of band # decreases from 3.63 eV at 240 nm to 3.60 eV at 266 nm.

In the 300 nm spectrum in Figure 4d, band X, band *, band A, and band # show similar relative intensities as at 240 nm. Band A is stronger than band X. Bands * and # show stronger intensity than in the 266 nm spectrum. The peak in band * at 3.06 eV has become only slightly lower than band X; band #, located at $EBE = 3.605$ eV, has become so strong that it has equal height as band A.

The 355 nm spectrum in Figure 4e has the highest energy resolution, and shows some clearly resolved vibrational peaks. The feature at $EBE = 3.07$ eV has become the strongest peak in the spectrum, and the envelope of band X has completely changed.

Taken together, the five NIPE spectra displayed in Figure 4 show that the relative intensities of bands X, A, *, and # vary considerably at different detachment photon energies. There is no monotonic relationship between detachment photon energy and the peak intensity. The spectral feature at $EBE \approx 3.06$ eV, first appears with similar intensity as X in the 240 nm spectrum (Figure 4b), then becomes weaker in the 266 nm spectrum, and stronger again at 300 nm. In the spectrum at 355 nm, in Figure 4e, this peak becomes the dominant one. Resonant autodetachment (AD) may contribute to the bands at $EBE \sim 3.06$ and ~ 3.6 eV, and it will be discussed later.

Calculated NIPE Spectrum and the Vibrational Progressions in It

Geometries and Energies of the Electronic States of $\text{NQ}^{\bullet-}$ and NQ

The CASPT2 geometries of the two lowest electronic states of $\text{NQ}^{\bullet-}$ and the three lowest electronic states of NQ are given in Table 1, and their relative energies are provided in Table 2. The CASPT2 results for NQ have been previously published¹³ and are given here for comparison with those for $\text{NQ}^{\bullet-}$. In Table 2 the relative CASPT2 energies are also compared with the experimental values, obtained from the NIPE spectra.

Figure 5. Definitions of the bond lengths in NQ .

Table 1. (12/12)CASPT2 C–C and C–O bond lengths (Å) in the $^2\text{A}_2$ and $^2\text{B}_1$ states of $\text{NQ}^{\bullet-}$ and the $^3\text{B}_2$, $^1\text{A}_1$, and $^1\text{B}_2$ states of NQ , optimized using the aug-cc-pVDZ basis set. The bond lengths are defined in Figure 5.

R State	R1	R2	R3	R4	R5	R6	R7
$^2\text{A}_2$	1.273	1.457	1.423	1.438	1.426	1.391	1.455
$^2\text{B}_1$	1.279	1.426	1.422	1.464	1.432	1.380	1.479
$^3\text{B}_2$	1.255	1.456	1.416	1.453	1.434	1.379	1.470
$^1\text{A}_1$	1.269	1.439	1.434	1.415	1.445	1.374	1.465
$^1\text{B}_2$	1.242	1.476	1.407	1.490	1.421	1.389	1.476

As shown in Table 2, $\text{NQ}^{\bullet-}$ is calculated to have a $^2\text{A}_2$ ground state, but with a $^2\text{B}_1$ excited state lying only 0.28 eV above it. In the former state of $\text{NQ}^{\bullet-}$ the a_2 π non-bonding (NB) MO is singly occupied, and the b_1 π NBMO is doubly occupied; and in the latter state the a_2 NBMO is doubly occupied and the b_1 NBMO is singly occupied. Removal of the appropriate electron from the doubly occupied NBMO in either state of $\text{NQ}^{\bullet-}$ gives rise to the $^3\text{B}_2$ ground state of NQ . The a_2 and b_1 NBMOs of the $^3\text{B}_2$ state are shown in Figure 6.

Table 2. CASPT2/aug-cc-pVDZ relative energies (ΔE in eV) of the low-lying electronic states of $\text{NQ}^{\bullet-}$ and NQ , including CASSCF/aug-cc-pVDZ zero-point energy corrections. The assignments of the three major peaks in the NIPE spectrum of $\text{NQ}^{\bullet-}$ and the experimental electron binding energy (EBE) (eV) of each are given for comparison with the CASPT2 energies. Relative energies of the low-lying electronic states, with reference to the ground state of NQ ($\Delta E'$ in kcal/mol) are also presented.

	$^2\text{A}_2$	$^2\text{B}_1$	$^3\text{B}_2$	$^1\text{B}_2$	$^1\text{A}_1$
Wave function	$ \text{b}_1^2\text{a}_2\rangle$	$ \text{b}_1\text{a}_2^2\rangle$	$ \text{b}_1\text{a}_2(\alpha\beta+\beta\alpha)\rangle$	$ \text{b}_1\text{a}_2(\alpha\beta-\beta\alpha)\rangle$	$ \text{b}_1^2\rangle - \text{a}_2^2\rangle$
ΔE (CASPT2, eV)	0	0.28	2.98	3.45	3.53
NIPES Peak, EBE (eV) ^a			X, 2.88(1)	A, 3.43(1)	3.59
$\Delta E'$ (CASPT2, kcal/mol)				11.0	12.9
$\Delta E'$ (NIPES, kcal/mol)				12.7	16.4

^a The numbers in parentheses represent experimental uncertainty in the last digits. The $EBE = 3.59$ eV for $^1\text{A}_1$ is an estimated value.

Figure 6. The a_2 and b_1 NBMOs of the $^3B_2$ ground state of **NQ**

Assignment of the NIPE Spectra

The calculated CASPT2/aug-cc-pVDZ energy of the $^3B_2$ state of **NQ** of 2.98 eV, relative to the $^2A_2$ ground state of **NQ**⁺, is in good agreement with the experimental value of $EBE = 2.88$ eV of band X in the NIPE spectrum. However, due to the appearance of the features * and # and the considerable change in the relative peak intensities at different energies of the detaching photons, the assignment of the peaks in the NIPE spectrum is not straightforward. In order to obtain a convincing assignment of the peaks, the origins of features * and # need to be explained.

The 355 nm NIPE spectrum shows a series of well resolved peaks, with the predominant peak being band *, which is located at $EBE = 3.07$ eV. Does the lower intensity of band X, relative to band *, in the 355 nm NIPE spectrum come from band X being a hot band? An experiment that assessed the temperature dependence of the 355 nm NIPE spectrum was performed, in order to test this possibility. The NIPE spectra with 355 nm photons at both room temperature (303K) and at low temperature (20 K) were taken and plotted together for comparison. (See Figure S4 in the Supporting Information). Comparison of these two spectra indicates that hot bands do, indeed, exist at 303K; but they only contribute to the threshold

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3 region between 2.8 to 2.85 eV below the energy of band X. The resolved peaks of band X at 355
4 nm in spectrum (e) of Figure 4 are not due to hot bands.
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8 Photodetaching fragments are another possible reason for the appearance of peaks * and
9 # in the NIPE spectra, and this possibility was checked by experiments with different photon
10 fluxes. NIPE spectra of $\text{NQ}^{\bullet-}$ with 266 nm photons were taken at photon fluxes of 0.01 mJ/pulse
11 and 0.11 mJ/pulse (Figure S5). If peaks * and # were due to detachment of daughter ions, formed
12 by photodissociation of the parent anion by the first photon, peaks * and # would be formed by a
13 process involving two photons. Therefore, significant intensity changes in the 266 nm NIPE
14 spectrum should be observed as the photon flux is changed an order of magnitude. However,
15 Figure S5 shows that essentially same spectrum was obtained for the two different photon fluxes.
16 This observation indicates that the appearance of the NIPE spectrum is overwhelmingly dictated
17 by a one-photon process, and it thus rules out the possibility of a photodetaching fragment
18 process.
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34 **Resonant Autodetachment and Direct Electron Detachment in $\text{NQ}^{\bullet-}$**

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37 Based on the above experimental evidence, which rules out hot bands and two-photon
38 processes as being responsible for bands * and # in the NIPE spectrum in Figure 4, we believe
39 that the most likely explanation of their origin is that they come from resonant autodetachment in
40 $\text{NQ}^{\bullet-}$. Resonant autodetachment from an anion occurs by a pathway that is different from
41 formation of the corresponding neutral molecule by direct electron loss. In resonant
42 autodetachment, photoexcitation leads to creation of an excited electronic state of the anion,
43 from which electron loss subsequently occurs. Such a pathway gives 'extra' bands in NIPE
44 spectra, bands that are higher in energy than the threshold for direct electron loss. The
45 contribution of these extra bands to a NIPE spectrum depends on the energy of the laser that is
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used for electron photodetachment, since resonant autodetachment bands are strongest when the laser energy matches the energy of an excited state from which autodetachment occurs.

Such 'extra' bands, due to resonant autodetachment, have been observed before in NIPE spectra. For example, the 266 nm NIPE spectrum of C_{60}^- shows an extra band at 3.7–4.0 eV, a region that is supposed to be "clean", because it lies between the energy of the singlet and triplet state of C_{60} .²⁷ Autodetachment from resonant excited states is commonly observed in the anions of aromatic organic molecules. Weinkauff and Schiedt studied resonant autodetachment from the anion of *p*-benzoquinone at 0.15–0.65 eV above the direct detachment threshold, and they showed that the resonant autodetachment, not direct excitation into the continuum, is responsible for the bands in this region.²⁸ Lineberger and co-workers found the appearance of autodetachment peaks at a laser wavelength of 351 nm and disappearance of those peaks at a laser wavelength of 364 nm in the NIPES study of phenoxide.²⁹ Very recently, Verlet et al. studied resonant autodetachment in the anthracenyl anion, and they showed that a number of π^* resonances are active in leading to electron loss in the first 2.5 eV above the threshold.³⁰

We believe that in the $NQ^{\bullet-}$ radical anion, electronic transitions from the $^2A_2$ ground state to certain excited states of the anion, followed by electron loss, give rise to the autodetachment bands at $EBE = 3.06$ eV (*) and $EBE = 3.63$ eV (#) in the NIPE spectra in Figure 4. However, we assign bands X and A in the NIPE spectrum of $NQ^{\bullet-}$ to direct electron detachment from the ground state of the radical anion to, respectively, the ground state and a low-lying excited state of neutral NQ .

On the basis of good agreement in Table 2 between the CASPT2 EBE of the $^3B_2$ state of NQ and the EBE measured for peak X in the NIPE spectrum of $NQ^{\bullet-}$, we can confidently assign band X in the NIPE spectra to the direct transition from the $^2A_2$ ground state of $NQ^{\bullet-}$ to the $^3B_2$

ground state of neutral **NQ**. Band A is thus, presumably, due to formation of an excited singlet electronic state of **NQ**. We tentatively assign band A to formation of the $^1B_2$ state, since it is calculated to be lower in energy than the $^1A_1$ state.

However, the calculated CASPT2 energy difference between $^1B_2$ and $^1A_1$ is small, amounting to only 1.9 kcal/mol. Therefore, we performed Franck-Condon (FC) simulations of the NIPE spectra of **NQ**^{•-}, in order to make a more convincing assignment of $^1B_2$ or $^1A_1$ as being responsible for peak A in the experimental spectrum.

Franck-Condon Simulation of the NIPE Spectra

The FC simulations were performed with the ezSpectrum program, using the CASPT2/aug-cc-pVDZ optimized geometry, vibrational frequencies, and normal mode vectors for each electronic state. The $^2A_2$ ground state of **NQ**^{•-} was taken as the initial state, and the three, low-lying states of **NQ** – $^3B_2$, $^1B_2$, and $^1A_1$ – were each taken as the final state. The results of the FC simulations are shown in Figure 7.

In Figure 7 the energy and the intensity of the 0–0 peak in the vibrational progression computed for each state have been adjusted to match those in experimental spectrum. The full-width-half-maxima (FWHM) of the simulated peaks were set to match the experimental resolution. Because the experiment was performed at low temperature (20 K), no peaks from hot bands appeared in the FC simulations.

The spectra obtained with 355 nm photons show the strongest * peak. Consequently the resonant autodetachment that gives rise to this peak resonance is likely to alter the intensities of vibrational bands in the nearby X peak. Therefore, only the spectra obtained with 240 nm, 266 nm, and 300 nm photons are used in Figure 7 for comparison with the FC simulations. The

comparison of the 355 nm spectrum with the FC simulations of it and the assignment of the observed peaks in this spectrum are given in the Supporting Information.

On the basis of the comparison of the calculated *EBEs* and FC intensities, with those in the experimental NIPE spectrum, the 0-0 transitions within bands X and A can be confidently assigned to the $^3B_2$ and $^1B_2$ states respectively, giving experimental values of $EBE = 2.88$ eV for the triplet and $EBE = 3.43$ eV for the lowest singlet state. However, the assignment of the 0-0 transition in $^1A_1$ is more difficult, due to the complexity of the spectra and the size of the gap between $^1B_2$ and $^1A_1$ states, which is calculated to be small. The peak for the 0-0 band of the $^1A_1$ state is probably buried under the A and # bands.

By carefully comparing the NIPE spectra at different photon energies, we find some clues about the location of the 0-0 peak for $^1A_1$ from the difference in the appearance of the # band. The *EBE* of the first small peak of the # band is 3.63 eV in the 240 nm spectrum, but 3.60 eV in the 266 nm spectrum, and 3.605 eV in the 300 nm spectrum. The ~ 30 meV *EBE* difference may be caused by the presence of the $^1A_1$ state. By carefully moving the $^1A_1$ state location, changing its intensity, and comparing the experimental spectrum with the simulated spectrum, the 0-0 transition of $^1A_1$ has been provisionally located at 3.59 eV.

However, the assignment of the *EBE* of $^1A_1$ is challenging. For example, if the $^1A_1$ peak is shifted closer to the $^1B_2$ peak, reducing the gap between the two states to 2.7 kcal/mol, the simulated spectrum could also fit the experimental spectrum at a similar level of quality as in Figure 7. (see Figure S1 in the SI). However, $EBE = 3.59$ eV is still the best estimation for the position of the 0–0 transition in the $^1A_1$ state.

Figure 7. Simulated NIPE spectra for formation of the three lowest electronic states of NQ, using the calculated CASPT2/aug-cc-pVDZ stick spectra, convoluted with Gaussian line broadening. The simulated spectra are superimposed onto the experimental spectra of NQ^{•-} at (a) 240 nm, (b) 266 nm, and (c) 300 nm. The simulated peak intensities and positions of the 0-0 bands have been adjusted to match those in the experimental spectrum. The FWHMs of Gaussians for $^3B_2$, $^1B_2$, and $^1A_1$ peaks are set to 60, 50, 50 meV at 240 nm; 50, 35, 35 meV at 266 nm; and 45, 35, 35 meV at 300 nm, respectively. The energy difference between $^1B_2$ and $^1A_1$ is set to 3.7 kcal/mol.

The simulated spectra with 240 nm, 266 nm, and 300 nm photons are displayed in Figure 7, together with the experimental NIPE spectra for comparison. The CASPT2/aug-cc-pVDZ simulated spectrum at 193 nm, and more simulations using different theoretical methods [i.e., (12/12)CASSCF and B3LYP], are given in the SI of this manuscript. Overall, the simulated NIPE spectra provide a good fit to the experimental spectra, except for the peaks * and #, which we believe are due to resonant autodetachment. The energies, derived from the NIPE spectrum, of the two singlet states of **NQ**, relative to the triplet ground state, are listed in Table 2. The experimental value of ΔE_{ST} is estimated to be 0.55 eV = 12.7 kcal/mol. The previously calculated value of the energy difference between $^3B_2$ and $^1B_2$ states of $\Delta E_{ST} = 11.0$ kcal/mol agrees well with this experimental value.

The experimental *EBE* of the $^1A_1$ state is, as discussed above, less reliable than the *EBEs* of the $^3B_2$ and $^1B_2$ states. The *EBE* of $^1A_1$ is estimated to be 3.59 eV, which is 0.71 eV (16.4 kcal/mol) higher than that of the $^3B_2$ ground state and 0.16 eV (3.7 kcal/mol) higher than that of the $^1B_2$ state. The calculated CASPT2 energy differences are, respectively, 12.9 kcal/mol and 1.9 kcal/mol.

As shown in Figure 7, the FC simulations find that, of the two **NQ** singlet states, the open-shell singlet $^1B_2$ state is calculated to have the longer vibrational progression. It is easy to see that the green $^1B_2$ peaks extend over a much wider binding energy range than the purple $^1A_1$ peaks. The reason is that, as shown in Table 1, the difference in geometry between the $^1B_2$ state of **NQ** and the $^2A_2$ state of **NQ**^{•−} is larger than the difference between $^1A_1$ and $^2A_2$; and large changes in geometry between radical anion and neutral give rise to long vibrational progressions.

In particular, as shown in Table 1, the C=O bond lengths (R_1) are calculated to be 0.027 Å shorter in $^1B_2$ than in $^1A_1$. The greater change in the C=O bond lengths should result in a longer progression in the symmetrical C=O stretching mode in the peaks for formation of $^1B_2$ than of $^1A_1$. This predicted difference between the two singlet states provides, at least in principle, a way to distinguish between them in the NIPE spectrum of $NQ^{\bullet-}$.

Summary and Conclusions

NIPE spectra of $NQ^{\bullet-}$ have been taken at 20 K, using 193, 240, 266, 300, and 355 nm lasers for electron photodetachment. CASPT2/aug-cc-pVDZ calculations predict with reasonable accuracy the *EBEs* of the 0–0 bands in the three lowest electronic states of NQ . In addition, the FCFs, calculated from the CASPT2/aug-cc-pVDZ optimized geometries, vibrational frequencies, and normal modes, successfully simulate the appearance of the first two of these three bands.

The following assignments of the *EBEs* of the electronic states of NQ in the NIPE spectrum of $NQ^{\bullet-}$ have been made on the basis of the simulations of the NIPE spectra in Figure 7. Peak X at $EBE = 2.88$ eV is the origin of the $^3B_2$ state; peak A at $EBE = 3.43$ eV is the origin of the $^1B_2$ state; and the origin of the $^1A_1$ state is estimated to have $EBE = 3.59$ eV. These assignments of the bands in the NIPE spectrum confirm that, as predicted,¹³ NQ has a $^3B_2$ triplet ground state, and the energy of the $^1B_2$ state is slightly lower than that of the $^1A_1$ state. NIPES provides an experimental value of $\Delta E_{ST} = 12.7$ kcal/mol in NQ , about 1.7 kcal/mol larger than the CASPT2 calculated value of $\Delta E_{ST} = 11.0$ kcal/mol,¹³ and the $^1B_2$ – $^1A_1$ gap = 3.7 kcal/mol, which is about 1.8 kcal/mol larger than the calculated value.

The experimental NIPE spectrum of $NQ^{\bullet-}$ gives not only the same state ordering as that predicted by the calculations in Reference 13, but also energetic separations between the states

that are similar to those predicted by these calculations. Consequently, the experimental NIPE spectrum of $\text{NQ}^{\bullet-}$ provides evidence, albeit circumstantial, that these calculations are likely also to have also predicted correctly the still experimentally unknown NIPE spectrum of $\text{NQDM}^{\bullet-}$.

Obtaining the latter NIPE spectrum is, of course, necessary, in order to fully test the prediction that the substitution of both methylene groups in NQDM by the oxygens in NQ will be found to *increase* ΔE_{ST} , rather than to *decrease* ΔE_{ST} by 17.5 kcal/mol, as has been found to be the case for $\text{TMM} \rightarrow \text{OXA}$,^{7,8} or to leave ΔE_{ST} almost unchanged, as has been found to be the case for $\text{MQBDM} \rightarrow \text{MBQ}$.⁹⁻¹¹

Supporting Information. (12/12)CASSCF and CASPT2 optimized geometries, energies, frequencies, and thermal corrections for the low-lying states of NQ and $\text{NQ}^{\bullet-}$; Simulated NIPE spectrum with a different $^1\text{B}_2$ and $^1\text{A}_1$ separation (2.7 kcal/mol); Simulated NIPE spectra using different levels of theory, i.e., (12/12)CASPT2, (12/12)CASSCF, and B3LYP; Simulated 193 nm and 355 nm spectrum and assignment of the vibrational peaks in the 355 nm spectrum; Comparison of the hot (303 K) and cold (20 K) 355 nm spectrum; Comparison of the 266 nm spectra with different photon fluxes.

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Notes

The authors declare no competing financial interest

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