Substitution effects on the absorption spectra of nitrophenolate isomers†

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Charge-transfer excitations highly depend on the electronic coupling between the donor and acceptor groups. Nitrophenolates are simple examples of charge-transfer systems where the degree of coupling differs between ortho, meta and para isomers. Here we report the absorption spectra of the isolated anions in vacuo to avoid the complications of solvent effects. Gas-phase action spectroscopy was done with two different setups, an electrostatic ion storage ring and an accelerator mass spectrometer. The results are interpreted on the basis of CC2 quantum chemical calculations. We identified absorption maxima at 393, 532, and 399 nm for the para, meta, and ortho isomer, respectively, with the charge-transfer transition into the lowest excited singlet state. In the meta isomer, this π–π* transition is strongly redshifted and its oscillator strength reduced, which is related to the pronounced charge-transfer character, as a consequence of the topology of the conjugated π-system. Each isomer’s different charge distribution in the ground state leads to a very different solvent shift, which in acetonitrile is bathochromic for the para and ortho, but hypsochromic for the meta isomer.

1 Introduction

We have recently investigated the intrinsic optical properties and solvatochromism of a series of extended p-nitrophenolates by state-of-the-art gas-phase action spectroscopy and quantum chemical calculations.3 These compounds are text book examples of donor–acceptor chromophores with the phenolate oxygen as a donor group and the nitro as an acceptor group. The position of the charge-transfer (CT) excitation in the absorption spectrum was found to depend strongly on the π-conjugated spacer between the donor and acceptor groups. Thus, extending the spacer resulted in a bathochromically shifted CT excitation, which we ascribe to an increased conjugation at both ends of the molecule—the donor and acceptor groups—along with a decreased electronic coupling between them. Moreover, we found that one has to be very careful in relating solution absorption characteristics of these anionic chromophores to their intrinsic absorption properties. Thus, chromophores may show a different progression of absorption maxima in solution relative to that observed in the gas phase. In the monodisperse oligomer approach, the optical properties of a series of conjugated oligomers are usually investigated in solution and from extrapolation of these data, the properties of an infinite polymer are predicted.4,5 For charged compounds, such as phenolates, solution experiments may provide misleading results.

As a continuation of our work on nitrophenolates, we have now turned to the three possible substitution motifs, p-, m-, and o-nitrophenolate. The new fundamental questions we seek to answer in this work are how substitution determines the donor–acceptor coupling, i.e., mixing of donor HOMO with acceptor LUMO, and how this coupling affects the intrinsic absorption characteristics and the sensitivity to solvent effects.

2 Experimental

We used two different experimental setups for our action spectroscopy measurements, which are complementary in the covered range of wavelengths, the kind of fragments that are detected, and the fragmentation time window. Compounds for both experiments were purchased from Sigma-Aldrich.

2.1 ELISA experiments

These were carried out at the electrostatic ion storage ring in Aarhus (ELISA).6,7 Electrospray ionization was used to produce...
the ions that were subsequently accumulated in a 22-pole ion trap and thermally equilibrated by collisions with a helium buffer gas therein. The ions were accelerated in a bunch to kinetic energies of 22 keV, and a bending magnet was used to select the appropriate ions according to their mass-to-charge ratio. The revolution time of the ions in the ring is ca. 50 μs. Following injection into the ring, the ions were stored for about 40 ms before being irradiated by a nanosecond light pulse from a tunable EKSPLA laser. This is an Nd:YAG laser where the third harmonic (355 nm) pumps an optical parametric oscillator (OPO). The visible output from this OPO is frequency doubled in a crystal, providing UV light. The repetition rate of the experiment was 10 Hz. Lifetimes were obtained from measurements of the yield of neutrals hitting a microchannel plate (MCP) detector located at the end of the straight section opposite to the side where photoexcitation was performed. From fits to the spectrum, it is possible to extrapolate back to time zero, defined as the time when the laser was fired, to obtain the total number of photoexcited ions for each wavelength used (relative, not absolute, number) and subsequently deduce the absorption from this information by normalizing to both the average number of photons in the laser pulses and the neutrals yield prior to photoexcitation.

2.2 Sep1 experiments

In this setup, operating at a repetition rate of 40 Hz, the yield of fragment ions was monitored as a function of excitation wavelength, up to 10 μs after photoexcitation in a single pass experiment. Ions were again produced by electrospray ionization and accumulated in a 14-pole ion trap. An ion bunch was accelerated to 50 keV energies and appropriate ions were selected by a magnet. These were photoexcited by light from a similar laser system as that used at ELISA, again in a merged beam configuration. The laser was operated at 20 Hz, irradiating every second ion bunch, so that the difference signal—“laser on” minus “laser off”—could continuously be measured. The shortest wavelength that the laser provides is 420 nm. An electrostatic analyzer allowed NO$_2^-$ or ions that had lost NO to reach a channeltron detector where they were counted. The yields of these two ion fragments were summed to obtain the action spectra.

It is important to keep the differences between the two setups in mind. In the ELISA experiment, slow delayed dissociation is monitored after one-photon absorption, whereas in the Sep1 setup, fast dissociation is monitored after non-coherent absorption of two photons (see Section 5.1). Also the photo-induced signal (the action) is measured in different ways: in the ring experiment, the sum of neutrals formed from all the dissociation channels is sampled, whereas in the other setup, a single dissociation channel, involving one ionic fragment with a particular mass-to-charge ratio, is sampled in one experiment.

3 Computational details

Ground-state geometries were optimized using the MP2 level of theory and the TZVPP basis set. Theoretical calculations were performed using the linear-response CC2 coupled-cluster model and the aug-cc-pVDZ basis set, if not denoted otherwise. These calculations were done with turbomole code. CC2 has been successfully applied to $p$-nitrophenolates of different sizes before. To validate the CC2 results for the meta isomer and study solvent shifts, the $ab$ initio multi-reference method SORCl was used in combination with the aug-cc-pVDZ basis set and the SV(P) basis set augmented with diffuse functions of the aug-cc-pVDZ set, as implemented in the ORCA program package. The MR-DDC12 calculation that produces the average natural orbitals employed a CAS(6,4) reference of the frontier π-orbitals, truncated with $T_{pre} = 10^{-3}$. In the final MR-DDC13 + Q calculation, the entire π-electron system is included in a RAS(12; 5 / 2 / 3 2) reference. Thresholds $T_{nat}$ and $T_{sel}$ were both set to $10^{-6}$. For calculations of solvent shifts, geometries were optimized in the presence of the COSMO reaction field, using the PBE0 hybrid functional and the TZVP basis set. Electron vertical detachment energies (VDE) at the CCSD(T) level of theory were calculated using the aug-cc-pVDZ basis set and the ORCA code. TDDFT absorption energies can be found in the ESI.

4 Results

4.1 Gas-phase spectra

Fig. 1 shows the absorption spectra of the three nitrophenolate isomers in vacuo, as obtained from the two experimental setups, together with the results of theoretical calculations at the CC2 level. The two experiments resolve different features of the absorption spectrum, each of which would lead to different conclusions when considered alone. The ELISA spectra of the three isomers show one broad band that peaks at 393 nm (3.15 eV, para), 363 nm (3.42 eV, meta), and 399 nm (3.11 eV, ortho), respectively. The spectra obtained from the combined fragment ion yields in the Sep1 experiment differ in several aspects. The para- and ortho-isomer spectra show bands peaking at 434 nm (2.86 eV) and 453 nm (2.74 eV), respectively, hence are significantly red-shifted compared to the ELISA spectra. The meta-isomer spectrum shows a very broad band peaking at 532 nm (2.33 eV), which is not resolved in the ELISA spectrum and is strongly red-shifted compared to the bands of para and ortho isomers. This is in contrast to the blue-shifted feature visible in the ELISA spectrum of the meta isomer. The neutral and fragment ion yields are arbitrarily scaled, hence the relative intensities of the features are unknown.

In the ELISA data for the meta isomer, the 532 nm (2.33 eV) band cannot be distinguished from the background counts. In the case of the para and ortho isomers, neither experiment detects absorption for wavelengths longer than 500 nm (2.48 eV). The lowest band in these two isomers shows the same onset in both experiments, but is broadened and/or red-shifted in the Sep1 experiment, which does not cover the entire band due to the wavelength limitation.

Theoretical calculations at the CC2 level find only one low-lying dipole-allowed transition for the para and the ortho isomer. Its energy reproduces the absorption maximum of the ELISA spectrum with great accuracy. This allows a safe assignment of
the experimental band to the $S_0$–$S_1$ transition. The $S_1$ state is dominated by the $\pi^*\pi^*$ singly-excited configuration involving the frontier $\pi$ orbitals. The oscillator strength is smaller for the ortho isomer by a factor of three.

The theoretical spectrum of $m$-nitrophenolate agrees perfectly with the Sep1 spectrum, but does not reproduce the feature that dominates the ELISA spectrum. Vertical excitation into the $S_1$ state, which is the lowest $\pi^*\pi^*$ excited state, is predicted at 515 nm (2.41 eV), with an oscillator strength (0.03) smaller by a factor of 5-7 compared to the ortho isomer. Hence, the $S_0$–$S_1$ excitation in $m$-nitrophenolate is predicted to be weak and significantly red-shifted. The reason for this redshift and the differences in the experimental data will be discussed below.

Theoretical calculations at the DFT and MP2 level yield planar para and meta isomers. For ortho, MP2/TZVP finds a non-planar minimum 0.4 kcal mol$^{-1}$ below the planar transition state. Due to the flatness of the potential energy surface, the O–N–C–C dihedral angle depends strongly on the method (HF: 4°, PBE0: 13°, PBE: 18°, MP2/aug-cc-pVTZ: 26°). In the MP2/TZVP geometry, used for the spectra calculations, the dihedral is 31° and thus somewhat larger than that at the basis set limit of MP2. The effect of non-planarity on the spectrum, however, is limited. As shown in Fig. 1, the $S_1$ excitation is red-shifted by 0.11 eV (14 nm) and an energetically close $n^*-\pi^*$ transition, which is dipole forbidden in the planar geometry, borrows some oscillator strength from the $\pi^*\pi^*$ state.

![Fig. 1](image1.png) Measured and calculated absorption spectra of the nitrophenolate isomers in vacuo. Neutral yields from the ELISA experiment are compared with joined fragment ion yields from the Sep1 experiment and theoretical excitation energies. Theoretical vertical detachment energies from Table 2 are indicated by orange lines.

The theoretical spectra also show two strong transitions to resonant states above the ionization threshold (see Table 2 for VDE’s), which are missing in the ELISA spectra. In all three systems, there is a dipole-forbidden $n^*-\pi^*$ state below the VDE.

To test whether non-planarity affects states in the region of the experimental absorption spectra of $m$-nitrophenolate, we performed CC2 calculations on geometries with varying O–N–C–C dihedral (Fig. 2). With increasing twist, the $S_0$–$S_1$ transition is blue-shifted, reaching 472 nm (2.63 eV) at 45°, which is still far lower in energy than the prominent feature in the ELISA spectrum. Further twist is energetically prohibitive and has little effect on the excitation energies. Note that the oscillator strength of the $S_0$–$S_1$ transition does not change with non-planarity and that the $n^*-\pi^*$ transition is still not visible. Therefore, we exclude the possibility of a strongly blue-shifted $S_1$ state due to non-planarity at room temperature. The latter rather leads to a broadening of the spectrum, as can be seen in the solution spectrum (see below).

4.2 Solution spectra

Absorption spectra of the three isomers in acetonitrile solution are shown in Fig. 3, together with the computed gas-phase line spectra. The lowest band maxima are located at 430 nm (2.88 eV, para), 473 nm (2.62 eV, meta), and 443 nm (2.80 eV, ortho), respectively. Furthermore, three bands are visible in the near-UV, which are not observed in the gas-phase experiment.

Apart from the expected solvent shifts, the experimental solution spectra agree surprisingly well with the theoretical gas-phase spectra, including the meta isomer. Both energies and oscillator strengths are reproduced for the $S_1$ state as well as for the states in the near-UV region (experimental absorptivities are arbitrarily scaled). In particular, the $m$-nitrophenolate solution spectrum confirms the red-shifted and weak $S_1$ transition, which is visible in the Sep1 spectrum and predicted by theory. Note that the $S_1$ band and the second peak in the near-UV band are red-shifted compared to the theoretical excitation energies for the ortho and para isomers. For $m$-nitrophenolate, a small blueshift occurs.

4.3 Theoretical solvent models for $m$-nitrophenolate

To further elucidate the discrepancies for the meta isomer between the ELISA data on the one hand and the theoretical gas-phase and experimental solvent and Sep1 gas-phase spectra...
on the other hand, we theoretically modeled the solvent effect on the S0–S1 absorption energy using a series of solvent models. For a number of 1–7 explicit solvent molecules, the lowest energy complex was determined using molecular dynamics and geometry optimization techniques. The bulk solvent was represented by the conductor-like screening model (COSMO). Table 1 shows the S1 excitation energies with and without the COSMO reaction field. It also shows the total binding energy \( E_{\text{bind}} \) of the acetonitrile molecules to the complex within the COSMO medium. \( E_{\text{bind}} \) accounts for effects missing in the COSMO model, like H-bond formation and QM effects. For 1–3 solvent molecules, the binding energies are largest for salt bridges to the phenolate group, which accepts up to 4 direct hydrogen bonds. Salt bridges to the nitro group are weak (O–H distance of 2.4–2.5 Å) and only two solvent molecules are bound simultaneously.

By excluding the bulk solvent from the calculation, the effect of microsolvation can be studied. As is expected from the excitation-induced CT (vide infra), hypsochromic shifts result each time when additional acetonitrile molecules are binding to the phenolate group (see Fig. 4). Salt bridges to the nitro group, in contrast, lead to bathochromic shifts. The picture changes when the bulk solvent is included (COSMO). The S1 energy converges rapidly to a value slightly above that obtained from the gas-phase calculation. Note that no explicit counter ion was included in the calculations. This procedure is justified by two observations. (1) In strongly polar solvents, the shift is widely independent from the exact position of the counter ion. (2) As reported previously,² the hypsochromic solvent shift of nitrophenolates in acetonitrile is grossly overestimated when including the counter ion explicitly but not any solvent molecules. Thus, including the counterion would not improve the convergence of the mixed QM/COSMO solvent model.

### Table 1 SORCI S1 excitation energies of m-nitrophenolate in acetonitrile

<table>
<thead>
<tr>
<th>( N_S )</th>
<th>( N_{\text{HB}}^{\text{CO}} )</th>
<th>( N_{\text{HB}}^{\text{NO2}} )</th>
<th>( E_{\text{bind}}^{\text{QM}} ) (kcal mol(^{-1}))</th>
<th>( S_1 ) (eV)</th>
<th>( \text{VDE} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0</td>
<td>0.0</td>
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<td>2.46</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>−0.9</td>
<td>2.15</td>
<td>2.30</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>−1.7</td>
<td>2.26</td>
<td>2.25</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>0</td>
<td>−2.3</td>
<td>2.37</td>
<td>2.15</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>1</td>
<td>−2.6</td>
<td>2.20</td>
<td>2.13</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>2</td>
<td>−2.9</td>
<td>2.05</td>
<td>2.15</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>2</td>
<td>−3.3</td>
<td>2.35</td>
<td>2.25</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>2</td>
<td>−3.9</td>
<td>2.37</td>
<td>2.23</td>
</tr>
</tbody>
</table>

Columns 1–3 contain the number of explicit solvent molecules, hydrogen bonds to the phenolate and to the nitro group. The bulk solvent is either excluded (vacuum) or represented by the COSMO model. All geometries were optimized in the presence of the COSMO reaction field. \( E_{\text{bind}}^{\text{QM}} \) is the binding energy inside the COSMO medium (no BSSE correction), which would be zero if the solvent model was exact.

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5 Discussion

5.1 Differences in the two gas-phase experiments

Different from the case of the meta isomer, the data from the ELISA and the Sep1 setups are consistent for p- and o-nitrophenolate, but the redshift in the Sep1 spectrum calls for an explanation and can be related to the different fragmentation processes and time windows monitored in the two setups.

The ELISA setup uses a weak laser field and measures neutrals produced essentially after 1-photon absorption, either due to slow fragmentation or electron autodetachment from the vibrationally hot ground state. The resulting spectrum may be quenched towards longer wavelengths if the photon energy is insufficient to overcome the fragmentation barrier and the ionization threshold. For short wavelengths, i.e., energies above the ionization threshold, fast electron detachment from excited resonance states may compete with internal conversion (IC) and quench the signal, because the neutrals would be produced before being deflected to the detection lap of the storage ring. The same applies to excited-state or fast ground-state fragmentation processes.

The Sep1 setup only detects fast dissociation channels, which result predominantly from the non-coherent absorption of two photons (Fig. S4 in ESI†), where the ns pulse duration allows for IC and vibrational energy redistribution, according
to mechanism (1). The Sep1 spectrum should therefore be associated with the convolution of the 1-photon cross-sections of the vibrationally hot and cold systems. This is not to be confused with coherent two-photon absorption processes where the photon energy is half the excitation energy.

\[ A^- \overset{hv}{\rightarrow} A^0 \overset{IC}{\rightarrow} A^+ \]

Neither neutrals nor free electrons are detected in the Sep1 experiment. Therefore, the Sep1 spectrum may be quenched by electron detachment, even below the ionization threshold, owing to the excess energy of the two absorbed photons. The electron detachment can occur (a) from the vibrationally hot excited state \((A_u^+ \rightarrow A^0 + e^-)\), competing with IC, or (b) as slow autodetachment from the vibrationally hot ground state \((A_u^- \rightarrow A^0 + e^-)\). Mechanism (b) has been suggested before to explain photodetachment spectra below the ionization threshold.18 Mechanism (a) might be relevant in the case of a resonance enhancement of the coupling between continuum and strongly allowed valence states, e.g., when the VDE is close to the vertical excitation energy of the \(S_0\)–\(S_1\) transition, as is the case for \(p\)- and \(o\)-nitrophenolate (see Table 2). This has been suggested to explain sub-microsecond decay of photoexcited anions of a model chromophore (pCA) of the photoactive yellow protein (PYP).19 The PYP chromophore has quite similar electronic properties with its frontier \(\pi\) orbitals partially localized on the donor (phenolate) and acceptor (propenoic acid) groups. Pump-probe experiments on another model of the PYP chromophore found evidence for the competition between IC and electron detachment at the ps timescale for the decay of a resonant state near the ionization threshold.20 On the other hand, IC was found after excitation into resonant states.21

The signal in the Sep1 experiment may also be quenched by electron detachment after single-photon absorption \((A_u^- \rightarrow A^0 + e^-)\). This process would be relevant for photon energies above the adiabatic detachment energy if IC is slow and the excited state is close to the continuum, which is the case for \(p\)- and \(o\)-nitrophenolate. This mechanism would best explain the observed quenching of the \(S_0\)–\(S_1\) absorption band towards shorter wavelengths (Fig. 1).

It is interesting to compare our results with another recent study on the methylated pCA model chromophore of PYP.22 Rocha-Rinza et al. measured the gas-phase absorption at ELISA using a different setup that allows illumination and neutral detection at the same lap of the ring, hence detecting neutrals from both electron detachment and fragmentation. The recorded spectra of different isomers show both valence and resonance states, but no additional features due to direct electron detachment, such as \(A^- \overset{hv}{\rightarrow} A^0 + e^-\). In particular, their \(meta\) spectrum shows no absorptivity in the region of the VDE. This indicates that the direct ionization channel has a negligible cross-section compared with that of transitions into valence or resonance states.

### 5.2 Assignment of the \(S_1\) state in \(m\)-nitrophenolate

When we associate the lowest band in the experimental solution spectrum with the band resolved in the Sep1 experiment, we obtain a hypsochromic solvent shift of +0.24 eV for acetonitrile. Our calculations predict a smaller shift of +0.05 eV, but this error can easily be accounted for by the same effects that cause the shifts in the yield maxima between the two experimental setups (see Section 5.1) and by the expected errors of the computational model (basis-set superposition and size-consistency errors). In view of the agreement between the theoretical calculations, the Sep1 data, the experimental solution spectra, and the small predicted solvent effect, we conclude that the 532 nm (2.33 eV) absorption band in the Sep1 spectrum originates from the \(S_0\)–\(S_1\) transition, whereas the dominant feature in the ELISA spectrum must be of different origin.

Rigorous tests of the methodological approach support this conclusion. The differences in the ground-state geometry of the \(meta\) isomer, which will be discussed in the next section, are confirmed at the DFT and at the CASSCF level of theory (see ESI†). Spectra calculated at the SORCI level of theory corroborate the CC2 data, showing a constant redshift of the \(S_1\) and higher-lying \(\pi^*\)–\(\pi^*\) states (see ESI†).

In none of the gas-phase spectra, the higher-lying bright resonant states are resolved that appear in the solution spectra and the theoretical data. Therefore, it must be explained why these bands do not appear in the gas-phase experiments with the \(ortho\) and \(meta\) isomers. The most likely reasons are rapid fragmentation and electron detachment, as discussed in Section 5.1. The hypothesis of electron detachment is supported by our calculations of the vertical detachment energies (Table 2), e.g., 2.98 eV (416 nm) for the \(ortho\) isomer. As the experimental spectrum extends to at least 3.65 eV (340 nm), IC competes with autodetachment from the \(S_1\) excited state in this energy region. The same situation has been observed in a recent study on the HBTDI chromophore of the green fluorescent protein.23 Also in negatively charged DNA strands of adenine, IC was found after excitation above the VDE.21

In solution, the VDE is considerably higher, e.g., for \(m\)-nitrophenolate in acetonitrile, employing the continuum-electrostatic COSMO model. PBE0 predicts a VDE of 4.95 eV (250 nm). Adding the six QM MeCN molecules that form salt-bridges to the chromophore, the VDE increases to 5.16 eV (240 nm). An additional MeCN molecule on top of the ring causes a further distinct blueshift. Completing the first solvation shell, the VDE can be expected to exceed 5.6 eV (220 nm), which is clearly above the intense bands in the near UV region of the solution spectrum.

In the absence of the bright resonant states and a clear \(S_1\) absorption band, the ELISA spectrum of the \(meta\) isomer lacks any reference for the absolute absorptivity and the physical origin of the feature peaking at 363 nm (3.42 eV)

### Table 2 Properties of the ground-state and the \(S_1\) excitation of nitrophenolate isomers

<table>
<thead>
<tr>
<th>Isomer</th>
<th>(S_1) (eV)</th>
<th>(f)</th>
<th>(\Delta H_{10}) (D)</th>
<th>VDE (eV)</th>
<th>(\Omega^{CD}_{\text{NPA}})</th>
<th>(\Omega^{NO}_{\text{NPA}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>para</td>
<td>3.21</td>
<td>0.53</td>
<td>5.2</td>
<td>3.33</td>
<td>0.25</td>
<td>0.61</td>
</tr>
<tr>
<td>meta</td>
<td>2.41</td>
<td>0.03</td>
<td>9.1</td>
<td>2.98</td>
<td>0.36</td>
<td>0.28</td>
</tr>
<tr>
<td>ortho</td>
<td>3.01</td>
<td>0.11</td>
<td>4.4</td>
<td>3.27</td>
<td>0.23</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>(3.12)</td>
<td>(0.21)</td>
<td></td>
<td>(3.1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Excitation energies, oscillator strengths, and difference-dipole moments from CC2. VDE from CCSD(T)/aug-cc-pVDZ (see Section 3). NPA fragment charges (see text) from HF/TZVP. Values for the planar (transition state) geometry of \(ortho\) are given in parentheses.
remains unclear. Our CC2 calculations find a dipole-forbidden resonant transition at 3.84 eV and transitions into diffuse states that are strongly basis-set dependent (Fig. S8 in the ESI), but any assignment to the feature peaking at 363 nm would be highly speculative.

Also the action spectroscopic study on the PYP model chromophore\textsuperscript{22} investigated the substitution effect. For the meta substitute, they find merely a weak and broad signal that they associate with the $S_1$ state, as predicted by their CC2 calculations. In contrast to our ELISA spectrum, they resolve higher-lying resonant states, which are also predicted by their CC2 calculations. Different from our ELISA spectrum, their meta-isomer spectrum does not show any absorbance in the region between $S_1$ and the resonant states, and therefore shows a good overall agreement with theory. As stated above, the main difference in their experimental setup is the detection of neutrals that are produced immediately after illumination, including neutrals produced by electron detachment.

### 5.3 Origin of the strong substitution effect in $m$-nitrophenolate

In the following, we develop a rationale for the anomalous properties of the $S_1$ state in the meta isomer and its relation to the topology of the molecule. The ground state of the meta isomer shows distinct differences in geometry (Fig. 5) and charge distribution, which can be understood when considering the canonical Lewis structures that dominate the ground-state wave function (Fig. 6). To analyze the charge distribution, Table 2 provides fragment charges obtained by summing the atomic charges of a natural population analysis\textsuperscript{24} (NPA) of the HF wave function. The energy of the aromatic structure, which locates the excess charge on the phenolate oxygen, is essentially independent of the isomer, as both substituents form a single bond to the aromatic ring. The quinoid (or alternated) structure that assigns the formal charge to the nitro group features one additional bond and is thus more stable and dominates the wave function of the para and ortho isomers. Correspondingly, ca. 60% of the excess charge are located on the nitro group (Table 2), which forms a relatively strong C–N bond. For the topology of the meta isomer, this structure cannot be realized due to the even number of bonds between the substituents. The most stable alternated structures for $m$-nitrophenolate assign the formal charge on ring carbons and form the triple resonance indicated in Fig. 6. Structures with a negative nitro group require two radical centers in the ring and therefore hardly contribute. As a consequence, the NPA net charge in the nitro group is merely $-0.28\,e$, whereas the charge on the ring and on the phenolate oxygen is increased to 36% of the excess charge, each. The bond length alternation is reduced in the ring and enhanced in the nitro fragment.

The topology-related difference in the electronic structure is reflected in the frontier $\pi$ molecular orbitals. As shown in Fig. 7, HOMO (LUMO) natural orbitals are more localized on the phenolate (nitro) fragment, respectively. Therefore, the $S_0-S_1$ excitation in $m$-nitrophenolate has more CT character (see $|\Delta \mu_{\text{in}}|$ in Table 2) and a strongly reduced transition-dipole moment, compared to $p$- and $o$-nitrophenolate. The bathochromic shift in the $m$-nitrophenolate $S_0-S_1$ excitation originates from the low energy of the “intrinsic” CT state corresponding to the phenolate–nitrobenzene donor–acceptor system. As a model, consider $p$-biphenolate (see ref. 2): when rotating the C–C bond connecting the nitrobenzene with the phenolate from the planar to the perpendicular orientation, donor and acceptor systems are fully separated. This shifts the CC2 $S_1$ excitation energy from 2.23 to 1.60 eV. The locally-excited states of nitrobenzene (phenolate) in contrast, are located at 4.5 (4.0) eV, respectively, employing the same level of theory.
6 Conclusions

We studied the optical absorption properties of $p$-, $m$-, and \( \alpha \)-nitrophenolate in vacuo and in bulk solution. Due to the different topology and the emerging resonance structures, the \textit{meta} isomer features widely decoupled donor and acceptor regions, whereas the donor HOMO and acceptor LUMO are strongly mixed in the \textit{para} and \textit{ortho} isomers. As a consequence, the $S_0\rightarrow S_1$ excitation, which is characterized by a HOMO–LUMO $\pi$–$\pi^*$ excitation in all three cases, is strongly red-shifted in the \textit{meta} isomer, carries little oscillator strength, and has a strong CT character. Different from previously studied push–pull systems, like the anionic PYP chromophore $p\text{CA}^-$,\textsuperscript{22} this does not necessarily lead to a strong solvent shift for the \textit{meta} isomer, because donor and acceptor regions share the negative excess charge, which is stabilized by the solvent on both fragments. In acetonitrile, \textit{e.g.}, the nitro group is better solvated than the phenolate group in the \textit{para} and \textit{ortho} isomers, leading to strong bathochromic shifts, whereas the opposite applies to the \textit{meta} isomer, which shows a smaller hypsochromic shift.

Our comparison of data from two different experimental setups demonstrates the potential problems involved in photo-destruction spectroscopy with limitations in the energy- or time-window for detection of the fragmentation channels. In the case of the \textit{meta}-isomer, the ELISA spectrum lacks the expected strong absorption bands of the resonant transitions and does not resolve the weak $S_0\rightarrow S_1$ band. This calls for further experiments to resolve the complete gas-phase UV–vis spectrum of \( m \)-nitrophenolate and accommodate the observed feature in the 363 nm region.

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