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On the Effect of a Single Solvent Molecule on the Charge-Transfer Band of a Donor–Acceptor Anion

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Supporting Information

ABSTRACT: Many biochromophore anions located within protein pockets display charge-transfer (CT) transitions that are perturbed by the nearby environment, such as water or amino acid residues. These anions often contain the phenolate moiety as the electron donor and an acceptor group that couples to the donor via a π-conjugated system. Here we show using action spectroscopy that single molecules of water, methanol, and acetonitrile cause blue shifts in the electronic transition energy of the bare *m*-nitrophenolate anion by 0.22, 0.22, and 0.12 eV, respectively (uncertainty of 0.05 eV). These shifts are similar to CC2-predicted ones and are in accordance with the weaker binding to the phenolate end of the ion by acetonitrile in comparison with water and methanol. The nitro acceptor group is almost decoupled from the phenolate donor, and this ion therefore represents a good model for CT excitations of an anion. We found that the shift caused by one acetonitrile molecule is almost half of that experienced in bulk acetonitrile solution, clearly emphasizing the important role played by the microenvironment. In protic solvents, the shifts are larger because of hydrogen bonds to the phenolate oxygen. Finally, but not least, we provide experimental data that serve to benchmark calculations of excited states of ion–solvent complexes.

Charge-transfer (CT) excitations play a significant role in chemistry and biology. For example, organic donor–acceptor compounds, which are characterized by CT excitations, have found use as nonlinear optical (NLO) chromophores.[1] Protein biochromophores such as the one from photoactive yellow protein (PYP) undergo CT excitations,[2] while the oxyluciferin anion responsible for light emission from fireflies and located within the luciferase enzyme may be formed biochemically in a CT excited state.[3] In a CT excitation, an electron (or, more appropriately, charge density) moves from one part of the molecule (the donor) to another (the acceptor) or from one molecule to another. The energy of CT excitations strongly depends on the donor–acceptor coupling. At infinite separation, the excitation energy is simply the difference between the ionization energy of the donor and the electron affinity of the acceptor, which is typically smaller than the energy of local excitations on any of the moieties. Effective coupling via a π-conjugated system allows the donor and acceptor states to delocalize and overlap, which reduces the gap between the local and CT excitations and gives oscillator strength to the latter. Such CT transitions can often be identified in the absorption spectrum from a strong dependence on solvent polarity. They are, however, hard to predict theoretically; in particular, time-dependent density functional theory (TDDFT) using local exchange–correlation functionals generally fails.[4,5]

An important question up for debate is the spectral shift caused by a single solvent molecule or other hydrogen-bonding interactions on a molecular anion that displays a CT transition.[2,6−8] The issue is of particular relevance for understanding the absorption by proteins in which a biochromophore is located in a binding pocket that provides shielding against bulk water. In this environment, specific interactions with immobile waters or charged or polar groups can widely tune the optical properties of the chromophore.[9] Often there is limited access to water molecules, just one or two.[10] The shift in absorption caused by a nearby water molecule depends on the character of the electronic transition (i.e., the degree of CT) and the geometry of the complex within the cavity. If a water molecule binds to the negative donor site, a blue shift is expected for a CT transition on the basis of simple electrostatic reasoning, since the interaction energy between the donor site and the water is lowered upon electron transfer to the acceptor site. The shift cannot be higher than the solvent binding energy unless the solvent molecule is unbound in the excited state. On the other hand, the polarizability is higher in the excited state than in the ground state, which reduces the blue shift. As the energy for binding to anions is larger than that to neutral chromophores, the microenvironment is expected to be of larger importance for anions, but the actual size of the induced shift by, say, a single water molecule still needs to be better established experimentally. This is the topic of the present work, in which we compared experimental results with theoretical ones.

A textbook example of a donor–acceptor chromophore anion is *m*-nitrophenolate (m^-), in which phenolate is the donor group and the nitro substituent is the acceptor group (Figure 1). Phenolate is a common motif among biochromophores and typically represents the donor state of these. In contrast to the other two isomers, ortho and para, the phenolate anionic group is widely decoupled from the nitro group in the meta isomer (see

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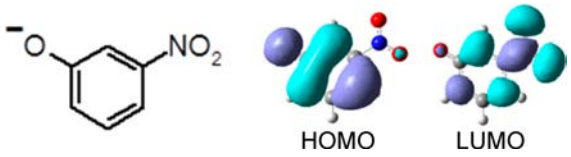

Figure 1. (a) Structure of the *m*-nitrophenolate anion. (b) Frontier natural orbitals from the state-averaged (S_0 and S_1) MR-DDCI2 density matrix (data from ref 11).

the valence orbitals in Figure 1). For the ortho and para isomers, there exists an important resonance structure in which the negative charge is moved from the phenolate oxygen to the nitro group, and as a result of this strong coupling between the donor and acceptor states, the absorption is shifted much further to the blue than for the isolated meta ion, as recently reported.[11] Hence, m^- is an excellent and well-defined model system for testing the importance of microsolvation on the CT transition energy. Also the ion is small enough to allow for high-level quantum-chemical calculations and a benchmarking of these by comparison to experimental results. Here we report the results from a joint spectroscopic and theoretical characterization of *m*-nitrophenolate with a single water, methanol, or acetonitrile molecule attached. Water and methanol can make hydrogen bonds to the phenolate oxygen, while acetonitrile binds more as a dipole.

We note that gas-phase electronic absorption spectroscopy has earlier been done on several microsolvated protonated molecules such as amino acids, crystal violet, and polycyclic aromatic hydrocarbons[12] as well as metal cations and metal-ion complexes.[13] Also the cross sections for photodetachment as functions of wavelength have been measured for anion complexes,[14] as have photodestruction spectra of hydrated electron clusters.[15]

Action spectroscopy experiments were done in the present work with a home-built mass spectrometer.[16] *m*-Nitrophenolate was purchased from Sigma-Aldrich, and ions were formed by electrospray ionization of the sample dissolved in acetonitrile. They were passed through an octopole transmission guide surrounded by a chamber with a gas inlet, where they were allowed to undergo ion−molecule reactions. The chamber was filled with water, methanol, or acetonitrile at a pressure of at least 0.01 mbar. All ions were collected in a 14-pole ion trap filled with helium buffer gas at room temperature. The trap was emptied with a repetition rate of 40 Hz, and the ion bunches were accelerated to kinetic energies of 50 keV. Those of interest according to m/z ratio were selected by a bending magnet, and every second ion bunch was photoexcited by light from an EKSPLA laser system operated at 20 Hz. In this laser system, the 1064 nm fundamental of an Nd:YAG laser was frequency-tripled to give 355 nm light, which was used to pump an optical parametric oscillator to produce visible light. Photofragment ions were selected by a hemispherical electrostatic analyzer (ESA) and counted by a channeltron detector. As the binding energies of the complexes are less than 1 eV (vide infra), the dissociation is expected to be complete before arrival at the analyzer (travel time of a couple of microseconds), avoiding kinetic shifts for which corrections must be made in cases where the dissociation time constant is long. Thus, even though the yield of complexes is low, the experiment benefits from complete photodissociation. We measured a low yield of fragment ions when the laser was off, which was due to collisions with residual gas in the beamline. This signal was proportional to the parent ion beam current but was too low to correct for ion-beam fluctuations. The experiment was therefore repeated several times to average out these fluctuations. The "laser-off" signal was, however, subtracted from the "laser-on" signal to obtain a pure photoinduced yield of fragment ions. The laser wavelength was scanned from 420 to 700 nm. At each wavelength, the number of injections was at least 500.

Photodissociation of the bare m^- ion led to several fragment ions (Figure 2a) that were formed after the absorption of two

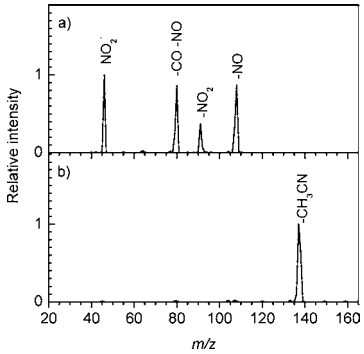

Figure 2. Photodissociation mass spectra of (a) bare m^- and (b) $m^-(CH_3CN)$ obtained with 510 and 500 nm light, respectively.

photons. The dominant fragment ions were NO_2^- (m/z 46) and ions formed by the loss of NO (m/z 108), NO_2 (m/z 92), or CO and NO (m/z 80). Photodissociation mass spectra of the complexes of m^- with a solvent molecule [denoted as m^-(solvent)] were also recorded to identify the fragment ions. The most dominant fragment was the bare ion (m/z 138) formed by evaporation of the solvent molecule [e.g., for $m^-(CH_3CN)$, see Figure 2b]. Its yield increased linearly with laser power [see the Supporting Information (SI)], and one photon was therefore sufficient for the dissociation. This indicates that the dissociation energies are less than the photon energies (>2 eV). Indeed, the solvent binding energies calculated using DFT (PBE0 functional, aug-cc-pVDZ basis set; see Table S1 in the SI) were 0.64, 0.71, and 0.55 eV for water, methanol, and acetonitrile, respectively. These calculations were performed with TURBOMOLE.[17] Similar binding energies were predicted by Zuev et al.[6] for complexes of water with the PYP and green fluorescent protein (GFP) anions in their phenolate forms. When zero-point vibrational energy and corrections for the basis-set superposition error were included,[18] we obtained binding energies of 0.54, 0.65, and 0.50eV, respectively. For a simple dissociation process in which one bond is cleaved, the barrier for the reverse reaction is low or zero. Hence, the dissociation energy is similar to the activation energy, and the excess energy after photoexcitation is at least 1 eV (photon energy minus dissociation energy). It can therefore be assumed that all of the photoexcited ions dissociated within the experimental time window of a few microseconds. The action spectra of the complexes are therefore good representations of the corresponding gas-phase absorption spectra. Photoexcitation of $m^-(CH_3OH)$ at high laser power also led to OH loss and dissociation of the nitrophenolate ion via two-photon processes.

The action spectra of the complexes are shown in Figure 3 together with the previously reported spectrum for the bare ion.[11] The band maxima and shifts relative to the bare ion are summarized in Table 1. The bare ion absorbs maximally at 2.34 eV (530 nm), and it is clearly evident that a single solvent molecule causes a blue shift in the absorption. It is worth

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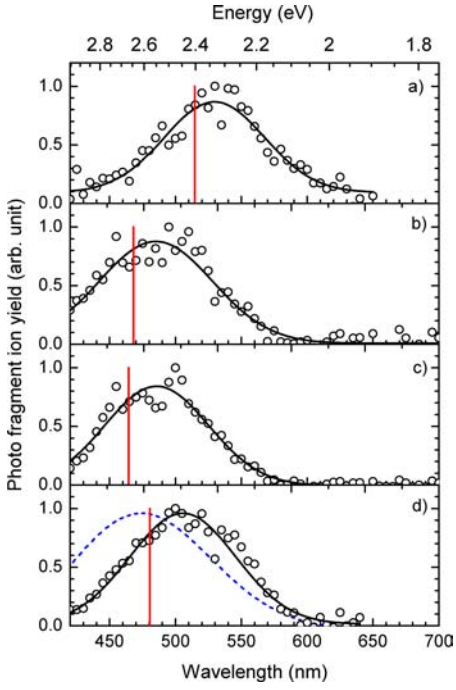

Figure 3. Action spectra of (a) bare m^-, (b) $m^-(H_2O)$, (c) $m^-(CH_3OH)$, and (d) $m^-(CH_3CN)$. Gaussian curves are included to guide the eye. The red sticks show CC2-calculated values. The blue dashed curve in (d) is the spectrum in bulk acetonitrile solution.

Table 1. Absorption Band Maxima (λ_{max}) and Shifts from the Bare Ion (Δ)

ion	λ_{max} (nm)[a]	λ_{max} (eV)[a]	Δ (eV)[a]	λ_{max} (eV)[b]	Δ (eV)[b]
m^-	530	2.34		2.41	
$m^-(H_2O)$	485	2.56	0.22	2.65	0.25
$m^-(CH_3OH)$	485	2.56	0.22	2.67	0.26
$m^-(CH_3CN)$	505	2.46	0.12	2.58	0.17

[a]From experiment (Figure 3). [b]CC2-calculated.

emphasizing that the band shapes of the bare ion and the complexes are very similar and can be approximated by Gaussians with band widths of ~0.4 eV.

The shifts for water and methanol are the same [0.22 eV (45 nm)], and that for acetonitrile is about a factor of 2 smaller [0.12 eV (25 nm)]. In all three cases, the solvatochromic shift is merely a fraction of the solvent binding energy, with that of acetonitrile being the smallest (24%). Obviously, the strong hydrogen bonds formed with water and methanol (Figure 4) cause a stronger perturbation of the electronic structure of the chromophore than the interaction with acetonitrile. The latter still achieves a comparable binding energy, as it has the largest dipole moment

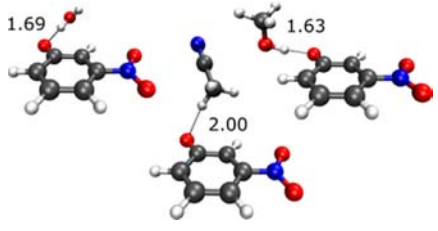

Figure 4. Minimum-energy structures of $m^-(H_2O)$, $m^-(CH_3OH)$, and $m^-(CH_3CN)$ calculated at the MP2 level using the TZVPP basis set. Hydrogen-bond distances in Å are given.

and polarizability. Water has a slightly larger dipole moment than methanol, whereas methanol has a larger polarizability and forms a slightly stronger hydrogen bond (Figure 4), but the shifts are similar.

We also calculated vertical excitation energies at the CC2 level of theory using the optimized structures shown in Figure 4 (see Table 1). For the bare ion as well as the three complexes, the obtained values are ~0.1 eV higher in energy than the experimental absorption maxima, but the solvation shifts agree rather well (0.25, 0.26, and 0.17 eV for water, methanol, and acetonitrile, respectively). This result is satisfactory; the deviation of 0.1 eV is within the typical error of the CC2 method.[19] Moreover, an inhomogeneous line broadening can be expected because of the orientational flexibility of the solvent molecule at room temperature, which is not taken into account by the calculations. We note that in the case of water binding to the PYP anion, Krylov and co-workers[6] predicted a blue shift of 0.06 eV for the phenolate (electron donor) site and a red shift of 0.07 eV when water binds to the carboxyl group. When we placed the solvent molecule at the nitro group of m^-, we obtained red shifts of 0.27 and 0.25 eV for methanol and acetonitrile, respectively, demonstrating the strong CT character of the electronic transition in m^- compared with that in the PYP anion. Figure S4 in the SI shows that the density changes upon excitation are essentially localized on the phenolate oxygen and the nitro group. This is consistent with the observed strong perturbation due to hydrogen bonds.

In bulk acetonitrile solution, the absorption band maximum is at 2.62 eV (473 nm), which represents a blue shift of 0.28 eV relative to the bare ion. Interestingly, almost half of this shift is caused by a single solvent molecule, which clearly demonstrates the importance of the nearby environment on the electronic structure of the ions. In the protic solvents water and methanol, the band maxima are at 3.18 eV (390 nm) and 3.20 eV (387 nm), respectively. Hence, full completion of the solvation shell in these two solvents induces a larger blue shift than in acetonitrile. This is most likely linked to the fact that the phenolate oxygen can hydrogen-bond to two or three water or methanol molecules, rendering a CT excitation less favorable.

Finally, we did measurements on the bare m^- ion at another setup, the electrostatic ion storage ring in Aarhus (ELISA), where neutrals were measured instead of ionic fragments.[20] Ion bunches were stored in the ring for 24 ms before being irradiated with laser light. Neutrals produced within ~10 μs were counted by a secondary emission detector (SED). The obtained yield of photoneutrals as a function of wavelength is shown in Figure 5 together with the spectrum from Figure 3. The spectra follow each other nicely on the low-energy side from ~2.3 eV and down. In the 2.4–2.7 eV region, the yield of photoneutrals decreases with energy, but the relative yield is higher than in the photofragment ion experiment. At higher energies, the yield increases. A power dependence study at 2.95 eV (420 nm) revealed that the signal is mainly due to the absorption of two photons, though some contribution from one-photon absorption cannot be excluded (see the SI). We calculated the vertical detachment energy to be 2.98 eV, and we assign the signal to electron photodetachment of hot m^- anions, as this would account for the asymmetry of the absorption band and a skewing toward the blue. The band maximum from this experiment is at ~2.4 eV. Taken together, we estimate the experimental uncertainty in the band maximum to be 0.05 eV.

In conclusion, we have shown that the attachment of single solvent molecules of water, methanol, and acetonitrile causes

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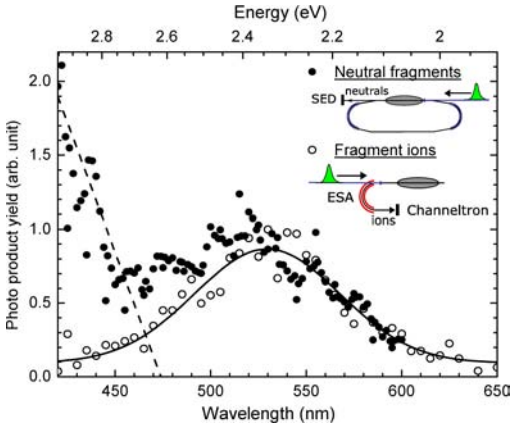

Figure 5. Action spectra of m^- recorded at two different setups. Solid circles: Photoneutrals were counted by an SED right after photoexcitation in a storage ring. A straight line fits the data at high energies. Open circles: Photodissociation followed by deflection of fragment ions in an ESA (same as Figure 3a).

blue shifts in the electronic absorption of *m*-nitrophenolate by 0.22, 0.22, and 0.12 eV, respectively (uncertainty of 0.05 eV). The CC2-calculated vertical excitation energies differ by ~0.1 eV from the experimental absorption maxima, but the predicted shifts for the complexes relative to the bare ion are nearly identical to the experimental ones. The smaller shift found for acetonitrile is ascribed to a weaker interaction with the electron-donating oxygen, which results in a smaller perturbation of the CT excitation energy. Interestingly, a single acetonitrile molecule provides nearly half of the solvent shift seen in bulk solution. Our data provide clear benchmarks for theoretical calculations of CT excitation energies of weakly bound ion−molecule complexes. This is highly relevant to shed light on the shifts induced by single water molecules or amino acid residues on biochromophore anions in protein pockets. Future work will address the role of stepwise solvation, which is an experimental challenge because of very low ion beam currents.

■ ASSOCIATED CONTENT

Supporting Information

Additional experimental and computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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