On the role of a single solvent molecule on the charge-transfer band of a donor-acceptor anion

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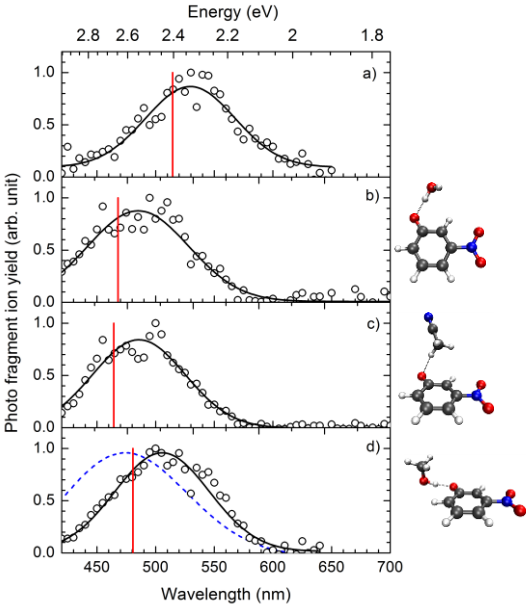
Charge-transfer excitations play significant roles in chemistry and biology. For example, organic donor-acceptor compounds, characterized by charge-transfer excitations, have found use as nonlinear optically (NLO) chromophores. Charge-transfer excitation is highly dependent on the electronic coupling between the donor and acceptor groups. Nitrophenolates are simple model systems for studying the effects of solvent binding on the charge-transfer process. The coupling between the acceptor and donor group is broken for the meta isomer, which makes this the perfect system to test the effect of single solvent molecules on a charge-transfer system. Single solvent molecules of water, methanol and acetonitrile were added to the meta isomer. Action spectroscopy was done in the gas-phase at an accelerator mass spectrometer. We identified a hypsochromicshift for all the solvent complexes. The bare meta ion has an absorption maxima at 532 nm, which blue shifts to 487 nm, 485 nm and 505 nm for the addition of water, methanol and acetonitrile respectively. This experiment shows the effect of solvent molecules on a pure charge transfer excitation, and sets a benchmark for quantum chemical calculations of charge transfer states.



Absorption band maxima and shifts Δ from the bare ion.

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

[a] From experiment. [b] CC2 method.