Supporting Information

for

"Substitution effects on the absorption spectra of nitrophenolate isomers"

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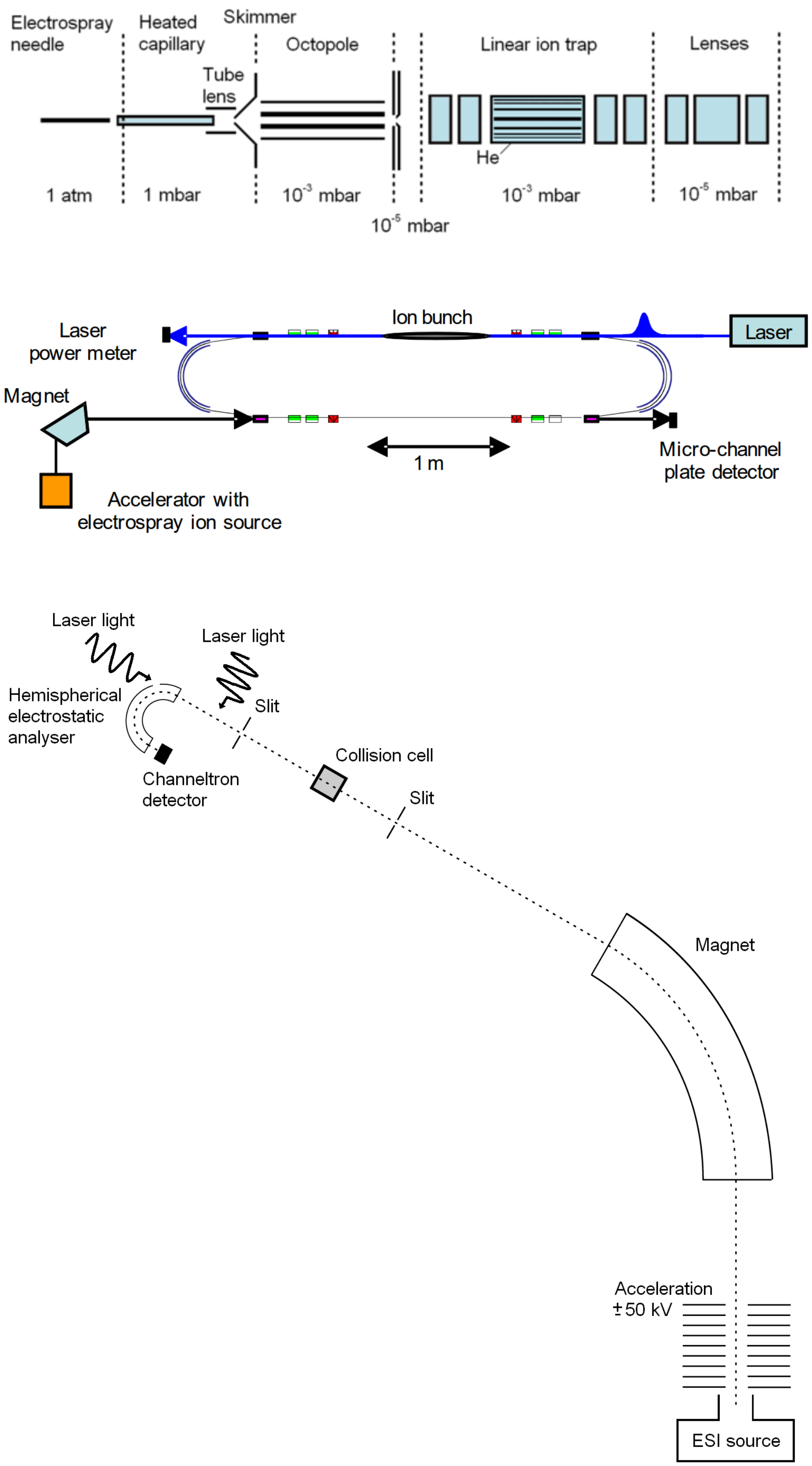

Figure S-1: Top: Electrospray ion source combined with a linear ion trap. Middle: The electrostatic ion storage ring in Aarhus, ELISA. Bottom: Accelerator mass spectrometer used for single pass experiments (Sep1).

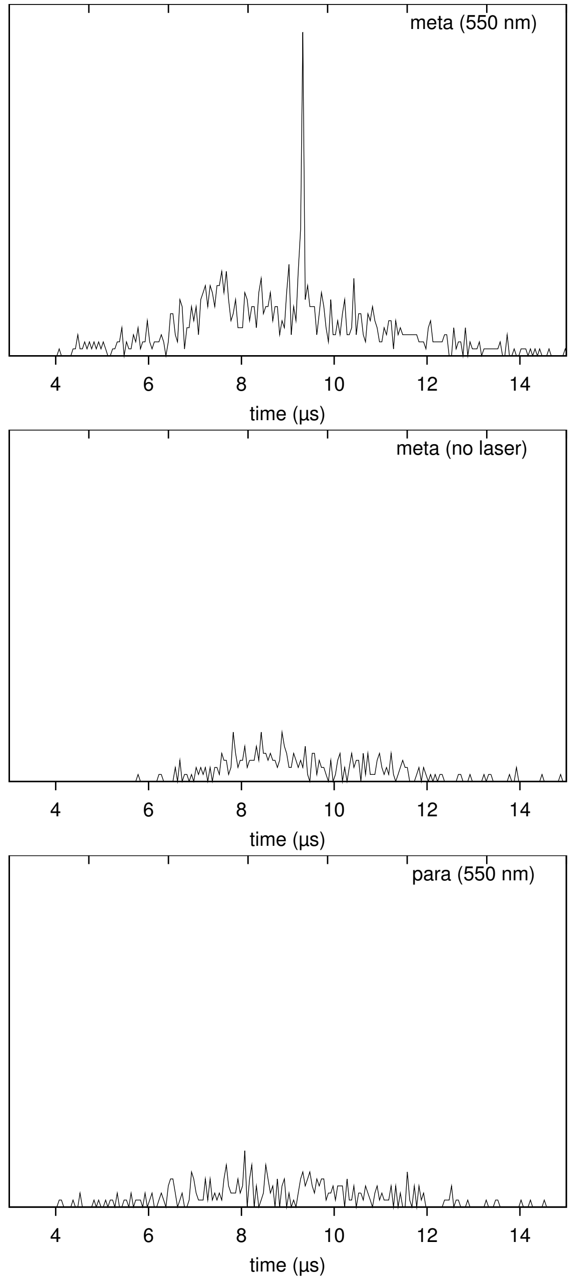

Figure S-2: Sep1 time spectra of the m/z 108 fragment ions of meta- and para-nitrophenolate. The ion bunch is 10 μs long and the laser is fired in the middle of the bunch (see upper panel). Increased ion formation due to photo induced dissociation is found at 550 nm for the meta isomer only.

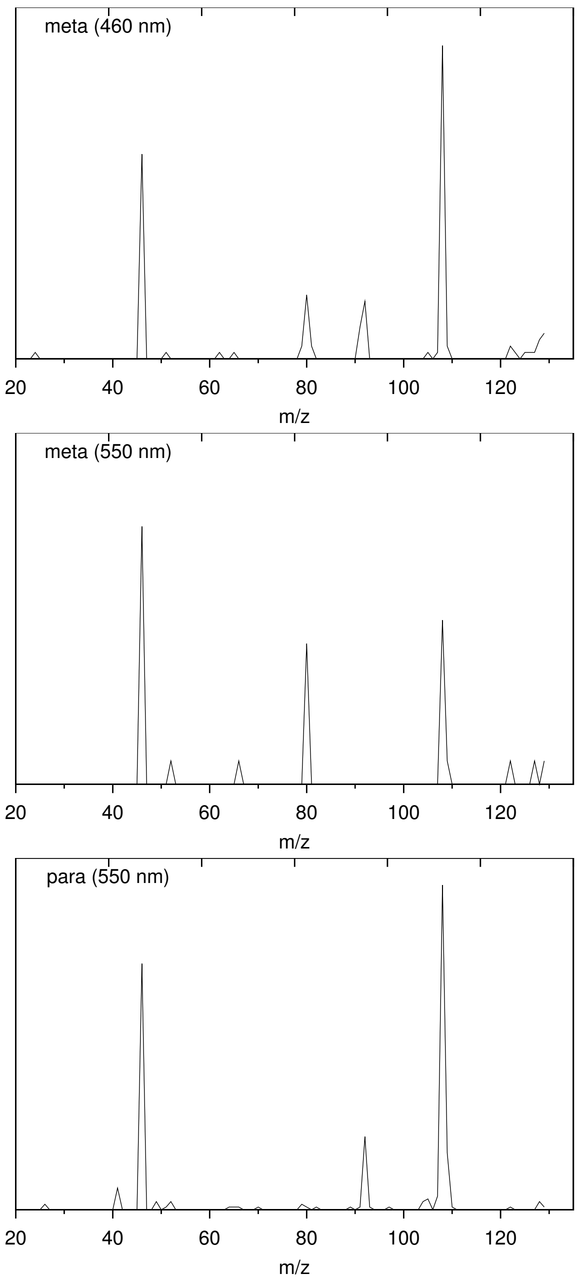

Figure S-3: Photoinduced dissociation mass spectra of meta- and para-nitrophenolates in the Sep1 experiment. The NO_2^- fragment ion (m/z=46) and NO loss channel (m/z=108) are found to be the dominant fragments.

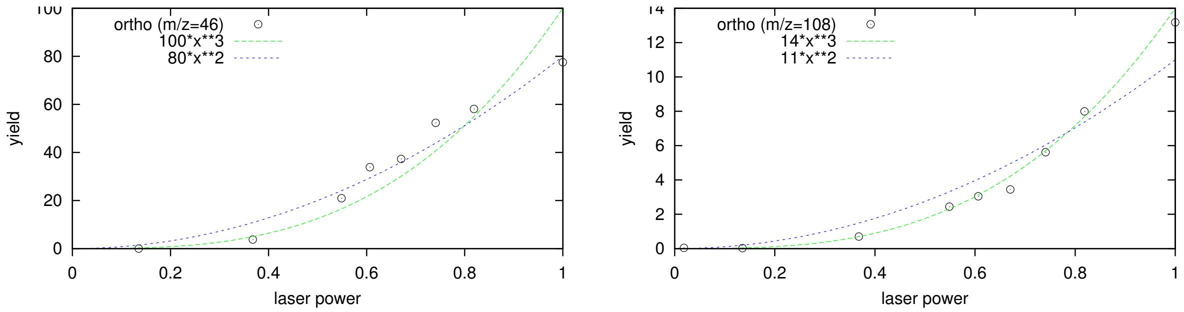

Figure S-4: Sep1 power spectra of *o*-nitrophenolate at 450 nm: The yields of NO_2^- fragments (left) and anions after NO loss (right) are plotted against laser power (arbitrary units).

Table S-1: S_1 excitation energies of nitrophenolate isomers.

	CC2	SORCI[a]	PBE[b]	PBE0[b]	exp (vacuo)	exp (MeCN)
para[c]	3.21	3.07	3.27	3.51	3.16	2.88
meta	2.41	2.08	1.18	1.81	—	2.62
ortho	3.01	2.63	2.71	2.88	3.08	2.80
ortho (planar)	3.12	2.87	2.87	3.19		

All excitation energies were calculated on the same MP2/TZVPP optimized geometries. [a]2-root SORCI/aug-SV(P) calculation. [b]TDDFT linear response calculation with a 6-311++G(d,p) basis set. [c]From ref 1.

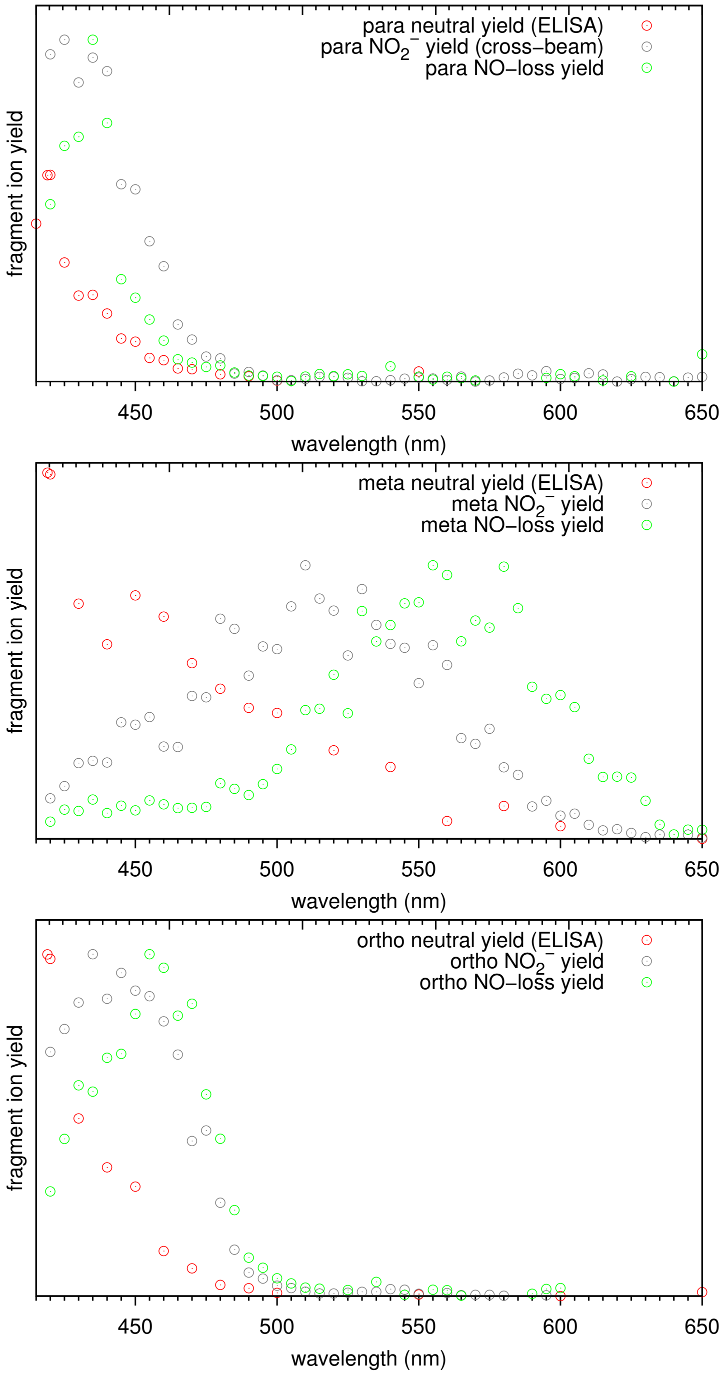

Figure S-5: Absorption spectra of para-, meta-, and ortho-nitrophenolate in vacuo: Comparison of ion yields of different fragments. Note, that the scaling of the yields is arbitrary.

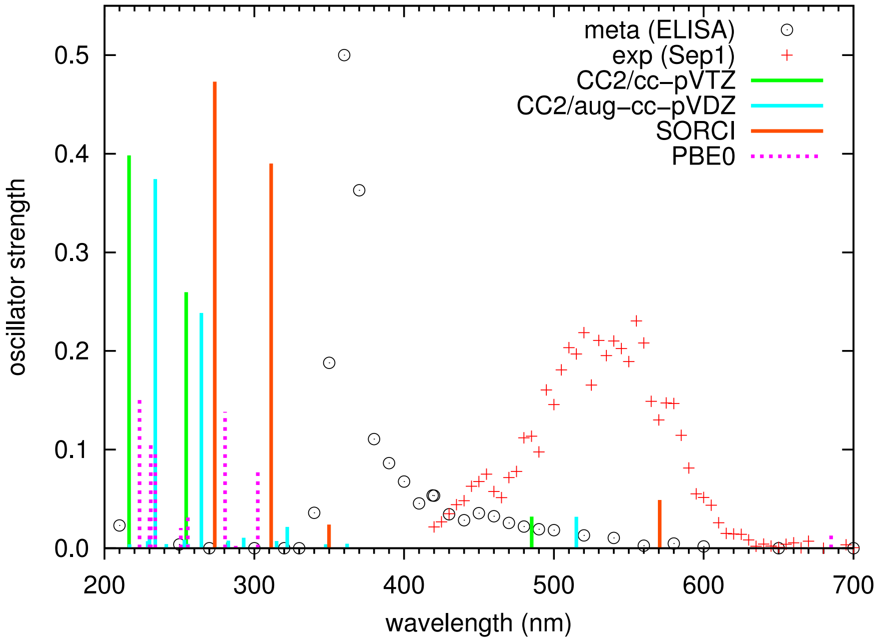

Figure S-6: Absorption spectra of meta-nitrophenolate in vacuo: Comparison between different QM methods and experimental spectra.

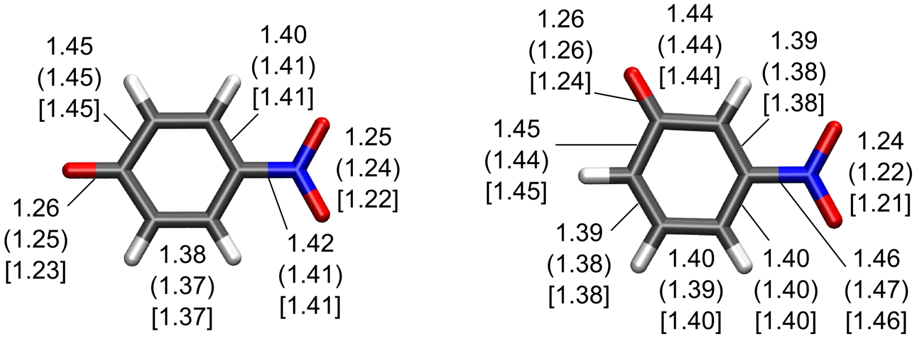

Figure S-7: Bondlenghts (Å) of the MP2/TZVPP ground-state geometries of para and meta. Values from PBE0/6-311++G(d,p) and CASSCF(12,10)/6-31G(d) calculations are given in parentheses and brackets, respectively.

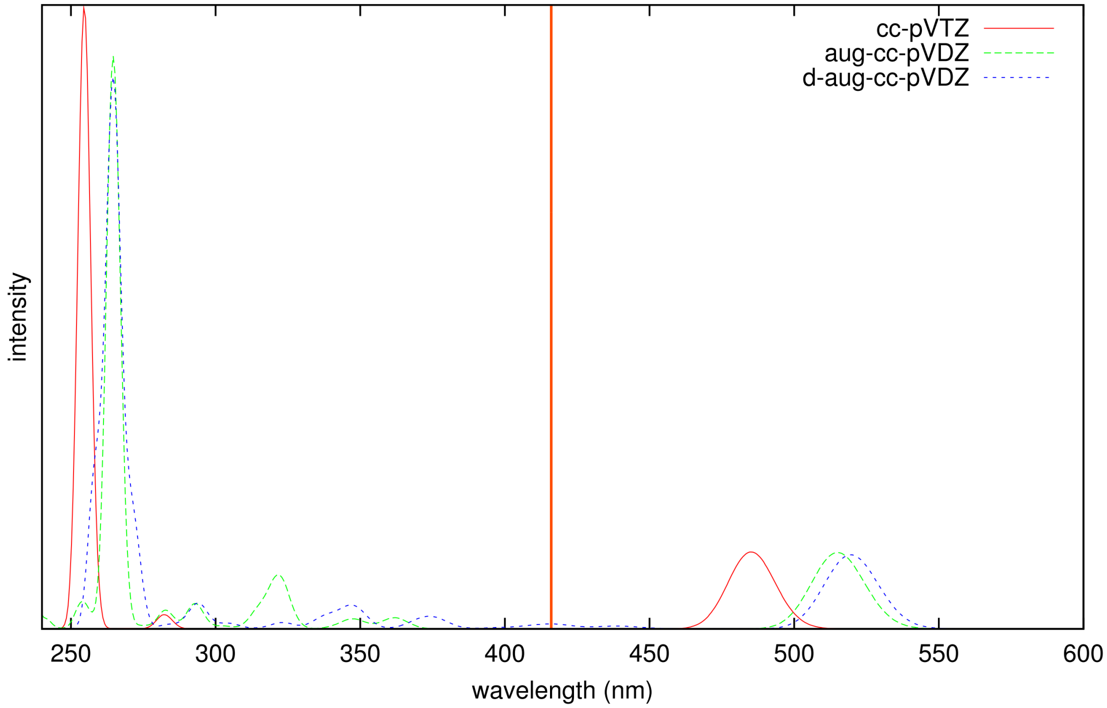

Figure S-8: CC2 absorption spectrum of *m*-nitrophenolate (peaks are convoluted with Gaussians of 0.1 eV width). Weak transitions into diffuse states appear when the basis set is augmented by diffuse functions. Towards the basis-set limit, these transitions are expected to appear further red-shifted and with smaller oscillator strengths, as their spacial overlap with the valence states will diminish. With the doubly augmented d-aug-cc-pVDZ set, some of these already appear below the vertical detachment energy (orange line), indicating the possibility of dipole-bound states.

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p-nitrophenolate MP2/TZVPP Min

C	-1.214175	0.000000	-0.066647
C	-1.213653	0.000000	-1.442805
C	0.000000	0.000000	-2.231559
C	1.213653	0.000000	-1.442805
C	1.214175	0.000000	-0.066647
C	0.000000	0.000000	0.638540
H	-2.138622	0.000000	0.493556
H	-2.151320	0.000000	-1.985599
H	2.151320	0.000000	-1.985599
H	2.138622	0.000000	0.493556
O	0.000000	0.000000	-3.489061
N	0.000000	0.000000	2.057164
O	-1.089622	0.000000	2.661481
O	1.089622	0.000000	2.661481

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m-nitrophenolate MP2/TZVPP Min

C	0.225126	-1.501290	0.000000
C	-1.129566	-1.844173	0.000000
C	-2.131347	-0.884059	0.000000
C	-1.866707	0.537391	0.000000
C	-0.461029	0.858212	0.000000
C	0.510579	-0.133799	0.000000
H	1.016041	-2.232512	0.000000
H	-1.403441	-2.893977	0.000000
H	-0.166267	1.897171	0.000000
N	1.917030	0.269031	0.000000
O	2.782017	-0.615088	0.000000
O	2.192655	1.472308	0.000000
O	-2.774941	1.413357	0.000000
H	-3.172823	-1.185889	0.000000

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o-nitrophenolate MP2/TZVPP Min

C	-0.089716	0.480944	1.441191
C	-0.119726	1.862915	1.504199
C	-0.046208	2.583613	0.298765
C	0.047582	1.932446	-0.912852
C	0.081467	0.491398	-1.068453
C	-0.025106	-0.185429	0.214718
H	-0.140481	-0.123213	2.336774
H	-0.198179	2.368337	2.456986
N	-0.027816	-1.624116	0.279024
O	0.438900	-2.173853	1.294020
O	-0.504375	-2.260410	-0.665721
H	-0.069714	3.668522	0.316582
H	0.113211	2.498213	-1.835182
O	0.222312	-0.053465	-2.188156

References

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