

Electronic Spectroscopy of Isolated DNA Polyanions

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SUPPORTING INFORMATION: supplementary figures as described in the text

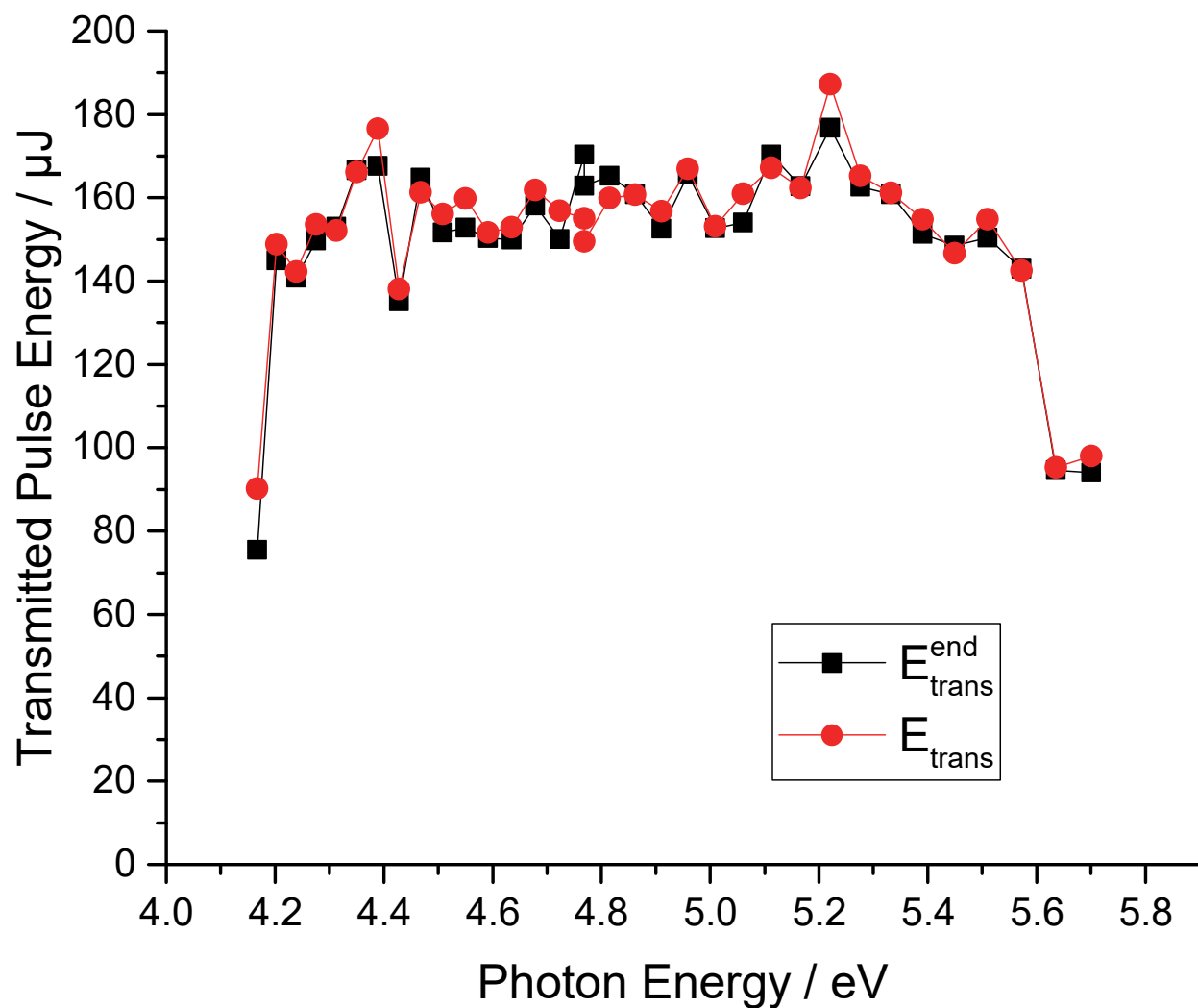


Figure S1. Representative data for the transmitted pulse energy as a function of the photon energy. The black points were measured immediately following acquisition of a mass spectrum, concurrently with measurement of the reflected pulse energy. The red points are calculated pulse energy used to irradiate ions during acquisition of a mass spectrum (see main text). The extreme photon energy points have lower pulse energy due to reaching the edge of the tuning range of the OPO.

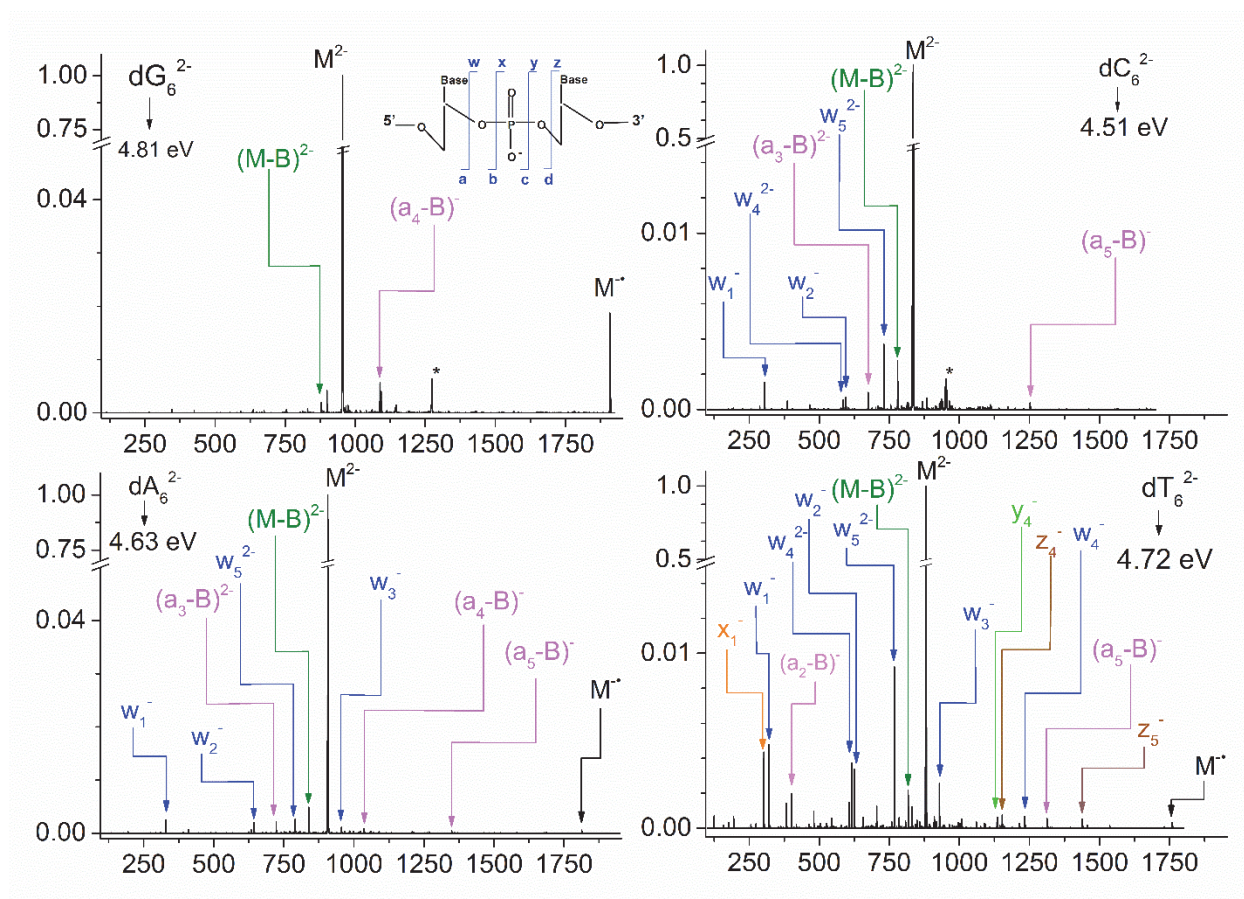


Figure S2. Mass spectra following irradiation with a single UV laser pulse (160 μ J transmitted through the trap) at 4.81 eV (257.5 nm) for dG_6^{2-} (top left), 4.51 eV (275 nm) for dC_6^{2-} (top right), 4.63 eV (267.5 nm) for dA_6^{2-} (bottom left) and 4.72 eV (262.5 nm) for dT_6^{2-} (bottom right). Major fragmentation channels are labelled according to the nomenclature in the inset, and EPD products are shown in red. Note that the vertical scale for purines (A and G) differs from that of the pyrimidines (C and T). The asterisks denote fragmentation channels come from 4- dimer (which is isobaric). These fragments are excluded from the analysis.

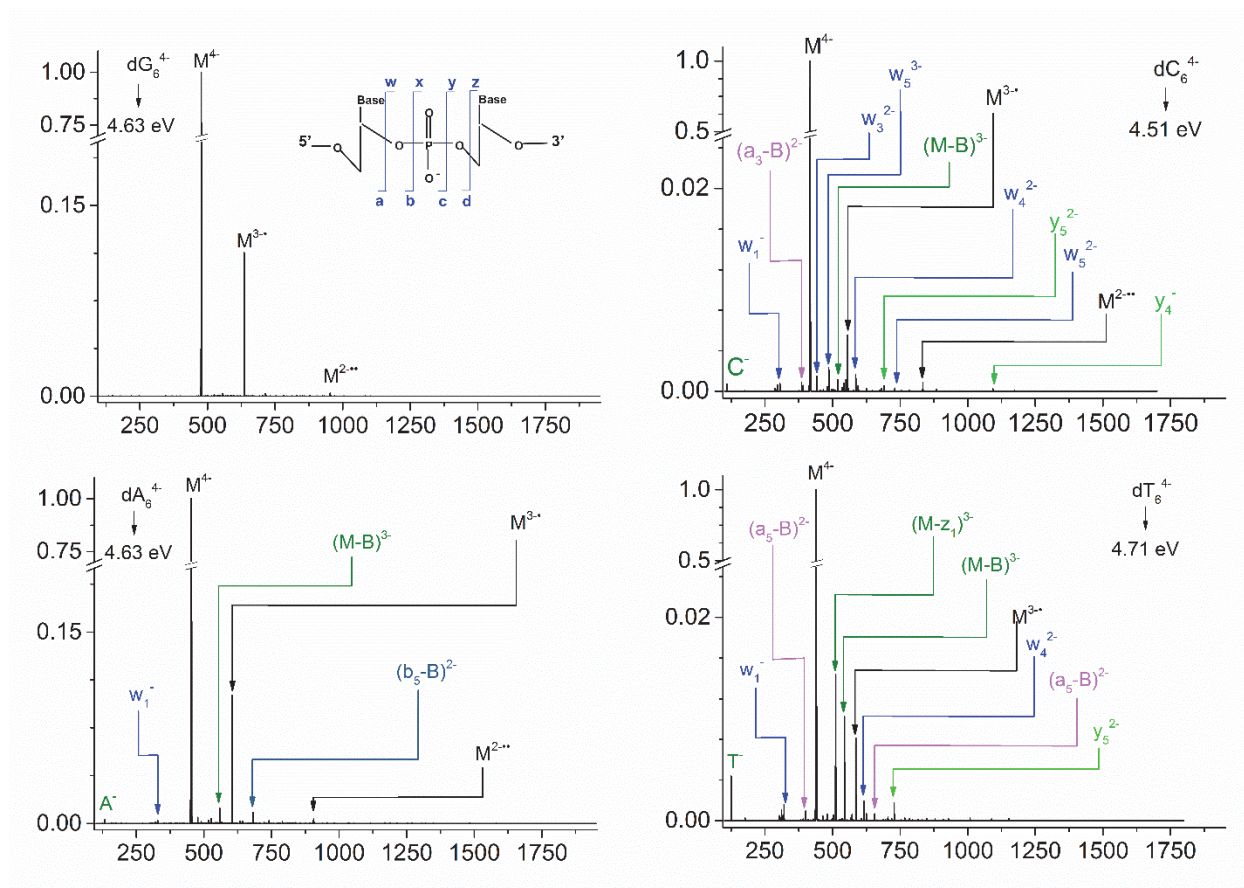


Figure S3. Mass spectra following irradiation with a single UV laser pulse (160 μ J transmitted through the trap) at 4.81 eV (257.5 nm) for dG₆⁴⁻ (top left), 4.51 eV (275 nm) for dC₆⁴⁻ (top right), 4.63 eV (267.5 nm) for dA₆⁴⁻ (bottom left) and 4.72 eV (262.5 nm) for dT₆⁴⁻ (bottom right). Major fragmentation channels are labelled according to the nomenclature in the inset, and EPD products are shown in red. Note that the vertical scale for purines (A and G) differs from that of the pyrimidines (C and T).

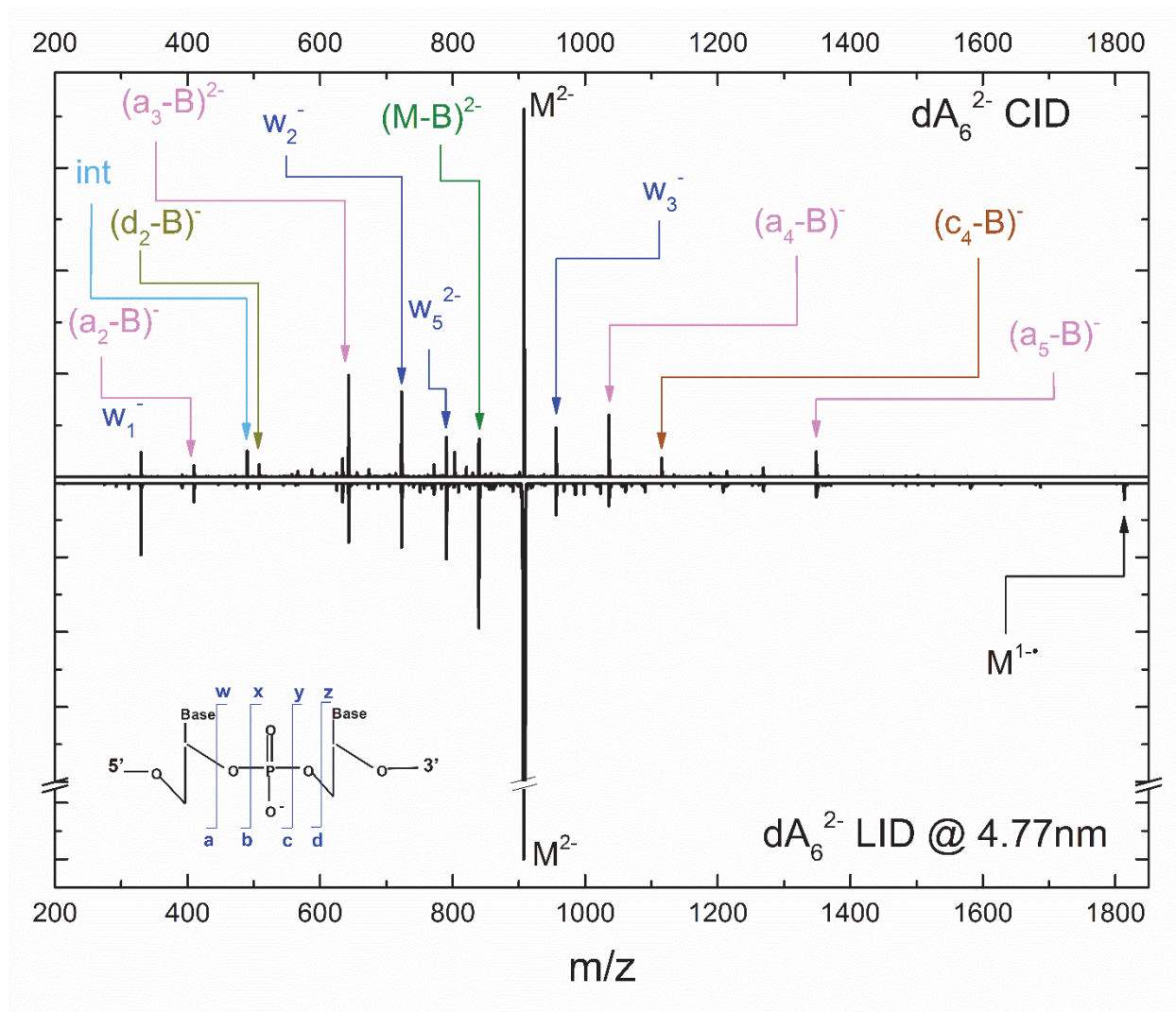


Figure S4. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.67V (top) and irradiation with 4.77 eV photons (bottom) for A_6^{2-} . The major peaks are annotated according to the scheme in the bottom panel. Here int refers to an internal fragment.

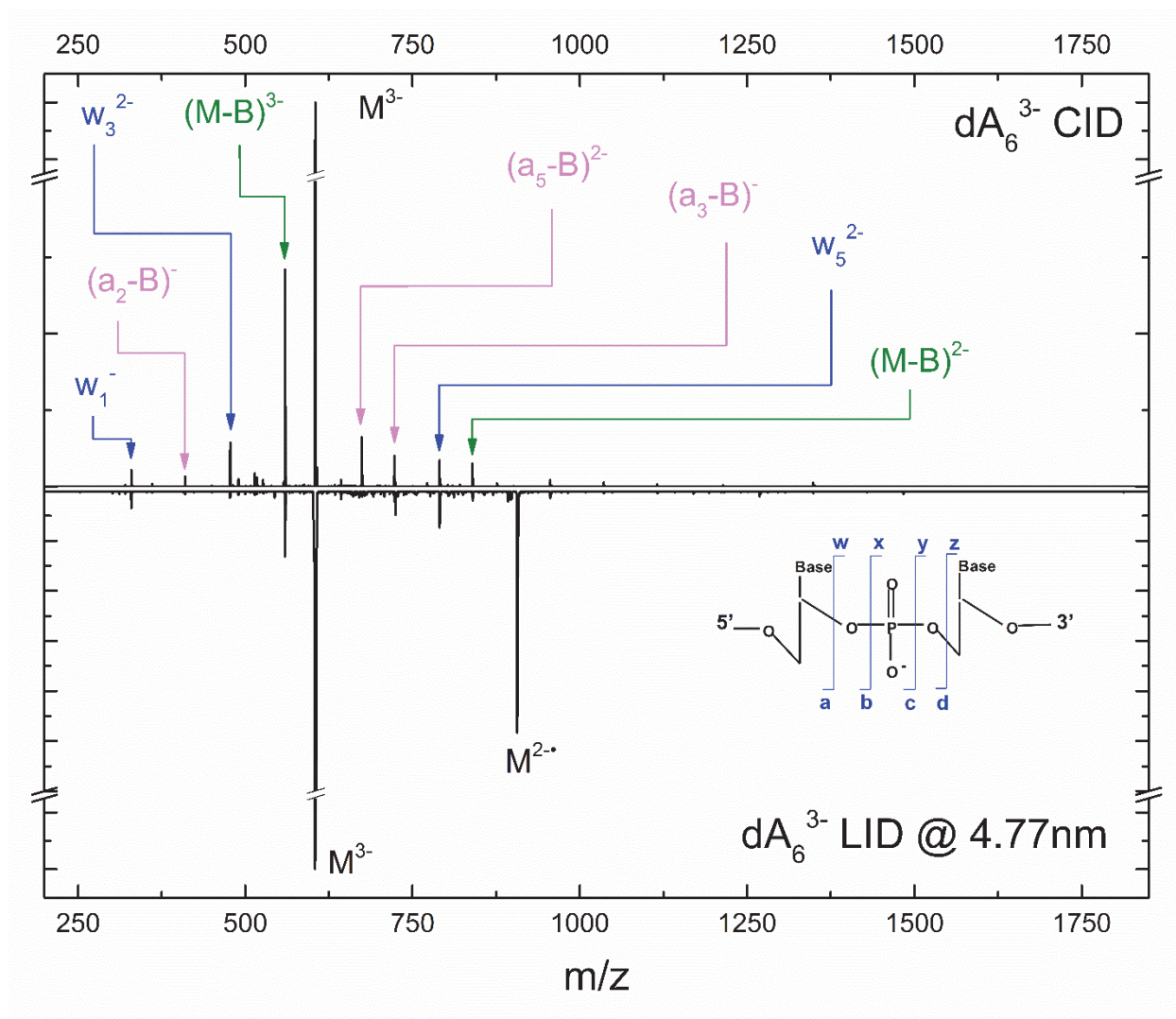


Figure S5. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.70V (top) and irradiation with 4.77 eV photons (bottom) for A_6^{3-} . The major peaks are annotated according to the scheme in the bottom panel.

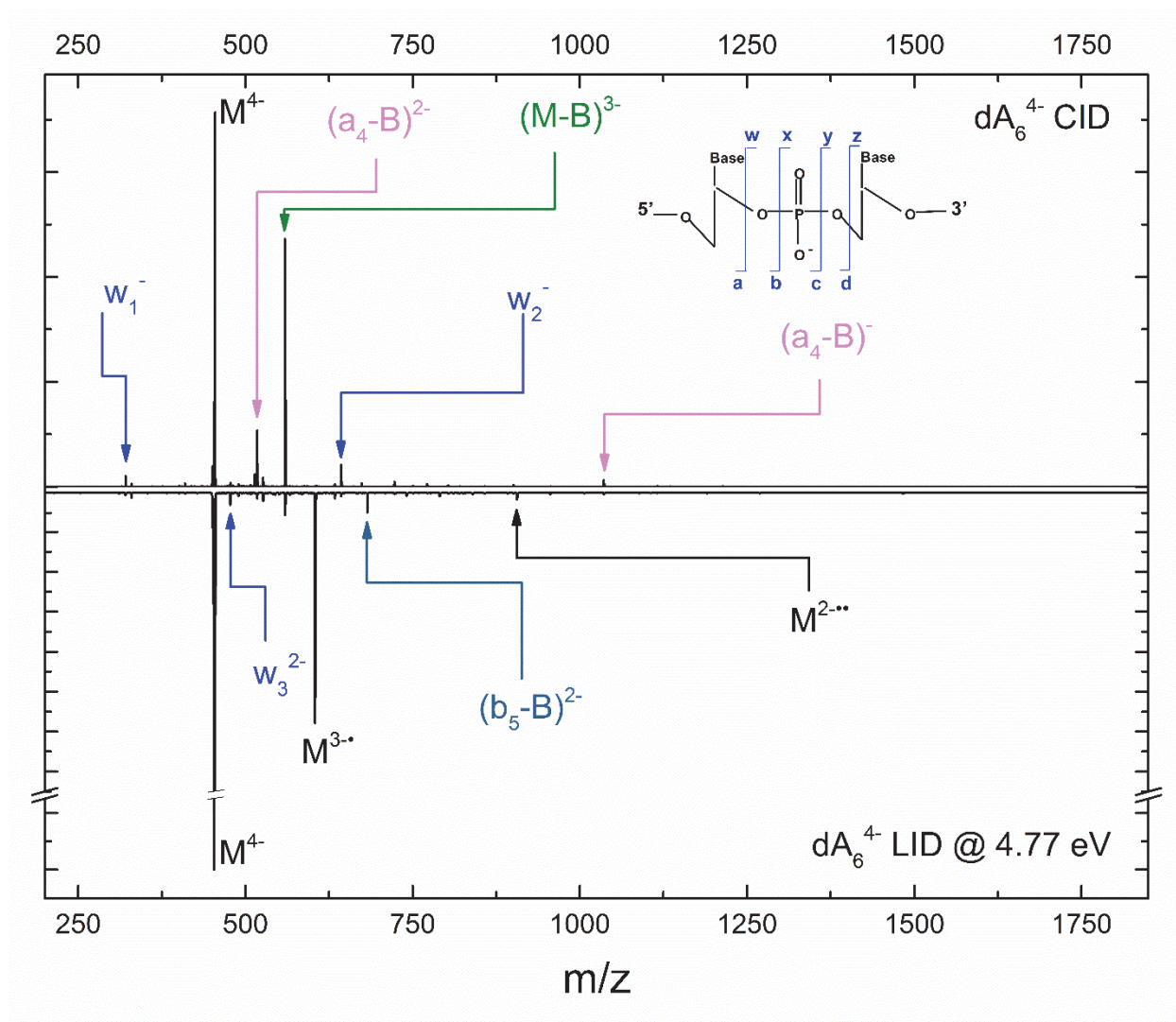


Figure S6. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.70V (top) and irradiation with 4.77 eV photons (bottom) for A_6^{4-} . The major peaks are annotated according to the scheme in the top panel.

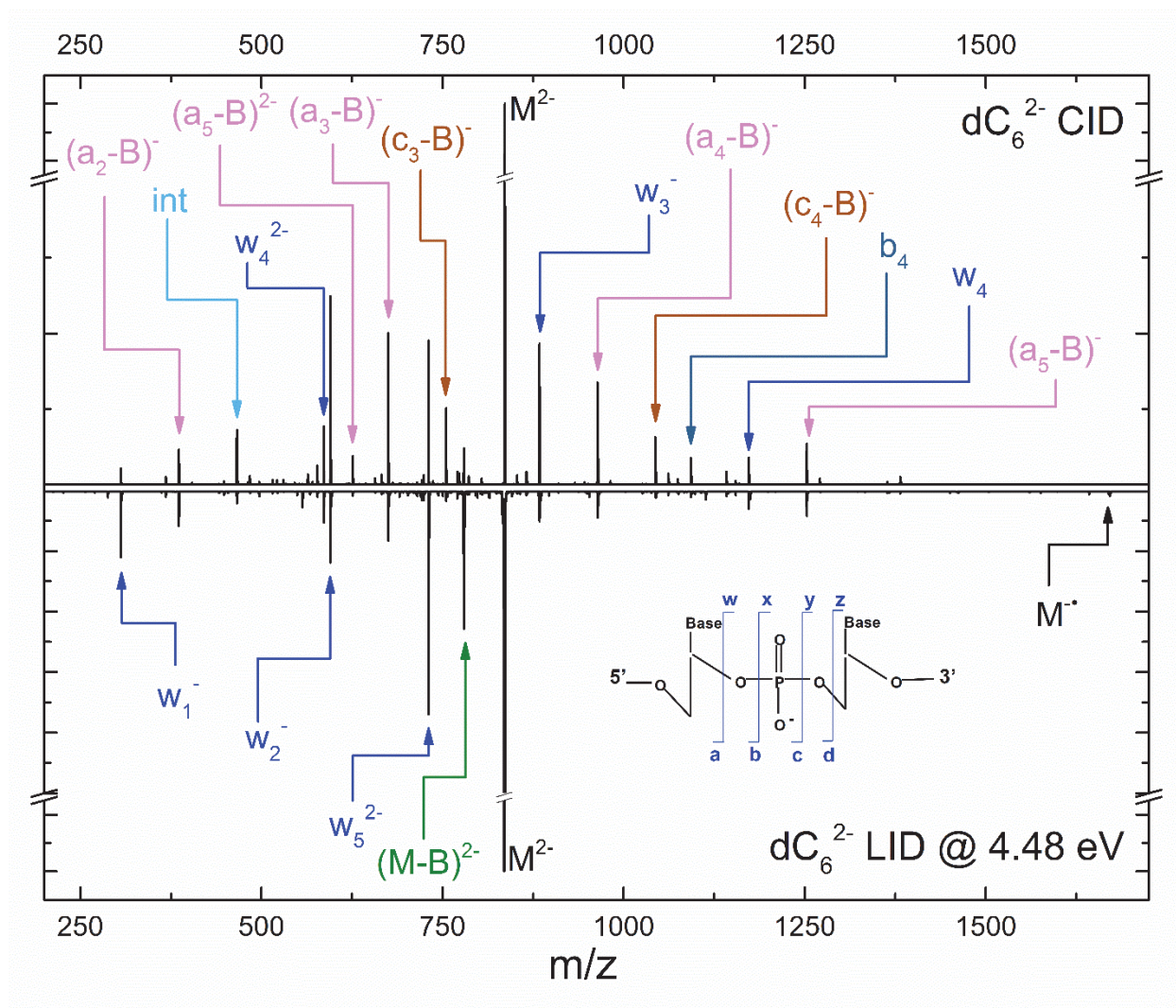


Figure S7. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.70V (top) and irradiation with 4.48 eV photons (bottom) for C_6^{2-} . The major peaks are annotated according to the scheme in the bottom panel.

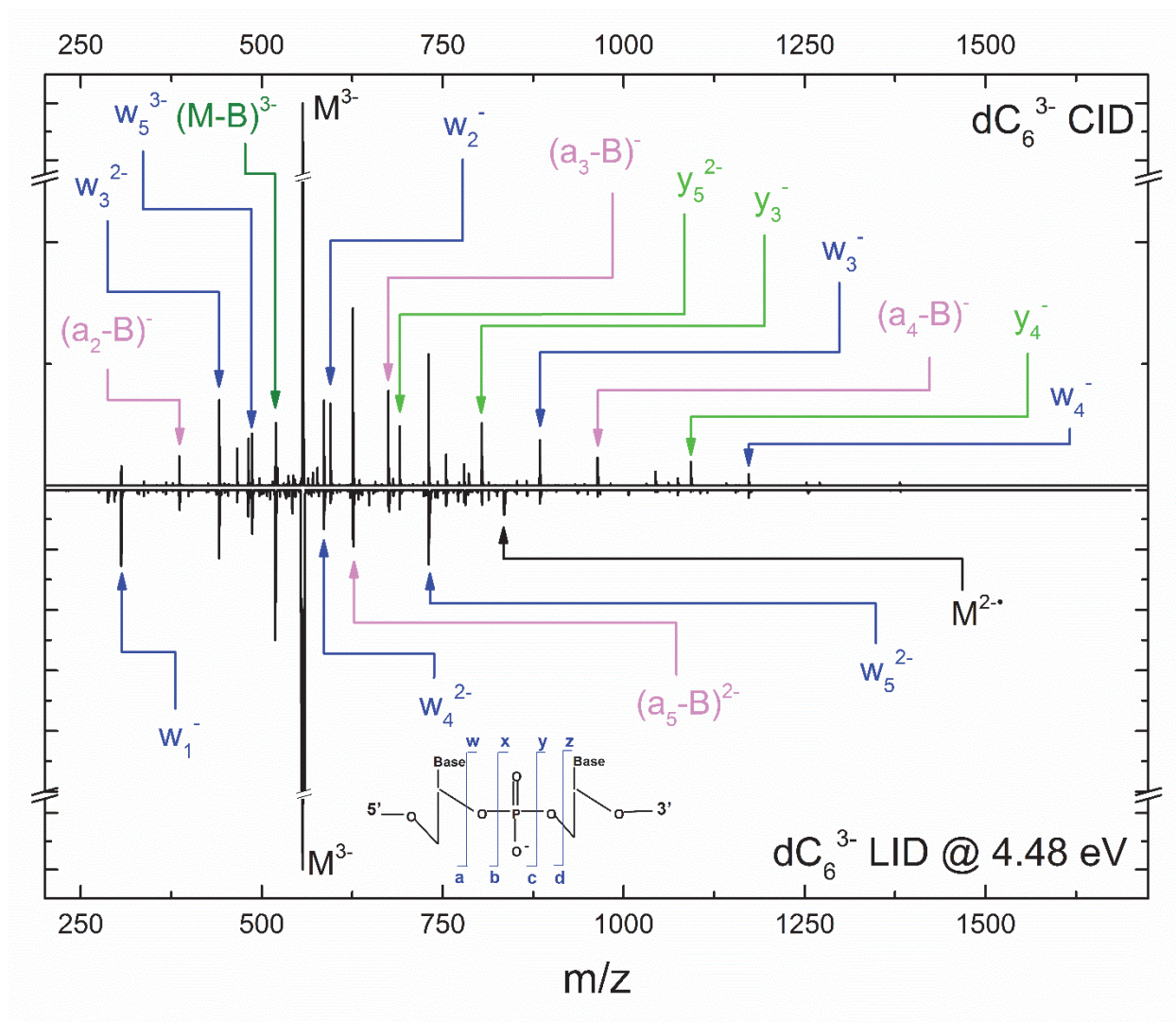


Figure S8. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.70V (top) and irradiation with 4.48 eV photons (bottom) for C_6^{3-} . The major peaks are annotated according to the scheme in the bottom panel.

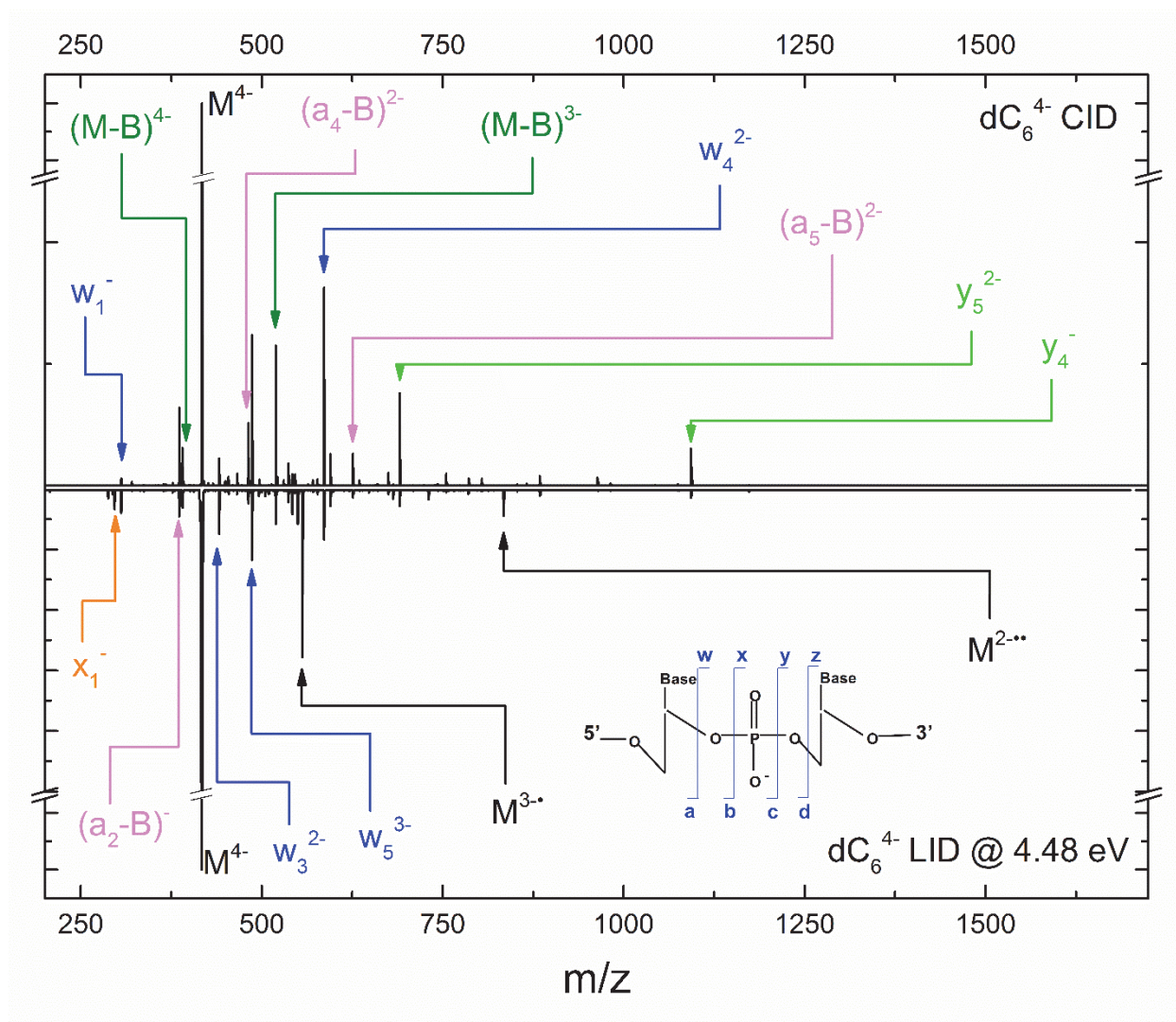


Figure S9. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.9V (top) and irradiation with 4.48 eV photons (bottom) for C_6^{4-} . The major peaks are annotated according to the scheme in the bottom panel.

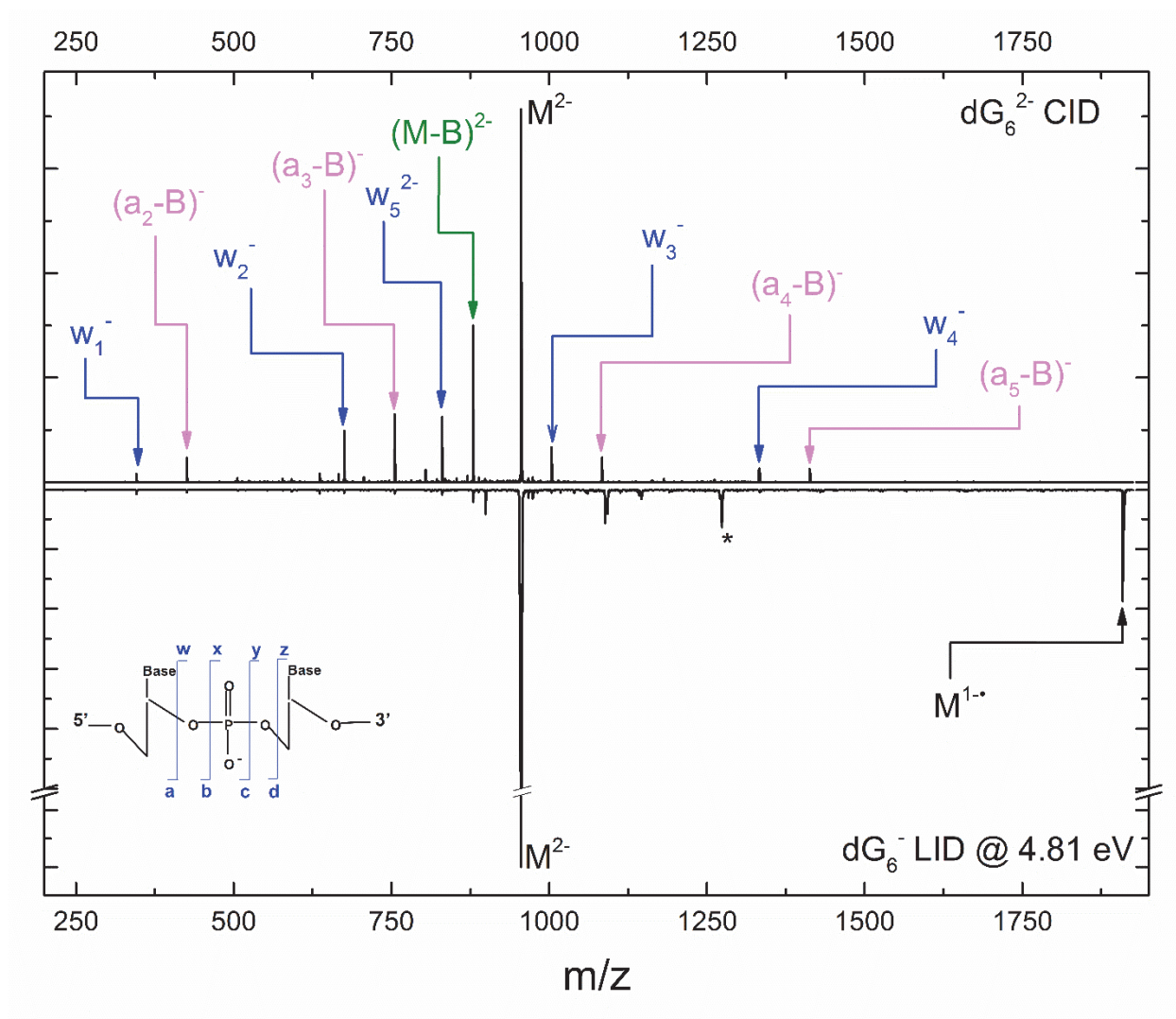


Figure S10. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.47V (top) and irradiation with 4.81 eV photons (bottom) for G_6^{2-} . The major peaks are annotated according to the scheme in the bottom panel.

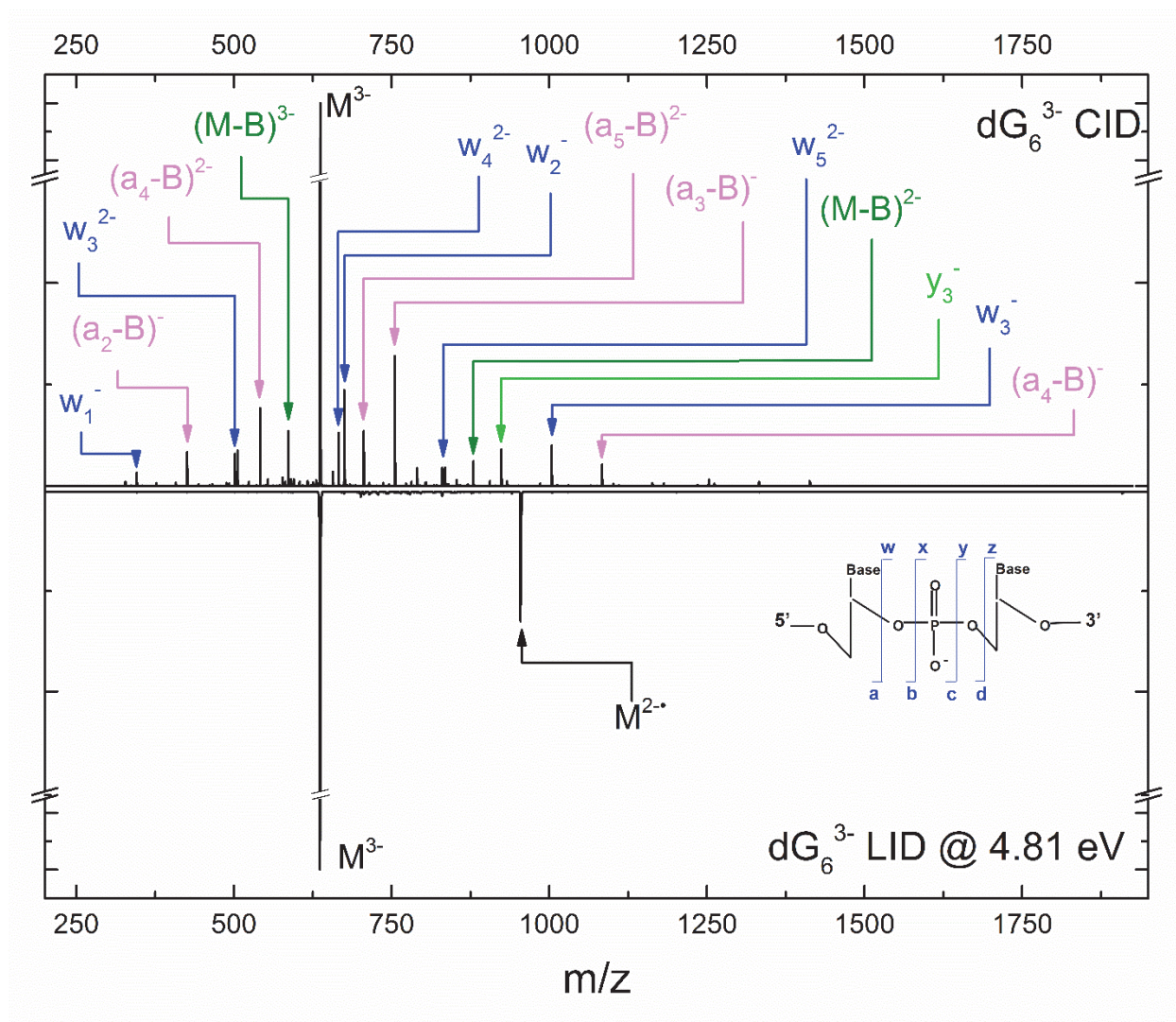


Figure S11. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.80V (top) and irradiation with 4.81 eV photons (bottom) for G_6^{3-} . The major peaks are annotated according to the scheme in the bottom panel.

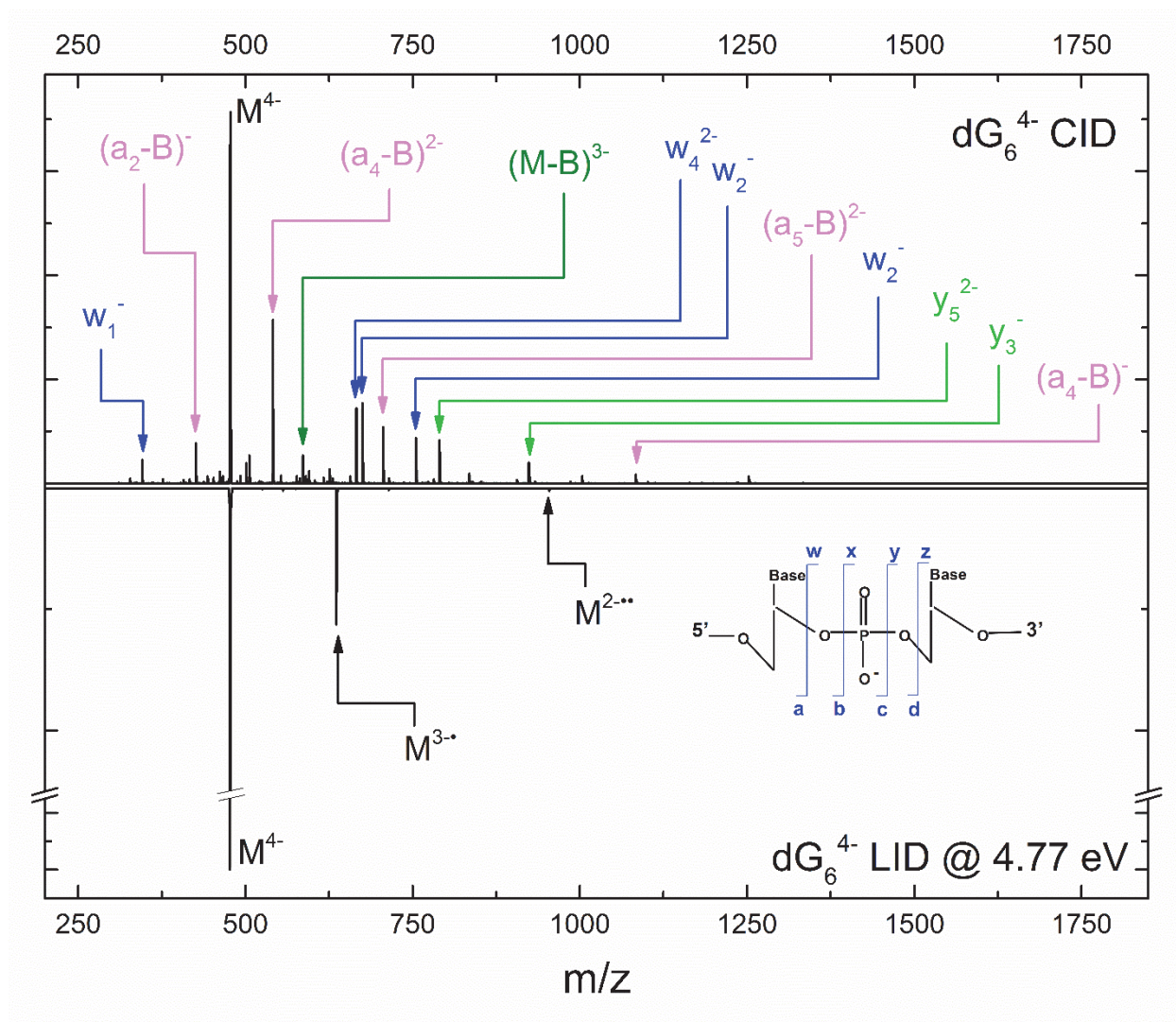


Figure S12. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.90V (top) and irradiation with 4.81 eV photons (bottom) for G_6^{4-} . The major peaks are annotated according to the scheme in the bottom panel.

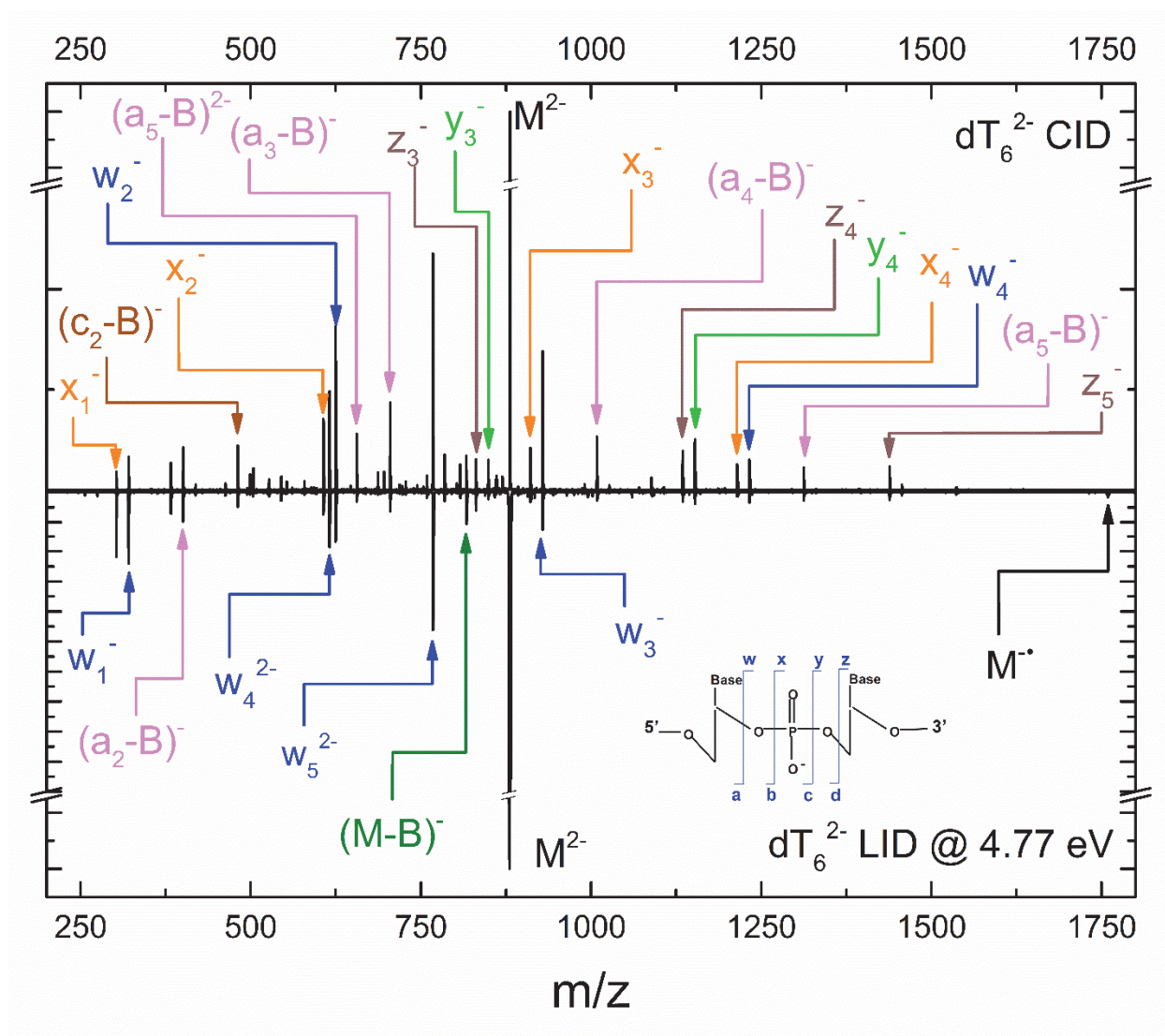


Figure S13. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.73V (top) and irradiation with 4.77 eV photons (bottom) for T_6^{2-} . The major peaks are annotated according to the scheme in the bottom panel.

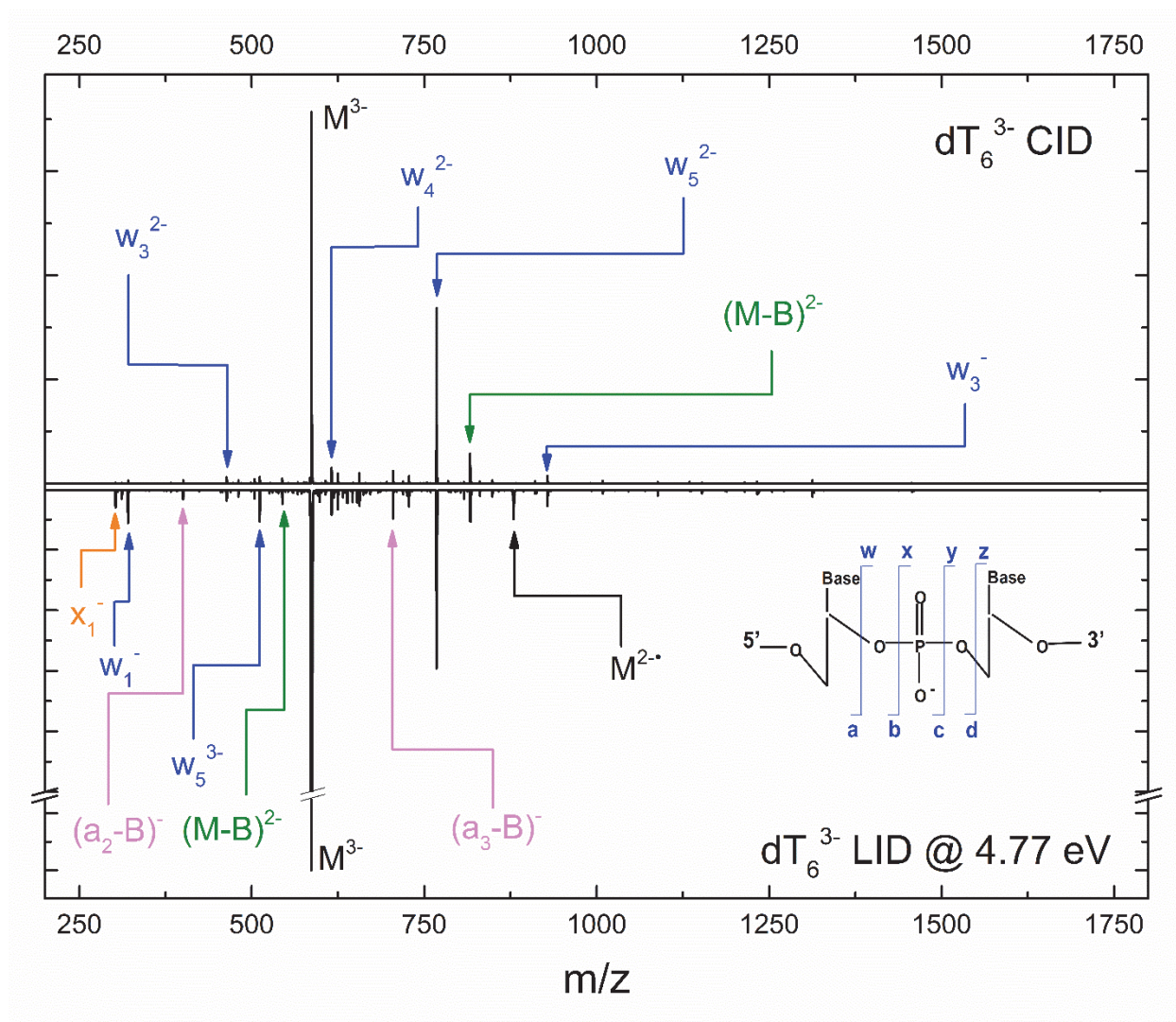


Figure S14. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.70V (top) and irradiation with 4.77 eV photons (bottom) for T_6^{3-} . The major peaks are annotated according to the scheme in the bottom panel.

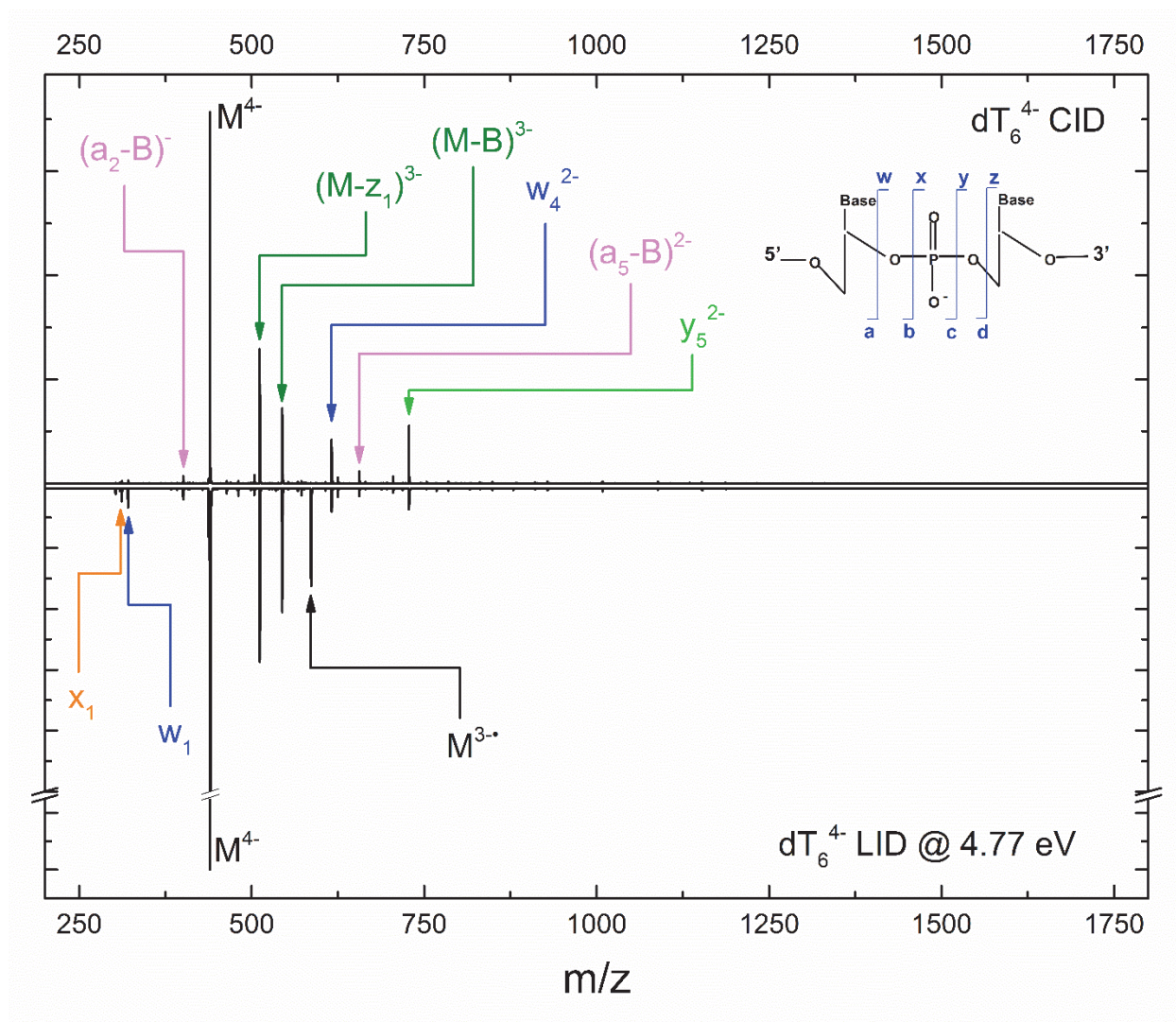


Figure S15. Mass spectra following 10ms collision induced dissociation with an activation voltage of 0.7V (top) and irradiation with 4.77 eV photons (bottom) for T_6^{4-} . The major peaks are annotated according to the scheme in the top panel.

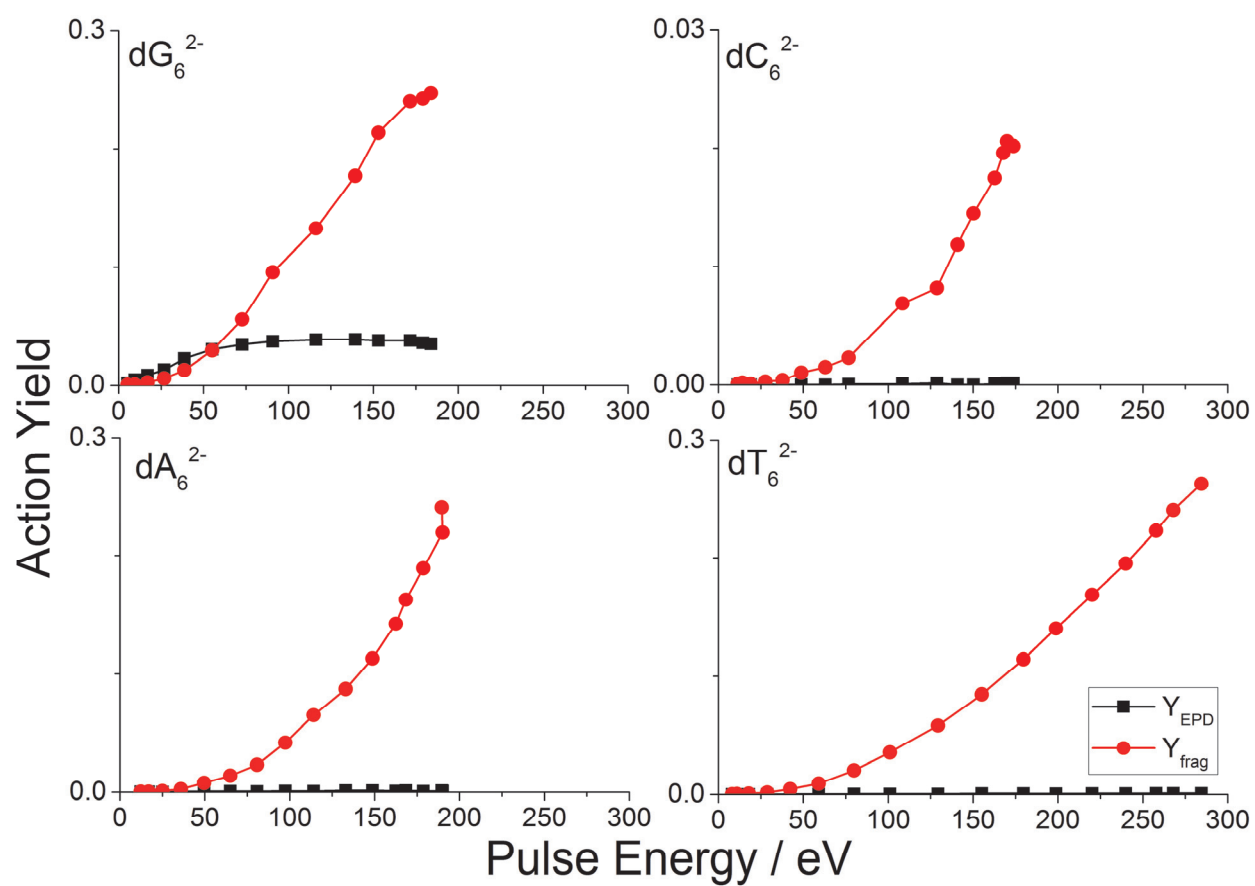


Figure S16. Photoreaction yields versus transmitted pulse energy E_{trans} for EPD (black) and PF (red) for the 2- charge states of dG₆ (top left, 4.81 eV), dC₆ (top right, 4.51 eV), dA₆ (bottom left, 4.63 eV) and dT₆ (bottom right, 4.72 eV).

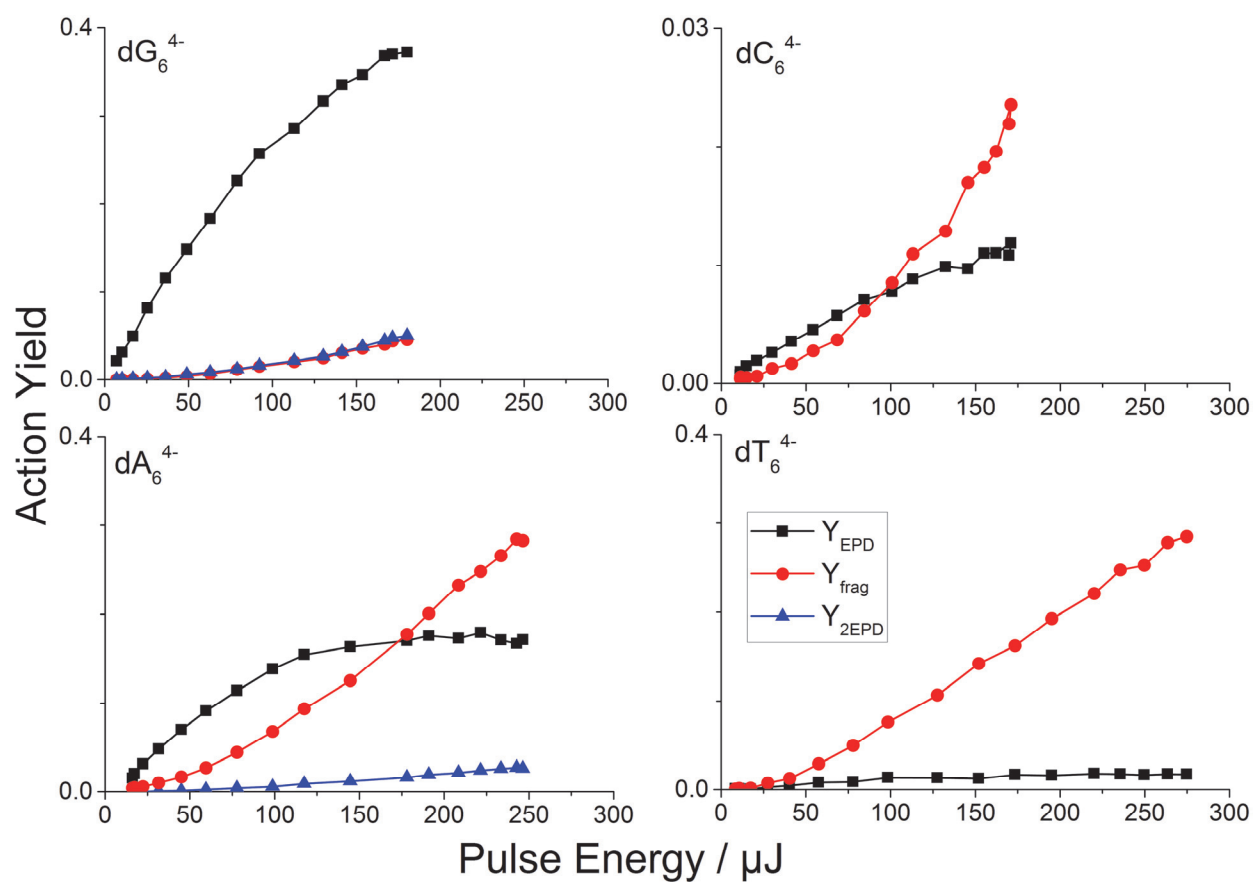


Figure S17. Photoreaction yields versus transmitted pulse energy E_{trans} for EPD (black), PF (red, and loss of two electrons (2EPD) (blue) for the 4- charge states of dG_6 (top left, 4.81 eV), dC_6 (top right, 4.51 eV), dA_6 (bottom left, 4.63 eV) and dT_6 (bottom right, 4.72 eV). The dependence of loss of two electrons is quadratic, indicating two sequential electron losses: $M^{4-} \rightarrow M^{3\bullet} \rightarrow M^{2\bullet\bullet}$.

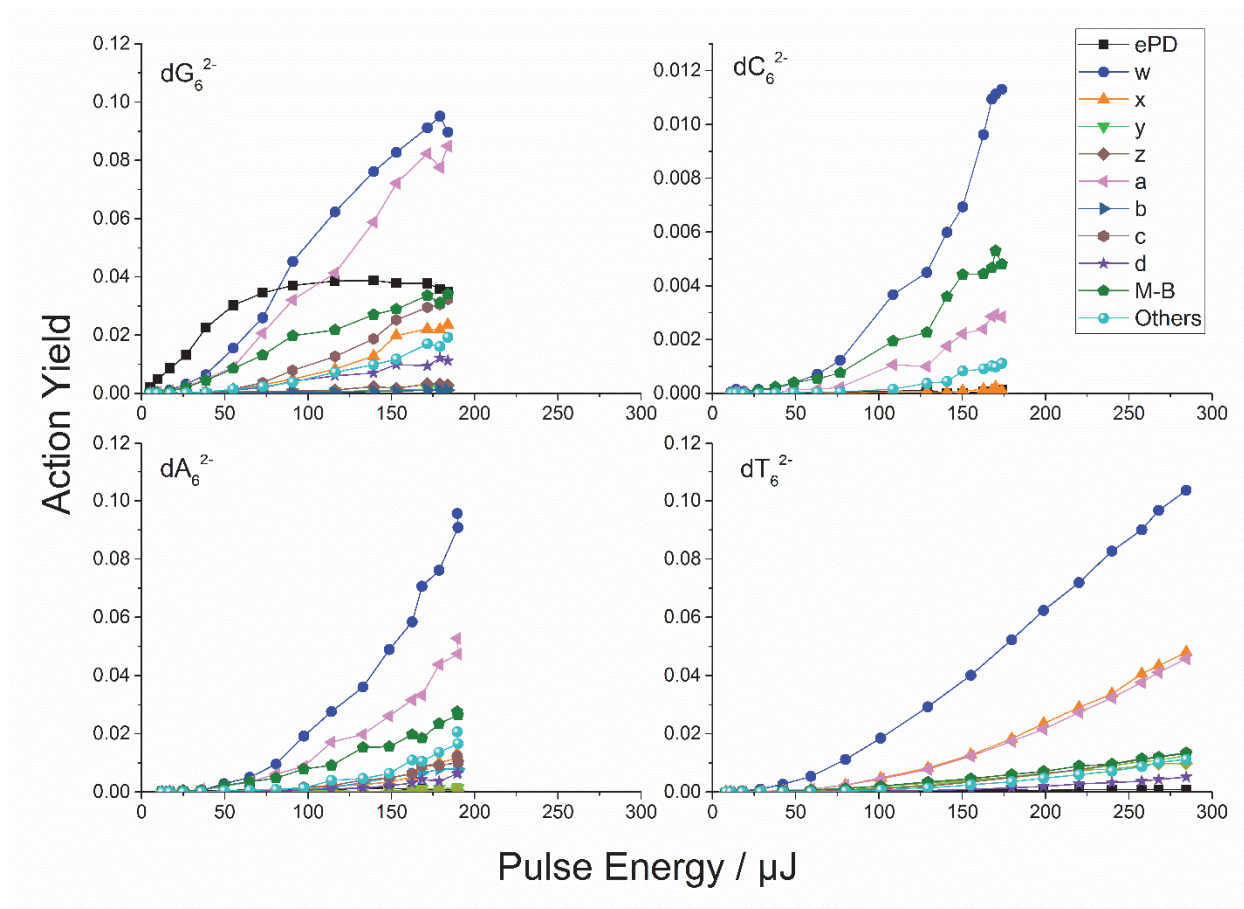


Figure S18. Action yield versus pulse energy for fragments assigned to different families for the 2- charge states of G_6 (top left), C_6 (top right), A_6 (bottom left) and T_6 (top right). Note the choice of colour reflects the colours used in the annotated MS. None of these are linear, and no individual component is either.

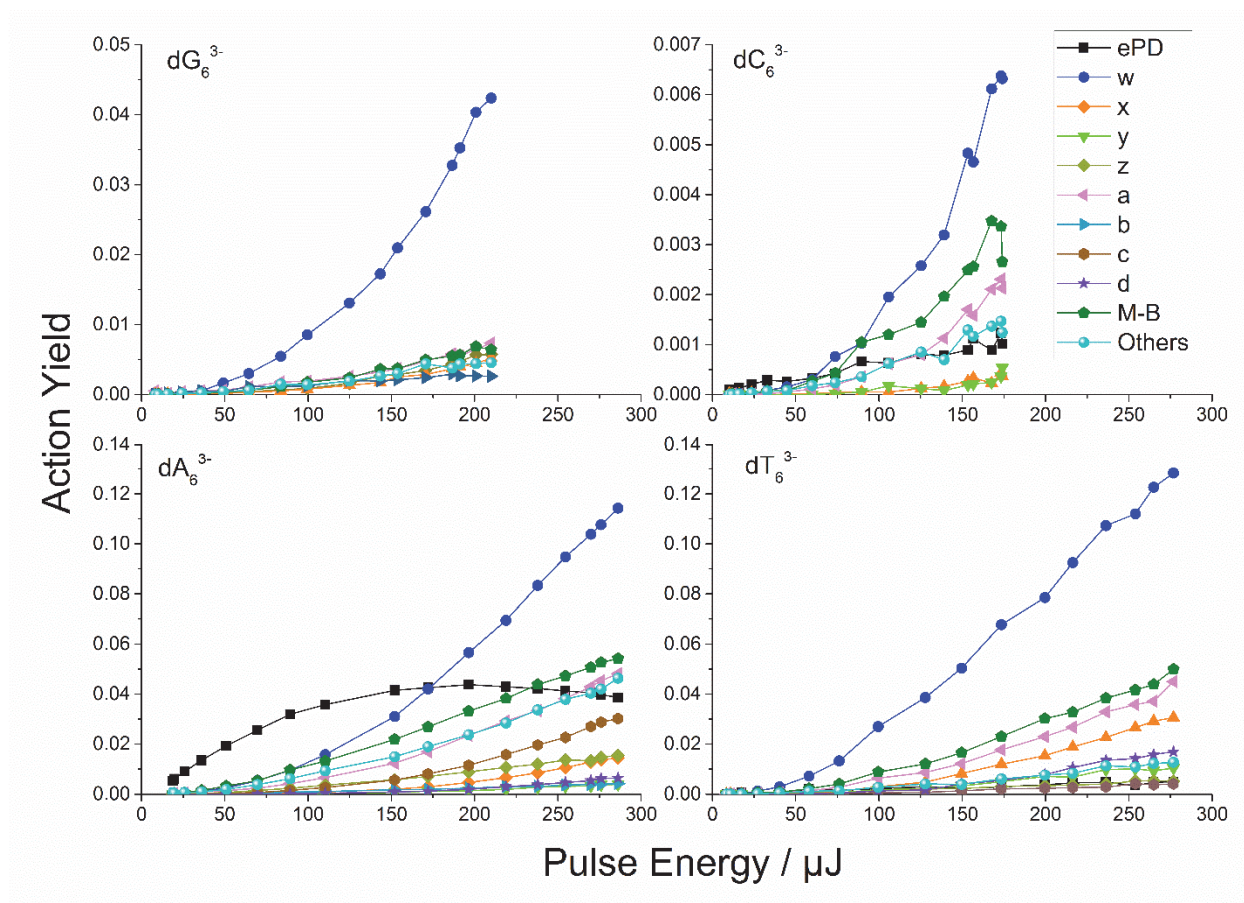


Figure S19. Action yield versus pulse energy for fragments assigned to different families for the 3- charge states of G_6 (top left), C_6 (top right), A_6 (bottom left) and T_6 (top right). Note the choice of colour reflects the colours used in the annotated MS. None of these are linear, and no individual component is either. The ePD is omitted from the G_6 panel for clarity.

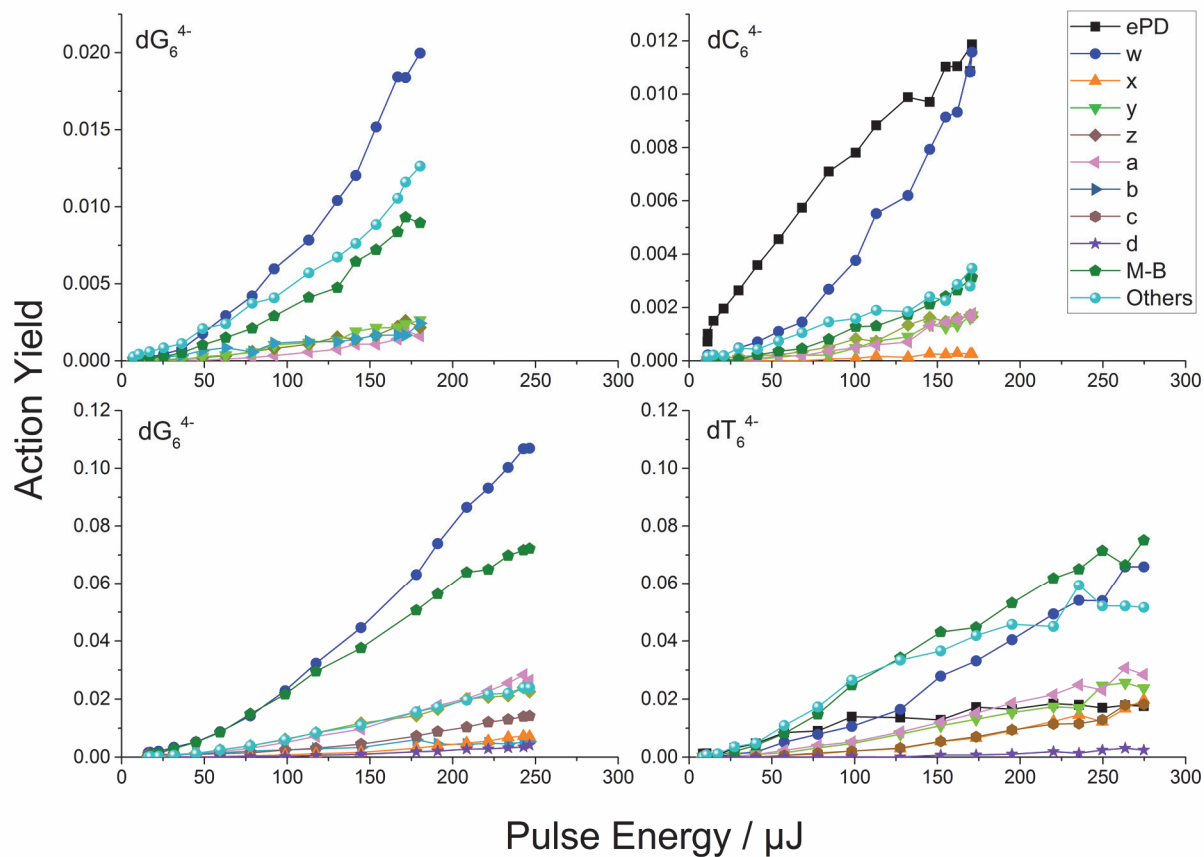


Figure S20. Action yield versus pulse energy for fragments assigned to different families for the 4- charge states of G_6 (top left), C_6 (top right), A_6 (bottom left) and T_6 (top right). Note the choice of colour reflects the colours used in the annotated MS. None of these are linear, and no individual component is either. The ePD is omitted from the G_6 panel for clarity.

dG ₆ ²⁻	P1	P2	P3	P4	P5
cf1	-0.33	-0.33	-0.33	-0.5	-0.5
cf2	-0.5	-0.5	0	-1	0
cf3	-0.5	-0.5	0	-0.5	-0.5
cf4	-0.33	-0.33	-0.33	-0.5	-0.5

dA ₆ ²⁻	P1	P2	P3	P4	P5
cf1	-0.33	-0.33	-0.33	-0.5	-0.5
cf2	-0.33	-0.33	-0.5	-0.5	-0.33
cf3	-0.33	-0.33	-0.33	-0.5	-0.5

dc ₆ ²⁻	P1	P2	P3	P4	P5
cf1	-0.33	-0.33	-0.33	-0.5	-0.5
cf2	-0.33	-0.33	-0.33	-0.5	-0.5

dT ₆ ²⁻	P1	P2	P3	P4	P5
cf1	-0.33	-0.33	-0.33	-0.5	-0.5
cf2	-0.33	-0.33	-0.33	-0.5	-0.5
cf3	-0.33	-0.33	-0.33	-0.5	-0.5
cf4	-0.5	-0.5	-0.33	-0.33	-0.33

dG ₆ ³⁻	P1	P2	P3	P4	P5
cf1	-1	-0.5	-0.5	-0.5	-0.5
cf2	-0.5	-0.5	-0.5	-0.5	-1
cf3	-1	-0.33	-0.33	-0.33	-1
cf4	-1	-0.33	-0.33	-0.33	-1
cf5	-0.5	-0.5	-0.5	-0.5	-1
cf6	-1	-0.33	-0.33	-0.33	-1

dA ₆ ³⁻	P1	P2	P3	P4	P5
cf1	-1	-0.5	-0.5	-0.5	-0.5
cf2	-1	-0.33	-0.33	-0.33	-1
cf3	-1	-0.5	-0.5	-0.5	-0.5
cf4	-1	-0.33	-0.33	-0.33	-1
cf5	-1	-0.5	-0.5	-0.5	-0.5

dc ₆ ³⁻	P1	P2	P3	P4	P5
cf1	-1	-0.33	-0.33	-0.33	-1
cf2	-1	-0.33	-0.33	-0.33	-1
cf3	-1	-0.33	-0.33	-0.33	-1
cf4	-1	-0.5	-0.5	-0.5	0.5
cf5	-1	-0.33	-0.33	-0.33	-1
cf6	-1	-0.33	-0.33	-0.33	-1

dG ₆ ⁴⁻	P1	P2	P3	P4	P5
cf1	-1	-1	0	-1	-1
cf2	0	-1	-1	-1	-1

Figure S21. Summary of charge localization (linked to proton distribution in proximity to each of the phosphate groups) in each optimized “conformer” (dX₆⁴⁻: 1 proton; dX₆³⁻: 2 protons; dX₆²⁻: 3 protons). We take the crude assumption that a phosphate group bear a charge = -1 and a neutralized phosphate group by a proton has a charge = 0. When a proton is shared between two phosphate groups, the charge is -0.5, and when 2 proton are shared between three phosphate groups, the charge of -0.33. The DFT calculations show that the charges are much more spread on the structure. The table is only helping to infer next to which phosphate group(s) the protons are located. The colors mean the following. When one proton is shared between two phosphate groups, the phosphate charge is assigned (-0.5 -0.5), written in the same color. When two protons are shared between 3 phosphates groups, they are assigned respective charges of (-0.33, -0.33, -0.33), with the same color. A phosphate group neutralized by a proton not shared by other groups is marked in green. This occurs only for some conformers of dG₆. Note that the phosphate groups with value of -1 (not neutralized) are all nevertheless making H-bonds with base or sugar groups, a phenomenon that “dilutes” the charges in practice.

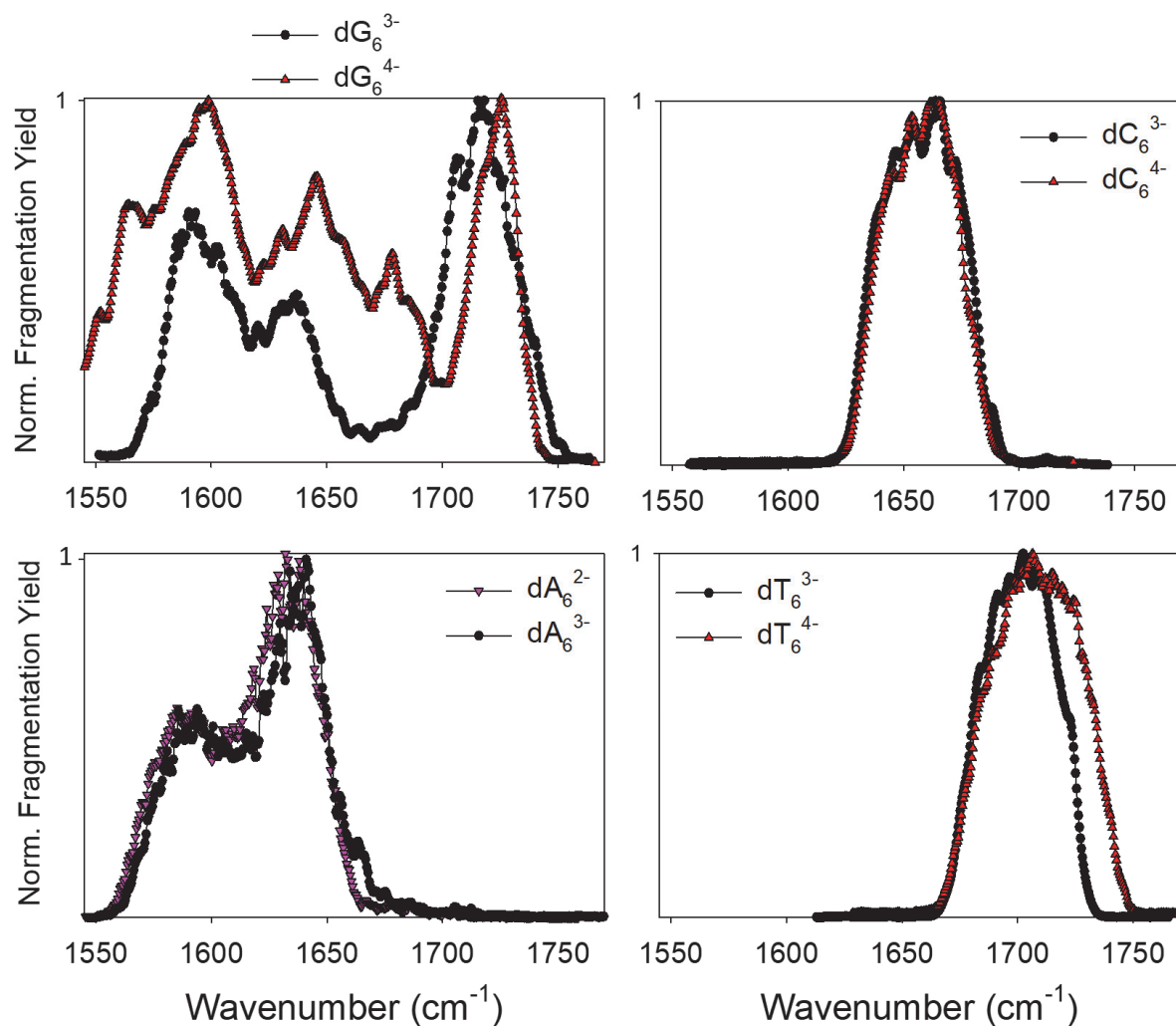


Figure S22. Experimental IRMPD spectrum of the single strands, as annotated in the legends. For the 3- single strands, the fragments (according to Mc Luckey nomenclature) taken into account are $d_1\text{-H}_2\text{O}^-$, w_1^- , w_4^{2-} , w_2^{2-} , $a_5\text{-B}^{2-}$, $a_3\text{-B}^-$, y_3^- , w_3^- , $a_4\text{-B}^-$, and base loss from the strand $ss\text{-B}^{2-}$ and internal fragments. For the other charge states, the fragments are of the same nature.

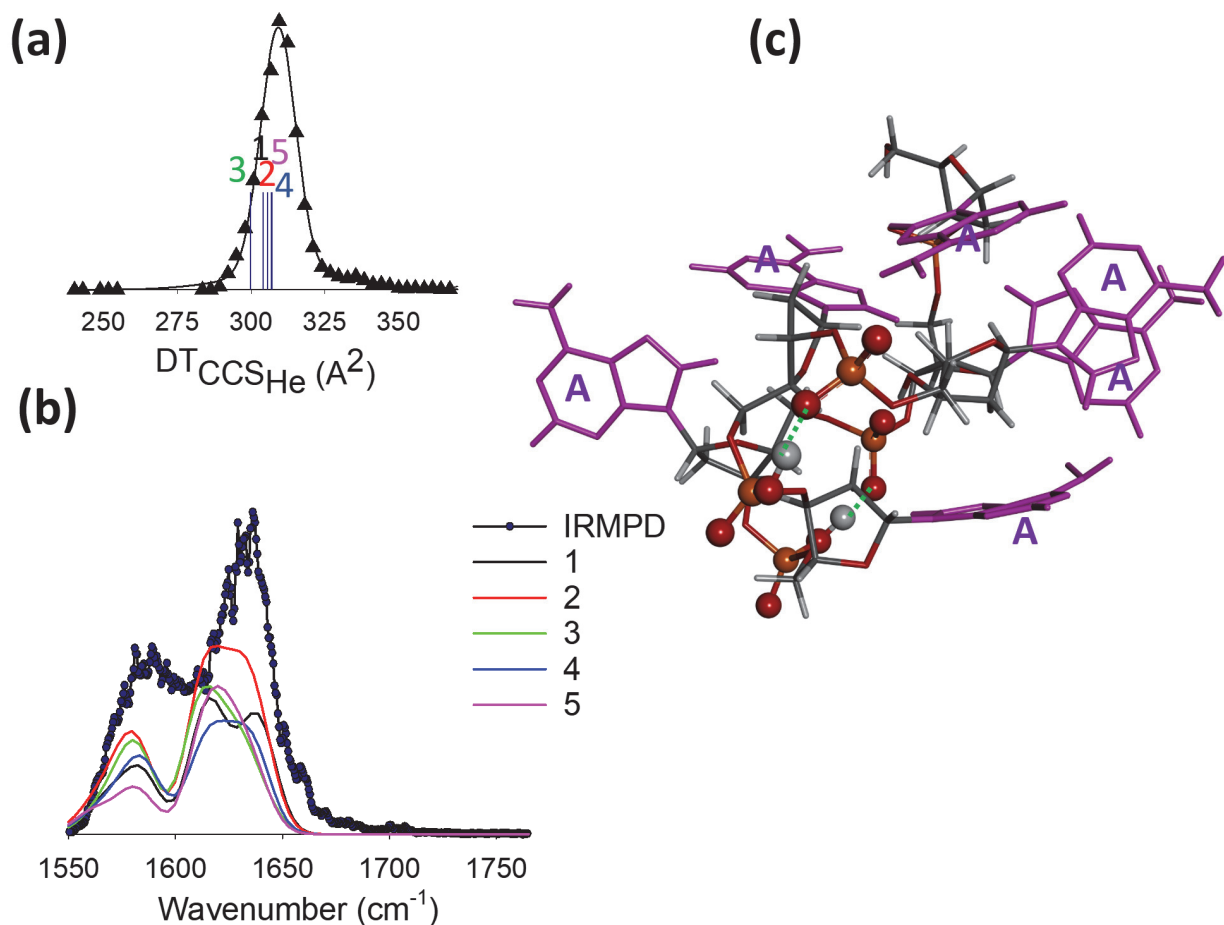


Figure S23. A) Ion mobility spectrometry of the single strand dA_6^{3-} ($^{\text{DT}}\text{CCS}_{\text{He}}$). The vertical bars are the theoretical collisional cross section obtained on the different conformers of dA_6^{3-} using the trajectory model (TM, mobcal). B) Experimental IRMPD spectrum of the single strand dA_6^{3-} and the calculated IR spectra of different conformers of dA_6^{3-} . The calculations were performed using Gaussian 16 rev. B01 (DFT, B3LYP, 6-31G(d,p)+GD3) and frequencies were scaled by a factor of 0.97. C) Structure of conformer 5 of dA_6^{3-} . Hydrogen bonds between two pairs of phosphate groups are represented in ball and stick.

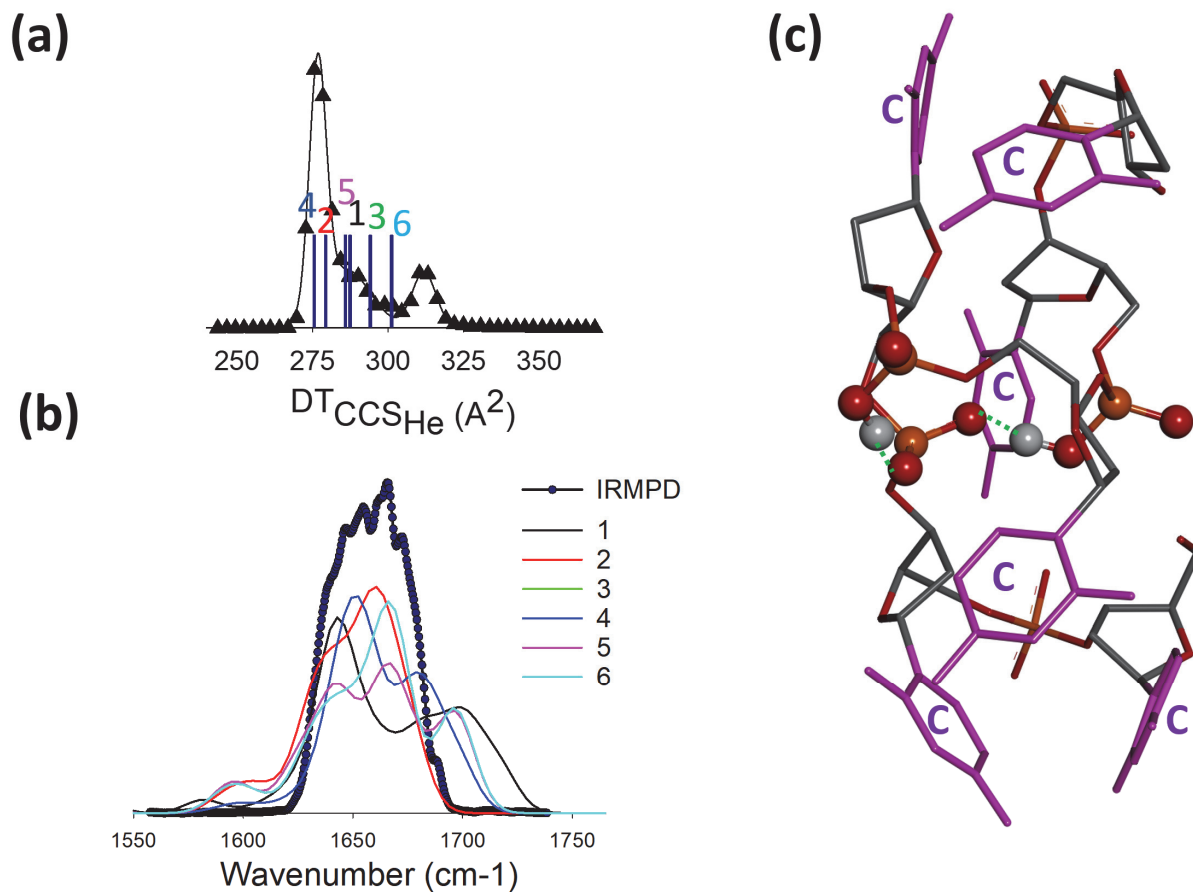


Figure S24. A) Ion mobility spectrometry of the single strand dC_6^{3-} (DTCCS_{He}). The vertical bars are the theoretical collisional cross section obtained on the different conformers of dC_6^{3-} using the trajectory model (TM, mobcal). B) Experimental IRMPD spectrum of the single strand dC_6^{3-} and the calculated IR spectra of different conformers of dC_6^{3-} . The calculations were performed using Gaussian 16 rev. B01 (DFT, B3LYP, 6-31G(d,p)+GD3) and frequencies were scaled by a factor of 0.97. C) Structure of conformer 5 of dC_6^{3-} . Hydrogen bonds between two pairs of phosphate groups are represented in ball and stick.

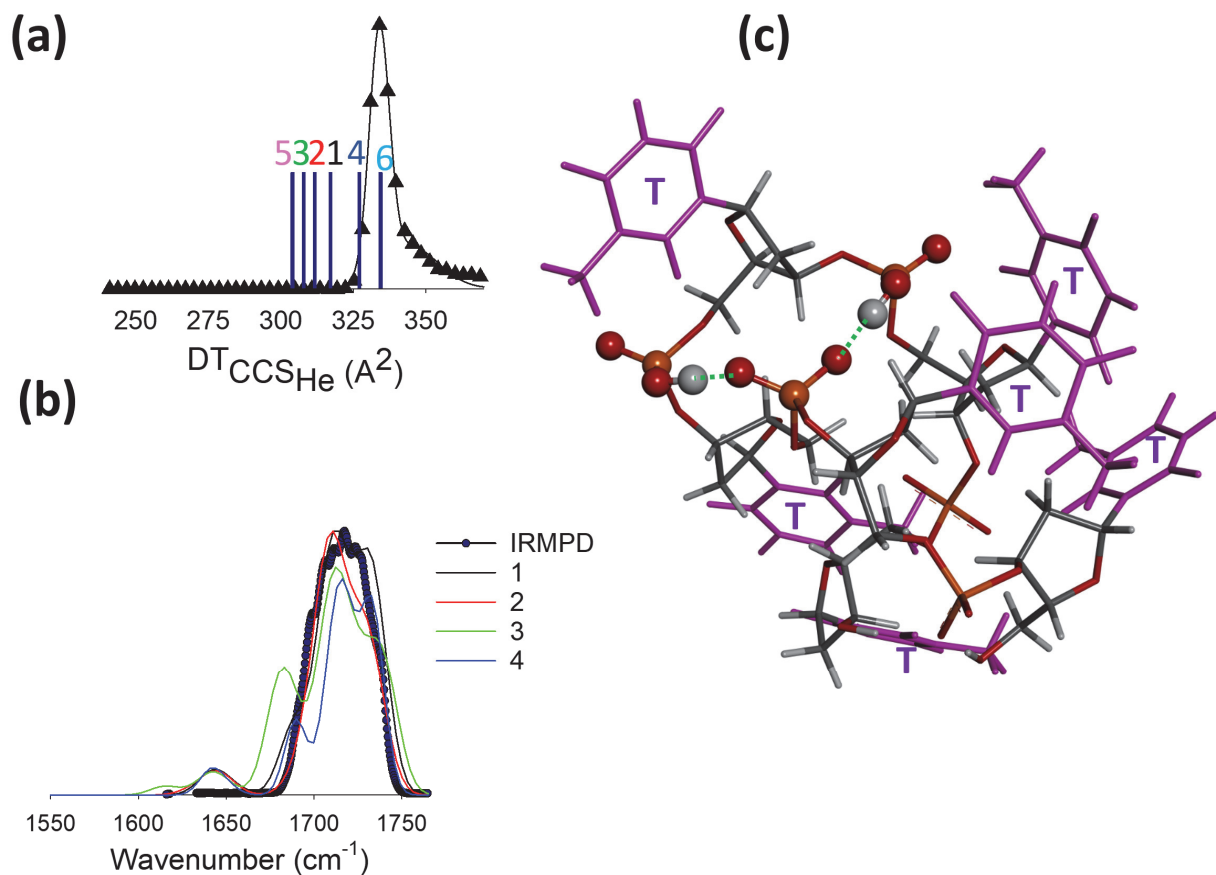


Figure S25. A) Ion mobility spectrometry of the single strand dT_6^{3-} (DTCCS_{He}). The vertical bars are the theoretical collisional cross section obtained on the different conformers of dT_6^{3-} using the trajectory model (TM, mobcal). B) Experimental IRMPD spectrum of the single strand dT_6^{3-} and the calculated IR spectra of different conformers of dT_6^{3-} . The calculations were performed using Gaussian 16 rev. B01 (DFT, B3LYP, 6-31G(d,p)+GD3) and frequencies were scaled by a factor of 0.97. C) Structure of conformer 3 of dT_6^{3-} . Hydrogen bonds between two pairs of phosphate groups are represented in ball and stick.

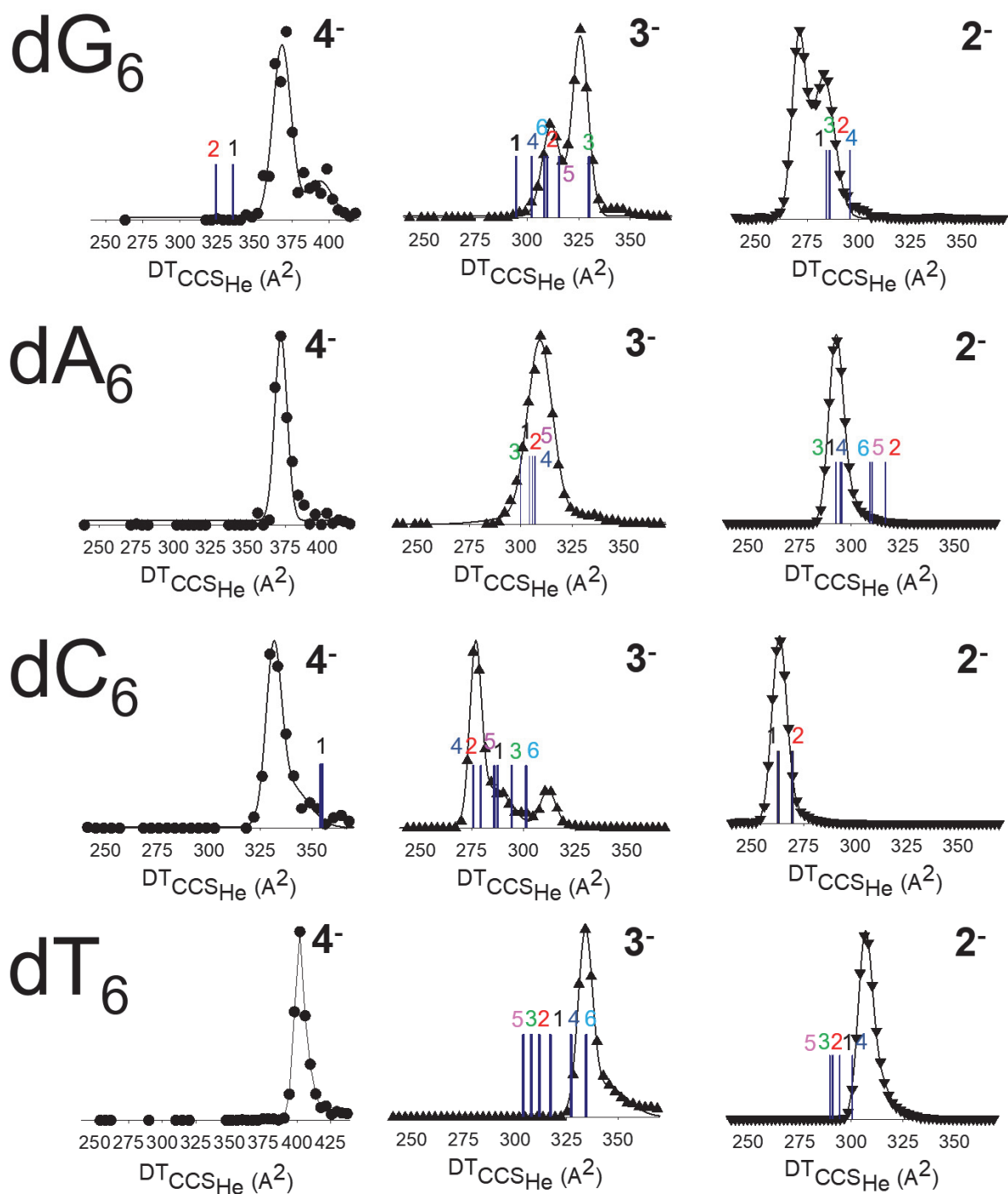


Figure S26. Collision cross section distributions (DT_{CCSHe}) for all charge states, and matching of the calculated collision cross section distributions (TM calculation, Mobcal, helium, 300K) for each conformer.

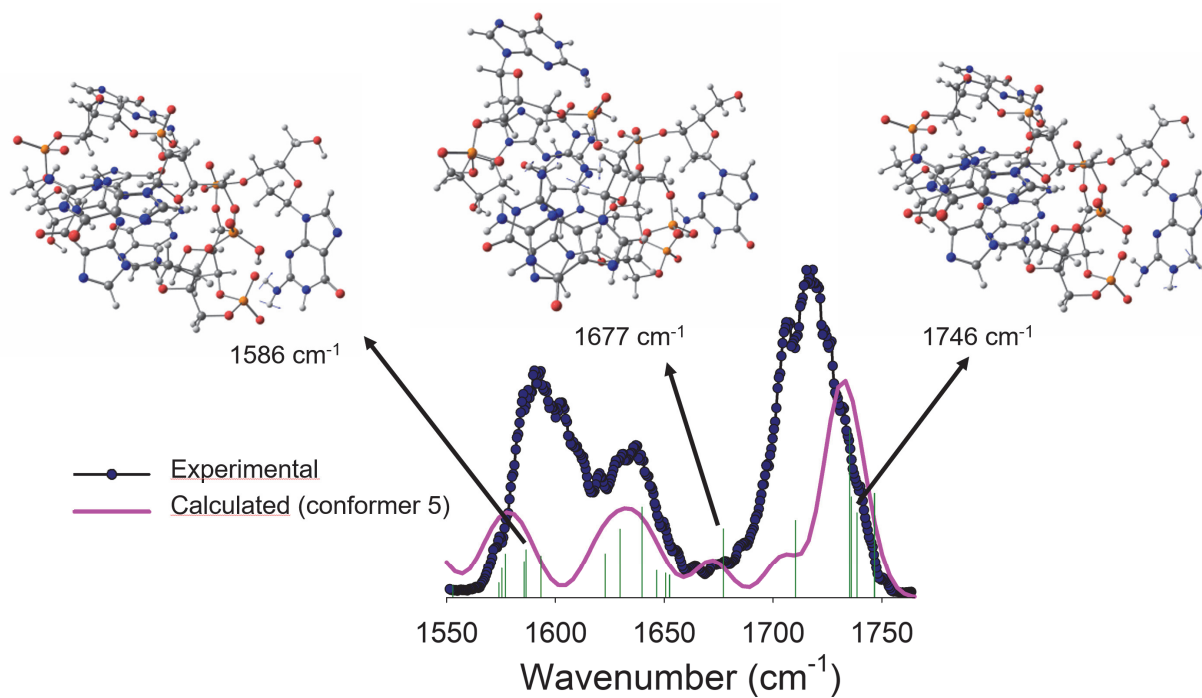


Figure S27. Examples of vibrational modes in the calculated spectra. An supporting animated version of this figure is available in PowerPoint format (Figure_S27.pptx). The animation is visible by activating the “presentation” mode.

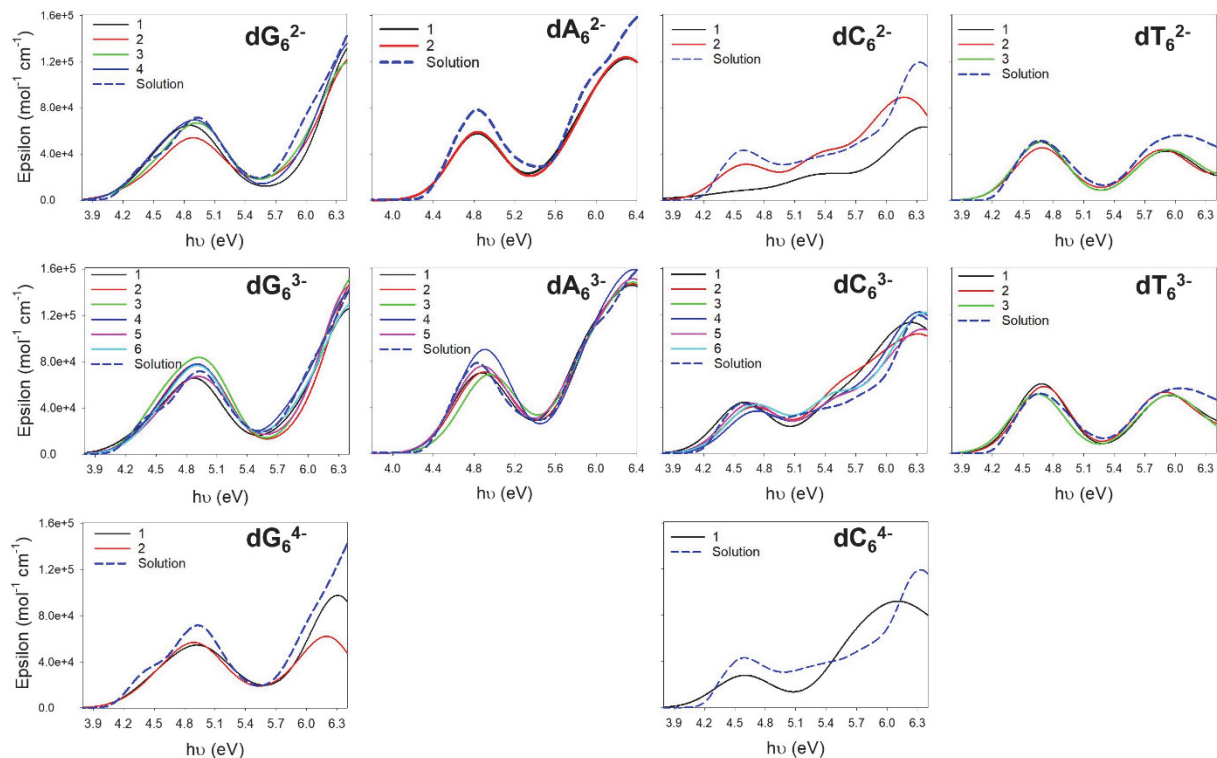


Figure S28. Comparison of experimental solution absorption spectra (dashed blue line) and calculated gas-phase absorption spectra (TD-DFT/MO6-2X/6-31G(d,p)) for all calculated conformers (the legend refers to the conformer number).

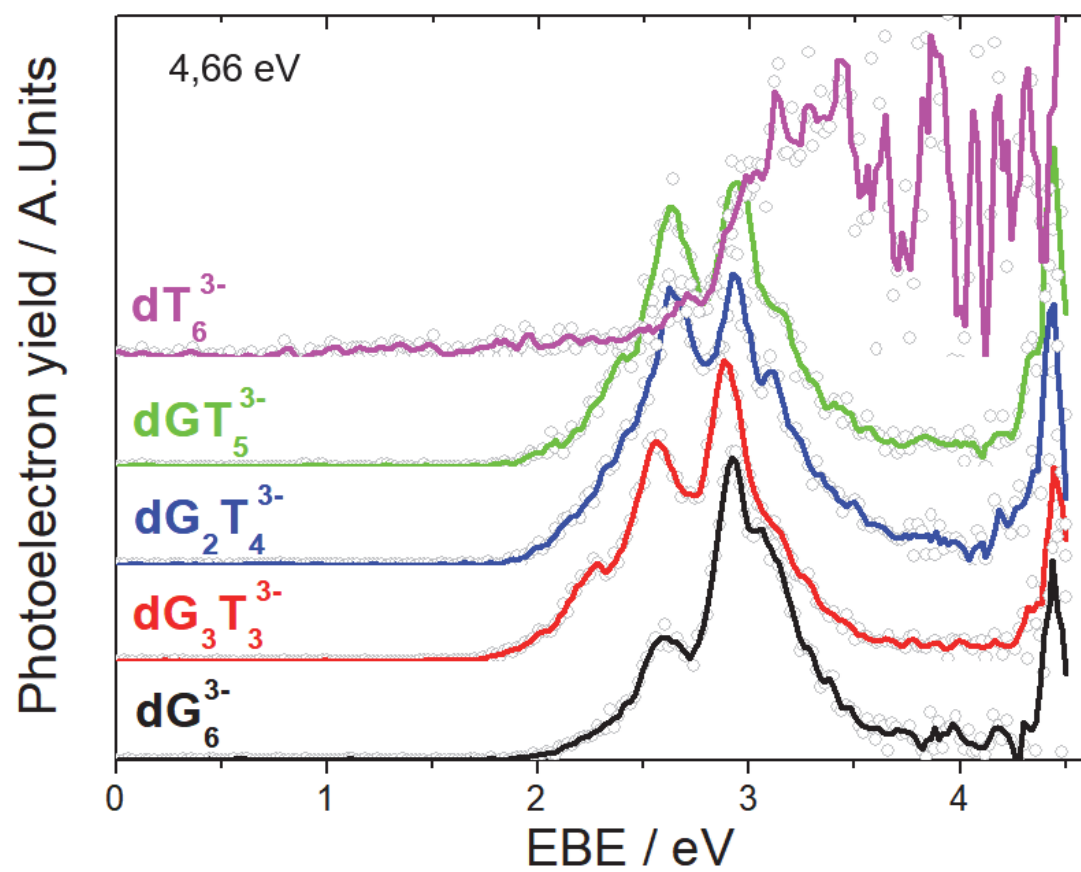


Figure S28. Photoelectron spectra of dT_6^{3-} , dGT_5^{3-} , $\text{dG}_2\text{T}_4^{3-}$, $\text{dG}_3\text{T}_3^{3-}$, and dG_6^{3-} , with an excitation wavelength of 266 nm ($h\nu = 4.66$ eV).

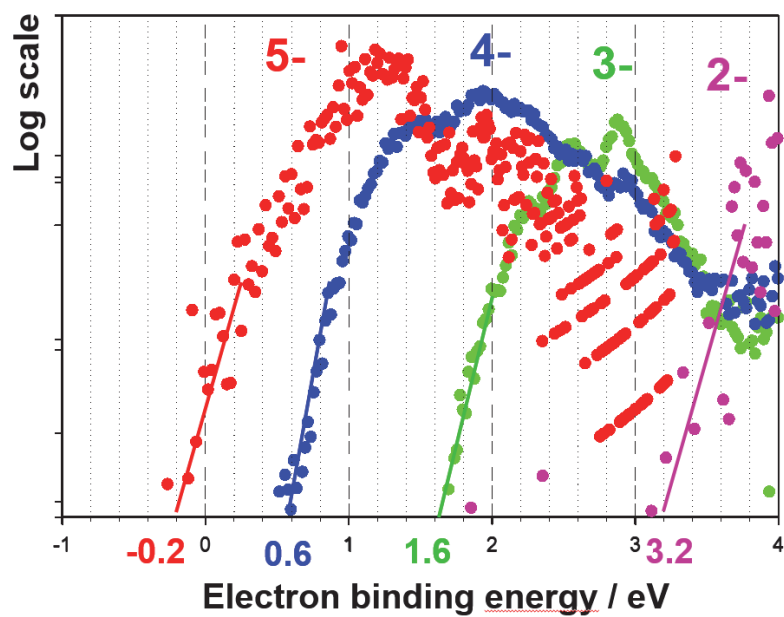


Figure S30. Photoelectron spectra of dG_3T_3 at charge states 5-, 4-, 3- and 2- (presented on a log scale to estimate the adiabatic detachment energy), recorded with an excitation wavelength of 266 nm ($h\nu = 4.66$ eV).

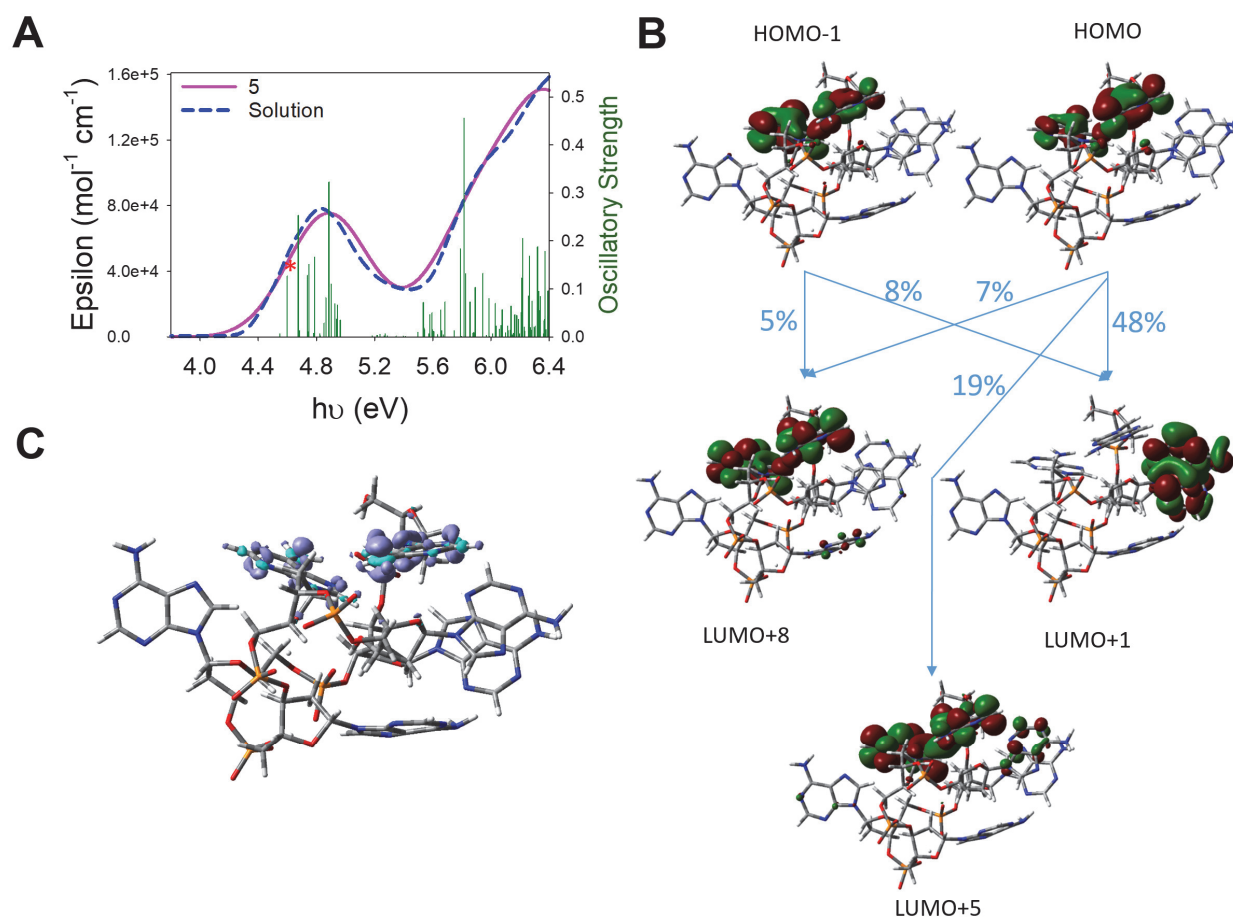


Figure S31. A) Experimental solution absorption spectrum and calculated gas-phase absorption spectrum (conformer 5) of dA_6^{3-} . B) Molecular orbitals involved in the first electronic transition of significant oscillator strength (shown by a star in panel A). C) Calculated difference of electronic densities between dA_6^{3-} and the product of vertical electron detachment, $\text{dA}_6^{2-\bullet}$.

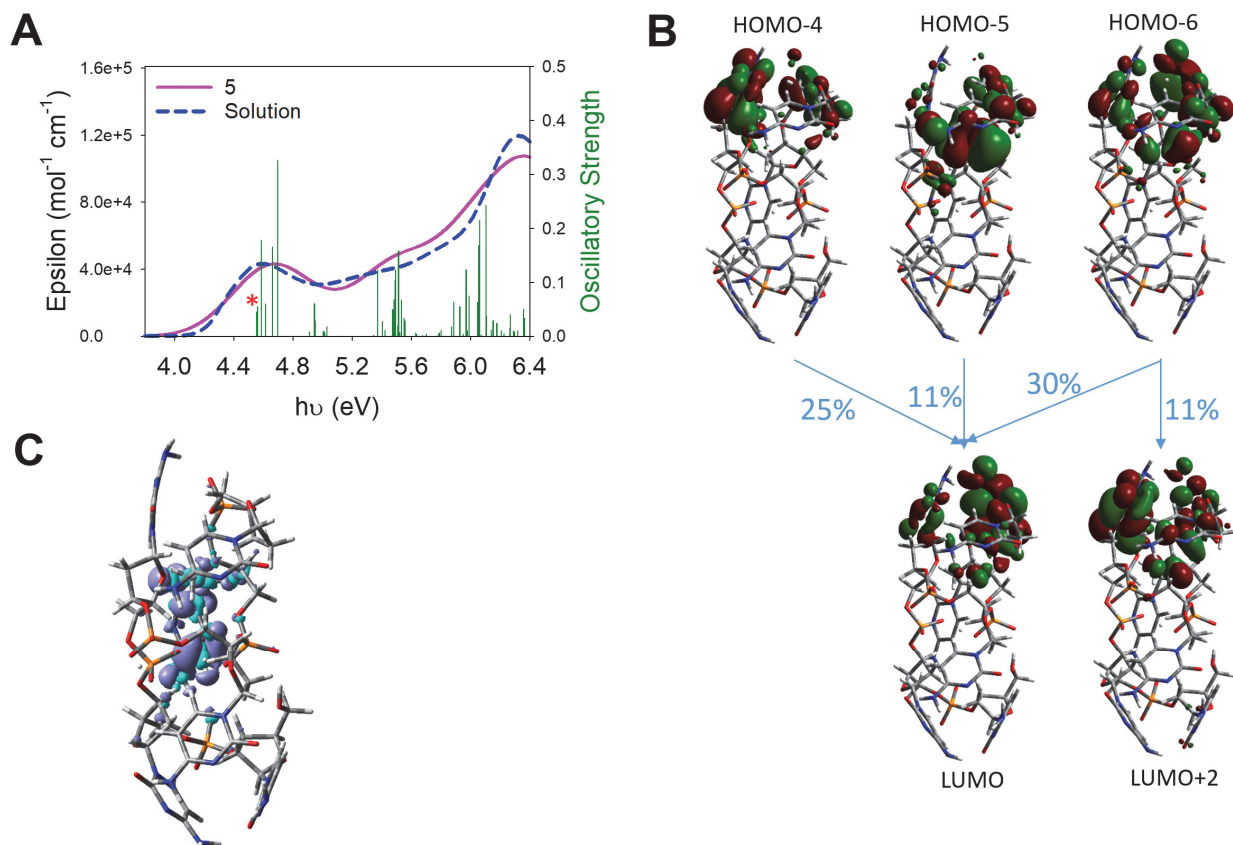


Figure S32. A) Experimental solution absorption spectrum and calculated gas-phase absorption spectrum (conformer 5) of dC_6^{3-} . B) Molecular orbitals involved in the first electronic transition of significant oscillator strength (shown by a star in panel A). C) Calculated difference of electronic densities between dC_6^{3-} and the product of vertical electron detachment, $\text{dC}_6^{2\cdot}$.

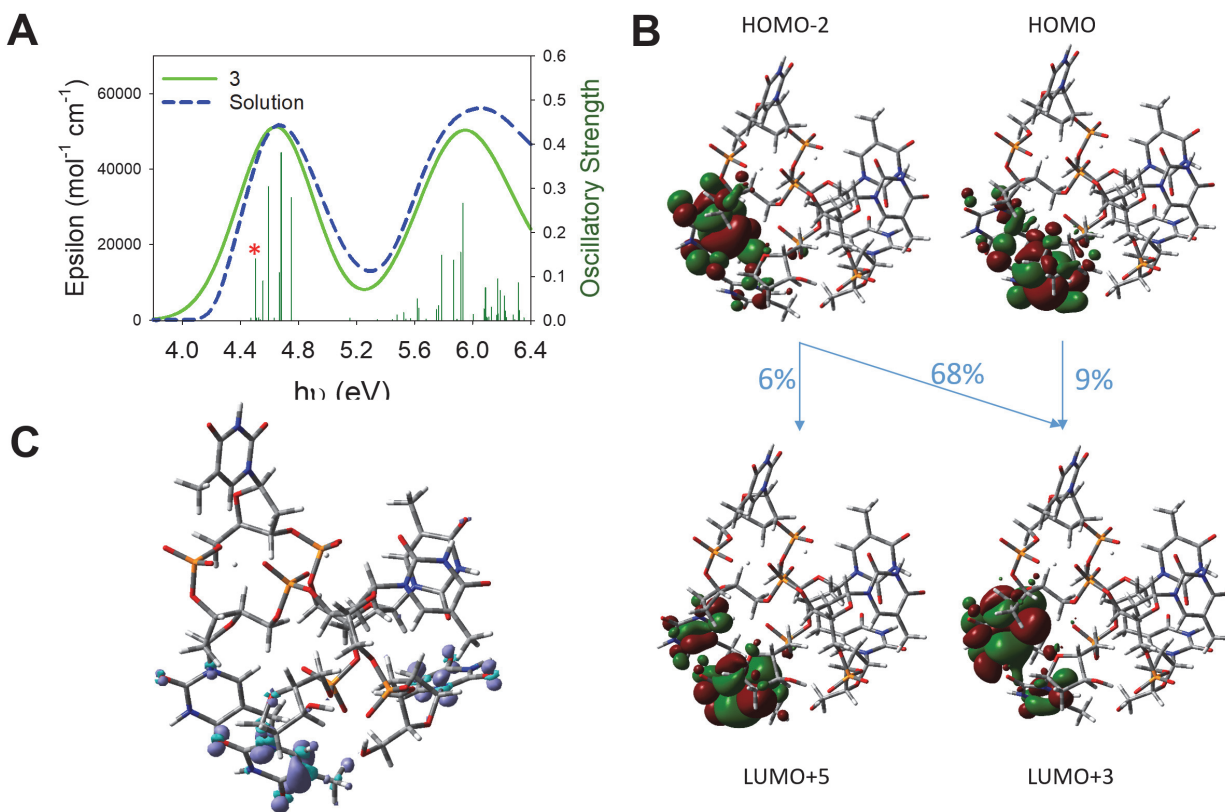


Figure S33. A) Experimental solution absorption spectrum and calculated gas-phase absorption spectrum (conformer 3) of dT_6^{3-} . B) Molecular orbitals involved in the first electronic transition of significant oscillator strength (shown by a star in panel A). C) Calculated difference of electronic densities between dT_6^{3-} and the product of vertical electron detachment, $\text{dT}_6^{2-\bullet}$.