Electronic Supporting Information

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The Soret absorption band of isolated chlorophyll a and b tagged with quarternary ammonium ions

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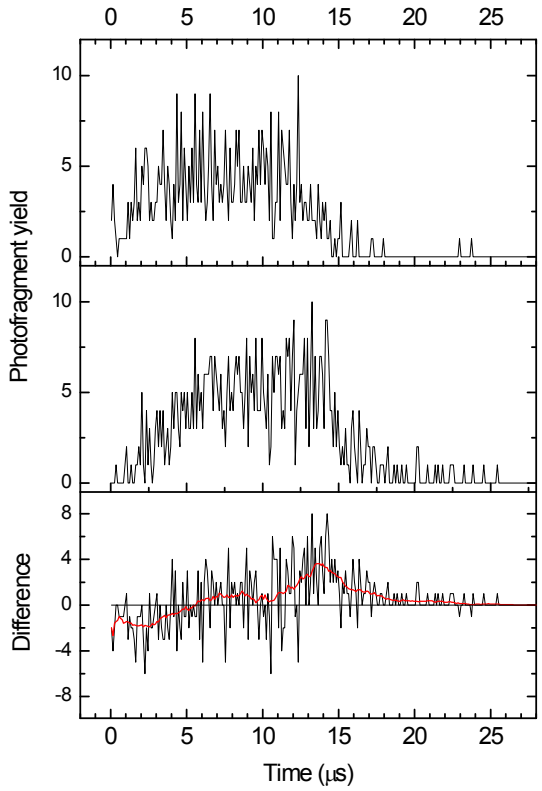
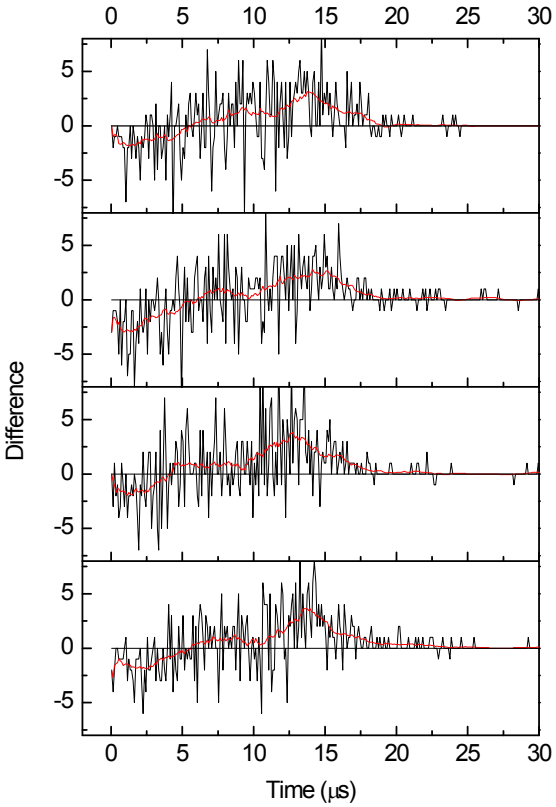
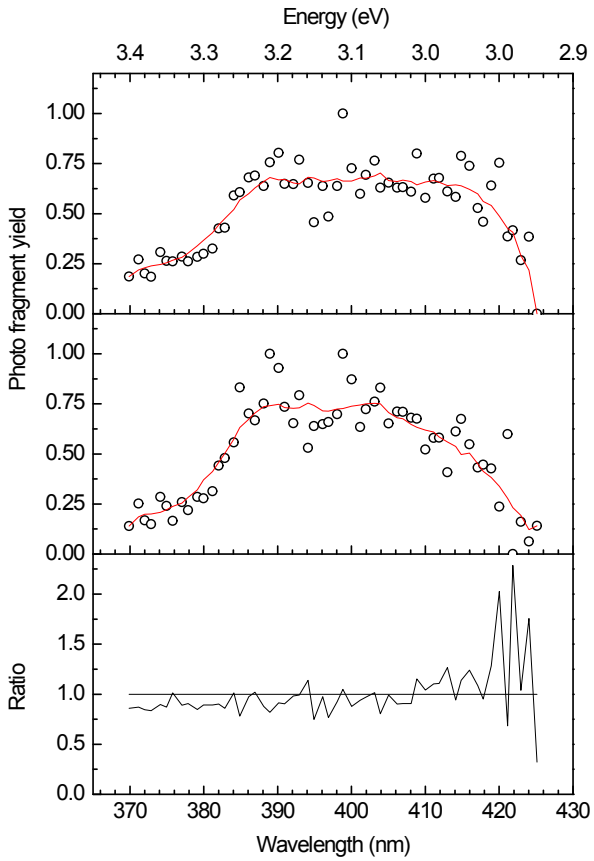


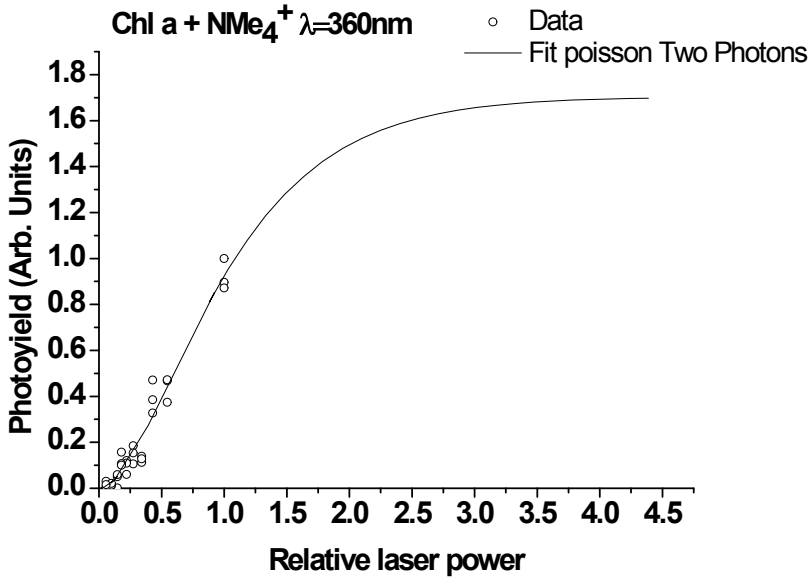
Ion bunch profiles at 50 kV and 25 kV acceleration sampling $\mathbf{3}^+$ from Chl a • $\mathbf{3}^+$. The time is the flight time to the electrostatic analyser after the laser was fired. The difference between the two ion bunch profiles (25 kV – 50 kV) shows that more ions arrive late at 25 kV acceleration.



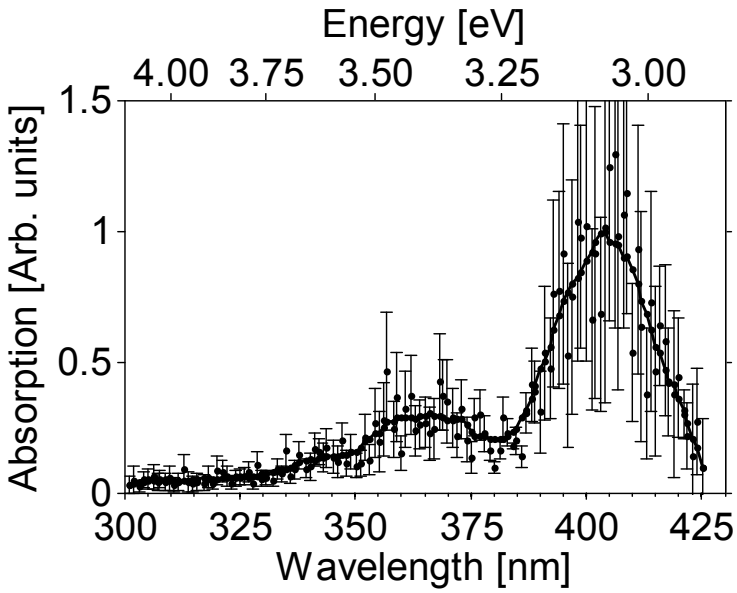
Difference between the two ion bunch profiles (25 kV – 50 kV). From top to bottom: 372 nm, 374 nm, 380 nm and 382nm.



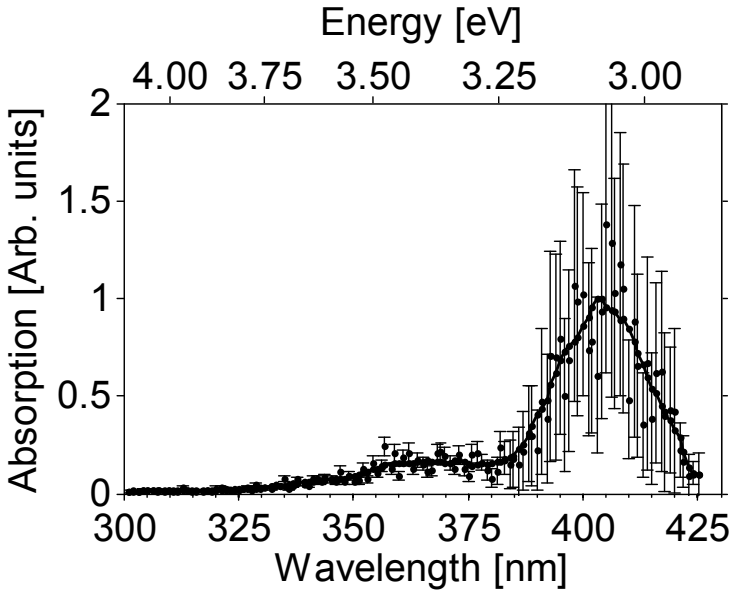
Gas-phase action spectra of Chl a • $\mathbf{3}^{+}$ recorded at 50 kV and 25 kV and the ratio between the two spectra at each wavelength (50 kV / 25 kV). At low wavelengths there is no indication of too little dissociation at 50 kV due to too long dissociation times. The scatter in the ratio is highest when the absorption is low.



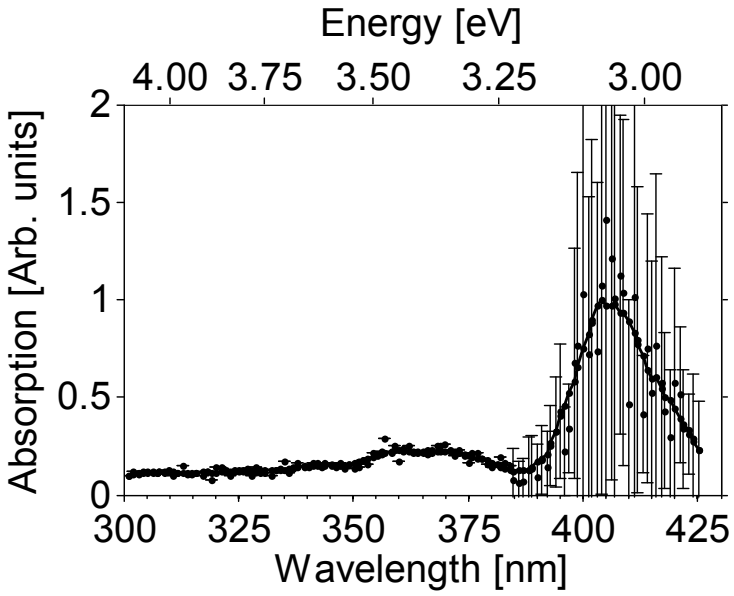
Power-dependence data. The fit is a two-photon Poisson fit with saturation, A(1-(1+b)exp(-b x))



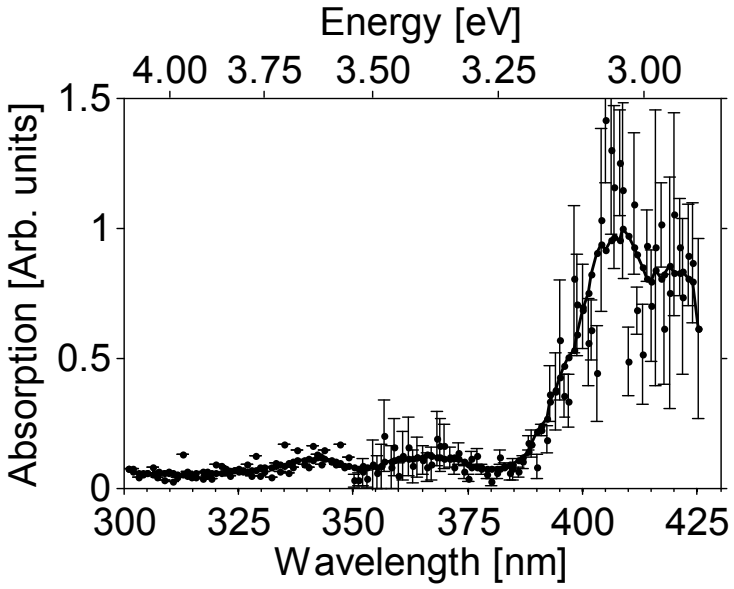
Action spectrum for Chl a + acetylcholine dissociating into acetylcholine.



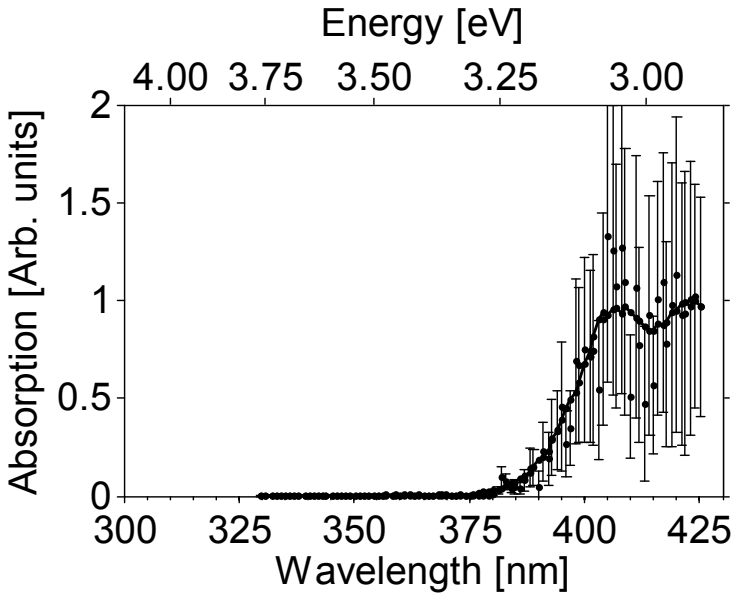
Action spectrum for Chl a + NMe_4^+ dissociating into NMe_4^+.



Action spectrum for Chl a + NBu_4^+ dissociating into NBu_4^+.



Action spectrum for Chl b + acetylcholine dissociating into acetycholine.



. Action spectrum for Chl b + NMe_4^+ dissociating into NMe_4^+.

Table S1. Chl *a* orbital contributions to calculated TD-CAM-B3LYP/Def2-SVP excitations. Lesser contributions having transition probabilities ~½ of those of the main transitions are given in parentheses. Minor contributions with probabilities less than ½ not shown.

Chl *a*		eV	Contributing orbital transitions
1^{+}	Soret-band	3.422	HOMO→LUMO+1 (HOMO-1→LUMO)
	Soret-band	3.666	HOMO-1→LUMO+1 (HOMO→LUMO)
	Minor peak	3.991	HOMO→LUMO+2 HOMO-1→LUMO+1
	Minor peak	4.068	HOMO-5→LUMO
2^{+}	Soret-band	3.378	HOMO→LUMO+1 (HOMO-1→LUMO)
	Soret-band	3.363	HOMO-1→LUMO+2 (HOMO-3→LUMO) (HOMO→LUMO) (HOMO→LUMO+2)
	Minor peak	4.067	HOMO-5→LUMO (HOMO→LUMO+2)
3^{+}	Soret-band	3.361	HOMO→LUMO+2 (HOMO-1→LUMO)
	Soret-band	3.603	HOMO-1→LUMO+2 (HOMO→LUMO) (HOMO→LUMO+2)
	Minor peak	3.919	HOMO→LUMO+2 (HOMO-1→LUMO+2)
	Minor peak	4.084	HOMO-5→LUMO
	Minor peak	4.141	HOMO-5→LUMO HOMO-1→LUMO+2
	Minor peak	4.170	HOMO-5→LUMO HOMO-5→LUMO+2
No tag	Soret-band	3.335	HOMO-2→LUMO HOMO-1→LUMO
	Soret-band	3.450	HOMO-2→LUMO HOMO-1→LUMO HOMO-2→LUMO+1 HOMO→LUMO+1
	Soret-band	3.613	HOMO-1→LUMO+1 HOMO→LUMO
	Minor peak	3.999	HOMO-4→LUMO HOMO-2→LUMO

Table S2. Chl *b* orbital contributions to calculated TD-CAM-B3LYP/Def2-SVP excitations. Lesser contributions having transition probabilities ~½ of those of the main transitions are given in parentheses. Minor contributions with probabilities less than ½ not shown.

Chl *b*		eV	Contributing orbital transitions
1^{+}	Soret-band	3.251	HOMO→LUMO+1 (HOMO-1→LUMO)
	Soret-band	3.429	HOMO-1→LUMO+1 (HOMO→LUMO)
	Minor peak	4.018	HOMO→LUMO+2 HOMO-1→LUMO+2
	Minor peak	4.134	HOMO-5→LUMO
2^{+}	Soret-band	3.226	HOMO→LUMO+1 (HOMO-1→LUMO)
	Soret-band	3.406	HOMO-1→LUMO+2 (HOMO→LUMO)
	Minor peak	4.140	HOMO-5→LUMO
3^{+}	Soret-band	3.195	HOMO→LUMO+2 (HOMO-1→LUMO)
	Soret-band	3.383	HOMO-1→LUMO+2 (HOMO→LUMO)
	Minor peak	3.930	HOMO→LUMO+2 HOMO-1→LUMO+2
	Minor peak	4.111	HOMO-10→LUMO (HOMO-6→LUMO) (HOMO-10→LUMO+2)
	Minor peak	4.134	HOMO-6→LUMO
	Minor peak	4.142	HOMO-1→LUMO+2 HOMO→LUMO+2 (HOMO-10→LUMO)
No tag	Soret-band	3.156	HOMO→LUMO+1 HOMO-1→LUMO
	Soret-band	3.320	HOMO-2→LUMO HOMO-1→LUMO+1 (HOMO-1→LUMO) (HOMO→LUMO) (HOMO→LUMO+1)
	Soret-band	3.370	HOMO-1→LUMO+2 HOMO-2→LUMO (HOMO-2→LUMO+1)
	Minor peak	4.214	HOMO-5→LUMO (HOMO-4→LUMO)