In-Situ Generation and Reaction of Sub-Picosecond Electron Pulse: Ultrafast Broadband Spectroscopy

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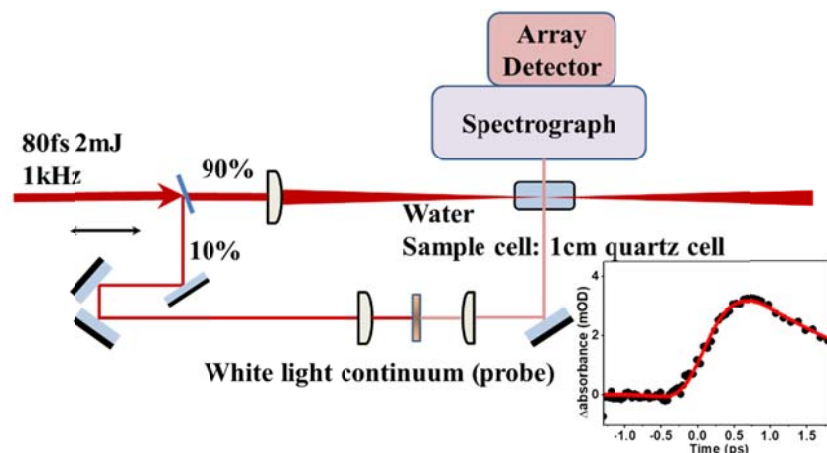[b]Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094, India

Figure S1: (A) Schematic of the broad band pump-probe setup to measure the dynamics of electrons generated in-situ by multiphoton ionization of water using 800 nm femtosecond laser pulse. Inset: Transient signal for electron recorded at 1050 nm with 100 uJ/pulse energy. The fitted instrument response function (IRF) is 0.55 (±0.05) ps.
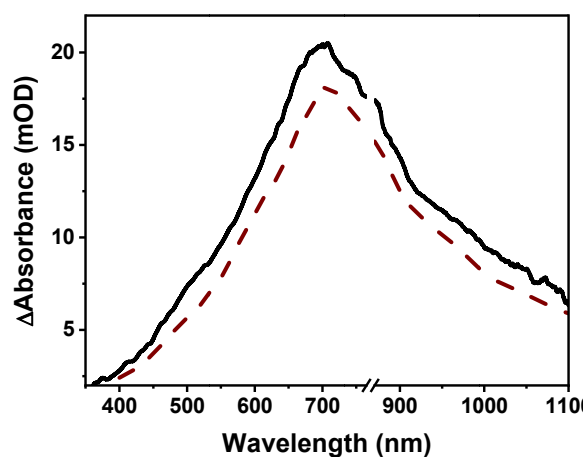

Figure S2: Solvated electron spectrum in pure water recorded at 4 ps following the multiphoton ionization of water. Solvated electron spectra recorded at 1 µs using a linear electron accelerator[1] is also shown as dashed line for the comparison.
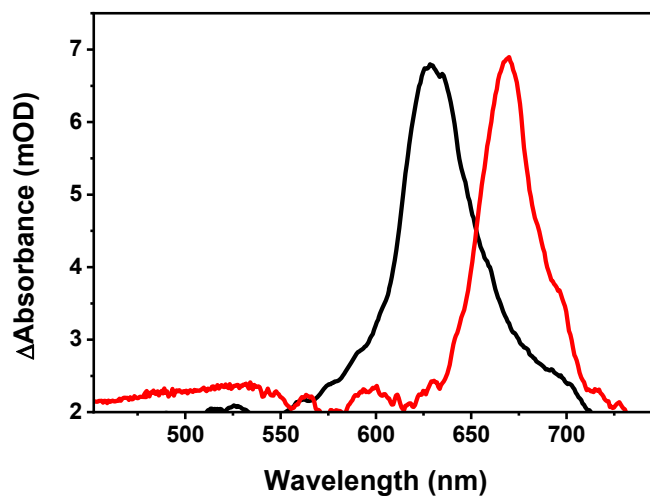
Figure S3: Transient absorption spectra recorded at 100 fs following the multiphoton ionization with 800 nm laser pulse for H_2O (black) and D_2O (red)
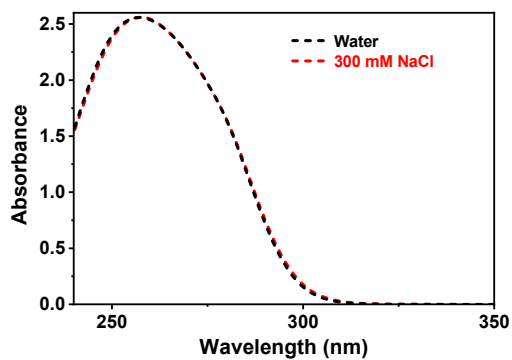

Figure S4: Absorption spectra of aqueous solution of 2 mM MV^{2+} in the absence and presence of 300 mM NaCl.
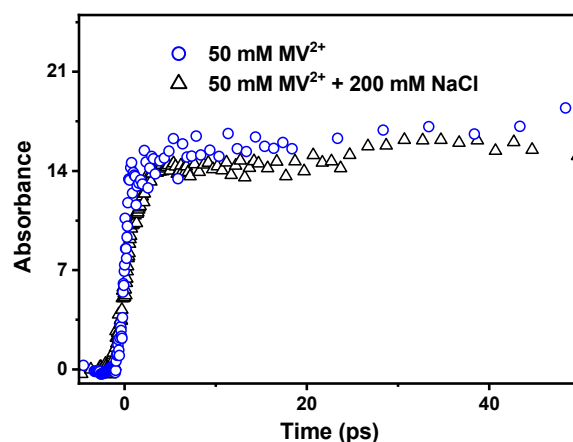
Figure S5: Transient decay kinetics recorded at 396 nm for 50 mM aqueous solution of MV^{2+} in the absence and presence of 200 mM sodium chloride.

Calculations of electron concentration:

Solvated electron extinction coefficient[2,3] (ε) in pure water at 715nm is 19700 M^{-1} cm^{-1}

Absorbance at 715 nm is 17 mOD at 3 ps with 220 µJ/pulse energy

The pump beam (800 nm) diameter at the sample is 185 µm. Due to perpendicular pump-probe geometry, the pump beam diameter can be considered as the optical path for probe. Considering same extinction coefficient for the pre-hydrated and hydrated electrons, the concentration of electron within the monitoring volume is calculated to be 4.6×10^{-5} M.

MV^{2+} is being reduced to $MV^{\bullet+}$ by accepting an electron. Since, the $MV^{\bullet+}$ is reported to have much longer lifetime[4] as compared to the temporal window of our experiment, we can neglect the decay of $MV^{\bullet+}$. Considering the molar extinction coefficient (ε) of $MV^{\bullet+}$ at 396 nm[3,5] as 42100 M^{-1} cm^{-1}, we can also determine the concentration $MV^{\bullet+}$ which is equivalent to the fraction of electron is reacting with MV^{2+}.

Absorbance at 396 nm at 1ns with 150 mM MV^{2+} (A) = 31.8 mOD

Considering negligible contribution of solvated electron at 396 nm at longer time delay, the concentration of $MV^{\bullet+}$ is estimated to be 4.1×10^{-5} M.

The rate of reaction between solvated electron and methyl viologen was calculated from the variation in the lifetime of solvated electron with MV^{2+} concentration (Fig S4). The slope of the linear fitting of the experimental data represents the bimolecular reaction rate constant

and found to be $8.6\pm0.6 \times10^9$ M^{-1}s^{-1}. This value matches well with the value obtained by nanosecond pulse radiolysis experiment.[6]

Estimation of ponderomotive shift under high laser field:

A ponderomotive potential can be given as[7]

$$U_p = \frac{e^2 E^2}{4m\omega^2}$$

Where e, and m represent the charge and mass of the electron, respectively. E and ω represent the applied electric field and angular frequency of light, respectively.

In term of intensity (I) the above equation can be written as

$$U_p(eV) = 9.33 \times I \left(\frac{10^{14}W}{cm^2}\right) \times \lambda^2(\mu m^2)$$

Our experiments were performed using 200 µJ/pulse energy. The pump diameter of 180 µm at the sample corresponds to 1.5×10^{13} W/cm^2 fluence. Considering laser central wavelength of 0.8 µm, the ponderomotive potential is calculated to be 0.9 eV. Such value of the ponderomotive force is responsible for the multiphoton ionization of water with less number of photon than predicted by its ionization energy (6.5 eV).
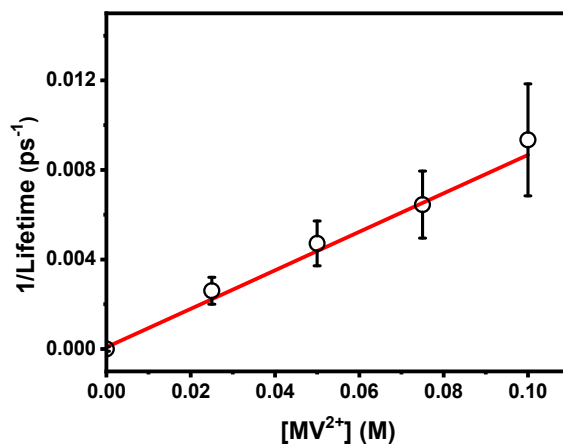

Figure S6: Variation in the lifetime of solvated electron with the concentration of MV^{2+} concentration. The solid line is the linear fit of the experimental data.

Table S1: Fitting parameters for kinetics at different wavelengths for pure water.

Wavelength/nm	Time constant/ ps (Amplitude)
1080	0.86±0.2 (0.81), 298±22 (0.09), >1000 (0.1)
1050	0.92±0.3 (0.83), 307±24 (0.07), >1000 (0.1)
1000	1.16±0.3 (0.74), 293±25 (0.11), >1000 (0.16)
980	1.31±0.2 (0.58), 313±22 (0.15), >1000 (0.27)
900	1.55±0.2 (0.45), 297±27 (0.17), >1000 (0.38)
870	2.1±0.3 (0.33), 311±24 (0.19), >1000 (0.48)
710	0.83±0.2 (-0.56), 7.8±1 (0.07), 315±20 (0.09), >1000 (0.28)

Table S2: Fitting parameters for kinetics at different wavelengths for 50 mM MV^{2+} aqueous solution.

Wavelength/nm	Life Time/ps (Amplitude)
396	1.34±0.4 (-0.35), 176±22(-0.16)
870	1.88±0.2 (0.51), 191±22 (0.49)
900	1.49±0.3 (0.56), 199±20 (0.44)
950	1.52±0.3 (0.67), 198±23 (0.33)
980	1.25±0.2 (0.67), 181±32 (0.33)
1050	0.78±0.4 (0.88), 185±25 (0.12)
1080	0.77±0.3 (0.89), 177±26 (0.11)

Table S3: Fitting parameter at 396 nm and 980 nm wavelength at different concentrations of MV^{2+} in pure water

$[MV^{2+}]$\ mM	Life Time/ps (Amplitude)	
	396 nm	980 nm
25	1.83±0.5(-0.19), 352±42(-0.29), Residual (0.52)	1.3±0.4(0.63), 350±39(0.37)
50	1.34±0.4(-0.35), 176±22(-0.16), Residual (0.49)	1.25±0.2(0.67), 181±32(0.33)
75	1.51±0.2(-0.41), 130±29(-0.11), Residual (0.48)	1.31±0.3(0.68), 135±23(0.32)
100	1.37±0.1(-0.45), 88±9.3(-0.06), Residual (0.49)	1.41±0.4(0.69), 92±19(0.31)
125	1.26±0.3(-0.46), 15±5.9(-0.04), Residual (0.50)	1.3±0.3(0.71), 19±3(0.29)
150	1.46±0.3(-0.46), 3±0.9(-0.03), Residual (0.51)	1.7±0.4(0.77), 4.5±2(0.23)

Table S4: Concentration of $MV^{\bullet+}$ at 3ps and at 1ns

$[MV^{2+}]$/ mM	$[MV^{\bullet+}]$ at 3ps /10^{-5} M	$[MV^{\bullet+}]$ at 1ns /10^{-5} M
25	1.15	3.05
50	2.33	3.4
75	2.74	3.75
100	3.29	3.94
125	3.48	4.1
150	3.67	4.1

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