मल्टीफ़ोटॉन आयनीकरण-लघु इलेक्ट्रॉन स्पंद

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पानी के मल्टीफ़ोटॉन आयनीकरण द्वारा अल्ट्राशॉर्ट इलेक्ट्रॉन स्पंद का मूलस्थानस्थ जनन

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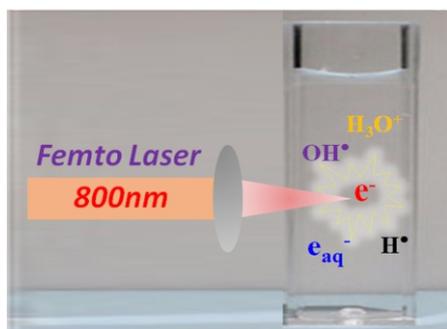
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ABSTRACT

विकिरण रसायन विज्ञान और जीव विज्ञान अनुसंधान से संबंधित विकिरण प्रेरित रासायनिक परिवर्तनों की गतिकी का अध्ययन करने के लिए नियमित रूप से स्पंदित विकिरणी अपघटन प्रयोग किया जाता है। मानक स्पंदित विकिरणी अपघटन सुविधाएँ नैनोसेकंड समय पैमाने में समय विभेदन को सीमित करती हैं। फेमटोसेकंड और पिकोसेकंड समय पैमाने में विकिरण प्रभाव की प्रारंभिक घटनाओं तक पहुँचने के लिए एक अल्ट्राशॉर्ट इलेक्ट्रॉन स्रोत की आवश्यकता होती है जिसके लिए एक फेमटोसेकंड लेजर संचालित फोटोकैथोड आधारित इलेक्ट्रॉन त्वरक की आवश्यकता होती है। हालाँकि, तकनीकी चुनौतियाँ और अत्यधिक लागत ऐसे जटिल उपकरणों के विकास को सीमित करती हैं। यहाँ हम एक प्रवर्धित फेमटोसेकंड लेजर का उपयोग करके पानी के मल्टी फोटान आयनीकरण द्वारा सब-पिकोसेकंड इलेक्ट्रॉन स्पंद की मूलस्थानस्थ जनन के लिए एक अपेक्षाकृत सरल वैकल्पिक तकनीक प्रस्तुत करते हैं। टेबल-टॉप कमर्शियल फेमटोसेकंड लेजर का उपयोग करके, हमने सब-पिकोसेकंड विभेदन वाले इलेक्ट्रॉनों के जनन और अस्थायी पहचान के लिए एक कॉम्पैक्ट पंप-प्रोब स्पेक्ट्रोमीटर विकसित किया है।

मुख्य शब्द : अल्ट्राफास्ट स्पेक्ट्रोस्कोपी, मल्टीफ़ोटॉन आयनीकरण; इन-सीटू इलेक्ट्रॉन उत्पादन; इलेक्ट्रॉन विलयन

In-Situ Generation of Ultrashort Electron Pulse by Multiphoton Ionization of Water

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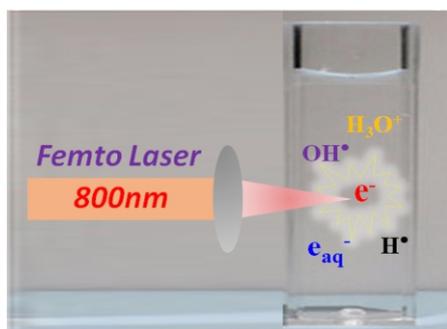
Femtolysis

ABSTRACT

Pulsed radiolysis experiment is routinely employed to study kinetics of radiation induced chemical changes relevant to radiation chemistry and biology research. Standard pulsed radiolysis facilities limit the time resolution in nanosecond time scale. Accessing early events of radiation effect in femtosecond and picosecond timescale requires an ultrashort electron source which demands a femtosecond laser driven photocathode-based electron accelerator. However, technological challenges and exorbitant costs limit the development of such complex instrumentation. Herein we present a relatively simpler alternative technique for in-situ generation of sub-picosecond electron pulse by multiphoton ionization of water using an amplified femtosecond laser. Using a table-top commercial femtosecond laser, we have developed a compact pump-probe spectrometer for the generation and temporal detection of electrons with sub-picosecond resolution.

KEYWORDS: *Ultrafast spectroscopy, Multiphoton ionization; In-situ electron generation; Electron solvation*

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Introduction

The ionizing radiations have a severe impact on chemical and biological species due to radiation induced generation of energetic electrons and radicals which induce chemical modification such as DNA damage. Understanding radiation induced chemical and biological effects requires the study of electron and ion induced chemical kinetics in real time. To extract dynamic information and to identify the radiolytic product, an electron based pulsed radiolysis setup is commonly being used? Thermionic gun based few MeV pulsed electron linear accelerator (LINAC) is now an established technology and is routinely employed for pulsed radiolysis experiments with nanosecond time resolution [1]. However, a complete understanding of radiation induced damage in chemistry and biology requires early timescale information in picosecond and femtosecond timescale. Accessing femtosecond and picosecond timescale information in a pulsed radiolysis study needs a femtosecond electron pulse which can only be generated by a photocathode gun driven by a femtosecond laser [2]. A high current photocathode gun requires use of Cesium-telluride (CsTe) material which is susceptible to atmospheric degradation. Thus, a CsTe photocathode needs to be prepared, transported and maintained at high vacuum ($< 10^{-9}$ mbar) and requires frequent replacement. In addition, the time synchronization of the laser and radiofrequency (RF) field and phase synchronization of RF in photocathode and LINAC are important technological barriers for the implementation of femtosecond pulse radiolysis facility. Fig.1(a) & Fig.1(b) shows the original photograph of the ELYSE facility [3], which gives an idea of the complexity of a picosecond accelerator setup. In addition, the exorbitant cost involved in such multi-component complex instrumentation limits the widespread development of such facilities.

Herein we show an alternative approach for in-situ generation of sub-picosecond electron pulse in water using a femtosecond amplified laser through multiphoton ionization (photolysis) process [4]. By using moderate energy (100-300 μJ/pulse) commercially available femtosecond laser pulse, we generate and detect sub-picosecond electron pulse in water as a table-top facility. The dynamics of pre-solvated and solvated electrons have been monitored in 350-1100 nm region by pump-probe technique. Broadband measurement of transient absorption spanning visible and near IR region allowed us to probe the relaxation of semi-solvated electrons, which mainly absorb beyond 900 nm and the reaction kinetics of both pre-solvated and solvated electrons. This setup is proposed to act as a viable alternative to a picosecond electron accelerator-based pulse radiolysis facility, at least in the aqueous medium.
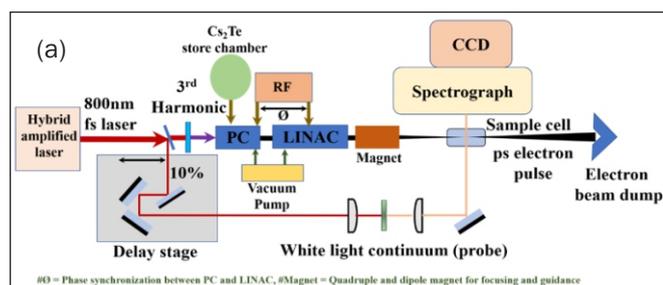
Method

The sub-picosecond photolysis setup was developed by modifying the existing ultrafast transient absorption (TA) spectrometer as shown in Fig.2. The setup is coupled to a commercial amplified femtosecond laser 50 fs, 800 nm, kH1z from Amplitude Technologies, France. About 200 μJ/pulse laser energy is strongly focused within a quartz cuvette filled with water. A small fraction of the remaining pulse energy (about 1 μJ) is used to generate a broadband white light continuum (350-1100 nm) in a rotating calcium fluoride plate which is used as probe light. In the present setup, the probe pulse is propagated perpendicular to the pump pulse to minimize the interference from the pump induced light generated in the optical cell. The pump induced changes in the probe light were monitored using a dual diode array detector coupled with a spectrograph. The relative temporal delay between the pump and probe pulse was controlled using a computer controlled optical translational stage. Considering strong absorption at ~800 nm, IR-140 dye was used as a reference sample for the determination of zero time of the setup. IR-140 has an excited state absorption (ESA) band in 500-650 nm region which is due to the absorption of its first excited singlet state (S_1). The appearance of the ESA signal of IR-140 provides information about the zero time of the setup.

Fig.1: (a) Schematic of the conventional picosecond pulse radiolysis setup, (b) Actual facility of ELYSE [Source: https://www.icp.universite-paris-saclay.fr].
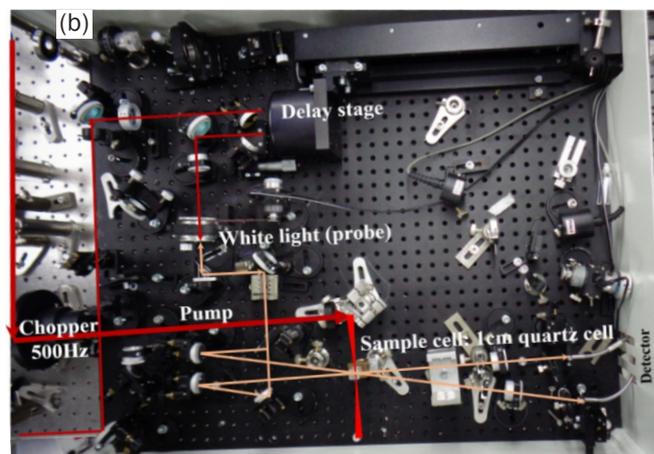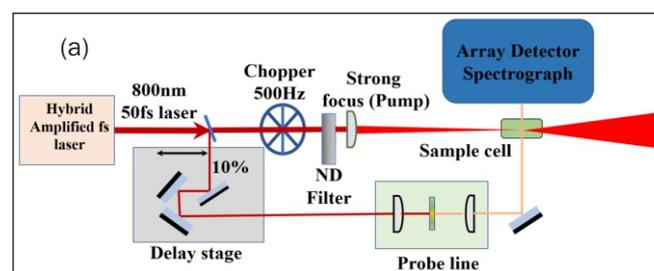
Fig.2: (a) Schematic of the broad band pump-probe setup to measure the dynamics of electrons generated in-situ by multiphoton ionization of water. (b) Photograph of the modified transient absorption setup.

Results & Discussion

The transient absorption (TA) spectra recorded at 1 ps and 5 ps with pure water as a medium of ionization are shown in Fig.3(a). The omission of the data in the 770-870 nm region is due to the large scattering of the pump light. The pure water spectrum at 5 ps time delay closely matches the solvated electron spectrum recorded with a LINAC based nanosecond pulse radiolysis facility. This result suggests the formation of electrons by multiphoton ionization of water using an intense femtosecond laser. Whereas pure water spectrum recorded at 1 ps time delay shows a significant absorption in the 1000-1070 nm region, which is a signature of the pre-hydrated electron. However, we could not see the signature of the dry electron due to the limited temporal window of our setup. The decay kinetics (Fig.3(b)) of the pre-hydrated electron (1050 nm) and hydrated electron (710 nm) were analysed with multiexponetial decay function. Our analysis shows a rise component at 710 nm with a time constant of 0.83±0.2 ps and a correlated decay at 1050 nm with a time constant of 0.86±0.2 ps. This observed time scale suggests the growth of solvated electron at 710 nm at the cost of the decay of the pre-hydrated electrons.

Thus, the present setup has the capability of detecting pre-hydrated electrons and solvated electrons separately. Some electron quenchers can be added to the medium and their reaction can be monitored in real time using our setup. We have shown that the decay of pre-solvated electrons leads to the rise of solvated electron signals which are correlated with each other. In the presence of an electron quencher, the surviving probability of pre-hydrated electron will be dependent on the concentration of the electron quencher. Hence the solvated signal strength at 710 nm will be dependent on the quencher concentration. Thus, we have investigated the reaction of pre-hydrated electrons with a well-known electron quencher, nitrate ion. The effect of nitrate ions on the yield of solvated electrons is shown in Fig.4. It is evident from the figure that the addition of potassium nitrate (KNO₃) results in a gradual decrease in the signal of the hydrated electron at 710 nm. The scavenging of pre-hydrated electrons by nitrate ions will compete with the solvation of electrons. The reciprocal of the surviving (S) percentage of pre-hydrated electron will be in a linear relation with scavenger's concentration (C) as shown in equation 1.
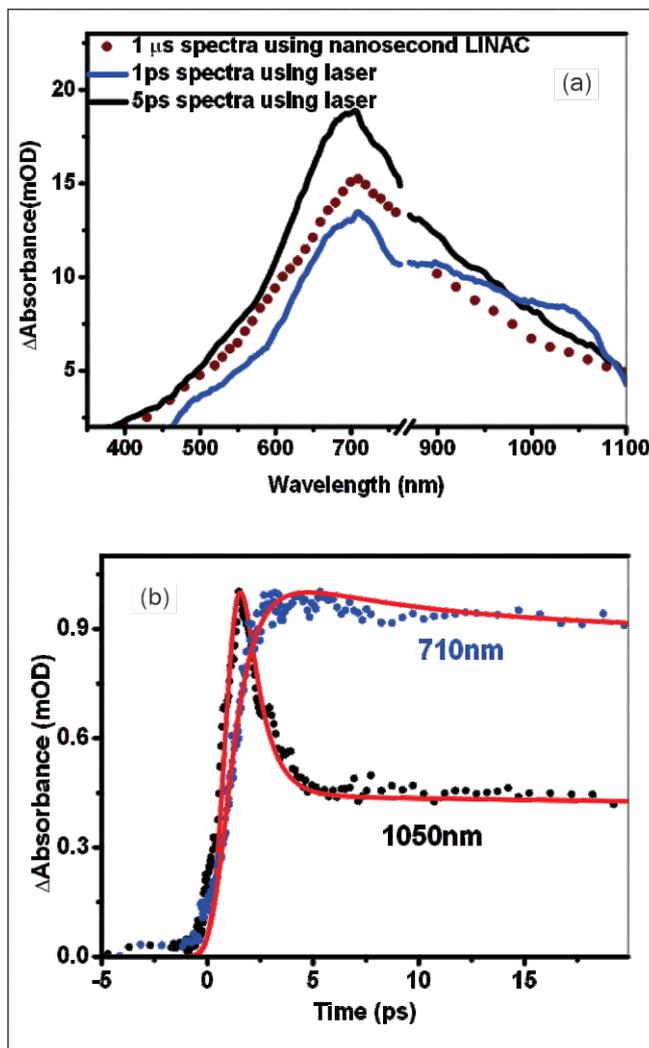
Fig.3: (a) Time-resolved spectra of electron (350-1100 nm) recorded by multiphoton ionization of water at 1 and 5 ps time delay. Solvated electron spectrum measured at 1μs using LINAC based nanosecond pulse radiolysis setup is also shown for comparison. (b) Normalized transient decay kinetics at 1050 nm and 710 nm. The solid lines through experimental data points are fitting using multiexponential decay function.
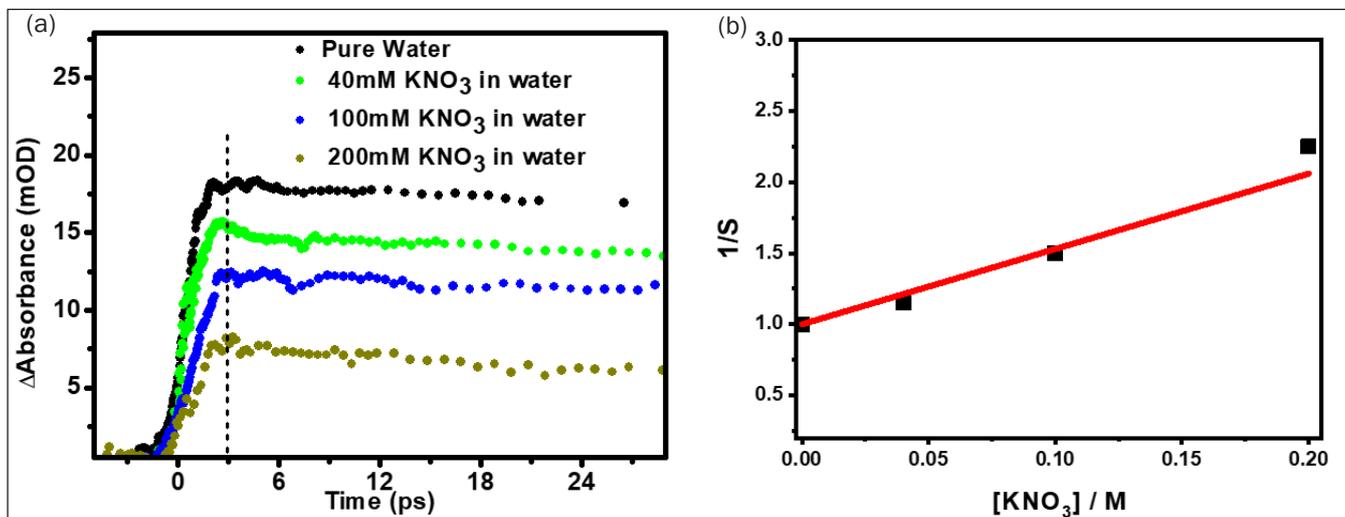
Fig.4: (a) Real time observation of 710 nm kinetics in presence of different concentrations of KNO₃ (b) Variation in the survival probability(S) of pre-hydrated electron with the concentration of KNO₃. The solid line is the fitting of the experimental data by equation 1.

$$\frac{1}{S} = \tau_{pre} k_{pre} [C] + 1 \qquad (1)$$

Where τ_{pre} is the lifetime of the pre-hydrated electron and k_{pre} is the rate of reaction between pre-hydrated electrons and the nitrate ions. The reported average lifetime of pre-hydrated electrons (τ_{pre}) is about 540 fs [5]. The variation in the survival probability of pre-hydrated electron with the concentration of nitrate ion is shown in Fig.4(b). The fitting of the experimental data with equation 1 results in the rate constant (k_{pre}) value of 1 x 10^{13} $M^{-1}s^{-1}$. This large value of the rate constant clearly indicates the strong electron scavenging ability of nitrate ion. Thus, our setup was able to measure the very fast reaction of electron with a suitable scavenger.

Conclusion

In conclusion, we report development of a compact table top sub-picosecond resolved broadband transient absorption spectroscopic set up for generation and study of pre-hydrated solvated and hydrated electron produced by multiphoton ionization of water using femtosecond 800 nm laser pulse. Our set up can be employed to record temporal evolution of electron dynamics over full visible and NIR spectral window (350 to 1100 nm) and can act as a viable alternative to picosecond electron accelerator-based pulse radiolysis facility, at least in aqueous medium.

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