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1990 J. Phys.: Condens. Matter 2 SA171

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Femtosecond spectroscopy of ultrafast reactions in aqueous media

Y Gauduel, S Pommeret and A Antonetti

Laboratoire d'Optique Appliquée, Ecole Polytechnique—ENS Techniques Avancées,
91120 Palaiseau, France

Received 9 July 1990

Abstract. The elucidation of detailed mechanisms of ultrafast events that occur in molecular charge transfer or reaction dynamics has been made possible by recent advances in spectroscopy techniques that use ultrashort laser pulse generation. Ultrashort laser pulses (100 femtoseconds duration, $1 \text{ fs} = 10^{-15} \text{ s}$) allow initiation of selective photochemical processes (photoejection of epithermal electrons), and obtaining of unique information on the dynamics of primary steps of radical reactions involving ultrafast electron or proton transfer: formation of the hydration cage around an electron, encounter pair formation, ion–molecule reactions. Recent investigations on the non-equilibrium reactional processes in the universal protic solvent (water) are presented.

1. Introduction

Liquid water is considered as a universal solvent whose chemical and physical properties have a determinant influence on the reactivity of numerous compounds in physical chemistry and biology. From a general point of view, the knowledge of the early events immediately following the interaction of ionizing radiation with polar liquid represent a fundamental aspect of the reactivity of non-equilibrium electronic states in condensed matter [1, 2].

The exact structure of liquid water is not fully understood at ambient temperature, and single charges (electron, proton or derived radicals) can be used as microprobes to investigate the local structure or the molecular response of the liquid following a local perturbation (existence of an electric field). Excess electrons implicate intriguing issues on its coupling with the solvent, since bound states exist only through interaction with the surrounding medium. Following a dielectric continuum picture of the solvent it has been suggested that the transition from a quasi-free electron to the fully relaxed state (hydrated state) is initiated by long-range dipolar interactions followed by self-trapping of the electron [3].

Technological advances in ultrashort laser pulses [4, 5] now allow investigations with femtosecond accuracy in the field of chemical or biochemical reaction dynamics and

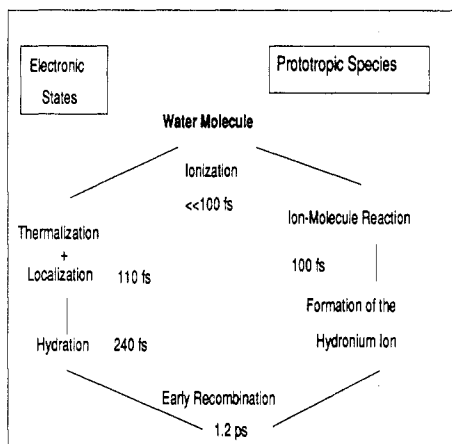


Figure 1. Primary events occurring in pure liquid water following femtosecond photoionization by ultraviolet pulses.

have been applied with success to the study of ultrafast radical reactions or intramolecular and intra-ionic dynamical processes in liquid matter [6–9].

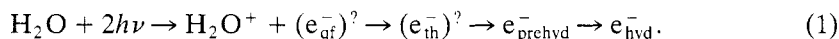
2. Ultrafast physico-chemical events in pure liquid water

The primary species initiated by interactions of ionizing energy with polar liquids have been subject to numerous studies and investigations in various fields such as radiation chemistry, photochemistry and photophysics [10–15].

During the interaction of ionizing radiation with an aqueous phase, absorption of energy initiates the ionization process. This step is followed by energy exchanges between excess electrons and solvent molecules. The energy exchange within a local region leads to complex couplings between the elementary charge and the protic solvent. Ultrafast reactions lead, in less than 10^{-12} s, to the formation of primary species: hydronium ion or hydrated proton (H_3O^+), OH radical, hydrated electron and dissociation products of the excited state of water molecule (H_2O^*): H, OH [13].

Direct photoionization of water by near-UV femtosecond pulses ($I > 10^{12} \text{ W m}^{-2}$) is possible since the light can be absorbed through a non-linear process. In such experiments, the 8 eV two-photon excitation is above the ionization threshold for liquid water estimated at a very low quantum yield to be around 6.5 eV [15]. The two-photon absorption coefficient of pure water at 310 nm (4 eV) has been estimated to be $4 \times 10^{-13} \text{ mW}^{-1}$ which yields a non-negligible absorption when dealing with multi-gigawatt peak power pulses.

Figure 1 represents some of the primary events on charge transfer which have been identified in the sub-picosecond timescale following the injection of an epithermal electron through two-photon ionization of water molecules. The initial energy deposition in the bulk phase is followed, within 0.3 ps, by the formation of the fully relaxed hydrated electron (e_{hyd}^-) (reaction 1):



Spectroscopic investigations have shown that electron hydration in water proceeds through at least one intermediate state (localized or prehydrated electron) where the

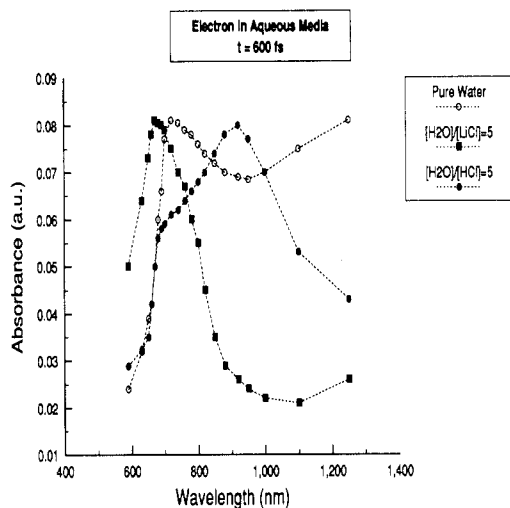


Figure 2. Transient spectra obtained at 600 fs (0.6×10^{-12} s) after femtosecond electron photo-detachment in pure liquid water, or in concentrated ionic aqueous solutions ($[\text{H}_2\text{O}]/[\text{XCl}] = 5$ with $\text{X} = \text{H}$ or Li). The points are calculated from the experimental kinetics and the amplitude of the signal obtained at different test wavelengths.

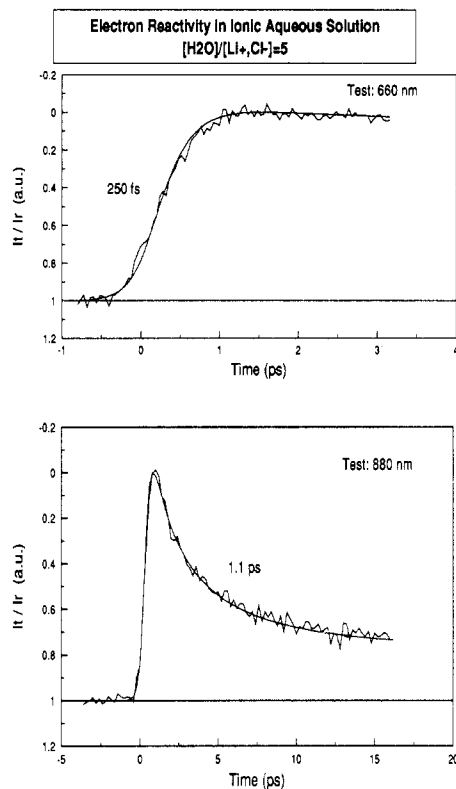


Figure 3. Kinetic data obtained at 660 and 880 nm after femtosecond laser photoionization of concentrated ionic solution ($[\text{H}_2\text{O}]/[\text{LiCl}] = 5$). At 660 nm the risetime (250 fs) is mainly due to the direct electron capture by deep traps. At 880 nm, an early ($\text{e}^- - \text{Cl}$) recombination can be observed with a time constant of 1.1 ps.

lifetime is in the femtosecond regime [16]. This non-equilibrium configuration, characterized by an infrared absorption band extending above 1250 nm, appears in 110 fs and then disappears in 240 fs while a structureless absorption band arises in the visible (figure 2). The very fast appearance of $\text{e}^-_{\text{prehyd}}$ is on a timescale short compared to any nuclear motion, solvent dipole orientation or thermal motion of water molecules and it implies that efficient mechanisms involved in the localization process do not require large molecular and dynamical reorganization. Experimentally, the absence of a significant continuous shift between the infrared and visible bands suggests that the relaxation of water molecules in the vicinity of excess electrons involves extremely small water motions. In other words an epithermal electron gets to a fully relaxed hydrated state without a dominant dielectric response of the polar medium. Several groups have deduced information on the structural aspects of the fully relaxed hydrated electron using a molecular dynamic simulation of water by the Monte Carlo and path integral techniques [17–20].

Following the photoionization of H_2O the resulting water cation (H_2O^+) undergoes, concomitantly to the electron hydration process, an ultrafast charge transfer with one of the surrounding water molecules. The reactivity of this cation (i) is considered as one of the fastest ion–molecule reactions occurring in liquid phase, (ii) is believed to take place in less than 10^{-13} s, i.e. the time required for a vibration of a molecule [12, 13] and (iii) leads to the formation of the hydronium ion or hydrated proton (H_3O^+) and the hydroxyl radical OH (reaction 2).

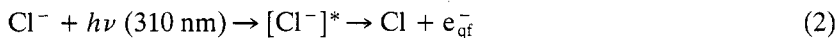


Femtosecond spectroscopic investigations in the near-UV have allowed the identification of an induced absorption, characterized by an ultrashort lifetime and which can be tentatively assigned to the existence of the water cation H_2O^+ . The relaxation following a mono-exponential law would then correspond to the ion–molecule reaction $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$ for which the cleavage rate constant is measured to be 10^{13} s^{-1} at 294 K (figure 1). We think it reasonable to assume that the ultrafast proton transfer from H_2O^+ to H_2O is dependent on specific properties of the protic solvent such as the vibrational energy of antisymmetric stretch. The limiting factor of the cleavage rate constant of the water cation would correspond to the activation energy of a bond cleavage leading to an ultrafast proton transfer from H_2O^+ to a surrounding water molecule.

The knowledge of free-radical reactions involving electron and prototropic species (H_3O^+ , OH) in aqueous media provides unique information on the dynamical compartment of a protic solvent. During the first picoseconds which follow an electron photodetachment from water molecules, a non-negligible fraction of e_{hyd}^- population (55%) reacts rapidly with the two possible nearest neighbours (H_3O^+ and OH) [21, 22]. The electron–radical pair ($\text{H}_3\text{O}^+ \dots e_{\text{hyd}}^-$ or $\text{OH} \dots e_{\text{hyd}}^-$) executes a one-dimensional (1D) walk before undergoing geminate recombination [22]. The analytical solution of a recombination controlled by 1D diffusion is $\text{erf}(T_d/t)^{1/2}$ yielding $T_d = 1.2$ ps (jump rate of $0.83 \times 10^{12} \text{ s}^{-1}$). The role of both the hydrogen bonds and the structure of H_3O^+ during this recombination remain to be clarified (figure 1).

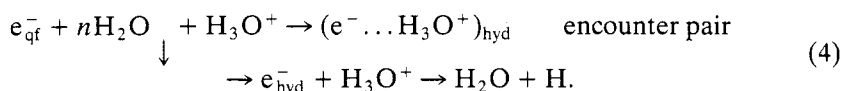
3. Ultrafast charge transfer in concentrated ionic aqueous solutions

Femtosecond photochemistry of ionic aqueous solutions allow the investigation of the reactivity of electrons as a function of the ionic strength. Electron photodetachment from a halide (Cl^-), through charge transfer to solvent spectra (CTTS) was achieved by pumping at 310 nm. It has been suggested that the femtosecond photolysis channel occurs through a highly excited state of the chloride anion which dissociates to give an epithermal electron and chlorine atom [23, 24].



For $R = [\text{H}_2\text{O}]/[\text{HCl}] = 5$, the transient absorption spectrum obtained following the electron attachment from chloride ion consists of three bands ($\lambda_{\text{max}}^1 < 1 \text{ eV}$, $\lambda_{\text{max}}^2 = 1.35 \text{ eV}$, $\lambda_{\text{max}}^3 = 1.72 \text{ eV}$) which are assigned to a non-fully-hydrated electron (e_{prehyd}^-), an encounter electron–ion pair ($\text{H}_3\text{O}^+ : e^-$)_{hyd} and an electron stabilized in normal aqueous traps (e_{hyd}^-) respectively (figure 2).

The important structureless spectral distribution clearly observed between 800 and 1000 nm has been assigned to the fact that a significant fraction of excess electrons can be localized in the solvation shell of the cation $[(\text{H}_3\text{O}^+)_{n\text{H}_2\text{O}}]$:



The formation of the encounter pair $(e^-:\text{H}_3\text{O}^+)_{\text{hyd}}$ is found to follow a rate constant of $4 \times 10^{12} \text{ s}^{-1}$. The single exponential law relaxation (time constant of 850 fs) corresponds to the deactivation of this transient encounter pair; the cleavage rate constant $[(\text{H}_3\text{O}^+:\text{e}^-)_{n\text{H}_2\text{O}} \rightarrow \text{H}_2\text{O} + \text{H}]$ equals $1.17 \times 10^{12} \text{ s}^{-1}$ at ambient temperature (equation (4)). Indeed, the encounter pair deactivation dynamics is faster than the average lifetime of H_3O^+ but is comparable to the H-bond timescale. These data clearly demonstrate that the single electron transfer: $e_{\text{qf}}^- + n\text{H}_2\text{O} + \text{H}_3\text{O}^+ \rightarrow (e^- \dots \text{H}_3\text{O}^+)_{\text{hyd}}$ occurs prior to the electron hydration phenomenon [25].

It is interesting to note that the charge transfer channel and the lifetime of this encounter pair are true to type for the hydronium ion. Let us consider here the case of LiCl aqueous solution with $[\text{H}_2\text{O}]/[\text{LiCl}] = 5$. When the hydration shell around Li^+ or Cl^- corresponds to tightly bound water, an important band peaking in the red spectral region can be observed (figure 2). The existence of a blue shift is assigned to a change of the electron hydration energy. For the test wavelength (660 nm), the dynamics of this ultrafast electron capture by deep traps equals 250 fs (figure 3). At 880 nm, an early $(e^- - \text{Cl})$ recombination can be observed with a time constant of 1.1 ps.

It seems reasonable to assume that in concentrated ionic aqueous solution the density and configurational fluctuations provide a potential well into which the excess epithermal electron may be directly hydrated. In this hypothesis, the favourable spatial distribution of deep traps created by the presence of a stable counter ion (Li^+) would represent a specific order of the liquid for direct electron capture and subsequent stabilization.

4. Conclusions

In conclusion, the investigation of early steps following the femtosecond photoionization of halide (Cl^-) in aqueous solution has shown the existence of specific photochemical channels which are dependent on the nature of the counter ion. In highly-concentrated aqueous solutions of hydronium ions, excess electrons will be mainly ejected inside the hydration shell of a hydronium ion $(\text{H}_3\text{O}^+)_{n\text{H}_2\text{O}}$ with a subsequent radical pair relaxation. In the case of Li^+ with low electronic affinity, the electron transfer leads to the formation of relaxed electron-ion pairs.

References

- [1] Castner E W, Fleming G R, Bagchi B and Maroncelli M 1988 *J. Chem. Phys.* **89** 3519–34
- [2] Williams R J P 1989 *Mol. Phys.* **68** 1–23
- [3] Kenney-Wallace G A and Jonah C D 1982 *J. Phys. Chem.* **86** 2572–86
- [4] Fork R L, Shank C V and Yen R T 1982 *Appl. Phys. Lett.* **41** 223–5
- [5] Migus A, Antonetti A, Etchepare J, Hulin D and Orszag A 1985 *J. Opt. Soc. Am. B* **2** 584–94
- [6] Wiesenfeld M and Ippen P 1980 *Chem. Phys. Lett.* **73** 47–50

- [7] Gauduel Y, Migus A, Martin J L, Lecarpentier Y and Antonetti A 1985 *Ber. Buns. Phys. Chem.* **89** 218–22
- [8] Gauduel Y, Migus A and Antonetti A 1988 in *Chemical Reactivity in Liquids; Fundamental Aspects* ed M Moreau and P Turcq (New York: Plenum) pp 15–32
- [9] Rosker M J, Dantus M, Zewail A H 1988 *J. Chem. Phys.* **89** 6113–28
Dantus M, Rosker M J, Zewail A H 1988 *J. Chem. Phys.* **89** 6129–40
- [10] Baxendale J H 1977 *Can. J. Chem.* **78** 1996–2008
- [11] Huppert D, Kenney-Wallace G A and Rentzepis P M 1981 *J. Chem. Phys.* **75** 2265–9
- [12] Buxton G V 1987 in *Radiation Chemistry* ed Farhataziz and M A J Rodgers (VCH) pp 321–49
- [13] Klassen N V 1987 in *Radiation Chemistry* ed Farhataziz and M A J Rodgers (VCH) pp 29–64
- [14] Gauduel Y, Pommeret S, Migus A and Antonetti A 1989 *Radiat. Phys. Chem.* **34** 5–14
- [15] Nikogosyan D N, Oraevsky A O and Rupasov V I 1983 *Chem. Phys.* **77** 131
- [16] Gauduel Y, Martin J L, Migus A, Yamada N and Antonetti A 1986 in *Ultrafast Phenomena V* ed C R Fleming and A E Siegman (New York: Springer) pp 308–11
Migus A, Gauduel Y, Martin J L and Antonetti A 1987 *Phys. Rev. Lett.* **58** 1559–62
- [17] Schnitker J, Rossky P and Kenney-Wallace G A 1986 *J. Chem. Phys.* **85** 2986–98
- [18] Wallqvist A, Thirumalai D and Berne B J 1986 *J. Chem. Phys.* **85** 1583–91
- [19] Motakabbir K A and Rossky P J 1989 *J. Chem. Phys.* **129** 253 (and references therein)
- [20] Barnett R N, Landman U and Nitzan A 1989 *J. Chem. Phys.* **91** 5567–80
- [21] Lu H, Long F H, Bowman R M and Eisenthal K B 1989 *J. Phys. Chem.* **93** 27
- [22] Gauduel Y, Pommeret S, Migus A and Antonetti A 1989 *J. Phys. Chem.* **93** 3880
- [23] Matheson M S, Mulac W A, Rabani J 1975 *J. Phys. Chem.* **67** 541
- [24] Gauduel Y, Pommeret S, Yamada N, Migus A, Antonetti A 1989 *J. Am. Chem. Soc.* **111** 4974–80
- [25] Gauduel Y, Pommeret S, Migus A, Yamada N and Antonetti A 1990 *J. Am. Chem. Soc.* **112** 2925–31