Solvation dynamics of electron produced by two-photon ionization of ethylene glycol

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The solvated electron is characterized by an intense absorption band in the visible or near infrared spectral domain depending on the solvent[1]. Thanks to the development of ultrashort laser pulses, great strides have been made towards the understanding of the solvation and early reactivity of the solvated electron, mainly in water and also in a few polar solvents. Recently, the recombination dynamics in ethylene glycol (EG) of electrons produced with femtosecond laser either by photodetachment of I^- or by ionization of the pure solvent was studied from the kinetics signals recorded at two different wavelengths[2]. Moreover, according to pulse radiolysis studies, the electron seems to have a "special" behavior in EG: the energy of the solvated electron absorption band is quite high (2.17 eV *i.e.* 570 nm) and the electron trapping is more efficient in EG than in other alcohol glasses[3-5].

Within this context, to get a better insight into the formation and the reactivity of the solvated electron in EG, we investigated the solvation dynamics of electrons produced by two photon-ionization of the solvent with a 263 nm femtosecond laser pulse. The two photon absorption coefficient of EG at 263 nm was determined to be $\beta = (2 \pm 0.5) \times 10^{-12}$ m/W. The dynamics of electron solvation in EG was studied by pump-probe transient absorption spectroscopy. So, time resolved absorption spectra ranging from 450 to 725 nm were measured. A shrinkage and a blue shift of the spectra were observed for the first tens of picoseconds.[6] The observed picosecond solvation dynamics were reconstructed using two different models, a stepwise mechanism with two localized electronic species and the continuous blue shifting model involving only one species.

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[1] F.J. Jou and G.R. Freeman, "Band resolution of optical spectra of solvated electrons in water, alcohols and tetrahydrofuran", Can. J. Chem., **1979**, 57, 591-597.

[2] J.A. Kloepfer, V.H. Vilchiz, V.A. Lenchenkov, A.C. Germaine, and S.E. Bradforth, " The ejection distribution of solvated electrons generated by one-photon photodetachment of aqueous I^- and two-photon ionization of the solvent", J. Chem. Phys., **2000**, 113, 6288-6307.

[3] G.V. Buxton, J. Kroh and G.A. Salmon, "Electron trapping in glassy normal alcohols. A pulse radiolysis study at temperatures down to 6K", J. Phys. Chem., **1981**, 85, 2021-2026.

[4] J. Cygler, H.A. Gillis, N.V. Klassen and G.G. Teather, "The effect of accumulated dose at 6 and 72 K on electron trapping in ethylene glycol-water glass", Rad. Phys. Chem., **1981**, 17, 379-382.

[5] J.P. Suwalski and J. Kroh, "Dynamics of the blue shift of e^-_{tr} optical absorption spectra in ethanol-water glasses", Rad. Phys. Chem., **2002**, 64, 197-201.

[6] B. Soroushian, I. Lampre, P. Pernot*, V. De Waele, S. Pommeret and M. Mostafavi, "Formation and geminate recombination of solvated electron upon two-photon ionization of ethylene glycol", Chem. Phys. Lett., **2004**, 394, 313-317.