Ultrafast solvation dynamics in ionic liquids

Bernhard Lang and Eric Vauthey

Physical Chemistry Department, University of Geneva, 30, quai Ernest Ansermet,
CH-1211 Geneva 4, Switzerland, tel. +41 22 379-6535, fax -6518,
bernhard.lang@chiphy.unige.ch,
http://www.unige.ch/sciences/chifi/Vauthey/welcome.html

During last years, room temperature ionic liquids (RTILs) have attracted considerable attention as an alternative reaction medium for organic catalysis, for liquid-liquid extraction and as ultralow volatilty liquid matrices[1]. RTILs commonly have melting points below 0°C and are stable at temperatures above 300°C, but due to the strong Coulombic interaction their vapor pressures are negligible. The ease of product separation and catalyst recycling promises RTILs as replacements for conventional synthesis and separation processes and for electrochemical applications as in batteries and solar cells. Due to the largely diminuished evaporation losses they are often called "green solvents". The liquid state dynamics of the RTILs is espected to be interesting because of the molecular nature of the ions. However, up to now only few is known about ultrafast dynamics of these species.

This works presents the first study of solvation dynamics in ionic liquids with femtosecond time-resolution. Using different laser dyes as chomophores we investigate the ultrafast dynamics of 1-(3-cyanopropyl)-3-methyl-imidazolium. As described by Maroncelli and Fleming[2], the reconstructed spectra from time-resolved fluorescence measurements permit the calculation of the Stokes shift correlation function. A complementary and more direct approach provides a three-pulse photon-echo peak shift (3PEPS) measurement which has been shown to yield directly the solute-solvent correlation function in many common cases[3].

First fluorescence up-conversion experiments using coumarin 153 (Cu153) and coumarin 30 as fluorescence probe show highly non-exponential dynamics, ranging from a few picoseconds to about half a nanosecond. These results are compared with existing data for Cu153 in various conventional solvents[2]. We also present first results of the 3PEPS measurements using IR140 as chomophore and compare with correlation functions reported for different alcohols[4].

[1] T. Welton, Chem. Rev. 99, 2071 (1999)
[2] M. Maroncelli and G. R. Fleming, J. Chem. Phys. **1987**, 86 (11), 6221
[3] W. P. de Boeij, M. Pshenichnikow and D. A. Wiersma, Chem. Phys. Lett. **1996**, 253, 53
[4] G. R. Fleming et al., J. Phys. Chem. A **1997**, 101, 725