

Service des Photons, Atomes et Molécules
SÉMINAIRE

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CEA-Saclay Bât 522, p 138

Taking the plunge: chemical reaction dynamics in liquid solutions

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Modern molecular-beam and laser-based experiments, using methods such as velocity map imaging, can unravel detailed stereodynamical features of gas-phase collisions. Similar approaches are being employed to study scattering from solid and liquid surfaces, and within small molecular clusters, from which dynamics at interfaces and some of the consequences of solvation can, respectively, be quantified. Reaction dynamics in bulk liquids, however, remain largely unexplored because the fast interactions of a solute with the surrounding solvent destroy velocity and quantum-state specific information. The pioneering work of Polanyi demonstrated the dynamical insights that can be obtained from the degree of vibrational excitation of the products of chemical reactions. Persistence of vibrational excitation of molecules in solution on the picosecond timescale provides a comparable opportunity to explore reaction dynamics in the environment of a bulk liquid. We have used picosecond time-resolved vibrational spectroscopy with broadband, ultrafast infra-red laser pulses to study the dynamics of H(D)-atom abstraction reactions by CN radicals in various organic solvents. The ULTRA Laser Facility at the Rutherford Appleton Laboratory was used to probe the vibrational content of the HCN (or DCN) products in the C-H (C-D) and C-N stretching regions. Results will be presented that demonstrate excitation of the C-H stretching and the HCN bending modes at early times, followed by relaxation to the solvent. Kinetic analysis of populations of specific vibrational levels reveals preferential formation of HCN products with vibrational energy above that of the ground state, and comparable results are obtained for DCN. These outcomes are contrasted with the known dynamics of CN radical reactions in the gas phase. The mode specificity can be understood with the aid of quasi-classical trajectory calculations and dynamical calculations that incorporate the solvent. Reference: S.J. Greaves et al., Science in press (to be published 18 March 2011); DOI: 10.1126/science.1197796

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