SOLVENT CONTRIBUTION TO VIBRATIONAL ENERGY RELAXATION OF TERMINAL ACETYLENES AND ALCOHOLS

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For all molecules, including diatomics, interactions with the solvent will induce vibrational relaxation. For larger molecules, the solvent-induced relaxation is expected to remove only a small part of the total energy in each step leading to a cascade process for the full relaxation of the energy. This process is often called solvent assisted intramolecular vibrational energy redistribution (IVR). However, for a large molecule, the excited state population will also decay for an isolated molecule. This purely intramolecular process is the result of extensive local perturbations to the spectrum. We have recently completed the first systematic study of the modification of the purely intramolecular vibrational relaxation dynamics by measuring the excited state lifetime of the first excited hydride stretch in alcohols and terminal acetylenes. Using picosecond transient absorption infrared spectroscopy, the effects of solvent on vibrational energy redistribution have been examined for a wide range of solvents. In all cases, there is a simple competition between the purely intramolecular vibrational energy redistribution (also IVR) and solvent-induced vibrational energy relaxation (VER), giving a total relaxation rate that is the sum of the rate due to molecule- dependent IVR and the rate due to solvent-dependent VER. This simple relaxation model is observed in both simple CCl_4-like solvents and more complex solvents, including benzene and 1,3- dichlorobenzene. The measurements provide the first insight into the mechanism for solvent-assisted IVR in large molecules.