SEMINAIRE ISMO

Jan Helbing

Department of Chemistry, University of Zurich

Ultrafast Vibrational Spectroscopy of Highly Symmetric Molecules

Selection rules for highly symmetric molecules often simplify their vibrational spectra but also make IR absorption highly sensitive to a lowering of symmetry due to solvation or electronic excitation. This can be exploited in multiple ways by ultrafast IR-spectroscopy to obtain information about energy relaxation as well as solvent structure and dynamics, both in the ground and the electronic excited state. Three examples will be discussed :
The observation of multiple CN stretch bands after metal-to-ligand charge transfer (MLCT) excitation of ferricyanide $[Fe(CN)_6]^{3-}$ has been interpreted as a signature of ultrafast electron localization in polar solvents. Comparison of electronic and direct IR excitation of the complex reveals, however, that octahedral symmetry is conserved while electronic excess energy is impulsively converted into multiple quanta of high frequency vibrational excitation. The D_{3h} symmetry of the nitrate ion NO_3^-, on the other hand, is permanently broken in water due to different hydrogen-bonding interactions between the three oxygen atoms and the surrounding H_2O. The degeneracy of the asymmetric NO stretch band is lifted and becomes an ideal observable for monitoring H-bond fluctuations and solvation shell dynamics by polarization-resolved two-dimensional IR (2D-IR) spectroscopy. 2D-IR spectroscopy can also be used to study solvent shell dynamics after electronic excitation. This is particularly interesting for quadrupolar acceptor-donor-acceptor molecules, which acquire a strong dipole moment only after asymmetric charge transfer in the excited state. In very strongly hydrogen bonding liquids, this can lead to complete freezing of solvent motion in the vicinity of the chromophore.

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Université Paris-Sud - 91405 ORSAY Cedex