

Short Visit Grant - Final Report on “Time Resolved mid Infrared Studies of Photo-induced Bimolecular Electron Transfer”

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The aim of the period in the IR application laboratory of the Max-Born-Institute in Berlin was to study the primary reaction products of photo-induced bimolecular electron transfer reactions.

During this stay, time-resolved mid-infrared measurements on perylene and methylperylene as electron donor and trans-1,4-dicyanoethylene (DCE) and tetracyanoethylene (TCNE) as acceptors in acetonitrile (ACN) and dichloromethane (DCM) have been carried out. The large amount of collected experimental data will need a substantial time of evaluation before quantitative results can be reported. However, qualitative conclusions can already be drawn.

Spectral dynamics on the band of the antisymmetric cyano stretching vibration of TCNE⁻ on a timescale of a few tens to a few hundreds of picoseconds show for the first time clearly distinguishable signatures of the primary reaction products, namely strongly and loosely bound ion pairs. The former are to be seen in both employed solvents and appear within time resolution. Charge recombination takes place on a timescale of the order of ten to several tens of picoseconds. Separation to free ions occurs only in the more polar ACN. These ions show in our measurements a narrower and blue-shifted CN stretching band. The rate constant of formation is much slower than that of the strongly bound pair and depends on the acceptor concentration, a clear indication of a diffusion controlled reaction. The picture is consistent with more indirect considerations based on a comparison of rate constants and free ion yields from transient absorption measurements in the visible domain and photo-conductivity experiments [1,2].

The results of this research visit provide the missing link many research groups have been after for decades, allowing by direct observation to distinguish the reaction products of on-contact pairs from the reaction products of those pairs which meet by diffusional motion only after excitation. The quantitative analysis of the obtained experimental data will lead to at least two publications.

As the results of this visit are very promising and the employed spectroscopic approach is rather general, a continuation of the project is planned to enlarge the data basis for a better understanding of ultrafast bimolecular photo-induced electron transfer reactions on a molecular basis.

[1] S. Pagès and B. Lang and E. Vauthey, *J. Phys. Chem. A* **108** (4), 549 (2004)

[2] V. Gladkikh, A.I. Burshtein, G. Angulo, S. Pagès, B. Lang and E. Vauthey, *J. Phys. Chem. A*, **108** (32), 6667 (2004)