

# **Final Report on "Femtosecond Time Resolved Mid-Infrared Studies of Photoinduced Bimolecular Electron Transfer in Condensed Phase"**

*Omar F. Mohammed*

*Department of Physical Chemistry, University of Geneva,  
30, quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland*

Despite the numerous studies carried out on photoinduced bimolecular electron transfer (ET), important questions still remain unanswered, such as the nature of the primary ET quenching product and the various steps leading to the formation of free solvated ions in polar solvents. Transient absorption and time-resolved Raman measurements have shown that the electronic absorption spectra and the high frequency vibrational modes of the transient species do not change upon separation of a contact ion pair into free ions [1]. Recently, we have shown that time resolved mid-infrared spectroscopy is a promising tool which permits direct insight into structural dynamics by following vibrational marker modes on both donor and acceptor sides in real time [2-4].

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(Pe) and methyl-perylene(MePe) as electron donor and trans-1,4-dicyanoethylene (DCE) and tetracyanoethylene (TCNE) as electron 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(tight complex) and loosely bound(loose complex) ion pairs. The former (tight complexes) 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 [5,6]. 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.

## References

- [1] E. Vauthey, A.W. Parker, B. Nohova and D. Phillips, *J. Am. Chem. Soc.* 116 (20), 9182 (1994)
- [2] O. F. Mohammed, N. Banerji, B. Lang, E. T. J. Nibbering, and E. Vauthey, *J. Phys. Chem. A* 110(51), 1367 (2006).
- [3] O. F. Mohammed, D. Pines, J. Dreyer, E. T. J. Nibbering, E. Pines, *Angew. Chem. Intl. Ed*, In press
- [4] O. F. Mohammed, D. Pines, J. Dreyer, E. Pines and E. T. J. Nibbering. *Science* 310 83 86 (2005).
- [5] S. Pages and B. Lang and E. Vauthey, *J. Phys. Chem. A* 108 (4), 549 (2004)
- [6] V. Gladkikh, A.I. Burshtein, G. Angulo, S. Pages, B. Lang and E. Vauthey, *J. Phys. Chem. A*, 108 (32), 6667 (2004)