UP2: Electron transfer in aminobenzonitriles

Cooperations: TP A2 / A7

Isolated molecules

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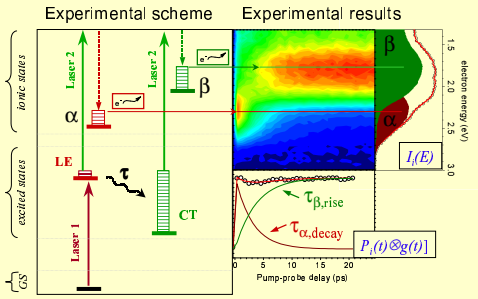
Time-resolved photoelectron spectroscopy

Yields spectroscopic and dynamic information

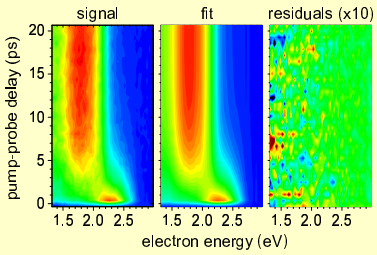
⇒ *reliable identification of ionization channels*



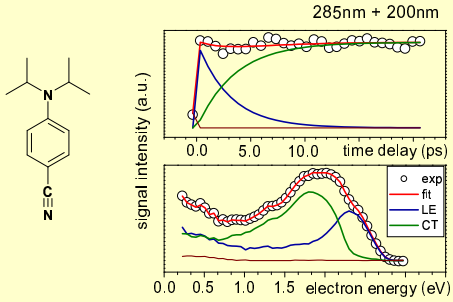
Example diisopropylaminobenzonitrile: transition from locally excited state (LE) to charge transfer state (CT)

The signal is fitted with function *(1)* to extract:
(a) the excited state *population dynamics* $P_i(t)$ and
(b) the *photoelectron spectra* $I_i(E)$.

$$S(E,t) = \sum_i I_i(E)\cdot[P_i(t)\otimes g(t)] \qquad (1)$$



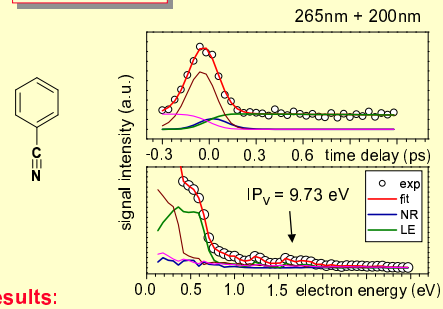
Diisopropylaminobenzonitrile



Results: ***We observe charge transfer!***

- locally excited state *(LE)* with τ_{decay} = 3.0 ps, IP_V = 8.4 eV.
- charge transfer state *(CT)* with τ_{rise} = 3.5 ps IP_V = 8.9 eV.

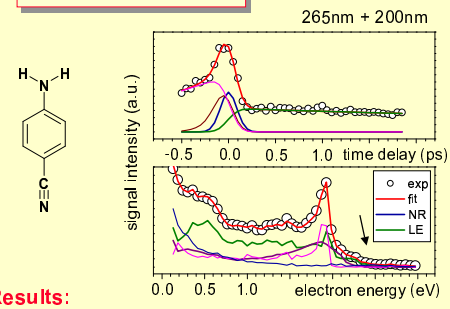
Benzonitrile



Results:

- non-resonant or short-lived signal *(NR)*
- long lived excited state *(LE)* with IP_V = 10.6 eV. (Ground state IP_V = 9.73 eV¥: arrow)

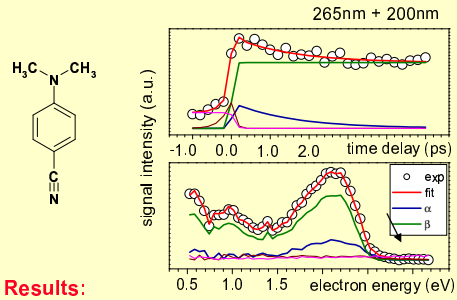
Aminobenzonitrile



Results:

- non-resonant or short-lived signal *(NR)*
- long lived excited state *(LE)* with IP_V = 9.0 eV. (Ground state IP_V = 8.51 eV¥: arrow)

Dimethylaminobenzonitrile



Results:

- short lived excited state *(α)* with τ = 1.3 ps
- long lived excited state *(β)* with IP_V = 8.5 eV. (Ground state IP_V = 7.91 eV¥: arrow)

¥*NIST Chemistry WebBook, NIST Standard Reference Database Number 69*

Microsolvated clusters

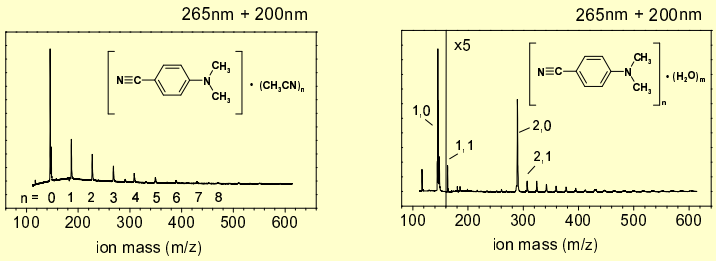
Dimethylaminobenzonitrile (solvens)$_n$ clusters

Electron transfer was observed for solvated clusters[1,2]

Reaction dynamics are not yet characterized

[1] Q.-Y. Shang, E.R. Bernstein, J. Chem. Phys. **97**, 60 (1992).
[2] O. Krauß, U. Lommatsch, C. Lahmann, B. Brutschy, W. Rettig, J. Herbich, Phys. Chem. Chem. Phys. **3**, 74 (2001).

Pump-probe mass spectra



First results:

- ***Good clustering with acetonitrile, water and methanol***
- ***No charge transfer dynamics observed in mass spectra***
- ***Strong fragmentation of DMABN $(H_2O)_{n>1}$ clusters?***

Future work

- electron transfer in chromophor-solvens clusters ⇒ ***characterize solvation effects***
- analysis of cluster fragmentation ⇒ ***coupled to charge transfer reaction?***
- cluster selection by hole burning methods or alignment
- spatially resolved detection of cluster fragments