Laser-induced intermolecular electron transfer calculated by means of TD-CIS

Stefan Klinkusch, Tillmann Klamroth, and Peter Saalfrank

Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany

TD-CIS method

Theory

- Goal: Solution of the time-dependent molecular electronic Schrödinger equation:

$$i\frac{\partial \Psi_{mol,el}(t)}{\partial t} = \hat{H}_{mol,el}(t)\Psi_{mol,el}(t)$$

with the time-dependent Hamiltonian $\hat{H}_{mol,el}(t)$ within the semiclassical dipole approximation:

$$\hat{H}_{mol,el}(t) = \hat{H}_0 - \hat{\vec{\mu}}\vec{F}(t)$$

- Concept: CIS$^{(1)}$ coefficients D_a^r become time-dependent$^{(2,3,4)}$

$$\Psi^{CIS}(t) = D_0(t)\Psi_0^{HF} + \sum_{a,r} D_a^r(t)\Psi_a^r = \sum_j C_j(t)\Phi_j$$

Types of laser pulses

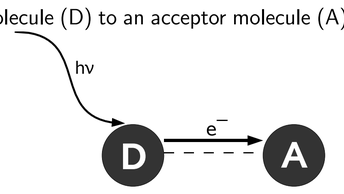
- $\cos^2$-shaped pulses:

$$\vec{F} = \begin{cases} \vec{f}_0 \cos^2\left[\frac{\pi}{2\sigma}(t-t_p)\right]\cos\left[\omega(t-t_p)\right] & \text{if} \quad |t-t_p| < \sigma \\ \vec{0} & \text{else} \end{cases}$$

  - π-pulses: $|\vec{\mu}_{f,i}||\vec{f}_0|\sigma = \pi$ (if $\vec{\mu}_{f,i} \parallel \vec{f}_0$)
  - manually optimized pulses, usually: $|\vec{\mu}_{f,i}||\vec{f}_0|\sigma < \pi$

Aim

- Electron transfer from a donor molecule (D) to an acceptor molecule (A) within a state-to-state transition



- Selective generation of wavepackets

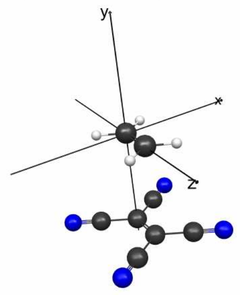
Contributions to the excitation energy E_{ex} to the CT-state

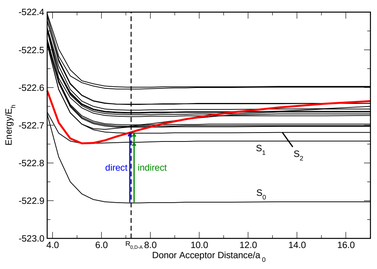
- Ionization potential of the donor molecule, IP_D
- Electron affinity of the acceptor molecule, EA_A
- Work to transfer electron from the donor to the acceptor

$$E_{ex} \approx IP_D - EA_A - \frac{1}{R}$$

System

Stationary calculations in an ethylene-tetracyanoethylene (TCNE)-system (CIS$^{(1)}$/6-31G*$^{(6)}$)

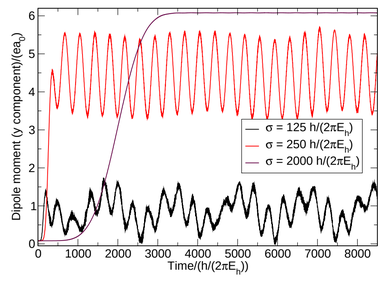


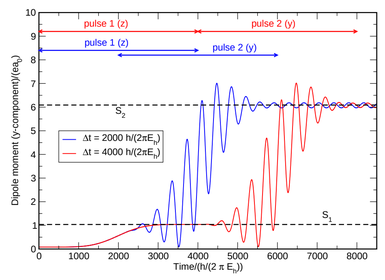


- CT state exists

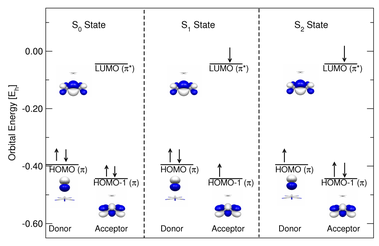
State-to-state excitations

- direct: $S_0 \rightarrow S_2$
- pulse sequence: $S_0 \rightarrow S_1 \rightarrow S_2$





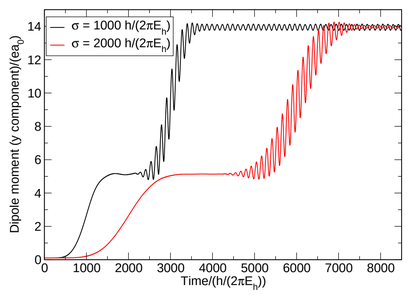
- Laser-induced intermolecular charge transfer is possible
- A longer pulse ($\sigma \geq 500\frac{h}{2\pi E_h}$) achieves at least a target state population of 0.90
- Orbital picture:

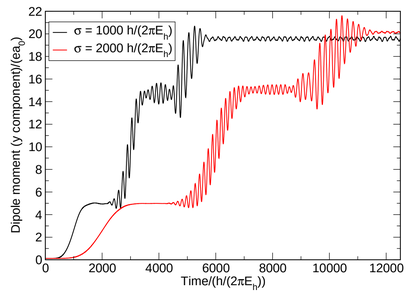


Larger systems

State-to-state excitations in multiple-donor systems

- System can be enlarged by adding more donor or acceptor molecules
- Excitation only with pulse sequences
- system with two donor molecules: DDA
- system with three donor molecules: DDDA

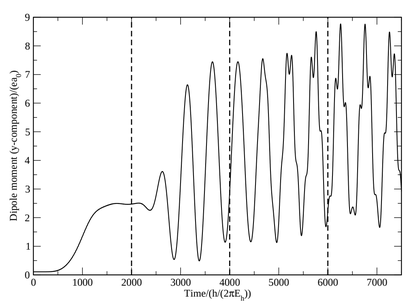


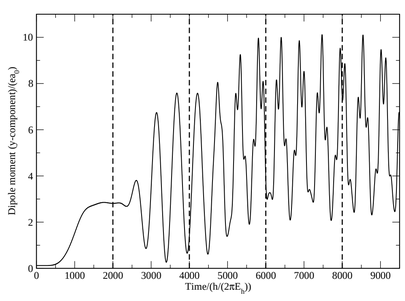


Selective Excitation of Wave Packets in large systems

- Aim: Generation of a wave packet with a hole moving between two or more donor molecules
- Result: Generation of an excitonic wave packet
- Wave Packet can be induced by a pulse sequence with π-pulses and manually optimized pulses to achieve a defined population scheme

- system DDA
- system DDDA





Summary

Conclusions

- Intermolecular electron transfer can be described with TD-CIS
- Electron transfer can be induced using several ways:
  - Direct transition (only in smaller systems due to a small transition dipole moment)
  - Sequential transition (possible in most cases)
- Generation of an excitonic wave packet is possible in systems with more than one donor molecule with a pulse sequence

Outlook

- Including photoionization
- Including finite lifetime of excited states
- Switch between excited states with opposing dipole moments
- Calculations for more realistic systems

References

1. J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, *J. Phys. Chem.* **96**, 135 (1992).
2. T. Klamroth, *Phys. Rev. B* **68**, 245421 (2003).
3. C. Huber and T. Klamroth, *Appl. Phys. A* **81**, 91 (2004).
4. P. Saalfrank, T. Klamroth, C. Huber, and P. Krause, *Isr. J. Chem.* **45**, 205 (2005).
5. A. D. Bandrauk, E. Aubanel, and S. Chelkowski, in J. Manz, L. Wöste (Eds.) *Femtosecond Chemistry* Vol. 2, Chap. 25, p. 731, Verlag Chemie, Weinheim (1995).
6. P. C. Hariharan, and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973).