Simulations of time-resolved photoelectron spectra using extended time-dependent configuration interaction methods

Stefan Klinkusch and Jean Christophe Tremblay
Freie Universität Berlin, Physikalische und Theoretische Chemie, Takustraße 3, 14195 Berlin, Germany
Contact: stefan.klinkusch@fu-berlin.de, jc.tremblay@fu-berlin.de

Aim

- Reconstruction of a time-resolved photoelectron spectrum of an Au_7^- cluster
  - Excitation of the cluster to higher states or to a wavepacket using a first laser pulse
  - Excitation of the relaxed wavepacket to the ionization continuum using a second pulse
  - Varying delay times between the two pulses
  - Reconstruction of the spectrum from the kinetic energies of the ionized species
- Improvement of the temporal behaviour of the signal
- Possibility to improve the signal by taking higher excitations into account and to use every arbitrarily chosen laser field

The ρ-TDCI method[1,2]

Theory

- Goal: Solution of the Liouville-von-Neumann equation

$$\frac{\partial\hat{\rho}(t)}{\partial t} = -i\left[\hat{H}_{el},\hat{\rho}\right] + i\left[\underline{\hat{\mu}}\underline{F}(t),\hat{\rho}(t)\right] + \hat{\hat{\mathcal{L}}}_D\hat{\rho}(t)$$

within the space of CI eigenfunctions $|n\rangle$ with time-dependent expansion coefficients $\rho_{nm}(t)$

$$\hat{\rho}(t) = \sum_{nm}\rho_{nm}(t)|n\rangle\langle m|$$

Photoionization[3,4]

- Photoionization rate of an electronic state $|n\rangle$ is calculated as

$$I_n = \begin{cases} 0 & \text{, if } E_n < IP \\ \sum_{a,r}|D^r_{a,n}|^2\Omega^r_a & \text{, if } E_n \geq IP \end{cases}$$

with the ionization rate of a configuration state function

$$\Omega^r_a = \begin{cases} 0 & \text{, if } \varepsilon_r \leq 0 \\ \frac{\sqrt{\varepsilon_r}}{d} & \text{, if } \varepsilon_r > 0 \end{cases}$$

Relaxation

- Non dipole interactions and internal conversion is described using

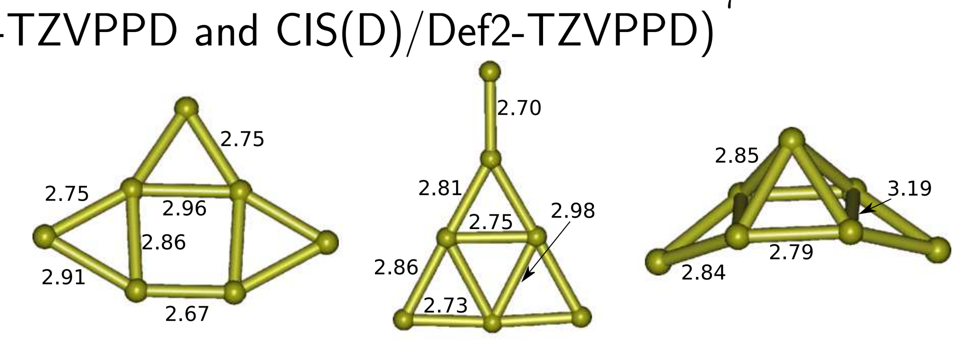
$$\Gamma_{m\rightarrow n} = \frac{|\langle H\rangle_{NAC}|^2}{\hbar^2(\omega_{nm}+\omega_c)^2}$$

with $|\langle H\rangle_{NAC}|^2$ as a system-dependent parameter and ω_c as the Matsubara frequency in an Ohmic expression of the phonon density of states

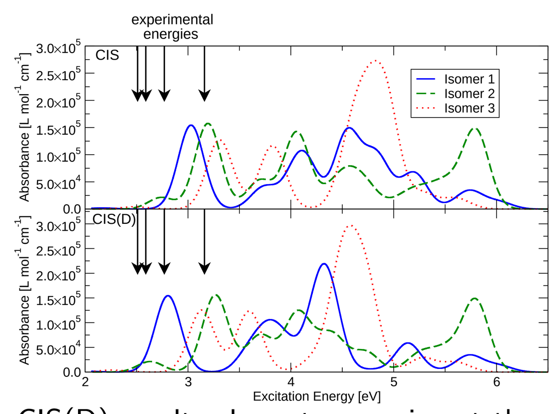
$$J(\omega) = \eta\omega e^{-\omega/\omega_c}$$

System[5,6]

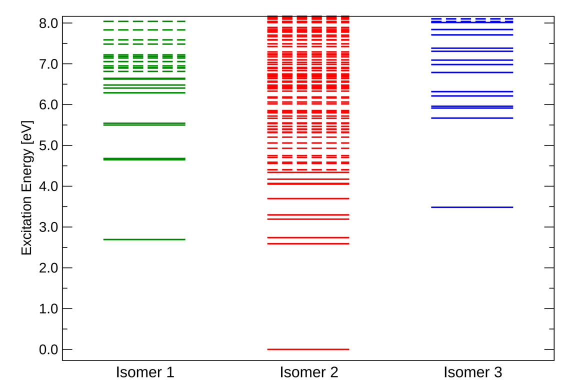
Stationary calculations for three isomers of the Au_7^- cluster (CIS/Def2-TZVPPD and CIS(D)/Def2-TZVPPD)



- Spectra

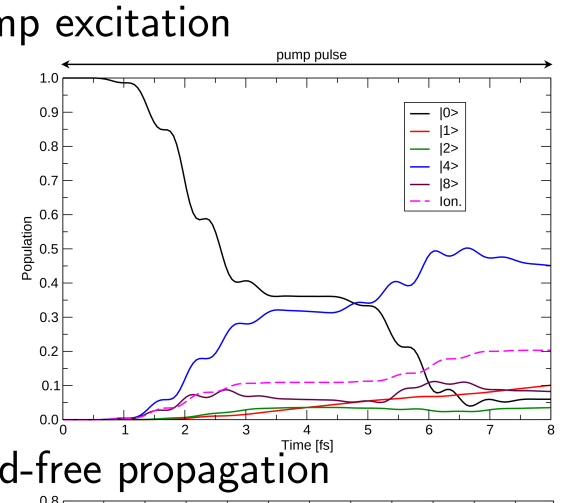


- Energies



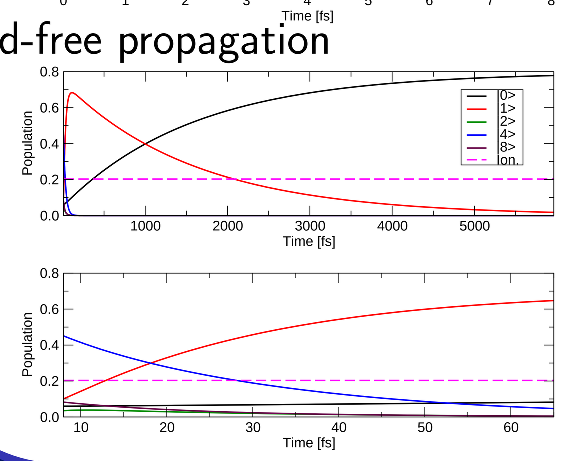
- CIS(D) results closer to experiment than CIS results
- CIS(D) correction for the lowest 20 states of each isomer
- Treatment of the three isomers as one system (with internal conversion)

Pump excitation



- Non-resonant pump pulse of $4\,\mathrm{fs}$ width
- Frequency lower than ionization potential
- Depopulation of ground state
- Significant population in four excited states
- Loss of norm at about 0.2

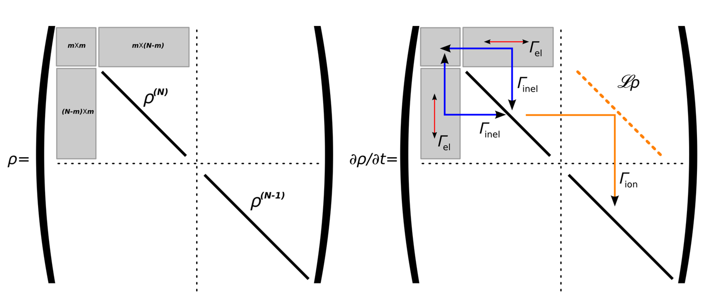
Field-free propagation



- Fast relaxation of the four-level-system to a two-level-system with the states $|0\rangle$ and $|1\rangle$
- Higher population in the ground state for longer delay times

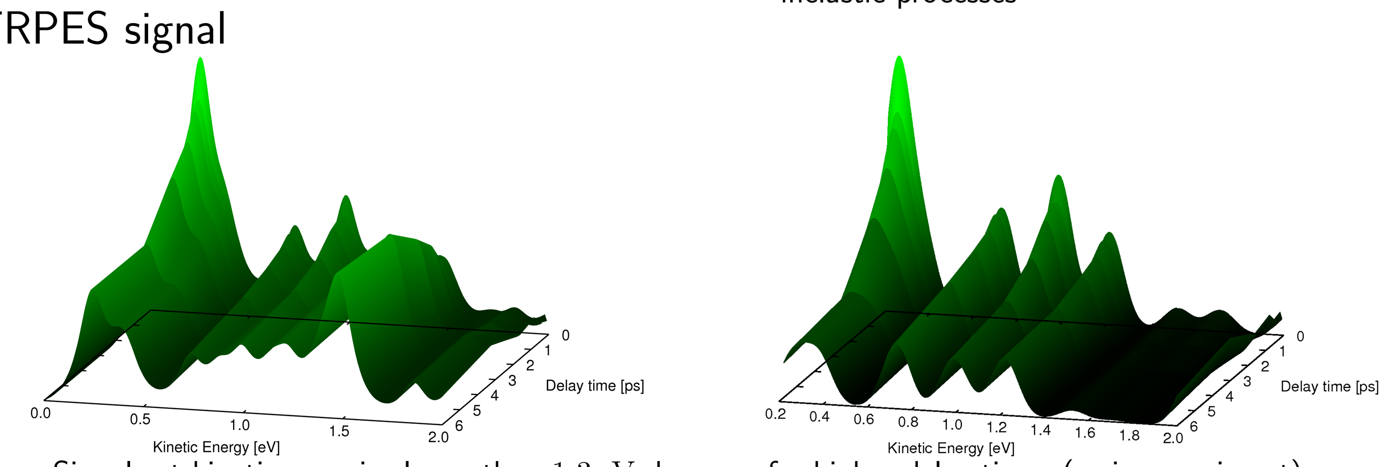
Probe excitation

Signal reconstruction



- N electron system consists of m nonionizing and $(N-m)$ ionizing states
- coherences among ionizing states are neglected, populations are kept
- only populations of $(N-1)$ electron system are kept, no coherences
- coupling between N and $(N-1)$ electron system via ionization
- coupling within N electron system via elastic and inelastic processes

TRPES signal

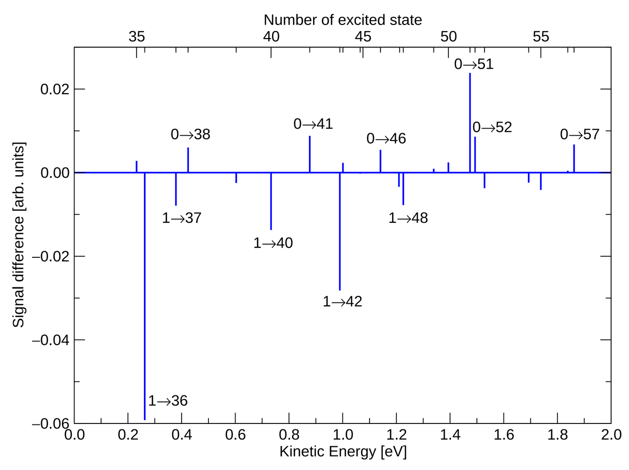


- Signals at kinetic energies lower than $1.3\,\mathrm{eV}$ decrease for higher delay times (as in experiment)
- Signals at kinetic energies higher than $1.3\,\mathrm{eV}$ increase for higher delay times (artifact)

Interpretation

- Difference signal is calculated as

$$\Delta S_{probe}(E_{kin}) = S_{probe}(E_{kin}, t_{delay} = 6\,\mathrm{ps}) - S_{probe}(E_{kin}, t_{delay} = 100\,\mathrm{fs})$$



- Positive signals arise from excitations from the ground state
- Negative signals arise from excitations from the first excited state
- Below $1.3\,\mathrm{eV}$ stronger signals on negative side
- Above $1.3\,\mathrm{eV}$ stronger signals on positive side
- Reason is a high transition dipole moment from the ground state to ionization continuum

Summary

Conclusions

- Photoelectron spectrum can be reconstructed from a ρ-TDCI calculation
- Improved dependence of the signal on the delay time vs. TDDFT/FISH[5]
- Dependence of the signal on the delay time can be explained from transition dipole moments
- Advantages of this method:
  - Description of the system is systematically improvable
  - Strong field excitations can be treated variationally (linear extension)
  - Photoionization, relaxation, and internal conversion are included
- Disadvantages:
  - HF/CIS description is insufficient
  - Better description of the experiment requires (D) calculation (more expensive)

Outlook

- Improve description of the experiment with various density functionals → TDCIS/DFT
- Improve description of photoionization, relaxation, and internal conversion
- Reduce computational requirements → propagation in CSF space and resolution of identity

References

1. T. Klamroth, *Phys. Rev. B* **68**, 245421 (2003).
2. J. C. Tremblay, T. Klamroth, and P. Saalfrank, *J. Chem. Phys.* **129**, 084302 (2008).
3. S. Klinkusch, P. Saalfrank, and T. Klamroth, *J. Chem. Phys.* **131**, 114304 (2009).
4. J. C. Tremblay, S. Klinkusch, T. Klamroth, and P. Saalfrank, *J. Chem. Phys.* **134**, 044311 (2011).
5. J. Stanzel, M. Neeb, W. Eberhardt, P. G. Lisinetskaya, J. Petersen, and R. Mitrić, *Phys. Rev. A* **85**, 013201 (2012).
6. F. Furche, R. Ahlrichs, P. Weis, C. Jacob, S. Gilb, T. Bierweiler, and M. M. Kappes, *J. Chem. Phys.* **117**, 6982 (2002).