



Hylleraas

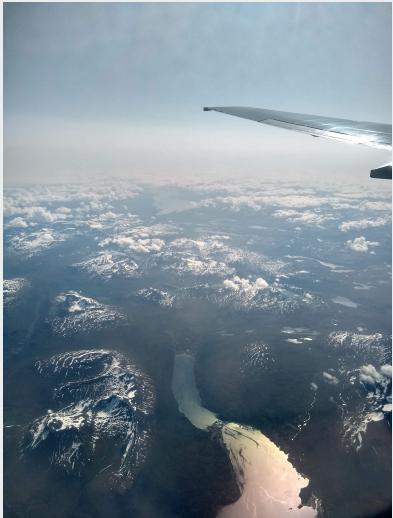


ISTCP-X debrief

July 11-17, Tromsø, Norway

10th Triennial Congress of the International Society for Theoretical Chemical Physics

~35 hr journey



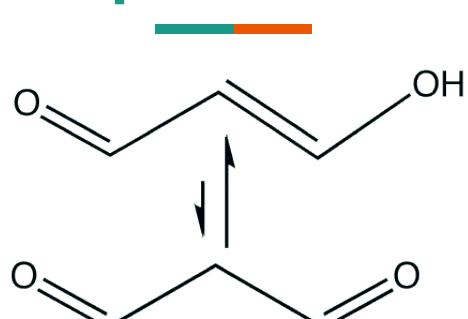
Several fjords



~150 speakers, ~550 attendees



Propanedial and UV-x-ray pump-probe spectroscopy



NATIONAL
ACCELERATOR
LABORATORY

Nana List



In Silico proof-of-concept for experimental method to study photodecay processes

Collaboration with SLAC, proposing uses for new X-ray light sources.

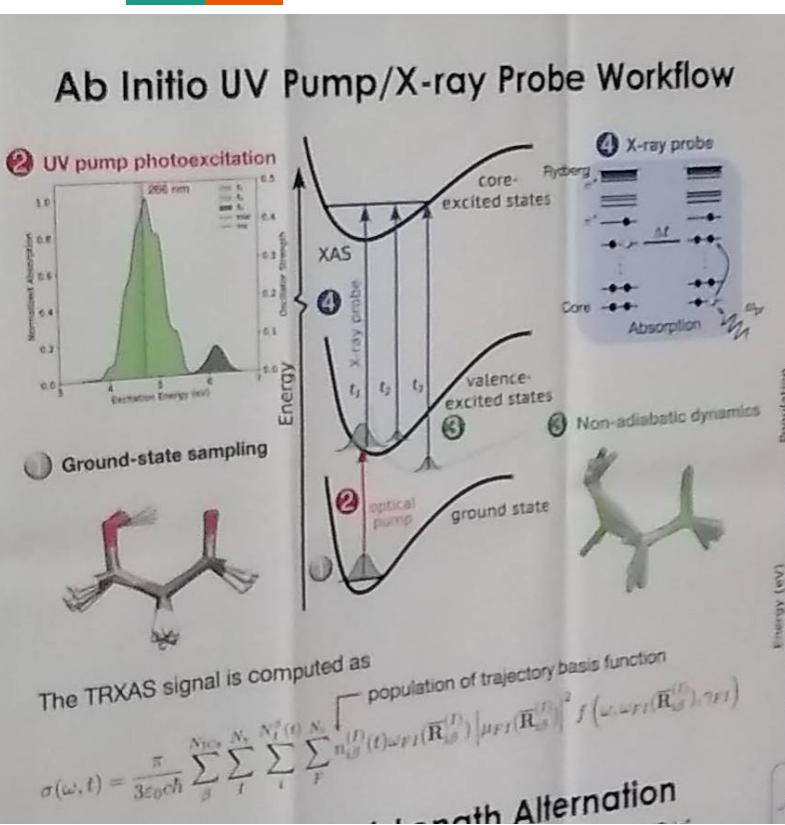
UV pump prepares (π, π^*) state. Decay to (n, π^*) . X-ray excites core into vacancy. Sensitive to chemical environment.

Studying intermolecular H-transfer, and conical intersection. (*Think Norrish Type II*)

They can't access information on photoproducts and photodissociation dynamics.



Proposed Technique



Apologies for the phone photo - unpublished work

In silico workflow designed to match forthcoming experiments

Ground state sampling to sample different FC initial configurations

Pump with 266 nm UV → $S_2 (\pi, \pi^)$*

Propagate nonadiabatic dynamics by AIMS

X-ray probe excites core into different vacancies due to S_2, S_1, S_0

Separation of atomic K-edge spectra clear, several eV difference

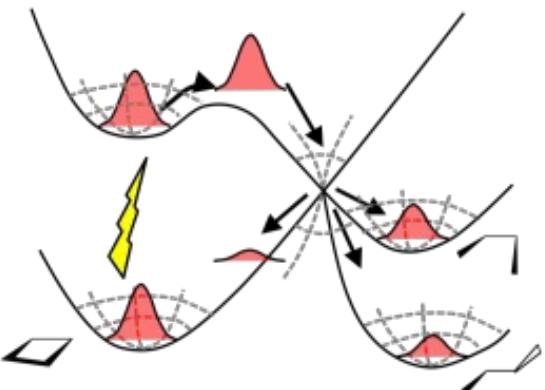
Can detect chemical environment, bond-length alteration, etc.

Enol peak particularly sensitive to bond-length alteration

Ultrafast excited state dynamics - AIMS

AIMS - Ab Initio Multiple Spawning

Photo-isomerism



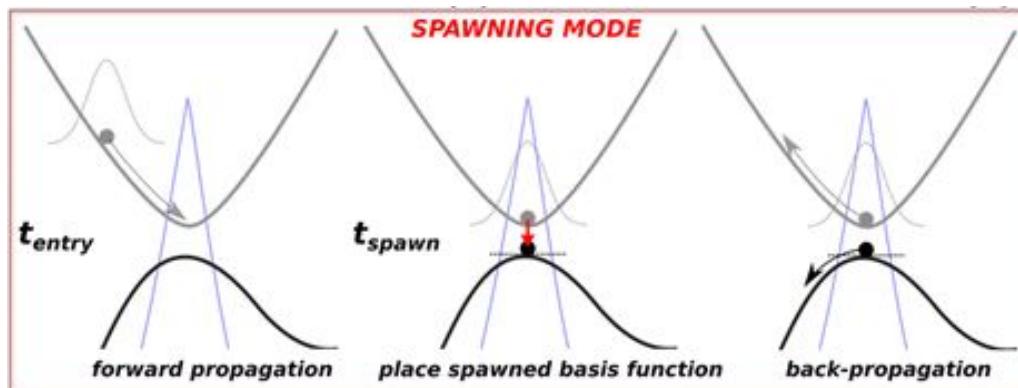
Need to couple both electronic and nuclear wavefunction dynamics

Nuclear wavefunction: linear combinations of gaussians with time-dependent coeffs.

1D gaussian basis function for each nuclear d.o.f. TD: R, P, Y non-TD: gaussian width

Need to adaptively expand the nuclear basis set to account for QM phenomena

Expand only when classical dynamics fail - spawn (FC) when ↑ nonadiabatic couplings



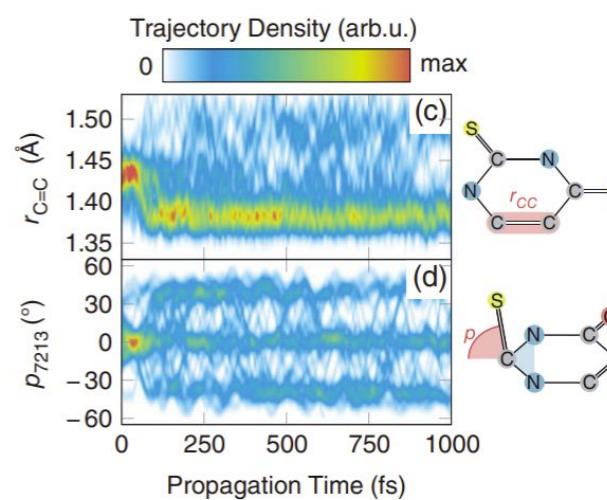
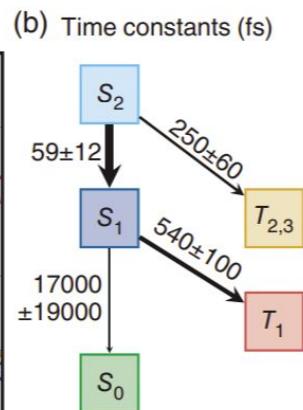
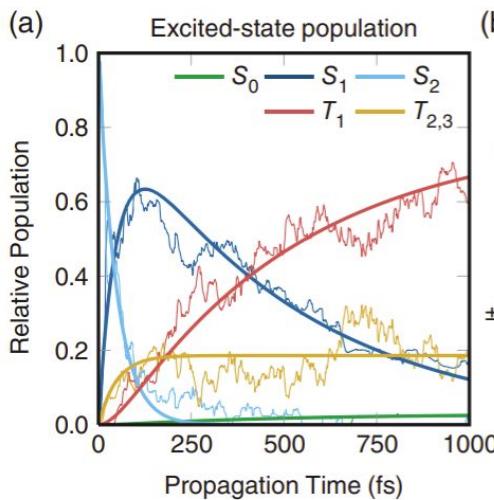


SHARC - Surface Hopping including ARbitrary Couplings



<https://sharc-md.org>

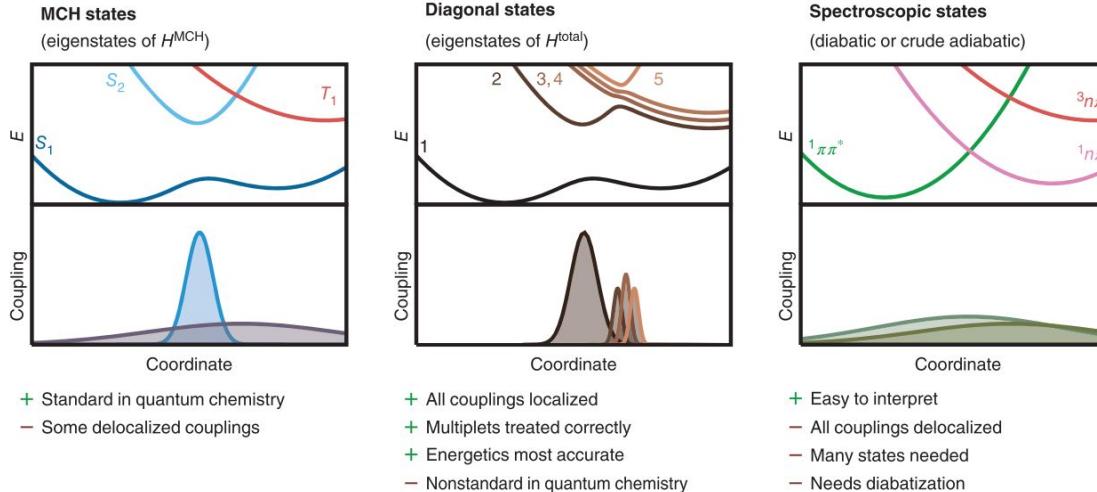
"Mr. SHARC"



Sebastian Mai



SHARC - Nonadiabatic, also spin-orbit, dipole, couplings



Misses quantum effects (ZPE, tunneling), but so does AIMS in a small nuclear basis

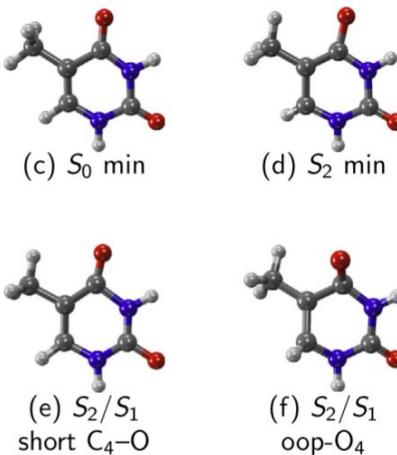
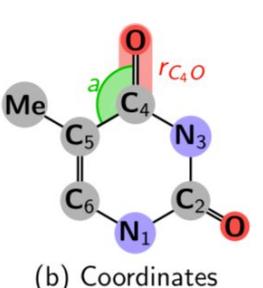
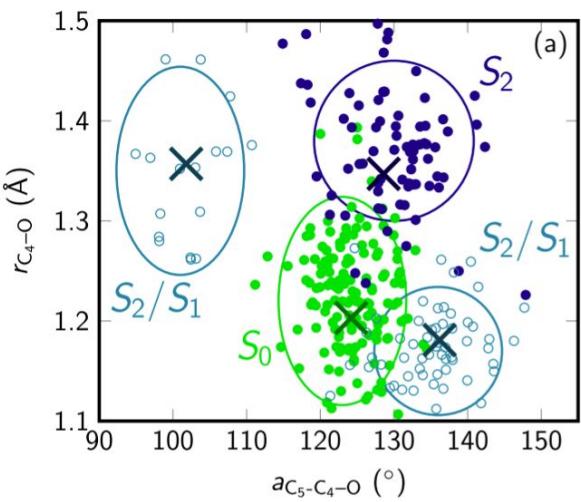
“Least switching” - switch stochastically only when the population of electronic state decreases

Electronic structure ‘on-the-fly’ - can even use QM/MM

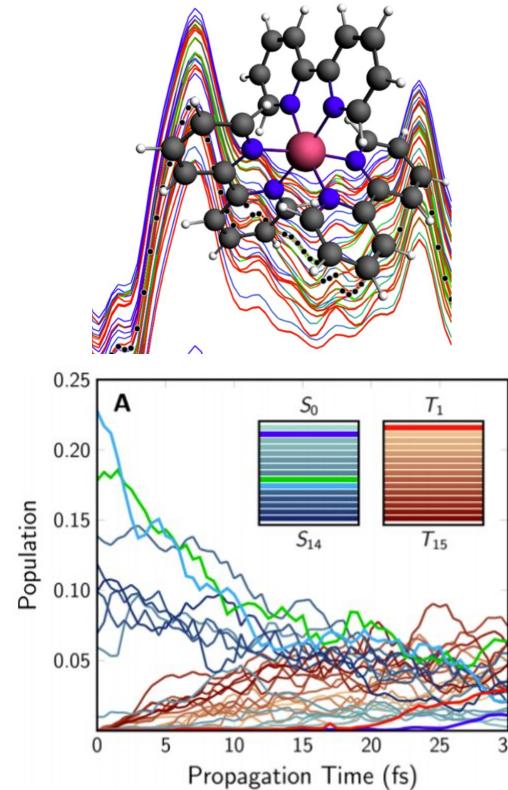
Shortcomings: lacks decoherence, needs ensembles (stochastic), velocity scaling upon hops, EST wavefunction sign

SHARC - Example applications

DNA bases



Organometallics



Interfaces: MOLPRO, MOLCAS, TURBOMOLE, COLUMBUS, ADF, GAUSSIAN, ORCA

Other interesting talks

- **Eric Neuscamman** - Variational excited states in electronic structure theory
- **Peter Gil** - MP2 correlation energies by quadrature methods
- **Todd Martinez** - Nonadiabatic dynamics of photoactive proteins using GPUs
- **Denis Jacquemin** - Searching for super-accuracy in excited state calculations
- **Stefan Grimme** - New tight-binding quantum chemistry methods
- **Satoshi Maeda** - Automatic reaction path networks by Artificial Force Induced Reaction method
- **Heather Kulik** - Transition metal catalysts through high-throughput and machine learning tools
- **Julien Blonio** - A ‘virtual spectrometer’ to predict and interpret vibration spectra
- **David Clary** - Semiclassical transition state theory (SCTST) and nerve agents
- **Morgane Vacher** - Chemiluminescence of 1,2-dioxetane from MD and machine learning
- **Cristina Puzzarini** - Rotational spectroscopy and quantum chemistry for astrochemistry (glycolaldehyde)

Thank you!

