Nuclear Quantum Effects Nuclear Quantum Effects in Chemical Reactivity: from Ground State Reactions to Photochemistry

A.Chin, P.Depondt, F.Finocchi, S.Huppert (INSP)
Riccardo Spezia (LCT)
`riccardo.spezia@sorbonne-unversite.fr`

Journée UFR de Chimie / UFR de Physique

Chemistry and Physics

- Dynamic Simulations: Structure and Reactivity at LCT
- NQEs: F.Finocchi, S.Huppert, Ph.Depondt $\rightarrow$ ISCD project: Quo vadis hydronium ?
- MPS/Tensor Network at ISCD: A.Chin $\rightarrow$ ISIM project: Theory of Photoinduced Proton-Coupled Electron Transfer in Nanozymes and Polaritonic Optical Cavities
- F.Angiolari PhD with S.Huppert (graduated in September)
- N.Avallone ISCD PhD co-direction with F.Finocchi (will graduate in December)
- B.Le Dé ISIM PhD co-direction with A.Chin and S.Huppert (2nd year PhD)

The Feynman's Club

Chemical Reaction

- $A + B \rightarrow C + D$
- reactants (old species) become products (new species)
- A,B,C,D: molecules, so finally nuclei + electrons
- Chemical reaction: a rearrangement of nuclei and electrons
- Electron arrangement: electronic structure theory

$$\mathcal{H}_{el}\Psi(r; R) = E\Psi(r; R) \tag{1}$$

- Nuclear dynamics (ground state)

$$U(R) = \min_{\Psi_0}\langle\Psi_0(r; R)|\mathcal{H}_{el}|\Psi_0(r; R)\rangle \tag{2}$$

$$F = -\frac{\partial U(R)}{\partial R} \tag{3}$$

Chemical Reaction

Electrons always quantum (adiabatic or not)
Nuclei ?

- Molecular dynamics: $F_I = M_I \ddot{R}_I(t)$
- "Classical" MD : F from force fields (e.g. proteins ...)
- "Ab initio" MD : $F_I = -\nabla_I \langle \Psi_0 | \mathcal{H}_{el} | \Psi_0 \rangle$
- But nuclei are "particles" so in general TDSE holds, e.g. in the adiabatic approximation

$$\left[-\sum_I \frac{1}{2M_I} \nabla_I^2 + E_k(R) + \mathcal{C}_{kk}(R) \right] \chi_k = i \frac{\partial}{\partial t} \chi_k \qquad (4)$$
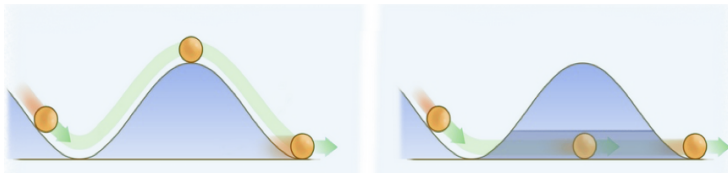
Nuclear Quantum Effects in Chemical Reactivity

- Light nuclei
  Thermal De Broglie wavelength

$$\lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \tag{5}$$

  where $\lambda_{th} \sim 1$ Å for H at 300 K.

- Tunneling (not only involving H atoms)

- Vibrational quantization (classical vs quantum partition function)
- Classical MD with initial quantization $\rightarrow$ Leakage !

Quantum Thermal Bath

- Quantum Thermal Bath (QTB)[1]

$$m_i \ddot{q}_{i,\alpha} = -\frac{\partial V}{\partial q_{i,\alpha}} - m_i \gamma \dot{q}_{i,\alpha} + R_{i,\alpha}(t) \qquad (6)$$

following the Wiener-Khinchin theorem

$$\langle R_{i,\alpha}(t) R_{i,\alpha}(t+\tau) \rangle = \int_{-\infty}^{+\infty} I_{R_i}(|\omega|) e^{-i\omega\tau} \frac{d\omega}{2\pi} \qquad (7)$$

$$I_{R_i}(\omega) = 2m_i \gamma \hbar \omega \left[\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1} \right] \qquad (8)$$

- Adaptative QTB at INSP[2]

[1] H.Dammak, Y.Chalopin, M.Laroche, M.Hayoun, J.-J.Greffet, Phys.Rev.Lett. 103, 190601 (2009)

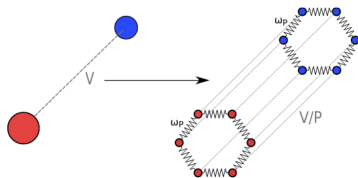[2] E.Mangaud, S.Huppert, T.Plé, P.Depondt, S.Bonella, F.Finocchi, J.Chem.Theory Comput. 15, 2863 (2019).

Ring Polymer Molecular Dynamics

Based on Path-Integral theory , which gives an exact quantum partition function

$$\mathcal{Z} = \lim_{P \to \infty} \frac{1}{(2\pi\hbar)^P} \int d\mathbf{p} \int d\mathbf{q} \exp\left(-\beta_P \hat{H}_P(\mathbf{p}, \mathbf{q})\right) \tag{9}$$

Ring Polymer MD[3] on an extended Hamiltonian

$$H_P(\mathbf{x}, \mathbf{p}) = \sum_{i=1}^{3N} \sum_{j=1}^{P} \left\{ \frac{[p_i^{(j)}]^2}{2m_i} + \frac{1}{2} m_i \omega_P^2 [x_i^{(j)} - x_i^{(j-1)}]^2 \right\} + \sum_{j=1}^{P} V(\mathbf{x}^{(j)}) \tag{10}$$

---

[3] Craig and Manolopoulos J.Chem.Phys. 121, 3368 (2004)

NQE in MD: from spectroscopy to reactivity

- QTB provides good NQE on spectra and phase transitions
- What about "chemical reactions" ?
- Tests on model systems: 1-D Morse and CH_4-like molecules fragmentation, H diffusion in 2D lattice

Rate constant:[4] $k(T) = \frac{1}{Q} Re \left\{ \mathrm{Tr} \left[e^{-\beta \hat{H}} \hat{F} \hat{P} \right] \right\} = \frac{1}{Q} \lim_{t \to \infty} C_{f,s}(t)$
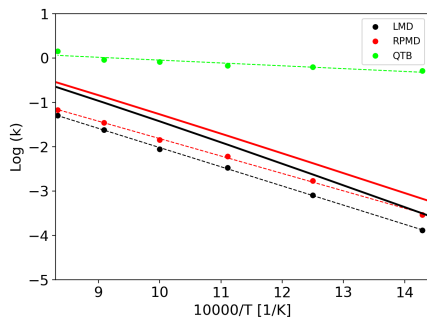

---

[4] Miller and co-workers J. Chem. Phys., 1974, 61, 1823; J. Chem. Phys., 1983, 79, 4889

1-D Morse reactive model
D_e = 10 kcal/mol; ZPE = 2 kcal/mol

The quantum rate constant can be obtained for 1-D Morse by using a discrete basis-set and results compared with simulations, in particular classical-quantum differences in the 800–1200 K range.
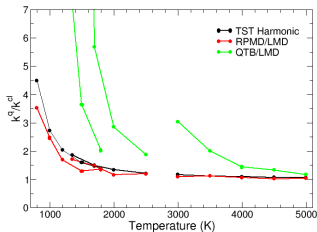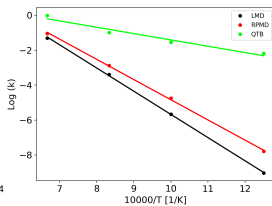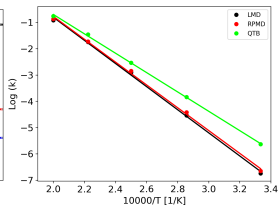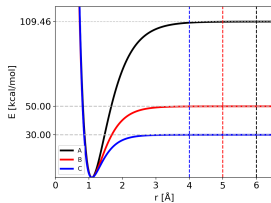

	E^a	ΔE
Classical	9.49	
Quantum (SoS)	8.74	0.75
LMD	8.6	
T-RPMD	7.8	0.8
QTB	1.3	7.3
H.A. – Classical	8.11	–
H.A. – Quantum	7.33	0.78

F.Angiolari, S.Huppert, RS - Phys. Chem. Chem. Phys. 24, 29357(2022).
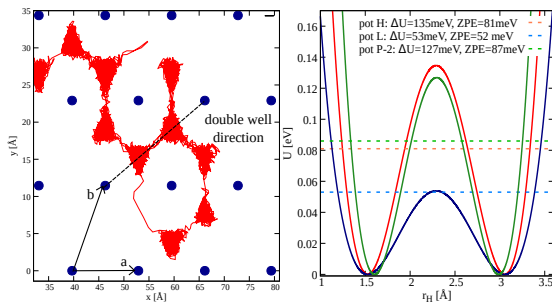
CH$_4$ and modified models
ΔZPE ∼ 10 kcal/mol

CH$_4$ → CH$_3$ + H

TST and RPMD are in agreement
RPMD can catch also relatively small
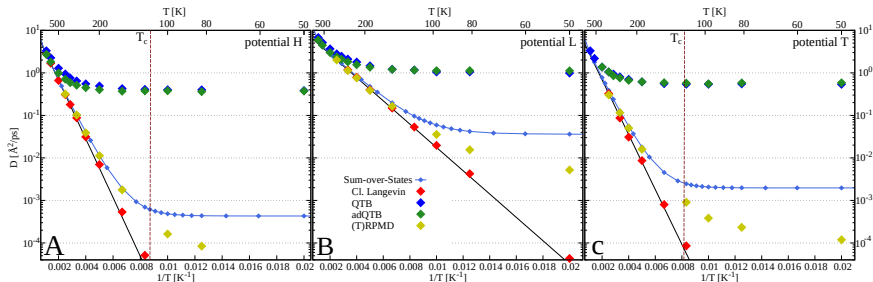effects and low temperatures are
quite high ..

H diffusion in 2D lattice

Quantum diffusion coefficient (see derivation in Avallone PhD thesis)

$$D(T) = \frac{1}{2}\tilde{C}_{vv}(\omega = 0) = \frac{1}{\eta}\sum_{n,k}\frac{e^{-\beta\mathcal{E}_{n,k}}}{\mathcal{Z}}\frac{1}{\hbar^2}\left(\frac{d\mathcal{E}_{nk}}{dk}\right)^2 \tag{11}$$

H diffusion in 2D lattice

- QTB overestimates D
- AdQTB does not improve the behavior
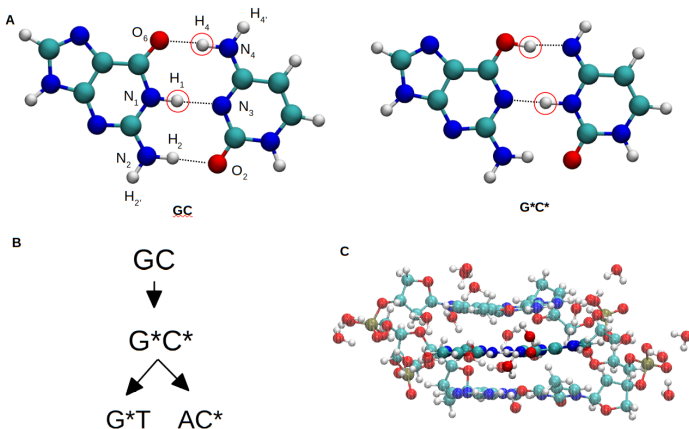- RPMD improves the classical picture and is similar to full quantum

N.Avallone, Ph.Depondt, F.Finocchi, RS, T.Plé and S.Huppert. In preparation.

Nuclear Quantum Effects in Chemical Reactivity: MARS code

Multiple trAjectory Reactive Simulations

- LMD and T-RPMD dynamics
- Dynamics in cartesian coordinates
- Analytical models (Morse, Proton Transfer), interface with DFTB+
- Interface with PLUMED for enhanced sampling (Umbrella Sampling, MetaDynamics) and Quantum Free Energy
- Parallelized on the beads
- Chemistry under Vibrational Strong Coupling (in progress)
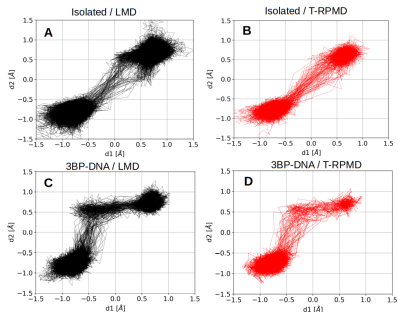- Fortran90 + OpenMP

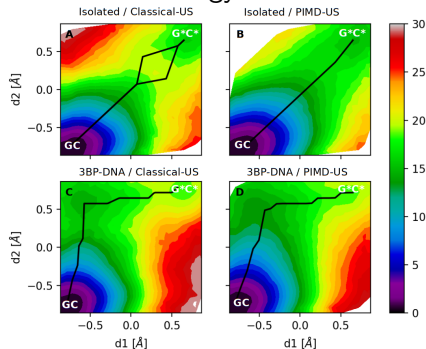# Double Proton Transfer in DNA base pair

RPMD with DFTB: Direct Dynamics and Umbrella Sampling

Double Proton Transfer in DNA base pair

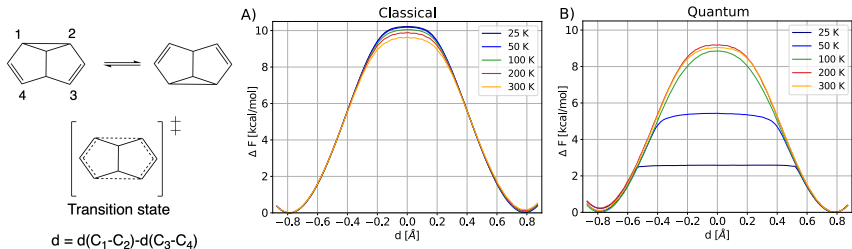Direct dynamics : G*C* → GC

Free energy surface

Free energy surfaces provide same pathways as reaction dynamics

F. Angiolari, S. Huppert, F. Pietrucci, RS. J. Phys. Chem. Lett. 14, 5102 (2023)

Heavy Atom Tunneling

Combining DFTB (3OB) with Umbrella Sampling: Classical (LMD) and Quantum (RPMD): Free Energies profiles from 300 to 25 K.

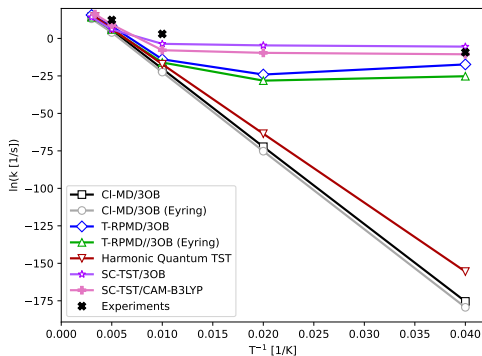$d = d(C_1\text{-}C_2) - d(C_3\text{-}C_4)$

- Classical: barrier almost temperature independent
- Quantum: for "high" temperatures the barrier is similar to the classical
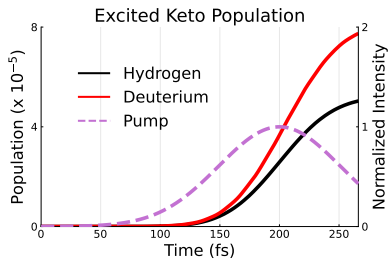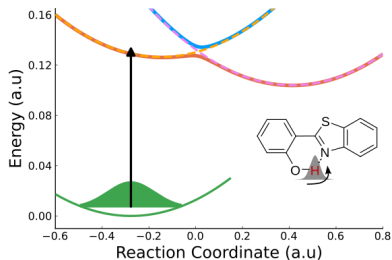- Quantum: for "low" temperatures the barrier drops down almost reaching a plateau

Heavy Atom Tunneling

Rate constant from dynamics: $k^{TST}(T)$ from free energy + recrossing factor $\kappa(T)$ from post-TS dynamics: $k(T) = \kappa(T)k^{TST}(T)$
Comparable with : semi-classical TST and experiments

F. Angiolari, G.Mandelli, S. Huppert, C.Aieta, RS. To be submitted

Excited state proton transfer → See Poster/Flash B.Le Dé

$$\boxed{\hat{H}(t) = \hat{H}^{elec} + \hat{H}^{vib} + \hat{H}^{phon} + \hat{H}^{phot} + \hat{H}^{drive}(t)} \qquad \hat{H}^{drive}(t) = \epsilon(t)\left(|e\rangle\langle e^*| + h.c.\right)\cos(\omega_{e^*}t)$$

$$\hat{H}^{elec} = \omega_e |e\rangle\langle e| + \omega_k |k\rangle\langle k| + \omega_{e^*} |e^*\rangle\langle e^*| + \omega_{k^*} |k^*\rangle\langle k^*| + \Delta\left(|e^*\rangle\langle k^*| + h.c.\right)$$

$$\hat{H}^{vib} = \left(|e^*\rangle\langle e^*| + |k^*\rangle\langle k^*|\right)\omega_{vib}\hat{a}^\dagger\hat{a} + \left[|e^*\rangle\langle e^*| g_{e^*} + |k^*\rangle\langle k^*| g_{k^*}\right]\left(\hat{a}^\dagger + \hat{a}\right)$$
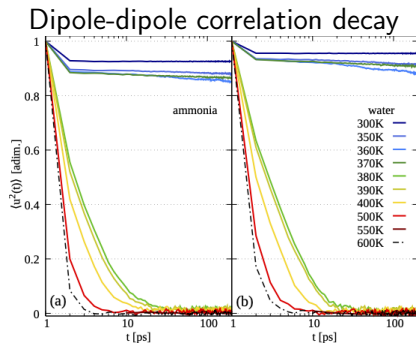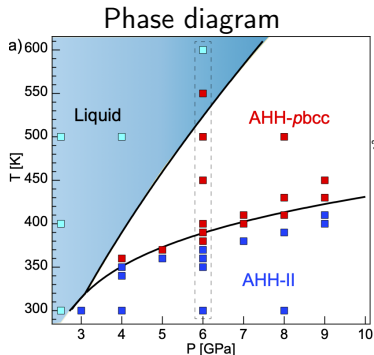
$$\hat{H}^{phon} = \sum_{k'} \omega_{k'}\left(\hat{c}_{k'}^\dagger\hat{c}_{k'}\right) + \left(\hat{a}^\dagger + \hat{a}\right)\sum_{k'} y_{k'}\left(\hat{c}_{k'}^\dagger + \hat{c}_{k'}\right)$$

$$\hat{H}^{phot} = \sum_{k} \omega_{k}\left(\hat{b}_{k}^\dagger\hat{b}_{k}\right) + (|e^*\rangle\langle e| + |k^*\rangle\langle k| + h.c)\sum_{k} g_{k}\left(\hat{b}_{k}^\dagger + \hat{b}_{k}\right)$$

B. Le Dé, S. Huppert, RS, A.Chin. In preparation

Ammonia HemiHydrate $H_2O:(NH_3)_2$ under high pressure

Orientational disorder drives site disorder in plastic AHH
INSP-IMPMC-LCT collaboration

Phase diagram

Dipole-dipole correlation decay

N.Avallone, S.Huppert, P.Depondt, L.Andriambariarijaona, F.Datchi, S.Ninet, T.Plé, R.Spezia, F.Finocchi.

Conclusions

- VENUS $\longrightarrow$ MARS: *Multiple trAjectory Reactive Simulations*
- Nuclear quantum effects with DFTB Hamiltonian (DFTB+ code) and rare events methods (metadynamics, umbrella sampling ...)
- MARS is coupled with DFTB+ and PLUMED and is parallel (OpenMP) on the beads
- RPMD provides good picture of chemical reaction kinetics
- Large systems and low temperatures can be studied
- Heavy atom tunneling: NQE in both thermodynamics AND dynamics

Perspectives

- MARS: Vibrational Strong Coupling (BoCavMD), Gaussian/ORCA/XTB, ML interface ...
- Semi-classical methods, NQEs with fixed vibrational states
- Excited State PT : MPS vs atomistic simulations (RPMD+SH)
- Investigating more chemical (organic) reactions at low-T (heavy atom tunneling?)

Acknowledgments

- F.Angiolari, T.Plé, J.Bowles, J.Richardi – LCT (SU)

- N.Avallone, B.Le Dé, S.Huppert, Ph.Depondt, A.Chin, F.Finocchi – INSP (SU)

- F.Pietrucci – IMPMC (SU)

- G.Mandelli, C.Aieta, M.Ceotto (U Milano)

Feynman's Club

1-D Morse reactive model

Canonical rate constant

$$k(T) = \frac{1}{Q} Re \left\{ Tr \left[e^{-\beta \hat{H}} \hat{F} \hat{P} \right] \right\} \tag{12}$$

where the flux and projection operators can be expressed in terms of the step function operator :

$$\hat{F} = \frac{i}{\hbar} [\hat{H}, \hat{h}(q - q^{\ddagger})] \tag{13}$$
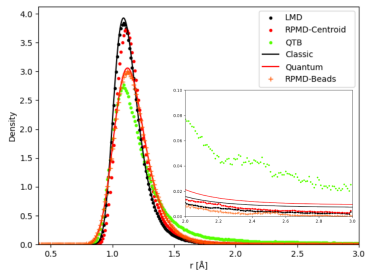
and following Miller and co-workers [5]

$$k(T) = \frac{1}{Q} \lim_{t \to \infty} C_{f,s}(t) \tag{14}$$

$$C_{f,s}(t) = Tr[\hat{\bar{F}} e^{i\frac{\hat{H} t_c^*}{\hbar}} \hat{h}(s) e^{-i\frac{\hat{H} t_c}{\hbar}}] \tag{15}$$
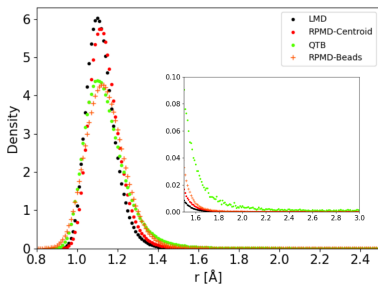
[5] J. Chem. Phys., 1974, 61, 1823; J. Chem. Phys., 1983, 79, 4889

Distance distributions

1-D Morse

Potential C (low barrier)

- QTB gives too broad distribution
- Beads distribution is very close to quantum distribution
- In reactivity the tails are VERY important
- Distance distribution $\longleftrightarrow$ energy fluctuations $\longleftrightarrow$ anharmonicity

Path Integral with Enhanced Sampling

If the barrier is too high for the temperature we are interested in, the direct dynamics cannot observe the processes.

Enhanced sampling methods were developed and they can be coupled with Path Integral based MD.
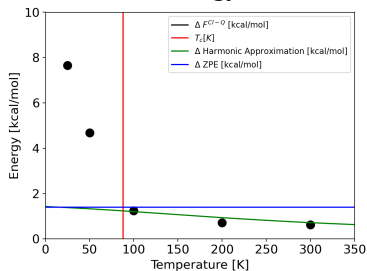
For example Umbrella Sampling:

$$U(s) = \frac{1}{2}k_{US}(s - s_0)^2 \tag{16}$$

$$s = CV(\mathbf{q}) \tag{17}$$

$$\mathbf{q} = \frac{1}{P}\sum_{i=1}^{P}\mathbf{q}_i \tag{18}$$

Heavy Atom Tunneling

Classical-Quantum energy barrier difference

A transition corresponding to the crossover temperature:

$$T_c = \frac{\hbar \Omega}{2 \pi k_B} \tag{19}$$

For $T > T_c$ it follows the Harmonic approximation (ZPE effect)

For $T < T_c$ it increases much more than expected (tunneling)

Heavy Atom Tunneling

Rate constant: dynamics vs semi-classical TST vs experiments

- RPMD-TST

$$k^{TST}(T) = \frac{1}{2}\langle|v_s|\rangle \frac{e^{-F(0)/k_b T}}{\int_{-\infty}^{0} e^{-F(s)/k_b T} ds} \qquad (20)$$

- SC-TST (Aieta et al. J. Phys. Chem. A 120, 4853 (2016); J. Chem. Theory Comput. 14, 2142 (2019))

$$\begin{aligned}
k(T) &= \frac{1}{2\pi\hbar Q^r(T)} \int N(E) e^{-\beta E} dE \qquad (21) \\
&= \frac{1}{h} \frac{Q_{tra}^{\ddagger}(T) Q_{rot}^{\ddagger}(T)}{Q_{tra}^r(T) Q_{rot}^r(T)} \frac{\int N_{SC}(E) e^{-\beta E} dE}{Q_{vib}^r(T)} \qquad (22)
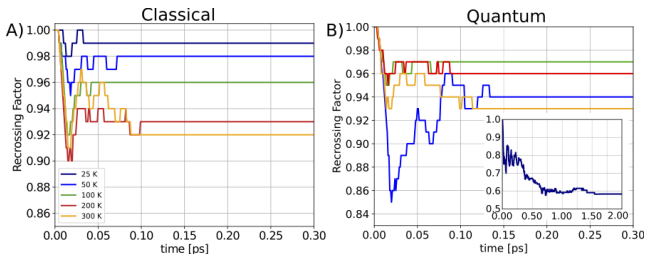\end{aligned}$$

- Experiments: Sander and co-workers (Chem. Eur. J. 2020, 26, 10452)

Heavy Atom Tunneling

Dynamics to estimate the recrossing factor (Suleimanov, J Phys Chem C 2012, 116, 11141.)

$$k(T) = \kappa k^{TST}(T) \tag{23}$$

$$\kappa(t) = \frac{\langle \delta(s_0)\dot{s}_0 h(s_t)\rangle}{\langle \delta(s_0)\dot{s}_0 h(\dot{s}_0)\rangle} \tag{24}$$

- Classical : as T decreases, $\kappa \to 1$
- Quantum : at lower T, κ strongly decreases