Theory of Photoinduced Excited State Proton Transfer

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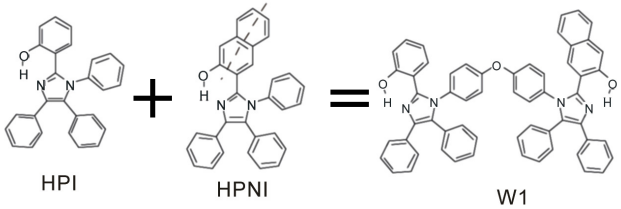
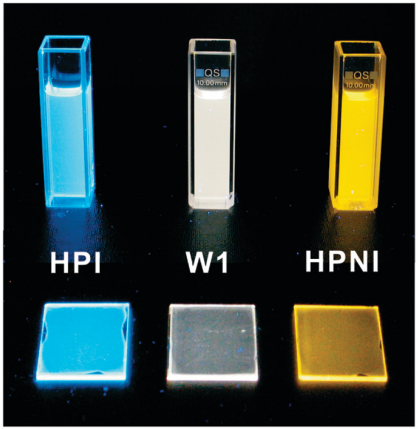
VISTA seminar 04/08/2026

Excited-state Intramolecular Proton Transfer (ESIPT) applications

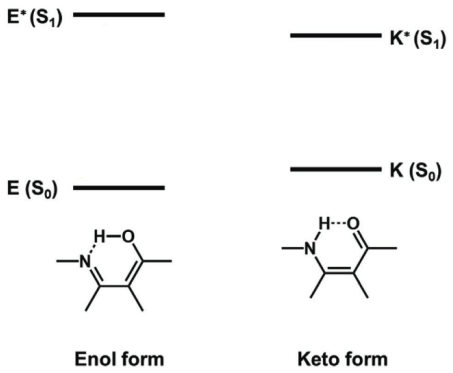
- Used for drug delivery, fluorescent probes, white organic light-emitting devices (OLEDs)





S. Park, J. E. Kwon et al. *JACS* 131 (39), 14043-14049 (2009)

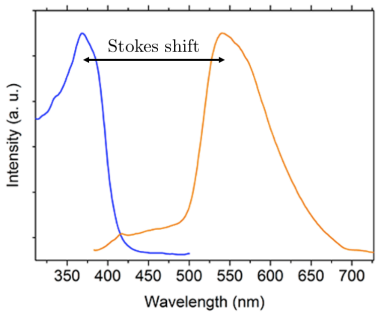
Excited-state Intramolecular Proton Transfer (ESIPT)

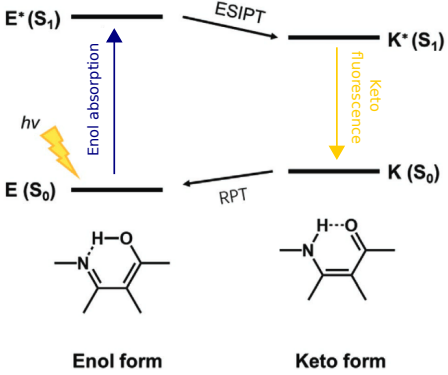


Chen L. P.Y Lan et al., *Adv. Optical Mater.* 9, 2001952 (2021)

F. Borbone, A. Tuzi et al. *Crys. Growth Des.* 17, 5517-5523 (2017)

Excited-state Intramolecular Proton Transfer (ESIPT)





Chen L. et al., *Adv. Optical Mater.* 2001952 (2021)

F. Borbone, A. Tuzi et al. *Crys. Growth Des.* 17, 10, 5517-5523 (2017)

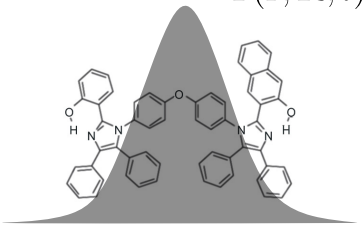
ESIPT challenges

- Ultrafast (tens of fs): out-of-equilibrium vibronic states, possible quantum effects

  $\rightarrow$ The proton has to be described on a quantum level

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t) = \hat{H}(\mathbf{r},\mathbf{R},t)\Psi(\mathbf{r},\mathbf{R},t)$$

$$\Psi(\mathbf{r},\mathbf{R},t)$$



ESIPT challenges

- Ultrafast (tens of fs): out-of-equilibrium vibronic states, possible quantum effects

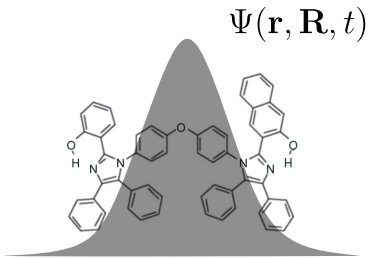
  $\rightarrow$ The proton has to be described on a quantum level

- Need to excite the system for ESIPT to occur

  $\rightarrow$ The rest of the molecule is out-of-equilibrium

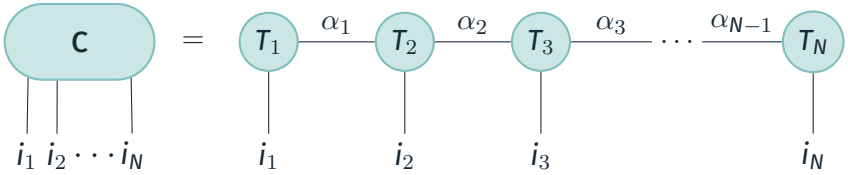
- Quantum effects become a numerical challenge for big systems : curse of dimensionality

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t) = \hat{H}(\mathbf{r},\mathbf{R},t)\Psi(\mathbf{r},\mathbf{R},t)$$



Matrix Product State (MPS)

- The wavefunction can be written as : $|\psi\rangle = \sum_{\{i\}} C_{i_1\ i_2 \ldots i_N} |\phi_{i_1} \ldots \phi_{i_N}\rangle$
- The high-dimensional tensor $C_{i_1\ i_2 \ldots i_N}$ can be separated into smaller tensors to rewrite $|\psi\rangle$.



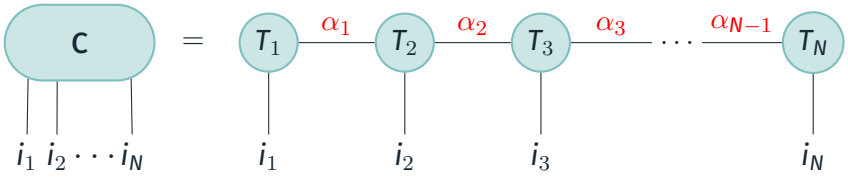
elements $\simeq d^N$

$\forall i\,,\ \alpha_i \leq D_{\text{max}}$

elements $\leqslant NdD_{\text{max}}^2$

Matrix Product State (MPS)

$\Rightarrow$ **MPS can efficiently capture and reduce the dimension of chain-like systems !**



elements $\simeq d^N$

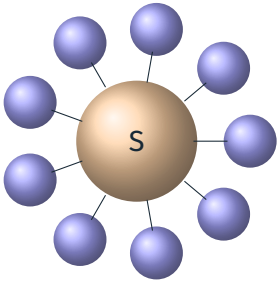
$\forall i\,,\ \alpha_i \leq D_{\max}$

elements $\leqslant NdD_{\max}^2$

SVD on α

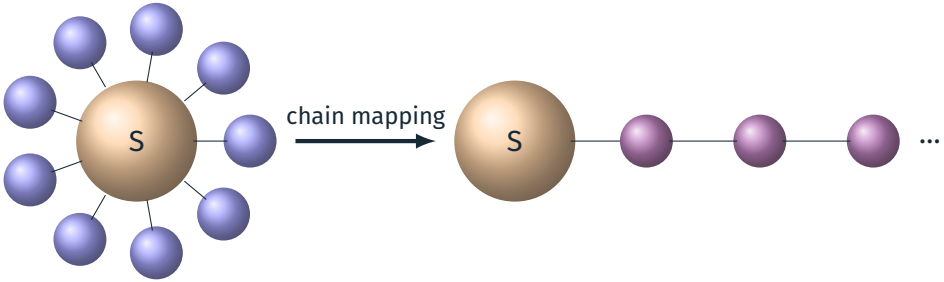
An environment ...

Pictorial representation of an Hamiltonian :



The system is surrounded by different modes
Not efficient description for MPS

An environment mapped into a chain (TEDOPA)



The linear bath becomes a mix of the initial environment.

It can be seen as a change of basis : Unitary Tranformation.

Now suitable for MPS.

TEDOPA = Time Evolving Density operator with Orthonormal Polynomials Algorithm

J. Prior, A.W. Chin, S.F. Huelga, M.P. Plenio *Phys. Rev. Lett.* 105, 05040 (2010)
M.P. Woods, R. Groux, A.W. Chin, S.F. Huelga, M.B. Plenio *J. Math. Phys.* 55, 032101 (2014)

MPSDynamics.jl

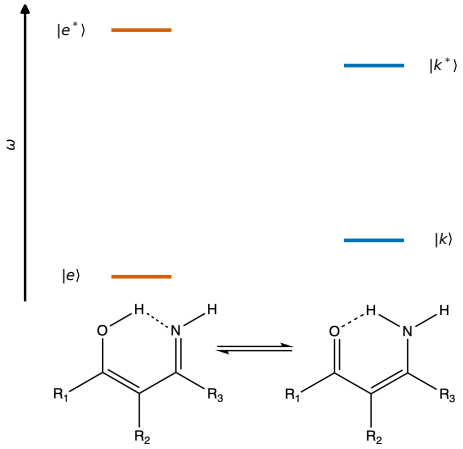
- Julia package developed in Chin's group
- Open access, GitHub webpage
- `https://github.com/shareloqs/MPSDynamics.jl`
- Examples, theoretical background, documentation

T. Lacroix, BLD, A. Riva, A.J. Dunnett, A.W. Chin *J. Chem. Phys.* **161**,084116 (2024)

BLD, A. Jaouadi, E. Mangaud, A.W. Chin, M. Desouter-Lecomte *J. Chem. Phys.* 160, 244102 (2024)

Y. Wang, A. Benny, BLD, A.W. Chin, G.D. Scholes *PNAS*, 122 (9) e2416542122 (2025)

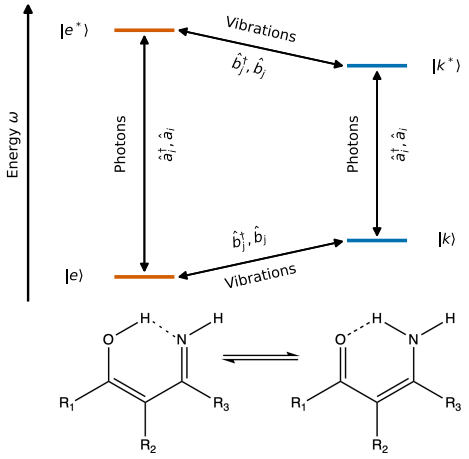
ESIPT Four-level



$$\hat{H} = \hat{H}_S$$

$$\hat{H}_S = \omega_e |e\rangle\langle e| + \omega_{e^*} |e^*\rangle\langle e^*| + \omega_k |k\rangle\langle k| + \omega_{k^*} |k^*\rangle\langle k^*|$$

ESIPT Four-level open-system description



$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{SB}$$

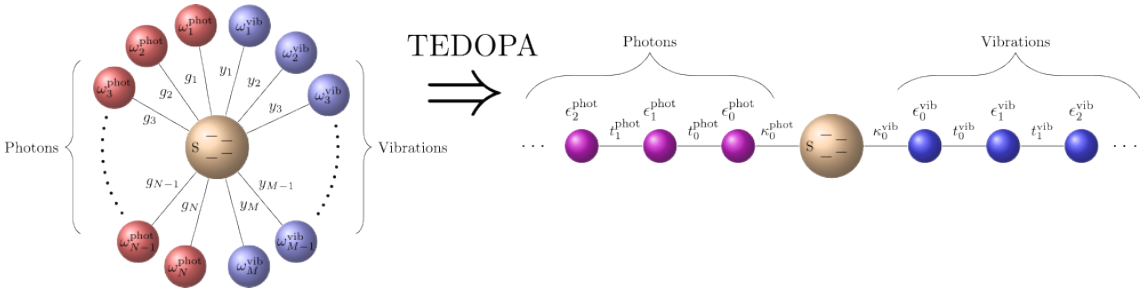
$$\hat{H}_S = \omega_e |e\rangle\langle e| + \omega_{e^*} |e^*\rangle\langle e^*| + \omega_k |k\rangle\langle k| + \omega_{k^*} |k^*\rangle\langle k^*|$$

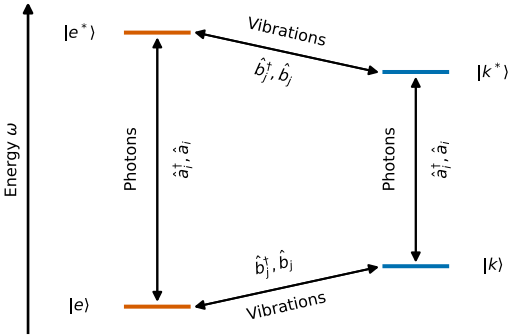
$$\hat{H}_B = \overbrace{\sum_i \omega_i^{\text{phot}} \left(\hat{a}_i^\dagger \hat{a}_i\right)}^{\text{Photons}} + \overbrace{\sum_j \omega_j^{\text{vib}} \left(\hat{b}_j^\dagger \hat{b}_j\right)}^{\text{Vibrations}}$$

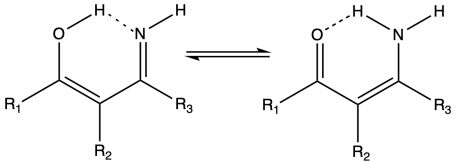
$$\hat{H}_{SB} = \left(|e^*\rangle\langle e| + |k^*\rangle\langle k| + \text{h.c.}\right) \sum_i g_i \left(\hat{a}_i^\dagger + \hat{a}_i\right) + \left(|e^*\rangle\langle k^*| + \text{h.c.}\right) \sum_j y_j \left(\hat{b}_j^\dagger + \hat{b}_j\right)$$

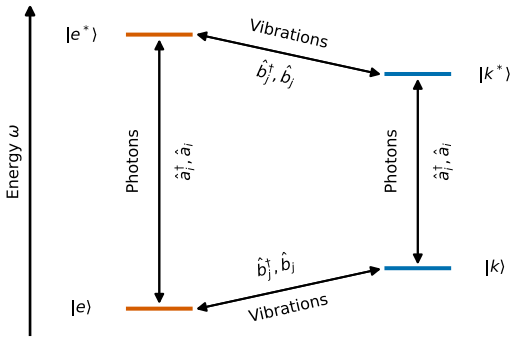
$$J^{\text{phot}}(\omega) = \sum_i^N g_i^2 \delta(\omega_i^{\text{phot}} - \omega) \quad , \quad J^{\text{vib}}(\omega) = \sum_i^M y_i^2 \delta(\omega_i^{\text{vib}} - \omega)$$

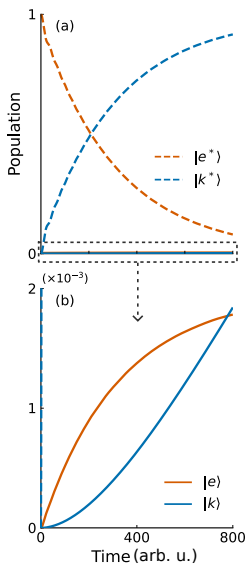
ESIPT Four-level open-system description

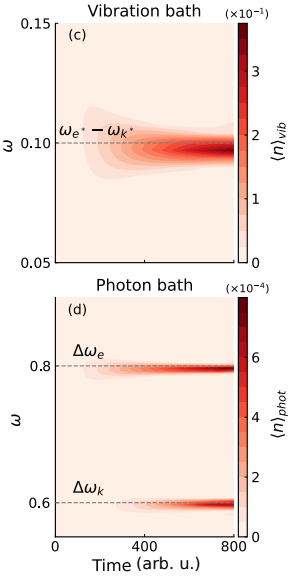



Energy ω
|e*⟩
Vibrations
$\hat{b}_j^\dagger, \hat{b}_j$
|k*⟩
Photons
$\hat{a}_i^\dagger, \hat{a}_i$
Photons
$\hat{a}_i^\dagger, \hat{a}_i$
$\hat{b}_j^\dagger, \hat{b}_j$
|k⟩
|e⟩
Vibrations


H
O
N
H
R1
R3
R2
H
O
N
H
R1
R3
R2



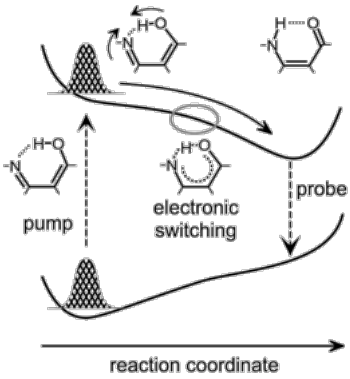




BLD, S. Huppert, R. Spezia, A.W. Chin , *J. Chem. Theory Comput*,20, 20, 8749–8766 (2024)

Towards a continuous description

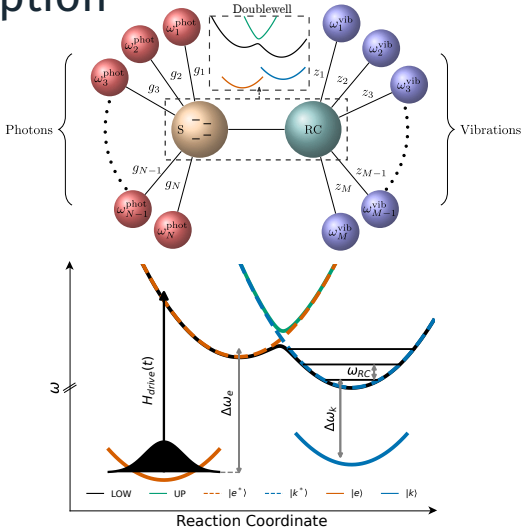
- The proton transfer can have a description in space $\rightarrow$ reaction coordinate



S. Lochbrunner, A. J. Wurzer and E. Riedle, *J. Phys. Chem. A*, Vol. 107, No. 49 (2003)

Towards a continuous description

- The proton transfer can have a description in space $\rightarrow$ reaction coordinate
- Insert additional dimension into the system



Towards a continuous description

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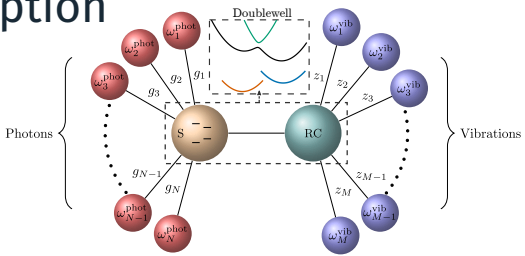
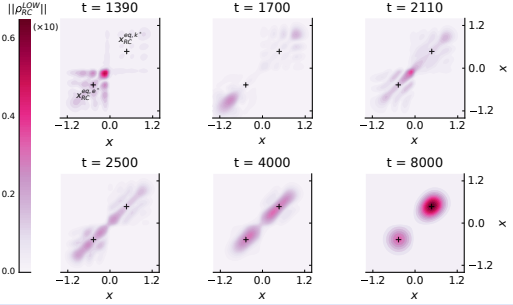
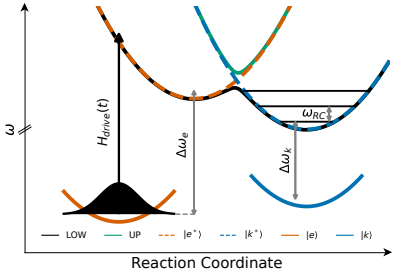






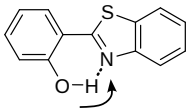
Case study : HBT and HBQ

S. Lochbrunner et al. *J. Chem. Phys.*, 112, 10699 (2000)
S. Pijeau et al. *J. Phys. Chem. A* , 121, 4595 (2017)
D. Picconi *Photochem. Photobiol. Sci.* 20, 1455 (2021)

- Ultrafast proton transfer
- Small molecule, ideal to compare experimental and numerical results
- Different kinetic isotope effect (KIE) : mass and frequency $\neq$
  $\rightarrow$ interaction with vibrations $\neq$
- Deuterium less damped

HBT/DBT : no KIE

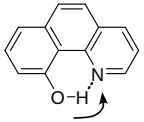
$\tau_{\mathrm{H}} = \tau_{\mathrm{D}} = 62$ fs



HBT : 2-(2 hydroxyphenyl)benzothiazole

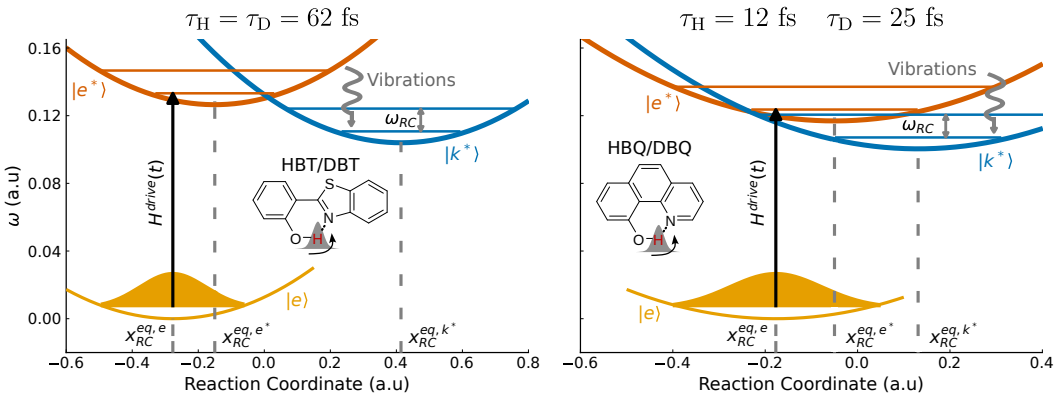
HBQ/DBQ: KIE

$\tau_{\mathrm{H}} = 12$ fs $\quad \tau_{\mathrm{D}} = 25$ fs



HBQ : 10-hydroxybenzo[*h*]quinoline

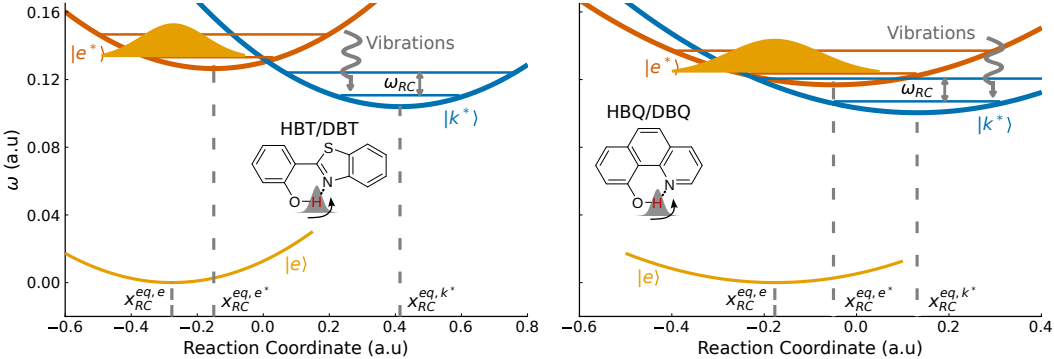
Study of kinetic isotope effect



Previous study with Redfield approach. 800 vibrations for the damping in MPS

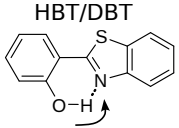
⋆ L. Zhang, F. Fassioli, B. Fu, Z. She, G. D. Scholes, *ACS Phys. Chem Au* 3, 107-118 (2023)

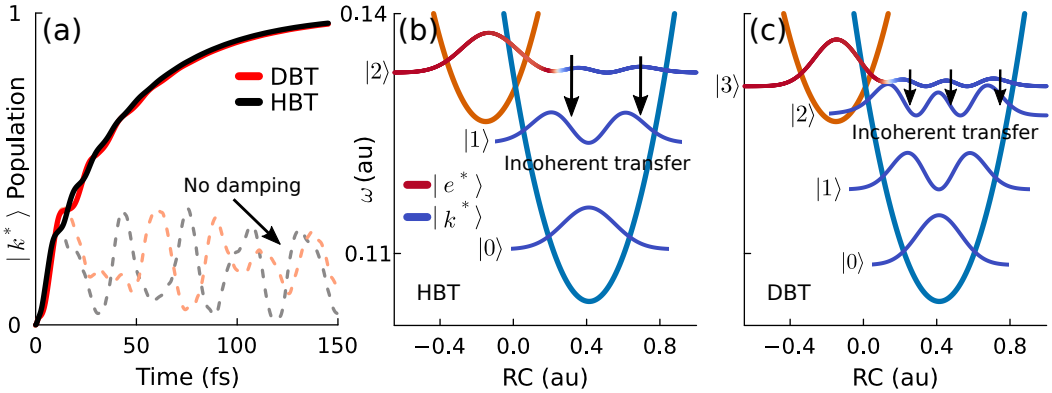
Franck-Condon dynamics : delta pulse



Franck-Condon dynamics

HBT/DBT

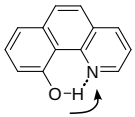




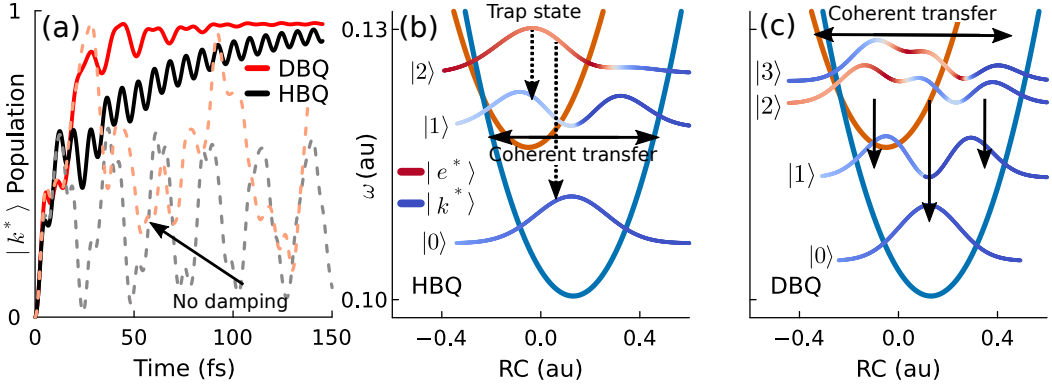
- Balance between damping strength and state overlaps

BLD, S. Huppert, R. Spezia, A.W. Chin *J. Phys. Chem. Lett.* 16, 2514–2521 (2025)

HBQ/DBQ



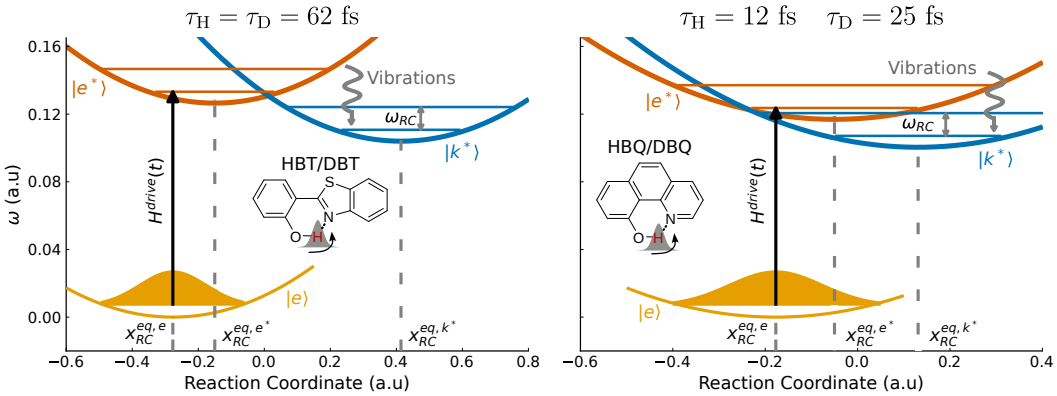
Franck-Condon dynamics



- Enol/Keto combination leads to a coherent and fast transfer

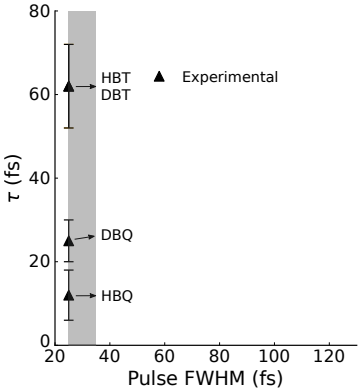
BLD, S. Huppert, R. Spezia, A.W. Chin *J. Phys. Chem. Lett.* 16, 2514–2521 (2025)

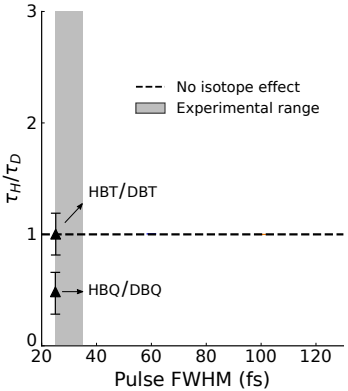
Effect of the pulse



Effect of the pulse

FWHM $= 0$ fs
Delta pulse
Franck-Condon dynamics





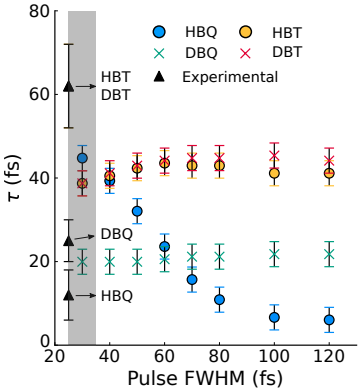
Experimental : J. Lee, C.H. Kim, T. Joo *J. Phys. Chem A* 117, 1400-14005 (2013)

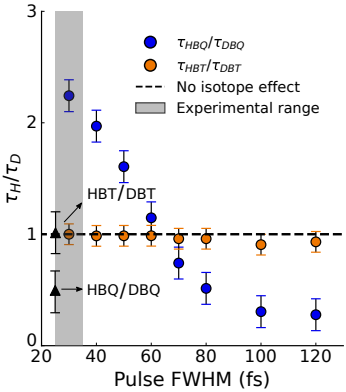
Effect of the pulse

- HBT/DBT/DBQ stay similar, no matter the pulse
- HBQ/DBQ isotope flip effect with FWHM

⇒ Trap state of HBQ is less populated with longer pulses

⇒ Initial conditions are important





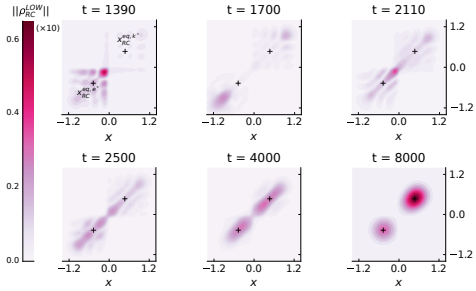
Experimental : J. Lee, C.H. Kim, T. Joo *J. Phys. Chem A* 117, 1400-14005 (2013)
BLD, S. Huppert, R. Spezia, A.W. Chin *J. Phys. Chem. Lett.* 16, 2514–2521 (2025)

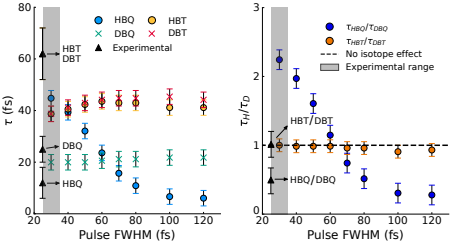
Conclusions

- Ultrafast ESIPT has been studied with MPS
- Continuous variable in the system to study high-dimensional exact quantum dynamics
- Isotope effect of HBT and HBQ analyzed

→ Initial conditions (pulse duration) are important

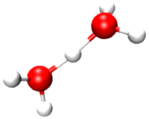
- MPS powerful but results are model dependent

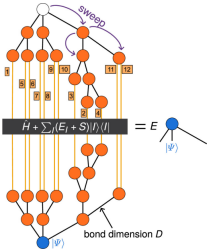




Acknowledgments

- Alex Chin, Riccardo Spezia and Simon Huppert
- Thibaut Lacroix, Angela Riva, Angus Dunnett
- Michèle Desouter-Lecomte
- Yuanheng Wang, Alfy Benny, Gregory D. Scholes
- Henrik Larsson





Thank you for your attention