Quantum dynamics with wave packet approaches: applications to the Infrared spectroscopy of protonated molecules

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Grenoble, Mars 2025

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(2) Theoretical Chemistry, University of Heidelberg

Molecular Quantum dynamics

Molecular Quantum Dynamics, Springer, 2014, Ed. F. Gatti

Quantum Physics: applications in chemistry,
Lectures Notes in Chemistry, F. Gatti, B. Lasorne, H.-D. Meyer and A. Nauts,
Springer, 2017.

Full quantum mechanical time-dependent treatment

Quantization of eigenstates, Quantum Resonances
Non-Born-Oppenheimer processes
Tunneling
Quantum phase transition
Quantum Coherence (laser pulses)

Molecular Quantum dynamics

$$\hat{H}(R,t)\Psi(R,t) \quad = \quad (\hat{T}(R)+\hat{V}(R))\Psi(R,t) = i\frac{\partial\Psi(R,t)}{\partial t}$$

A method to solve the Schrödinger equation for the nuclei: in quantum dynamics, **very strong correlation**: very large primitive (or mathematical) basis set. We are very limited in the size of the systems

Necessity to have, first, the ab initio data, for instance the potential energy surfaces **in a form adapted to the methods used in Quantum Dynamics**

Choice of the set of coordinates (motions of large amplitude) and the Kinetic Energy Operator: **the polyspherical coordinates** (F. Gatti and C. Iung Phys. Rep. (2009)), TANA Package (M. Dong, L. Joubert Doriol, H.-D. Meyer, A. Nauts F. Gatti , D. Lauvergnat JCP (2013)).

Quantum dynamics

The Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) package

http://www.pci.uni-heidelberg.de/cms/mctdh.html

H.-D. Meyer, U. Manthe, and L.S. Cederbaum, Chem.Phys.Lett. **165** (1990), 73.

Multidimensional Quantum Dynamics : MCTDH Theory and Applications Wiley-VCH Edited by H.-D. Meyer, F. Gatti and G. Worth.

Quantum dynamics

The MultiConfiguration Time Dependent Hartree (MCTDH) algorithm is a computational method to propagate wave packets. The MCTDH wavefunction *ansatz* writes

$$\begin{aligned}
\Psi(q_1,\ldots,q_f,t) \quad &\equiv \Psi(Q_1,\ldots,Q_p,t), \\
&= \sum_{m_1}^{n_1} \cdots \sum_{m_p}^{n_p} A_{m_1,\ldots,m_p}(t) \prod_{\kappa=1}^{p} \varphi_{m_\kappa}^{(\kappa)}(Q_\kappa,t), \\
&= \sum_{M} A_M \Phi_M, \qquad (1)
\end{aligned}$$

$$\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t) = \sum_{l_1=1}^{N_{1,\kappa}} \cdots \sum_{l_d=1}^{N_{d,\kappa}} c_{j_\kappa l_1 \cdots l_d}^{(\kappa)}(t)\, \chi_{l_1}^{(\kappa)}(q_{1,\kappa}) \cdots \chi_{l_d}^{(\kappa)}(q_{d,\kappa}) \qquad (2)$$

$$i\dot{A}_M = \sum_{L} \langle \Phi_M | H | \Phi_L \rangle A_L, \qquad (3)$$

$$i\dot{\varphi}^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \left(\rho^{(\kappa)}\right)^{-1} \langle H \rangle^{(\kappa)} \varphi^{(\kappa)}. \qquad (4)$$

Multi-Layer MCTDH (H. Wang and M. Thoss)

$$
\begin{aligned}
\Psi(q_1, q_2, q_3, t) &= \sum_{j_1=1}^{n_1}\sum_{j_2=1}^{n_2}\sum_{j_3=1}^{n_3} A_{j_1,j_2,j_3}(t)\varphi_{j_1}^{(1)}(q_1,t)\varphi_{j_2}^{(2)}(q_2,t)\varphi_{j_3}^{(3)}(q_3,t) \\
\varphi_{j_1}^{(1)}(q_1,t) &= \sum_{i_1=1}^{N_1} c_{i_1}^{(1,j_1)}(t)\chi_{i_1}^{(1)}(q_1) \\
\Psi(q_1, q_2, q_3, t) &= \sum_{j_{12}=1}^{n_{12}}\sum_{j_3=1}^{n_3} A_{j_{12},j_3}(t)\varphi_{j_{12}}^{(12)}(q_1,q_2,t)\varphi_{j_3}^{(3)}(q_3,t) \\
\varphi_{j_{12}}^{(12)}(q_1,q_2,t) &= \sum_{k_1=1}^{n_1}\sum_{k_2=1}^{n_2} B_{k_1,k_2}^{(12,j_{12})}(t)\xi_{k_1}^{(1)}(q_1,t)\xi_{k_2}^{(2)}(q_2,t)
\end{aligned}
$$

Up to thousands of degrees of freedom !

Necessity to have the potentials in the right form

Fast strong quantum effects

Calculate the Potential and express it in an adequate form

Sum of products of one-particle operators

$$V(q_{i_1}^{(1)}, \ldots, q_{i_p}^{(p)}) = \sum_{j_1=1}^{m_1} \cdots \sum_{j_p=1}^{m_p} C_{j_1 \ldots j_p} v_{j_1}^{(1)}(q_{i_1}^{(1)}) \cdots v_{j_p}^{(p)}(q_{i_p}^{(p)}) \tag{5}$$

The potential is in MCTDH form only when dealing with model problems

Monte Carlo Canonical Polyadic Decomposition (MCCPD): Markus Schröder JCP 2020

Neural Network-Potential Energy Surface S. Wille; A. Kandratsenka et al., Phys. Chem. Chem. Phys. 22, 26113 (2020)

Kinetic Energy Operator

Polyspherical coordinates: X. Chapuisat and C. Iung Phys. Rev. A 1992.

Separation into subsystems: G. Brocks, A. van der Avoird, B. Sutcliffe, J. Tennyson, Mol. Phys. (1983).

The polyspherical approach

F. Gatti and C. Iung Phys. Rep. (2009).

TANA Package

M. Dong, L. Joubert Doriol, H.-D. Meyer, A. Nauts F. Gatti , D. Lauvergnat 181 JCP 139 (2013) 204107.

General strategy

Dynamics with MCTDH or ML-MCTDH (Heidelberg package). Allows one to treat a large number of degrees of freedom.

Potential energy surfaces (Kandratsenka, Bowman, Marx, Zhang).

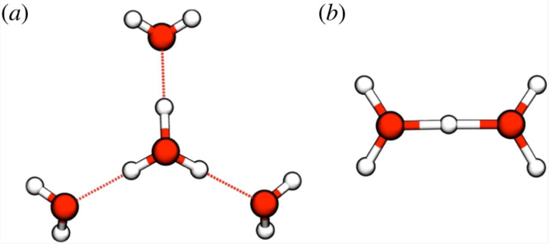
Re-expression with MCCPD (Monte Carlo Canonical Polyadic Decomposition, Markus Schröder): sum of products.

Curvilinear coordinates: KEO in polyspherical coordinates.

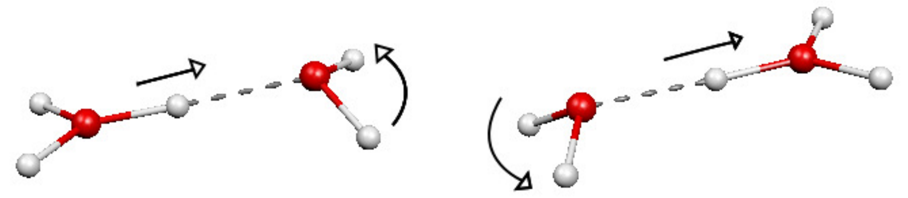
Outline

$(H_2O)_3H_3O^+$

Zundel and Eigen cations: the two “idealized” forms of an excess proton in liquid water. Essential to describe the diffusion of protons in water (Grotthuss mechanism).

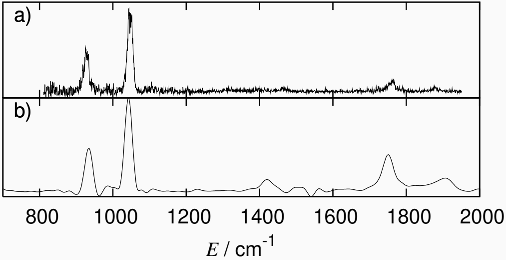


Zundel cation



Strong coupling (Fermi resonance) between the proton-transfer motion and the wagging (or pyramidalization) bending mode of vibration. Description in terms of curvilinear (involving angles) coordinates.

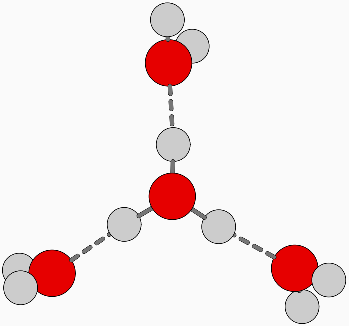
Zundel cation



O. Vendrell, F. Gatti, and H.-D. Meyer, Angewandte Chemie Int. Ed (VIP) 46 (2007) 6918. "Dynamics and Infrared Spectroscopy of the Protonated Water Dimer."

S. S. Xantheas, Nature 457 (2009) 673.

Eigen cation $H_9O_4^+$ (Markus Schröder)



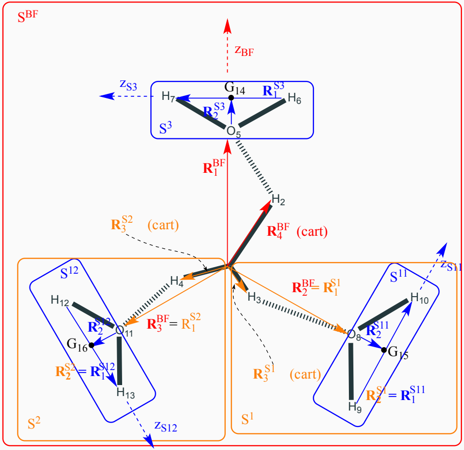
Three water molecules around a central hydronium

33-D, highly correlated and very floppy molecule

Global description of the potential and dipoles are available[1]

[1] PES by Yu et al., J. Phys. Chem. A 123, 1399 (2019)

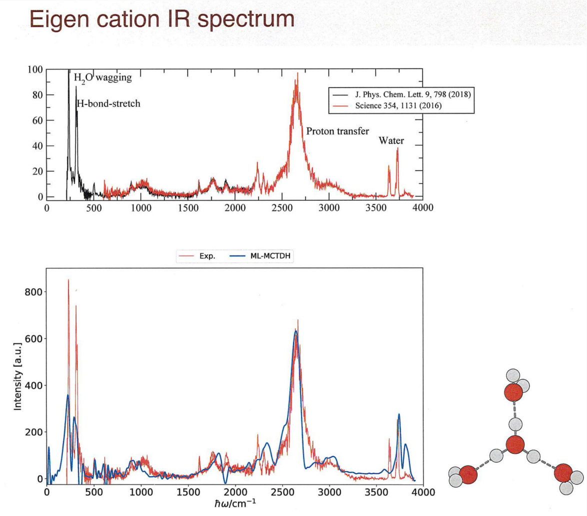
Eigen cation $H_9O_4^+$



33 Internal coordinates:

- 3 times Water internal (9)
- 3 times wagging of Water (3)
- 3 times rocking of Water (3)
- 3 times O-O distance (3)
- 3 times Water rotation around O-O (3)
- Cartesian coordinates for inner H's (9)
- 2 Angles between O-O vectors (2)
- 1 Umbrella (1)

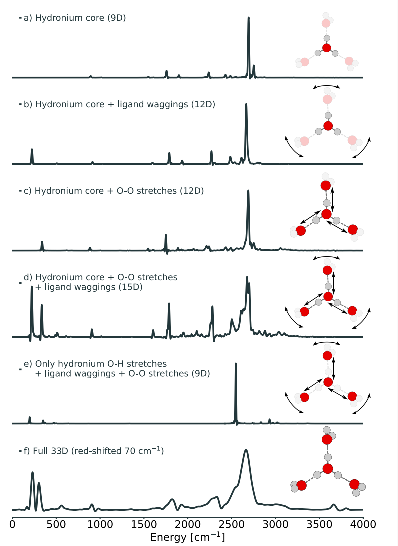
Eigen cation



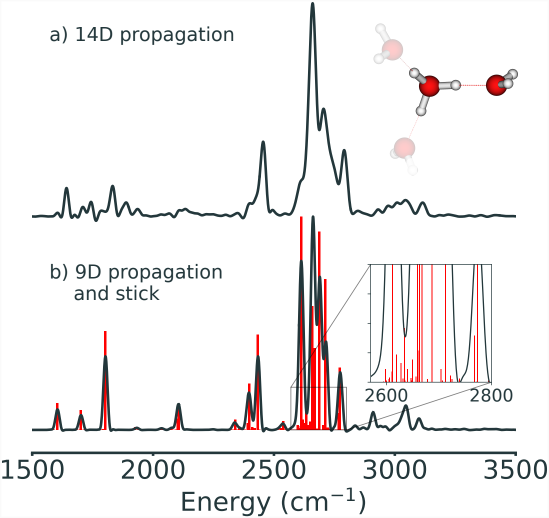
Eigen cation IR spectrum

M Schröder, F Gatti, D Lauvergnat, HD Meyer, O Vendrel "The coupling of the hydrated proton to its first solvation shell" Nat. Comm. 13 (2022) 6170.

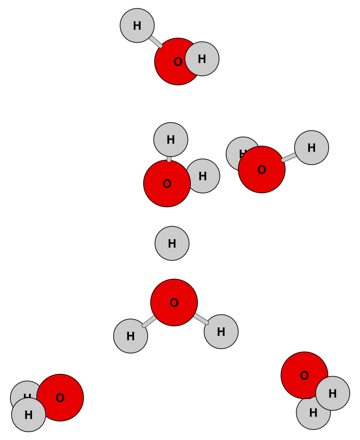
Eigen cation



Eigen cation



Extended Zundel Cation (David Mendive Tapia) (51D)



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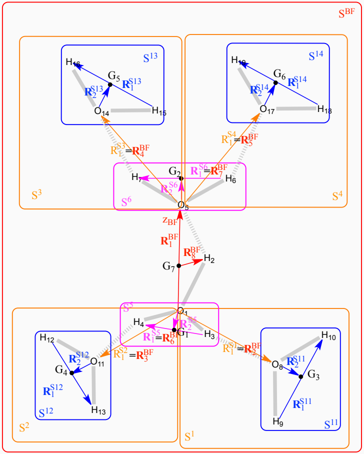

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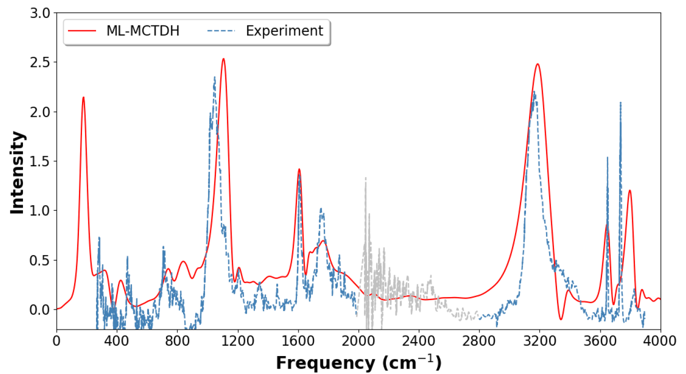
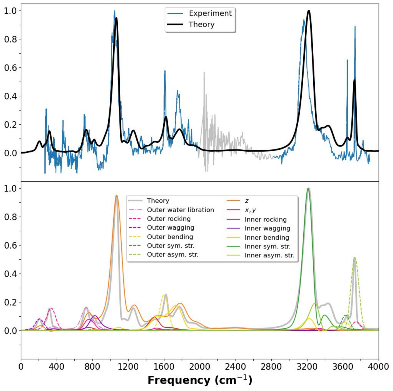


Exp: Nadja Heine, Matias R. Fagiani, Mariana Rossi, Torsten Wende, Giel Berden, Volker Blum, and Knut R. Asmis, JACS, 2013, 135, 8266–8273.

PES from D. Marx.

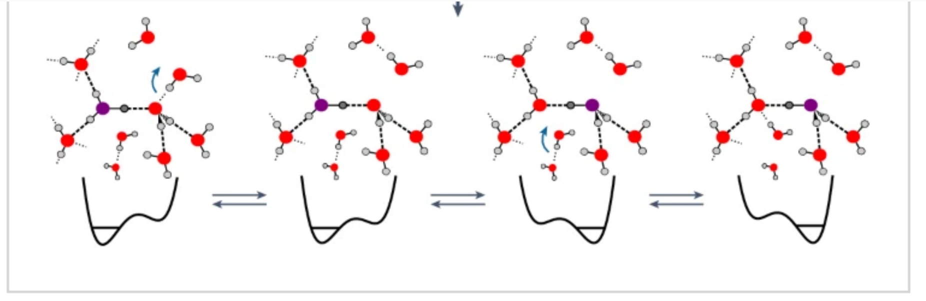
Extended Zundel Cation (David Mendive Tapia) (51D)



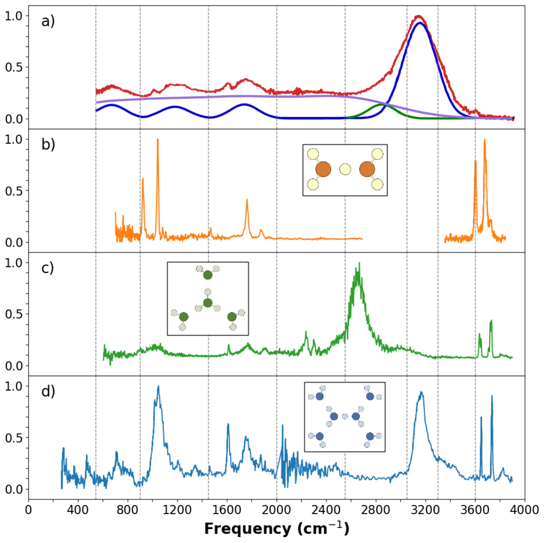
Top: calculated (black) and experimental (blue) absorption spectrum of the protonated water hexamer, i.e. $H^+(H_2O)_6$.

Bottom: characterization of the most relevant peaks.

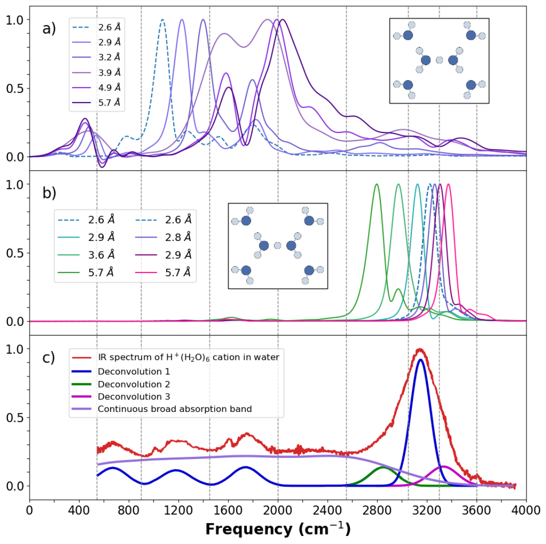
Extended Zundel Cation (David Mendive Tapia) (51D)



Proton Transfer: A Gomez, WH Thompson, D Laage Nature Chemistry 16 (2014), 1838-1844.



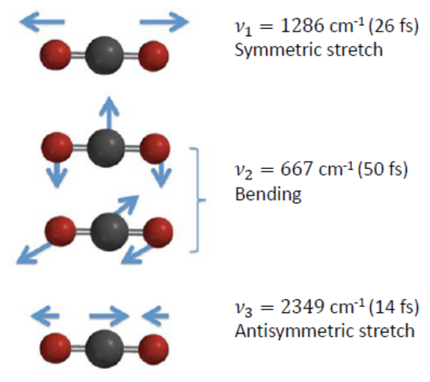
Experimental IR spectra a) $H^+_{(aq)}$ in a water solution of perchloric acid (red), b) Zundel ($H_5O_2^+$), c) Eigen ($H_9O_4^+$) and d) protonated water hexamer ($H_{13}O_6^+$).



Spectroscopic signals associated with the excitation of the shared-proton modes in $H^+(H_2O)_6$ for the (a) central proton and (b) outer-protons when detaching one second shell solvation molecule.

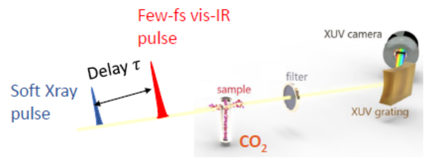
Bulk water: a water hexamer surrounded by a vast fluctuating network of water molecules yielding to the so-called continuous absorption band and the chameleonic spectroscopic character of the hydrated proton that cannot always be idealized as the pure Eigen nor Zundel prototypes.

Attospectroscopy of coherent vibration of CO_2



Collaboration with Lou Barreau (Orsay) and John Stanton

Attospectroscopy of coherent vibration of CO_2

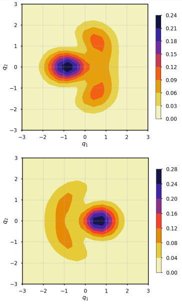


Pump/Probe experiment: Lou Barreau (Orsay).
Pump: duration around 15 fs, frequency : 1.5498 ev.
Creation of a wavepacket that is a superposition of the vibrational ground state and of FRL and FRH at 1208 cm^{-1} and 1378.6 cm^{-1}.
States coming from a Fermi resonance that are Raman active.

Three periods at 26.3, 24.2 and 300 fs.

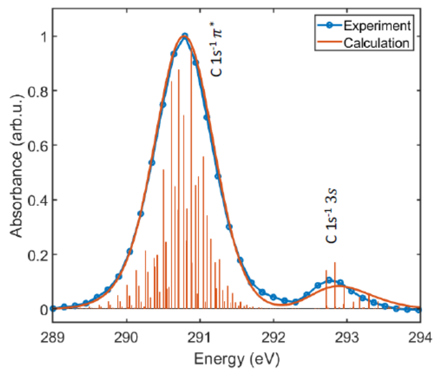
Probe: XUV Attosecond pulses around 290 eV.

Attospectroscopy of coherent vibration of CO_2



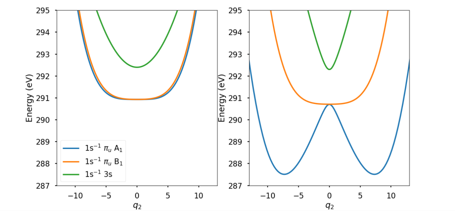
a) Density of the nuclear wavefunction in the lower state of the Fermi resonance $|\psi_l|^2$ as a function of the bending q_2 and symmetric stretching q_1 normal coordinates. **b)** Same as a for the upper state $|\psi_u|^2$.

Attospectroscopy of coherent vibration of CO_2



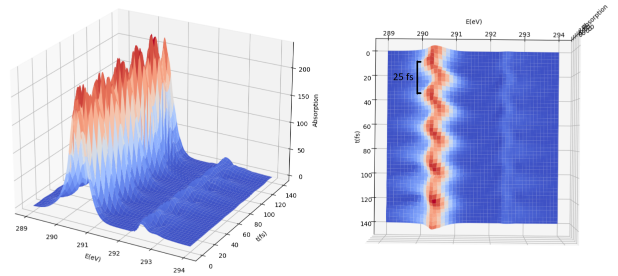
Probe spectrum

Attospectroscopy of coherent vibration of CO_2



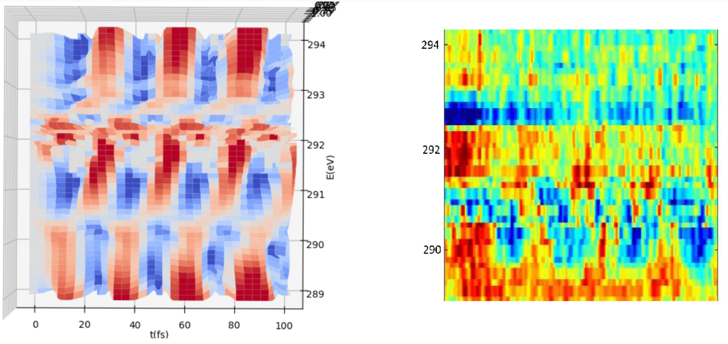
Adiabatic curves including the 3s state: pseudo-Jahn Teller effect!!! Not Renner Teller.

Attospectroscopy of coherent vibration of CO_2



Calculation of the probe spectrum as a function of time with the dipole-dipole correlation function

Attospectroscopy of coherent vibration of CO_2

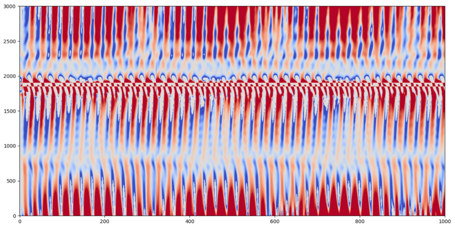


Comparison theory/experiment:

log of the spectrum at time t divided by the spectrum at $t = 0$.

Red: log > 0, blue: log < 0.

Attospectroscopy of coherent vibration of CO_2



Log of the spectrum at time t divided by the spectrum at $t = 0$.

Red: $\log > 0$, blue: $\log < 0$.

On 1000 fs. We see a period of 300 fs.

Conclusions

Combination of polyspherical coordinates with MCTDH and MCCPD: very efficient.

Necessity to have the PESs.

Opens direct collaborations with experimentalists.

Acknowledgements

University of Heidelberg: M. Schröder, D. Mendive Tapia, H.-D. Meyer, and O. Vendrell (protonated water clusters).

University of Paris-Saclay: Lou Barreau, Alexis Texier (CO_2).

University of Florida: John Stanton (CO_2).

University of Bochum: D. Marx.

CNRS International Research Network MCTDH.