

**Quantum Dynamics with the Multi-Configuration Time-Dependent
Hartree (MCTDH) Approach. Applications to Infra-red
spectroscopy and Intramolecular Energy Redistribution.**

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Quantum dynamics

- **Why using quantum dynamics to study the motion of the nuclei?**
- **Strong quantum mechanical effects.**
- **Tunneling effects : reactions involving a light atom (H, H⁺, electron), Hydrogen bonds in water or between the base pairs of nucleotides that build the double helical structure of DNA.**
- **Dynamics around a strong coupling between electronic states. For instance conical intersections in the first step of photosynthesis or vision. (Strong interference effects).**

Quantum dynamics

- **Necessity to have, first, the ab initio data, for instance the potential energy surfaces**
- **In quantum dynamics, very strong correlation: very large primitive (or mathematical) basis set. We are very limited in the size of the systems**
- **MCTDH tries to replace this very large primitive (or mathematical) basis set by a much smaller basis set of time-dependent vibrational orbitals.**

Multi-Configuration Time Dependent Hartree

- **MCTDH package of Heidelberg: see**

<http://www.pci.uni-heidelberg.de/tc/usr/mctdh/>

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

H.-D. Meyer, F. Gatti, and G. Worth, Multidimensional Quantum Dynamics: MCTDH Theory and Applications Wiley-VCH, 2009, (BOOK).

- **A MCSCF algorithm for the nuclear coordinates:
"contraction" of the primitive basis set which
allows to treat larger systems.**
- **A Time-Dependent approach : propagation of
wave packets**

A Time-Dependent MCSCF approach for the nuclei

$$\begin{aligned}\Psi(Q_1, \dots, Q_p, t) &\equiv \Psi(q_1, \dots, q_f, t) \\ &= \sum_{j_1}^{n_1} \cdots \sum_{j_p}^{n_p} A_{j_1, \dots, j_p}(t) \prod_{\kappa=1}^p \varphi_{j_\kappa}^{(\kappa)}(Q_\kappa, t) = \sum_J A_J \Phi_J\end{aligned}$$

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

A Variational Principle.

$$i\dot{A}_J = \sum_L \langle \Phi_J | \hat{H} | \Phi_L \rangle A_L$$

$$i\dot{\varphi}_j^{(\kappa)} = \left(1 - P^{(\kappa)}\right) \sum_{k,l} \rho_{j,k}^{(\kappa)-1} \langle \hat{\mathbf{H}} \rangle_{k,l}^{(\kappa)} \varphi_l^{(\kappa)}$$

Examples of problems treated so far with MCTDH

Photo-dissociation: absorption spectra (NOCl, NO₂, CH₃I, ICN, ArHBr, Ar₂HBr, HCl/ice).

Computation of absorption spectra of polyatomic molecules.

Vibronically coupled systems: Pyrazine; Allene; Butatriene; Benzene, Furan, Pentatetraene.

Molecule-surface scattering : (H₂/LiF, N₂/LiF). Dissociation from a surface. (CH₄/Ni, CH₃I/MgO).

Dissociative adsorption of H₂ on Cu(100), N₂ on stepped Ru(0001), and H₂ on Pt(111).

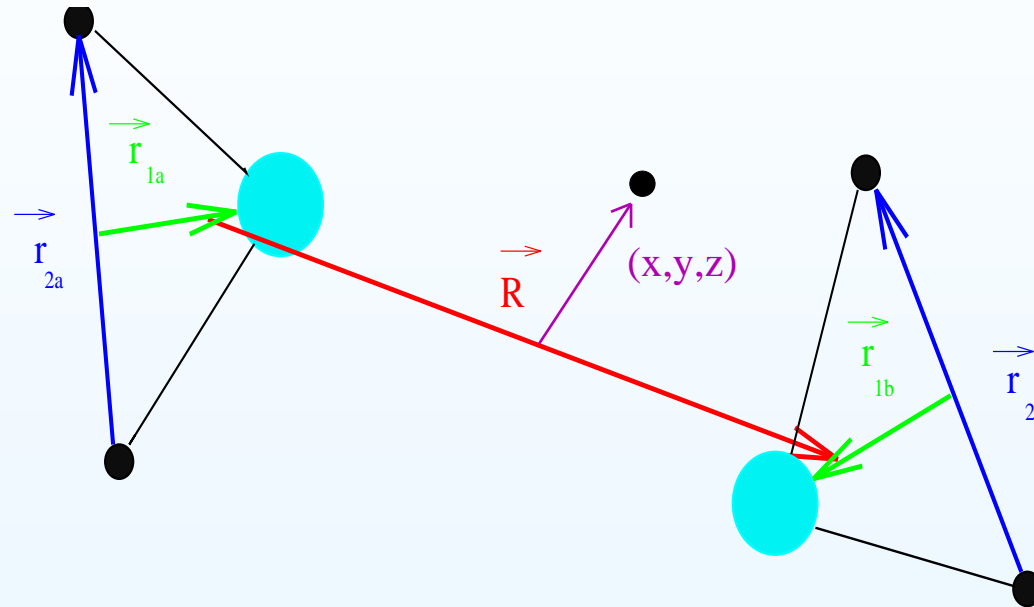
Reactive scattering, thermal reaction rates.

Nuclear dynamics during electron-scattering processes: CO₂ + e⁻ , H₂O + e⁻ .

Intra-molecular vibrational-energy redistribution (IVR)

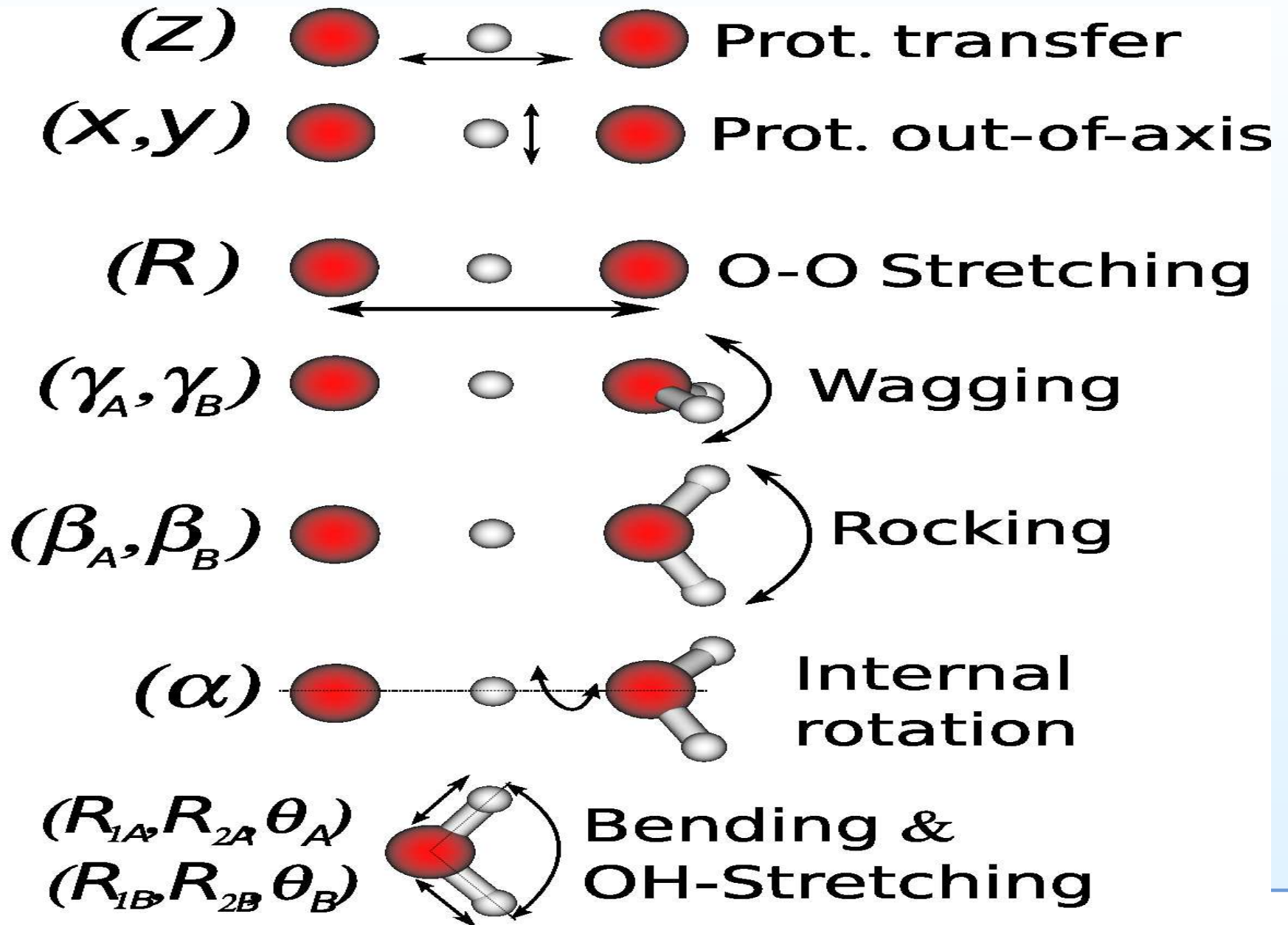
- IVR: we start from one well-defined initial vibrational excitation.
- Where does the energy go? Is the energy redistribution statistic or mode-specific?
- If specific: possibility to control reactions by short laser pulses.
- Infrared-spectroscopy of the molecules: Fermi resonances.
- Examples: Infrared spectrum of the Zundel cation and Cis/Trans Isomerization of HONO.
(Electronic ground state)
- Extension to organic molecules involving conical intersections.

Infra-red Spectrum of H_5O_2^+ (Protonated Water Dimer):



Very floppy system.
Very strong anharmonicity.

15 internal degrees of freedom



15 internal degrees of freedom

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Very strong anharmonicity.

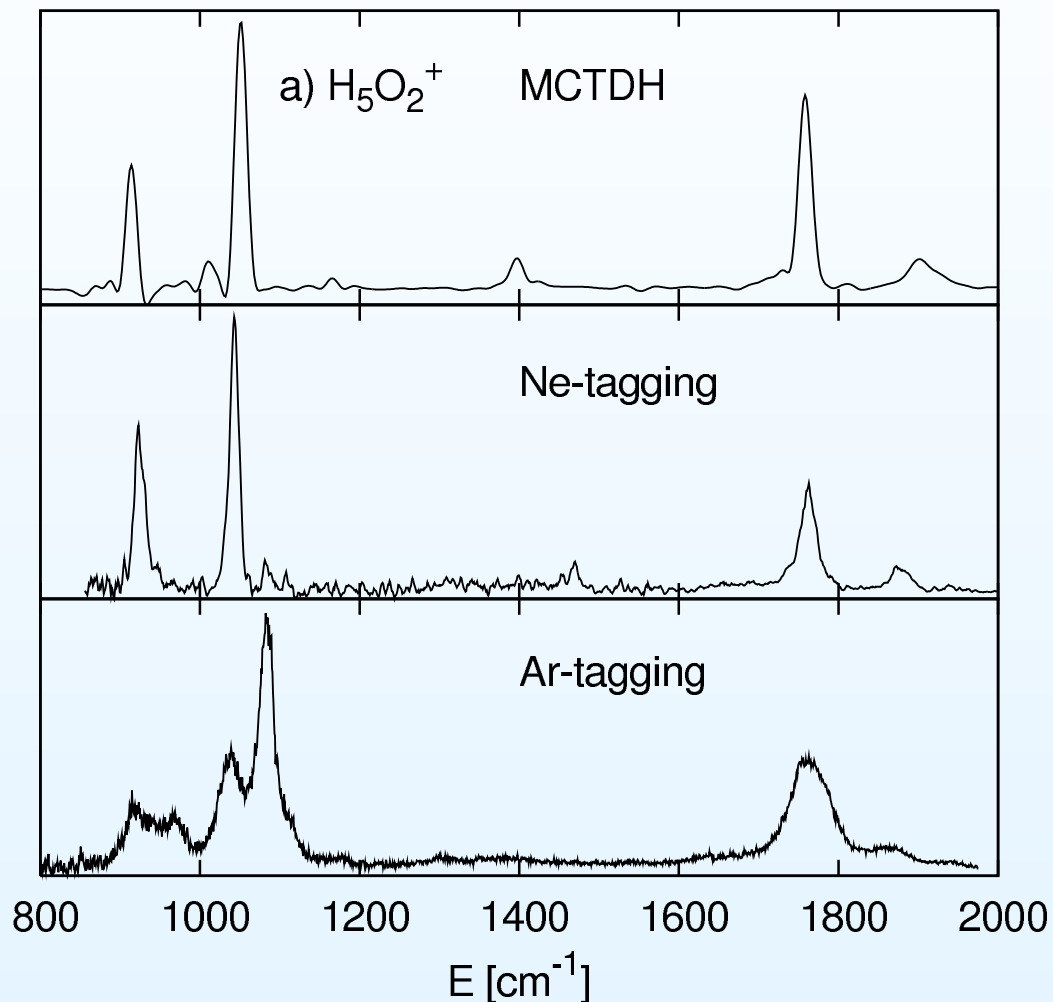
Necessity to use curvilinear coordinates.

F. Gatti, and C. Iung *Physics Reports*, 484 (2009), 1 .

"Exact and constrained kinetic energy operators for polyatomic molecules: The polyspherical approach."

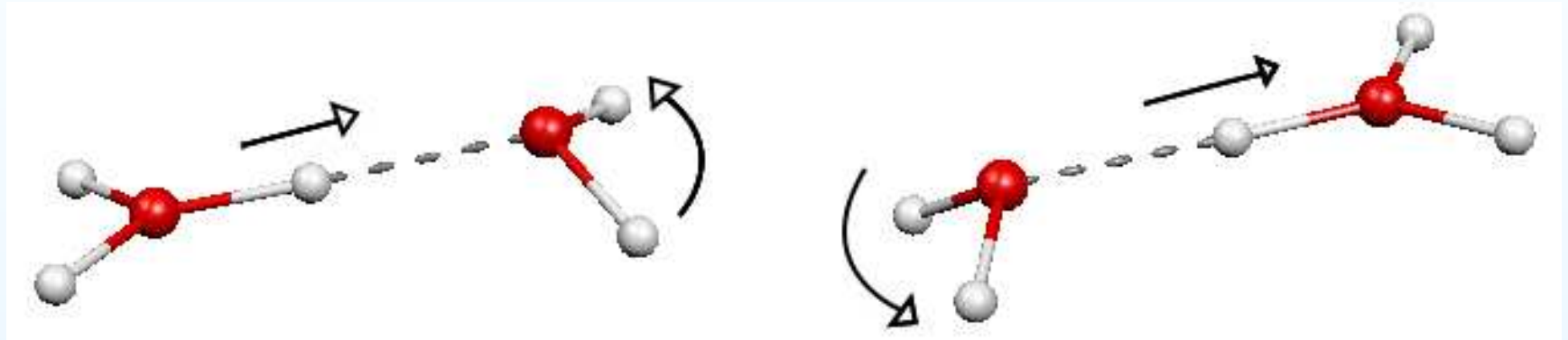
Use of the program TNUM from David Lauvergnat.

Interpretation of the eigenstates:



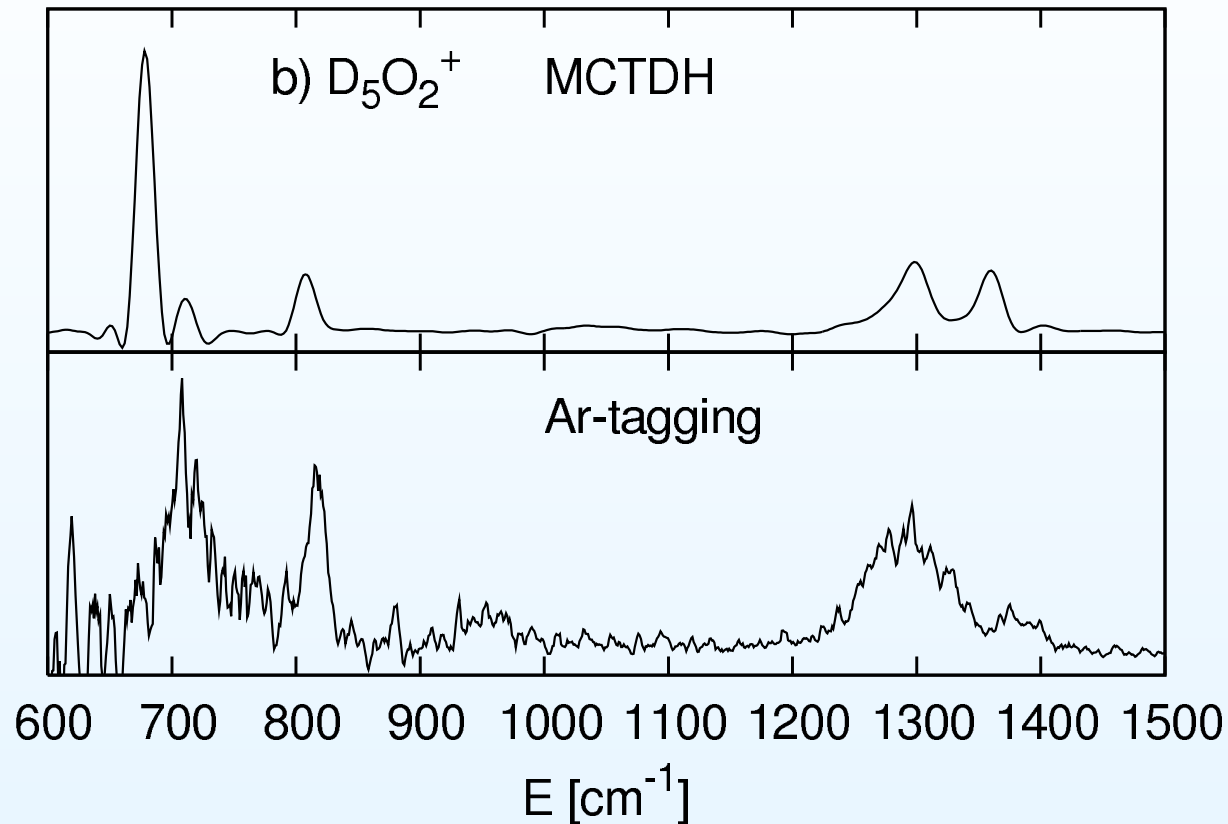
O. Vendrell, F. Gatti, and H.-D. Meyer, *Angewandte Chemie Int. Ed (VIP)* 46 (2007) 6918.
"Dynamics and Infrared Spectroscopy of the Protonated Water Dimer."

Pyramidalisation of H_3O^+



Strong coupling (Fermi resonance) between the proton-transfer motion and the wagging (or pyramidalization) bending mode of vibration.

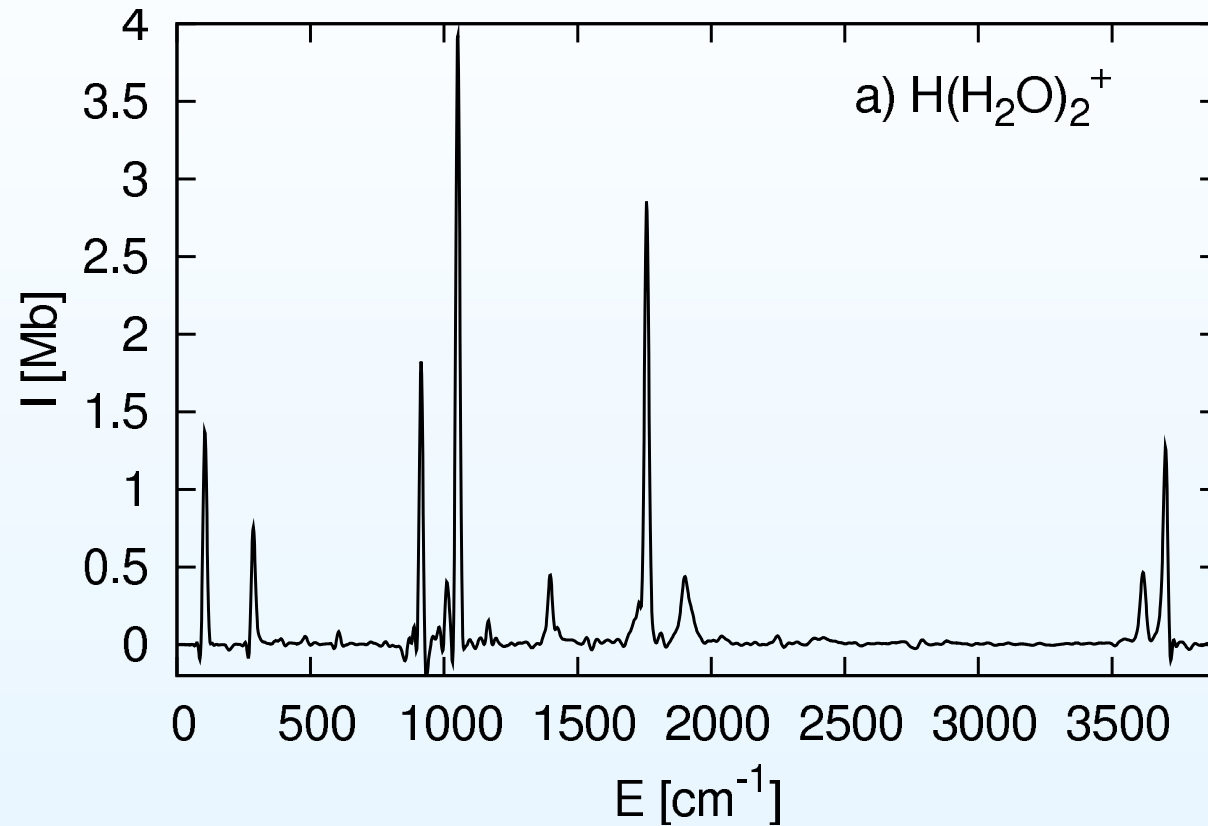
Deuterated protonated Water Dimer: $D(D_2O)_2^+$



O. Vendrell, F. Gatti, and H.-D. Meyer, *Angewandte Chemie Int. Ed (VIP)* 48 (2009)352.

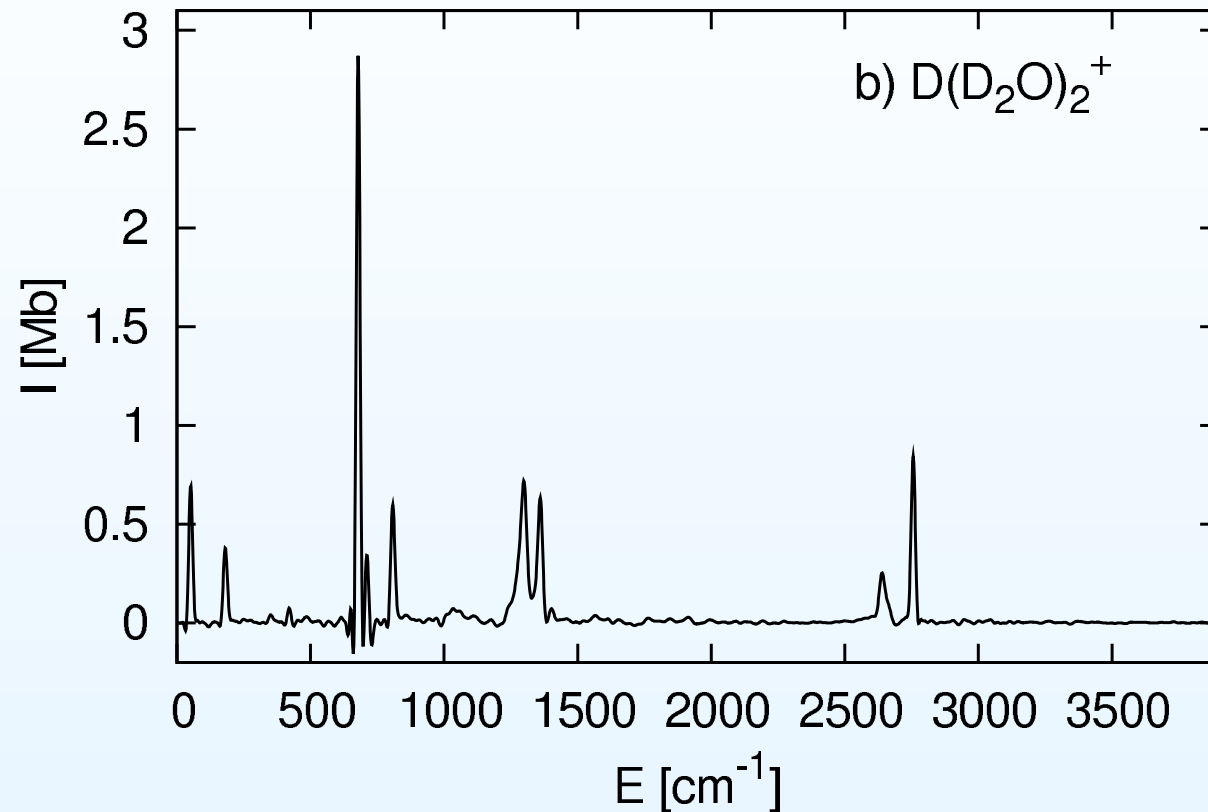
"Strong Isotope Effects in the Infrared Spectrum of the Zundel Cation."

Protonated Water Dimer: $H(H_2O)_2^+$



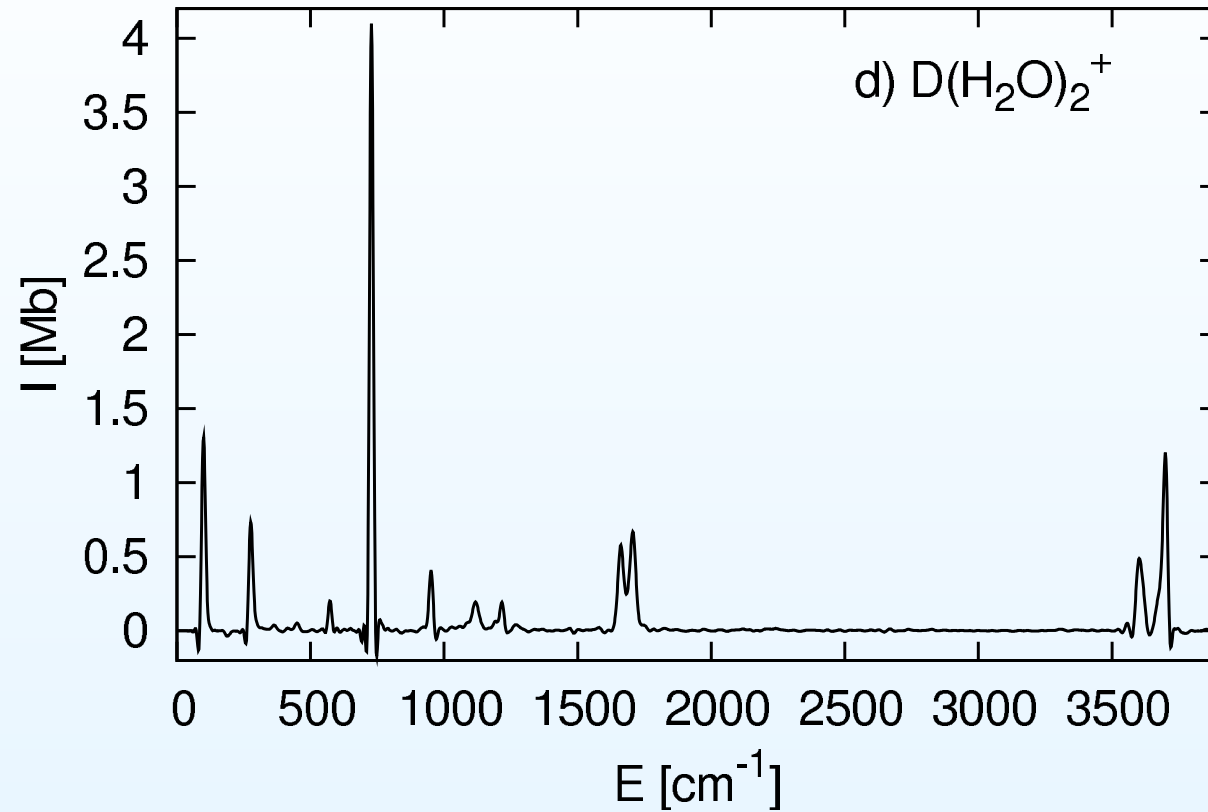
O. Vendrell, D. Lauvergnat, F. Gatti, and H.-D. Meyer, J. Chem. Phys. 127 (2007)184302

Deuterated protonated Water Dimer: $D(D_2O)_2^+$

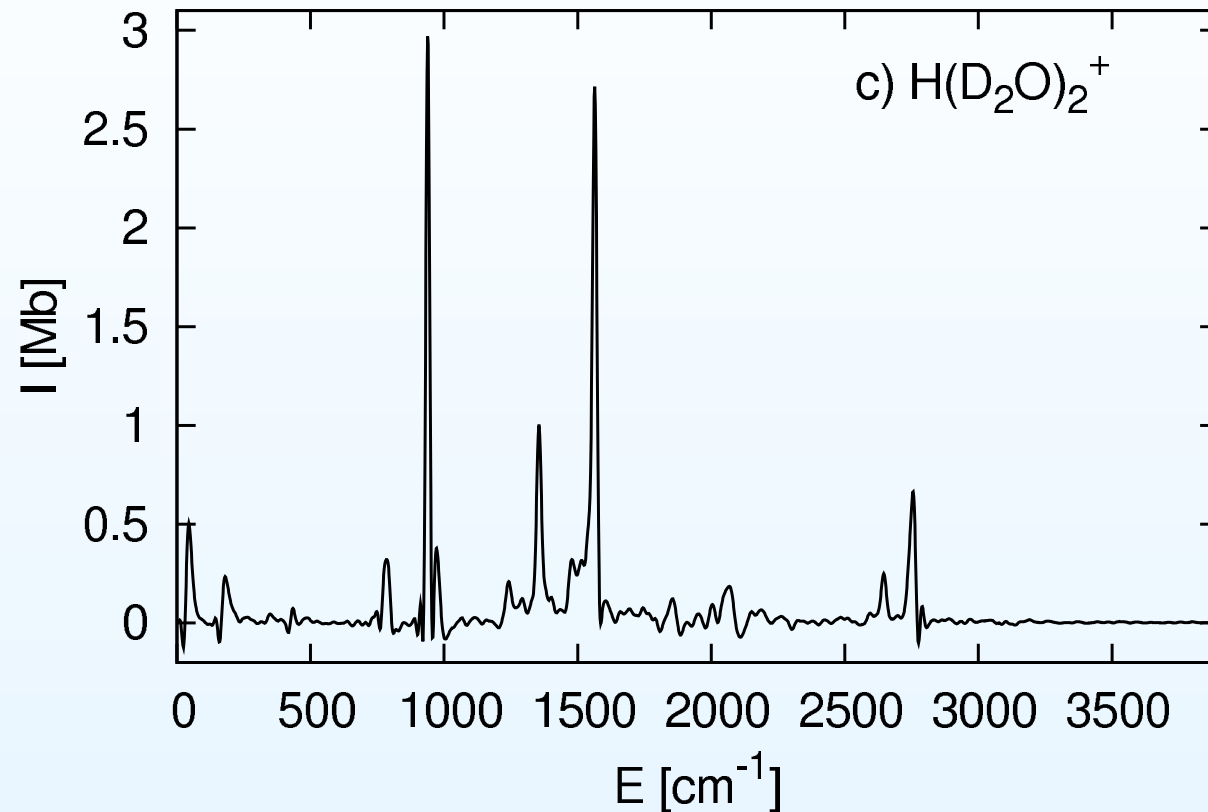


O. Vendrell, M. Brill F. Gatti, D. Lauvergnat and H.-D. Meyer,
J. Chem. Phys. 130 (2009)234305

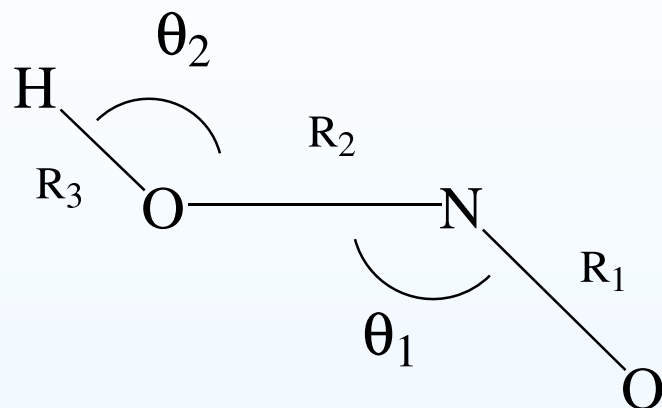
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Polyspherical valence coordinates for HONO



$$R_1 = 2.21 \text{ bohr}$$

$$R_2 = 2.70 \text{ bohr}$$

$$R_3 = 1.81 \text{ bohr}$$

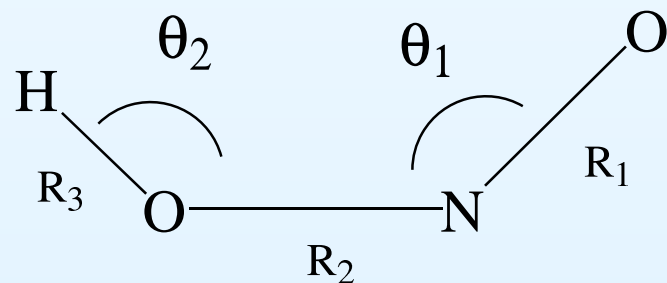
$$\theta_1 = 110.7^\circ$$

$$\theta_2 = 102.1^\circ$$

$$\tau = 180^\circ$$

τ = out-of-plane rotation angle

trans



$$R_1 = 2.24 \text{ bohr}$$

$$R_2 = 2.63 \text{ bohr}$$

$$R_3 = 1.85 \text{ bohr}$$

$$\theta_1 = 113.6^\circ$$

$$\theta_2 = 104.0^\circ$$

$$\tau = 0^\circ$$

cis

HONO: strong mode selectivity

The Cis-geometry lies 93 cm^{-1} ($< 0.02eV$) only above the Trans geometry. However, the cis-trans process proceeds much faster than the opposite direction

We focus on the *cis* \rightarrow *trans* isomerization.

Barrier height: $4105 \text{ cm}^{-1} \approx 0.5eV$

$$\hat{H}_{tot} = \hat{H}_0 - \hat{\vec{\mu}} \cdot \vec{E}(t)$$

$$\vec{E}(t) = E_0 \cos(\omega t) \sin^2(\pi t/t_p) \Theta(t) \Theta(t - t_p) \vec{e}$$

(2)

Calculation of new six-dimensional potential energy surface and dipole moment surface.

Transition energies and moments for the Cis Geometry

F. Richter, F. Gatti, C. Léonard, F. LeQuéré and H.-D. Meyer, *J. Chem. Phys.* 127 (2007) 164315.

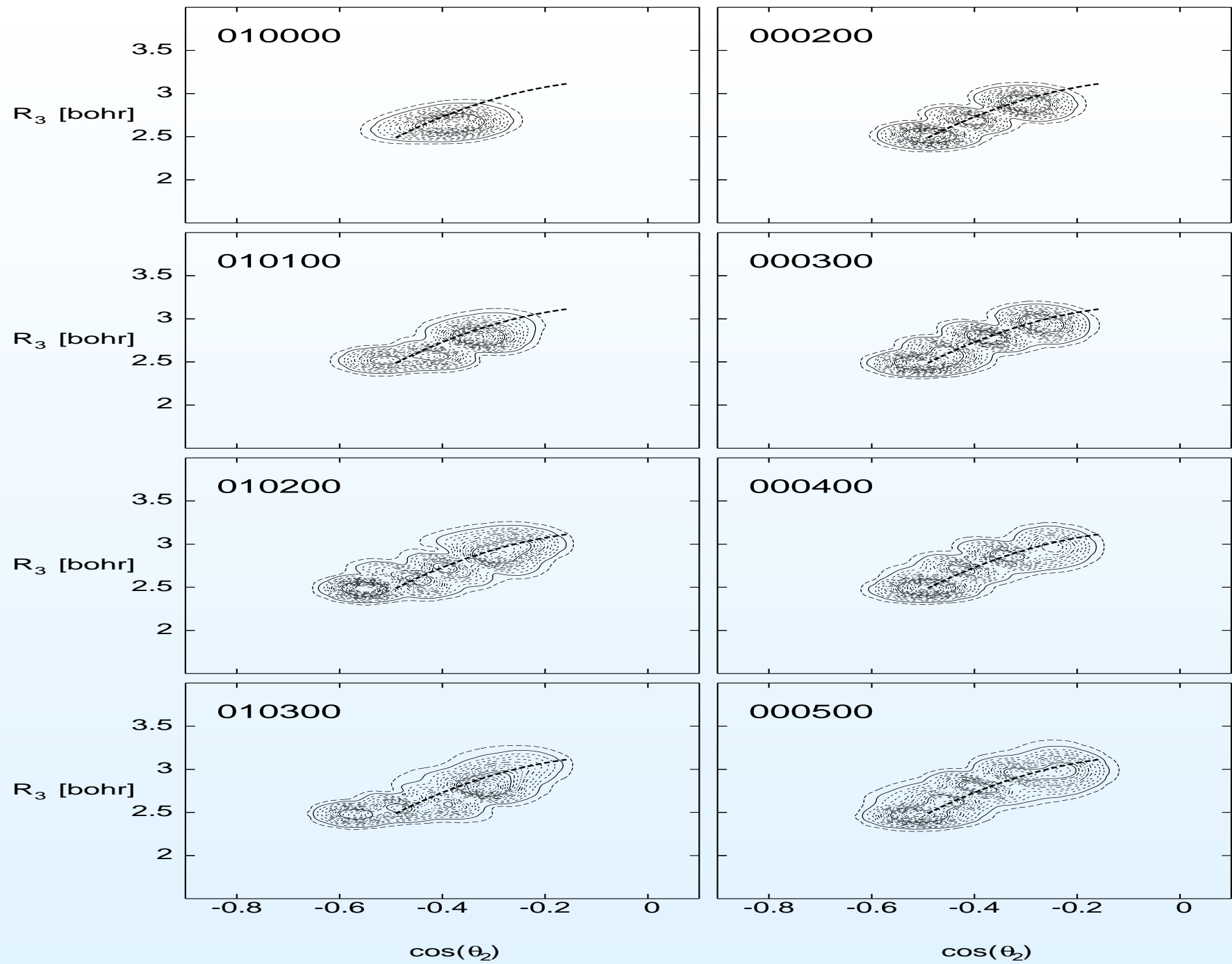
	ν_{exp}	Exp.	Calc. CCSD(T)/DFT
000010	(ONO)	609	616.7(33.7)
000100	(ON)	852 (291)	850.1(281)
001000	(HON)	-	1311.6(7.5)
010000	(N=O)	1641	1632.0(177)
100000	(OH)	3426	3438.1(18.0)
000002	(out-of-plane)	-	1212.7 (0.2)

Transitions energies in cm^{-1} .

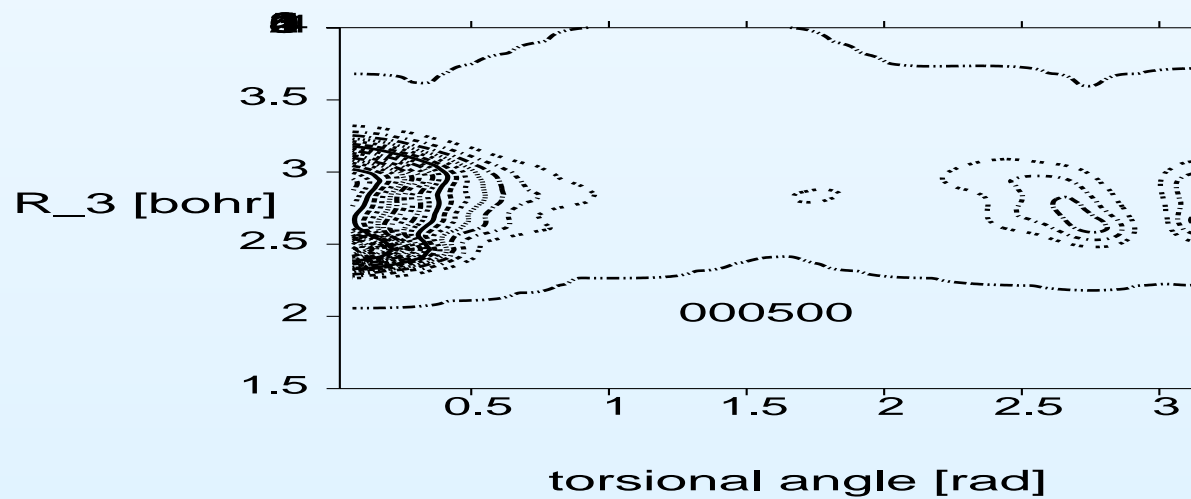
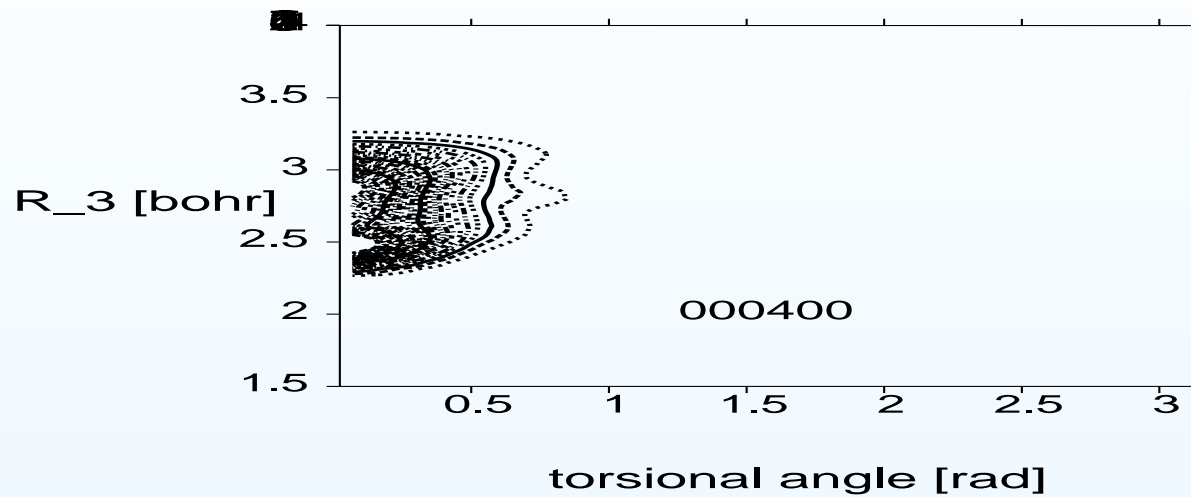
In parentheses: Transitions moments in km/mol.

How is it possible to trigger the isomerization?

- Not possible to directly excite the isomerization.
- An efficient and **selective IVR-pathway** leading to the *cis* → *trans* isomerization.
- **Optimal path: simultaneous increase of the (middle) ON bond length and of the cosine of the ONO bending angle.**
- **Optimal orientation of the laser is parallel to the ON bond. Laser frequency of about 850 cm^{-1} .** Pulse-envelope with a duration of 500 fs. After irradiation, we have simulated the dynamics during 2000 fs.



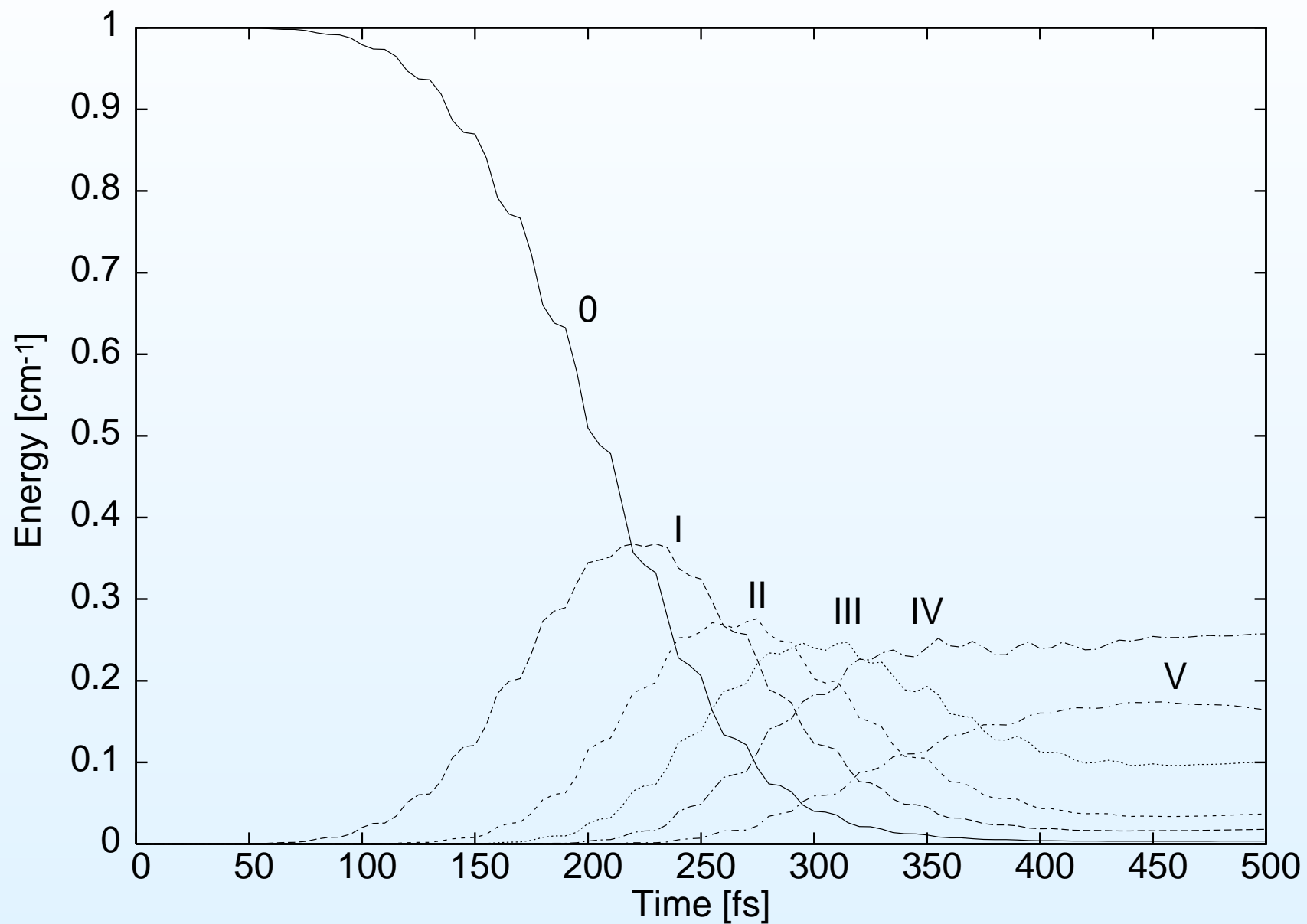
Tunneling



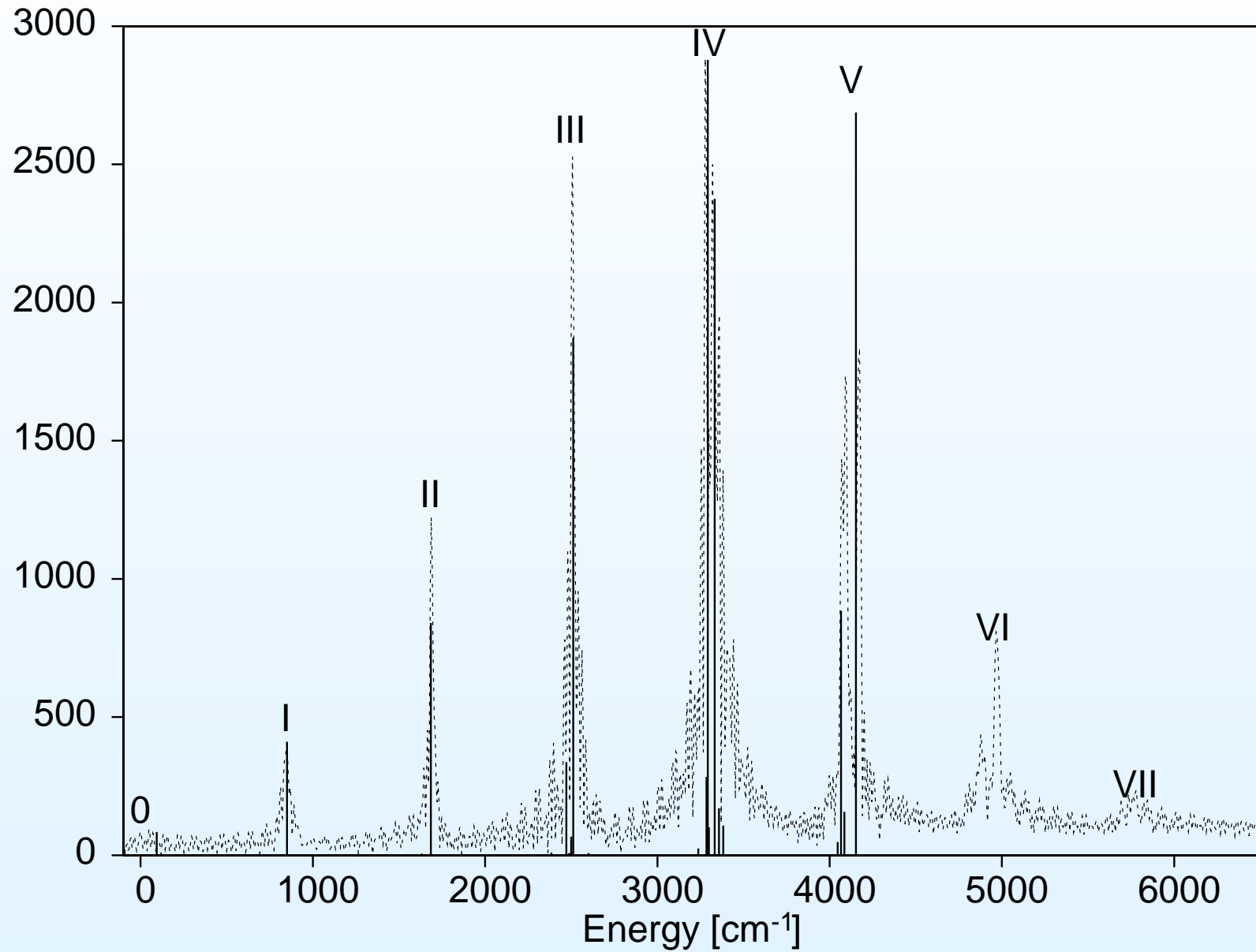
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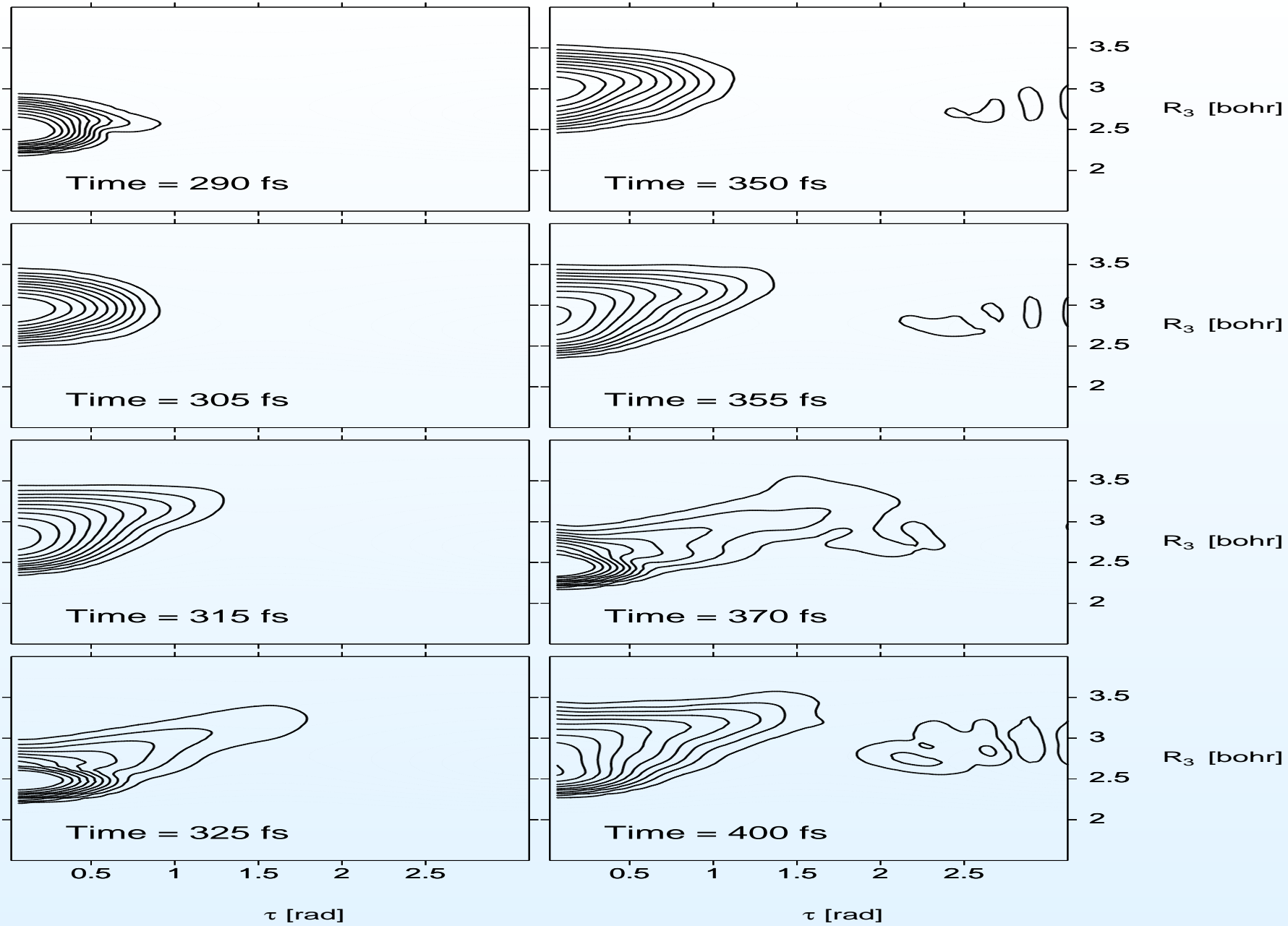
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Evolution of the population of the eigenstates:



Fourier transform of the autocorrelation function:





How is it possible to trigger the isomerization?

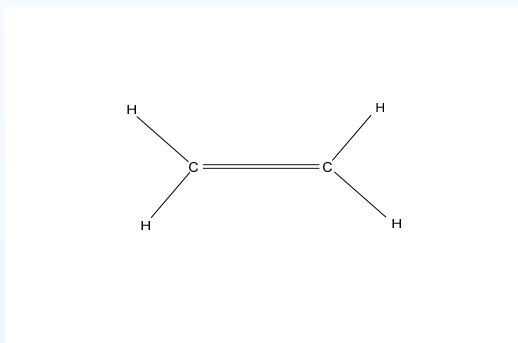
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laser intensity [Watt/cm ²]	total Energy [eV]	k [ps ⁻¹]	P_{trans}^F
$1.225 \cdot 10^{14}$	1.045	0.67	0.17
$1.714 \cdot 10^{14}$	1.363	2.66	0.34

Conical intersection.

Photochemical mechanisms in organic compounds involving conical intersections.

Example: calculation of the photabsorption spectrum of ethene.



Calculation with 6D of the absorption spectrum.

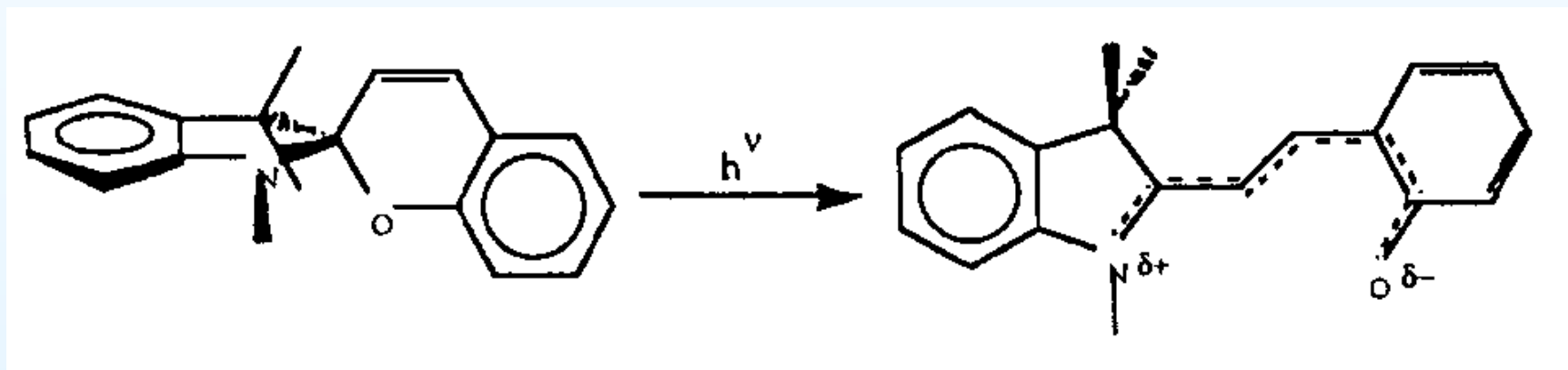
M. Brill, F. Gatti, D. Lauvergnat and H.-D. Meyer, Chem. Phys. 338 (2007)186.

Addition of some Rydberg states.

Conical intersections.

Example: Spiropyran: ring opening through a conical intersection.

Absorption of the light by the 'symmetric' stretching mode of vibration of the phenyl group.



Conclusion:

- MCTDH has been parallelized
- MCTDH 'Multi-Layer' or 'cascading' (5000 degrees of freedom)
- Very large systems: one core (chromophore) described precisely and the rest (protein) described as an environment.

Acknowledgements:

- **Montpellier: C. Jung, B. Lasorne, F. Richter**
- **Heidelberg: O. Vendrell and H.-D. Meyer**
- **Marne-la-vallée: C. Léonard**
- **Orsay: D. Lauvergnat**