Unravelling the Pathways of Ultrafast Vibrational Energy Flow in Hydrogen Bonds

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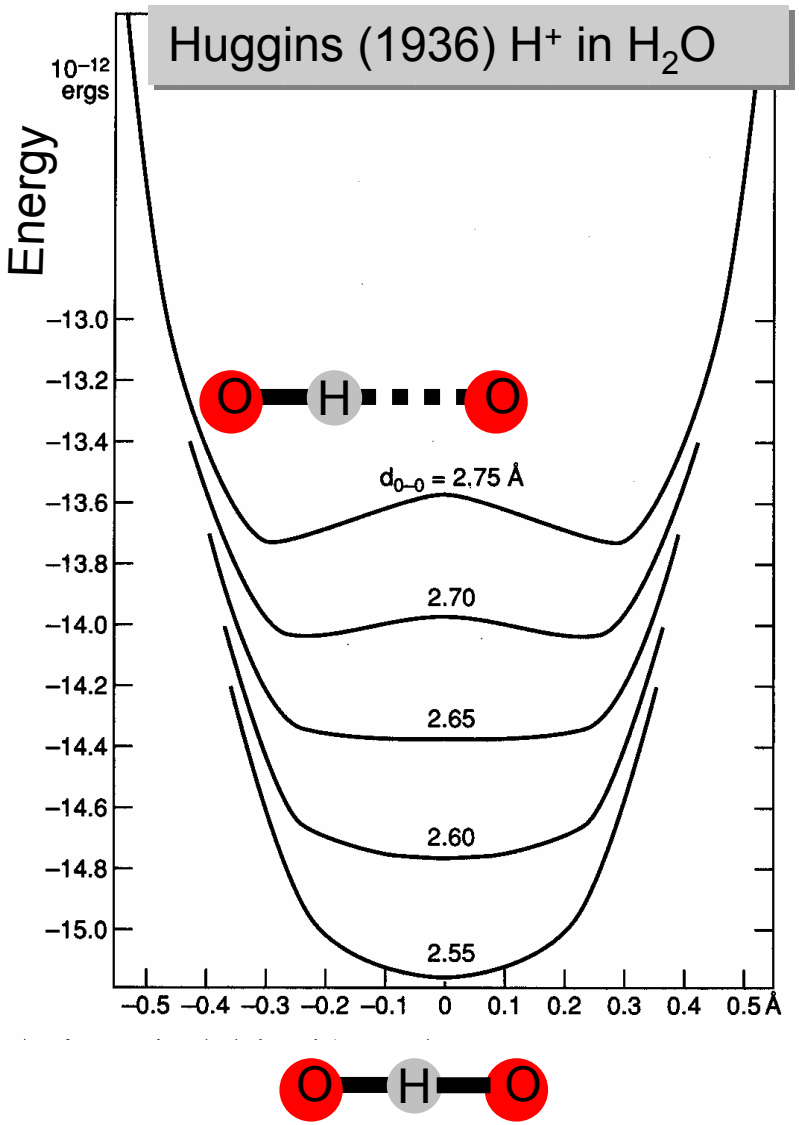
AGENDA



correlation

H-atom ↔ H-bond

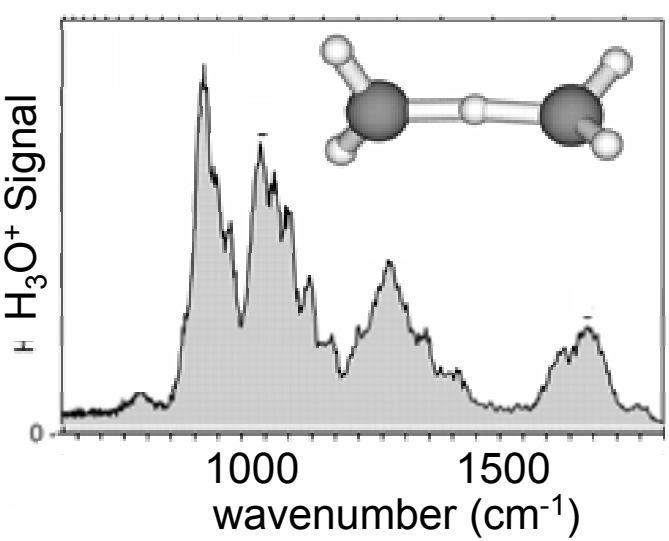
multidimensional quantum dynamics

potential energy surfaces
equations of motion

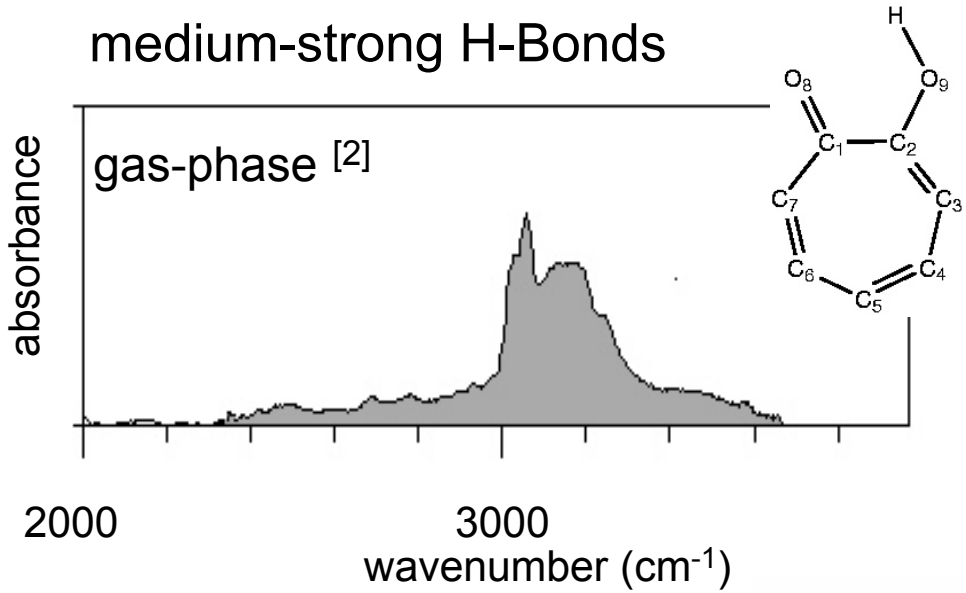
M. L. Huggins, JPC 40, 723 (1936)

MULTIDIMENSIONALITY & IR SPECTRUM

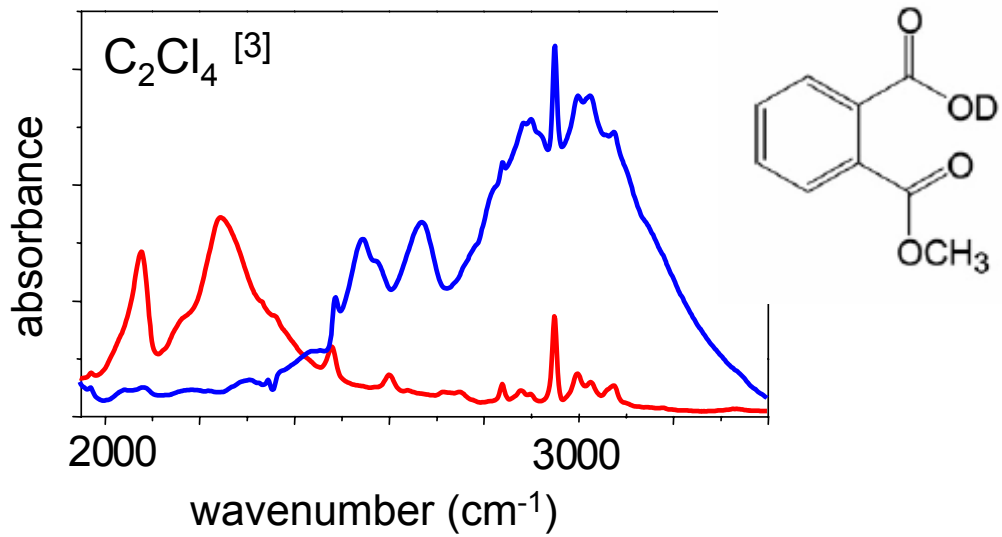
strong H-Bond [1]



medium-strong H-Bonds

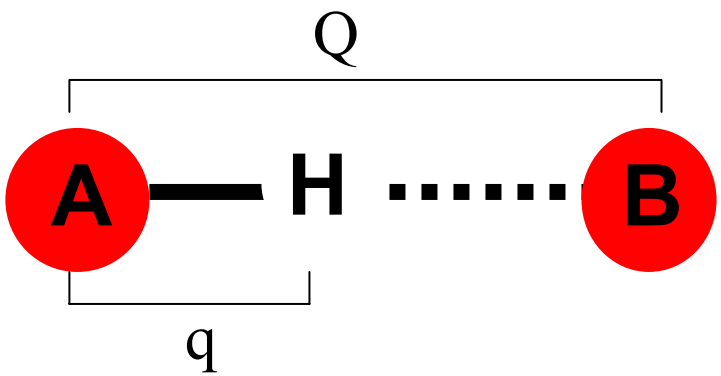


red-shift
broadening
substructure

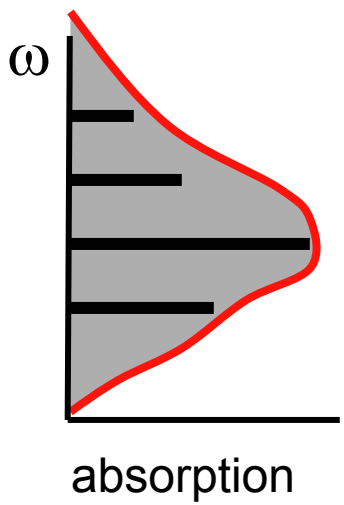


[1] K. Asmis et al., Science 299, 1375 (2003), [2] NIST, [3] J. Stenger et al. □

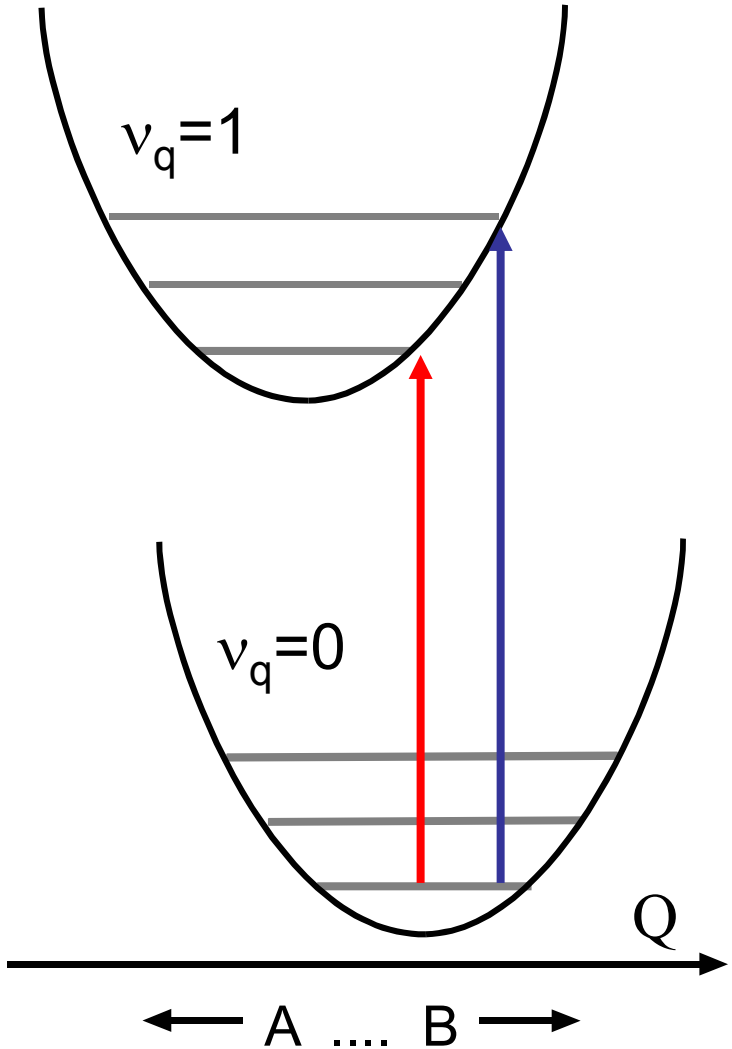
A SIMPLE ADIABATIC MODEL



Franck-Condon-like transition

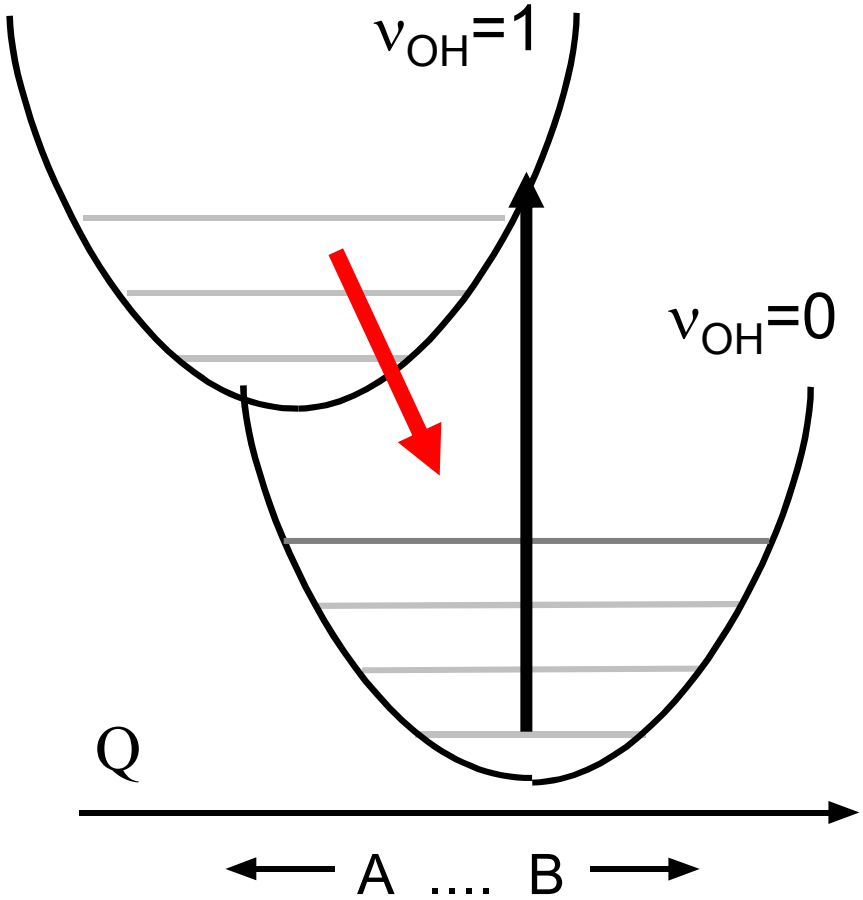


?

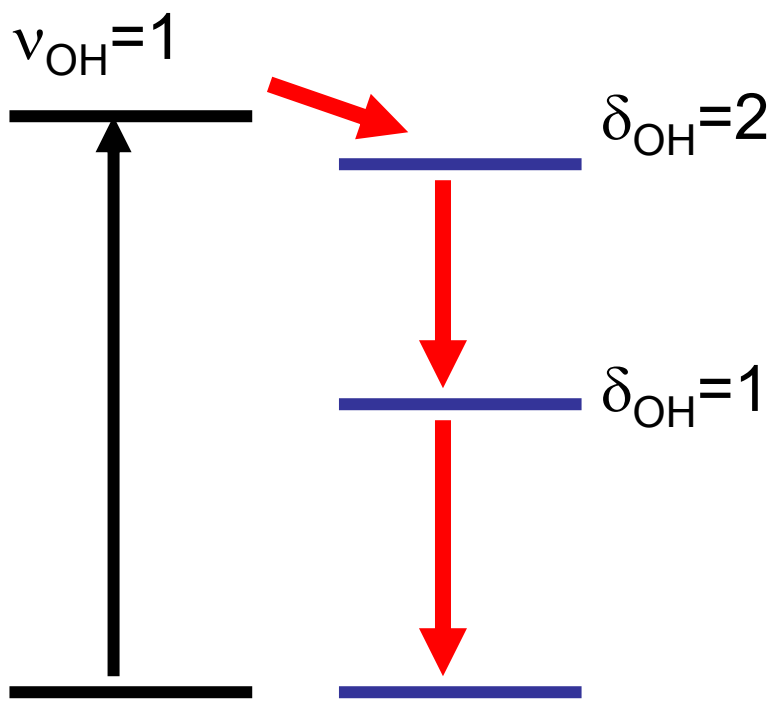


VIBRATIONAL RELAXATION MODELS

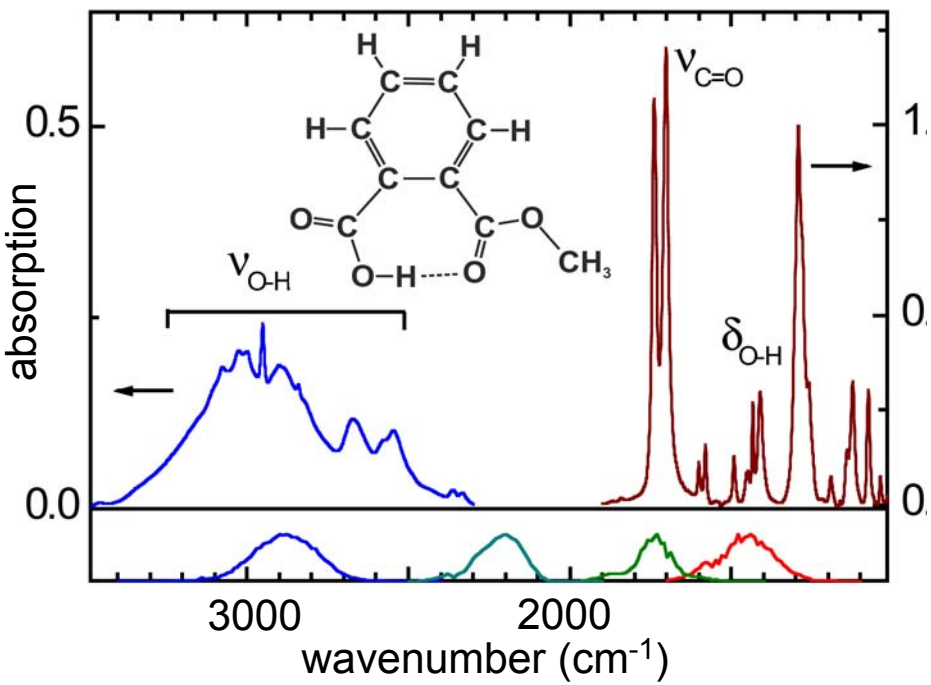
via H-bond motion

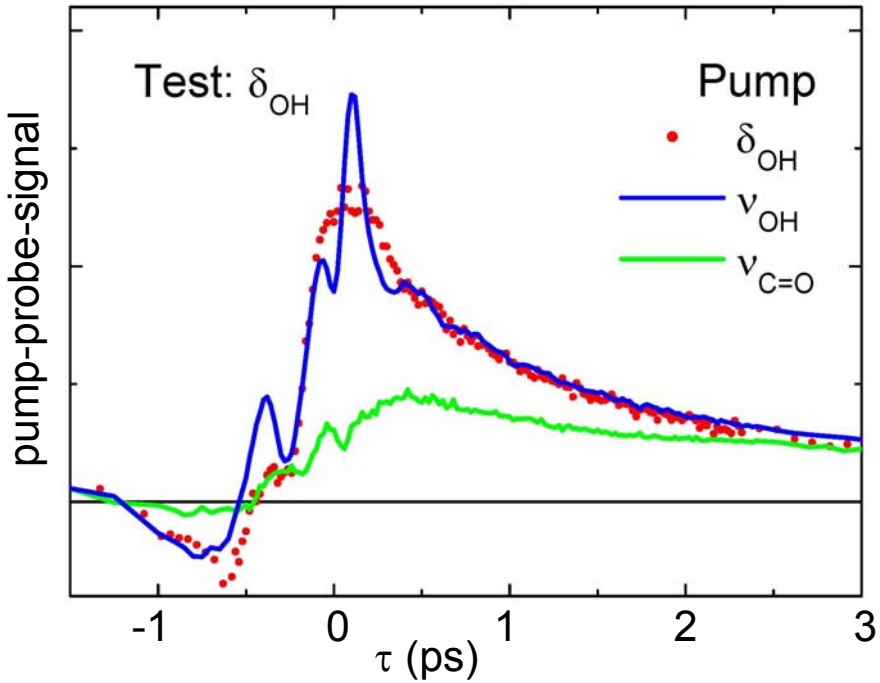


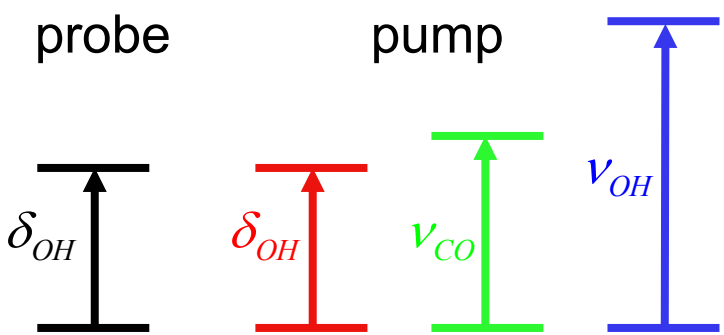
via Fermi-resonance



PMME-H: 2-COLOR IR SPECTROSCOPY





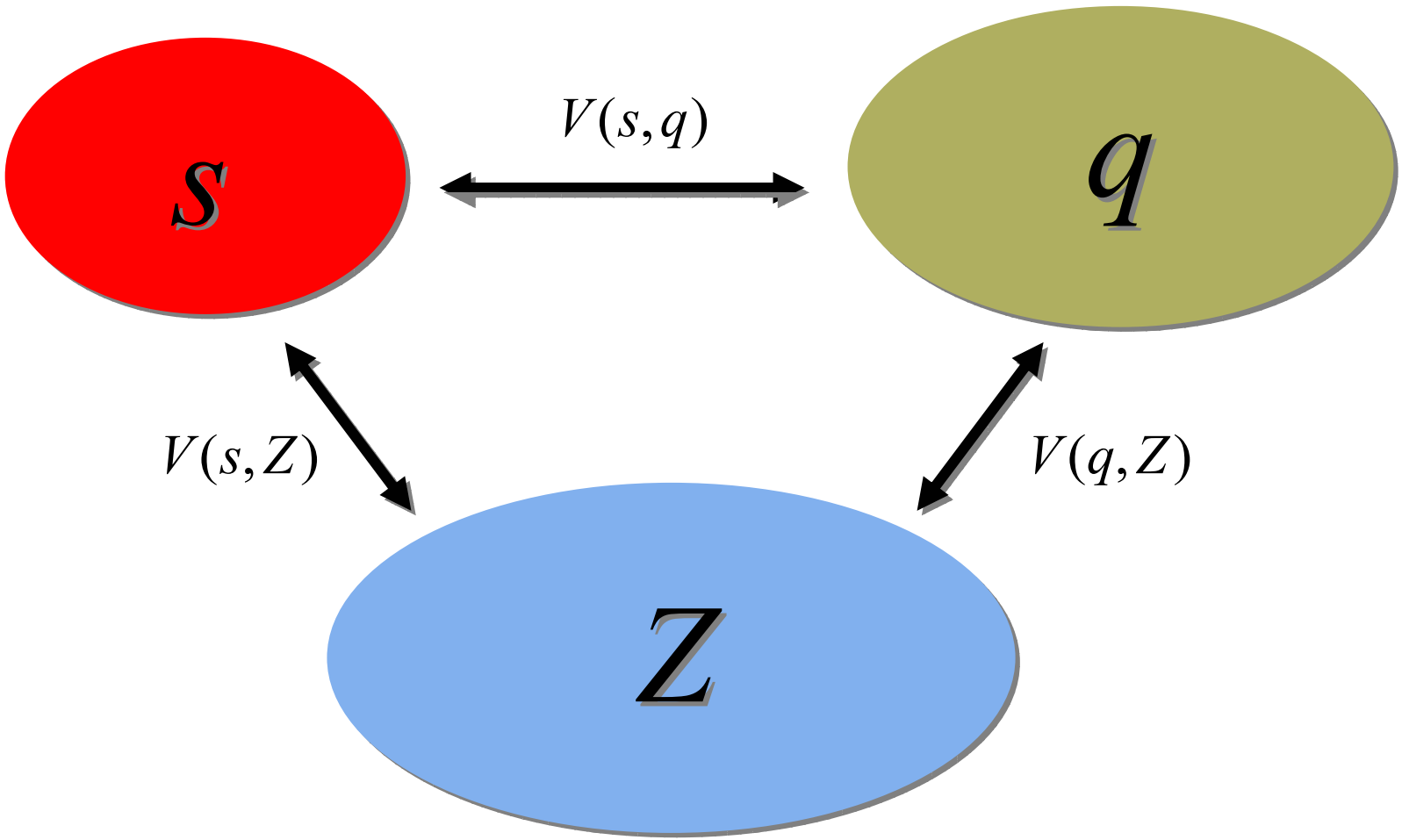


$T_1(\nu_{OH})$=200fs, $T_1(\delta_{OH})$=800fs
relaxation via δ_{OH}=1 (>30%)
T_{cool} ~ 20 ps
ν_{osc} ~ 100 cm^{-1}

K. Heyne et al. JPCA 108, 6083 (2004)

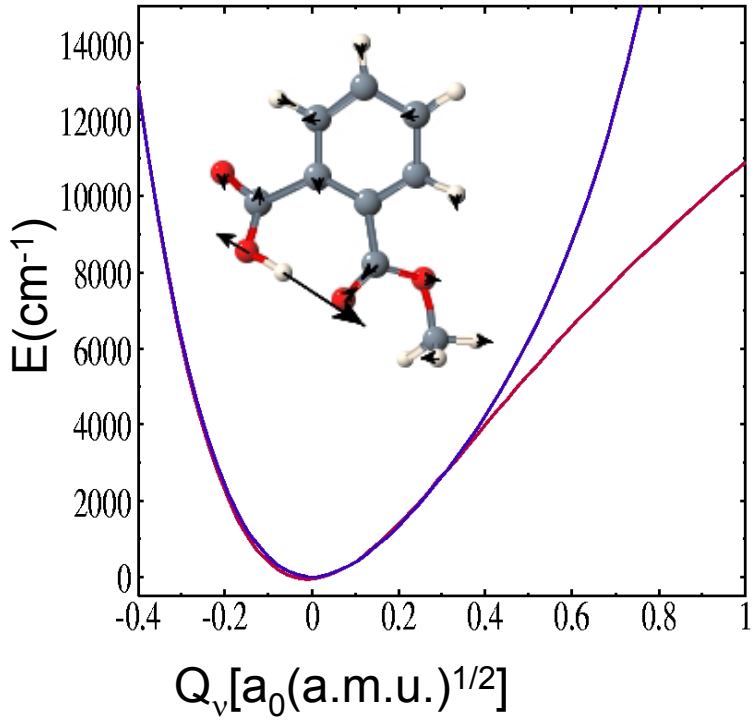
SYSTEM-BAD APPROACH

$$H = H_{SYS}(s;t) + H_{BATH}(q,Z) + H_{SB}(s,q,Z)$$



POTENTIAL ENERGY SURFACES

- Reaction Surface Hamiltonian
  - ➢ no proton transfer
  - ➢ no bond dissociation
- normal mode representation

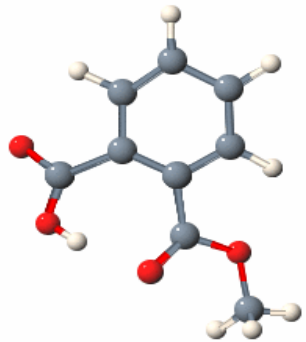


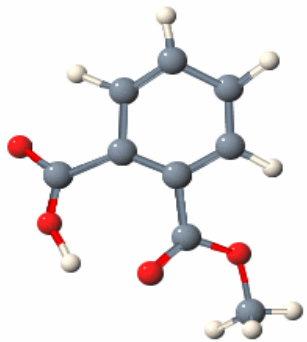
$$V(\mathbf{Q}) = \sum_i V^{(1)}(Q_i) + V_{corr}(\mathbf{Q})$$

$$V_{corr}(\mathbf{Q}) = \sum_{i \neq j} V^{(2)}(Q_i, Q_j) + \sum_{i \neq j \neq k} V^{(3)}(Q_i, Q_j, Q_k) + \sum_{i \neq j \neq k \neq l} V^{(4)}(Q_i, Q_j, Q_k, Q_l) + \ldots$$

- ➢ choice of relevant coordinates
- ➢ calculation of correlation potential

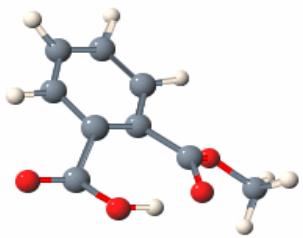
PMME: 5D DISSIPATIVE MODEL

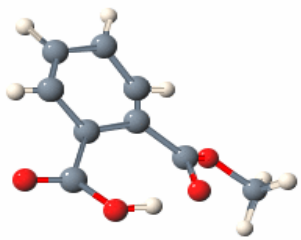


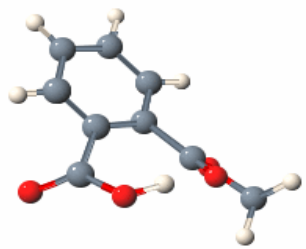


ν_{OH} = 3036 cm^{-1}

δ_{OH} = 1455 cm^{-1}



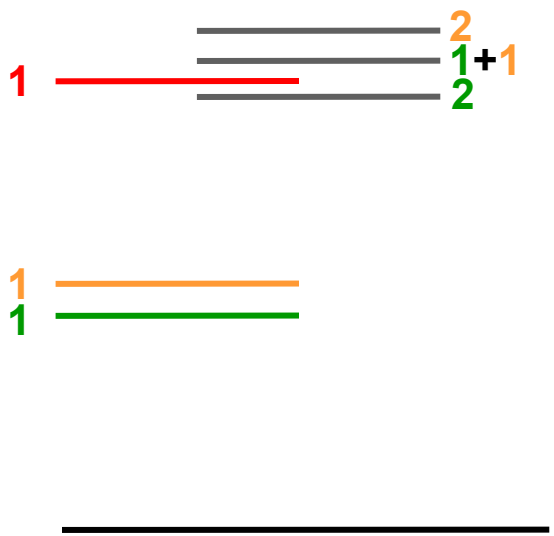




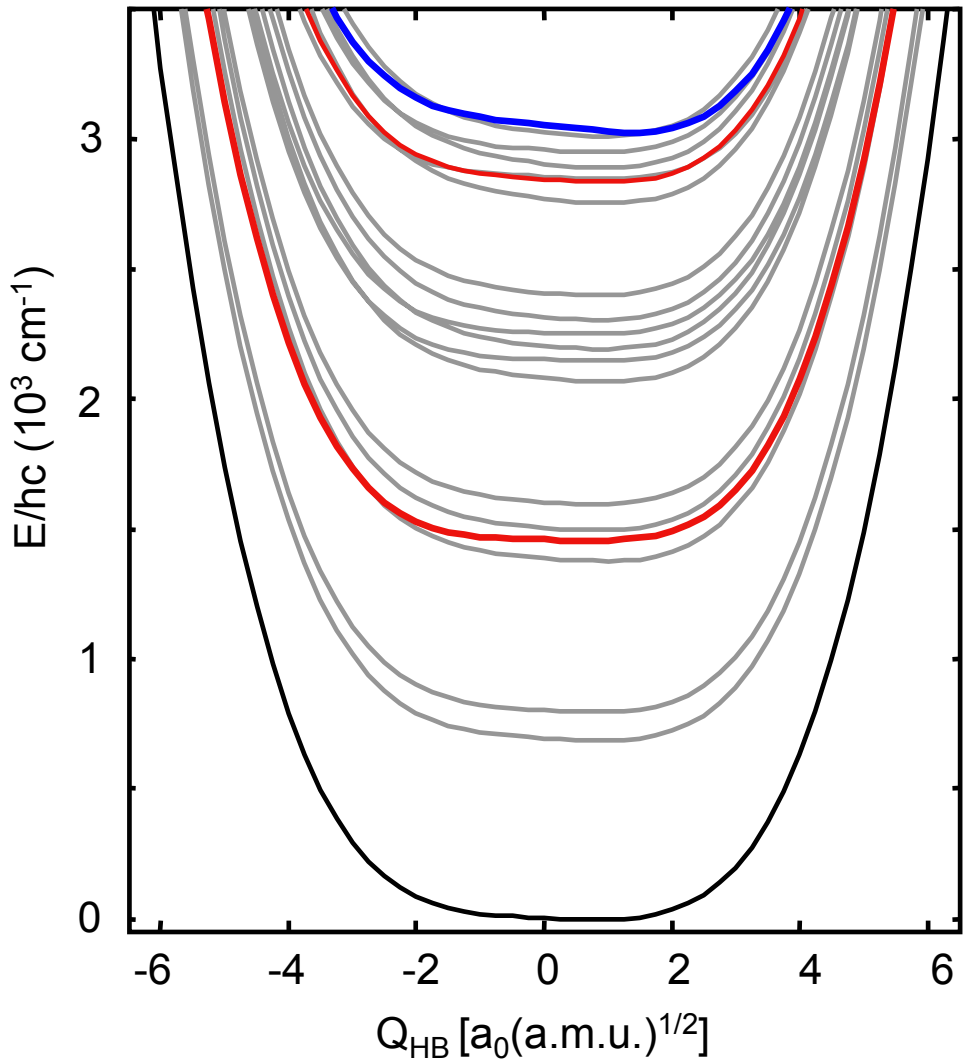
γ_1 = 792 cm^{-1}

γ_2 = 690 cm^{-1}

ν_{HB} = 63 cm^{-1}

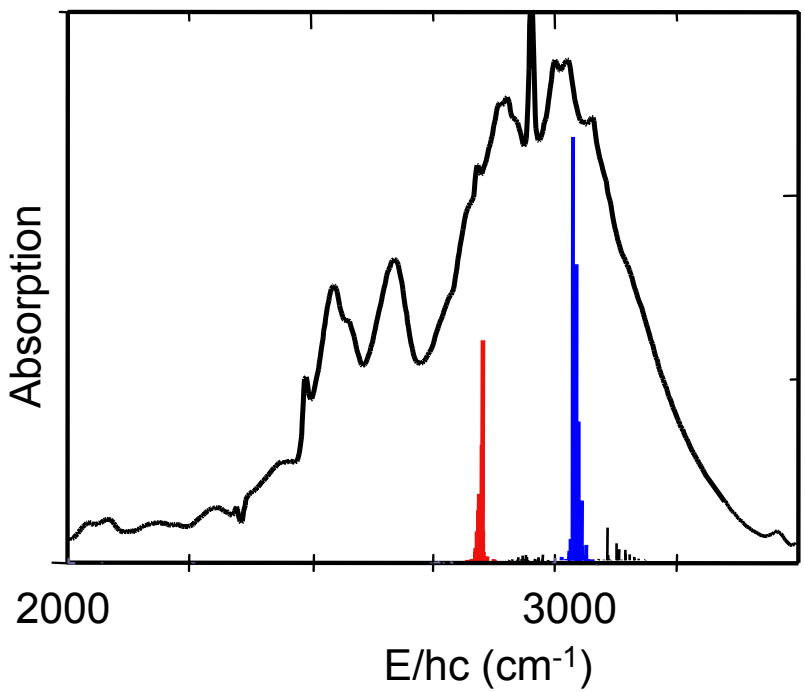


PMME-H: IR SPECTRUM



diabatic states

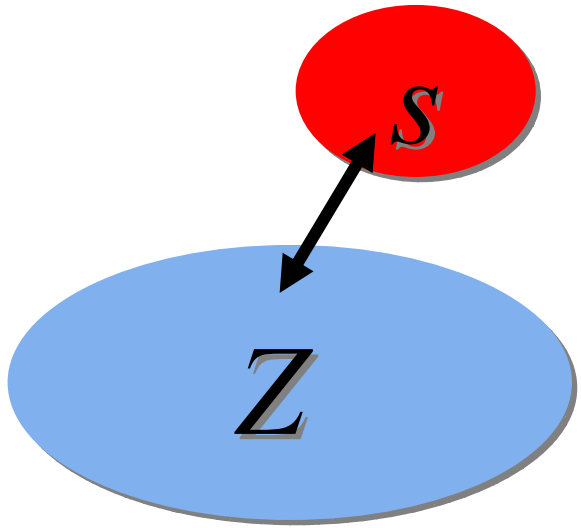
$$\rightarrow \quad (v_\nu, v_\delta, v_{\gamma_1}, v_{\gamma_2})$$



DISSIPATIVE QUANTUM DYNAMICS

observables $$O(s,t) = \mathrm{tr}_{SYS}\left(\hat{O}(s)\,\hat{\rho}(t)\right)$$

reduced density operator $$\hat{\rho}(t) = \mathrm{tr}_{BATH}\left(\hat{\rho}_{total}(t)\right)$$



Quantum-Master Equation

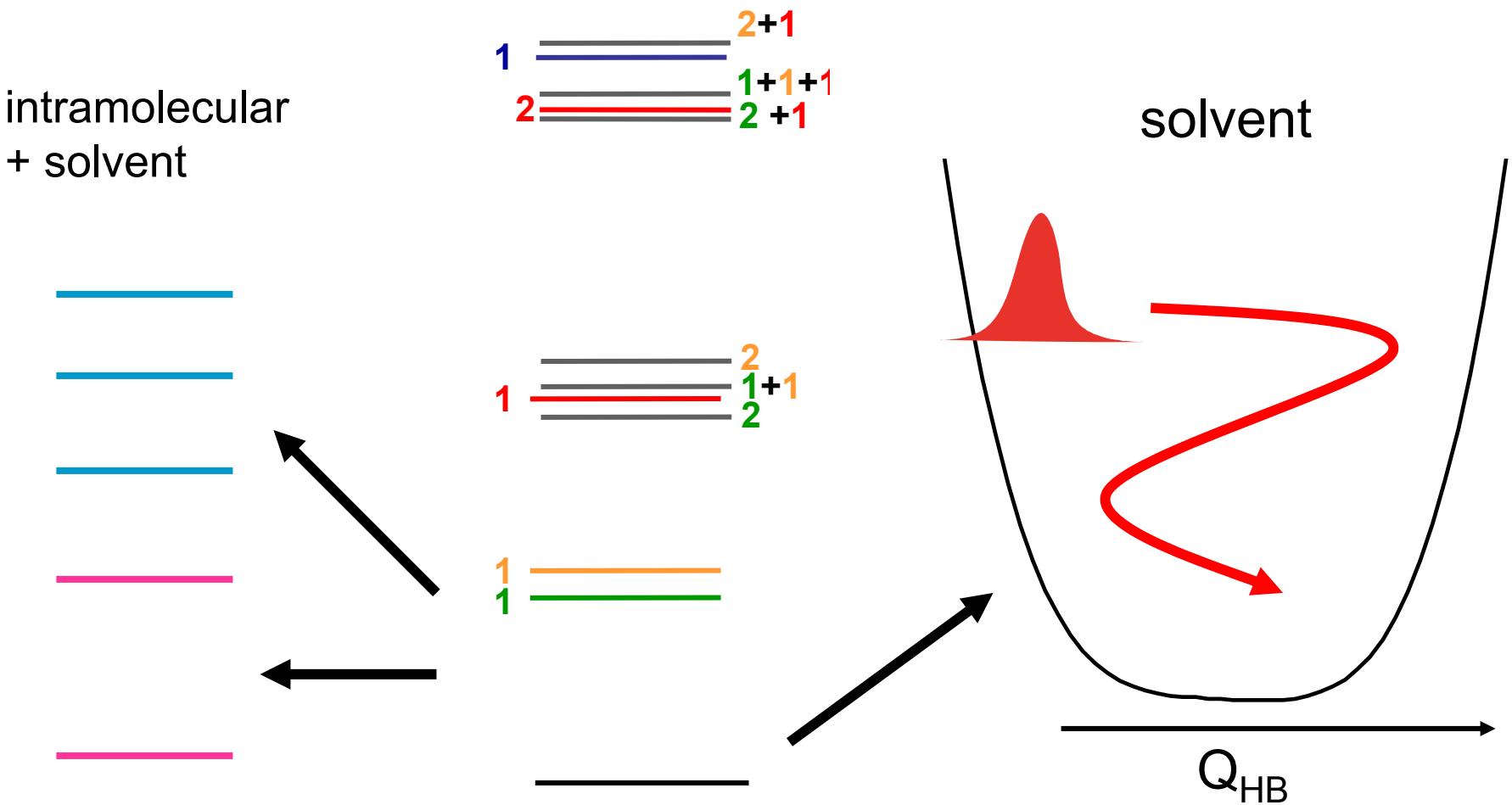
$$\frac{\partial \rho_{ab}}{\partial t} = -i\omega_{ab}\rho_{ab} + iE(t)\sum_{c}(d_{ac}\rho_{cb} - d_{cb}\rho_{ac}) - \sum_{cd} R_{ab,cd}\rho_{cd}$$

coherent dynamics

relaxation/dissipation

PMME: SYSTEM-BATH MODEL

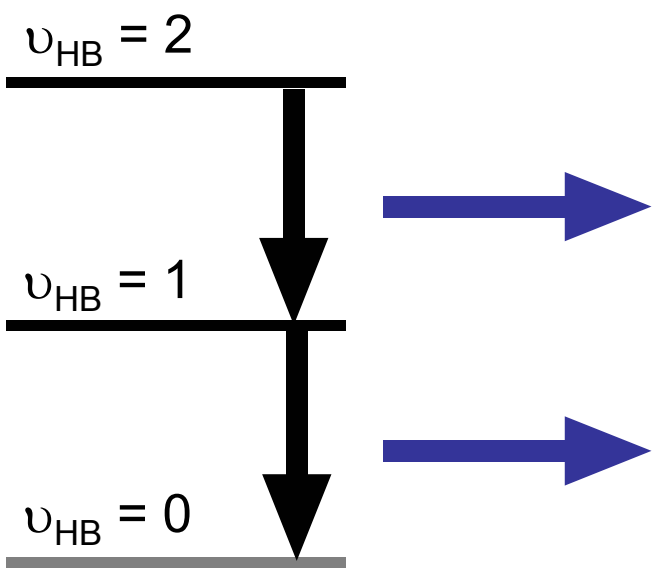
$V(s = Q, q, Z)$ ➡ relevant interactions



PMME: RELAXATION OF HB-MODE

bilinear coupling

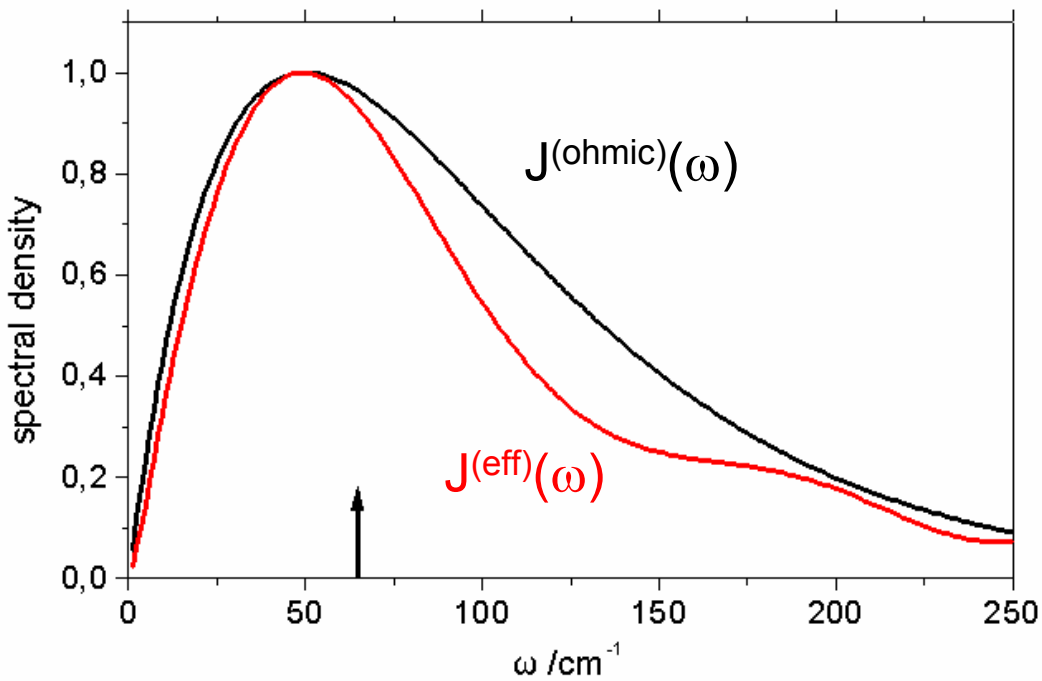
$$H_{SB}^{(I)} = Q_{HB} \sum_{\lambda} g_{HB,\lambda}^{(I)} \; Z_{\lambda}$$



T_1~1.6ps

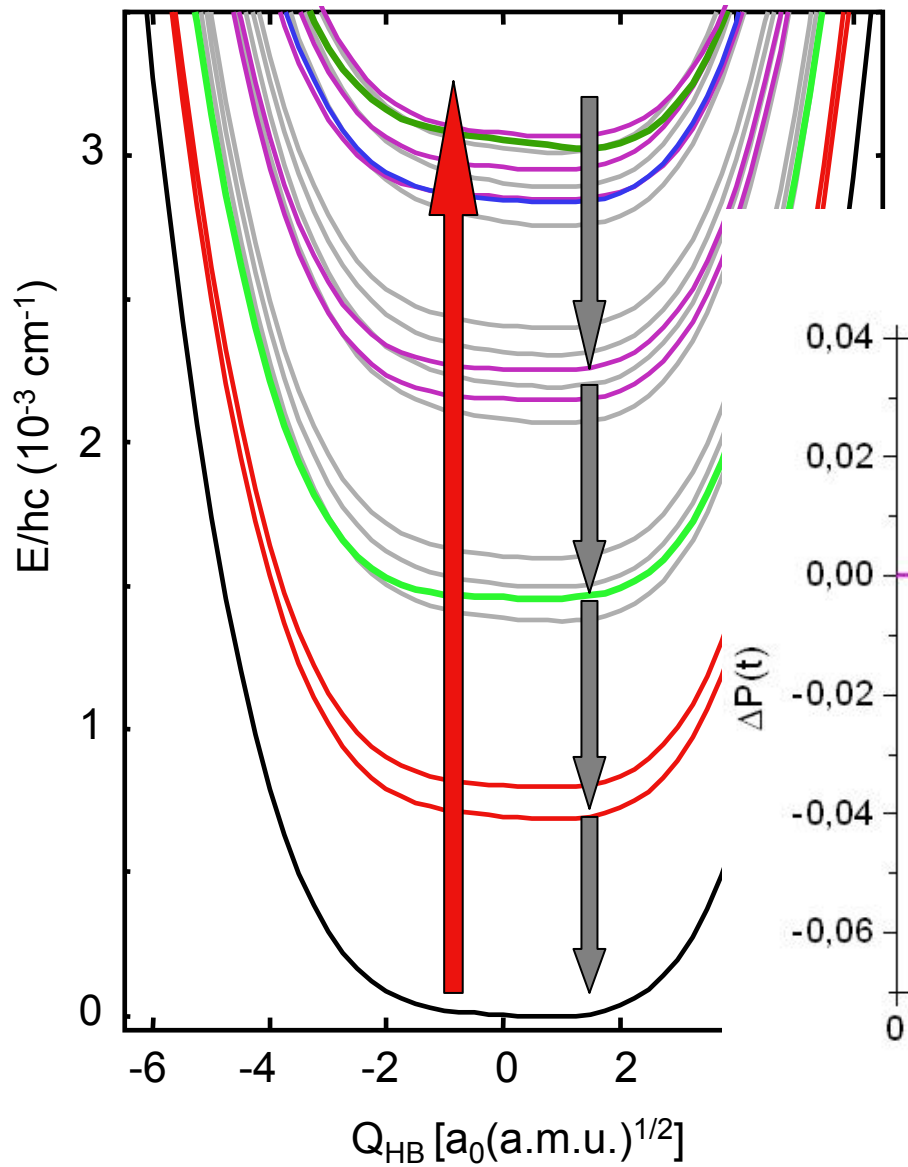
spectral density

classical MD PMME/CCl_4 at T=300K



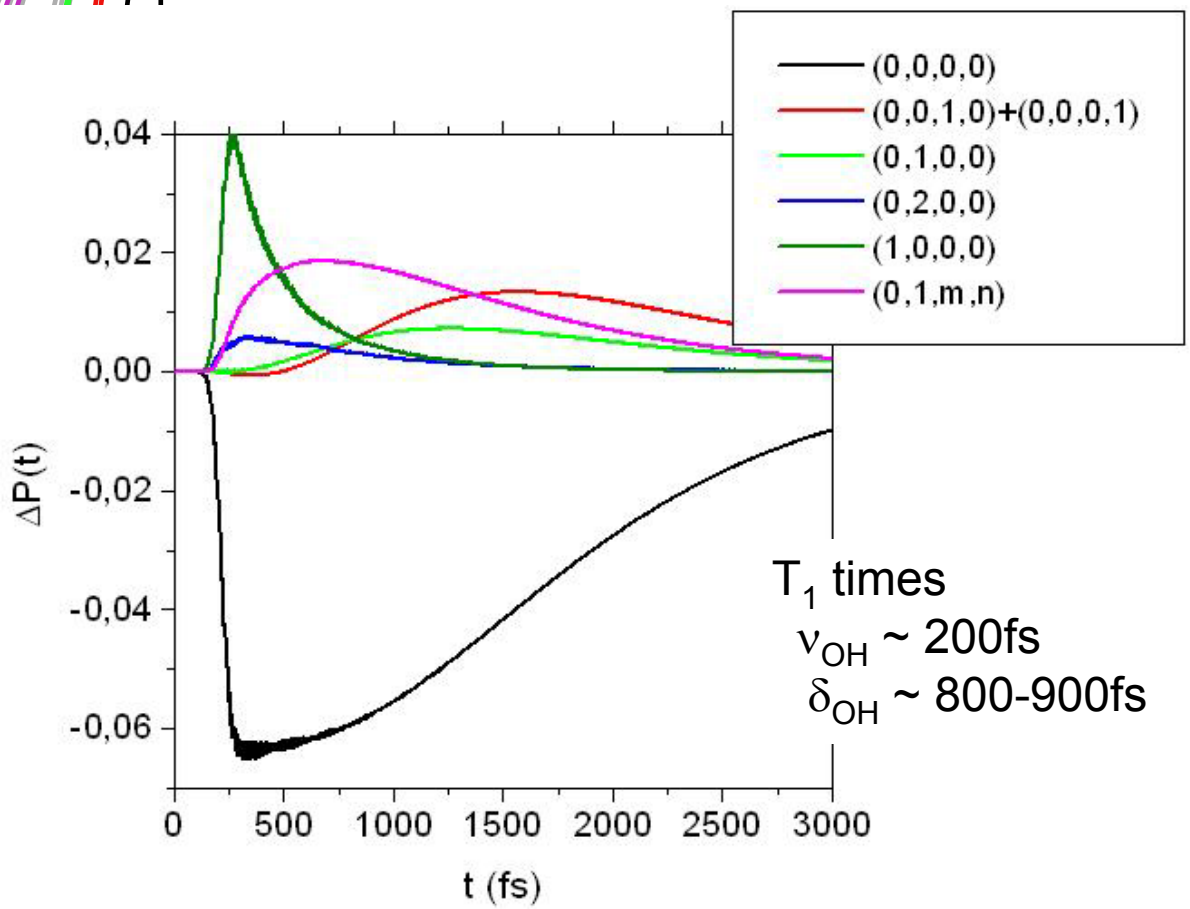
H. Naundorf, O.K. PCCP 5, 79 (2003)

OH-STRETCH RELAXATION



diabatic states

$(v_\nu, v_\delta, v_{\gamma_1}, v_{\gamma_2})$

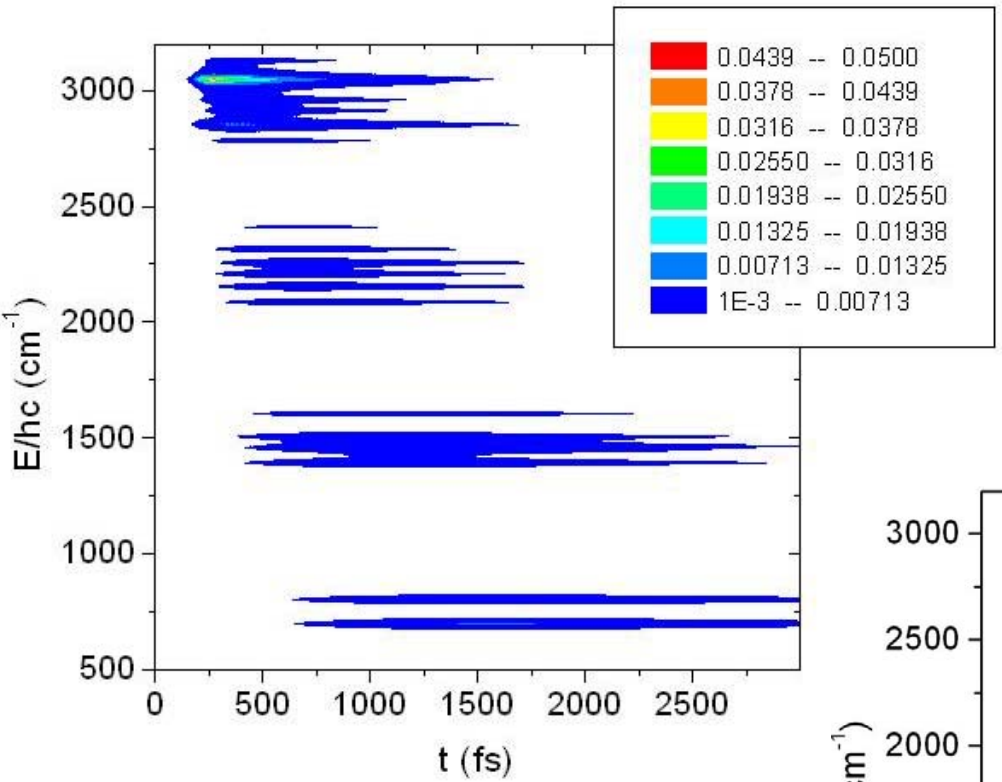


T_1 times

ν_{OH} ~ 200fs

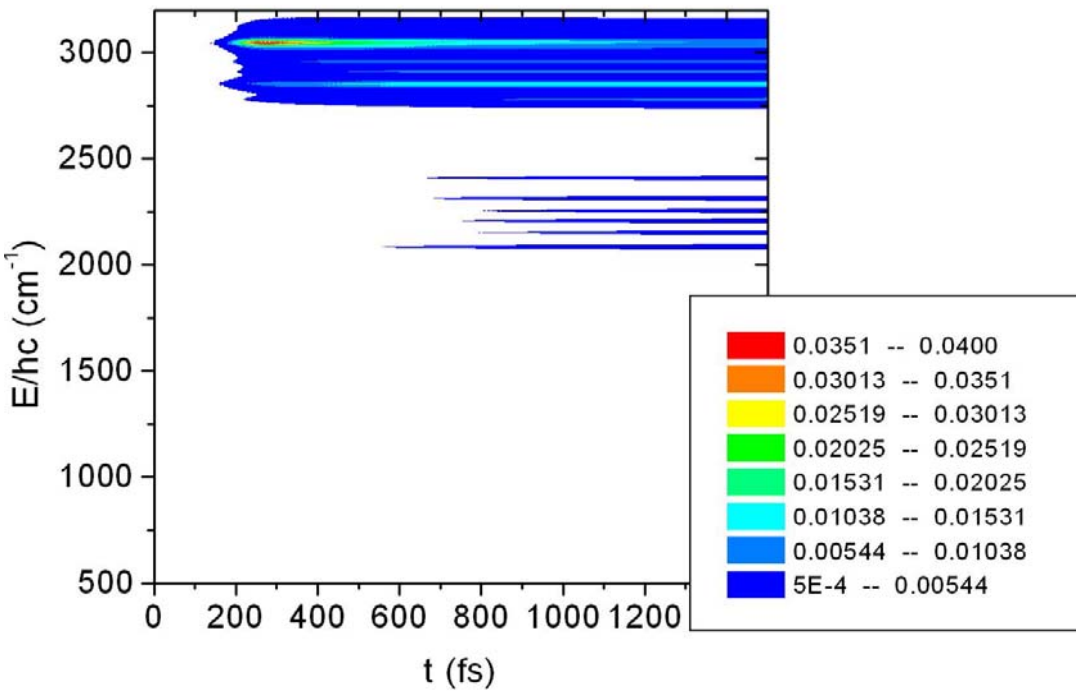
δ_{OH} ~ 800-900fs

RELAXATION MODELS

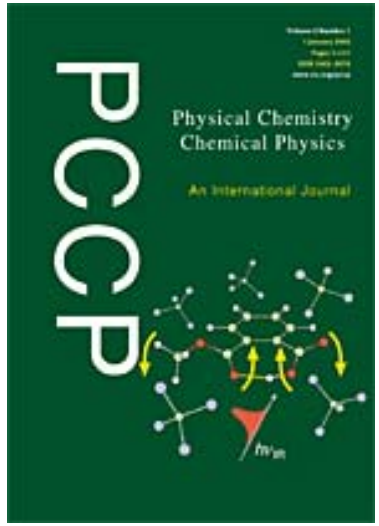


relaxation via bending modes

relaxation via HB-mode



SUMMARY



quantum chemistry

classical MD

Quantum Master Equation

vibrational relaxation pathways in H-bonds

nonlinear IR spectroscopy

OH-relaxation via in- and out-of-plane bendings

T_1 relaxation times

ν_{OH} ~ 200fs

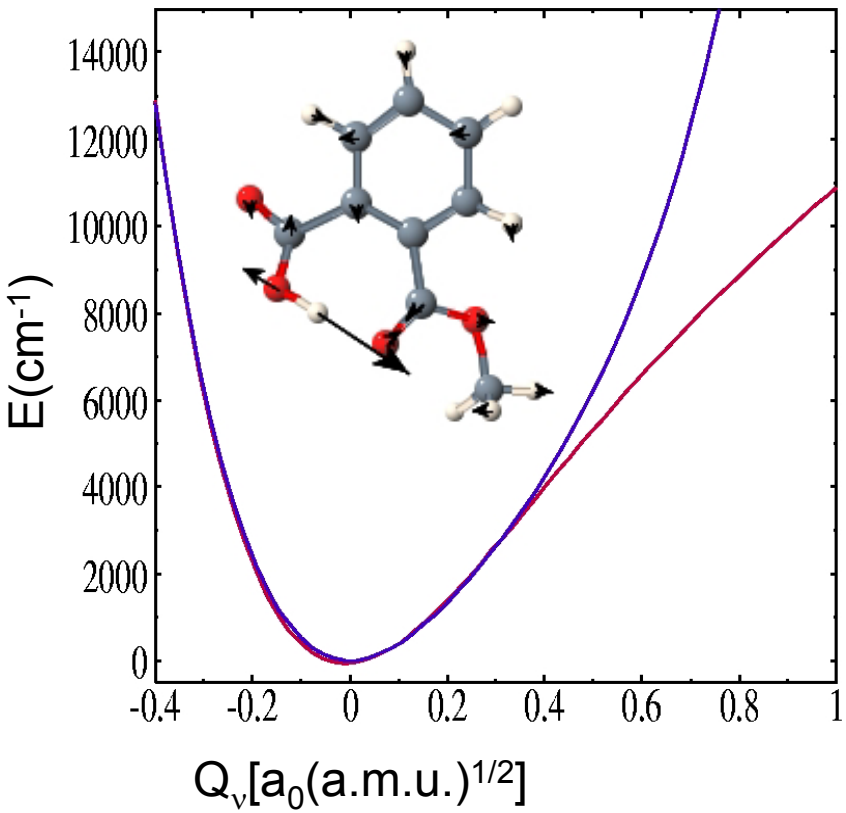
δ_{OH} ~ 800-900fs

ν_{HB} ~ 1.6ps

COHERENT WAVE PACKET MOTION

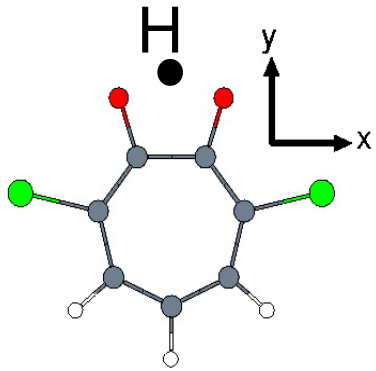
PMME: nonreactive

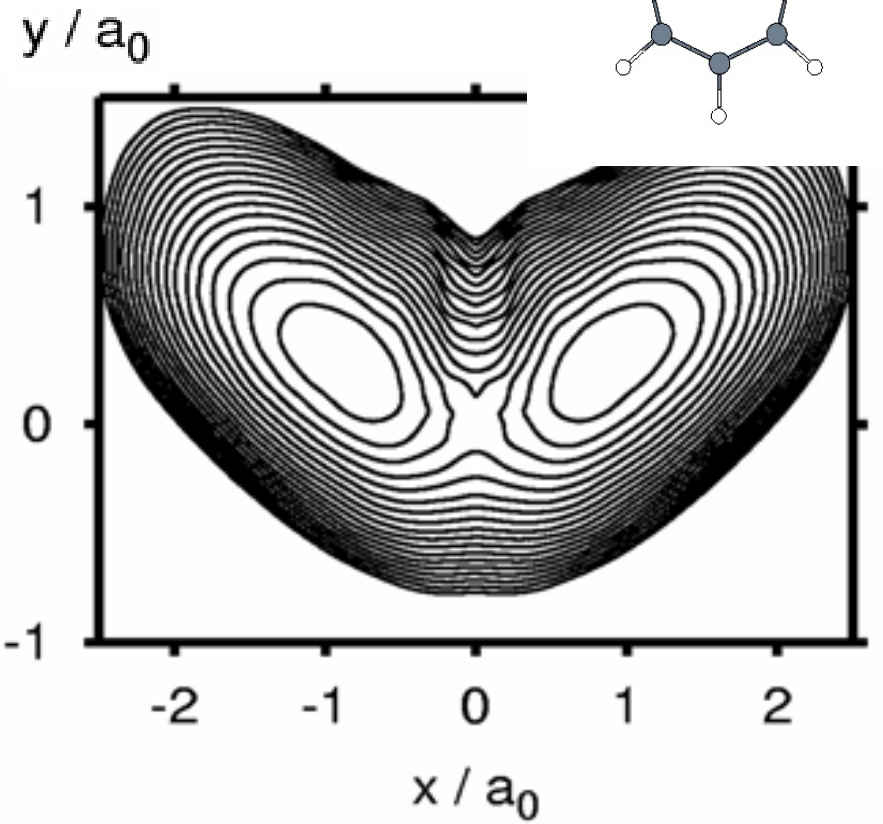
➢ moderate anharmonicity



Tropolone: reactive

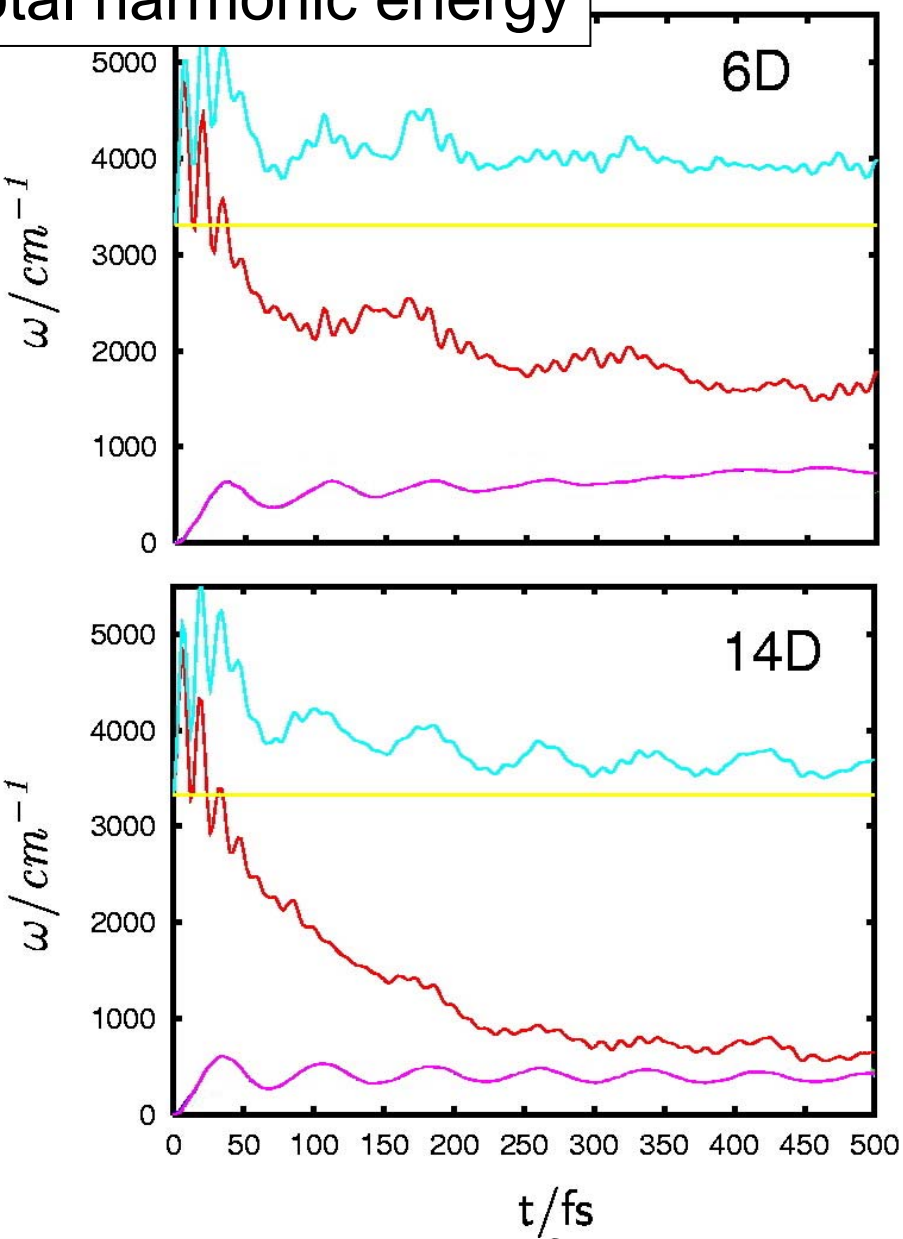
➢ strong anharmonicity



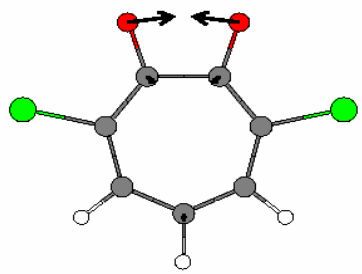


H-TRANSFER AND ENERGY FLOW

total harmonic energy



ω_{str}
ω_{as}
ω_{b}
ω_{sy}
harmonic
initial



quasi-coherent wave packet dynamics

K. Giese et al. JTCC 3, 567 (2004)

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