

Symmetry and the Entangled Ro-vibrational Quantum States of a Fluxional Molecule

Uwe Manthe
Theoretische Chemie
Universität Bielefeld

Introduction: rotations and vibrations

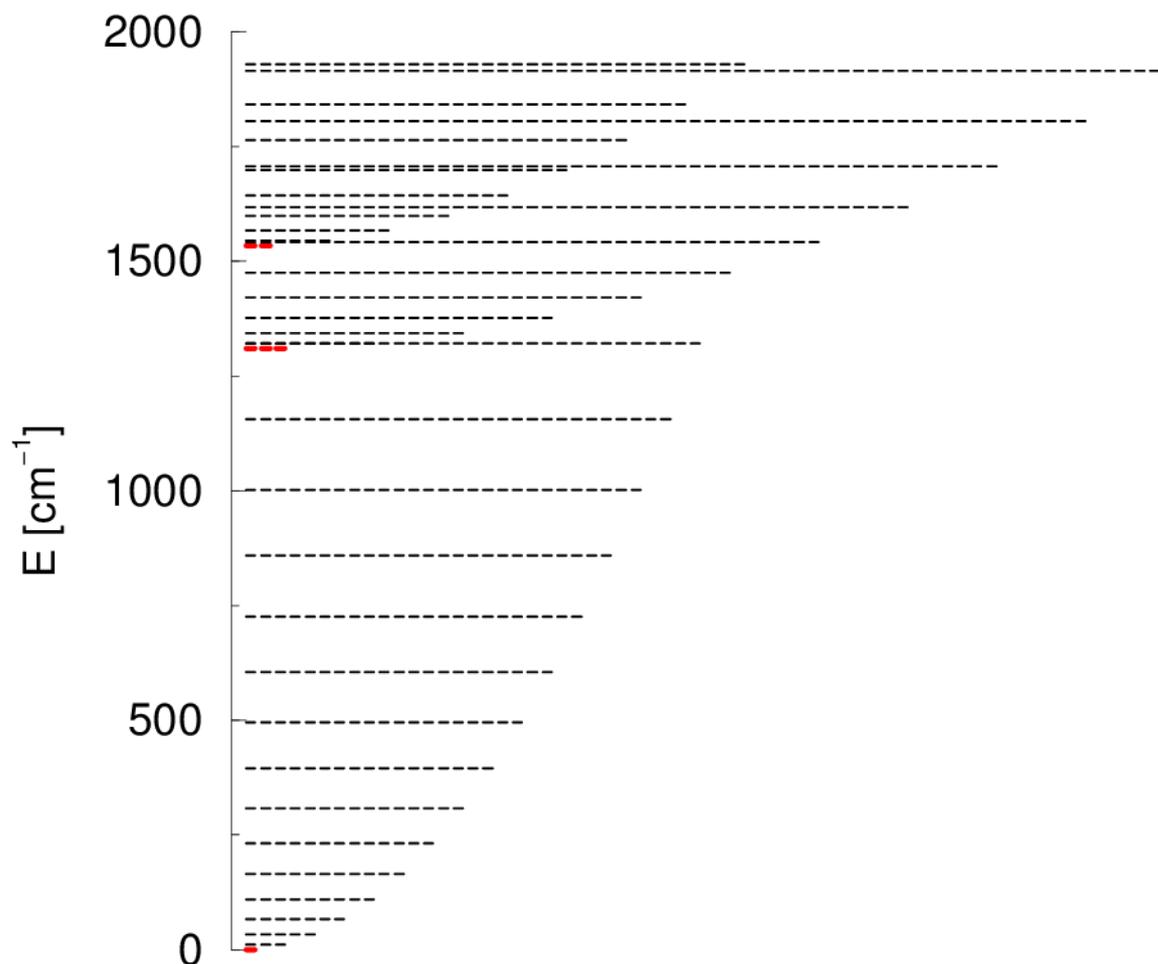
Quantum states of isolated molecules:
separation of rotation and vibration essential

Quantum states of CH_4

- vibrational states

- rotational and
ro-vibrational states

(rotational quantum number
 $M=0$ only)



Symmetry and the Entangled Ro-vibrational Quantum States of a Fluxional Molecule

Separation of rotation and vibrations

Molecular symmetry groups

Floppy molecules

The breakdown of separability: A_n and AB_n with $n > 4$

A prominent example: CH_5^+

Separation of rotation and vibrations

Vibrational motion is described by coordinates \mathbf{Q} in a body fixed frame

Rotational motion of the body fixed frame is described by the Euler angles α, β, γ

Rotational invariance of the Hamiltonian:

$$\Psi_{J,M}(\alpha, \beta, \gamma, \mathbf{Q}) = \sum_{K=-J}^J \sqrt{\frac{2J+1}{8\pi^2}} D_{MK}^J(\alpha, \beta, \gamma) \cdot \psi_{J,K}(\mathbf{Q})$$

$D_{MK}^J(\alpha, \beta, \gamma)$: Wigner rotation matrices

Separability of rotational and vibrational motion:

$$\Psi_{J,M}(\alpha, \beta, \gamma, \mathbf{Q}) = \left(\sum_{K=-J}^J \sqrt{\frac{2J+1}{8\pi^2}} D_{MK}^J(\alpha, \beta, \gamma) \cdot c_{J,K} \right) \cdot \psi(\mathbf{Q})$$

$\psi(\mathbf{Q})$: vibrational wavefunction

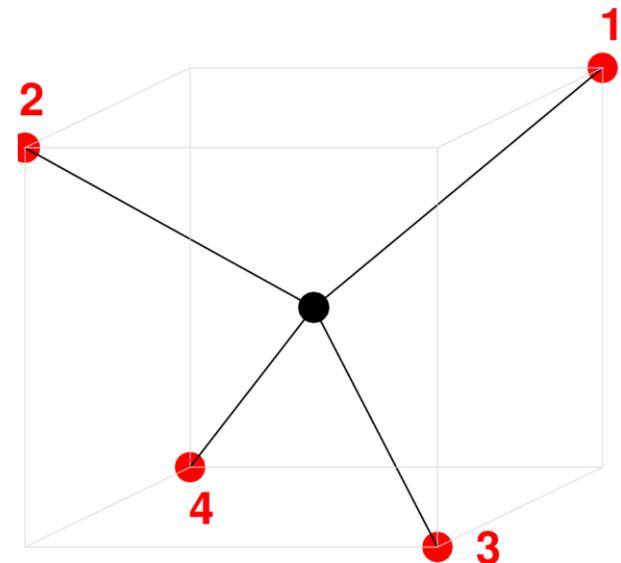
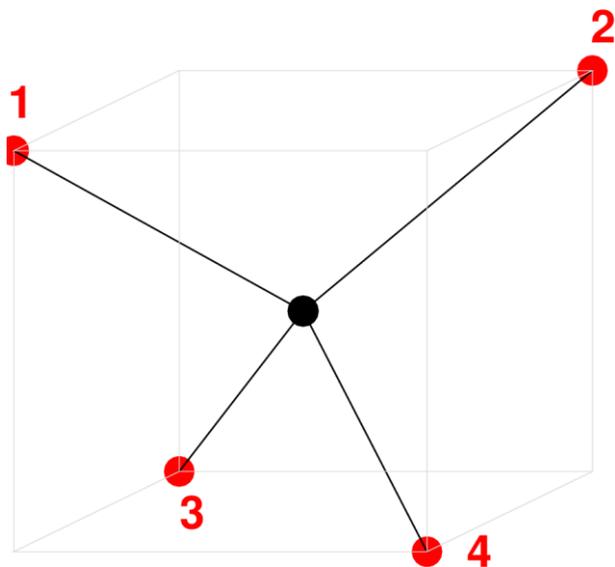
Molecular symmetry groups

Hamiltonian invariant with respect to **inversion** and **permutation of identical atoms**

Rigid or semirigid molecules:
permutation-inversion symmetry mapped on point groups,
vibrational wavefunctions transform according to the irreducible representations of the point group

Identical atoms used in the definition of the body fixed frame
→ permutations affect rotational wavefunctions

Permutations are mapped on equivalent rotations



Floppy molecules

Molecules showing long range motion:
identical nuclei can dynamically exchange their positions
→ feasible permutations (and inversion)

Separation of rotational and vibrational motion:

$$\Psi(\alpha, \beta, \gamma, \mathbf{Q}) \approx \psi_{rot}(\alpha, \beta, \gamma) \cdot \psi_{vib}(\mathbf{Q})$$

Vibrational wavefunction transforms according to the group of feasible permutations (and inversion).

Rotational wavefunction transforms according to the rotation group $SO(3)$.

It must also transform according to the group of feasible permutations which affect the definition of the body fixed frame (→ equivalent rotations).

The breakdown of separability: A_n and AB_n with $n > 4$

All permutation dynamically feasible

and relevant for the definition of the body fixed frame:

A_3 , AB_3 : S_3 isomorphic to C_{3v} (\rightarrow subgroup of SO_3), **triangle**

A_4 , AB_4 : S_4 isomorphic to T_d (\rightarrow subgroup of SO_3), **tetrahedron**

A_5 , AB_5 : S_5 not isomorphic to any subgroup of SO_3

... (analogous for all $n > 4$)

\rightarrow rotational wavefunction of correct symmetry can not exist

\rightarrow breakdown of separability of rotational and vibrational motion

A prominent example: CH_5^+

PES with 120 symmetry-equivalent minima separated by tiny barriers

→ delocalized quantum states

PES by Brown et al.

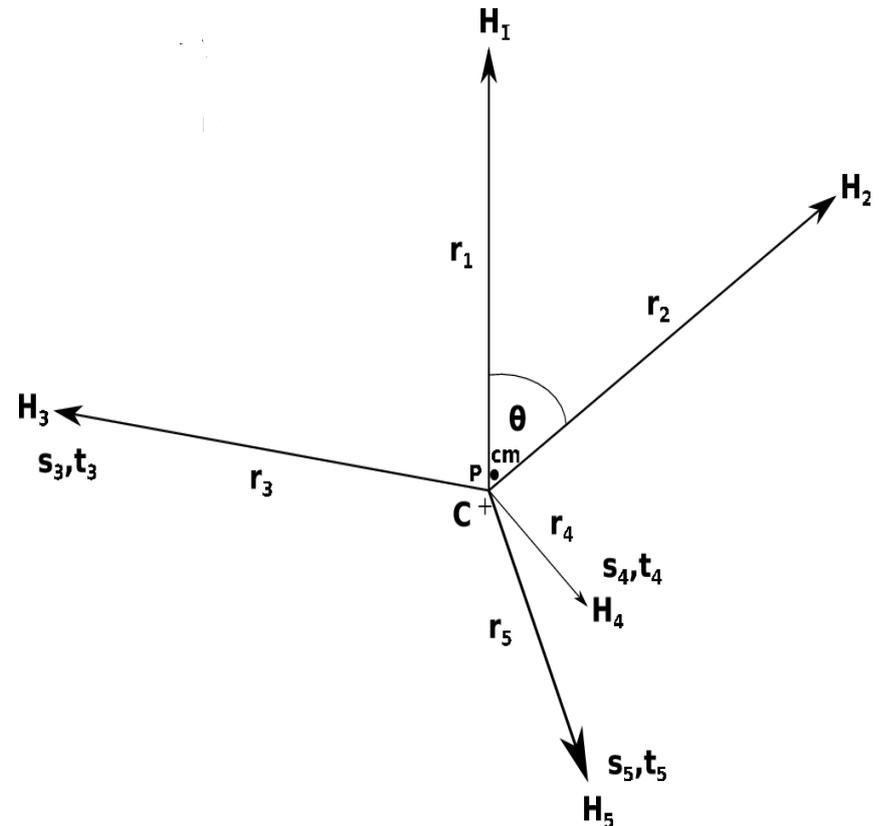
MCTDH calculations:

iterative diagonalization approach

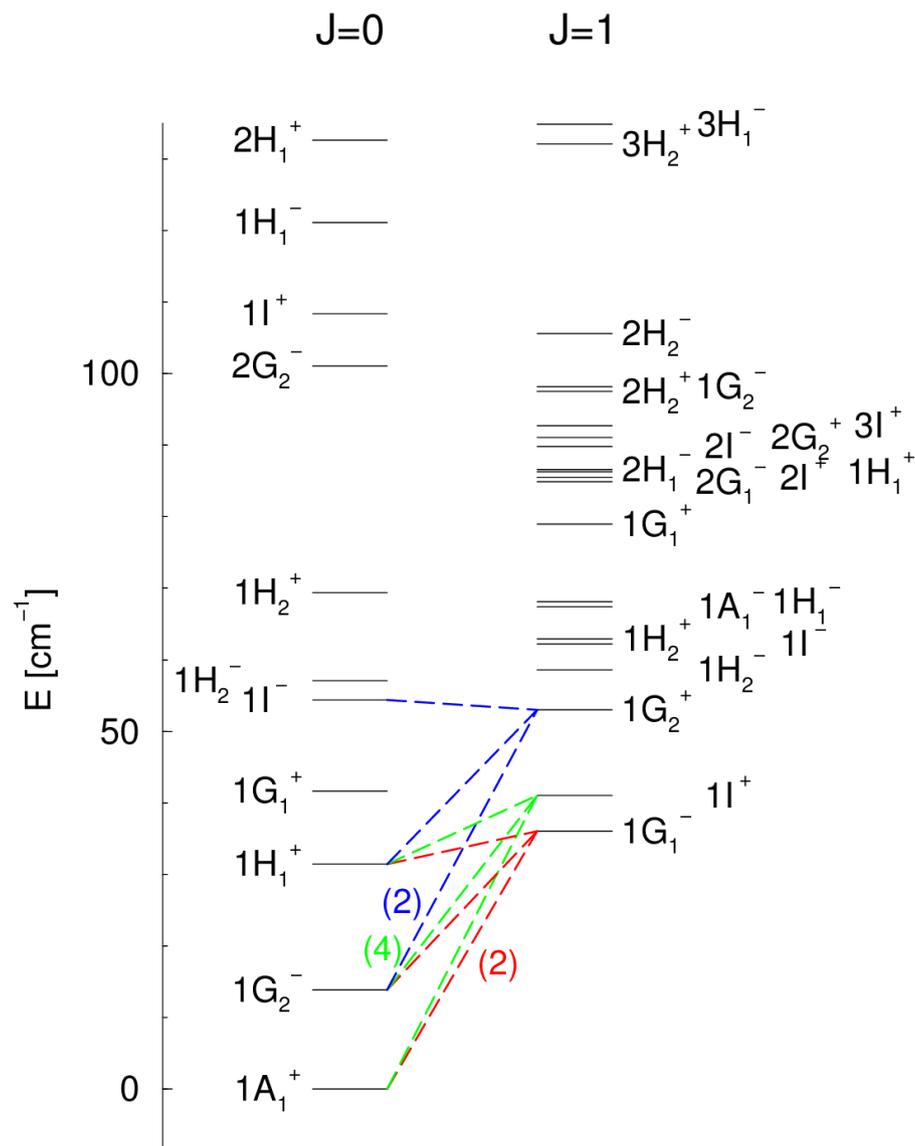
adapted to multi-well systems,

explicit symmetrization

(incompletely converged)



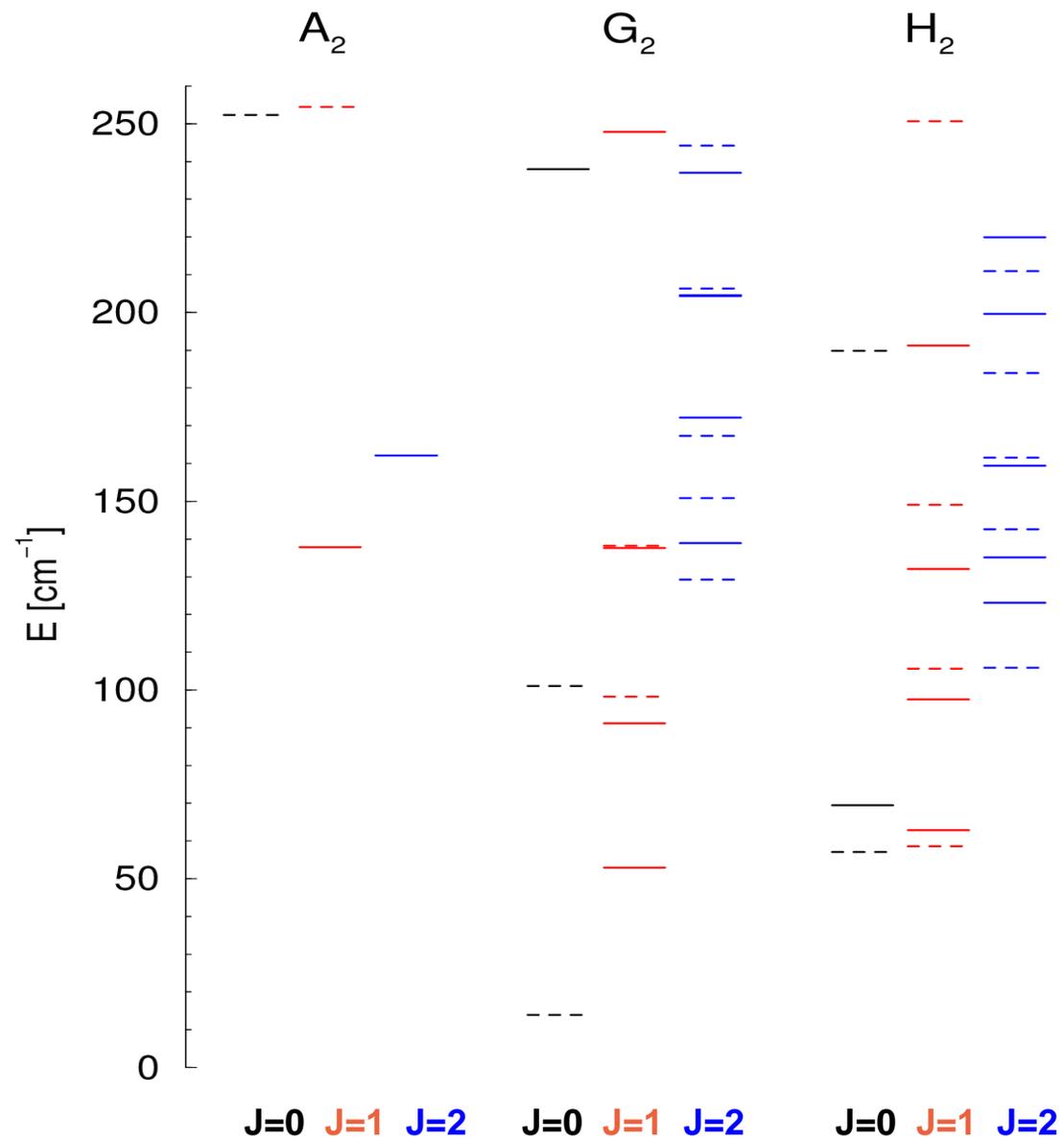
Ro-vibrational states of CH_5^+



numerical result:
 contributions from a small
 number of vibrational states
 dominate in the wavefunctions

Symmetry?

Pauli-allowed ro-vibrational states of CH_5^+



Thanks

Robert Wodraszka

Roman Ellerbrock, Daniela Schäpers, Tim Lenzen, Ralph Welsch

Wolfgang Eisfeld (Bielefeld)

Juliana Palma (Quilmes)

Alexandra Viel (Rennes)

Fermin Huarte (Barcelona)

Gunnar Nyman (Göteborg)

Finanical Support:

DFG, AvH, Univ. Bielefeld