Generalized Critical Points Analysis of Acetylene Vibrational Dynamics

Ph. D. Oral Defense

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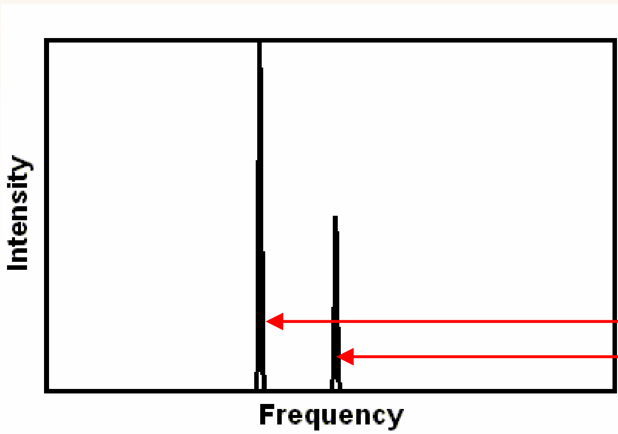
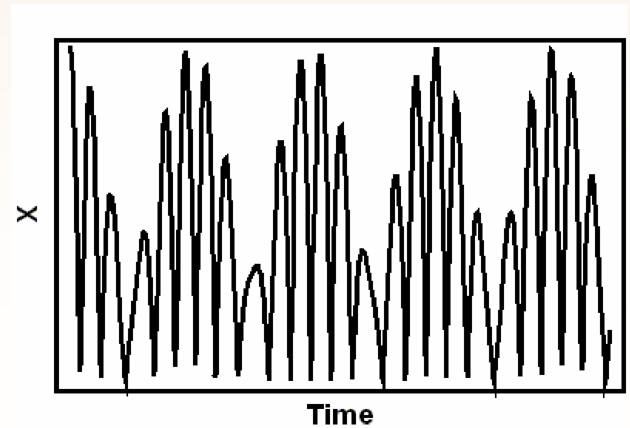
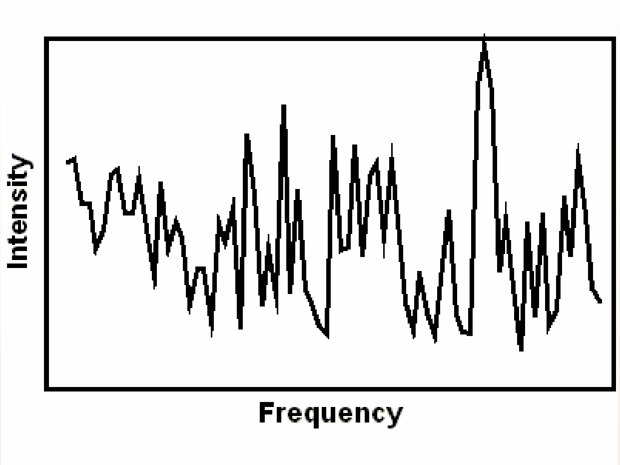
Molecular Spectra and Vibrations

Spectra $\xrightarrow{\mathcal{F}^{-1}}$ **Dynamics**

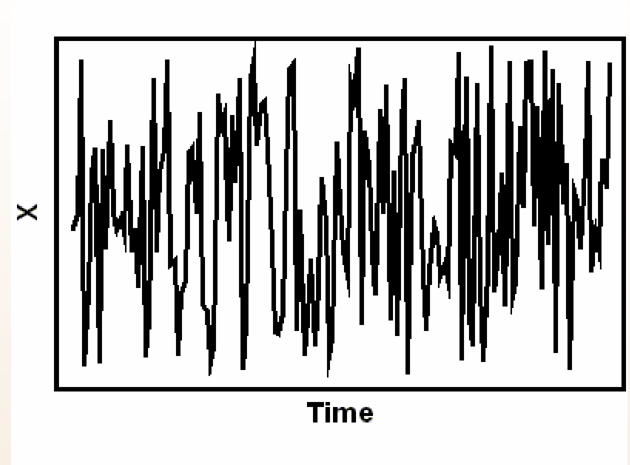


Regular spectrum: motion can be decomposed into periodic oscillations (modes)

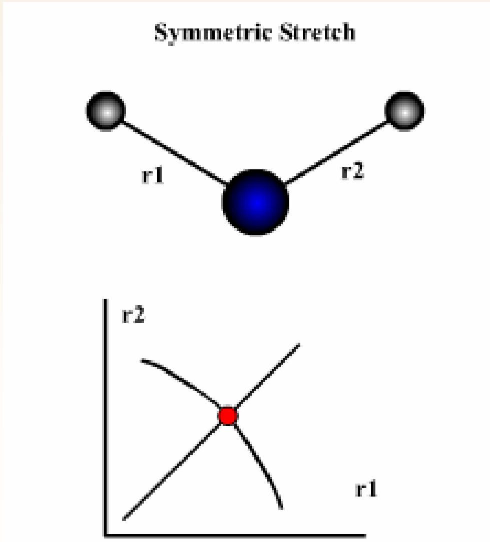


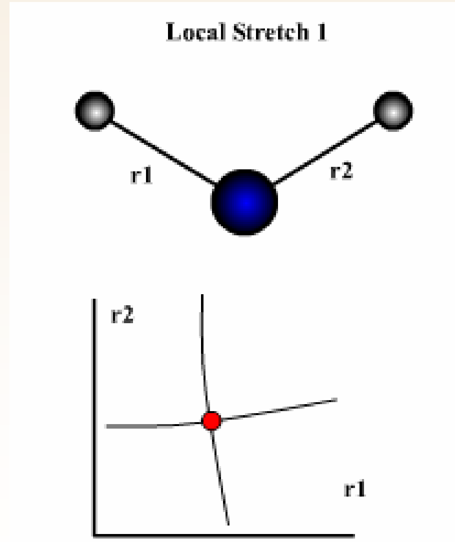


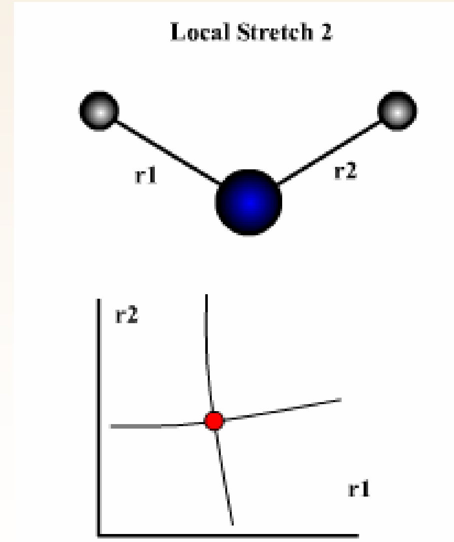
Irregular spectrum: motion is completely random



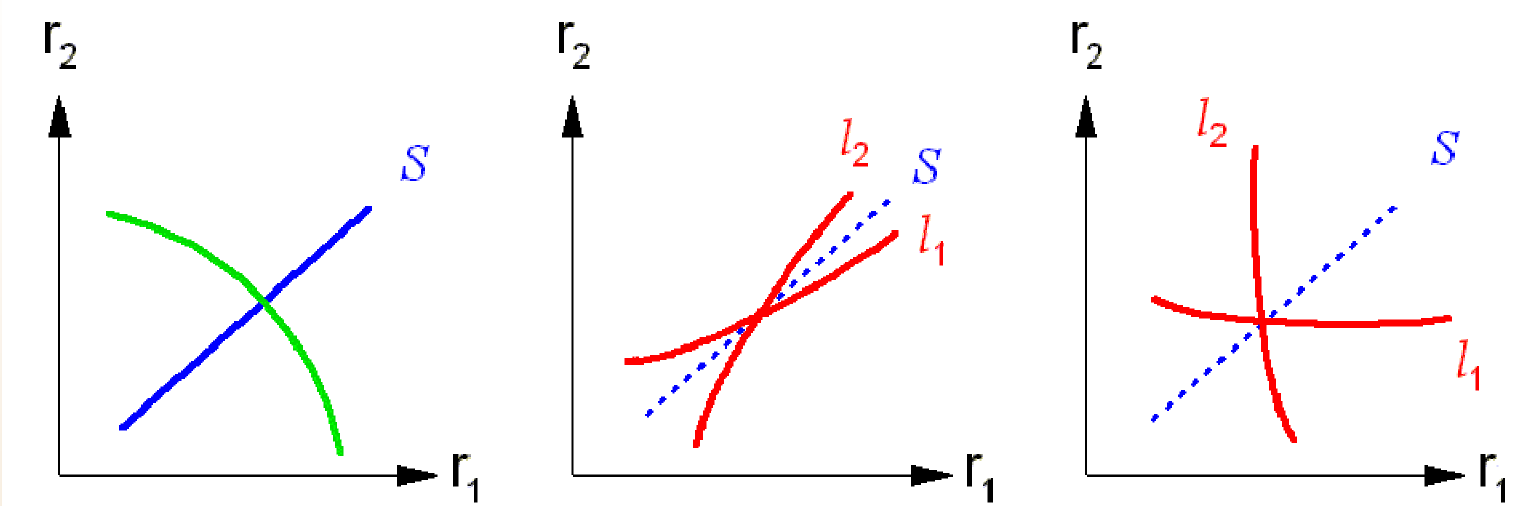
Modes of Vibration







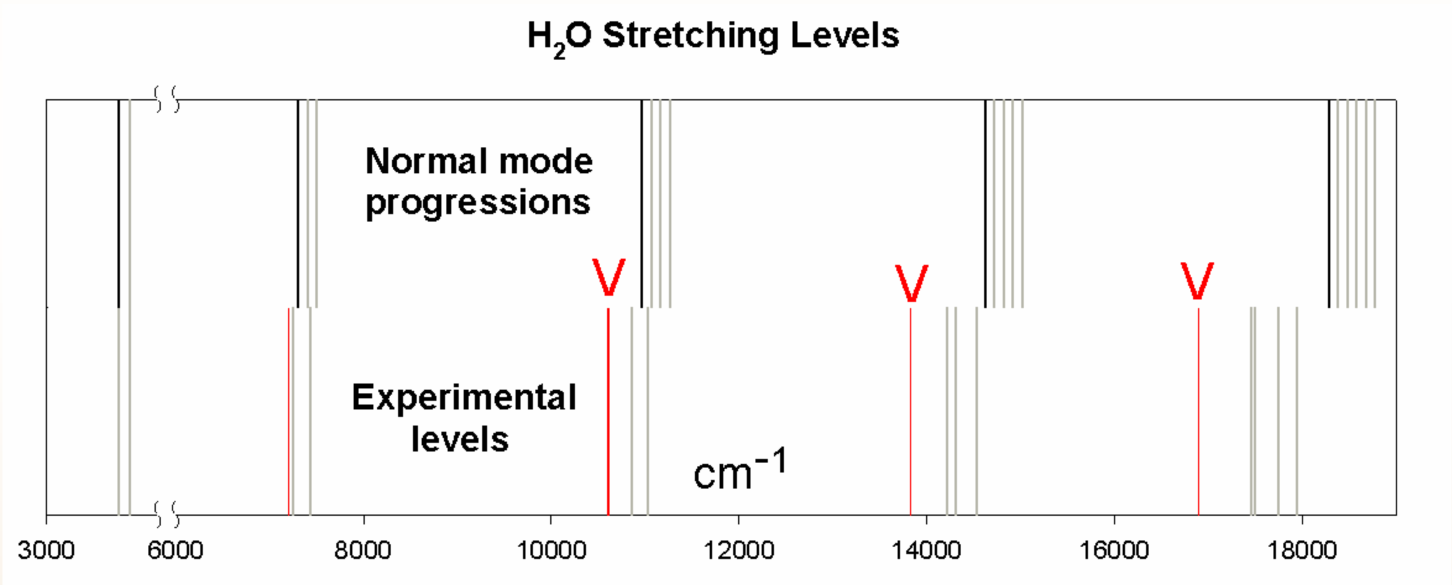
Normal → Local Transition (Bifurcation)



Our Research

A. **Vibrational modes are important for characterizing the molecular dynamics.**

B. **Bifurcations of these modes reflect qualitative changes in both dynamics and spectral patterns.**

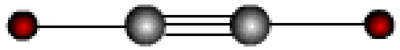


C. **We extract the modes and their bifurcations from the effective Hamiltonian (H_{eff}), obtained from fitting the spectra.**

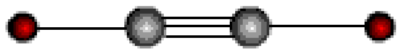
C_2H_2 Pure Bending Spectra

Normal mode zero-order states: $|n_4^{l_4}, n_5^{l_5} >$

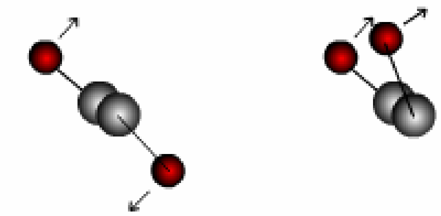
n4: Trans bend



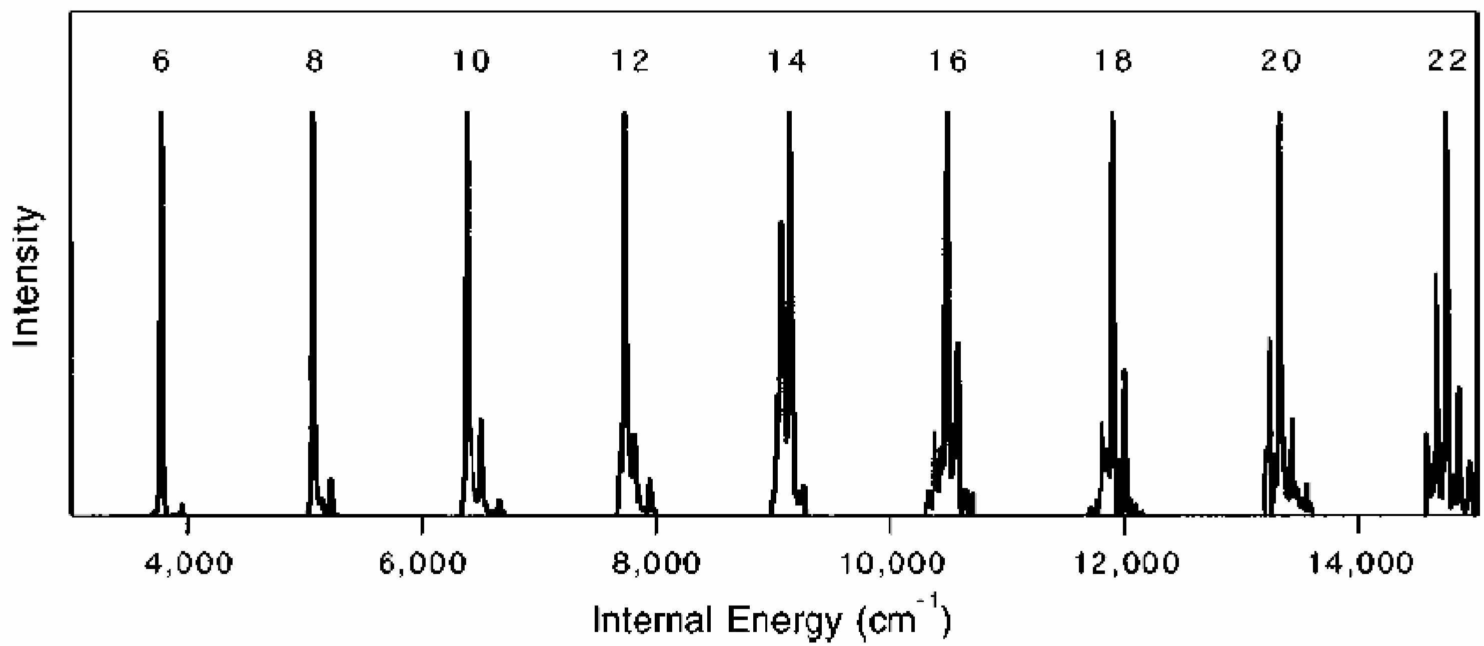
n5. Cis bend



Vibrational angular momenta l4, l5



Dispersed Fluorescence spectrum recorded by Field *et al.*
Resolved into "clumps" (polyads)



Quantum Effective Hamiltonian

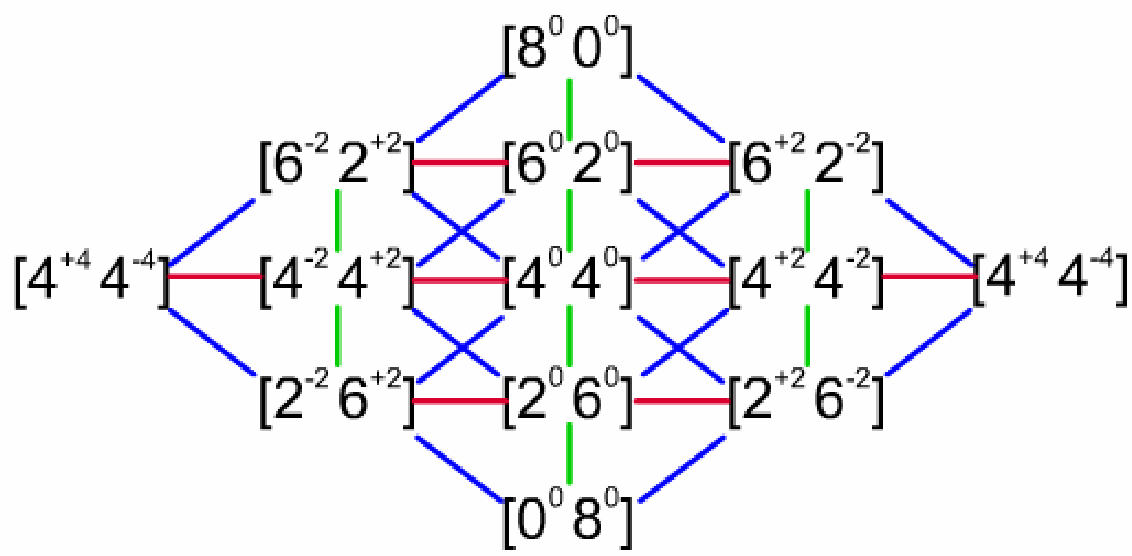
Ground electronic state (S_0)
Vibrational part only:

$$H_{bend} = H_0 + V_{DDI} + V_{l} + V_{DDII}$$

$$H_0 = \sum_{4,5} \omega_i n_i + \sum_{4,5} x_{ij}\, n_i\, n_j + \sum_{4,5} y_{ijk}\, n_i\, n_j\, n_k + \sum_{4,5} g_{ij}\, l_i\, l_j$$

Polyad {8, 0}^{g}

$$[n_4^{l_4}\; n_5^{l_5}]$$



V_{DDI} (green line)
V_{l} (red line)
V_{DDII} (blue line)

2 polyad numbers:

$$\{N_b, l\}^{g/u} = \{n_4+n_5,\; l_4+l_5\}^{g/u}$$

Only states with the same polyad numbers are coupled.

Classical Hamiltonian

- **Heisenberg's Correspondence Principle:**

$a_i^+ \rightarrow I_i^{1/2}\exp[i\phi_i]$
$a_i \rightarrow I_i^{1/2}\exp[-i\phi_i]$ → $H_{bend}(I_i, \phi_i)$ i=4d, 4g, 5d, 5g

- **New canonical variables**

Trivial: $(K_a, \theta_a, K_b, \theta_b)$

$K_a=(N_b+2)/2$ $K_b=l/2$: constants of motion. θ_a, θ_b : cyclic angles

Nontrivial: $(J_a, \psi_a, J_b, \psi_b)$ $J_a=(n_4-n_5)/2$ $J_b=(l_4-l_5)/2$

- **Simplified Classical Hamiltonian**

$$H_{bend}(K_a, K_b, J_a, J_b, \psi_a, \psi_b)$$

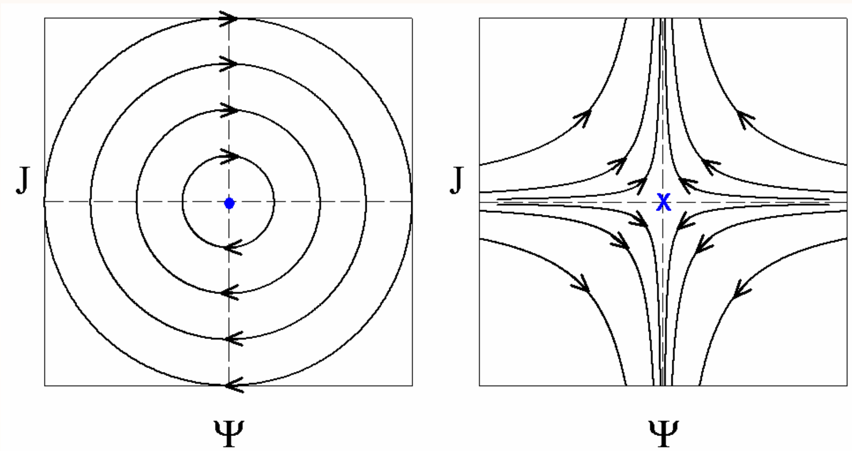
- **Equations of motion in reduced phase space**

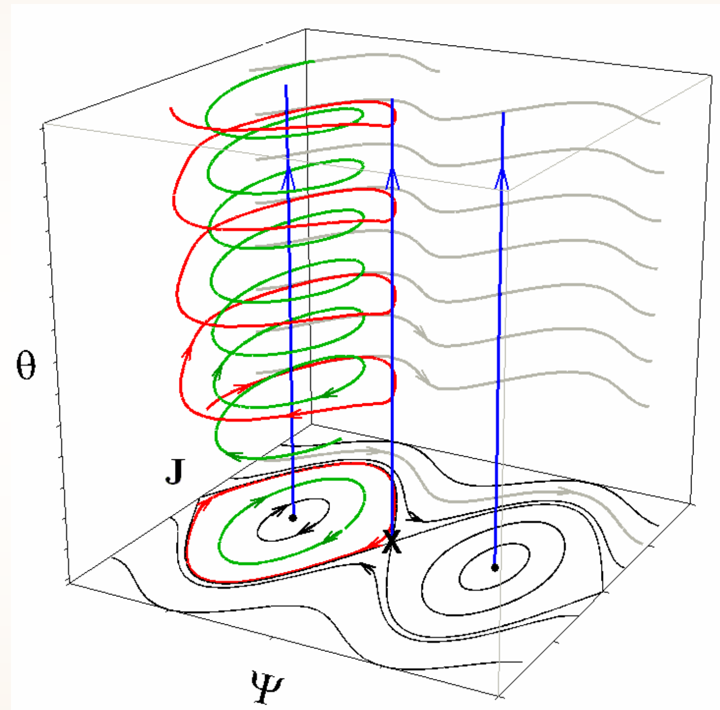
$$\dot{\psi}_i = \frac{d\psi_i}{dt} = \frac{\partial H_{bend}}{\partial J_i}, \quad \dot{J}_i = \frac{dJ_i}{dt} = -\frac{\partial H_{bend}}{\partial \psi_i}$$

- **Flow in the reduced phase space is organized by critical points.**

$$\dot{J}_i = \dot{\psi}_i = \frac{\partial H_{bend}}{\partial \psi_i} = \frac{\partial H_{bend}}{\partial J_i} = 0$$

Stable (Elliptic) | Unstable (Hyperbolic)





- **In the full phase space, the critical points move along the cyclic angle (s) θ_i.**

- **Near a stable critical point, trajectories can be decomposed into periodic oscillations → vibrational modes.**

Critical Points in $\{N_b, 0\}$ Polyads

Solving 4 simultaneous equations
for <u>continuously</u> varying K_a (N_b) values:

$$\frac{\partial H_{bend}}{\partial J_a} = \frac{\partial H_{bend}}{\partial J_b} = \frac{\partial H_{bend}}{\partial \Psi_a} = \frac{\partial H_{bend}}{\partial \Psi_b} = 0$$

(1) (2) (3) (4)

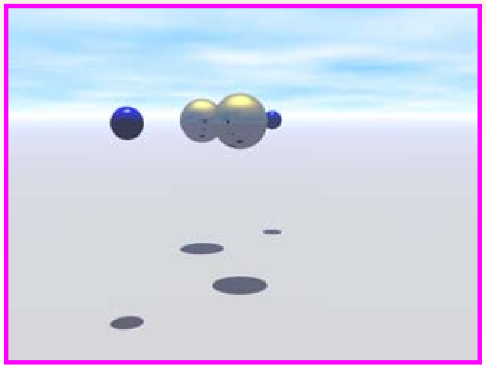
From (3), (4):	$(\psi_a, \psi_b) = (0, 0), (0, \pi/2), (\pi/2, 0), (\pi/2, \pi/2)$
From (2):	$J_b = 0$
From (1):	$J_a (K_a, \psi_a, \psi_b)$

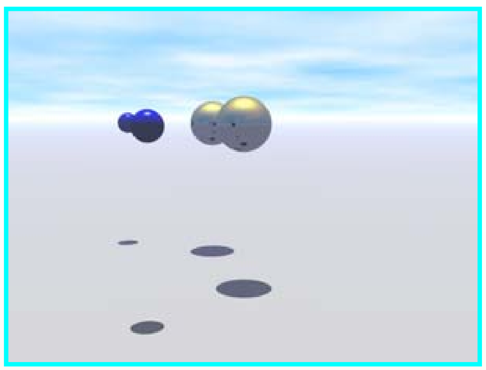
These critical points are periodic orbits in the full phase space since

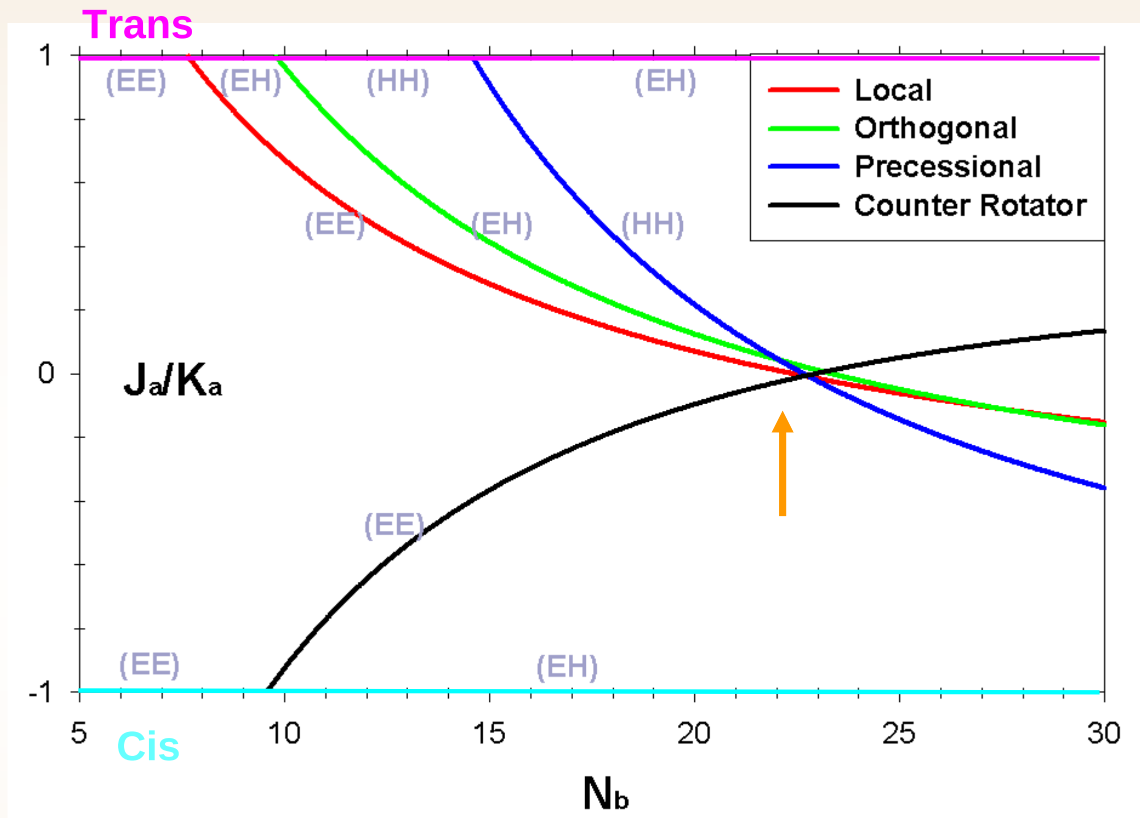
$$\dot{\theta}_a \neq 0 \qquad \dot{\theta}_b = 0$$

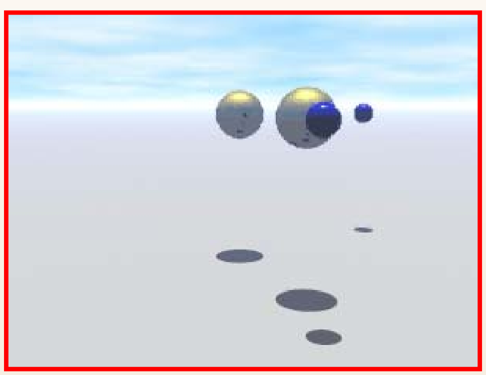
Results for $\{N_b, 0\}$ Polyads

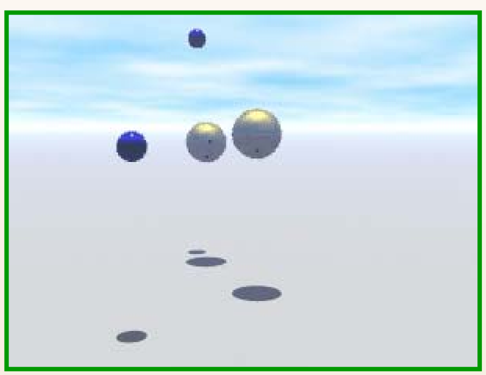
(Click on each picture to see the animation.)

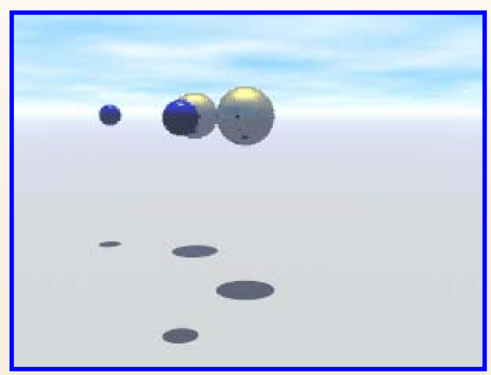


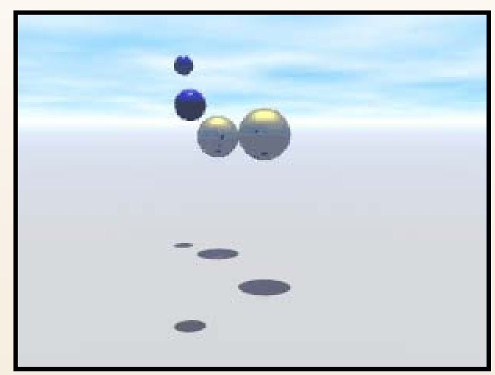








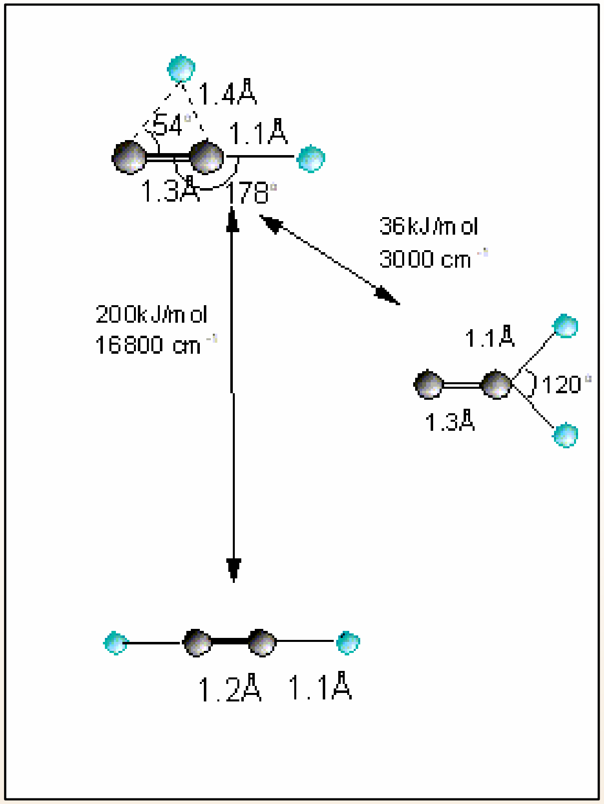




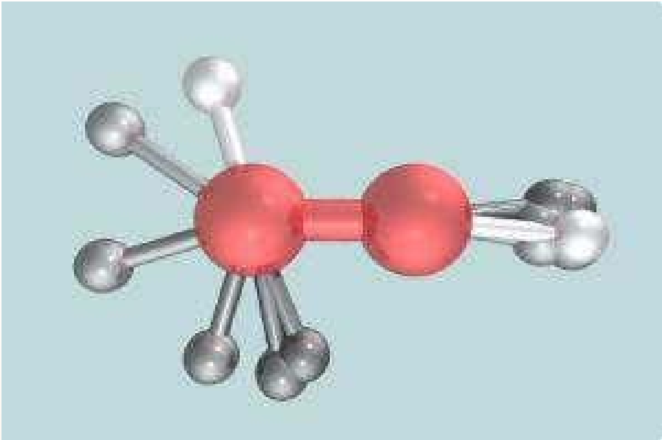
Acetylene-Vinylidene Isomerization

Long-living vinylidene observed in acetylene-vinylidene system

= “local mode” inferred from acetylene H_{eff}?



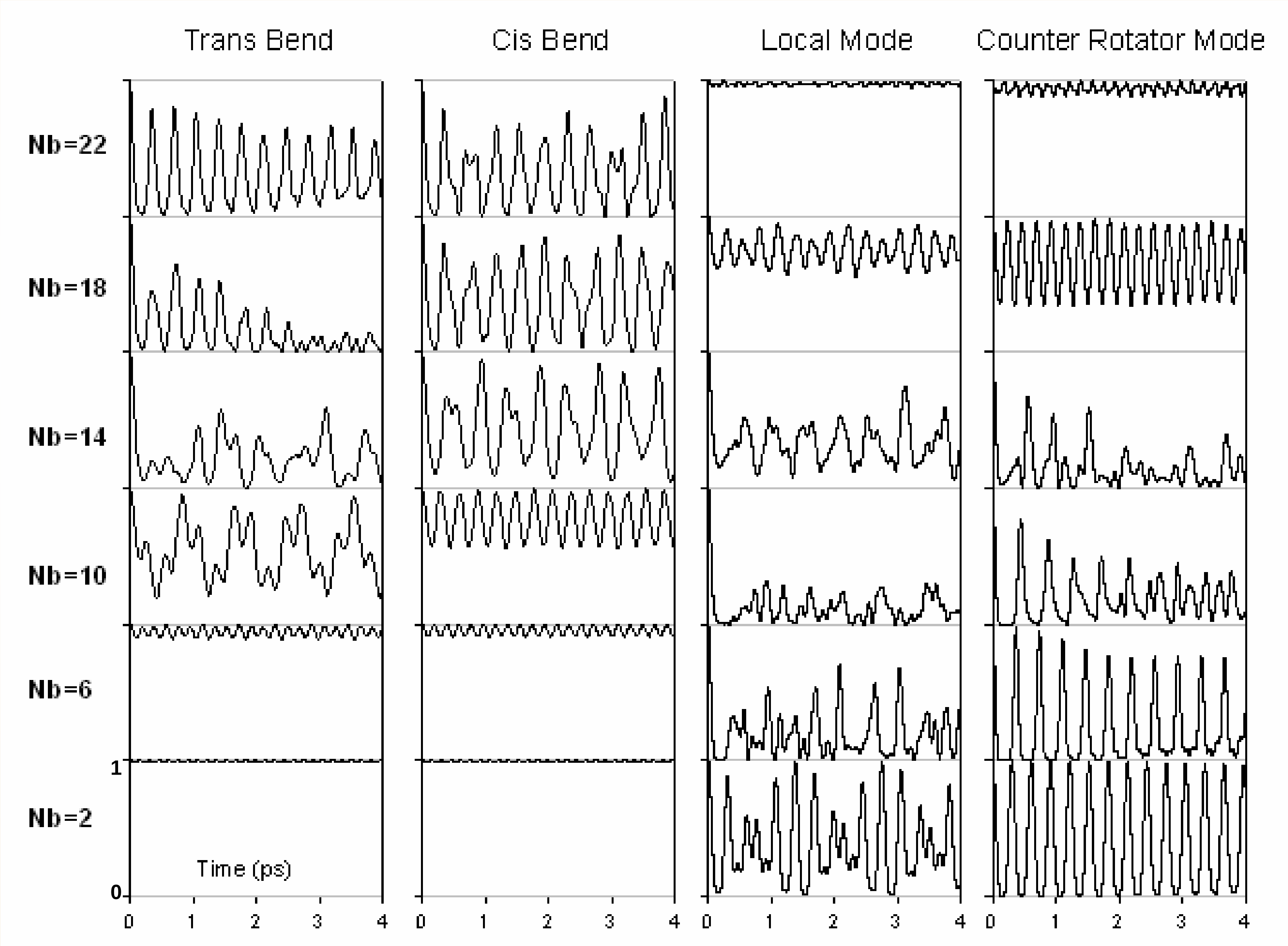
(Click on the picture to see the animation.)



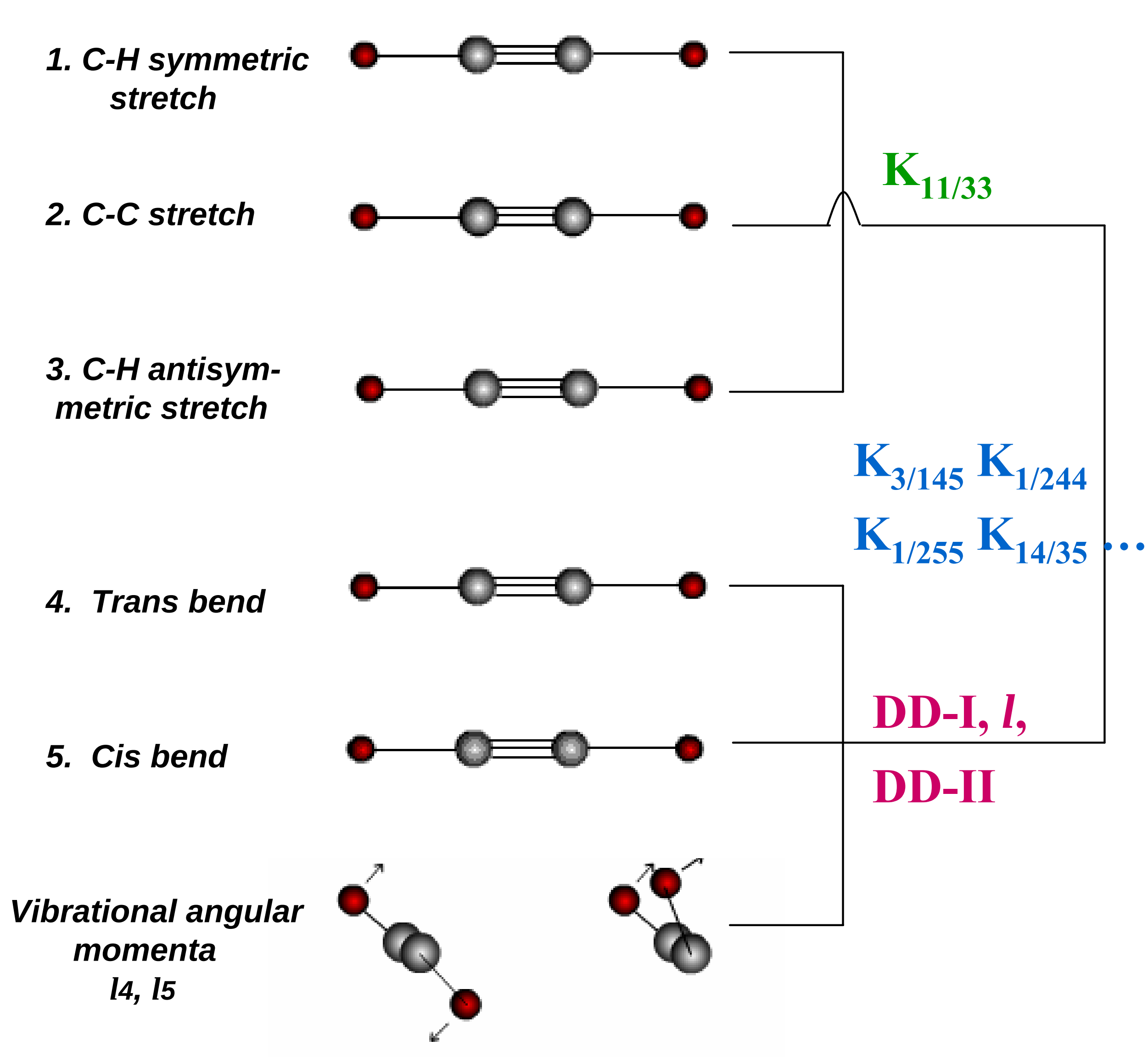
From Carter et al. @ UCLA

Quantum Survival Probability

$$P(t) = |\langle\Psi_{(t)}|\Psi_{(0)}\rangle|^2$$



C_2H_2 Stretch-Bend System



$\omega_1 : \omega_2 : \omega_3 : \omega_4 : \omega_5$

$= 3372:1975:3289:608:729$

$\sim 5:3:5:1:1$

3 polyad numbers:

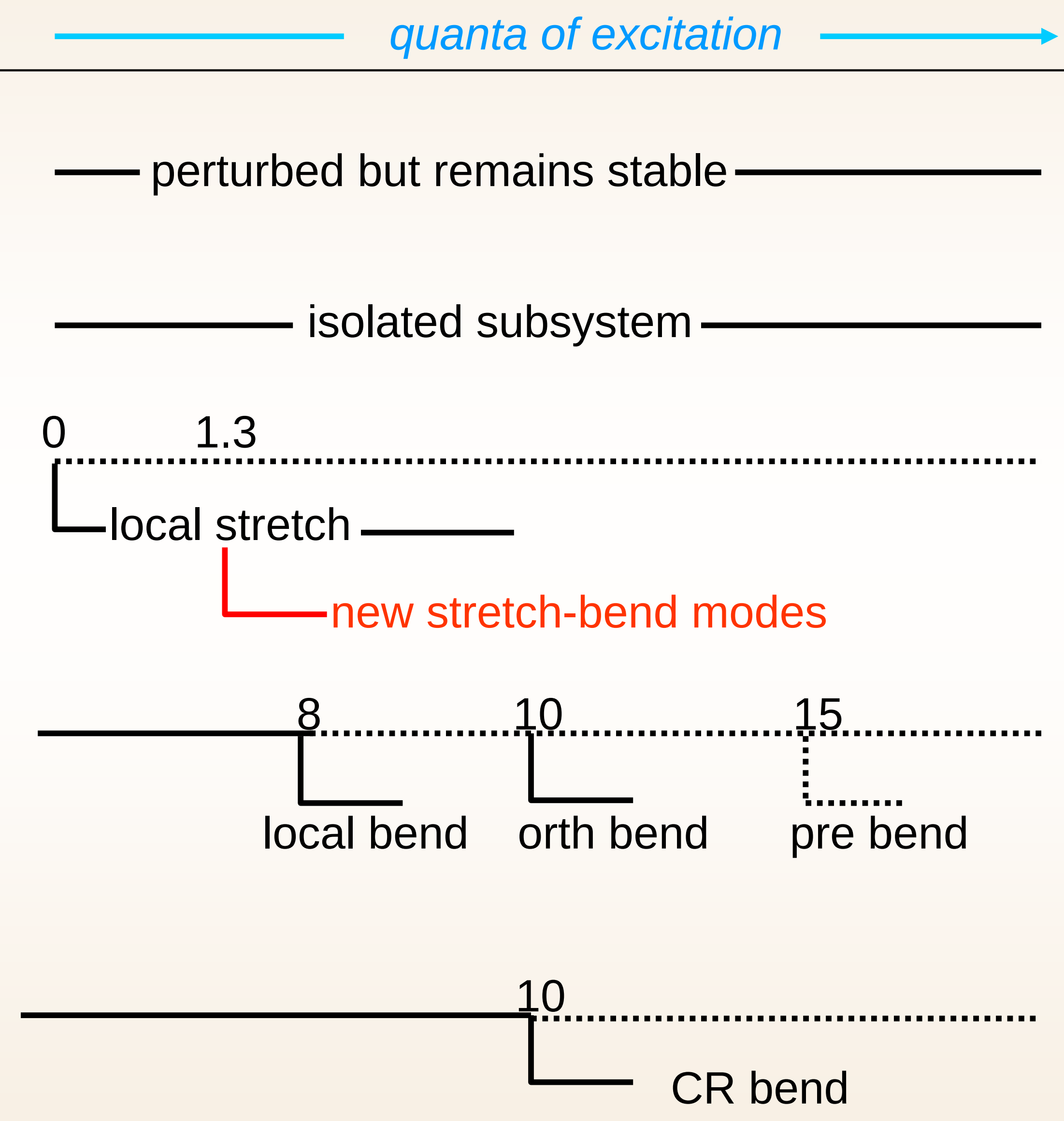
$N_{tot} = 5n_1+3n_2+5n_3+n_4+n_5$

$N_s = n_1+n_2+n_3$

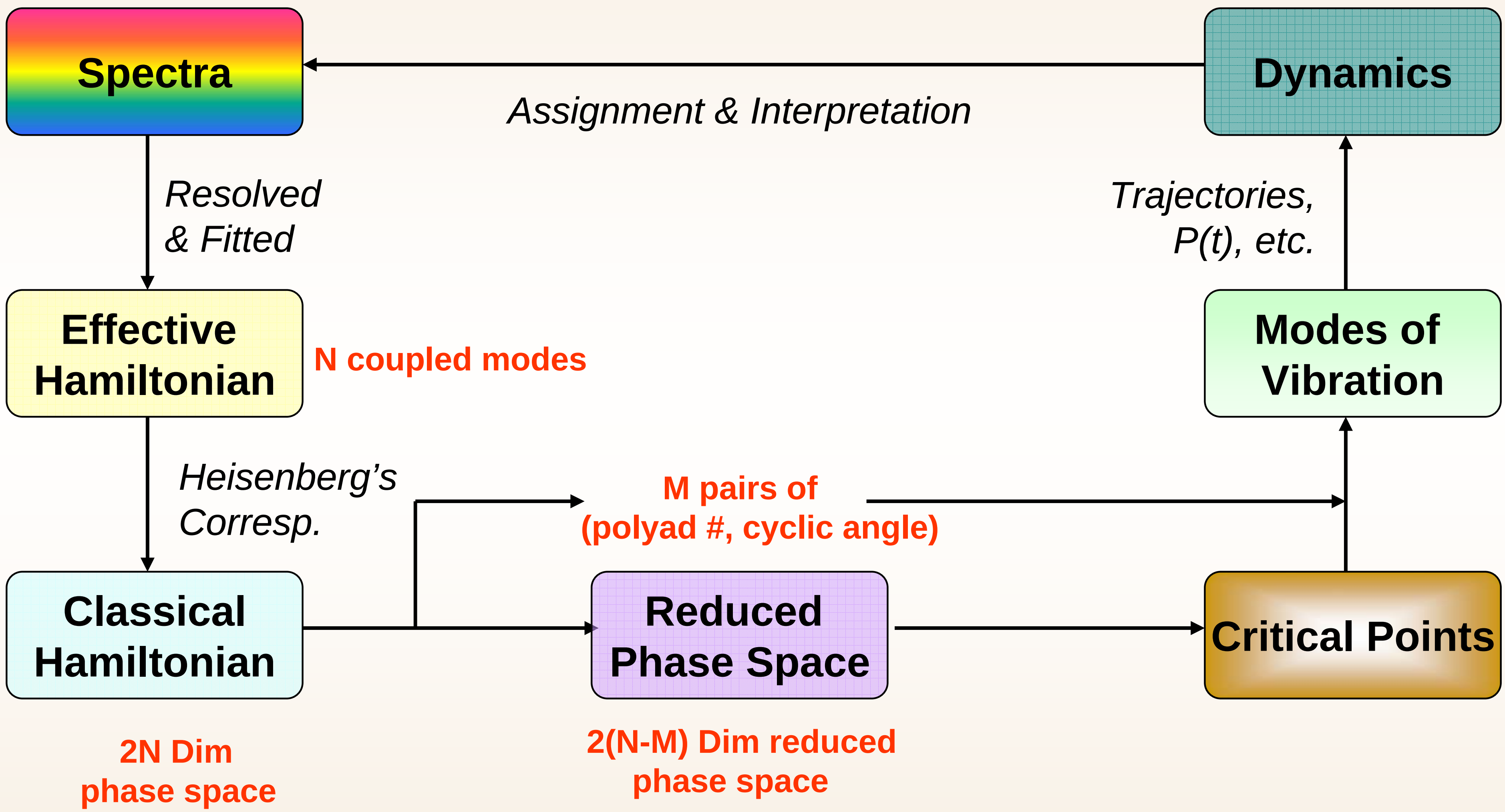
$l = l_4+l_5$

Fate of 5 Normal Modes

1. C-H symmetric stretch	$\|n_1, 0, 0, 0^0, 0^0\rangle$
2. C-C stretch	$\|0, n_2, 0, 0^0, 0^0\rangle$
3. C-H antisym-metric stretch	$\|0, 0, n_3, 0^0, 0^0\rangle$
4. Trans bend	$\|0, 0, 0, n_4^0, 0^0\rangle$
5. Cis bend	$\|0, 0, 0, 0^0, n_5^0\rangle$



Generalized Critical Points Analysis



Advantages of Our Method

A. H_{eff} vs molecular potential energy surface (PES)

- Current limitations in *ab initio* calculation
- Polyad numbers

B. Analytic detection of critical points

- Solvable regardless of stability
- Scales linearly with dimensionality
- Does not rely exclusively on visualization
- Considers multiple interacting resonances

C. Efficiency of the method

- Simple & gives an overview of the features
- Starting point for further exploration of the dynamics

Future Work

A. **Full analysis of the stretch-bend dynamics of C_2H_2**

Overtones → All combinational states

B. **Other systems: C_2H_2 isotopomers, CH_4, CH_2O …**

Effective Hamiltonians with multiple polyad numbers

C. **Effect of polyad breaking terms**

Important at high energy, esp. near a reaction barrier

Acknowledgements

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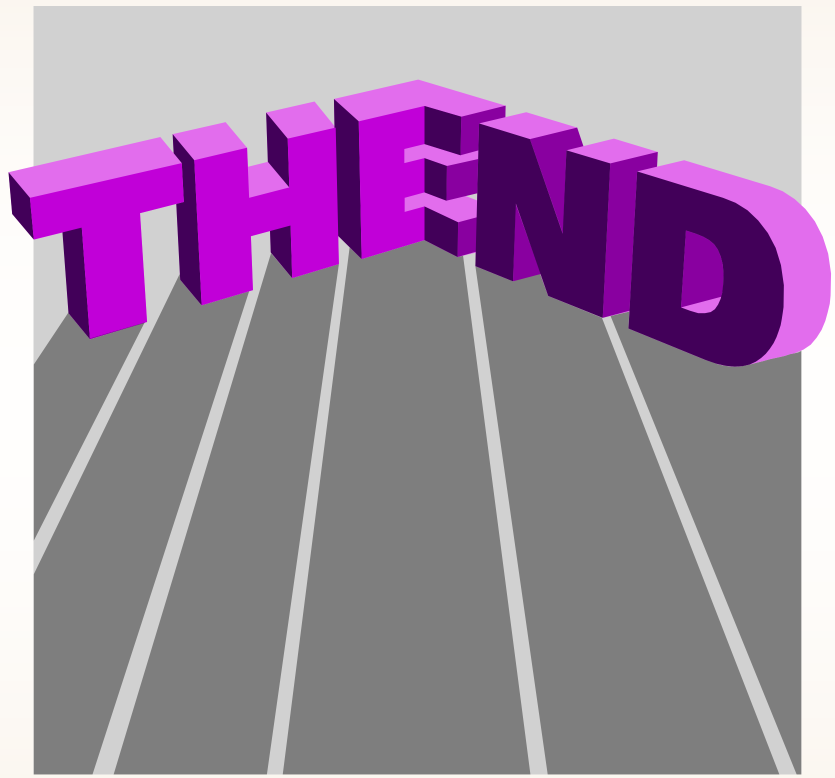
- Travis Humble, Mary Rohrdanz
- Erich Wolf

- Financial Support: Department of Energy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