Generalized Critical Points Analysis of Acetylene Vibrational Dynamics

Ph. D. Oral Defense

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Molecular Spectra and Vibrations

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

Irregular spectrum: motion is completely random
Modes of Vibration

Symmetric Stretch

Local Stretch 1

Local Stretch 2

Normal $\rightarrow$ 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 \((\text{H}_{\text{eff}})\), obtained from fitting the spectra.
C$_2$H$_2$ Pure Bending Spectra

Normal mode zero-order states: $|n_4^{l4}, n_5^{l5}>$

$n4$: Trans bend

$n5$: Cis bend

Dispersed Fluorescence spectrum recorded by Field et al.
Resolved into “clumps” (polyads)
Quantum Effective Hamiltonian

Ground electronic state ($S_0$)
Vibrational part only:

$$H_{\text{bend}} = H_0 + V_{\text{DDI}} + V_l + V_{\text{DDII}}$$

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

Polyad \{8, 0\}^g

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

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

- **New canonical variables**
  - **Trivial:** \((K_a, \theta_a, K_b, \theta_b)\)
    \[ K_a = (N_b + 2)/2 \quad K_b = l/2 : \text{ constants of motion.} \quad \theta_a, \theta_b : \text{ cyclic angles} \]
  - **Nontrivial:** \((J_a, \psi_a, J_b, \psi_b)\)
    \[ J_a = (n_4 - n_5)/2 \quad J_b = (l_4 - l_5)/2 \]

- **Simplified Classical Hamiltonian**
  \[ H_{\text{bend}} (K_a, K_b, J_a, J_b, \psi_a, \psi_b) \]

- **Equations of motion in reduced phase space**
  \[ \psi_i = \frac{d\psi_i}{dt} = \frac{\partial H_{\text{bend}}}{\partial J_i}, \quad J_i = \frac{dJ_i}{dt} = -\frac{\partial H_{\text{bend}}}{\partial \psi_i} \]
• Flow in the **reduced phase space** is organized by **critical points**.

\[
\dot{J}_i = \dot{\psi}_i = \frac{\partial H_{\text{bend}}}{\partial \psi_i} = \frac{\partial H_{\text{bend}}}{\partial J_i} = 0
\]

- Stable (Elliptic)
- Unstable (Hyperbolic)

• In the **full phase space**, the **critical points** move along the cyclic angle (s) \( \theta_i \).

• Near a stable critical point, trajectories can be decomposed into periodic oscillations \( \rightarrow \) vibrational modes.
Critical Points in \( \{N_b, 0\} \) Polyads

Solving 4 simultaneous equations for continuously varying \( K_a \) (\( N_b \)) values:

\[
\begin{align*}
\frac{\partial H_{\text{bend}}}{\partial J_a} &= \frac{\partial H_{\text{bend}}}{\partial J_b} = \frac{\partial H_{\text{bend}}}{\partial \psi_a} = \frac{\partial H_{\text{bend}}}{\partial \psi_b} = 0 \\
(1) & \quad (2) & \quad (3) & \quad (4)
\end{align*}
\]

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

\[
\dot{\theta}_a \neq 0 \quad \dot{\theta}_b = 0
\]
Results for \( \{N_b, 0\} \) Polyads

(Click on each picture to see the animation.)
Long-living vinylidene observed in acetylene-vinylidene system

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

(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$_2$H$_2$ Stretch-Bend System**

1. C-H symmetric stretch
2. C-C stretch
3. C-H antisymmetric stretch
4. Trans bend
5. Cis bend

Vibrational angular momenta $l_4, l_5$

The polyad numbers are:

$\omega_1 : \omega_2 : \omega_3 : \omega_4 : \omega_5 = 3372:1975:3289:608:729 \sim 5:3:5:1:1$

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
   $|n_1, 0, 0, 0^0, 0^0\rangle$
   ____________ perturbed but remains stable ____________

2. C-C stretch
   $|0, n_2, 0, 0^0, 0^0\rangle$
   ____________ isolated subsystem ____________

3. C-H antisymmetric stretch
   $|0, 0, n_3, 0^0, 0^0\rangle$
   0
   local stretch

4. Trans bend
   $|0, 0, 0, n_4, 0^0\rangle$
   8
   local bend
   10
   orth bend
   15
   pre bend

5. Cis bend
   $|0, 0, 0, 0^0, n_5^0\rangle$
   10
   CR bend

new stretch-bend modes
Generalized Critical Points Analysis

- Spectra
  - Effective Hamiltonian
    - Classical Hamiltonian
      - Heisenberg’s Corresp.
        - Reduced Phase Space
          - Critical Points
            - Dynamics
              - Trajectories, $P(t)$, etc.

Resolved & Fitted

N coupled modes

M pairs of (polyad #, cyclic angle)

2N Dim phase space

2(N-M) Dim reduced phase space
Advantages of Our Method

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

   Current limitations in \textit{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 C₂H₂

Overtones $\rightarrow$ All combinational states

B. Other systems: C₂H₂ isotopomers, CH₄, CH₂O ...

Effective Hamiltonians with multiple polyad numbers

C. Effect of polyad breaking terms

Important at high energy, esp. near a reaction barrier
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