Intra- and intermolecular dynamics of cyanoacetylene and its complexes with helium

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Outline of the talk

1. **Cyanoacetylene molecule: discovery and history of spectroscopic studies**

2. **Intramolecular dynamics of cyanoacetylene**
    - **Potential energy surface: state-of-the-art ab initio calculations**
    - **Theoretical spectroscopy in the microwave and infrared regions: nearly exact dynamical calculations**

3. **Numerical results**

   - **Molecular structure from ab initio calculations**
   - **Potential energy surface: role of the anharmonic effects**
   - **Rovibrational energy levels: impact of various approximations**
   - **Perturbed levels: a stringent test of the theory**

4. **Intermolecular dynamics of complexes with helium**

5. **Forthcoming new developments**

Cyanoacetylene molecule: discovery and history of spectroscopic studies

1. **First synthesis: Moureu and Bongrand, 1920**
2. **First spectroscopic observation and structure determination: Westenberg and Bright Wilson, 1950**
3. **High-resolution laboratory spectroscopy: over 40 experimental studies covering the frequency range from the microwave to the near-infrared regions**
4. **Theoretical studies: scarce, less than 20 papers published, accurate data ina few papers, no systematic study of the intramolecular dynamics**

5. Astrophysical observations

- first detection: Turner, 1971
- assignment of interstellar rotational transitions: de Zafra, 1971
- observation of cyanoacetylene in dense interstellar clouds: Morris et al., 1976
- detection of interstellar vibrationally excited cyanoacetylene: Clark et al., 1976
- obervation of cyanoacetylene in Titan's atmosphere: Kunde et al., 1981
- obervation of vibrationally excited cyanoacetylene in Orion: Goldsmith, 1983
- observation of *all* vibrational fundamentals bands of cyanoacetylene in hot molecular cores: Wyrowski et al., 1999

Intramolecular dynamics of cyanoacetylene

1. **Linear molecule with $N = 5$ atoms**
   - **$3N - 5 = 10$ degrees of freedom**
   - **$N - 4 = 6$ bending vibrational modes**
   - **$N - 6 = 4$ stretching vibrational modes**
2. **Low-frequency modes almost harmonic → no large amplitude motions expected → the use of normal coordinates correct**
3. **Very small rotational constant ≈ 0.15 cm^{-1} → high density of molecular states**
4. **Bending modes doubly degenerate → carrying vibrational angular momentum → l-doubling of rovibrational levels with $J \neq 0$**

Potential energy surface: state-of-the-art ab initio calculations

1. Method: CCSD(T)
   - based on the many-body theory of fermionic systems
   - size-consistent
   - highly-correlated
   - preserving spin and spatial symmetry
2. One-particle basis: cc-pVQZ

Potential energy surface: symmetries

1. Terms depending on a single set of bending coordinates (q, α)
   - leading term harmonic in q, independent of α
   - anharmonic terms: even powers of products of q, $\cos\alpha$, and $\sin\alpha$
2. Coupling terms depending on two bending coordinates (q_1, α_1) and (q_2, α_2)
   - at least quartic or higher-order

3. Terms depending on a single stretching coordinate z
    - leading term harmonic in z
    - anharmonic terms: cubic or higher order in z
4. Coupling terms depending on two stretching coordinates z_1 and z_2
    - at least quartic or higher order
5. Coupling terms depending on one set of bending coordinates (q, α) and one stretching coordinate z
    - at least cubic or higher order

Theoretical spectroscopy in the microwave and infrared regions: nearly exact dynamical calculations

1. **Watson's isomorphic Hamiltonian**
   - kinetic term

$$T = T_{\mathrm{rot}} + T_{\mathrm{vib}} + T_{\mathrm{rot-vib}}$$

   - rotational term

$$T_{\mathrm{rot}} = b(z_1, z_2, z_3)(J^2 - J_z^2)$$

   - vibrational term

$$T_{\mathrm{vib}} = \frac{1}{2} b(z_1, z_2, z_3)(L^+L^- + L^-L^+)$$

$$-\frac{1}{2}\sum_{i=1}^{3}\left(\frac{\partial^2}{\partial q_i^2} + \frac{1}{q_i^2}\frac{\partial^2}{\partial \alpha_i^2}\right) - \frac{1}{2}\sum_{j=1}^{4}\frac{\partial^2}{\partial z_j^2}$$

   - rotation-vibration coupling term

$$T_{\mathrm{rot-vib}} = b(z_1, z_2, z_3)(L^+J^- + L^-J^+)$$

3. Total wave function

$$\Psi^{p}_{JM} = \sum_{\{n_i\}} \sum_{\{n_j\}} \sum_{K} c_{\{n_i\},\{n_j\},K} \Phi^{JMp}_{\{n_i\},\{n_j\},K}(\phi, \theta, \alpha, q_1, q_2, q_3, z_1, \ldots, z_4)$$

4. Basis functions

$$\Phi^{JMp}_{\{n_i\},\{n_j\},K}(\phi, \theta, \alpha, q_1, q_2, q_3, z_1, \ldots, z_4) =$$
$$(D^{(J)\star}_{MK}(\phi, \theta, \alpha) + p(-1)^J D^{(J)\star}_{M,-K}(\phi, \theta, \alpha))$$
$$\times \mathcal{R}_{\{n_i\},\{n_j\},K}(q_1, q_2, q_3, z_1, \ldots, z_4)$$

– rotational part

$$D^{(J)\star}_{MK}(\phi, \theta, \alpha)$$

– bending functions

$$\prod_{i=1}^{3} \chi_{n_i k_i}(q_i)$$

– stretching functions

$$\prod_{j=1}^{4} \phi_{n_j}(z_j)$$

5. Hamiltonian matrix

$$\langle \Phi^{JMp}_{\{n_i\},\{n_j\},K} | T + V | \Phi^{JMp}_{\{n'_i\},\{n'_j\},K'} \rangle$$

6. Size of the matrix $\sim 10^6 \rightarrow$ Davidson algorithm for diagonalisation

7. Possible approximations

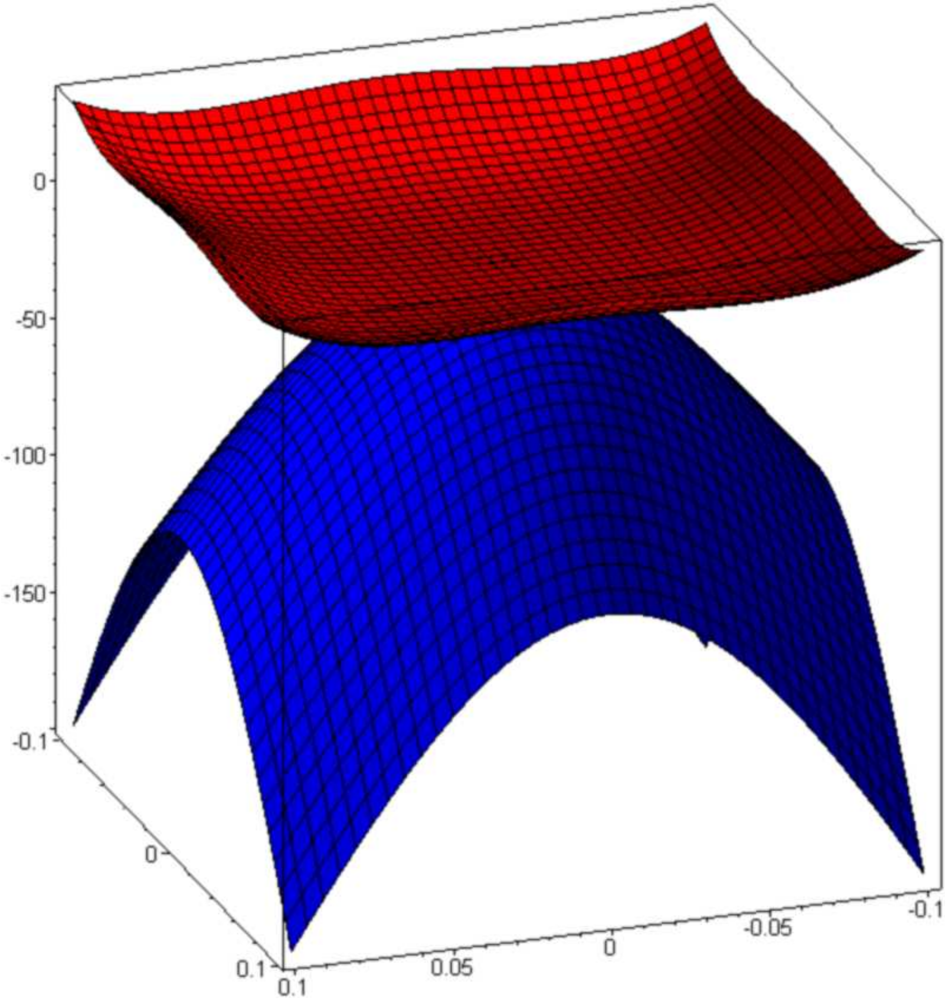
   - in the potential: harmonic, anharmonic without intermode couplings, etc.
   - in the kinetic operator: harmonic plus rigid rotor, anharmonic without rotation-vibration coupling, etc.

Numerical results: molecular structure

Spectroscopic constants of cyanoacetylene: comparison of the theory with experiment

	theory	experiment
$r(\mathrm{HC_1})$	1.062	1.057
$r(\mathrm{C_1C_2})$	1.206	1.205
$r(\mathrm{C_2C_3})$	1.376	1.378
$r(\mathrm{C_3N})$	1.161	1.159
B_0	4549.059	4550.140
α_7	–14.388	–14.455

Numerical results: potential energy surface



Numerical results: rotational transitions and comparison with experiment

$J' = 7 \rightarrow J'' = 6$ transition frequency in the ν_7 vibrational band: comparison with the experiment

	theory		experiment	
	e	f	e	f
harmonic	21.3111			
anharmonic pot. only	21.2843			
anharmonic no vib.-rot.	21.2105			
full calculation	21.1772	21.2436	21.2453	21.2574
l dubling	0.0664		0.0121	

Forthcoming new developments

1. further checks of the codes, and inclusion of the multimode couplings → work in progress in Warsaw
2. increase of the efficiency of the code, larger basis calculations → work in progress in Warsaw
3. generalization of the dynamics to the He–cyanoacetylene case → work in progress in Warsaw and in Meudon
4. computation of the potential energy surface for He interacting with flexible cyanoacetylene → work in progress in Warsaw
5. (full close-coupling???) calculations of the rate constants for rovibrational deexcitations of cyanoacetylene in collisions with He → work in progress in Meudon