Saddle Point Localization of Molecular Wavefunctions

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Intuitive understanding of molecules

Exact quantum mechanics

Nuclei:

Electrons:

Born-Oppenheimer model

Nuclei:

Electrons:

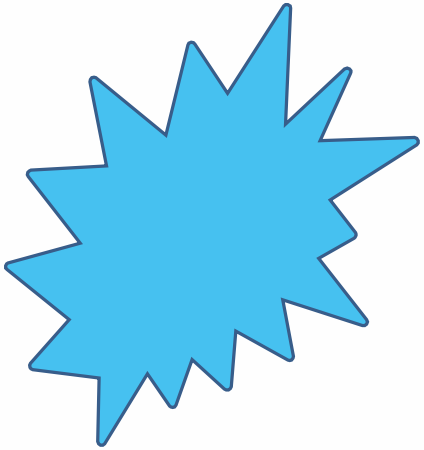
Classical coupling of electrons

Nuclei:

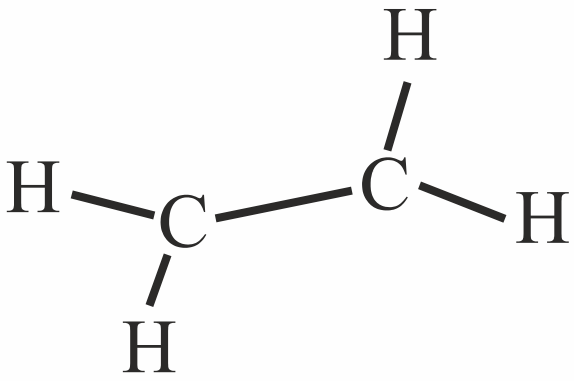
Electrons:

Physics → Chemistry

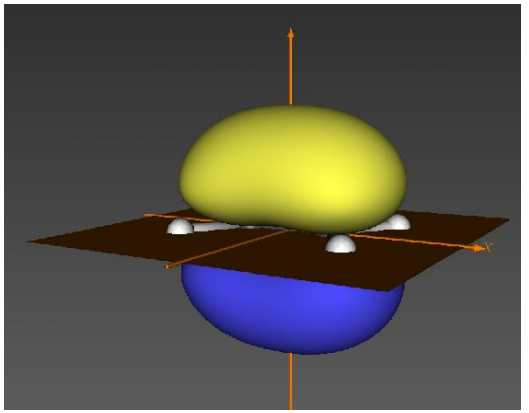
Molecular quantum mechanics	Quantum chemistry	Quasi-electron theory of molecules



Molecules described by the molecular formula



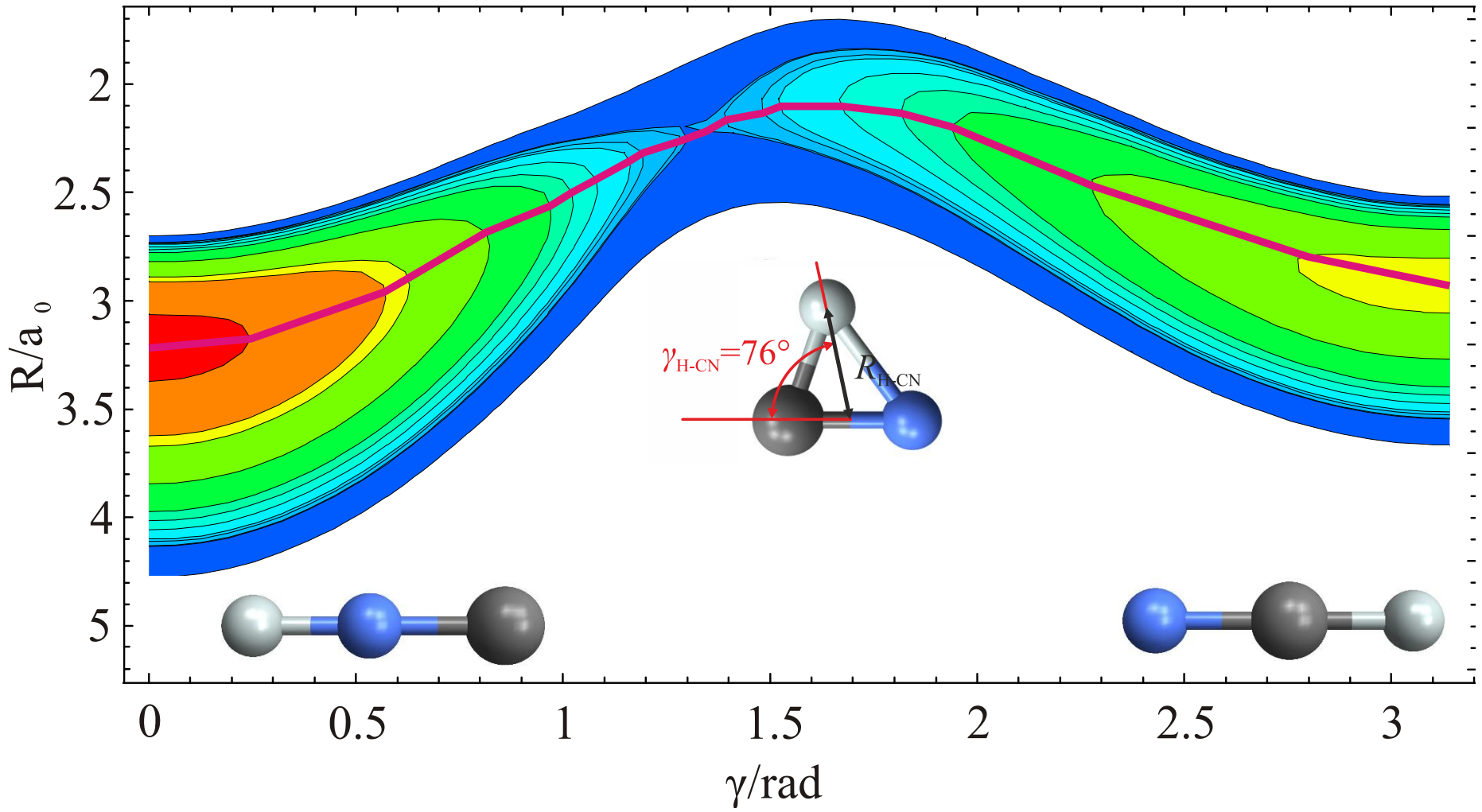
Molecules with a shape described through the geometry of the nuclear configuration



Molecules with a shape made up from individual quasi-electrons

H. Primas, *Chemie in unserer Zeit, 19*, 109 (1985), G. Ch. Mellau, in preparation

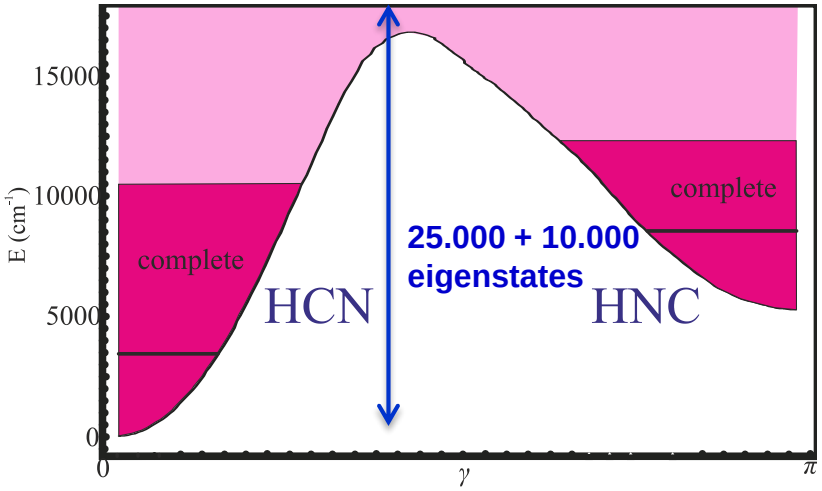
[H,C,N] molecular system

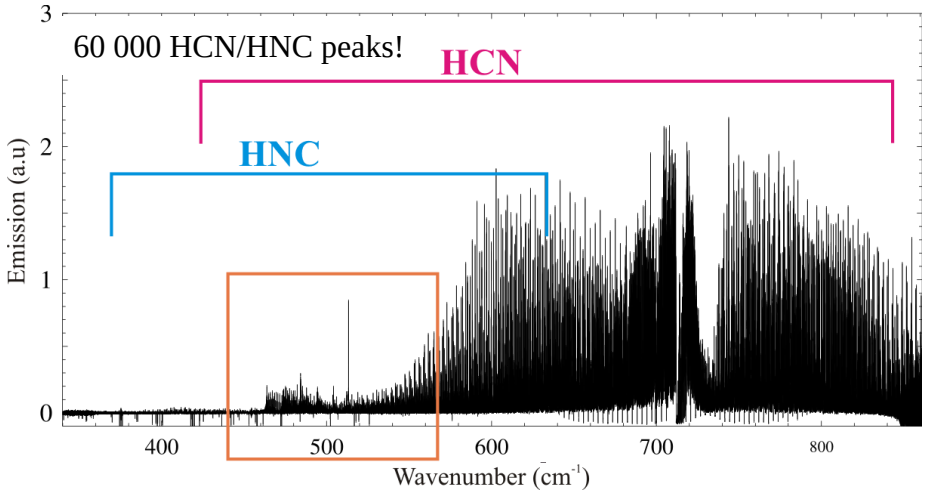


Potential function form: Mourik *et al. J. Chem. Phys.*, **2001**, *115*, 3706-3718

HCN/HNC eigenenergy and eigenvector data sets

from experiments





G.Ch. Mellau, *J. Chem. Phys.* 133, 164303 (2010),
G.Ch. Mellau, *J. Chem. Phys.* 134, 234303 (2011),… 11 papers

Complete (v_1,v_2,v_3,l) assigned ab initio up to the isomerization barrier

e, J=0	e, J=1		e, J=60	f, J=60
0.0000	2.9100	00^00	5376.5455	
	718.7979	01^10	6091.7720	6118.0706
1414.9159	1417.8414	02^00	6797.5744	
2100.5823	2103.4725	02^20	6852.9351	6832.6549
…	…		…	…
18754.768	18150.834	?????	18033.7293	18057.3009
18770.643	18159.392	?????	18036.1204	18063.0370

Complete pattern based assignment of all 168.110 ab initio rotation-vibration eigenenergies

G.Ch. Mellau, *J. Chem. Phys.*,134, 234303 (2011) … & this work

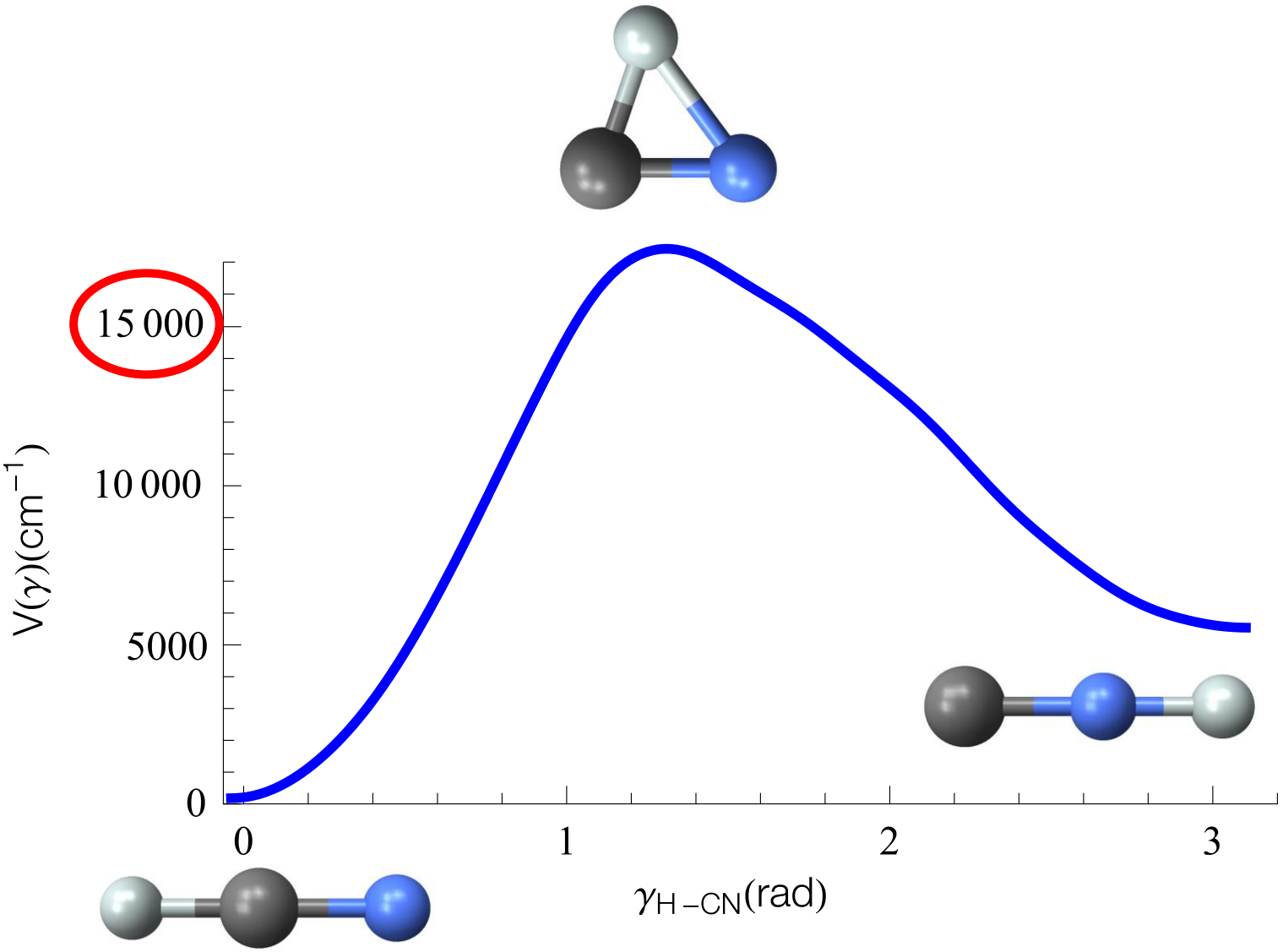
Source 1): UCL Exomol ab initio list

Mourik *et al. J. Chem. Phys.* 115, 3706 (2001), G. J. Harris *et al.*, *MNRAS* 367, 400 (2006)

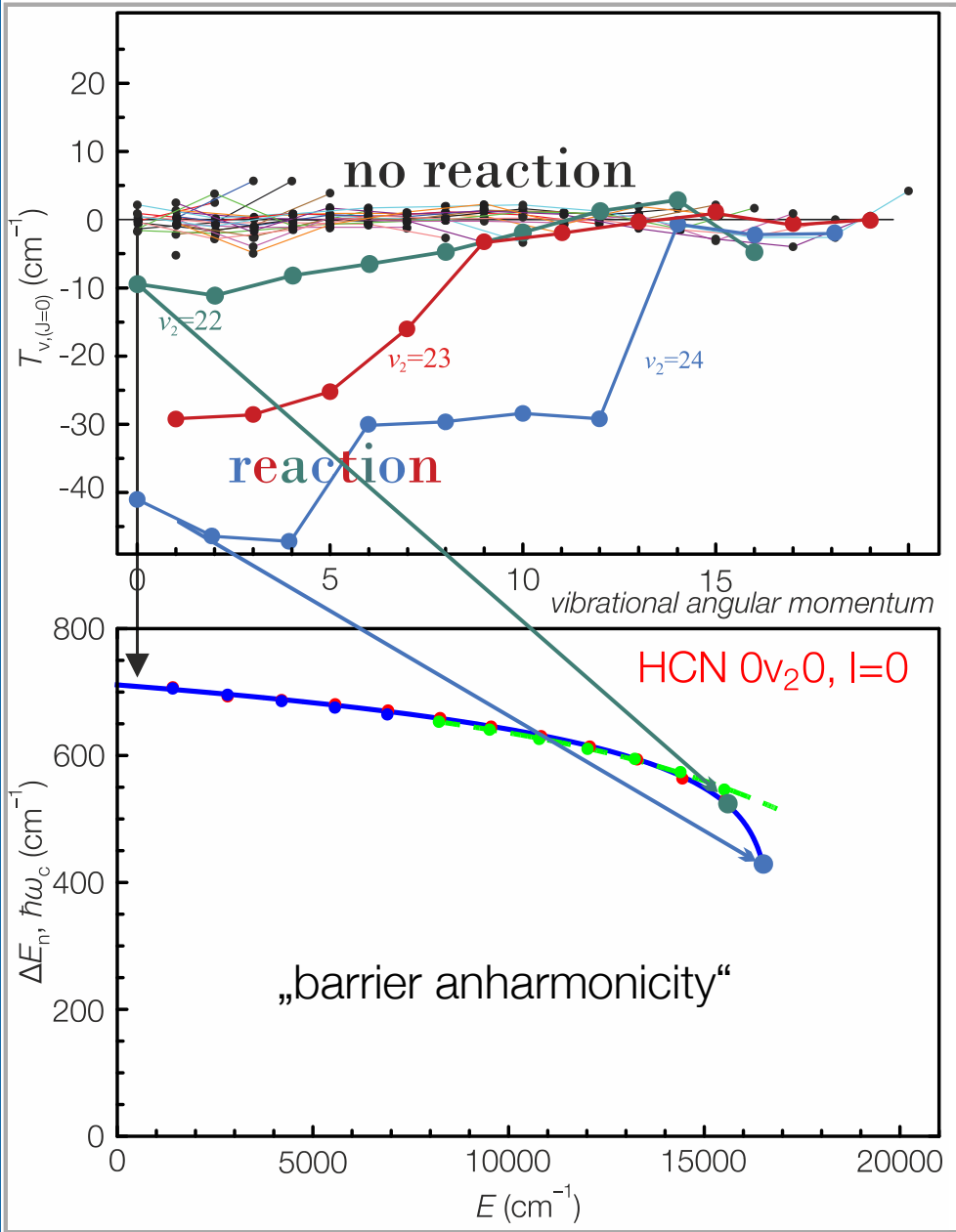
Source 2): extended 1) to higher energies with stored eigenvectors and improved convergence (A. Kyuberis, O. Polyansky, N. F. Zobov)



Molecular double well problem



Vibrational signature of the isomerization
Vibrational signature of a transition state



THE JOURNAL OF CHEMICAL PHYSICS **134**, 234303 (2011)

Complete experimental rovibrational eigenenergies of HCN up to 6880 cm^{-1} above the ground state

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Spectroscopic characterization of isomerization transition states

Joshua H. Baraban,[1]* P. Bryan Changala,[1] Georg Ch. Mellau,[2] John F. Stanton,[3] Anthony J. Merer,[4,5] Robert W. Field[1]

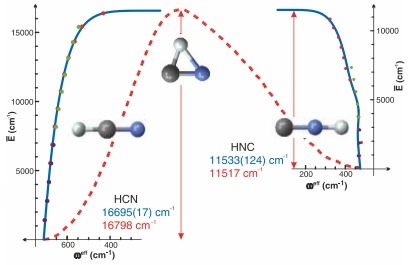

Fig. 4. The ω_2^{el} (r = 0) effective frequency analysis for HCN and HNC. Shown are experimental data points (blue), Dunham polynomial expansion predictions using only experimental data (green), and the assigned ab initio data points (red) (*26*) (see supplementary text for details). The fitted E_{Ts} parameters using Eq. 4 (blue) are compared with the ab initio barrier heights (red). A one-dimensional cut through the potential energy surface is shown as a red dashed line. The unusual shapes of the HNC potential and ω^{el} plot near 5000 cm^{-1} result from interaction with a low-lying excited diabatic electronic state (*44*).

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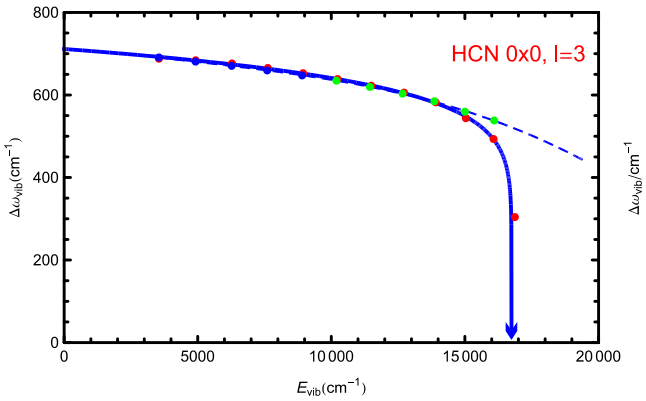
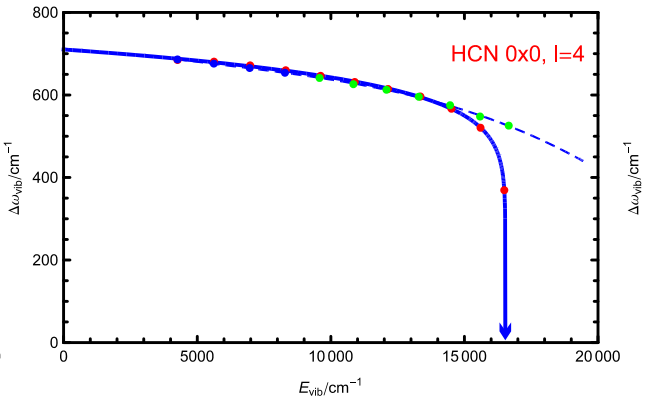
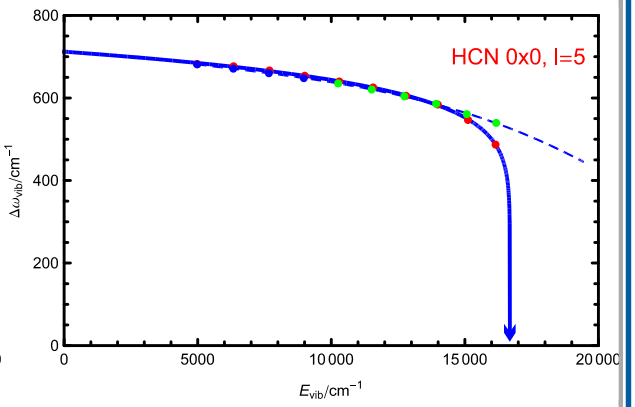
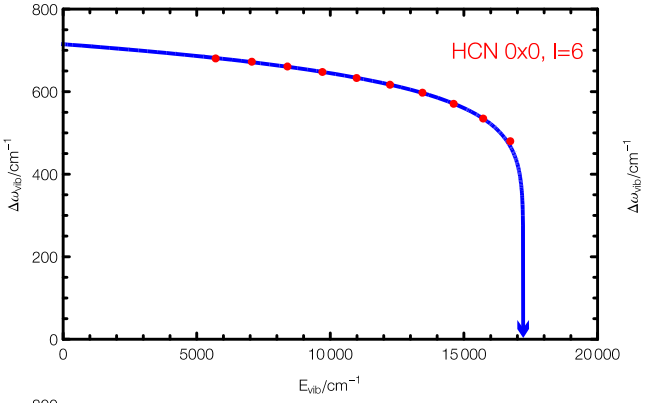
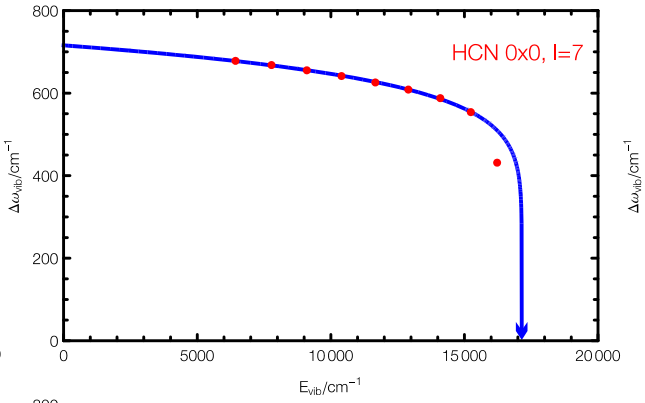
HCN $0v_20$ l=3… bending series

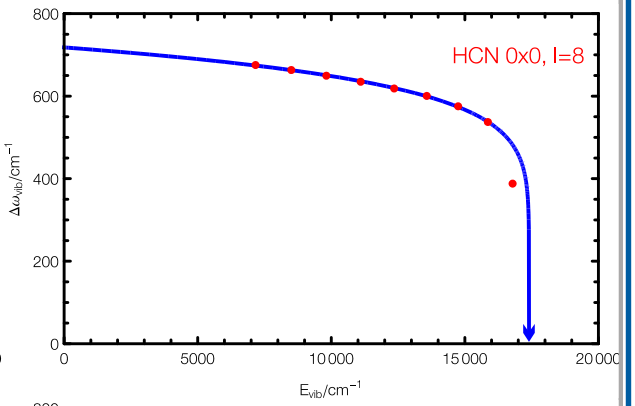


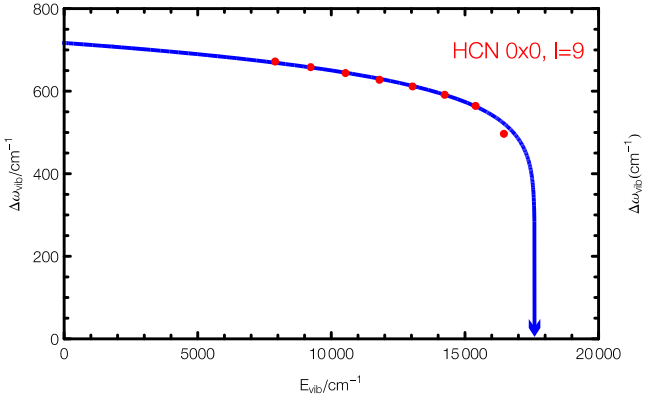


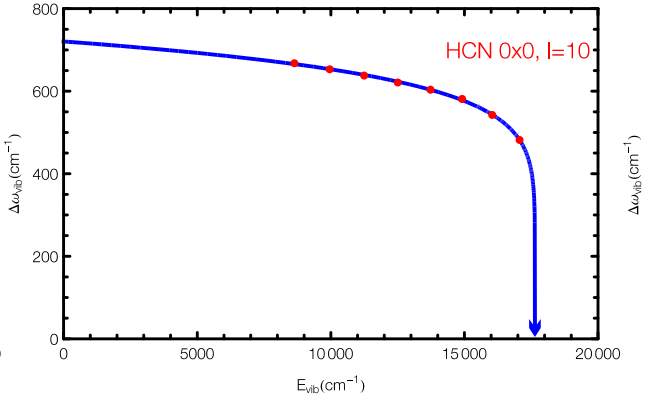


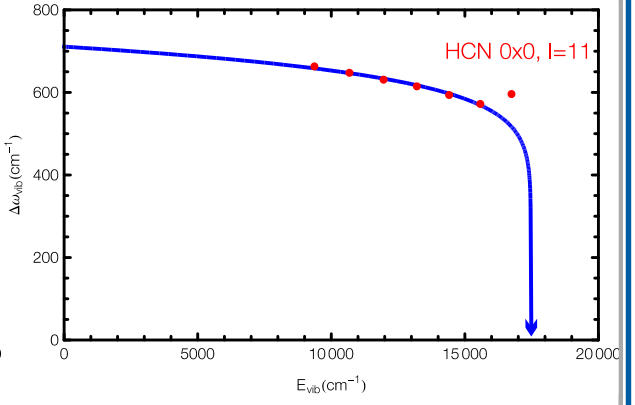




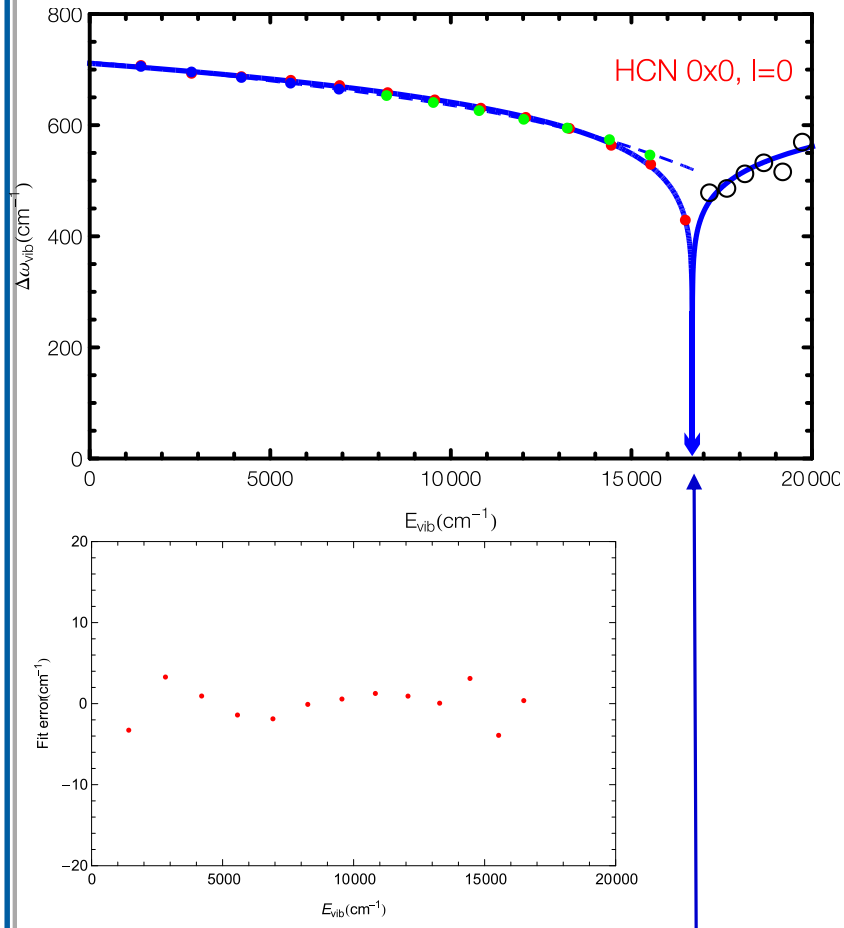


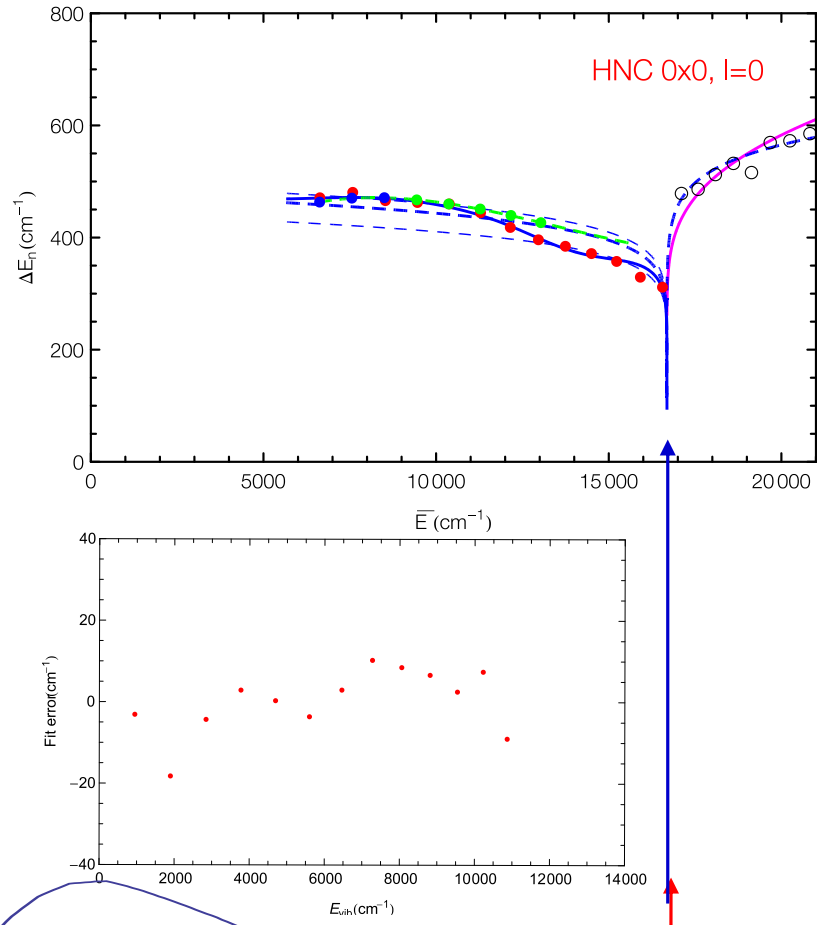




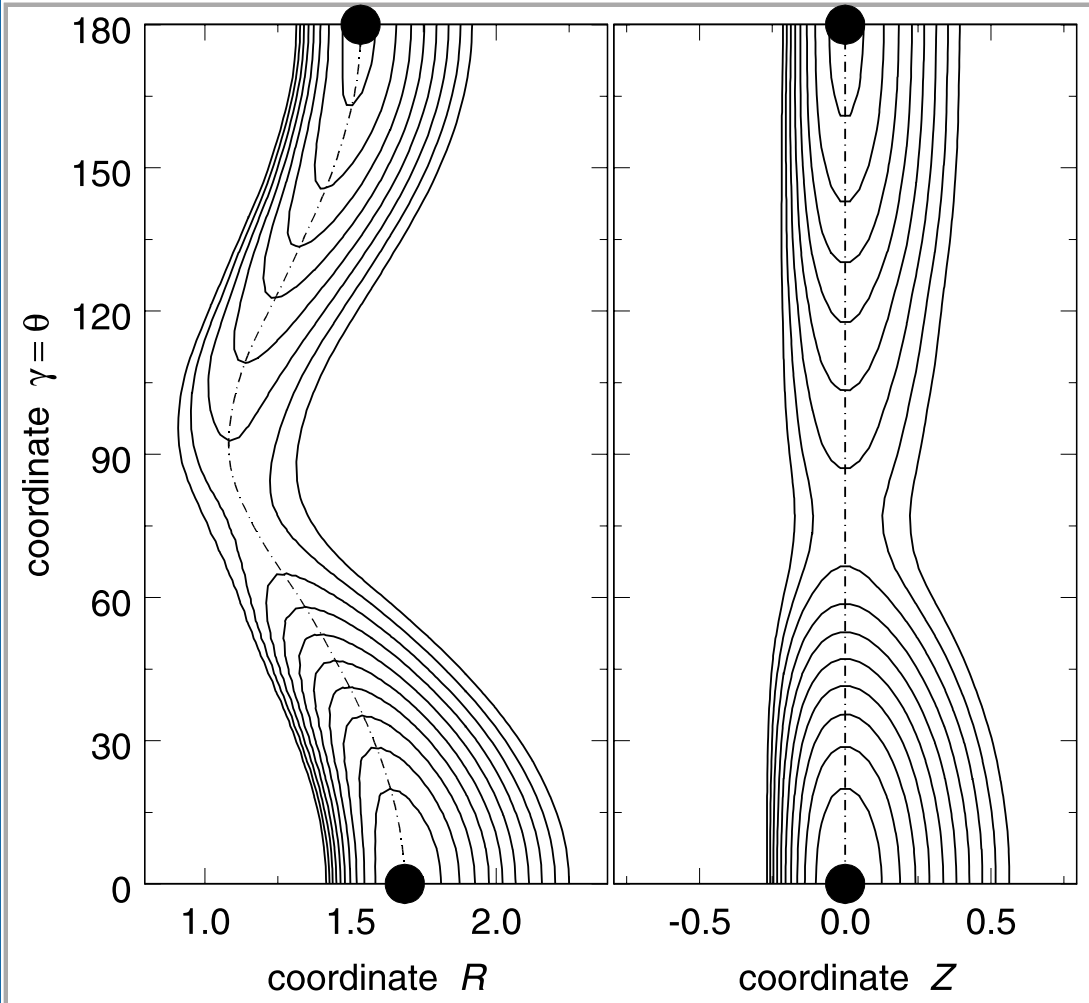


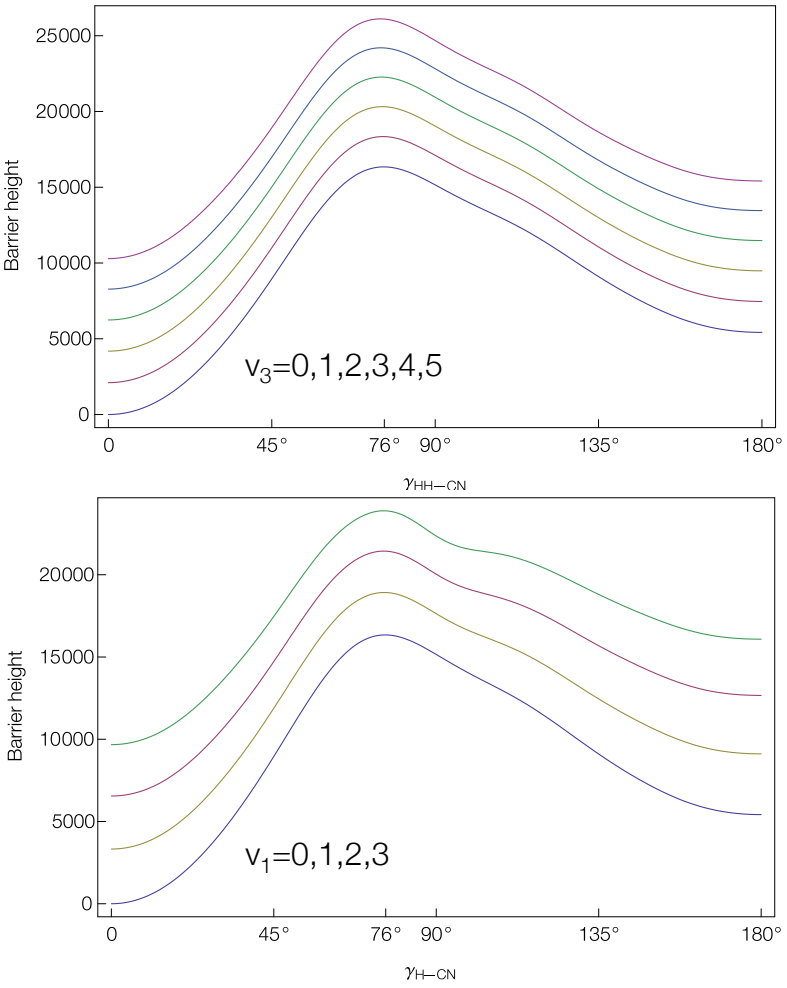
HCN/HCN *l*=0 bending frequency analyis





Nearly separable isomerizing system



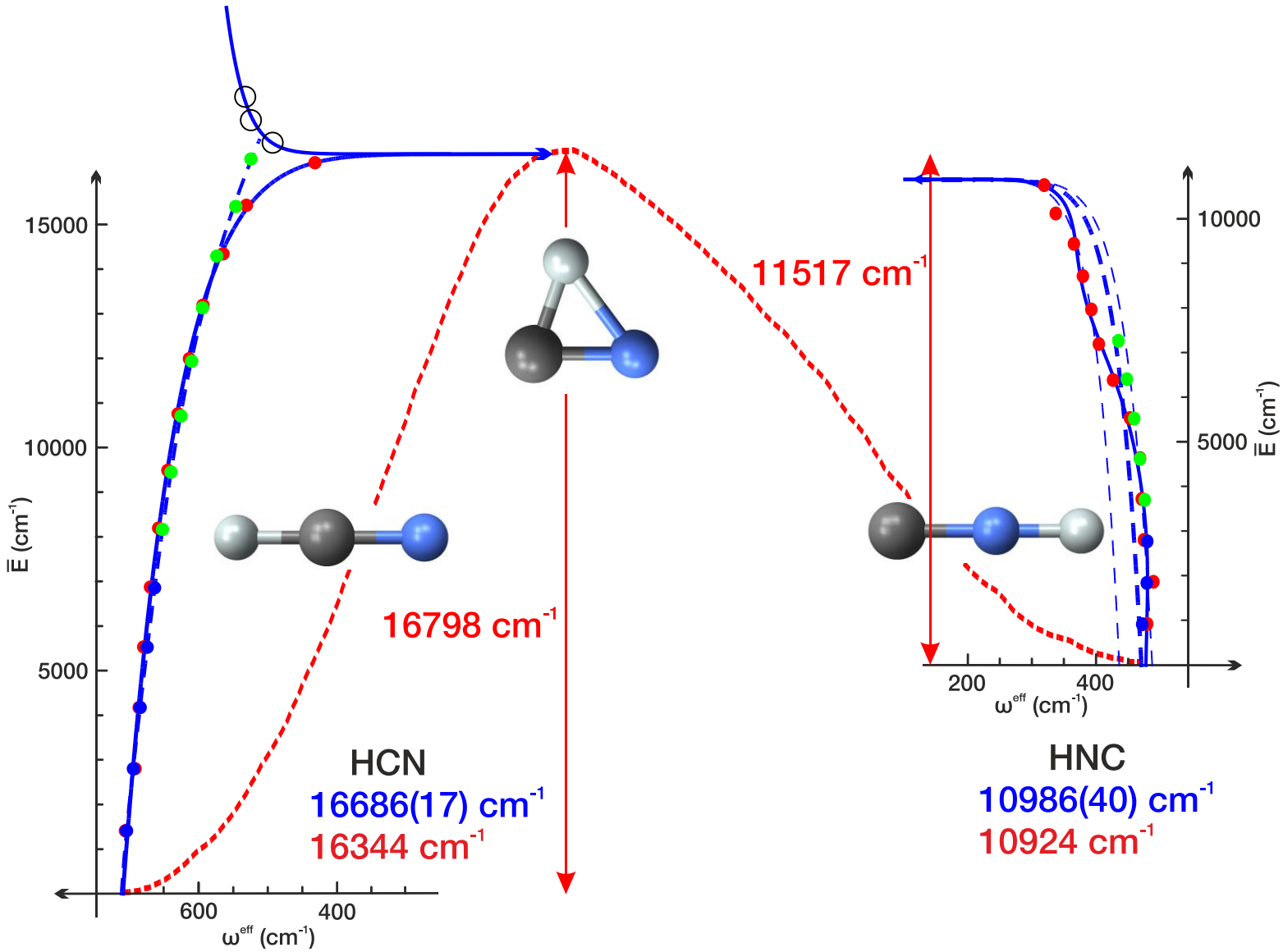


Canonical Perturbation Theory

Separation of motion: one-dimensional Hamiltonian in the bending angle parameterized by the v_1 and v_3 stretch quantum numbers -> $V_{v1;v3}$ (γ) pseudopotentials

M. Joyeux et al. *Adv. Chem. Phys.***136** 267 (2005) Z. Bacic and J.C. Light, J. Chem. Phys. 86 3065 (1987)

Transition state spectroscopy ↔ "frequency analysis"



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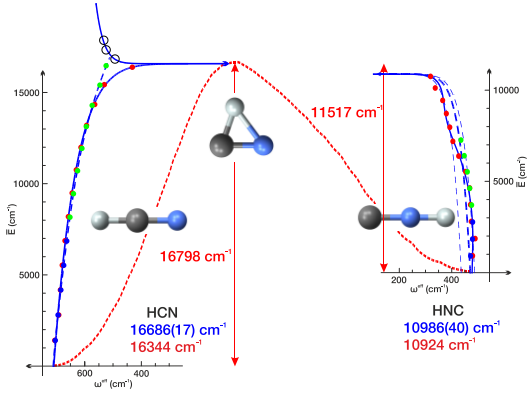

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S. Coy

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