Quantum monodromy and quantum phase transitions in floppy molecules

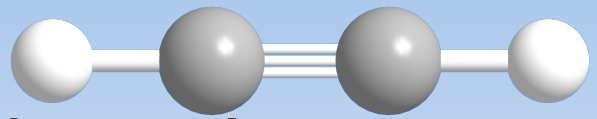
Danielle Larese
Yale University

In honor of the occasion of
Franco Iachello's
70th birthday

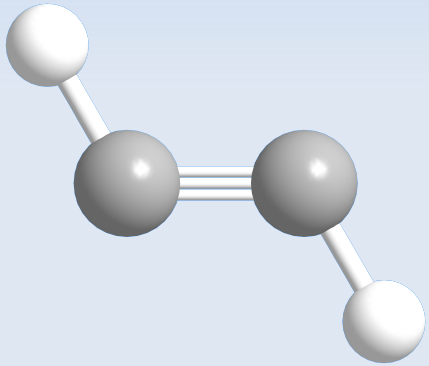
road map

- molecular physics: vibrations and rotations
- short history of vibron model
- quantum phase transitions (QPT)
- excited state quantum phase transitions (ESQPT)
- results for floppy molecules

molecular I

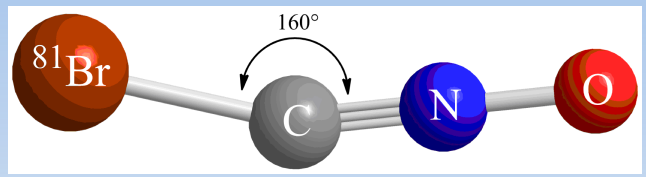


- energy scales (acetylene as example)
  - electronic excitation: ~42,000 cm^{-1} (= 5 eV)



  - vibrational excitation: ~600 and 1000 cm^{-1} (= 0.07 and 0.1 eV)
  - rotational excitation: ~10 cm^{-1} (= 0.001 eV)

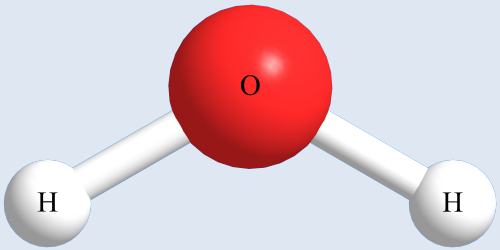
molecular II

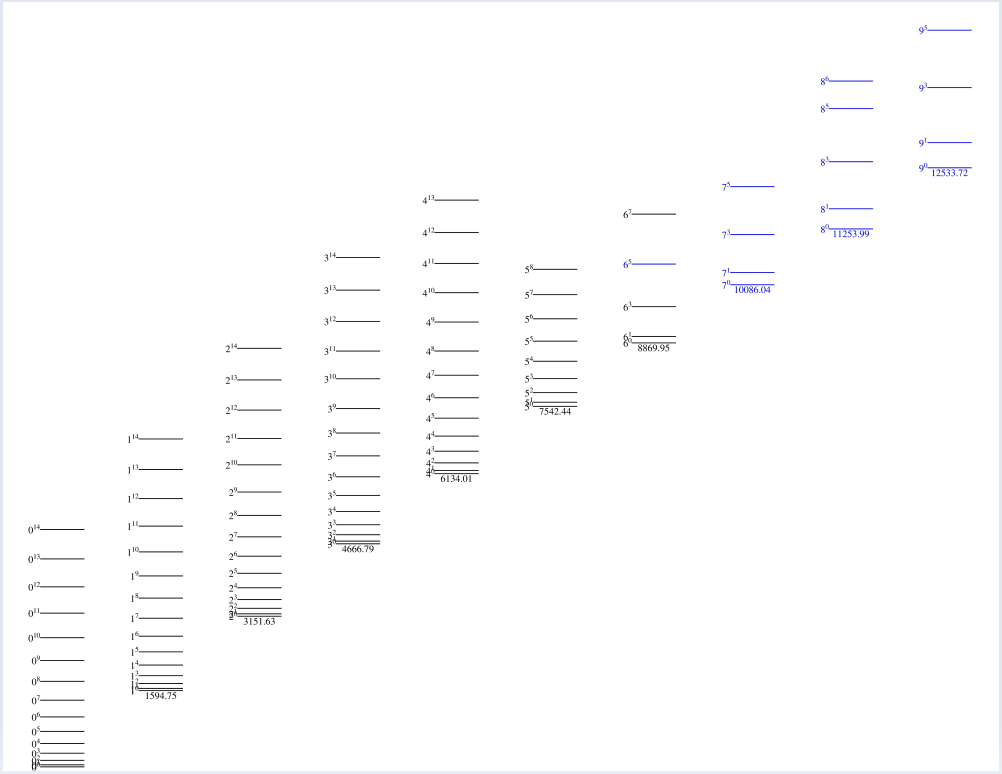


- precision
  - high precision with several methods
  - example: bromofulminate
  - vibrational and rotation levels measured infrared, photoelectron and millimeter-wave spectroscopy
  - used with ab initio calculations to assign levels
  - energy levels with 1:1000 precision
  - prediction of barrier in potential surface to 1:1000 precision
  - equilibrium bending angle to hundredth of degree

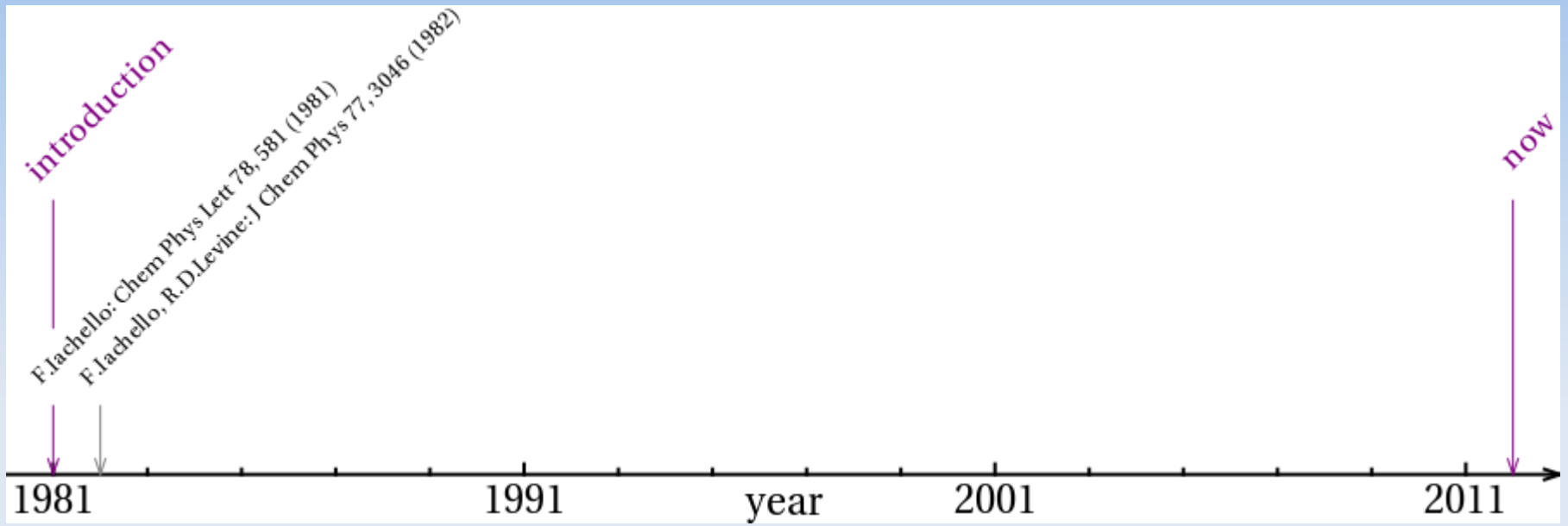
molecular III

- over 10,000 experimental levels available for water
- recent work bring levels up to dissociation
- experimental accuracy of ±0.03cm^{-1} at highest levels





timeline


introduction
F.Iachello: Chem Phys Lett 78, 581 (1981)
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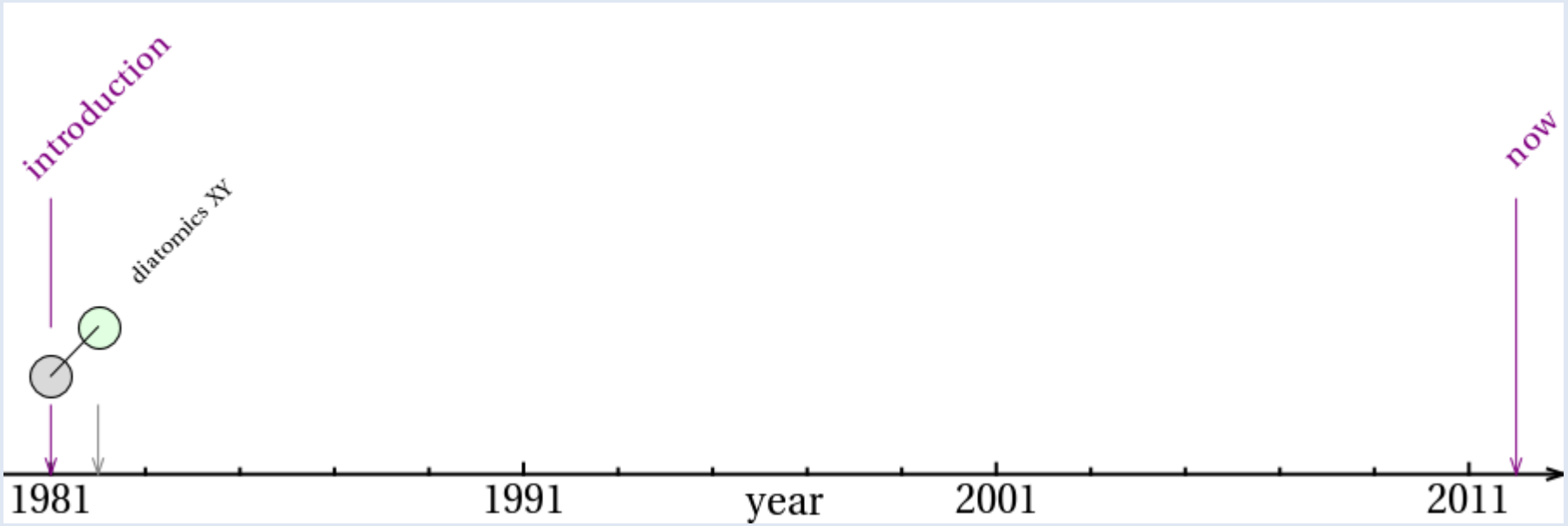
now
1981
1991
year
2001
2011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diatomics XY
now
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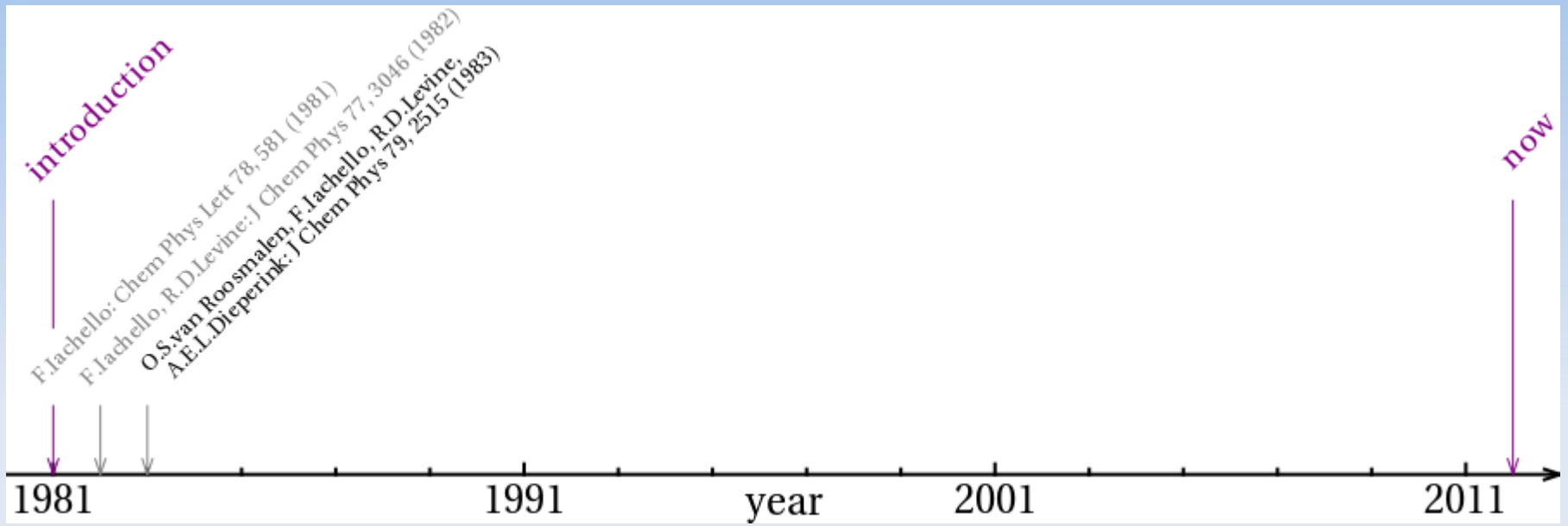
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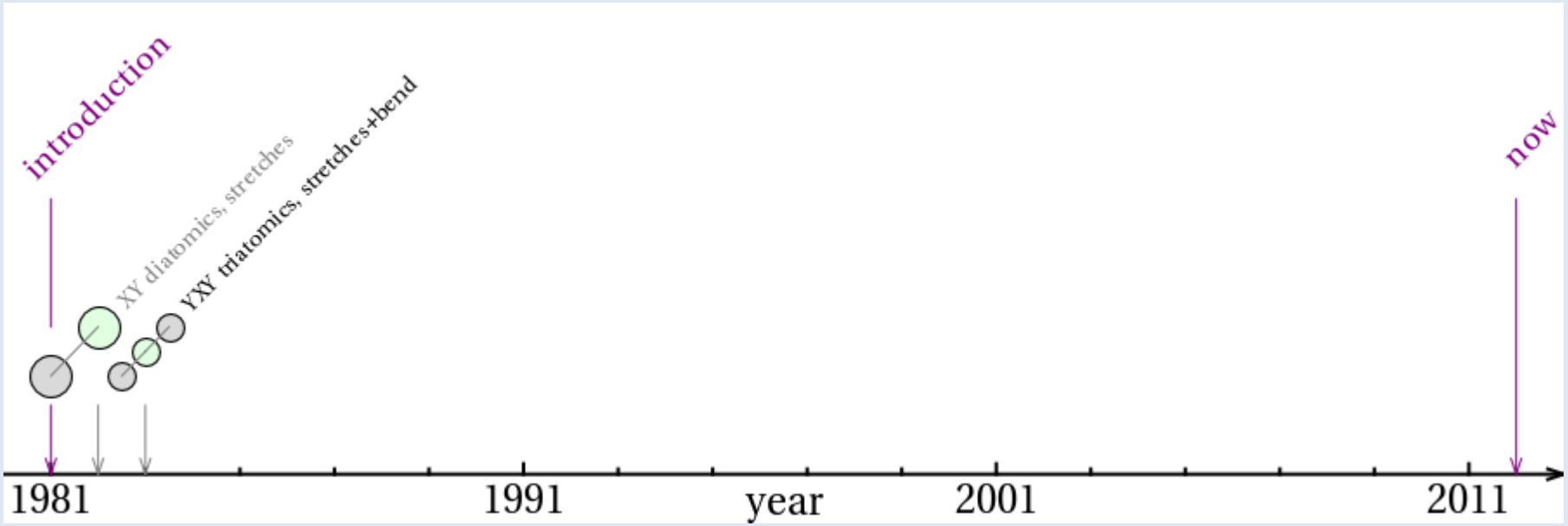
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XY diatomics, stretches
YXY triatomics, stretches+bend
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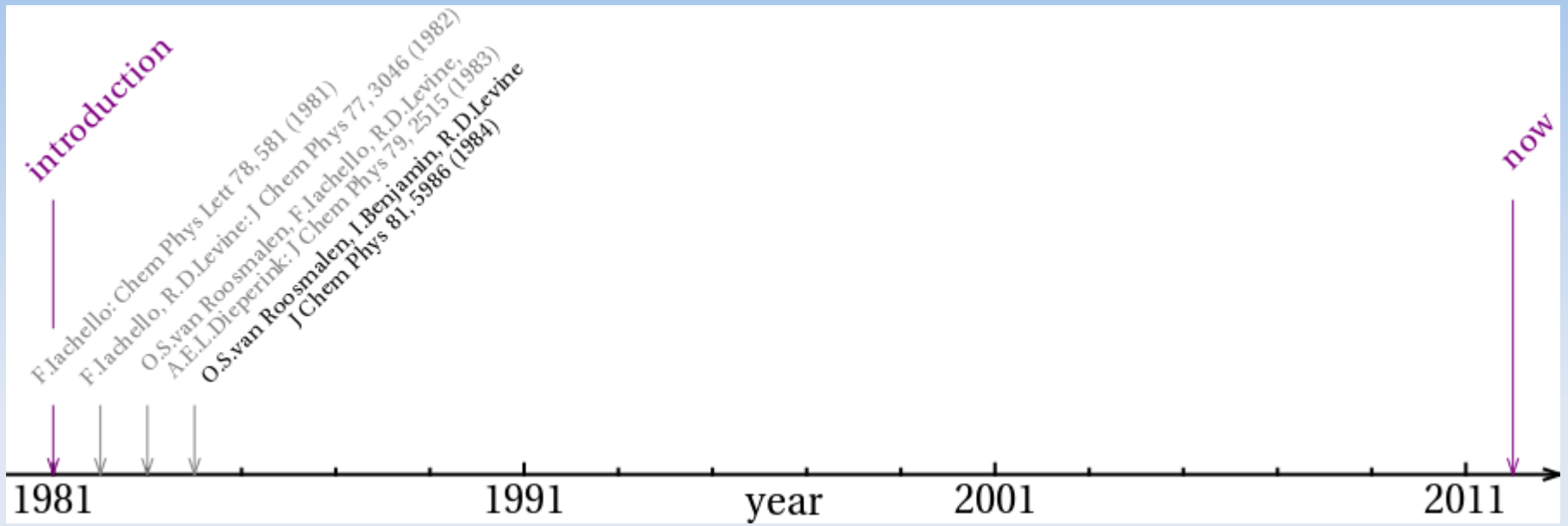
timeline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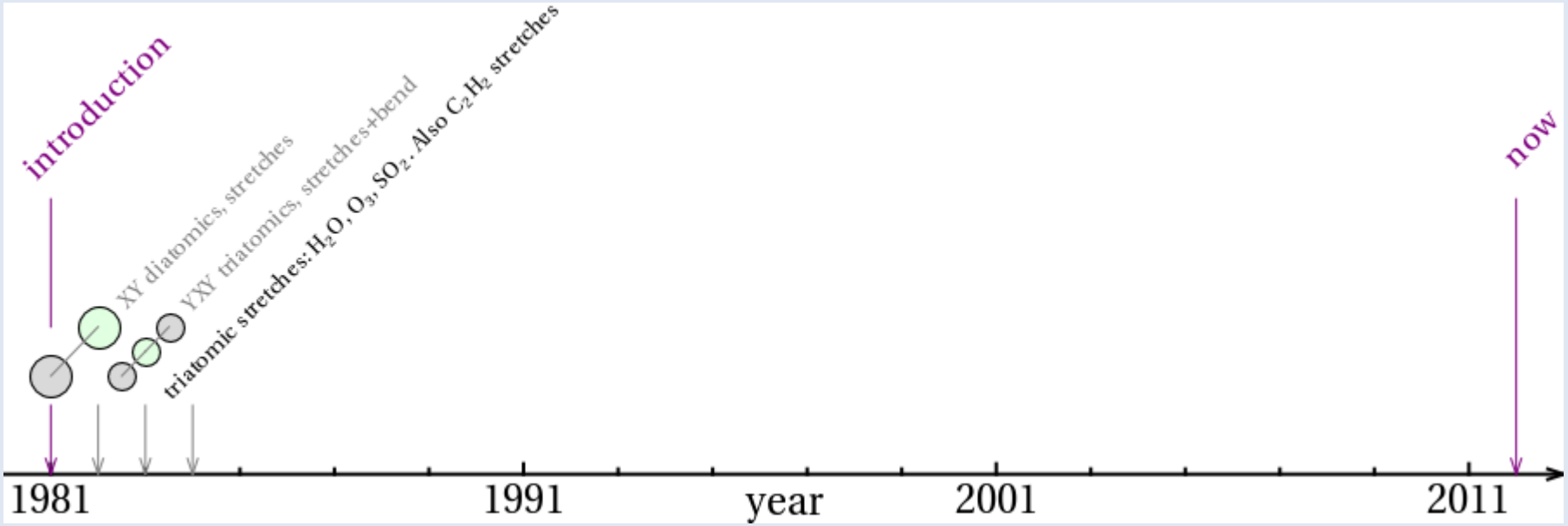
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triatomic stretches: H_2O, O_3, SO_2. Also C_2H_2 stretches
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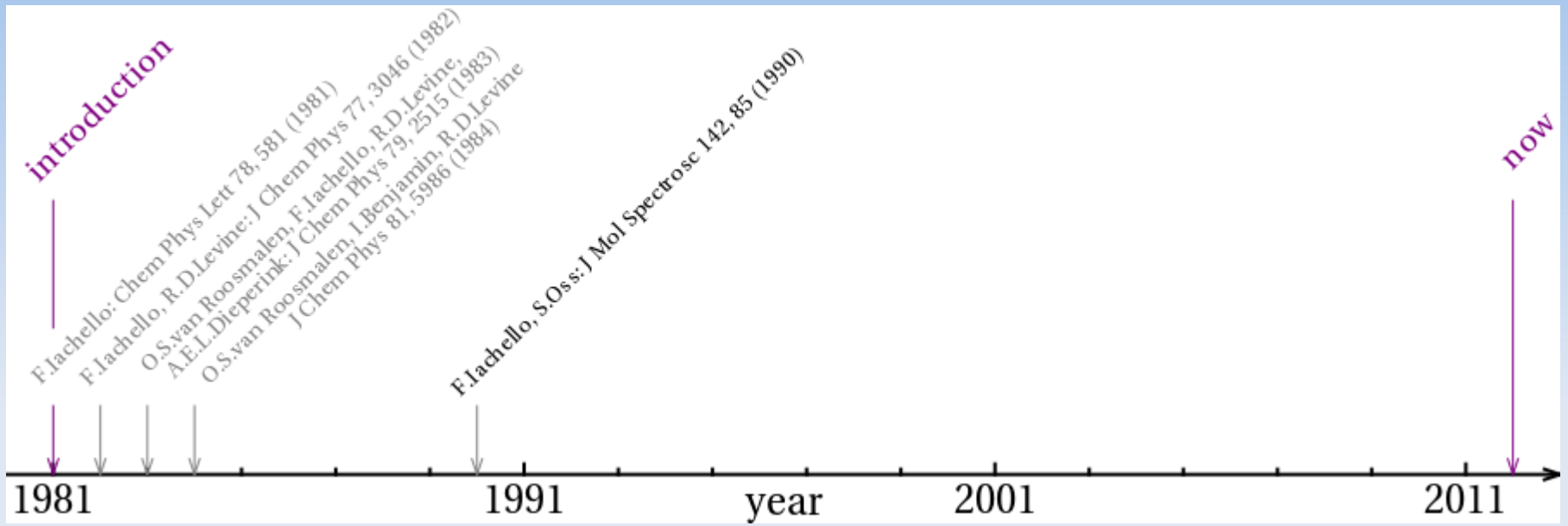
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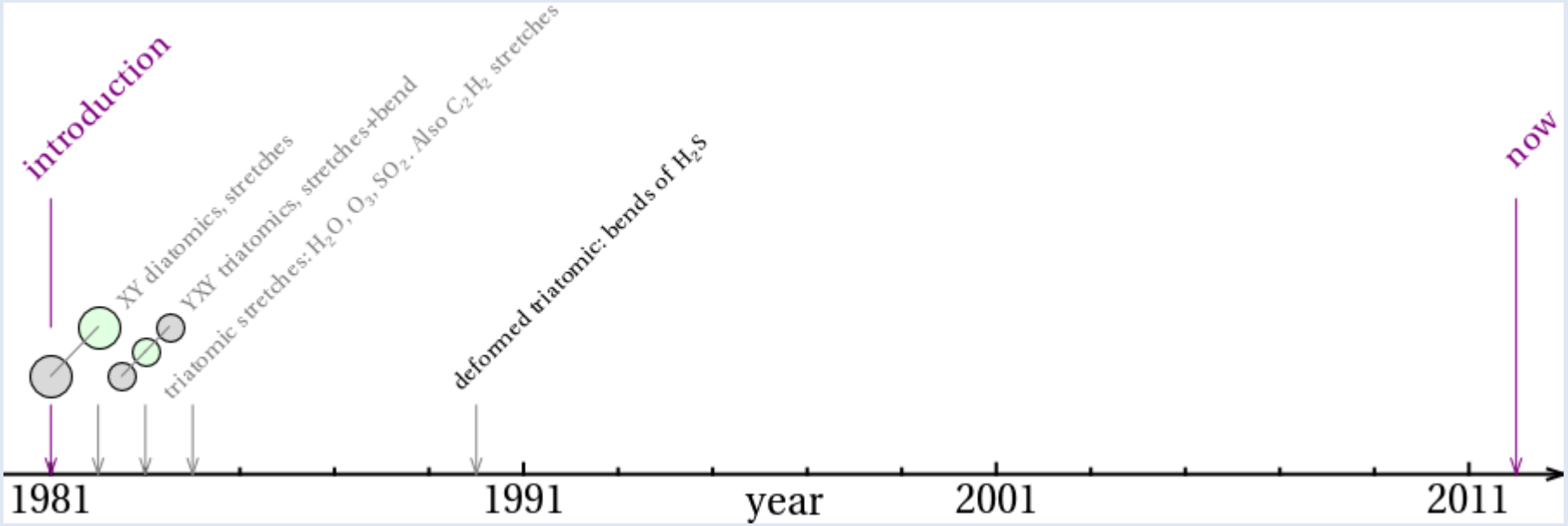
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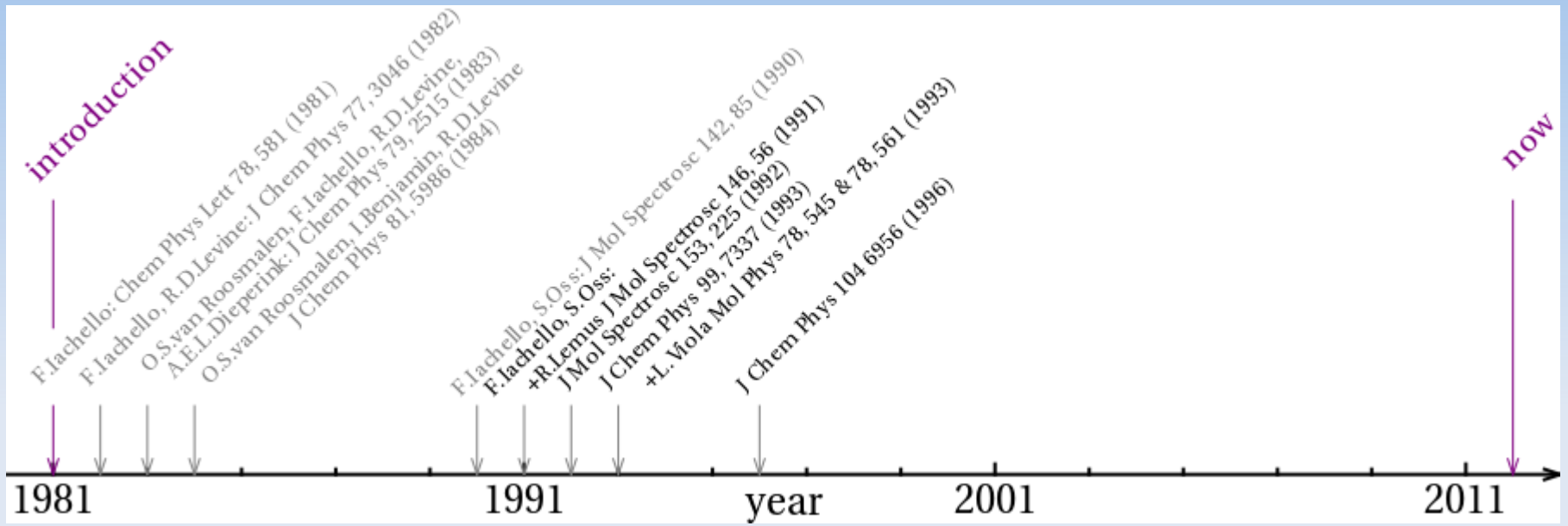
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+R.Lemus J Mol Spectrosc 153, 225 (1992)
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+L. Viola Mol Phys 78, 545 & 78, 561 (1993)
J Chem Phys 104 6956 (1996)
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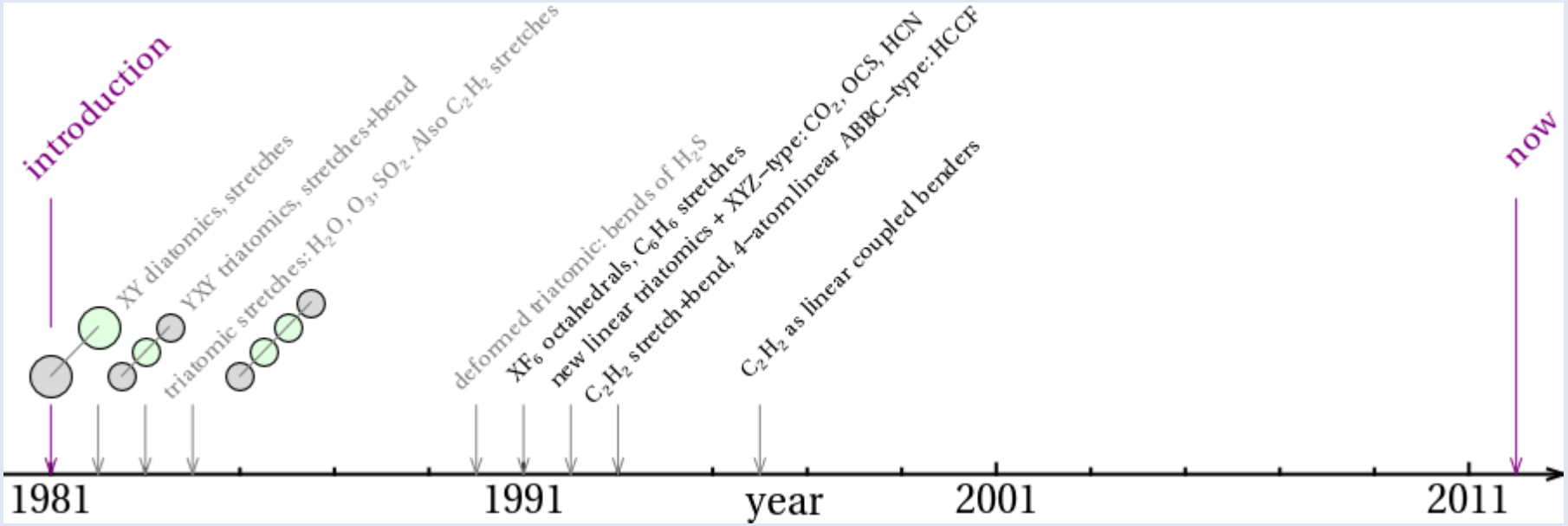
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deformed triatomic: bends of H_2S
XF_6 octahedrals, C_6H_6 stretches
new linear triatomics + XYZ–type: CO_2, OCS, HCN
C_2H_2 stretch-bend, 4–atom linear ABBC–type: HCCF
C_2H_2 as linear coupled benders
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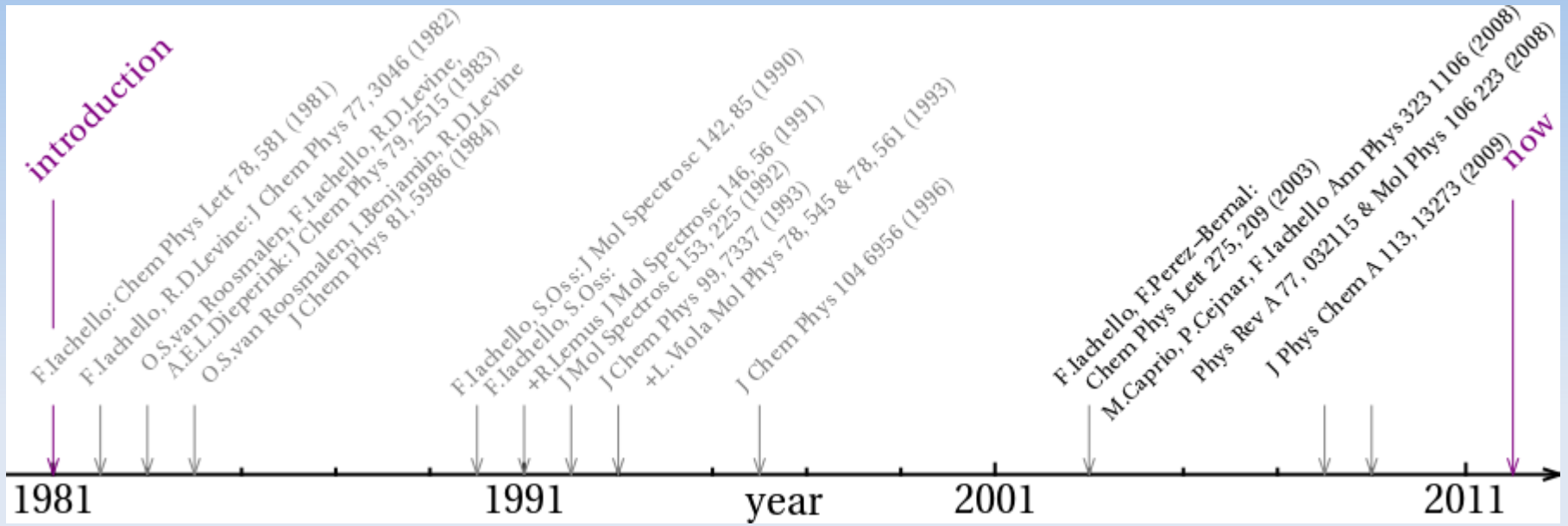
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F.Iachello, F.Perez-Bernal: Chem Phys Lett 275, 209 (2003)
M.Caprio, P.Cejnar, F.Iachello Ann Phys 323 1106 (2008)
Phys Rev A 77, 032115 & Mol Phys 106 223 (2008)
J Phys Chem A 113, 13273 (2009)
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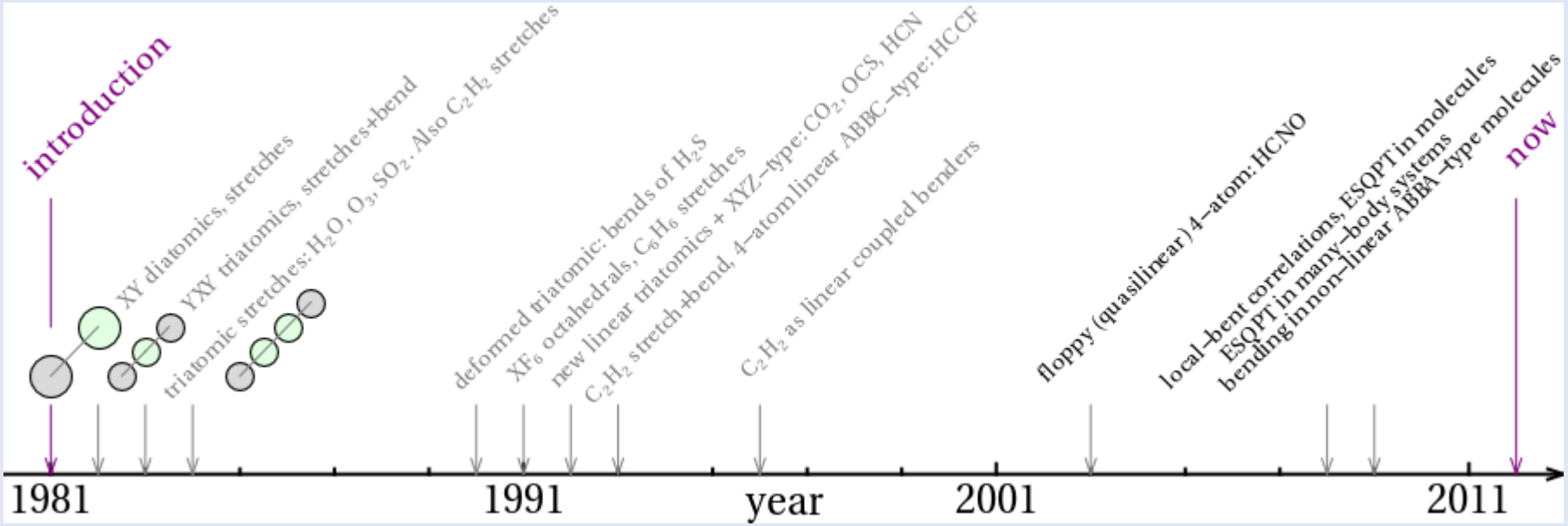
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deformed triatomic: bends of H_2S
XF_6 octahedrals, C_6H_6 stretches
new linear triatomics + XYZ-type: CO_2, OCS, HCN
C_2H_2 stretch-bend, 4-atom linear ABBC-type: HCCF
C_2H_2 as linear coupled benders
floppy (quasilinear) 4-atom: HCNO
local-bent correlations, ESQPT in molecules
ESQPT in many-body systems
bending in non-linear ABBA-type molecules
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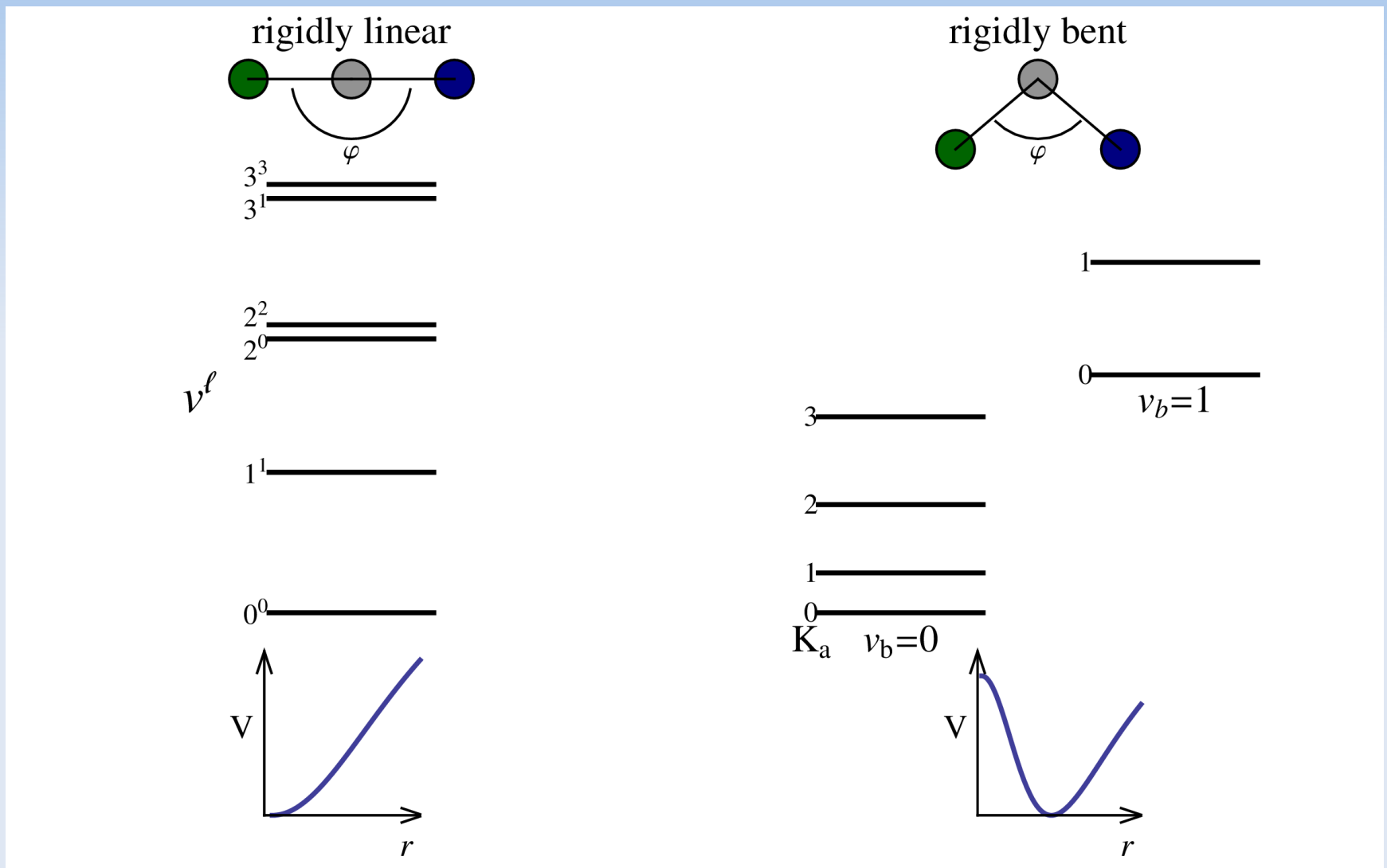
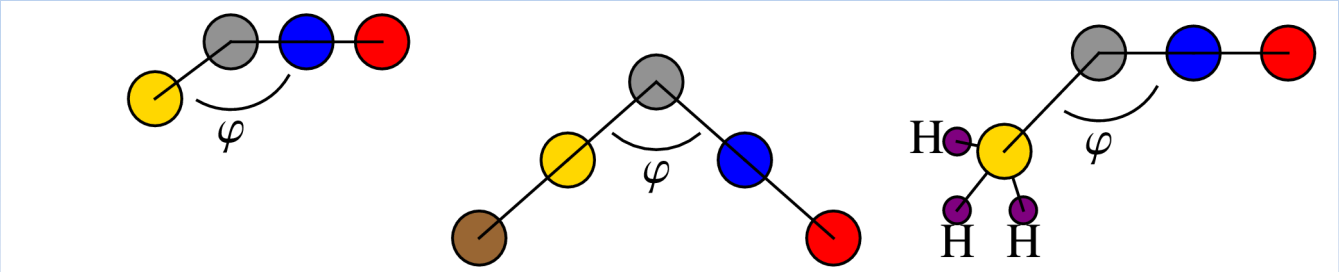
rigid molecules



bending in floppy molecules

- small molecules, 4-7 atoms total



  - have an isolated bending vibration mode
  - for which vibration-rotation spectrum is known
  - non-rigid or ”floppy”
- vibron model has few, physically relevant parameters, values of which are obtained by a fit to experimental data
  - harmonicity ε
  - anharmonicity α
  - angular momentum β
  - pairing (interaction) A

F. Iachello, S. Oss, J. Chem. Phys. 104 (1996) 6956
F. Iachello, F. Pérez-Bernal, P. Vaccaro, Chem. Phys. Lett. 375 (2003) 309

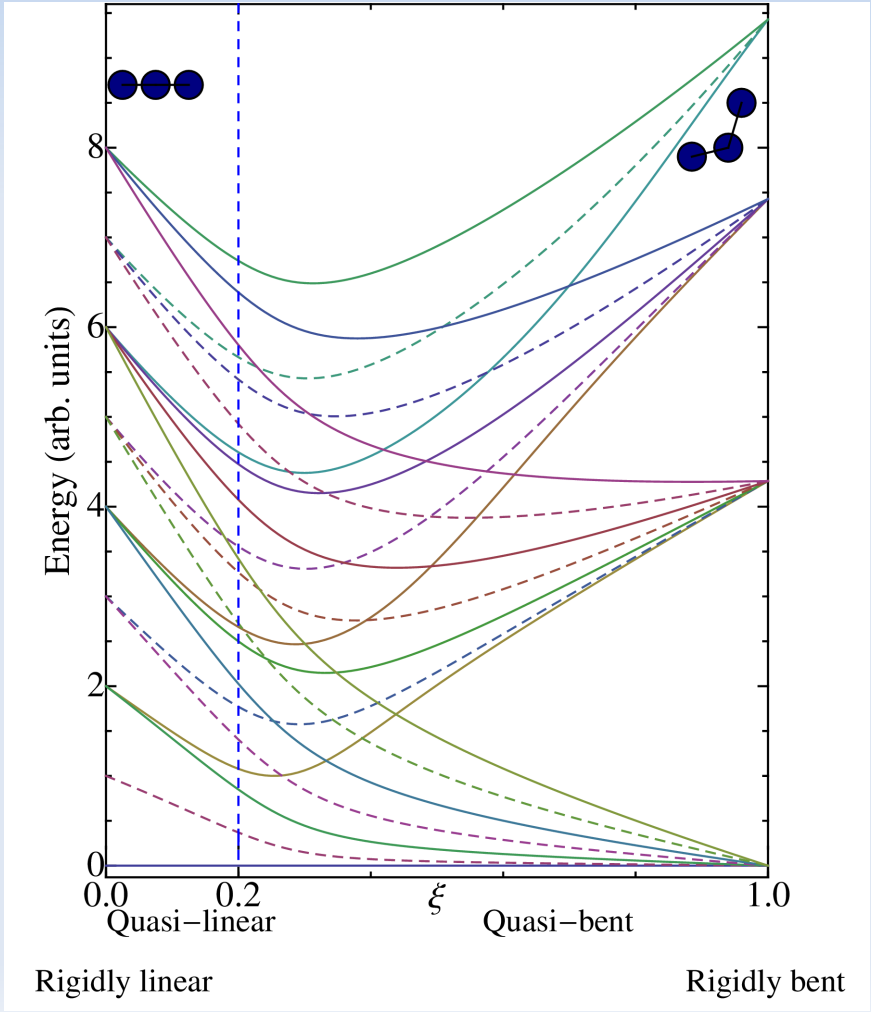
quantum phase transition (QPT) in molecules

- QPT: qualitative changes in the state of a system as a function of a parameter in Hamiltonian

$$H_{total} = (1-\xi) H_{linear} + \xi H_{bent}$$

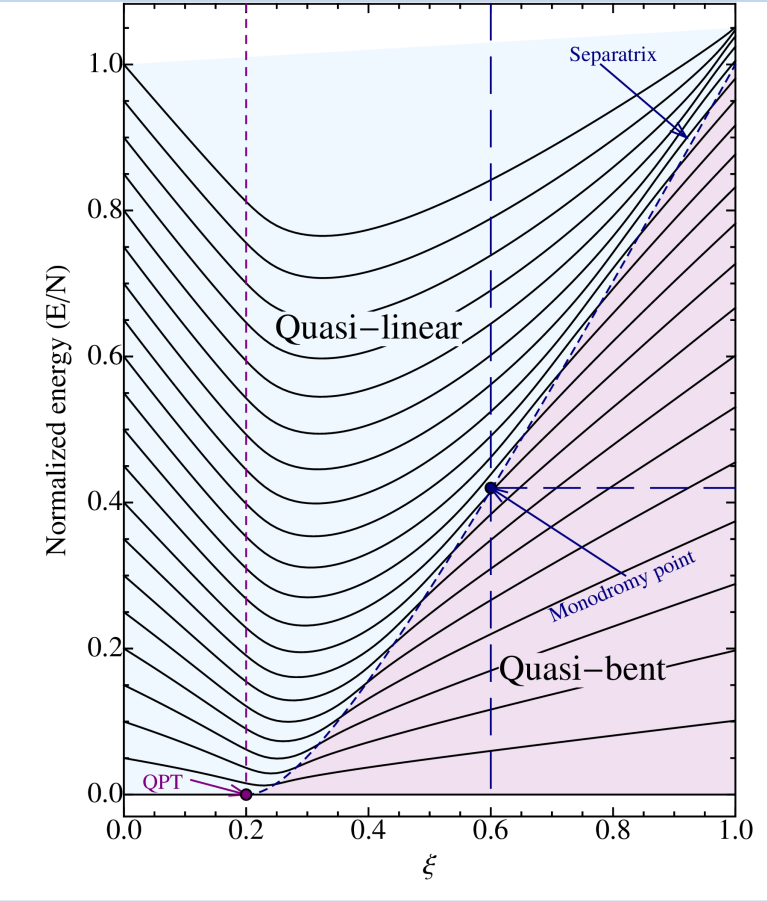
F. Pérez-Bernal, F. Iachello, Phys. Rev. A 77 (2008) 032115

- Evolution of energy levels as a function of ξ: correlation diagram

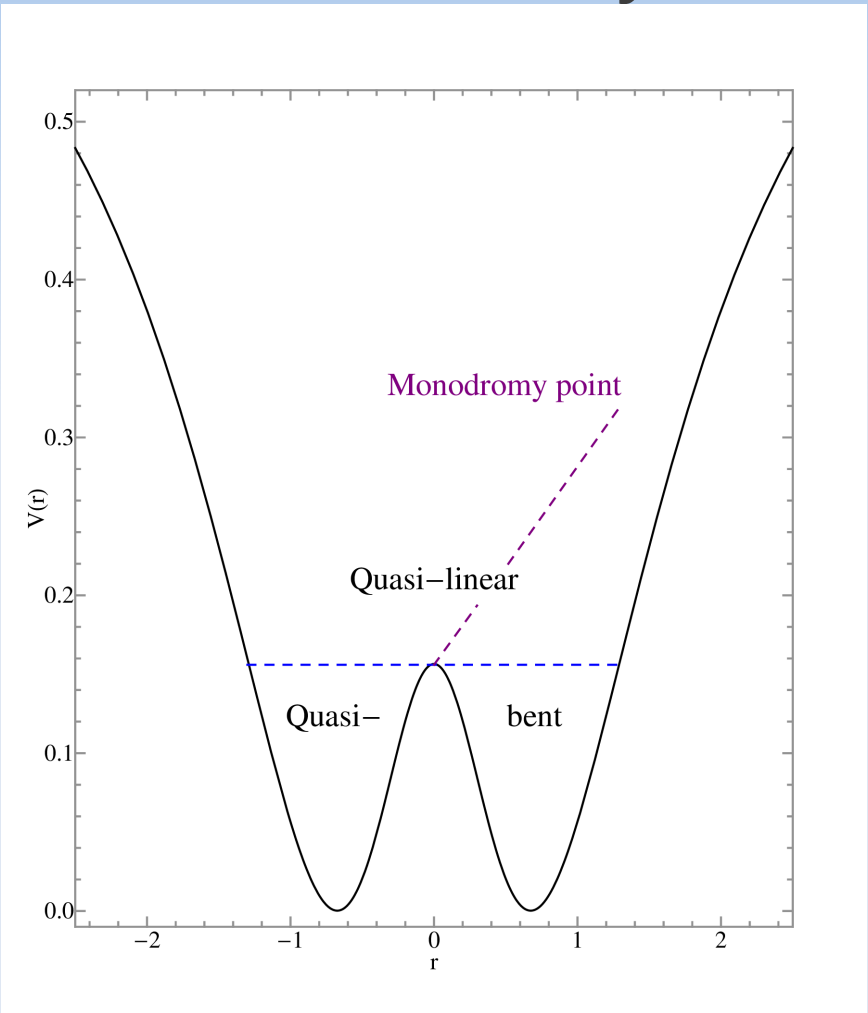


Excited State QPT in molecule

- ESQPT: qualitative changes in the state of the system as a function of excitation energy



Monodromy

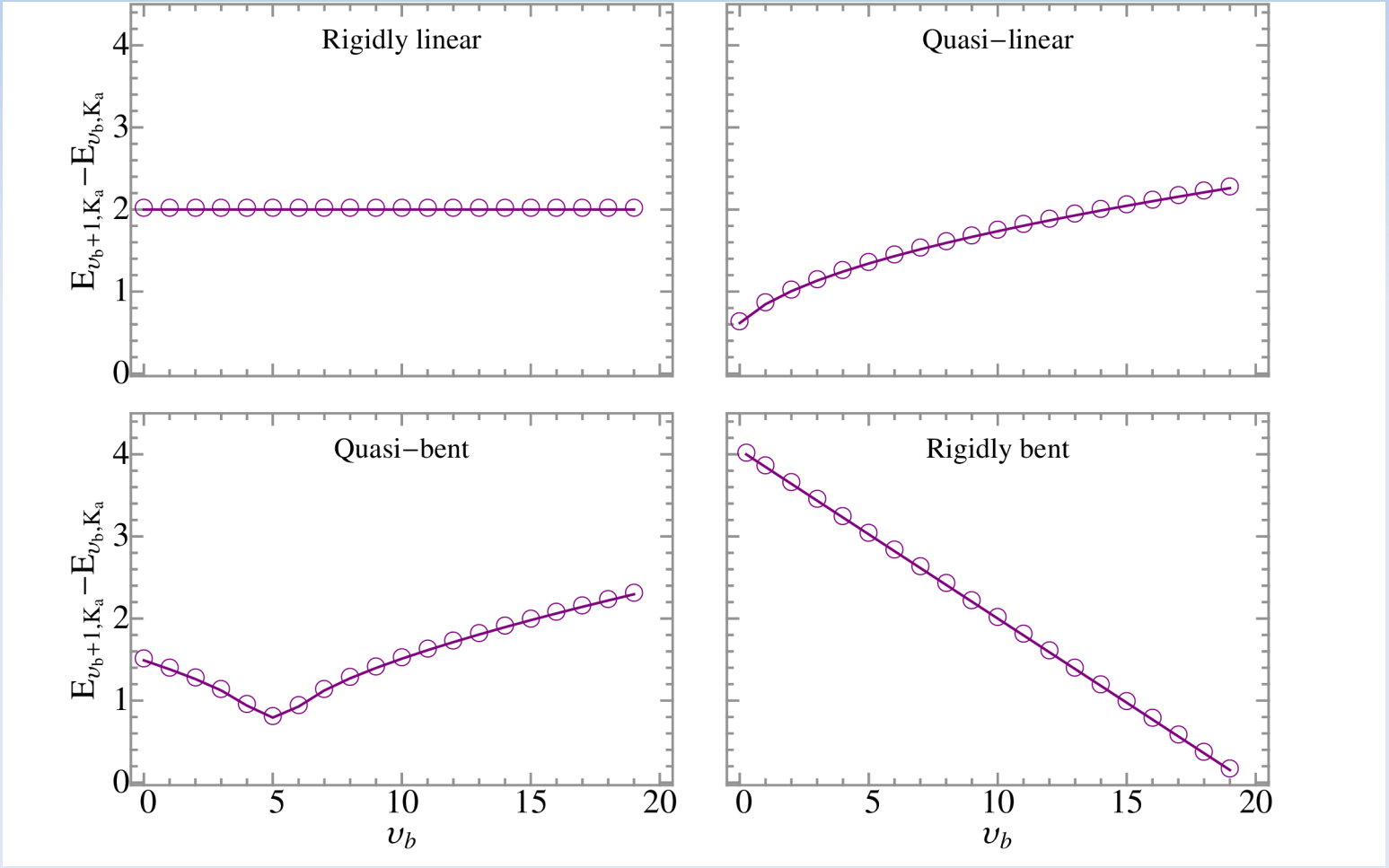


ESQPT ≡ monodromy

M. Child, T. Weston, J. Tennyson, Mol. Phys. 96 (1999) 371
M. Winnewisser, B. Winnewisser, I. Medvedev, F. DeLucia, S. Ross, J. Mol. Struct. 798 (2006) 1
M. Caprio, P. Cejnar, F. Iachello, Annals of Phys. 323 (2008) 1106

spectroscopic signatures of QPT and ESQPT

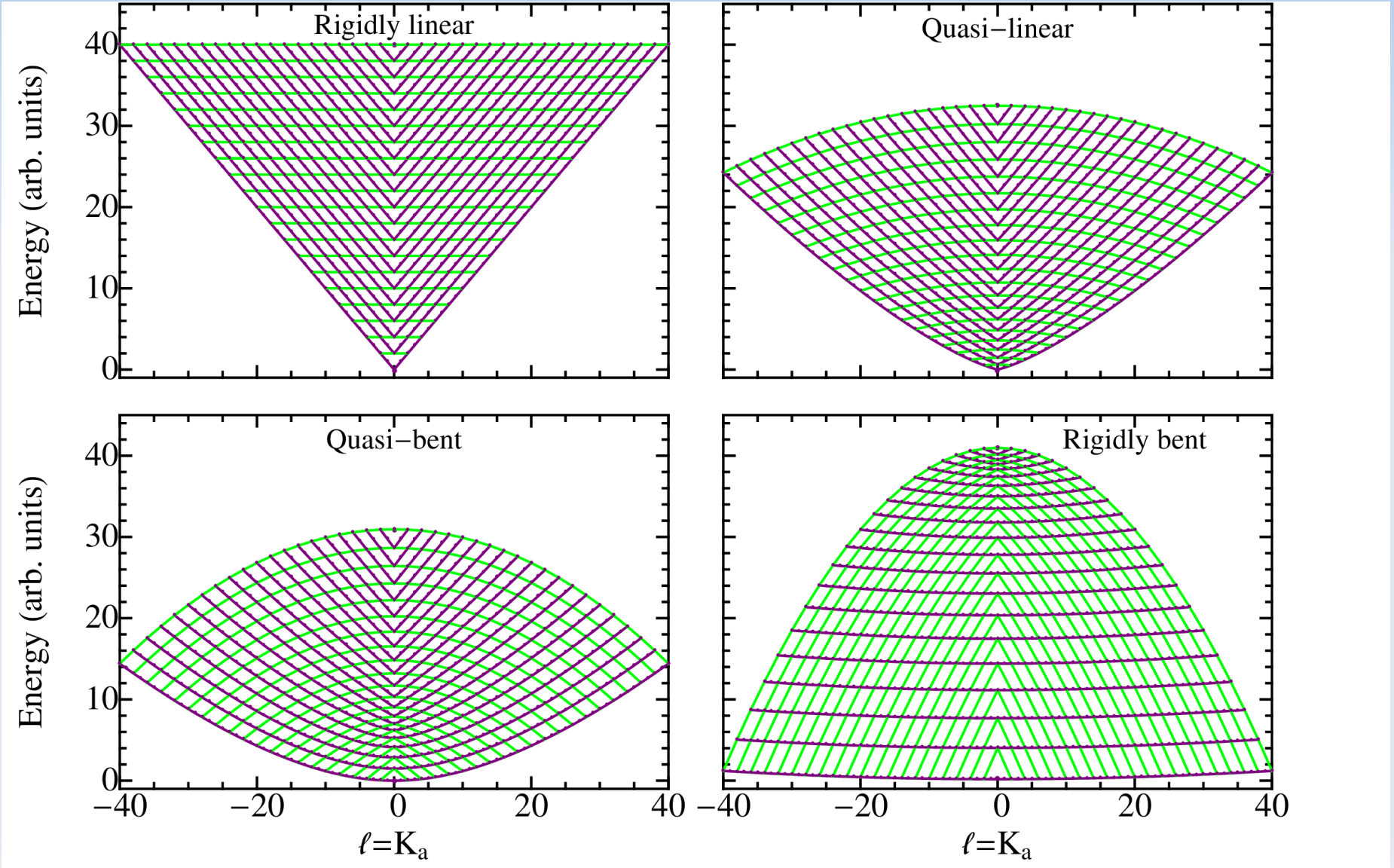
Birge-Sponer plots



R. Dixon, Trans. Of Farady Soc. 60 (1964) 1363

spectroscopic signatures of QPT and ESQPT

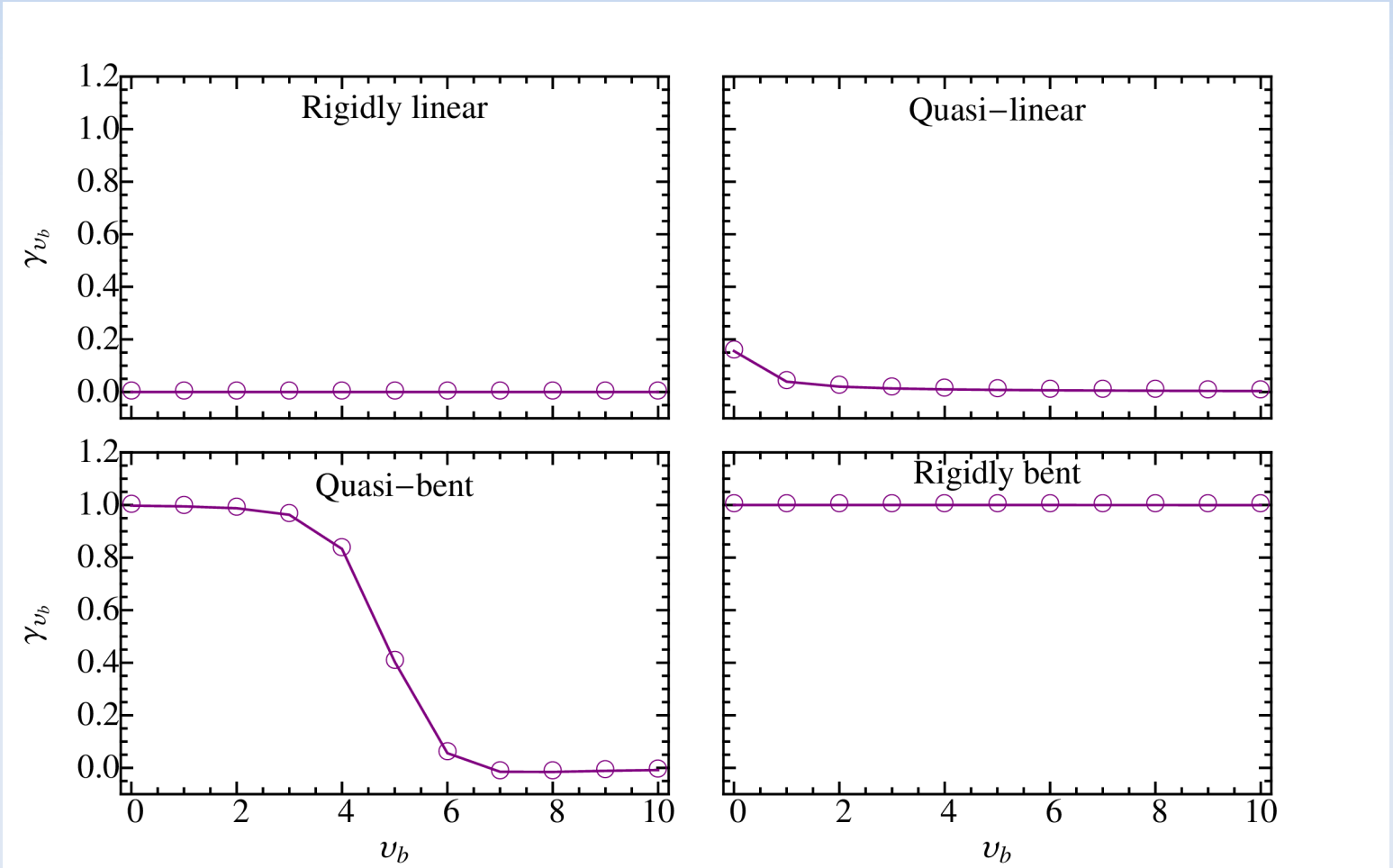
Monodromy plot



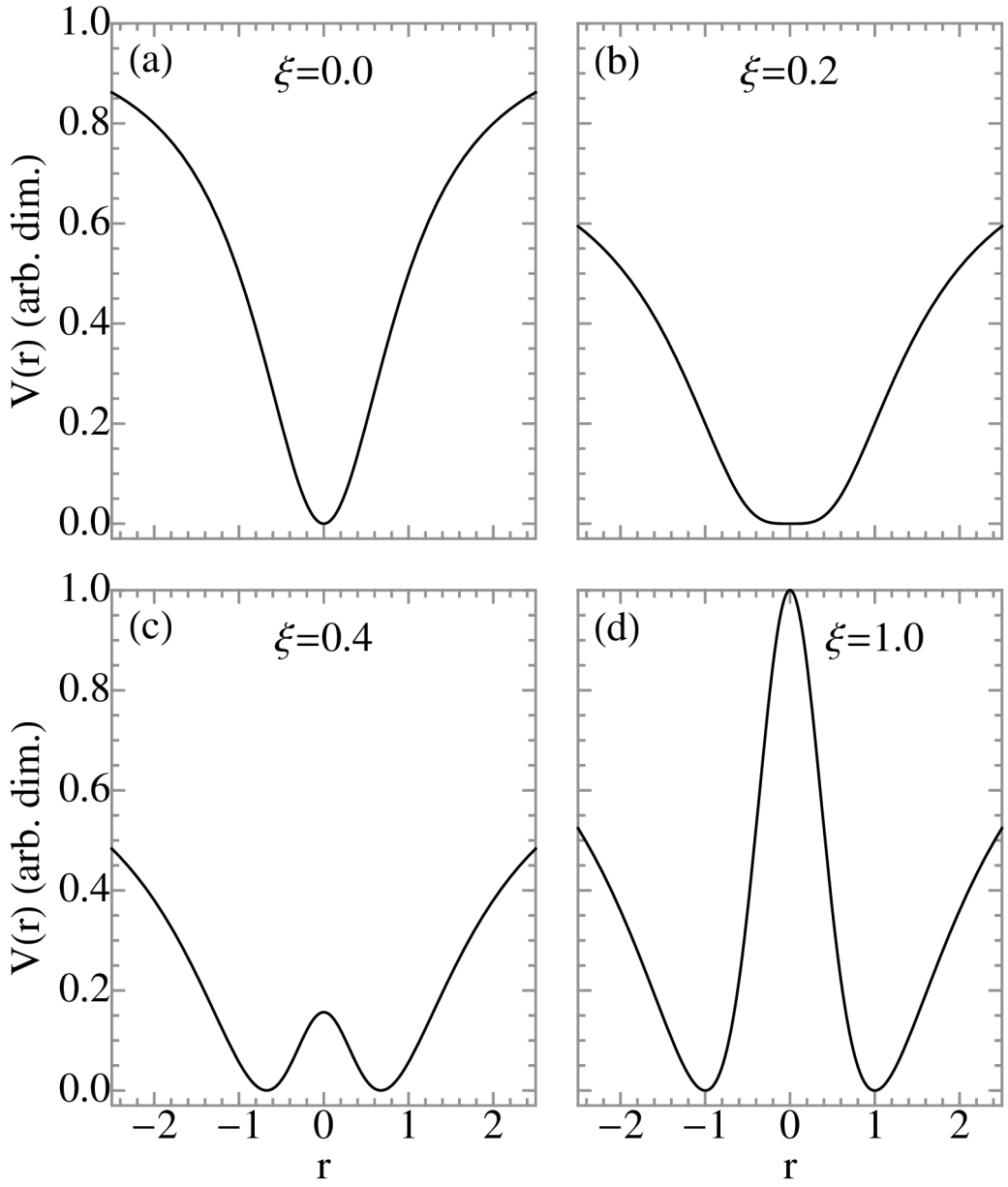
spectroscopic signatures of QPT and ESQPT

Angular momentum exponent plot

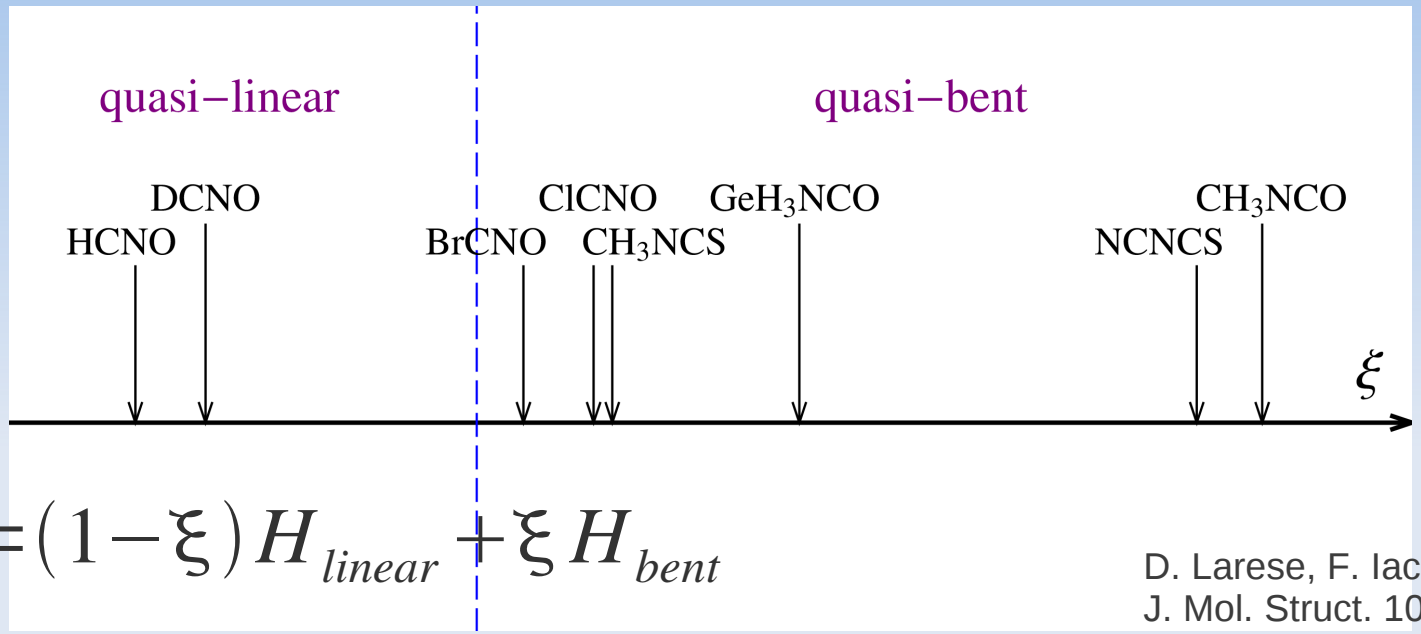
$$E(\ell) = E_0 + a\,\ell^{\gamma_{\upsilon_b}+1}$$



potential surfaces



summary of our study



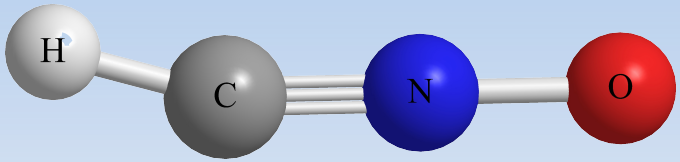
$$H_{total} = (1-\xi) H_{linear} + \xi H_{bent}$$

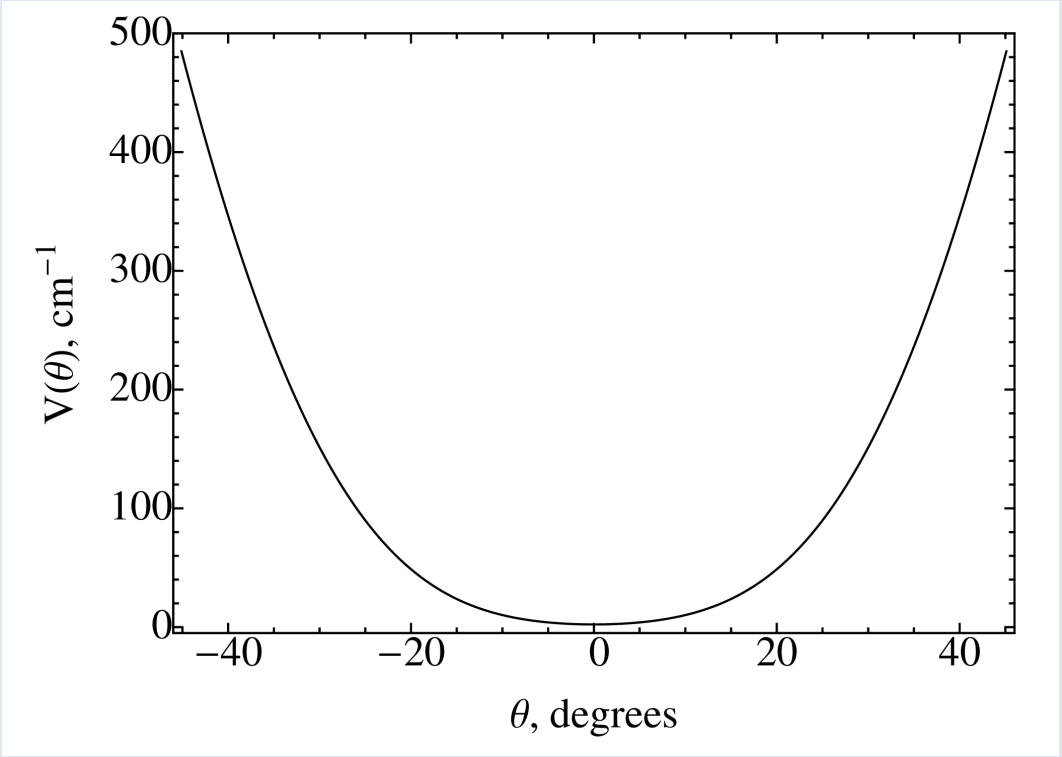
D. Larese, F. Iachello
J. Mol. Struct. 1006, 611 2011

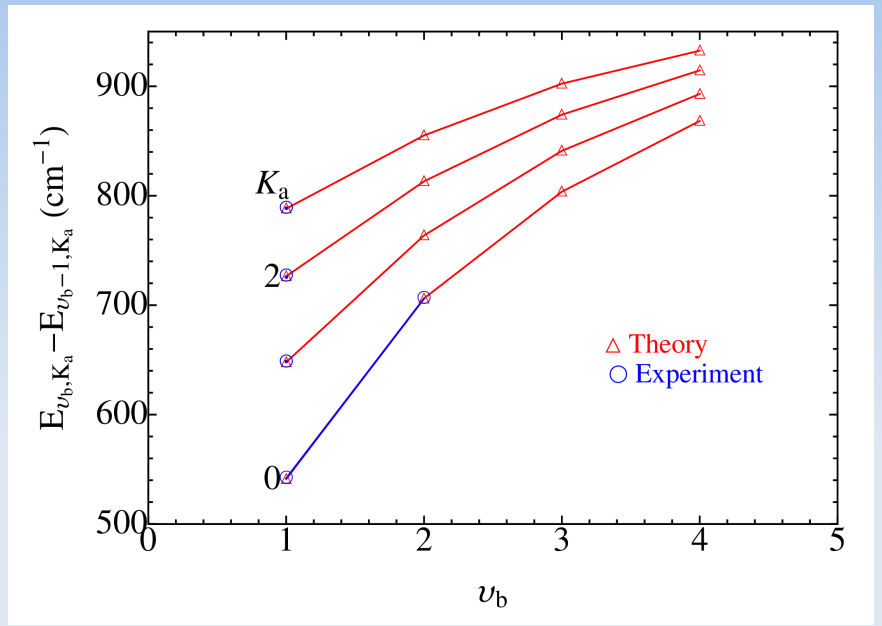
Table 1: Best-fit values of Hamiltonian parameters. N (the integer vibron number) and ξ (control parameter value) are both dimensionless, while ε, α, β, A, and rms deviation are in cm^{-1}.

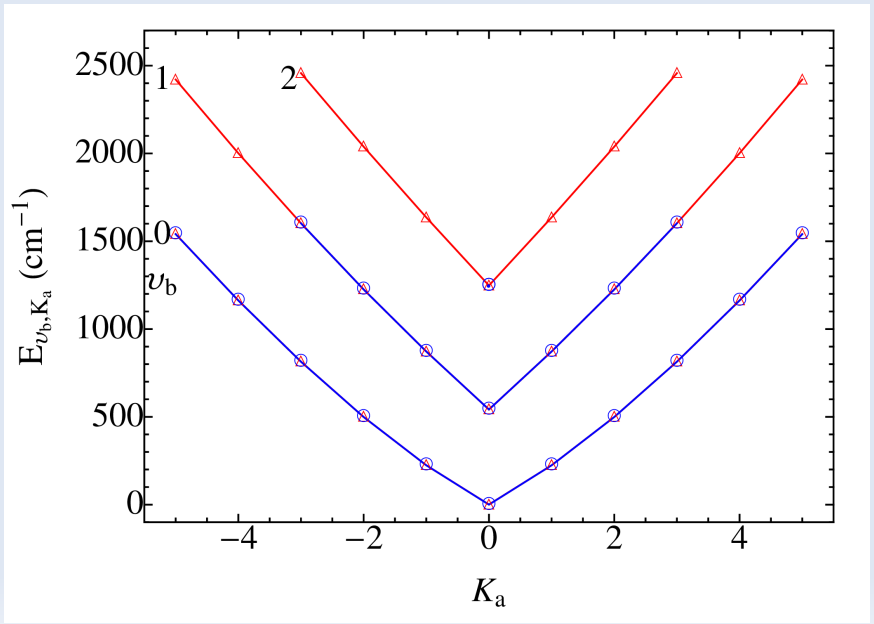
Molecule	N	ε	α	β	A	rms	ξ
CH_3NCO	78	453.756	-5.5741	7.6712	1.6313	1.34	0.2168
NCNCS	70	203.572	-2.5766	1.4957	0.81344	2.18	0.2154
GeH_3NCO	90	385.319	-4.1902	4.6941	1.1172	0.38	0.2069
CH_3NCS	73	523.947	-6.8652	7.8193	1.8524	0.48	0.2029
ClCNO	92	638.079	-6.4925	3.2283	1.7766	0.71	0.2025
BrCNO	96	642.047	-6.4154	3.1938	1.6980	0.57	0.2010
DCNO	30	634.902	-12.5727	8.4958	5.2775	0.25	0.1942
HCNO	24	716.715	-13.0168	10.7685	7.4363	0.09	0.1927

fulminic acid

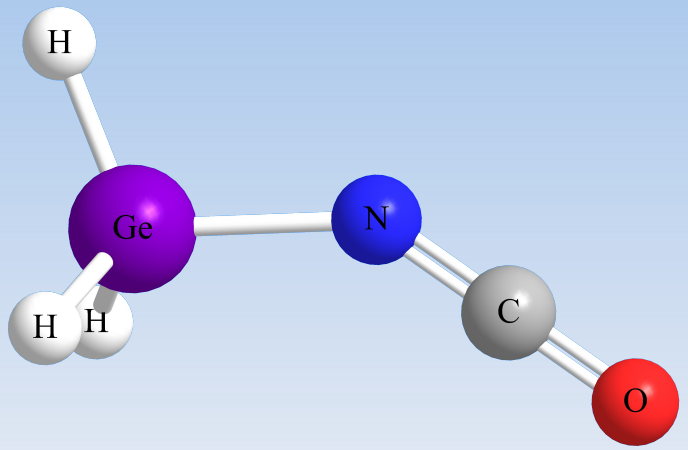


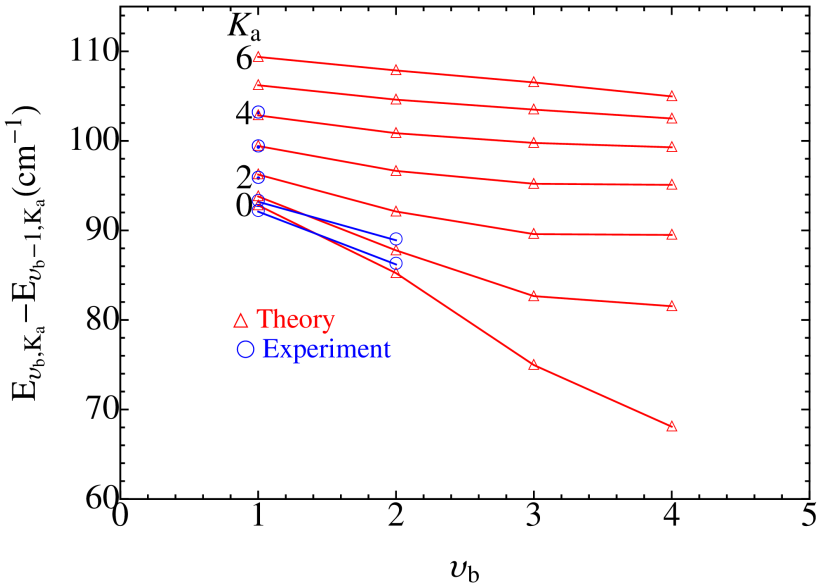


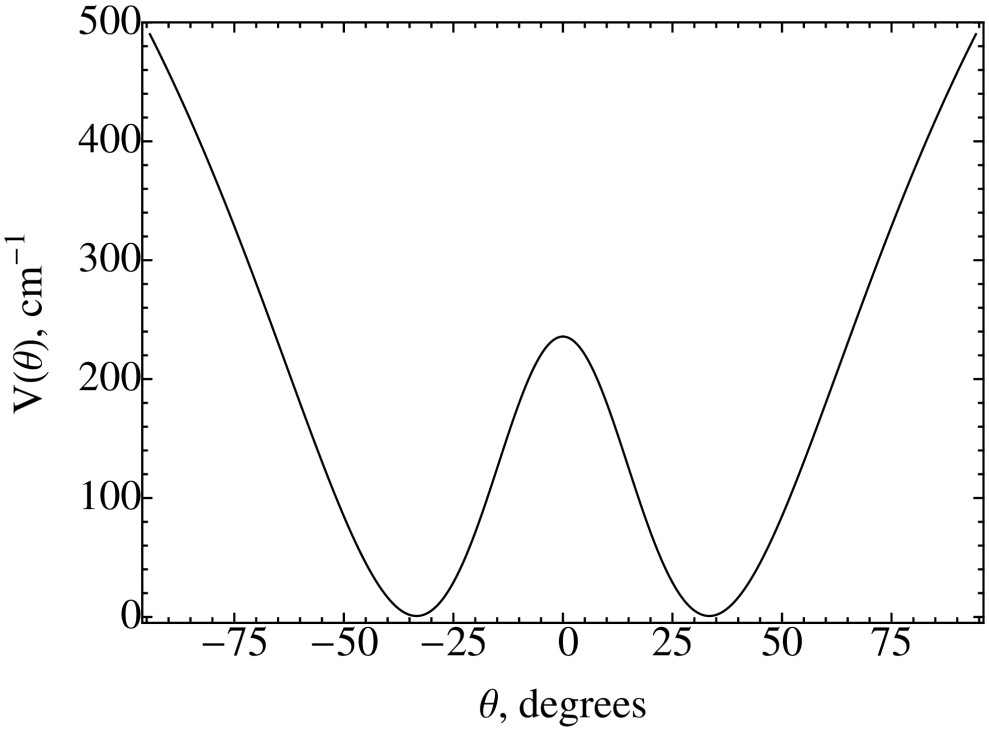


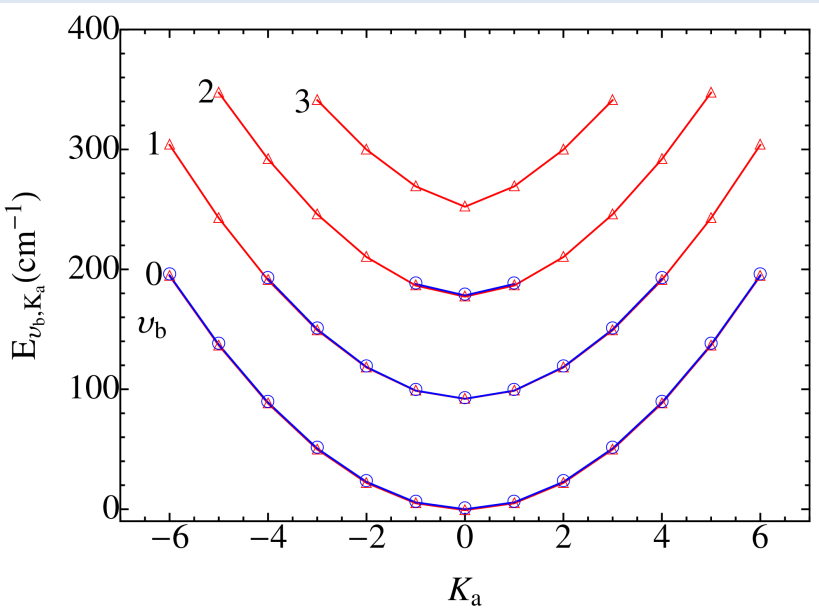


germyl isocyanate

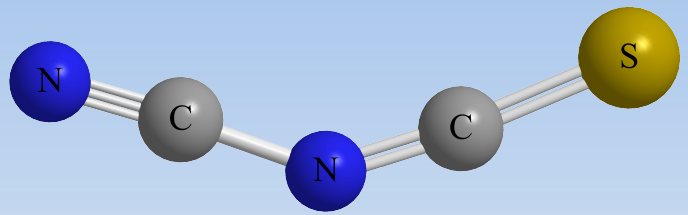








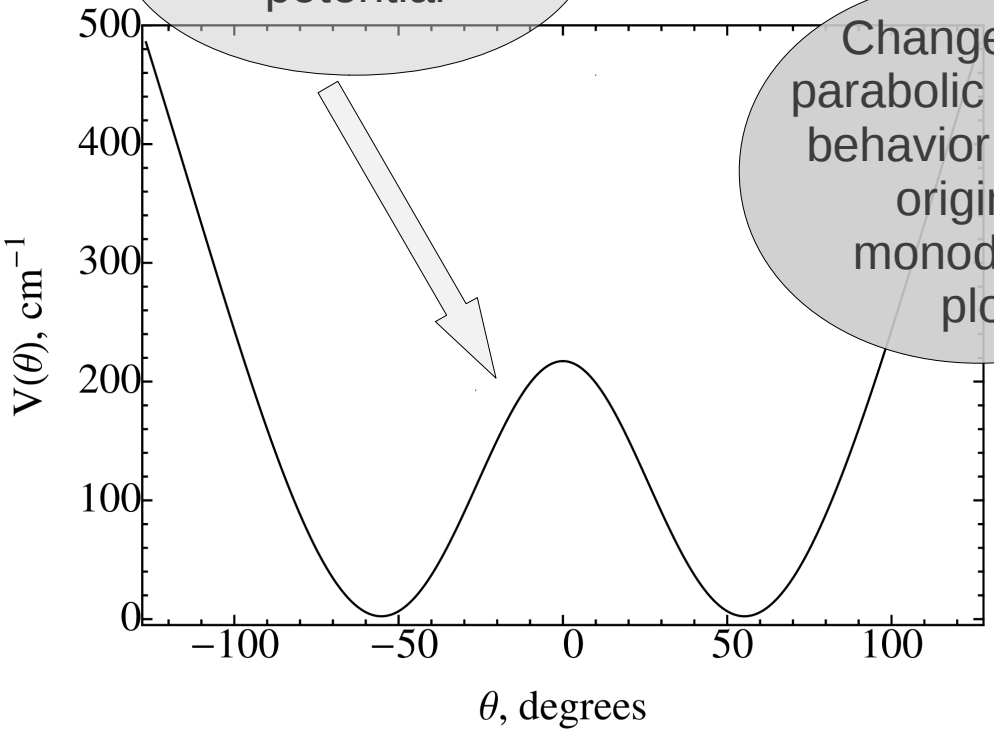
spectroscopic signatures

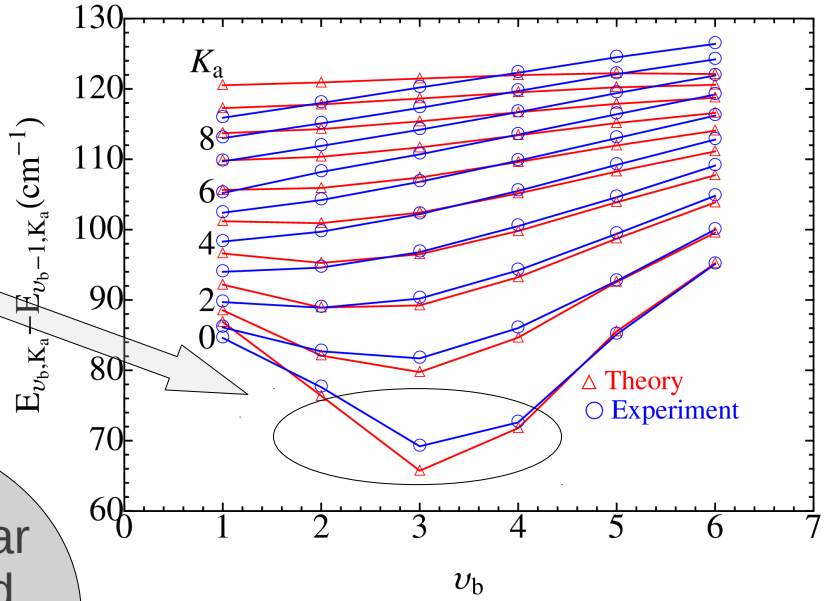


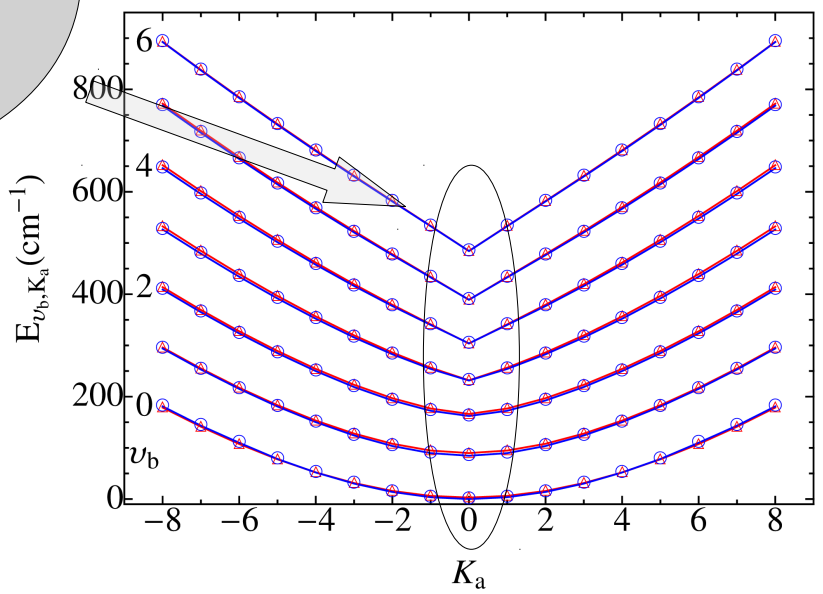
Champagne-bottle hump in bending potential

Dixon dip in Birge-Sponer plot

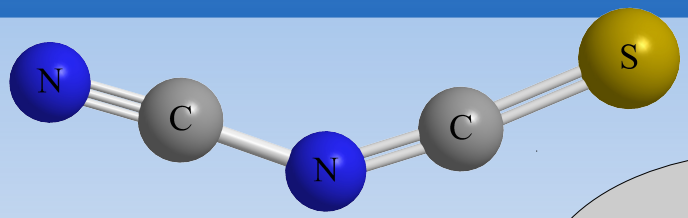
Change from parabolic to linear behavior around origin in monodromy plot



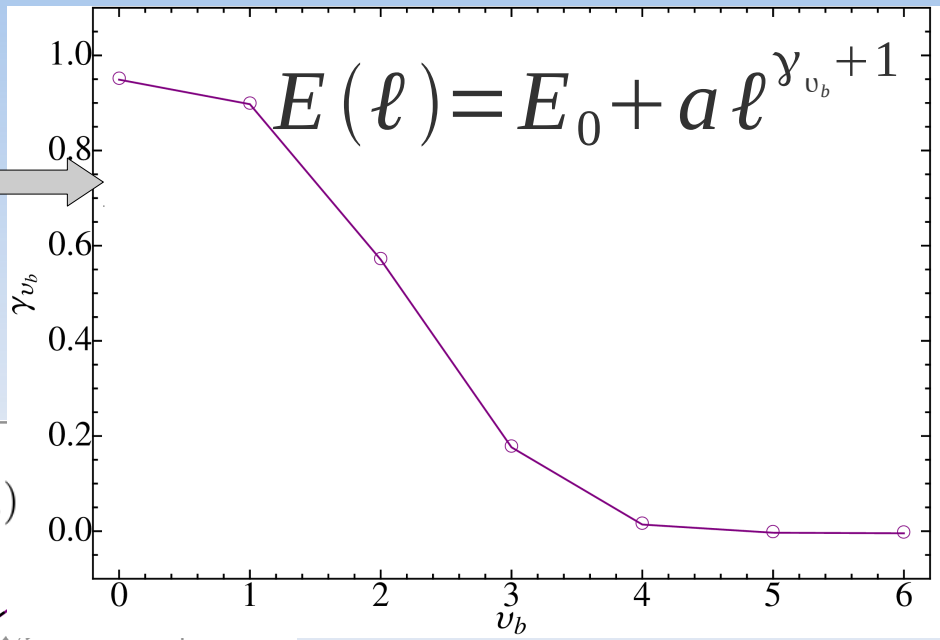


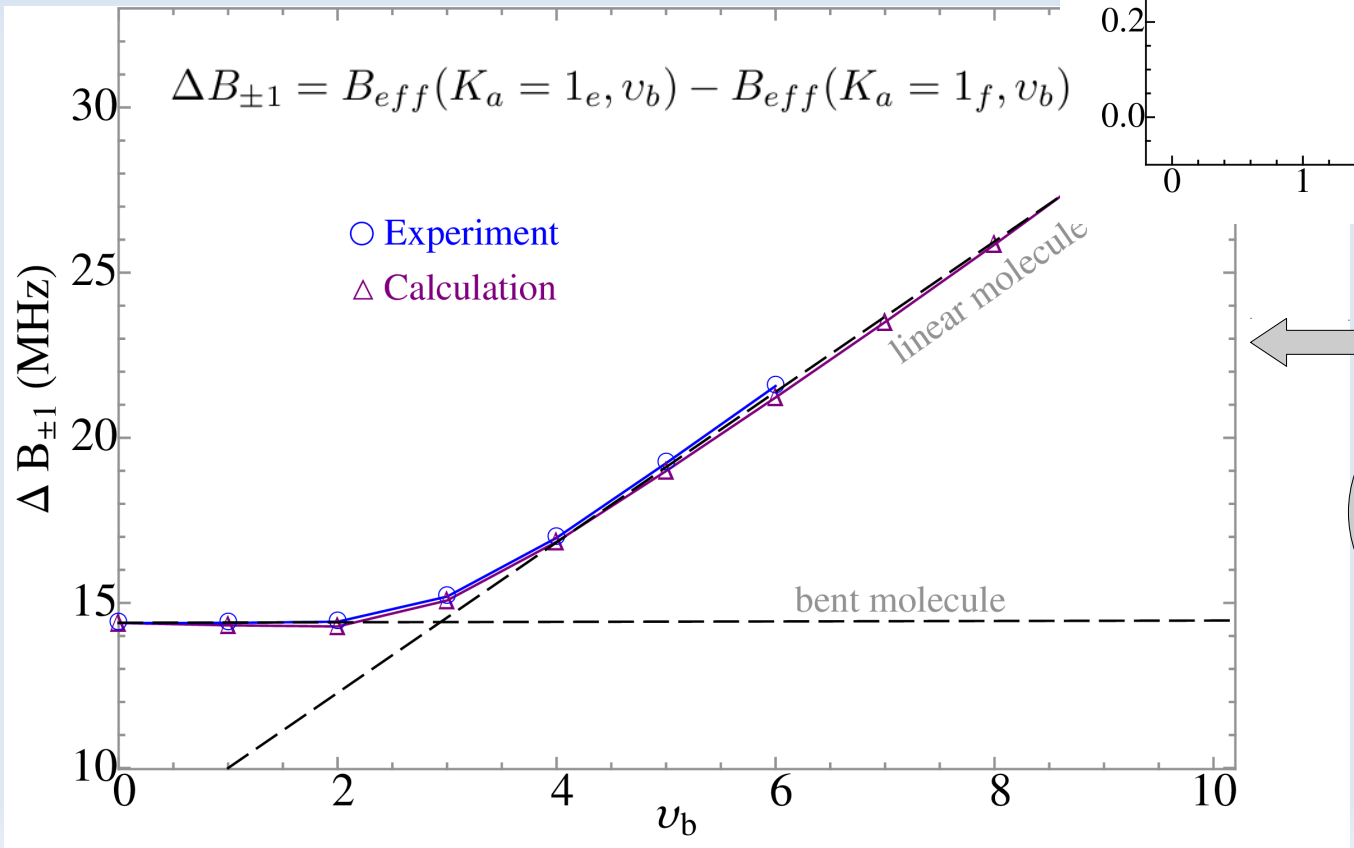


more evidence of ESQPT in NCNCS



Angular momentum exponent plot





Vibration-rotation interaction: rotational constants *e-f* splitting changes abruptly

next project: coupled benders

- Molecules with two bending sites that are coupled
- Acetylene
  - Ground electronic state, linear molecule
    - F. Iachello, F. Pérez-Bernal J. Phys. Chem. A 113 (2009) 13273
  - Excited electronic state, trans-bent
    - Three large-amplitude motions: two bends, one torsion
    - Makes trans-cis transition?
    - A.J. Merer, A.H. Steeves, J.H. Baraban, H.A. Bechtel, R.W. Field, J. Chem. Phys. 134 (2011) 244310

next project: water

- Vast experimental data available
  - J. Chem. Phys. Ref. Data 30 (2001) 735
  - J. Che. Phys. 131 (2009) 221105
  - J. Quant. Spectros. & Rad. Transf. 111 (2011) 1043
- Bend + anti-symm. stretch + symm. Stretch

- ESQPT at high energy
  - ~11 000 cm^{-1}
  - $v_b = 8$

conclusion

- Simple algebraic Hamiltonian can describe rigidly linear, quasi-linear, quasi-bent, and rigidly bend molecules
- QPT and ESQPT (monodromy) can be seen in bending modes of small non-rigid molecules
- More complex systems (e.g., coupled benders and isomerization) may also be described

Thanks!

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Correlation diagram