Groupe de Chimie Théorique
du MSME

Renner-Teller Effect in Tetra-Atomic Molecules

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(non linear) Outline

General Presentation

Structure of Vibronic Levels & Hund's Cases

A New Variational Method

Application to the Acetylene Cation

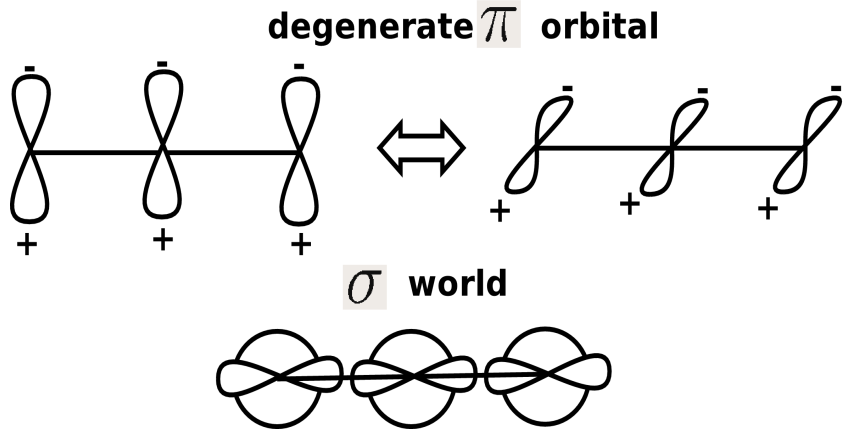
Rotational Structures

HCCS : A Challenging System

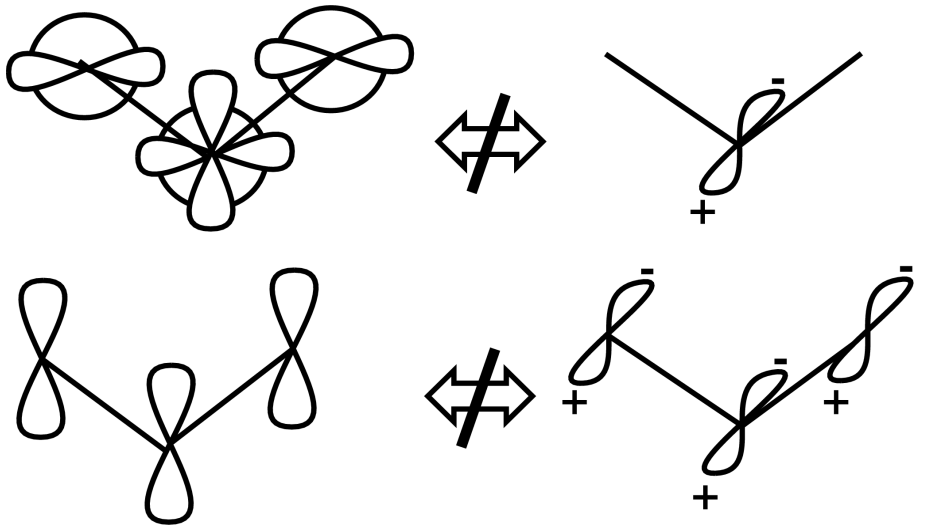
Where does the RT Effect come from ?

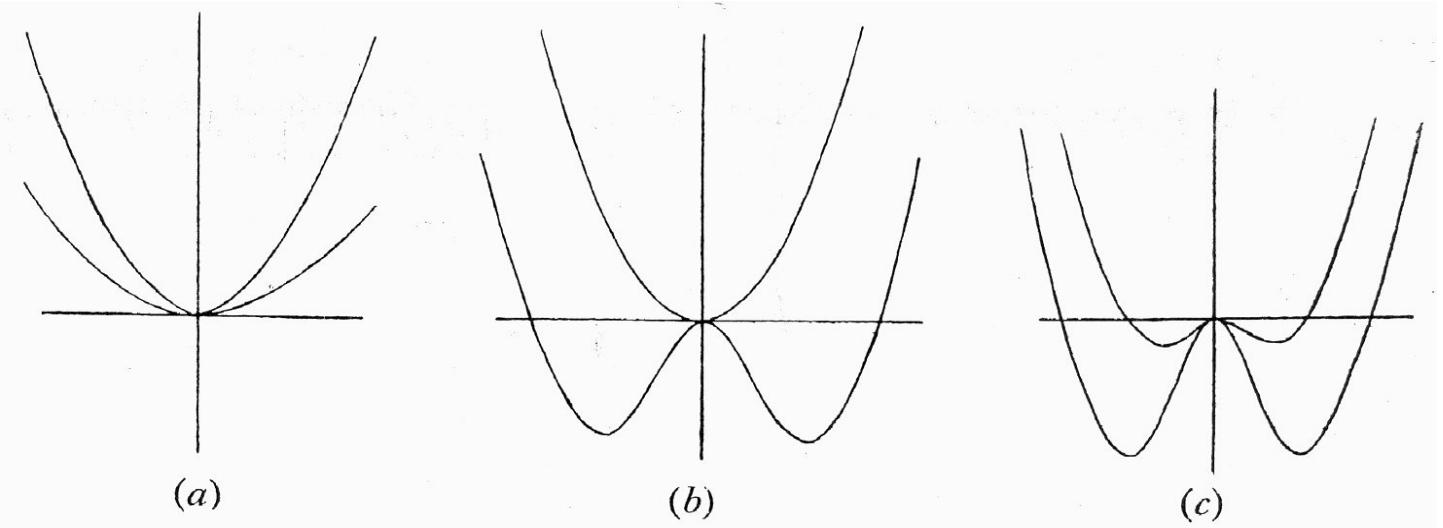
§ Chain systems exploring linearity with a degenerate electronic state

At linearity



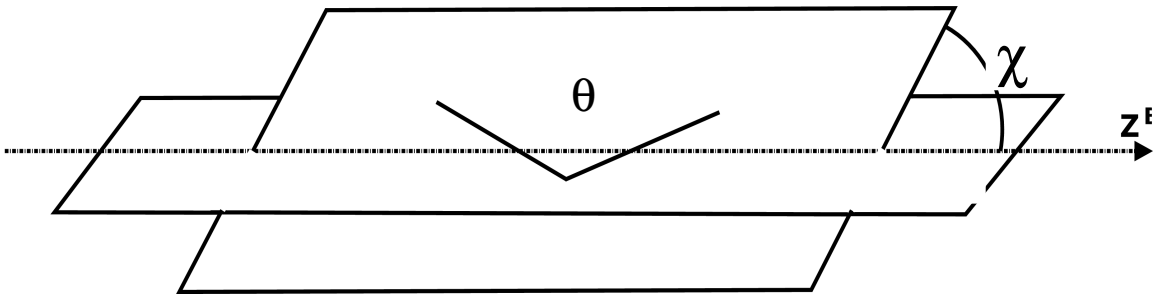
Out of linearity





Pople & Longuet-Higgins
Mol. Phys. 1, p. 372 (1958)

Non Adiabatic Couplings (triatomics)



§ In the (A',A'') representation:

$$\begin{cases} \psi_X^I = f_X \, cos\left[\Lambda\left(\vartheta_e - \chi\right)\right] \\ \psi_X^{II} = f_X \, sin\left[\Lambda\left(\vartheta_e - \chi\right)\right] \end{cases} \Rightarrow \begin{cases} \frac{\partial}{\partial\chi}\psi_X^I = \Lambda\psi_X^{II} \quad ; \quad \frac{\partial}{\partial\chi}\psi_X^{II} = -\Lambda\psi_X^I \\ \frac{\partial^2}{\partial\chi^2}\psi_X^I = -\Lambda\psi_X^I \quad ; \quad \frac{\partial^2}{\partial\chi^2}\psi_X^{II} = -\Lambda\psi_X^{II} \end{cases}$$

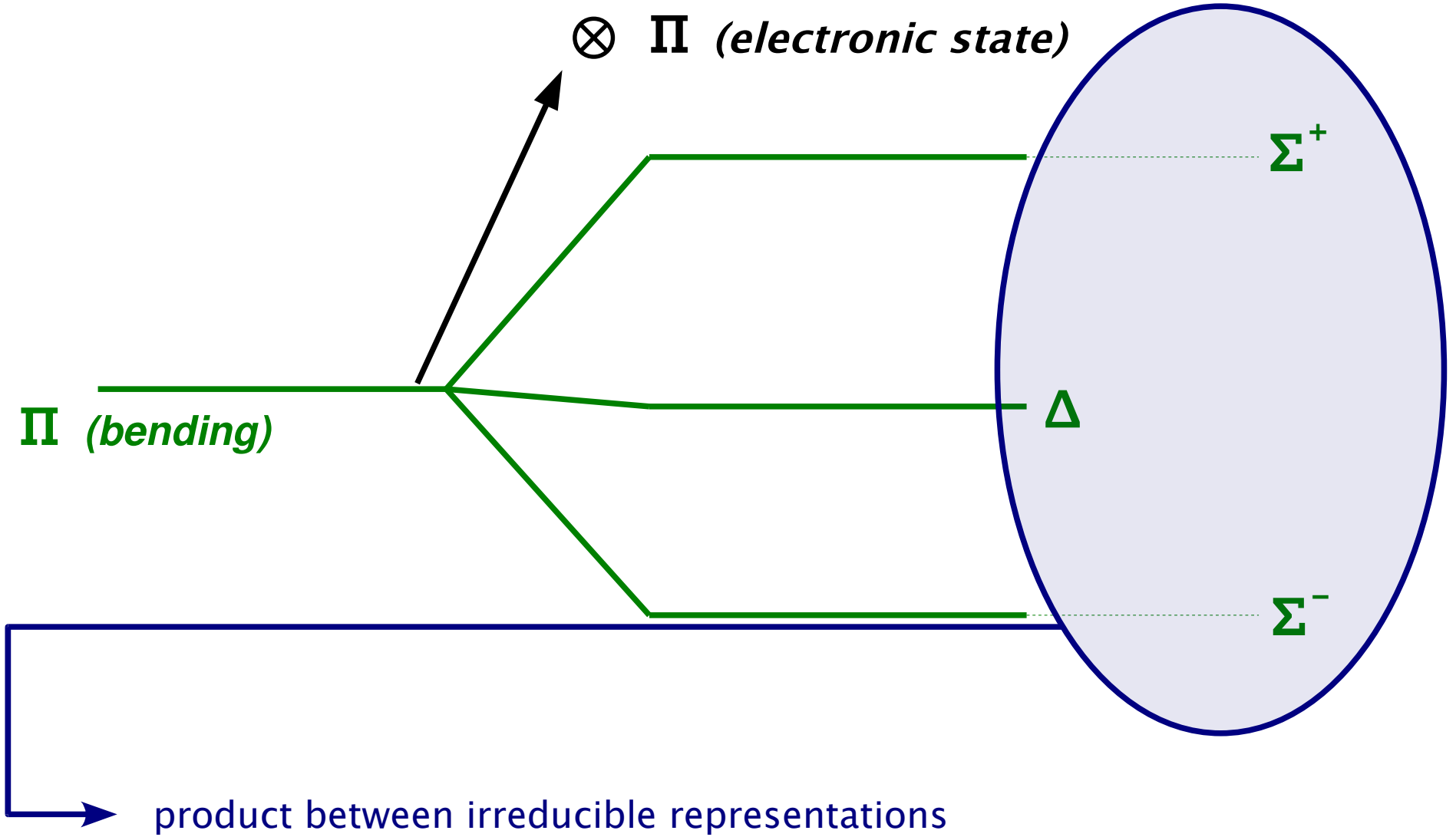
R. Renner, Z. für physik 92, p. 172 (1934)

Function of all nuclear displacements (except χ)

Single azimuthal electronic angle

Structure of Vibronic States (without SO)

§ With one quantum in the bending mode:



product between irreducible representations

> Σ-states well localized on one of both components

> Δ-state delocalized on both components

Hund's cases

Hund's Cases (a)

§ Total wavefunction factorized by:

$$|+\rangle = (\psi_k^I + i\psi_k^{II})/\sqrt{2}$$

or

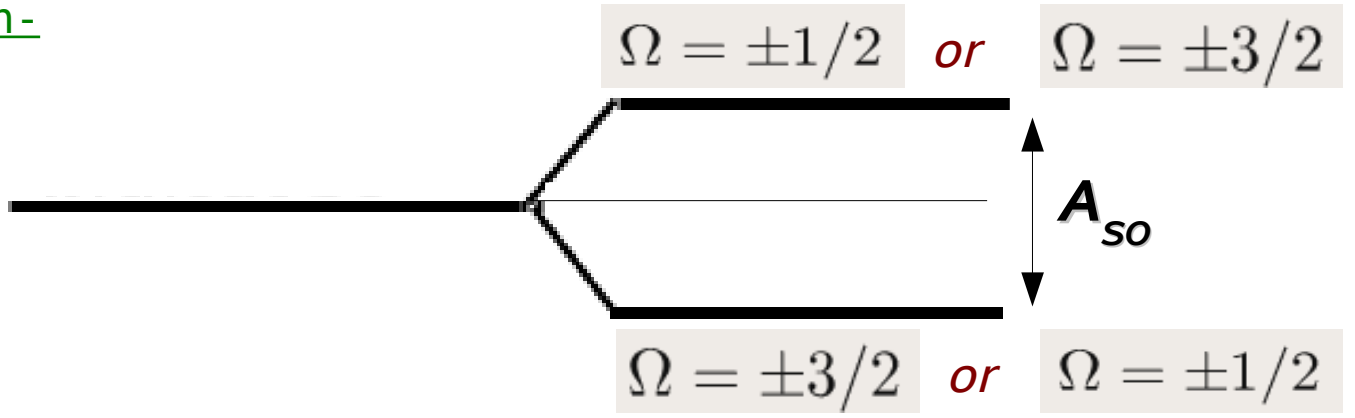
$$|-\rangle = (\psi_k^I - i\psi_k^{II})/\sqrt{2}$$

=> delocalized on both components

=> Λ is a good quantum number

§ Effects of the spin-orbit coupling:

$A \times L_z \cdot S_z$ =>



Hund's Cases (b)

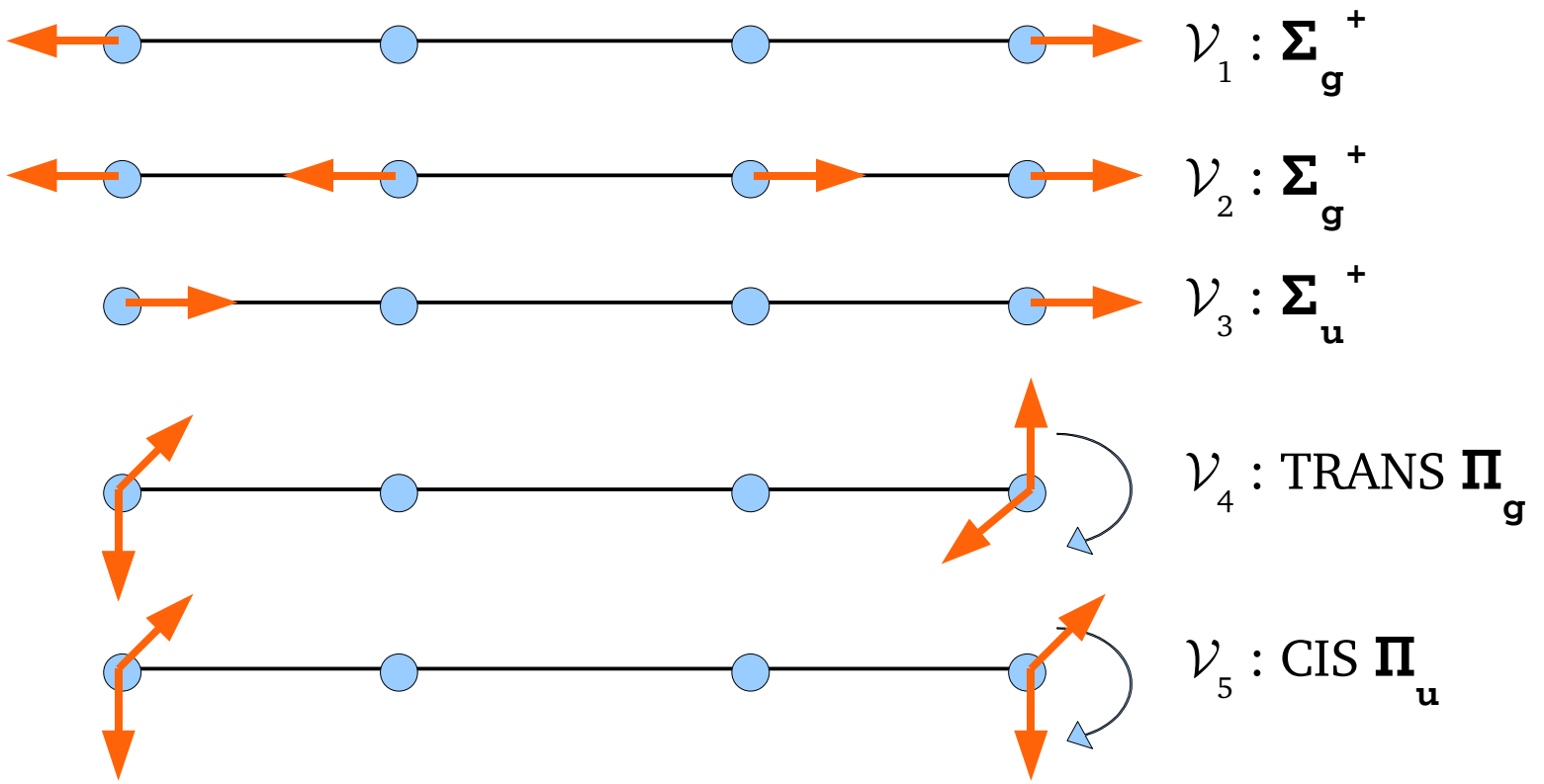
§ Total wavefunction factorized by: ψ_k^I *or* ψ_k^{II}

=> localized on one of both electronic potential

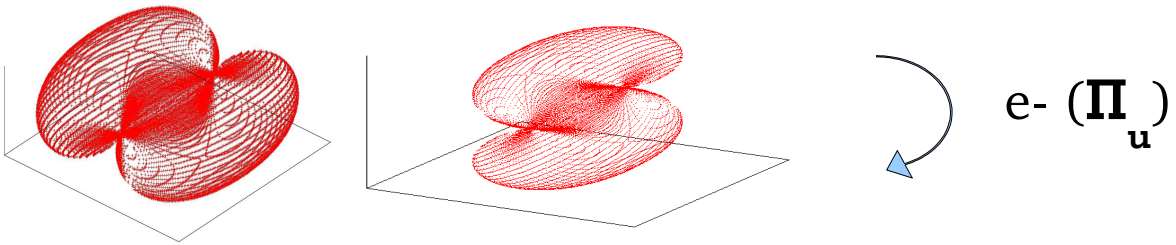
=> SO coupling almost cancels

Degrees of Freedom in Tetra-Atomic Molecules

§ Vibrational modes



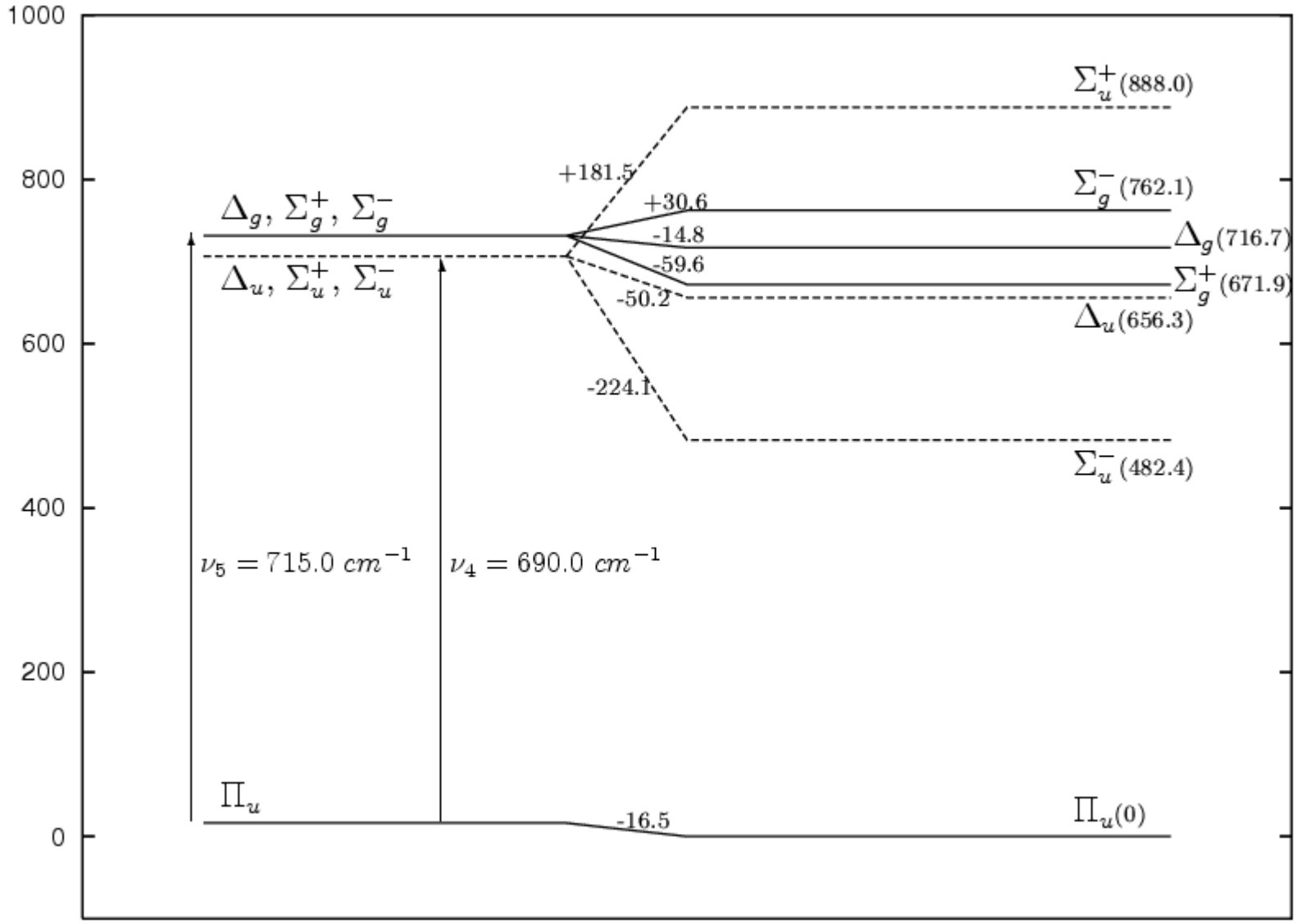
§ Electronic motion



+ Rotation
+ Spin (S = 1/2)

Consequences for the IR Spectrum

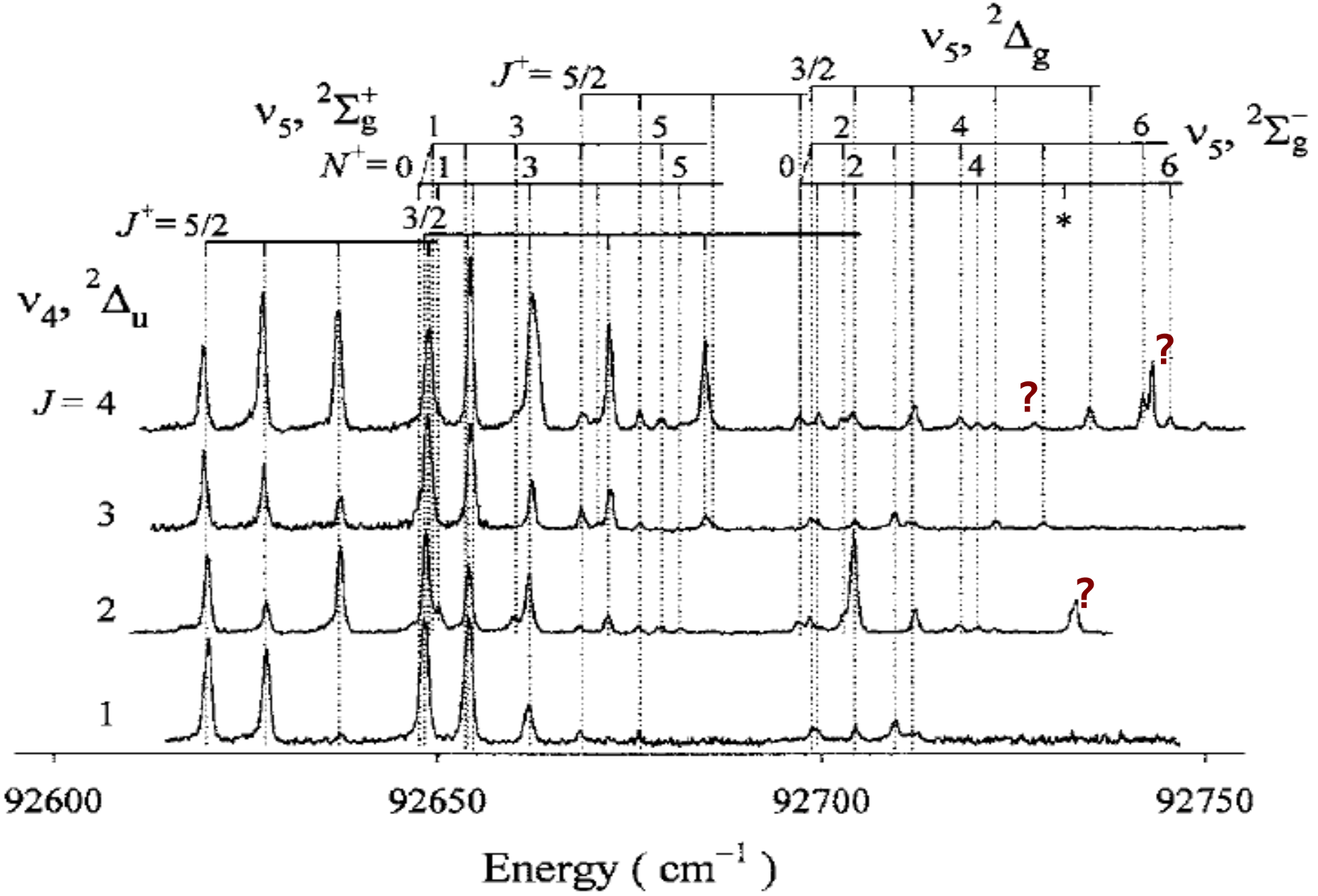
Example of the acetylene cation ($HCCH^+$) :



\+ Spin + Rotation

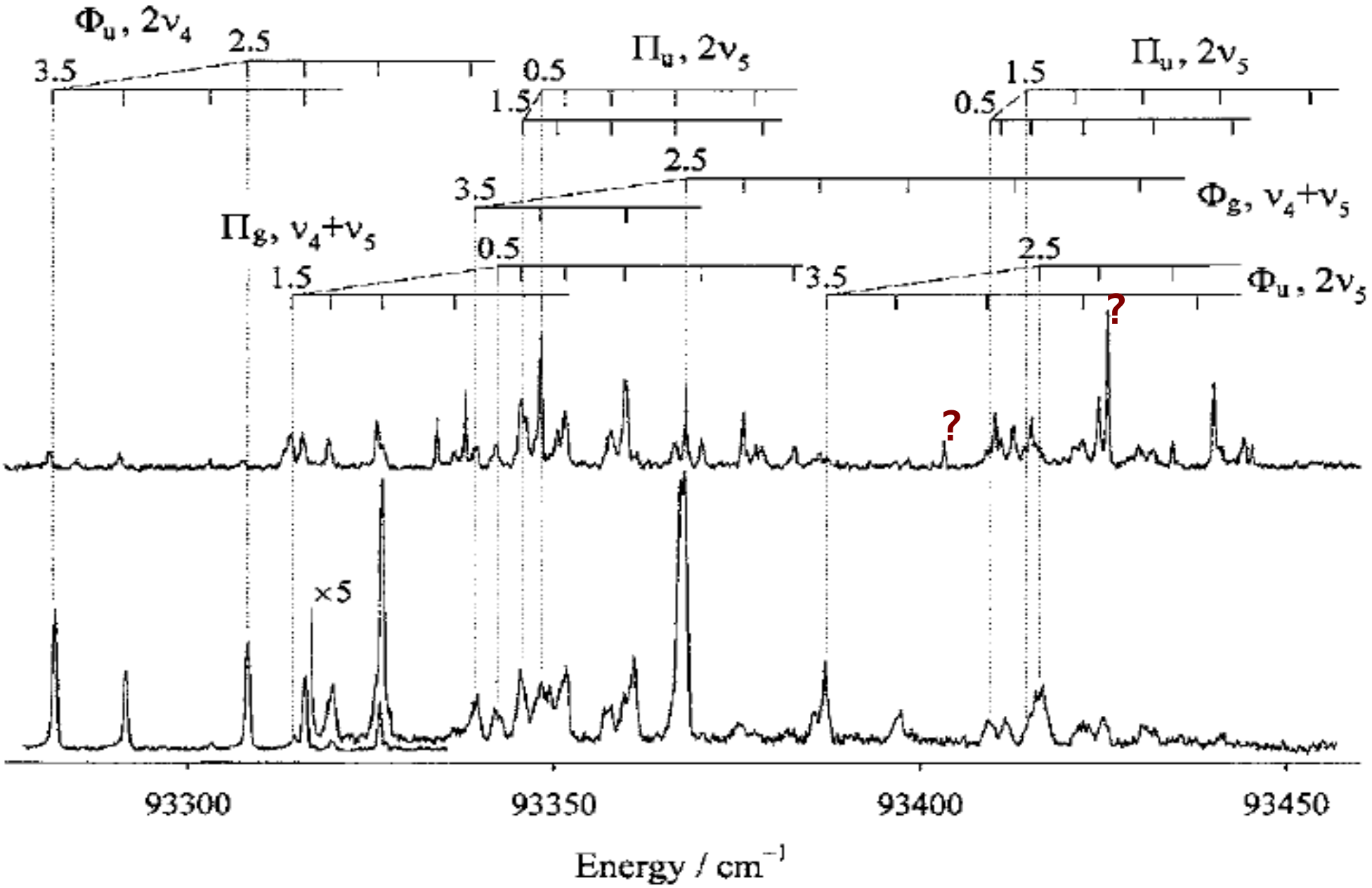
L. Jutier, C. Léonard et F. Gatti, JCP **130**, 134301 / 134302 (2009)

Spectrum Around the First Two Σ_g



Tang et al. JCP **125**, 133201 (2006)

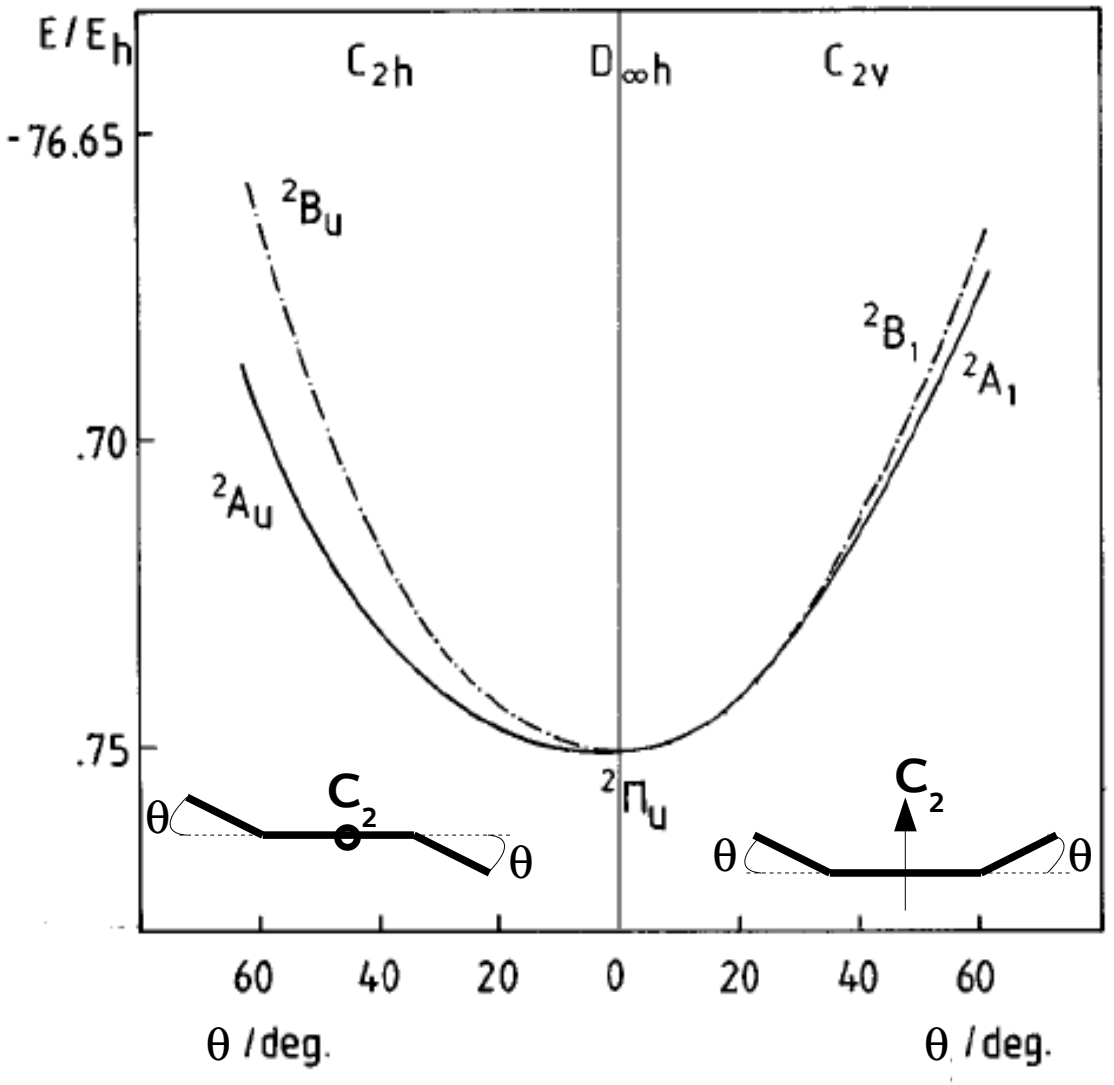
Spectrum Around 1400 cm^{-1}



Tang et al. JCP **125**, 133201 (2006)

Model by Peric et al.

§ Angular motions for HCCH+



> one-dimensional curves

> separation of TRANS and CIS bendings

> model Hamiltonian for near-equilibrium geometries, with 4 degrees of freedom

Peric et al, JCP **102** p. 3685 (1995)

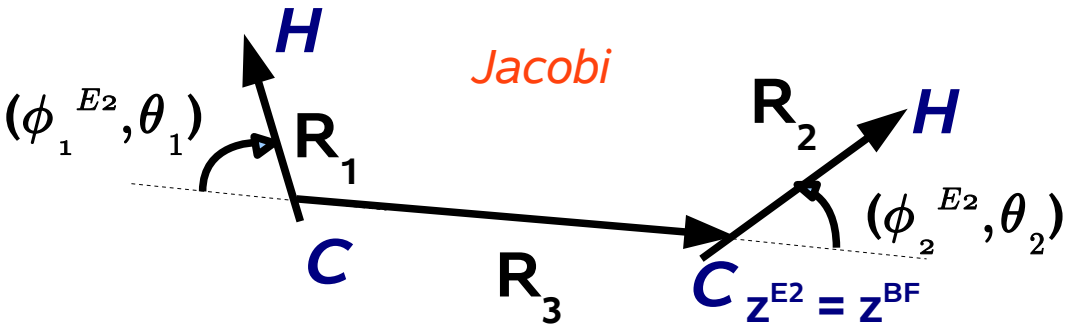
§ No coupling between rotation, bendings and stretches

Internal Coordinates

Simplicity of the nuclear Hamiltonian

$$2\hat{T} = \sum_{i=1}^{3}\left(-\frac{1}{\mu_i}\frac{1}{R_i}\frac{\partial^2}{\partial R_i^2}R_i\right) + \frac{(\hat{\mathbf{j}}_1^2)_{\mathrm{BF}}}{\mu_1 R_1^2} + \frac{(\hat{\mathbf{j}}_2^{\dagger}\hat{\mathbf{j}}_2)_{\mathrm{BF}}}{\mu_2 R_2^2}$$

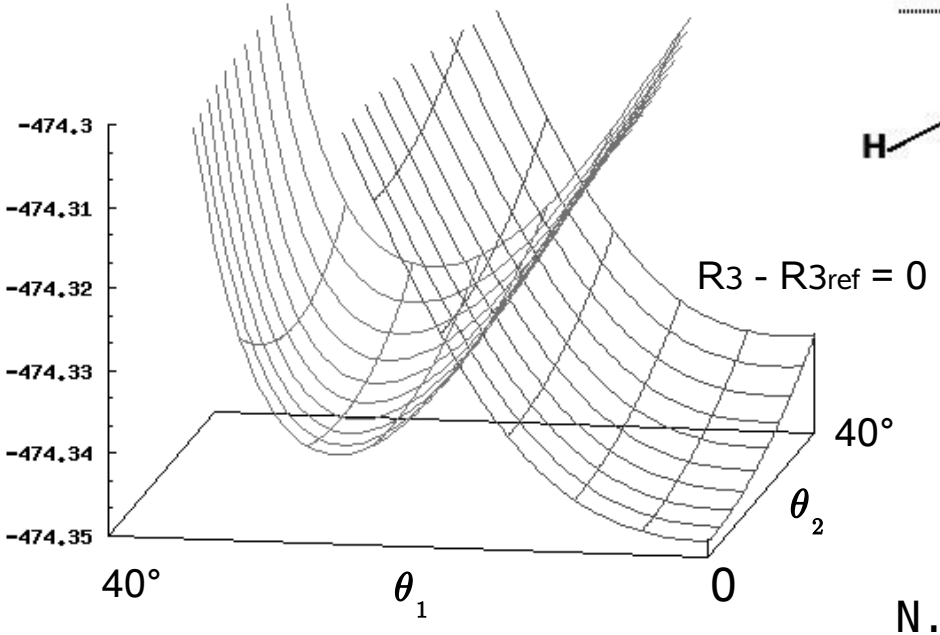
$$+ \frac{(\hat{\mathbf{J}}^2 + (\hat{\mathbf{j}}_1 + \hat{\mathbf{j}}_2^{\dagger})(\hat{\mathbf{j}}_1 + \hat{\mathbf{j}}_2) - 2\hat{\mathbf{J}}(\hat{\mathbf{j}}_1 + \hat{\mathbf{j}}_2))_{\mathrm{BF}}}{\mu_3 R_3^2}.$$



F. Gatti et al, JCP **123** 174311 (2005)

Reduction of the crossing terms in the EPSs

R3 – R3ref = -0.3 bohr



R3 - R3ref = 0

Valence Coordinates required

Hamiltonian by N. C. Handy

N. C. Handy, Mol. Phys. **61** 207 (1987)

Corrective Terms

§ Spin-Orbit Coupling

$$A \times L_z \cdot S_z$$

> for $HCCH^+$, fixed at the equilibrium value : ***A*** = -30.23 cm^{-1}

(Breit-Pauli operator, basis cc-pv5z + diffuse orbitals)

§ Rewriting of the angular part

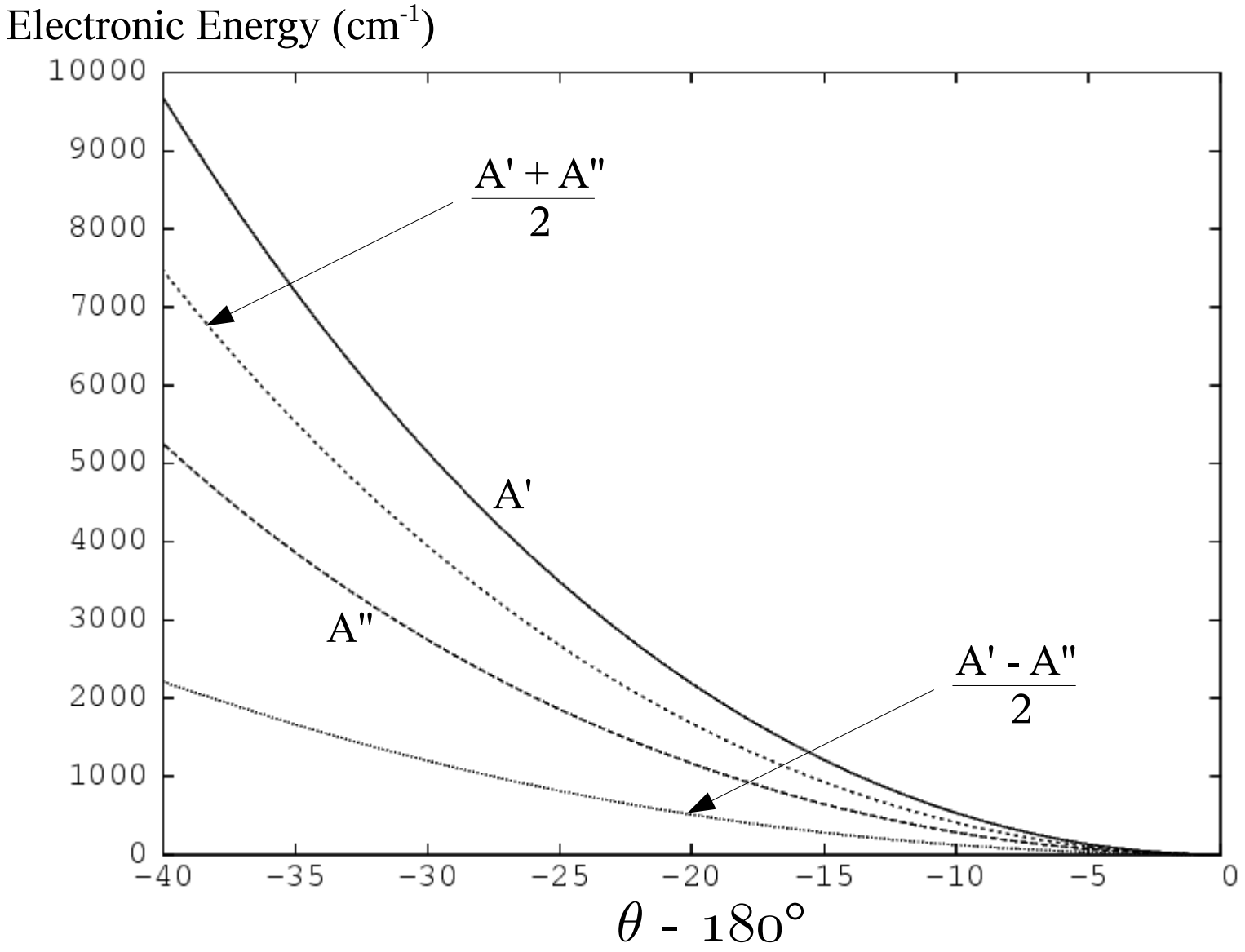
$$\overrightarrow{J_{noy}} = \overrightarrow{J_{tot}} - \overrightarrow{S} - \overrightarrow{L_e}$$

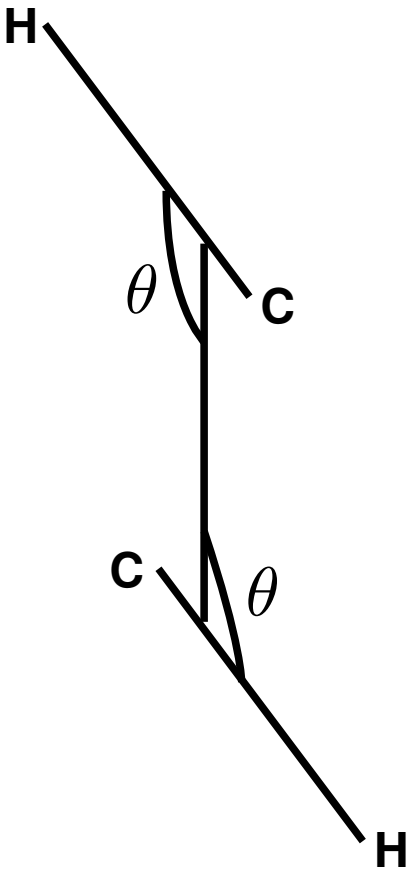
supplementary terms

$$\frac{1}{2\mu_3 R_3^2} \cdot (\vec{S}^2 - \widehat{L_{ez}}^2 - 2\widehat{S_z}(\widehat{S_z} + \widehat{L_{ez}}) - 2(\widehat{j_{1z}} + \widehat{j_{2z}}) \cdot (\widehat{L_{ez}} + \widehat{S_z}))$$

$$- \frac{1}{2\mu_3 R_3^2} \cdot [\widehat{S_+}(\widehat{J_-} - \widehat{j_{1,-}} - \widehat{j_{2,-}}) + \widehat{S_-}(\widehat{J_+} - \widehat{j_{1,+}} - \widehat{j_{2,+}})]$$

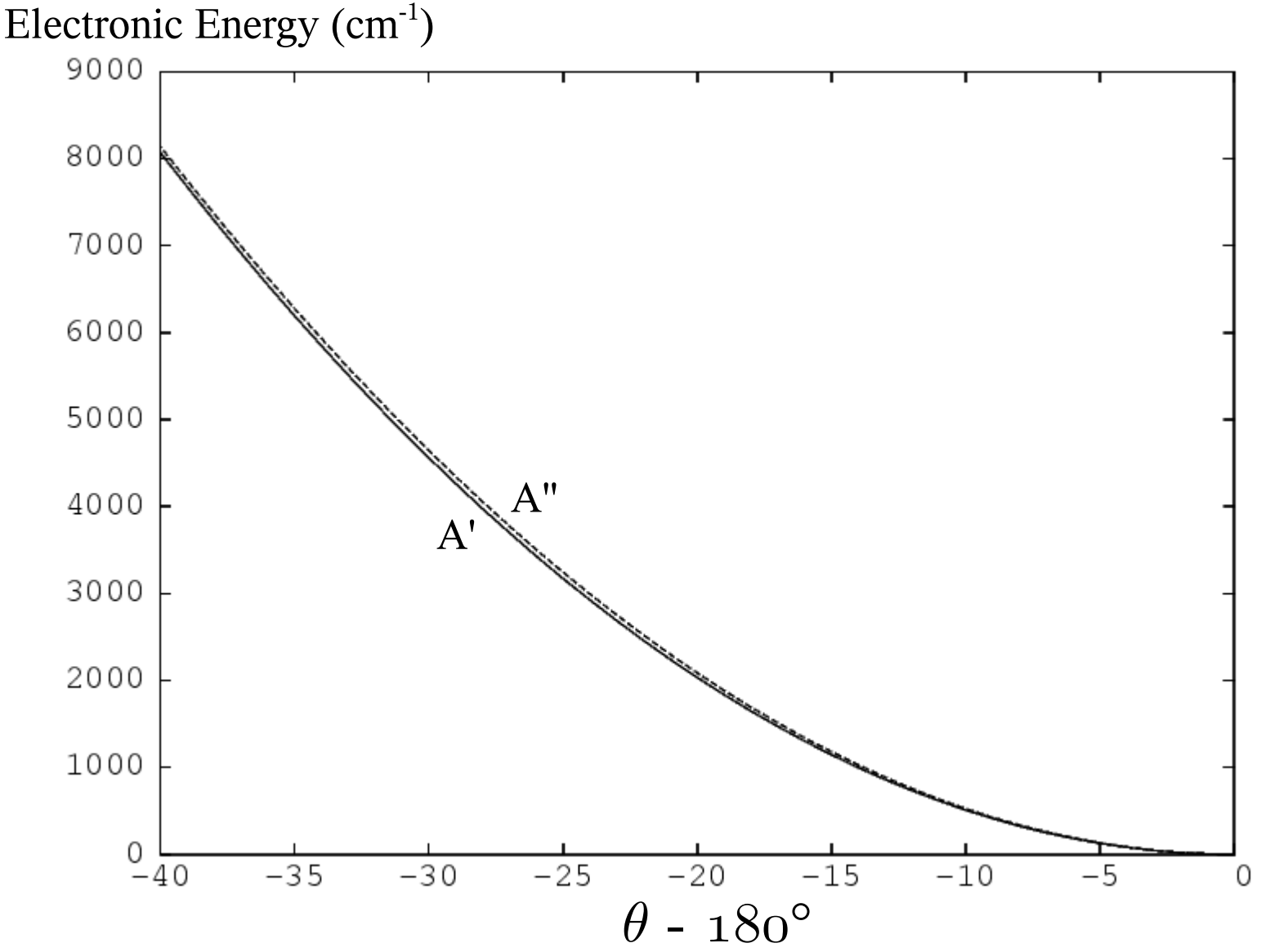
trans Configuration

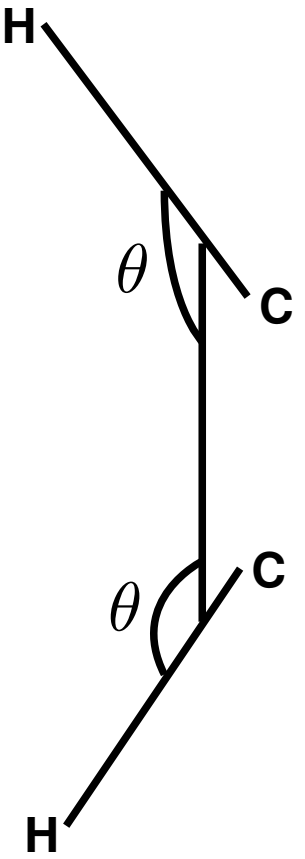




> $\omega_{A'} \sim 1.85\,\omega_{A''}$

cis Configuration (1D)

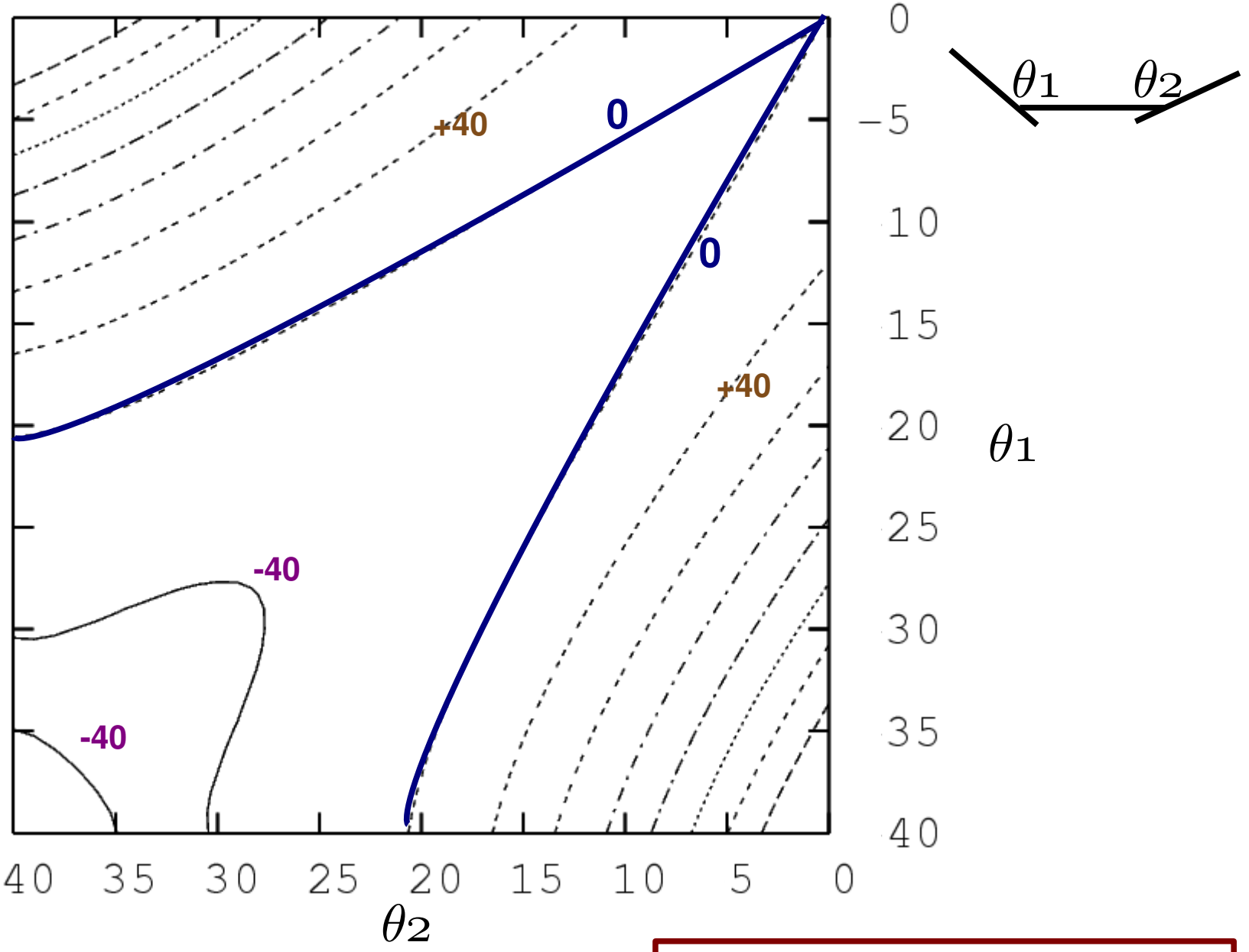




almost the same harmonic terms

cis Configuration (2D)

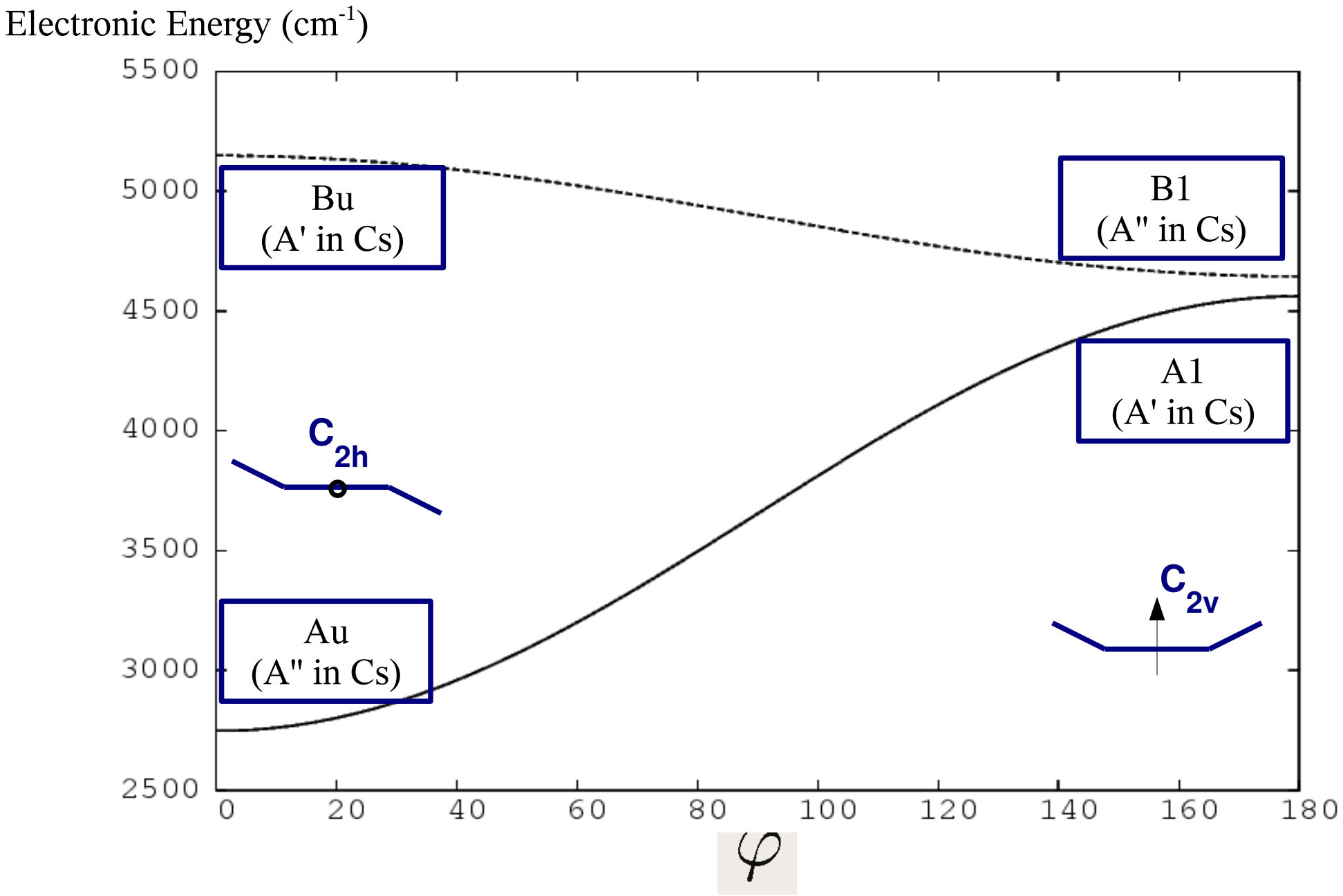
$\frac{A' - A''}{2}$ (cm^{-1})



V(A') ~ V(A'') for $\theta_1 = \theta_2$
V(A') > V(A'') for $\theta_1 \neq \theta_2$

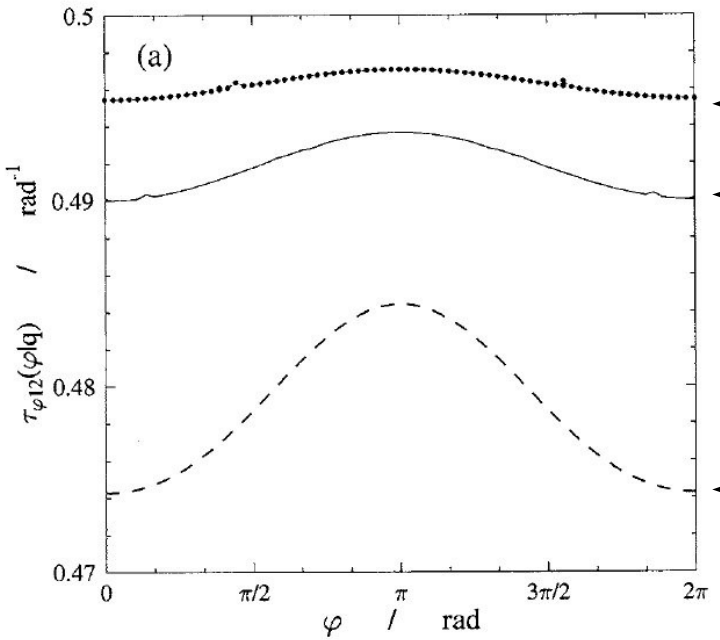
Torsion

$\theta_1 = \theta_2 = 30°$



Torsion & Non adiabatic Coupling Terms

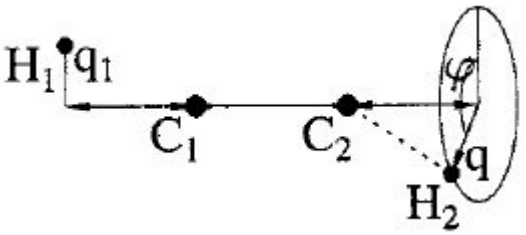
Symetric Case



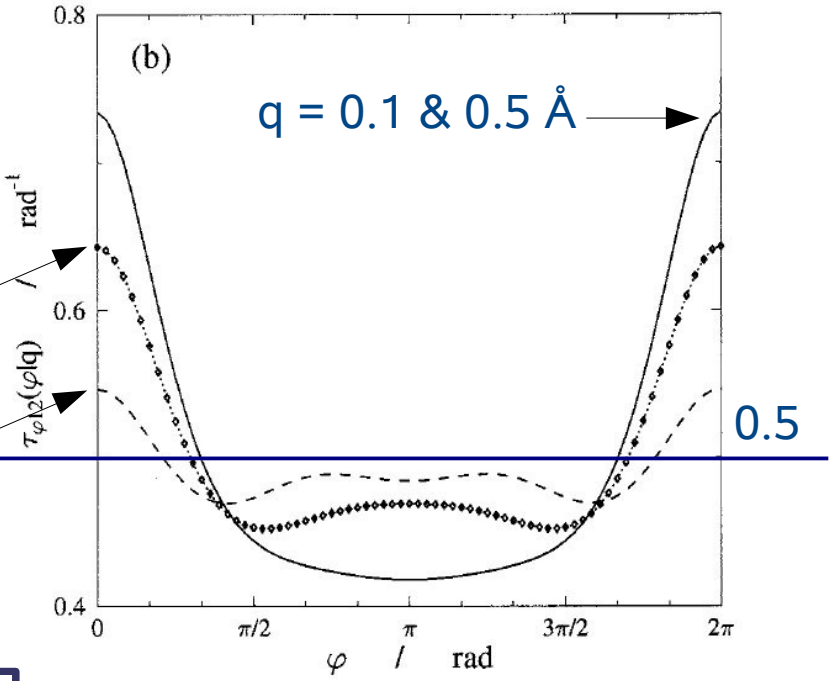
q = 0.2 Å

q = 0.3 Å

q = 0.5 Å



Non Symetric Case



Halasz et al JCP **126**, 154309 (2007)

q = 0.1 & 0.8 Å

q = 0.3 & 0.5 Å

$$\frac{1}{2\pi}\int_{\phi=0}^{\phi=2\pi}\left\langle X\left|\frac{\partial}{\partial\phi}\right|Y\right\rangle d\phi \simeq \frac{1}{2}$$

Basis Functions

- Electronic orbital part:

$$\Psi_e^{\pm|\Lambda|} = \frac{X \pm iY}{\sqrt{2}} exp\left[\pm i\,|\Lambda|\left(\gamma + \frac{\phi}{2}\right)\right]$$

where the phase factor depends on the definition of the third Euler angle

- Electronic spin part:

$$|S, M_S\rangle$$

- Rotation :

$$|J, P\rangle$$

- Stretches: eigenfunctions of the harmonic oscillator

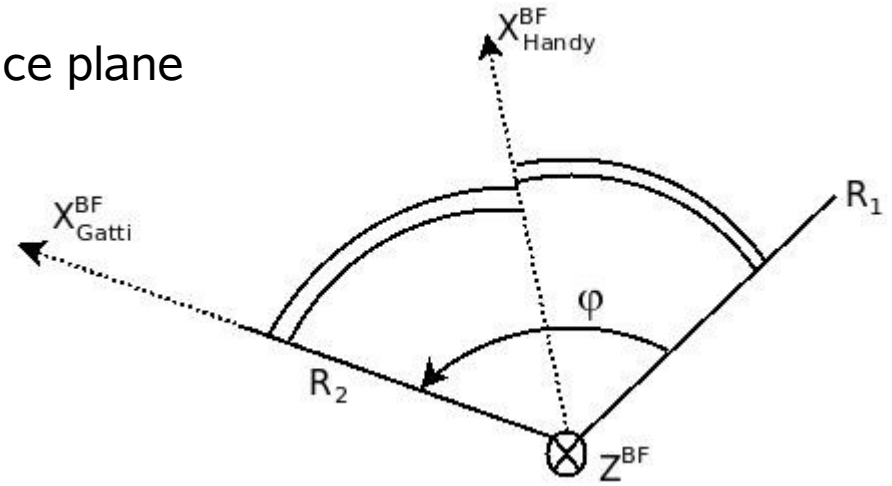
- Bendings

$$Y_{l_1}^{m_1}\left(\theta_1, \phi_1^{E2}\right) \times Y_{l_2}^{m_2}\left(\theta_2, \phi_2^{E2}\right)$$

modified for improving convergence

e- Basis Functions and the Third Euler Angle

γ is defined from the (Z^{BF},X^{BF}) reference plane



- with Gatti et *al.*'s convention:

$$\frac{1}{2\pi}\int_{\phi=0}^{\phi=2\pi}\left\langle X\left|\frac{\partial}{\partial\phi}\right|Y\right\rangle d\phi \simeq \frac{1}{2}$$

$$\Psi_e^{\pm|\Lambda|} = \frac{X \pm iY}{\sqrt{2}} exp\left[\pm i\,|\Lambda|\left(\gamma + \frac{\phi}{2}\right)\right]$$

- with Handy et *al.*'s convention:

$$\frac{1}{2\pi}\int_{\phi=0}^{\phi=2\pi}\left\langle X\left|\frac{\partial}{\partial\phi}\right|Y\right\rangle d\phi \simeq 0$$

$$\Psi_e^{\pm|\Lambda|} = \frac{X \pm iY}{\sqrt{2}} exp\left[\pm i\,|\Lambda|\,\gamma\right]$$

About Spherical Harmonics

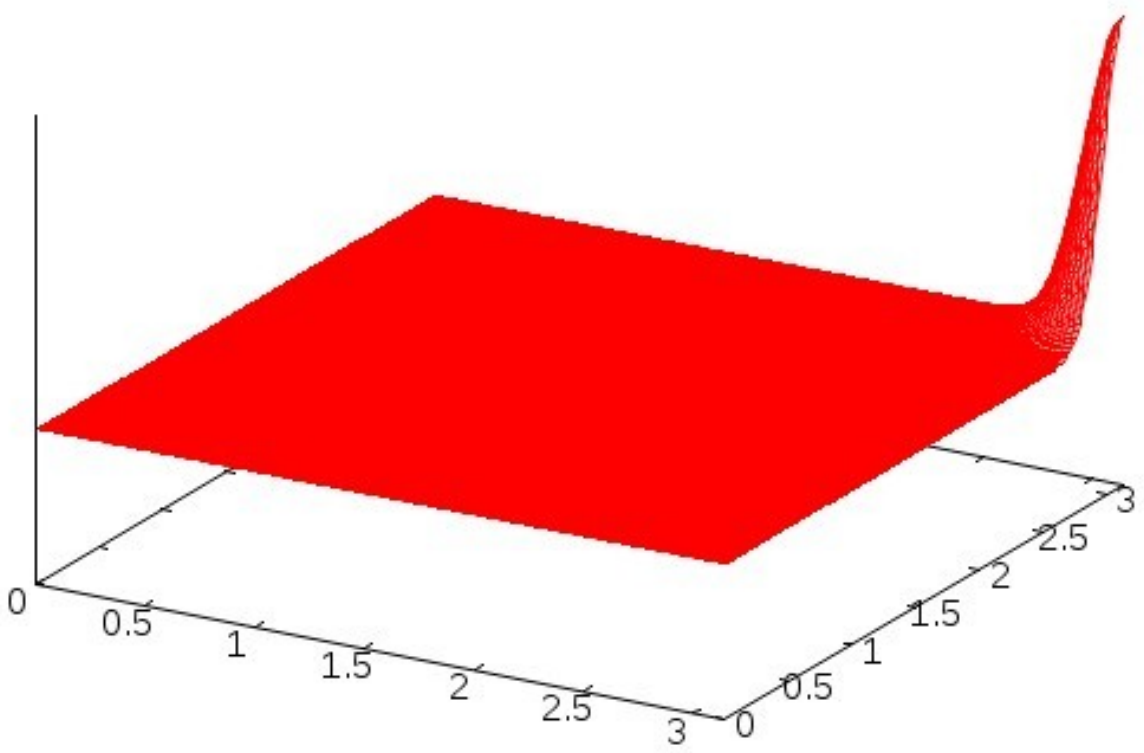
$$Y_l^m(\theta,\phi) = N_l^m \left[\sum_{i=0}^{l-|m|} {}^iC_l^m \, cos^i\theta \right] sin^{|m|}\theta \, \frac{e^{im\phi}}{\sqrt{2\pi}}$$

§ Avoid singularities at linearity, due to:

$$\hat{j}^2 = -\hbar^2 \cdot \left[\frac{1}{sin^2\theta} \cdot \frac{\partial^2}{\partial\phi^2} + \frac{1}{sin\theta} \cdot \frac{\partial}{\partial\theta} \left(sin\theta \cdot \frac{\partial}{\partial\theta} \right) \right]$$

§ But...

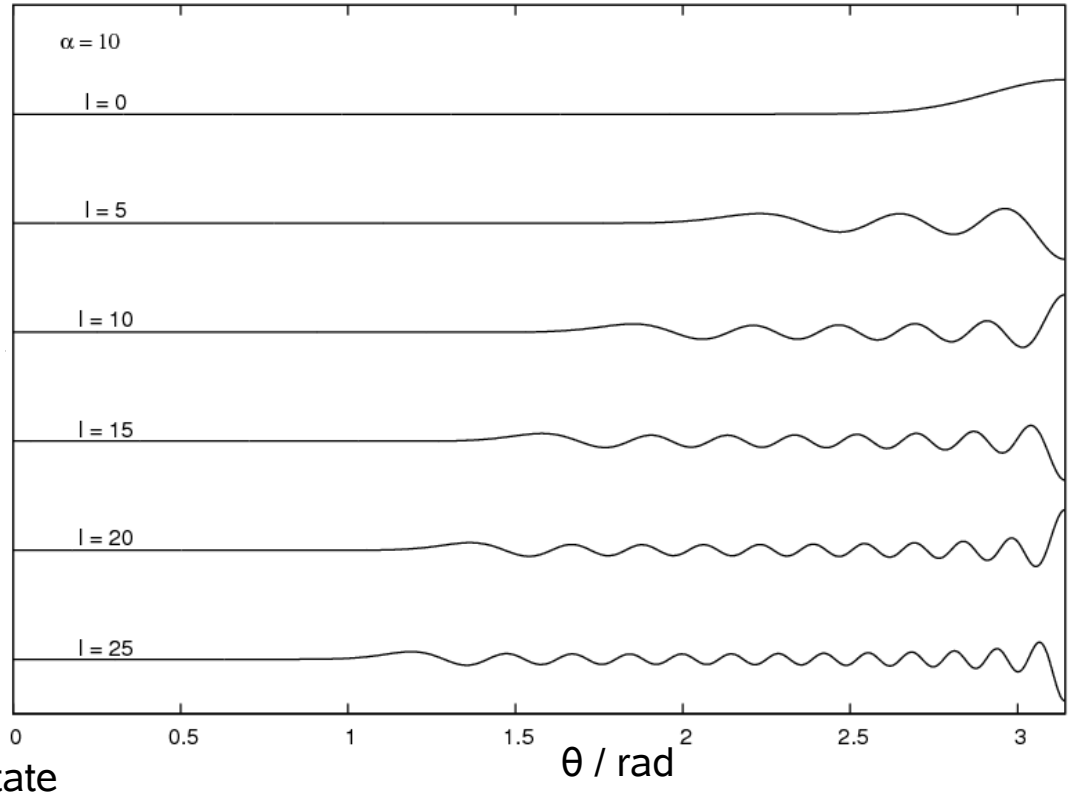
> They are not optimzed for describing this kind of wavefunction:



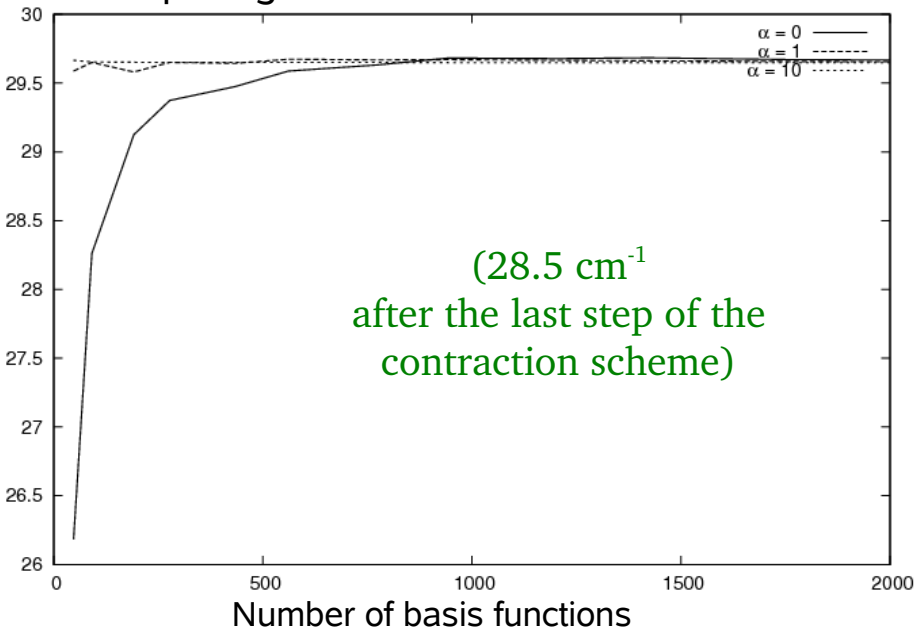
Reduction of the number of basis functions

- Inclusion of an exponential term:

$$\left[\sum_i \gamma_i \, e^{-\alpha_i(\theta-\theta_{max_i})^2}\right]$$



$HCCH^+$:
spin-orbit splitting from the vibronic fundamental state



(28.5 cm^{-1}
after the last step of the
contraction scheme)

⇒ *Economy of one order of magnitude in the number of basis functions*

L. Jutier, JCP **133** 034107 (2010)

Rotational Band Origins ($HCCH^+$)

state	assignment	previous work[2]	Tang[7]	Yang[8] [b]	this work
$^2\Pi_{u3/2}$	0	0.0	0.0	0.0	0.0[c]
$^2\Pi_{u1/2}$		28.5	30.8	29.8	28.5
$^2\Sigma_{u1/2}$	ν_4	496.2	502.7	499.5	506.3
$^2\Delta_{u5/2}$		658.6	666.4	672.9	665.0
$^2\Delta_{u3/2}$		685.8	695.8	701.4	692.3
$^2\Sigma_{u1/2}$		902.3	912.6	909.9	897.3
$^2\Sigma_{g1/2}$	ν_5	685.4	697.5	694.9	691.8
$^2\Delta_{g5/2}$		718.9	715.1	713.4	718.7
$^2\Delta_{g3/2}$		747.5	746.0	743.0	747.4
$^2\Sigma_{g1/2}$		776.2	746.6	738.2	769.9
$^2\Pi_u$	$2\nu_4$	1090.7	1109.4	1108.3	1105.1
$^2\Phi_{u7/2}$		1313.5	1327.0	1316.0	1323.2
$^2\Phi_{u5/2}$		1338.8	1354.3	1342.7	1348.8
$^2\Pi_u$		1685.5		1683.5	1682.3
$^2\Pi_g$	$\nu_4 + \nu_5$	1214.9	1210.8[a]	1210.2	1236.8
$^2\Pi_{g3/2}$		1365.6	1361.6	1373.1	1373.2
$^2\Pi_{g1/2}$		1392.9	1390.7	1401.6	1403.8
$^2\Phi_{g7/2}$		1384.5	1384.1	1370.4	1392.0
$^2\Phi_{g5/2}$		1411.9	1414.2	1398.9	1420.0
$^2\Pi_g$		1613.7	1616.8[a]	1620.6	1608.5
$^2\Pi_u$	$2\nu_5$	1392.5	1393.5	1404.8	1399.3
$^2\Phi_{u7/2}$		1423.8	1432.7	1410.7	1439.3
$^2\Phi_{u5/2}$		1452.6	1462.8	1440.5	1468.1
$^2\Pi_u$		1496.4	1459.0[a]	1451.2	1487.4
$^2\Pi_{u3/2}$	ν_2	1819.0		1817.5	1818.9
$^2\Pi_{u1/2}$		1847.5			1846.8
$^2\Pi_{g3/2}$	ν_3	3151.9[d]			3134.3
$^2\Pi_{u3/2}$	ν_1	3236.4[d]			3221.8

- Previous work :

  Code in Jacobi coordinates
  ab initio pts MRCI+Q

- Tang *et al.* :

  ZEKE experiment
  J. Chem. Phys. **125**, 133201 (2006)

- Yang *et al.* :

  ZEKE experiment
  J. Phys. Chem. A **110**, 11001 (2006)

- this work :

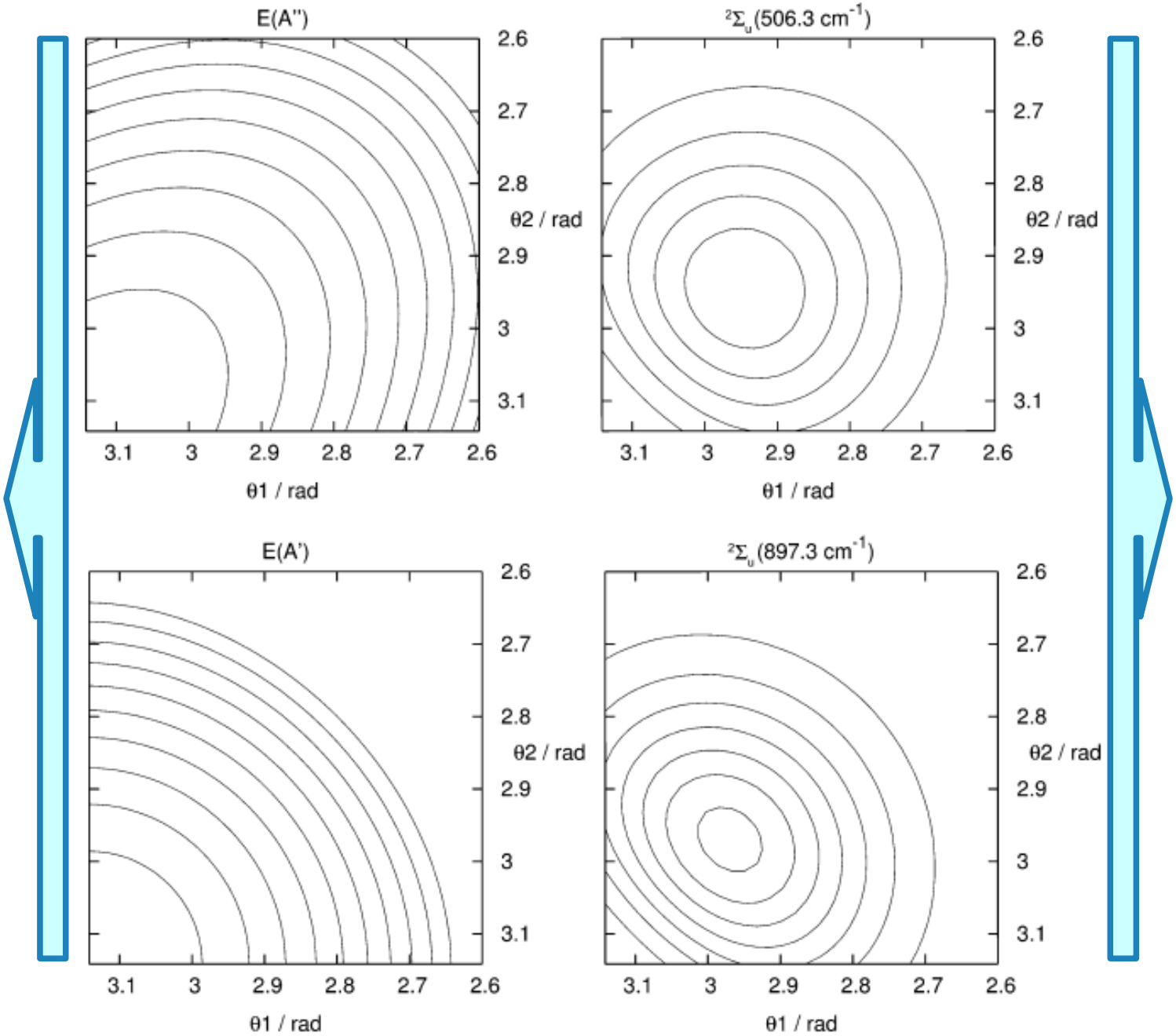
  Code in valence coordinates
  ab initio pts CCSD(T)

L. Jutier et C. Léonard, J. Chem. Theory Comput. **6**, 1565 (2010)

How to Assign

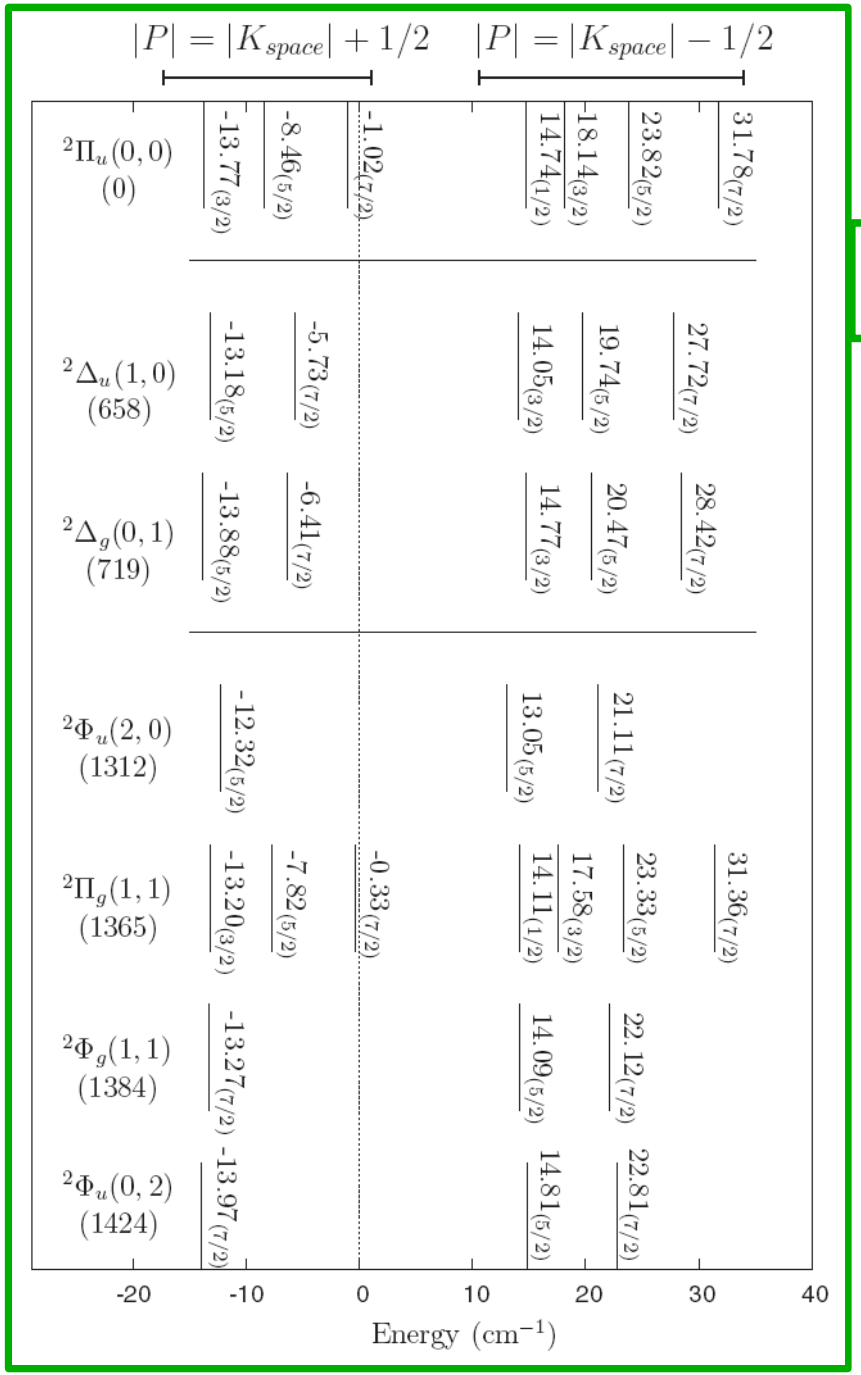
Σ staes with 1 quantum in the *trans* bending mode

A' and A" electronic potentials in trans shape



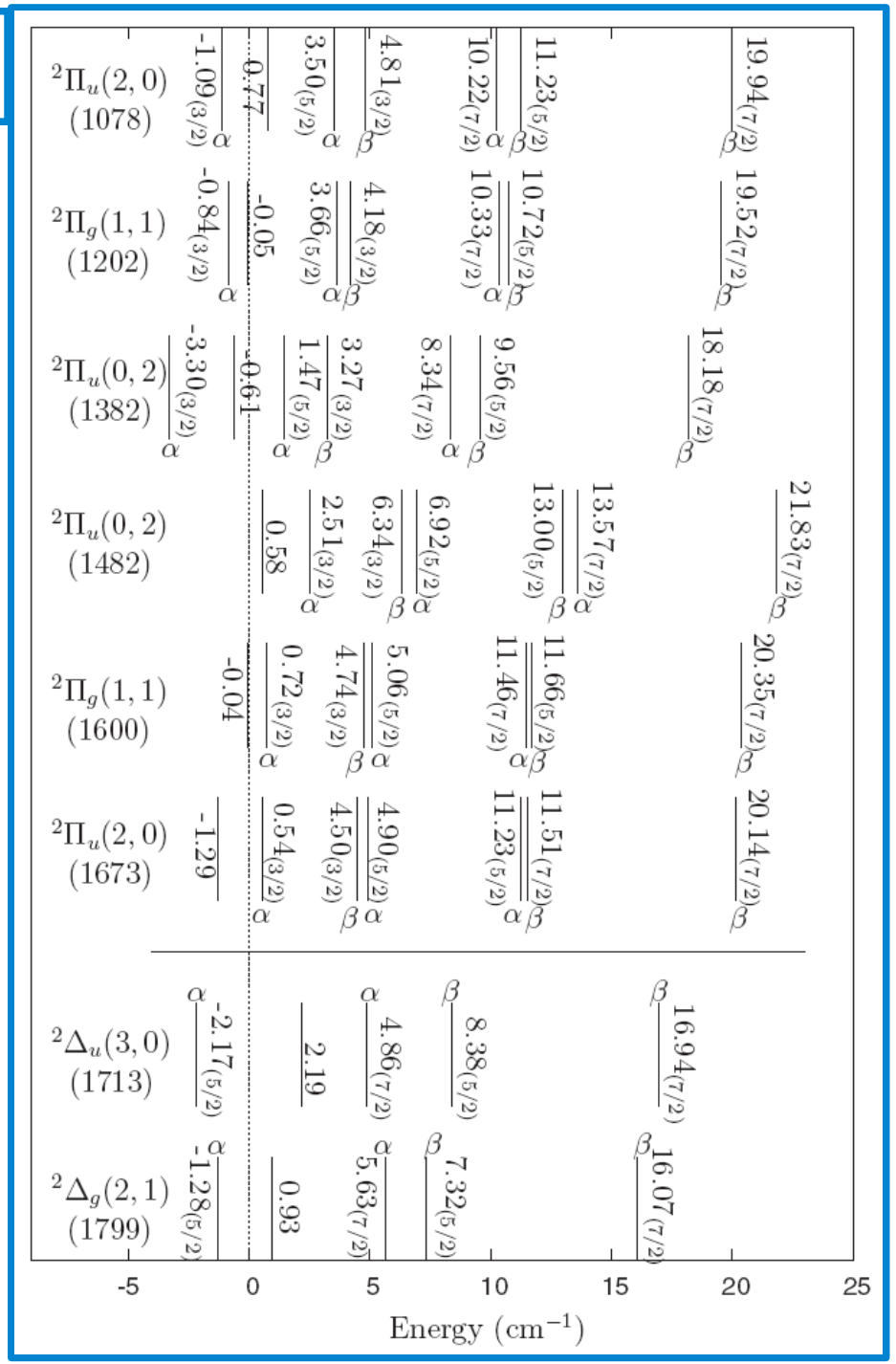
$|\Psi|^2$ *for both Σ states*

Rotational Structures ($HCCH^+$)



Hund's case (a)

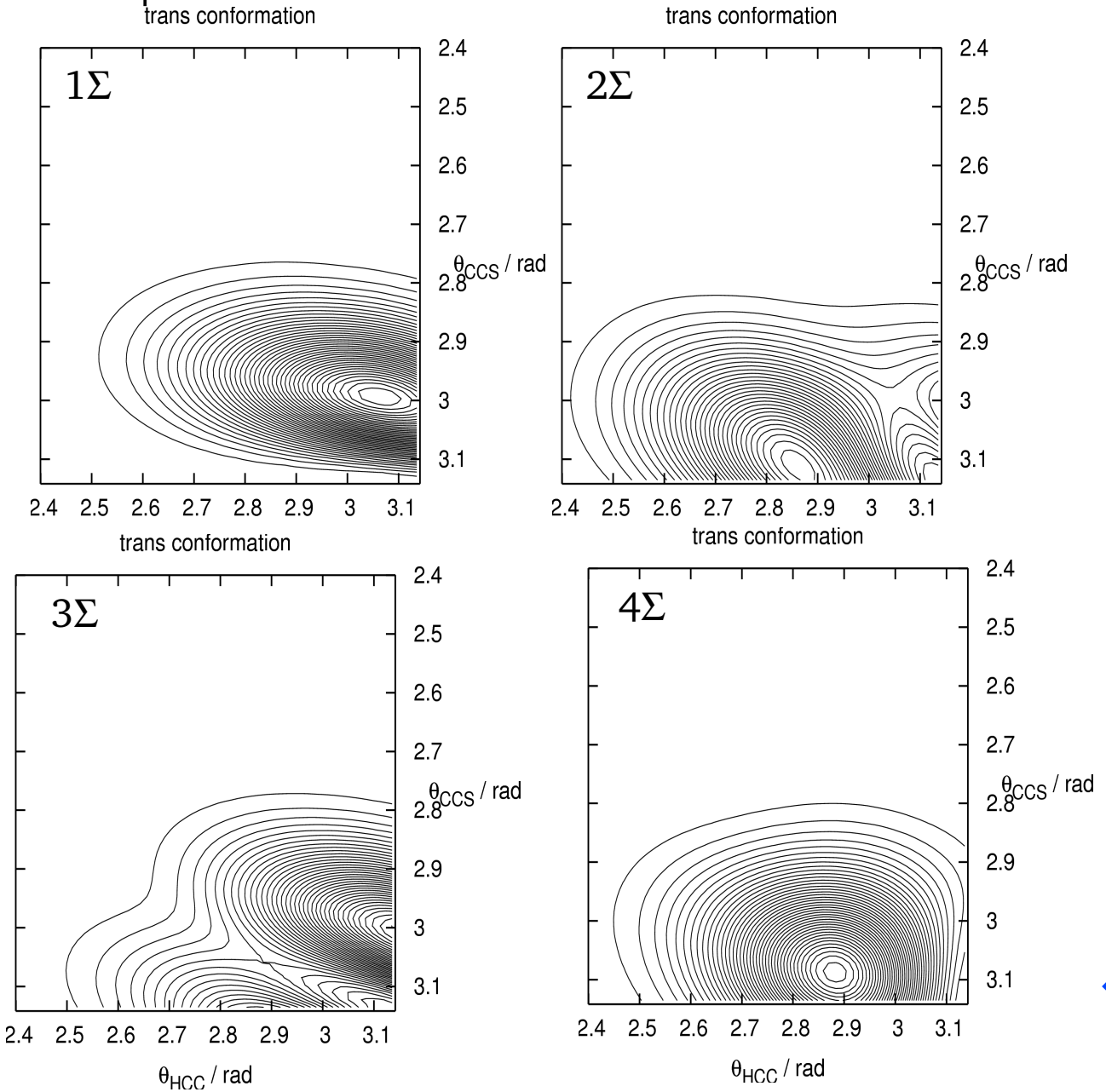
Hund's case (b)



HCCS: a Challenge

§ A non symmetrical system:

> Both bending modes belong to the same irreduscible representation => all resonances allowed



§ High value of the spin-orbit constant:

> Non standard vibronic structure in term of Hund's cases

> Impossibility of using 'pure spacial' symmetries, for instance Σ^+ or Σ^-

L. Jutier et G. Dhont, *to be submitted*

Vibronic Structure

State	our work	He & Clouthier	Serie
$1\Pi_{3/2,v_3=0}$	0	0.0	A
$1\Pi_{1/2,v_3=0}$	251	260.5	B
$1\Sigma_{v_3=0}$	333	—	
$1\Delta_{5/2,v_3=0}$	353	—	
$2\Sigma_{v_3=0}$	458	—	
$2\Delta_{5/2,v_3=0}$	512	—	
$1\Delta_{3/2,v_3=0}$	601	607.3	C
$3\Sigma_{v_3=0}$	637	—	
$2\Pi_{3/2,v_3=0}$	685	675.9	A
$2\Pi_{1/2,v_3=0}$	691	—	
$1\Phi_{7/2,v_3=0}$	707	—	
$2\Delta_{3/2,v_3=0}$	747	726	C
$1\Pi_{3/2,v_3=1}(49\%)$ - $3\Pi_{3/2,v_3=0}$ (31%)	780	776.5	A
$3\Pi_{3/2,v_3=0}$ (57%) - $1\Pi_{3/2,v_3=1}(38\%)$	799	822.2	A
$3\Pi_{1/2,v_3=0}$	807	753.0	B
$4\Sigma_{v_3=0}$	842	—	
$4\Pi_{3/2,v_3=0}$	843	870.3	A
$2\Phi_{7/2,v_3=0}$	866	—	
$4\Pi_{1/2,v_3=0}$	929	856.1	B
$1\Phi_{5/2,v_3=0}$	954	—	
$5\Pi_{3/2,v_3=0}$	972	—	
$5\Pi_{1/2,v_3=0}$	980	969.9	B
$6\Pi_{3/2,v_3=0}$ (70%) - $3\Delta_{3/2,v_3=0}$ (24%)	1006	993.8	A

> No pure stretching excitations

?

> Pbs with $\Pi_{1/2}$-$\Pi_{1/2}$ transitions

?

> Sears resonances

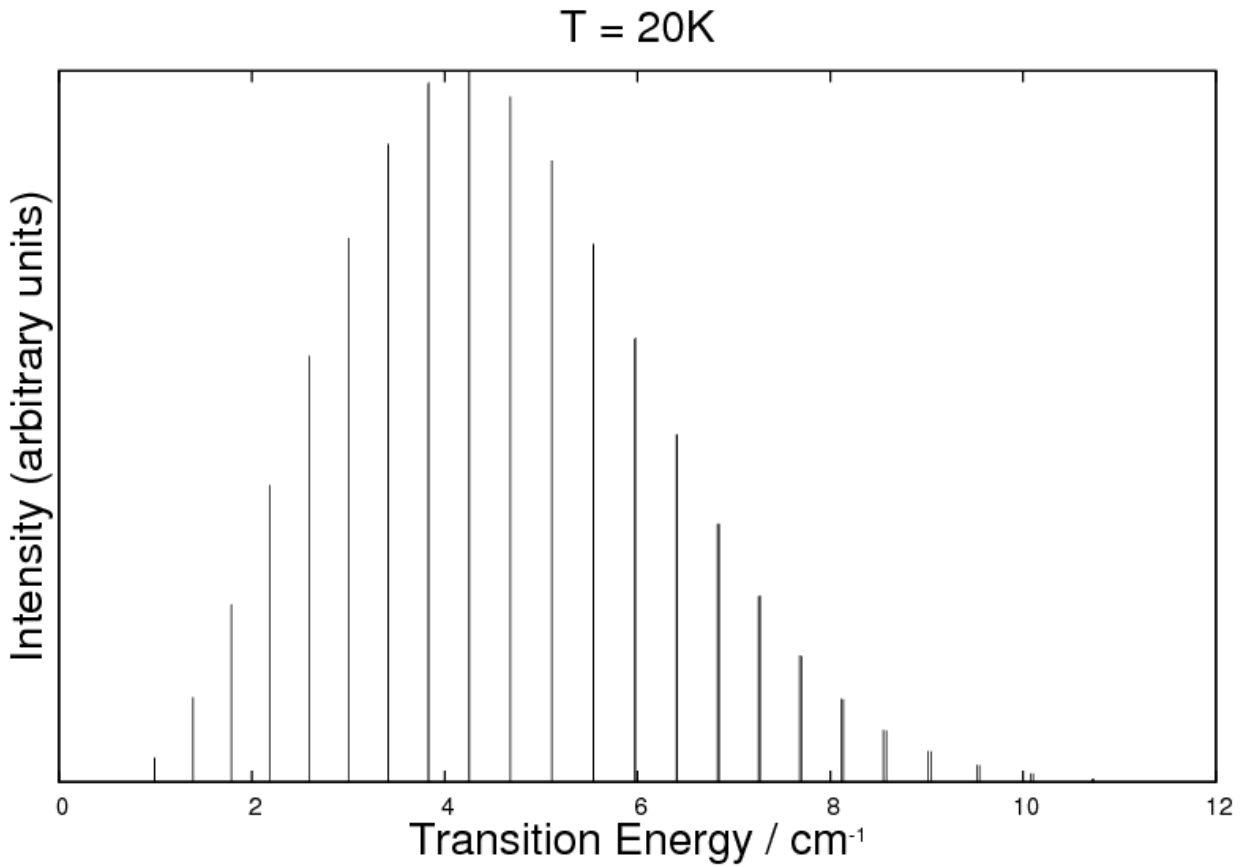
S.-G. He and D. Clouthier, *JCP* **123** 014317 (2005)

Pure Rotational Intensities

> Only considering the permanent dipole moment:

$$R^2_{ab}(J \rightarrow J+1) = \mu_0^2 \frac{1}{J+1} \left| \sum_{i,j} c_i^* \, c_j \sqrt{(J+1)^2 - P_i^2} \, \delta_{\eta(a,i),\eta(b,j)} \right|^2$$

$$I_{a \rightarrow b} \propto \nu_{ab} \left[exp\left(-\frac{E_a}{k_B T}\right) - exp\left(-\frac{E_b}{k_B T}\right) \right] \times R^2_{ab}$$



Perspectives

Intensities for infrared transitions

> Require 6-D surfaces for the dipole moment components

Improving the description of the electronic wavefunctions following the torsion

> Require expensive *ab initio* calculation (MRCI in the C1 point group)

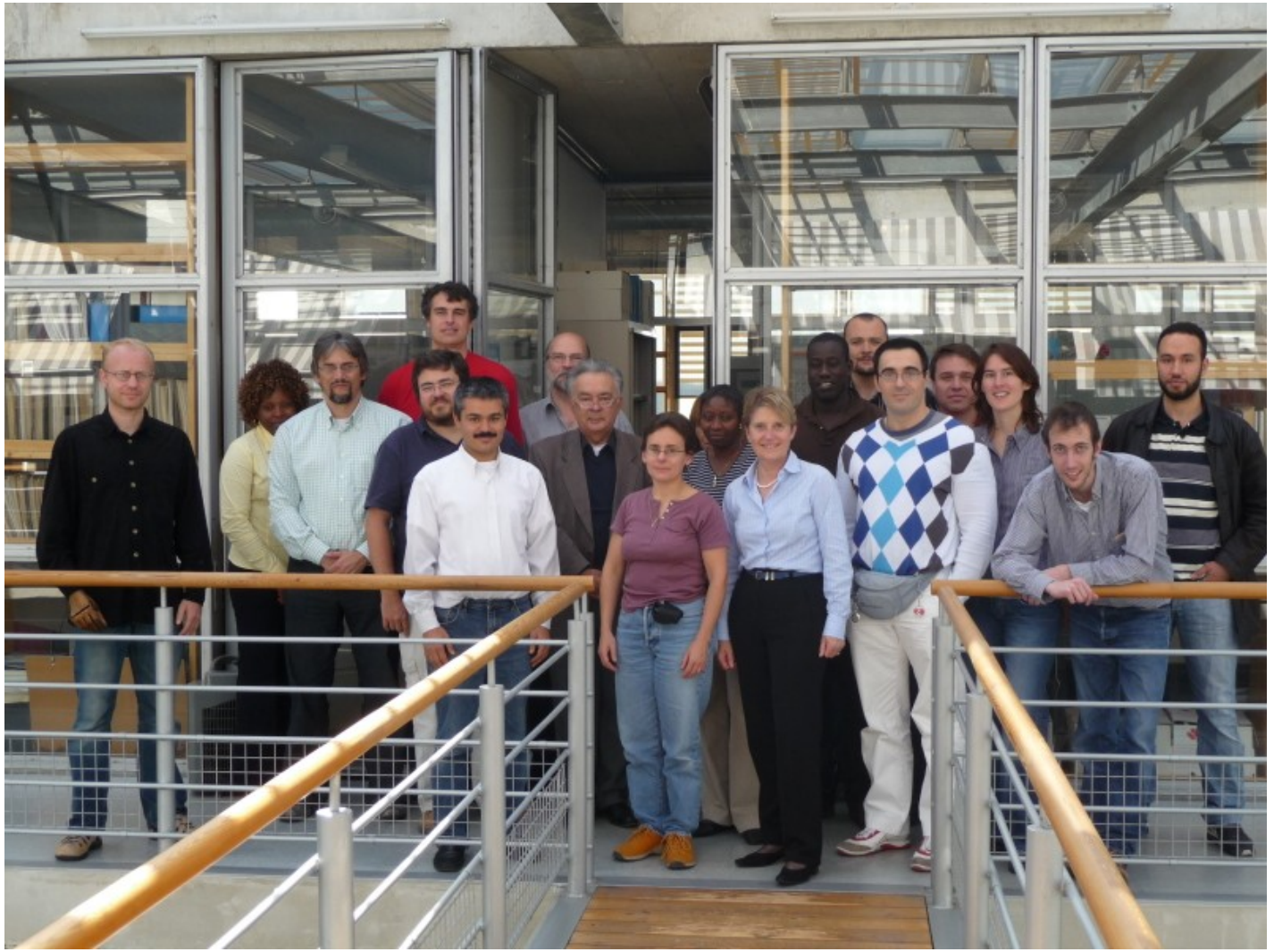
More than 4-atom systems

> Require the implementation of a complicated nuclear Hamiltonian (depending on coordinates)

> Flexibility of the contraction scheme

Non linear equilibrium geometries
More than two electronic surfaces
...

Acknowlegdments



Theoretical Chemistry Group (UMPEMU)

... AND YOU FOR YOUR ATTENTION