Computing spectra of Van der Waals clusters

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- Complexes consist of stable molecules held together by Van der Waals interactions
- Extract information about these interactions or confirm ab initio or pairwise potentials.
- A lot of detailed experimental data is available

How do spectroscopists usually extract potential information ?

- Use normal coordinates and a molecule-fixed axis system (Eckart) chosen to minimise Coriolis coupling
- Use perturbation theory. Energy levels are eigenvalues of an effective rotational Hamiltonian :

$$G(\mathbf{n}) + F_{\mathbf{n}}(J_x, J_y, J_z)$$

where

$$G(\mathbf{n}) = \sum_r \omega_r (n_r + \frac{1}{2}) + \sum_{r \geq s} x_{rs} (n_r + \frac{1}{2})(n_s + \frac{1}{2}) + \cdots$$

and

$$F_{\mathbf{n}}(J_x, J_y, J_z) = A_{\mathbf{n}} J_x^2 + B_{\mathbf{n}} J_y^2 + C_{\mathbf{n}} J_z^2 + \frac{1}{4} \sum_{\alpha,\beta} \tau_{\alpha,\alpha,\beta,\beta} J_\alpha^2 J_\beta^2$$

This approach works poorly for Van der Waals clusters

It treats perturbatively the effects of

- anharmonicity
- Coriolis coupling
- centrifugal coupling

The zeroth-order model is harmonic + rigid rotor.

An alternative is to numerically solve the Schroedinger equation

$$H\psi_n = E_n\psi_n$$

$$H = T + V$$

To compute a spectrum one must choose coordinates that describe the shape and orientation of the molecule and find the associated kinetic energy operator (KEO).

- the chain rule

To obtain the potential

- solve the electronic Schroedinger equation for many different shapes
- fit a function to these points

How does one solve the Schroedinger equation ?

- represent wavefunctions with basis functions

$$\psi_n(\mathbf{r}, \boldsymbol{\theta}) = \sum_k c_k^n \quad f_k(\mathbf{r}, \boldsymbol{\theta})$$

- compute eigenvalues and eigenvectors of the Hamiltonian matrix

The most obvious basis functions are product functions :

$$f_{k_1,k_2,\cdots} = \phi_{k_1}(r_1)\phi_{k_2}(r_2)\cdots\phi_{k_N}(\theta_1)\cdots$$

Between 10 and 100 1-d functions required for each coordinate.

$\Rightarrow > 10^{3N-6}$ multi-d basis functions required.

Diagonalization of the Hamiltonian matrix is very costly.

Both the CPU time [(basis size)^3] and the memory [(basis size)^2] scale very badly.

Alternatives

- Semi-classical methods
  - accuracy
  - feasibility (many trajectories, long-time propagations)
- Monte Carlo methods
  - great for the ground state

Diagonalization can be avoided by using iterative methods

- Energy levels, intensities, rate constants, cross sections can be computed from time-independent methods that require only evaluating matrix-vector products
- Matrix-vector products can be done without storing the matrix
- Only a few vectors are stored
- NB A spectrum is obtained without storing or computing a Hamiltonian matrix

Lanczos Algorithm

$$\mathbf{H} = \begin{pmatrix} \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} \rightarrow \begin{pmatrix} \cdot & \cdot & 0 & 0 \\ \cdot & \cdot & \cdot & 0 \\ 0 & \cdot & \cdot & \cdot \\ 0 & 0 & \cdot & \cdot \end{pmatrix} = \mathbf{T}$$

- Among the eigenvalues of $\mathbf{T}$ are eigenvalues of $\mathbf{H}$
- Eigenvectors of $\mathbf{H}$ are obtained from those of $\mathbf{T}$

Symmetry Adapted Lanczos Algorithm

Eigenvalues and eigenvectors for all irreps are generated from a single set of matrix-vector products.

This is done by using projection operators and exploiting the fact that

$$\mathbf{H}\mathbf{v}^{(m)} = \mathbf{H}\hat{P}^{(m)} \sum_{n=1}^{N} \mathbf{v}^{(n)} = \hat{P}^{(m)} \left[\mathbf{H} \sum_{n=1}^{N} \mathbf{v}^{(n)} \right]$$

At each iteration one applies $\mathbf{H}$ to the sum of the Lanczos vectors computed at the previous iteration.

Wang and Carrington, J. Chem. Phys. 114, 1473 (2001)

Adiabatic Approximation

We assume that the intra-molecular motion is much faster than the inter-molecular motion

Ideally, we would use effective potentials for the slow coordinates that are obtained by averaging the full potential with intra-molecular wavefunctions.

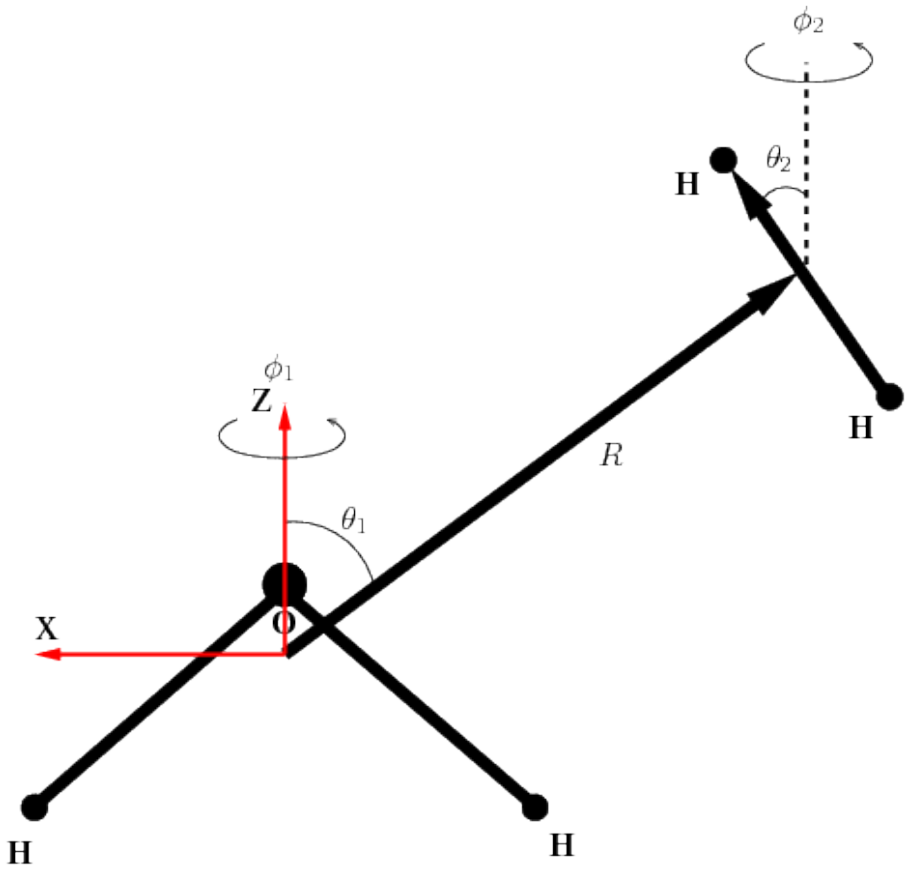
Instead we fix the geometry of the monomers and compute a 4-d (when both monomers are linear) potential.

Choose coordinates and derive the KEO

Option I : Polar coordinates defined using axes attached to two vectors of one monomer

- attach an axis system to monomer A
- Coordinates are :
  - the length of the inter-monomer vector ;
  - θ and ϕ angles that specify the orientation of $\vec{R}$ and the vectors required to describe the orientation of monomer B ;
  - Euler angles that specify the orientation of the axis system attached to monomer A with respect to the space-fixed axes.

Axis system attached to one monomer

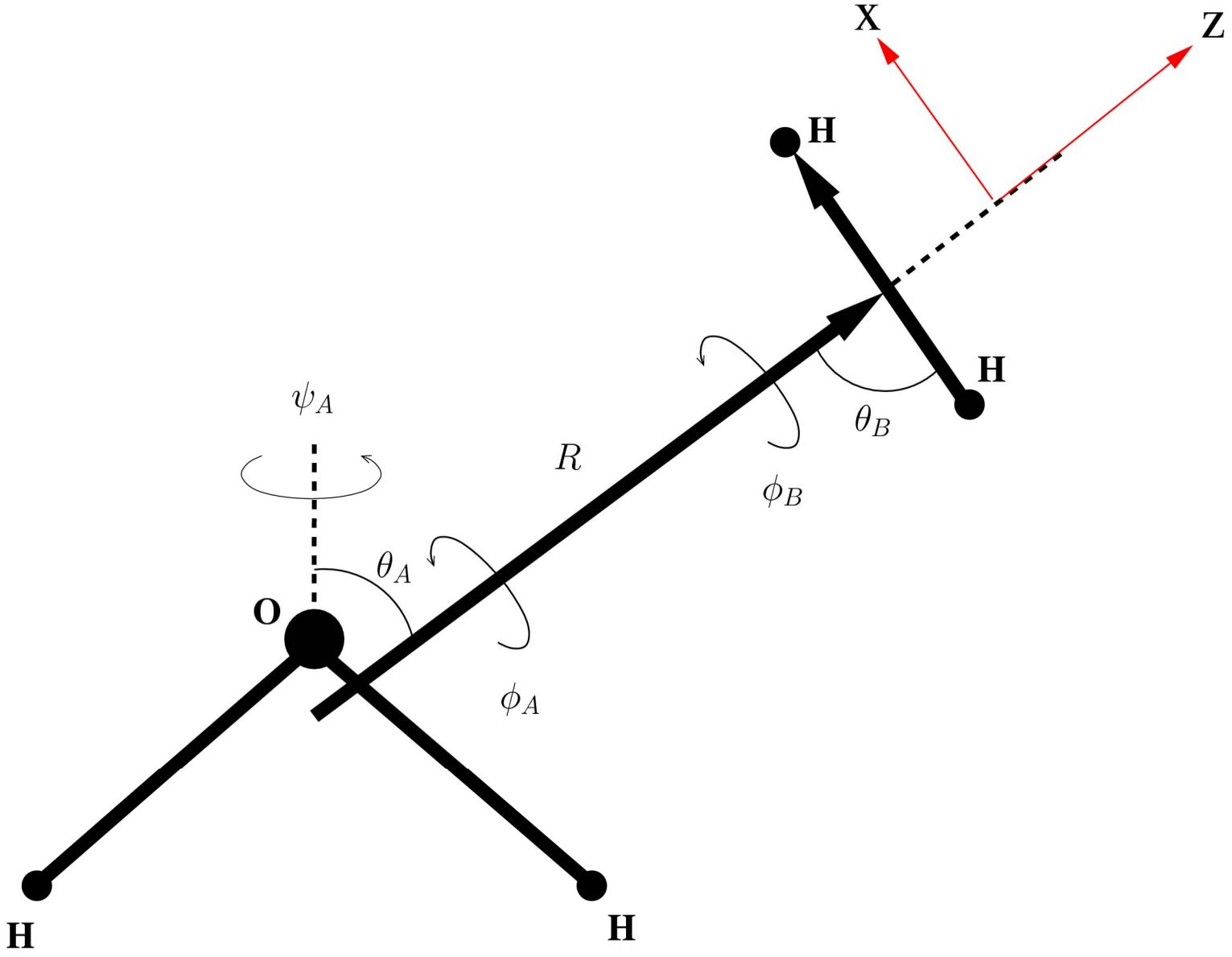


Option II : Euler angles wrt a frame attached to the dimer axis

- If the monomers are non-linear the coordinates are
  - ϕ^A, θ^A, ψ^A and ϕ^B, θ^B, ψ^B
  - α, β, which specify the orientation of the inter-monomer vector.

  In the linear monomer case there are no ψ^σ angles.

Axis system attached to the dimer axis



The KEO in polar coordinates attached to one monomer

$$K = B_x^A(J_x - j_x^R - j_x^B)^2 + B_y^A(J_y - j_y^R - j_y^B)^2 + B_z^A(J_z - j_z^R - j_z^B)^2 + T_R + T_B \quad ,$$

where

$$T_R = B_R\, j_R^2 - \frac{1}{2\mu}\frac{\partial^2}{\partial R^2}$$

$$T_B = B_x^B(j_x^B)^2 + B_y^B(j_y^B)^2 + B_z^B(j_z^B)^2$$

The KEO in Euler coordinates wrt the dimer frame

$$K = T_A + T_B + T_{couple} + T_R$$

where

$$T_\sigma = B_x^\sigma \, ({}^\sigma j_x)^2 + B_y^\sigma \, ({}^\sigma j_y)^2 + B_z^\sigma \, ({}^\sigma j_z)^2; \quad \sigma = A, B$$

$$T_{couple} = B_R(\vec{J} - \vec{j^A} - \vec{j^B})^2$$

Angular basis functions

Using a frame attached to one monomer

$$Y_{j_1,m_1}(\theta_1,\phi_1)Y_{j_2,m_2}(\theta_2,\phi_2)D^{J*}_{MK}(\alpha,\beta,\gamma)$$

Using a frame attached to the dimer axis

$$D^{j_A*}_{m_A,k_A}(\phi_A,\theta_A,\psi_A)D^{j_B*}_{m_B,0}(\phi_B,\theta_B,0)D^{J*}_{MK}(\alpha,\beta,0)$$

Why these basis functions ?

- Matrix elements of the kinetic energy operator are simple and in closed form
- Singularities in the kinetic energy operator cause no trouble
- Uncoupled basis yields efficient matrix-vector products

Which coordinates are best ?

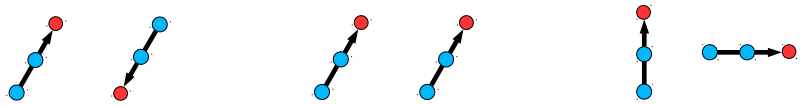
The dimer frame coordinates are best if

- it is possible to identify two pieces of the complex between which coupling is weak.

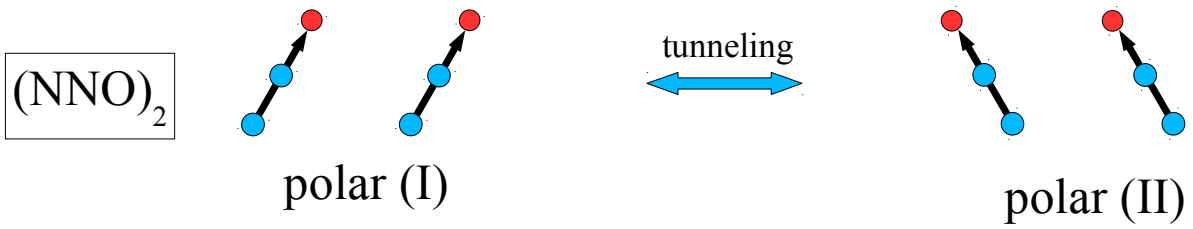
The monomer frame coordinates are best if

- one monomer is much heavier than the other
- the $R = 0$ singularity is important.

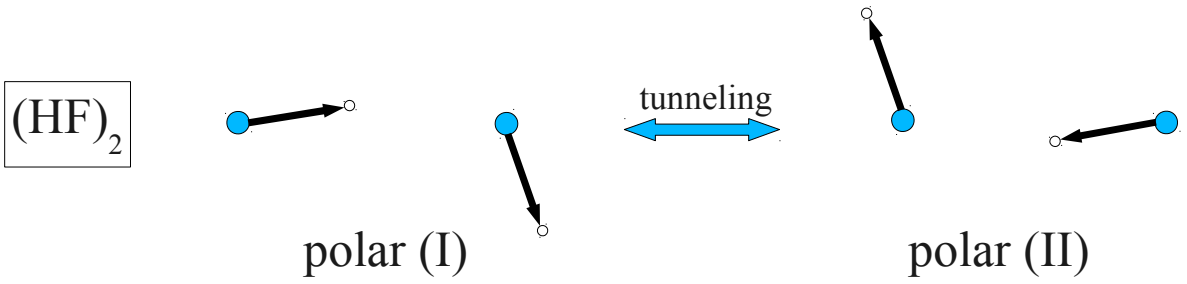
NNO dimer

- Multiple minima
- 
- Non-polar global minimum with O in
- Two polar wells of identical depth and shape
- Two T-shaped wells with N in

Tunneling between the two polar wells

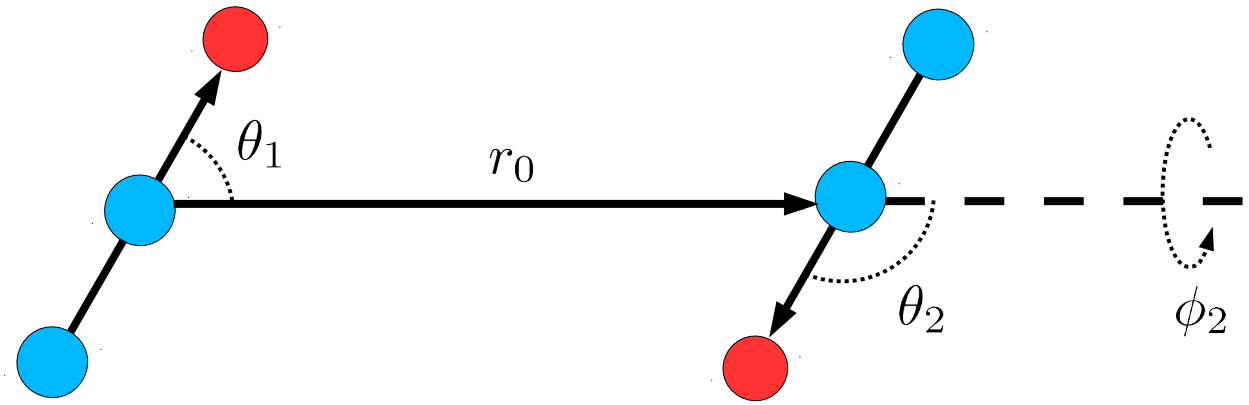


The situation is a bit like $(HF)_2$



Coordinates

Non-polar O-in isomer : $(\theta_1 = 61.2\,^\circ, \theta_2 = 118.8\,^\circ)$



Experimental work

- The non-polar O-in structure has been studied in several papers and an IR band was first reported in R. E. Miller and R. W. Watts, Chem. Phys. Lett., (1984)
- The polar isomers were discovered in 2007.

THE JOURNAL OF CHEMICAL PHYSICS **126**, 164310 (2007)

Nitrous oxide dimer: Observation of a new polar isomer

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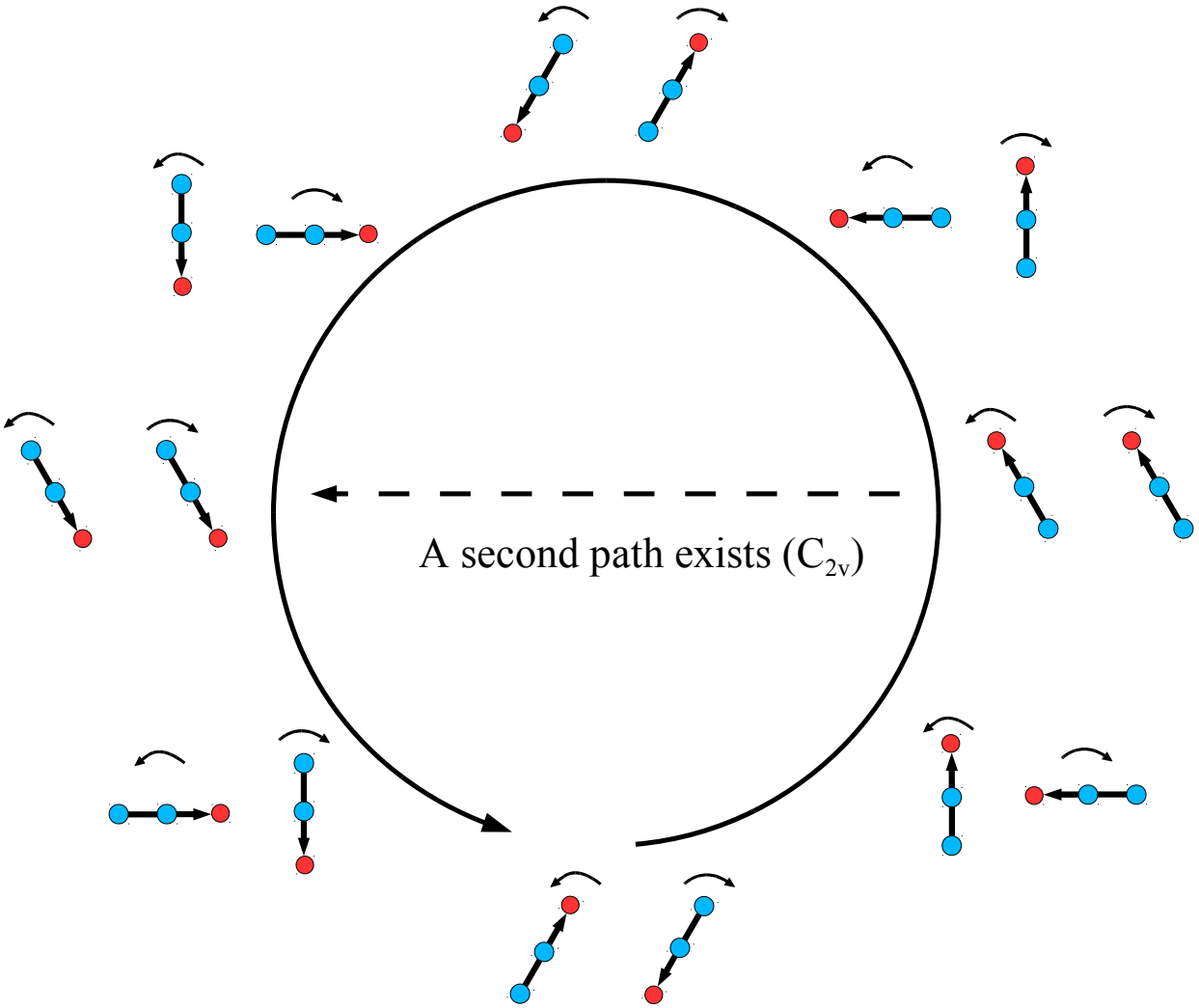
Previous theoretical work

Berner, East, Afshari, Dehghany, Moazzen-Ahmadi, and McKellar, J. Chem. Phys. (2009)

They found stable structures and computed harmonic frequencies.

Disrotatory motion

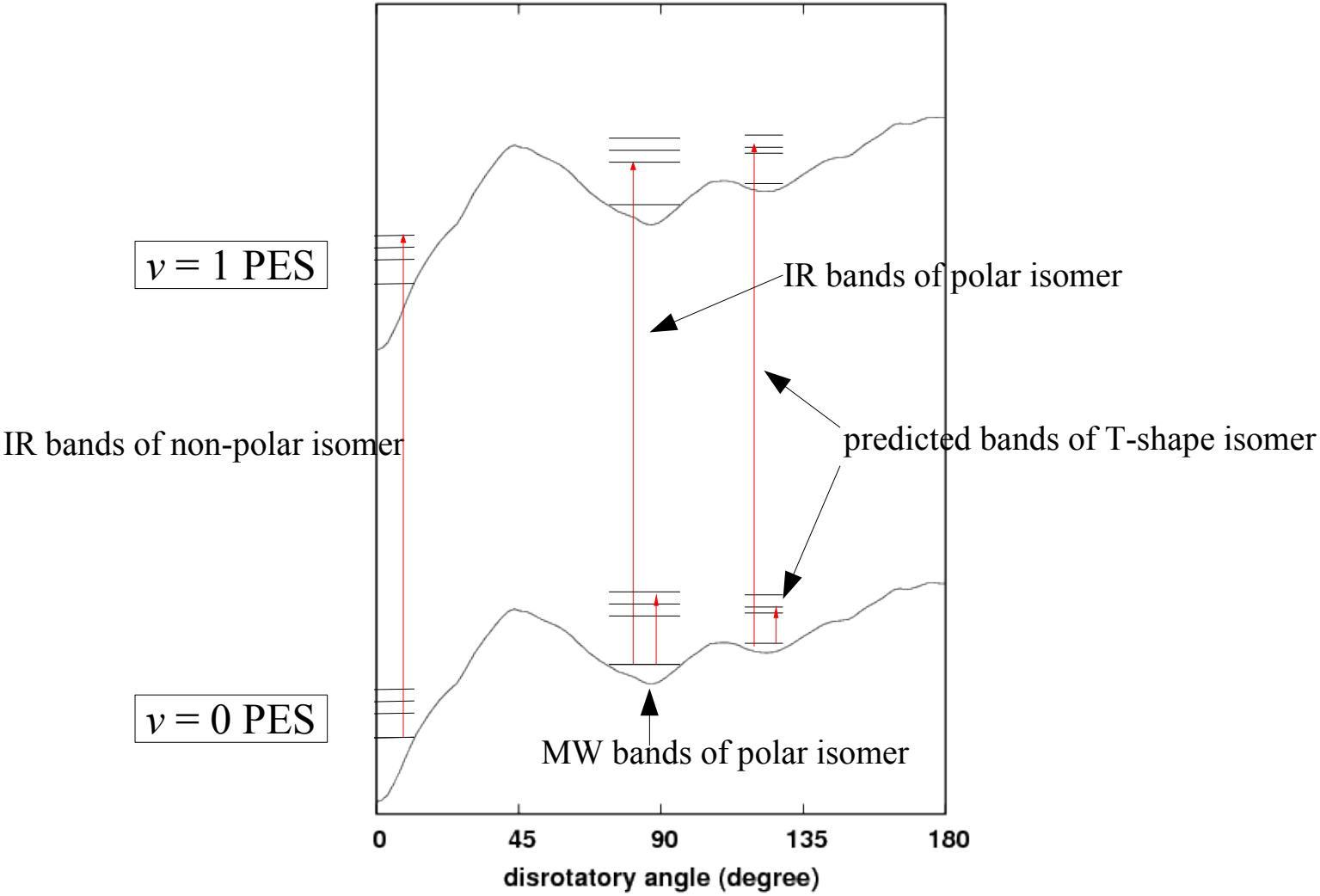


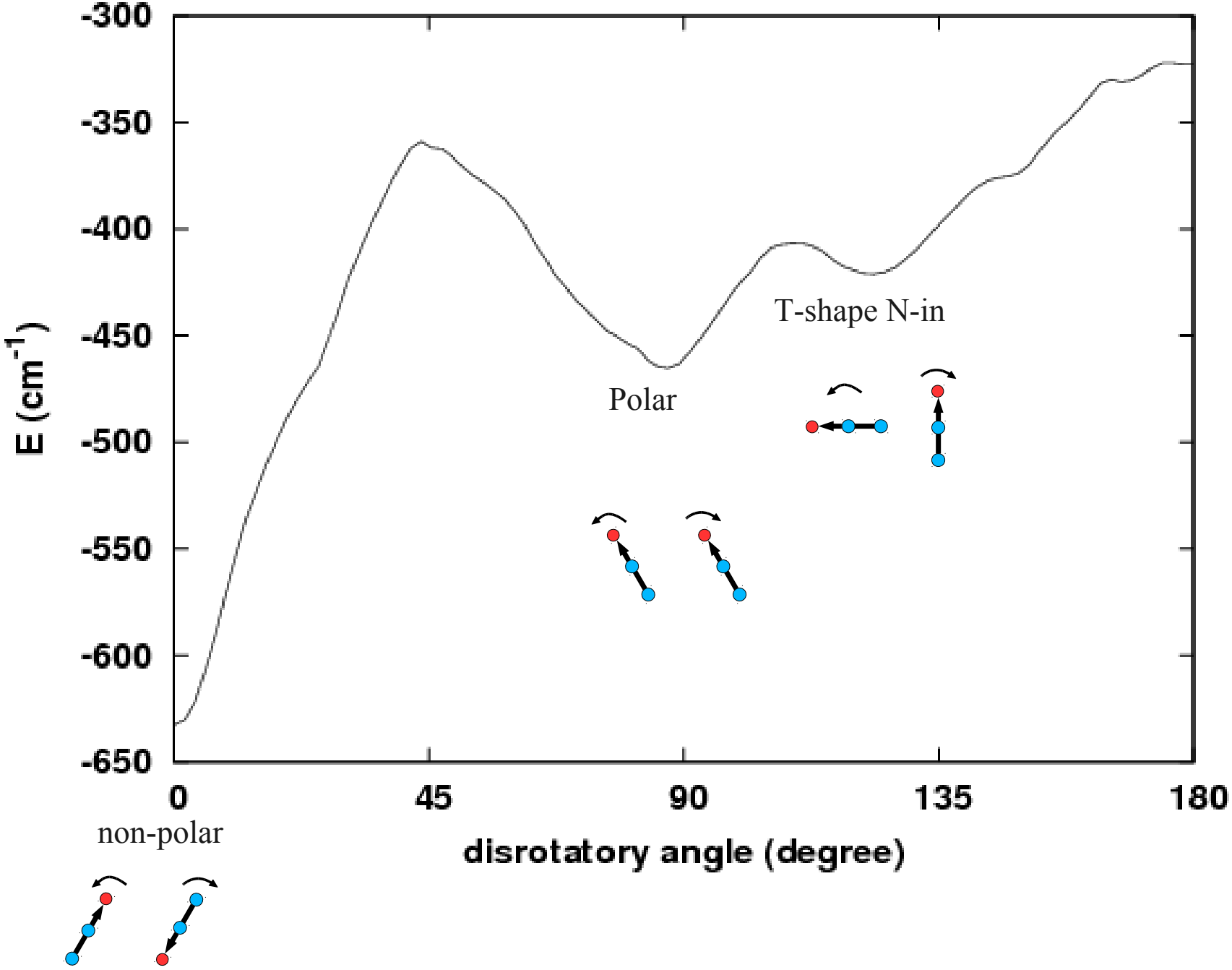
4-d potential energy surface

Richard Dawes and Ahren Jasper

- Energies are computed with the explicitly correlated CCSD(T)-F12b method and the VTZ-F12 basis.
  - G. Knizia, T. B. Adler, and H.-J. Werner, J. Chem. Phys., 130, 054104 (2009)
  - K.A. Peterson, T. B. Adler, and H.-J. Werner, J. Chem. Phys., 128, 084102 (2008)
- about 2000 points
- A 4-d surface is made by interpolating between local fits (IMLS)
  - Dawes et al. J. Chem. Phys., 130, 144107 (2009)

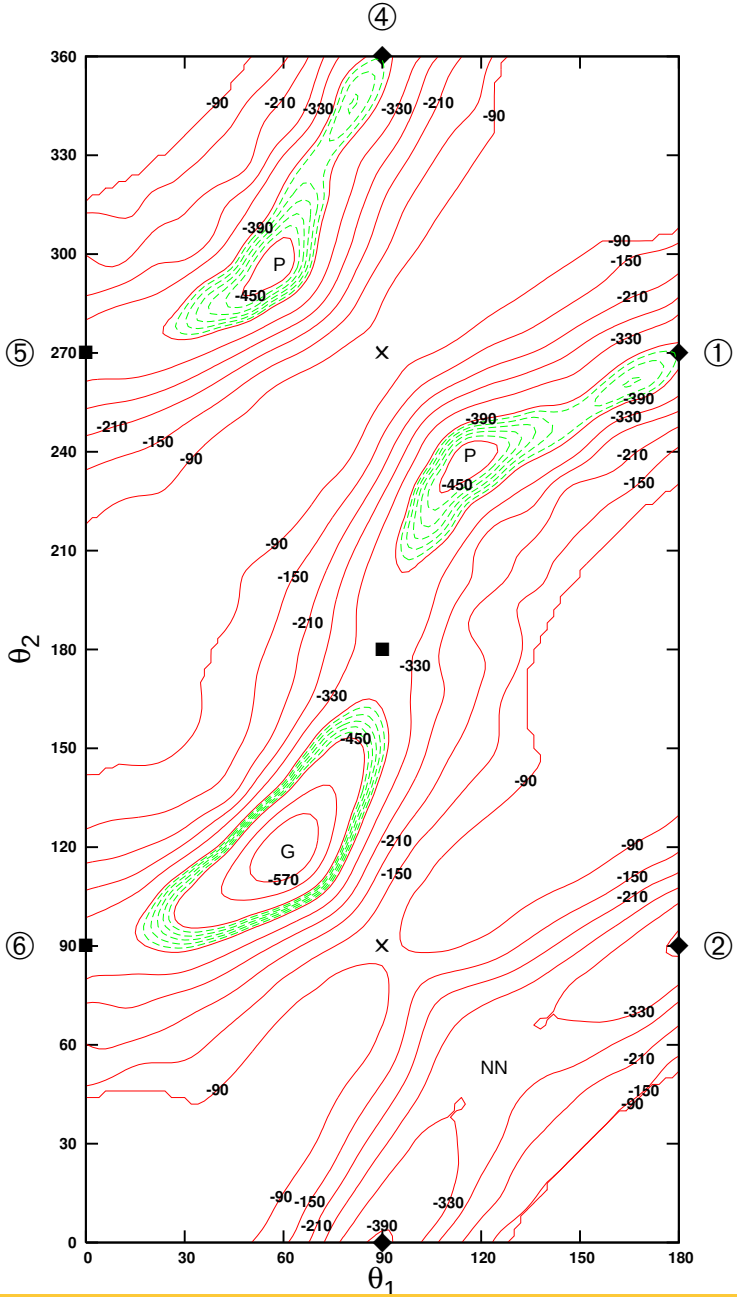
What is observed ?



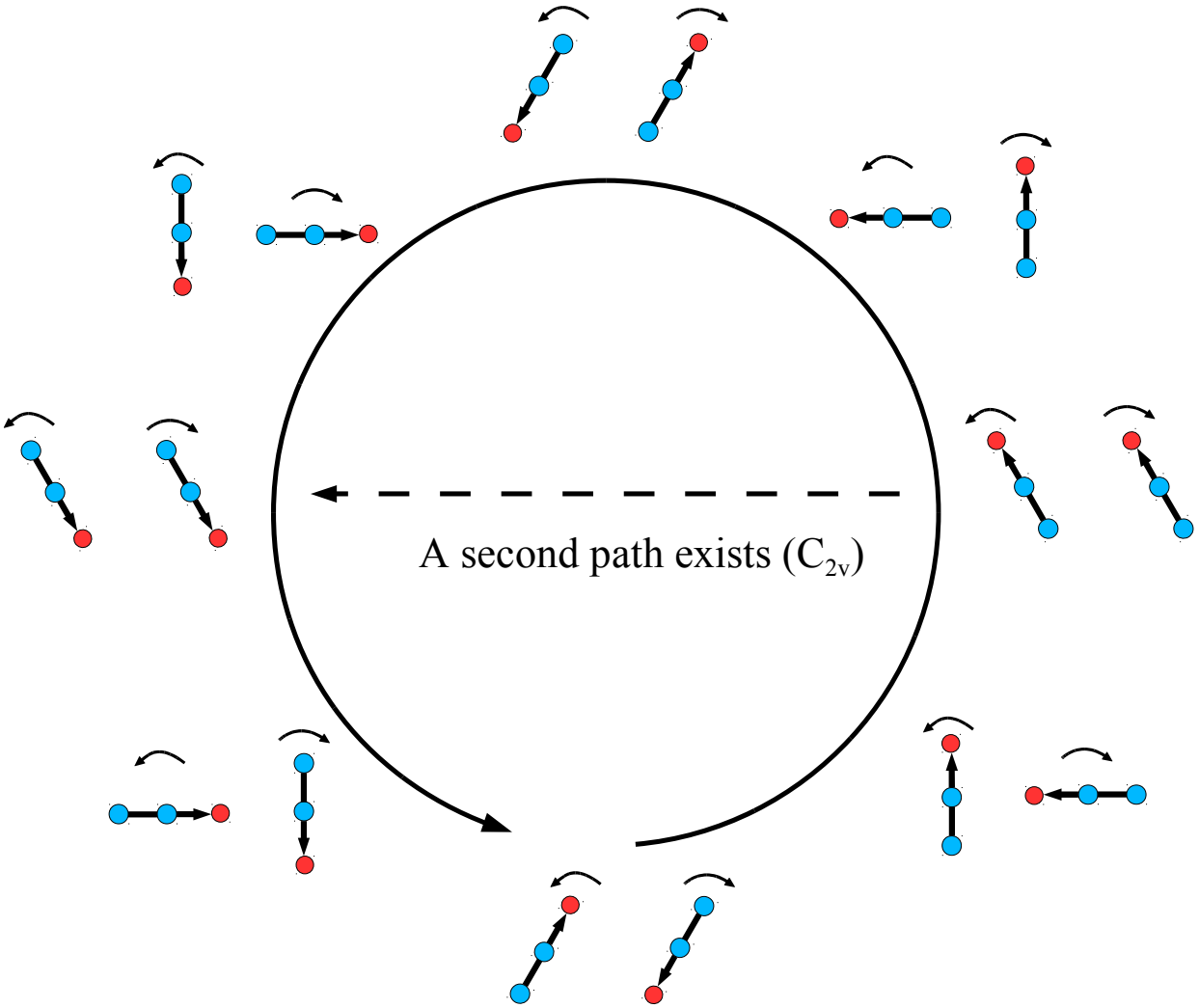

-300
-350
-400
-450
-500
-550
-600
-650
E (cm-1)
0
45
90
135
180
disrotatory angle (degree)
T-shape N-in
Polar
non-polar

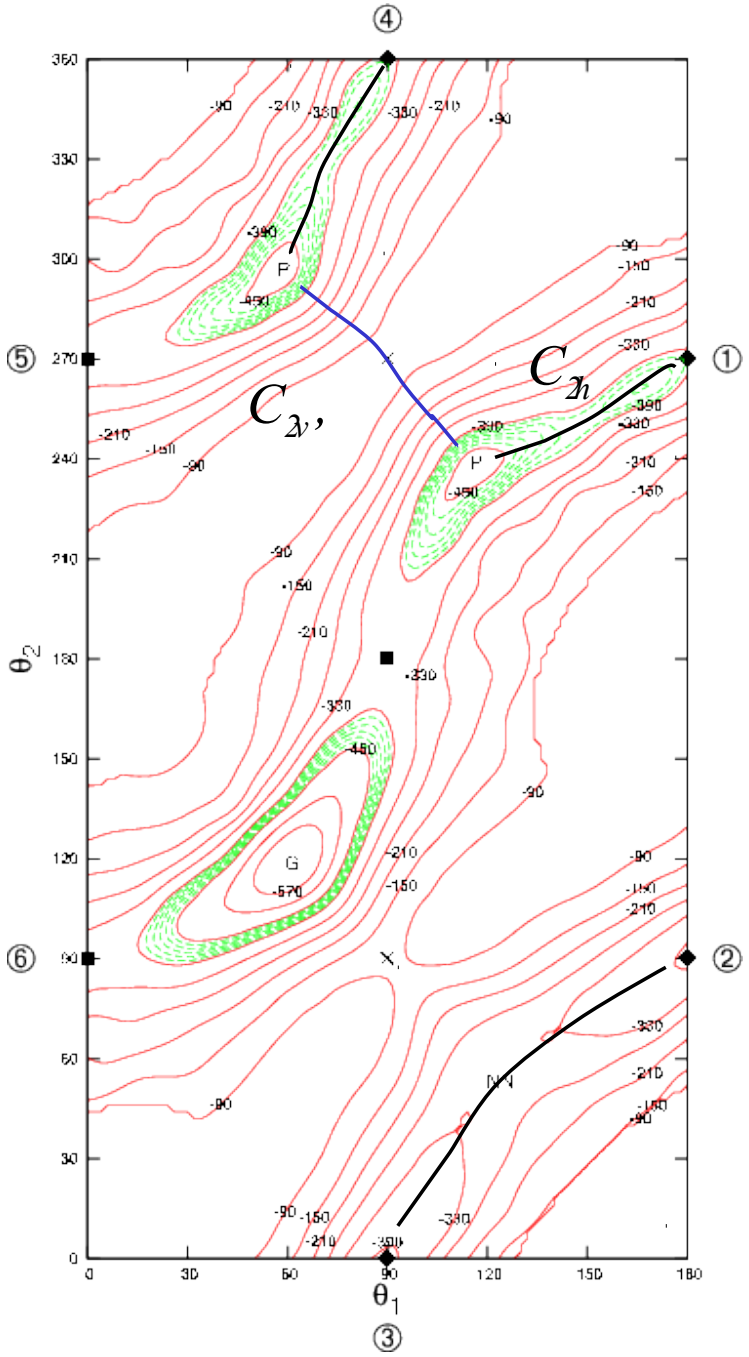
In the bottom half of this figure $\phi = 0$ and the O atoms are on opposite sides.

In the top half, $\phi = \pi$, the O atoms are on the same side, and $\theta_2^{plot} = 2\pi - \theta_2$



Disrotatory motion

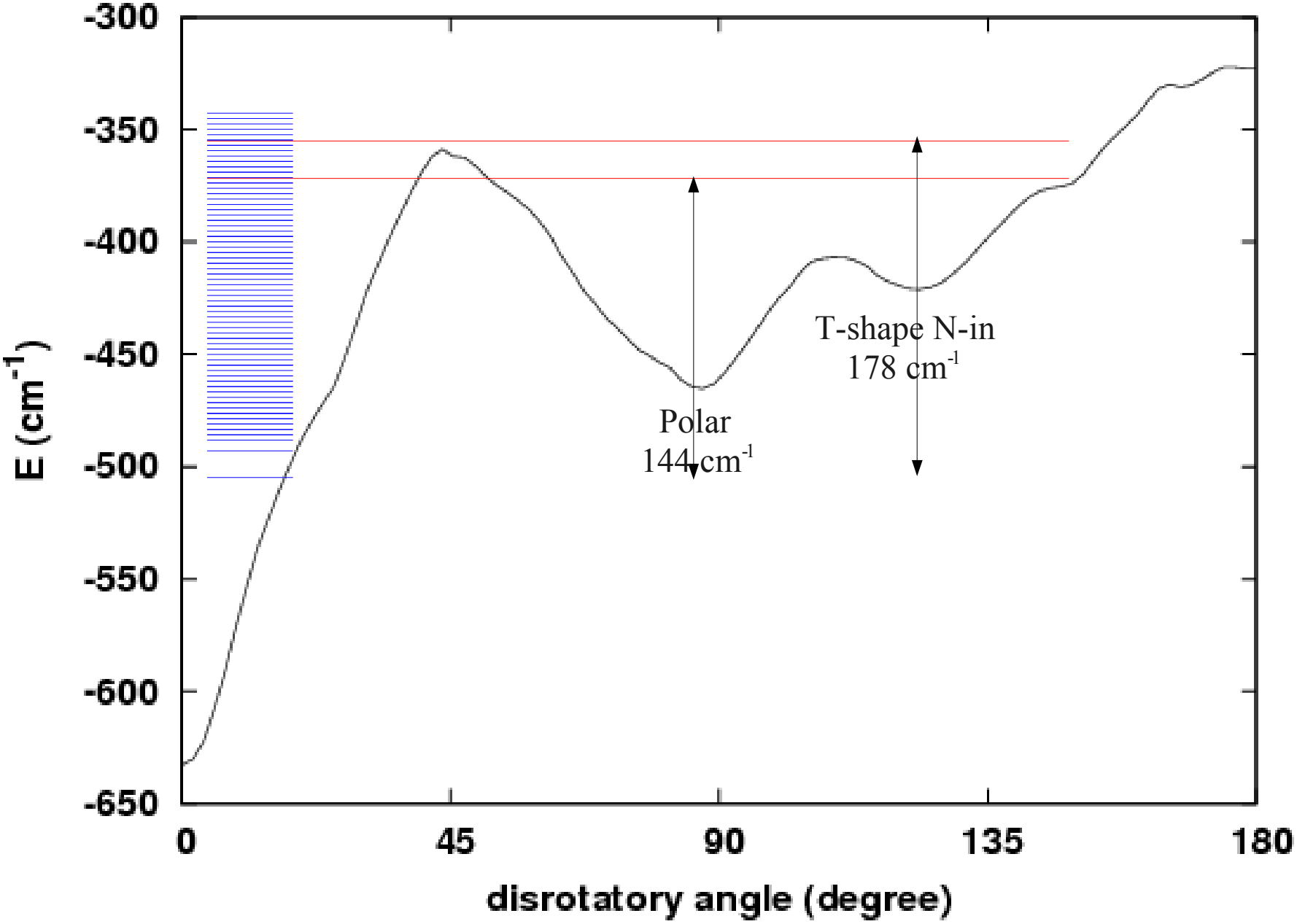



④
⑤
①
⑥
②
③
C_{2v},
C_{2h}
P
P
G
X
NN
θ_1
θ_2

Compute the spectrum

- We use the coordinates and angular basis of Option II (frame attached to the inter-monomer vector $\vec{R}$).
- Sine discrete variable representation (DVR) functions are used for R
- Potential integrals are done with Gauss quadrature
- Matrix-vector products are evaluated by doing sums sequentially
- We compute levels labelled by the irreps of the group $\{E, P\} \times \{E, E^*\}$ using the symmetry adapted Lanczos algorithm

Identification of polar levels is difficult



Non-polar isomer

Many ro-vibrational levels for overtones of 4 vibrational bands are assigned

- torsion,
- geared bend
- anti-geared bend
- VDW stretch

Ro-vibrational transitions agree well with existing experimental data.

TABLE I: Intermolecular vibrational levels of non-polar isomer (cm^{-1}). The experimental results are estimated from combination bands

Mode	Sym	harmonic[1]	This work	Expt[1–3]
torsion	$A-$	30.	25.76	27.3 (1.0)
geared	$B+$	49.	41.86	42.3 (1.0)
VDW stretch	$A+$	69.	52.76	
anti-geared	$A+$	121.	97.52	

[1] G. M. Berner, A. L. L. East, M. Afshari, M. Dehghany, N. Moazzen-Ahmadi and A. R. W. McKellar, J. Chem. Phys. **130**, 164305 (2009)

[2] M. Dehghany, M. Afshari, N. Moazzen-Ahmadi and A. R. W. McKellar, Phys. Chem. Chem. Phys. **10**, 1658 (2008)

[3] M. Dehghany, M. Afshari, Z. Abusara and N. Moazzen-Ahmadi, Phys. Chem. Chem. Phys. **11**, 7585 (2009)

TABLE I: Rotational constants of first three vibrational states of the non-polar isomer (cm^{-1}).

vib state	A	B	C
ground state	0.3005	0.05988	0.04985
Refs. 1,2	0.2995	0.05992	0.04984
torsion	0.2900	0.05945	0.05011
Ref. 3	0.2864	0.05948	0.05009
geared	0.3149	0.05863	0.04867
Ref. 4	0.3118	0.05876	0.04862

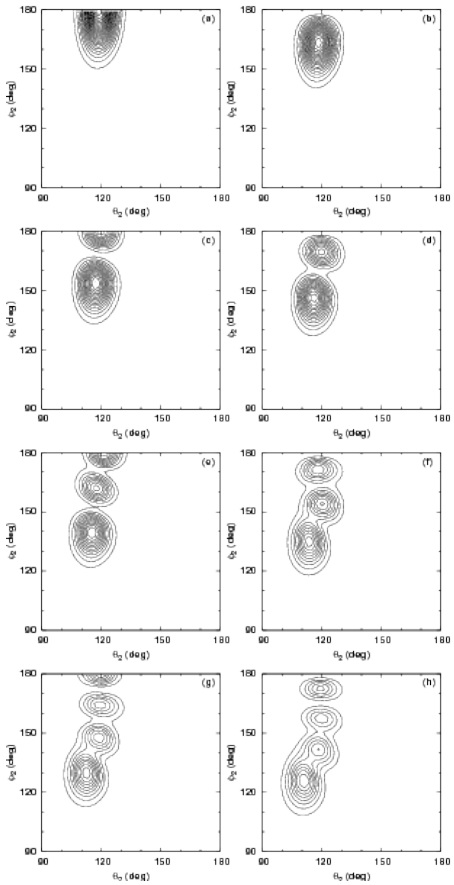
[1] M. Dehghany, M. Afshari, Z. Abusara, N. Moazzen-Ahmadi and A. R. W. McKellar, J. Chem. Phys. **126**, 164310 (2007)

[2] M. Dehghany, M. Afshari, Z. Abusara, C. Van Eck and N. Moazzen-Ahmadi, J. Mol. Spectrosc. **247**, 123 (2008)

[3] M. Dehghany, M. Afshari, N. Moazzen-Ahmadi and A. R. W. McKellar, Phys. Chem. Chem. Phys. **10**, 1658 (2008)

[4] M. Dehghany, M. Afshari, Z. Abusara and N. Moazzen-Ahmadi, Phys. Chem. Chem. Phys. **11**, 7585 (2009)

Torsion of non-polar isomer : 25.76 cm^{-1}



$v = 0, 1$

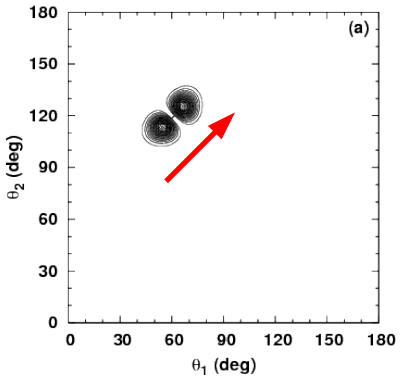
$v = 2, 3$

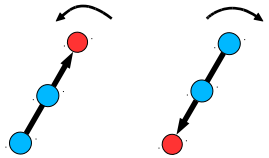
$v = 4, 5$

$v = 6, 7$

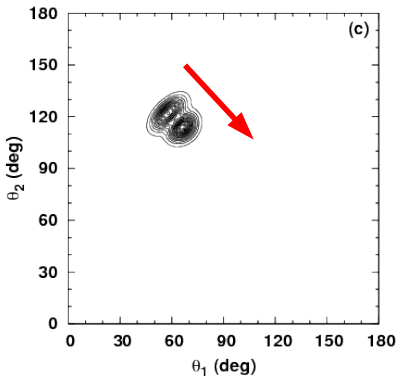
Geared-bend and anti-geared bend of non-polar isomer

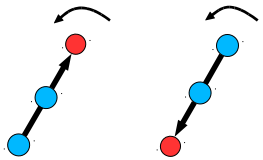
Geared bend : 41.86 cm^{-1}





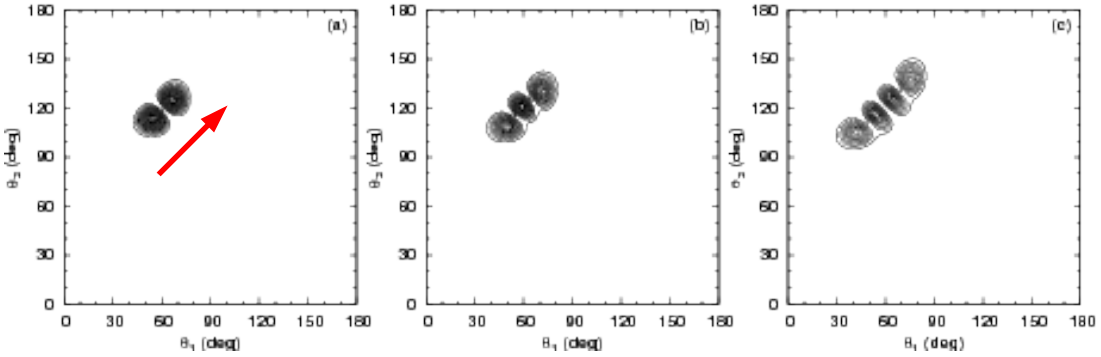
Anti-geared bend : 52.76 cm^{-1}

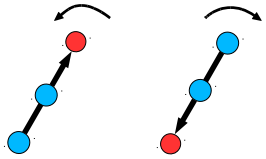




Geared-bend overtones of non-polar isomer

Geared bend : 41.86 cm^{-1}

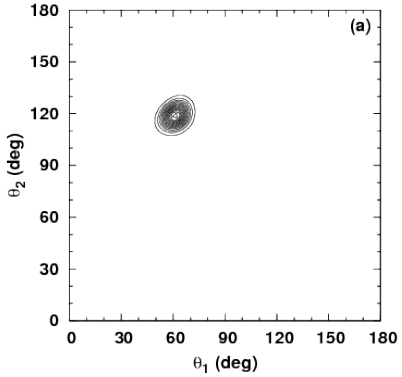


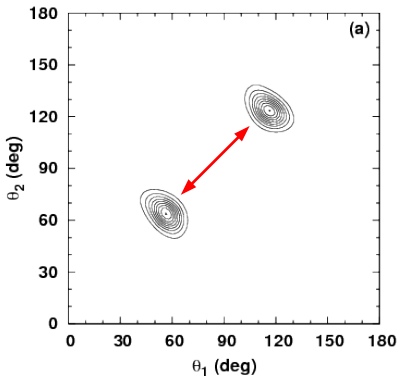


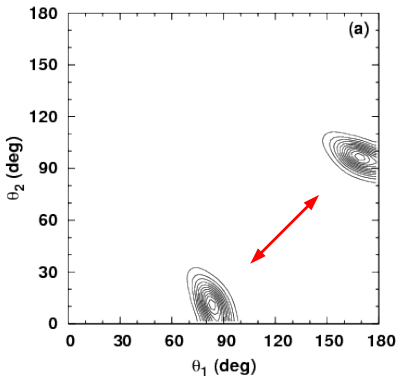
Ground state of the three isomers

tunneling

tunneling







Nonpolar, 0 cm^{-1}

$(\theta_1, \theta_2) \approx (60^\circ, 120^\circ)$

Polar, 143.53 cm^{-1}

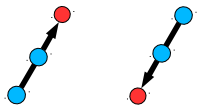
$(\theta_1, \theta_2) \approx (60^\circ, 60^\circ)$

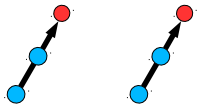
$\approx (120^\circ, 120^\circ)$

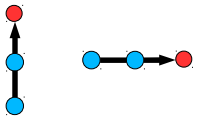
T-shape N-in, 178.03 cm^{-1}

$(\theta_1, \theta_2) \approx (90^\circ, 0^\circ)$

$\approx (180^\circ, 90^\circ)$

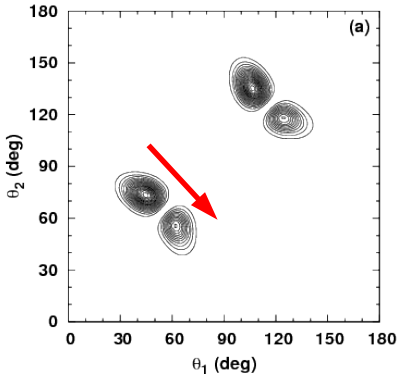


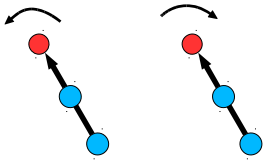




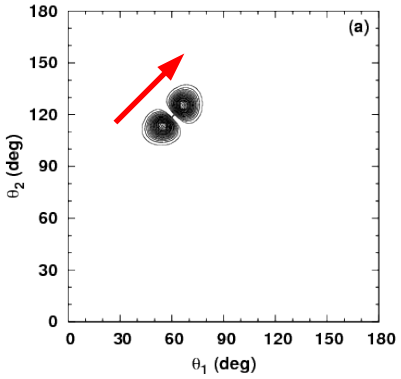
Geared-bend of polar isomer

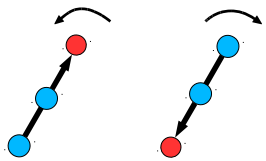
geared bend of polar: 20.31 cm^{-1}





Geared bend : 41.86 cm^{-1}





20.31 cm^{-1} = 163.84 - 143.53cm^{-1} (polar ground state)

How do we identify these "polar" states ?

For $J = 0$ we plot wavefunctions

For $J > 0$ we use a sum-of-monomer-dipoles approximation and compute intensities for all possible transitions from lower J states.

When the initial state is a polar ro-vibrational state, the final state is assumed to also be a polar state if the intensity is appreciable.

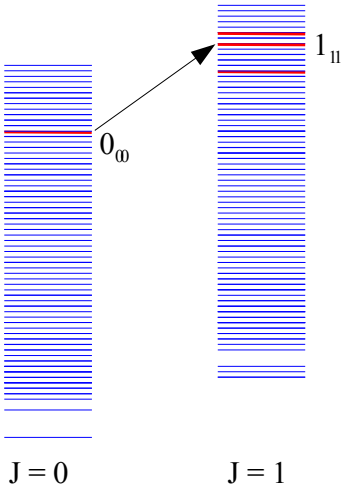


TABLE I: Rovibrational transitions and intensities of polar isomer. The experiment is from Walker, Minei, Novick and Lego, J. Mol. Spectrosc. (2008)

$J''_{K''aK''c} \rightarrow J'_{K'aK'c}$	ν(cal)	ν(obs)	S
$0_{00} \rightarrow 1_{01}$	0.1006		1.45
$0_{00} \rightarrow 1_{11}$	0.3545	0.35510	2.45
$1_{10} \rightarrow 1_{01}$	0.2622	0.26325	3.67
$1_{10} \rightarrow 1_{11}$	0.0083		2.17

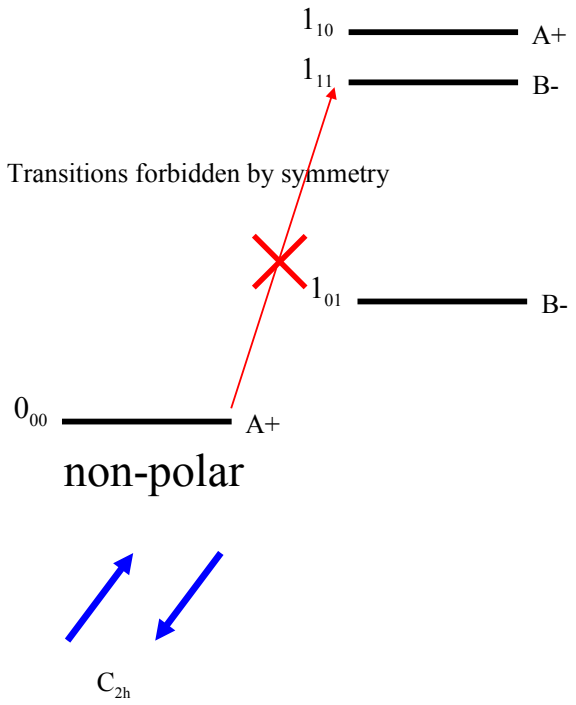
In the non-polar case the $\Delta J = 1$ transitions are symmetry forbidden

States are labelled by $A+, B+, A-, B-$.

- A/B for permutation of the monomers
- +/- for parity

Selection rule is $A+ \leftrightarrow A-$; $B+ \leftrightarrow B-$

We can assign $J_{Ka,Kc}$ labels to levels we compute.

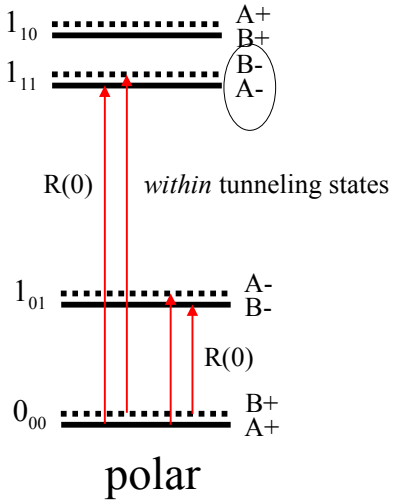


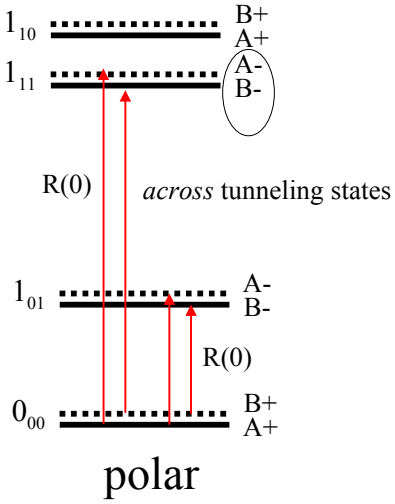
Which transitions occur among polar states ?

All the rotational levels come in pairs.

We know that the $A+ \quad 0_{00} \rightarrow A- \quad 1_{11}$ will occur, but we do not know if the $A- \quad 1_{11}$ level is above or below the $B- \quad 1_{11}$ level.

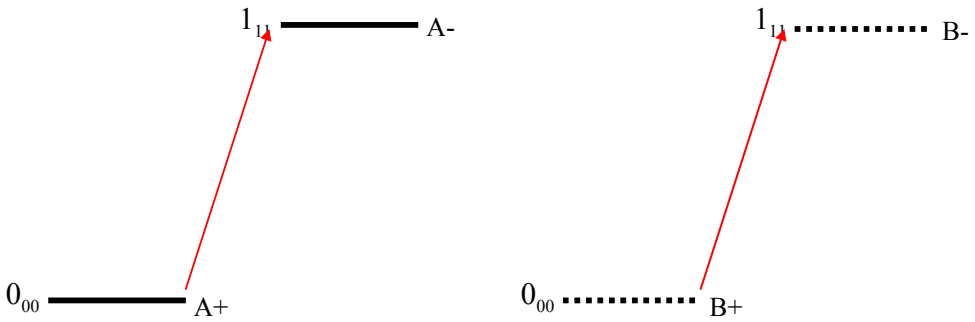
The tunneling splitting is so small ($\approx 10^{-13}$ cm^{-1}) that we cannot distinguish between the options.



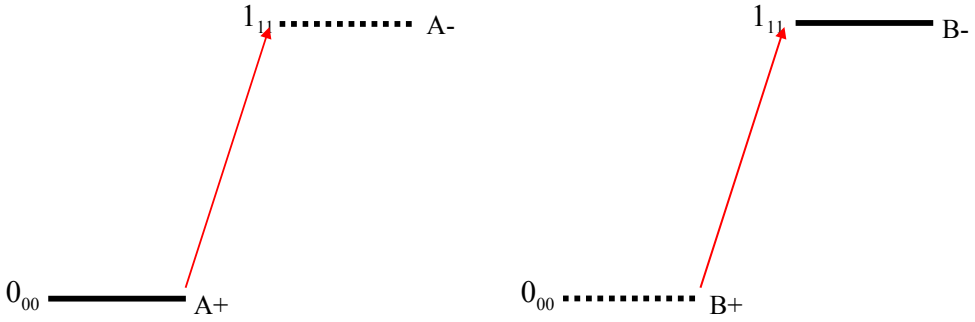


Which case is right ?

Case I : transition within a tunneling state

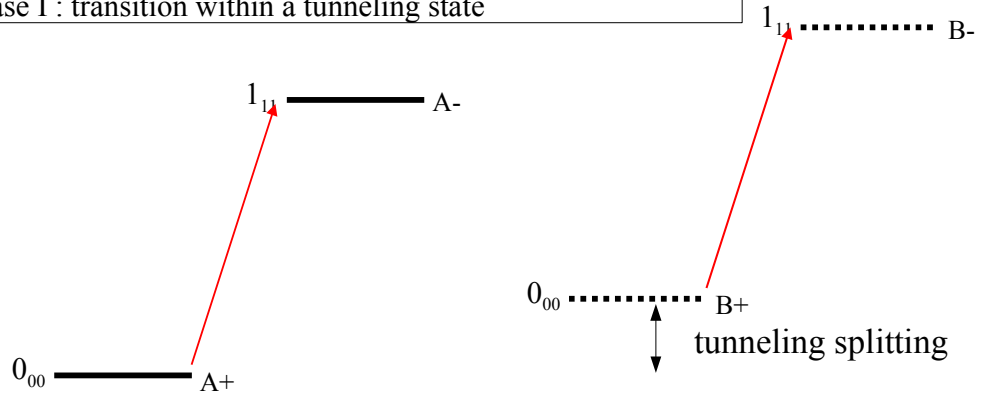


Case II : transition between different tunneling states

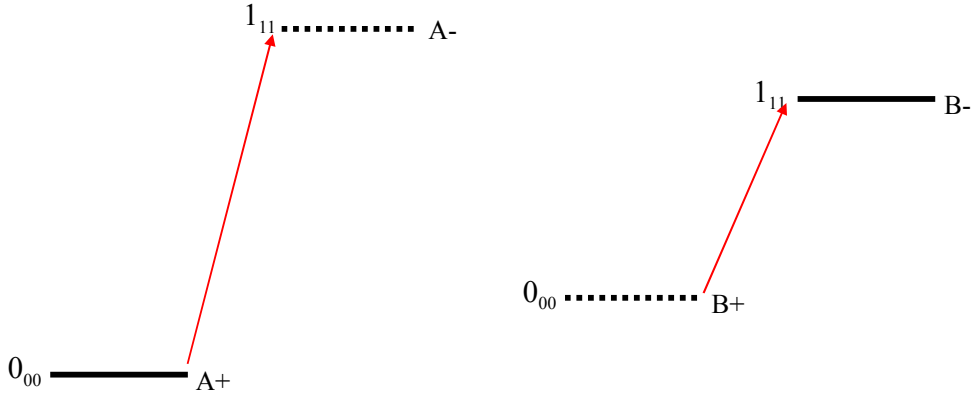


If the tunneling splitting were larger, e.g. $(HF)_2$

Case I : transition within a tunneling state



Case II : transition between different tunneling states



A new tool : vibrational parent analysis of rovibrational levels

- Given the J=1 rovibrational wavefunctions and a set of vibrational wavefunctions,

$$\Psi^{(J)} = \sum_{l_1,l_2,m_2;K} c_{l_1,l_2,m_2;K} |l_1, l_2, m_2(K)\rangle |JK\rangle$$

$$\Phi_v = \sum_{l_1,l_2,m_2} d_{l_1,l_2,m_2} |l_1, l_2, m_2\rangle$$

- Re-expand the J=1 state in terms of vibrational wavefunction Φ_v

$$\Psi^{(J)} = \sum_{v,K} \tilde{c}_{K,v} |\Phi_v\rangle |JK\rangle$$

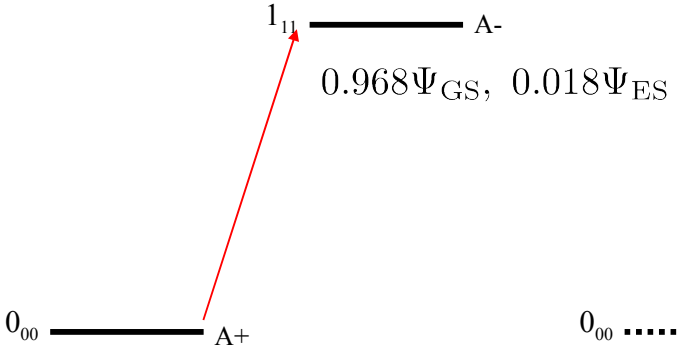
$$\tilde{c}_{K,v} = \sum_{l_1,l_2,m_2} c_{l_1,l_2,m_2} (\Phi_v | l_1, l_2, m_2(K))$$

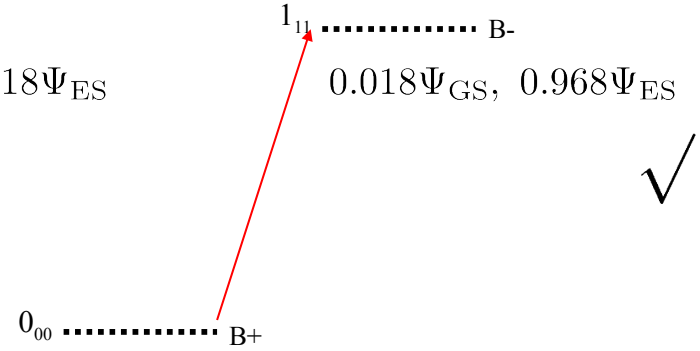
- The contribution of state Φ_v is given by

$$P_v = \sum_K \tilde{c}^2_{K,v}$$

Which case is right ?

Case I : transition within a tunneling state





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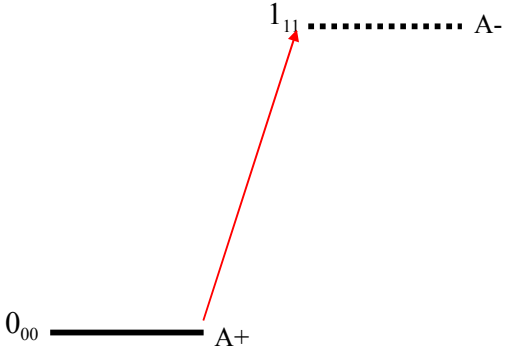
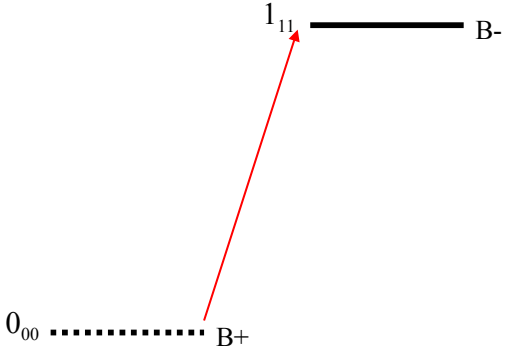
Case II : transition between different tunneling states



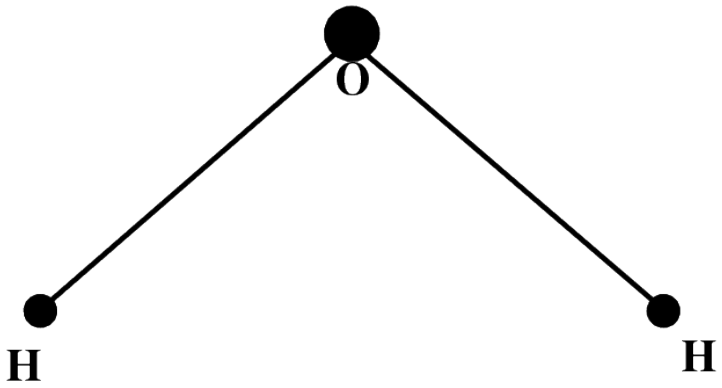


×

H_2O-H_2

Ab initio potential energy surfaces :
Hodges, Wheatley, Schenter, Harvey, J. Chem. Phys. (2004) ;

Valiron, Wernli, Faure, Wisenfeld, Rist, Kedzuch, Noga, J. Chem. Phys. (2008)



Experimental study : infrared spectra probing the bending band of H_2O Weida and Nesbitt, J. Chem. Phys. (1999)

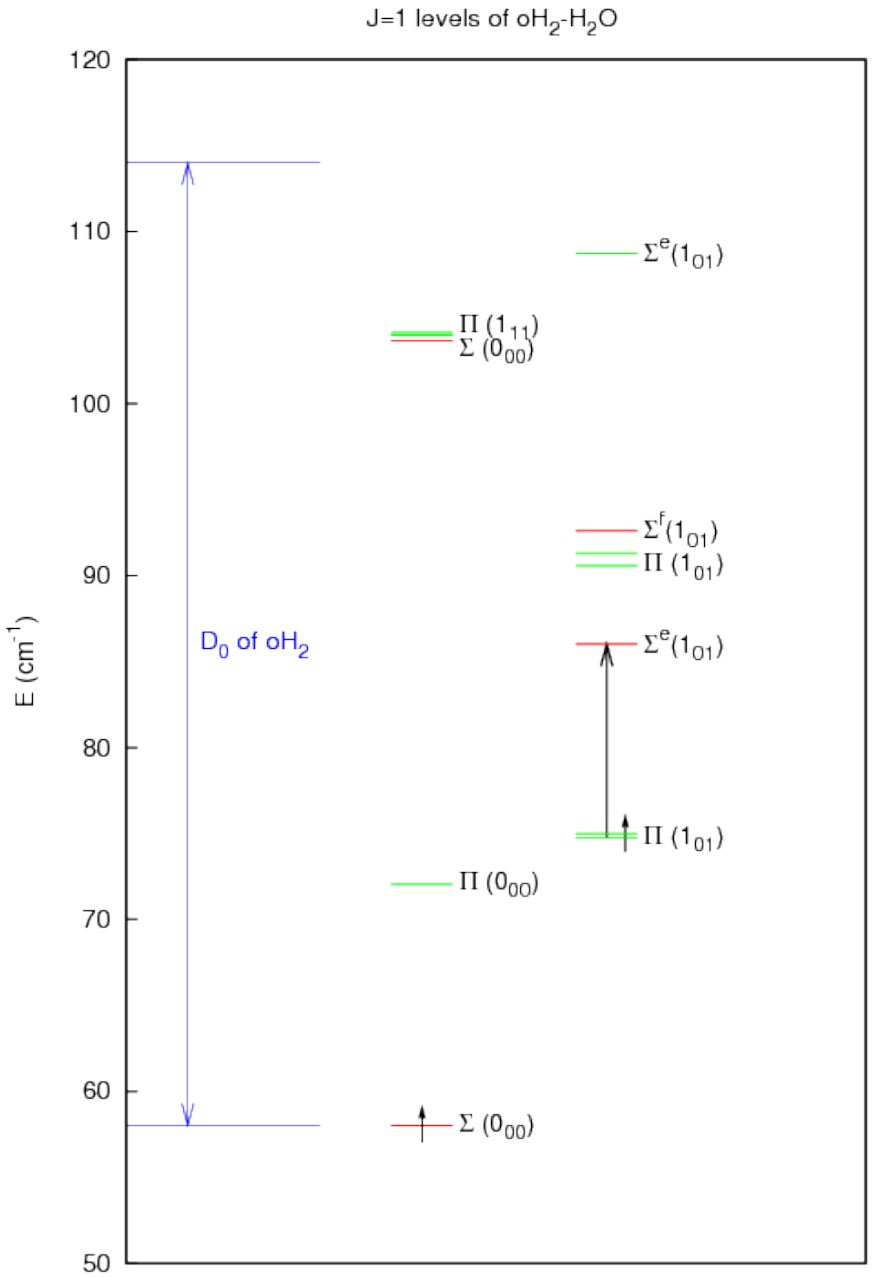
Coordinates

The dimer frame is better because $B_R = 1.0$ cm^{-1}

Calculations done in both coordinates give idenical results, but

- dimer frame coordinates : $j_{max} = 8, n_R = 45$. Basis size = 125'000 for $J = 0$
- monomer frame coordinates : $j_{max} = 12, n_R = 45$. Basis size = 646'000 for $J = 0$

Some $J = 1$ levels



Well depth $= 241\ \mathrm{cm}^{-1}$

zpe ($= D_0$ for pH_2-H_2O) $=$ -36.34 cm^{-1}

Density

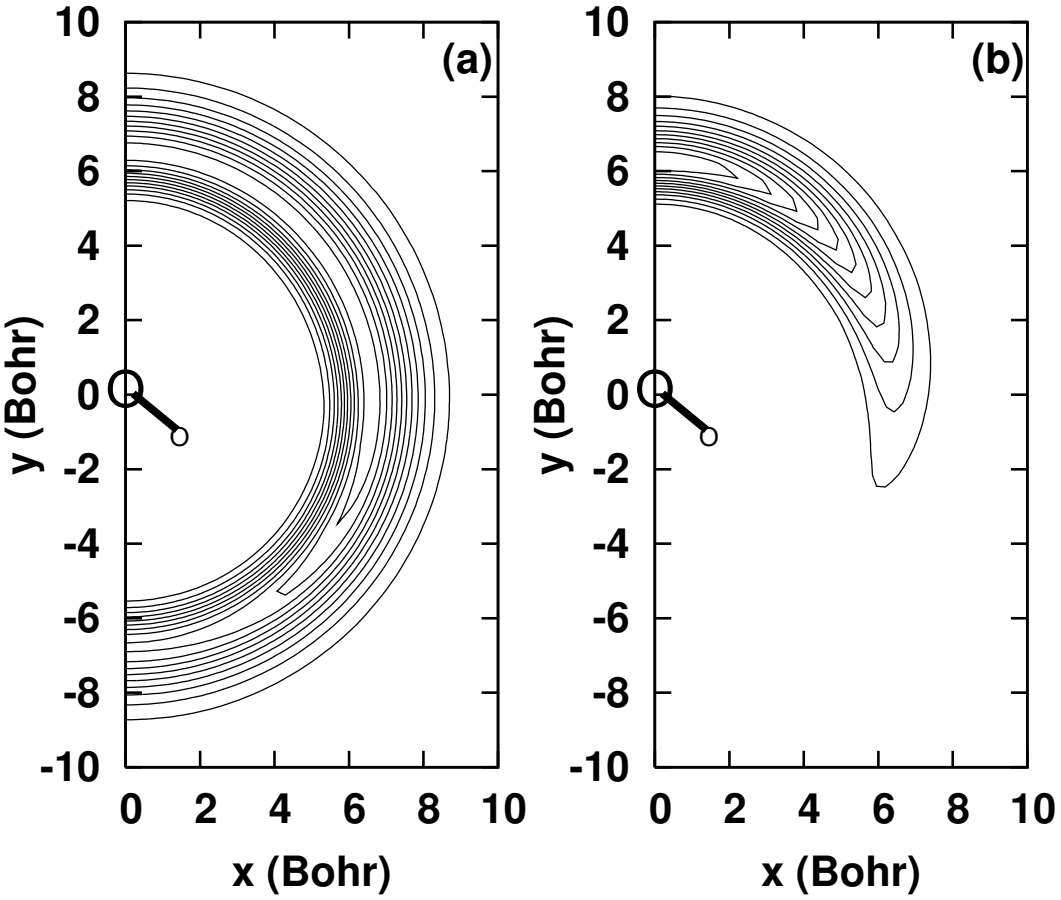


FIG. 1: Ground state of pH_2-H_2O with E=-33.78 cm^{-1} (a) and oH_2-H_2O with E=60.06 cm^{-1}(b)

How bands are computed : an example

Band I of W&N

$\Sigma(0_{00}) \longrightarrow \Sigma(0_{00})$ band of o H_2 - p H_2O.

	E''	E'	cal	obs	o - c
P(4)	70.919	65.996	1589.877	1589.909	0.032
P(3)	65.219	61.708	1591.289	1591.315	0.026
P(2)	60.909	58.833	1592.724	1592.741	0.017
P(1)	58.021	57.392	1594.171	1594.176	0.005
R(0)	56.572	58.833	1597.061	1597.037	-0.024
R(1)	58.021	61.708	1598.487	1598.446	-0.041
R(2)	60.909	65.996	1599.887	1599.827	-0.060
R(3)	65.219	71.667	1601.248	1601.169	-0.079
R(4)	70.919	78.677	1602.558	1602.458	-0.100

o H_2 - p H_2O levels : $\Sigma(0_{00}) \longrightarrow \Sigma(0_{00})$ and $\Pi(0_{00}) \longrightarrow \Pi(0_{00})$ bands

Levels below 113.8 cm^{-1} are bound.

J	even	odd
0	56.572 $\Sigma(0_{00})$	–
1	72.094 $\Pi(0_{00})$	58.021 $\Sigma(0_{00})$
	–	72.044 $\Pi(0_{00})$
2	60.909 $\Sigma(0_{00})$	74.995 $\Pi(0_{00})$
	74.845 $\Pi(0_{00})$	–
3	79.317 $\Pi(0_{00})$	65.219 $\Sigma(0_{00})$
	–	79.022 $\Pi(0_{00})$
4	70.919 $\Sigma(0_{00})$	85.027 $\Pi(0_{00})$
	84.547 $\Pi(0_{00})$	–

is the $\Sigma \rightarrow \Sigma$ band (R branch) observed by Weida and Nesbitt

is the $\Pi \rightarrow \Pi$ new band (only show Q branch) !

Conclusion

- Using modern electronic structure (explicitly correlated CC) and quantum dynamics (symmetry adapted Lanczos algorithm) methods it is possible to compute very accurate spectra of Van der Waals molecules
- For $(NNO)_2$ our calculated transition frequencies agree very well with those that have been measured
- $(NNO)_2$ has very small tunneling splittings that might be measurable in excited states
- T-shaped N-in states are predicted

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