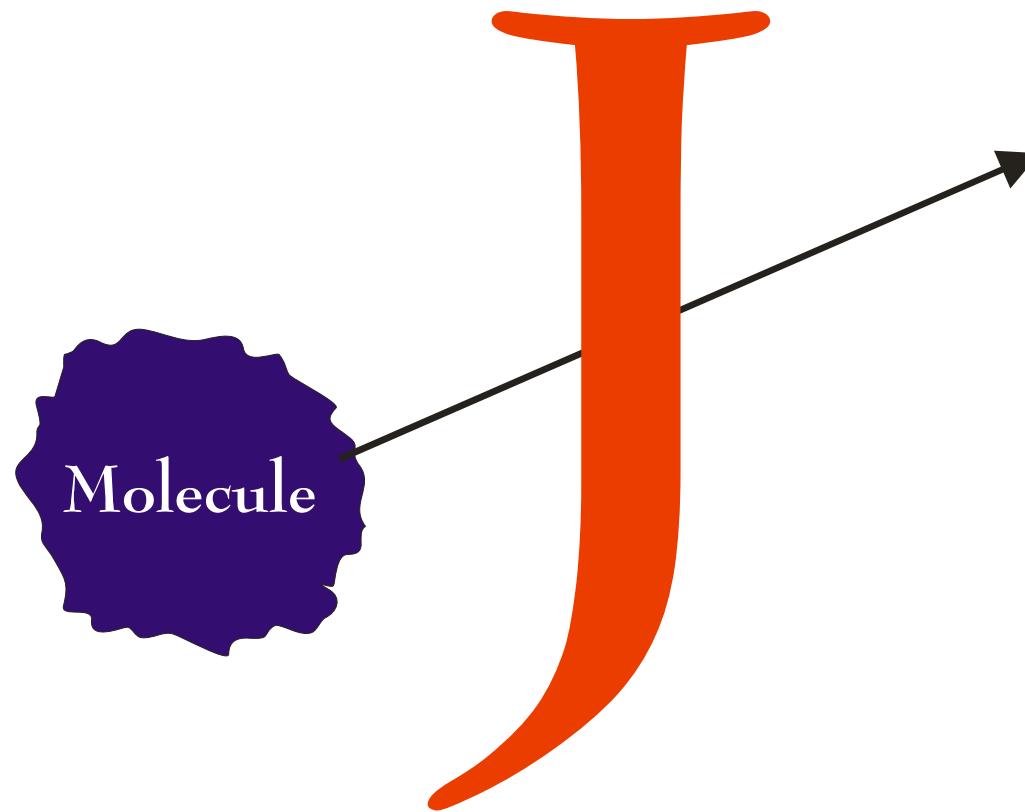


***Where is
Wuppertal?***

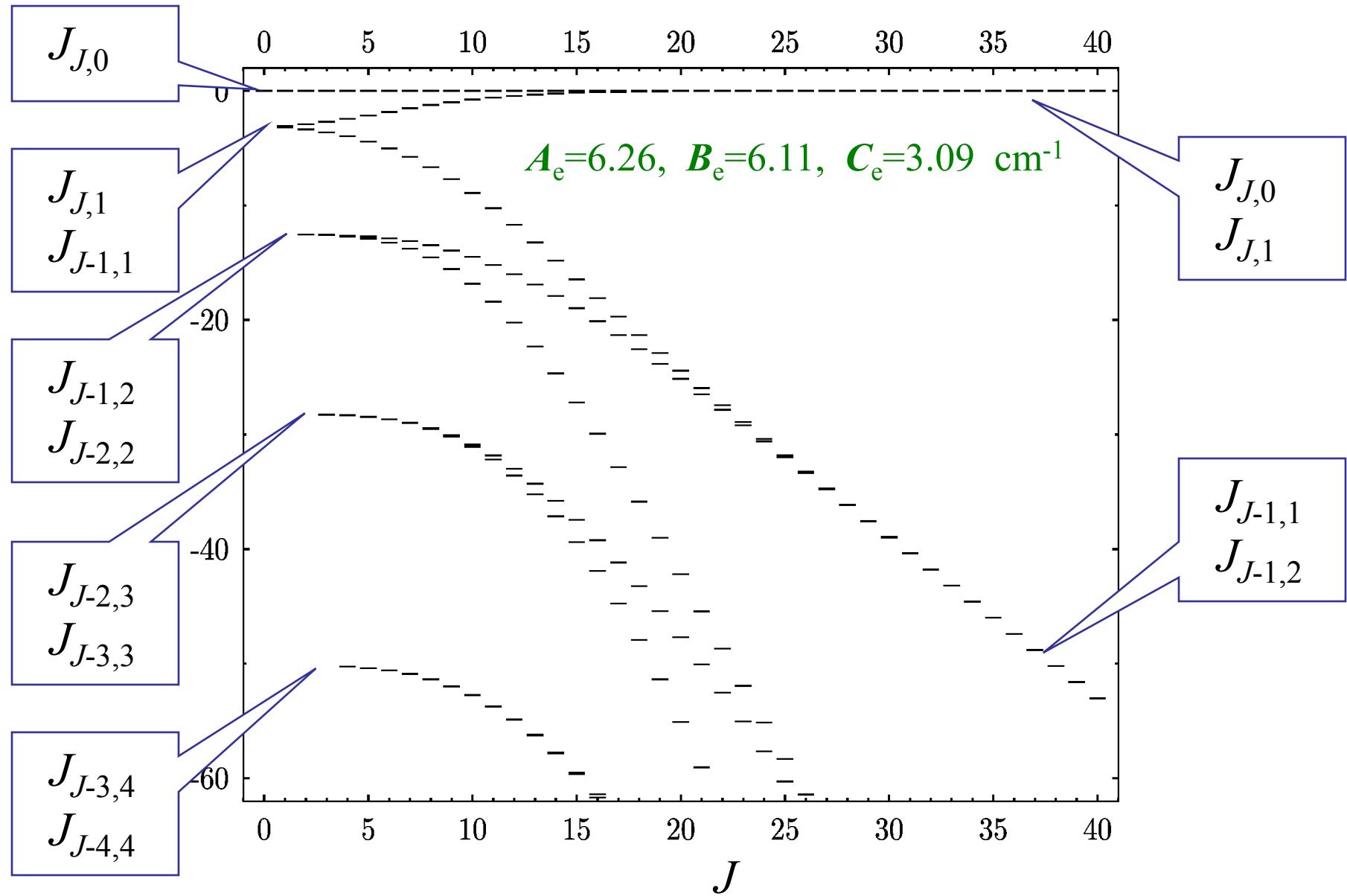


Molecules in highly excited rotational states

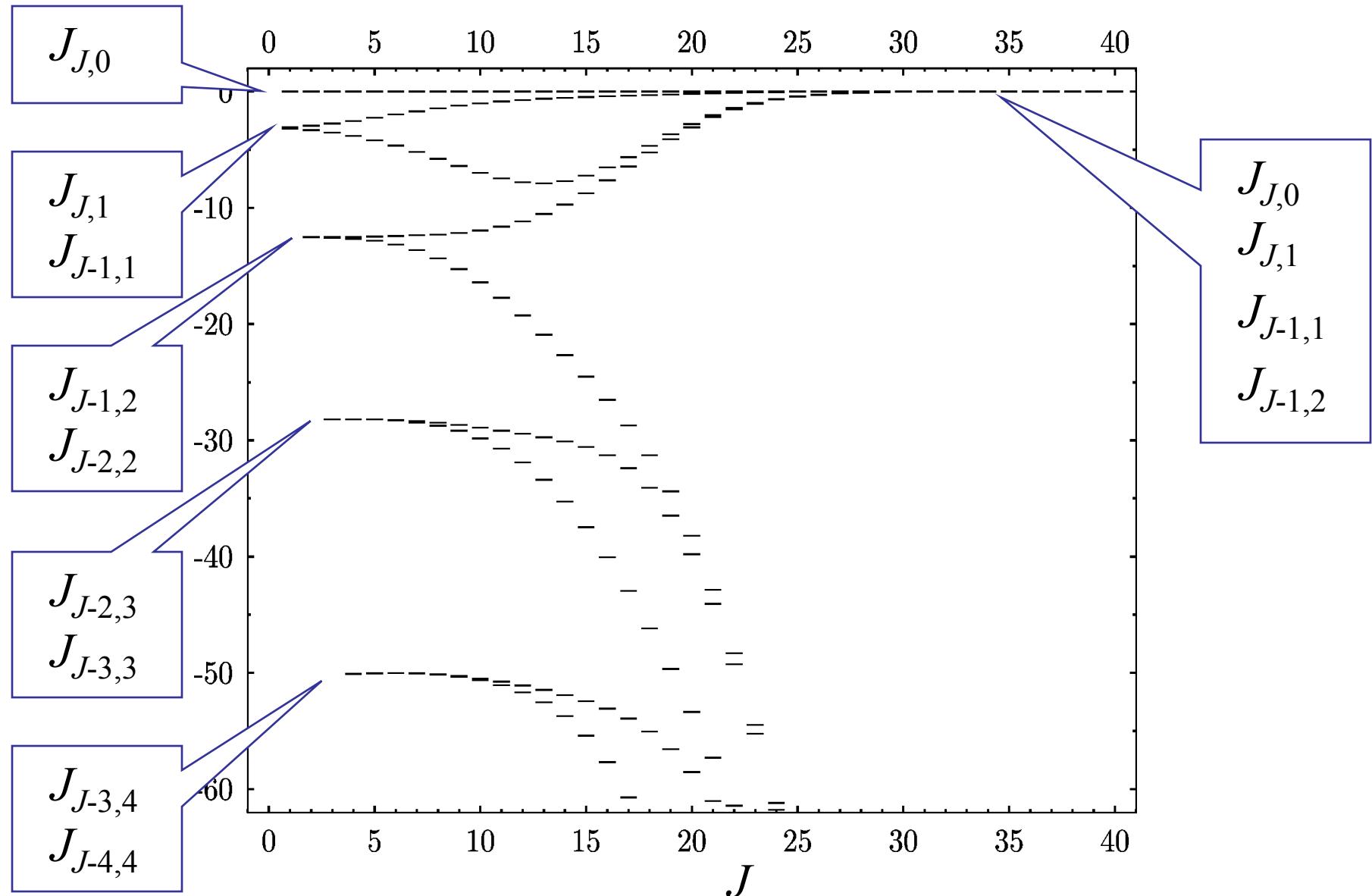


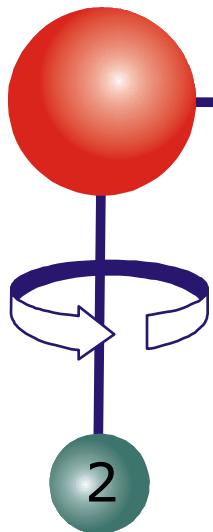
$J \sim 100$

H₂Te Rigid Rotor Energy Levels [$E(J_{KaKc}) - E(J_{J0})$]

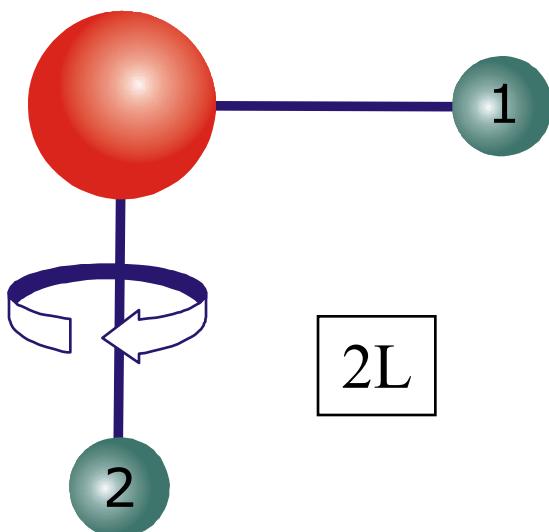


Actual H₂Te Energy Levels [$E(J_{KaKc}) - E(J_{J0})$]

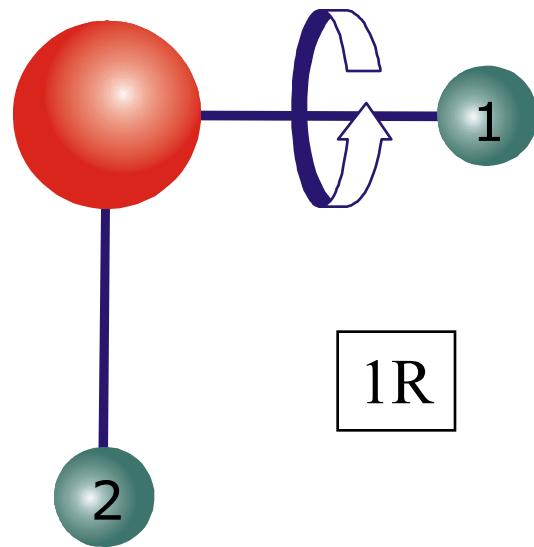




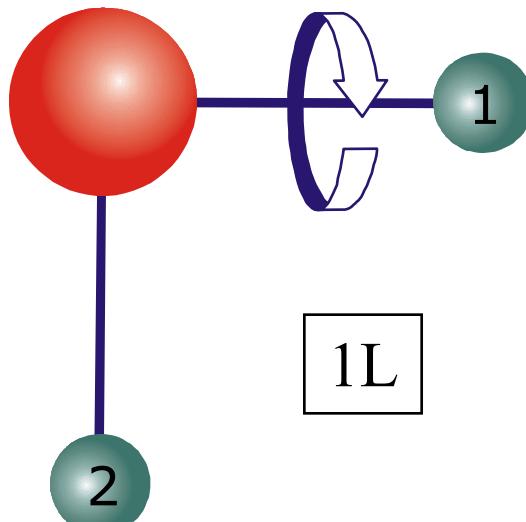
$2R$



$2L$



$1R$



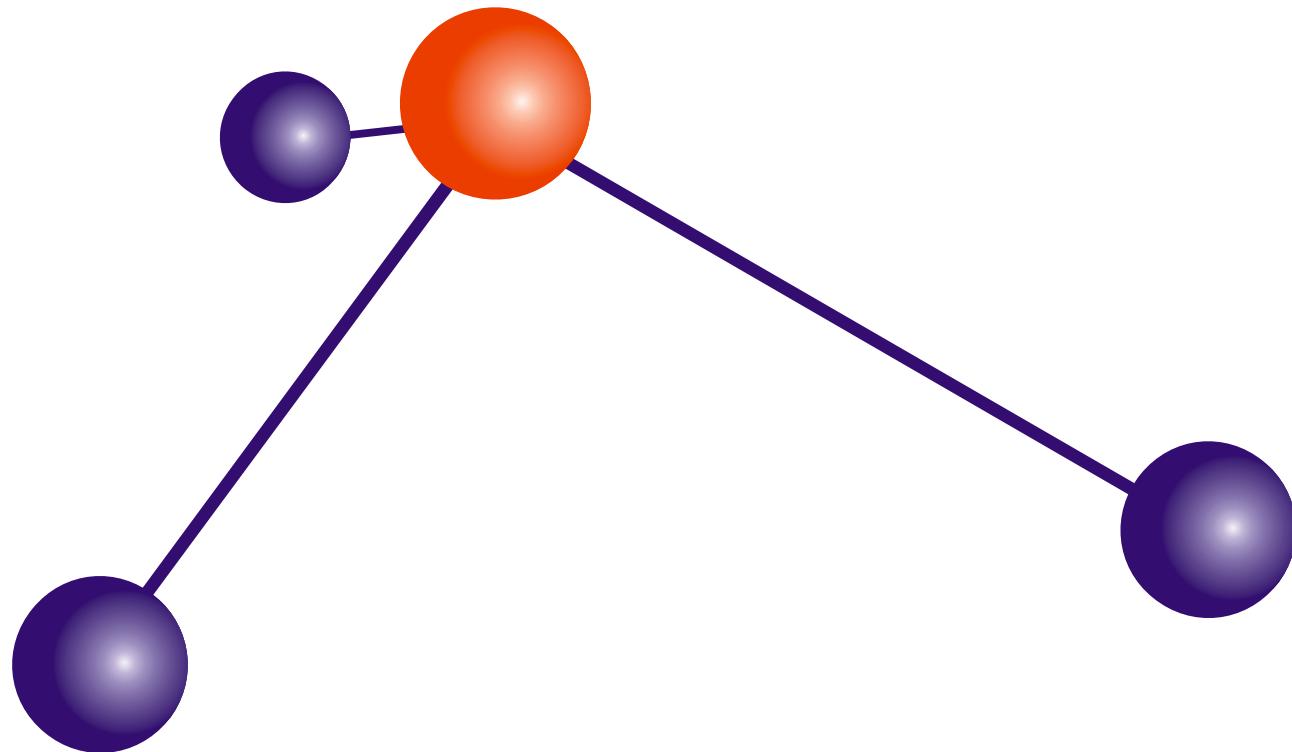
$1L$

$$\left. \begin{array}{l} J_{J,0} \\ J_{J,1} \\ J_{J-1,1} \\ J_{J-1,2} \end{array} \right\} \equiv \dots$$

$$\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \quad \text{in} \quad C_{2v}(\mathbf{M})$$

Rotational Energy Level Clusters

1972	Dorney and Watson	CH ₄	8-fold and 6-fold clusters
1978	Zhilinskii and Pavlichenkov	H ₂ O	4-fold clusters (E_{rb})
1978	Harter and Patterson		Rotational energy surfaces and clusters
1991	Lehmann		Local mode theory and clusters
1992	Kozin et al	H ₂ Se	4-fold clusters observed
1993	Kozin and Jensen	H ₂ Se	4-fold cluster theory (E_{rbs})
1994	Jensen and Bunker	H ₂ X	4-fold cluster symmetry
1996	Kozin et al	H ₂ Te	4-fold clusters (exp and theory)
1997	Jensen et al		Review paper on 4-fold clusters
2000	Jensen		Review paper on LMT and clusters [Mol. Phys. 98 , 1253-1285 (2000)]



**Are there similar effects for
XH₃ molecules – say PH₃?**

We investigate by variational rotation-vibration calculations

Basis functions:

$$|\Psi_{Basis}\rangle = |J, K, m\rangle |v_{inv}, J, K\rangle \Psi_{v_1}^{MO}(\xi_1) \times \Psi_{v_2}^{MO}(\xi_2) \times \Psi_{v_3}^{MO}(\xi_3) \times \Psi_{V,l}^{HO}(\xi_{4a}, \xi_{4b})$$

Rigid rotor
eigenfunctions

Morse oscillators

Two-dimensional
isotropic harmonic
oscillators for doubly
degenerate bending
vibrations

Numerov-Cooley
solution of inversion
Schrödinger
equation for

$$V_0(\rho) = V(\rho, \xi_\lambda = 0)$$

**Hougen-Bunker-Johns theory:
Eckart & Sayvetz conditions**
 $\Rightarrow \widehat{T}_{\text{nuc}} = \text{expansion in the } \xi_i$

[1] H. Lin *et al.*, *J. Chem. Phys.* **117**, 11265 (2002)

[2] S.N. Yurchenko *et al.*, *Mol. Phys.* **103**, 359 (2005) and references given there.

Variational rotation-vibration calculations for PH₃

$J \leq 80$

Vibrational basis set:

$$2(\nu_1 + \nu_2 + \nu_3) + \nu_{inv} + V_{bend} \leq 6$$

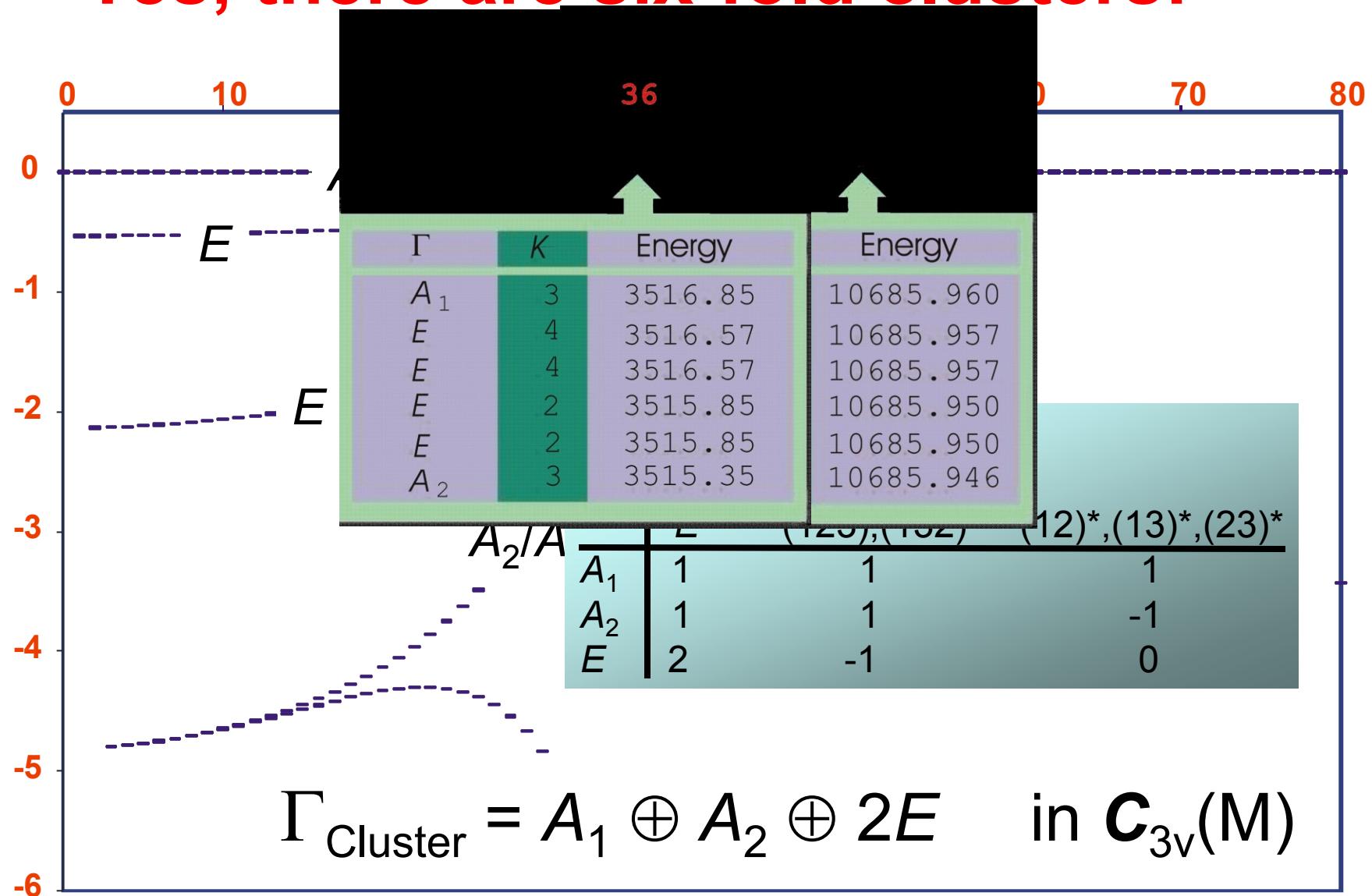
Potential energy surface:

cc-pwCVTZ [1]
refined by fitting to experimental
vibrational term values [2]

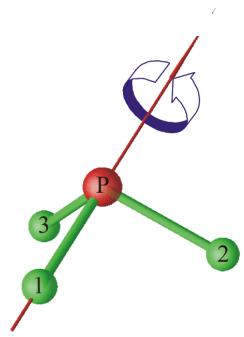
[1] D. Wang, Q. Shi, and Q.-S. Zhu, *J. Chem. Phys.*, **112**, 9624 (2000)

[2] S.N. Yurchenko *et al.*, *Chem. Phys.* **290**, 59 (2003)

Yes, there are six-fold clusters!

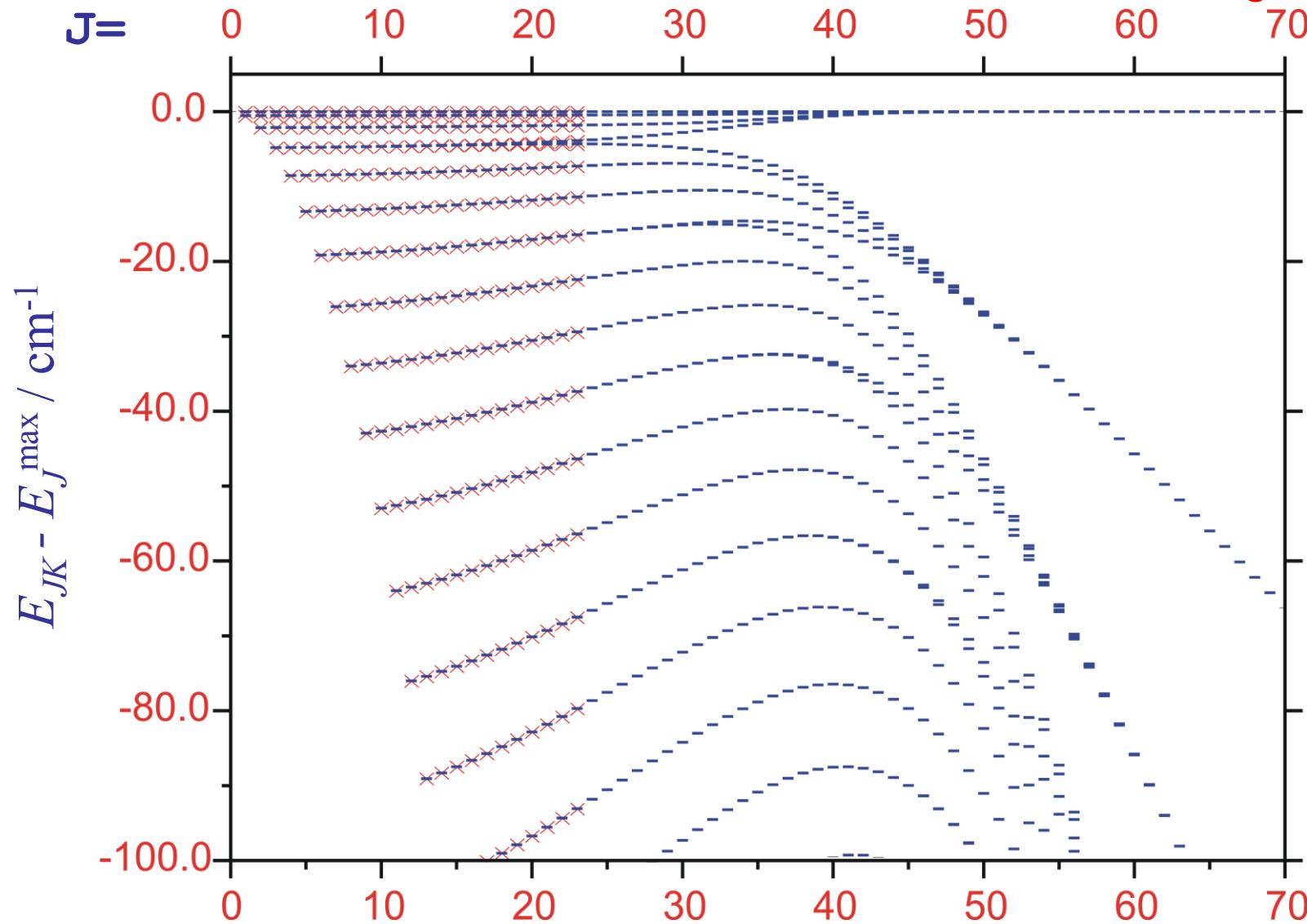


$$|1 \text{ PCS}\rangle = E |1 \text{ PCS}\rangle$$

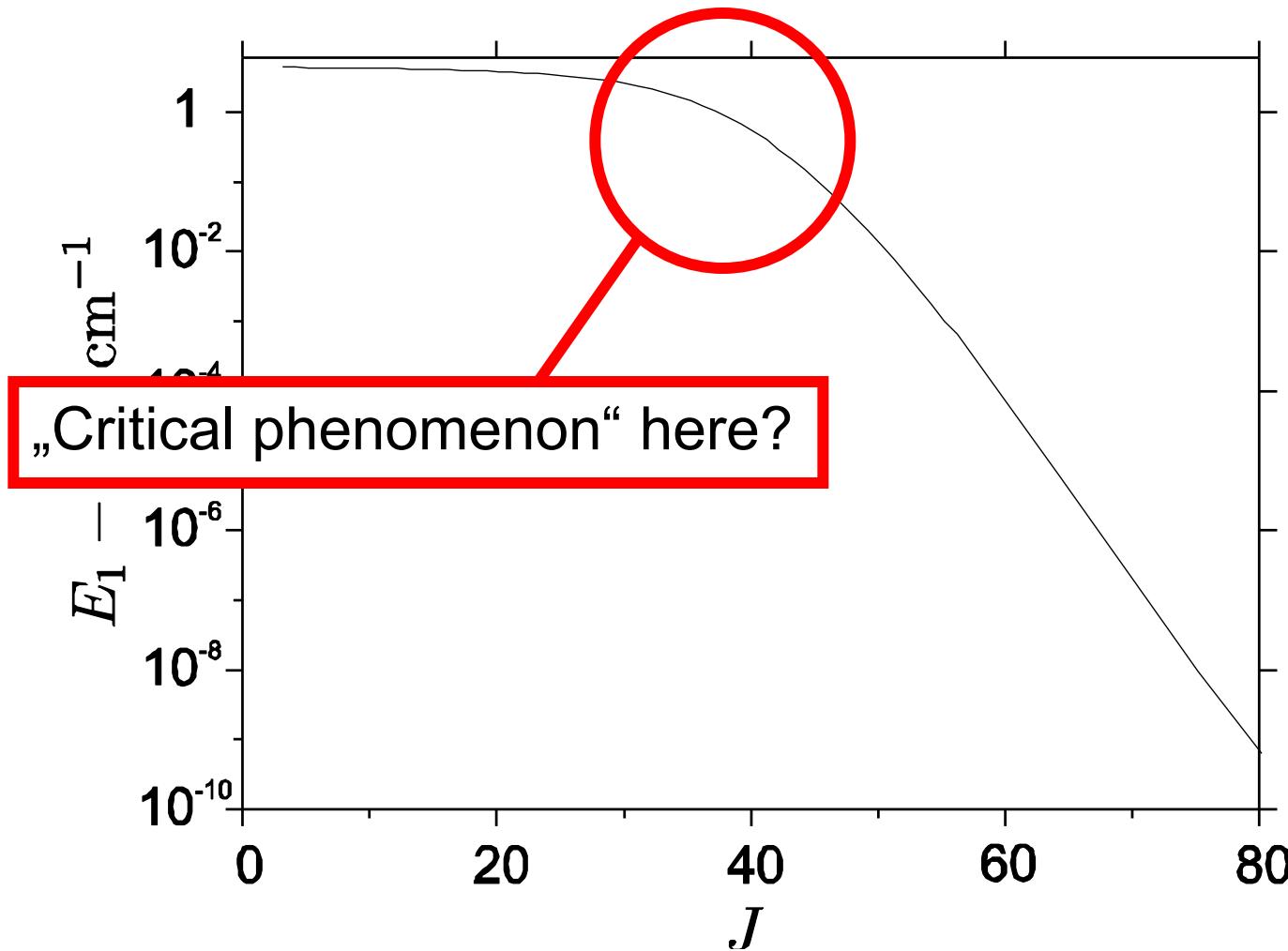


$$\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus 2E \quad \text{in } C_{3v}(M)$$

Watson-type Hamiltonian for PH₃

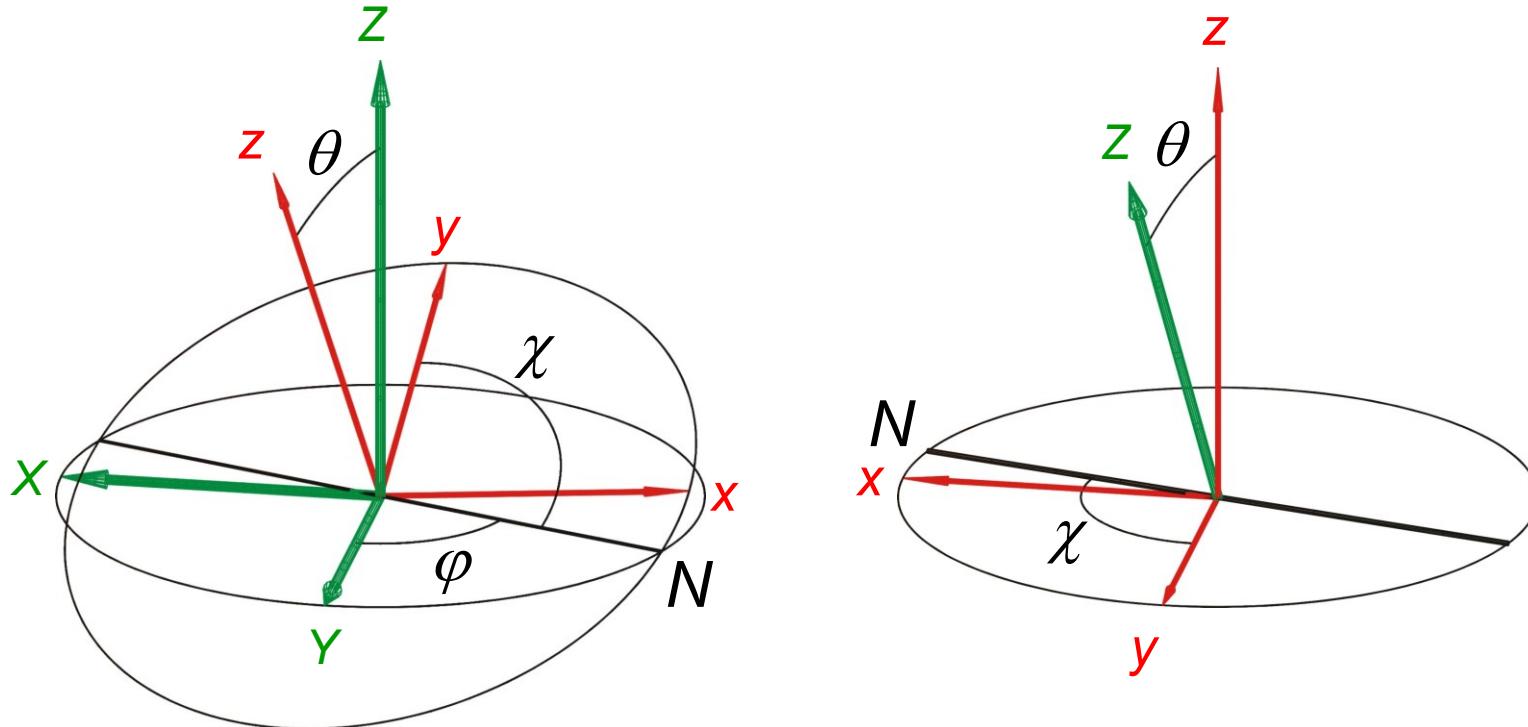


“Cluster spread”, vibrational ground state of PH₃



Rotational coordinates

xyz is molecule-fixed; XYZ is space-fixed



- (θ, φ, χ) define orientation of molecule (xyz) relative to laboratory (XYZ).
- (θ, χ) define orientation of Z axis relative to molecule (xyz).

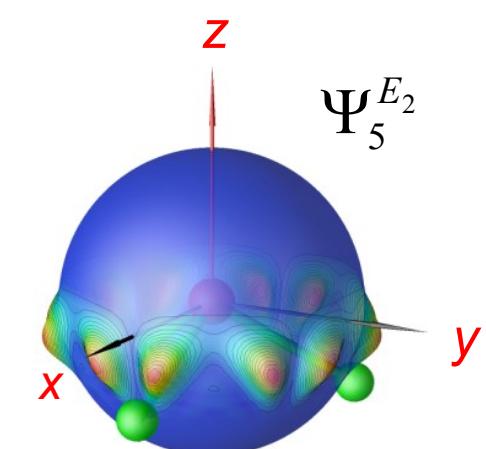
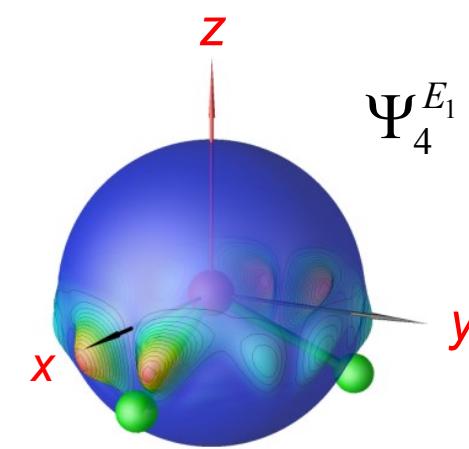
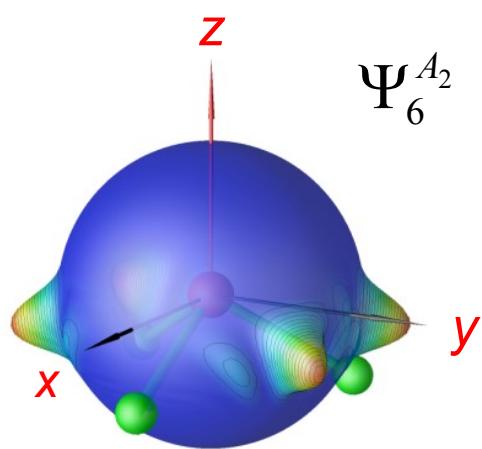
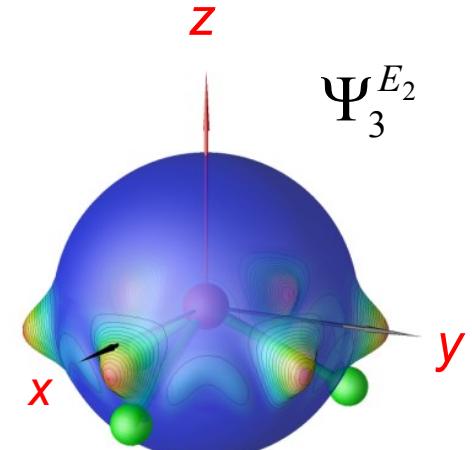
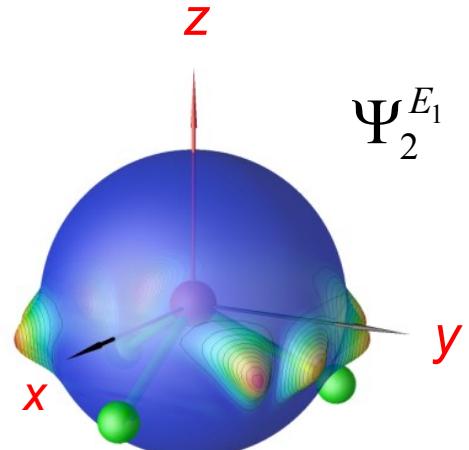
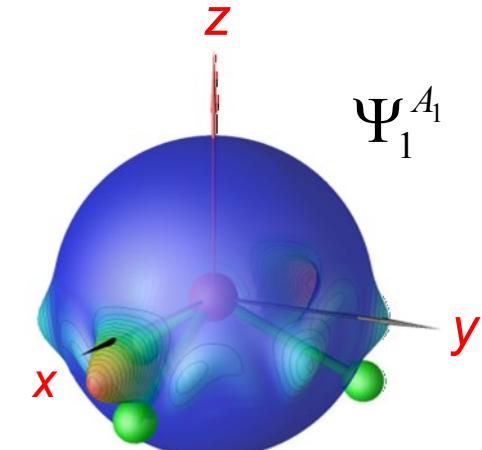
For a rovibronic eigenstate Φ_i

$$F_{J,m}(\theta, \chi) = \int (\Phi_i)^* \Phi_i \sin \theta dV$$

Integration over all vibronic coordinates and φ

is the probability distribution for the orientation of the Z axis relative to the molecule.

$$F_{J,m}(\theta, \chi)$$



**“Top cluster states” for $J = m = 40$,
vibrational ground state of PH_3**

Primitive cluster states $|j \text{ PCS}\rangle$

First symmetrize, e.g.

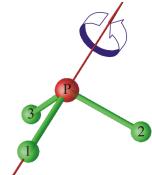
$$\Psi_1^{A_1} = \frac{1}{\sqrt{6}} (|1 \text{ PCS}\rangle + |2 \text{ PCS}\rangle + |3 \text{ PCS}\rangle + |4 \text{ PCS}\rangle + |5 \text{ PCS}\rangle + |6 \text{ PCS}\rangle)$$

$$\Psi_6^{A_2} = \frac{1}{\sqrt{6}} (|1 \text{ PCS}\rangle + |2 \text{ PCS}\rangle + |3 \text{ PCS}\rangle - |4 \text{ PCS}\rangle - |5 \text{ PCS}\rangle - |6 \text{ PCS}\rangle)$$

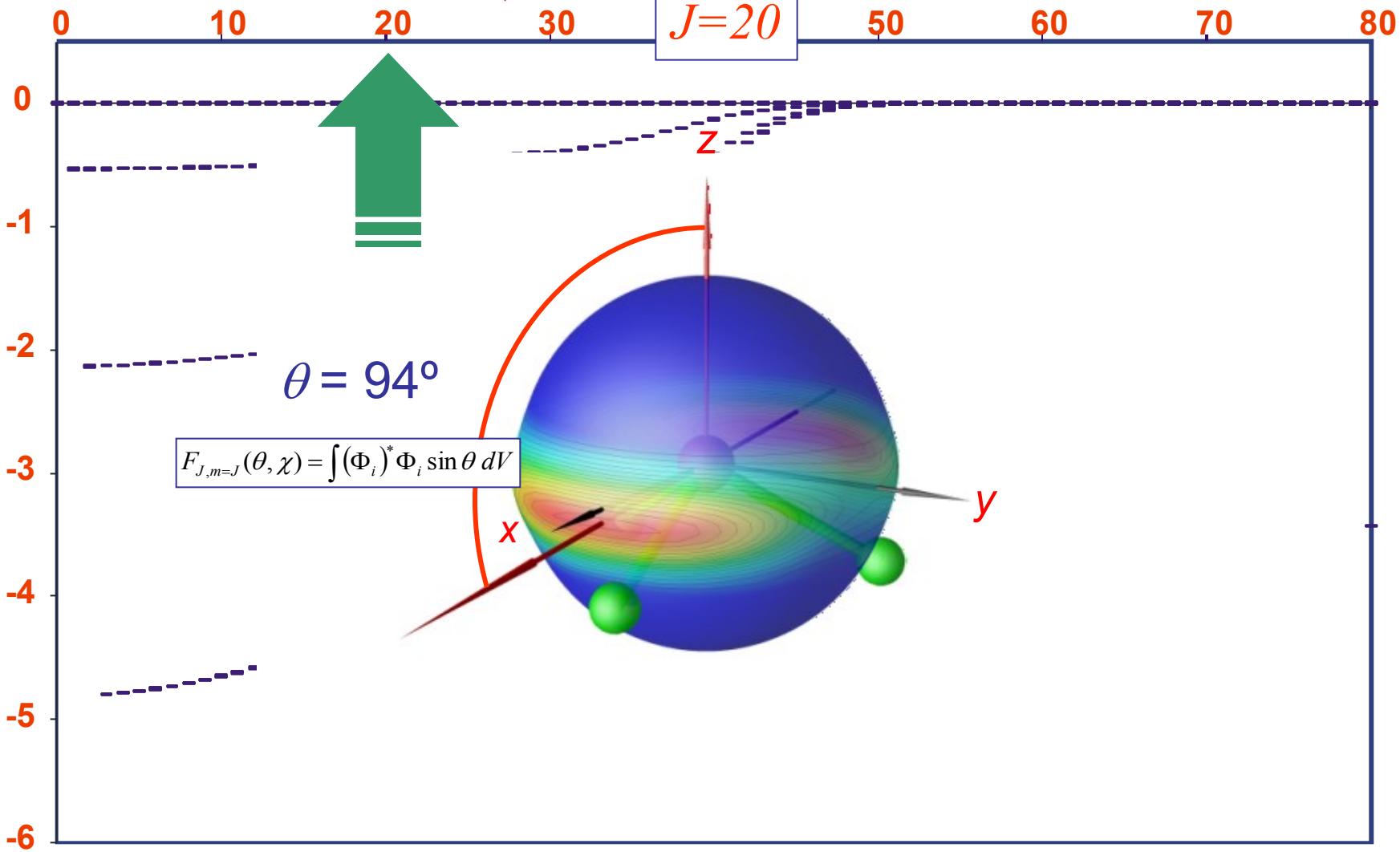
with similar expressions for the E functions....



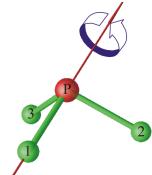
$| 1 \text{ PCS} \rangle$



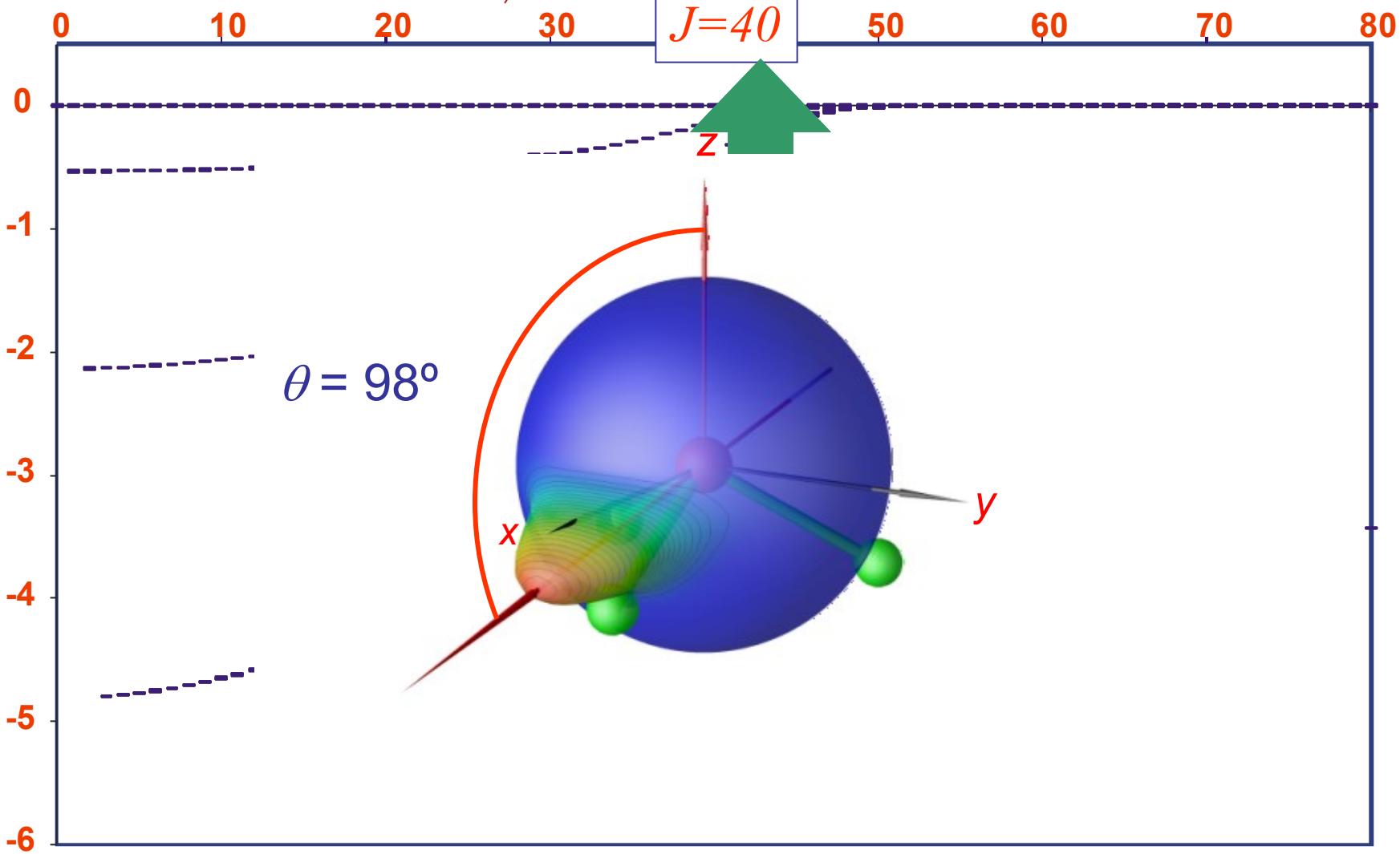
$J=20$



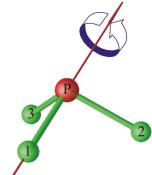
$| 1 \text{ PCS} \rangle$



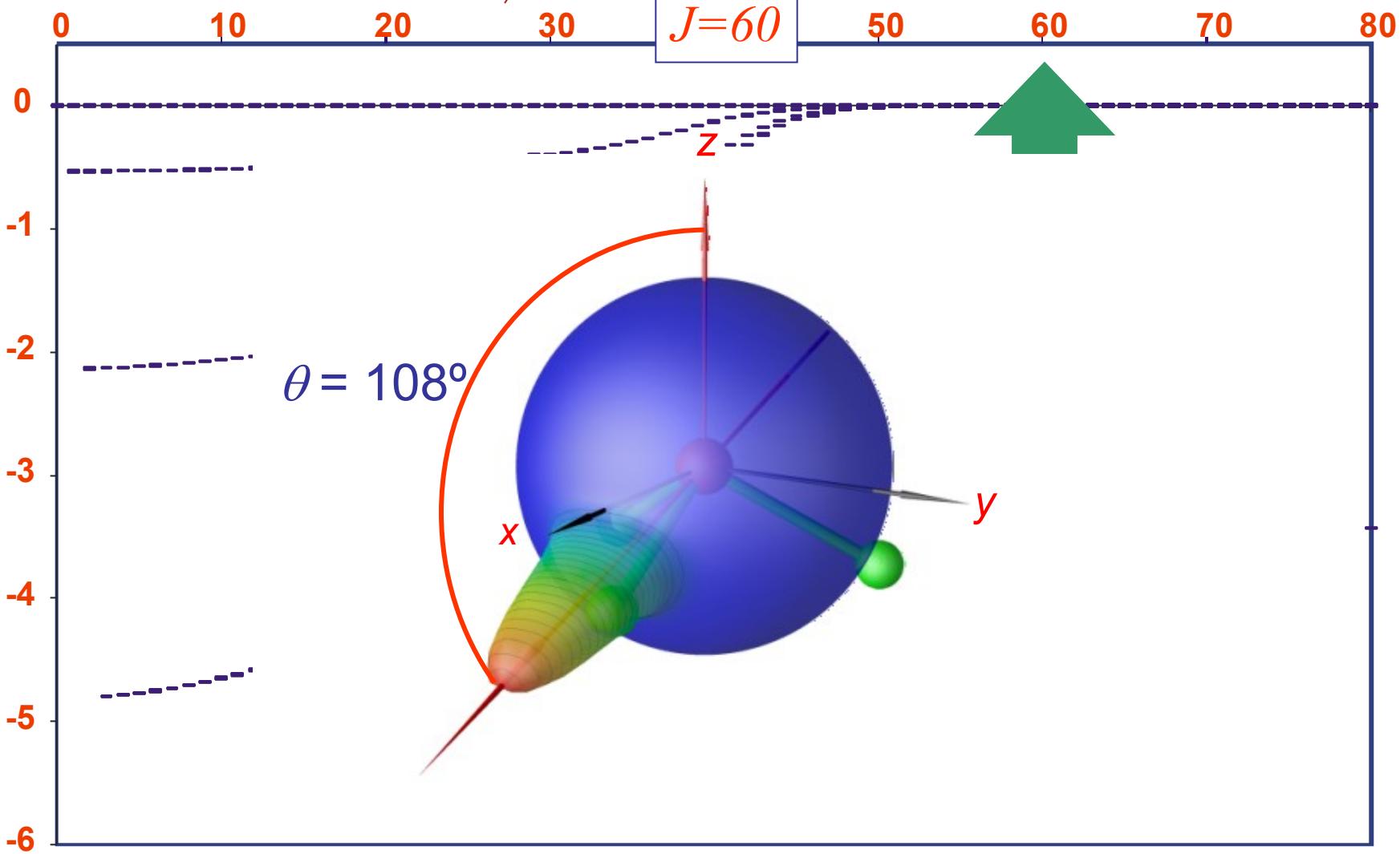
$J=40$



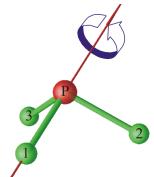
$| 1 \text{ PCS} \rangle$



$J=60$

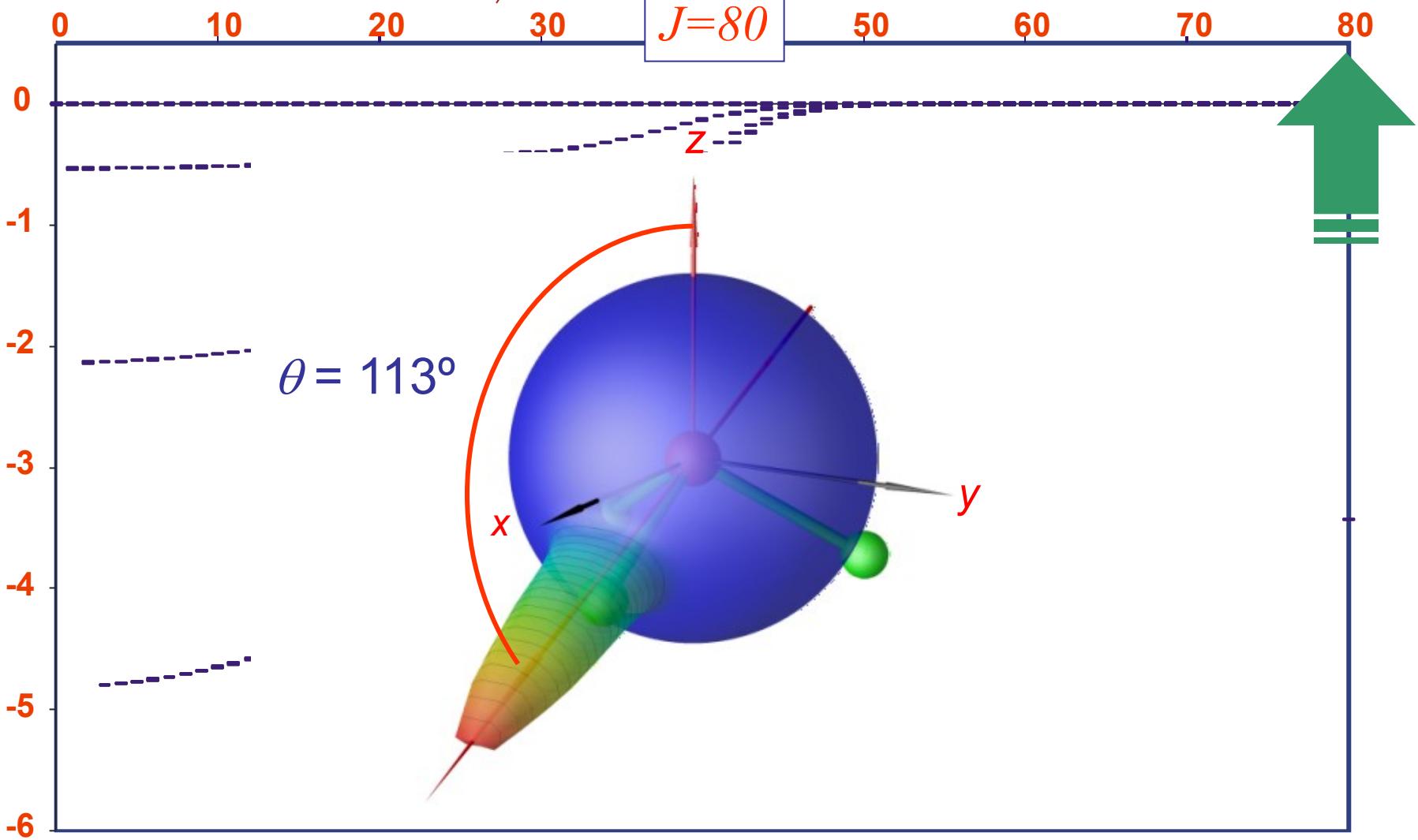


$| 1 \text{ PCS} \rangle$

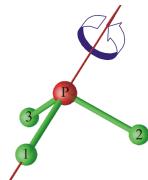


$\theta_{\text{eq}} = 123^\circ$

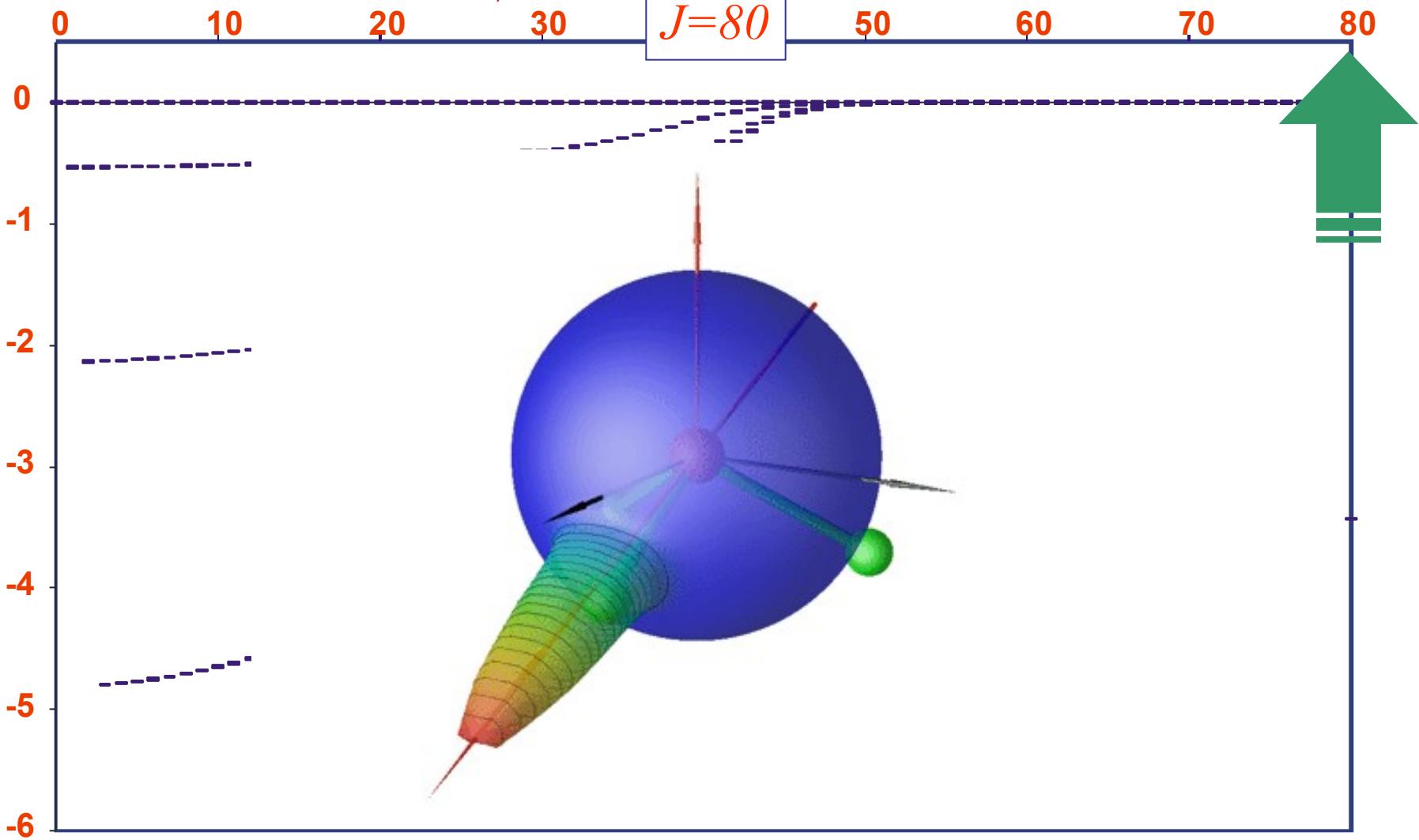
$J=80$



$| 1 \text{ PCS} \rangle$



$J=80$

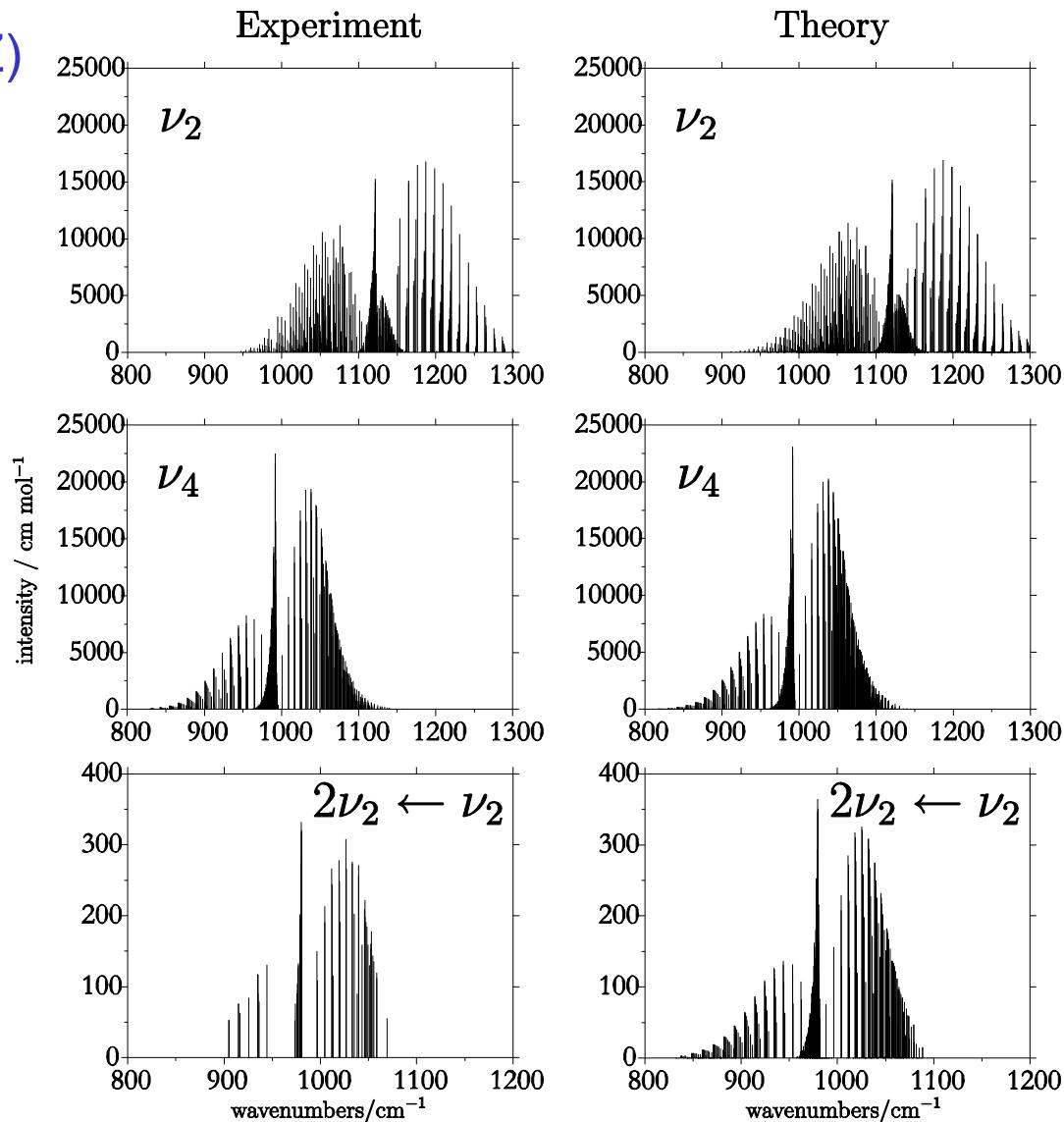


PH_3 intensity calculations

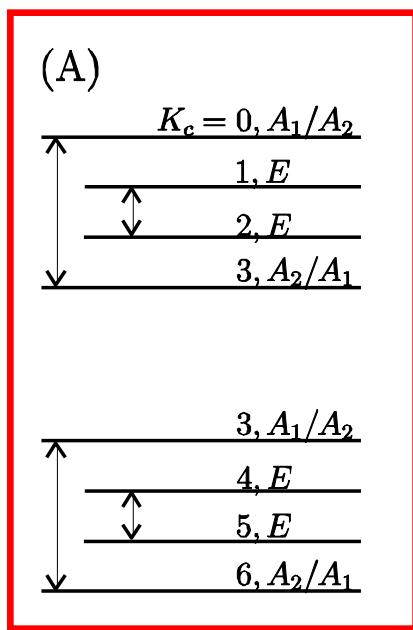
Ab initio (CCSD(T)/aug-cc-pVTZ)
dipole moment surfaces

Rotation-vibration
wavefunctions from
the variational
calculation

Experimental data
from L. R. Brown,
R. L. Sams, I. Kleiner,
C. Cottaz, and L. Sagui,
J. Mol. Spectrosc. **215**,
178-203 (2002)

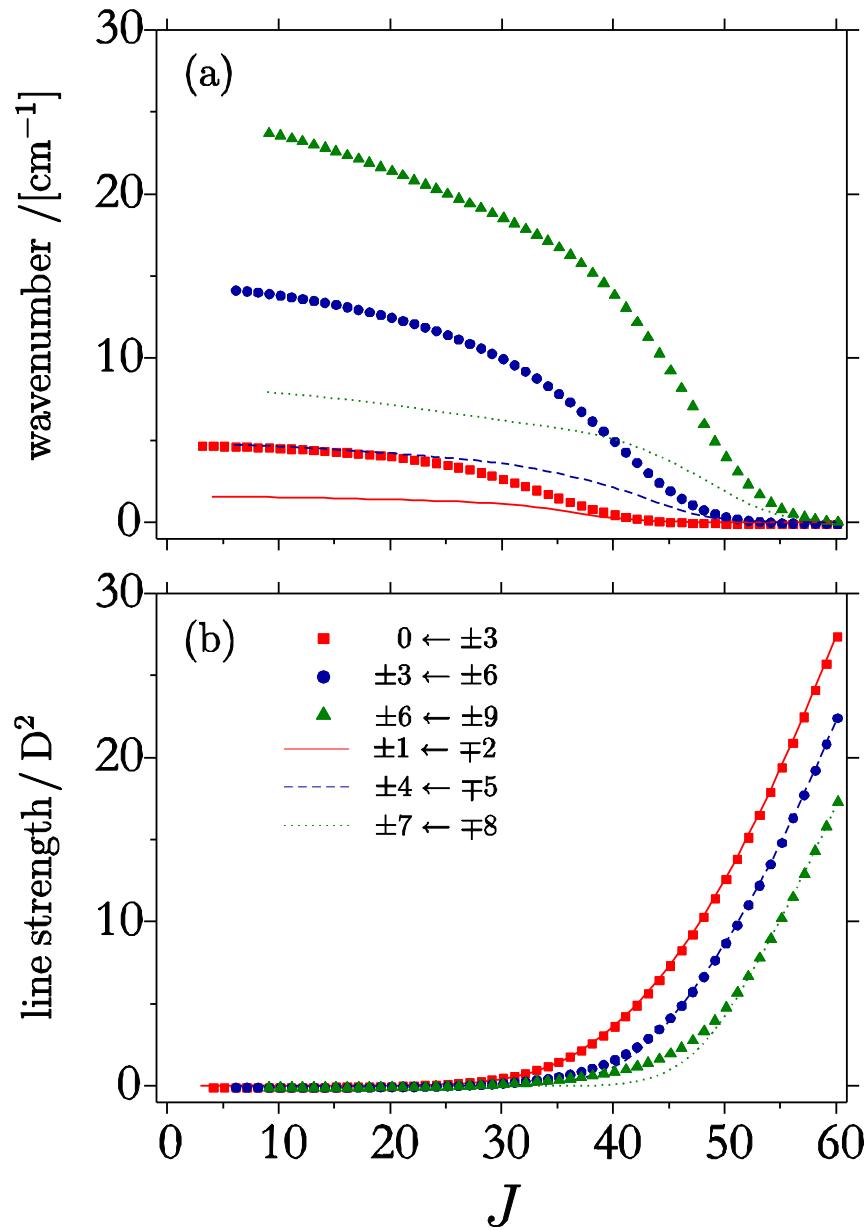


PH₃ cluster transitions

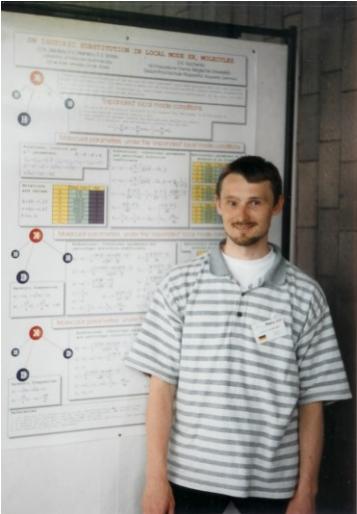


Large line strengths
at high J

Can the lower states
be populated somehow?



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Serguei Patchkovskii, Ottawa

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