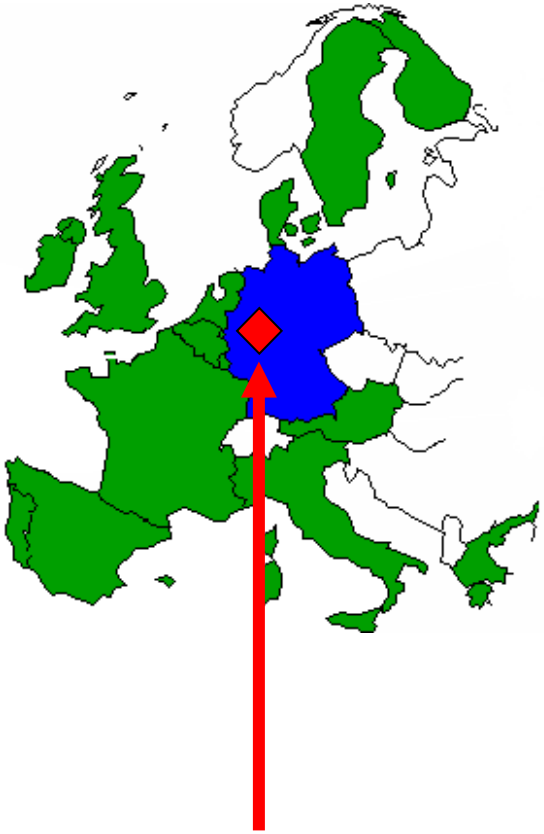
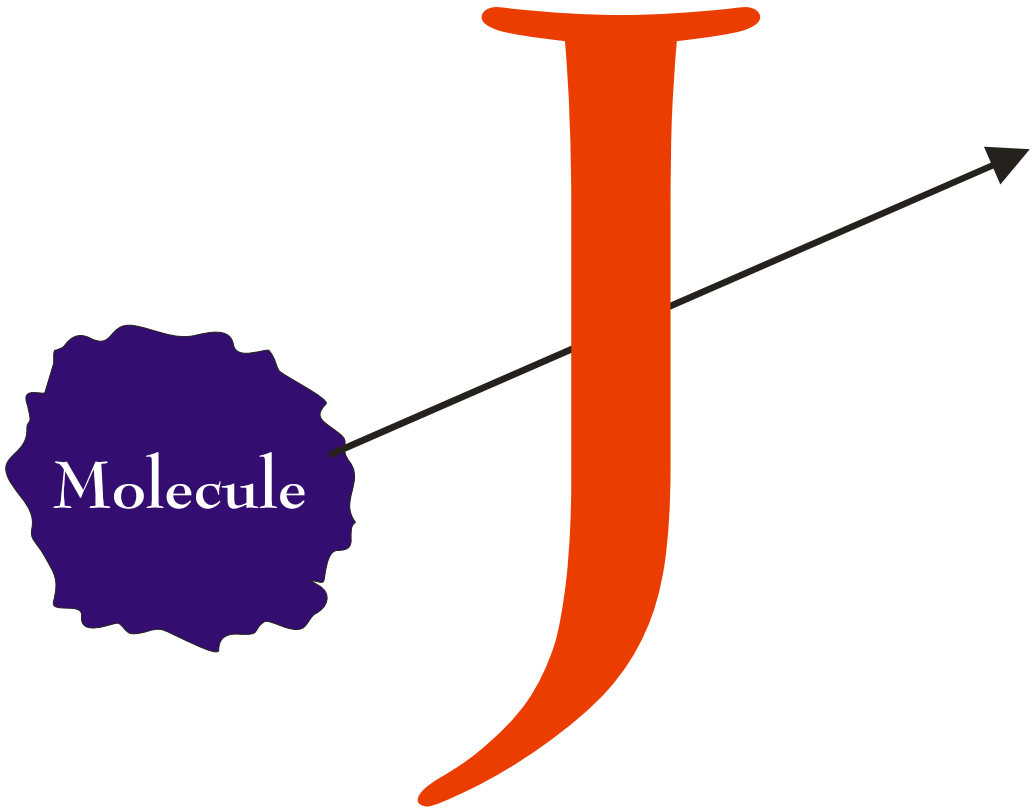


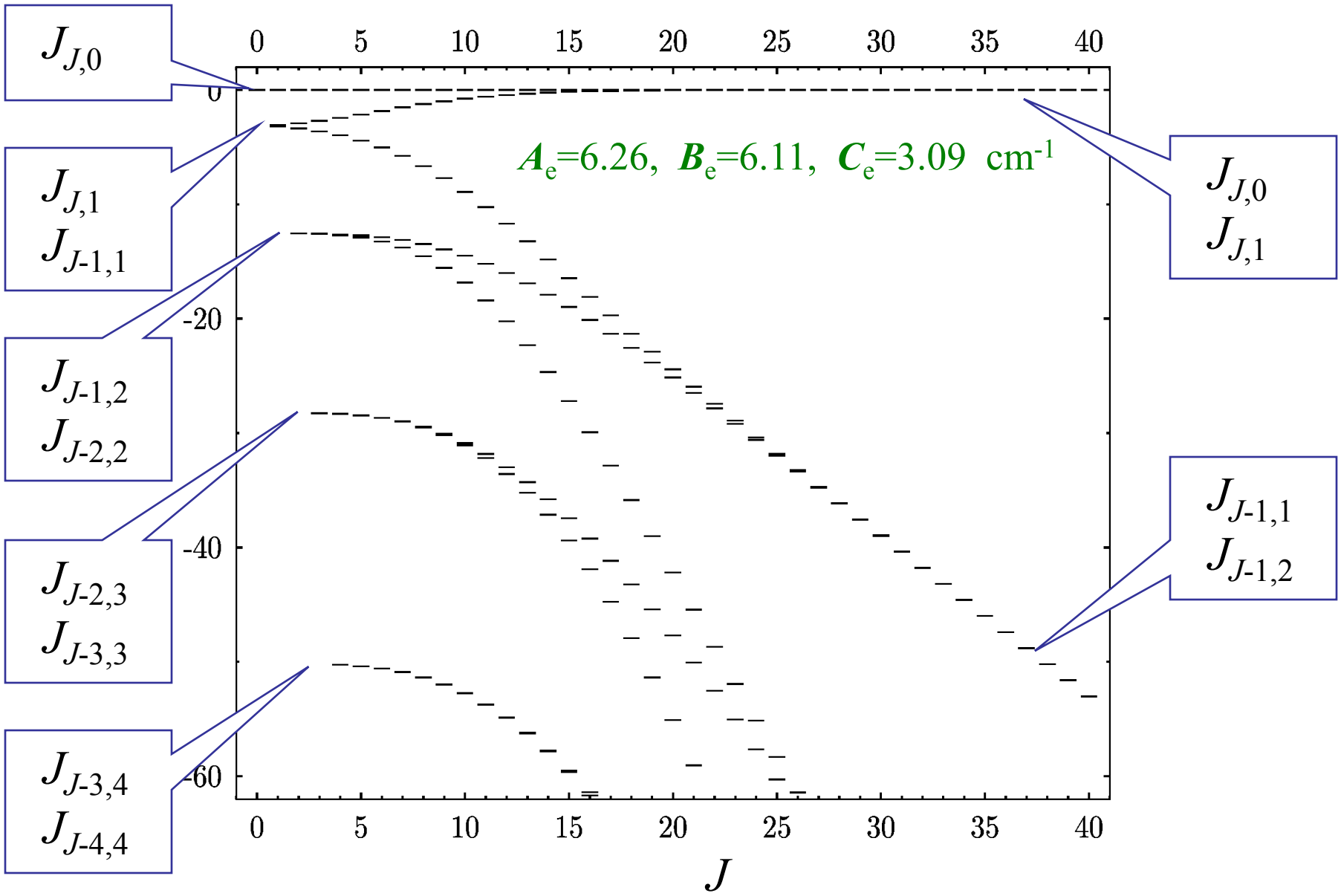
Where is Wuppertal?

Molecules in highly excited rotational states

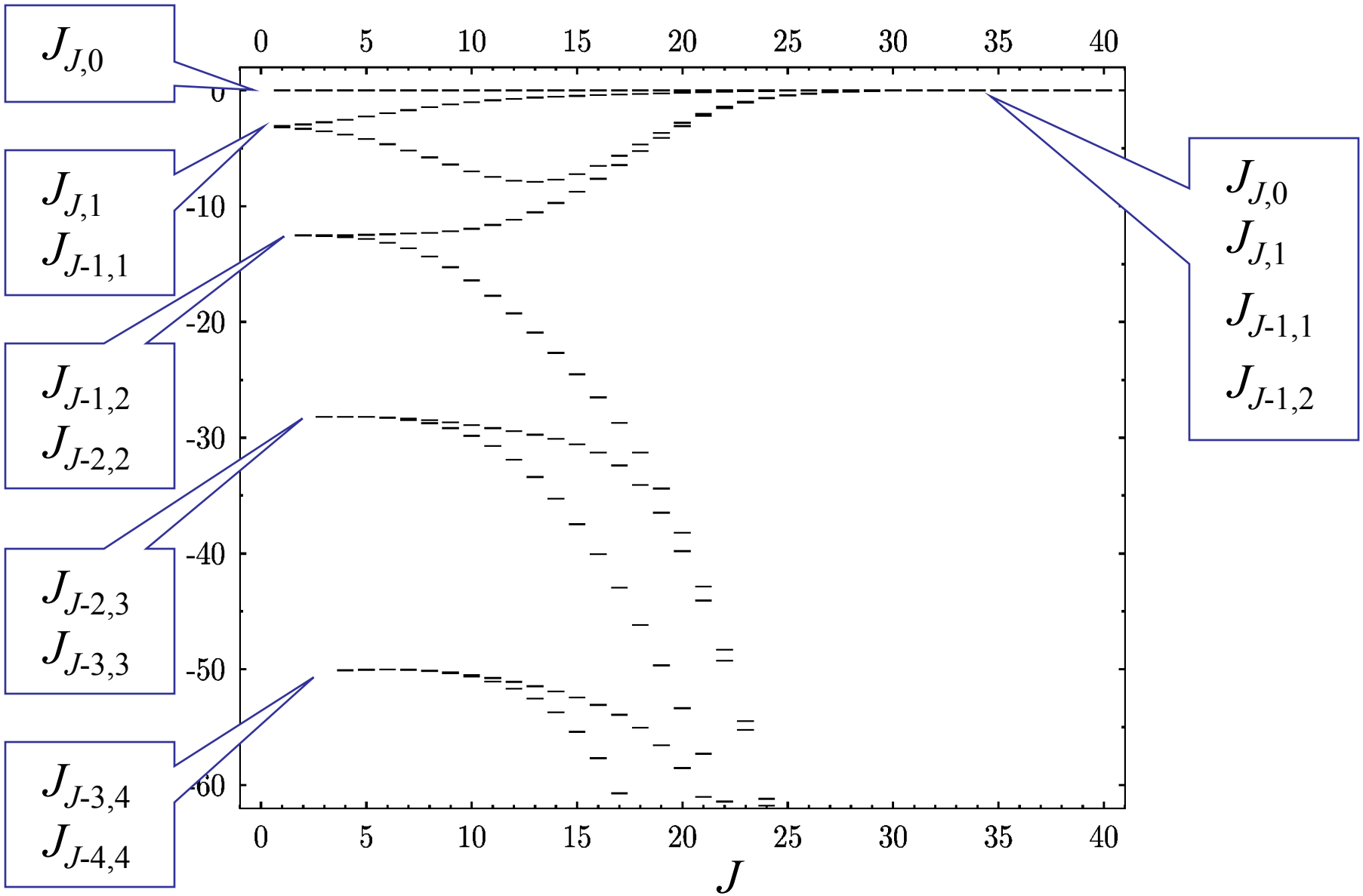


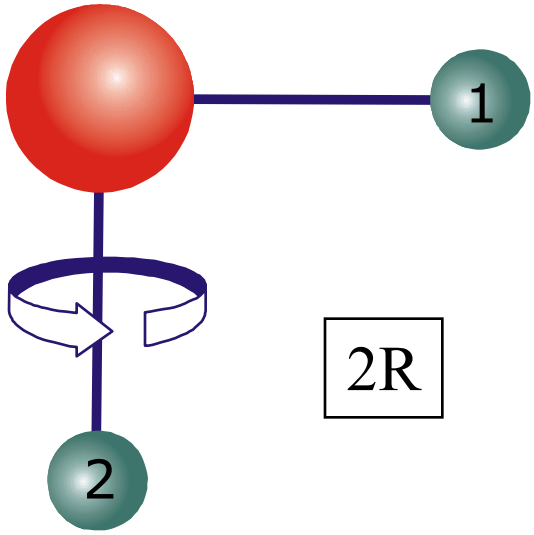
$J \sim 100$

H_2Te Rigid Rotor Energy Levels [$E(J_{KaKc})$-$E(J_{J0})$]

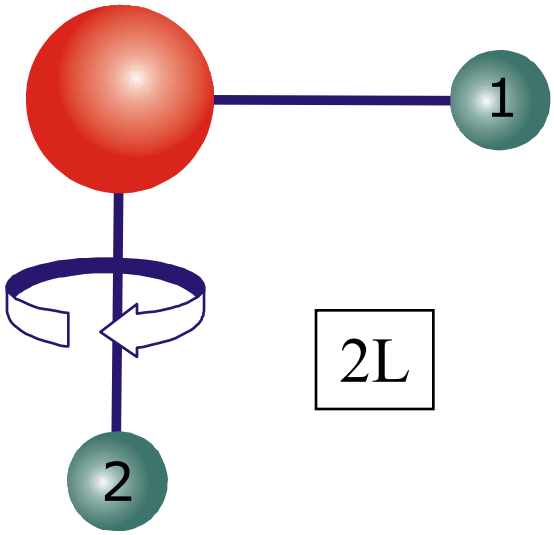


Actual H_2Te Energy Levels [$E(J_{KaKc})$-$E(J_{J0})$]

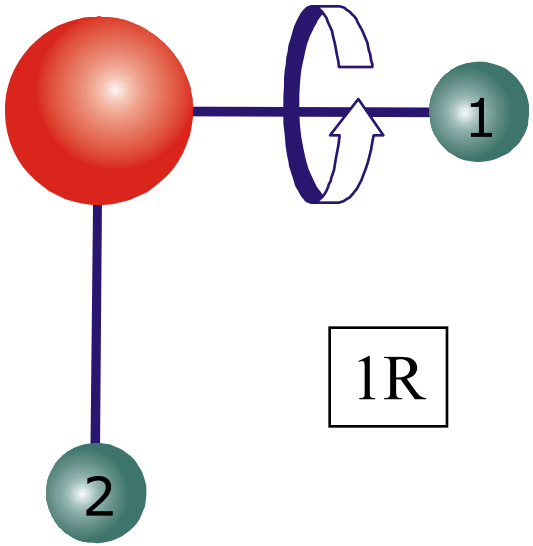




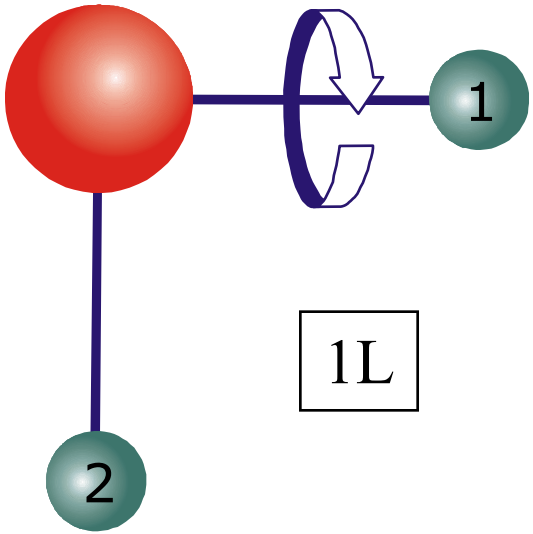
2R



2L



1R



1L

$J_{J,0}$

$J_{J,1}$

$J_{J\text{-}1,1}$

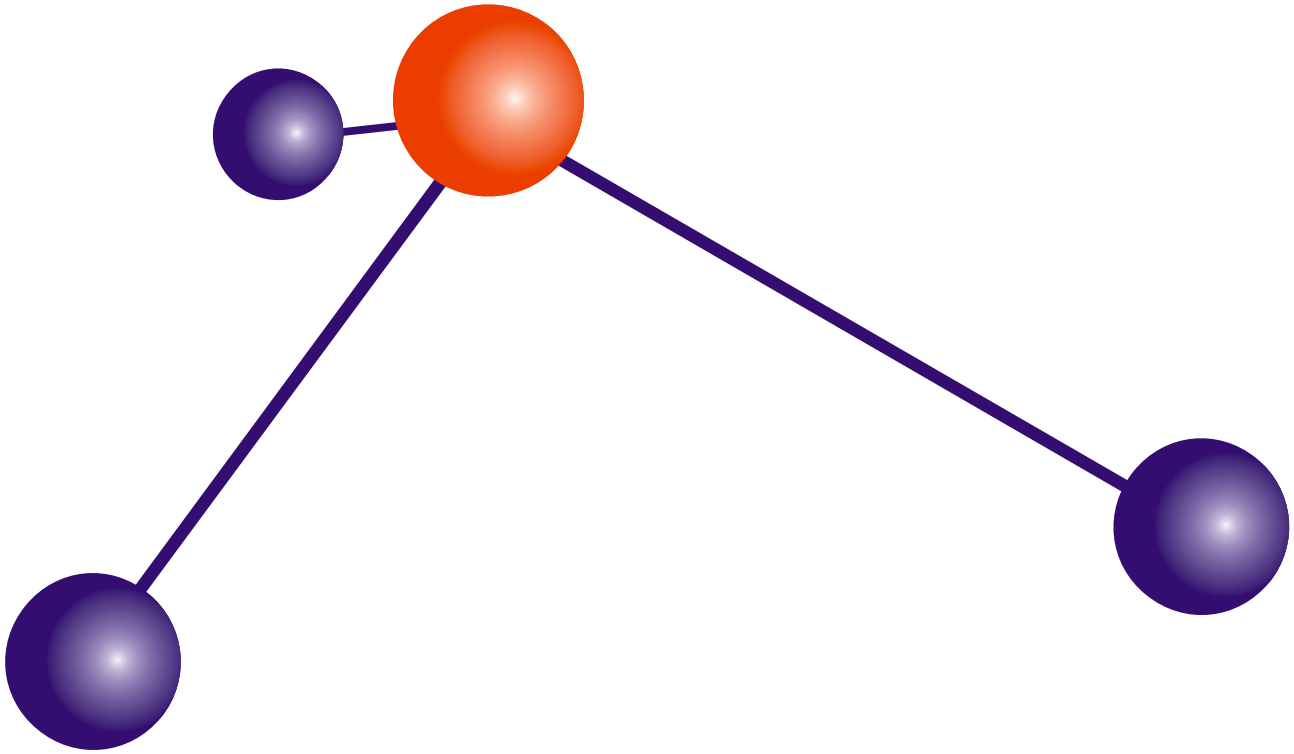
$J_{J\text{-}1,2}$

$\equiv$

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

Rotational Energy Level Clusters

1972	Dorney and Watson	CH_4 8-fold and 6-fold clusters
1978	Zhilinskii and Pavlichenkov	H_2O 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_2Se 4-fold clusters observed
1993	Kozin and Jensen	H_2Se 4-fold cluster theory (E_{rbs})
1994	Jensen and Bunker	H_2X 4-fold cluster symmetry
1996	Kozin et al	H_2Te 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 XH_3 molecules – say PH_3?

We investigate by variational rotation-vibration calculations

Basis functions:

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

Rigid rotor eigenfunctions

Numerov-Cooley solution of inversion Schrödinger equation for

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

Morse oscillators

Two-dimensional isotropic harmonic oscillators for doubly degenerate bending vibrations

Hougen-Bunker-Johns theory: Eckart & Sayvetz conditions

$\Rightarrow \hat{T}_{nuc}$ = expansion in the ξ_i

Programs: XY3 and TROVE

(Theoretical Rotation-Vibration Energies)

XY3: Rotation-vibration energies for pyramidal, ammonia-type molecule in isolated electronic state.

[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.

TROVE: Rotation-vibration energies for any molecule in isolated electronic state.

[3] S.N. Yurchenko, W. Thiel, and P. Jensen, *J. Mol. Spectrosc*. **245**, 126 (2007)

Variational rotation-vibration calculations for PH_3

$J \leq 80$

Vibrational basis set:

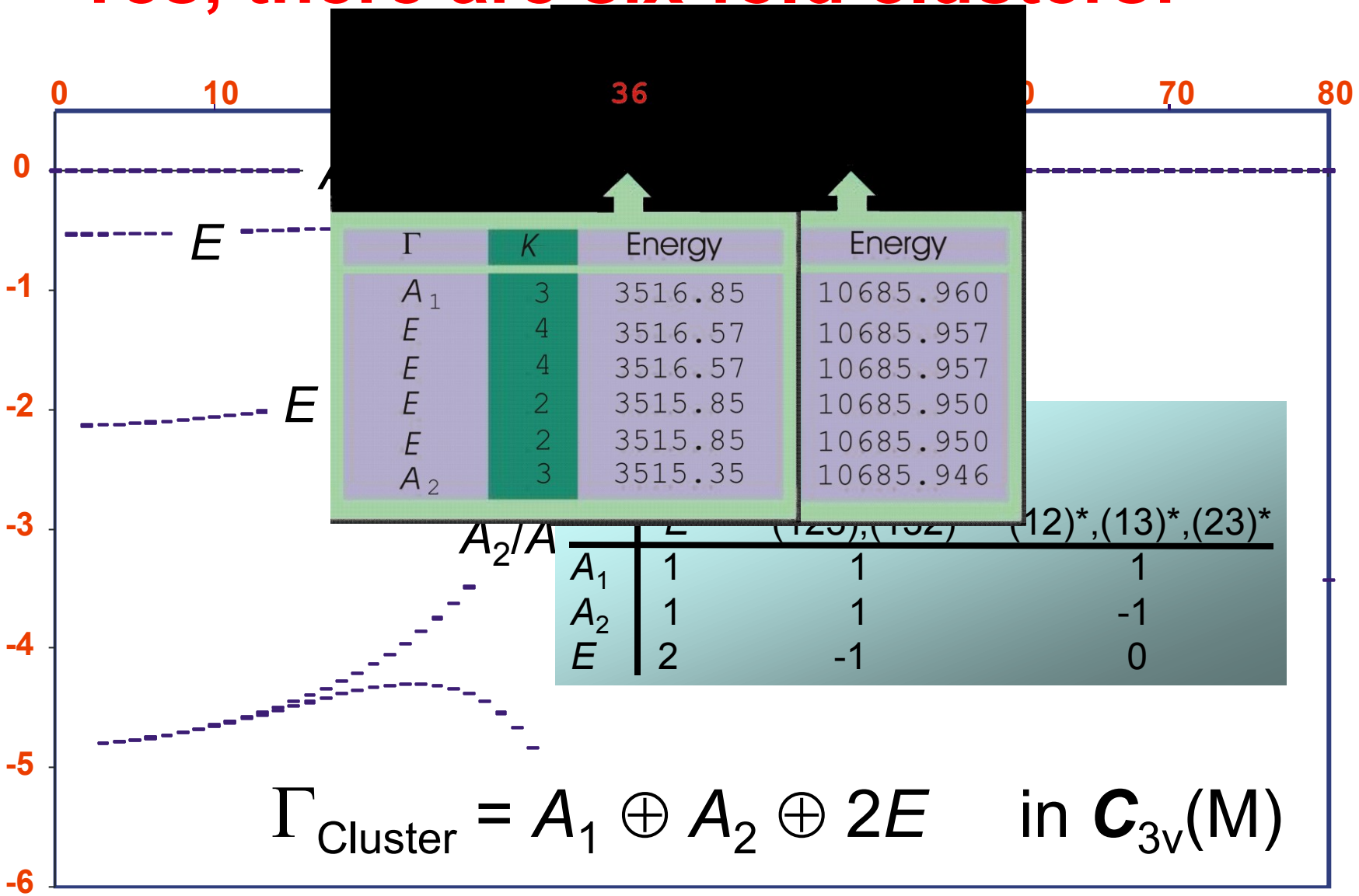
$$2(v_1 + v_2 + v_3) + v_{inv} + V_{bend} \leq 6$$

Potential energy surface:

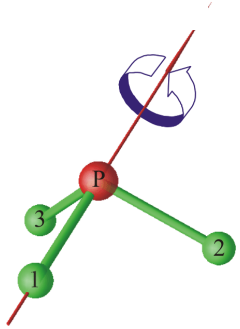
cc-pwCVTZ [1]
refined by fitting to experimental vibrational term values [2]

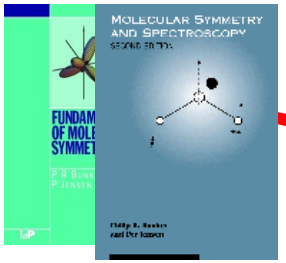
[1] D. Wang,Q. Shi, and Q.-S. Zhu, *J. Chem. Phys.*, **112**, 9624 (2000)
[2] S.N. Yurchenko *et al*., *Chem. Phys.* **290**, 59 (2003)

Yes, there are six-fold clusters!



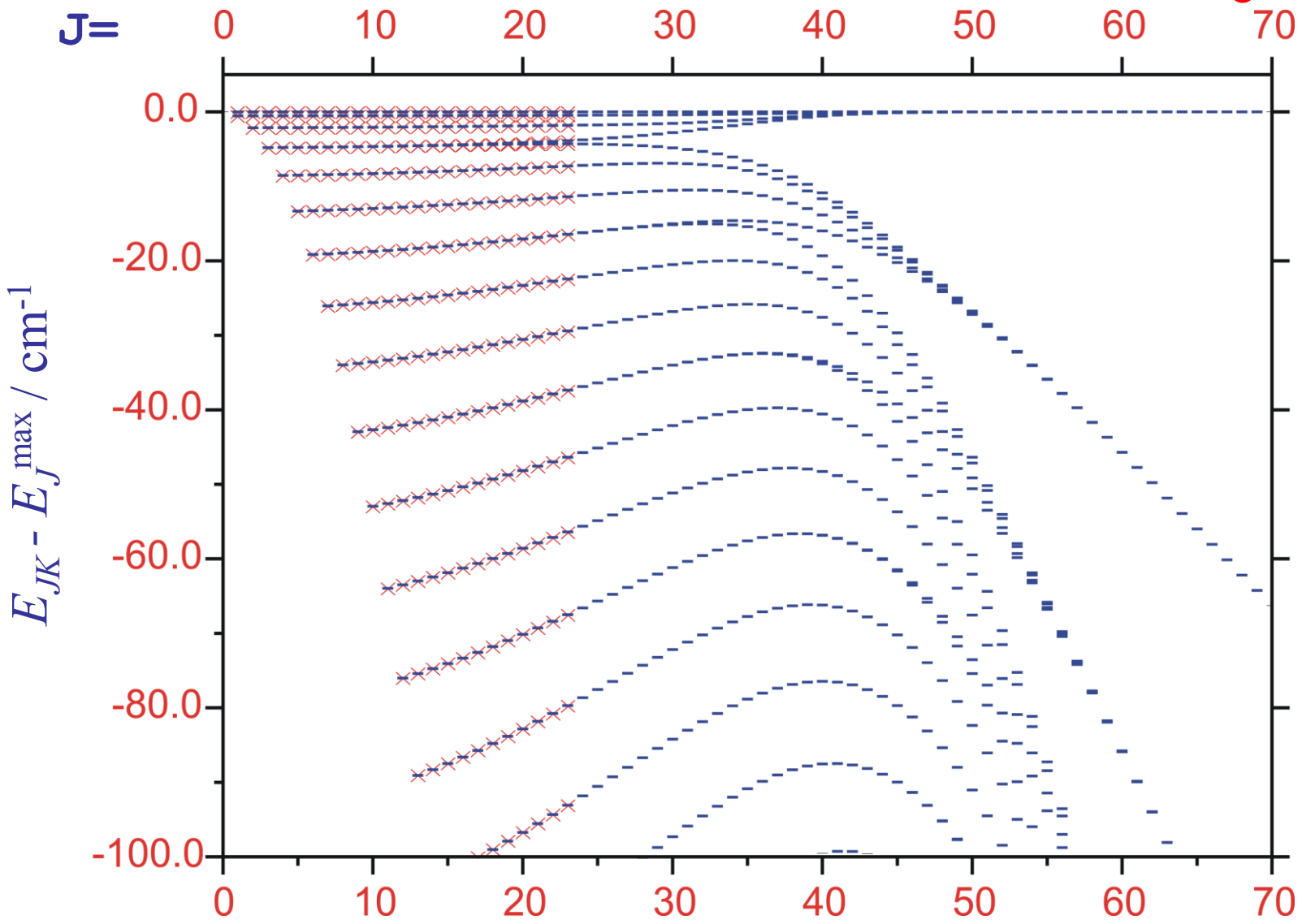
$$|\,1\ \mathrm{PCS}\,\rangle = E\,|\,1\ \mathrm{PCS}\,\rangle$$





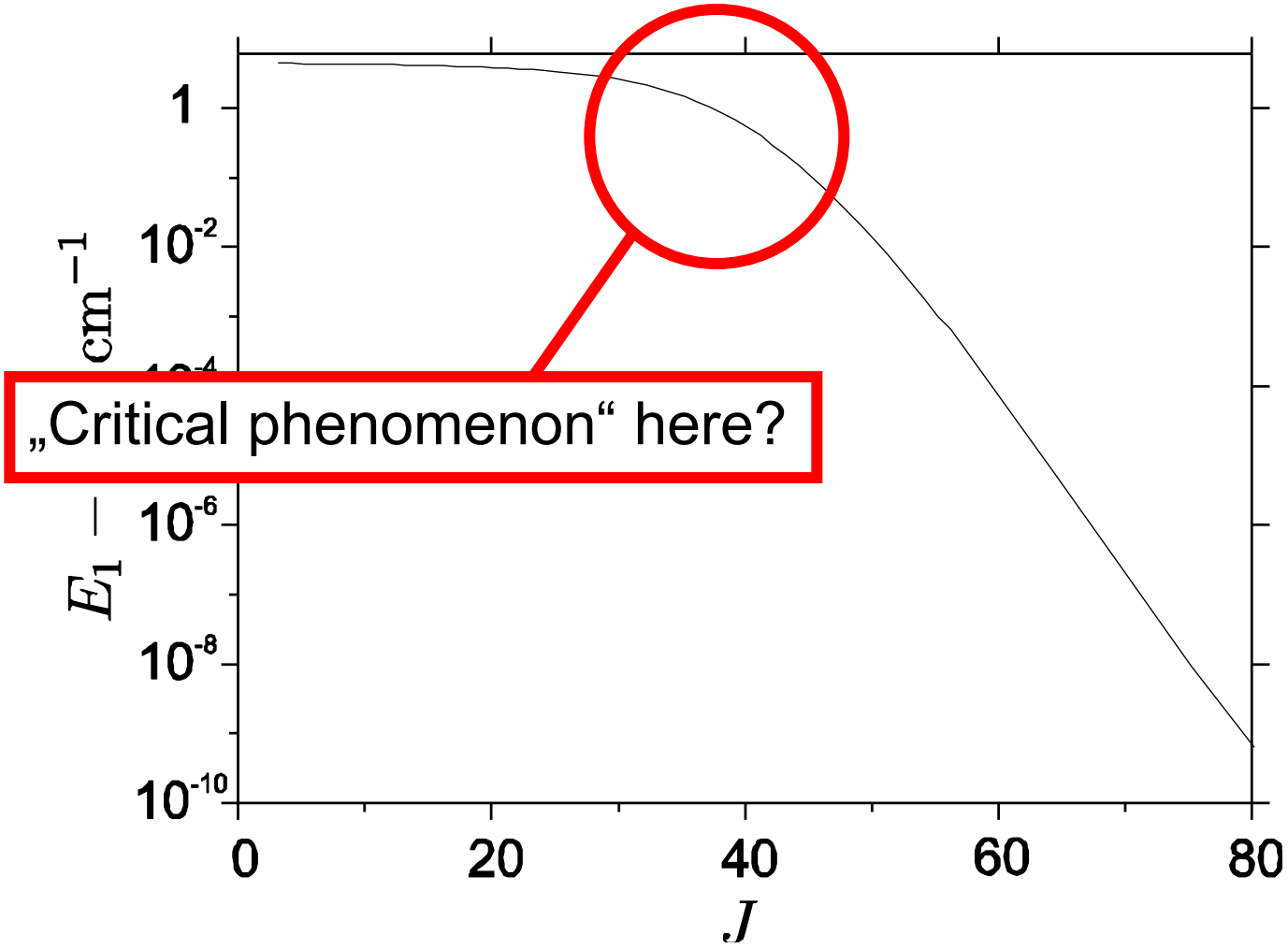
$$\Gamma_{\mathrm{Cluster}} = A_1 \oplus A_2 \oplus 2E \qquad \text{in } \boldsymbol{C}_{3v}(\mathrm{M})$$

Watson-type Hamiltonian for PH_3



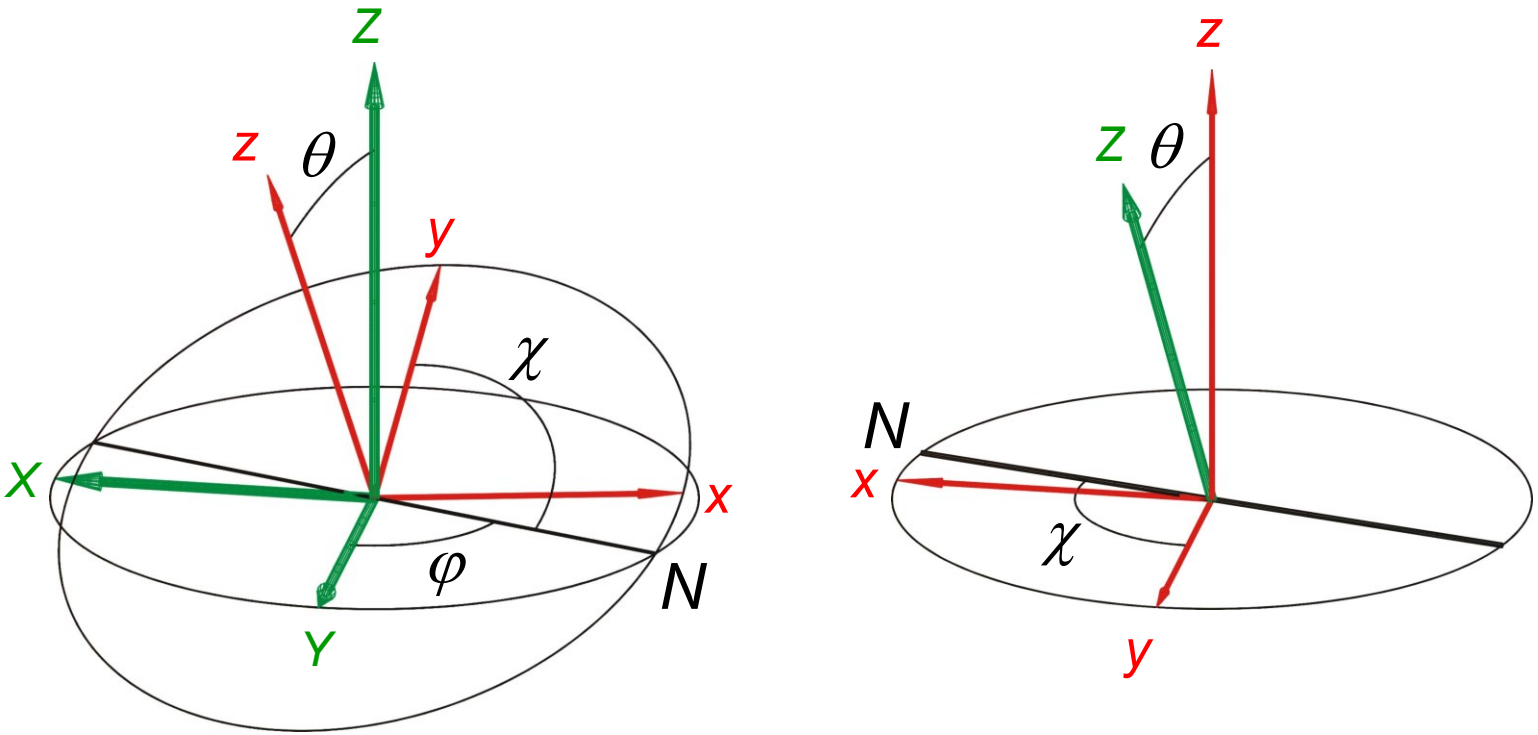
L. Fusina, G. Di Lonardo, *J. Mol. Struct.* **517-518,** 67 (2000)

“Cluster spread”, vibrational ground state of PH_3



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*).

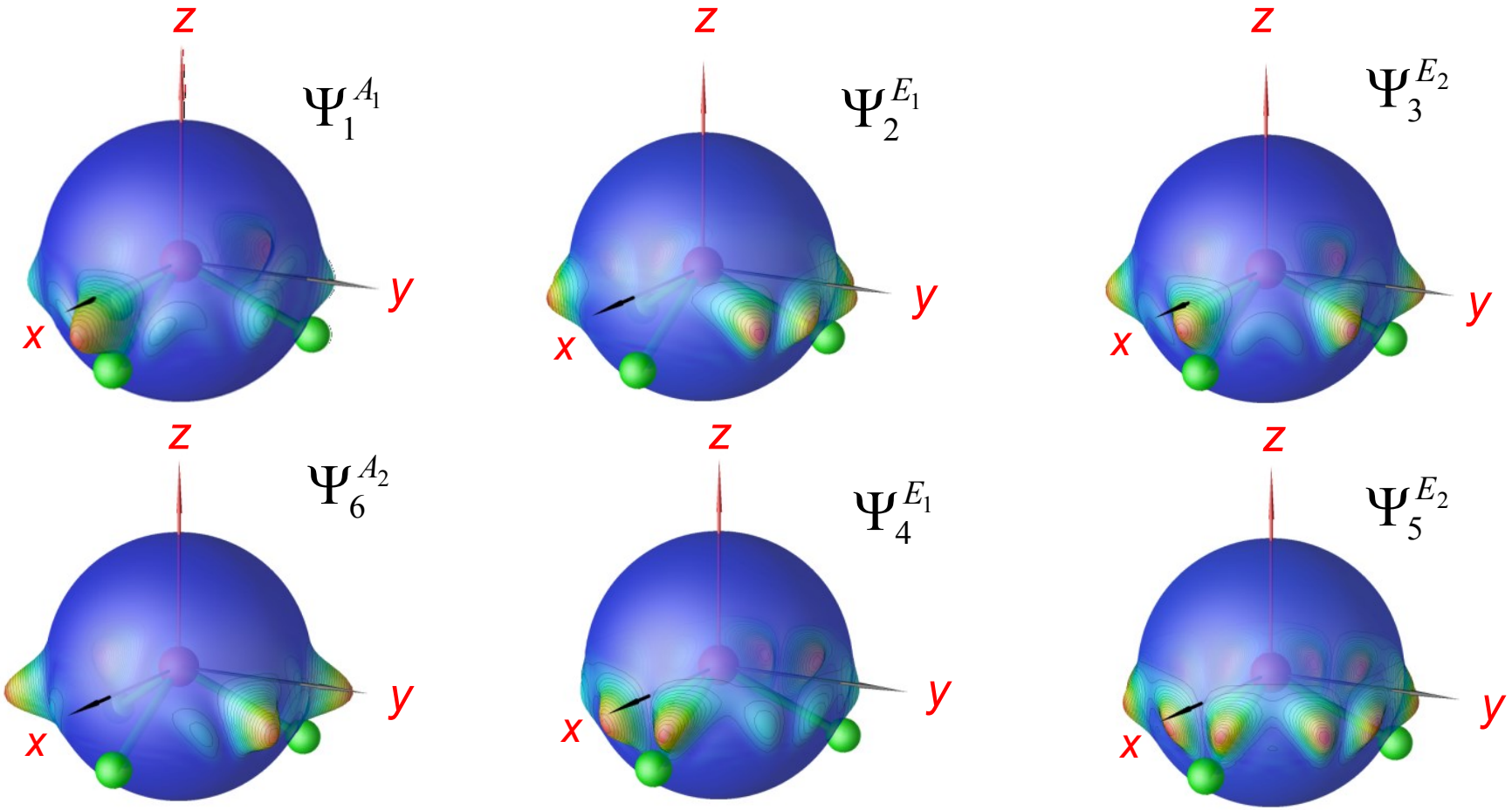
For a rovibronic eigenstate Φ_i

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

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

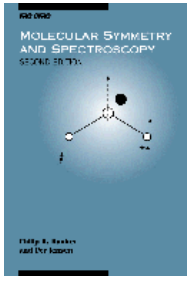
Primitive cluster states $|j\,\mathrm{PCS}\rangle$

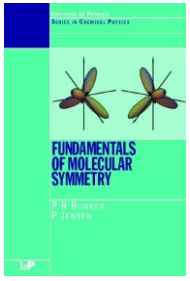
First symmetrize, *e.g.*

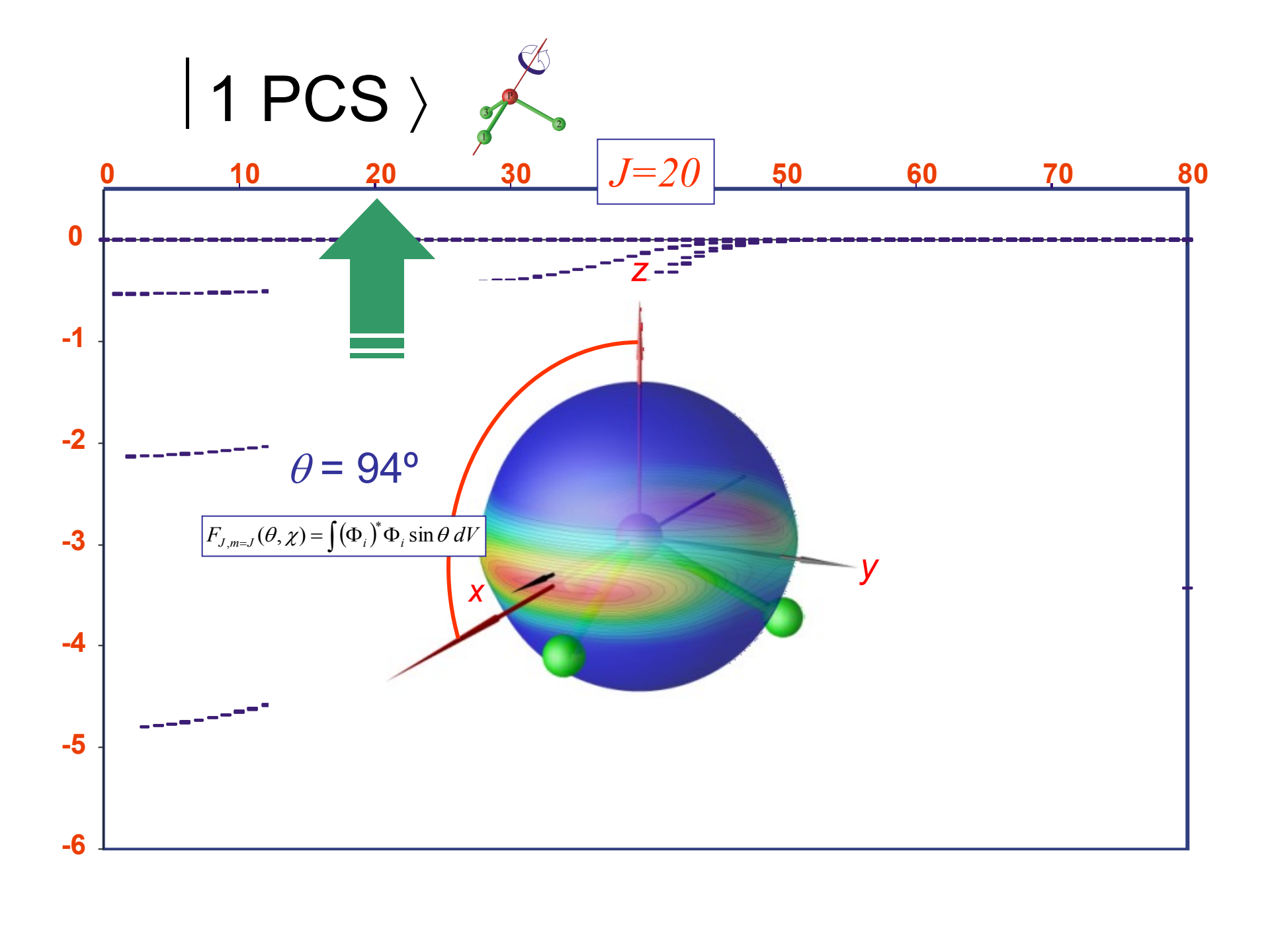
$$\Psi_1^{A_1} = \frac{1}{\sqrt{6}}\left(|1\,\mathrm{PCS}\rangle + |2\,\mathrm{PCS}\rangle + |3\,\mathrm{PCS}\rangle + |4\,\mathrm{PCS}\rangle + |5\,\mathrm{PCS}\rangle + |6\,\mathrm{PCS}\rangle\right)$$

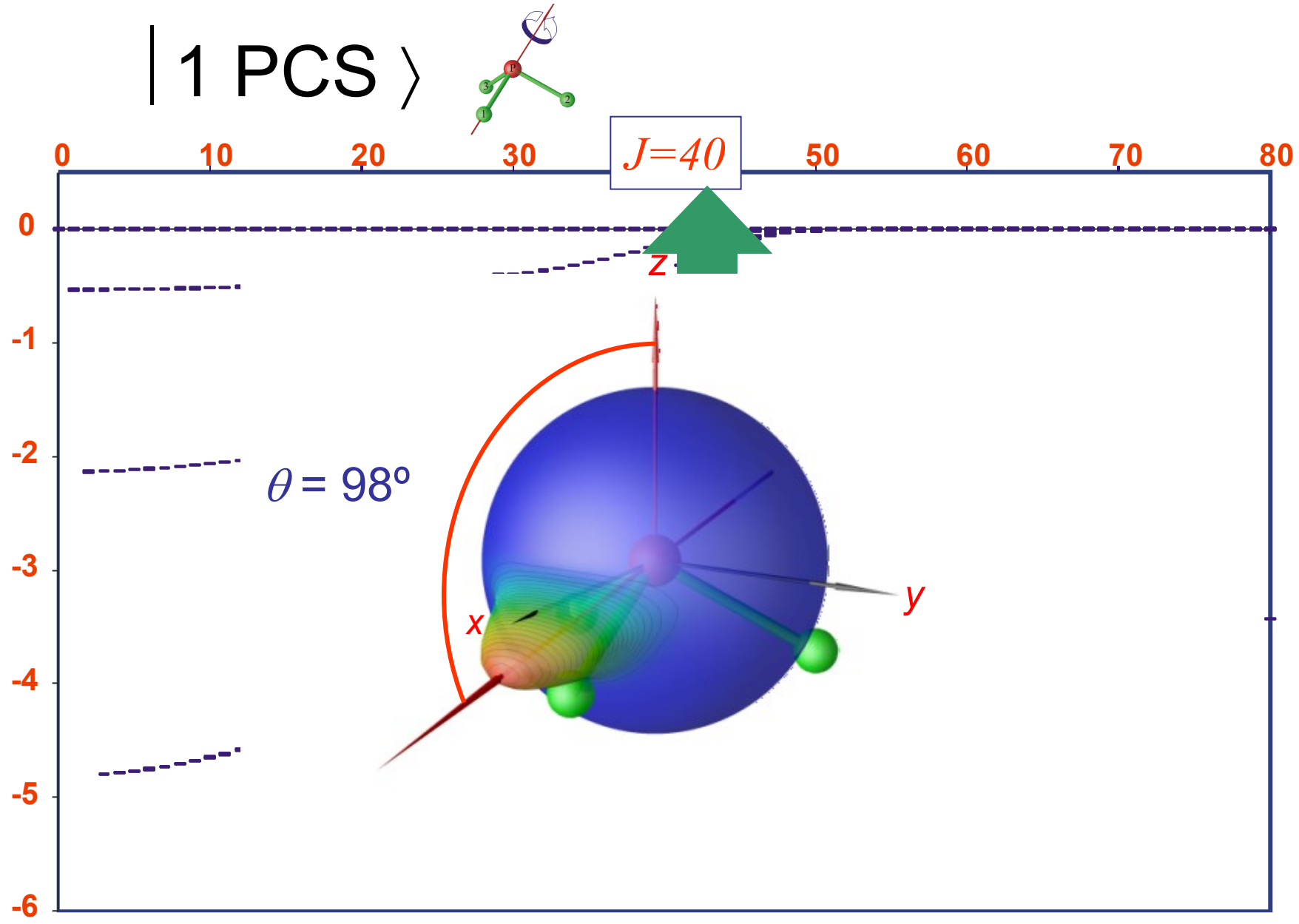
$$\Psi_6^{A_2} = \frac{1}{\sqrt{6}}\left(|1\,\mathrm{PCS}\rangle + |2\,\mathrm{PCS}\rangle + |3\,\mathrm{PCS}\rangle - |4\,\mathrm{PCS}\rangle - |5\,\mathrm{PCS}\rangle - |6\,\mathrm{PCS}\rangle\right)$$

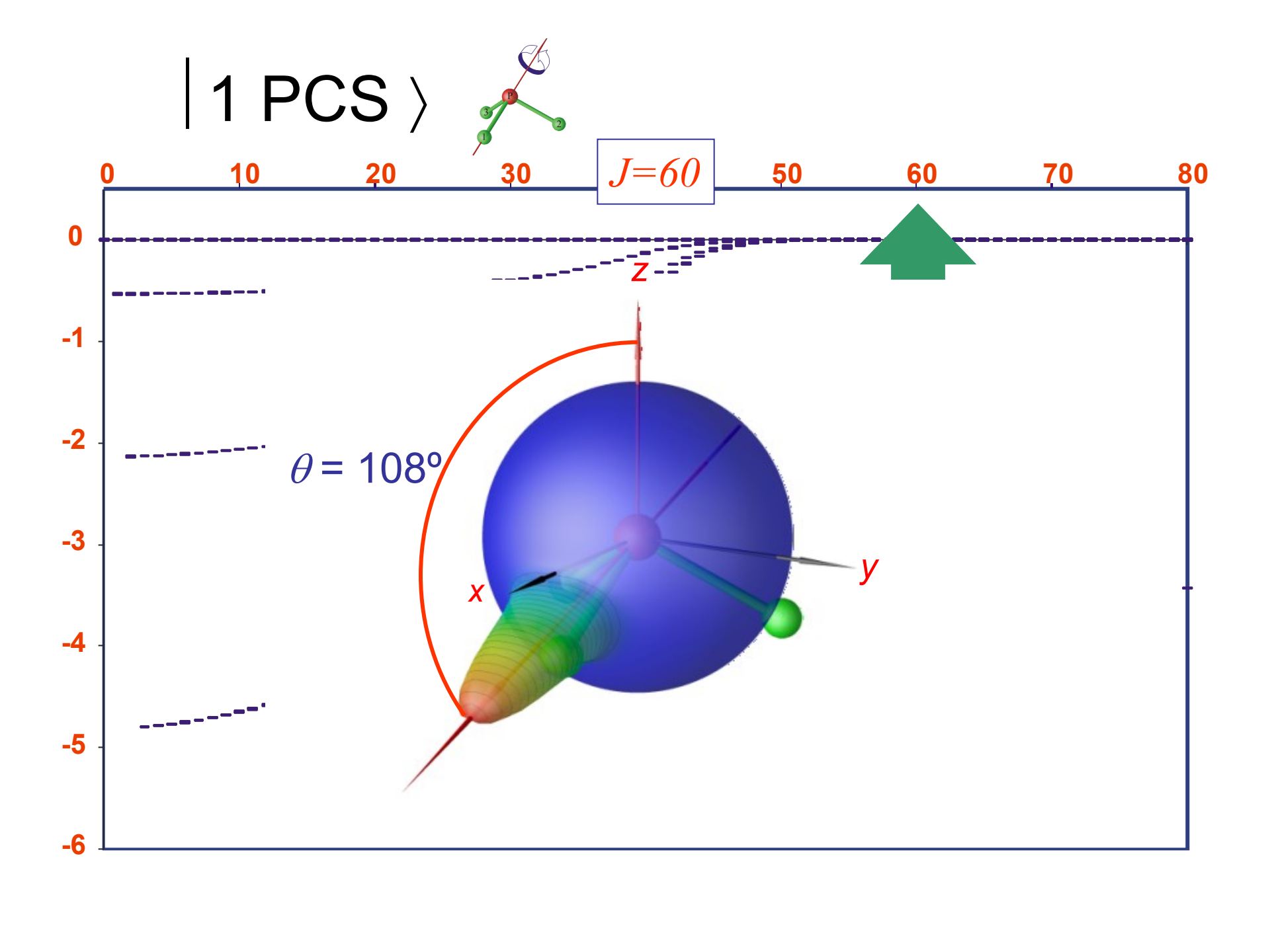
with similar expressions for the *E* functions....

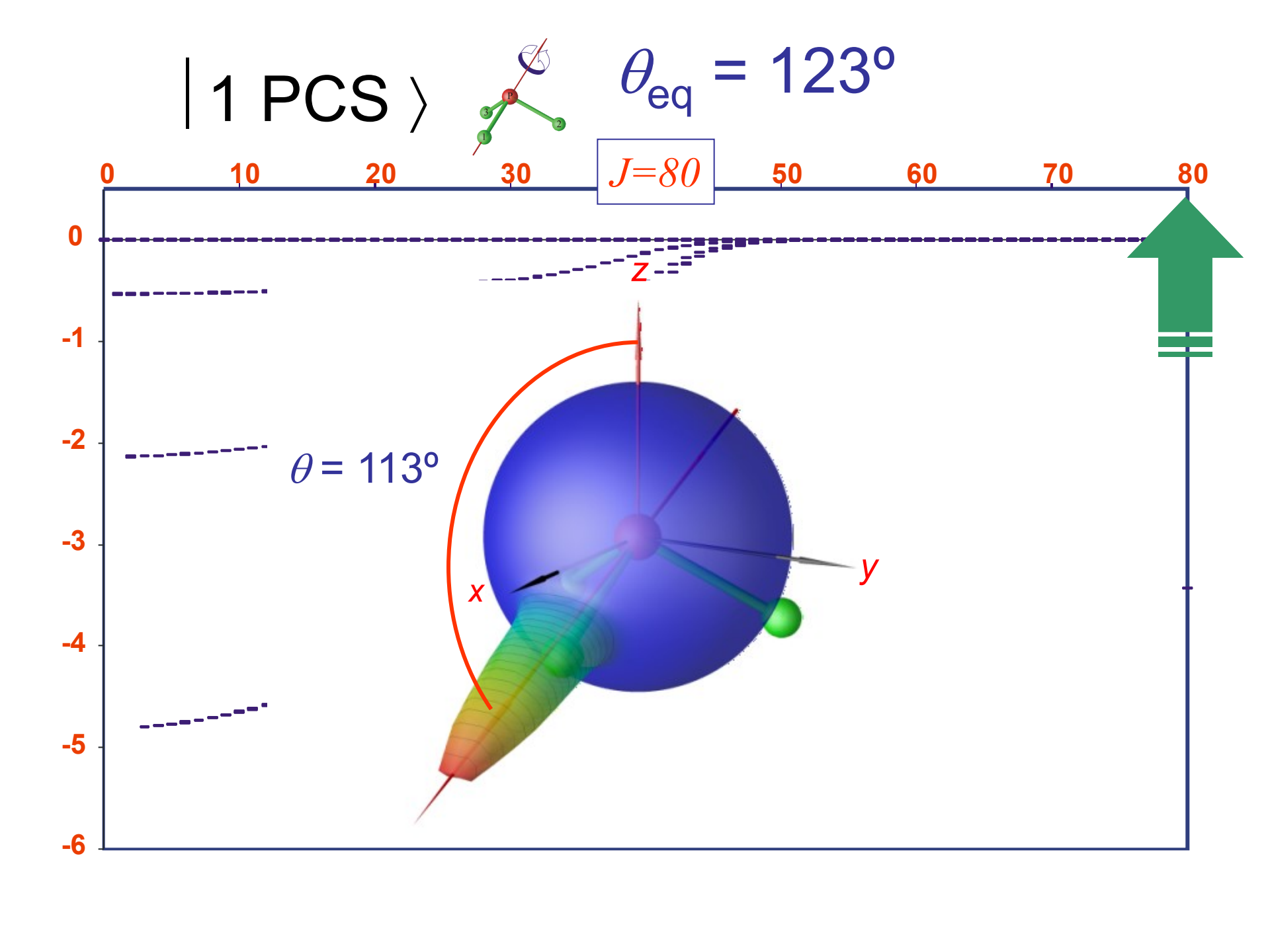


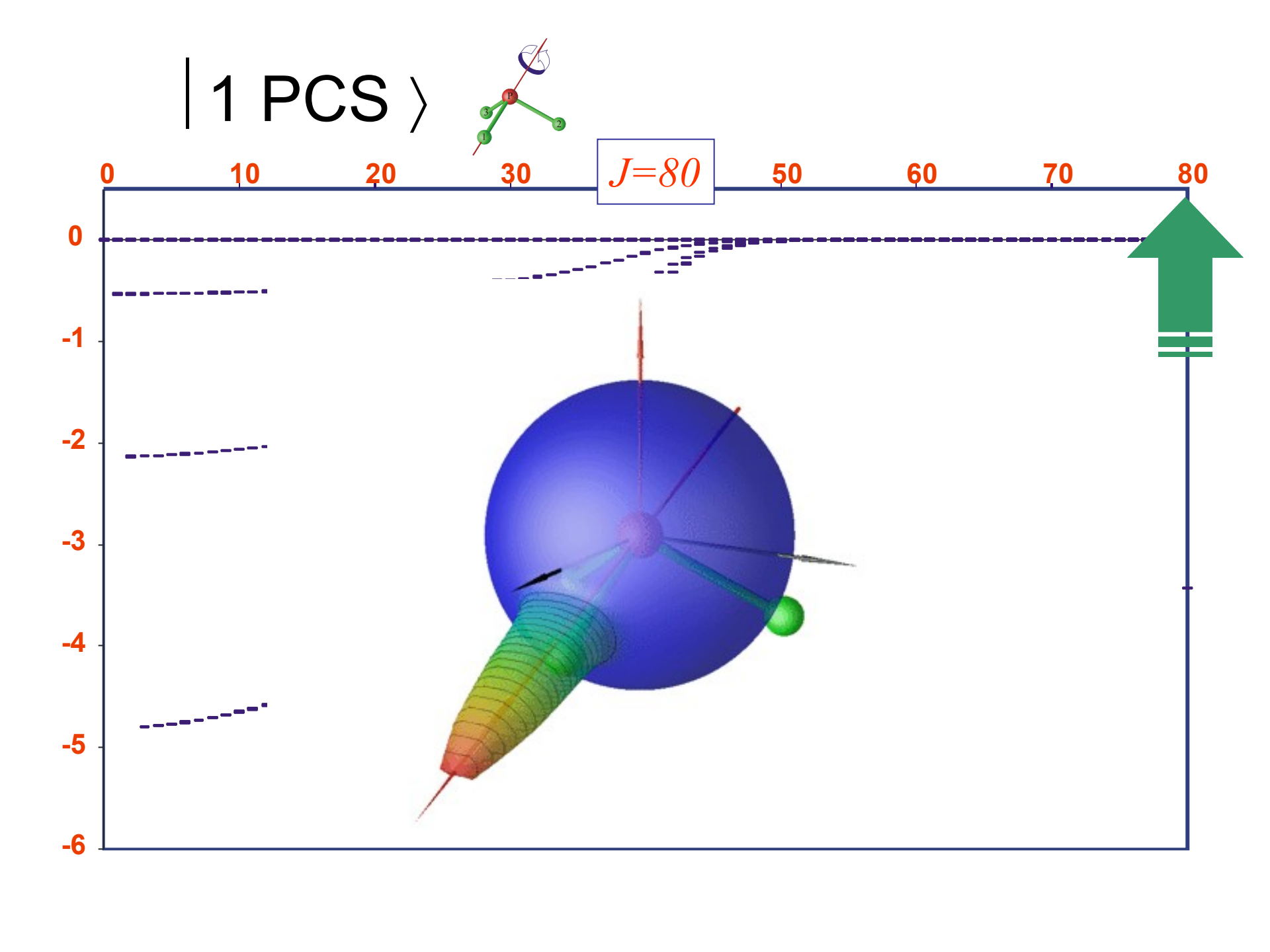



| 1 PCS ⟩
J=20
0
10
20
30
40
50
60
70
80
0
-1
-2
-3
-4
-5
-6
z
y
x
θ = 94°
$F_{J,m=J}(\theta,\chi) = \int (\Phi_i)^* \Phi_i \sin\theta \, dV$


| 1 PCS ⟩
0
10
20
30
J=40
50
60
70
80
0
-1
-2
-3
-4
-5
-6
z
θ = 98°
x
y


| 1 PCS ⟩
J=60
0
10
20
30
50
60
70
80
0
-1
-2
-3
-4
-5
-6
z
θ = 108°
x
y


| 1 PCS ⟩
θeq = 123°
J=80
0
10
20
30
40
50
60
70
80
0
-1
-2
-3
-4
-5
-6
z
θ = 113°
x
y

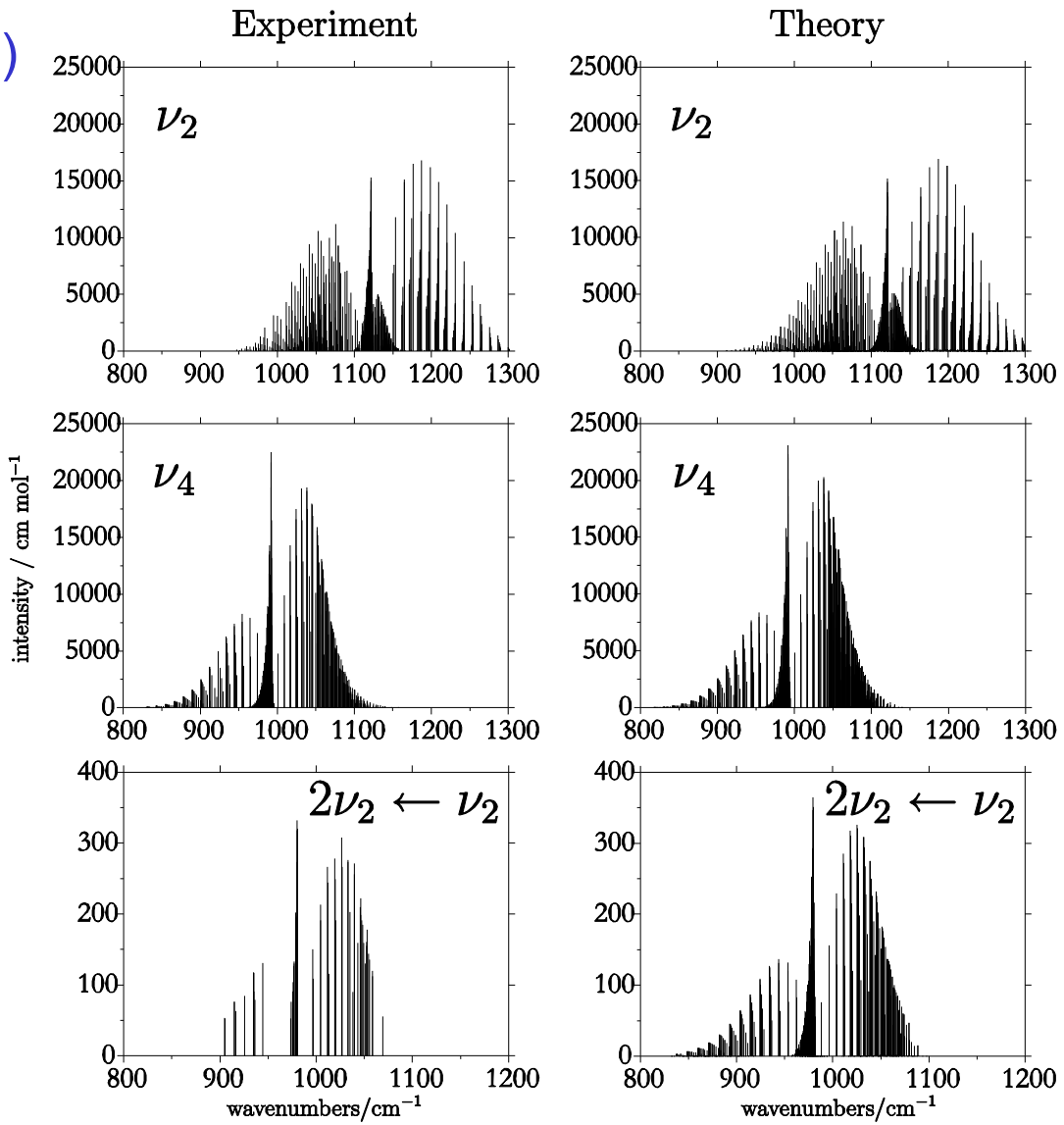

| 1 PCS ⟩
J=80
0
10
20
30
50
60
70
80
0
-1
-2
-3
-4
-5
-6

PH_3 intensity calculations

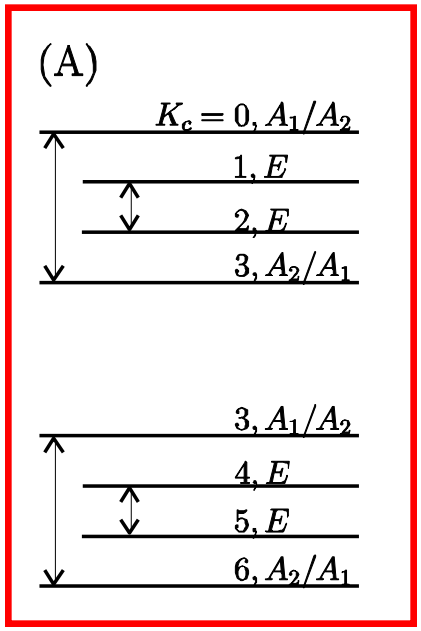
Ab initio (CCSD(T)/aug-cc-pVTZ) dipole moment surfaces

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)

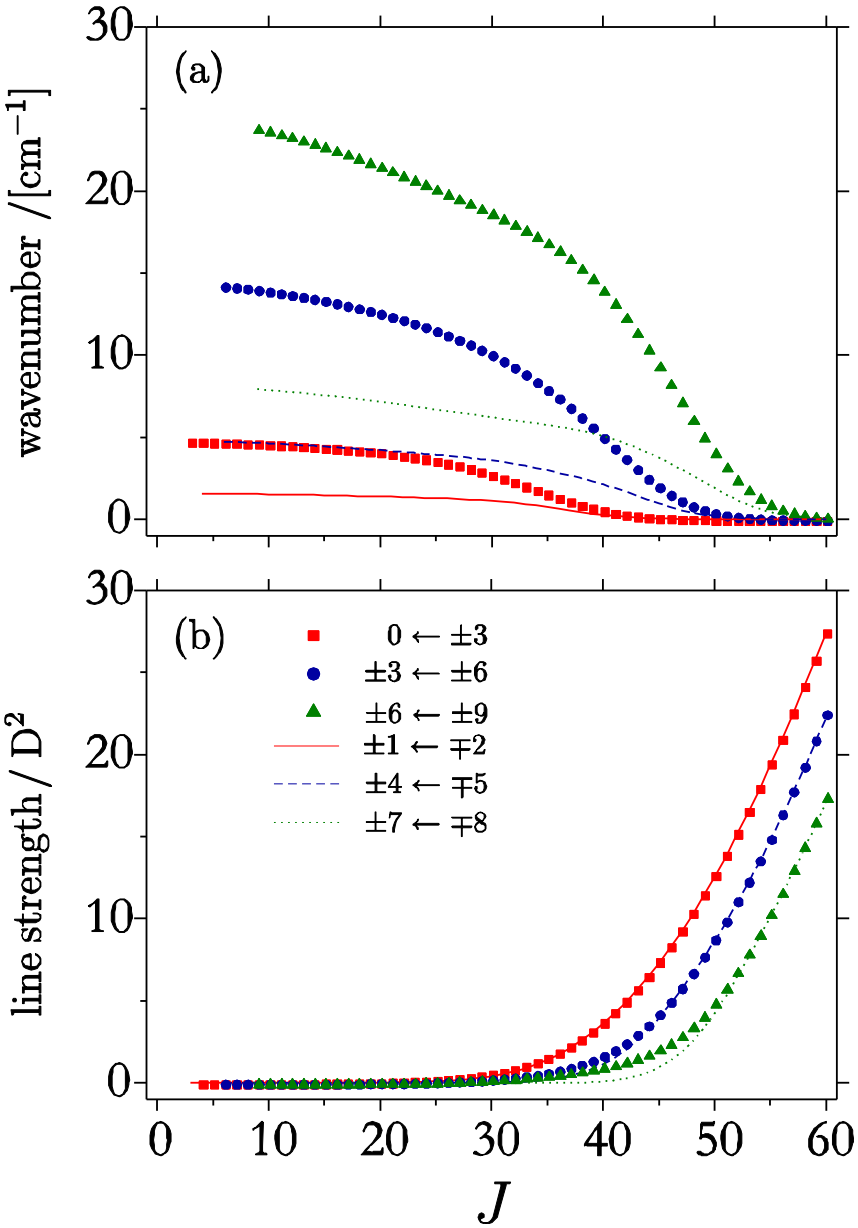


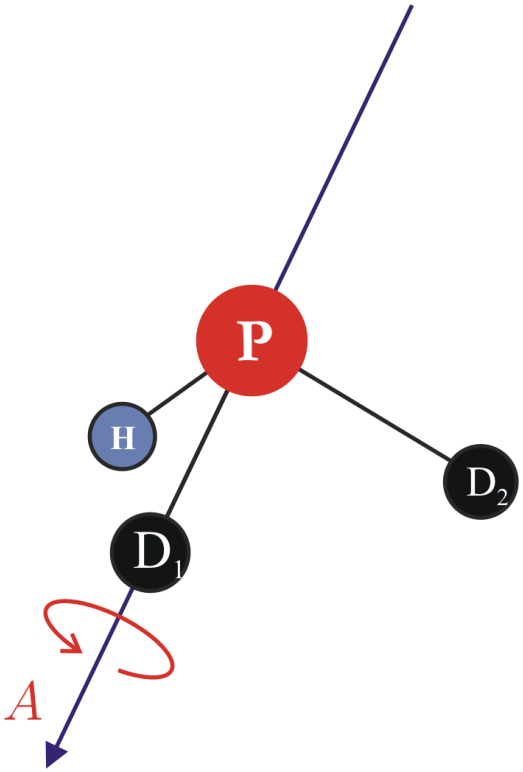
PH_3 cluster transitions

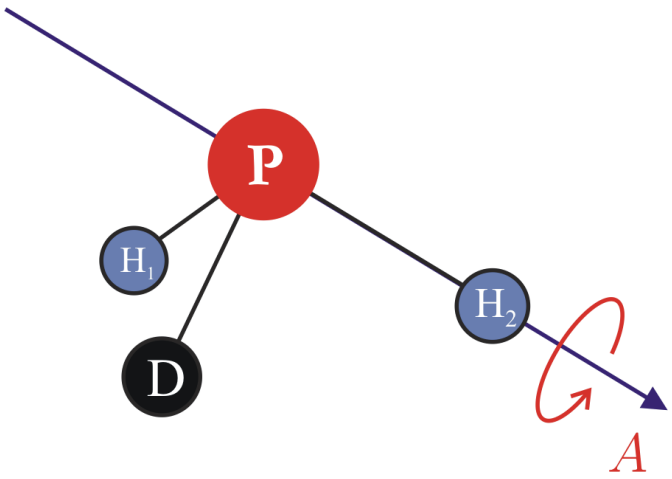


Large line strengths at high J

Can the lower states be populated somehow?



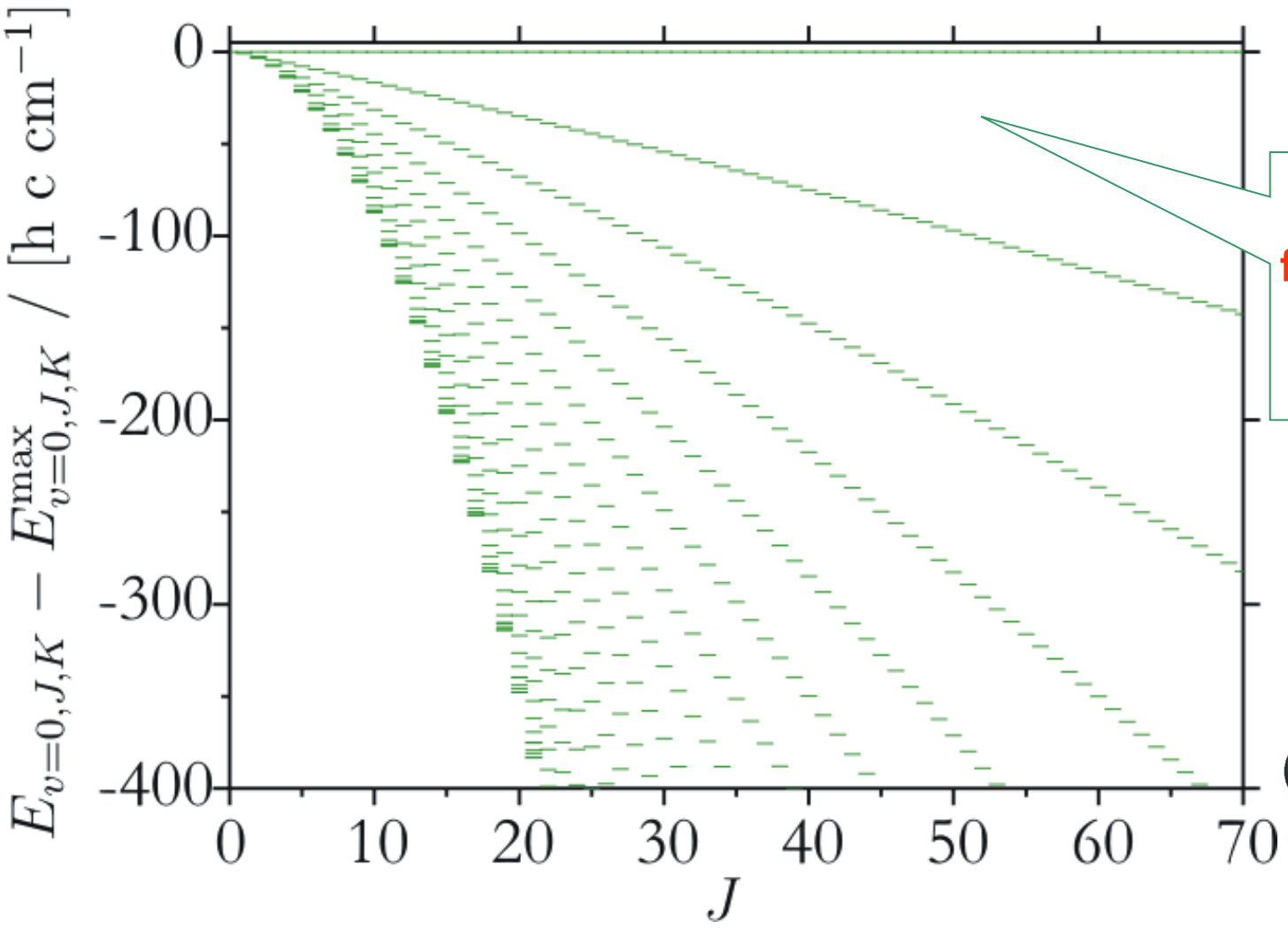




?

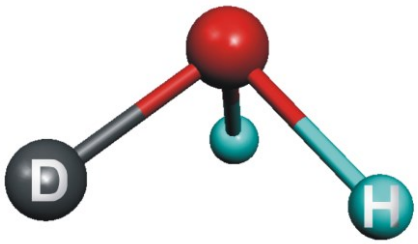
Also similar effects for XHD_2 or XH_2D molecules, say PHD_2 or PH_2D?

PH_2D rotational energies: TROVE calculations

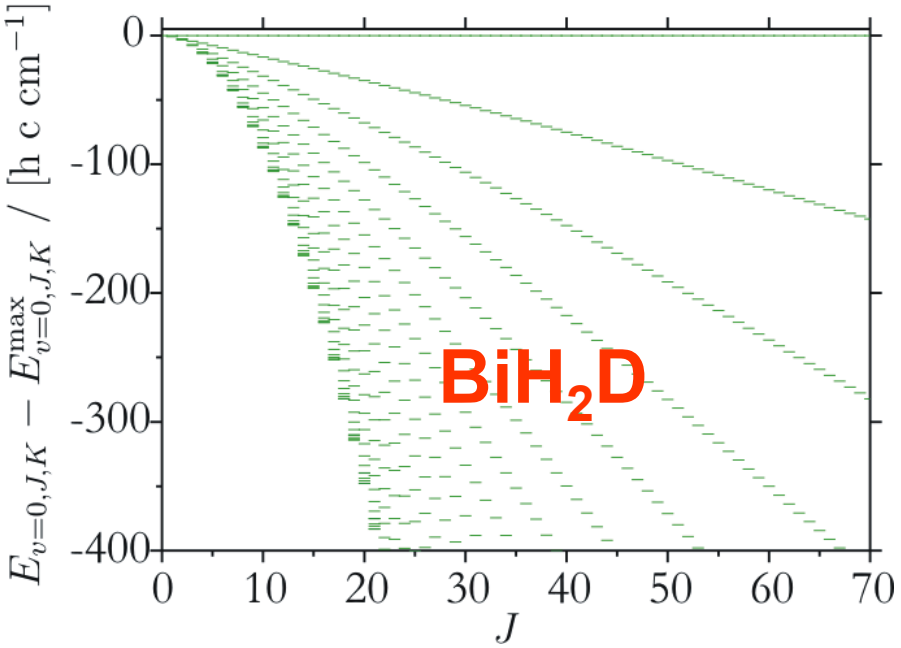


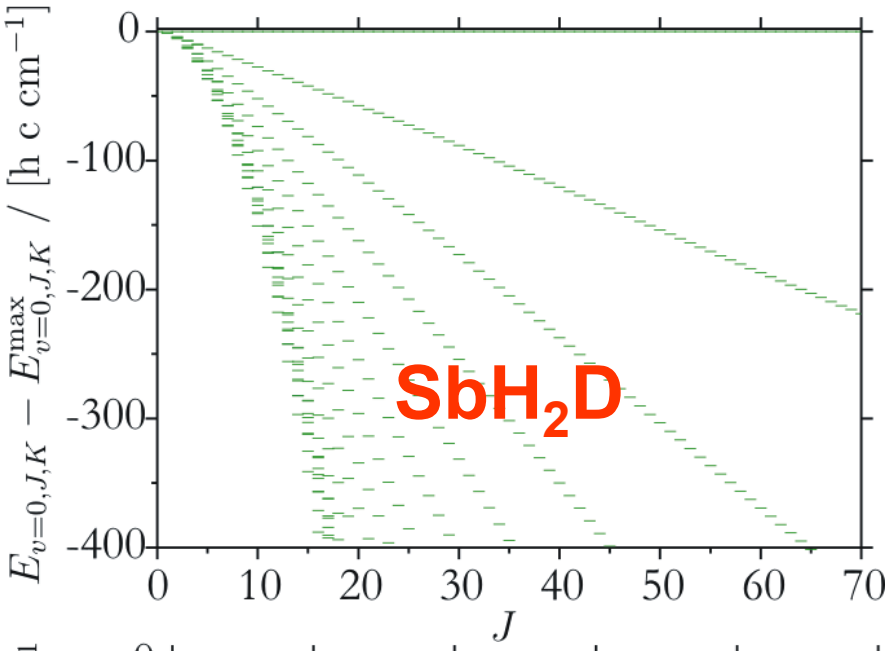
No cluster formation found for PH_2D

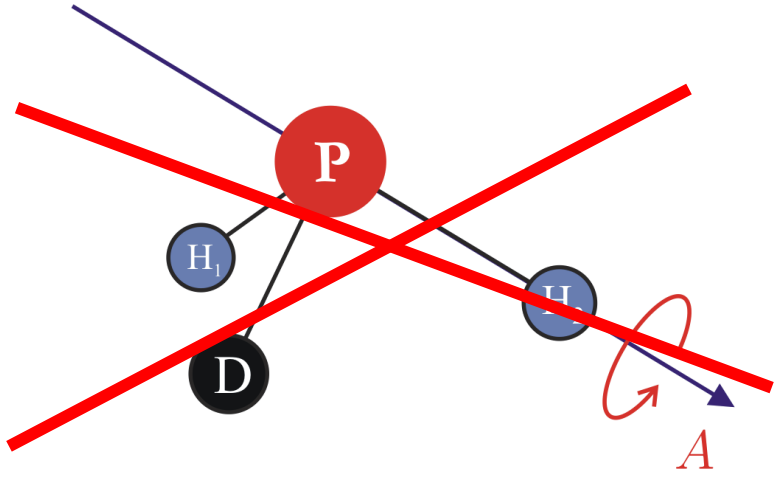
PH_2D

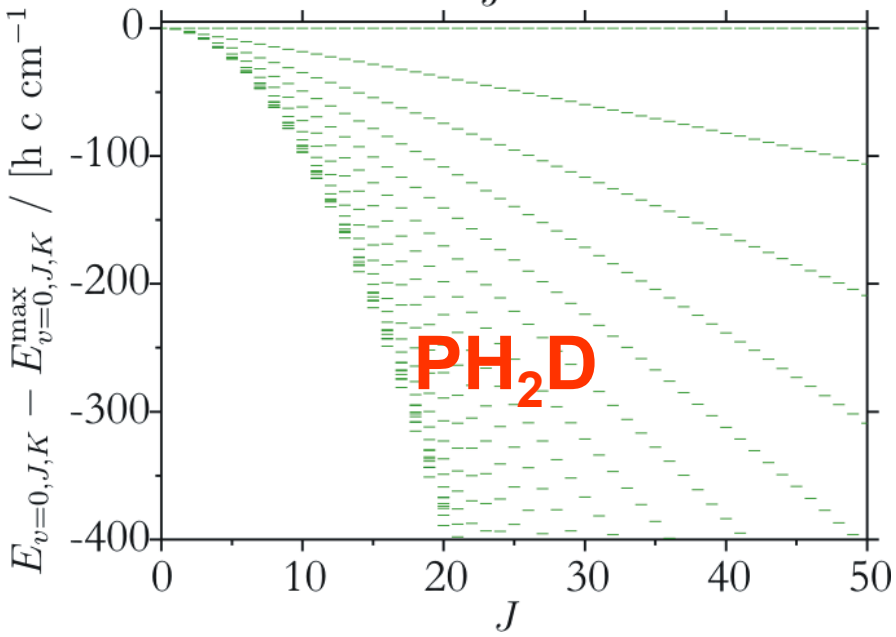


XH_2D: Cluster-free molecules



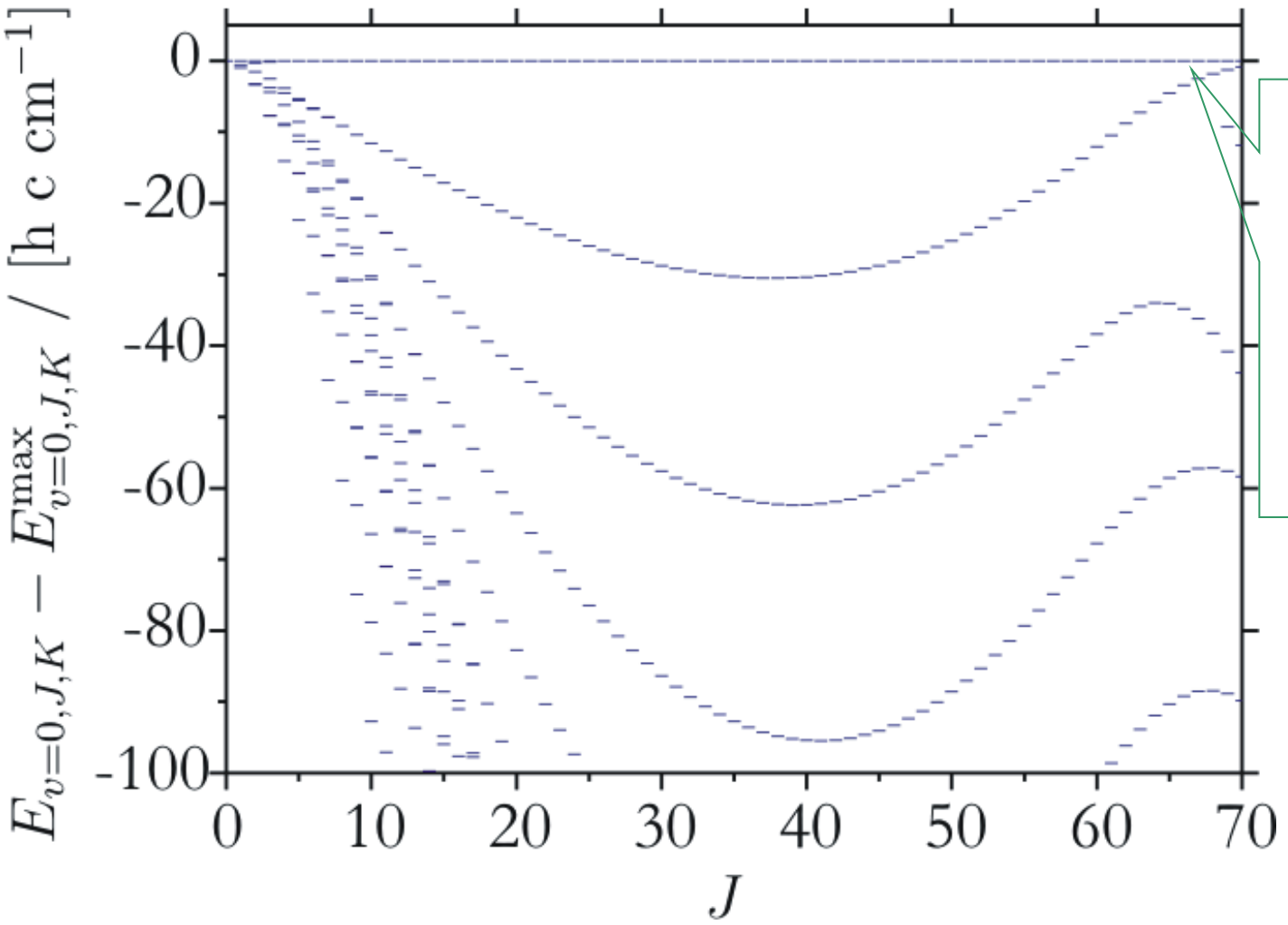






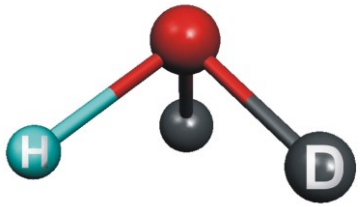
Reduced rotational term values

PHD_2 rotation energies: TROVE calculations



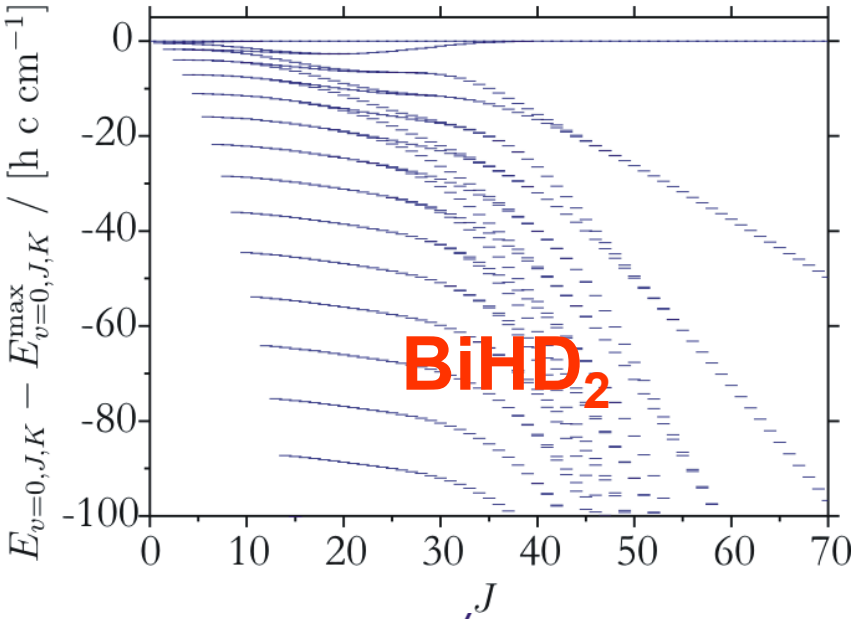
Cluster formation for PHD_2

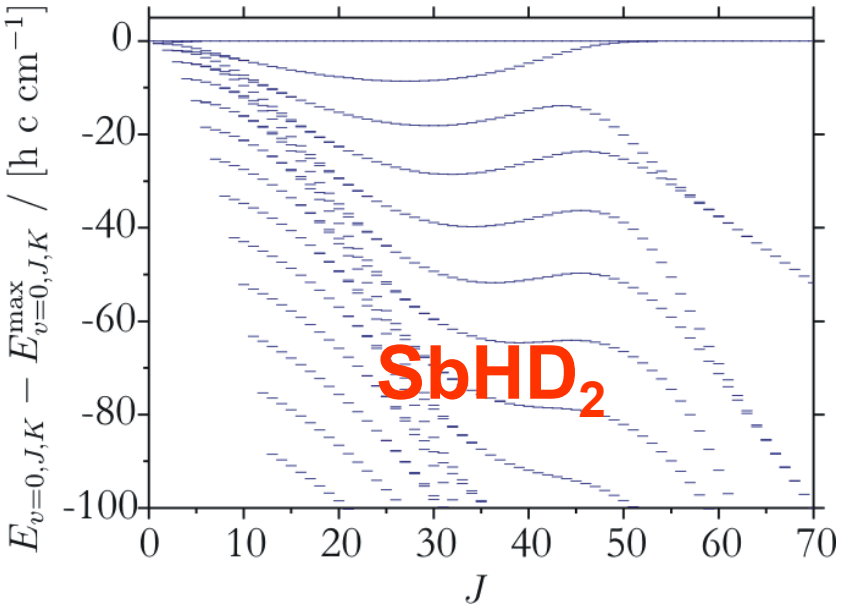
PHD_2

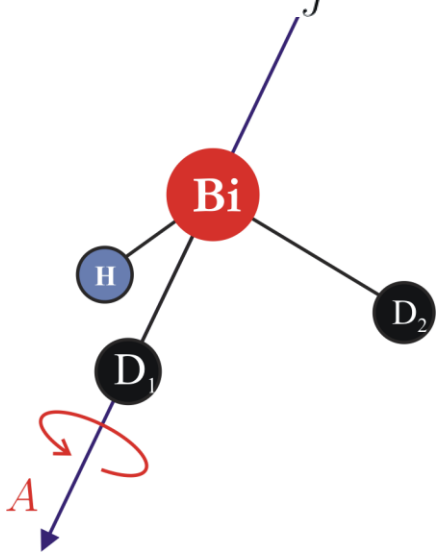


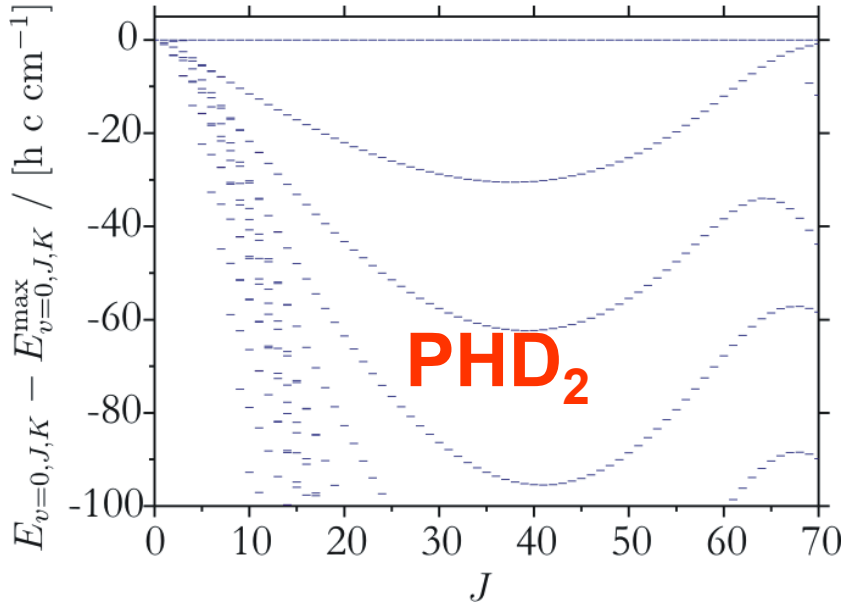
Reduced rotational term values in the vibrational ground state of PHD_2

XHD_2: Molecules with rotational energy cluster formation



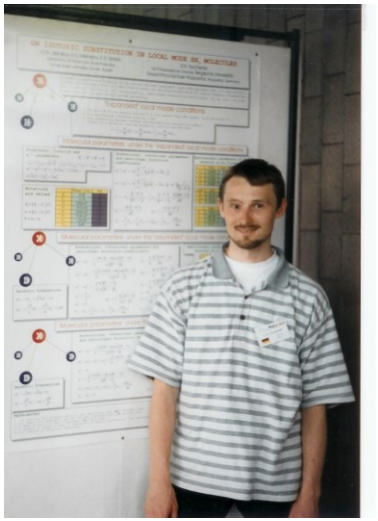






Reduced rotational term values

Thanks & Acknowledgments



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