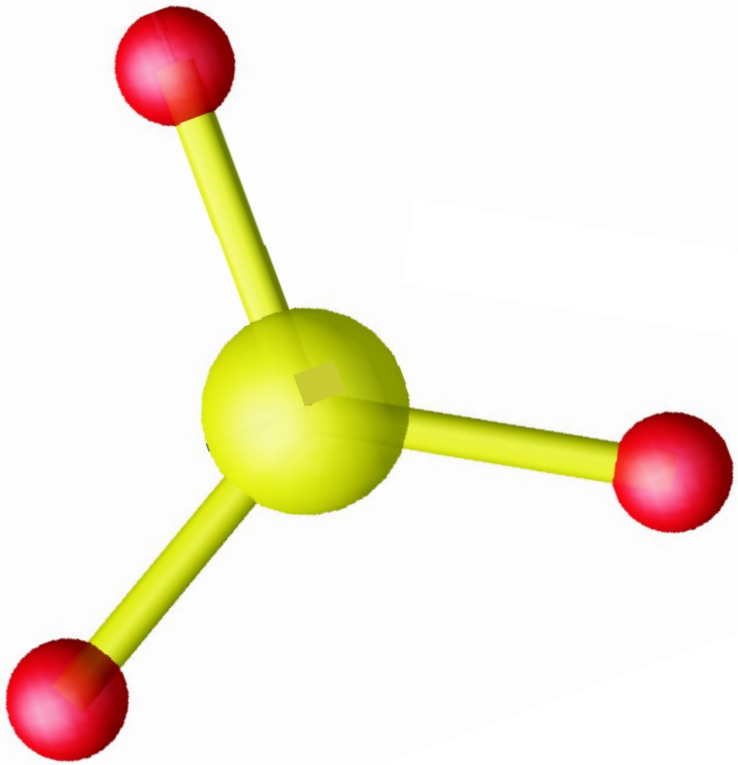
SO_3

- Forbidden rotational spectrum
- Rovibrational energy cluster formation



SO_3 calculations

- Nuclear-motion calculations carried out with TROVE[1]
- Potential-energy surface obtained by *ab initio* methods[2]

[1]S.N. Yurchenko, W. Thiel, and P. Jensen, *J. Mol. Spectrosc*. **245**, 126 (2007).
[2]D. S. Underwood, J. Tennyson, and S. N. Yurchenko, *Phys. Chem. Chem. Phys.* **15**, 10118 (2013).

SO_3: All nuclei are zero-spin bosons

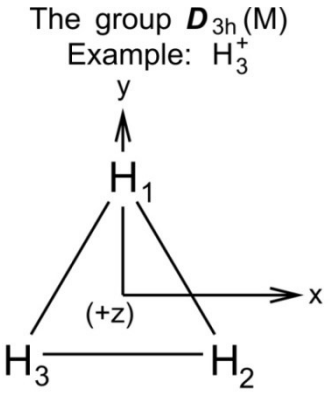
Only levels with

$\Gamma_{\mathrm{rve}} = A_1' \quad \text{or} \quad A_1''$

exist in Nature

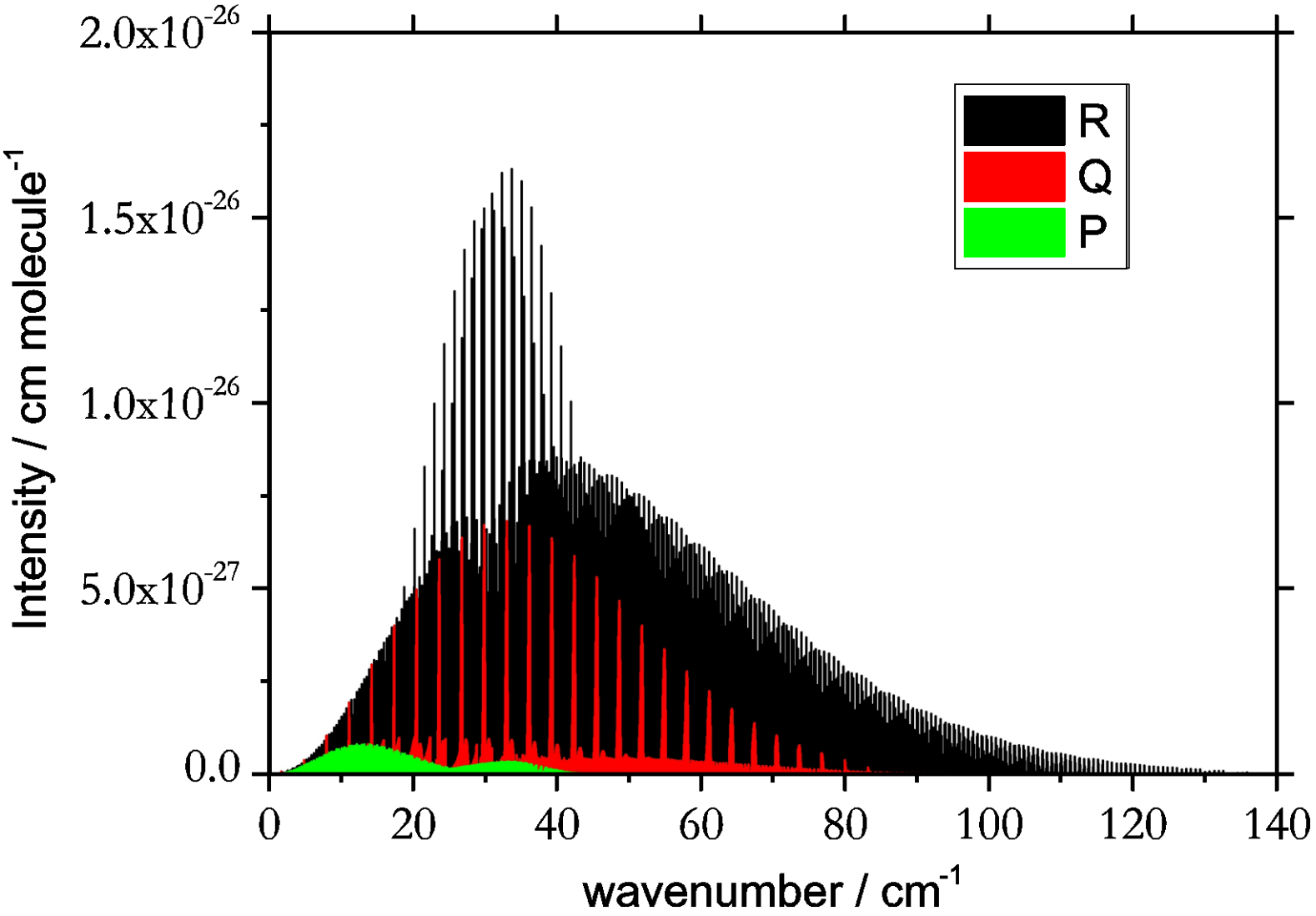
All other levels are missing!

K = 3*t* in vib. ground state



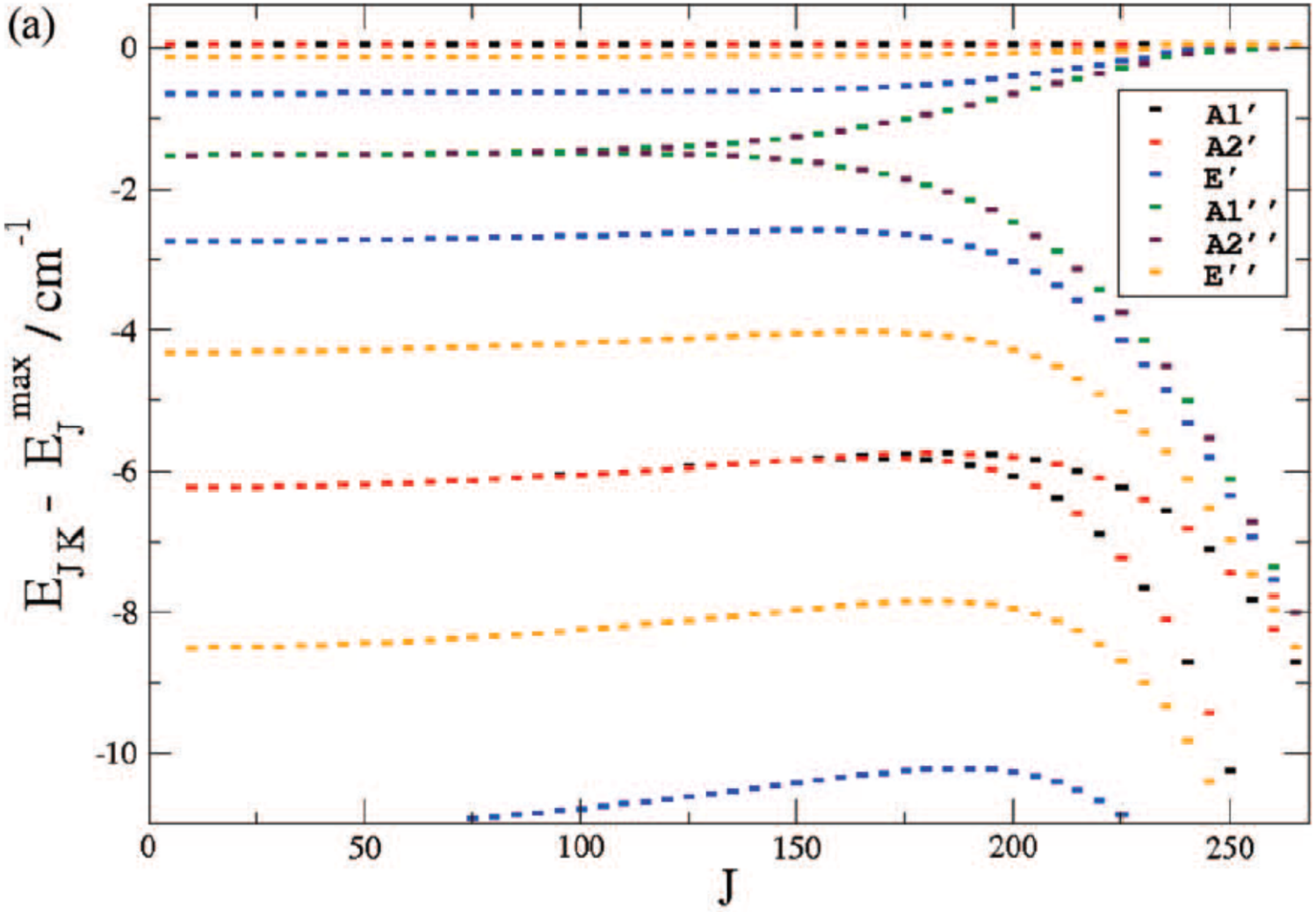
D_{3h}(M):	E	(123)	(23)	E^*	$(123)^*$	$(23)^*$	
	1	2	3	1	2	3	
D_{3h}:	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
Equiv. rot.:	R^0	$R_z^{2\pi/3}$	$R_{\pi/2}^{\pi}$	R_z^{π}	$R_z^{5\pi/3}$	R_0^{π}	
A_1' :	1	1	1	1	1	1	: $\alpha_{zz}, \alpha_{xx} + \alpha_{yy}$
A_1'' :	1	1	1	−1	−1	−1	: $\Gamma(\mu_A)$
A_2' :	1	1	1	1	1	1	: $\hat{J}_z$
A_2'' :	1	1	−1	−1	−1	1	: T_z
E' :	2	−1	0	2	−1	0	: (T_x, T_y),
							: $(\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
E'' :	2	−1	0	−2	1	0	: $(\hat{J}_x, \hat{J}_y)$,
							: $(\alpha_{xz}, \alpha_{yz})$

SO_3 Forbidden rotational spectrum



SO_3 Reduced energies

Vibrational ground state

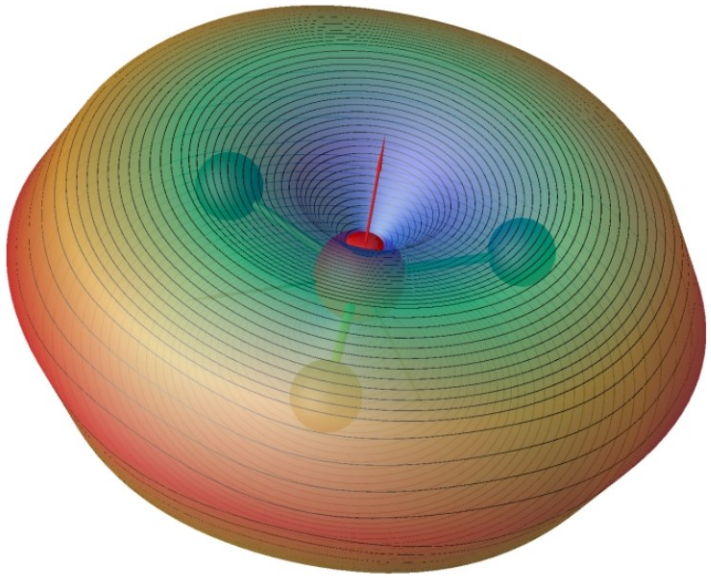


Sixfold energy clusters!

Confirmation: Rotational energy surface[1]

Energy as function of angles θ and ϕ that define the classical angular momentum

$J = 200$



$$J_x = \sqrt{J(J+1)}\,\hbar\,\sin\theta\,\cos\phi,$$

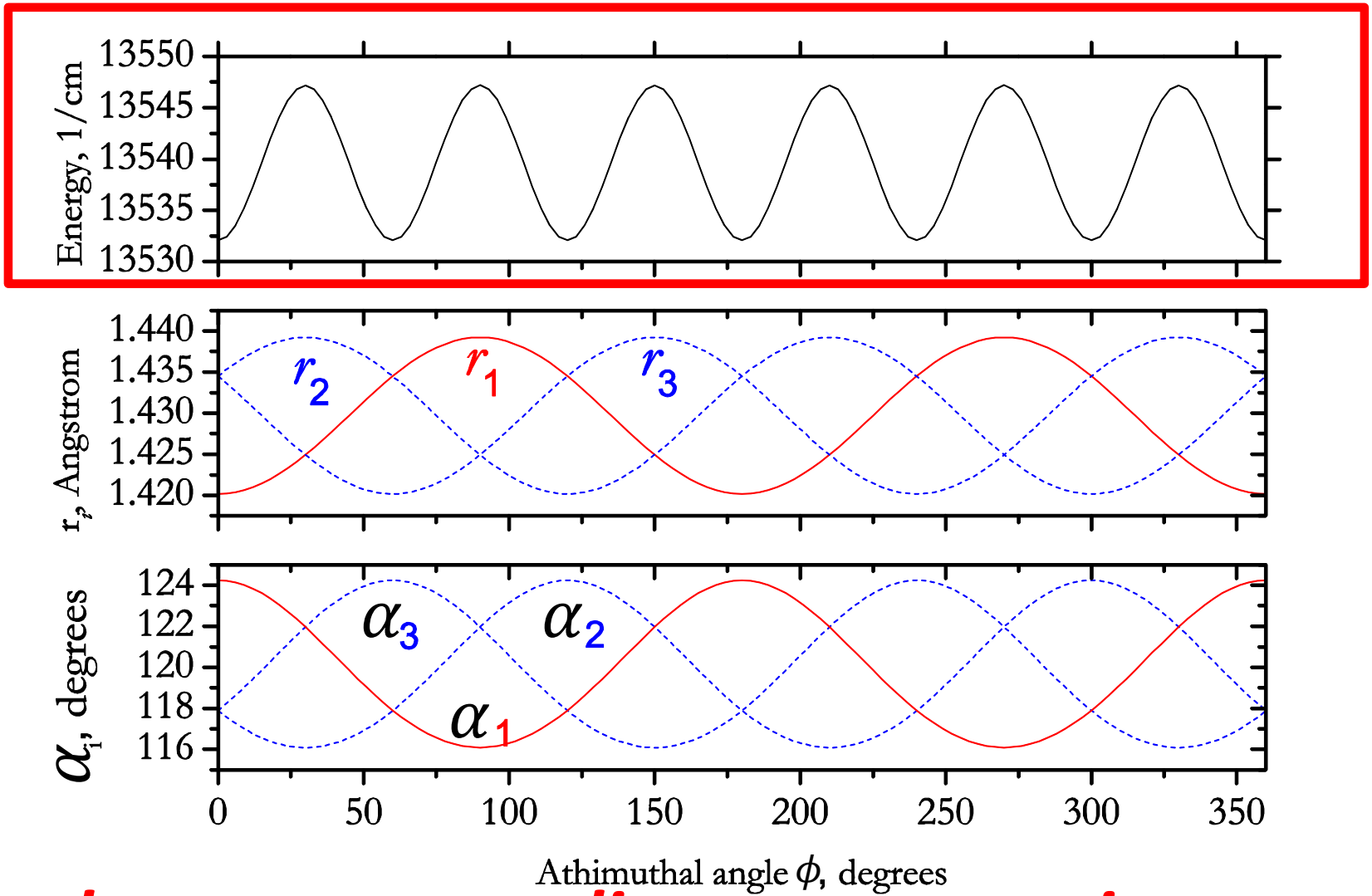
$$J_y = \sqrt{J(J+1)}\,\hbar\,\sin\theta\,\sin\phi,$$

$$J_z = \sqrt{J(J+1)}\,\hbar\,\cos\theta\,,$$

in the molecule-fixed axis system.

[1]W. G. Harter, Phys. Rev. A **24**, 192 (1981).

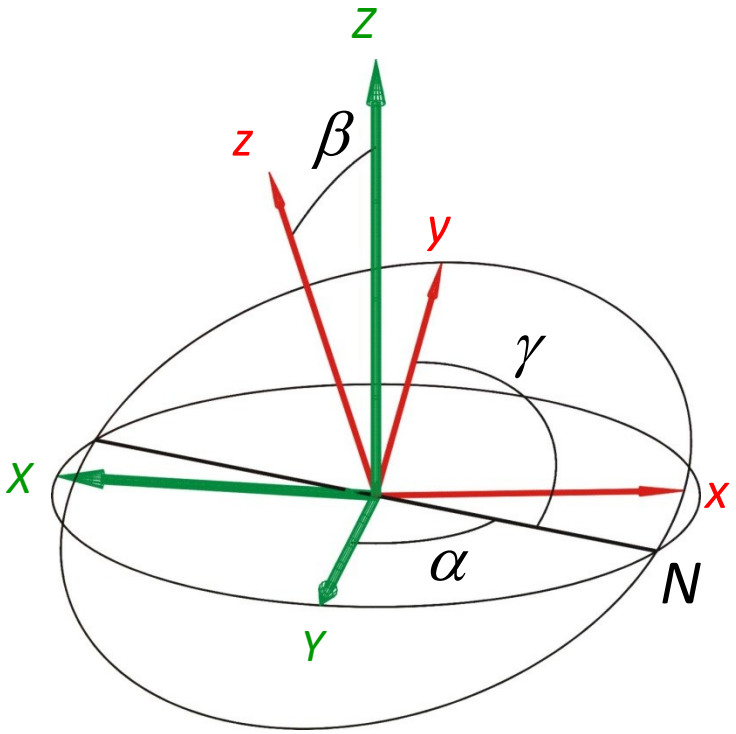
Six maxima along the equator, θ = 90°



Angular momentum lies on equator in cluster states!

$$F(\beta,\gamma) = \int_0^{2\pi} \mathrm{d}\alpha \int_{\mathrm{vib}} \mathrm{d}V \left(\psi_n^{\mathrm{PCS}}\right)^* \psi_n^{\mathrm{PCS}},$$

xyz is molecule-fixed; *XYZ* is space-fixed



F(β,γ) is the probability density of β,γ or of *Z* axis relative to molecule

- (α,β,γ) define orientation of molecule (*xyz*) relative to laboratory (*XYZ*).
- (β,γ) define orientation of *Z* axis relative to molecule (*xyz*).

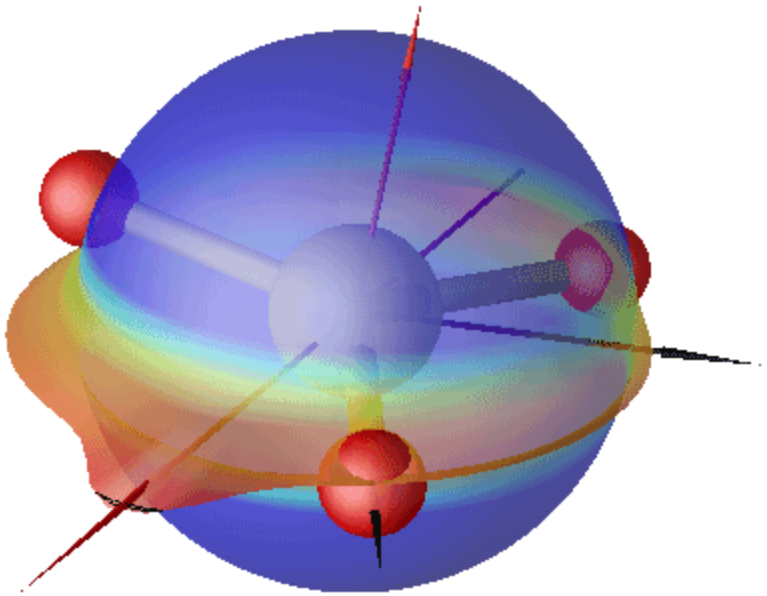
$$F(\beta, \gamma) = \int_0^{2\pi} \mathrm{d}\alpha \int_{\mathrm{vib}} \mathrm{d}V \ \left(\psi_n^{\mathrm{PCS}}\right)^* \ \psi_n^{\mathrm{PCS}},$$

ψ_n^{PCS} is "Primitive Cluster State"

- A cluster is described by six symmetrically equivalent PCS states
- The correspondence between PCS states and symmetrized states can be determined, for example, by projection operator methods

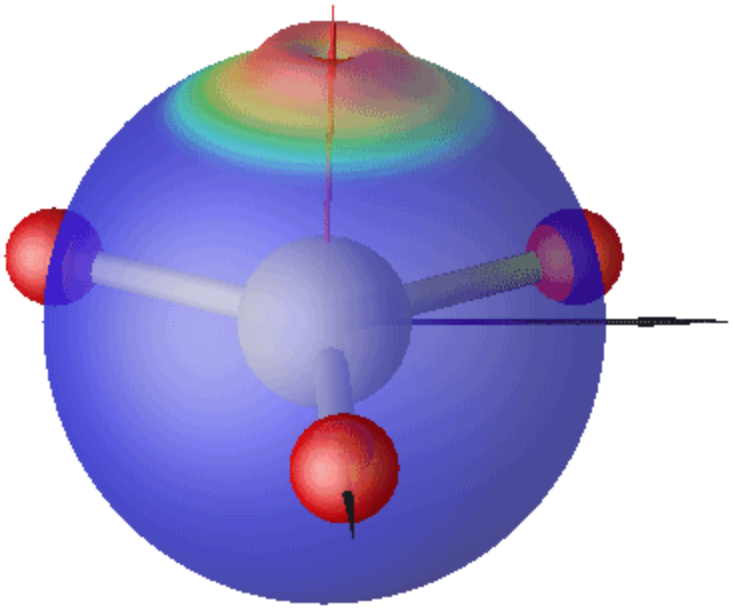
We consider states with $m = J$ to align Z axis with $\boldsymbol{J}$

$F(\beta,\gamma)$ for $^{32}S^{16}O_3$, $J = m = 250$



Angular momentum (rotation axis) lies on equator!

Contrast: $F(\beta,\gamma)$ for $^{32}S^{16}O_3$, (J,K) = (100,99) – at bottom of J manifold.



Angular momentum (rotation axis) lies towards north pole!

SO_3

- Rovibrational energy clusters determined by QM calculations
- Surprising, but borne out by semiclassical RES theory