Quantum Rotations in Methyl Iodide

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What are quantum rotations?

- Molecules in molecular solids can undergo reorientational motion

- H_2 is a dumbell rotor and its quantum rotations are nearly “free” (i.e. no barrier hinders its motion)

$$E_l = Bl(l+1), \quad l = 0,1,2,K$$

$$B = \frac{\eta^2}{2I}$$

- Hindered rotors can perform torsional oscillations and even rotational tunneling through the barrier!

Why study quantum rotations?

- Rotational dynamics as studied with neutrons reflect the molecular environment, i.e. the *energy landscape*

- Neutron tunneling spectroscopy provides extremely detailed information on the shape and magnitude of the potential energy of the molecular groups.

- Rotational tunneling measurements can be used to quantify interatomic interactions.

- Good test of first-principles/DFT calculations

Bulk CH_3I

A Canonical Rotational System

Properties

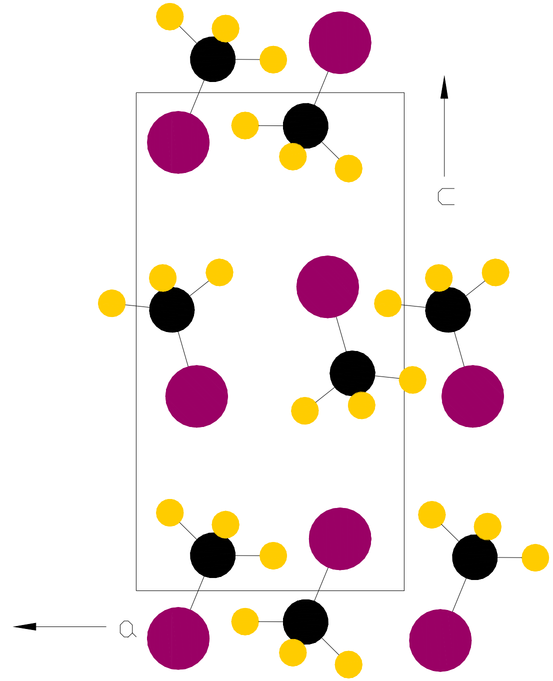
MP: -66.5°C

MW: 141.94 g/mol

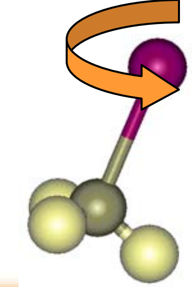
Dipole moment: μ = 1.62 debye

Projection onto the a-c plane

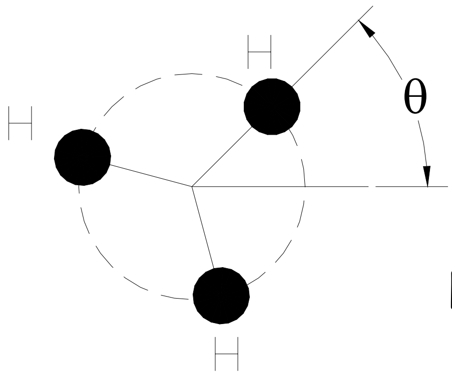
(Prager et.al.,J.Chem.Phys. **86**, 2563 (1987))



The Methyl Group: CH_3



- We want to study the dynamics about the main molecular axis



$I[CH_3] = 5.3 \times 10^{-47}\ \mathrm{kg \cdot m^2}$

$$B = \frac{\eta^2}{2I} = 0.65\ \mathrm{meV}$$

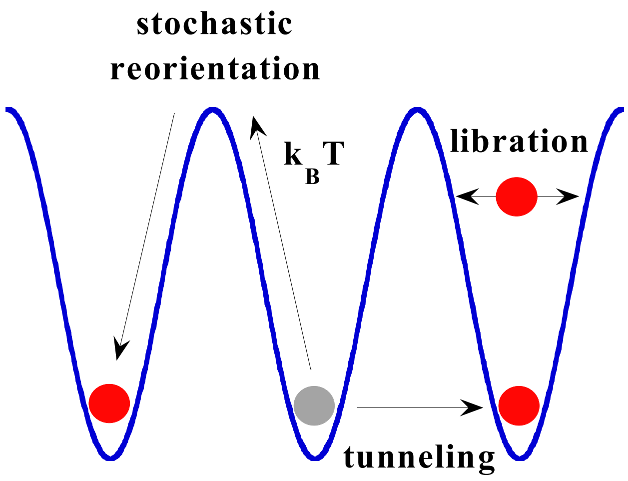
Free rotor energy levels: $E_j = Bj^2, \quad j = 0,1,2,K$

Useful conversions
1 meV $\leftrightarrow$ 4 ps
1 μeV $\leftrightarrow$ 4 ns

Bulk CH_3I Dynamics

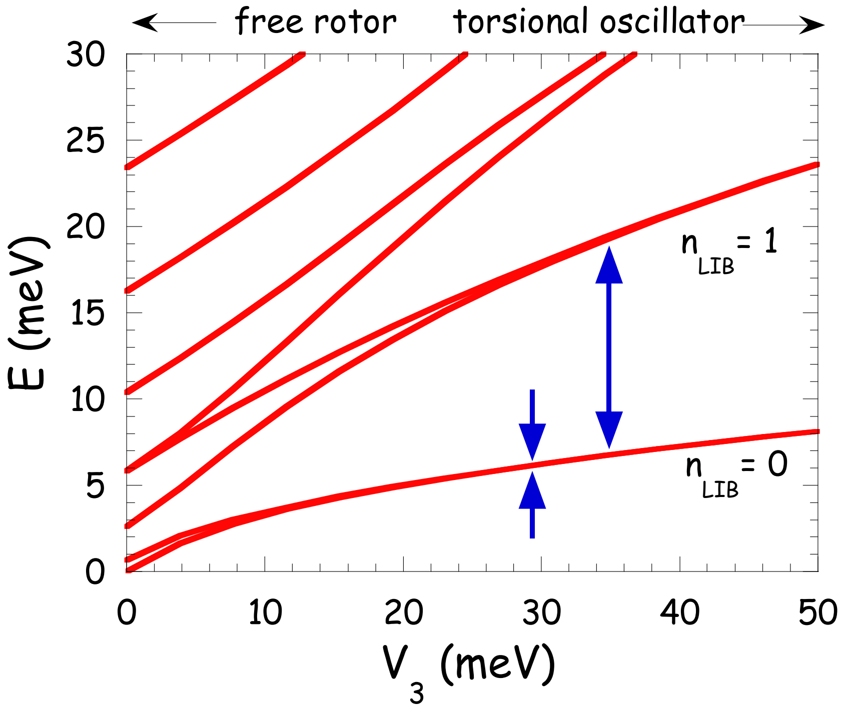
- Interaction potential of methyl group (1) van der Waals term, (2) short-range steric repulsion, and (3) additional multipole terms

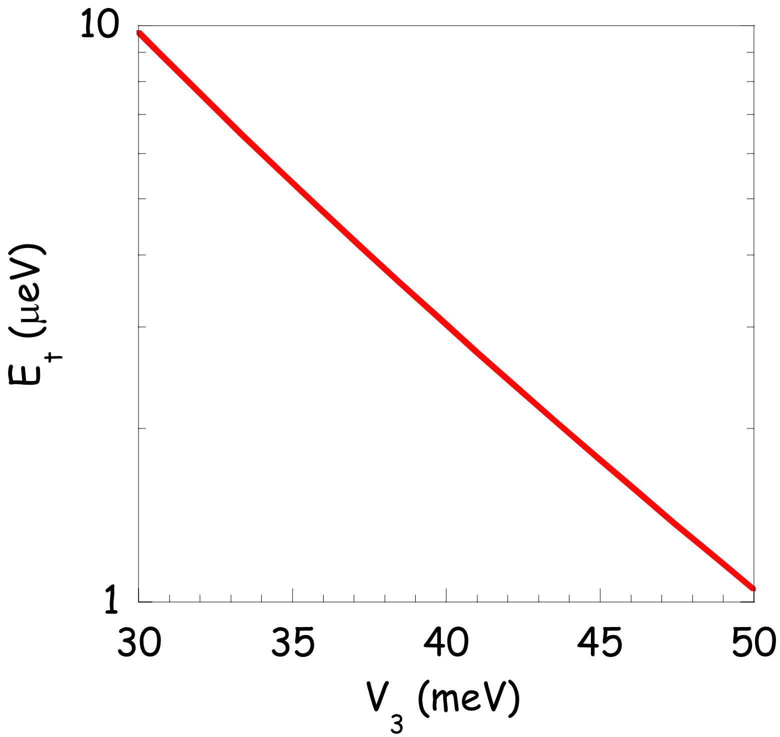
- Simplified model based on symmetry alone: $V(\theta)=\frac{V_3}{2}(1-\cos 3\theta)$



Bulk CH_3I Dynamics

$$H = -B\frac{d^2}{d\theta^2} + \frac{V_3}{2}\left(1 - \cos 3\theta\right)$$



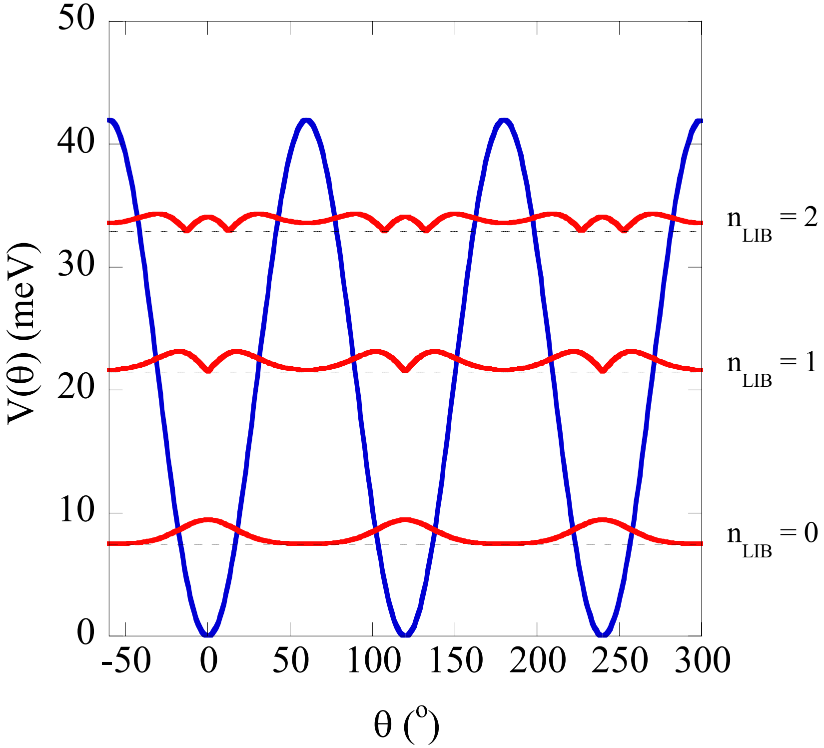


Tunneling energy very sensitive to the barrier height!

Rotational Tunneling

- Tunneling rate (…and energy) proportional to the overlap of the wavefunctions through the barrier

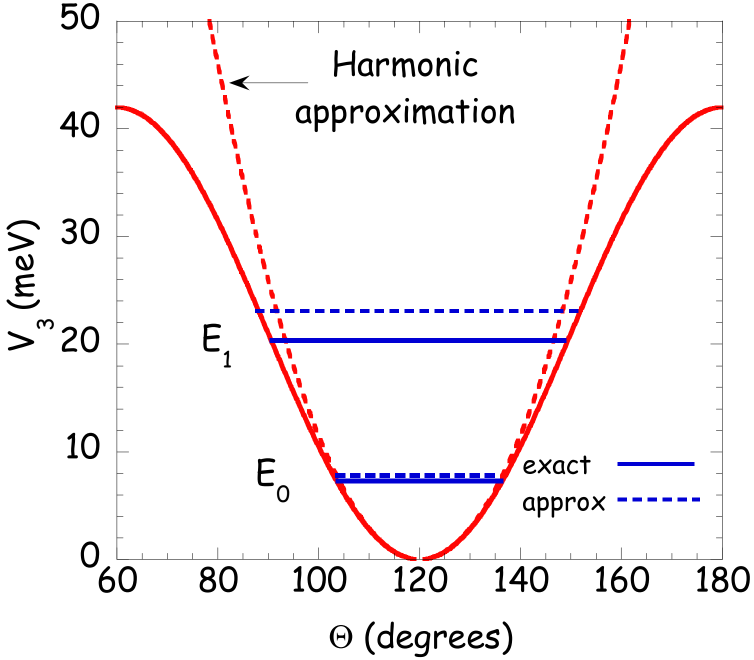
- Overlap increases with librational level (n_{LIB}) hence tunneling rate increases with librational level

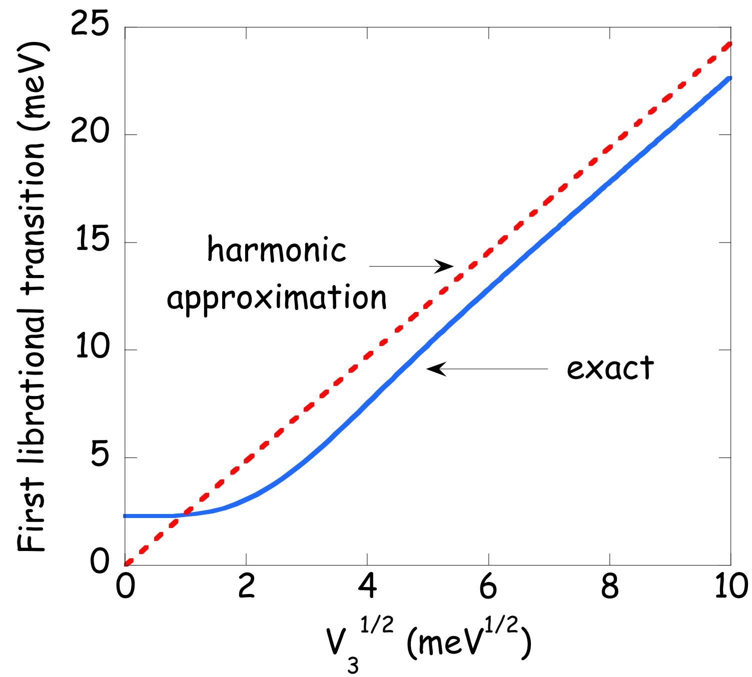


Librational Motion

- Librations are torsional oscillations
- Harmonic approximation:

$$\boxed{E_n = \left(n_{LIB} + \frac{1}{2}\right)\eta\omega_0} \qquad \boxed{\eta\omega_0 = 3\sqrt{BV_3}}$$





Measurement Technique
Inelastic Neutron Scattering

- Neutrons are highly penetrating
- Wavelengths on order of intermolecular spacing (~Å)
- Energies on order of molecular excitations (~μeV-meV)
- No symmetry-based selection rules as in optical techniques
- Simple interpretation of spectra

Using Inelastic Neutron Scattering to See Quantum Rotations

- **Neutrons can induce a spin flip in hydrogenous species**
- **Incoherent scattering**
- Simple case: H_2

$\Psi = \psi_{rot}\,\psi_{ns}\,\psi_{el}\psi_{vib}$ ($\psi_{el}\psi_{vib}$ are in the totally symmetric ground state)

Ψ must be AS upon nuclear exchange (composed of 2 fermions)

ψ_{ns} must be AS(S) if ψ_{rot} is S(AS)

$$\psi_{ns}^{S} = \begin{cases} |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \end{cases} \qquad J = 1, \text{ ortho}$$

$$\psi_{ns}^{AS} = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \qquad J = 0, \text{ para}$$

Using Inelastic Neutron Scattering to See Quantum Rotations

- For a methyl group rotation three spins involved so must construct the S and AS spin functions

A

$$\psi_{ns}^{S} = \begin{cases} |\uparrow\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{3}}\left(|\uparrow\uparrow\downarrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\downarrow\uparrow\uparrow\rangle\right) \\ \frac{1}{\sqrt{3}}\left(|\downarrow\downarrow\uparrow\rangle + |\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\rangle\right) \\ |\downarrow\downarrow\downarrow\rangle \end{cases}$$

$$\varepsilon = e^{i2\pi/3}$$

E

$$\psi_{ns}^{AS} = \begin{cases} \frac{1}{\sqrt{3}}\left(|\uparrow\uparrow\downarrow\rangle + \varepsilon|\downarrow\uparrow\uparrow\rangle + \varepsilon^*|\uparrow\downarrow\uparrow\rangle\right) \\ \frac{1}{\sqrt{3}}\left(|\downarrow\downarrow\uparrow\rangle + \varepsilon|\uparrow\downarrow\downarrow\rangle + \varepsilon^*|\downarrow\uparrow\downarrow\rangle\right) \\ \frac{1}{\sqrt{3}}\left(|\uparrow\uparrow\downarrow\rangle + \varepsilon^*|\downarrow\uparrow\uparrow\rangle + \varepsilon|\uparrow\downarrow\uparrow\rangle\right) \\ \frac{1}{\sqrt{3}}\left(|\downarrow\downarrow\uparrow\rangle + \varepsilon^*|\uparrow\downarrow\downarrow\rangle + \varepsilon|\downarrow\uparrow\downarrow\rangle\right) \end{cases}$$

- Observed transitions: $A \rightarrow E$ and $E \rightarrow E$
- Situation is more complex but still need to flip a spin to induce a transition between rotational states

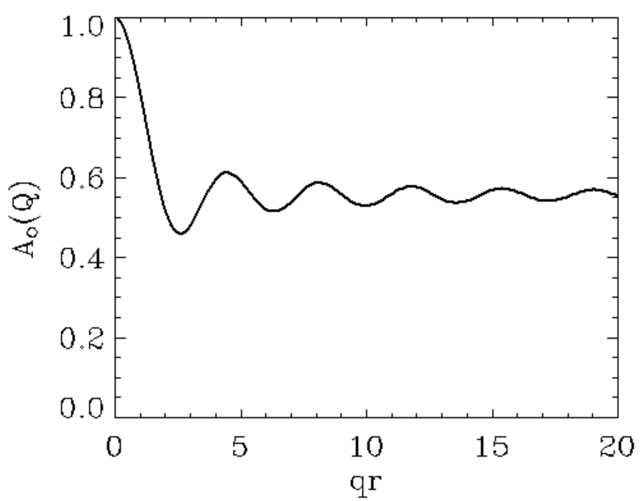
Using Inelastic Neutron Scattering to See Quantum Rotational Tunneling

Neutron scattering law for methyl tunneling

$$S(Q,\omega) = A_0(Q)\delta(\omega) + (1 - A_0(Q))\frac{1}{2}\left[\delta(\omega - \omega_t) + \delta(\omega + \omega_t)\right]$$

$$A_0(Q) = \frac{5 + 4j_0\left(QR\sqrt{3}\right)}{9}$$

R: radius of methyl group
ω_t: tunneling energy
A_0: elastic incoherent structure factor



High Flux Backscattering Spectrometer

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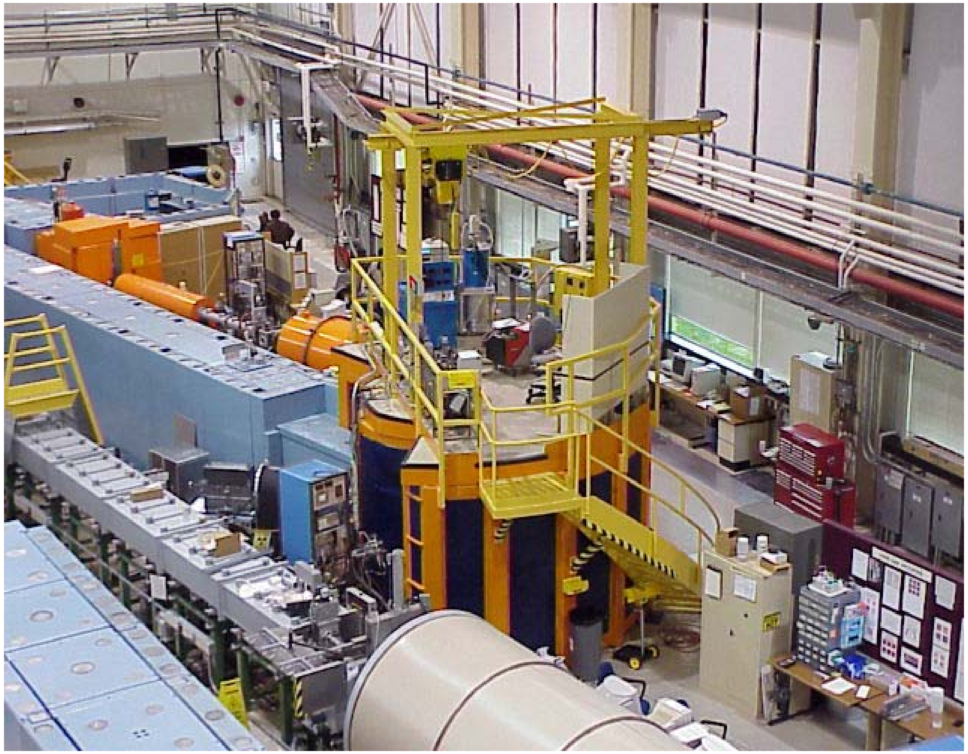
- High energy resolution is often necessary to observe rotational tunneling directly.
- Typical neutron techniques to study tunneling include TOF, backscattering, and neutron spin-echo
- No other neutron spectrometer in North America is capable of measuring the tunnel splitting of CH_3I!



Are the HFBS measurements enough?

- Measuring the tunneling energy allows you to estimate the barrier height V_3

Can we stop here and declare victory?….NO!

- With knowledge of the barrier height you can estimate the librational transition energy E_0

- Confirmation that this model is correct requires that we perform an independent measurement like measuring the librational transition and comparing the measurement with our estimate

Filter Analyzer Neutron Spectrometer

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- S(Q,E) reflects density of vibrational (librational) modes, G(E)
- Vary initial energy, fix final energy
- Measures energy transfers of order 10's-100's meV