Nuclear Quadrupole Resonance Spectroscopy

Review nuclear quadrupole moments, Q – A negative value for Q denotes a distribution of charge that is "football-shaped", i.e. a sphere elongated at the poles; a positive value corresponds to a flattened sphere.]

Some examples of nuclear quadrupole moments

Nucleus	I	Q $/10^{-28}m^2$
^{2}H	1	2.8×10^{-3}
^{14}N	1	1.06×10^{-3}
^{23}Na	3/2	9.7×10^{-2}
^{35}Cl	3/2	-7.9×10^{-2}
^{63}Cu	3/2	-0.157
^{93}Nb	9/2	-0.2

The (2I + 1) values of m_I that correspond to the different orientations of the nuclear "spin-axis" with respect to a defined direction are degenerate **unless**

(1) a magnetic field is applied (this is the NMR expt.) or

(2) there is a nonzero electric field gradient (efg) at the nucleus.

The splitting of the m_I levels by the efg is the nuclear analog of the zero-field splitting of m_S levels in ESR spectroscopy.

In the appropriate coordinate system, the electric field gradient has three components,

$$V_{xx},\ V_{yy},\ \text{and}\ V_{zz}, \quad \text{where}\ V_{xx} + V_{yy} + V_{zz} = 0$$

In an axially-symmetric situation, $V_{xx} = V_{yy}$, and the efg is defined by V_{zz}, or q (= V_{zz}/e).

In a non-axial case, a second parameter (the "asymmetry parameter", η) is needed,

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

There are two contributions to q

$$q = q_{\text{valence electrons}} + q_{\text{lattice}}$$

$$q_{valence} = K_p[-N_{p(z)} + \frac{1}{2}(N_{p(x)} + N_{p(y)})]$$

or

$$q_{valence} = K_d[-N_{d(z^2\}} + N_{d(x^2-y^2)} + N_{d(xy)} - \frac{1}{2}(N_{d(xz)} + N_{d(yz\}})]$$

where the N's are the populations of the orbitals indicated (taking into account any effects of covalency).

Note the sign convention that concentration of charge along the z-axis contributes to a **negative** field gradient.

$q_{lattice}$ is affected by the symmetry of the neighboring atoms or ligands, e.g. an octahedron with two long trans bonds would have $q_{lattice} > 0$

Obviously, calculation of absolute q-values from structural data is virtually impossible because of the many contributing factors to $q_{valence}$ and $q_{lattice}$.

The splitting of m_I levels

For axial cases ($\eta = 0$)

The general equation for the splitting of m_I levels in an efg (q) is

$$E_m = \frac{e^2Qq[3m_I^2 - I(I+1)]}{4I(2I-1)}$$

where E is the energy of a specified m_I level.

Thus for I = 1

$E(m_I = 0) = e^2Qq(-2/4) = -e^2Qq/2$

$E(m_I = \pm1) = e^2Qq(1/4) = (+)e^2Qq/4$

Energy separation = $\frac{3}{4}(e^2Qq)$

e^2Qq is known as the Quadrupole Coupling Constant and can be positive or negative quantity depending upon the sign of Qq.

In NQR spectroscopy, transitions are induced between the m_I states
Selection rule $\Delta m_I = \pm1$

So for an I=1 sample, a single transition should be observed when $h\nu = \frac{3}{4}(e^2Qq)$.

We can also show that for I = 3/2, only two levels (one NQR transition) can be observed.

$E(\pm1/2) = -\frac{1}{4}(e^2Qq)$

$E(\pm3/2) = (+)\frac{1}{4}(e^2Qq)$

So in this case $h\nu = \frac{1}{2}(e^2Qq)$

The energy differences are very small, e.g. for some ^{35}Cl compounds $|e^2Qq|$ may be 20 MHz, which corresponds to
7×10^{-4} cm^{-1}

NOTE NQR must be done on solid samples, for molecular tumbling in liquids averages field gradients to zero. Sample must also be diamagnetic (unpaired electrons affect relaxation times of nuclei).

Some examples....

^{75}As (I = 3/2; 100%; Q is positive)

AsR_3 compounds.
We can anticipate that q will be dominated by the unshared electron pair on As, giving rise to a negative efg.

	R = Et	Ph	C_2F_5
e^2Qq =	89.6	98.9	108.9 MHz

(Since there is only one allowed transition, only the absolute value of e^2Qq can be determined.}

The above data can be interpreted to show increased (negative) q_{zz} as inductive withdrawal of electron density in p_x and p_y orbitals.

Case of ^{55}Mn (I = 5/2; 100%; Q is positive)

For I = 5/2 there are three energy levels in an axially symmetric compound. The allowed transitions are $\pm 1/2 \leftrightarrow \pm 3/2$ ($\Delta = 3/10\ e^2Qq$) and $\pm 3/2 \leftrightarrow \pm 5/2$ ($\Delta = 6/10\ e^2Qq$). When $q > 0$, $\pm 1/2$ is ground state and when $q < 0$, $\pm 5/2$ is ground state.

For $XMn(CO)_5$

X	e^2Qq
:[a]	(-)67.1
D	(-)45.7
$Co(CO)_4$	(-)20
$Re(CO)_5$	(-)8.7
$Mn(CO)_5$	3.3
I	19.8
Br	17.5
Cl	13.9

[a] $Li^+[Mn(CO)_5]^-$

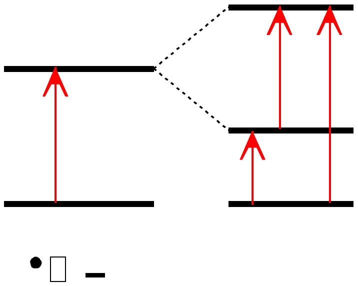
We can interpret these values in terms of e^2Qq which is expected to become more **negative** as the sigma-donor power of X **increases** and/or as the pi-acceptor power of X **decreases.**

NQR of non-axial systems, $\eta \neq 0$

I = 1

When $\eta = 0$, there are two levels $m_I = 0$ and ±1 and <u>one allowed transition.</u>

When $\eta \neq 0$ the ±1 level is split and there are <u>three allowed transitions.</u>



Observation of three transitions gives values for e^2Qq and η.

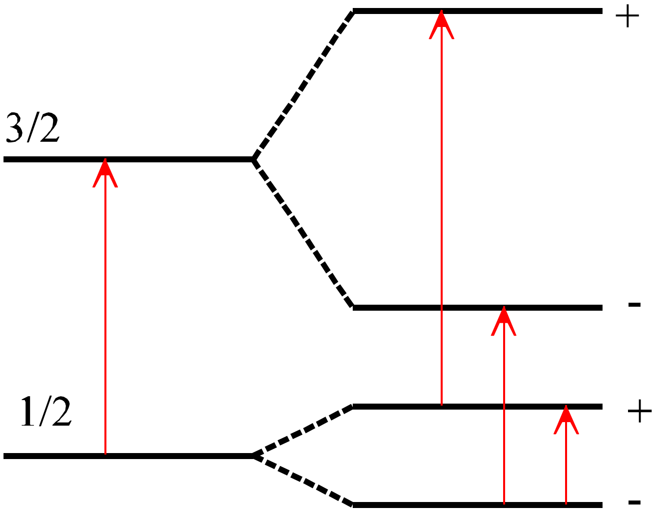
$$E_0 = \frac{-2e^2Qq}{4I(2I-1)} \quad \text{and} \quad E_{\pm 1} = \frac{e^2Qq(1 \pm \eta)}{4I(2I-1)}$$

I = 3/2

Nonzero η does not split $\mathbf{m_I = n/2}$ levels, so there is only a single allowed transition, from which the two “unknowns” e^2Qq and η cannot be extracted.

$$h\nu = \frac{e^2Qq}{2}\sqrt{1+\eta^2/3}$$

What to do? Record spectrum in magnetic field (which removes all degeneracy of the m_I levels)



This results in three transitions from which three unknowns can be extracted: e^2Qq, η, and the sign of q.

For I = 2 or greater, there are two or more allowed transitions from which e^2Qq and η can be determined directly. Comparison of spectra recorded with and without a magnetic field allows determination of the sign of q.

Read:

Ebsworth	pp 130 - 136
Drago	pp 607 - 612; 618-620

Do Problems (p. 624) 2, 6, 7, 8, 9

Problem 10: ^{14}N lines of pyridine at 3.90 and 2.95 MHz.

If $\eta = 0$, there would be one line at $(3.90+2.95)/2 = 3.42$ MHz

Therefore $h\nu = 3.42h = \frac{3}{4}(e^2Qq)$

$e^2Qq/h = 4(3.42)/3 = 4.56$ MHz

From above equation the separation between the two lines $(3.90-2.95 = 0.95 \text{ MHz}) = \frac{1}{4}e^2Qq(2\eta) = \frac{1}{2}\eta(4.56)$

$$\eta = 2(0.95)/4.56 = 0.42$$