This proposal is essentially to study the induced field distributions within the magnetized specimen and the factors, which determine the distribution patterns. This proposal envisages studies on two aspects of the induced field distributions within magnetized materials. This would enable the resolution of the manifestations in spectra. The magnitudes of contributions to induced fields and the corresponding anisotropies can account for a "shift" in the line positions, which are usually associated with chemical shifts. On the contrary, the distribution of induced field can also result in line-shape variations. Then, what would be the consequences due to the variety of spin space and coordinate space averaging for line narrowing for purposes of Shielding tensors particularly for HR PMR in solids. Will all such efforts cumulatively further enhance the resolutions obtainable? If the chemical shift tensors are experimentally determined unequivocally, then to the extent the theoretical (quantum chemical) calculations can yield, the shielding mechanisms can be discerned for the benefit of electronic structure information.

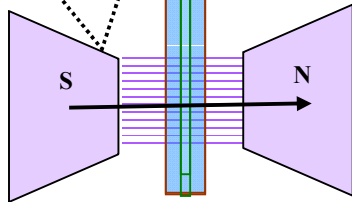Photographs sent by BrukerBioSpin during the course of correspondences after the purchase

Aspect-1:

The induced field distributions are dependent on the equations, which depend on the coordinate space parameters. And, the factors occurring in the equation have precisely the same functional dependences which get averaged in the case of magic angle spinning [MAS] for line narrowing in solids where in it is essentially the chemical shift anisotropy & dipole-dipole interactions among the spins which are sought to be averaged. Hence, the effect of MAS on the induced field exclusively could be sometimes trivial consequences. However, in some context the same would require explanations by calculating the induced field distributions within the medium. The descriptions in the following pages explain the principles of the basic phenomenon, by which, in NMR, paramagnetic shifts are measured in a pure liquids surrounded by a paramagnetic solution with a larger paramagnetic susceptibility. *Even though this phenomenon is used in the studies in inorganic chemistry, the full implication of the context has not been comprehended yet*. In particular, the above situation is to be prominently emphasized in view of the availability of variety of magnetic field strengths and the probes for the techniques like the spinning of samples oriented at Magic angle w.r.to the direction of applied magnetic fields. The variations in the observed shifts due to the variation in the available magnet configurations and the NMR probes seem worth studying from the point of view of (i) the calculation of the induced fields described by this applicant in the following Webpage: http://www.geocities.com/inboxnehu_sa/nmrs2005_icmrbs.html , (ii) the results obtained as in http://saravamudhan.tripod.com/csir_schm_sa/id22.html and, (iii) the results of calculations as reported in the website http://nehuacin.tripod.com/ . In particular, noting the discussions in the 4th Alpine Conference on SSNMR reported at http://nehuacin.tripod.com/id3.html makes it an interesting study trying to experimentally verify the various consequences of size and shapes of macroscopic specimen on the induced field distributions within the specimen.
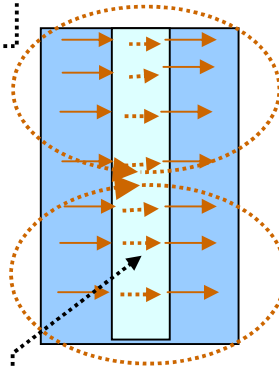
For the construction of a probe, a design to enable the detection of NMR signal near the criticalities of the validity of selection rules is described. The availability of a probe with such features would pave the way for designing experiments with the probe specifically to follow the trends of induced field distribution patterns within the specimen in a more detailed manner.

An explanation of the observations reported earlier in the contexts of the (a) Advanced NMR Instruments available at High Field (b) Construction of the MASS probe to be completed (c) All the efforts of this PI in evolving a simple procedure for calculations of induced fields in the contexts of magnetic resonance parameters (page# 5 to9)
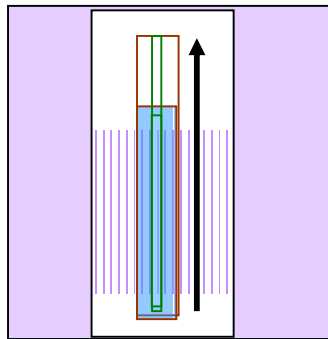
FASS Probes: Fixed Angle Sample

spinning probes:
Only perpendicular-to-the-magnetic field
Configurations **(a) & (b)** below

FASS coils: (a)
Electro Magnet Systems and
Permanent Magnets:
(up to 100Mhz Proton NMR
frequency)

S   N

Field at the inner
capillary water

Applied field + the
induced field
FASS (a)

VASS Probes: Variable Angle Sample Spinning Probes.

By construction in these
probes the sample can be
inside a coil whose solenoidal
axis can be changed in
orientation from Parallel to the
magnetic field gradually to
perpendicular to the field.
Mostly the probe heads for
Supercon Systems have the
MAS versions.
Below is an illustration of how
the same coil can be rotated to
have different angles with
magnetic field direction.

MAS satator with
coil for which this
assembly was
imported from
Bruker

Parallel to Field
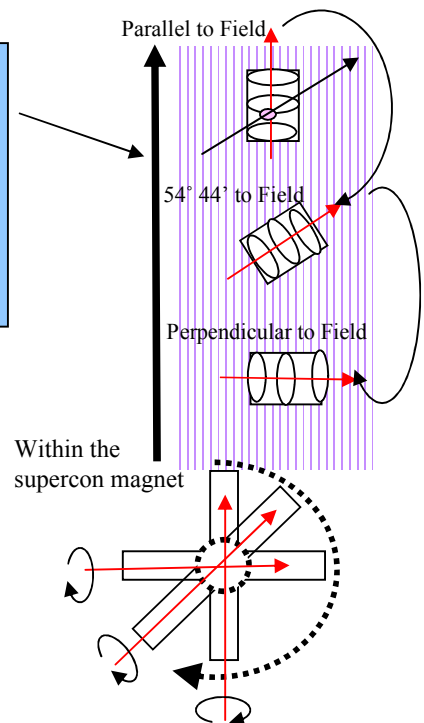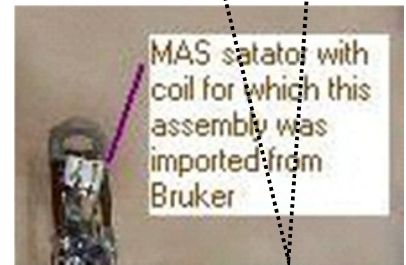
54° 44' to Field

Perpendicular to Field

FASS Coils (b)
Superconducting [Supercon]
Magnet Systems : 200 MHz
and onwards up to currently
highest value of 900 MHz
proton NMR frequency

Field at the inner
Capillary water

Applied field ▬ the induced
field **FASS (b)**

Within the
supercon magnet

An explanation of the manifestations in the spectra when the magnetic configuration with respect to laboratory axes changes; consequences of induced fields for the variations in relative dispositions of sample coil and magnetic field directions

$$H\upsilon_{Res} = g\beta H_{Res}$$

υ_{Res} = Resonance Frequency is held fixed. [Consider the Resonance of Capillary water for different contents in the outer tube surrounding that capillary.
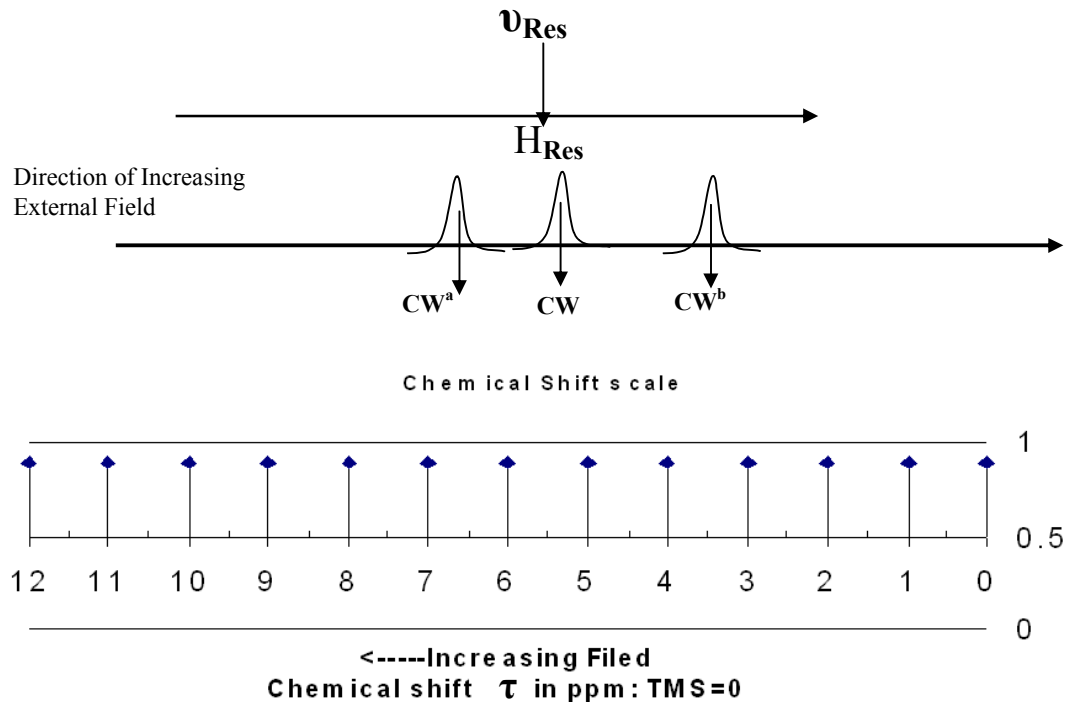
H_{cw} stands for the resonance field for the Capillary Water when no paramagnetic material is placed in the outer tube. This means $H_{Res} = H_{cw}$

For FASS (a) the induced field [due to the paramagnetic substance in the outer tube] adds to the Field experienced by the Capillary Water. Hence the field at Capillary would be more than what the value was without paramagnetic substance:

$$H_{cw}{}^a = H_{cw} + \Delta H^a{}_{induced}.$$

That is $H_{cw}{}^a > H_{cw}$; this would require externally adding a field "- $\Delta H^a{}_{induced}$" to bring the field at the capillary to the required resonance value for υ_{Res}. Or as the field value is slowly scanned near resonance, the resonance can be observed only at an external field value lower than the previous filed value.
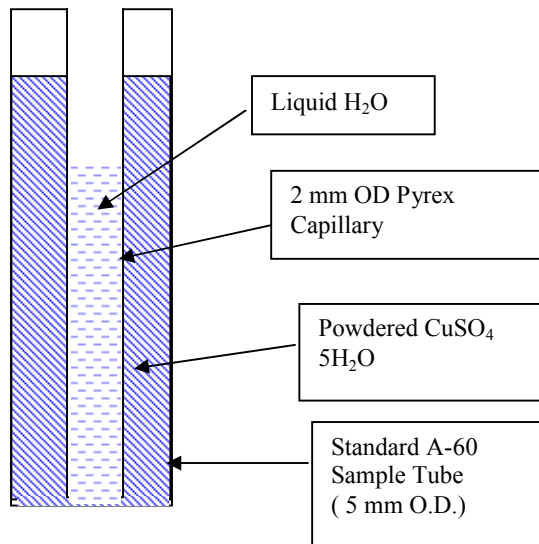
CW

Chemical Shift scale

<-----Increasing Filed
Chemical shift τ in ppm: TMS=0

For the context of current efforts of Aspect-1 a consideration of the published NOTE from literature:
These aspects though conspicuous, are not a matter routinely taken note of for the awareness of the spectacular trends due to the revolution which technology brings about in the instrumentation and the spectrometer capabilities.
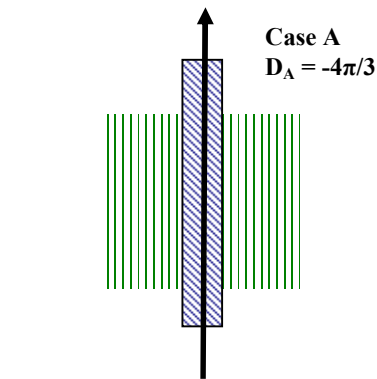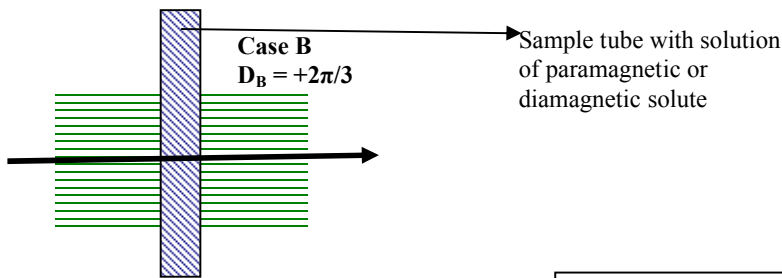A60 NMR Spectrometer is of the type, which comes under the systems with Electromagnets, which can be categorized under the **FASS (a)** probe systems. The author used a sample tube with inner

capillary within a sample tube of 5mm OD. When Coppersulphate-pentahydrate powder sample is filled in the outer tube, the water sample inside the capillary recorded a downfield shift (a direction towards the TMS reference) of 90 Hz from the water sample, which was not surrounded by Copper Sulphate powder. This was conclusively a 1.5 cgs / Hz of susceptibility value measure for the copper sulphate.

Liquid H_2O

2 mm OD Pyrex Capillary

Powdered $CuSO_4$ $5H_2O$

Standard A-60 Sample Tube (5 mm O.D.)

This corresponds to the FASS (a) configuration for the Magnetic Filed Direction, Sample coil Axis and the Spinning axis of the sample tube.

For $CuCl_2$ and $CuBr_2$ 27.2 x 10^{-6} cgs units and 14.1 x 10^{-6} cgs units are the volume susceptibility values measured with respect to $CuSO_4$ $5H_2O$ by these experiments.

Case B
$D_B = +2\pi/3$

Sample tube with solution of paramagnetic or diamagnetic solute

Case A
$D_A = -4\pi/3$

The demagnetization factor, for an infinitely long cylinder (ellipsoid), when the filed is applied parallel [**Case A ;** Supercon magnet systems above 100 MHz] to the cylinder axis is **0.0000.** Then the effective Demagnetization inside a Lorentz Cavity in this sample would be
$D_A = 4\pi. \{0.0- (1/3)\} = -4\pi/3.$
For **Case B (**electro magnet or permanent magnet systems at and below 100 MHz**), $D_B = 4\pi. \{1/2-1/3) = 4\pi /6 = +2\pi/3$**.

For Paramagnetic Samples the Susceptibility values are **+ve** and for diamagnetic samples the susceptibility values are **–ve.** This implies that the induced fields will be along the direction of the external

magnetic field for paramagnetic systems. For purposes of NMR the shifts are measured with respect to a reference

and the correction is given by $\delta_{A, B} = D_{A, B} \{\chi^{ref} - \chi^{sample}\}$. The χ^{ref} is for the diamagnetic (-ve susceptibility values << paramagnetic +ve Susceptibility values) substance inside the capillary. Hence for a DPPH solution (paramagnetic) δ_A will be negative and hence downfield from reference; δ_B will be positive and up field to the reference peak.

A careful scrutiny of this situation would indicate the differences from the induced fields within a *capillary of pure liquid inside this solution* in the sample tube. These points as above are to be appreciated for explaining the experimental measurements reported in the article entitled: *"Bulk Susceptibility Corrections in Nuclear magnetic Resonance Experiments Using Superconducting Solenoids"* by D.Live and S.I.Chan, **Analytical Chemistry,** Vol.42, No.7, pages 791 &792 (1970).

Relevance of the above descriptions on demagnetization effects can be found at the following URLs of this E.S.
http://nehuacin.tripod.com/id3.html
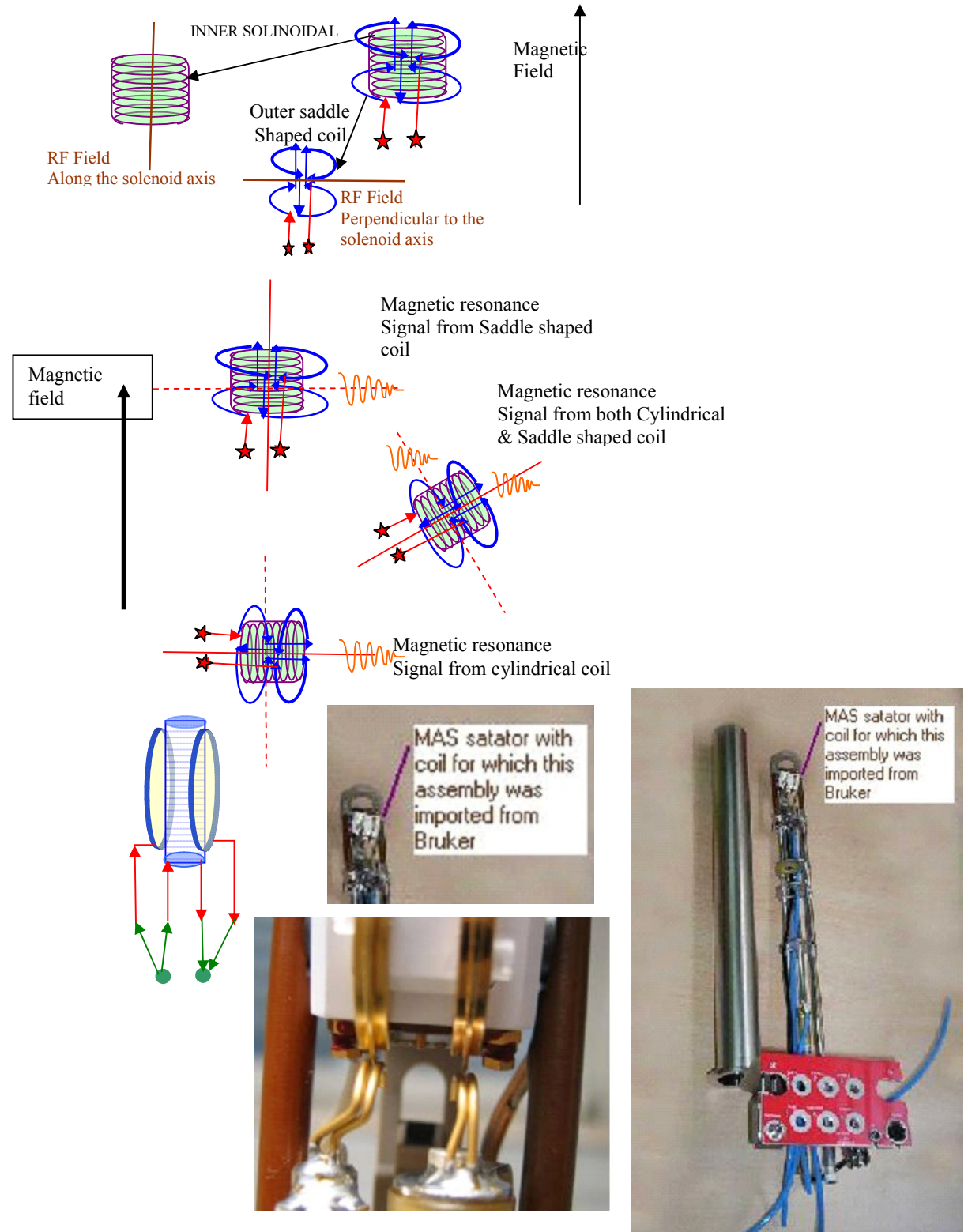http://nehuacin.tripod.com/pre_euromar_compilation/

The spectra till now obtained at several institutions where FT NMR facilities are available indicate that an extra effort has to be put in to setup the spectrometer conditions for acquisition of spectra in the absence of a deuterium signal to secure a field frequency lock. Spectra could be acquired without field frequency locking in most of the spectrometer systems (Bruker, 200,300. Jeol 400Mhz, 60MHz and Varian 600MHz, 400MHz, 90MHz). The required trends for the shifts due to paramagnetic outer sample could be observed for a inner capillary water sample using the standard 5mm NMR sample tubes. This preliminary effort was necessary because the first observation of this type was reported with one of the early Varian A60 spectrometer and subsequently with 100MHz and 200MHz spectrometers. The usage of the possible variation of angles with VASS probes is a significant feature in this proposal. The induced field calculations reported by this author in various conference/symposia till now by this author would require a few experiments to be carried out to prove its utility and applications in the context of NMR. http://nehuacin.tripod.com/id1.html

<u>Probe design for</u> construction *With reference to the possibility of the coil axis parallel and perpendicular to the Magnetic Field direction in the MASS probe (within a supercon system) the following are to be considered as further developmental considerations for the instrumentation.*
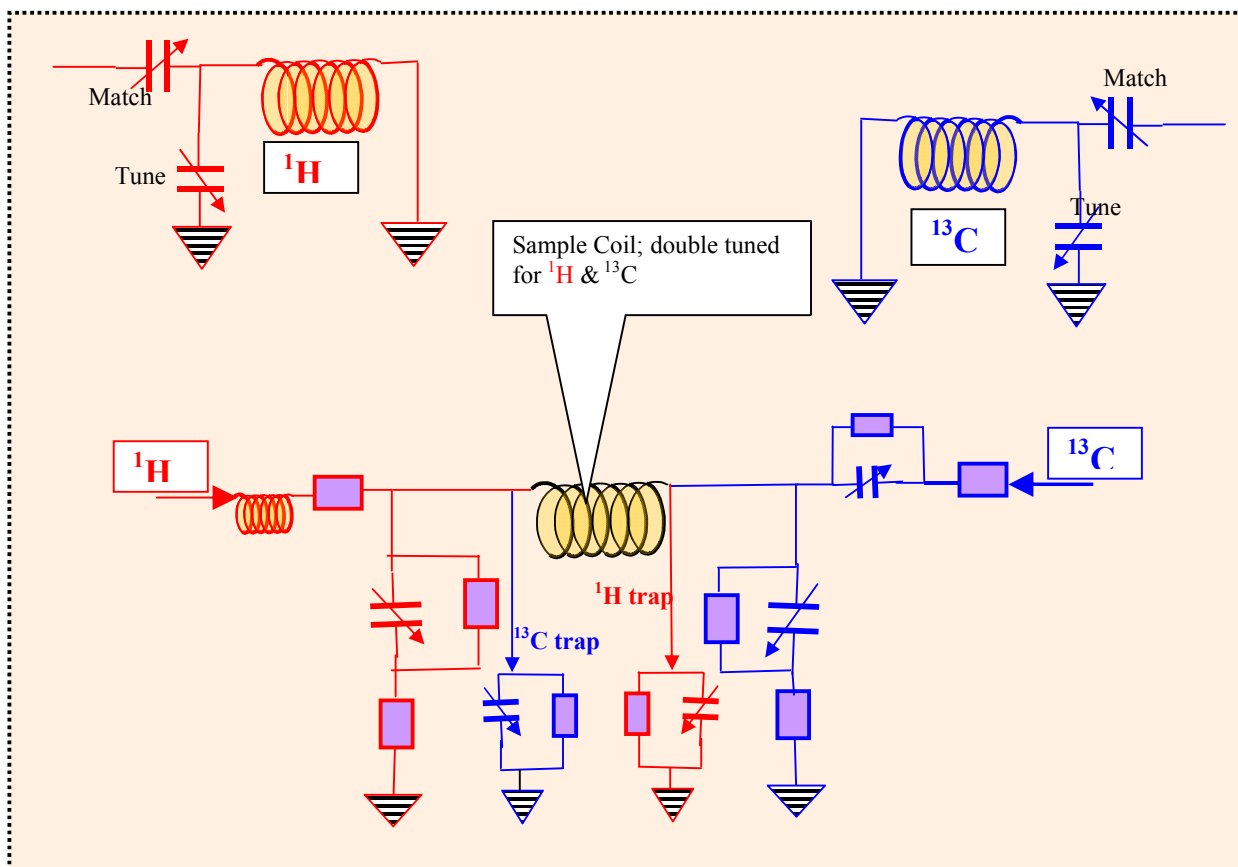
Since for the coil axis parallel to the field direction, "**No Magnetic Resonance signal**" could be detectable because of the requirements of selection rule the following are the novel experiments to be considered. (1) Since a slight angle (small angle with respect to magnetic field direction) of tilt, from the totally parallel orientation, would have a small XY component of the RF field (with Z as the magnetic field direction) , there could be induced rotating magnetization cutting the coil axis. If the pulse is applied with off-parallel orientation, and (mechanically) the coil is set to parallel orientation "within the T_2 time scales," then, there would be NMR signal even while the coil axis is parallel to the magnetic field. Can this become demonstrable? And, what would be the significance of such a NMR signal obtained while the sample coil axis is parallel to the magnetic field?. Can a pulse scheme be thought of for a coherent manipulation in spin space equivalent to the special angle rotation of the coil axis from near zero to exact zero?
2. Alternately, is it possible to have a double resonance type of arrangement where there is a solenoid sample coil and surrounding the Hemholtz coil configuration whose axis is perpendicular to the other solenoid? And when the first coil axis is parallel to the magnetic field, the other will have a perpendicular orientation and can be used to excite and detect the signal of the same sample, which the

first coil also surrounds. The sample filling factor and signal to noise considerations could be different and hence the sensitivity

INNER SOLINOIDAL

Magnetic Field

Outer saddle Shaped coil

RF Field
Along the solenoid axis

RF Field
Perpendicular to the solenoid axis

Magnetic resonance
Signal from Saddle shaped coil

Magnetic field

Magnetic resonance
Signal from both Cylindrical & Saddle shaped coil

Magnetic resonance
Signal from cylindrical coil

MAS satator with coil for which this assembly was imported from Bruker

MAS satator with coil for which this assembly was imported from Bruker

What would be the optimum configuration and values of inductances o f the two coils, to connect them as effectively a single coil to the transmitter-receiver of the spectrometer console.

Match

Tune

^1H

Sample Coil; double tuned for ^1H & ^{13}C

Match

^{13}C

Tune

^1H

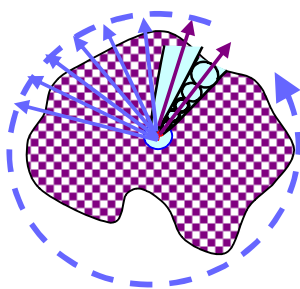^{13}C

^{13}C trap

^1H trap

Aspect-2:

This aspect arises because of the results reported by this Investigator in the conferences cited below with the relevant excerpts:

EUROMAR2007 Abstract/   http://nehuacin.tripod.com/id4.html

Such consideration would make it possible to envisage a protocol of procedure to extract the intra molecular Shielding Tensor Parameters of Protons in organic molecular single crystal by the HR PMR techniques in solids.
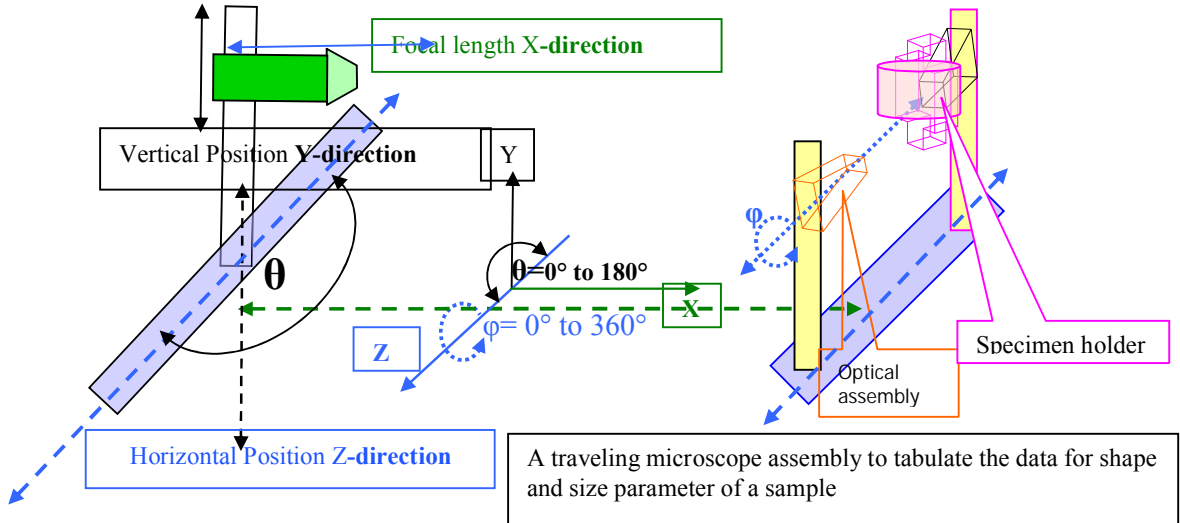
ICS_FDNMR: http://nehuacin.tripod.com/id6.html

With the help of an optical Goniometer and a Traveling microscope, it should be possible to measure the sets of r,θ,φ values conveniently define the specimen shape with respect to a internal coordinate reference frame, even though an analytical equation may not be possible. Since it is only a question of finding appropriate 'n' (number of dipoles for given polar coordinates, the task of arbitrary shape can be within the realms of calculation by this summation procedure.

1. Define φ to be equal to zero, for the disposition of ZX plane above.
2. Every setting along the vertical Y-axis would define the parallel set of [1 N_y 1 / 'ZX'] planes, every setting along the y-axis at equal intervals (convenient & arbitrary) counted sequentially by serial index N_y = 0,1,2,3,4…. and this sampling is made as much smaller an interval value as possible.
3. At each 'N_y' value (corresponding to that assigned y coordinate) sampling along the X-axis, at equal intervals serially from left to right with index N_x = 0,1,2,3,4… would result in recording at specified X-coordinates, and from the focal length for the give setting of x,y would result in the z-coordinate.
4. Thus a table of x,y,z can be constructed for φ = 0
5. These are (x,y,z) values with origin(0,0,0) located outside the specimen, and a transformation, shifting of origin can be effected to get these set of values (x,y,z) with respect to an origin located inside the specimen.
6. With respect to the internal location of the origin, and using the same disposition for the coordinate axes directions, the following identities can be used to get a set of polar coordinates.
   $x = r \cdot \sin(\theta) \cdot \cos(\varphi)$; $y = r \cdot \sin(\theta) \cdot \sin(\varphi)$; $z = r \cdot \cos(\theta)$
7. The measurements can be similarly made for other values of 'φ'. Depending on how regular (non-ellipsoidal) shape and what symmetries are conspicuous for the shape, the values of 'φ' can be chosen. For example in certain shapes, a measurement for φ = 0°, 90° would suffice to describe the macroscopic shape in terms of the set of r, θ, φ values.
8. Then the 'complete' set of θ, φ values thus measured at experimentally convenient mesh of sampling may have to be subjected to a smoothening appropriately, define 'complete' set of values to be able to describe the close packing criterion for calculation by the summation procedure.

What are the optimum orientations? ; And, how many samples are required to get the morphological details without losing information on the shape factors is a matter of concern similar to the Concerns in the article in Advances in Magnetic Resonance, Vol. (?), Academic Press, year? by **John A Weil** (*Reference No.7* (?) listed in "Pyromellitic Acid…….Proton Shielding", S.Aravamudhan, U.Haeberlen, H.Irngartinger and C.Krieger, Molecular Physics, 38, 241 (1979)

The above is intended to take into account comprehensively the (continuum) bulk susceptibility contributions at given proton site, which along with the (discrete) intermolecular near neighbor contributions gets added on to the **INTRA MOLECULAR** shielding tensor, while obtaining the Proton Shielding Tensor parameters by a measurement on Single Crystal specimen by the Multiple Pulse Line Narrowing Technique.

A traveling microscope assembly to tabulate the data for shape and size parameter of a sample

An outlook for the future trends of this research proposal

Line Shapes in Magnetic Resonance and the Average Static Magnetic Field at a Site: The Role of Discreteness and Continuum within the Material

When there are no time averaged fields (**1**) to be accounted for, then, within the materials it is the totality of the static fields at every one of the sites [distributed within the material] which manifests in a magnetic resonance spectrum. This essentially implies the spatial distribution of the static magnetic field which contributes to the line shape. Since the discreteness of the contribution from adjacent sites [to be resulting in a summed up total contribution], depends on the nature of material constituents within a small range of distance compared to the macroscopic extent, this contribution can be obtained as a calculated sum for a typical site within the material, [this can be taken to be the Contribution from within Lorentz Sphere (**2**)] and further considered to be the same for every one of the sites in a homogeneous medium. But the contribution from the remaining bulk of the material could be much more difficult to track and estimate at each site by the methods known till now (**3**) particularly when the material has such shapes to be causing inhomogeneous induced field distributions even in a homogeneous medium. The methods, used since early days to calculate demagnetization factors, make evident the kind of complications that arise in estimating induced fields within material specimen of arbitrary shapes. All these complications in estimating the induced field distributions and analyzing the observed patterns in spectra, require stringent experimental conditions for implementing certain techniques for their obvious utilities. The case of HR PMR studies in single crystals for determining molecular shielding tensors is such a complication which required invariably making single crystal spheres from single crystals of every organic molecular systems of interest (**4**). There have been efforts to device rapid computational methods to calculate such induced field distributions within materials (**5**).

It has been possible, since recently, to evolve (**6**) a simple summation approach to calculate induced fields within a material which can reproduce the known, standard demagnetization factors with comparable accuracy. This method seems capable of simplifying the procedure to estimate the induced fields within the material [and, even outside a magnetized material (**7**)] and provides a diversion to circumvent the necessities to be considering an "average field" as being represented by the calculated values. This method has been described (**8**) earlier with an enumeration (**9**) of the associated advantages. The impact of these results can be effectively enunciated with specific reference to the analysis of line shapes of magnetic resonance spectra of materials.

(**1**) W.C.Dickinson, Phys. Rev., **81**, 717 (1951). (**2**) S.Aravamudhan, Ind. J. Phys., **88**, 985 (2005). (**3**) G. Mozurkewich, H.I.Ringermacher, and D.I.Bolef, Phys. Rev. B, **20**, 33 (1979)

(**4**) http://www.geocities.com/saravamudhan1944/eenc_ampere_lille.html

(**5**) P. Vallabh Sharma, Pure Appl. Geophys., **64**, 89 (1966)

(**6**) http://nehuacin.tripod.com/pre_euromar_compilation/id7.html

(**7**) http://saravamudhan.tripod.com/id6.html

(**8**) Poster Sheet_7 to Sheet_10 at http://www.geocities.com/inboxnehu_sa/nmrs2005_icmrbs.html

(**9**) Sheet_11 at http://www.geocities.com/inboxnehu_sa/nmrs2005_icmrbs.html

This Investigator has contributed to the National symposia of Indian Biophysical Society and International Biophysics Congresses where in the possible applications of Chemical shift Tensors (aromatic ring current shifts) and the Induced Fields in the context of paramagnetic shift reagents in MRI experiments have been considered. The PI has published to the Internet an article on NMR entitled: NMR as a Tool for Structure Determination which can be displayed at the URL: http://www.geocities.com/saravamudhan2002/nmr_article.html . In addition a consideration of the NMR techniques in the context of standardizing the medicinal plants and an initiative would be made to contribute an appropriate article on the use of solid state NMR techniques: http://www.geocities.com/inboxnehu_sa/Proj_bicnehu.html . A progress is being made to envisage curricular requirements for facilitating an appreciation of advanced aspects of Magnetic Resonance in early enough stages of the post graduate level courses http://www.geocities.com/saravamudhan1944/ugc_inno_proposal.html

http://www.geocities.com/inboxnehu_sa/conference_events_2005.html
http://www.geocities.com/inboxnehu_sa/conference_events_2006.html