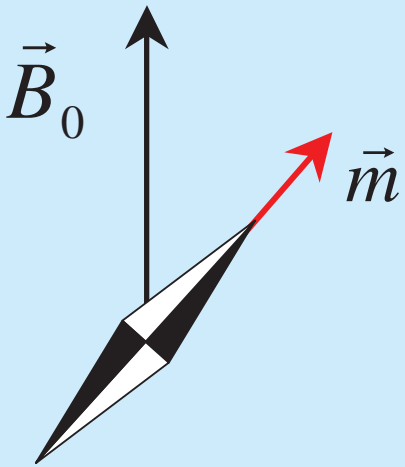
Ressonância Magnética Nuclear

Prof. José Schneider

IFSC

O que é a Ressonância Magnética Nuclear?

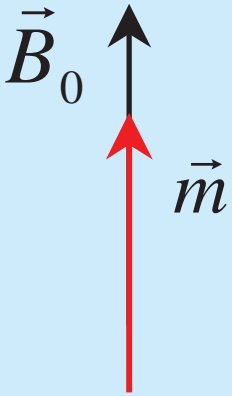
Momento magnético na presença de um campo



$\vec{m}$: Momento de dipolo magnético

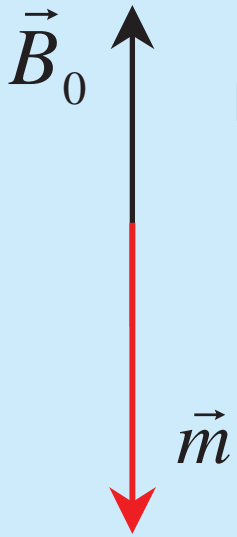
Energia potencial magnética:

$$E_{MAG} = -\vec{m} \cdot \vec{B}_0$$



Estado paralelo:
Mínima energia

$$E_{MAG} = -m\,B_0$$



Estado anti-paralelo:
Máxima energia

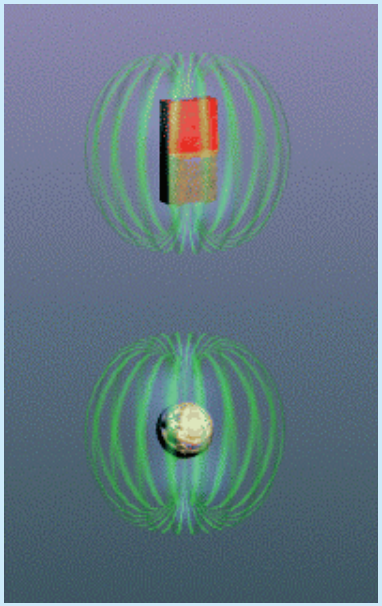
$$E_{MAG} = m\,B_0$$

Diferença de energia : $\Delta E_{MAG} = 2\,m\,B_0$

Spin

As partículas materiais possuem:

- Massa
- Carga elétrica
- Momento magnético ⇔ "Spin"



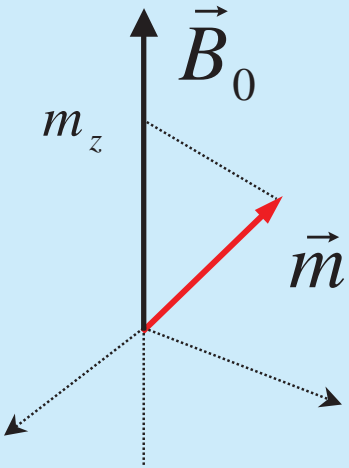
Spin = Momento angular intrínseco

Partículas com momento magnético:

- Elétrons (RPE)
- Prótons
- Nêutrons
- *Núcleos atômicos (RMN)*

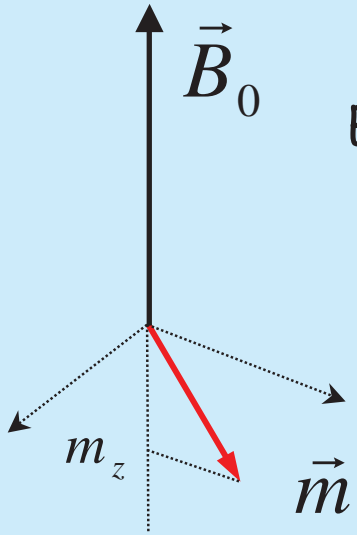
Física Quântica:

- O spin é uma grandeza física quantizada (I = 0, 1/2, 1 , 3/2,...).
- As orientações possíveis para o vetor momento magnético são limitadas.
- Para I = 1/2 : duas orientações



Estado "paralelo":
Mínima energia

$$E_{MAG} = -\, m_z\, B_0$$

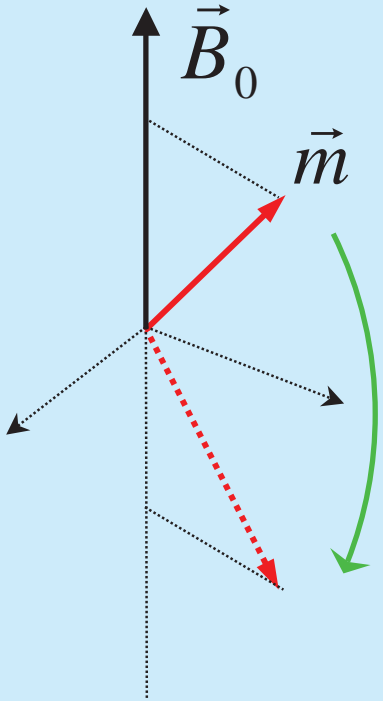


Estado anti-paralelo:
Máxima energia

$$E_{MAG} = m_z\, B_0$$

Diferença de energia : $\Delta E_{MAG} = 2\, m_z\, B_0$

Transições



Física Quântica:

A transição entre estados acontece somente quando é entregue <u>exatamente</u> a energia ΔE_{MAG}

$$\Delta E_{MAG} = 2\, m_z\, B_0 = 2\left(\gamma \frac{h}{2}\right) B_0$$

$$\boxed{\Delta E_{MAG} = h\, \gamma\, B_0}$$

h : Constante de Planck = 6,63 10^{-34} J.s (unidades de momento angular)

γ : Constante dependente da espécie de núcleo

B_o : Campo magnético

Absorção Ressonante: Quantum de energia

Física Quântica:

A energia eletromagnética é absorvida/emitida em múltiplos discretos do *quantum*:

$$\boxed{E = h\,f}$$

h : Constante de Planck

f : Freqüência de oscilação dos campos eletromagnéticos (Hz)

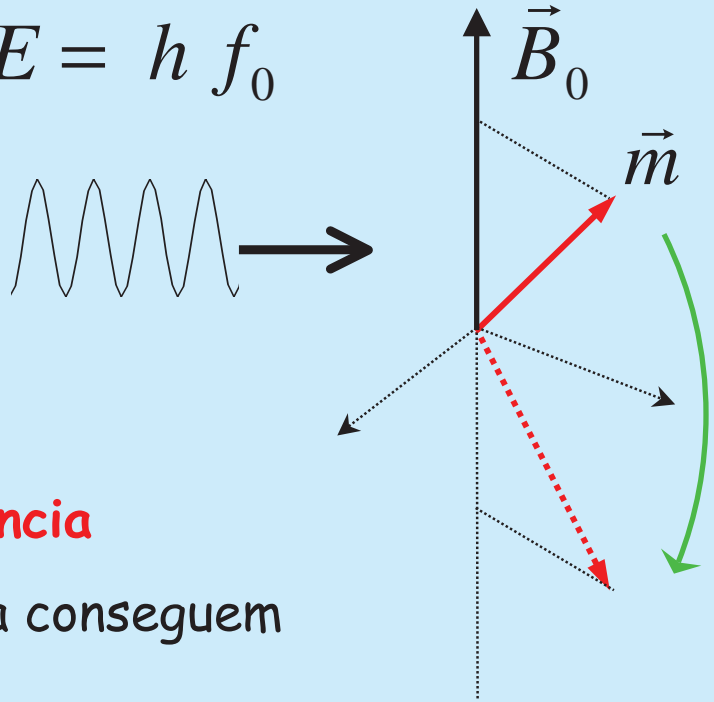
E: Energia de um fóton

Absorção/Emissão Ressonante

$$\Delta E_{MAG} = h\,\gamma\,B_0 \qquad E = h\,f_0$$

Se $E = \Delta E_{MAG}$

então: $\boxed{f_0 = \gamma\,B_0}$



f_0 : Freqüência de ressonância

Unicamente fótons com esta energia conseguem produzir uma transição.

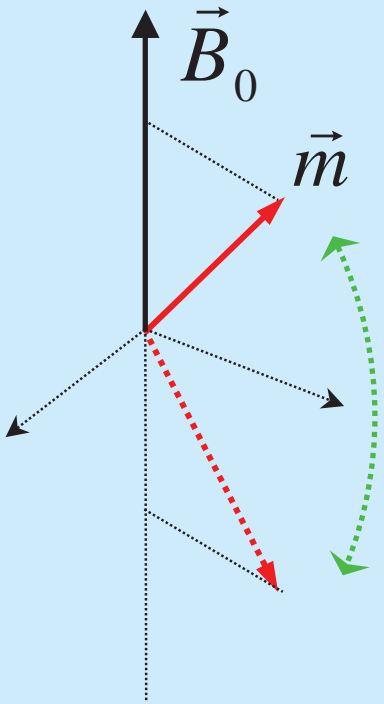
f_0 na faixa dos MHz:

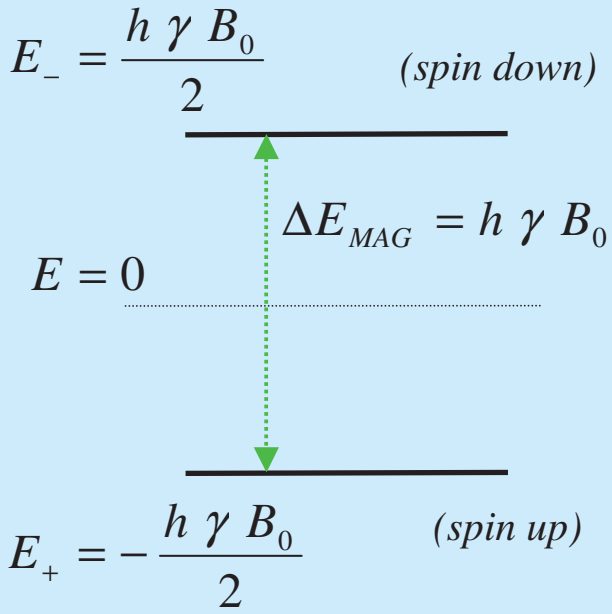
Radio-freqüências

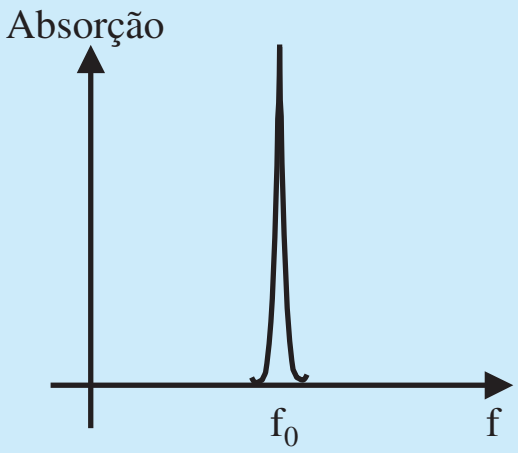
Isótopo	f_0 [MHz]	Abundancia Natural [%]
^{1}H	425.5769	100
^{13}C	107.002	1,1
^{17}O	57.772	$3{,}7\ 10^{-2}$
^{23}Na	112.62	100
^{29}Si	84.58	4,7
^{31}P	172.36	100

(B_0 = 10T)

Ressonância Magnética Nuclear



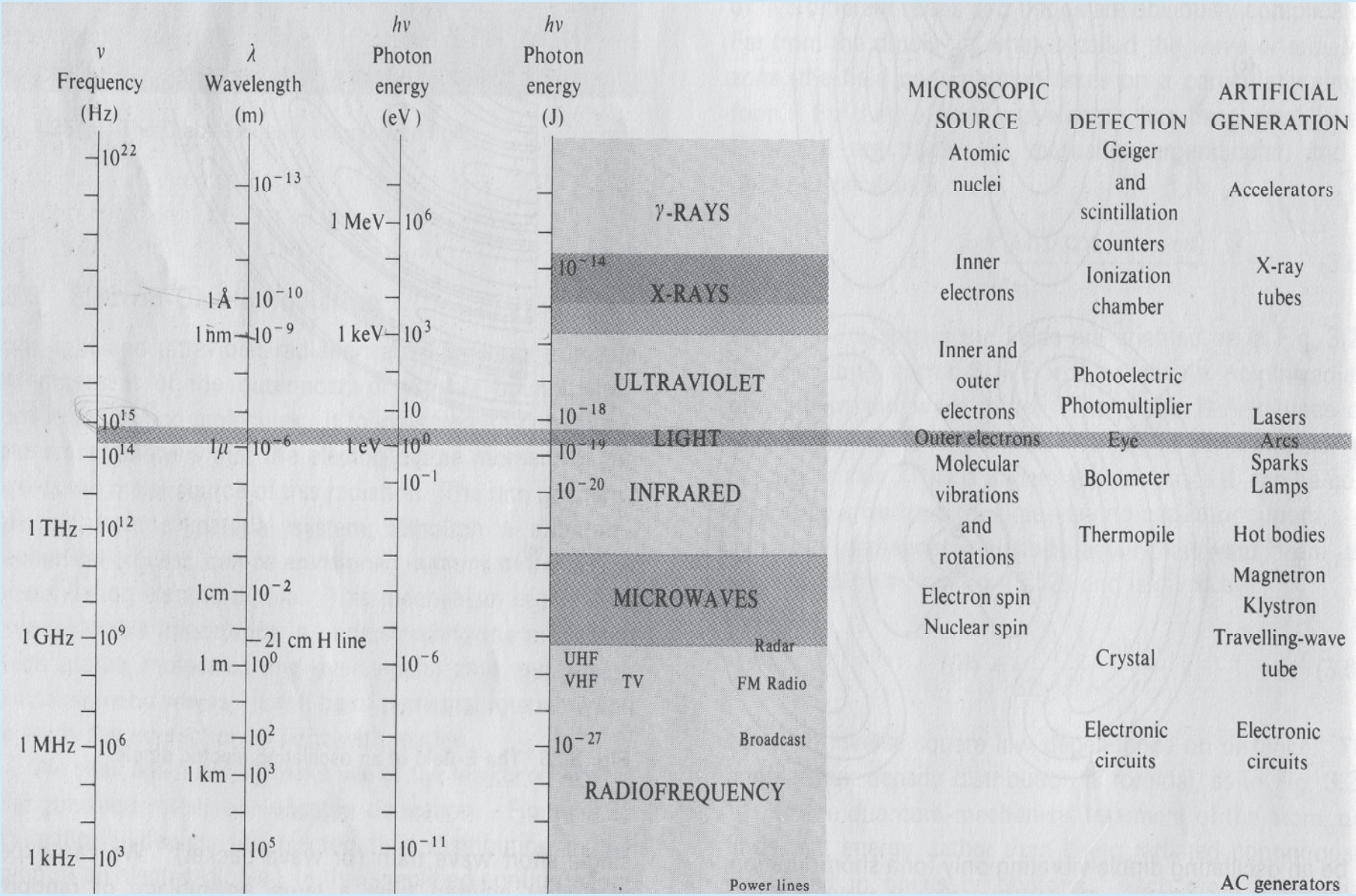




Espectro de RMN:

Representação da absorção de energia em função da freqüência.

Espectro eletromagnético



Técnicas Espectroscópicas

Espectroscopia	Freqüências	Informação:
RMN	~10×10^6 to 900×10^6 Hz	Campo magnético no núcleo
RPE	~1×10^9 to 30×10^9 Hz	Campo magnético nos elétrons
Microondas	~1×10^9 to 600×10^9 Hz	Rotações moleculares
Infravermelho	~6×10^{11} to 4000×10^{11} Hz	Vibrações e oscilações das ligações atômicas
Visível/Ultravioleta	~7.5×10^{14} to 300×10^{14} Hz	Níveis de energia dos elétrons mais externos
Mössbauer	~3×10^{16} to 300×10^{16} Hz	Níveis de energia dos elétrons mais externos Níveis de energia no núcleo

RMN: Quem e quando

The Nobel Prize in Physics 1943

"for his contribution to the development of the molecular ray method and his discovery of the magnetic moment of the proton"

Otto Stern

USA

Carnegie Institute of Technology
Pittsburgh, PA, USA

b. 1888
(in Sorau, then Germany)
d. 1969

The Nobel Prize in Physics 1944

"for his resonance method for recording the magnetic properties of atomic nuclei"

Isidor Isaac Rabi

USA

Columbia University
New York, NY, USA

b. 1898
(in Rymanow, then Austria-Hungary)
d. 1988

The Nobel Prize in Physics 1952

"for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith"

Felix Bloch

1/2 of the prize

USA

Stanford University
Stanford, CA, USA

b. 1905
(in Zurich, Switzerland)
d. 1983

Edward Mills Purcell

1/2 of the prize

USA

Harvard University
Cambridge, MA, USA

b. 1912
d. 1997

http://nobelprize.org/physics/

Sendo que a freqüência de ressonância é

$$\boxed{f_0 = \gamma B_0}$$

Então para que serve a RMN?

Espectroscopia por RMN

Os núcleos interagem com o campo magnético *total*:

$$B_{Total} = B_0 + B_{Local}$$

Origem do campo local:

- correntes eletrônicas ao redor do núcleo
- momentos magnéticos de núcleos vizinhos

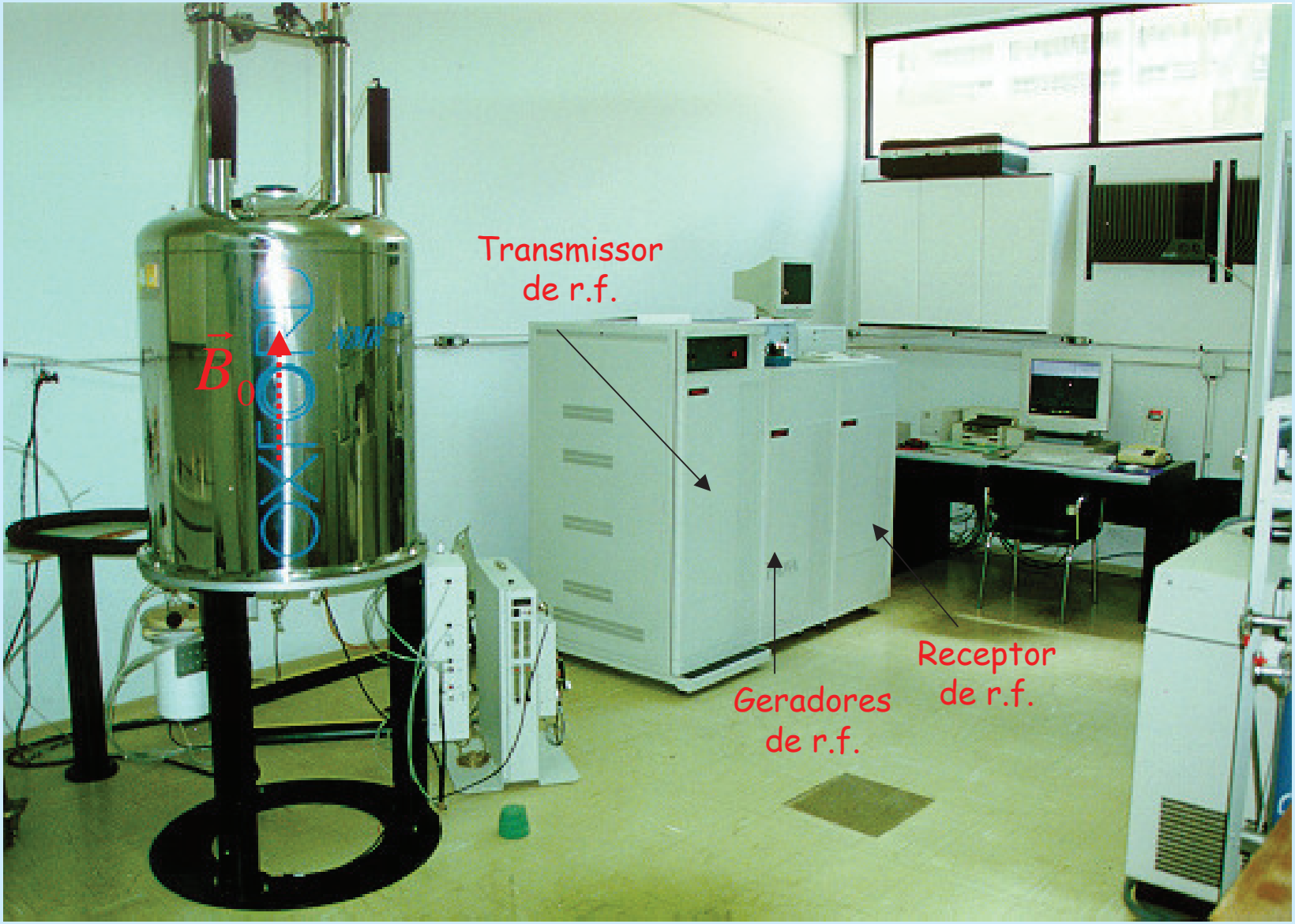
$$B_0 >> B_{Local}$$

A freqüência de ressonância depende do campo local!

$$\boxed{f_0 = \gamma\, B_{Total} = \gamma \left(B_0 + B_{Local}\right)}$$

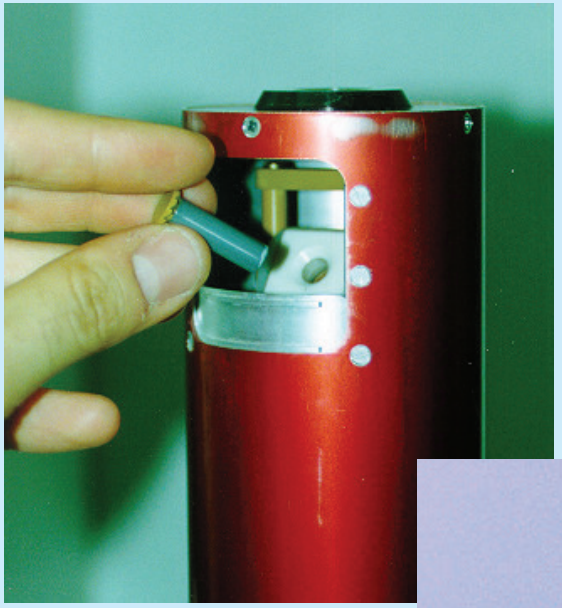
O espectro de RMN contem informação da vizinhança atômica do núcleo estudado

Espectrômetro de RMN

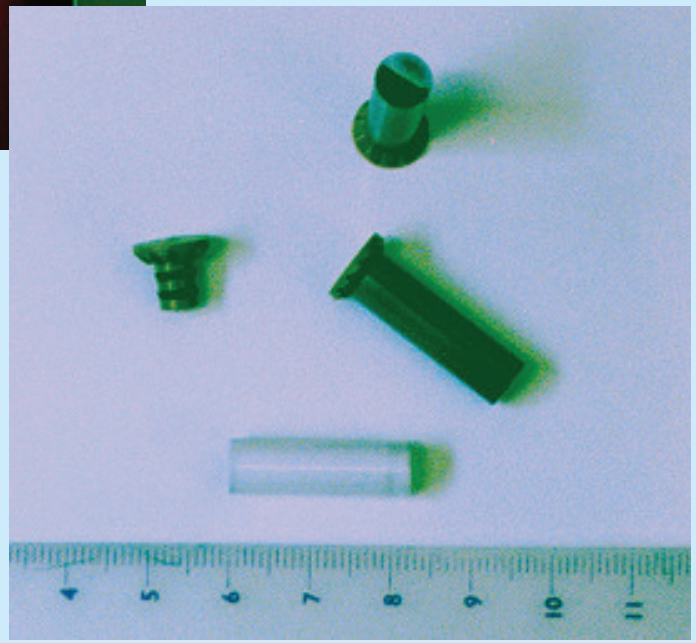


Espectrómetro de RMN (9.4Tesla, 400MHz)

Magneto superconductor vertical

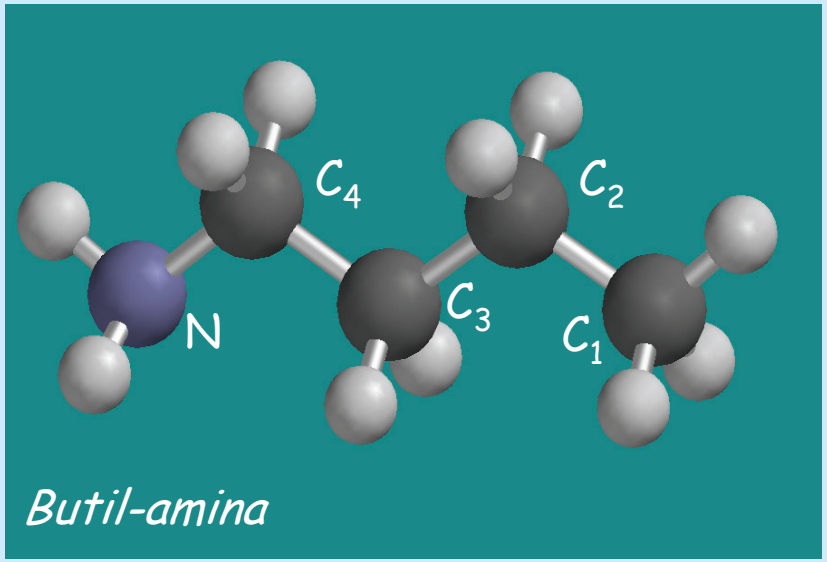


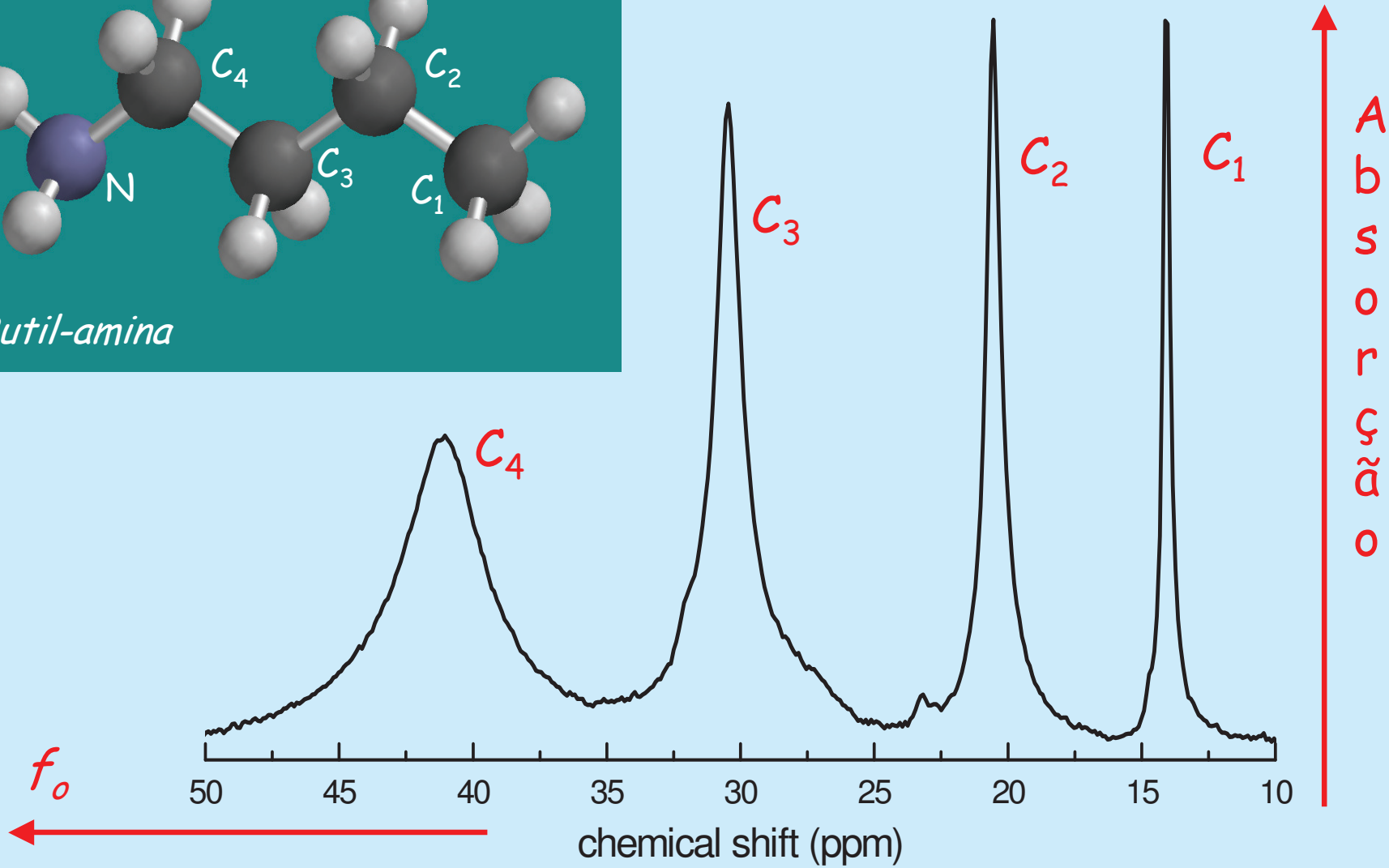
Sonda de RMN



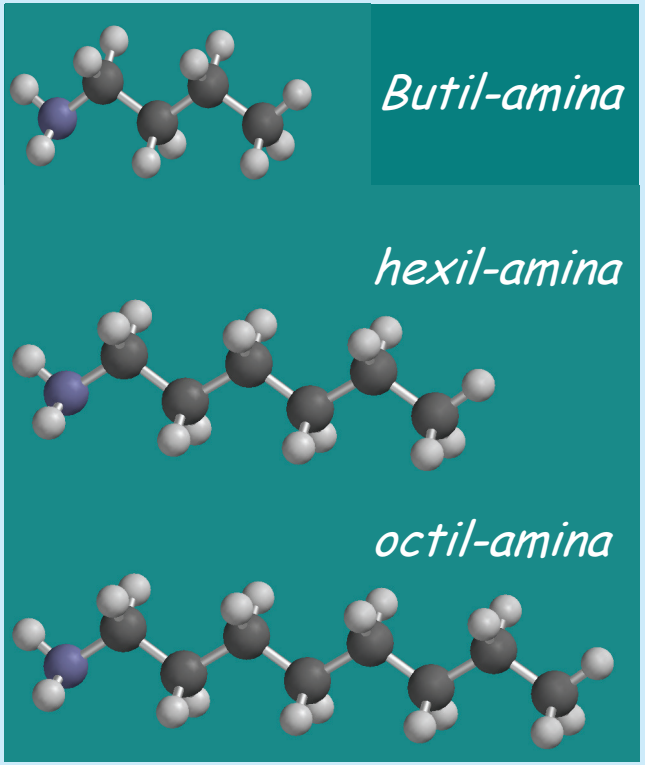
Porta-amostras de RMN: Zircônio e nitreto de silício

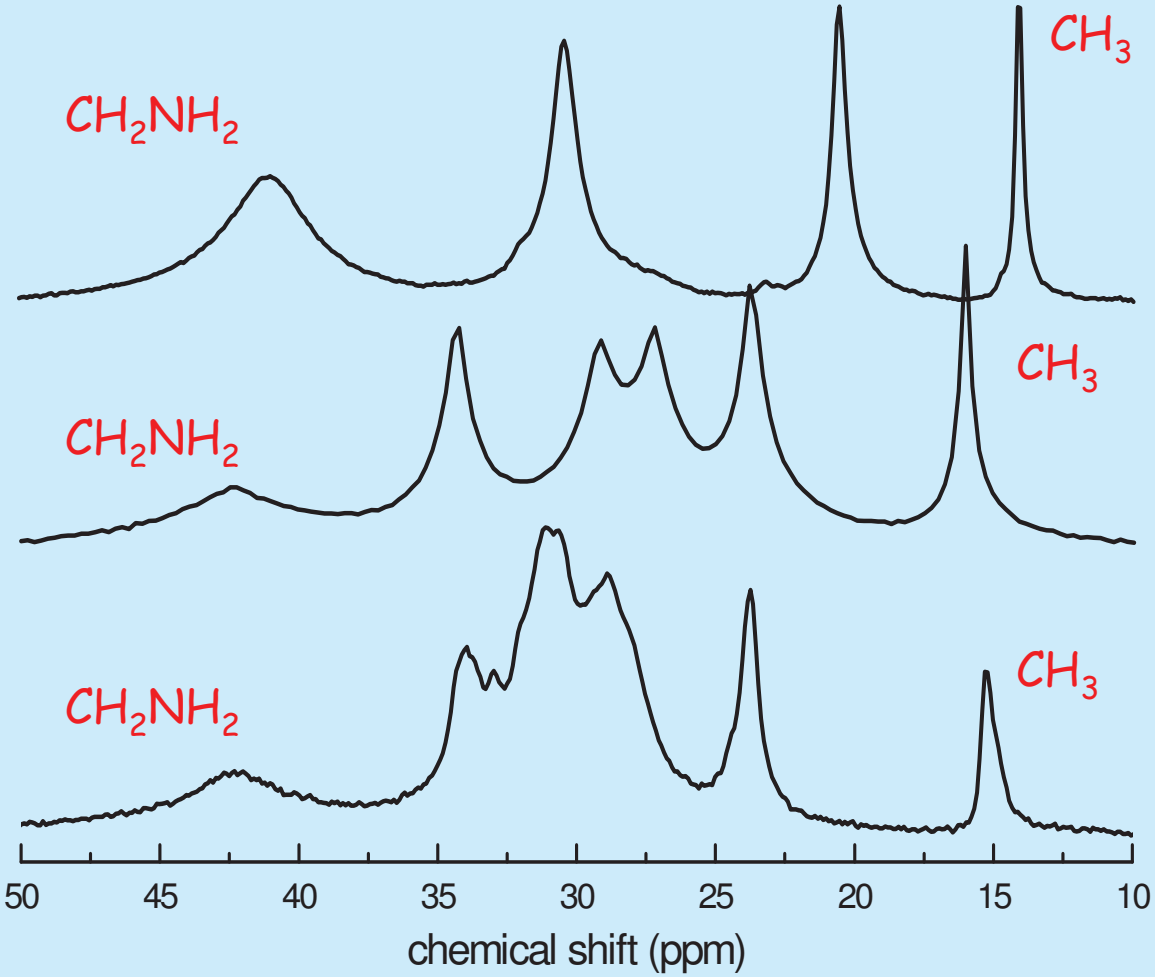
Espectroscopia por RMN (^{13}C)



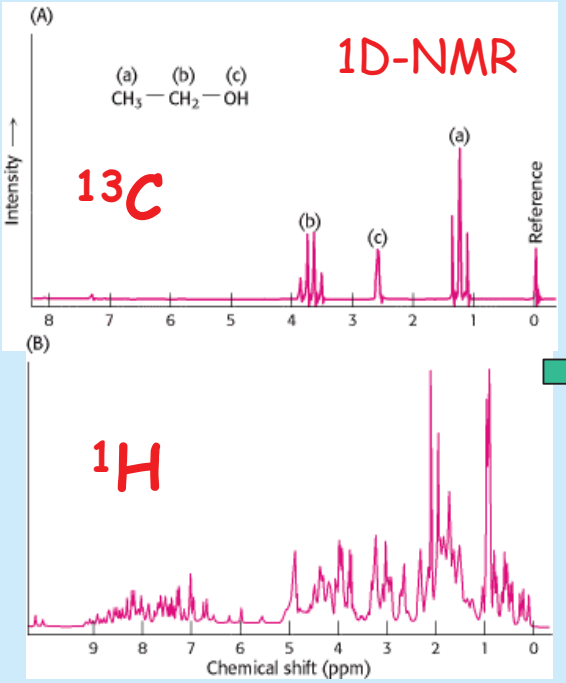


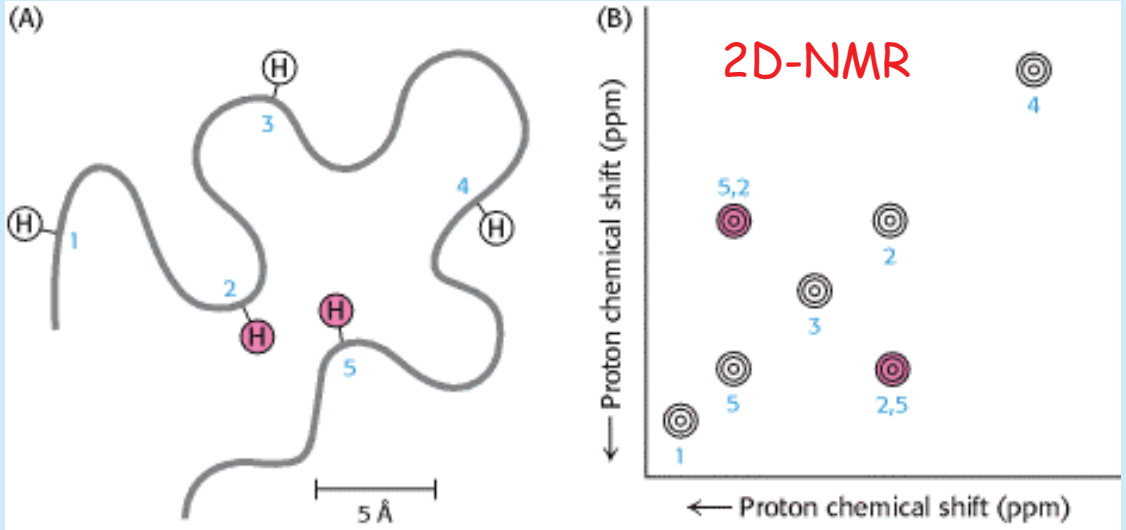
Espectroscopia por RMN (^{13}C)

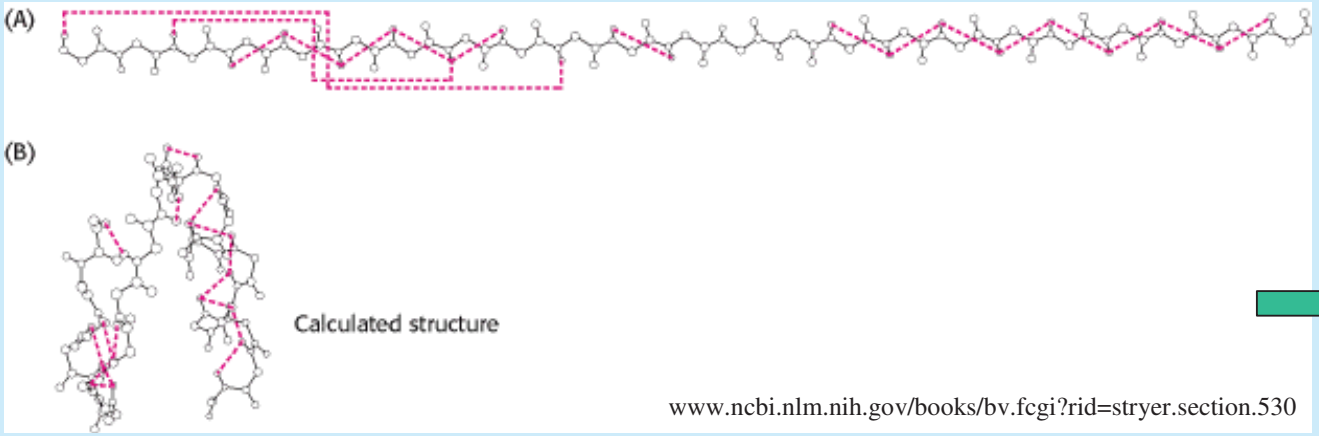




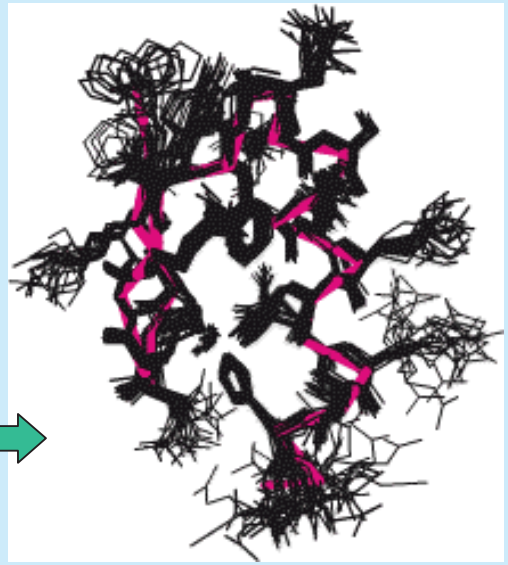
RMN e estrutura: proteinas







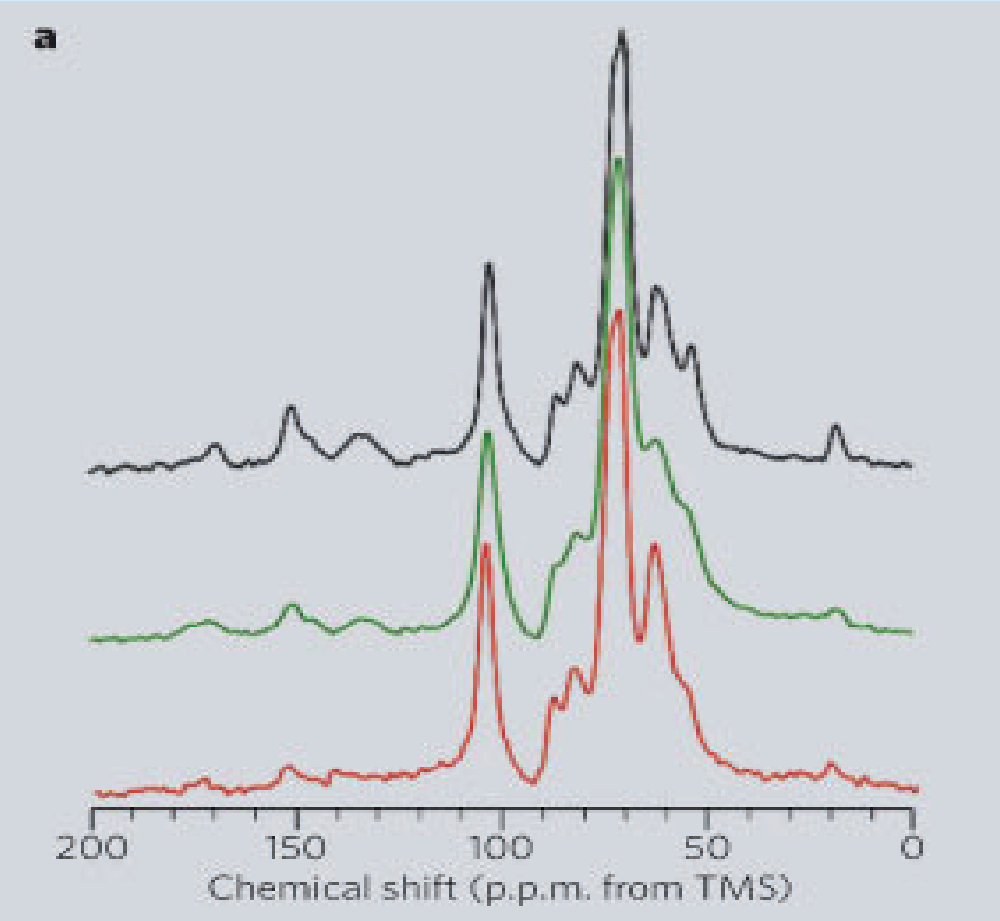
www.ncbi.nlm.nih.gov/books/bv.fcgi?rid=stryer.section.530



VARIAN

Wood used by Stradivari and Guarneri

Nature **444**, 565 (30 November 2006) | doi:10.1038/444565a
Joseph Nagyvary[1], Joseph A. DiVerdi[2], Noel L. Owen[3] and H. Dennis Tolley[4]

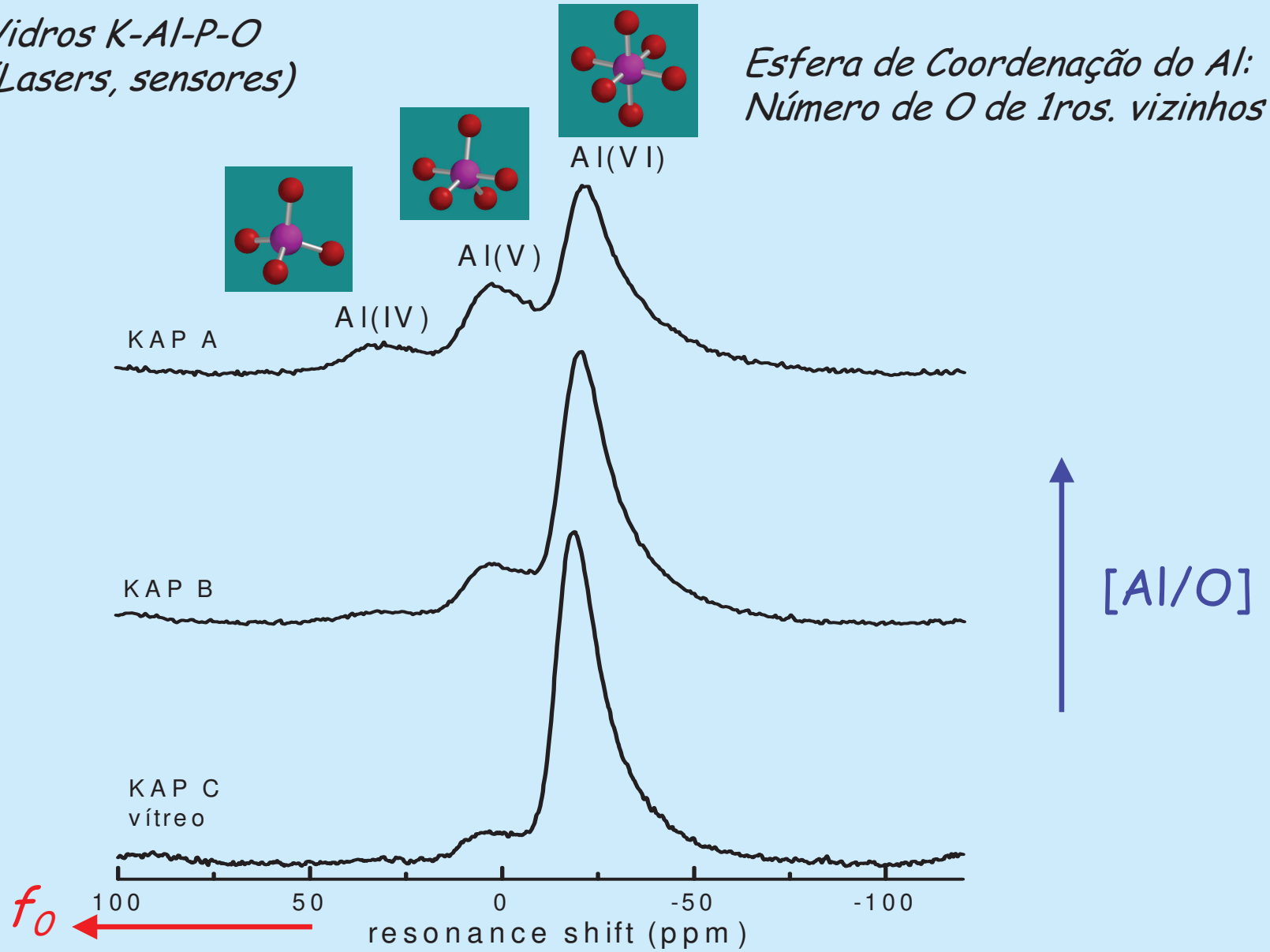


^{13}C solid-state NMR spectra.
Black trace: recent untreated Bosnian maple;
Green: violin of Stradivari;
Red: violin of Guarneri del Gesu.

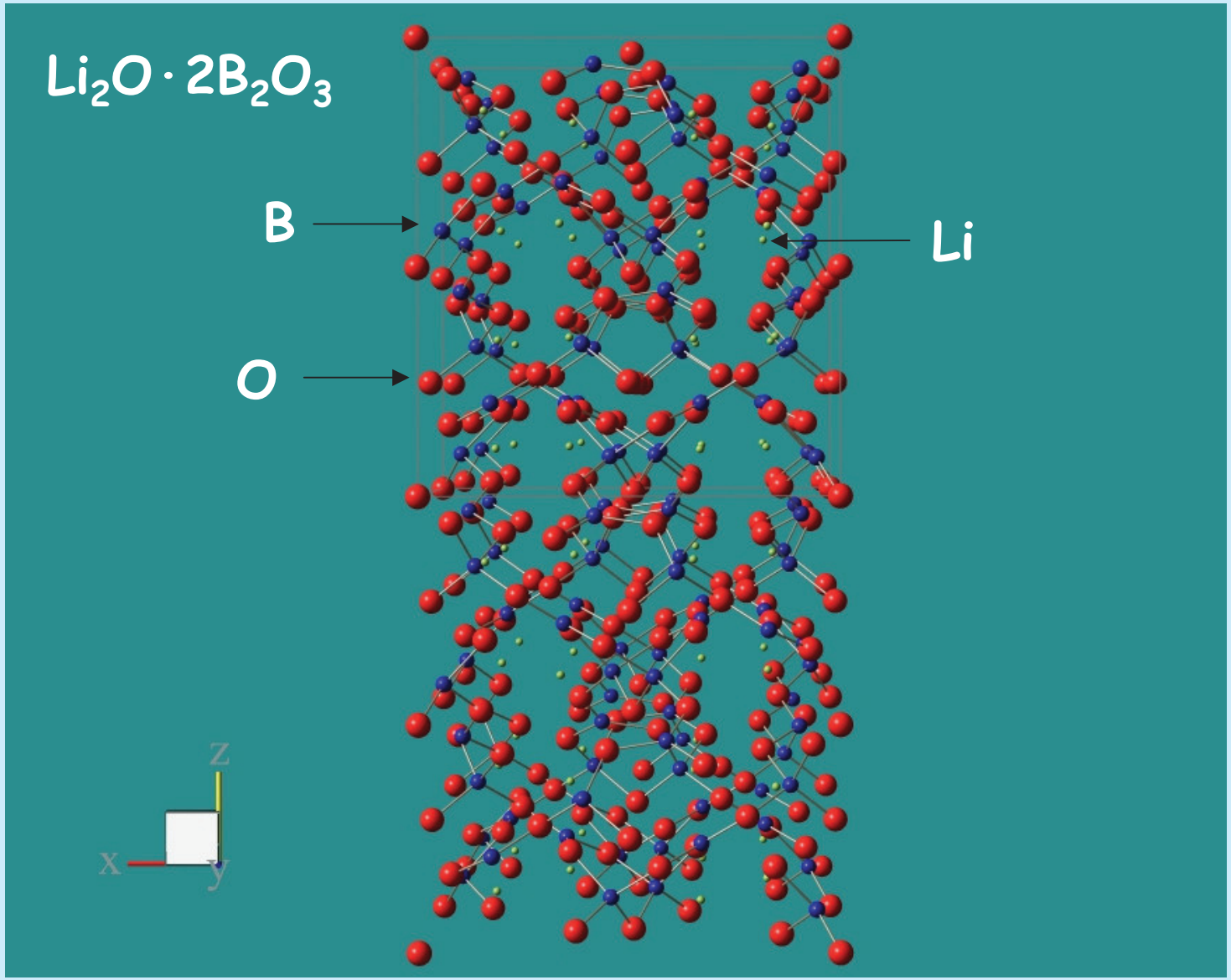
Espectroscopia por RMN (^{27}Al)

Vidros K-Al-P-O
(Lasers, sensores)

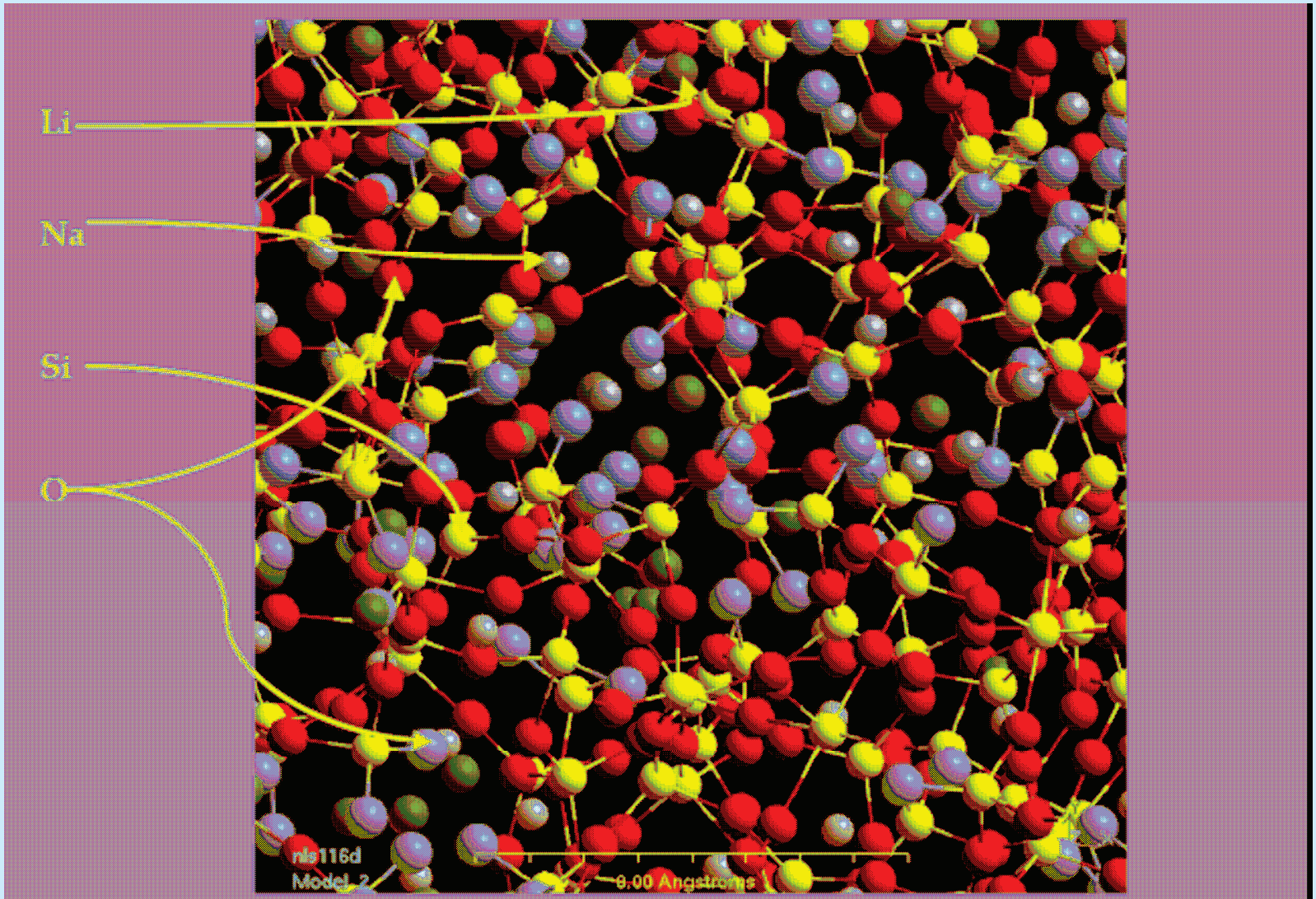
Esfera de Coordenação do Al:
Número de O de 1ros. vizinhos



Ordem: o estado cristalino



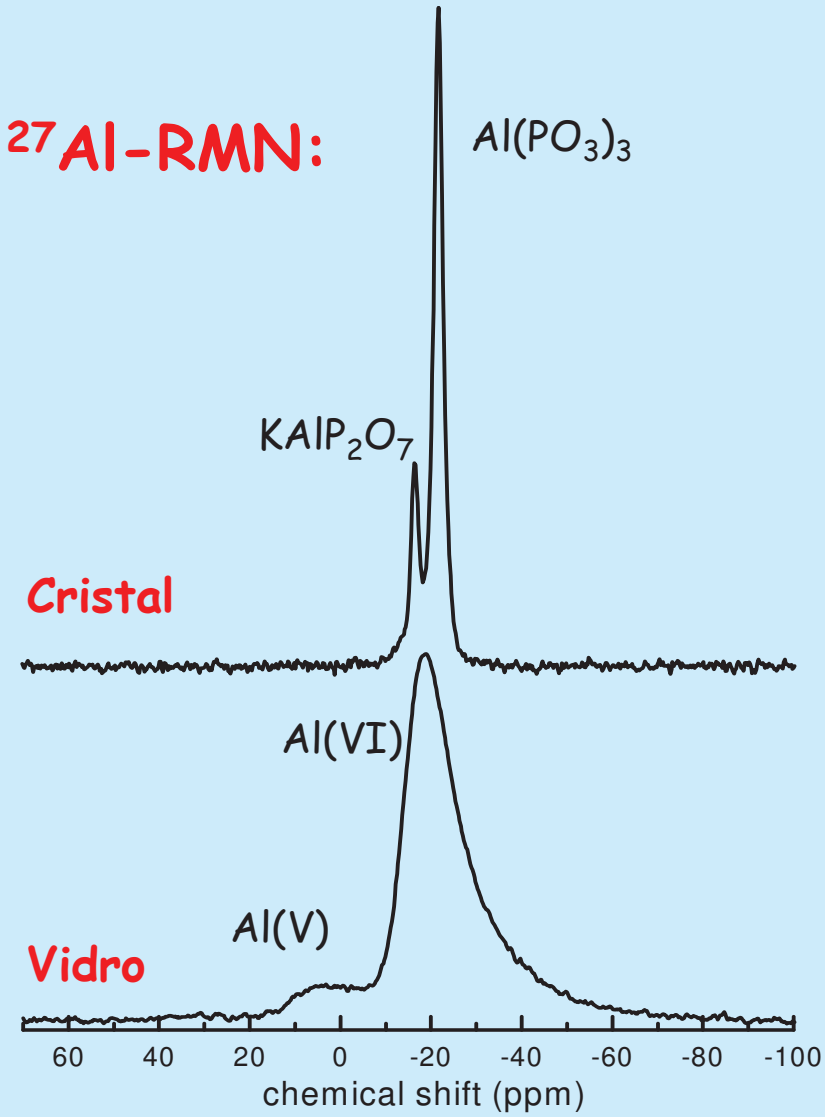
Desordem

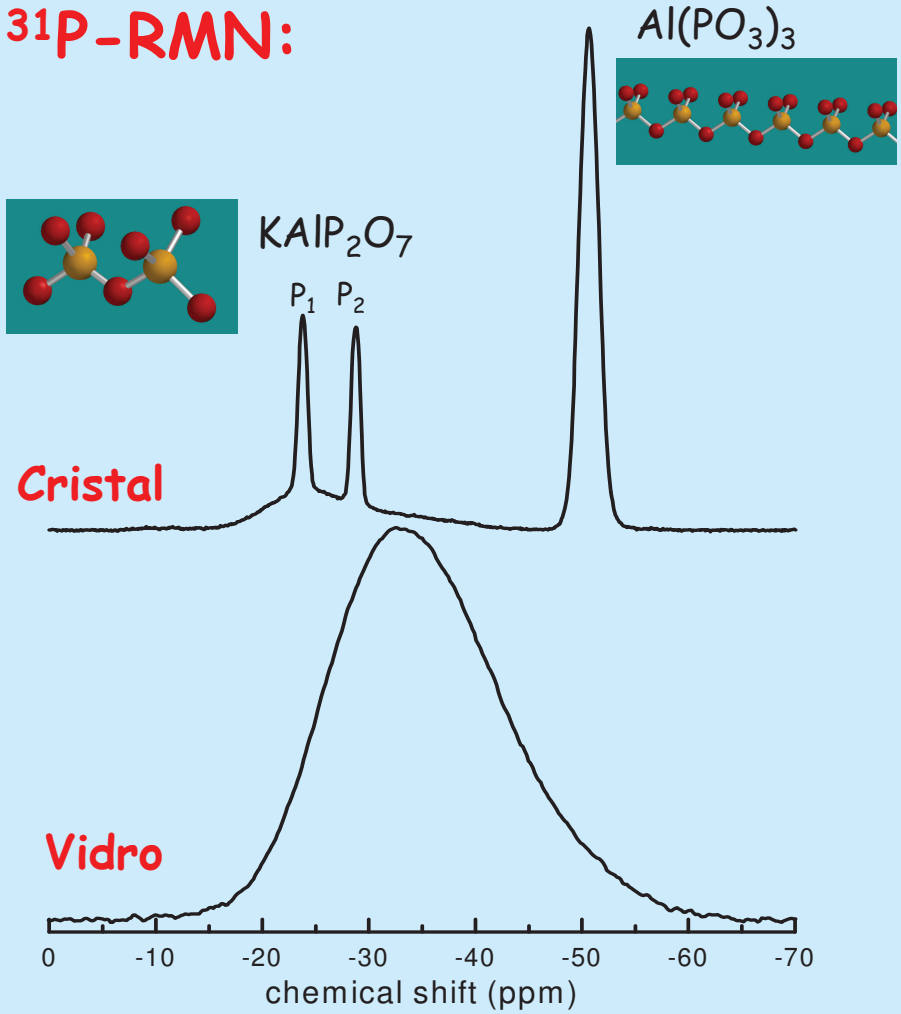


Snap-shot structure of a lithium sodium silicate glass

Espectroscopia por RMN:

Ordem-desordem, coexistência de fases (K-Al-P-O)





Espectroscopia por RMN

- Estrutura em escala atômica

(sólidos, moléculas, transições de fase)

- Dinâmica atômica/molecular

(íons, fragmentos moleculares)

Abrangência

Física, Química, Ciências de Materiais,

Biologia, Medicina

Espectroscopia por RMN

The Nobel Prize in Chemistry 1991

"for his contributions to the development of the methodology of high resolution nuclear magnetic resonance (NMR) spectroscopy"

Richard R. Ernst

Switzerland

Eidgenössische Technische Hochschule (Swiss Federal Institute of Technology)
Zurich, Switzerland

b. 1933

The Nobel Prize in Chemistry 2002

"for the development of methods for identification and structure analyses of biological macromolecules"

"for their development of soft desorption ionisation methods for mass spectrometric analyses of biological macromolecules"

"for his development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution"

John B. Fenn

1/4 of the prize

USA

Virginia Commonwealth University
Richmond, VA, USA

b. 1917

Koichi Tanaka

1/4 of the prize

Japan

Shimadzu Corp.
Kyoto, Japan

b. 1959

Kurt Wüthrich

1/2 of the prize

Switzerland

Eidgenössische Technische Hochschule (Swiss Federal Institute of Technology)
Zurich, Switzerland;
The Scripps Research Institute
La Jolla, CA, USA

b. 1938

Imagens por RMN

Tomógrafo por RMN desenvolvido no IFSC

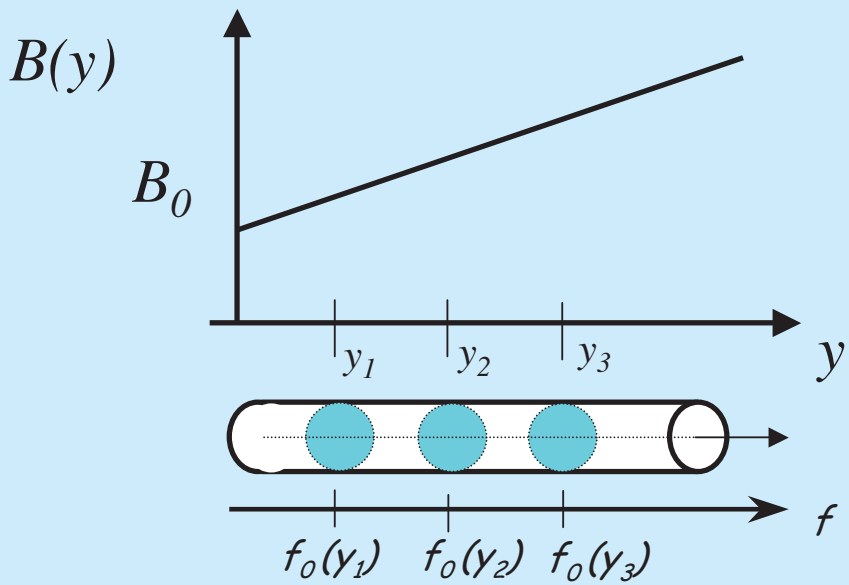
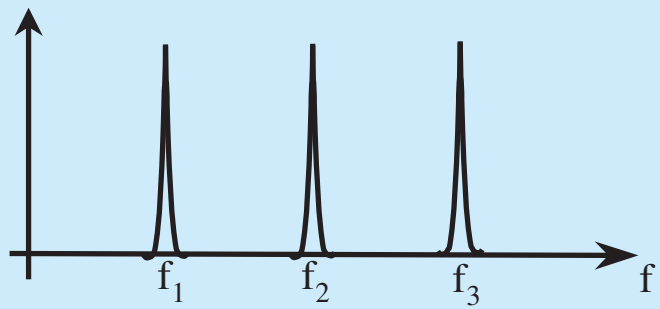
Imagens por RMN: o principio

Espectroscopia por RMN:

$$f_0 = \gamma \left(B_0 + B_{Local} \right)$$

$\vec{B}_0$: *Uniforme em toda a amostra*

Imagens por RMN:

$$f_0(y) = \gamma\, B(y) = \gamma \left(B_0 + g\ y \right)$$

O campo varia linearmente sobre a amostra !