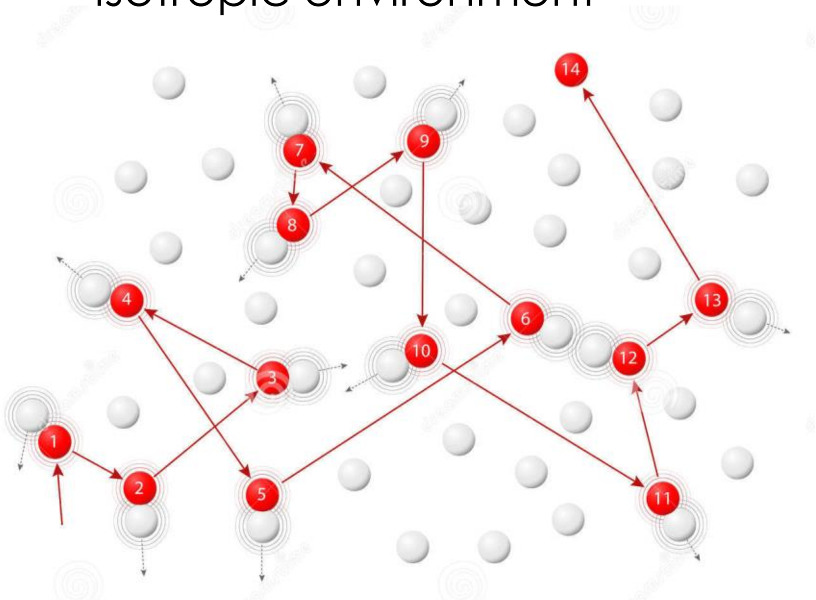
15. Anisotropic interactions

Liquid ≡ Brownian movement
isotropic environment



Very fast molecular motion (10^{12} Hz)
ALL the orientations coexist…

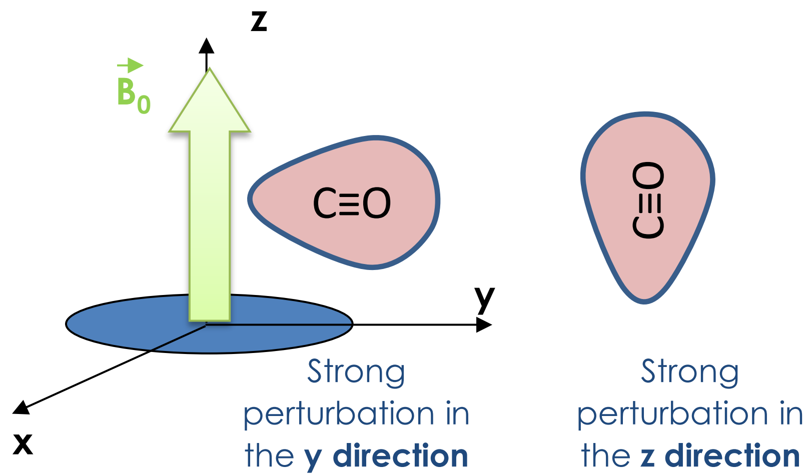
Solid ≡ anisotropic environment

The environment depends on the orientation respect to magnetic field B_0

15 Chemical shift anisotropy

La perturbation de B_0 autour noyau n’est pas parfaitement sphérique.
Dans une poudre, la perturbation dépend de la position du cristallite par rapport au champ magnétique statique B_0.
The chemical shift is ANISOTROPIC

Example $\delta^{13}C$ of carbon monoxyde



$$\vec{B}' = (1 - \sigma)\,\vec{B}_0 = \vec{B}_0 - [\sigma]\,\vec{B}_0$$

Perturbation term
$[\sigma]$ is not a scalar value !

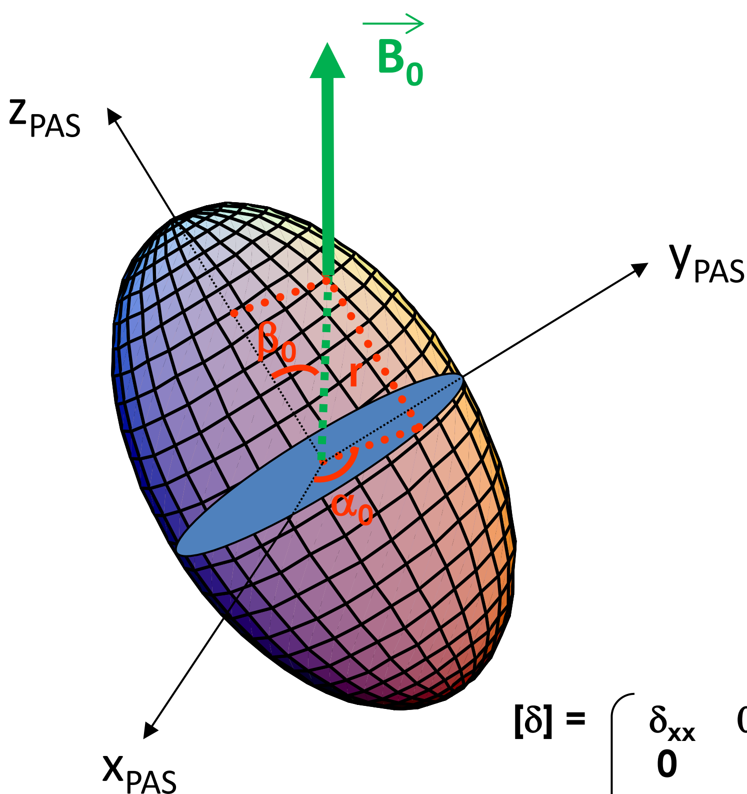
$$[\sigma] = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$

Thus, a diagonalization is possible !
In the Pincipal Axis System (PAS)

$$[\sigma_{PAS}] = \begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$$

15 Chemical shift anisotropy

Mathematical representation of the chemical shift can be achieved by an ellipsoid : $\delta_{xx}X^2 + \delta_{yy}Y^2 + \delta_{zz}Z^2 = 1$



L'ellipsoïde coupe les axes du PAS en des points qui dépendent de δxx, δyy, δzz

Les valeurs propres du tenseur d'anisotropie de déplacement chimique

Pour une poudre, B_0 coupe l'ellipsoïde en un point :
Le déplacement chimique qui dépend de l'orientation par rapport au champ B_0

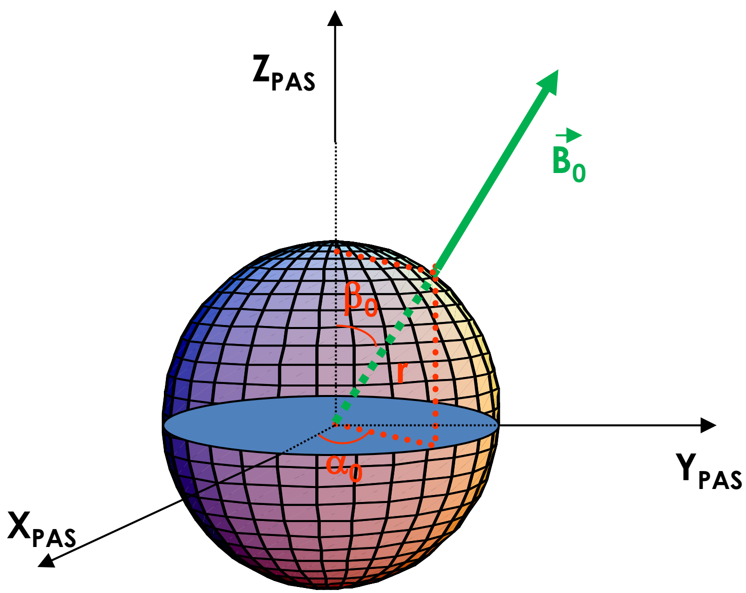
$$[\delta] = \begin{pmatrix} \delta_{xx} & 0 & 0 \\ 0 & \delta_{yy} & 0 \\ 0 & 0 & \delta_{zz} \end{pmatrix}$$

$$\delta_{iso} = 1/3\,(\delta_{xx} + \delta_{yy} + \delta_{zz})$$

NMR principles

15 Chemical shift anisotropy

Particular cases : the CSA tensor is spherical



In this representation the PAS is fixed, orientation of B0 is varied

$\delta xx = \delta yy = \delta zz$

Whatever the position respect to the magnetic field, δ is always the same.

Highly symmetric environment

OR solution state (brownian movement that average the CSA)

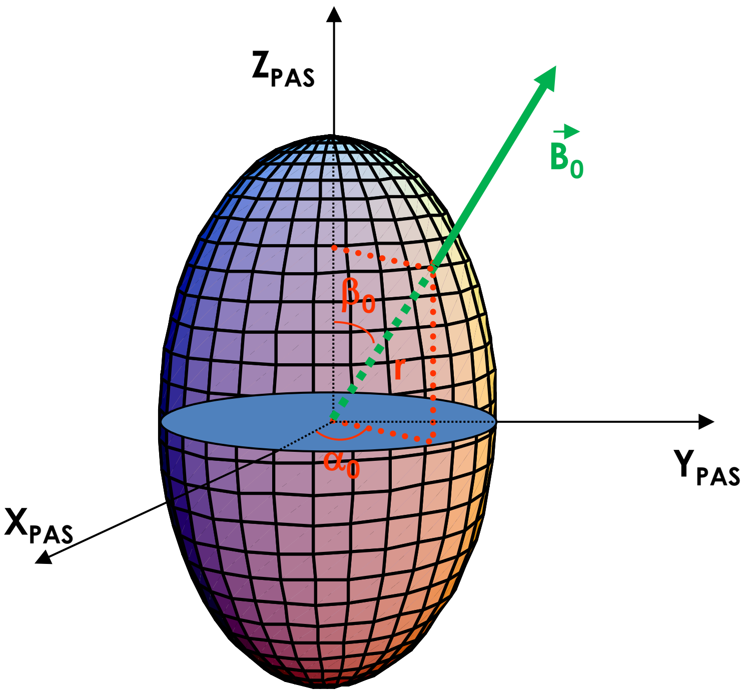
$$\delta_{iso} = \delta_{xx} = \delta_{yy} = \delta_{zz}$$

15 Chemical shift anisotropy

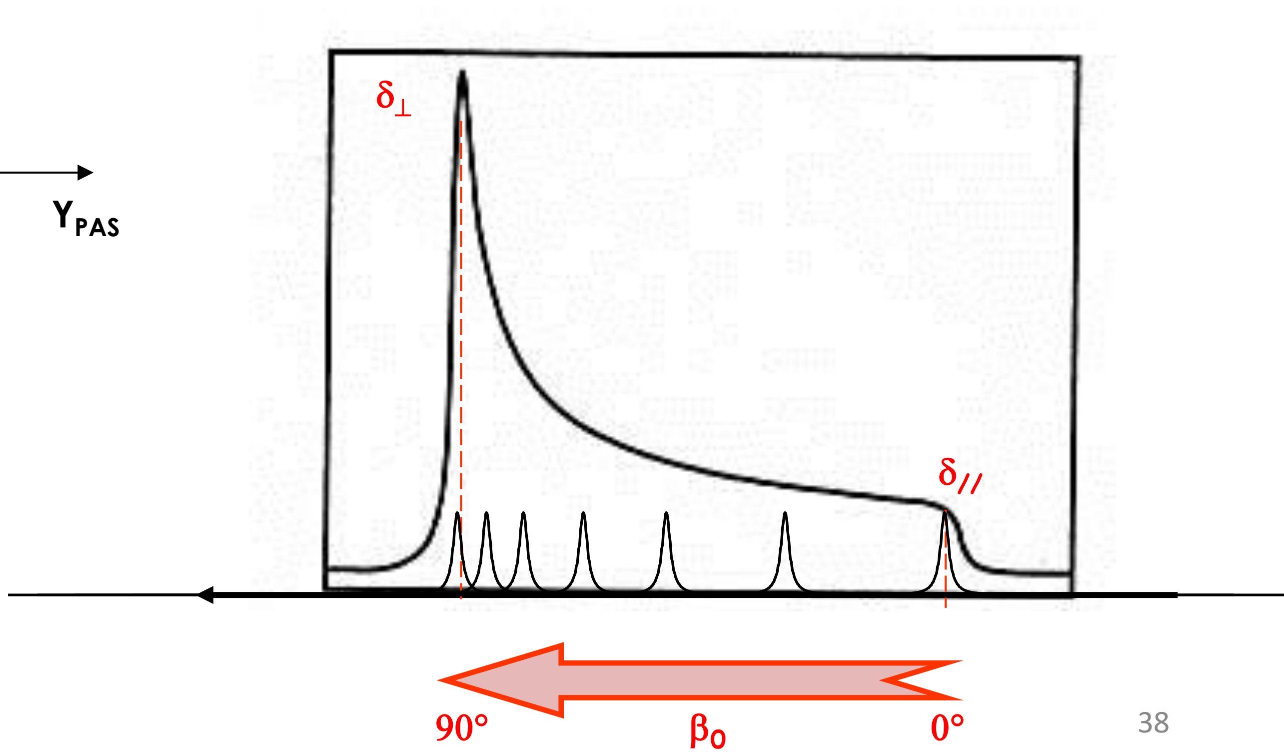
Particular cases : the CSA tensor is symmetrical

Ex : $\delta xx = \delta yy \neq \delta zz$ $\delta_{XX} = \delta_{YY} = \delta_{\perp}$
$\delta_{ZZ} = \delta_{//}$

Pas de dépendance en α_0, seulement en β_0



In this representation the PAS is fixed, orientation of B0 is varied



15 Chemical shift anisotropy

Example of powder spectrum

For one given δiso

General symetry

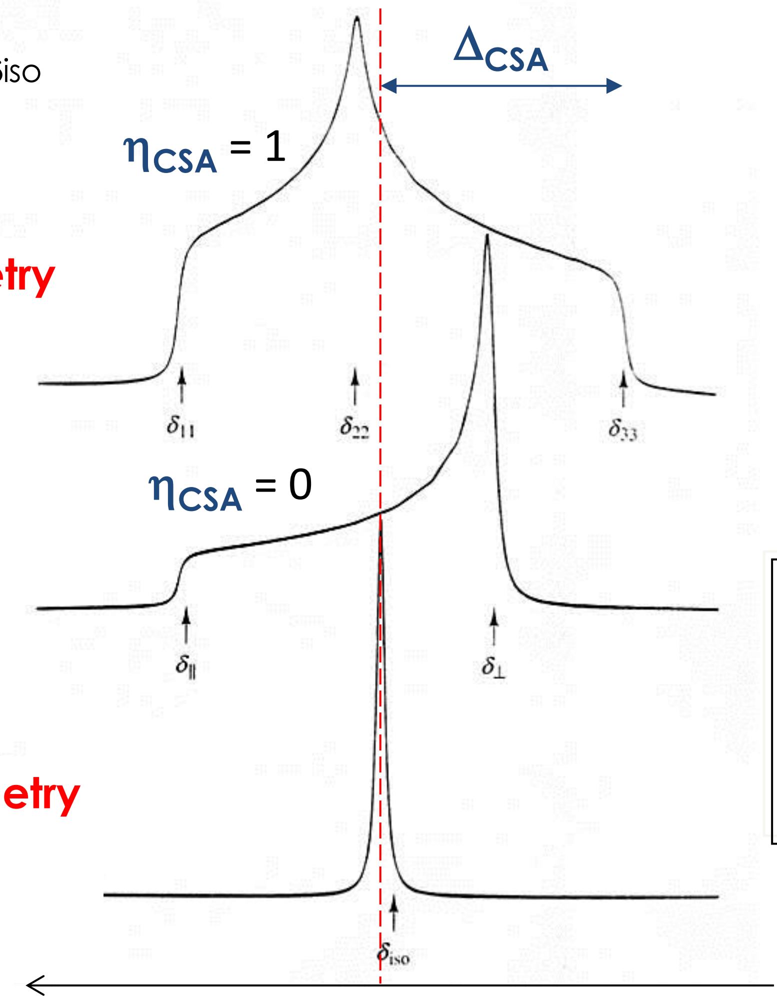
$\delta_{11} \neq \delta_{22} \neq \delta_{33}$

Axial symetry

$\delta_{11} \neq \delta_{22} = \delta_{33}$

Spherical symetry

$\delta_{11} = \delta_{22} = \delta_{33}$



Two parameters are defined :

The “width” Δ_{CSA}

The “shape” η_{CSA}

Convention

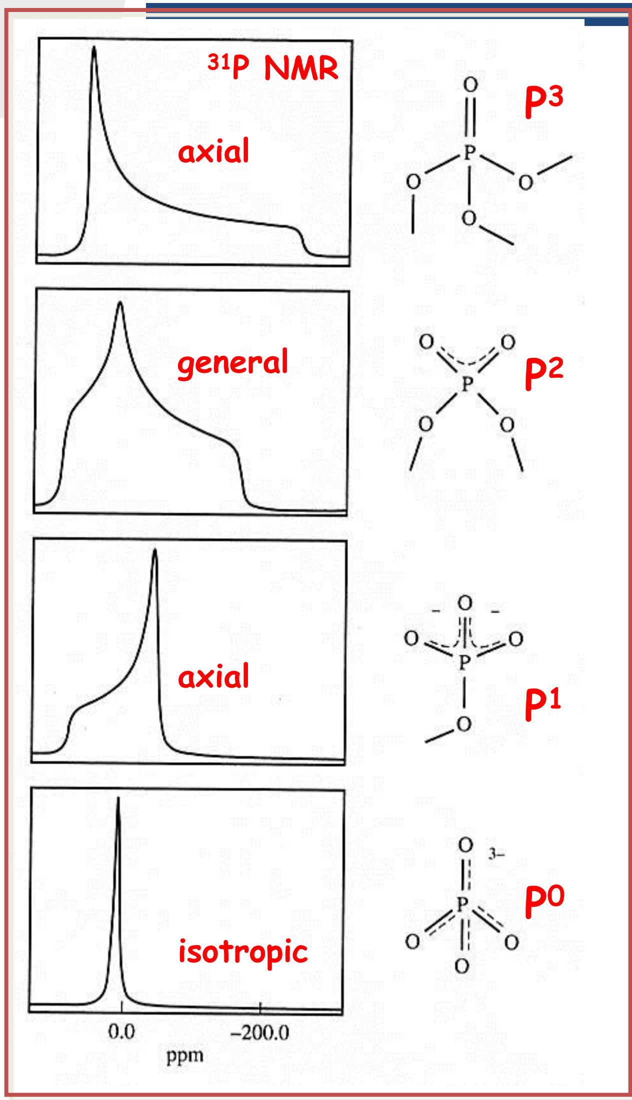
δ_{11}, δ_{22}, δ_{33} avec

$$|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$$

$$\Delta_{CS} = \delta_{33} - \delta_{iso}$$

$$\eta_{CS} = (\delta_{22} - \delta_{11}) / (\delta_{33} - \delta_{iso})$$

15 Chemical shift anisotropy



Eckert, Prog. Nucl. Magn. Reson., 1992, 24, 159.

Typical case of phosphates

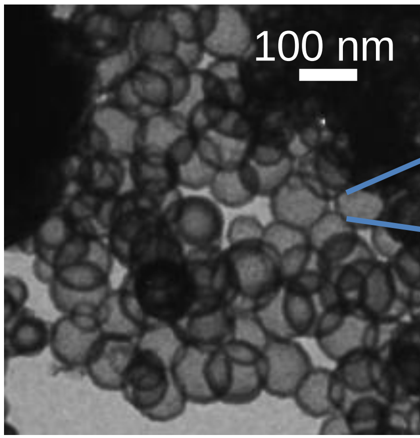
P^n with n : number of P-O-P bridges

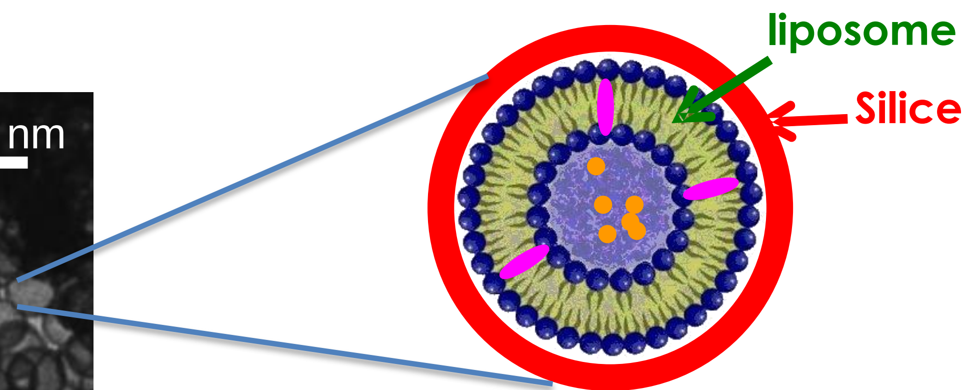
Relation symétrie vs CSA

Exemple :

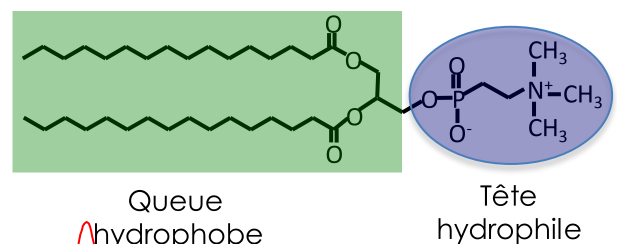
- ^{31}P (sels de phosphates)
- ^{29}Si (silicates - zéolites)
- ^{13}C (carbones sp^3, sp^2, sp^1)

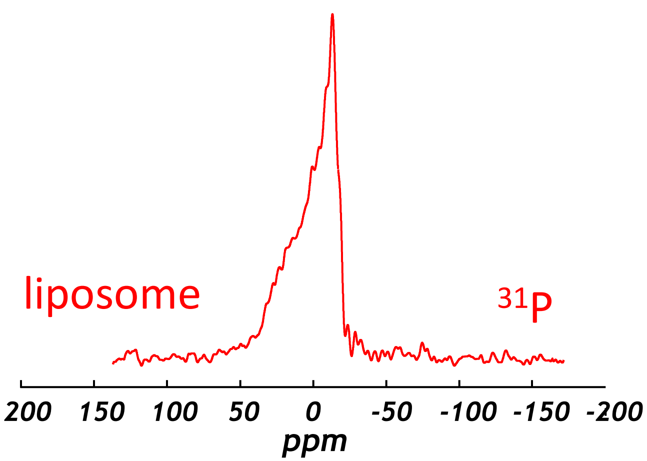
15 Chemical shift anisotropy

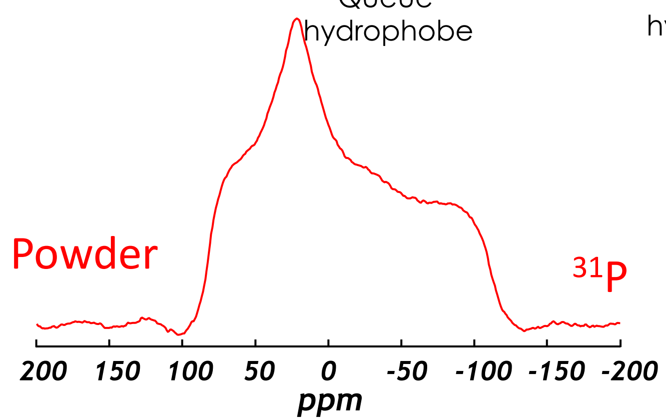




Phospholipide :
DPPC (Dipalmitoylphosphatidylcholine)







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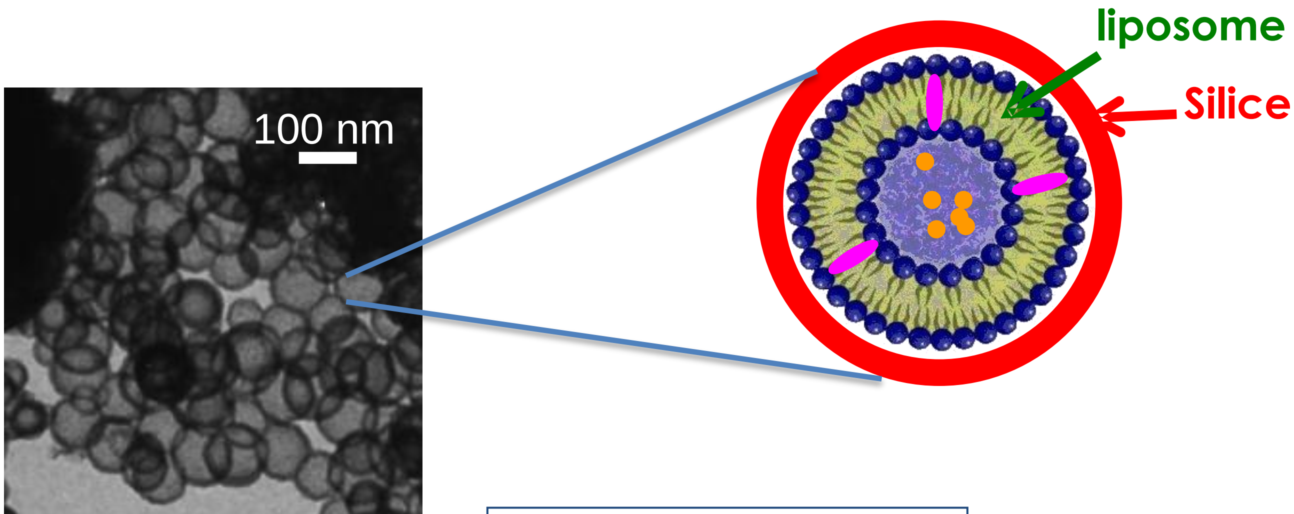
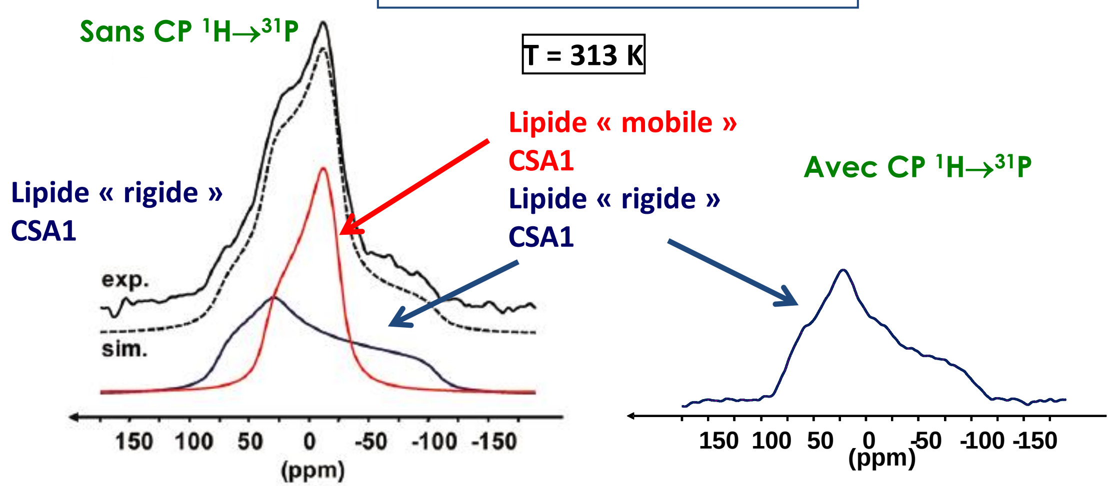
15 Chemical shift anisotropy



Echo ^{31}P condition statique



CSA1 $\Delta_{CSA1} \approx$ -105 ppm et $\eta_{CSA1} \approx 0,6$

CSA2 $\Delta_{CSA2} \approx$ 35 ppm et $\eta_{CSA2} \approx 0,0$

N. Folliet *et al. J. Am. Chem. Soc.* **2011**