Solid-state NMR of organic polymers

$^{13}$C NMR under MAS is an important tool for the study of organic polymers including biopolymers. By means of cross-polarization, often also constituents in smaller concentrations can be detected. We study for example natural rubbers in order to reveal its composition (industrial collaboration, projet CANAOPT). Another line is the study of modern materials used in fine arts (collaboration with Pratt Institute, New York). A common problem is the degradation of these materials with time. These processes are studied in vitro by solid state NMR as well as non-invasively by unilateral low field NMR.
- composition of natural rubber, industrial collaboration (project CANAOPT, coordinator JF Pilard, MSP)
- degradation of polymeric materials used in fine arts – collaboration with C. Kehlet, Pratt Institute, New York
- the chemical structure of the green-blue pigment marennine, a 10 kDa polymer found in diatoms (and in green oysters) at the French atlantic coast – collaboration with JL Mouget, MMS, and MMS Nantes

NMR-crystallography for inorganic fluorides and oxyfluorides

Our laboratory is specialized on the structural study of fluorides and oxyfluorides in close collaboration with groups from the French Fluorine Network. NMR can help to fine tune the structure by (i) comparing the
experimental parameters with those issued from DFT calculations on the base of structural models; (ii) applying high resolution solid state NMR sequences, including 2D correlation experiments, to characterize the environment of probed nuclei. As an example, the assignment of fluorine sites to NMR lines from 2D $^{19}$F DQ-SQ experiment is shown for #-$\text{LaZr}_2\text{F}_{11}$.

Projects

- structure refinement of oxyfluorides by means of measurements and DFT calculations of NMR parameters ($^{19}$F and cation) (thesis Jamal Dabachi)
- characterization of fluorine environments in anodes and electrolytes for fluoride ionic conductor batteries (ANR project FLUOBAT, coordinator V. Maisonneuve, FLUO)

Solid-state NMR in the presence of paramagnetic centers
NMR is the art of dealing with various interactions that locally change the resonance frequency and that are usually treated as perturbations of the Zeeman interaction. Chemical shift, $J$, dipolar, and quadrupolar coupling are well studied, and there have been techniques developed to deal with them. The hyperfine interaction of the nucleus with unpaired electron(s) in the presence of paramagnetic centers is however less investigated in solid state NMR. Line broadening and very fast relaxation make common techniques not applicable. We develop new methods that allow NMR experiments despite the hyperfine interactions and that exploit this interaction. It has for example allowed to measure copper-carbon distances in a Cu-cyclam complex.

Projects
- Cu-cyclam as model system for testing new methods in NMR of paramagnetics (thesis S. Kumara Swamy, collaboration with A. Kassiba (NF) and M Makowska (Czestochowa, Poland))

NMR of ion conductors
In addition to the structure, the ion mobility is the central interest in the study of ion conductors. In particular the lithium ions can well be investigated by NMR of the isotopes $^6\text{Li}$ and $^7\text{Li}$. The quadrupolar relaxation of the latter reflects the Li motion. Its interpretation yields a measure for the average time for hopping from site to site, $t_c$, and the activation energy needed for this hopping.

Projects

- Li$^+$ and H$^+$ mobility in the Li garnet Li$_{7-x}$H$_x$La$_3$Sn$_2$O$_{12}$ (with F Le Berre and MP Crosnier-Lopez, OETPS)

- the distribution of phosphorus dopants in LAMOX (with G. Corbel and P. Lacorre, OETPS)

Publications (since 2009)

Incorporation of antimicrobial peptides into membranes: a combined liquid-state NMR and Molecular Dynamics study of alamethicin in DMPC/DHPC bicelles
Sensitivity enhancement of $^{29}$Si double-quantum dipolar recoupling spectroscopy by Carr-Purcell-Meiboom-Gill acquisition method

M. Goswami, P.K. Madhu, J. Dittmer, N.C. Nielsen, and S. Ganapathy

Efficient Ion Exchange of H\textsuperscript{+} for Li\textsuperscript{+} in (Li\textsubscript{0.30}La\textsubscript{0.57}\textsuperscript{−}0.13)TiO\textsubscript{3} Perovskite in Water: Protons As a Probe for Li Location
A. Boulant, P. Maury, J. Emery, J.-Y. Buzaré, O. Bohnke
Chem. Mat. 21 (2009), 2209-2217

Effect of fluoride ion incorporation on the structural aspects of barium–sodium borosilicate glasses

On the assignment of F-19 MAS NMR spectra of fluoroaluminates using through-space spectral edition of F-19-(27) Al and $^{19}$F-$^{19}$F connectivities
C. Martineau, C. Legein, J.-Y. Buzaré, F. Fayon
Phys. Chem. Chem. Phys. 11 (2009), 950-957

NMR investigations of Li\textsuperscript{+} ion dynamics in the NASICON ionic conductors Li\textsubscript{1-x}La\textsubscript{x/3}Zr(PO\textsubscript{4})\textsubscript{3}
J. Physics: Cond. Matter 21 (2009), 175404

Peculiarities of ionic transport in Li\textsubscript{1.3}Al\textsubscript{0.15}Y\textsubscript{0.15}Ti\textsubscript{1.7}(PO\textsubscript{4})\textsubscript{3} ceramics
J. Phys.: Condensed Matter 21 (2009), 185502

Properties of amorphous silica generated by the fluoride method
L. P. Demyanova, A. Tressaud, J.Y. Buzaré, C. Martineau, C. Legein, Y. N. Malovitski, V. S. Rimkevich
Inorg. Mat. 45 (2009), 151-156

Highly Fluorinated Silica Obtained by Direct F\textsubscript{2}-Gas Fluorination: Stability and Unprecedented Fluorosilicate Species Revealed by Solid State NMR Investigations
E. Lataste, C. Legein, M. Body, J.-Y. Buzaré, A. Tressaud, A. Demourgues

Double-quantum F-19-F-19 dipolar recoupling at ultra-fast magic angle spinning NMR: application to the assignment of F-19 NMR spectra of inorganic fluorides
Solid-state F-19 MAS NMR investigation of fluoride ion mobility in lead fluorides: correlation with anionic conductivity
C. Martineau, F. Fayon, C. Legein, J.Y. Buzaré, G. Corbel
Chem. Mat. 22 (2010), 1585-1594

Reaction mechanisms of Li$_{0.30}$La$_{0.57}$TiO$_3$ powder with ambient air: H$^+$/Li$^+$ exchange with water and Li$_2$CO$_3$ formation
A. Boulant, J.F. Bardeau, A. Jouanneaux, J. Emery, J.Y. Buzaré, O. Bohnke
Dalton Trans. 39 (2010), 3968-3975

Evolution of guanazolium fluoroaluminates within the composition-space diagram and with the temperature

New oxyfluoride pyrochlores Li$_{2-x}$La$_{(1+x)/3}$#$(2x-1)/3$B$_2$O$_6$F (B = Nb, Ta): average and local structure characterization by XRD, TEM and $^{19}$F solid-state NMR spectroscopy

Probing short and medium range order in Al-based fluorides using high resolution solid state nuclear magnetic resonance and parameter modelling in "Functionalized Inorganic Fluorides

2D zirconium fluorides: synthesis, structure and NMR spectroscopy
A. Ben Ali, M. Body, M. Leblanc, V. Maisonneuve

NMR parameters in alkali, alkaline earth and rare earth fluorides from first principle calculations
A. Sadoc, M. Body, C. Legein, M. Biswal, F. Fayon, X. Rocquefelte, F. Boucher

In-115 and F-19 MAS NMR study of (NH$_4$)$_3$InF$_5$ phases
G. Scholz, T. Krahl, M. Ahrens, C. Martineau, J.-Y. Buzaré, C. Jaeger, E. Kemnitz

From micro- to nanostructured fast ionic conductor Li$_{0.30}$La$_{0.57}$TiO$_3$: size effects on NMR properties
A. Boulant, J. Emery, A. Jouanneaux, J.-Y. Buzaré, J.-F. Bardeau

Characterizing gum natural rubber samples through advanced techniques
J. L. Leblanc, J.-F. Pilard, E. Pianhanuruk, I. Campistron, J.-Y. Buzaré
H+/Li+ exchange property of Li$_{3x}$La$_{2/3-x}$TiO$_3$ in water and in humid atmosphere
O. Bohnke, Q. N. Pham, A. Boulant, J. Emery, T. Salkus, M. Barré

Structural investigation of $\#-$ and $\#-$sodium hexafluoroarsenate, NaAsF$_6$, by variable temperature X-ray powder diffraction and multinuclear solid-state NMR and DFT calculations
M. Biswal, M. Body, C. Legein, G. Corbel, A. Sadoc, F. Boucher

Instability of lithium garnets against moisture. Structural characterization and dynamics of Li$_{7-x}$H$_x$La$_3$Sn$_2$O$_{12}$ and Li$_{5-x}$H$_x$La$_3$Nb$_2$O$_{12}$
C. Galven, J. Dittmer, E. Suard, F. Le Berre, M.-P. Crosnier-Lopez
*Chem. Mat.* 24 (2012), 3335-3345, doi: 10.1021/cm300964k

Analysis of the local structure of phosphorus-substituted LAMOX oxide ion conductors
B. Pahari, N. Mhadhbi, G. Corbel, P. Lacorre, J. Dittmer

Structural investigation of $\#-$LaZr$_2$F$_{11}$ by coupling X-ray powder diffraction, $^{19}$F solid state NMR and DFT calculations
C. Martineau, C. Legein, M. Body, O. Peron, B. Boulard, F. Fayon

NbF$_5$ and TaF$_5$: assignment of $^{19}$F NMR resonances and chemical bond analysis from GIPAW Calculations
M. Biswal, M. Body, C. Legein, A. Sadoc, F. Boucher

Solid-state NMR correlation experiments and distance measurements in paramagnetic metalorganics exemplified by Cu-cyclam

Non-invasive characterization of polymeric materials in relation to art conservation using unilateral NMR combined with multivariate data analysis

Noncovalent chalcogen bonds and disulfide conformational change in the cystamine-based hybrid perovskite [H$_3$N(CH$_2$)$_2$SS(CH$_2$)$_2$NH$_3$]PbI$_4$
N. Louvain, G. Frison, J. Dittmer, C. Legein, N. Mercier
NMR parameters in column 13 metal fluoride compounds (AlF$_3$, GaF$_3$, InF$_3$ and TIF) from first principle calculations
A. Sadoc, M. Biswal, M. Body, C. Legein, F. Boucher, D. Massiot, F. Fayon

Marennine, promising blue pigments from a widespread Haslea diatom species complex

$F^-/OH^-$ substitution in [H$_4$tren]$^{4+}$ and [H$_3$tren]$^{3+}$ hydroxyfluorotitanates(IV) and classification of tren cation configurations
J. Lhoste, M. Body, C. Legein, A. Ribaud, M. Leblanc, V. Maisonneuve

Degradation of natural rubber in works of art studied by unilateral NMR and high field NMR spectroscopy
C. Kehlet, A. Catalano, J. Dittmer