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Résumés des conférences

Organisateurs : Francesca Ingrosso et Erwan André.

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Experimental and numerical investigation of water confined in swelling clays.

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Swelling clay minerals are ubiquitous in surface environments, both terrestrial and marine, where they often represent one of the main mineral components. Their structure involves colloidal size ($< 2\mu\text{m}$) negatively charged layers constituted with two tetrahedral layers sandwiching an octahedral one. The charge deficit resulting from cationic substitutions in either the tetrahedral or octahedral layer is compensated for by exchangeable cations located in the interlayer space. The moderate charge of the layers (between -0.1 and -0.2 C/m²) allows water molecules to penetrate the interlayer space and hydrate the interlayer cations, which results in a swelling of the crystal structure.

As a function of relative humidity (RH) and under non-saturated conditions, smectite typically shows a stepwise hydration behaviour corresponding to the intercalation of 0, 1 or 2 discrete sheets of water molecules in its interlayer. However, heterogeneities of charge location (between octahedral and tetrahedral sheets) and/or of charge amount (from one interlayer to the other or within a given interlayer) most often lead to the coexistence of different hydration states within smectite crystals. These heterogeneities are best revealed by comparing X-ray diffraction (XRD) patterns recorded on the same smectite sample under contrasting RH conditions. Calculated XRD patterns can then be fitted to experimental profiles using a trial-and-error procedure. The obtained structural models allow describing the hydration behaviour of the swelling smectite layers, and more especially their hydration heterogeneity and the evolution of layer hydration as a function of RH. The water content determined from XRD profile modelling can then be compared with gravimetric isotherm water desorption measurements. Such comparison allows discriminating the relative contributions of H₂O molecules from 1W and 2W interlayers (crystalline water) and from the pore space network.

By taking into account smectite hydration heterogeneity it is possible to further refine the interlayer structure of hydrated smectite layers. However, common crystallographic approaches account poorly for the actual statistical positional disorder of confined water and therefore do not provide a comprehensive characterisation of the structure and organisation of interlayer species. Computational simulations can supply detailed molecular pictures of the system, notably by discriminating water molecules forming the cation hydration shell from those filling the interlayer space but question regarding the validity of the semi-empirical atomic interaction parameters used in these theoretical simulations still remains. A specific quantitative collation procedure between computational simulations and experimental diffraction data has been developed in order to tackle this problem. Recent examples of the application of such a procedure combining experimental diffraction data and molecular simulations will be presented for the specific case of deciphering the molecular organization of interlayer water and cations in the different swelling clay hydrates (mono-, bi-, and tri-hydrated layers).



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Functionalization of layered hydroxides and oxides: an extended chemical toolbox.

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Since the discovery of the extraordinary properties of graphene or metal dichalcogenide single layers, research on nanosheet-based systems and hybrid layered materials have increased considerably. In this presentation, I will illustrate some synthetic approaches to functional layered hybrids used in our laboratory. I will focus on two different classes of materials: Layered Simple Hydroxide and ion-exchangeable layered perovskites.

In the first part, I will show how copper- and cobalt-based Layered Simple Hydroxides can be functionalized by a series of carefully designed fluorene mono- and diphosphonic acids, using anionic exchange reactions and a preintercalation strategy. Detailed characterization of the internal structure and chemical bonding properties for copper- and cobalt-based hybrids has been performed via ancillary experimental techniques.[1] For the copper-based LSH class, for which more elusive findings are found, first-principles molecular dynamics simulations unravel the fundamental stabilizing role of the H-bonding network promoted within the local environments of the fluorene mono- and diphosphonic acids. The cobalt series of compounds constitute a new class of hybrid magnets, with magnetic ordering temperatures ranging from 11.8 to 17.8 K and show a clear magnetoelectric effect.[2]

The second part will deal with another class of layered materials, namely ion-exchangeable layered perovskites which can exhibit especially interesting physical properties such as ferroelectricity or optical properties for instance. We are particularly interested in the functionalization of an Aurivillius phase of formula $\text{Bi}_2\text{SrTa}_2\text{O}_9$ (BST), known for its ferroelectric properties. Yet, the published synthetic methods for its functionalization have the important drawback of being extremely long. To overcome this problem, we have explored the microwave-assisted protonation of BST phase and its subsequent functionalization by various amines which can be performed in a few hours instead of more than a week via classical conditions. In addition, we will show that using microwave activation, we have been able to functionalize BST with more "interesting" amines, including chiral or aromatic amines and poly-amines, and with (poly)alcohols, which enables a better understanding of the reaction mechanisms at stake.[3,4] Finally, it is possible to go beyond "simple" insertion, using a microwave assisted post-synthetic modification, during which an organic reaction takes place within the interlamellar spacing of the layered oxide.[5]

1. Q. Evrard, C. Leuvrey, P. Farger, E. Delahaye, P. Rabu, G. Taupier, K. D. Dorkenoo, J.-M. Rueff, N. Barrier, O. Pérez, G. Rogez, *Cryst. Growth Des.* 18, 1809 (2018).

2. Q. Evrard, Z. Chaker, M. Roger, C. M. Sevrain, E. Delahaye, M. Gallart, P. Gilliot, C. Leuvrey, J.-M. Rueff, P. Rabu, C. Massobrio, M. Boero, A. Pautrat, P.-A. Jaffrès, G. Ori, G. Rogez, *Adv. Funct. Mater.*, 1703576 (2017).

3. Y. Wang, E. Delahaye, C. Leuvrey, F. Leroux, P. Rabu, G. Rogez, *Inorg. Chem.* 55, 4039 (2016).

4. Y. Wang, M. Nikolopoulou, E. Delahaye, C. Leuvrey, F. Leroux, P. Rabu, G. Rogez, *Chem. Sci.*, 2018, 9, 7104-7114.

5. Y. Wang, E. Delahaye, C. Leuvrey, F. Leroux, P. Rabu, G. Rogez, *Inorg. Chem.* 55, 9790 (2016).



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Nanoconfinement de complexes à transition dans les films minces de silice ordonnée et orientée verticalement pour l'élaboration de capteurs.

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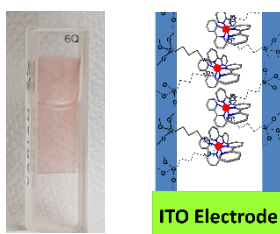
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The phenomenon of spin crossover (SCO) for the FeII consist to the change of molecular spin state by the effect of either photoexcitation, temperature or pressure¹. [FeII(bpy)₃]²⁺ is an SCO complex which can switch from low-spin (LS) to high-spin (HS) state only by photoexcitation.

We present here a novel methodology employed to confine this mononuclear complex, [FeII(bpy)₃]²⁺, in the matrix of a sulfonate-functionalized vertically-aligned mesoporous silica thin film electrodeposited on indium-tin oxide electrode by an electrochemically-assisted self-assembly (EASA) method.² Transmission electronic microscopy (TEM) reveals that the mesostructure and orientation of the sulfonate-functionalized silica films is maintained up to 30% of mercaptopropylsilane in the starting sol.

The electrochemical characterization of the [FeII(bpy)₃]²⁺ confined in the mesoporous silica shows a stable and reversible signal around 0.86 V. Comparison of the Raman spectrum of the [FeII(bpy)₃]²⁺ functionalized silica thin films with the [FeII(bpy)₃]²⁺ microcrystalline powder presents the same vibrational bands except in the low wavenumber region corresponding to Fe-N stretching vibrations modes suggesting a change of the conformation of the complex upon its confinement in the silica matrix. the UV-Vis shows the metal-to-ligand charge-transfer band at 526 nm Furthermore, the UV-Visible spectrum shows an absorption due to the metal to ligand charge transfer (MLCT) transition of [FeII(bpy)₃]²⁺ in silica at 526 nm which is slightly shifted compared to the bulk observed at 519 nm indicating a possible drop of energy gap between LS and HS due to the confinement. This could be then exploited to induce unprecedented thermally induced SCO by modifying the bipyridine (bpy) ligand³ with methyl group. Such compounds could be interesting for opto-magnetic or opto-electronic sensors.



Picture of [Fe(bpy)₃]²⁺ confined in a mesoporous silica thin film

1. Kröber, J.; Audière, J.-P.; Claude, R.; Coddjovi, E.; Kahn, O.; Haasnoot, J. G.; Grolière, F.; Jay, C.; Bousseksou, A.; Linares, J.; Varret, F.; Gontier-Vassal, A. Chem. Mater. 1994, 6, 1404

2. Goux, A.; Etienne, M.; Aubert, E.; Lecomte, C.; Ghanbaja, J.; Walcarius, A. Chem. Mater. 2009, 21, 731.

3. Donald C Craig, Harold A. Goodwin and Djulia Onggo. J. Chem., 1988, 41, 1157-69



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Structure et dynamique de l'espace interfoliaire d'hydroxydes doubles lamellaires.

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Les hydroxydes double lamellaires (HDL) sont des matériaux lamellaires formés par empilement de feuillets d'octaèdres d'hydroxydes de cations aux degrés d'oxydation +II et +III. La proportion de cations trivalents dans les feuillets définit une densité de charge positive qui est compensée par l'insertion d'anions (pouvant être solvatés) entre les feuillets. L'espace interfoliaire des HDL est le lieu où prend place l'interaction entre les feuillets et l'anion intercalé. Bien que possédant des similitudes avec la surface du matériau, le fait d'être entre deux feuillets définit un espace en trois dimensions qui s'adapte, dans une certaine mesure, aux dimensions de l'espèce chimique intercalée (de quelques Å à quelques nm), et qui la sépare du milieu extérieur sans complètement l'isoler. Il existe en effet un équilibre chimique entre l'espace interfoliaire et le milieu extérieur. Si cet équilibre peut être exploité en solution pour échanger l'anion intercalé, il existe également entre le matériau sec et l'atmosphère.

Les interactions entre feuillets, anions et eau interfoliaire dépendent du taux d'hydratation, de la nature du couple cationique ou encore de la densité de charge des feuillets. Pour sonder la structure du matériau et de son milieu interfoliaire, mais également pour suivre la dynamique des espèces présentes, nous avons couplé une approche expérimentale multi techniques (DRX, spectroscopies de vibration, RMN) en conditions contrôlées, à une approche théorique de modélisation (DFT, Dynamique Moléculaire).

Nous illustrerons cette double approche au travers de différents exemples, en partant de systèmes intercalant des anions inorganiques simples (Cl^- , NO_3^- , CO_3^{2-}), pour aller vers des hybrides organo-minéraux.



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*Les interactions fluides/minéraux à haute pression :
une approche expérimentale.*

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Cette conférence est centrée sur l'approche expérimentale des interactions fluides (eau+gaz) / roches dans des conditions de haute pression (jusque 1500 bar) et de haute température. Le but est de reproduire des conditions de profondeur envisagées dans le stockage géologique et d'appréhender les mécanismes responsables de la réactivité de phases fluides et minérales dans des conditions extrêmes. Une attention particulière sera portée aux expériences en micro-capillaires de silice qui permettent de manipuler à très haute pression des systèmes dangereux (e.g. SO_x, NO_x, H₂S...) et de réaliser les analyses des différentes phases en présence par micro-spectrométrie Raman. Des exemples tirés d'études sur la séquestration géologique du CO₂ illustreront la conférence.



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*Transport in hydrated clays at the nanoscale:
simulations and experiments.*

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Clays are porous lamellar materials. Their wide use in industrial applications, energy and environmental engineering (oil recovery, ground water remediation, geological barrier for radioactive waste and CO₂) is partly due to their remarkable properties of retention at the mineral surface. In environmental engineering, the role of water on clay permeability and their retention properties is crucial. Indeed, the water is the vector of the motion of the species present in the medium, including for instance the hazardous elements. Clays can show different behaviors towards water, depending in particular on the value of the negative structural charge carried by the mineral layers and the relative interactions between water, cations and clay surfaces. Provided that the interatomic interactions are properly defined, classical molecular simulations can help to better understand what happens at the clay/water interface because they allow a detailed picture of the structure, thermodynamics and dynamics of the system. The first part of my talk will be dedicated to the dynamical properties of water in clays obtained by classical molecular dynamics and quasi-elastic neutron scattering. I will show how the comparison between both is crucial in order to interpret experiments on the one hand and to test the validity of simulations parameters (force-field) on the other hand. In a second part, I will indeed explain how to improve the existing classical force-fields by including atomic polarisability.



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Effet du confinement et des interactions de surface sur la structure et la dynamique de molécules confinées.

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Lorsque les molécules sont confinées dans des matrices poreuses, leurs propriétés physiques sont le plus souvent modifiées. Ceci peut se traduire par un changement des propriétés structurantes à l'intérieur des pores. Le confinement à échelle nanométrique peut ainsi se révéler être une stratégie intéressante pour ajuster ces propriétés afin d'optimiser les applications. L'espace disponible pour l'organisation des molécules, les interactions avec la surface poreuse et la présence de molécules de solvant résiduelles sont les principaux facteurs qui régissent ces changements. Changements qui s'expriment généralement par une incapacité à cristalliser selon la structure originelle et qui induisent même le maintien d'états liquides bien en dessous des températures de solidification des composés purs.

L'inhomogénéité structurale, souvent présente dans ces matériaux, est un véritable défi quant à la caractérisation de ces systèmes. Ces problématiques peuvent cependant être abordées par des approches expérimentales complémentaires telles que la diffusion totale des rayons X couplée à la RMN du solide [1-3], la relaxométrie RMN et la DSC.

A partir de deux études pratiquées sur l'encapsulation d'un principe actif et sur le comportement de l'eau dans des verres bioactifs, nous présentons dans cette contribution les résultats pouvant être obtenus par notre approche sur ce type de nanomatériaux fonctionnels. Dans ce cadre, les analyses à partir des mesures de diffusion totale de rayons X couplées à l'analyse de distribution de paires (PDF) sont utilisées afin d'établir des modèles structuraux. En particulier, l'analyse PDF permet la détermination des paramètres structuraux à plusieurs échelles, à savoir l'ordre local ainsi que les modifications structurales induites par les effets de confinements. La caractérisation RMN étant également sensible à la structure locale, elle permet de valider les modèles structuraux mais aussi d'étudier l'éventuelle dynamique moléculaire grâce son influence sur les mécanismes de relaxation RMN. La DSC vient compléter cette caractérisation en apportant des informations sur les transitions de phase en milieu confiné.

[1] K.-Y. Hsieh, E.-E. Bendeif, A. Gansmüller, S. Pillet, T. Woike and D. Schaniel, RSC Adv., 2013, 3, 26132.

[2] E.-E. Bendeif, A. Gansmüller, K.-Y. Hsieh, S. Pillet, T. Woike, M. Zobel, R. B. Neder, M. Bouazaoui, H. El Hamzaoui and D. Schaniel, RSC Adv., 2015, 5, 8895.

[3] F. Deligey, S. Bouguet-Bonnet, A. Doudouh, P.-L. Marande, D. Schaniel and A. Gansmüller, J. Phys. Chem. C, 2018 (in press)



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A mechanistic description of the containment of iodomethane in nanoporous silver zeolites by ab initio molecular dynamics.

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The radioactive iodine species belong to the most dangerous components of nuclear effluents and waste produced in nuclear facilities and this fact motivates a significant effort in development of technologies for their efficient trapping. In this work we use computer simulations at the periodic DFT level [1] to investigate dissociative adsorption of iodomethane on silver exchanged mordenite, which is among the most effective sorbents of iodine species available as of today [2]. The structural models for the Ag-MOR have been selected on the basis of systematic analysis of energetics of diverse Ag sites [3]. The structure, energetics, and mobility of complexes $\text{Ag}-(\text{CH}_3\text{I})_n$ formed upon adsorption of iodomethane on Ag^+ sites are investigated using the molecular dynamics approach (MD). The free-energy profiles for the reaction $\text{CH}_3\text{I} + \text{Ag-MOR} \rightarrow \text{AgI} + \text{CH}_3\text{-MOR}$ are determined using MD blue-moon ensemble technique [4] and compared with the results of static approach. The AgI species formed as a product of dissociative adsorption are shown to combine spontaneously into small clusters $(\text{AgI})_m$ with the size and geometry restricted by the size of confining void. The geometry and energetics of the $(\text{AgI})_m$ species are analyzed in detail and our findings are shown to agree well with the available experimental results [2,5]. The internal energy of formation of clusters in mordenite is shown to contribute significantly to the shift of equilibrium from the undissociated to dissociated form of adsorbed CH_3I . The influence of the Ag content on the mechanism of dissociative adsorption is also discussed [6].

[1] T. Bučko, S. Chibani, J.-F. Paul, L. Cantrel, M. Badawi, *Phys. Chem. Chem. Phys.* 19, 27530 (2017).

[2] K.W. Chapman, P.J. Chupas, T.M. Nenoff, *J. Am. Chem. Soc.* 132, 8897 (2010)

[3] S. Chibani, M. Chebbi, S. Lebègue, T. Bučko, M. Badawi, *J. Chem. Phys.* 144, 244705 (2016).

[4] T. Bučko, *J. Phys.: Condens. Matter* 20, 064211 (2008).

[5] T. M. Nenoff, M.A. Rodriguez, N.R. Soelberg, K.W. Chapman, *Micropor. Mesopor. Mater.* 200, 297 (2014).

[6] S. Chibani, M. Chebbi, S. Lebègue, L. Cantrel, M. Badawi, *Phys. Chem. Chem. Phys.* 18, 25574 (2016).

Acknowledgments

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