Experimental Report

24/04/2014

Proposal:	**7-05-408**	**Council:**	10/2012
Title:	INS study of solvatochromic effectinduced by host-guest interactionsin zeolites		

This proposal is a new proposal

Researh Area: Chemistry

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Samples: ZSM-5, M6(SiO2)90(AlO2)6 (M=Li, Na, K, Rb, Cs) ; salicylidene aniline (C13H11NO)

Instrument	Req. Days	All. Days	From	To
IN1 LAG	4	4	27/05/2013	31/05/2013

Abstract:

The aim of this proposal is to understand the role of zeolite structure and the nature of extraframework cations (M=Li+, Na+, K+, Rb+, Cs+)on the solvent behavior of zeolites. The goal is planned to be achieved by a combined experimental and modelling study of salicylidenaniline molecule sorbed in cation-exchanged zeolites. The molecule, which is well known for its solvatochromic and photochromic properties, is expected to be a sensitive indicator of the details of host-guest interactions. Results of the study performed with a large palette of methods of electronic and vibrational spectroscopies and assisted by molecular modeling, will provide new data allowing a better understanding of reactivity of zeolites. The outcome of the project should provide a new insight on the acid-base characteristics of non-Brønsted acid zeolite and on the parameters controlling these characteristics.

INS study of solvatochromic effect induced by host-guest interactions in zeolites

Introduction. There has been a considerable interest in molecular compounds exhibiting photochromic and solvatochromic properties, which are of crucial importance for the development of photosensible devices such as optical memories and photoswitches. Among such molecules, 2-hydroxybenzylideneaniline (hereafter referred to as salicylideneaniline, SA) belongs to the Shiff bases family and is often considered as a prototype molecule revealing reversible photoreactivity. [1-3] The SA molecule can exist in several tautomer forms, as shown in Fig. 1. It is generally agreed that the ground state SA isomer is the cis-enol form (Fig. 1a) and that the reactivity of the molecule is related to the proton transfer that leads to the formation of the cis-keto structure (Fig. 1b) in the excited state.

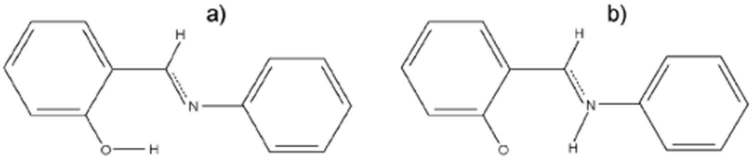

Fig. 1 Isomers of the salicylideneaniline molecule: cis-enol (a), cis-keto (b)

Among different experimental techniques used to study photochromic molecules, methods of conventional vibrational spectroscopy provide the information at the length- and time-scale relevant to the process of interest. Despite the long history of studies on the photochromism of SA, vibrational spectroscopic investigations of the molecule in both the solid state and solution are few in number. Furthermore, the assignments of bands to the vibrational modes of the molecule were incomplete. The first goal pursued in the present work is to investigate the vibrational dynamics of the SA molecule in a solid phase with particular attention to covering whole spectral interval characteristics of molecular vibrations and on the assignment of observed spectral features to the vibrational modes. The second goal of the study is to characterize salicylideneaniline confined in an inorganic matrix. The reason for this second objective is that such a matrix (**acting like a solvent**) has a number of advantages over the classical fluid solvents because it provides a controlled geometrical and chemical environment, a degree of confinement, and a high thermal stability. Silicalite-1 zeolite (all-silica analog of ZSM-5 zeolite) is chosen in the present study as such a host medium. Because of the inert nature of silica walls and the fact that the size of zeolite pores tightly fits the size of the molecule, one can expect that SA sorbed in silicalite-1 should exist in an immobile quasi-isolated state. These goals are achieved by using a number of experimental techniques such as the Raman, infrared, and inelastic neutron scattering (INS) spectroscopies. The complementary information obtained by these methods are supplemented by results of quantum-chemical calculations and molecular modeling.

Experimental. Weighed amounts (ca. 1.2 g) of silicalite-1 were introduced into an evacuable and heatable glass cell placed in a vertical oven connected to a piping network. The sample was heated stepwise up to 450°C under a flow of dry argon for 3 hours and then cooled to room temperature in the argon atmosphere. Amounts of salicylideneaniline corresponding to one molecule per two unit cells of silicalite-1 structure were introduced into the cell under a dry argon atmosphere. The process of sorption of the SA molecule into silicalite-1 was monitored by conventional diffuse reflectance UV-visible absorption spectroscopy and Raman spectroscopy. After six months, the UV-vis and Raman spectra of the system did not show any further evolution, thus indicating that the system had come to equilibrium and that SA was present in the zeolite void in a molecular form. Inelastic neutron scattering experiments were carried out using the new spectrometer LAGRANGE at the Institut Laue-Langevin, Grenoble, France. This spectrometer combines an extended energy range, a higher resolution, and an increased detected flux compared with the previous instrument. The scattering cross-section for hydrogen being much larger than of other elements, INS traditionally emphasizes vibrational modes involving hydrogen atoms. In this work, measurements were performed using a Cu(220) monochromator. The estimated accuracy on the frequency values is ±10 cm^{-1}. The samples were transferred inside a glovebox, into cylindrical aluminum cells. The cells were placed in a cryostat and cooled to 10 K to decrease the influence of the Debye-Waller factor, and thus sharpen peaks in the vibrational spectra.

Results.

1. Vibrational spectra of SA in the solid phase. The analysis of the experimental Raman and INS spectra of the SA powder unambiguously indicates that the molecule in the solid phase exists in the cis-enol form. A slight difference in the position of peaks and/or intensities of some modes can be ascribed to a systematic error inherent to the theoretical level used in the calculations, and to the fact that the calculations were performed for an isolated molecule.

2. Vibrational spectra of the SA molecule adsorbed in silicalite-1zeolite. Silicalite-1 has the MFI structure type and its framework is characterized by a porous system consisting of intersecting channels formed by rings of ten oxygen atoms. Straight channels run along the b crystallographic axis and have a nearly circular shape with dimensions of 5.3 Å x 5.6 Å, while sinusoidal channels have an average direction along the a axis with dimensions of 5.1 Å x 5.5 Å. The analysis of the spectra in Fig. 2 shows that the Raman and INS spectra of the molecule in the solid and sorbed states are very similar to each other.

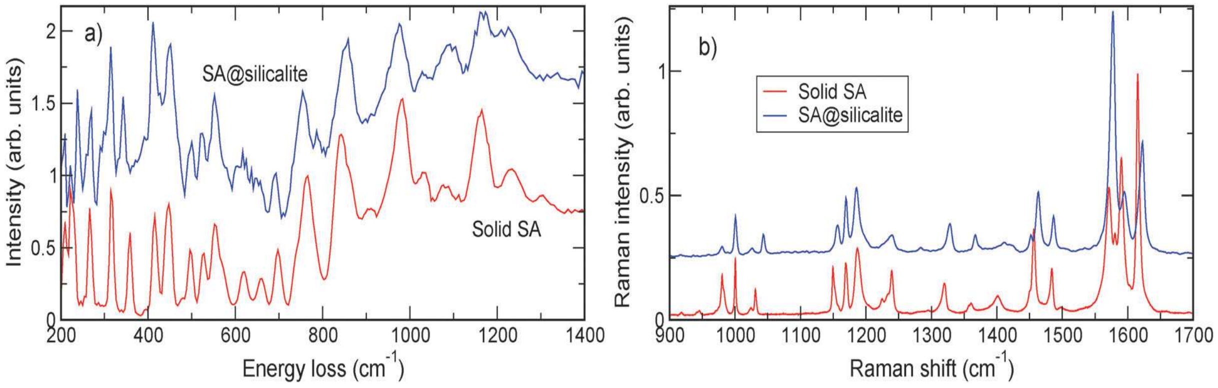

Fig. 2. INS (a) and Raman (b) spectra of the SA molecules sorbed in silicalite-1compared with the spectra of the molecule in solid phase.

The comparison of the frequencies of the vibrational modes of the molecule in the solid and sorbed states shows that the frequency differences are relatively small and the maximum difference does not exceed 18 cm^{-1} and indicates that silicalite-1 is a relatively inert environment. It is worthy to note that the Raman spectrum of the sorbed molecules does not contain the peak at 111 cm^{-1}, which supports the assignment of this peak to an intermolecular mode. Analysis of the atomic displacements reveals that these modes have a similar form that can be described as the anti-phase motion of the phenol and benzene rings in the direction perpendicular to the plane of the rings. A possible explanation for the downward shift of their vibrational frequencies is that the intermolecular interactions in the solid phase constrains these vibrations to a larger extent than the interactions with the silicalite-1 lattice. This hypothesis is in line with the disappearance of the peak at 111 cm^{-1} in the Raman spectrum of sorbed salicylideneaniline. Most of the modes are shifted upward upon sorption. Analysis of the potential energy distribution in the modes shows that the dominant contributions to PED come from the internal coordinates of the phenol ring. Therefore it is of interest to analyse the atomic displacements and their localization in the modes that are shifted upon sorption. Such different behaviours of the vibrational mode frequencies reflects a different degree of confinement of the phenol and benzene rings of the molecule by the silicalite-1 framework. Indeed, large frequency shifts of the modes localized on the phenol ring indicate that this part of the sorbed molecule is more constrained than the benzene ring. Given the size and shape of the molecule and the topology of the zeolite void, one can suggest that the benzene ring of SA resides in the intersection of the straight and sinusoidal channels, whereas the phenol ring is situated in the section of the straight channel between two intersections, where the ring is subjected to a larger confinement than the benzene one. From the structural view-point it is unlikely that the molecule can reside in a sinusoidal channel because the topology of the zeolite pore system would apply too strong constraints on the molecular geometry. Consequently, we propose that the most probable adsorption site of the SA molecule is the straight channels of the silicalite-1 framework. This assumption is supported by results of molecular modeling.

Conclusion. The comparison of Raman, infrared, and inelastic neutron scattering spectra of the SA molecule with the theoretical spectra obtained by using results of quantum-chemical calculations of different SA isomers in a free state, unambiguously shows that the molecule exists in the cis-enol form in a condensed phase. The analysis of the experimental data is greatly facilitated by the complementary nature of the techniques and by the comparison of the experimental and calculated peak intensities. Making use of the results of the calculations, a complete assignment of the observed spectral features to the vibrational modes of the molecule is performed. All experimental spectroscopic data indicate that the sorbed SA molecules are present in the cis-enol form in the zeolite channels. The confinement induces only a weak perturbation of the vibrational dynamics of the molecule in comparison with that in solid SA. The displacements of spectral peaks in the Raman and INS spectra of SA upon sorption and the analysis of the corresponding vibrational modes show that the confinement mostly affects the vibrational modes whose amplitude is localized on atoms of the phenol ring. This finding allows the suggestion that the sorbed SA molecule is located in the zeolite channel, such that the phenol ring lies in the section of the straight channel between two intersections, whereas the benzene ring is situated at the channel intersection. This assumption is corroborated by results of molecular modeling using a combination of Monte-Carlo and energy minimization techniques.

In addition, note that the nature of extraframework cations (M=Li+, Na+, K+, Rb+, Cs+) on the solvent behavior of zeolites was also investigated using such complementary techniques. The molecular modelling and interpretations are still on progress and the outcome of the project should provide a new insight on the acid-base characteristics of non-Brønsted acid zeolite and on the parameters controlling these characteristics.

[1] I. Casades, M. Alvaro, H. Garcia, M. N. Pillai, *Eur. J. Org. Chem.*, (2002), 2074-2079.
[2] P. K. Dutta, W. Turbeville, *J. Phys. Chem.*, 95 (1991), 4087-4092.
[3] W. Turbeville, P. K. Dutta, *J. Phys. Chem.*, 94 (1990), 4060-4066.

The INS experiments permit the following paper :
M. Hureau, K. Smirnov, A. Moissette, H. Jobic *Phys.Chem.Chem.Phys. 2014, 16, 7562−7570.*