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Detection and use of small *J* couplings in solid state NMR experiments

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Abstract

Over the years, solid-state nuclear magnetic resonance (NMR) spectroscopy has become an important tool for materials science, with its local point of view that is highly complementary to the structural information provided by diffraction techniques, electron microscopy, and molecular modeling, for example. As compared to other interactions that determine the spectral expression of the local structure of the observed nuclei in solid-state NMR experiments, the *J* coupling, characteristic of the chemical bonds, has received far less attention because of its being generally so small that it is masked in the line-widths. Nevertheless, the scalar or isotropic part of *J* couplings, which is not averaged by magic angle spinning (MAS), can be evidenced in many systems, and exploited to unequivocally characterize the extended coordination sphere. In a first step we describe the different experiments that permit the observation and the measurement of *J* couplings, even when dealing with quadrupolar nuclei. We then present new and recently-published results that illustrate the state of the art of NMR methodologies based on or intended for measuring *J* couplings in solids and the novel perspectives that they open towards better understanding of ordered and disordered materials at the subnanometric scale, a length scale that is otherwise difficult to access. ***To cite this article: D. Massiot et al., C. R. Chimie 13 (2010).***

Keywords: NMR; High resolution solid-state NMR; *J* coupling; Dipolar interaction

1. Introduction

Because of its ability to selectively observe and characterize the local environments of most constituting atoms of ordered or disordered solids, high-resolution solid-state nuclear magnetic resonance (NMR) spectroscopy has become a tool of choice for materials science. The rapid development of new methods now not only provides means for spectrally resolving and quantifying different chemical environment characterized by their chemical shifts but also allows one to explore the structure of the surrounding of the observed atoms at different length scales using interactions characteristic of distances (dipolar interaction) [1,2] or chemical bonds (*J* indirect coupling) [3]. These methods can take different forms ranging from spectral edition to measurement and use the through-space or through-bond interactions in multidimensional experiments. The aim of this contribution is to focus on the measurement and use of indirect *J* couplings, even when involving

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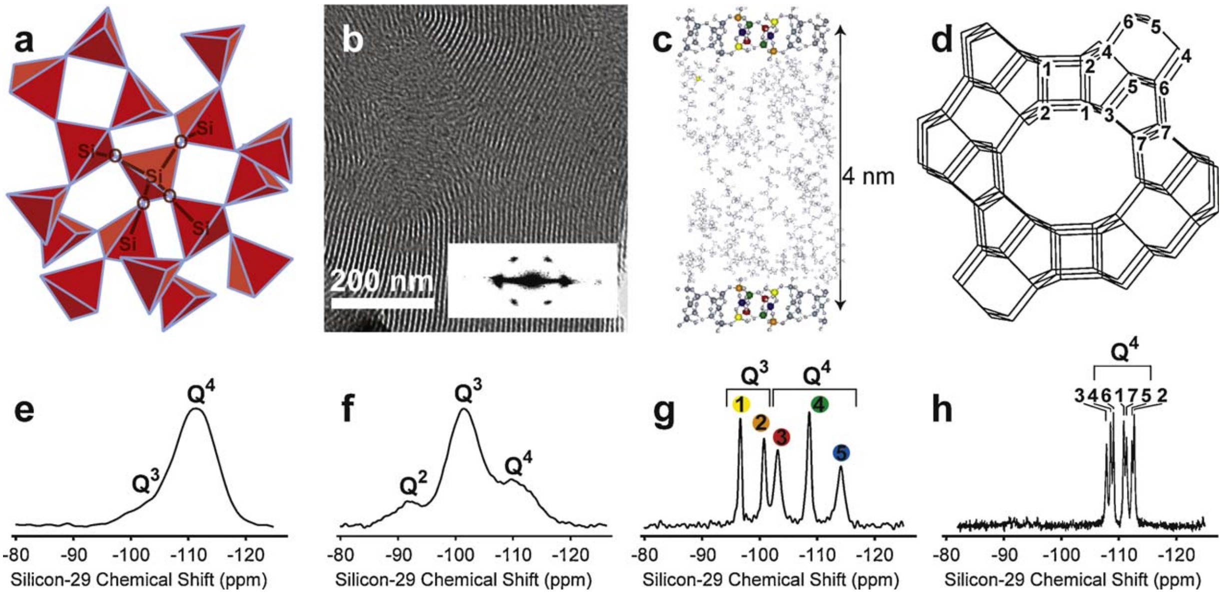

Fig. 1. a: schematic representation of an amorphous SiO_2 structure, with SiO_4 tetrahedra shown in red, and (e) ^{29}Si spin-echo MAS NMR spectrum of commercial silica with 99% enrichment in ^{29}Si; b: transmission-electron microscopy (TEM) image and electron diffraction pattern (inset) and (f) $^{29}Si\{^1H\}$ CPMAS NMR spectrum of an hexagonal mesoporous silica composite [4]; c: in-plane view of a layered silicate–surfactant mesophase consisting of thin (0.8 nm) molecularly-ordered silicate sheets with five distinct (colored) Si atom sites giving rise to five narrow ^{29}Si resonances in the corresponding $^{29}Si\{^1H\}$ CPMAS NMR spectrum (g), and separated by alkylammonium surfactant species [5]; d: schematic representation of the highly ordered silicate framework structure and (h) ^{29}Si MAS NMR spectrum with extremely narrow resonances of zeolite ZSM-12 (courtesy D.H. Brouwer).

quadrupolar nuclei, and to emphasize new developments and perspectives.

Silica-based materials can be used as a starting point to illustrate the general problems of materials science that can be assessed using solid-state NMR, including by the exploitation of molecular interactions such as *J* couplings. These materials are of paramount importance in many different fields of materials sciences in the form of inorganic glasses, sol–gel derived materials, biocompatible or bioinspired materials, porous or mesoporous materials, zeolites, or organic–inorganic hybrids. The structures of silica-based materials are characterized in particular by various extents of order and disorder at length scales that range from molecular to micrometric dimensions, as illustrated with a few typical examples on Fig. 1. Amorphous structures, such as silicate glasses or commercial SiO_2, which may be used as a silicon source for silicate materials synthesis, have highly disordered molecular structures that are associated with a wide range of local silicon environments giving rise to broad (ca. 10 ppm, full width at half maximum [fwhm]) ^{29}Si NMR lineshapes (Fig. 1e) that barely allow resolution of chemically different Q^3 (*i.e.*, $(SiO)_3Si–OH$ or $(SiO)_3Si–O^-$) and fully condensed Q^4 $(Si(SiO)_4)$ ^{29}Si moieties. Similar molecularly-disordered SiO_2 structures are also generally found in the walls of self-assembled mesoporous silica despite potentially high degrees of long-range order in their pore architectures, as illustrated on Fig. 1f by the broad lineshapes associated with Q^2, Q^3, and Q^4 environments in the $^{29}Si\{^1H\}$ cross-polarization (CP) magic angle spinning (MAS) spectrum of the block-copolymer-silica composite whose representative transmission electron microscopy (TEM) image is shown on Fig. 1b [4]. Increasing extents of molecular order, on the other hand, may be clearly evidenced by narrow ^{29}Si NMR resonances that allow distinguishing between chemically similar environments on the basis of subtle differences in their bonding geometries. This is for example the case for non-crystalline surfactant-templated layered silicates with short-range molecular order [5] (Fig. 1c and g) and even more so for high-zeolites such as ZSM-12 [6] (Fig. 1h), where high degrees of long-range three-dimensional (3D) molecular order yield extremely narrow (ca. 0.4 ppm) ^{29}Si MAS NMR lineshapes (Fig. 1h).

However, even if the simple 1D ^{29}Si MAS spectra (direct observation or CP from ^1H) obviously already provide valuable information on the nature and composition of complex materials at the molecular level, the exact attribution of the different resonances in highly ordered compounds or the understanding of the