Advances in the characterization of inorganic solids using NMR correlation experiments
Andrew G. M. Rankin, Frédérique Pourpoint, Nghia Tuan Duong, Laurent Delevoye, Jean-Paul Amoureux, Olivier Lafon

To cite this version:

Andrew G. M. Rankin, Frédérique Pourpoint, Nghia Tuan Duong, Laurent Delevoye, Jean-Paul Amoureux, et al.. Advances in the characterization of inorganic solids using NMR correlation experiments. Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, Elsevier, 2023, 10.1016/B978-0-12-823144-9.00192-8 . hal-03995696

HAL Id: hal-03995696
https://cnrs.hal.science/hal-03995696
Submitted on 3 Mar 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Advances in the characterization of inorganic solids using NMR correlation experiments

Andrew G. M. Rankin¹, Frédérique Pourpoint², Nghia Tuan Duong³, Laurent Delevoye¹, Jean-Paul Amoureux², Olivier Lafon¹,*

¹ Univ. Lille, CNRS, INRÉA, Centrale Lille, Univ. Artois, FR 2638 – IMEC – Fédération Chevreul, 59000 Lille, France
² Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, 59000 Lille, France.
³ Aix Marseille Univ, CNRS, ICR, 13397 Marseille, France.
⁴ Bruker Biospin, 34 rue de l'industrie, 67166 Wissembourg, France.

* corresponding author: olivier.lafon@univ-lille.fr

Keywords: solid-state NMR, correlation, homonuclear, heteronuclear, through-bond, through-space, INADEQUATE, HETCOR, HMQC, INEPT, microporous materials, catalysts, minerals, biomaterials

Abstract: As a local characterization technique endowed with atomic resolution, solid-state NMR spectroscopy provides unique insights on the atomic-level structure and dynamics of inorganic and hybrid materials. In particular, two-dimensional through-bond and through-space correlation experiments allow the observation of covalent bonds and proximities between identical or distinct isotopes, thus providing detailed information on the arrangement of atoms in the materials. Compared to biological and organic samples, inorganic and hybrid materials contain additional NMR-active nuclei, and notably quadrupolar isotopes with nuclear spin I ≥ 1, such as ¹¹B, ²⁷Al and ⁷¹Ga, which are often subject to large quadrupolar interaction. Therefore, specific NMR correlation experiments have been developed to probe the local environment of these quadrupolar isotopes. We provide here an in-depth overview of correlation experiments, which have been employed for the characterization of inorganic and hybrid materials. We present first the through-space and through-bond correlation experiments to probe connectivities and proximities between identical nuclei, and then their counterparts for distinct isotopes. In both cases, we describe the experiments employed for spin-1/2 and quadrupolar isotopes. We indicate the state-of-the-art technique and the isotopes, for which they have been applied. Finally we present how these correlation NMR experiments have provided essential information on the atomic-level structure of different classes of inorganic hybrid materials, including (i) microporous materials (aluminophosphates, zeolites, metal-organic frameworks (MOFs)), (ii) metal oxide catalysts, such as amorphous silica alumina as well as supported metal complexes on alumina or silica, (iii) minerals and biomaterials and (iv) glasses.

1. Introduction

Correlation NMR techniques are a given class of two-dimensional (2D) NMR experiments. They provide information on the through-bond connectivities and through-space proximities between nuclei in solids by coherence transfers during the mixing period through J- and dipolar couplings, respectively. The 2D correlation NMR spectra indicate between which spins the coherences are transferred. For improving resolution and sensitivity, these experiments are performed under magic-angle spinning (MAS) conditions. These experiments are classified into two types: the homo- and hetero-nuclear correlation NMR experiments, which probe the connectivities or proximities between
identical and distinct nuclei, respectively, which can be either spin-1/2 or quadrupolar isotopes (see Figure 1).

![Diagram of 2D correlation NMR experiments](image)

**Figure 1.** Schematic classification of 2D correlation NMR experiments, which can be employed to probe connectivities and proximities in solids under MAS conditions. $S \geq 1$ denotes the integer and half-integer spin quadrupolar isotopes, whereas $I$ or $S = n/2$ with $n \geq 1$ denotes solely the half-integer quadrupolar nuclei. In the case of quadrupolar nuclei, the coherence transfer in 2D heteronuclear correlation experiment can be mediated by the sum of $J$-coupling and the second-order quadrupolar-dipolar cross terms, which are not average out by MAS.$^{1,2}$

Correlation NMR experiments, including correlation spectroscopy (COSY)$^{3}$ between identical nuclei and heteronuclear single-quantum coherence (HSQC)$^{4}$ scheme between distinct isotopes, have been initially introduced at the end of the 1970s to probe connectivities between spin-1/2 nuclei in isotropic solutions. In 1980s and 1990s, these correlation experiments were adapted for the study of spin-1/2 isotopes in solids under MAS conditions. Solid-state correlation experiments were first introduced to probe heteronuclear proximities in organic and inorganic solids.$^{5,6}$ Then they were applied to observe homonuclear connectivities in plastic crystals$^{7,8}$ and later in inorganic solids$^{9,10}$. As regards covalent bonds between distinct isotopes, they have been detected using correlation experiments first in inorganic solids$^{11}$, before their observation in organic solids$^{12}$. Correlation experiments to probe homonuclear proximities have been reported first for solid-state amino-acids$^{13}$, before their use for phosphate compounds$^{14}$.

The correlation solid-state NMR experiments, which are listed above, were first demonstrated for spin-1/2 isotopes. A further advance was their use for quadrupolar nuclei with spin $I \geq 1$, which was demonstrated in the 1990s and 2000s. Heteronuclear correlation experiments have been developed to probe proximities$^{15,16}$ and later connectivities$^{17}$ between spin-1/2 and half-integer quadrupolar nuclei, such as $^{31}$P and $^{27}$Al with $I = 5/2$. Then these experiments were also applied to observe proximities$^{18}$ and later connectivities$^{19}$ between distinct half-integer quadrupolar nuclei, such as $^{27}$Al and $^{17}$O with $I = 5/2$. These heteronuclear correlation experiments were also combined with the multiple-quantum MAS (MQMAS) scheme to refocus the second-order quadrupolar broadening and hence, allow the acquisition of high-resolution NMR spectra$^{20,21}$. Homonuclear correlation experiments have also been introduced to detect proximities between identical half-integer quadrupolar nuclei, such as $^{23}$Na and $^{11}$B with $I = 3/2$$^{22,23}$. Conversely, to the best of our knowledge, these experiments have not yet been applied to detect connectivities between quadrupolar nuclei. Another major advance was the development of heteronuclear correlation for the indirect detection of $^{14}$N nuclei, which does not exhibit a central transition (CT) contrary to half-integer quadrupolar nuclei, via spin-1/2 isotopes, such as $^1$H.$^{1,2}$ This approach has more recently been applied for the indirect detection of spin-1/2 nuclei subject to large chemical shift anisotropy (CSA), such as $^{195}$Pt$^{24}$. 
The robustness of through-space correlation NMR experiments has also been improved by the development of more robust dipolar recoupling schemes designed using symmetry 25 and built from composite 26 or adiabatic pulses 27. These experiments have also been modified so that they enable (i) the observation of longer-range proximities 28, (ii) are compatible with high MAS frequencies 29 and (iii) are less affected by the random fluctuations of MAS frequencies, which cause $t_1$-noise 30,31. The sensitivity of these heteronuclear correlation experiments has notably been improved using indirect detection via protons at high MAS frequencies 32. Several reviews about homo- and hetero-nuclear recoupling sequences, mainly for spin-1/2 nuclei, have been published 33-41. Through-bond correlation experiments, primarily for spin-1/2 isotopes in organic solids, 42,43 as well as correlation experiments for quadrupolar nuclei44-48 have also been surveyed. Furthermore, through-bond and through-space correlation experiments for both spin-1/2 and quadrupolar nuclei were presented in reviews about solid-state NMR of a specific class of inorganic materials, including oxide glasses 49-51, crystalline and amorphous aluminophosphates 52, heterogeneous catalysts 53-56, zeolites 57-59 and metal-organic frameworks 58,60.

We provide here an overview of correlation NMR experiments for inorganic solids. We notably highlight the state-of-the-art techniques to probe homo- and hetero-nuclear connectivities and proximities of spin-1/2 and quadrupolar nuclei. We also show how these techniques have provided new insights into the atomic-level structure of inorganic materials, including microporous materials, heterogeneous catalysts, minerals, biomaterials and glasses.

2. Correlation between identical nuclei

Connectivities and proximities between identical nuclei can be probed by homonuclear correlation experiments employing coherence transfers based on $J$- and dipolar-couplings, respectively. These experiments can be classified based on the coherences, which are selected during the indirect evolution period, $t_1$, and which can be either single-, double- or triple-quantum (1Q, 2Q or 3Q) coherences, whereas the 1Q coherences are always detected during the acquisition period, $t_2$ 35,61. The sensitivity of these experiments decreases with increasing coherence order during the $t_1$ period. Nevertheless, 2Q-1Q correlation allows probing the connectivities or proximities between sites with close resonance frequencies, whereas 3Q-1Q correlation permits the observation of triplets of nuclei 61. We present first the through-bond homonuclear correlation, before the discussion of through-space variants.

2.1 Through-bond homonuclear correlations

Connectivities between spin-1/2 nuclei in inorganic solids have been first probed using the COSY experiment, which is a 1Q-1Q correlation and is identical to the experiments used for liquids 8-10,62. Nevertheless, the conventional COSY experiment suffers from disadvantages that (i) the diagonal and cross-peaks cannot be displayed simultaneously in double absorption mode, (ii) the intense diagonal peaks can obscure cross-peaks in 2D COSY spectra and (iii) the anti-phase components of the cross peaks reduce their overall intensity. The first and second of the above difficulties can be circumvented by the use of the double-quantum filtered COSY (DQF-COSY) experiment, for which the diagonal and cross peaks can be phased in double-absorption mode 62. Nevertheless, the DQF-COSY experiment is not optimal for the characterization of solids since it yields anti-phase line shapes, which reduces the intensity of the cross peaks for unresolved couplings. This limitation can be circumvented by using total through-bond correlation spectroscopy (TOBSY), in which radiofrequency (rf) irradiation synchronized with MAS removes the anisotropic interactions, such as dipolar interactions and CSA, as well as the isotropic chemical shifts and only allows the homonuclear $J$-couplings 63. In particular, this selection of homonuclear $J$-coupling can be achieved using the symmetry-based R30 14 scheme, which is highly
robust to offset and rf field inhomogeneity. The TOBSY sequence has been used to record 2D $^{31}\text{P}$ 1Q-1Q through-bond homonuclear correlations and hence, to probe $^{31}\text{P}$-O-$^{31}\text{P}$ connectivities in phosphate crystalline phases. Nevertheless, the 1Q-1Q correlations, such as DQF-COSY and TOBSY, do not allow the observation of connectivities between nuclei with close resonance frequencies, which is an important limitation for the use in inorganic solids, since these samples often contain nearby sites with similar resonance frequencies.

This limitation can be side-stepped by the use of 2Q-1Q correlation using the incredible natural abundance double quantum transfer experiment (INADEQUATE). The technique was originally introduced in 1980 by Freeman and co-workers in order to probe natural abundance $^{13}\text{C}$-$^{13}\text{C}$-$J$-couplings in the solution state. Fyfe et al. were amongst the first to recognise the potential for the sequence to be used to study solid materials, reporting in the early 1990s the use of $^{29}\text{Si}$ INADEQUATE for the elucidation of the three-dimensional (3D) lattice structures of zeolites. However, one difficulty in applying the INADEQUATE sequence used for liquids to the solid-state is that it yields anti-phase correlations, leading to reduced intensity for unresolved couplings. Hence, this sequence is only suited to solid samples that generate narrow spectral lineshapes, such as the well-defined framework structures studied in the aforementioned works.

In 1999, Lesage et al. proposed a modified version of the pulse sequence designed to overcome the limitations of the original technique. This variant, termed “refocused INADEQUATE”, is displayed in Figure 2. The evolution under homonuclear dipolar interactions and CSA is suppressed by the synchronization with MAS, i.e. the delays between the centers of the rf pulses are equal to an integer multiple of rotor period, $\tau_R = 1/\nu_R$, where $\nu_R$ is the MAS frequency, whereas the 180° pulses in the middle of the first and second $\tau$ delays, termed defocusing and refocusing delays, respectively, refocus the evolution under isotropic chemical shifts. During the defocusing delay, the transverse magnetization evolves under homonuclear $J$-couplings into anti-phase 1Q coherences, which are converted into 2Q coherences by the second 90° pulse. In the absence of losses, the creation of 2Q coherences for an isolated $S_2$ spin pair is maximum for $\tau = 1/(2J_{SS})$, where $J_{SS}$ denotes the $J$-coupling constant between the observed $S$ spins. These coherences evolve at the sum of the isotropic chemical shifts of the correlated nuclei during the $t_1$ period and are converted back into anti-phase 1Q coherence by the third 90° pulse. In contrast with the original INADEQUATE sequence, the refocused INADEQUATE scheme includes a refocusing delay between the third 90° pulse and the acquisition to transform the anti-phase 1Q coherences into in-phase signal before the acquisition. This sequence is especially useful for the study of disordered solids exhibiting NMR signals broader than the strength of the homonuclear $J$-couplings.
Figure 2. Pulse sequence of 2D $^{31}$P refocused INADEQUATE experiment along with desired coherence transfer pathways. Figure adapted from ref. 73. The initial 90° pulse can be replaced by $^1$H→$^{31}$P cross-polarization (CP) transfer to enhance the sensitivity and/or to select the $^{31}$P nuclei near protons.

If the refocused INADEQUATE sequence was first applied for the observation of connectivities between $^{13}$C nuclei in organic solids, its utility to detect $J$-coupling between $^{31}$P nuclei, which has a 100% natural isotopic abundance, has been later demonstrated in phosphorus-containing crystalline and amorphous solids, notably by the solid-state NMR group at CNRS Orleans, France. Several publications have demonstrated the use of 2D $^{31}$P refocused INADEQUATE for the structural characterisation of P-O-P connectivities in $\text{Zn}_2\text{P}_2\text{O}_7$ and $\text{SnP}_2\text{O}_7$ crystalline powders (see Figure 3) 75 as well as lead phosphate glasses 74,76. The $J$-coupling constants between $^{31}$P nuclei through P-O-P linkage typically range from 16 to 34 Hz 75,77. It has also been shown that the 2D INADEQUATE spectrum can exhibit diagonal peaks in the absence of $J$-coupling between $^{31}$P nuclei with the same isotropic chemical shift but distinct magnitude or orientation of their CSA tensors since the $n = 0$ rotational resonance ($R^2$) reintroduces the dipolar interaction between them 73. The intensity of these anomalous diagonal peaks decreases at higher MAS frequency and lower static magnetic field. 2D $^{31}$P 3Q-1Q homonuclear correlation spectra have also been recorded for $\text{Pb}_3\text{P}_4\text{O}_{13}$ crystalline compound and
phosphate glasses using the same sequence as refocused INADEQUATE but distinct phase cycling\textsuperscript{61}. These spectra allow for the observation of P-O-P-O-P trimers.

Figure 3. 2D \textsuperscript{31}P refocused INADEQUATE spectrum of SnP$_2$O$_7$ crystalline powder acquired at a static magnetic field $B_0 = 7$ T with $\nu_R = 10$ kHz. This spectrum shows 46 pairs of cross-correlation peaks resulting from P-O-P connections. Reprinted with permission from reference \textsuperscript{75}. Copyright 2003, American Chemical Society.

As mentioned above, INADEQUATE experiments have also been used to probe connectivities between $^{29}$Si nuclei in solids. The two-bond $J$-coupling constant, $2J_{\text{SiOSi}}$, between $^{29}$Si nuclei of Si–O–Si linkages is typically lower than 15 Hz in silicate materials\textsuperscript{78}. Furthermore, the natural abundance of the $^{29}$Si isotope is only 4.68\% and hence, the probability of having two sites containing $^{29}$Si isotope is as low as 0.2\%. Therefore, the first reported 2D $^{29}$Si INADEQUATE experiments on isotopically unmodified zeolites lasted several days\textsuperscript{69}. The sensitivity of this experiment has been improved by $^{29}$Si isotopic enrichment\textsuperscript{79} and/or dynamic nuclear polarization (DNP) under MAS (see Figure 4)\textsuperscript{80–82}. This latter technique enhances the NMR signal by transferring the polarization of unpaired electrons to the nuclear spins through microwave irradiation\textsuperscript{83}. The unpaired electrons can be exogenous biradicals, which are incorporated into the sample by impregnation with a solution of biradicals. In these conditions, DNP primarily enhances the NMR signals of nuclei located near surfaces\textsuperscript{84,85}. Therefore, DNP-enhanced 2D $^{29}$Si INADEQUATE experiments have been mainly applied to probe the $^{29}$Si-$^{29}$Si connectivities near the surface of particles\textsuperscript{80,81}. Nevertheless, unpaired electrons in the bulk region of the materials, such as oxygen vacancies in γ-irradiated fused quartz, can also be used as a source of polarization for DNP to enhance the sensitivity of $^{29}$Si INADEQUATE experiment\textsuperscript{86}. Furthermore, the use of the 2D $^{29}$Si refocused INADEQUATE sequence allows the observation of $^{29}$Si-$^{29}$Si connectivities in disordered and amorphous materials, for which the linewidths exceed the $^{29}$Si-$^{29}$Si $J$-coupling constants\textsuperscript{87,88}. In addition, a variant of the 2D $^{29}$Si refocused INADEQUATE sequence incorporating a z-filter between the refocusing delay and the acquisition period has been employed to eliminate undesired antiphase contributions due to multiple couplings\textsuperscript{88,89}. Finally, the sensitivity of 2D $^{29}$Si INADEQUATE experiments can be improved by the Carr-Purcell Meiboom-Gill (CPMG) scheme, i.e. the acquisition of a train of echoes during the acquisition period by applying a train of 180° pulse\textsuperscript{90}. 
More recently, a DNP-enhanced refocused INADEQUATE scheme has been applied to probe the connectivities between surface and core $^{113}$Cd nuclei of CdS quantum dots. This experiment relies on $^{113}$Cd–S–$^{113}$Cd $J$-coupling constants, which are approximately equal to 100 Hz.

To the best of our knowledge, 2D homonuclear correlation between quadrupolar nuclei via homonuclear $J$-couplings has not been reported. Conversely, connectivities between $^{27}$Al nuclei connected via O bridges to the same $^{31}$P nucleus in microporous crystalline AlPO$_4$-14 compounds have been probed using relay via two-bond $^{31}$P–$^{27}$Al $J$-couplings and 2D through-bond homonuclear correlation experiment derived from heteronuclear single-quantum correlation (HSQC) sequence.

2.2 Through-space homonuclear correlations

Through-space homonuclear correlations, which rely on coherence transfer via homonuclear dipolar couplings, allow the observation of proximities between identical nuclei and hence, complement through-bond homonuclear correlations. For isotopes in the first periods of the periodic table, the homonuclear dipolar couplings are usually larger than the $J$-couplings and yields faster coherence transfers. As a result, through-space homonuclear correlation experiments are usually more efficient than their through-bond counterparts. These experiments can be classified based on the order of the Hamiltonian governing the through-space coherence transfer as well as the coherence order during $t_1$ period. Through-space homonuclear correlation experiments have been applied to both spin-1/2 and half-integer quadrupolar nuclei.

2.2.1 Between spin-1/2 nuclei

Through-space homonuclear correlations can be achieved through either the first- or second-order Hamiltonian involving the homonuclear dipolar interaction.
First-order recoupling. The contribution of dipolar interactions to the first-order Hamiltonian is averaged out by MAS. Nevertheless, this interaction is reintroduced between spins having isotropic chemical shifts differing by a multiple of the MAS frequency, i.e. the $R^2$ condition $93-95$. This approach has been recently applied to record 2D $^{89}$Y 1Q-1Q through-space homonuclear correlation spectrum of yttrium-doped ceria $96$. To compensate the long longitudinal relaxation time of the $^{89}$Y isotope, which typically reaches hundreds of seconds, and its low gyromagnetic ratio ($|\gamma(\text{H})|/|\gamma(\text{Y})| = 4.92\%$), the sensitivity of this 2D $^{89}$Y homonuclear correlation was enhanced using DNP transfer from paramagnetic Gd(III) dopants. Nevertheless, the $R^2$ approach is a frequency-selective recoupling, which reintroduces the dipolar couplings only between specific sites at a given MAS frequency.

A more broadband and versatile approach to reintroduce the homonuclear dipolar couplings under MAS in the first-order Hamiltonian relies on the application of rf pulses, which prevents its refocusing by MAS. In particular, some first-order homonuclear dipolar recoupling schemes have been developed, which selectively restore the homonuclear dipolar coupling, while removing the unwanted interactions, such as isotropic and anisotropic chemical shifts as well as heteronuclear $J$- and dipolar couplings. The first-order recoupling schemes allow the detection of proximities between the nearest neighbors. Weak cross-peaks are observed for nuclei further apart owing to the dipolar truncation, i.e. the large homonuclear recoupled dipolar interactions between nearby nuclei attenuates the coherence transfers between distant nuclei $97$.

A widely used first-order homonuclear dipolar recoupling to acquire 2D 1Q-1Q correlation is the radio-frequency driven-recoupling (RFDR), where one 180° pulse is applied every rotor period $13$. This recoupling is robust, easy to set-up and works at all MAS frequencies. Nevertheless, when the pulse length represents a significant fraction of the rotor period, the amplitude of the recoupled dipolar interaction depends on the rf field strength. This variant has been called finite-pulse RFDR (fp-RFDR) $98$. The RFDR scheme has notably been employed to acquire 2D 1Q-1Q through-space correlation spectra of $^{31}$P, $^{29}$Si and $^1$H nuclei of inorganic and hybrid materials $99-101$.

Nevertheless, the 1Q-1Q through-space correlation does not allow the observation of proximities between nuclei with close resonance frequencies. This limitation can be circumvented by the acquisition of 2Q-1Q through-space correlation spectra. Various first-order homonuclear dipolar recoupling have been designed to excite and reconvert the 2Q coherences between identical nuclei, including back-to-back (BaBa) scheme $14,102$, RFDR bracketed by 90° pulses (denoted $[\text{fp-RFDR}]$) $103,104$, and symmetry-based sequences, such as POST-C7 $26$, SPC5 $105$, SR2$64$ $1106,107$ and R20$2^9$ $108$. The choice of the recoupling sequence depends on the MAS frequency and the strength of the spin interactions. The 2D $^{31}$P and $^{29}$Si 2Q-1Q through-space correlation spectra are usually acquired at moderate MAS frequencies, $v_b \approx 10$ kHz, which are compatible with the use of POST-C7 and SR2$64$ sequences, which require nutation frequencies, $v_1 = 7v_b$ and $6.5v_b$, respectively $107,109$. In particular, the SR2$64$ recoupling benefits from high robustness and hence, is especially beneficial to observe the small $^{29}$Si-$^{29}$Si dipolar couplings. Conversely, 2D $^1$H 2Q-1Q through-space correlation experiments are carried out at high MAS frequencies, $v_b \geq 50$ kHz, to improve the spectral resolution by averaging out the $^1$H-$^1$H dipolar interactions. For that purpose, symmetry-based first-order homonuclear dipolar recoupling schemes, such as R12$5^2$, with short cycle time and low rf field requirement ($v_1 = 3v_b$) have been introduced $110$. Besides organic solids, these recoupling sequences have been used to probe $^1$H-$^1$H proximities in hybrid solids, including metal-organic frameworks, as seen in Figure 6 $111$. 
During the excitation (exc.) and reconversion (rec.) blocks, the $I-I$ dipolar interaction are reintroduced in the first-order Hamiltonian by recoupling schemes, such as BaBa, [fp-RFDR], POST-C7, SPC5, SR26[11] or R12[12]. The initial longitudinal magnetization can be created by $^1\text{H}$→$I$ CP transfer followed by a flip-back 90° pulse on the $I$ channel.

The pulse sequence and the coherence transfer pathway of 2D $2Q$-$1Q$ through-space homonuclear correlation are displayed in Figure 5. The first recoupling scheme transforms the longitudinal magnetization into $2Q$ coherences, which evolve during the $t_1$ period. The second recoupling scheme reconverts these coherences into longitudinal magnetization, which is transformed into observable transverse magnetization by the 90° pulse. Signals passing through $2Q$ coherences during the $t_2$ period are selected by a four-step phase cycle of the recoupling scheme used either for excitation or reconversion. Like for through-bond correlation, the sensitivity of $^{29}\text{Si}$ through-space correlation can be enhanced by CPMG[12] as well as DNP to detect $^{29}\text{Si}$-$^{29}\text{Si}$ proximities near surfaces[80,113]. Similarly the sensitivity gain provided by DNP has been leveraged to observe proximities between $^{31}\text{P}$ sites near the surface of nanoparticles[114]. 2D $2Q$-$1Q$ through-space homonuclear correlation experiments have also been employed to probe $^{19}\text{F}$-$^{19}\text{F}$ proximities in inorganic fluorides[115–118]. These experiments require robust first-order homonuclear dipolar recoupling since $^{19}\text{F}$ nuclei often exhibit large isotropic and anisotropic chemical shifts. Note also that the proximities between three protons have also been probed using 2D $3Q$-$1Q$ through-space homonuclear correlation experiments[119–121].

Figure 5. Pulse sequence of 2D $2Q$-$1Q$ through-space homonuclear correlation for isotope $I$ along with desired coherence transfer pathways. During the excitation (exc.) and reconversion (rec.) blocks, the $I-I$ dipolar interaction are reintroduced in the first-order Hamiltonian by recoupling schemes, such as BaBa, [fp-RFDR], POST-C7, SPC5, SR26[11] or R12[12]. The initial longitudinal magnetization can be created by $^1\text{H}$→$I$ CP transfer followed by a flip-back 90° pulse on the $I$ channel.
Second-order recoupling. These schemes rely on cross-terms between distinct homonuclear dipolar interactions or homo- and hetero-nuclear dipolar interactions in the second-order Hamiltonian. Hence, these cross-terms contain products of operators of three distinct spins. These recoupling schemes are less susceptible to dipolar truncation than first-order recoupling and they allow probing longer-range distance. Nevertheless, the magnitude of the second-order Hamiltonian is inversely proportional to the MAS frequency and hence, these second-order recoupling are less efficient at high MAS frequency.

In the case of nuclei subject to several large homonuclear dipolar interactions, such as protons and $^{19}$F nuclei, proximities can also be probed using spin diffusion experiments, which have been first introduced for polymer blends and then have been applied for organic molecules adsorbed in zeolites and later inorganic fluorides. The pulse scheme used for these spin diffusion experiments is identical to NOESY sequence and is shown in Figure 7a. The 1Q coherences excited by the first 90° pulse evolve during the $t_1$ period. The second 90° pulse stores the magnetization along the direction of the $B_0$ field during a mixing time, $\tau$. During this delay, spin diffusion can exchange magnetization between distinct sites. The last 90° pulse converts the longitudinal magnetization into transverse magnetization, which is detected during the acquisition period, $t_2$. After 2D Fourier transform, we obtain a 2D 1Q-1Q through-space correlation spectrum, as seen in Figure 7b.

Nevertheless, these 2D 1Q-1Q correlation experiments do not allow the observation of proximities between nuclei with close resonance frequencies. This limitation can be circumvented by the use of 2D 2Q-1Q through-space correlation relying on cross-terms between homonuclear dipolar couplings, such as the dipolar homonuclear homogeneous Hamiltonian (DH$^3$) scheme, which has notably been employed to probe proximities between $^{19}$F nuclei in inorganic fluorides and fluorinated aluminophosphates.
Figure 7. (a) Pulse sequence of 2D $^1$H or $^{19}$F spin diffusion experiment along with desired coherence transfer pathways. (b) 2D $^1$H spin diffusion spectrum of methyl ammonium lead iodide containing 4% tetrapropylammonium at $B_0 = 18.8$ T with $v_R = 35$ kHz. (c) Pulse sequence of 2D 1Q-1Q SHHS experiment. (d) DNP-enhanced 2D $^{13}$C CHHC spectrum of bifunctionalized mesoporous silica nanoparticles. (e) Pulse sequence of 2D 1Q-1Q homonuclear correlation experiments, such as PDSD, DARR and PARIS, between $S = ^{13}$C or $^{31}$P nuclei. These experiments differ by the rf irradiation applied on $^1$H channel during the mixing time $\tau$. (f) DNP-enhanced 2D $^{13}$C DARR spectrum of $^{13}$C-enriched methionine adsorbed on Pd nanoparticles supported on $\gamma$-alumina and impregnated with a TEKPol solution in 1,1,2,2-tetrachloroethane (TCE) at $B_0 = 9.4$ T and 105 K with $v_R = 12$ kHz. Figures b, d and f adapted from refs. 129–131, respectively. Copyright 2020, Wiley, 2017, American Chemical Society, 2016, Royal Society of Chemistry.

Nuclei other than $^1$H and $^{19}$F, such as $^{13}$C or $^{31}$P, are subject to smaller homonuclear dipolar couplings and spin diffusion due to cross-terms between homonuclear dipolar couplings is quenched under MAS. A first possibility to circumvent this issue is to 2D 1Q-1Q SHHS sequence, in which the $S$-edited $^1$H longitudinal magnetization is exchanged by $^1$H-$^1$H spin diffusion during a mixing period placed between two CP transfers (see Figure 7c). This experiment has been applied to probe the proximities between organic functional groups bound to silica surface (see Figure 7d)\textsuperscript{113}. Nevertheless, cross-terms between homonuclear dipolar interactions and heteronuclear dipolar interaction with protons can transfer magnetization between nuclei with different frequencies. This process is referred to as proton-driven spin diffusion (PDSD)\textsuperscript{132}. The corresponding pulse sequence is shown in Figure 7e and is identical to that of spin diffusion experiment for the detected nucleus, $I$, except that the initial 90° pulse is replaced
by a $^1$H→$^1$I CP transfer and heteronuclear dipolar decoupling schemes are applied on $^1$H channel during the $t_1$ and $t_2$ periods to suppress $^1$H-$^1$I dipolar couplings. Conversely, during the mixing time, $\tau$, no irradiation is applied in the case of PDSD sequence so that the cross-terms between $^1$H-$^1$I and $^1$I-$^1$I dipolar couplings transfer magnetization between $^1$I spins. Nevertheless, the efficiency of this transfer decreases for MAS frequency and $B_0$ field strength above 20 kHz and 14.1 T ($^1$H Larmor frequency of 600 MHz). Irradiation on the $^1$H channel can be applied during the mixing time, $\tau$, to restore these cross-terms under fast MAS and at high magnetic field. For instance, the sequences called dipolar-assisted rotational resonance (DARR) \cite{133} or radio frequency assisted diffusion (RAD) \cite{134} employ continuous wave rf irradiation with nutation frequency equal to 1 or 2 times the MAS frequency during the mixing time, whereas phase-alternated irradiation, such as phase-alternated recoupling irradiation scheme (PARIS) \cite{135,136}, improves the magnetization transfer at high MAS frequencies. The 1Q-1Q correlation techniques have been widely employed for the observation of $^{13}$C-$^{13}$C proximities in biomolecules \cite{41}. Nevertheless, they have also been recently applied to probe proximities between C sites of $^{13}$C-enriched organic molecules adsorbed at the surface of nanoparticles or in zeolites (see Figure 7f) \cite{131,137}. Homonuclear correlation experiments for $^{31}$P nuclei have also been applied to probe the proximities between Lewis and Brønsted acid sites in zeolites using P-containing probe molecules \cite{138}.

### 2.2.2 Between half-integer quadrupolar nuclei

Like for spin-1/2 nuclei, through-space homonuclear correlation experiments have been developed to probe proximities between identical half-integer quadrupolar nuclei, including $^{11}$B, $^{17}$O, $^{23}$Na and $^{27}$Al \cite{44,47,139}. Nevertheless, these experiments are more challenging for these isotopes than for spin-1/2 nuclei owing to the larger size of the density matrix, equal to $(2I+1)^2$ for a spin-$I$ nucleus, and the presence of large anisotropic quadrupolar interaction. This interaction has a magnitude much larger than the rf irradiation and the MAS frequency, resulting in complicated spin dynamics during rf irradiation under MAS conditions. Therefore, 2D through-space homonuclear correlation experiments were initially achieved using recoupling techniques, which do not involve rf irradiation, such as (i) cross-terms between homonuclear dipolar couplings and either first-order quadrupolar interaction \cite{140,141} or heteronuclear dipolar couplings to protons \cite{142,143} in the second-order Hamiltonian, (ii) $R^2$ condition \cite{144} or (iii) off-magic-angle spinning \cite{23,145,146}. Nevertheless, this latter approach reintroduces other unwanted interactions and hence, decreases the spectral resolution, whereas $R^2$ method requires MAS frequency matching the difference in isotropic chemical shifts between the recoupled spins and the transfer efficiency of second-order recoupling decreases at higher MAS frequencies.

Dipolar couplings between identical half-integer quadrupolar nuclei have also been restored by the rf irradiation of the CT between energy levels $m_i = -1/2$ and $+1/2$ with $m_i$ the magnetic quantum number \cite{147,148}. This approach has the advantage to be more versatile than those without rf irradiation. Nevertheless, the applied rf field should be weak to avoid the excitation of satellite transitions (STs) and the related signal losses. In particular, efficient recoupling has been achieved using homonuclear rotary recoupling (HORROR) condition, $\nu_{\mathrm{CT}} = (I + 1/2)\nu_1 = \nu_R/2$, where $\nu_{\mathrm{CT}}$ is the nutation frequency of the CT and $\nu_1$ is the rf field strength \cite{149}. The robustness to offset and rf field inhomogeneity has been improved by the use of $R\nu^2_{\mathrm{H}}$ symmetry-based recoupling and supercycling \cite{150-155}. Zero-quantum (0Q) dipolar recoupling, such as SR2$^2_2$, can be employed to acquire 2D 1Q-1Q correlation spectra \cite{150,153,154}, whereas 2Q recoupling, such as BR2$^2_2$, can be applied to record 2D 2Q-1Q correlation experiments \cite{151,152,155}. The 1Q-1Q correlation pulse sequence is identical to that shown in Figure 7a, except that the 90° pulse are selective of the CT and 0Q recoupling scheme is applied during the $\tau$ delay. The 2Q-1Q correlation spectra between half-integer quadrupolar nuclei are acquired using the pulse sequence of Figure 5. Nevertheless, a CT-selective 180° pulse must be applied during the $t_1$ period
to eliminate 2Q coherences between energy levels $m_i$ and $m_i+2$ of a single $I$-spin nucleus\textsuperscript{140}. The 2Q-1Q variant has the advantage to allow the observation of proximities between nuclei with close resonance frequencies. Furthermore, the BR2\textsuperscript{2} recoupling benefits from high robustness to offset, which contributes to the reintroduction of the homonuclear dipolar couplings\textsuperscript{155}. Nevertheless, the efficiency of this recoupling drops on resonance and hence, the carrier frequency must be carefully chosen. The intensity of these homonuclear correlation experiments between CTs of half-integer quadrupolar nuclei can be enhanced by the irradiation of the STs at the beginning of the pulse sequence, in such way that the population difference across the CT is enhanced\textsuperscript{150-152}. Note that 3D $^{14}$N/$^{15}$N/$^1$H through-space correlation has been developed to probe proximities between $^{14}$N nuclei since their lack of CT prevents the application of the above correlation experiments based on the selective irradiation of the CT\textsuperscript{156}. Nevertheless, they have only been applied so far to solid-state peptides.

Figure 8. 2D $^{27}$Al 2Q-1Q through-space correlation spectrum of HY zeolite calcined at 700 °C. The isotropic shifts are indicated near the peaks. The peak resonating at 59 ppm is assigned to framework $\text{AlO}_4$ species of Brønsted acid sites SiOHAl, whereas those at 32 and 3 ppm stem from extra-framework $\text{AlO}_5$ and $\text{AlO}_6$ sites, respectively, acting as Lewis acid sites. The auto-correlation peaks on the diagonal indicate proximities between identical sites, whereas the cross peaks outside the diagonal reveal proximities between distinct Al sites. Figure adapted from ref.\textsuperscript{157}. Copyright, 2010, Wiley.

3. Correlation between distinct nuclei

Connectivities and proximities between distinct isotopes, $I$ and $S$, can be observed using heteronuclear correlation experiments based on coherence transfers through $J$- and dipolar couplings, respectively. These experiments rely on either a single coherence transfer $I \rightarrow S$, when the excited and detected isotopes differ, or two successive coherence transfers $S \rightarrow I \rightarrow S$, when the excited isotope is identical to that detected. The relative sensitivity of these two approaches depends on the gyromagnetic ratios, longitudinal relaxation times, $T_1$, coherence lifetimes and line widths of the correlated nuclei\textsuperscript{32}. The heteronuclear correlation experiment, in which the $S$ spin is detected and the $I$ spin is indirectly observed, is denoted $S(I)$ hereafter.

3.1 Through-bond heteronuclear correlations
The connectivities between distinct isotopes in inorganic solids have been probed using through-bond heteronuclear correlation experiments \(^1\) similar to those used in isotropic solution, including the refocused insensitive nuclei enhanced by polarization transfer (\(J\)-RINEPT) based on a single transfer \(I \rightarrow S\) \(^2,15,18,19\) as well as the heteronuclear multiple-quantum coherence (\(J\)-HMQC) scheme relying on a double transfer \(I \rightarrow S \rightarrow I\) \(^12,16,16\). These experiments are carried out under MAS to average out anisotropic interactions and hence, to improve the resolution. Furthermore, the \(J\)-coupling constants between nuclei separated by two or more covalent bonds usually do not exceed a few tens of hertz. Hence, these coherence transfers are only efficient when at least one of the correlated isotope exhibits sufficiently long time constant, \(T_2'\), for the decay of transverse magnetization, which is not refocused by a 180° pulse.

### 3.1.1 Between spin-1/2 isotopes

The \(J\)-RINEPT pulse sequence is displayed in Figure 9. The first 90° pulse on the \(I\) channel excites the \(I\)-spin transverse magnetization, which is encoded by the isotropic chemical shift during the \(t_1\) period since the 180° pulse applied to the \(S\) channel in the middle of the \(t_1\) period refocuses the evolution under \(I-S\) \(J\)-couplings. During the defocusing delay, \(\tau\), the simultaneous 180° pulses on \(I\) and \(S\) channels refocus the evolution under the isotropic chemical shifts but not that under \(I-S\) \(J\)-couplings. This evolution converts the in-phase transverse magnetization of the \(I\) nuclei into antiphase magnetization with respect to the \(I-S\) \(J\)-couplings. The simultaneous 90° pulses on \(I\) and \(S\) channels convert this antiphase magnetization of the \(I\) spin into antiphase magnetization of the \(S\) spin, which is subsequently converted into in-phase magnetization of the \(S\) spin during the refocusing delay, \(\tau'\). This in-phase magnetization is detected during the \(t_2\) period. For an isolated \(I-S\) pair and in the absence of losses, the optimal \(\tau\) and \(\tau'\) delays are equal to \(1/(2J_{IS})\).

\[\begin{array}{c}
90°\ y & 180°\ y & 90°\ y & 180°\ y \\
\hline
\end{array}\]

\[\begin{array}{c}
\tau/2 & 180°\ y & \tau/2 & \text{het. dec.} & \tau'/2 & \text{het. dec.} \\
\hline
180°\ y & 90°\ y & 180°\ y \\
\hline
\end{array}\]

![Figure 9. Pulse sequence along with desired coherence transfer pathways of 2D \(S(I)\) through-bond heteronuclear correlation using \(I \rightarrow S\) \(J\)-RINEPT transfer. The evolution under \(I-S\) \(J\)-couplings is refocused during \(t_1\) and \(t_2\) periods.](image)

The \(J\)-coupling constants between covalently bonded \(^1\)H-\(^{13}\)C nuclei, \(^1J_{\text{CH}}\), are typically equal to 140 Hz and the \(^{13}\)C\(^1\)H) \(J\)-RINEPT sequence based on these coupling has been employed to observe H–C bonds of organic molecules, such as surfactants, in mesoporous silica \(^16\). It has been shown that the transfer efficiency of \(^1\)H-\(^{13}\)C \(J\)-RINEPT scheme can be improved by reducing the coherence losses due to \(^1\)H-\(^1\)H dipolar couplings during \(\tau\) and \(\tau'\) delays using \(^1\)H homonuclear dipolar decoupling \(^16\) or fast MAS \(^16\). In particular, the \(T_2'\) time constants of \(^1\)H and \(^{13}\)C nuclei are proportional to the MAS frequency \(^16\). Furthermore, a three-fold enhancement in sensitivity of 2D \(^1\)H-\(^{13}\)C \(J\)-RINEPT experiment, which
corresponds to a time saving by almost an order of magnitude, has been achieved using indirect detection of $^{13}$C nuclei via protons ($^1H^{13}C$) under fast MAS (see Figure 10)\(^\text{164}\).

Similarly the H–Si bonds in poly(cyclosilane) have been observed using $^{29}$Si($^1$H) J-RINEPT scheme incorporating $^1$H homonuclear dipolar decoupling and based on coherence transfer via $^1$$^1$J$^\text{SiH}$ coupling constants, which are typically equal to 170 Hz\(^\text{108}\). The sensitivity of this experiment has been improved using DNP to detect silicon hydride sites (SiH) at the surface of silicon nanoparticles\(^\text{91}\). The strength of the $J$-coupling constant decreases for increasing number of bonds between the coupled spins. Nevertheless, geminal couplings through two covalent bonds can be large enough to achieve J-RINEPT transfer. For instance, the geminal $^{29}$Si-$^{31}$P $J$-coupling constants typically range from 4 to 15 Hz and have been leveraged to correlate the $^{29}$Si and $^{31}$P signals of a mixture of silicophosphate crystalline phases\(^\text{159}\).

![Figure 10](image_url)

Figure 10. (a) 2D $^1$H($^{13}$C) J-RINEPT spectrum of cetyltrimethyl ammonium bromide (CTAB) surfactant in mesoporous silica recorded in 50 min at $B_0 = 14.1$ T with $\nu_R = 40$ kHz. The initial 90° pulse on $I = ^{13}$C channel is replaced by $^1$H$\rightarrow$$^{13}$C CP transfer. Furthermore, the residual initial $^1$H magnetization, which is not transferred to $^{13}$C nuclei, is eliminated by the application of purge pulses. (b–c) Selected cross sections along the (b) $^1$H and (c) $^{13}$C dimensions of the 2D $^{13}$C($^1$H) (top traces) and $^1$H($^{13}$C) (bottom traces) J-RINEPT spectra acquired under the same experimental conditions. The noise level is shown as an inset with a vertical expansion by a factor of 10. Figure adapted from ref.\(^\text{164}\). Copyright, 2009, Elsevier.

Figure 11 shows the pulse sequence of $J$-HMQC experiment. The first 90° pulse on $S$ channel creates transverse magnetization of $S$ nuclei, which evolves under $J_{IS}$ coupling into antiphase magnetization during the first $\tau$ delay and then is converted into heteronuclear multiple-quantum coherences by the 90° pulse on $I$ channel. These coherences are encoded during $\tau_1$ period by the isotropic chemical shift of $I$ nuclei before being converted back into antiphase magnetization of $S$ nuclei by the second 90° pulse on $I$ channel. For an isolated $I$-$S$ pair and in the absence of losses, the optimal $\tau$ delays are equal to $1/(2J_{IS})$. The $J$-HMQC experiment has notably been employed to correlate the $^{29}$Si and $^{31}$P signals of a mixture of silicophosphate crystalline phases (see Figure 12)\(^\text{161}\) as well as to probe $^{19}$F-$^{207}$Pb and $^{19}$F-$^{31}$P covalent bonds in β-Pb$_2$ZnF$_6$\(^\text{165}\) and oxyfluoride glass-ceramics\(^\text{166}\), respectively. More recently, as shown in Figure 13, the sensitivity of $^{77}$Se($^{113}$Cd) $J$-HMQC experiment has been enhanced by DNP to probe the $^{77}$Se–$^{113}$Cd covalent bonds near the surface of CdSe nanocrystals\(^\text{167}\).
Figure 11. Pulse sequence along with desired coherence transfer pathways of 2D $S(l)$ $J$-HMQC experiment.

Figure 12. 2D $^{31}P$($^{29}Si$) $J$-HMQC spectrum of a mixture of Si$_3$O($PO_4$)$_3$ and SiP$_2$O$_7$ polymorphs acquired at $B_0 = 7$ T with $\nu_R = 14$ kHz. The 1D $^{29}Si$ and $^{31}P$ MAS NMR spectra are displayed along the $^{29}Si$ and $^{31}P$ dimensions of the 2D spectra, beside the projections. The bottom spectrum displays an expansion of the circled region in the top spectrum. Figure adapted from ref. 161. Copyright, 2009, Elsevier.
Figure 13. DNP-enhanced 2D $^{77}$Se($^{113}$Cd) J-HMQC spectrum of CdSe nanoplatelets mixed with hexagonal boron nitride and impregnated with 16 mM TEKPol solution in TCE. The $^{77}$Se transverse magnetization is excited using $^1$H→$^{77}$Se CPMAS transfer. A structural model of the surface of CdSe nanoplatelets along with the observed connectivities is shown on the left of the figure. Figure adapted from ref. 167. Copyright, 2021, American Chemical Society.

3.1.2 Between spin-1/2 and half-integer quadrupolar isotopes

3.1.2.1 Without high-resolution

$J$-RINEPT and $J$-HMQC experiments have also been used to probe connectivities between spin-1/2 and half-integer quadrupolar isotopes in inorganic solids. The employed pulse sequences are identical to those used to correlate the signals of spin-1/2 isotopes, except that CT-selective pulses are applied to the quadrupolar nuclei. Furthermore, when the excited nucleus is half-integer quadrupolar nucleus, the signal intensity can be enhanced by irradiating the STs at the beginning of the sequence, in such way that the population difference across the CT is increased 168. When the $T_2^*$ time constant is much longer than that of the apparent decay of the transverse magnetization, $T_2$, the signal intensity can be enhanced by the acquisition of a train of echoes using CPMG scheme for spin-1/2 nuclei or the quadrupolar CPMG (QCPMG) variant for half-integer quadrupolar nuclei, in which 180° pulses are CT-selective 169,170. When half-integer quadrupolar nuclei are indirectly detected using $J$-HMQC sequence, the losses can be reduced by accelerating the coherence transfer through the irradiation of STs during the $t$ delays 171,172. DNP has been recently employed to enhance the sensitivity of $J$-RINEPT experiments in order to probe connectivities of surface sites 81.

As seen in Table 1 and Table 2, the $J$-RINEPT and $J$-HMQC experiments have been applied for several spin-1/2 isotopes, including $^1$H, $^{13}$C, $^{19}$F, $^{29}$Si, $^{31}$P and $^{77}$Se, as well as a few half-integer quadrupolar nuclei, such as $^{11}$B, $^{27}$O, $^{27}$Al, $^{51}$V and $^{71}$Ga. An example of 2D $^{19}$F($^{27}$Al) $J$-HMQC spectrum allowing the observation of $^{19}$F-$^{27}$Al covalent bonds is shown in Figure 14. These experiments have been demonstrated for isotopes with high or moderate gyromagnetic ratio, since the strength of the $J$-coupling increases with increasing gyromagnetic ratios. Furthermore, the $J$-coupling constants usually decrease when the number of bonds between the coupled nuclei increases. Isotopic enrichment and/or DNP are often required to detect connectivities of isotopes with low natural abundance, such as $^{17}$O (0.0373%) and $^{29}$Si (4.67%). Heteronuclear correlation experiments between isotopes exhibiting close Larmor frequencies, such as $^{13}$C and $^{27}$Al, for which these frequencies are only 3.6% apart, are not possible with conventional MAS NMR probes and require the use of a frequency splitter 173,174.
Table 1. List of the pairs of spin-1/2 and quadrupolar isotopes, between which covalent bonds have been probed by 2D J-RINEPT or J-HMQC experiments in hybrid or inorganic solids.

<table>
<thead>
<tr>
<th>I = 1/2</th>
<th>S ≥ 1/2</th>
<th>2J_{IS} /Hz</th>
<th>2D experiments</th>
<th>Sample</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H</td>
<td>27Al</td>
<td>376</td>
<td>J-HMQC</td>
<td>Al hydride on γ-Al₂O₃</td>
<td>175</td>
</tr>
<tr>
<td>13C</td>
<td>27Al</td>
<td>71</td>
<td>J-HMQC</td>
<td>alkylaluminium</td>
<td>174</td>
</tr>
<tr>
<td>19F</td>
<td>11B</td>
<td>-b</td>
<td>J-HMQC</td>
<td>fluoroborosilicate glass</td>
<td>176</td>
</tr>
<tr>
<td>19F</td>
<td>27Al</td>
<td>-b</td>
<td>J-HMQC</td>
<td>fluorinated aluminophosphate</td>
<td>128</td>
</tr>
<tr>
<td>29Si</td>
<td>17O</td>
<td>23-34</td>
<td>J-HMQC</td>
<td>silica</td>
<td>168</td>
</tr>
<tr>
<td>31P</td>
<td>17O</td>
<td>120-130</td>
<td>J-HMQC</td>
<td>Na₅P₃O₁₀ crystals</td>
<td>177</td>
</tr>
<tr>
<td>77Se</td>
<td>71Ga</td>
<td>500-800</td>
<td>J-RINEPT</td>
<td>gallium selenide crystal and glass</td>
<td>170</td>
</tr>
</tbody>
</table>

*In this table, the I and S symbols do not denote the indirectly detected and spy isotopes, contrary to Figure 9 and Figure 11. b Not measured.

Table 2. List of the pairs of spin-1/2 and quadrupolar isotopes, between which two-bond connectivities have been probed by 2D J-RINEPT or J-HMQC experiments in hybrid or inorganic solids.

<table>
<thead>
<tr>
<th>I = 1/2</th>
<th>S ≥ 1/2</th>
<th>2J_{IS} /Hz</th>
<th>2D experiments</th>
<th>Sample</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>29Si</td>
<td>11B</td>
<td>-b</td>
<td>J-HMQC</td>
<td>layered borosilicates</td>
<td>178</td>
</tr>
<tr>
<td>29Si</td>
<td>27Al</td>
<td>1-6</td>
<td>DNP+J-RINEPT</td>
<td>silicated alumina</td>
<td>81</td>
</tr>
<tr>
<td>31P</td>
<td>11B</td>
<td>-b</td>
<td>J-HMQC</td>
<td>aluminosilicate glasses</td>
<td>179</td>
</tr>
<tr>
<td>31P</td>
<td>27Al</td>
<td>15-25</td>
<td>J-RINEPT</td>
<td>borophosphate glass</td>
<td>180</td>
</tr>
<tr>
<td>31P</td>
<td>51V</td>
<td>40</td>
<td>J-HMQC</td>
<td>aluminophosphate crystals</td>
<td>17</td>
</tr>
<tr>
<td>31P</td>
<td>71Ga</td>
<td>12</td>
<td>J-HMQC</td>
<td>gallophosphate crystal</td>
<td>182</td>
</tr>
</tbody>
</table>

*In this table, the I and S symbols do not denote the indirectly detected and spy isotopes, contrary to Figure 9 and Figure 11. b Not measured.

Figure 14. 2D 19F{27Al} J-HMQC spectrum of crystalline fluorinated aluminophosphate AlPO₄·CJ2 at B₀ = 9.4 T with νR = 10 kHz. This spectrum allows probing 19F-27Al covalent bonds and hence, the local OH/F distribution in this material. Figure adapted from ref. 128. Copyright, 2011, Royal Society of Chemistry.

3.1.2.2 With high-resolution
In 2D J-RINEPT and J-HMQC spectra, the signals of quadrupolar nuclei are broadened by second-order quadrupolar interaction. This broadening, which can mask differences in isotropic chemical shifts, can be removed using 2D MQMAS scheme, which combines the evolution of multiple-quantum and 1Q coherences. These 1Q coherences of the quadrupolar isotope at the end of the MQMAS block can be transferred to spin-1/2 nucleus via J-coupling using J-RINEPT sequence, as shown in Figure 15, which displays the sequence of 3Q-J-RINEPT experiment. The sensitivity of this experiment can be enhanced by the use of soft pulse added mixing (SPAM), i.e. the insertion of a 90° CT-selective pulse after the reconversion pulse of the MQMAS block. The 3Q-J-RINEPT sequence has been applied to acquire 2D \(^{31}\text{P}\{^{27}\text{Al}\}\) and \(^{29}\text{Si}\{^{27}\text{Al}\}\) through-bond correlation spectra of aluminophosphate and aluminosilicate materials, respectively, with high-resolution along the \(^{27}\text{Al}\) dimension (see Figure 16). High-resolution J-HMQC spectra can also be acquired by substituting the initial CT-selective 90° pulse on the S channel (see Figure 11) by a MQMAS block exciting 3Q coherences of the detected quadrupolar isotope. Nevertheless, this experiment requires a 3D acquisition, instead of a 2D one for 3Q-J-RINEPT technique.

![Pulse sequence along with desired coherence transfer pathways of 2D S/I 3Q-J-RINEPT experiment for I \(\geq 5/2\). The first pulse on I channel employs high rf power to excite the 3Q coherences. The second and third pulses on this channel corresponds to the SPAM block, whereas the other pulses are selective of the CT.](image-url)
3.1.3 Between two half-integer quadrupolar isotopes

The $^{27}$Al-$^{17}$O covalent bonds in $^{17}$O-enriched aluminate glass and alumina have been observed using 2D $^{27}$Al($^{17}$O) $J$-HMQC experiment based on one-bond $^{17}$O-$^{27}$Al $J$-couplings, as seen in Figure 17\textsuperscript{19,172}. The sensitivity of this experiment has been improved by the irradiation of $^{27}$Al STs at the beginning of the sequence to enhance the population difference across the CT, but also the irradiation of $^{17}$O STs during the defocusing and refocusing delays to accelerate the coherence transfers, and hence, to reduce the losses during this delay \textsuperscript{172}. These losses can also be limited by spinning slightly off the magic angle, which lengthens the $T_2^*$ time constant of the $^{27}$Al and $^{17}$O nuclei \textsuperscript{189}.

Figure 16. Comparison of 2D $^{29}$Si($^{27}$Al) (a) $J$-RINEPT and (b) 3Q-$J$-RINEPT spectra of a mixture of microcline and albite aluminosilicate minerals acquired at $B_0 = 9.4$ T with $\nu_R = 10$ kHz. Figure reprinted from ref. \textsuperscript{187}. Copyright, 2006, Royal Society of Chemistry.

Figure 17. (a) Build-up of the signal of 1D $^{27}$Al($^{17}$O) population transfer (PT)-$J$-HMQC and $J$-HMQC experiment of $^{17}$O-enriched $\gamma$-$\text{Al}_2\text{O}_3$ sample. In PT-$J$-HMQC variant, the $^{17}$O STs are irradiated during the defocusing and refocusing delays, $\tau$, which accelerates the coherence transfer by approximately a factor of 2 and hence, reduces the losses. (b) 2D $^{27}$Al($^{17}$O) PT-$J$-HMQC of the same sample. The spectra are acquired at $B_0 = 18.8$ T with $\nu_R = 20$ kHz. Figure reprinted from ref. \textsuperscript{172}. Copyright, 2015, American Institute of Physics.
3.2 Through-space heteronuclear correlations

Coherence transfers based on heteronuclear dipolar couplings can be used to acquire 2D heteronuclear correlation spectra. These through-space heteronuclear correlation complement their through-bond counterparts. Furthermore, for isotopes in the first periods of the periodic table, the heteronuclear dipolar couplings are usually larger than the J-couplings, which results in faster coherence transfers and hence, higher sensitivity. Like the through-bond heteronuclear correlation, the through-space variants have been applied for pairs of spin-1/2 isotopes, pairs of spin-1/2 and quadrupolar isotopes as well as pairs of half-integer quadrupolar nuclei.

3.2.1 Between spin-1/2 isotopes

The NMR signals of distinct spin-1/2 nuclei distant by a few angstroms have been mainly correlated using 2D heteronuclear correlation (HETCOR) sequence based on CP transfer. This CP-HETCOR sequence shown in Figure 19 is a direct detection method employing a single 

\[ I \rightarrow S \]

polarization transfer. The 90° pulse on the I channel creates transverse magnetization of the I nuclei, which is encoded by the isotropic chemical shift during the \( t_2 \) period. This magnetization is then transferred to the S spin by CP during the contact time, \( t_{CP} \). This CP transfer relies on the simultaneous rf irradiation of I and S isotopes. These rf fields lock the transverse magnetization of the two isotopes along a particular direction in the rotating frame. The CP transfer is effective provided the nutation frequencies of the I and S isotopes, denoted \( v_I \) and \( v_S \) hereafter, fulfill the Hartmann-Hahn conditions under MAS conditions:

\[
v_I + \epsilon v_S = n v_R
\]

where the coefficient \( \epsilon \) is equal -1 for the 0Q-CP and +1 for 2Q-CP and \( n = \pm 1 \) or \( \pm 2 \). The terms 0Q-CP and 2Q-CP are related to the rank of the spin operator in the Hamiltonian of the recoupled dipolar interaction. At slow MAS, the 0Q-CP condition is preferred, whereas at fast MAS, both 0Q-CP and 2Q-CP can be employed. The most efficient CP transfer is usually achieved for \( n = \pm 1 \). As most NMR coils produce inhomogeneous rf field, the Hartmann-Hahn condition is only fulfilled in a limited region of the sample volume. Hence, the rf field applied to I or S isotope is usually linearly swept so that the different regions of the sample contribute to the detected signal and hence, the signal intensity is enhanced. The optimal \( t_{CP} \) time depends on the I-S dipolar coupling and the relaxation during the spin locks. After the CP transfer, the free-induction decay (FID) of the S nuclei is detected during the \( t_2 \) period. If necessary, notably when \( I = ^1H \), the broadening of NMR signals of S nuclei due to residual dipolar couplings with I spin can be removed by applying heteronuclear dipolar decoupling sequence during the \( t_2 \) period. The sensitivity of CP-HETCOR experiments can be enhanced by using CPMG detection, when \( T_2(S) \gg T_2^*(S) \), notably for \( S = ^{29}\text{Si} \), and DNP. Table 3 lists pairs of spin-1/2 isotopes, for which 2D HETCOR spectra have been recorded using direct detection.

Table 3. List of the pairs of distinct spin-1/2 isotopes, for which their signals have been correlated using direct detection methods. Except 2D \(^{13}\text{C}^{(29}\text{Si})\) HETCOR spectrum, for which TEDOR transfer was employed, other HETCOR experiments were recorded using CP transfer.

<table>
<thead>
<tr>
<th>I</th>
<th>S</th>
<th>DNP</th>
<th>Sample</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>(^{13}\text{C})</td>
<td>no</td>
<td>mesoporous aluminosilicates</td>
<td>194</td>
</tr>
<tr>
<td>(^1\text{H})</td>
<td>(^{15}\text{N})</td>
<td>no</td>
<td>silica-supported Ta complexes</td>
<td>195</td>
</tr>
<tr>
<td>(^1\text{H})</td>
<td>(^{19}\text{F})</td>
<td>no</td>
<td>flourohectorite</td>
<td>196</td>
</tr>
<tr>
<td>(^1\text{H})</td>
<td>(^{29}\text{Si})</td>
<td>no</td>
<td>amorphous hydrogenated silicon</td>
<td>6</td>
</tr>
<tr>
<td>(^1\text{H})</td>
<td>(^{31}\text{P})</td>
<td>no</td>
<td>phosphate crystals and glasses</td>
<td>197,198</td>
</tr>
<tr>
<td>(^1\text{H})</td>
<td>(^{89}\text{Y})</td>
<td>yes</td>
<td>Y-doped BaZrO(_3)</td>
<td>199</td>
</tr>
<tr>
<td>(^1\text{H})</td>
<td>(^{113}\text{Cd})</td>
<td>yes(^a)</td>
<td>CdS nanoparticles</td>
<td>200</td>
</tr>
<tr>
<td>Isotope</td>
<td>Isotope</td>
<td>Value</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
<td>-------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>$^1$H</td>
<td>$^{119}$Sn</td>
<td>yes</td>
<td>Sn/SnOx nanoparticles</td>
<td></td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>$^{29}$Si</td>
<td>no $^a$</td>
<td>functionalized mesoporous silica</td>
<td></td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>$^{31}$P</td>
<td>no</td>
<td>fluorinated aluminophosphate</td>
<td></td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>$^{13}$C</td>
<td>yes $^b$</td>
<td>organically functionalized silicon nanoparticles</td>
<td></td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>$^{13}$C</td>
<td>yes</td>
<td>zirconium phosphate nanoparticles</td>
<td></td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>$^{29}$Si</td>
<td>no</td>
<td>silicophosphate</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Using CPMG detection. $^b$ Using TEDOR-HETCOR.

Figure 18. 2D $^{29}$Si($^1$H) CP-HETCOR-CPMG spectrum of mesoporous silica nanoparticles functionalized with allyl groups acquired at $B_0 = 14.1$ T with $\nu_R = 40$ kHz. Because of the CPMG detection, this direct detection experiment is more sensitive than indirect detection via protons. Figure adapted from ref. 90. Copyright, 2008, Elsevier.

Nevertheless, CP transfer has some limitations. In the case of CP-HETCOR experiment with protons, a first drawback is that $^1$H spin diffusion during $\tau_{CP}$ can exchange transverse magnetization between protons, which results in relayed correlation and may prevent the observation of proximities between a given nucleus and its nearest protons. This issue is particularly acute for long $\tau_{CP}$ delay and hence, notably for small heteronuclear dipolar couplings. It can be circumvented using Lee-Goldburg CP (LG-CP), which averages out $^1$H-$^1$H dipolar interaction during the CP transfer and hence, the $^1$H spin diffusion. This technique has been first introduced to record $^{13}$C($^1$H) CP-HETCOR spectra of organic solids, and then has been applied to acquire $^{31}$P($^1$H) CP-HETCOR spectra of phosphate materials.

Another drawback of CP transfer is the requirement to fulfill the Hartmann-Hahn condition. These conditions are narrower for small hetero- and homo-nuclear dipolar interactions as well as at high MAS frequencies. In particular, CP transfer involving isotopes other than $^1$H and $^{19}$F exhibits narrow Hartmann-Hahn conditions. Furthermore, the optimization of the rf field strength to fulfill the Hartmann-Hahn condition is only feasible in the case of sensitive CPMAS experiment. Therefore, for HETCOR experiments, which do not involve protons or $^{19}$F, an alternative to CPMAS is the use of transferred-echo, double-resonance (TEDOR) scheme, which derives from RINEPT transfer. In TEDOR scheme, a rotational-echo, double-resonance (REDOR) recoupling is applied to one of the two isotopes during the defocusing and refocusing delays to reintroduce the I-S dipolar couplings. The REDOR recoupling consists of a train of 180° pulses and hence, is easier to optimize than CPMAS transfer. Furthermore, contrary to CP, TEDOR recoupling is not affected by dipolar truncation and hence, is more efficient for long-range polarization transfer. For instance, DNP-enhanced TEDOR...
experiment has been employed to acquire 2D $^{13}\text{C}^{29}\text{Si}$ through-space HETCOR spectrum of functionalized silicon nanoparticles. 

For HETCOR experiments between protons and another isotope, the resolution along the $^1\text{H}$ dimension is improved by fast MAS, with $\nu_R \geq 40$ kHz. Under lower MAS frequencies, the resolution of $^1\text{H}$ signals can also be increased by the application of homonuclear dipolar decoupling sequences, such as frequency-switched Lee-Goldburg (FSLG), on the $^1\text{H}$ channel during the $t_1$ period. Nevertheless, fast MAS is more robust and is easier to set up.

Figure 19. Pulse sequence along with desired coherence transfer pathways of Si/I CP-HETCOR experiment. During the CP transfer, the rf field applied to the I isotope is linearly ramped.

In addition, under fast MAS, indirect detection via nuclei with high gyromagnetic ratio, such as $^1\text{H}$ or $^{19}\text{F}$, usually improves the sensitivity, in spite of the lower sample volume of rotors with small diameter. Pairs of distinct spin-1/2 isotopes, for which their NMR signals have been correlated using indirect detection methods, are listed in Table 4. For instance, it has been shown that the sensitivity for the detection of $^{13}\text{C}$ nuclei at the surface of organically functionalized mesoporous silica can be enhanced by a factor of 3 through the indirect detection nuclei via protons using double CP (DCP) scheme displayed in Figure 20. In this scheme, the transverse magnetization of the excited nuclei, S, is transferred to the I isotope using a first CP transfer. Then a 90° pulse stores the generated transverse magnetization of the I nuclei along the $B_0$ field direction, while the remaining S magnetization is destroyed by saturation blocks. For $S = ^1\text{H}$ or $^{19}\text{F}$, an efficient saturation can be achieved by rf irradiation with $\nu_1 = \nu_R/2$ corresponding to the HORROR condition, which reintroduces the S-S dipolar interaction. The second 90° pulse on the I channel converts the longitudinal magnetization of I nuclei into transverse magnetization, which is encoded by the isotropic chemical shift during the $t_1$ period. Finally a second I→S CP transfer reconverts the transverse magnetization of the I nuclei into transverse magnetization of S nuclei, which is detected during the $t_2$ period. The DCP scheme has been applied for the indirect detection of $^{13}\text{C}$ and $^{15}\text{N}$ nuclei via protons at the surface of organically functionalized mesoporous silica (see Figure 21). The $^{19}\text{F}$ nuclei have also been used as spy spin for the
indirect detection of $^{13}$C nuclei using DCP scheme in the case of mesoporous silica functionalized with fluorinated organic moieties $^{202}$. More recently, DCP sequence has been employed for the indirect detection via protons of low-$\gamma$ spin-1/2 isotopes, including $^{89}$Y, $^{103}$Rh and $^{183}$W, in inorganic and hybrid materials $^{217}$ as well as $^{31}$P nuclei in phosphane/borane $^{218}$. The sensitivity of DCP experiment with $^1$H detection has also been enhanced using DNP $^{200}$. 

![Diagram](image)
Figure 20. Pulse sequences along with desired coherence transfer pathways for the indirect detection of I nuclei via S spins: S/I (a) DCP, (b) TONE-2-D-HMQC and (c) T-HMQC schemes.

Like the 2D CP-HETCOR spectra, 2D DCP ones with $S = ^1\text{H}$ can exhibit relayed correlations owing to $^1\text{H}$ spin diffusion during the second CP transfer. This problem is more pronounced for long contact times, like in the case of low-$\gamma$ I isotopes subject to small dipolar couplings with protons. Therefore, DCP variant using LG-CP scheme during the I$\rightarrow^1\text{H}$ transfer has been introduced to suppress $^1\text{H}$ spin diffusion and relayed correlation. As mentioned above, a limitation of CP transfer is the need to optimize the rf field amplitudes in order to fulfill one of the Hartmann-Hahn condition. This issue can be circumvented by substituting in DCP sequence the CP transfers by $^1\text{H}$$\rightarrow$I and I$\rightarrow^1\text{H}$ dipolar-mediated RINEPT (D-RINEPT) schemes, which derive from J-RINEPT sequences shown in Figure 9 but heteronuclear dipolar recoupling blocks are applied on $^1\text{H}$ channel during the $\tau$ delays to reintroduce the $^1\text{H}$-S dipolar couplings. Nevertheless, the efficiency of this double D-RINEPT sequence was still lower than that of DCP for the employed SR$_1^2$ heteronuclear dipolar recoupling.

Figure 21. 2D $^1\text{H}$$\{^{15}\text{N}\}$ DCP spectrum of isotopically unmodified mesoporous silica nanoparticles functionalized with 3-(3-phenyl ureido)propyl groups (see the structure displayed as an inset) acquired at $B_0 = 14.1$ T with $\nu_R = 40$ kHz in 46 h. Figure adapted from ref. 216. Copyright, 2014, Elsevier.

Another drawback of DCP technique is the limited excitation bandwidth of the CP transfer owing to the use of long spin-lock irradiation. As a result, DCP sequence is not applicable for isotopes subject to large CSA, such as $^{113}\text{Cd}$ or $^{195}\text{Pt}$. For instance, the CSA of $^{195}\text{Pt}$ nuclei can exceed 7000 ppm, leading to spectral breadth of 500 kHz at $B_0 = 9.4$ T. An alternative for the indirect detection of $^{195}\text{Pt}$ nuclei is to use the same dipolar-mediated HMQC (D-HMQC) sequence, which derives from the J-HMQC scheme shown in Figure 11 but $^1\text{H}$-$^{195}\text{Pt}$ dipolar couplings are reintroduced during the $\tau$ delays by the application of heteronuclear dipolar recoupling schemes, such as SR$_4^1$$_2$, on the I channel. The D-HMQC sequence has been combined with magic-angle turning (MAT) scheme to refocus $^{195}\text{Pt}$ CSA during the $\tau_1$ period and correlate the $^1\text{H}$ signal with $^{195}\text{Pt}$ centerband. The D-HMQC experiment has also been used for the indirect detection of $^{111}\text{Cd}$ and $^{113}\text{Cd}$ nuclei via $^{13}\text{C}$ and $^{31}\text{P}$ isotopes near the surface of CdSe and Cd$_x$P$_{1-x}$ nanoparticles.

Nevertheless, a limitation of the basic D-HMQC scheme is the $\tau_1$-noise, which produces spurious streaks along the indirect spectral dimension and hence, reduces the sensitivity. These artefacts stem from the random fluctuations of the MAS frequencies, which prevent a correct refocusing of the $^1\text{H}$...
CSA reintroduced by the SR4 blocks at the end of the defocusing delay, and result in signal amplitude variation from scan to scan. As a result, the uncorrelated signal is not perfectly canceled by the phase cycling, which leads to $t_1$-noise. It has been shown that the $t_1$-noise can be decreased by refocusing the $^1$H CSA during the $\tau$ delays by inserting two simultaneous 180° pulses on the $^1$H and $^I$ channels in the middle of these delays. For $I = ^{195}$Pt, short high-powered adiabatic (SHAP) pulses can be employed as 180° pulses. Hence, these $t_1$-noise-eliminated (TONE) $D$-HMQC experiments must be preferred for the indirect detection via protons of spin-1/2 isotopes subject to large CSA. Furthermore, in the TONE-2-$D$-HMQC variant shown in Figure 20b, a 90° pulse at the end of the defocusing delay flips back the uncorrelated $^1$H magnetization along the $B_0$ field direction, thus reducing the intensity of the uncorrelated signal and that of the $t_1$-noise. The TONE-$D$-HMQC experiments have been applied for the indirect detection via protons of $^{195}$pt nuclei of platinum complexes grafted on silica surfaces. This sequence has also been combined with MAT to suppress the spinning sidebands of $^{195}$Pt nuclei and to correlate the $^1$H NMR signal only with its centerband. Furthermore, we recently showed that $^{195}$Pt nuclei can be indirectly detected via protons in solids using T-HMQC sequence shown in Figure 20c, in which the $^1$H-$^{195}$Pt dipolar interactions are reintroduced during the $\tau$ delay by the application of long rf pulses on $^{195}$pt channel. These long pulses also excite and reconver $^{195}$pt 1Q coherences, which are encoded by the isotropic chemical shifts during the $t_1$ period. Since the long pulses are applied to the $^{195}$Pt channel, they do not reintroduce the $^1$H CSA and hence, the 2D $^1$H($^{195}$Pt) T-HMQC spectra exhibit low $t_1$-noise (see Figure 22).

![Figure 22](image.png)

Figure 22. 2D $^1$H($^{195}$Pt) T-HMQC spectrum of an aged mixture of trans- and cis-platin acquired at $B_0 = 18.8$ T with $\nu_R = 64$ kHz. Figure adapted from ref. 229. Copyright, 2022, American Institute of Physics.

Table 4. List of the pairs of distinct spin-1/2 isotopes, for which their signals have been correlated using indirect detection methods employing two consecutive coherence transfers $S \rightarrow I \rightarrow S$.

<table>
<thead>
<tr>
<th>$S$</th>
<th>$I$</th>
<th>Sequence</th>
<th>Sample</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>$^{13}$C</td>
<td>DCP</td>
<td>organically functionalized mesoporous silica</td>
<td>215</td>
</tr>
<tr>
<td>$^1$H</td>
<td>$^{15}$N</td>
<td>DCP</td>
<td>organically functionalized mesoporous silica</td>
<td>216</td>
</tr>
<tr>
<td>$^1$H</td>
<td>$^{31}$P</td>
<td>DCP</td>
<td>phosphane/borane</td>
<td>218</td>
</tr>
<tr>
<td>$^1$H</td>
<td>$^{89}$Y</td>
<td>DCP</td>
<td>yttrium complex</td>
<td>217</td>
</tr>
</tbody>
</table>
3.2.2 Between spin-1/2 and quadrupolar isotopes

3.2.2.1 Without high-resolution

Through-space heteronuclear correlation experiments relying on one ($I \rightarrow S$) or two ($S \rightarrow I \rightarrow S$) coherence transfers have also been applied to probe proximities between spin-1/2 and quadrupolar isotopes in solids

\[^{1}H\]^{89}Y, \(^{1}H\)\(^{103}Rh\), \(^{1}H\)\(^{103}Rh\) double D-RINEPT, \(^{1}H\)\(^{113}Cd\), \(^{1}H\)\(^{119}Sn\) D-HMQC, \(^{1}H\)\(^{183}W\) DCP, \(^{1}H\)\(^{199}Pt\) D-HMQC, \(^{19}F\)\(^{13}C\) DCP, \(^{31}P\)\(^{113}Cd\) D-HMQC

Table 5 lists pairs of spin-1/2 and half-integer spin quadrupolar isotopes, which have been correlated using a single coherence transfer. The CP-HETCOR sequence is identical to that employed for spin-1/2 isotopes (see Figure 19). Nevertheless, it requires the spin locking of the magnetization of the quadrupolar isotope, which is difficult to achieve under MAS

During the spin lock, the modulation of the quadrupolar interaction by MAS results in crossing of energy levels. Adiabatic crossings are usually difficult to achieve since they require large rf fields, which are not compatible with the rf power specifications of most NMR probes. An alternative is to spin lock the magnetization of the CT using low rf field, which results in sudden-passage energy level crossings. Nevertheless, even under these conditions, some losses often occur during the energy level crossings, which decreases the efficiency of CPMAS transfer, and the magnetization of quadrupolar nuclei cannot be spin locked for some crystallite orientations, which results in line-shape distortions

Furthermore, the low rf field used to spin lock the magnetization of the CT leads to a high sensitivity to offset and CSA

In addition, the CPMAS experiment requires a careful adjustment of the rf field applied to the quadrupolar isotope to fulfill the Hartmann-Hahn conditions under MAS conditions:

\[ \nu_{1I} + \epsilon \left( S + \frac{1}{2} \right) \nu_{1S} = n \nu_{R} \]  \hspace{1cm} (2)

assuming the $S$ spin is the quadrupolar isotope, while avoiding the rotary resonance recoupling ($R^{3}$) condition

\[ \nu_{1S} = \frac{k \nu_{R}}{S + \frac{1}{2}} \]  \hspace{1cm} (3)

with $k = 0, 1, 2$ or 3

These issues are circumvented by the use of magnetization transfer, which do not employ spin lock of the quadrupolar isotope but instead two or three CT-selective pulses. These sequences include the dipolar-mediated RINEPT (D-RINEPT) techniques, such as TEDOR, and phase-shifted recoupling effects a smooth transfer of order (PRESTO) 240–243. In these sequences, the heteronuclear dipolar interactions are reintroduced by applying heteronuclear recoupling to the spin-1/2 isotope. In the case of spin-1/2 nuclei other than $^{1}H$ and $^{19}F$, which are subject to small homonuclear dipolar couplings,
heteronuclear recoupling schemes, such as REDOR or R^3 with \( v_{12} = v_{\text{H}} \), reintroducing the \( |m| = 1 \) space component of the heteronuclear dipolar interaction must be employed since they result in larger recoupled dipolar interaction and hence, faster magnetization transfer. The R^3 scheme has the advantage to be \( \gamma \)-encoded, which limits the \( t_1 \) noise.

Conversely when the spin-1/2 nuclei are subject to large homonuclear dipolar interactions, like in the case of protons, recoupling reintroducing the \( |m| = 2 \) space component of the heteronuclear dipolar interaction, such as those based on SR47 recoupling, are required since they suppress the contribution of homonuclear dipolar interactions to the first-order average Hamiltonian. Furthermore, we have recently demonstrated that the efficiency of the D-RINEPT transfer from protons to half-integer quadrupolar nuclei can be improved by employing SR47 recoupling built from composite or adiabatic tanh/tan inversion pulses, continuous wave irradiation during the windows and composite 90° and 180° pulses on the \( ^1\text{H} \) channel. These modifications limit the losses due to \(^1\text{H}-^1\text{H} \) dipolar interactions and improve the robustness to rf field inhomogeneity. The corresponding sequence termed D-RINEPT-CWc is shown in Figure 23a. The use of adiabatic pulses as basic inversion element of SR47 recoupling provides the highest transfer efficiency and robustness at low MAS frequencies, \( \nu_{\text{r}} \leq 15 \text{ kHz} \), whereas at higher MAS frequencies, 270°,90°, composite pulse must be employed since the rf requirement of adiabatic pulses is not compatible with the specifications of MAS probes. The D-RINEPT sequence using SR47 recoupling is not affected by dipolar truncation and hence, allows the observation of both short- and long-range proximities. The SR47 recoupling also reintroduces the \(^1\text{H} \) CSA but this term commutes with the recoupled \(^1\text{H}-^1\text{I} \) dipolar interactions, and hence, does not affect the magnetization transfer.

The PRESTO sequence is an alternative to the D-RINEPT sequence for the transfer of magnetization from protons to half-integer quadrupolar nuclei. This sequence displayed in Figure 23b employs a symmetry-based recoupling, RN\( _{12} \) which reintroduces the \( |m| = 2 \) space component and the 1Q terms of the heteronuclear dipolar interaction. R22 recoupling built from single 180° pulses results in good transfer efficiency and robustness at low MAS frequencies, \( \nu_{\text{r}} \leq 20 \text{ kHz} \), whereas at high MAS frequencies (\( \nu_{\text{r}} \approx 60 \text{ kHz} \), R16 recoupling using 270°,90°, composite pulse as a basic inversion element must be employed. These recoupling schemes are affected by dipolar truncation and hence, PRESTO experiment complements D-RINEPT by allowing the selective observation of short-range proximities. These recoupling sequences also reintroduce the \(^1\text{H} \) CSA, which does not commute with the recoupled \(^1\text{H}-^1\text{I} \) dipolar interactions and hence, can interfere with the magnetization transfer. In the case of large \(^1\text{H}-^1\text{I} \) dipolar interactions, e.g. for covalently bonded \(^1\text{H}-^1\text{I} \) nuclei, and moderate \(^1\text{H} \) CSA, notably at low \( B_0 \) fields, the PRESTO-II sequence with only two pulses applied to the quadrupolar isotope is generally the most efficient variant of PRESTO. Conversely the PRESTO-III scheme shown in Figure 23b results in higher efficiency in the case of small \(^1\text{H}-^1\text{I} \) dipolar interactions and large \(^1\text{H} \) CSA because the interference of \(^1\text{H} \) CSA are limited by the application of CT-selective 180° pulse to the quadrupolar isotope and the simultaneous overall phase shift of the recoupling applied to \(^1\text{H} \) channel, which refocus partly the \(^1\text{H} \) CSA while preserving the recoupled \(^1\text{H}-^1\text{I} \) dipolar interactions. In the PRESTO sequence, the first 90° pulse excites \(^1\text{H} \) transverse magnetization, which is encoded by the isotropic chemical shift during the \( t_1 \) period. The second 90° pulse flips back this transverse magnetization along the \( B_0 \) field direction. The RN\( _{12} \) 1Q heteronuclear recoupling converts the \(^1\text{H} \) longitudinal magnetization into \(^1\text{H} \) 1Q coherences antiphase with respect to the quadrupolar isotope, which is transformed into 1Q coherences of the quadrupolar isotope antiphase with respect to the protons by the 90° pulse on the \( S \) channel. These antiphase 1Q coherences of \( S \) spins evolves during the refocusing delay into in-phase transverse magnetization, which is detected during the \( t_2 \) period.
The sensitivity of 2D PRESTO experiments has been improved using DNP and QCPMG detection to correlate the signals of $^1$H and $^{17}$O isotopes in natural abundance (see Figure 24) $^{240,248}$.

The $^1$H resolution of heteronuclear correlation spectra between protons and quadrupolar isotopes is improved at high MAS frequencies ($\nu_R \geq 40$ kHz) $^{245}$. At lower MAS frequencies, the resolution can be enhanced by the application of homonuclear dipolar decoupling, such as FSLG, on $^1$H channel during the $t_1$ period $^{240}$. However, fast MAS is easier to set up and more robust than the homonuclear decoupling.

Table S. List of the pairs of spin-$1/2$ and half-integer quadrupolar isotopes, which have been correlated using single coherence transfer $I \rightarrow S$.

<table>
<thead>
<tr>
<th>I</th>
<th>S</th>
<th>Sequence</th>
<th>Sample</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>$^{17}$O</td>
<td>CP-HETCOR</td>
<td>zeolites</td>
<td>249</td>
</tr>
<tr>
<td>$^1$H</td>
<td>$^{17}$O</td>
<td>DNP+PRESTO-II</td>
<td>Mg(OH)$_2$ and Ca(OH)$_2$</td>
<td>240</td>
</tr>
<tr>
<td>$^1$H</td>
<td>$^{43}$Ca</td>
<td>DNP+CPMAS</td>
<td>hydroxyapatite nanoparticles</td>
<td>250</td>
</tr>
<tr>
<td>$^{11}$B</td>
<td>$^1$H</td>
<td>CP-HETCOR</td>
<td>borosilicate zeolite</td>
<td>251</td>
</tr>
</tbody>
</table>
As mentioned above, the choice of the excited and detected isotopes in heteronuclear correlation depend on the gyromagnetic ratios, longitudinal relaxation times, $T_1$, coherence lifetimes and line widths of the correlated nuclei. In the case of heteronuclear correlation experiment between spin-1/2 and half-integer quadrupolar isotopes relying on a single coherence transfer, the highest sensitivity is often achieved by exciting the quadrupolar isotope, which exhibits faster longitudinal relaxation than spin-1/2 nuclei. Furthermore, the sensitivity can be further improved by irradiating the STs at the beginning of the sequence to enhance the population difference across the CT. Nevertheless, in the case of DNP experiments, higher sensitivity is usually achieved by exciting the protons since the $^{1}$H-$^{1}$H spin diffusion efficiently transports the DNP-enhanced $^{1}$H polarization into the sample.

Figure 24. 2D $^{17}$O($^{1}$H) DNP-enhanced PRESTO-II-QCPMG spectrum of isotopically unmodified mesoporous silica nanoparticles with pore diameter of 3.4 nm dried in vacuo at 25 °C and impregnated with 16 mM TEKPol solution in TCE. This spectrum was acquired at $B_0 = 9.4$ T with $\nu_B = 12.5$ kHz. FSLG homonuclear decoupling was applied to the protons during the $t_1$ period to improve the spectral resolution of the $^{1}$H dimension. Figure adapted from ref. Copyright, 2016, American Chemical Society.

Nevertheless, the above heteronuclear correlation experiments relying on a single coherence transfer cannot correlate the signals of protons and the 1Q coherences of $^{14}$N nuclei, which are broadened over several megahertz by first-order quadrupolar interaction for this spin-1 isotope and hence, are difficult to spin lock or to invert by 180° pulse. CP-HETCOR and PRESTO-II sequences have been applied to correlate the signals of protons and $^{14}$N 2Q coherences between energy levels $m_I = \pm 1$ since these coherences are only broadened by second-order quadrupolar interaction. However, the overtone excitation and detection at twice the Larmor frequency are less efficient than those of $^{14}$N 1Q coherences at the $^{14}$N Larmor frequency. Therefore, through-space HMOC (D-HMQC) experiments have been proposed for the indirect detection of $^{14}$N coherences via $^{13}$C nuclei and later protons. These experiments, which derive from the J-HMQC scheme shown in Figure 11, are advantageous since they do not employ any spin lock or inversion pulse on $^{14}$N channel. They have
been applied for the indirect detection of $^{14}$N 1Q and 2Q coherences. The indirect detection of $^{14}$N 1Q coherences requires an accurate adjustment of the magic angle with an accuracy better than ±0.002° and fluctuations of the MAS frequency smaller than a few hertz to refocus the first-order quadrupolar interaction. The indirect detection of $^{14}$N 2Q coherences is less demanding in terms of accuracy and stability of the MAS but is often less efficient 263–266. Coherence transfers have been mediated by first residual dipolar splitting 1,2,262, which is the sum of the J-coupling and the second-order quadrupole-dipole cross term. Nevertheless, it has been shown that more efficient coherence transfers can be achieved by reintroducing S-$^{14}$N dipolar couplings through the application of heteronuclear recoupling on S channel during the defocusing and refocusing delays 263,267,268. When S = $^1$H, the $\text{SR}^{1/2}$ recoupling built from single 180° pulse is generally used 269. Furthermore, the through-space HSQC sequence has also been employed for the indirect detection of $^{14}$N coherences via protons but is less efficient than D-HMQC 270. An additional challenge for these experiments is the excitation of $^{14}$N coherences using rf field with amplitude of few tens of kilohertz, which is two orders of magnitude lower than the first-order quadrupolar interaction. Various schemes have been proposed but sideband selective long pulses combine good efficiency, high robustness and easy set up 266. The indirect detection via protons of $^{14}$N 1Q coherence using D-HMQC sequence has notably been employed to investigate host-guest interactions in MOFs 271 as well as the structure of layered aluminophosphate containing amine structure directing agents 272 (see Figure 25a). It has also been shown that the resolution along the $^{14}$N dimension can be improved by applying homonuclear decoupling schemes on $^1$H channel during $t_1$ period 273.

As mentioned in the section 3.2.1, a limitation of D-HMQC sequence is the $t_1$-noise produced by the random fluctuation of MAS frequency, which prevents the correct refocusing of $^1$H CSA and results in random signal amplitude modulation. In the case of the indirect detection of $^{14}$N nuclei, this issue cannot be circumvented by the use of TONE D-HMQC sequence, since this scheme includes 180° pulses, which are difficult to achieve for spin-1 nuclei. An alternative consists in reintroducing the $^1$H-$^{14}$N dipolar interactions by applying two identical long pulses, similar to those used in transfer of population in double resonance (TRAPDOR) 274,275, during the defocusing and refocusing delays on $^{14}$N channel instead of $^1$H channel 276–279. These pulses do not reintroduce the $^1$H CSA, which limits the $t_1$-noise. We have recently shown that this combination of TRAPDOR and HMQC schemes, called T-HMQC, can allow the indirect detection of either $^{14}$N 1Q or 2Q coherences with similar efficiency 229. Furthermore, the 2Q variant benefits from slightly higher resolution. Nevertheless, to the best of our knowledge, T-HMQC experiment has so far only been applied for the indirect detection of $^{14}$N nuclei in organic solids but not yet for inorganic or hybrid solids.

The D-HMQC experiment has also been applied to correlate the signals of spin-1/2 and half-integer quadrupolar nuclei in solids 46,236,237,280 since depending on the correlated isotopes and the sample, the $S \rightarrow I \rightarrow S$ consecutive transfers can be more sensitive than the $S \rightarrow I$ single transfer. Table 6 lists pairs of spin-1/2 and half-integer quadrupolar nuclei, which have been correlated using D-HMQC sequence. In that case, the recoupling scheme is applied to the spin-1/2 isotope to minimize the number of pulses applied to quadrupolar nuclei and the associated losses. The pulses applied to the quadrupolar isotope are selective of the CT. It is often preferable to detect indirectly the spin-1/2 nuclei via the quadrupolar isotope since the longitudinal relaxation of quadrupolar nuclei is often faster and the application of the recoupling on the indirect channel limits the $t_1$-noise. The recoupling employed in D-HMQC sequence reintroduces longitudinal two-spin order term ($S_1 L_1$) of the heteronuclear dipolar interaction. Hence, the D-HMQC sequence is not affected by dipolar truncation and CSA interference 280. Furthermore, it has been shown that the D-HMQC sequence is more efficient than the D-HSQC variant 281.

When the spin-1/2 isotope is not subject to large homonuclear dipolar interaction, the heteronuclear dipolar interaction can be reintroduced by the recoupling scheme with simultaneous
amplitude and frequency modulations equal to the MAS frequency (SFAM-1) (see Figure 25b). This recoupling reintroduces the $|m| = 1$ space component of the heteronuclear dipolar interaction and hence, results in fast coherence transfer \cite{282,283}. Furthermore, because of the amplitude and frequency modulations, it is more robust to offset, CSA and rf field inhomogeneity than REDOR and R$^3$ schemes. At low MAS frequencies, $\nu_R \leq 15$ kHz, the symmetry-based recoupling built from adiabatic tanh/tan (tt) pulses, such as $R_2^{-1}$, benefits from higher robustness than SFAM-1 and has been applied to correlate quadrupolar nuclei with spin-1/2 nuclei subject to large CSA, such as $^{207}$Pb \cite{284}.

Figure 25. (a) 2D $^1$H\{$^{14}$N\} D-HMQC-SR4$^2$ spectrum of layered aluminophosphate containing amine structure directing agents acquired at $B_0 = 18.8$ T with $\nu_R = 62.5$ kHz. Figure adapted from ref. \cite{272}. Copyright, 2013, American Chemical Society. (b) 2D $^{11}$B\{$^{29}$Si\} D-HMQC-SFAM-1 spectrum of boron nitride supported on dendritic fibrous silica nanoparticles acquired at $B_0 = 18.8$
When the indirectly detected isotope is subject to large homonuclear dipolar interactions, like $^1\text{H}$, a recoupling reintroducing the $|m|=2$ space component of the heteronuclear dipolar interaction, such as SR4$^2$, must be employed since they eliminate the contribution of homonuclear dipolar interactions to the first-order average Hamiltonian.\textsuperscript{270,280} Furthermore, the resolution along the $^1\text{H}$ dimension of proton-detected $D$-HMQC experiment can be improved by applying homonuclear decoupling schemes on $^1\text{H}$ channel during $t_1$ period.\textsuperscript{281} The $D$-HMQC sequence allows the indirect detection of half-integer quadrupolar nuclei via protons, which can enhance the sensitivity, notably at high MAS frequencies, $v_B \geq 40$ kHz.\textsuperscript{239} Nevertheless, this experiment exhibits $t_1$-noise, as already mentioned in section 3.2.1. When the indirectly detected isotope is a half-integer quadrupolar nucleus, TONE $D$-HMQC sequence, shown in Figure 20b, can be employed by applying CT-selective $180^\circ$ pulses during the defocusing and refocusing delays.\textsuperscript{225} This technique has been used for indirect detection via protons of $^{27}\text{Al}$ and $^{25}\text{Mg}$ quadrupolar nuclei (see Figure 25c). For $I = 3/2$, an alternative consists in the use of T-HMQC scheme, which has been recently applied for the indirect detection via protons of $^{35}\text{Cl}$ 1Q, 2Q and 3Q coherences.\textsuperscript{229,286} Nevertheless, to the best of your knowledge, it has not yet been employed for inorganic or hybrid materials.

Table 6. List of the pairs of spin-1/2 and half-integer quadrupolar isotopes, for which their signals have been correlated using $D$-HMQC sequence in inorganic or hybrid materials.

<table>
<thead>
<tr>
<th>$S$</th>
<th>$I$</th>
<th>Sequence</th>
<th>Sample</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{H}$</td>
<td>$^{14}\text{N}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>layered aluminophosphate</td>
<td>272</td>
</tr>
<tr>
<td>$^1\text{H}$</td>
<td>$^{23}\text{Na}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>layered double hydroxide</td>
<td>281</td>
</tr>
<tr>
<td>$^1\text{H}$</td>
<td>$^{25}\text{Mg}$</td>
<td>TONE $D$-HMQC</td>
<td>crystalline aluminophosphate AlPO$_4$-14</td>
<td>237</td>
</tr>
<tr>
<td>$^1\text{H}$</td>
<td>$^{27}\text{Al}$</td>
<td>$D$-HMQC-R$^1$</td>
<td>layered double hydroxide</td>
<td>225</td>
</tr>
<tr>
<td>$^1\text{H}$</td>
<td>$^{43}\text{Ca}$</td>
<td>$D$-HMQC-R$^1$</td>
<td>hydroxyapatite</td>
<td>287</td>
</tr>
<tr>
<td>$^1\text{H}$</td>
<td>$^{71}\text{Ga}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>gallium complex</td>
<td>239</td>
</tr>
<tr>
<td>$^{11}\text{B}$</td>
<td>$^1\text{H}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>B$_2$O$_3$/BN supported on silica</td>
<td>285</td>
</tr>
<tr>
<td>$^{11}\text{B}$</td>
<td>$^{29}\text{Si}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>borosilicate glass</td>
<td>46</td>
</tr>
<tr>
<td>$^{11}\text{B}$</td>
<td>$^{31}\text{P}$</td>
<td>$D$-HMQC-SFAM-1</td>
<td>borophosphate glass</td>
<td>236</td>
</tr>
<tr>
<td>$^{11}\text{B}$</td>
<td>$^{207}\text{Pb}$</td>
<td>$D$-HMQC-R2I$^{-1}$ (tt)</td>
<td>crystalline lead borate</td>
<td>284</td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td>$^7\text{Li}$</td>
<td>$D$-HMQC-SFAM-1</td>
<td>alkylaluminium</td>
<td>174</td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td>$^{27}\text{Al}$</td>
<td>$D$-HMQC-SFAM-1</td>
<td>alkylaluminium</td>
<td>174</td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>$^1\text{H}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>silica-supported catalysts</td>
<td>288</td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>$^{29}\text{Si}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>zeolites</td>
<td>289</td>
</tr>
<tr>
<td>$^{23}\text{Na}$</td>
<td>$^{29}\text{Si}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>crystalline sodium phosphate</td>
<td>290</td>
</tr>
<tr>
<td>$^{23}\text{Na}$</td>
<td>$^{31}\text{P}$</td>
<td>$D$-HMQC-R$^1$</td>
<td>crystalline aluminophosphate</td>
<td>237</td>
</tr>
<tr>
<td>$^{29}\text{Si}$</td>
<td>$^{17}\text{O}$</td>
<td>DNP+ $D$-HMQC-SR4$^2$</td>
<td>silica and silica alumina</td>
<td>291</td>
</tr>
<tr>
<td>$^{27}\text{Al}$</td>
<td>$^1\text{H}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>γ-alumina</td>
<td>292</td>
</tr>
<tr>
<td>$^{27}\text{Al}$</td>
<td>$^{13}\text{C}$</td>
<td>$D$-HMQC-SFAM-1</td>
<td>alkylaluminium</td>
<td>174</td>
</tr>
<tr>
<td>$^{27}\text{Al}$</td>
<td>$^{29}\text{Si}$</td>
<td>$D$-HMQC-SR4$^2$</td>
<td>montmorillonite clay</td>
<td>293</td>
</tr>
<tr>
<td>$^{27}\text{Al}$</td>
<td>$^{31}\text{P}$</td>
<td>$D$-HMQC-SFAM-1</td>
<td>aluminophosphate glass</td>
<td>237</td>
</tr>
<tr>
<td>$^{51}\text{V}$</td>
<td>$^{31}\text{P}$</td>
<td>$D$-HMQC-SFAM-1</td>
<td>vanadophosphate glass</td>
<td>236</td>
</tr>
<tr>
<td>$^{71}\text{Ga}$</td>
<td>$^{31}\text{P}$</td>
<td>$D$-HMQC-R$^1$</td>
<td>gallium-doped calcium phosphate ceramics</td>
<td>294</td>
</tr>
</tbody>
</table>

3.2.2.2 With high-resolution
As for through-bond HETCOR experiments, high-resolution version of through-space HETCOR sequence between spin-1/2 and half-integer quadrupolar isotopes have been developed. These high-resolution spectra have been first acquired using sequences deriving from 3Q-J-RINEPT scheme, in which the J-RINEPT block is substituted by CPMAS\(^{20,295}\), D-RINEPT\(^{238}\) or PRESTO\(^{296}\) transfer. As explained above, the D-RINEPT and PRESTO transfer are more robust than CPMAS. Furthermore, the sensitivity of these experiments is enhanced using soft pulse added mixing (SPAM), which increases the efficiency of the reconversion of 3Q coherences into 1Q ones of the quadrupolar isotope\(^{187,296}\). The sensitivity of these high-resolution HETCOR experiments can be further improved by a factor of 2 at least by substituting the 3QMAS block by a satellite transition MAS (STMAS) scheme, which correlates the satellite transition and the CT to remove the second-order quadrupolar broadening\(^{297,298}\). Nevertheless, this STMAS version requires the adjustment of the magic angle with an accuracy of 0.001° and a very stable MAS frequency. Therefore, its implementation is usually more difficult than that of 3QMAS version. These sequences have been employed to correlate the high-resolution spectra of half-integer quadrupolar nuclei, such as \(^{23}\)Na and \(^{27}\)Al, with the spectra of spin-1/2 isotopes, such as \(^1\)H and \(^{31}\)P (see Figure 26). Note also that in the case of spin \(I = 3/2\), STMAS technique can also be combined with D-HMQC scheme\(^{299}\).

![Figure 26. Comparison of 2D \(^{31}\)P\{\(^{27}\)Al\} (a) D-RINEPT and (b) 3Q-D-RINEPT spectra of layered aluminophosphate acquired at \(B_0 = 18.8\) T with \(v_\text{R} = 22.222\) kHz. Figure reprinted from ref. 238. Copyright, 2012, Royal Society of Chemistry.](image)

### 3.2.3 Between two half-integer quadrupolar isotopes

Proximities between distinct half-integer quadrupolar isotopes, such as \(^{11}\)B and \(^{27}\)Al, have been probed using CP-HETCOR using either continuous wave (CW) irradiation\(^{18,300}\) or train of rotor-synchronized pulses\(^{301}\). However, the spin-lock and the CPMAS transfer lack robustness in the case of quadrupolar nuclei. This issue has been circumvented by the use of D-HMQC and D-RINEPT sequences\(^{302,303}\). For these sequences, the highest robustness has been achieved using synchronous phase inversion R\(^3\) (SPI-R\(^3\)) scheme, which corresponds to the C\(^2\)\(^2\)\(^1\) symmetry\(^ {302}\). Furthermore, we have shown that this recoupling scheme must be applied to the dephaser isotope with magnetization parallel to \(B_0\) field to minimize the losses during the transfer\(^{303}\).

### 4. Applications
In this section, we review how correlation experiments have been employed for the characterization of different classes of materials: microporous materials, heterogeneous catalysts, minerals, biomaterials and glasses.

4.1 Microporous materials

Correlation experiments have provided unique insights into the structure of microporous materials (with pore diameters < 2 nm), including crystalline aluminophosphates (AlPOs), zeolites and MOFs.

4.1.1 AlPOs

Microporous crystalline aluminophosphates have been used for various applications, such as adsorption, gas separation and catalysis. These aluminophosphate materials are built from alternating aluminium polyhedra and phosphorus tetrahedra connected through bridging oxygen atoms. They are usually synthesized using a quaternary amine as structure-directing agents. The charge of these cations is balanced by $\text{F}^-$ and $\text{HO}^-$ anions coordinated to the Al atoms. Water can also be present in the pores for as-prepared or rehydrated AlPOs. In addition, it is possible to substitute the P atoms by Si ones and the Al atoms by di- or tri-valent metal atoms, including Mg or Zn. Solid-state NMR complements diffraction studies for the characterization of AlPOs and provides unique information on the defects, such as substitution, the interaction between AlPO framework and the host molecules as well as the motions of guest within the pores. Several reviews about solid-state NMR of crystalline AlPOs have been published [52,304–306]. As AlPOs contains several NMR active isotopes, such as $^{31}\text{P}$, $^{27}\text{Al}$, $^1\text{H}$, $^{19}\text{F}$, $^{14}\text{N}$, and $^{17}\text{O}$, 2D homo- and hetero-nuclear correlation experiments have been extensively employed to assign their NMR spectra and to probe their medium-range (0.3-1 nm) structure.

Through-space homonuclear 2Q-1Q experiments using POST-C7 and BaBa recoupling have been employed to probe $^{31}\text{P}$-$^{31}\text{P}$ [209,307–309] and $^1\text{H}$-$^1\text{H}$ [308] proximities, respectively, in AlPOs, whereas similar experiment using BR2$^2$ recoupling have been used to observe proximities between $^{27}\text{Al}$ nuclei [149,151,152].

The connectivities between Al and P sites in AlPOs have been probed using $^{27}\text{Al}$$^{[31}\text{P}]$ J-HMQC experiment [160] but also $^{31}\text{P}$$^{[27}\text{Al}]$ 3Q-J-RINEPT variant featuring high-resolution along the $^{27}\text{Al}$ dimension [310–312]. Furthermore, $^{27}\text{Al}$$^{[19}\text{F}]$ J-HMQC experiment has been employed to investigate the $\text{F}^-/\text{HO}^-$ distribution in fluorinated AlPOs (see Figure 14) [128].

Similarly proximities between Al and P sites have been observed using $^{31}\text{P}$$^{[27}\text{Al}]$ CP-HETCOR experiment [308], its variant with 3Q filter to suppress the second-order quadrupolar broadening of the $^{27}\text{Al}$ NMR spectra [187,307,313,314] and more recently the 3Q-$D$-RINEPT version [238,272,309,315]. The location of $\text{F}^-$ anions in fluorinated aluminophosphates has been investigated using 2D $^{31}\text{P}$$^{[19}\text{F}]$ and $^{27}\text{Al}$$^{[19}\text{F}]$ CP-HETCOR spectra (see Figure 27) [308,309]. Proximities between protons and half-integer quadrupolar isotopes, such as $^{23}\text{Na}$ and $^{27}\text{Al}$, in AlPOs have also been probed using high-resolution ST-CP-HETCOR experiments [297].
4.1.2 Zeolites

Aluminosilicate zeolites are microporous materials made of a 3D network of corner-sharing SiO$_4$ and AlO$_4$ tetrahedra. Furthermore, metals, such as Sn, Mo, Zn or Ga, can be introduced in the zeolites. They are widely employed for various applications, such as catalysis, ion exchange and separations. They contain several NMR active isotopes, such as $^{27}$Al, $^{29}$Si, $^{17}$O, $^1$H and $^{23}$Na and hence, solid-state NMR provides detailed information on the structure of the framework and notably the presence of defects, the extra-framework species, the host-guest interactions and the catalytic reactions within the zeolite pores 57–59,304,305. In particular, homo- and hetero-nuclear correlation NMR experiments are essential tools for the characterization of these materials.

The Si–O–Si connectivities can be identified by 2D $^{29}$Si INADEQUATE experiments 69,79,82,88,316,317. Owing to the low natural abundance of $^{29}$Si isotope (4.7%), the sensitivity of these experiments has been enhanced using $^{29}$Si isotopic enrichment 79,88,317 or DNP (see Figure 4) 82. The observation of proximities between $^{29}$Si nuclei using $^{29}$Si 2Q-1Q through-space homonuclear correlation also provides useful information on the structure of the zeolite framework 107,112,318. Proton 2Q-1Q through-space homonuclear correlations have been employed to probe the proximities between Lewis and Brønsted acid sites 319,320 and more recently the location of SiO$^-$–HOSi defects in zeolites and their interaction with structure-directing agent 321,322, whereas the presence of clusters of three silanol groups was demonstrated using the 3Q-1Q counterpart 121,323. The $^{13}$C PDSD experiment has been employed to observe adsorbed species and probe intermolecular interactions between cyclopentenyl cation intermediates and hydrocarbons during methane to olefins reaction over zeolite 324–328. The incorporation of Al atoms in the zeolite frameworks results in the formation of Brønsted acid sites made of bridging silanol SiOHAl. The dealumination converts some of these Brønsted acid sites into extra-framework Al sites, which act as Lewis acid sites, and hence, enhances the catalytic activity and the selectivity of zeolites. This process has been investigated by probing proximities between Al atoms using $^{27}$Al 2Q-1Q through-space homonuclear correlation, which show the proximity between Lewis and Brønsted acid sites (see Figure 8) 157.

Figure 27. 2D (a) $^{31}$P($^{19}$F) and (b) $^{27}$Al($^{19}$F) CP-HETCOR spectra of fluorinated aluminophosphate DNL-1 at acquired at $B_0 = 11.7$ T with $\nu_R = 28$ kHz. Figure reprinted from ref. 309. Copyright, 2011, American Chemical Society.
Furthermore, the position of Al atoms within the framework strongly influences the Brønsted acidity of zeolites. It has been investigated using $^{27}$Al($^{29}$Si) $J$- and $D$-HMQC experiments. Brønsted acid sites have also been observed using $^{27}$Al($^1$H) CP-HETCOR and $D$-HMQC experiments. In particular, the acquisition of 2D $^{27}$Al($^1$H) $D$-HMQC spectrum at 35.2 T revealed the presence of partially hydrolyzed Brønsted acid sites and provided unprecedented information on the distribution of Al atoms in the zeolites. Tri-coordinated framework Al atoms (Al(OSi)$_3$) acting as Lewis acid sites have also been revealed using trimethylphosphine oxide (TMPO) as a base probe molecules and $^{31}$P($^1$H) CP-HETCOR as well as $^{31}$P($^{27}$Al) PT-$D$-HMQC experiments. The $^{17}$O($^{29}$Si) $D$-HMQC experiment on doubly $^{17}$O- and $^{29}$Si-enriched zeolites has demonstrated the hydrolytic rearrangements occurring during the preparation of these zeolites. The acid sites created by the incorporation of Sn atoms into zeolite framework have also been observed using $^1$H($^{119}$Sn) $D$-HMQC experiments. Similarly $^{11}$B($^1$H) CP-HETCOR, $^1$H($^{11}$B) $D$-RINEPT and $^{11}$B($^{29}$Si) J-HMQC experiments have been used to probe the location of B atoms in zeolite substituted with boron. The $^{27}$Al($^{13}$C) $D$-HMQC experiment was also applied to probe the interactions between adsorbed $^{13}$C-enriched acetone molecules and the Lewis and Brønsted acid sites of dealuminated HY zeolite (see Figure 28). This double-resonance $^{13}$C-$^{27}$Al NMR experiment requires a frequency splitter owing to the close Larmor frequencies of these isotopes.

4.1.3 MOFs

Metal-organic frameworks are crystallized hybrids materials with promising applications in the field of gas storage, chemical separation, catalysis, depollution, sensing and drug delivery. They are built from an inorganic cluster and an organic ligand yielding to a porous framework. They contain a wide range of NMR-active isotopes, such as $^1$H, $^{13}$C, $^{27}$Al or $^{45}$Sc.

Correlation NMR experiments are essential techniques to probe the structure of MOFs, and notably the location of defects, as well as the host-guest interactions in these materials. For instance, 2D $^1$H 2Q-1Q homonuclear correlation at high MAS frequency has been used to assign the $^1$H signals of MOFs (see Figure 6) and probe the interactions of caffeine with UiO-66(Zr) MOFs, whereas 2D $^1$H spin diffusion measurements have been employed to probe the spatial arrangement of linkers in MOFs made of different linkers as well as the host-guest interactions and ethane/ethylene separation mechanism on zeolitic imidazolate frameworks.
The $^{13}$C($^1$H) CP-HETCOR, $^1$H($^{13}$C) J-HMQC experiments and their combination with $^1$H spin diffusion experiments have been applied to probe the host-guest interactions in MOFs 345–349, and notably the adsorption of CO$_2$ in MOFs functionalized with diamine or alcohol amine 349,350. The proximities between $^{13}$C and $^{27}$Al nuclei in MIL-100(Al) MOF have also been probed using DNP-enhanced $^{13}$C($^{27}$Al) and $^{27}$Al($^{13}$C) D-HMQC experiments 351. Similarly, $^{45}$Sc($^1$H) D-HMQC experiments were carried out to monitor the structural modification of the MIL-100(Sc) during thermal treatment (see Figure 29) 352.

![Figure 29: $^{45}$Sc($^1$H) D-HMQC spectra](image)

Figure 29. $^{45}$Sc($^1$H) D-HMQC 2D spectra of (a) as-synthesized MIL-100(Sc), and after thermal treatment at (b) 220, and (c) 300 °C. The 2D spectra were recorded at $B_0 = 18.8$ T with $\nu_R = 20$ kHz. Figure reprinted from ref. 352. Copyright, 2017, Wiley.

4.2 Metal oxide catalysts

Beside microporous materials, solid-state NMR can provide precious insights into the atomic-level structure and dynamics of other heterogeneous catalysts, including notably metal oxides and supported single-site catalysts 53–56,353–355. These materials contain several NMR-active isotopes, such as $^1$H, $^{13}$C, $^{17}$O, $^{19}$F, $^{29}$Si and $^{27}$Al. Through-bond and through-space correlation NMR experiments provide detailed information about the arrangement of atoms near the surface of the catalysts. Nevertheless, a difficulty is that the nuclei of the surface represent only a small fraction of the total amount of nuclei in the case of nanoparticles and mesoporous materials with surface area ranging from 10 to 100 m$^2$·g$^{-1}$ 356. Furthermore, several of the NMR active isotopes, such as $^{13}$C, $^{17}$O and $^{29}$Si, in these materials exhibit low natural abundance.

Therefore, 2D correlation on metal oxide catalysts were first demonstrated for sensitive spins, such as $^1$H, $^{19}$F or $^{27}$Al, or using isotope enrichment for isotopes, such as $^{13}$C and $^{17}$O. In particular, $^1$H 1Q-1Q, 2Q-1Q and 3Q-1Q through-space correlation experiments have been applied to probe the spatial distribution of organic functional groups as well as hydroxyl groups on surfaces as well as the ordering of mixed surfactants in mesoporous silica 55,195,292,357–359. The 3Q-1Q variant has the advantage to allow the unambiguous observation of proximities between CH$_2$ groups provided their $^1$H resonances are resolved. Similarly, $^{19}$F 1Q-1Q and 2Q-1Q through-space correlation spectra have been used to assign the signals of BF$_4^-$ and free F$^-$ anions for BF$_4^-$ salt of Pd(II) complex immobilized on silica 116. Furthermore, 2Q-1Q through-space correlation techniques have been applied to probe proximities between $^{27}$Al nuclei in amorphous silica alumina 360 and more recently between $^{17}$O sites in $^{17}$O-labeled γ-alumina (see Figure 30)361.
Moreover, metal oxide catalysts have also been characterized using conventional 2D heteronuclear correlation experiments. For instance, J-HMQC sequence has allowed the selective observation of AlH species on the surface of γ-alumina and OH groups on 17O-labeled silica and alumina. Through-bond and through-space heteronuclear correlation experiments have also been employed to probe 1H-13C connectivities and proximities in supported metal complexes and organic functional groups as well as surfactants (see Figure 10). These experiments were initially recorded for 13C-labeled samples. Nevertheless, it was later demonstrated that the sensitivity gain provided by indirect detection via protons allows their acquisition in natural abundance using conventional NMR. Similar approaches have been used to probe proximities between protons and other spin-1/2 isotopes, such as 15N, 19F, 29Si, and 195Pt, near surfaces (see Figure 18). Furthermore, through-space heteronuclear correlation experiments have also been applied to probe proximities between protons and half-integer quadrupolar nuclei, such as 11B, 17O, and 27Al nuclei located near the surface of oxide or nitride phases since their bulk region does not contain protons. In particular, 2D 27Al{1H} D-HMQC experiment has been employed to identify the hydroxyl groups at the surface of γ-alumina and the preferential grafting sites of metal complexes on these surfaces (see Figure 31) as well as the nature of Brønsted acid sites near the surface of amorphous silica alumina. Furthermore, 2D 11B{29Si} and 27Al{29Si} D-HMQC experiments have been used to probe the anchoring of BN/B2O3 and Al2O3 phases on silica nanoparticles (see Figure 25b).
In addition, the sensitivity enhancement offered by DNP, which can exceed two orders of magnitude\textsuperscript{83}, has been leveraged to acquire 2D correlation spectra involving surface nuclei of low natural abundance, such as \textsuperscript{13}C, \textsuperscript{29}Si and \textsuperscript{17}O. For instance, DNP-enhanced homonuclear correlation experiments have allowed the observation of \textsuperscript{13}C-\textsuperscript{13}C and \textsuperscript{29}Si-\textsuperscript{29}Si connectivities and proximities near surface, providing new insights into the structure of catalytic intermediates and products (see Figure 7f)\textsuperscript{131,374} as well as the spatial distribution of silica-bound organic functional groups (see Figure 7d)\textsuperscript{113,130}. Thanks to the sensitivity enhancement provided by DNP, some of these experiments were acquired in natural abundance, even if the probability of \textsuperscript{13}C-\textsuperscript{13}C and \textsuperscript{29}Si-\textsuperscript{29}Si pairs in that case is as low as 0.01 and 0.2\%, respectively. The sensitivity enhancement offered by DNP has also permitted the observation of \textsuperscript{1}H-\textsuperscript{17}O\textsuperscript{248,375} and \textsuperscript{17}O-\textsuperscript{29}Si\textsuperscript{291} pairs with probability of 0.038 and 0.0017\% in natural abundance, thus allowing the detection of silanol and siloxane groups at the surface of silica and amorphous silica alumina.

4.3 Minerals and biomaterials

Minerals make up both the surface and inner layers of the Earth’s geological structure, and are also used in industry as, for example, cements, ceramics, glasses, fertilisers and heterogeneous catalysts\textsuperscript{376–379}. Biomaterials are those materials interacting with biological systems. Modern applications of biomaterials include joint replacements, dental implants, tissue engineering (including bone repair) and the emerging field of “smart” biomaterials, that are capable of modifying their physicochemical and mechanical properties in response to external stimuli\textsuperscript{380,381}. Inorganic biomaterials notably include calcium phosphates, such as hydroxyapatite (\textsuperscript{10}Ca\textsubscript{10}(\textsuperscript{4}PO\textsubscript{4}\textsubscript{6})(OH\textsubscript{2}) and tricalcium phosphate (\textsuperscript{3}Ca\textsubscript{3}(PO\textsubscript{4}\textsubscript{2}), which are present in natural bones but are also used in the fabrication of components for the repair and reconstruction of damaged parts of the musculoskeletal system, but also due to their presence in\textsuperscript{382,383}. Minerals and inorganic biomaterials contain several NMR-active isotopes, such as \textsuperscript{1}H, \textsuperscript{17}O, \textsuperscript{19}F, \textsuperscript{29}Si, \textsuperscript{31}P, \textsuperscript{27}Al and \textsuperscript{43}Ca. Hence, solid-state NMR spectroscopy, including 2D correlation experiments, is
largely employed to characterize atomic-level structures, and notably defects lacking long-range positional order, in minerals and biomaterials 376–379,384.

The proximities between hydrogen sites have notably been probed using 2D $^1$H homonuclear correlation experiments 385–390. These 2D spectra provided information about the location of hydrogen in hydrous wadsleyite ($\beta-(\text{Mg,Fe})_2\text{SiO}_4$)388, which has received interest as a potential reservoir for hydroxyls (water) in Earth’s mantle (see Figure 32a), as well as the cation clustering in Mg/Al layered double hydroxides (LDH)386,387. Homonuclear correlation experiments have also been applied to probe $^{31}$P-$O$-$^{31}$P connectivities in calcium phosphate phases391,392 and $^{29}$Si-$^{29}$Si proximities in a feldspar mineral393. Furthermore, the sensitivity gain offered by DNP allowed to record 2D $^{13}$C 2Q-1Q homonuclear correlation of isotopically unmodified carbonated hydroxyapatite nanoparticles394. This spectrum demonstrated the clustering of carbonate anions. Proximities between Al sites in minerals were also probed by 2D $^{27}$Al 2Q-1Q homonuclear correlation151,393,395.

![Figure 32. (a) 2D $^1$H 2Q-1Q homonuclear correlation spectrum of hydrous wadsleyite recorded using the BABA recoupling sequence. 2Q correlations are indicated by dashed lines and the solid line denotes the autocorrelation diagonal. The spectrum was acquired at $B_0 = 14.1$ T with $\nu_R = 30$ kHz. (b) 2D $^{17}$O($^1$H) CP-HETCOR spectrum of $^{17}$O-enriched hydrous wadsleyite recorded at $B_0 = 20$ T with $\nu_R = 30$ kHz. Figure adapted from ref. 388. Copyright, 2013, Royal Society of Chemistry.](image)

Regarding heteronuclear correlation, 2D $^{31}$P($^1$H) CP-HETCOR experiment has widely used to investigate the nature of calcium phosphate phases in bones197,396–399 as well as the interaction of calcium phosphate surfaces with other compounds400–402. This experiment as well as 2D $^{13}$C($^1$H) CP-HETCOR and more recently, DNP-enhanced $^{13}$C($^{31}$P) CP-HETCOR experiments have provided information about the location of anionic substituents in calcium phosphate phases394,403,404. Heteronuclear correlation between protons and $^{43}$Ca isotope, which is low-$\gamma$ quadrupolar nucleus ($I = 7/2$ and $|\gamma(^{43}\text{Ca})/\gamma(^1\text{H})| = 6.7\%$), has also been reported, first for $^{43}$Ca-enriched hydroxyapatite and oxyhydroxyapatite287 and more recently, in natural abundance (0.14%) using DNP for carbonated hydroxyapatite (see Figure 33b). $^{1}$H($^{13}$C) CP-HETCOR experiments with $S = ^{13}$C196,405,406, 19F196 and $^{29}$Si405,407,408,409 have also been applied to study clay minerals and notably their interactions with organic cations and molecules. Correlation between $^1$H and $^{29}$Si nuclei as well as $^{17}$O($^1$H) CP-HETCOR experiment has also provided information about the location of protons in magnesium silicate phases (see Figure 32b)385,388,410. In addition, correlation experiments between $^{27}$Al isotope and spin-1/2 nuclei, such as $^1$H411,412, 19F412 and $^{29}$Si187,293,393, have been employed to gain insight into the location of cations, anions and vacancies in minerals and to identify impurities (see Figure 16).
Figure 33. DNP-enhanced solid state NMR spectra of carbonated hydroxyapatite nanoparticles recorded at $B_0 = 9.4$ T and ~100 K with $v_R = 8.5$ kHz. (a) 2D $^{13}$C($^1$H) CP HETCOR spectrum with associated $^{13}$C skyline projection (top). (b) 2D $^{43}$Ca($^1$H) CP-HETCOR spectrum with associated $^{43}$Ca (top) and $^1$H (right) skyline projections. Both 2D spectra were recorded using $^1$H FSLG homonuclear and SPINAL-64 heteronuclear decoupling. Also shown for comparison is the DNP-enhanced $^1$H Hahn-echo MAS NMR spectrum (far right, purple). Figure adapted from ref. 250. Copyright, 2017, American Chemical Society.

4.4 Glasses

Glasses are amorphous solids produced by the disequilibrium cooling of a liquid. These materials have a wide range of applications, including windows, containers, optical devices, nuclear waste storage and protective coatings. The characterization of atomic-level structures of glasses is challenging owing to their lack of long-range positional order. As a local characterization technique, solid-state NMR is particularly useful for investigating the structure glasses 49-52. Glasses contain several NMR active nuclei, such as $^{11}$B, $^{29}$Si, $^{27}$Al, $^{31}$P, $^{71}$Ga and $^{77}$Se. Correlation NMR experiments provide unique insight into the medium-range structure of glasses, i.e. the linkage between structural units, such as SiO$_4$, BO$_4$, BO$_3$, AlO$_4$ and PO$_4$ groups.

The P−O−P and Si−O−Si connectivities have been probed using 2D $^{31}$P/$^{29}$Si through-bond homonuclear correlation experiments, and notably the refocused INADEQUATE sequence,24,76,87. The $^{31}$P 3Q-1Q variant has been employed to observe trimers of phosphate units in lead phosphate glasses 61. Furthermore, through-space $^{31}$P/3Q and $^{29}$Si/4Q homonuclear correlation experiments have provide information on the proximities between these units. The homonuclear correlation experiments for $^{29}$Si isotope have been recorded on $^{29}$Si-enriched silicate glasses, given the low natural abundance of this isotope. Although 1Q-1Q homonuclear correlation spectra were recorded in the 1990s, their 2Q-1Q variants are usually preferred since they allow to probe connectivities and proximities between nuclei with close resonance frequencies. The proximities between hydrogen sites in weathered surface of phosphate was investigated using $^1$H 2Q-1Q homonuclear correlation and 1Q-1Q spin diffusion experiments 419. The 2Q-1Q homonuclear correlation experiments have also been employed to probe $^{11}$B-$^{11}$B 151 and $^{27}$Al-$^{27}$Al 420,421 proximities in glasses.

$J$-HMOCJ experiments have been applied to study connectivities between spin-1/2 and quadrupolar isotopes ($^{19}$F-$^{11}$B, $^{29}$Si–O–$^{27}$Al, $^{31}$P–O–$^{11}$B, $^{31}$P–O–$^{27}$Al) as well as distinct half-integer quadrupolar isotopes $^{17}$O–$^{27}$Al. The Se-Ga bonds in gallium selenide glass have also been probed using $J$-HMOCJ and $J$-RINEPT experiments 170. Furthermore, 2D through-space heteronuclear correlation
experiments have been used to reveal the proximities between $^{31}$P nuclei and various spin-1/2 ($^1$H$^{198}$, $^{29}$Si$^{422}$) and half-integer quadrupolar ($^{11}$B$^{253,253}$, $^{27}$Al$^{1236,256}$, $^{51}$V$^{424}$) isotopes. Similar experiments have been applied to probe the proximities between $^{29}$Si isotope and $^{11}$B$^{46,2}$ and $^{17}$O$^{254}$ quadrupolar nuclei. The 2D $^{29}$Si{$^{17}$O} CP-HETCOR spectra were acquired on $^{17}$O-enriched samples. The heteronuclear correlation between spin-1/2 and quadrupolar isotopes were initially acquired using CP-HETCOR sequence$^{252,253,256}$. Nevertheless, as explained in section 3.2.2.1, the $D$-HMQC sequence for that purpose is currently preferred owing to its higher robustness (see Figure 34)$^{46,236}$. Proximities between distinct half-integer quadrupolar nuclei, $^{11}$B and $^{27}$Al, have also been observed in glasses using CP-HETCOR experiments$^{18,301}$.

![Figure 34 Comparison of (a) 2D $^{31}$P{$^{27}$Al} CP-HETCOR and (b) 2D $^{27}$Al{$^{31}$P} $D$-HMQC-SFAM-1 spectra of 50K$_2$O–10Al$_2$O$_3$–P$_2$O$_5$ glass recorded at $B_0$ = 18.8 T with $\nu_R$ = 20 kHz. Figure adapted from ref. 52. Copyright, 2018, Elsevier.](image)

5. Conclusion

We have presented here the through-bond and through-space homo- and hetero-nuclear experiments, which have been developed and applied to probe connectivities and proximities in inorganic and hybrid solids. We have notably highlighted the state-of-the-art pulse sequences for each class of experiments. We also have shown how these correlation NMR experiments provide unique information on the atomic-level structure of a wide range of materials, including microporous materials, metal oxide catalysts, minerals, biomaterials and glasses. These experiments have also been employed for other types of materials, including cements$^{425-429}$, nanomaterials$^{80,91,167,201}$ and energy materials$^{129,430-436}$.

The recent advent of ultra-high field NMR magnet with $B_0 = 28$ T or even $35.2$ T$^{437,438}$ improves the sensitivity and the resolution of solid-state NMR, notably for quadrupolar nuclei and hence, will expand the application range of correlation NMR experiments by allowing their use for insensitive isotopes (with low gyromagnetic ratio or low natural abundance) as well as for nuclei subject to large quadrupolar interaction. Further gains in sensitivity are expected from the development of cryogenic MAS probes$^{439}$ and MAS DNP$^{83,440}$, which will facilitate the acquisition of correlation experiments for isotopes of low receptivity but also for diluted species (surfaces, interfaces, defects) or limited-volume materials (thin-films or cultural heritage samples).

Furthermore, the increased availability of fast MAS probes reaching MAS frequencies of 150 kHz or above combined with high magnetic fields$^{441,442}$ is expected to promote the use of detection via protons in correlation experiments.
At the same time, correlation experiments at ultra-high fields are a challenge owing to increased electronic shielding as well as the need to develop performant double- and triple-resonance probes at such high fields. Therefore, further methodological and instrumental developments will be required to apply correlation experiments at ultra-high fields.

Acknowledgements

Chevreul Institute (FR 2638), Ministère de l’Enseignement Supérieur, de la Recherche et de l’Innovation, Hauts-de-France Region, and FEDER are acknowledged for supporting and funding partially this work. Financial support from the IR INFRANALYTICS FR2054 CNRS for conducting the research is gratefully acknowledged. This project has received funding from the European Union’s Horizon 2020 research and innovation program under the Skłodowska-Curie agreement No. 847568. OL acknowledges financial support contract ANR-18-CE08-0015-01 (ThinGlass).

References


Calculations.


(272) Bouchevereau, B.; Martineau, C.; Mellot-Draznieks, C.; Tuel, A.; Suchomel, M. R.; Trébosc, J.; Lafon, O.; Amoureux, J.; Taulelle, F. High-Resolution Structural Characterization of Two
Layered Aluminophosphates by Synchrotron Powder Diffraction and NMR Crystallographies.  

*Journal of magnetic resonance (San Diego, Calif.: 1997)* **2014**, *245*, 38–49.  
https://doi.org/10.1016/j.jmr.2014.05.006.

https://doi.org/10.1016/0009-2614(90)87174-P.

(275) Grey, C. P.; Vega, A. J. Determination of the Quadrupole Coupling Constant of the Invisible Aluminum Spins in Zeolite HY with $^1$H–$^{27}$Al TRAPDOR NMR.  

(276) Jarvis, J. A.; Haies, I. M.; Williamson, P. T. F.; Carravetta, M. An Efficient NMR Method for the Characterisation of $^{14}$N Sites through Indirect $^{13}$C Detection.  
*Physical chemistry chemical physics : PCCP* **2013**, *15* (20), 7613–7620.  
https://doi.org/10.1039/c3cp50787d.

(277) Jarvis, J. A.; Haies, I.; Lelli, M.; Rossini, A. J.; Kuprov, I.; Carravetta, M.; Williamson, P. T. F. Measurement of $^{14}$N Quadrupole Couplings in Biomolecular Solids Using Indirect-Detection $^{14}$N Solid-State NMR with DNP.  
https://doi.org/10.1039/C7CC03462H.

(278) Jarvis, J. A.; Concistre, M.; Haies, I. M.; Bounds, R. W.; Kuprov, I.; Carravetta, M.; Williamson, P. T. F. Quantitative Analysis of $^{14}$N Quadrupolar Coupling Using $^1$H Detected $^{14}$N Solid-State NMR.  
https://doi.org/10.1039/C8CP06276E.

(279) Hung, I.; Gor’kov, P.; Gan, Z. Efficient and Sideband-Free $^1$H-Detected $^{14}$N Magic-Angle Spinning NMR.  
https://doi.org/10.1063/1.5126599.

https://doi.org/10.1063/1.4753987.

https://doi.org/10.1021/jp906099k.

https://doi.org/10.1016/S0009-2614(97)00537-X.

(283) Hu, B.; Trébosc, J.; Amoureux, J.-P. Comparison of Several Hetero-Nuclear Dipolar Recoupling NMR Methods to Be Used in MAS HMQC/HSQC.  
*Journal of magnetic resonance* **2008**, *192* (1), 112–122.  
https://doi.org/10.1016/j.jmr.2008.02.004.


https://doi.org/10.1021/acsuschemeng.0c04148.

https://doi.org/10.1021/acs.jpclett.0c01236.


(352) Giovine Raynald; Volkringer Christophe; Ashbrook Sharon E.; Trébosc Julien; McKay David; Loiseau Thierry; Amourex Jean-Paul; Lafon Olivier; Pourpoint Frédérique. Solid-State NMR Spectroscopy Proves the Presence of Penta-coordinated Sc Sites in MIL-100(Sc). Chemistry – A European Journal 2017, 23 (40), 9525–9534. https://doi.org/10.1002/chem.201700584.


Glasses from Feike, M.; Jäger, C.; Spiess, H. W. Connectivities of Coordination Polyhedra in Phosphate Resonance
Jäger, C.; Feike, M.; Born, R.; Spiess, H. W. Direct Detection of Connectivities in Glasses by 2D 3093(90)90685
Journal of Non-Knight, C. T. G.; Kirkpatrick, R. J.; Oldfield, E. The Connectivity of Silicon Sites in Silicate Structure and Phase Content on the Composition of Al


Glossary

Chemical shift anisotropy (CSA): for a solid, the shielding of the static magnetic field $B_0$ depends on its orientation because of the anisotropy of the electron density around the nuclei.
Central transition (CT): transition between energy levels, $m_i = +1/2$ and $-1/2$, with $m_i$ the magnetic quantum number, of a half-integer spin quadrupolar nucleus.

Connectivity: path of covalent bonds between two nuclei.

Correlation NMR experiments: 2D NMR experiment based on coherence transfer and allowing the observation of connectivities or proximities between identical or distinct isotopes.

Cross-polarization (CP): transfer of magnetization between distinct isotopes by irradiating simultaneously the transitions of these isotopes with rf fields satisfying the Hartmann-Hahn condition.

Dipolar interaction: magnetic interaction between the magnetic dipole moment of two nuclei.

Dipolar recoupling: NMR technique, usually a sequence of rf pulses, which reintroduces the dipolar interaction under MAS conditions.

Dipolar truncation: attenuation of the coherence transfer between distant nuclei by the large interaction between nearby nuclei.

Dynamic nuclear polarization (DNP): transfer of magnetization from unpaired electrons to nuclei used to enhance the sensitivity of NMR experiments.

Magic-angle spinning (MAS): rotation of the sample at 54.736° with respect to the static magnetic field $B_0$, which averages out the anisotropic NMR interactions, such as CSA and dipolar interaction, and hence, improves the resolution and the sensitivity of NMR spectra.

Multiple-quantum magic-angle spinning (MQMAS): 2D NMR experiments, which refocuses the second-order quadrupolar broadening of half-integer spin quadrupolar nuclei by correlating their triple-quantum coherences with the single-quantum coherences of their CT.

Quadrupolar interaction: interaction between the electric quadrupole moment of a quadrupolar nucleus and the surrounding electric field gradient.

Quadrupolar nucleus: nucleus with a spin $I \geq 1$.

Rotary resonance recoupling ($R^3$): reintroduction of anisotropic NMR interaction when the nutation of the coherences is equal to an integer multiple of the MAS frequency.

Rotational resonance ($R^2$): reintroduction under MAS of the homonuclear dipolar interaction occurring when the difference in resonance frequencies between two nuclei is equal to an integer multiple of the MAS frequency.

Satellite transitions (ST): transition between energy levels, $m_i$ and $m_i +1$, of a half-integer spin quadrupolar nucleus.

Nomenclature

$\gamma$: gyromagnetic ratio.

$t_1$: indirect evolution period of a 2D NMR experiment.

$t_2$: acquisition period of a 2D NMR experiment. The FID is detected during this period.

$T_{2}^{\prime}$: time constant for the decay of transverse magnetization, which is not refocused by a 180° pulse.

$\tau_R$: rotor period.
ν₁: rf field amplitude in Hz.

νₚ: MAS frequency.

Further reading


