Application of triple-channel $^{13}C\{^1H,^{19}F\}$ NMR techniques to probe structural properties of disordered solids

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Triple-channel ^{13}C MAS NMR experiments are carried out to characterize intermolecular interactions in disordered molecular solids containing fluorinated *n*-alkanes; an approach involving a combination of $^1H \rightarrow {}^{13}C$ and $^{19}F \rightarrow {}^{13}C$ cross-polarization experiments, with both single-channel (^1H) and double-channel ($^1H,^{19}F$) decoupling is developed to assign resonances for a given type of ^{13}C nucleus in different intermolecular environments.

In molecular crystals, structural disorder often arises when the molecules are able to take up more than one orientation (not necessarily with equal energy) within the space available to them. Fundamentally, such disorder raises important issues concerning the intermolecular interactions within the crystal. Although the space- and time-averaged crystal structure, as determined by diffraction-based techniques, can generally indicate the existence of disorder, it is often unable to provide information at a sufficiently detailed level. Techniques that can be used to study local structural and/or dynamic properties of solids must then come to the fore, and in this regard solid-state NMR spectroscopy proves to be a versatile and powerful approach. As described here, the application of triple-resonance techniques[1,2] can enhance considerably the scope and potential of solid-state NMR in this field. In particular, this paper reports solid-state ^{13}C NMR studies carried out to characterize intermolecular interactions in disordered molecular solids containing organofluorine compounds. Selective cross-polarization from ^1H or ^{19}F, together with decoupling of ^1H and/or ^{19}F, have been exploited to probe the local structure around organic functional groups that are disordered between local intermolecular environments that either contain fluorine or do not contain fluorine. The approach is applied to orientational disorder of 1-fluorotetradecane [$FH_2C(CH_2)_{12}CH_3$] 'guest' the molecules within the crystalline urea tunnel structure[3] in 1-fluorotetradecane–urea inclusion compound.

Carbon-13 CP MAS spectra recorded for the 1-fluorotetradecane–urea inclusion compound are shown in Fig. 1. An initial assignment of the resonances in the $^1H \rightarrow {}^{13}C$ CP MAS spectrum [Fig. 1(*a*)], acquired using ^1H and ^{19}F double-decoupling, was made, in part, on the basis of a previous study of alkane–urea inclusion compounds.[4] There are two resonances for $\mathit{C}H_2F$ (δ 84.1, 83.9) and two for $\mathit{C}H_3$ (δ 14.7, 14.4), whereas all other ^{13}C positions within the molecule give rise to only one distinguishable resonance (note that an italic letter is used to specify the assignment of resonances). As first proposed and demonstrated by Hollingsworth *et al.*[5,6] (see also ref. 3), such chemical shift differences for the end-groups of unsymmetric guest molecules $X(CH_2)_nY$ (abbreviated to X–Y) in urea inclusion compounds can arise from the existence of the different end-group interactions X···X, X···Y and Y···Y (rather than other possible sources such as conformational disorder). On this basis, the observation of two resonances for CH_2F in 1-fluorotetradecane–urea may be attributed tentatively to the $\mathit{C}H_2F\cdots FH_2C$ and $\mathit{C}H_2F\cdots H_3C$ end-group environments and the observation of two resonances for $\mathit{C}H_3$ may be similarly assigned to the $\mathit{C}H_3\cdots H_3C$ and $\mathit{C}H_3\cdots FH_2C$ end-group environments. Previously, assignments of such resonances to the different end-group situations have been made by comparing the spectrum for the urea inclusion compound containing X–Y guest molecules with: (*a*) spectra for urea inclusion compounds containing the corresponding symmetric guest molecules X–X and/or Y–Y; and/or (*b*) spectra for urea inclusion compounds containing mixtures of the guest molecules X–Y and X–X, and/or mixtures of the guest molecules X–Y and Y–Y.

In the approach devised here, the two resonances for CH_3 carbons in the 1-fluorotetradecane–urea inclusion compound can be assigned using two complementary experiments which exploit the ^{13}C–^{19}F dipole–dipole interaction. First, we consider a $^{19}F \rightarrow {}^{13}C$ CP MAS experiment with the spectrum [see Fig. 1(*b*)] acquired using both ^1H and ^{19}F decoupling; clearly, $^{19}F \rightarrow {}^{13}C$ CP gives rise to signals only from ^{13}C nuclei that have a dipolar interaction with (and therefore proximity to) ^{19}F. Second, we discuss a $^1H \rightarrow {}^{13}C$ CP MAS experiment with the spectrum [see Fig. 1(*c*)] acquired using only ^1H decoupling; although all ^{13}C nuclei will cross-polarize from ^1H, resonances arising from ^{13}C nuclei that experience ^{13}C–^{19}F dipole–dipole interactions will be broadened significantly in this experiment (note the absence of ^{19}F decoupling). In Fig. 1(*b*), the resonance at δ 14.4 is present, whereas the resonance at δ 14.7 is absent. In Fig. 1(*c*), the resonance at δ 14.4 is broadened severely, whereas the resonance at δ 14.7 is a narrow peak. These observations imply that the resonance at δ 14.4 arises from $\mathit{C}H_3\cdots FH_2C$ end-group environments, whereas the resonance at δ 14.7 arises from $\mathit{C}H_3\cdots H_3C$ end-group environments.

Clearly, the resonances for $\mathit{C}H_2F$ cannot be assigned using the above experiments, as the ^{13}C nucleus of interest is directly bonded to ^{19}F. Instead, the classic approaches[5,6] may be used. Thus, $^1H \rightarrow {}^{13}C$ CP MAS spectra, acquired using both ^1H and ^{19}F decoupling, for the 1,10-difluorodecane–urea and 1,12-di-

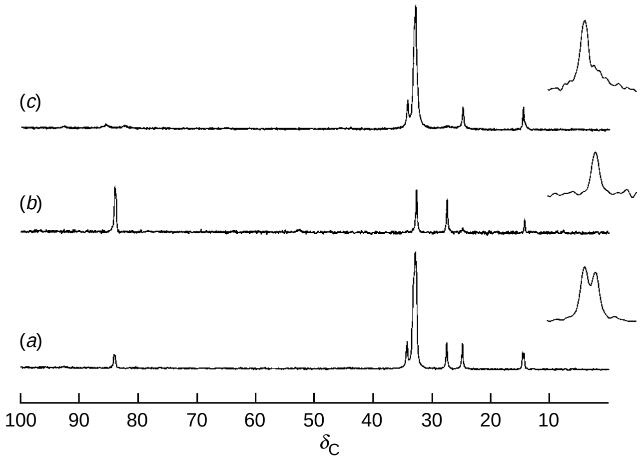

Fig. 1 Carbon-13 CP MAS spectra (guest region only) of the 1-fluorotetradecane–urea inclusion compound: (*a*) $^1H \rightarrow {}^{13}C$ cross-polarization spectrum acquired with $\{^1H,^{19}F\}$ double-decoupling; (*b*) $^{19}F \rightarrow {}^{13}C$ cross-polarization spectrum acquired with $\{^1H,^{19}F\}$ double-decoupling; (*c*) $^1H \rightarrow {}^{13}C$ cross-polarization spectrum acquired with only ^1H decoupling. In each case the inset shows the CH_3 signals on expanded scale.

Table 1 Carbon-13 chemical shifts and assignments for the 1-fluorotetradecane–urea inclusion compounds

δ_C	Assignment
14.4	$\mathit{C}H_3\cdots FH_2C$
14.7	$\mathit{C}H_3\cdots H_3C$
25.0	$\mathit{C}H_2CH_3$
27.6	$\mathit{C}H_2CH_2CH_2F$
32.8	$\mathit{C}H_2CH_2F$
33.0	'inner' $\mathit{C}H_2$
34.3	$\mathit{C}H_2CH_2CH_3$
83.9	$\mathit{C}H_2F\cdots H_3C$
84.1	$\mathit{C}H_2F\cdots FH_2C$

fluorododecane–urea inclusion compounds have single resonances due to $\mathit{C}H_2F$ at δ 84.1 for 1,10-difluorodecane–urea and at δ 84.2 for 1,12-difluorododecane–urea (in these inclusion compounds, all end-group interactions are of the type $CH_2F\cdots FH_2C$). This suggests that the resonance at δ 84.1 for 1-fluorotetradecane–urea arises from $\mathit{C}H_2F\cdots FH_2C$ end-group interactions. This assignment has been corroborated by considering the change in relative intensities of the two resonances in $^1H \rightarrow {}^{13}C$ CP MAS spectra for a urea inclusion system containing a mixture of 1-fluorotetradecane and tetradecane (for which the relative proportion of $CH_2F\cdots H_3C$ end-group environments should be higher than that in the 1-fluorotetradecane–urea inclusion compound).

All our assignments of isotropic chemical shifts for 1-fluorotetradecane in the urea tunnel structure are summarized in Table 1.

Although ^{19}F NMR has several advantages over ^{13}C NMR (including substantially greater sensitivity), it is noteworthy that we have been unable to distinguish different intermolecular environments for ^{19}F in the 1-fluorotetradecane–urea inclusion compound using ^{19}F MAS NMR (with ^1H decoupling). Presumably the ^{19}F chemical shift difference between the $CH_2\mathit{F}\cdots H_3C$ and $CH_2\mathit{F}\cdots FH_2C$ end-group environments is too small to be resolved, which in turn probably arises because ^{13}C linewidths are significantly smaller ($\Delta\nu_{\frac{1}{2}}$ *ca.* 12 Hz) than ^{19}F widths ($\Delta\nu_{\frac{1}{2}}$ *ca.* 125 Hz) for these systems.

The research described here has demonstrated that selective cross-polarization experiments in solid-state ^{13}C NMR can provide local structural information on intermolecular arrangements in disordered solids. This shows how triple-resonance solid-state NMR techniques may be exploited to extend our understanding of fundamental structural properties of solids.

Carbon-13 MAS NMR spectra were recorded on a Chemagnetics CMX200 NMR spectrometer operating at 50.33 MHz for ^{13}C, 200.13 MHz for ^1H and 188.27 MHz for ^{19}F. A Chemagnetics HFX triple-resonance probe was used, with the sample contained in zirconia rotors (7.5 mm outer diameter) fitted with boron nitride spacers and a Kel-F drive tip and end-cap. For ^{13}C CP MAS experiments, typical spectral conditions were: $\pi/2$ pulse duration, 4.5 μs; contact times, 1.0 ms ($^1H \rightarrow {}^{13}C$ CP) and 3.0–12.0 ms ($^{19}F \rightarrow {}^{13}C$ CP); spectral width, 20 kHz; recycle delay, 5–10 s; acquisition time, 102.4–153.6 ms; ^1H and ^{19}F decoupler powers, 56 kHz; MAS frequencies, 1.0–3.0 kHz. Chemical shifts were referenced externally, by rotor replacement, to the high-frequency resonance of adamantane (δ 38.4 with respect to the signal for tetramethylsilane). All urea inclusion compounds were prepared by slow cooling of solutions containing the guest molecules and urea in either methanol or a mixture of methanol and *tert*-amyl alcohol.

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Footnotes and References

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