BROADBAND HETERONUCLEAR SPIN DECOUPLING IN SOLIDS

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Experimental results demonstrate that recently introduced COMARO decoupling sequences can be used for broadband heteronuclear decoupling in solids, providing decoupling performance that is considerably less sensitive to off-resonance effects than cw decoupling and allowing good decoupling with relatively low rf power.

1. Introduction

While heteronuclear broadband decoupling by composite pulse sequences is a well established method in isotropic liquids [1–4], analogous decoupling sequences for oriented systems have been introduced only recently [5–9]. Those sequences [8,9], termed COMARO, were derived from a theoretical analysis of heteronuclear decoupling in the presence of homonuclear interactions like dipole–dipole and quadrupole interactions via computer simulations for various spin systems. The sequences consist of phase-shifted composite 90° pulses that are compensated for off-resonance effects. The sequence which was used in the experiments described in this paper is

$$\text{COMARO-2:} \quad YX\,YX\,YX \quad \bar{Y}X\,\bar{Y}X\,\bar{Y}X\,,$$

where X represents the composite pulse $385\ \overline{320}\ 25$. The predicted performance was verified experimentally in a liquid crystal sample [9]. Since the interactions between nuclear spins in a solid are basically the same as those in a liquid crystal, it is expected that the same sequences should also be applicable to solid samples. In this paper we provide experimental evidence verifying this prediction.

All experiments described here were performed on a Bruker CXP-200 spectrometer, equipped with an ASPECT-2000 computer. The experiments were designed to test the decoupling performance as a function of resonance offset and decoupling power and compare the result with spectra recorded with cw decoupling under otherwise identical conditions.

2. Offset dependence of decoupling performance in solid hexamethylbenzene

A polycrystalline sample of hexamethylbenzene was cross-polarized to enhance the carbon magnetization and the resulting signal acquired with cw or COMARO-2 decoupling. The decoupler field strength and resonance offset were the same during cross-polarization and decoupling. The experiment was repeated for different resonance offsets of the decoupler frequency. The results are shown in fig. 1. Only the methyl resonance is displayed. Clearly, cw decoupling is very sensitive to off-resonance effects. A resonance offset of the decoupler frequency of 4 kHz broadens the carbon resonance by a factor of two, leading to a corresponding reduction of the peak height. At the same decoupler offset, the COMARO-2 decoupled resonance lines are essentially unaffected. The apparent decrease in intensity of those resonances, starting at a decoupler offset of approximately 8 kHz is largely due to Hartmann–Hahn mismatch, leading to a decrease of the resulting car-

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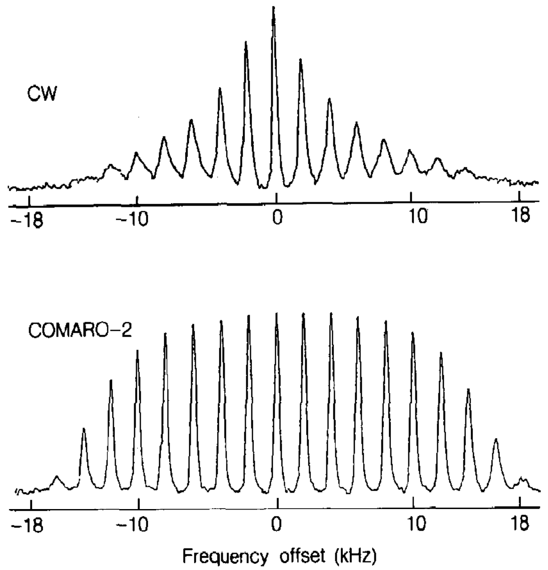

Fig. 1. The methyl resonance of the carbon spectrum of a polycrystalline sample of hexamethylbenzene is plotted as a function of decoupler offset for cw decoupling (top) and COMARO-2 composite pulse decoupling (bottom), showing the reduced sensitivity to resonance offset of the composite pulse sequence.

bon magnetization [10]. This is shown more clearly in fig. 2, where the linewidths of the carbon resonance is plotted versus decoupler offset for both COMARO-2 and cw decoupling.

An important aspect of composite pulse or multiple pulse sequences is their performance under non-

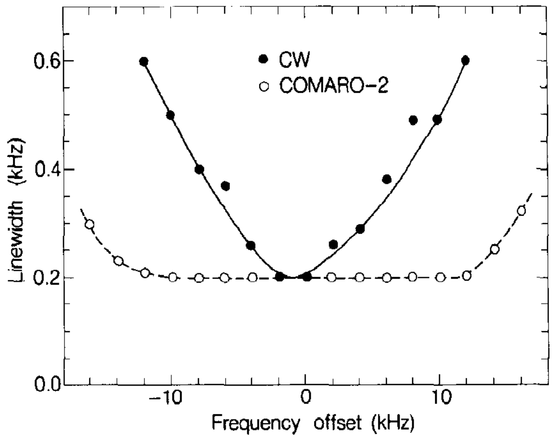

Fig. 2. Carbon linewidths of the spectra in fig. 1, plotted against resonance offset for cw decoupling (full circles) and COMARO-2 (open circles).

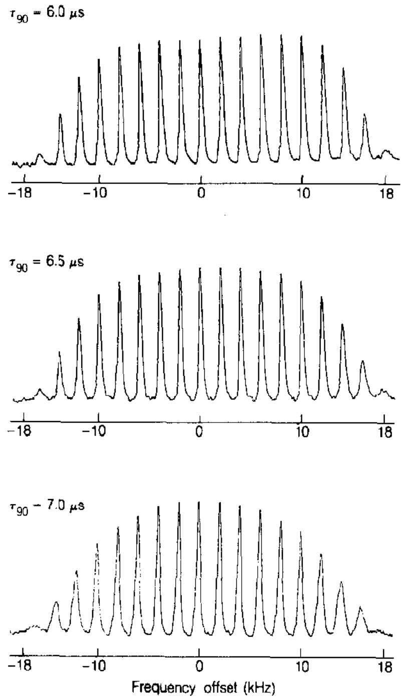

Fig. 3. Offset dependence of COMARO-2 decoupling with all pulse angles set shorter (top), equal (middle) and longer (bottom) than the nominal value of 6.5 μs.

ideal conditions. To test the performance of COMARO-2 in the presence of rf inhomogeneity or miscalibrated rf field strength, we repeated the above experiments, deliberately missetting the pulse lengths by ±15%. Fig. 3 shows the resulting offset dependence. For the spectra at the top of fig. 3, the ninety time was set to 6.0 μs, while its nominal value was 6.5 μs (middle). The spectra at the bottom of fig. 3 were recorded with a ninety time of 7 μs. Obviously, a less than nominal flip angle does not affect the decoupling performance significantly, even at this relatively large misset. A larger than nominal flip angle does affect the performance somewhat, although the result still compares favourably with the cw experiment.

3. Powder pattern lineshapes

Fig. 4 shows the powder pattern of a polycrystalline sample of the dipeptide alanylalanine (zwiter-

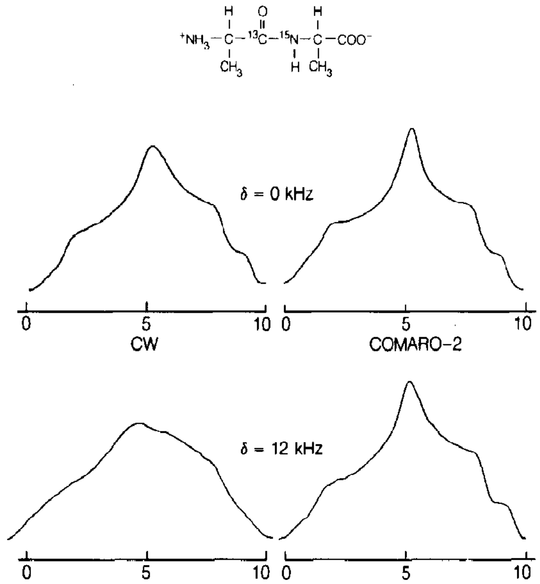

Fig. 4. Powder pattern of the carbon resonance of the doubly labeled dipeptide AlaAla, measured with cw decoupling (left) and COMARO-2 decoupling (right), with the decoupler frequency on resonance (top) and 12 kHz from resonance (bottom).

ionic), doubly labelled with ^{13}C and ^{15}N at the peptide bond [11]. The resulting tensor is due to chemical shift anisotropy and the carbon–nitrogen dipole coupling. The ^{13}C–^{15}N dipolar coupling is observed as a splitting of the σ_{11} and σ_{33} edges; σ_{22} is unsplit because it is about 60° from the peptide bond axis. If the decoupler frequency is set on resonance, both cw and COMARO-2 decoupling yield an undistorted powder pattern. At a decoupler offset of 10 kHz, cw decoupling leads to unsatisfactory decoupling, as is shown by the smearing out of the singularities. COMARO-2 on the other hand yields a practically undistorted powder line shape. The lower sensitivity with respect to decoupler frequency offsets allows one in many cases to reduce the decoupler field strength where the field strength must be kept high with cw decoupling in order to overcome off-resonance effects. This is demonstrated in fig. 5 for the same sample as fig. 4. Here, the decoupler frequency was set on resonance, while the decoupler level was lowered to a rf field strength of 21.27 kHz, corresponding to a 90° time of 11.75 μs. At this decoupler level, the powder pattern line shape is severely distorted with cw decoupling, while the COMARO-2 decoupled spectra remain well resolved.

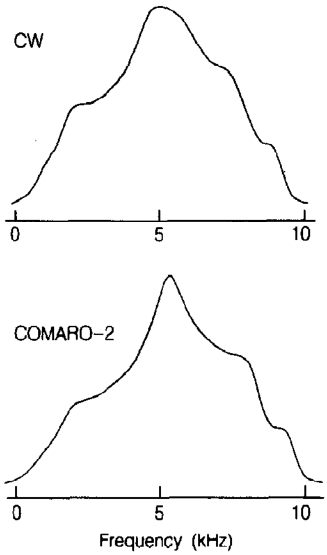

Fig. 5. Performance of cw-decoupling (top) and COMARO-2 (bottom) in AlaAla under low-power conditions. The decoupler frequency was set on resonance and the decoupler field strength was 21.27 kHz.

4. Magic angle spinning

In order to test the performance of the decoupling sequence during magic angle spinning, a sample of HMB was used. The decoupling performance was evaluated in the same way as for the static sample. As shown in fig. 6, the COMARO-2 decoupled spectra are still less sensitive to off-resonance effects than cw decoupling, but, its decoupling performance on resonance is inferior to that of cw decoupling. This is not too surprising since the rotor period of ≈500 μs is of the same order of magnitude as the period of the pulse cycle of 637 μs. The modulation of the offset and dipole–dipole couplings due to the sample rotation interferes therefore with the modulation scheme of the decoupling sequence. This interference destroys the refocusing effect of the multiple pulse sequence. In the language of coherent averaging theory, the combination of the two modulation schemes leads to an average Hamiltonian different from the one generated in a static sample. The compensation scheme of the composite pulse sequence,

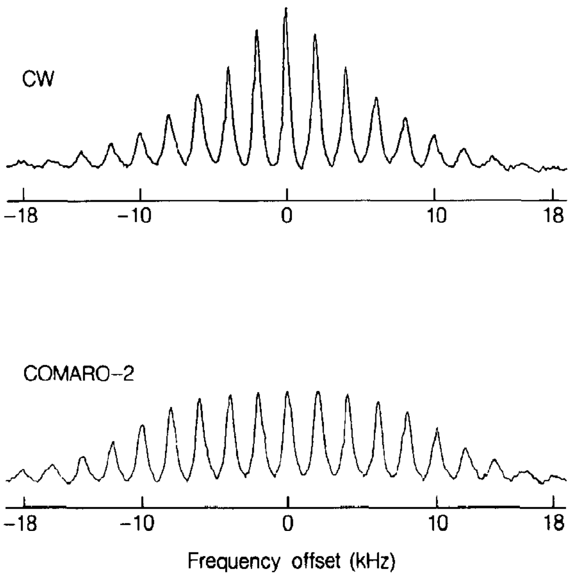

Fig. 6. Comparison of the decoupling performance of cw (top) and COMARO-2 (bottom) for a polycrystalline sample of hexamethylbenzene during magic angle spinning.

which was designed for application to static couplings can no longer refocus the different components of the magnetization. A decoupling sequence which can be used for magic angle spinning will therefore have to take the sample rotation into account.

5. Conclusions

The results presented here demonstrate that the composite pulse decoupling sequence COMARO-2 can be applied to static solids and yields a considerably less sensitive dependence of the decoupling performance on resonance offset than cw decoupling. The composite pulse decoupling sequence should be particularly usefull at high magnetic fields, where off-resonance effects become more pronounced.

Acknowledgement

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