Deuterium REDOR: Principles and Applications
for Distance Measurements

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The application of short composite pulse schemes (90°_x–90°_y–90°_x and 90°_x–180°_y–90°_x) to the rotational echo double-resonance (REDOR) spectroscopy of X–^{2}H (X: spin $\frac{1}{2}$, observed) systems with large deuterium quadrupolar interactions has been studied experimentally and theoretically and compared with simple 180° pulse schemes. The basic properties of the composite pulses on the deuterium nuclei have been elucidated, using average Hamiltonian theory, and exact simulations of the experiments have been achieved by stepwise integration of the equation of motion of the density matrix. REDOR experiments were performed on ^{15}N–^{2}H in doubly labeled acetanilide and on ^{13}C–^{2}H in singly ^{2}H-labeled acetanilide. The most efficient REDOR dephasing was observed when 90°_x–180°_y–90°_x composite pulses were used. It is found that the dephasing due to simple 180° deuterium pulses is about a factor of 2 less efficient than the dephasing due to the composite pulse sequences and thus the range of couplings observable by X–^{2}H REDOR is enlarged toward weaker couplings, i.e., larger distances. From these experiments the ^{2}H–^{15}N dipolar coupling between the amino deuteron and the amino nitrogen and the ^{2}H–^{13}C dipolar couplings between the amino deuteron and the α and β carbons have been elucidated and the corresponding distances have been determined. The distance data from REDOR are in good agreement with data from X-ray and neutron diffraction, showing the power of the method.   © 1999 Academic Press

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INTRODUCTION

In recent years solid state nuclear magnetic resonance (NMR) methods (*1–4*) have become an important tool for structure determination in solid systems, in particular when these systems exist in an amorphous or disordered phase, which cannot easily be studied by X-ray diffraction techniques. Moreover, solid state NMR has become, in conjunction with inelastic neutron scattering, the primary technique for studying proton or deuterium positions in solids, because of the well-known problem in locating hydrogen atoms of X-ray scattering. Some recent examples are the localization of protons or deuterons in H-bonded systems (*5, 6*).

There are two main interactions in NMR spectroscopy that

can be used to determine X–^{1}H or X–^{2}H distances between an $I = \frac{1}{2}$ nucleus X and a neighboring proton or deuteron, namely, the chemical shift and the nuclear magnetic dipolar interaction. The value of the chemical shift interaction is very sensitive to structural features such as the primary and secondary structure of molecules. For example, it has been shown recently that isotropic ^{15}N chemical shielding can be used to determine ^{15}N–^{1}H or ^{15}N–^{2}H distances (*7, 8*). However, there is no easy direct way to interpret the CS data in terms of nuclear distances, because calibration measurements on systems with well-known distances are needed to correlate these data to distances. Nuclear dipolar interactions, on the other hand, give direct geometrical information about intra- or intermolecular distances. Thus the study of these interactions between ^{1}H–X and ^{2}H–X is generally much more informative than CS data.

For simple systems consisting of pairwise ^{2}H–X-labeled molecules, the values of dipolar interactions can be obtained by simply recording the static NMR powder spectra and analyzing their lineshapes (*9, 10*). It is advantageous to record the X-spin spectra, because it is nearly impossible to elucidate any dipolar couplings from broad ^{2}H spectra, because of the strong quadrupolar interactions of the deuterons. In many systems the dipolar interactions are much smaller than the chemical shift anisotropy of the X spin, making it difficult to resolve the dipolar interaction in static solid state NMR spectra. This problem was already overcome in the sixties by the introduction of the spin echo double-resonance experiment (SEDOR) (*11*) technique and by separated local field experiments (*12, 13*).

When more complicated systems with several inequivalent deuterons and/or X nuclei are investigated, or when it is not possible to label only the interesting ^{2}H positions, special high-resolution solid state NMR techniques can be employed. By far the most important of these techniques is the rotational echo double-resonance (REDOR) experiment (*14, 15*), which monitors the dipolar interaction of spin pairs during magic angle spinning (MAS), often combined with proton–X cross-polarization (CP-MAS) (*16*) to enhance the X-spin signals. The dipolar REDOR dephasing of the signals is accomplished by the application of two 180° inversion pulses during each rotor period.

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