

Determination of Interatomic Distances by Zero-Quantum Correlation Spectroscopy under Rotational-Resonance Conditions

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Rotor-driven spin diffusion has become an established technique for determining internuclear distances and resolving structures in doubly labeled biomolecules (1, 2). Such techniques have also been utilized to probe intermolecular distances in polymeric blends (3). In the latter experiments, it is customary to use a single isotopically enriched site in order to eliminate the competing effects of intramolecular spin diffusion and to enhance the intermolecular exchange. Although the standard single-quantum (SQ) Zeeman exchange experiment is sufficient for identifying the presence of intermolecular spin diffusion in such polymeric systems, it is difficult to use this method to quantitatively determine distances. This arises because it is almost impossible to separate the spin-diffusion contribution to the signal from the effects of the larger population of nuclei which are not affected by Zeeman exchange and return to equilibrium by spin-lattice relaxation. In addition, to accurately determine internuclear distances from the final Zeeman exchange curve, an independent estimate of the decay time constant of the zero-quantum coherence of the two spins, T_2^{ZQ} , is necessary. The last complication in the SQ experiment arises from the use of a selective-inversion pulse or a Dante pulse train, both of which can have a significant duration relative to the rate of spin diffusion. Therefore, this makes it difficult to establish the initial stages of spin-diffusion exchange and leads to additional errors in the determination of internuclear distances.

Since spin diffusion occurs as the result of a zero-quantum (ZQ) transition, information analogous to that obtained from Zeeman exchange experiments is available from the two-dimensional ZQ correlation spectrum under rotational-resonance conditions. The latter technique is preferable because only those spins which are correlated by a zero-quantum transition are visible; hence, the main deficiencies of the Zeeman exchange experiment, as applied to singly labeled polymeric systems, can be avoided. Consequently, it is possible to determine the internuclear distance quantitatively from the ZQ correlation spectrum. In theory, the distance is derived from the cross-peak buildup measured as a function of the excitation delay, τ , in the sequence $\pi/2 - \tau/2 - \pi - \tau/2 - \pi/4 - t_1 - \alpha -$

ACQ (4). At time $\tau = \tau_{\max}$ under rotational resonance, zero-quantum cross peaks are most intense and the internuclear distance can be determined from the position of the maximum according to

$$r_{12} = \sqrt[3]{\frac{\gamma^2 \hbar \mu_0}{4\pi} b_{12}^{-1}}, \quad b_{12} = \frac{2\pi\sqrt{2}}{\tau_{\max}} \quad [1]$$

as given in Ref. (5). The intensity of the double-quantum (DQ) cross peaks also follows Eq. [1] under rotational-resonance conditions, and the similar use of DQ coherences has been demonstrated in this regard (5). The relative merit of the zero-quantum approach is that the homonuclear ZQ resonances are largely independent of magnetic field homogeneities and consist of frequency differences completely independent of the carrier. Thus, the linewidths will, in general, be less in the ZQ experiment, and the ZQ frequencies are independent of the exact choice of the spectral window (7). The dependence of the 2D DQ experiment on carrier frequency can compromise its usefulness in that the sensitivity changes with carrier frequency. The advantages of the smaller spectral window in the F_1 dimension for the ZQ case can also be significant.

We have investigated the viability of using cross-peak buildup for determining distances in $\text{Zn}(\text{}^{13}\text{CH}_3\text{}^{13}\text{COO})_2$ using the stated ZQ approach. We have modified the cited sequence to include cross polarization and have utilized a four-step phase cycle with a $\pi/4$ read-out pulse. In this way, connectivities arise at 45° angles in the $(2F_1, F_2)$ domain and provide more flexibility in the interpretation of complex systems. Figure 1 shows a typical 2D carbon-carbon zero-quantum power magnitude spectrum of solid $\text{Zn}(\text{}^{13}\text{CH}_3\text{}^{13}\text{COO})_2$ which contains residual NaAc remaining from synthesis. This spectrum was recorded on a Bruker MSL-300 spectrometer in a CP/MAS probe with $\omega_r = 12,432$ Hz ($n = 1$, rotational-resonance condition). The total number of scans was 8K with 1024 t_1 values and $\tau = 1$ ms. The horizontal axis corresponds to the F_2 dimension, and the projection through this axis results in a ZQ-filtered

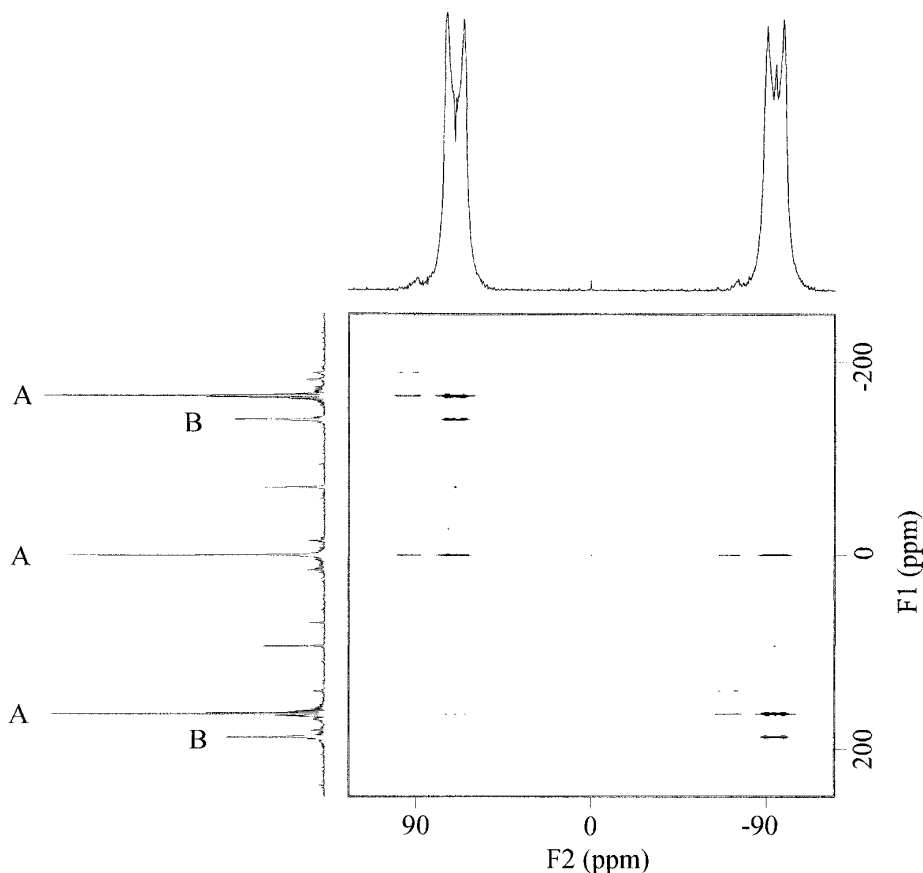


FIG. 1. Carbon-carbon zero-quantum spectrum of solid $\text{Zn}({}^{13}\text{CH}_3{}^{13}\text{COO})_2$.

single-quantum spectrum. The main peaks in this trace are due to ZnAc_2 , while the shoulders to the left of the main resonance are sidebands. The F_1 projection corresponds to the zero-quantum spectrum of the zinc/sodium acetate mixture. Resonances belonging to zinc acetate are labeled (A) along the projection and those originating from sodium acetate are labeled (B). This trace also shows artifacts due to the imperfect cancellation of the chemical shift and overexaggerated intensities due to t_1 truncation. In all, the zero-quantum linewidth is 50 Hz (T_2^{ZQ} lifetime approximately 6 ms). The zero-quantum cross peaks are connected by 45° lines through zero frequency in the 2D contour map. Couplings due to zinc acetate appear at F_1 frequencies 161 and -161 ppm, whereas residual sodium acetate appears at 190 and -140 ppm.

Furthermore, we have followed the cross-peak buildup in the zinc acetate system as a function of the excitation delay, τ , and have compared the integrated cross-peak volume to those computed with a GAMMA (6) simulation of the zero-quantum pulse sequence under rotational-resonance conditions. This is accomplished using the Hamiltonian

$$H = H^{\text{DI}} + H^{\text{CS},1} + H^{\text{CS},2} + H^{\text{RF}(\Omega, \Phi, t_p)}, \quad [2]$$

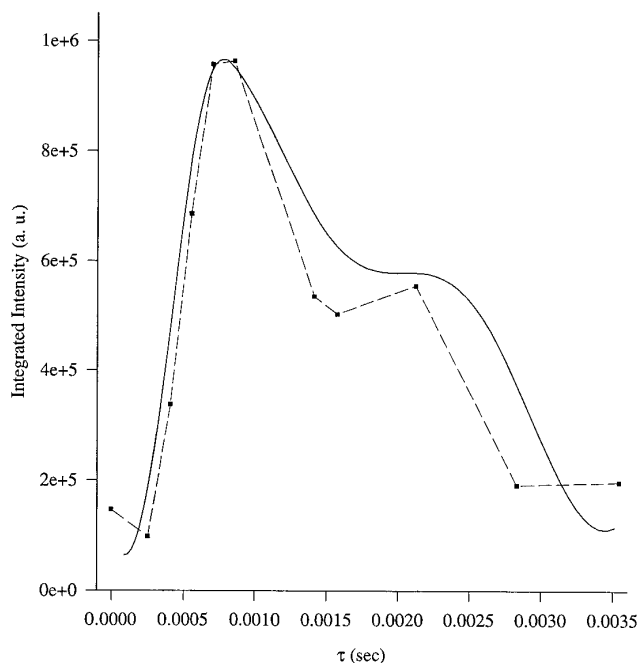


FIG. 2. Comparison of the experimental ZQ cross peak ($F_1 = -161$, $F_2 = 70$) integrated intensity in arbitrary units (\bullet) as a function of excitation delay, τ , with the results computed with the GAMMA simulation (—).

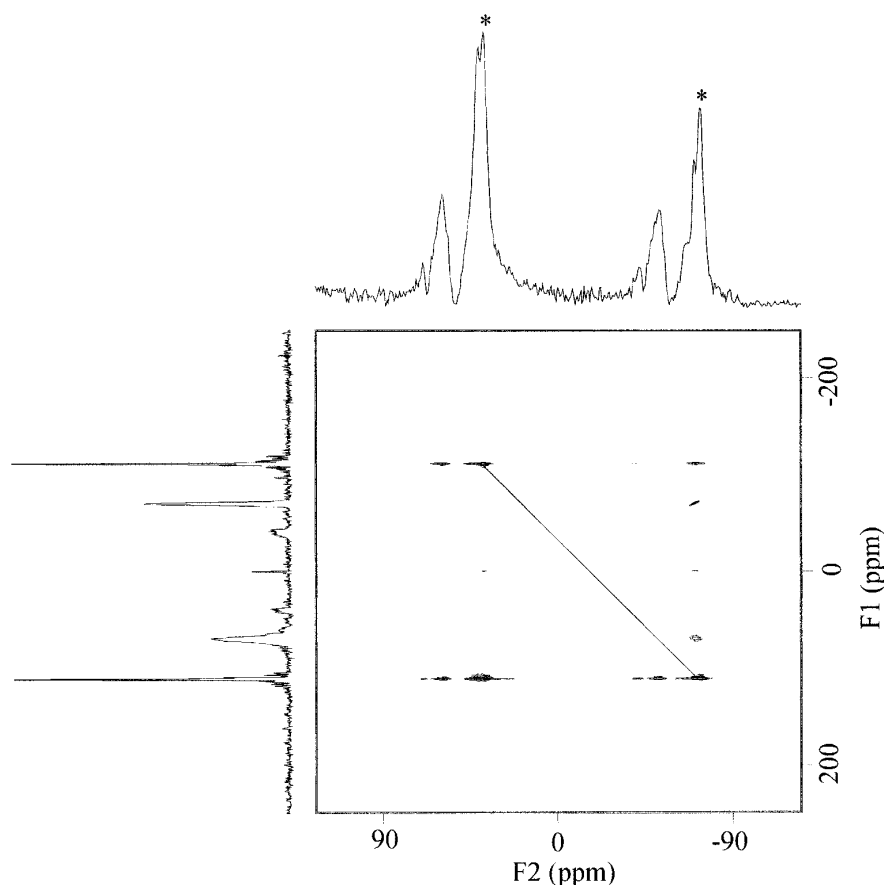


FIG. 3. Carbon-carbon zero-quantum spectrum of a solid polymer blend of ^{13}C -methyl-enriched poly(phenylene oxide) (PXE) and natural-abundance polystyrene (PS). The noted resonances (*) are the methyl carbon of PXE and the protonated aromatics of PS and PXE. These are rotor synchronized at 8405 Hz, and the ZQ coherence is shown in the 2D contour by the 45° diagonal.

where DI and CS refer to the dipolar and chemical-shift interactions and Θ , Φ , and t_p are the angle, phase, and duration of the pulses respectively in the sequence. In the current simulation, we utilize the Hamiltonian, pulse, evolution, and detection functions as provided in the GAMMA package. Furthermore, we have implemented the powder average, the t_1 incrementation, and the explicit coding of the phase cycles for this simulation as described in Ref. (6). The full details of the simulation will be presented in a subsequent publication. GAMMA version 3.5 β and gcc version 2.7.2 (libg++ version 2.7.0) were used, and calculations were performed on either an Intel Pentium 133 MHz computer running Linux 2.0 or a SPARC station IPX running SunOs 4.1.

Figure 2 shows that the two results are in good agreement. From Eq. [1] and the simulation results, the carbon-carbon bond distance was estimated to be between 1.52 and 1.62 Å, with the final determination being dependent upon the fine graining of the τ selection.

Two-dimensional ZQ correlation spectroscopy is potentially useful for determining distances in samples like compatible polymer blends, which have an inherent distance distribution. In Fig. 3, it is apparent that the ZQ coherence

between the methyl carbon (^{13}C enriched) of poly(phenylene oxide) and the natural-abundance aromatic carbons of polystyrene can indeed be observed in this manner in a compatible blend of these two polymers containing 10% poly(phenylene oxide). In this case, the intermolecular ZQ coherence is observed with rotor synchronization between the selected methyl and aromatic carbons. Selection of the methyl-aromatic intermolecular coherence over the shorter distance intramolecular coherence can be enhanced by appropriate τ selection. Again the ZQ cross peaks are connected by 45° lines in the 2D contour plot. In such systems, the determination of intermolecular distances is extremely important since it allows one to ascertain the relative spatial disposition of repeat units in two dissimilar polymer chains under conditions of total miscibility. This would assist in the identification of intermolecular interactions which lead to miscibility. To date, a full description of the intermolecular geometry remains to be developed. However, we believe that by combining zero-quantum correlation spectroscopy with rotational resonance such a description might be possible.

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REFERENCES

1. D. P. Raleigh, F. Creuzet, S. K. Das Gupta, M. H. Levitt, and R. G. Griffin, *J. Am. Chem. Soc.* **111**, 4502 (1989).
2. J. M. Griffiths, T. T. Ashburn, M. Auger, P. R. Costa, R. G. Griffin, and P. T. Lansbury, Jr., *J. Am. Chem. Soc.* **117**, 3539 (1995).
3. G. Pavlovskaya, M. Hansen, A. A. Jones, and P. T. Inglefield, *Macromolecules* **26**, 6310 (1993).
4. L. Muller, *J. Magn. Reson.* **59**, 326 (1984).
5. N. C. Nielsen, F. Creuzet, R. G. Griffin, and M. H. Levitt, *J. Chem. Phys.* **96**(8), 5668 (1992).
6. S. A. Smith, T. D. Levante, B. H. Meier, and R. R. Ernst, *J. Magn. Reson. A* **106**, 75 (1994).
7. W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.* **64**, 2229 (1976).