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COMMENTS

Comment on “Direct Determination of NMR Correlation Times from Spin−Lattice and Spin−Spin Relaxation Times”

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NMR relaxation studies provide useful information about the microdynamics of chemical systems. This information includes such properties as rotational correlation times and internuclear distances. The determination of rotational correlation times outside of the region of extreme narrowing ($\omega\tau \ll 1$) has been previously confined to low-temperature studies ($\omega\tau > 1$) where the correlation equation passes through a minimum and can be solved directly.[1,2]

In this journal, we recently reported a method that allows investigators to determine NMR rotational correlation times, τ, on the ns time scale (slightly viscous media) for dipolar nuclei including ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, and ^{113}Cd.[3,4] For dipolar nuclei, it is necessary to solve the rotational correlation time equations

TABLE 1: ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, and ^{113}Cd Coefficients for Eq 1 over the R_2/R_1 Range of 1−20

	magnetic field (T)		
coefficient	5.87	8.45	
			^{1}H
a_0	−0.376 279	−0.261 303	
a_1	0.522 971	0.363 173	
a_2	−0.046 764	−0.032 474	
a_3	0.002 382	0.001 654	
a_4	−0.000 046	−0.000 032	
			^{13}C
a_0	−1.579 786	−1.097 081	
a_1	2.634 350	1.829 418	
a_2	−0.264 513	−0.183 690	
a_3	0.014 271	0.009 911	
a_4	−0.000 284	−0.000 197	
			^{15}N
a_0	−3.933 477	−2.731 590	
a_1	6.249 786	4.340 167	
a_2	−0.624 121	−0.433 419	
a_3	0.033 541	0.433 419	
a_4	−0.000 665	0.000 462	
			^{19}F
a_0	−5.767 795	−4.005 187	
a_1	4.898 543	3.401 601	
a_2	−0.328 759	−0.228 293	
a_3	0.012 766	0.008 865	
a_4	−0.000 192	−0.000 133	
			^{31}P
a_0	−1.043 841	−0.724 892	
a_1	1.786 912	1.240 911	
a_2	−0.180 586	−0.125 407	
a_3	0.009 777	0.006 790	
a_4	−0.000 195	−0.000 135	
			^{113}Cd
a_0	−1.784 625	−1.239 313	
a_1	2.950 620	2.049 038	
a_2	−0.295 884	−0.205 473	
a_3	0.015 951	0.011 077	
a_4	−0.000 317	−0.000 220	

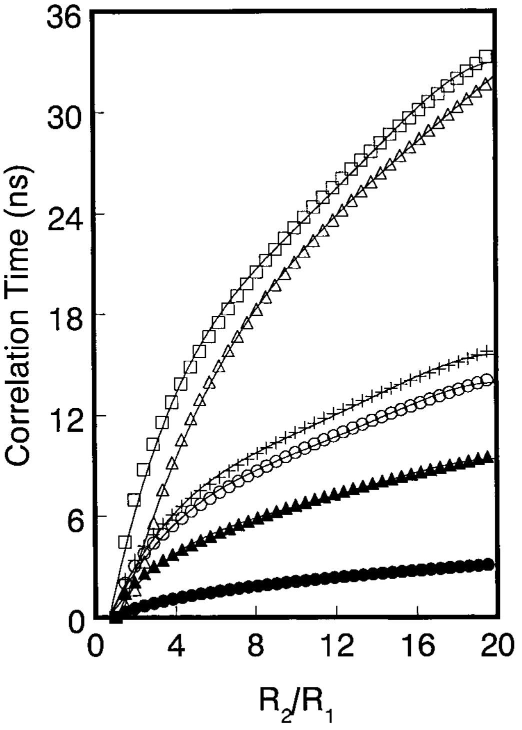

Figure 1. NMR correlation times (ns) for ^{1}H (●), ^{13}C (○), ^{15}N (□), ^{19}F (△), ^{31}P (▲) and ^{113}Cd (+) at 5.87 T (^{1}H = 250 MHz) vs R_2/R_1 from 0 to 20.

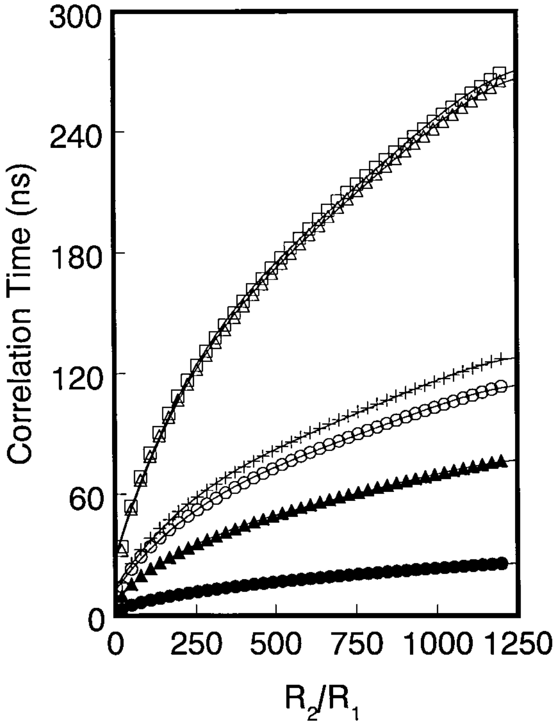

Figure 2. NMR correlation times (ns) for ^{1}H (●), ^{13}C (○), ^{15}N (□), ^{19}F (△), ^{31}P (▲) and ^{113}Cd (+) at 5.87 T (^{1}H = 250 MHz) vs R_2/R_1 from 20 to 1200.

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TABLE 2: ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, and ^{113}Cd Coefficients for Eq 1 over the R_2/R_1 Range of 20−1200

	magnetic field (T)		
coefficient	5.87	8.45	
			^{1}H
a_0	2.708 984	1.881 242	
a_1	0.049 312	0.034 244	
a_2	−0.000 068	−0.000 047	
a_3 ($\times 10^7$)	0.584 376	0.405 808	
a_4 ($\times 10^{10}$)	−0.190 593	−0.132 353	
			^{13}C
a_0	12.334 832	8.565 919	
a_1	0.218 668	0.151 852	
a_2	−0.000 301	−0.000 209	
a_3 ($\times 10^7$)	2.575 827	1.788 714	
a_4 ($\times 10^{10}$)	−0.839 361	−0.582 863	
			^{15}N
a_0	29.202 542	20.279 609	
a_1	0.518 711	0.360 225	
a_2	−0.000 713	−0.000 495	
a_3 ($\times 10^7$)	6.112 707	4.245 234	
a_4 ($\times 10^{10}$)	−1.991 979	−1.383 442	
			^{19}F
a_0	27.757 057	19.274 993	
a_1	0.516 974	0.358 993	
a_2	−0.000 717	−0.000 498	
a_3 ($\times 10^7$)	6.159 361	4.277 157	
a_4 ($\times 10^{10}$)	−2.010 468	−1.396 106	
			^{31}P
a_0	8.336 871	5.789 511	
a_1	0.147 509	0.102 437	
a_2	−0.000 203	−0.000 141	
a_3 ($\times 10^7$)	1.736 763	1.206 094	
a_4 ($\times 10^{10}$)	−0.565 895	−0.392 986	
			^{113}Cd
a_0	13.816 964	8.859 143	
a_1	0.245 046	0.176 616	
a_2	−0.000 037	−0.000 251	
a_3 ($\times 10^7$)	2.886 822	2.173 755	
a_4 ($\times 10^{10}$)	−0.940 715	−0.710 461	

at each magnetic field strength using iterative methods. The resulting solutions are fitted to pairs of polynomials ($R_2/R_1 = T_1/T_2 = 1.1{-}20$ and 20−1200) for each dipolar nucleus (^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, and ^{113}Cd) at individual magnetic field strengths. Consequently, NMR rotational correlation equations for dipolar relaxation can be solved for nuclei in moderately viscous media using R_2/R_1 ratios.[3,4] The investigator determines the R_2/R_1 ratio at a specific magnetic field and uses the appropriate polynomial (eq 1) to determine the rotational correlation time that can be used to study molecular properties and interactions.[5] The usefulness and limitations of this method are outlined elsewhere.[3,4,6]

$$\tau_c(\text{ns}) = a_o + a_1(R_2/R_1) + a_2(R_2/R_1)^2 + a_3(R_2/R_1)^3 + a_4(R_2/R_1)^4 \quad (1)$$

It has recently been brought to our attention that there are a number of NMR spectrometers operating at 5.87 and 8.45 T. This report extends our previous analysis to these magnetic field strengths (5.87 and 8.45 T). As a result of this and earlier reports, this technique is now available to a wide range of NMR spectrometers operating at field strengths between 4.7 and 14.1 T.

The intercepts and polynomial coefficients that can be used for the calculation of correlation times for R_2/R_1 ratios are given in Tables 1 and 2. Typical plots of the polynomials (cc = 0.999) that cover the two ranges of R_2/R_1 are shown in Figures 1 and 2 for ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, and ^{113}Cd relaxed by ^{1}H at 5.87 T.

References and Notes

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