

- York, 1975) mentions only Cr^{3+} photoracemization. Reference 2a notes that photoracemization accompanies photoredox processes for Co^{3+} and Rh^{3+} oxalato complexes.
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Time Development of Nuclear Overhauser Effects in Multispin Systems

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Abstract: Two methods are presented for the computation of the time development of z magnetizations in multispin systems during and following application of irradiation at the resonance frequency of one of the spins. Method A includes explicit consideration of the response of the irradiated nucleus to the irradiating field, and can be used in cases where the irradiating power is low ($\gamma H_2 \ll 1/T_1$). Method B assumes instantaneous saturation, and is appropriate when high irradiating power is used. In both cases the spin systems are assumed to consist of nuclei with distinct chemical shifts and negligible coupling constants. Sample calculations were performed on model proton systems, assuming long correlation times, typical of larger proteins or other biomacromolecules. These demonstrate that the time dependence of the nuclear Overhauser effect can be used in such systems to investigate relative internuclear distances and to probe for gaps separating islands or chains of nuclei. The use of high irradiating power is shown to be desirable.

Introduction

Steady-state NOEs have been much exploited for the establishment of spatial proximity between pairs of nuclei in complex molecules.² However, when the molecular weight becomes large enough that $\omega\tau_c \gg 1$ (for example, for all but the smallest proteins), the occurrence of spin diffusion causes the steady-state NOEs to be quite nonselective. For intermediate weight proteins, the existence of gaps separating groups of protons in the system will restore some selectivity, but little information can be obtained on spatial arrangement within the groups.⁶

In order to overcome this difficulty, one may observe the changes in intensity at short times after initiating irradiation. The macroscopic magnetization of the irradiated nuclei is then reduced more or less quickly to zero. Those nearby nuclei which cross-relax strongly with the irradiated nucleus will be excited quickly, and will be expected to show a NOE at short times. As spin diffusion occurs, nuclei more remote will also show effects. Thus the time dependence can be used to establish spatial proximity, restoring the capability lost by spin diffusion.

Wüthrich et al.^{7,8} have demonstrated the value of this approach, applying it to the assignment of proton signals in the

spectra of bovine pancreatic trypsin inhibitor and of horse heart ferricytochrome c .

The detailed calculation of the time dependences of the NOEs in a multispin system after initiation of irradiation at time $t = 0$ may be performed in several ways. We present two methods here applicable to polyspin systems where $\delta > J$ for all interacting spins; in the first, an explicit calculation of the effect of the irradiating field on the irradiated nucleus is included, so that cases where γH_2 is comparable to or less than the cross-relaxation rate may be analyzed. The second method is applicable to the situation where a strong irradiating field is used so that saturation is, in effect, instantaneous. A simpler analysis is then possible. In the limit of strong irradiating fields the two methods lead to identical results.

Methods of Calculation

Method A. In this case the approach starts with the density matrix equations,⁹ using the normal (or magnetization) mode coordinates of Werbelow and Grant,¹⁰ giving

$$d\nu_i/dt + \sum_j \Gamma_{ij}\nu_j = -\omega_2 V_i \quad (1)$$

Here $\nu_i = M_z^i - M_0^i$ is the z magnetization of one of the spins, and V_i is the sum over all of the transitions of spin i of the " V -mode" elements v_{kl} . In this paper we ignore the normal mode elements which do not correspond to z magnetiza-

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tions—this amounts to an independent relaxation model in which cross-correlation is neglected.

The derivation of a single equation for V_i requires that either (1) all transitions of spin i have the same frequency (scalar coupling constant $J = 0$) or (2) if the resonance is irradiated by an rf field H_2 , the power is large enough to decouple, $\gamma H_2 > 2\pi J$. We will also assume that only one spin is irradiated on resonance (the right-hand side of eq 1 is zero for all but that spin) and that that resonance is isolated—not overlapping with another—and the power is less than the chemical shift to the nearest resonance. Thus

$$dV_i/dt + R_2 V_i = \omega_2 M_{z_i} \quad (2)$$

with $R_2 = 1/T_2$ of that resonance and $\omega_2 = \gamma H_2$.

Equations 1 and 2 are most conveniently solved using Laplace transforms.¹¹ This gives for the irradiated spin (called α)

$$[(s + \rho_\alpha)(s + R_2) + \omega_2^2](M_z^\alpha - M_0) + (R_2 + s) \sum_{j \neq \alpha} \sigma_{\alpha j} (M_z^j - M_0) = \omega_2^2 M_0/s \quad (3)$$

and for the spins not irradiated

$$(s + \rho_i)(M_z^i - M_0) + \sum_{j \neq i} \sigma_{ij} (M_z^j - M_0) = 0 \quad (i \neq \alpha) \quad (4)$$

where $M_z = M_z(s)$ is the Laplace transform of $M_z(t)$ and s is the Laplace variable; ρ_i is the diagonal element of Γ and is the sum of all ρ_{ij} to that spin (see below). The σ_{ij} are the off-diagonal elements of Γ .

These equations can be written compactly as

$$\sum_j B_{ij}(s)[M_z^i(s) - M_0] = -\frac{1}{s} \omega_2^2 M_0 \delta_{\alpha i} \quad (5)$$

The characteristics of the B matrix are shown in Table I.

The relaxation elements of Table I are given by

$$R_2 = \sum_j \frac{\gamma^4 \hbar^2}{r_{j\alpha}^6} [0.25f(0) + 0.45f(\omega_0) + 0.3f(2\omega_0)] \quad (6)$$

$$\rho_i = \sum_j \frac{\gamma^4 \hbar^2}{r_{ij}^6} [0.1f(0) + 0.3f(\omega_0) + 0.6f(2\omega_0)] \quad (7)$$

$$\sigma_{ij} = \frac{\gamma^4 \hbar^2}{r_{ij}^6} [0.6f(2\omega_0) - 0.1f(0)] \quad (8)$$

where

$$f(\omega) = \tau_c / (1 + \omega^2 \tau_c^2) \quad (9)$$

r_{ij} is the distance between spins i and j , γ is the gyromagnetic ratio, ω_0 is the Larmor frequency of the spins, \hbar is Planck's constant divided by 2π , and τ_c is the rotational correlation time.

Formally, a solution to eq 5 can be written:

$$M_z^j(s) - M_0 = -\frac{1}{s} \omega_2^2 M_0 \frac{B^{\alpha j}}{|\mathbf{B}|} = -\frac{1}{s} \omega_2^2 M_0 \frac{P_j(s)}{Q(s)} \quad (10)$$

For N spins, $Q(s)$ is a polynomial of degree $N + 1$ representing $|\mathbf{B}|$. This was specified by calculating $|\mathbf{B}|$ for $N + 1$ values of s (chosen in our case so $R_2 < s < -R_2$) and then calculating the polynomial coefficients by the Vandermonde determinant method.¹² $P_j(s)$ is likewise a polynomial (of degree $N - 1$ or less) representing the cofactors $B^{\alpha j}$.

Now, taking the inverse Laplace transform of eq 10, we get the solution for the nuclear Overhauser effect (NOE) η_j of spin j :

$$\eta_j = (M_z^j - M_0)/M_0 \quad (11)$$

$$\eta_j = -\omega_2^2 \sum_k a_k^j \alpha_k (\exp(\alpha_k t) - 1) \quad (12)$$

Table I. The Laplace Matrix B

	saturated spin	spin not saturated
diagonal	$(R_2 + s)(\rho_i + s) + \omega_2^2$	$\rho_i + s$
off-diagonal	$(R_2 + s)\sigma_{ij}$	σ_{ij}

where the α_k are the $N + 1$ roots of $Q(s)$. If the roots of $Q(s)$ are not repeated (which they could be if the center spin of a symmetrical array were irradiated), the coefficients are given by

$$a_k^j = P_j(\alpha_k)/Q'(\alpha_k) \quad (13)$$

where Q' is the derivative of $Q(s)$.

One could reasonably expect that the roots of $Q(s)$ would either be real or occur in conjugate pairs. In fact, for N spins, $N - 1$ roots are real and negative and two are complex conjugates of each other (except at very small power H_2 when all are pure real). Hence we define

$$\alpha_k = X_k + iY_k \quad (14)$$

$$A_k^j = \omega_2^2 \operatorname{Re}(a_k^j \alpha_k) \quad (15)$$

$$B_k^j = \omega_2^2 \operatorname{Im}(a_k^j \alpha_k) \quad (16)$$

and

$$\eta_j = \sum_{k=1}^{N+1} \{A_k^j [1 - \cos(Y_k t) \exp(X_k t)] + B_k^j \sin(Y_k t) \exp(X_k t)\} \quad (17)$$

The steady-state NOE is obviously

$$\eta_j^\infty = \sum_{k=1}^{N+1} A_k^j \quad (18)$$

For up to eight spins, these computations can be done rapidly and efficiently on a computer. However, numerical problems arose with eight spins, especially at $\tau_c \gtrsim 10^{-8}$; these apparently involved overflow and loss of accuracy in evaluating the Vandermonde determinant. These problems were minimized by scaling the problem by R_2 . Then the polynomials were evaluated for $1 < s < -1$ and the real parts of roots were generally between 0 and about -2 . Even so, a DEC10 computer with a 36-bit word was barely accurate enough in single precision to solve the eight-spin problem. A B7700 computer with a larger word size was used in the computations of this paper.

Method B. As mentioned previously, two of the roots of $Q(s)$ are complex. At high powers, the imaginary parts of these roots approach $\pm\omega_2$. These oscillations never significantly affect any spin but the one irradiated; in the high-power limit (HPL) they dominate that one. Calculations show for the irradiated spin in the HPL

$$\eta_\alpha = \cos(\omega_2 t) e^{-R't} - 1 \quad (19)$$

with

$$R' = (R_2 + \rho_\alpha)/2 \quad (20)$$

Since the nonirradiated spins do not oscillate, it is permissible to neglect the oscillating term of eq 19 and solve eq 21 ($i \neq \alpha$):

$$\frac{dM_z^i}{dt} + \sum_{j \neq \alpha} \Gamma_{ij} (M_z^j - M_0) = \sigma_{i\alpha} M_0 \quad (21)$$

Defining the Γ' matrix as the relaxation matrix Γ excluding the irradiated spin, we get for the HPL

$$\eta_i(t) = \sum_k (\eta_k(0) - \eta_k(\infty)) \sum_j U_{ij}^{-1} U_{jk} \times \exp(-\lambda_j t) + \eta_i(\infty) \quad (22)$$

Table II. Half-Lives (τ) and Steady-State NOEs $\eta(\infty)$ for Six Spins—Uniform Chain of Protons at 360 MHz

$\tau_c = 1 \times 10^{-8}$, $r_{ij} = 2 \text{ \AA}$, $\omega_0\tau_c = 22.6$, $R_2 = 22.34$, $\sigma_{ij} = -8.87$, and $\rho_{ij} = 8.98$		$\tau_c = 5 \times 10^{-8}$, $r_{ij} = 2 \text{ \AA}$, $\omega_0\tau_c = 113.1$, $R_2 = 111.3$, $\sigma_{ij} = -44.49$, and $\rho_{ij} = 44.57$		
ν_2 (Hz) =	0.5	2	10	20
SATF =	0.05	0.8	20	79
spin	τ , s	η^∞	τ , s	η^∞
1	1.9 ^a	-0.335	<i>a</i>	-0.889
2	2.4	-0.305	0.4	-0.812
3	2.9	-0.283	0.8	-0.753
4	3.2	-0.268	1.2	-0.712
5	3.4	-0.259	1.4	-0.688
6	3.5	-0.256	1.5	-0.680

$\tau_c = 5 \times 10^{-8}$, $r_{ij} = 2 \text{ \AA}$, $\omega_0\tau_c = 113.1$, $R_2 = 111.3$, $\sigma_{ij} = -44.49$, and $\rho_{ij} = 44.57$		$\tau_c = 1 \times 10^{-8}$, $r_{ij} = 2 \text{ \AA}$, $\omega_0\tau_c = 22.6$, $R_2 = 22.34$, $\sigma_{ij} = -8.87$, and $\rho_{ij} = 8.98$		
ν_2 (Hz) =	1	10	20	100
SATF =	0.01	0.8	3.2	80
spin	τ , s	η^∞	τ , s	η^∞
1	7.2 ^a	-0.631	0.4 ^a	-0.994
2	7.4	-0.629	0.12	-0.990
3	7.5	-0.627	0.23	-0.987
4	7.5	-0.625	0.31	-0.984
5	7.5	-0.624	0.36	-0.983
6	7.6	-0.624	0.38	-0.983

^a Since the amplitude of the saturated spin oscillates, particularly at high power, it is not always possible to define a half-life.

Table III. Half-Lives and NOEs for Six Spins, 4/5 Broken Chain of Protons at 360 MHz, $r_{ij} = 2 \text{ \AA}$ Except $r_{45} = 3 \text{ \AA}$ ^a

τ_c (s) =	1×10^{-8}		5×10^{-8}		5×10^{-8}		5×10^{-8}	
ν_2 (Hz) =	20		1		20		100	
spin	τ , s	η^∞	τ , s	η^∞	τ , s	η^∞	τ , s	η^∞
1		-0.999	7.7	-0.677		-0.999		-1.000
2	0.11	-0.929	7.8	-0.675	0.04	-0.995	0.03	-0.997
3	0.38	-0.881	7.9	-0.673	0.10	-0.993	0.08	-0.994
4	0.50	-0.854	7.9	-0.672	0.14	-0.992	0.11	-0.993
5	2.23	-0.668	8.5	-0.665	0.61	-0.981	0.57	-0.982
6	2.34	-0.661	8.5	-0.664	0.63	-0.980	0.60	-0.981

^a Relaxation parameters for this case are the same as given in Table I except where the 4-5 interaction is concerned; σ_{45} and ρ_{45} are reduced by a factor of $(\frac{1}{2})^6 = 11.4$.

where U is a unitary matrix which diagonalizes Γ' , γ_j are the eigenvalue of Γ' , and the steady-state Overhauser effects, $\eta_i(\infty)$, are obtained from

$$\eta_i(\infty) = \sum_j (\Gamma')_{ij}^{-1} \sigma_{j\alpha} \quad (23)$$

This method can be applied to large systems, limited only by the computer's capability to diagonalize and invert large real symmetric matrices. A program for systems up to 20 spins has been written, and allows calculation of the time development of the Overhauser effects with high-power irradiation switched on or off on an arbitrary schedule or with the system prepared in an arbitrary state (for example, by inversion of one set of spins).

It will often be the case experimentally that the H_2 power applied will not be uniform across the sample, so that the nutation rate will be nonuniform and the magnetization in the rotating frame will quickly lose coherence. This will have the effect of suppressing the observable oscillations in the z magnetization of the irradiated nucleus, causing the behavior to approach more closely the HPL case.

Results

Sample computations were done for a chain of protons, including relaxation coupling to nearest neighbors only. All spins were assumed to have distinct Larmor frequencies. Since the buildup of the NOE is a sum of exponentials, it is difficult to characterize the growth in a simple manner. We choose to use the half-life (τ) at which the NOE reaches $\frac{1}{2}$ its steady-state value.

Table II shows the results of calculations for a uniform six-spin chain of protons at 360 MHz with a spacing of 2 Å and various powers (H_2). (In the table $\nu_2 = \gamma H_2/2\pi$ is the power in units of Hertz.) The correlation time 1×10^{-8} is barely in the spin-diffusion limit. The second calculation for $\tau_c = 5 \times 10^{-8}$ s is well within the spin-diffusion limit. In this table, SATF = $\gamma^2 H_2^2 / R_2 \rho \alpha$ is an attempt to approximate a saturation factor for the rf field at spin α . It is not entirely successful at long correlation times as can be seen.

Several important conclusions come from these calculations. At low powers, all spins (including the one irradiated) relax rather slowly and all at nearly the same rate. At higher power, sufficient to saturate the irradiated spin, the growth of the NOE depends very sensitively on the position in the chain of the observed spin relative to the irradiated spin. Indeed, the "contrast" grows with increasing power to a limit. Powers higher than those shown in Table II do not give significantly different results than those shown. It seems evident that the optimum power is the highest practical. (Other factors not included here such as indirect saturation of nearby resonances place a practical upper limit on the power level.)

Table III shows the result of calculations on a system of six spins in a chain with a "gap" introduced between protons 4 and 5. It is interesting that, even though the steady-state effects could not be used experimentally to reveal the gap, it is demonstrated very clearly in the sudden increase in half-life between the effects for protons 4 and 5 at the higher powers.

The calculations shown in Table IV are designed to show that the rate of growth of the NOE depends on the absolute distance to the saturated spin as well as on the relative position

Table IV. Time-Dependent NOEs—Broken Chain of Seven Protons^a

$r_{34} =$ saturate spin	3 Å 4		3 Å 3		4 Å 4		4 Å 3	
	τ, s	η^∞	τ, s	η^∞	τ, s	η^∞	τ, s	η^∞
1	0.59	-0.977	0.05	-0.998	2.72	-0.891	0.05	-0.998
2	0.58	-0.977	0.03	-0.998	2.70	-0.891	0.03	-0.998
3	0.56	-0.978	saturate	-1.000	2.69	-0.891	saturate	-1.000
4	saturate	-1.000	0.66	-0.968	saturate	-1.000	3.34	-0.847
5	0.03	-0.997	0.73	-0.966	0.03	-0.997	3.40	-0.845
6	0.08	-0.996	0.78	-0.965	0.08	-0.996	3.46	-0.844
7	0.11	-0.996	0.80	-0.964	0.105	-0.996	3.48	-0.844

^a For all $\nu_2 = 50$ Hz, $\tau_c = 5 \times 10^{-8}$ s, $\omega_0\tau_c = 113$, and $r_{ij} = 2$ Å except r_{34} , which is indicated.

in the chain. These calculations are for a seven-proton chain with a large distance between spins 3 and 4; either spin 3 or 4 is saturated. The increase in the half-lives as r_{34} is increased goes roughly as r_{34}^6 . For example, comparing the 4-Å calculation to the 3-Å calculation of the half-life of spin 3 when 4 is saturated gives $(3.34/0.66)^{1/6} = 1.31$ and for spin 4 when spin 3 is saturated $(2.69/0.56)^{1/6} = 1.30$.

Of the approximations made in this paper, the most serious is certainly our neglect of the indirect effect of the rf field on the other, off-resonance, spins. This effect is twofold: (1) the steady-state partial saturation of an off-resonance spin and (2) transient effects, commonly called Torrey¹³ oscillations. We are currently working on this problem. Extension of the theory to groups of equivalent spins will face complications inherent in degenerate spin systems detailed by ref 10. Reference 14 shows the difficulties which will be encountered if the theory is extended to include J coupling.

Listings of the computer programs are available from the authors on request.

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Optical Rotatory Dispersion Studies. 127.¹ Chirality Due to ¹³C Substitution. Synthesis and Chiroptical Properties of (1S)-2-Adamantanone-4-¹³C and (1S)-2,4-Adamantanedione-4-¹³C

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Abstract: The synthesis and circular dichroism spectra of (1S)-2-adamantanone-4-¹³C (**11**) and (1S)-2,4-adamantanedione-4-¹³C (**12**) are reported, two compounds which owe their chirality solely to ¹³C substitution. The monoketone **11** exhibits a negative Cotton effect, indicating that ¹³C makes a smaller octant contribution than ¹²C, while the diketone **12** shows three circular dichroism bands of remarkably large amplitude. Since no intensity changes were observed at 77 K it was concluded that the multiple band pattern does not reflect a dissymmetric solvation equilibrium but that each band corresponds to a different $n \rightarrow \pi^*$ transition.

Introduction

The recently recorded³ syntheses and detection of significant Cotton effects of deuterium-substituted cycloalkanones, whose chirality is solely due to the deuterium atom, have stimulated interest in theoretical work⁴ and proved to be of utility in

solving some subtle conformational problems.⁵ This encouraged us to undertake similar studies on cyclohexanones which owe their chirality only to replacement of one carbon by ¹³C. That such minor isotopic perturbations produce easily measurable Cotton effects⁶ was recently demonstrated¹ by the