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Monte Carlo simulation of NMR lineshapes in chemically exchanging spin systems

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Nomenclature*General*

i	complex unit, $\sqrt{-1}$
m	number of conformers
n	number of nuclei in the spin set
M	number of single quantum coherences of a spin system of n nuclei, $\frac{(2n)!}{(n-1)!(n+1)!}$
N	total number of nuclei, approximately $N = n \cdot m$ for a non-mutual exchange
n'	number of product functions for a spin set of n spin- $1/2$ nuclei, $n' = 2^n$
t	time elapsed since the start of detection
μ, μ'	indices of nuclei of a spin set
ν_μ	chemical shift of the μ th nucleus (in Hz)
$J_{\mu\mu'}$	coupling constant between nuclei μ and μ' (in Hz)
$fid(t)$	fid of a time slice at time t , as a complex number
$FID(t)$	fid of one set of spins at time t
$F(t)$	total simulated fid at time t

Indices

a, b, c, d	indices of the basis functions of the Hilbert space. Their values are between 1 and 2^n
k, l	indices of the eigenfunctions of the Hamiltonian. Their values are between 1 and 2^n
e, f	indices of the basis functions of the space spanned by the single quantum coherences. Their values are between 1 and M . As hyperindices, $e = (a, b)$ and $f = (c, d)$ (there are forbidden variations as well)
p, q	indices of the eigenfunctions of the space spanned by the single quantum coherences. Their values are between 1 and M . As hyperindex $p = (k, l)$
j, h	indices of conformers. Their values are between 1 and m
r	index of time slices and exchange points. The r th time slice starts at the $(r - 1)$ th exchange point and last until the r th. The 0th exchange point is the start of detection
s	index of scans

Kinetics

$A^{(j)}$	the j th conformer of the spin set
$[A^{(j)}]$	concentration of $A^{(j)}$
$t^{(r)}$	global time at the r th exchange point
Δt	the time elapsed since the last exchange, $\Delta t = t - t^{(r-1)}$
$\Delta t^{(r)}$	length of the r th time slice, $\Delta t^{(r)} = t^{(r)} - t^{(r-1)}$
k_{hj}	rate coefficient for the reaction $A^{(h)} \rightarrow A^{(j)}$
d_j	decay coefficient of the $A^{(j)}$ conformer
K_j	relative equilibrium concentration of $A^{(j)}$ conformer
κ_{jh}	the probability of the formation of $A^{(h)}$ conformer during decomposition of $A^{(j)}$

Hilbert space

$H^{(r)}$	Hamiltonian in the r th time slice (conformer dependent)
φ_a	product functions of the Hilbert space ($\alpha\alpha\dots\alpha, \beta\alpha\dots\alpha, \dots, \beta\beta\dots\beta$)
$\psi_k^{(j)}, \psi_k^{(r)}$	k th eigenfunction of the Hamiltonian of the j th conformer at r th time slice
$\rho(t)$	density matrix in the Hilbert space at time t (in the basis of φ functions)
ρ_{ab}	(a, b) element of the density matrix in the basis of the φ functions
λ_k	k th eigenvalue of the Hamiltonian in Hilbert space
$u_{ak}^{(r)}$	linear combination coefficient of φ_a in $\psi_k^{(r)}, \langle \psi_k^{(r)} \varphi_a \rangle$
$U^{(r)}$	unitary matrix of the $u_{ak}^{(r)}$ linear combination coefficients
$a_{kl}^{(r)}$	amplitude of the $\psi_k^{(r)} \rightarrow \psi_l^{(r)}$ transition
$A^{(r)}$	matrix of the $a_{kl}^{(r)}$ amplitudes

Liouville space

$L^{(r)}$	the equivalent of the $H^{(r)}$ Hamiltonian in Liouville space
$P^{(r)}(\Delta t)$	the operator that propagates the density matrix by time Δt
Φ_e	the basis functions of the space spanned by the single quantum coherences of Liouville space, the $\varphi_a \rightarrow \varphi_b$ transitions or coherences
$\Psi_p^{(j)}, \Psi_p^{(r)}$	eigenfunctions of the j th conformer or r th time slice
$\sigma(t)$	the vector of the density matrix in Liouville space (time dependent) in the basis of the Φ_e vectors
$\sigma^{(r)}$	the vector of the density matrix at the r th exchange point, abbreviation for $\sigma(t^{(r)})$
$\sigma_e(t)$	the e th element of $\sigma(t)$ vector, the coefficient of Φ_e in $\sigma(t)$
$\sigma_e^{(r)}$	abbreviation of $\sigma_e(t^{(r)})$
$\xi^{(r)}(t)$	the vector of the density matrix in Liouville space (time dependent) in the basis of the $\Psi_p^{(r)}$ vectors
$\xi_p^{(r)}(t)$	p th element of the $\xi^{(r)}(t)$ vector
$\omega_p^{(r)}$	p th characteristic frequency in the r th time slice
$\Omega^{(r)}$	diagonal matrix of the $\omega_p^{(r)}$ frequencies
$a_p^{(r)}$	the amplitude of the p th eigentransition in the r th time slice
$A^{(r)}$	row matrix of the $a_p^{(r)}$ amplitudes
I^+	row matrix of the I^+ operator in the basis of the Φ_e coherences
$c_{ep}^{(r)}$	linear combination coefficient of Φ_a in $\Psi_p^{(r)}, \langle \Psi_p^{(r)} \Phi_e \rangle$
$C^{(r)}$	unitary matrix of the $c_{ep}^{(r)}$ linear combination coefficients

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1. Introduction

One often meets with dynamic processes while dealing with experimental NMR spectroscopy [1–7]. Dynamic exchange may appear as the migration of acidic protons in a protic solution or as the

classical line broadening and coalescence phenomenon. The most common way for studying the exchange process of complicated spin systems is by simulation of the line broadening. This method is used in several fields of chemistry, e.g. in studying the stability and isomerization reactions of transition-metal and supramolecular

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