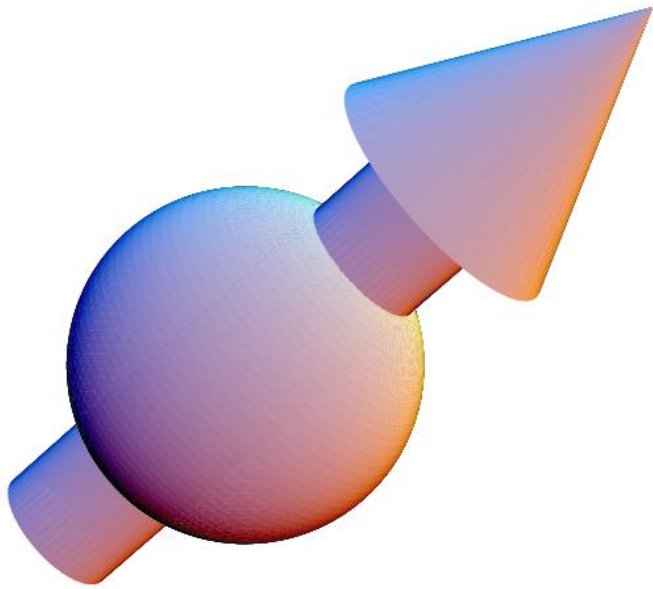


Spin Echoes

in Nuclear Magnetic Resonance Spectroscopy



Seoncheol cha
21.June.2014

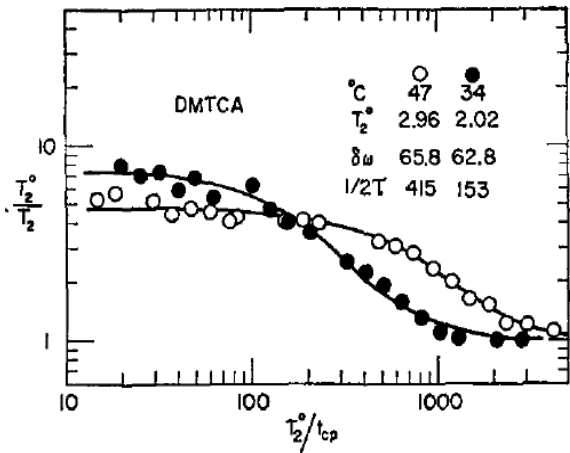
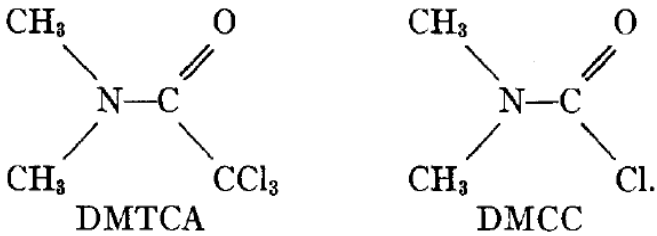
Sogang University
Soft Matter Optical Spectroscopy

Spin-Echo NMR Studies of Chemical Exchange. I. Some General Aspects*

ADAM ALLERHAND AND H. S. GUTOWSKY

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(Received 14 May 1964)



DMTCA			DMCC	
Method	E_a kcal	$\log \nu_0$	E_a kcal	$\log \nu_0$
Spin echo	14.6 ± 0.6	12.5 ± 0.4	14.0 ± 0.9	10.9 ± 0.6
Peak separation ^b	10.3 ± 1.7 (9.1 ± 1.0)	9.6 ± 1.3 (8.5 ± 0.8)	8.6 ± 1.7	6.9 ± 1.2
Intensity ratio ^b	12.6 ± 1.2 (13.6 ± 1.2)	11.0 ± 0.9 (11.8 ± 1.0)	9.7 ± 0.5	7.7 ± 0.4
Line narrowing ^b	14.1 ± 0.5 (15.8 ± 0.5)	12.0 ± 0.3 (13.5 ± 0.3)		
Intensity ratio ^c	9.9 ± 0.3	9.1 ± 0.2	7.3 ± 0.5	6.1 ± 0.3

Purpose – measuring chemical exchange phenomenon



Spin echoes

EL Hahn - Physical review, 1950 - APS

Intense radiofrequency power in the form of pulses is applied to an ensemble of spins in a liquid placed in a large static magnetic field H_0 . The frequency of the pulsed rf power satisfies the condition for nuclear magnetic resonance, and the pulses last for times which ...

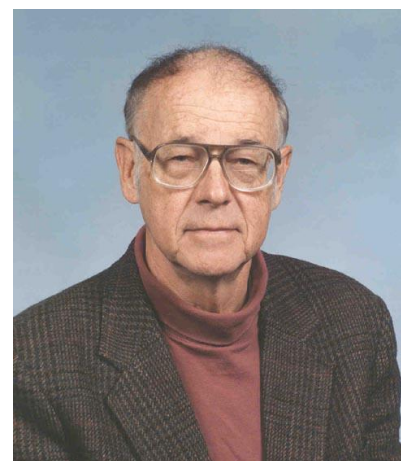
4632회 인용 관련 학술자료 전체 10개의 버전 인용 저장

Effects of diffusion on free precession in nuclear magnetic resonance experiments

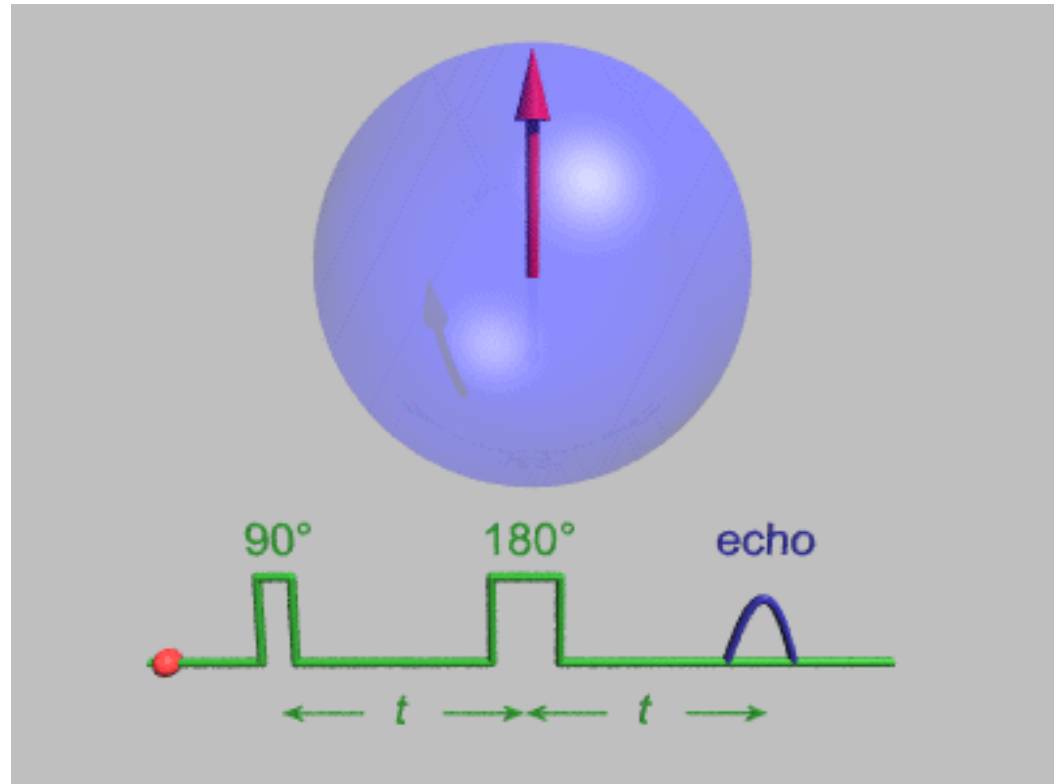
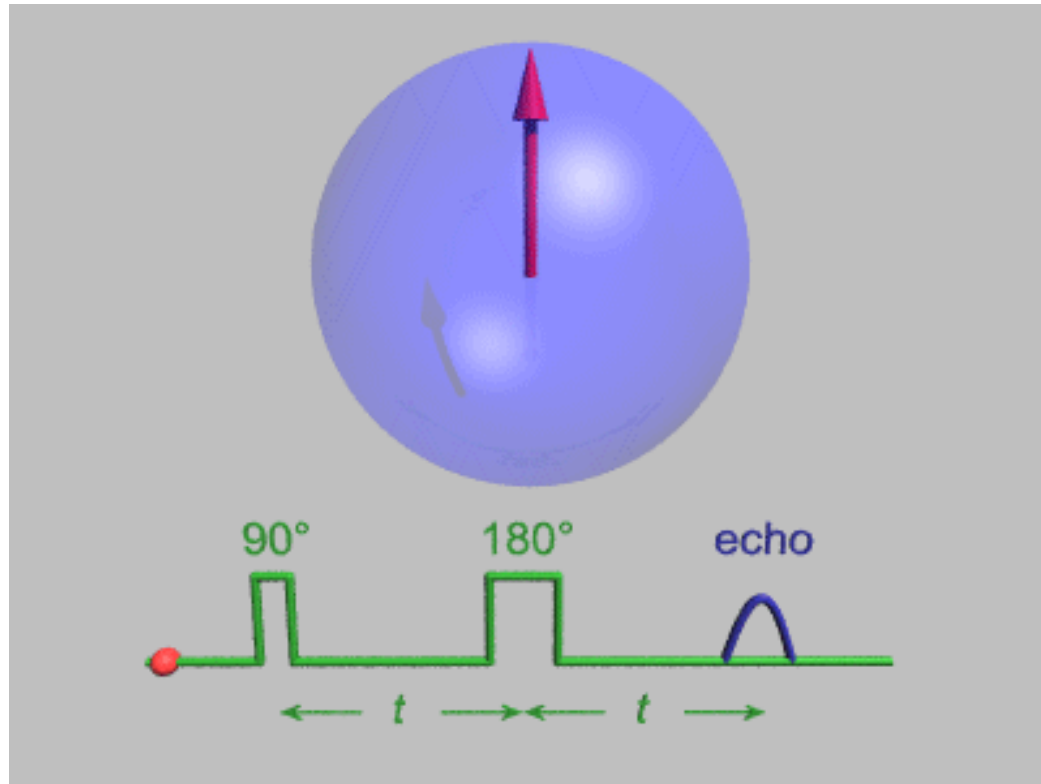
HY Carr, EM Purcell - Physical Review, 1954 - APS

... Page 3. H. Y. **CARR** AND F. M. **PURCELL** ... The **spin-echo** effect is associated with the successive application of two or more rf pulses. Hahn has described the effect for equal pulse widths. ...

4406회 인용 관련 학술자료 전체 16개의 버전 인용 저장

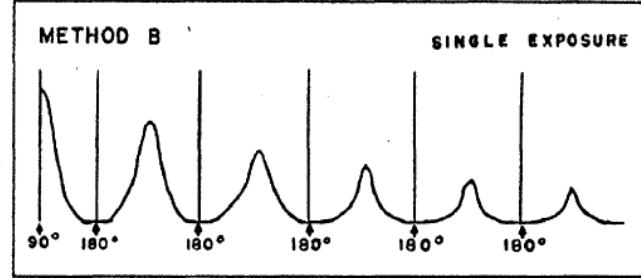
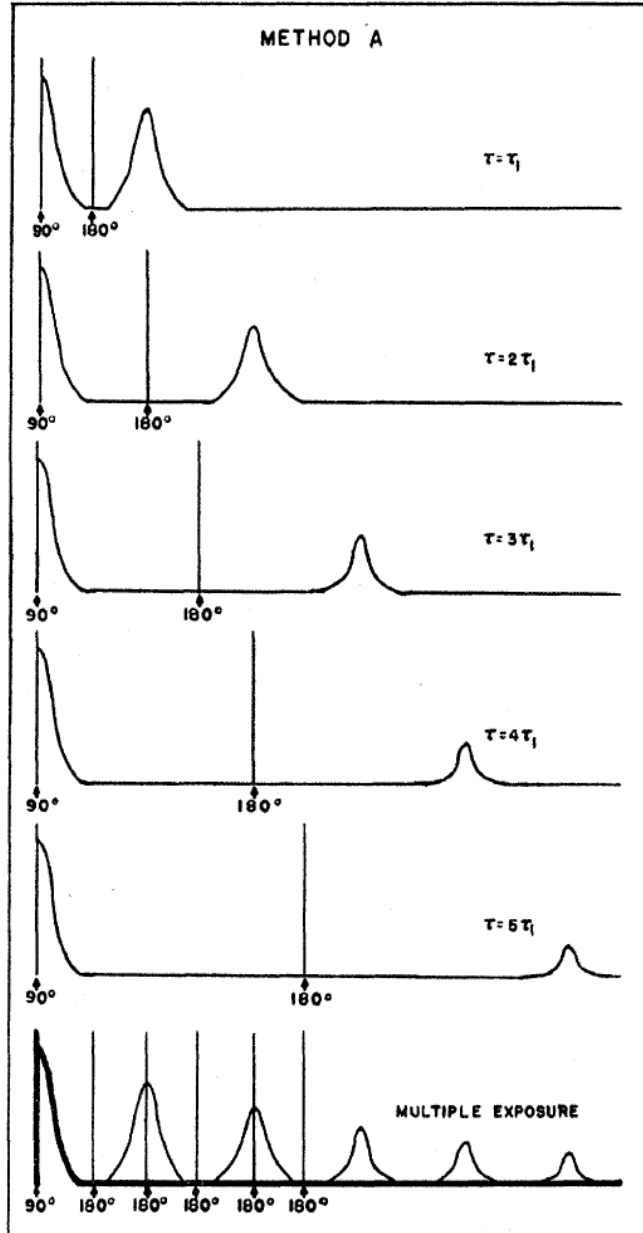


Spin echoes?



wikipedia

Spin echo – Carr & Purcell Version



Bloch's equation with a diffusion term (E. Hahn, Phys. Rev. 1950)

$$du/dt + [\Delta\omega + \delta(t)]v = -u/T_2$$

$$dv/dt - [\Delta\omega + \delta(t)]u + \omega_1 M_z = -v/T_2$$

$$dM_z/dt - \omega_1 v = -(M_z - M_0)/T_1.$$

Bloch's equation with a diffusion term (E. Hahn, Phys. Rev. 1950)

$$du/dt + [\Delta\omega + \delta(t)]v = -u/T_2$$

$$dv/dt - [\Delta\omega + \delta(t)]u + \omega_1 M_z = -v/T_2$$

$$dM_z/dt - \omega_1 v = -(M_z - M_0)/T_1.$$

Solution :

$$u(t) = (\Delta\omega/\beta)AQ + u(t_i)$$

$$v(t) = A \sin(\beta t + \xi)$$

$$M_z(t) = -(\omega_1 A/\beta)Q + M_z(t_i),$$

$$Q = \cos(\beta t + \xi) - \cos(\beta t_i + \xi) \text{ and } \beta = [(\Delta\omega)^2 + \omega_1^2]^{\frac{1}{2}}$$

$$F(t) = F(t_i') \exp\{- (t - t_i')/T_2$$

$$+ i[\Delta\omega(t - t_i') + \int_{t_i'}^t \delta(t'')dt'']\},$$

Bloch's equation with a diffusion term (E. Hahn, Phys. Rev. 1950)

$$F(t) = F(t_i') \exp \left\{ - (t - t_i') / T_2 \right. \\ \left. + i \left[\Delta \omega (t - t_i') + \int_{t_i'}^t \delta(t'') dt'' \right] \right\},$$

Bloch's equation with a diffusion term (H.Y.Carr & E.M Purcell , Phys. Rev. 1954)

$$H_z(j\tau) = H_z(0) + G\zeta \sum_{i=1}^j a_i.$$

a_i : 1 or -1
 τ : residence time of step
 ζ : distance of step

$$\begin{aligned} \phi_D = \phi - \phi_0 &= \sum_{j=1}^N \gamma\tau [H_z(j\tau) - H_z(0)] \\ &= G\zeta\gamma\tau \sum_{j=1}^N \sum_{i=1}^j a_i = G\zeta\gamma\tau \sum_{j=1}^N (N+1-j)a_j. \end{aligned}$$

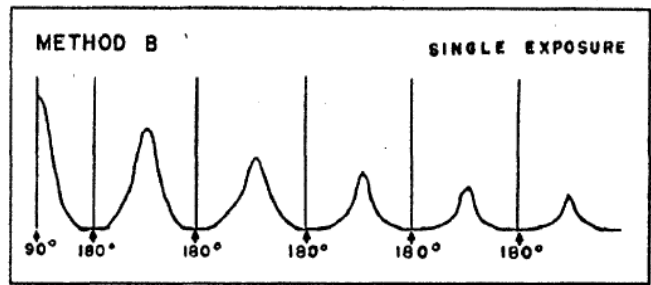
$$F(t) = F(t_i') \exp \left\{ -(t-t_i')/T_2 - \frac{1}{3}kt^3 + i[\Delta\omega(t-t_i') - \Phi(t_i')] \right\}$$

Hahn's results

Bloch's equation with a diffusion term (H.Y.Carr & E.M Purcell , Phys. Rev. 1954)

$$F(t) = F(t_i') \exp \left\{ - (t - t_i') / T_2 - \frac{1}{3} k t^3 + i [\Delta \omega (t - t_i') - \Phi(t_i')] \right\}$$

Hahn's results



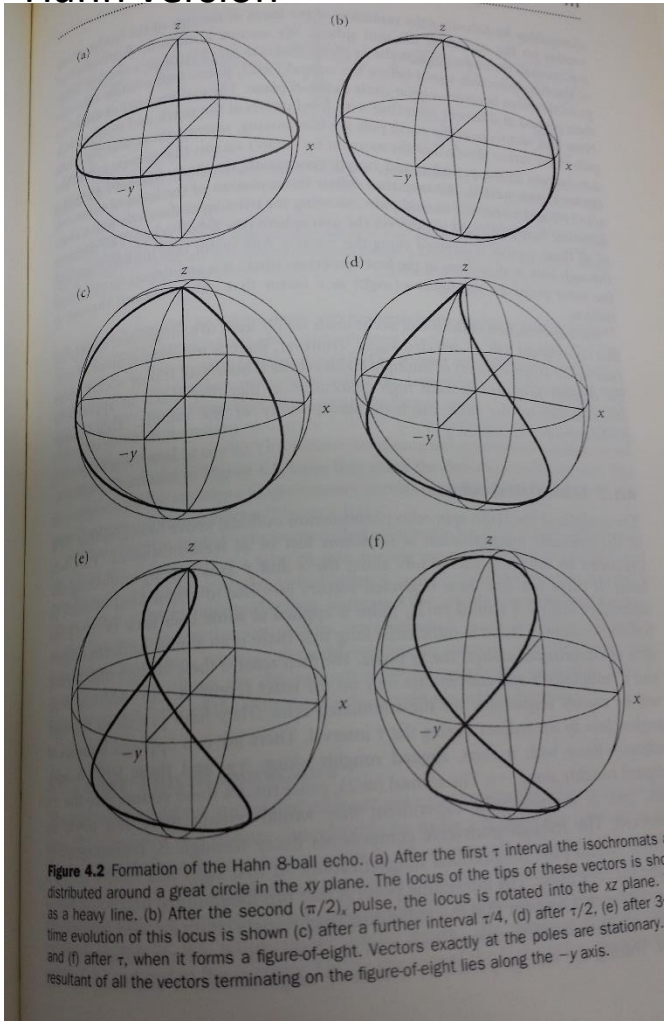
$$\phi_D = \phi - \phi_0 = G \zeta \gamma \tau \sum_{j=1}^N b_j \sum_{i=1}^j a_i, \quad t = N \tau / 2n,$$

$$M_{y'}(t) = M_0 \exp \left[(-t / T_2) + (-\gamma^2 G^2 D t^3 / 12 n^2) \right].$$

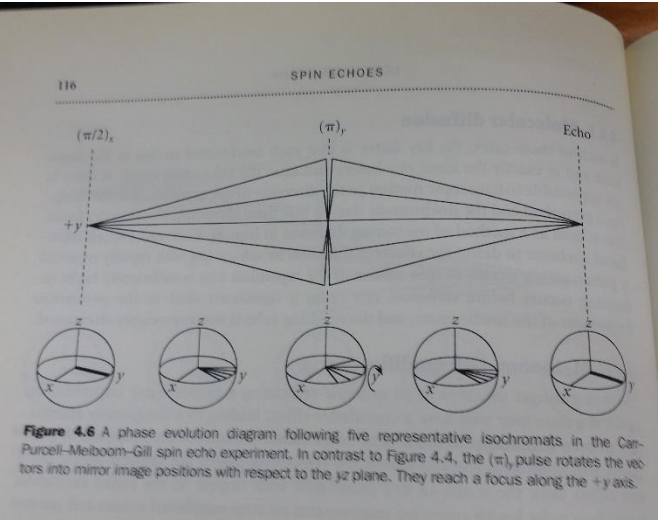
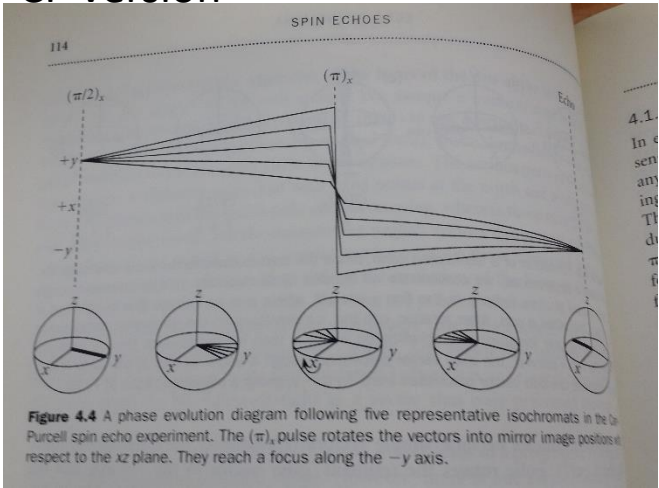
Carr&Purcell's results

Spin echo – Meiboom & Gill Modification (CPMG experiments)

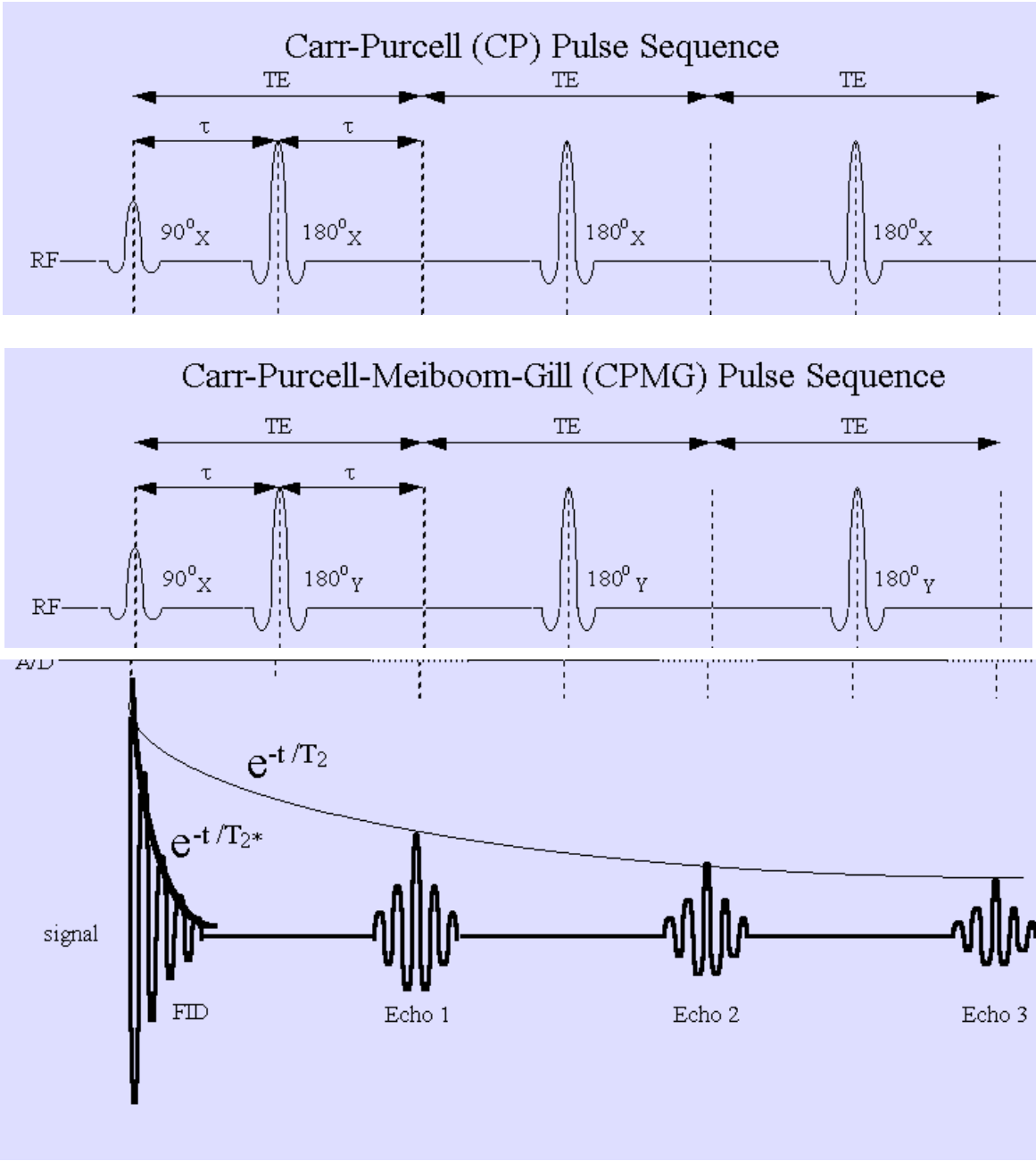
Hahn version



CP version



CPMG version



Spin-Echo NMR of chemical exchange I. Theory (A.Allerhand&H.S.Gutowsky, J. Phys. Chem 1964)

$$du_a/dt = -(\omega_a - \omega)v_a - (u_a/T_{2a}) - C_a u_a + C_b u_b,$$

$$du_b/dt = -(\omega_b - \omega)v_b - (u_b/T_{2b}) - C_b u_b + C_a u_a,$$

$$dv_a/dt = (\omega_a - \omega)u_a - (v_a/T_{2a}) - C_a v_a + C_b v_b - \omega_1 M_{za},$$

$$dv_b/dt = (\omega_b - \omega)u_b - (v_b/T_{2b}) - C_b v_b + C_a v_a - \omega_1 M_{zb}.$$

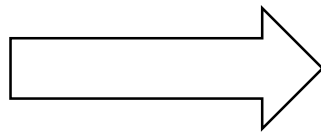
$$C_a = 1/\tau_a \quad \text{and} \quad C_b = 1/\tau_b,$$

$$dG_a/dt = -\alpha_a G_a + C_b G_b,$$

$$dG_b/dt = C_a G_a - \alpha_b G_b,$$

$$G_k = u_k + i v_k,$$

$$\alpha_k = (1/T_{2k}) + C_k - i(\omega_k - \omega).$$



$$(1/T_2) = (1/T_2^0)$$

$$+ P_a P_b (\delta\omega)^2 \tau [1 - (2\tau/t_{cp}) \tanh(t_{cp}/2\tau)].$$

Fast exchange limit
Approximation
(Z.Luz&S.Meiboom,
J. Phys. Chem 1963)

Numerical calculation Results (A.Allerhand&H.S.Gutowsky, J. Phys. Chem 1964)

TABLE I. Values of the "reduced" echo-decay time constant T_2^0/T_2 in the Carr-Purcell experiment, as a function of the pulse separation t_{cp} , calculated numerically and by the Meiboom analytical approximation,^a for the case of exchange between two sites,^b with $T_2^0\delta\omega = 150$.

P_a $T_2^0/2\tau$	0.5 20		0.5 50		0.5 150		0.5 500		0.3 500		0.1 500	
T_2^0/t_{cp}	Exact ^c	Approx. ^a	Exact ^c	Approx. ^a	Exact ^c	Approx. ^a	Exact ^c	Approx. ^a	Exact ^c	Approx. ^a	Exact ^c	Approx. ^a
16.67	26.61 ^d	43.93	18.70	17.67	6.47	6.44	5.57	5.57	2.93	2.96
25.00	19.34 ^e	24.90	35.14 ^f	30.14	17.50	16.62	6.37	6.34	5.49	5.49	2.90	2.92
50.00	7.44 ^g	8.05	14.21 ^h	14.41	13.97	13.53	6.09	6.06	5.26	5.25	2.80	2.82
62.50	5.33	5.61	10.34 ⁱ	10.56	12.35	12.06	5.94	5.92
83.33	3.54	3.64	6.77	6.90	10.00	9.89	5.71	5.69
100.00	2.80	2.84	5.18	5.26	8.49	8.43	5.52	5.50	4.78	4.78	2.60	2.62
125.00	2.17	2.19	3.78	3.82	6.73	6.72	5.23	5.22	4.55	4.54	2.51	2.52
166.67	1.66	1.67	2.61	2.63	4.82	4.83	4.77	4.76	4.16	4.16	2.34	2.35
250.00	1.30	1.30	1.73	1.74	2.96	2.97	3.92	3.91	3.45	3.45	2.04	2.05
500.00	1.07	1.07	1.19	1.19	1.54	1.54	2.34	2.34	2.13	2.13	1.48	1.48

^a T_2^0/T_2 calculated by means of Eq. (23).

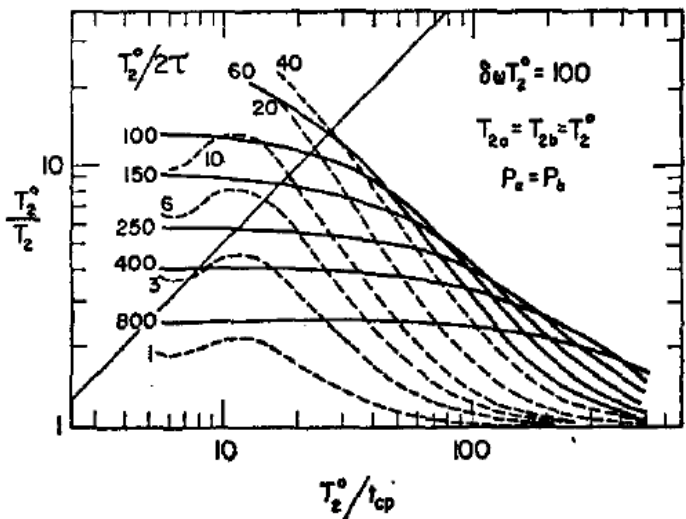
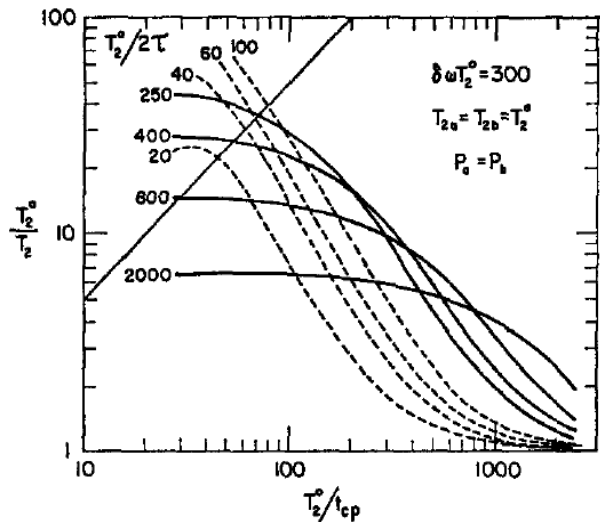
^b It is assumed that $T_{2a} = T_{2b} = T_2^0$.

^c T_2^0/T_2 obtained by numerical methods as described in the text following Eq. (13).

^{d-i} Of the cases given in the table, only for these did the decay deviate from exponential by a standard deviation in T_2^0/T_2 in excess 0.009, and 0.002.

$$(1/T_2) = (1/T_2^0)$$

$$+ P_a P_b (\delta\omega)^2 \tau [1 - (2\tau/t_{cp}) \tanh(t_{cp}/2\tau)].$$

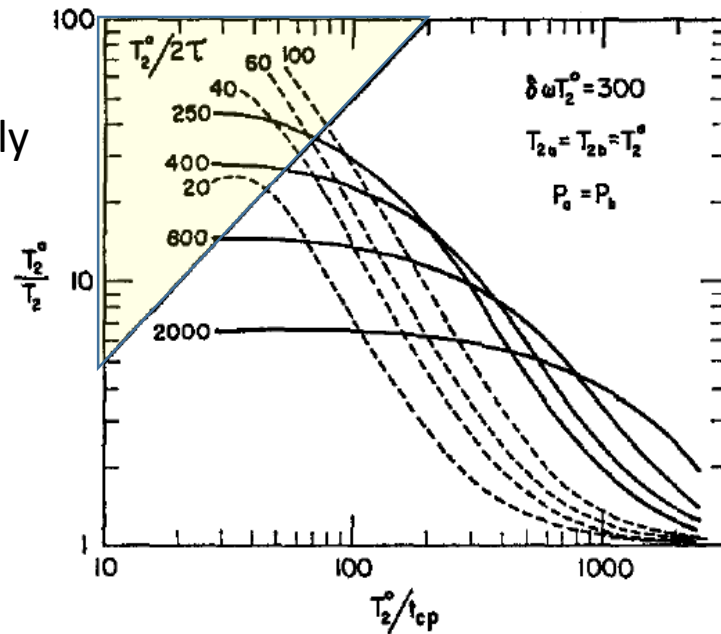


Numerical calculation Results (A.Allerhand&H.S.Gutowsky, J. Phys. Chem 1964)

Large pulse separation ($\tau_{cp} \rightarrow \infty$)

$$(1/T_2) = (1/T_2^0) + P_a P_b (\delta\omega)^2 \tau$$

$T_2 < 2t_{cp}$
Experimentally impossible



$$(1/T_2) = (1/T_2^0)$$

$$+ P_a P_b (\delta\omega)^2 \tau [1 - (2\tau/t_{cp}) \tanh(t_{cp}/2\tau)].$$

T_2 : transverse relaxation time with chemical exchange

T_2^0 : transverse relaxation time

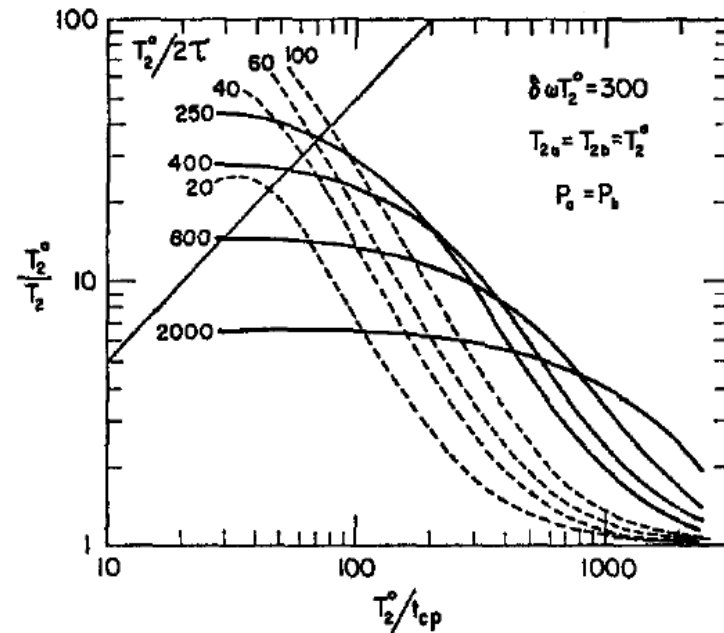
$$(1/T_2) = (1/T_2^0)$$

Short pulse separation ($t_{cp} \rightarrow 0$)

Numerical calculation Results (A.Allerhand&H.S.Gutowsky, J. Phys. Chem 1964)

Large pulse separation ($\tau_{cp} \rightarrow \infty$)

$$(1/T_2) = (1/T_2^0) + P_a P_b (\delta\omega)^2 \tau$$



$$(1/T_2) = (1/T_2^0) + P_a P_b (\delta\omega)^2 \tau$$

$$(T_2^0/T_2^m) - 1 = P_a P_b T_2^0 (\delta\omega)^2 \tau,$$



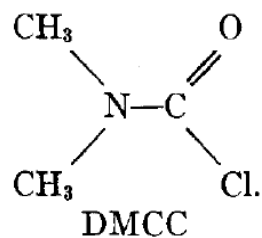
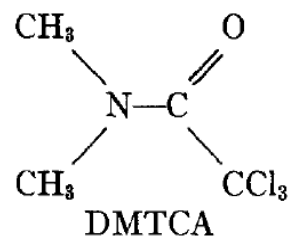
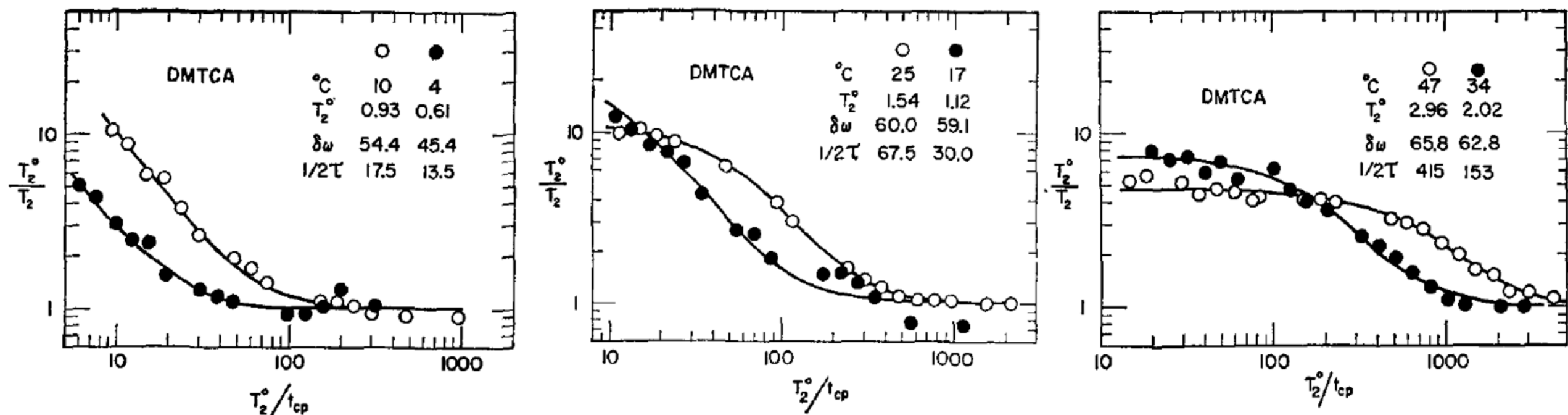
$$T_2^0/T_2 > 1.5$$

$$1/2\tau \leq P_a P_b T_2^0 (\delta\omega)^2$$

Limit of measurement

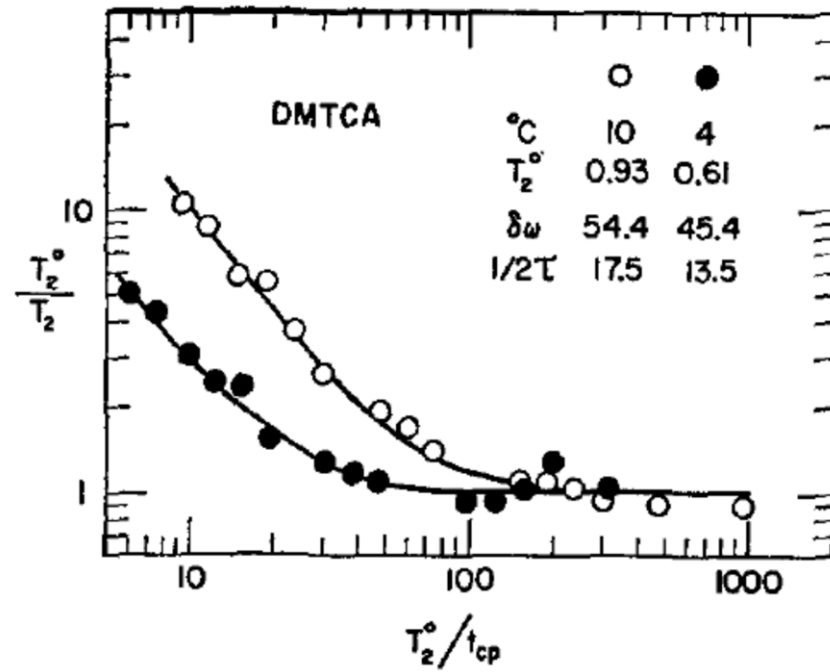
c.f. $\delta\omega = 750\text{Hz}$, $P_a = P_b = 0.5$, $T_2^0 = 0.01$
 $\tau \geq 3.5 \times 10^{-4} \text{ s}$

Spin-Echo NMR of chemical exchange II. Experiments

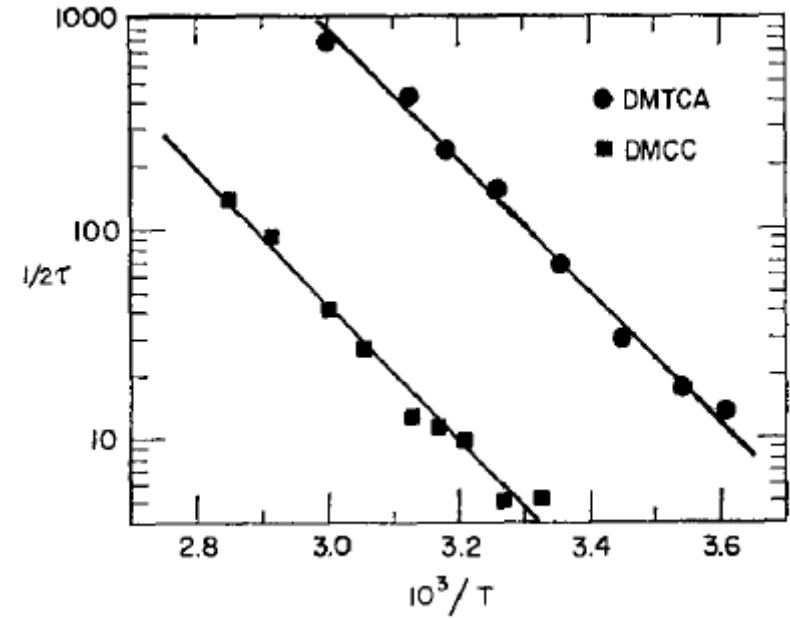


Temp. °C	(1/2τ) sec ⁻¹	δν ^a cps at 60 Mc	T ₂ ⁰ sec
N,N-dimethyltrichloroacetamide (DMTCA) ^b			
4	13.5±2.8 ^c	16.1±1.0 ^c	0.61±0.03 ^c
10	17.5±2.5	19.3±0.9	0.93±0.04
17	30.0±3.2	21.0±0.5	1.12±0.08
25	67.5±5.0	21.3±0.7	1.54±0.12
34	153±12	22.3±0.7	2.02±0.15
41	235±22	22.7±1.1	2.31±0.24
47	415±59	23.4±1.9	2.96±0.56
60	760±142	21.3±2.2	3.91±0.46

Spin-Echo NMR of chemical exchange II. Experiments



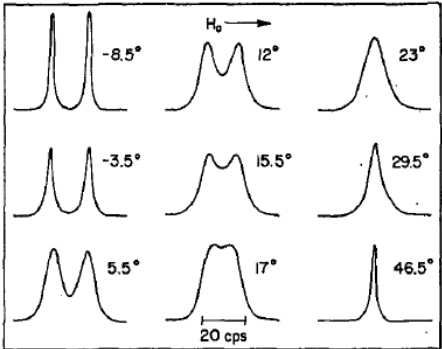
Internal rotation rates



$$\log(1/2\tau) = \log\nu_0 - (E_a/2.3RT),$$

Comparison between Spin-echo and High resolution

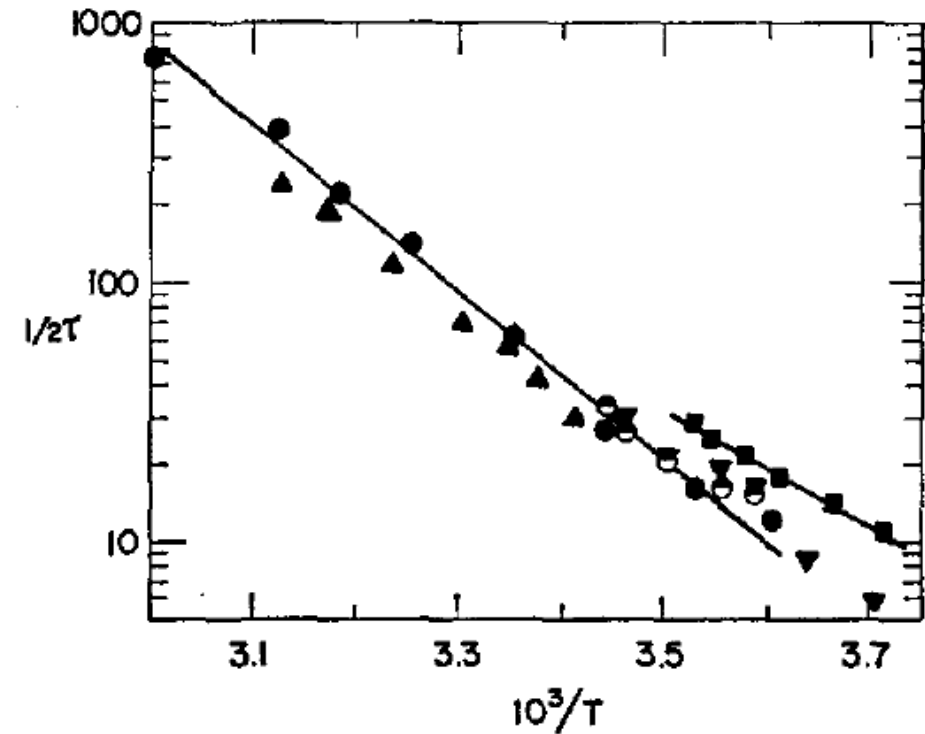
Method	DMTCA		DMCC	
	E_a kcal	$\log \nu_0$	E_a kcal	$\log \nu_0$
Spin echo	14.6 ± 0.6	12.5 ± 0.4	14.0 ± 0.9	10.9 ± 0.6
Peak separation ^b	10.3 ± 1.7 (9.1 ± 1.0)	9.6 ± 1.3 (8.5 ± 0.8)	8.6 ± 1.7	6.9 ± 1.2
Intensity ratio ^b	12.6 ± 1.2 (13.6 ± 1.2)	11.0 ± 0.9 (11.8 ± 1.0)	9.7 ± 0.5	7.7 ± 0.4
Line narrowing ^b	14.1 ± 0.5 (15.8 ± 0.5)	12.0 ± 0.3 (13.5 ± 0.3)		
Intensity ratio ^c	9.9 ± 0.3	9.1 ± 0.2	7.3 ± 0.5	6.1 ± 0.3



DMTCA
High
resolution
results

Advantages & Disadvantages

On this basis the reliabilities of the four methods decrease in the order: spin-echo > line narrowing > intensity ratio > peak separation.



A major **disadvantage** of the spin-echo method is that nuclei with chemical shifts within γH_1 of the exchanging nuclei cannot be present. In typical pulse experiments H_1 is 10 G, so that for proton-exchange studies, all nonexchanging protons have to be replaced by deuterium. However, there are a large number of systems with inter- or intramolecular exchange where there are no interfering nuclei.

Spin-Echo Studies of Chemical Exchange. II. Closed Formulas for Two Sites*

ADAM ALLERHAND AND H. S. GUTOWSKY

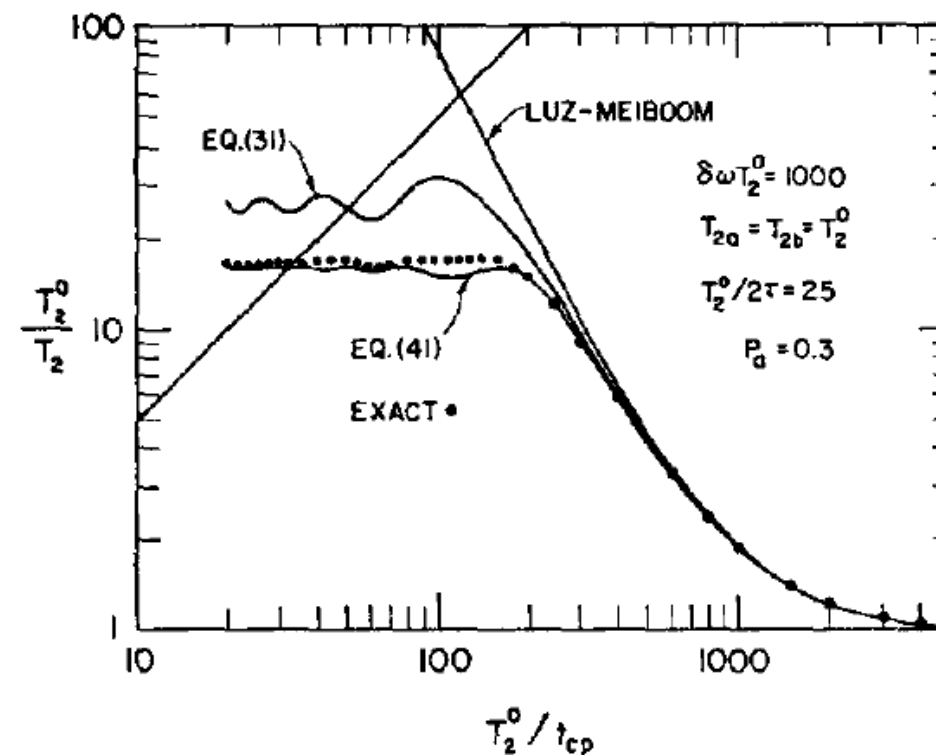
Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(Received 7 October 1964)

$$T_2^{-1} \cong T_+^{-1} = (T_2^0)^{-1} + (2\tau)^{-1} - (t_{cp})^{-1} \sinh^{-1} F,$$

with F defined by Eqs. (28) and (24) as

$$F = (1/\tau\sigma) \sinh(t_{cp}\sigma/2),$$



Spin-Echo NMR Studies of Chemical Exchange. III. Conformational Isomerization of Cyclohexane and d_{11} -Cyclohexane*

ADAM ALLERHAND,[†] FU-MING CHEN, AND H. S. GUTOWSKY

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

(Received 4 January 1965)

Equations derived previously for NMR chemical-exchange effects have been used in proton spin-echo studies at 26.85 Mc/sec of the chair-chair isomerization of cyclohexane and d_{11} -cyclohexane in 1:1 v/v solutions in CS_2 . The d_{11} -cyclohexane is particularly suited for such studies because of its very long natural relaxation time T_2^0 , and exchange rates of 0.53 to $3.8 \times 10^4 \text{ sec}^{-1}$ were determined for it in the temperature range between -98° and $+25^\circ\text{C}$. The heteronuclear coupling in d_{11} -cyclohexane does not affect the spin-echo results. However, in cyclohexane the homonuclear coupling and the shorter T_2^0 restricted the temperature range of accurate rate determinations to -60° and -25°C , respectively. The exchange rates are the same within experimental error for both compounds, as are ΔH^\ddagger , ΔF_{cb}^\ddagger , and ΔS_{cb}^\ddagger which were found to be 9.1 and 10.3 kcal/mole and -5.8 eu. The latter are compared with the results of several previous studies, and it is demonstrated that, in most if not all of the studies, there are systematic errors in the exchange rates. These errors have a modest effect upon ΔH^\ddagger but their effect upon ΔS^\ddagger is so large that the values for it are unreliable. Several factors governing the use of spin echoes to study chemical exchange are discussed.

