

DIFFUSION NMR

"Molecular diffusion", often simply called diffusion, is the thermal motion of all (liquid or gas) particles at temperatures above absolute zero. The rate of this movement is a function of temperature, size and shape of the particles and viscosity of the fluid. Applying of pulsed field gradients in NMR spectroscopy allows one to measure diffusion rates of nuclear spins. Diffusion of ions, molecules, intermolecular complexes, organometallic complexes and micelles can be studied by NMR.

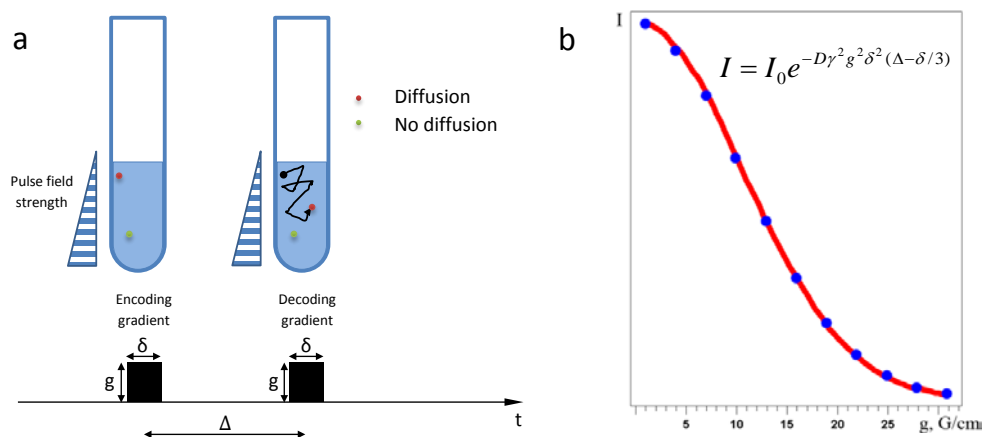


Fig. 1. (a) Applying of pulsed field gradients. (b) Dependence of the intensity of NMR signal on gradient strength, g .

A pulsed field gradient labels (encodes) molecules in the sample according to the spatial layer they occupy, and after diffusion time (Δ) new positions of molecules can be decoded by a second gradient pulse (Fig. 1a). Only those molecules which did not leave their spatial layer contribute to the resulting NMR signal. Attenuation of the intensity of the signal depends on the diffusion coefficient (D), diffusion time (Δ) and gradient parameters (strength g and duration δ). The value of diffusion coefficient can be found by fitting the signal attenuation curve (Fig. 1b).

Usually diffusion experiments are based on two types of pulse sequences:

- Spin echo (PGSE) [1]
- Stimulated echo (PGSTE) [2]

For samples with similar spin-lattice and spin-spin relaxation rates ($T_1 \approx T_2$), PGSE sequence is used. In case of $T_1 \gg T_2$ PGSTE sequence is preferable. The PGSTE sequence delivers only half of the signal intensity in comparison with the PGSE sequence.

Diffusion ordered spectroscopy (DOSY, Fig. 2) allows one to separate spectra of individual components in a mixture depending on their diffusion coefficients.

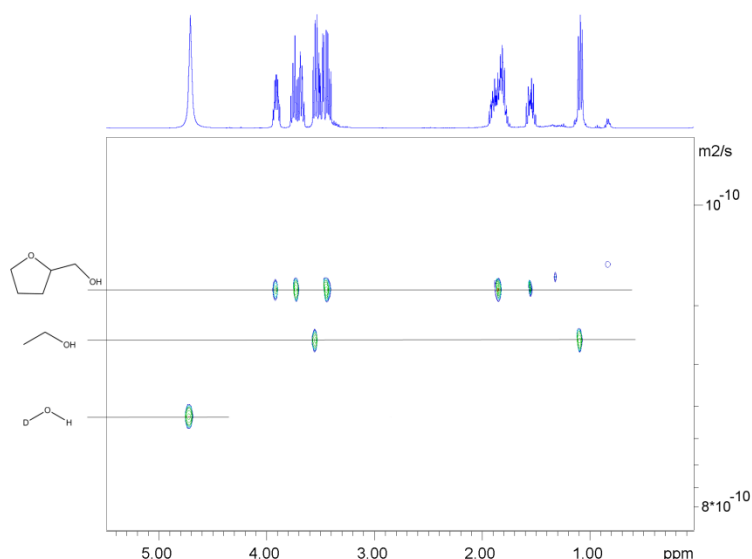


Fig. 2. Example of a DOSY spectrum.

1. Applications

Diffusion techniques are used for studying and analysis of solvation [3], formation of ion pairs [4], hydrogen bonds [5], inclusions [6], intermolecular complexes [7], organometallic complexes [8], micelles [9, 10], ionic liquids [11], microemulsions [12], determining size of molecules and aggregates [13], etc. A good review of diffusion NMR methods and applications is given in [14].

2. Temperature measurements. Reduction of convection in the sample

Depending on the viscosity of the solution and the temperature inside the sample convection flows can be produced. These flows have the same effect as diffusion and lead to increased molecular mobility. The reduction of the influence of convection in the sample can be achieved by the following:

- Using samples with decreased volume, such as Shigemi tube (Fig. 3a), sample tube with smaller diameter (Fig. 3b), or capillary (Fig. 3c).
- Using heat exchange medium inside the NMR sample tube, such as coaxial insert (Fig. 3d), or capillary (Fig. 3e).
- Using special pulse sequences for convection compensation, such as Double PGSTE [15].
- Using gradient cooling system for temperature stabilization (Fig. 8g) instead of standard air flow (Fig. 3f).

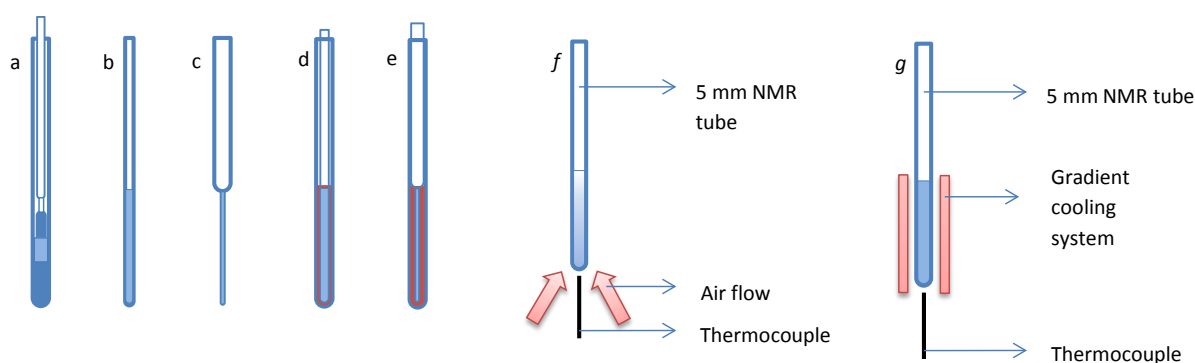


Fig. 3. (a)-(e) Various sample tube shapes used to decrease the effects of convection in the NMR sample. (f) Air flow temperature stabilization system. (g) Temperature stabilization by gradient cooling system.

3. Currently available at CMR

Apart of standard pulsed gradient field equipment available for liquid-state NMR instruments, Center for Magnetic Resonance has dedicated Bruker 60 Ampere gradient amplifiers with Bruker Diff50 probe and 5 mm coils for ^1H , ^2H , ^7Li , $^{13}\text{C}\{^1\text{H}\}$, ^{19}F , ^{23}Na , ^{31}P , ^{133}Cs nuclei. This extends the range of accessible diffusion coefficients to $10^{-9} \dots 10^{-13} \text{ m}^2/\text{s}$. Available temperature range is from -40 to $+80$ °C and from $+25$ to $+45$ °C for gradient cooling.

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