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Determination of Dipole - Dipole Couplings in Oriented n-Hexane by Two Dimensional NMR

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Abstract

A method is described for the experimental determination of dipolar coupling constants from NMR spectra of large molecules dissolved in liquid crystals. It is a combination of two dimensional and multiple quantum NMR techniques applied to randomly deuterated compounds. The method is exemplified for n-hexane which was randomly deuterated to 81%. The resulting NMR spectra of the mixture of isotopomers were separated and analysed by COSY-type and INADEQUATE-type 2D experiments and revealed all 16 dipolar coupling constants of n-hexane.

NMR spectra of molecules partially oriented in liquid crystals contain information about the anisotropic dipole-dipole interactions of the spins. It is of interest to recover the intramolecular dipolar coupling constants D_{ij} between each pair of spins since D_{ij} is proportional to $< (r_{ij})^{-3} >$ and quantitatively describes the molecular structure and the motions affecting the structure.[1] However, in conventional NMR spectroscopy the number of detectable transitions becomes intractably large as the number of active spins increases, and the individual lines may no longer be resolvable. In n-hexane, which is the molecule of interest here, the number of distinct transitions, even taking into account the symmetry of the molecule, can be as large as 217000, concealing the sixteen unique dipolar couplings between protons.

Several techniques have been proposed to overcome this problem. One useful approach is selective isotopic substitution, e.g. selective positioning of protons in otherwise deuterated molecules and measurement of the NMR spectrum under conditions of deuterium decoupling.[2,3] This allows an arbitrary reduction of the number of active spins but requires demanding synthetic effort. Another possible solution is the observation of high order multiple quantum spectra in order to reduce the redundant information in single quantum NMR spectra.[4]

We give here a preliminary report of an alternative method to analyse spectra and determine structures of molecules dissolved in liquid crystals. The basic idea is the use of randomly deuterated samples (a synthetically facile undertaking) which contain a mixture of all possible isotopomers of a molecule. This approach has been used before in the analysis of some cyclic compounds[3,5,6] in nematic liquid crystals. A highly deuterated sample will contain mostly isotopomers with just a few protons. Thus, the task of

interpreting one complex spectrum is reduced to one of analysing a large number of simple but overlapping spectra. The crucial point is the ability to recognize the individual signals which derive from the same spin system (arise from one isotopomer). This can be achieved by the combined application of two dimensional NMR[7] and multiple quantum NMR[8,9] techniques as is shown below for the case of n-hexane.

An 81% randomly deuterated sample of n-hexane was synthesized by exchange of n-hexane in the gaseous phase with D_2 over Pd on charcoal at 190°C. It was determined by mass spectroscopy to have a statistical distribution of isotopomers, as shown in Figure 1. Most molecules have between 0 and 5 protons on the chain. Figure 2 shows a two-quantum filtered[10,11] COSY-type spectrum of the mixture, taken with the pulse sequence:

$$(\tfrac{\pi}{2})_\phi - t_1 - (\tfrac{\pi}{2})_\phi - \frac{\tau_1}{2} - \pi_x - \frac{\tau_1}{2} - (\tfrac{\pi}{2})_x - \frac{\tau_2}{2} - \pi_x - \frac{\tau_2}{2} - \text{sample.}$$

The phase ϕ is incremented in 90° steps, alternating the receiver phase between 0 and 180°. The double quantum filter time τ_1 is varied to average out all double quantum coherences not refocussed at the end of τ_1. The spectrum effectively contains only signals from two proton isotopomers, since signals from one and three proton isotopomers are eliminated by the two quantum filter. Four or more proton molecules do not contribute due to a combination of low statistical probability of occurrence and a wide range of isomers. The COSY-type spectrum thus has 16 subspectra of the type A_2 or AB. Signals in the same spin system can easily be identified by off-diagonal correlations which form square patterns with diagonal peaks. All 16 dipole coupling constants could be read off this map and from a similar

experiment in which a π pulse was applied in t_1. The dipole coupling constants thus determined are listed in Table 1, together with a site assignment based on chemical shift.

The same information was corroborated in a second 2D-INADEQUATE-type[12] experiment. The pulse sequence used was:

$$(\tfrac{\pi}{2})_\phi - \frac{\tau_1}{2} - \pi_\phi - \frac{\tau_1}{2} - (\tfrac{\pi}{2})_\phi - t_1 - (\tfrac{\pi}{2})_x - \frac{\tau_2}{2} - \pi_x - \frac{\tau_2}{2} - \text{sample},$$

where ϕ is incremented by 90° while the receiver oscillates between 0 and 180°. Here two quantum and one quantum signals were correlated in a two dimensional map as shown in Figure 3. Six vertical lines were produced parallel to the one quantum axis, corresponding to the six possible double quantum frequencies

$$2\nu_M,\ \nu_M + \nu_{E_1},\ \nu_M + \nu_{E_2},\ 2\nu_{E_1},\ 2\nu_{E_2},\ \nu_{E_1} + \nu_{E_2}\ .$$

(See Figure 1 for the definition of M, E_1, and E_2.)
The six slices along the one quantum axis each contain A_2 or AB subspectra corresponding to their group type; thus there are 2 MM, 2 ME_1, 2 ME_2, 3 E_1E_1(2 shown), 3 E_2E_2(1 shown) and 4 E_1E_2(3 shown) subspectra. Subspectra are easily identified by their symmetric disposition around the central chemical shift position in ω_2. Different two quantum preparation times result in different relative intensities of the subspectra. Table 1 includes a list of dipole coupling constants obtained with two preparation times, 250 μs and 2.5 ms. The values of D_{ij} from the COSY-type and INADEQUATE-type experiments agree rather well. It remains to assign the couplings constants to specific pairs of protons on the molecule. These couplings can be used to test various theoretical models of conformational motions for hydrocarbon chains in anisotropic environments.[13-15] The fact

that D_{ij}'s for a molecule with 14 protons can be determined bodes well for the application of two dimensional and multiple quantum NMR to structure and motions of oriented molecules.

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Figure Captions

Fig. 1

Mass spectral data for a sample of n-hexane after 80 hours exchange with D_2: shown are the measured relative intensities (●) at masses 100 (0 protons) through 91 (9 protons) and calculated statistical fraction (O) assuming 81% deuteration.

Fig. 2

A two quantum filtered COSY-type spectrum of 81% randomly deuterated n-hexane, 23 mole% in EK 11650, taken with the pulse sequence described in the text. 128 x 1024 points deuterium-decoupled FIDs were collected on a 360 MHz spectrometer at -26°C (non-quadrature in t_1) with a spectral width of 16,667 Hz in both dimensions and a recycle delay of 5s. For each t_1 point 200 FIDs were accumulated while the double quantum mixing time τ_1 was incremented from 0 to 4900 μs in 100 μs steps after every fourth FID. For τ_2, 4 ms was used. The data set was zero filled to 512 x 2048 points prior to Fourier transformation. The square patterns which give the dipole coupling constants are illustrated for 4 of the 16 proton pairs.

Fig. 3

A part of a double quantum vs. single quantum spectrum of the same sample as in Fig. 2 obtained using the pulse sequence described in the text. 128 x 1024 points deuterium-decoupled FIDs were recorded at -26°C on a 360 MHz spectrometer with quadrature phase detection in both dimensions and a recycle delay of 5s. The spectral width was 3.3kHz in ν_1 and 7.35kHz in ν_2.

τ_1 was 250 μs and τ_2 4 ms. Vertical lines parallel to the single quantum axis illustrate the six double quantum frequencies of molecules with two protons along which the A_2- and AB-type spectra can be identified.

Table 1

List of dipole coupling constants obtained for the 8 AB and $8A_2$ coupling patterns of (a) the COSY-type and (b) the INADEQUATE-type experiment. The dipole coupling constants D_{ij} are defined by the equation:

$$H_D = \sum_{i<j} D_{ij} \frac{1}{2}(3I_{zi}I_{zj} - I_iI_j).$$

Table 1

Sites	D_{ij}(a)	D_{ij}(b)	Sites	D_{ij}(a)	D_{ij}(b)
E_1E_1	3974	3968	E_1E_2	186	183
E_1E_1	713	706	E_1E_2	81	81
E_1E_1	609	612	MM	1876	1862
E_2E_2	4487	4482	MM	206	203
E_2E_2	190	189	ME_1	386	382
E_2E_2	43	48	ME_1	322	314
E_1E_2	1616	1626	ME_2	1034	1041
E_1E_2	1086	1106	ME_2	598	591

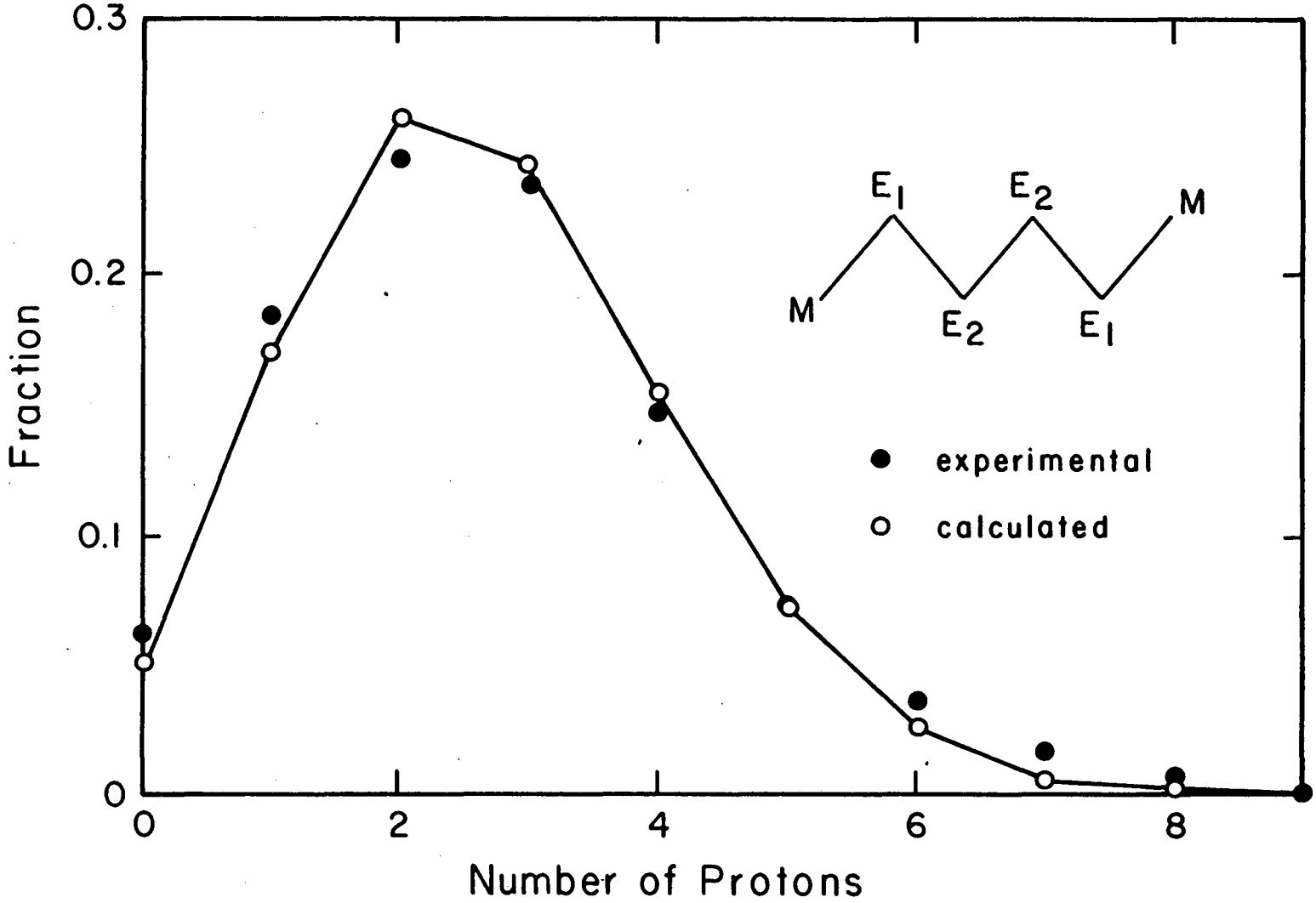

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Figure 1

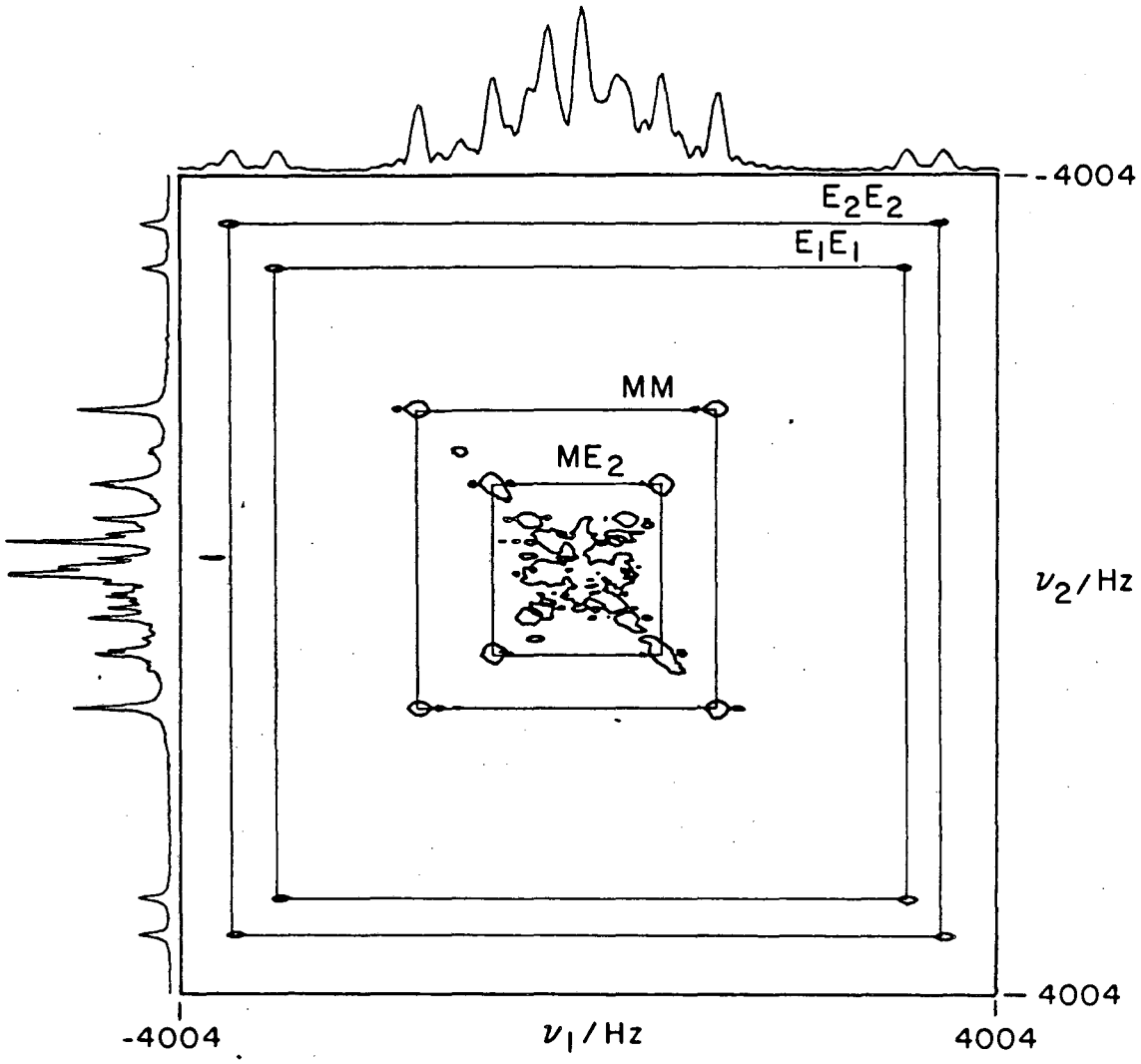

Figure 2

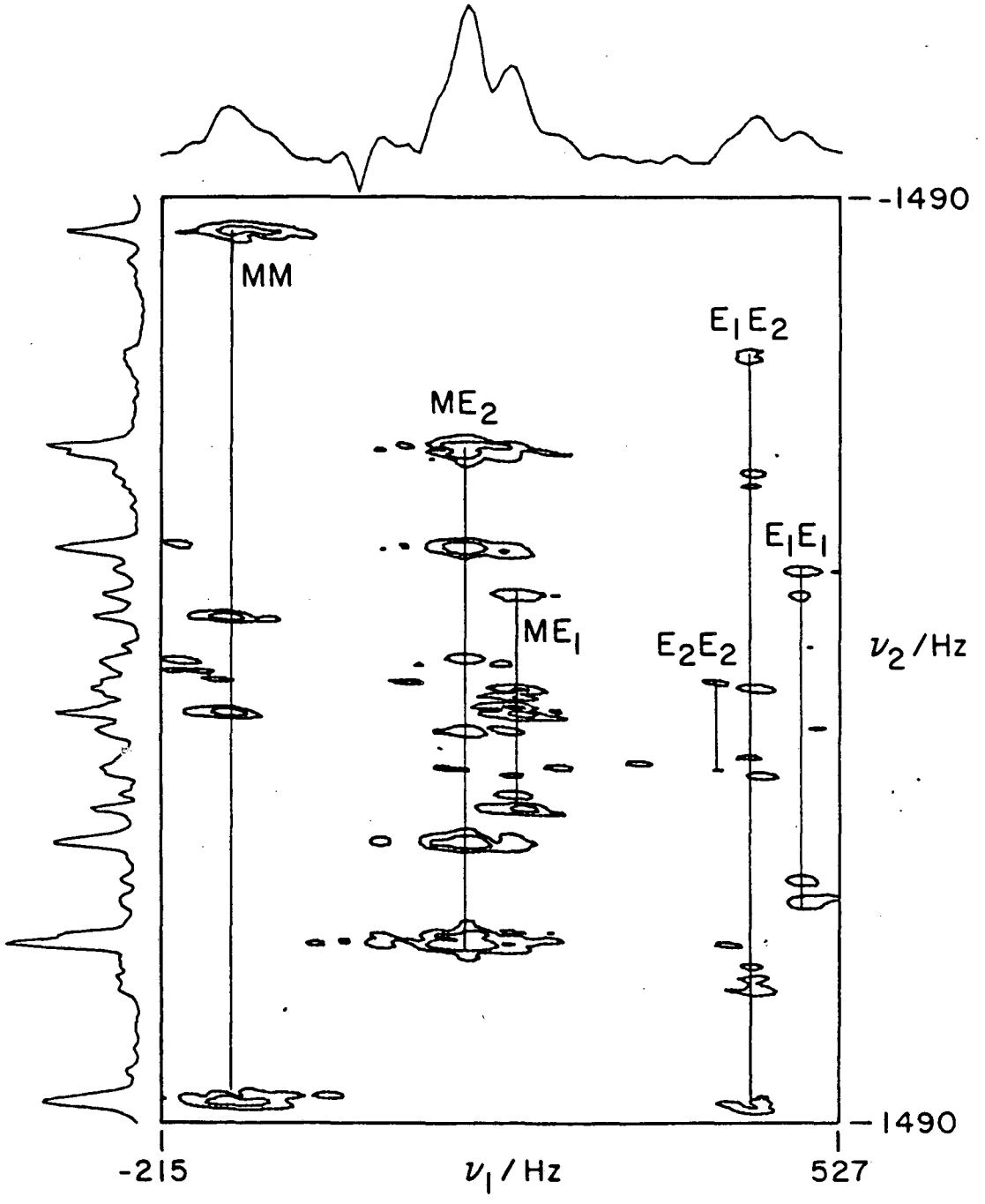
-1490
MM
E1E2
ME2
E1E1
ME1
E2E2
ν2/Hz
-1490
-215
ν1/Hz
527
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Figure 3

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