70. The ^2H,^2H-INADEQUATE Experiment: Detection of One- and Two-Spin Double Quantum Coherences

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The INADEQUATE experiment for spin-1 nuclei has been extended to deuteron spin systems of the *AX*, *AA'XX'*, and *AA'MM'X* type. Measurements with (3,3-D_2)norcampher, 4-chloro(2,3,5,6-D_4)pyridine, and (D_5)pyridine revealed correlation peaks due to two-spin double quantum coherences and additional one-spin double quantum peaks with coordinates $F_1 = 2\,\omega_i$, $F_2 = \omega_i$ (i = A, X) which were not observed in the ^{6}Li,^{6}Li-INADEQUATE experiment described earlier.

Introduction. – In the course of our work on the NMR spectroscopy of organolithium compounds [1], we have described the ^{6}Li,^{6}Li-INADEQUATE experiment and its application to structural problems in this field [2] [3]. Using this approach, neighbouring, chemically nonequivalent ^{6}Li nuclei in organolithium clusters, which are scalar coupled, can be detected *via* the observation of NMR signals which arise from double quantum coherences.

A closer look at the energy level diagram for a spin-1 *AX* system (*Fig. 1a*) reveals that aside from two-spin double quantum coherences (broken lines), one-spin double quantum coherences (dotted lines) should also be excited during the INADEQUATE pulse sequence and pass the phase cycle unhindered. Consequently, in a two-dimensional INADEQUATE experiment (*Eqn. 1* [4], $\Delta = 1/4\,J$ for spin-½ nuclei, $\Delta = 1/8\,J$ for spin-1

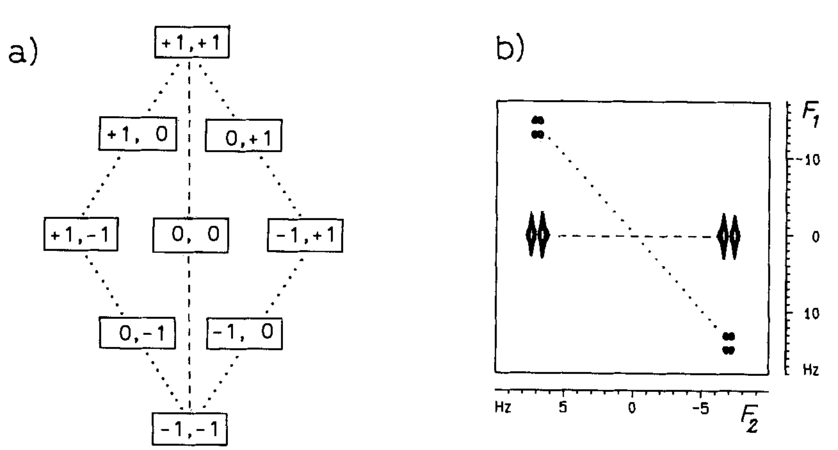


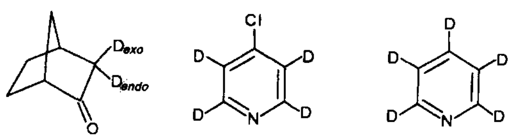
Fig. 1. a) *Energy-level diagram for an* AX *system of spin-1 nuclei.* b) *Result of a density matrix calculation for the 2D-INADEQUATE experiment of a spin-1* AX *system.* $\nu_A = 7.0$, $\nu_X = -7.0$, $J = 0.35$ Hz; magnitude calculation.

nuclei) one expects, after reconversion of double quantum coherences to observable one quantum magnetization, additional signals with coordinates $F_1 = 2\,\omega_i, F_2 = \omega_i\,(i = \mathrm{A, X})$, because evolution during t_1 proceeds with twice the *Larmor* frequency. These signals correspond to the 'type-II' signals observed for spin-$^1/_2$ nuclei in case of magnetic equivalence [5].

$$90° -- \Delta -- 180° -- \Delta -- 90° -- t_1 -- 135°, \mathrm{FID}\ (t_2) \quad (1)$$

This prediction is easily verified by a density matrix calculation with the program SMART [6] (*Fig. 1b*). However, experimentally, we never observed such signals in our ^{6}Li,^{6}Li experiments [2] [3]. We, therefore, investigated the 2D-INADEQUATE experiment for another spin-1 nucleus, ^{2}H, in order to solve this apparent discrepancy between theory and experiment.

Results and Discussion. – A number of ^{2}H spin systems of increasing complexity were studied with the compounds (3,3′-D_2)norcampher (**1**), 4-chloro(2,3,5,6-D_4)pyridine (**2**), and (D_5)pyridine (**3**). As *Fig. 2* demonstrates, the expected signals which arise from one-spin double quantum coherences are observed in all cases. Clearly, these peaks do not yield correlation information. It is interesting to note that, for the more complex spin systems in **2** and **3** (*AA'XX'* and *AA'MM'X* systems, respectively), their relative intensity



1 **2** **3**

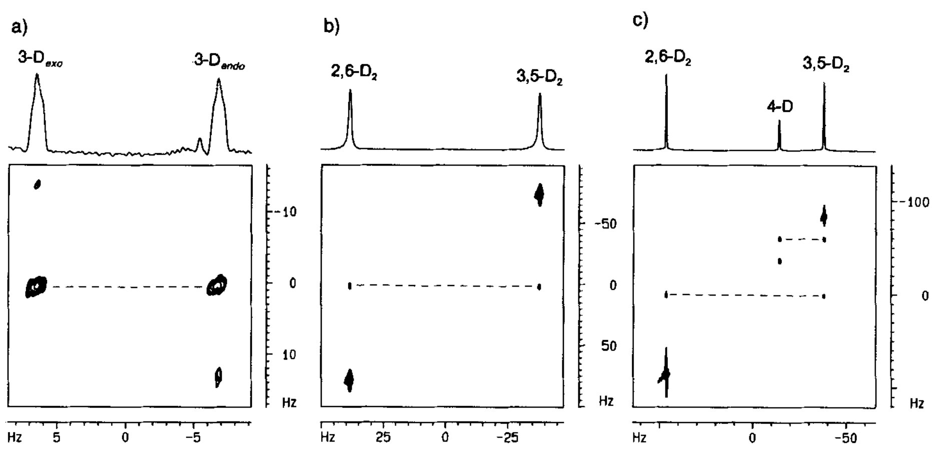


Fig. 2. *61.42-MHz ^{2}H,^{2}H-INADEQUATE experiments for three different ^{2}H spin systems. a) AX* System of **1** with ^{1}H broad-band decoupling; homonuclear ^{2}H,^{2}H coupling 0.35 Hz. *b) AA'XX'* system of **2**; *c) AA'MM'X* system of **3**. Magnitude calculation in each case; correlation peaks are connected by broken lines.

with respect to the signals which arise from two-spin double quantum magnetization has increased. Furthermore, signal selection for these higher spin systems leads to peaks with coordinates $+F_1,+F_2$ and $-F_1,-F_2$, while in the *AX* case we find $+F_1,-F_2$ and $-F_1,+F_2$.

Turning back to our product operator treatment [7] of the INADEQUATE experiment for a spin-1 AX system [3], we can complete the calculation for the 2D experiment, if we include the center line. For the magnetization after the spin-evolution time 2Δ, we then have

$$\sigma_1 = (\hat{I}_x\hat{S}_z + \hat{I}_z\hat{S}_x)\sin(2\pi J2\Delta) + (\hat{I}_y\hat{S}_z^2 + \hat{I}_z^2\hat{S}_y)\cos(2\pi J2\Delta) + (\hat{I}_y + \hat{S}_y) - (\hat{I}_z^2\hat{S}_y + \hat{I}_y\hat{S}_z^2) \quad (2)$$

With $2\Delta = 1/4J$, we obtain, after the second 90° pulse, two-spin double quantum coherence (term 1) and one-spin double quantum coherence (term 3) which evolve during t_1 with $\omega_A + \omega_X$ and $2\,\omega_i$ (i = A, X), relative to the carrier frequency ω_o, respectively:

$$\sigma_2 = (\hat{I}_y\hat{S}_x + \hat{I}_x\hat{S}_y) - (\hat{I}_z + \hat{S}_z) + (\hat{I}_y^2\hat{S}_z + \hat{I}_z\hat{S}_y^2) \quad (3)$$

The first term yields, after the read pulse, the correlation signals, while the last term leads to the additional peaks at $2\,\omega_i$, ω_i.

The reason why we did not observe the signals arising from one-spin coherences in the ^{6}Li,^{6}Li experiment are not clear. It seems possible that their relaxation behaviour as well as field inhomogeneity prevented their detection.

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Experimental. – *Compounds.* The synthesis of **1** and **2** followed published procedures [8] [9], **3** was commercially available (*Aldrich*).

Spectra. The ^{2}H,^{2}H-INADEQUATE spectra were measured with the standard *Bruker* software (INAD, UXNMR version 911101.1) on a *Bruker AMX-400* spectrometer at 61.42 MHz. The following parameters were used:

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
1	60	120	128	32	4K × 256	6.4	2	312.5	10.3
2	185	370	128	128	1K × 512	1.4	1	200	14
3	130	260	128	32	1K × 128	3.94	0.5	830	7

(a = sweep width in F_1 [Hz]; b = sweep width in F_2 [Hz]; c = number of t_1 experiments; d = number of scans; e = size of data matrix after zero-filling in F_1; f = acquisition time [s]; g = relaxation delay [s]; h = Δ delay = $1/8J$ [ms]; i = total measuring time [h])

Shifted sine bell window functions were applied in both frequency dimensions. The ^{2}H assignment follows the ^{1}H-NMR assignment from [10].

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