Accepted Manuscript

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Please cite this article as: L.M. Heist, C-D. Poon, E.T. Samulski, D.J. Photinos, J. Jokisaari, J. Vaara, J.W. Emsley, S. Mamone, M. Lelli, Benzene at 1 GHz. Magnetic field-induced fine structure, *Journal of Magnetic Resonance* (2015), doi: http://dx.doi.org/10.1016/j.jmr.2015.06.005

Benzene at 1 GHz. Magnetic field-induced fine structure

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Abstract

The deuterium NMR spectrum of benzene-d_6 in a high field spectrometer (1 GHz protons) exhibits a magnetic field-induced deuterium quadrupolar splitting $\Delta\nu$. The magnitude of $\Delta\nu$ observed for the central resonance is smaller than that observed for the ^{13}C satellite doublets $\Delta\nu'$. This difference, $\Delta(\Delta\nu) = \Delta\nu' - \Delta\nu$, is due to unresolved fine structure contributions to the respective resonances. We determine the origins of and simulate this difference, and report pulse sequences that exploit the connectivity of the peaks in the ^{13}C and ^2H spectra to determine the relative signs of the indirect coupling, J_{CD}, and $\Delta\nu$. The positive sign found for $\Delta\nu$ is consonant with the magnetic field biasing of an *isolated* benzene molecule—the magnetic energy of the aromatic ring is lowest for configurations where the C_6 axis is normal to the field. In the neat liquid the magnitude of $\Delta\nu$ is decreased by the pair correlations in this prototypical molecular liquid.

1

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1. Introduction

Molecular liquids and solutions subjected to a sufficiently strong magnetic field **B**, exhibit biased

Brownian motion that can be detected with nuclear magnetic resonance (NMR). This phenomenon was

initially observed by Lohman and MacLean using a 400 MHz spectrometer $(B = 9.36\,\text{T})$ and recording

deuterium NMR (^{2}H NMR) spectra of solutions containing aromatic hydrocarbons having large

diamagnetic anisotropies, e.g., phenanthrene-d_{10}, and triphenylene-d_{12}[1]. In that initial report there was

no evidence of biased rotational diffusion (orientational ordering) for the molecular liquid benzene-d_6.

The relatively small degree of magnetic field-induced ordering for benzene was subsequently inferred

from NMR relaxation (linewidth) measurements at a higher field of 11.7 T. It is now possible to study

the magnetic-field induced orientational ordering in benzene using an NMR spectrometer with

$B = 23.4\,\text{T}$, corresponding to a 1 GHz proton resonance frequency. In this case the magnetic torque has

been increased by a factor of $(1000/400)^2 = 6.25$ compared with the initial 400 MHz experiment. A ^{2}H

NMR experiment on neat perdeuterated benzene (C_6D_6) at 23.4 T reveals not only the expected increase

in magnitude of the field-induced quadrupolar splitting, $\Delta\nu$, but also that it is possible to record this

splitting on the two satellite peaks produced by the ~ 6% of molecules containing a single ^{13}C nucleus.

Quite unexpectedly, the magnitudes $\Delta\nu'$ obtained from the ^{2}H satellite doublets of the molecules

containing a ^{13}C nucleus are different from those obtained without the ^{13}C substitution $\Delta\nu$ (from the

central ^{2}H doublet) by an amount $\Delta(\Delta\nu) = \Delta\nu' - \Delta\nu$. The increased sensitivity at 1 GHz made it

possible to record spectra of C_6D_6 diluted in solvents whose constituent molecules are not aligned in a

magnetic field, such as the tetrahedral molecule tetramethyl silane (TMS). This dilution experiment

revealed that the magnitude of both $\Delta\nu$ and $\Delta\nu'$ increased, but that a difference $\Delta(\Delta\nu)$ remains. The

large increase in the sensitivity of detection at 23.4 T made it possible for the first time to detect field-

induced quadrupolar splittings on the center and ^{13}C satellite peaks from deuterium in a sample of

unlabeled benzene (C_6H_6, with both ^{13}C and ^{2}H at natural isotopic abundance). From these 1D NMR

experiments it is possible to obtain just the magnitudes of the field-induced quadrupolar splitting but not

2

their signs. We introduced a 2D NMR experiment on the sample of C_6D_6 in TMS, that we call the

QUASI-approach (QUAdrupolar SIgn), that makes it possible to obtain the relative signs of $\Delta\nu$ and the

one-bond, indirect scalar coupling, $^1J_{CD}$. The sign of $^1J_{CD}$ is known to be positive, and so for the first

time it is possible to obtain the absolute sign of a deuterium quadrupolar splitting. The sign of $\Delta\nu$

reflects the liquid state structure in the prototypical molecular liquid, benzene.

2. Experimental

2.1 NMR spectra

The NMR spectra at 23.4 T (1000.3 MHz for proton, 251.52 MHz for ^{13}C and 153.55 MHz for ^{2}H

Larmor frequencies) were acquired at the High-Field NMR Center of Lyon (Centre de RMN à Très

Hauts Champs de Lyon, ISA-CRMN), using an Avance III 1.0 GHz NMR Bruker instrument equipped

with a triple resonance TCI cryoprobe endowed with an additional channel for ^{2}H-lock. ^{2}H experiments

were performed using the ^{2}H-lock channel suppressing temporarily or permanently the lock stabilization

routine.

The ^{2}H $\pi/2$ radiofrequency (RF) pulse was calibrated to 174.0 μs, and the ^{13}C $\pi/2$ RF pulse was 16.3 μs. All

spectra were acquired at 298 K, and the chemical shifts referenced to TMS. Isotopically enriched

deuterated benzene (C_6D_6) was purchased from Cambridge Isotope Laboratory Inc.. Tetramethylsilane

(TMS) and natural abundance benzene were purchased from CortecNet and Sigma-Aldrich,

respectively.

2.2 Measuring the quadrupolar splittings $\Delta\nu$

The splittings of the center and satellite peaks were estimated by fitting the line shapes with the program

MestreNova (version 9.0.1). The program defines an optimized Lorentzian-Gaussian function for each

peak that varies the chemical shift, height, width, and area of the peak. There was some variation in the

splittings calculated from the direct measurement of the separation of the peak maxima, fitting the full

spectrum, or fitting each doublet separately. The fitting routines were tested by generating a spectrum

consisting of six lines centered approximately at the same positions as those in the experimental spectrum. This model spectrum had equal line separations and linewidths. The fitting routines obtained the correct line positions, and linewidths, and it was concluded that these routines are not introducing errors for the line positions. Hence in agreement with the experimental spectra (Figure 1), the magnitude of doublet splitting of the central line was different from those of the two ^{13}C satellite peaks.

3. Results and Discussion

3.1 Deuterium NMR spectra

1D Deuterium spectra of perdeuteriated benzene (C₆D₆)

1D Deuterium spectra of perdeuteriated benzene (C_6D_6)

^{2}H 1D spectra were acquired on two samples of C_6D_6. The first sample was of pure C_6D_6 and the spectrum is shown in Figure 1A. The spectrum in Figure 1B is of C_6D_6 dissolved in tetramethyl silane (TMS). The benzene concentration was 3% v/v and, to prevent the rapid TMS evaporation at 298 K, the sample was put into a pressure-sealed, NMR tube (CortecNet).

The use of a high sensitivity cryoprobe made it possible to detect, with a very good signal to noise ratio, both the central line, corresponding to the sum of the deuterium signals that are not coupled to a ^{13}C nuclear spin, and the satellite signals which account for the ^{2}H signals of the ^{13}C coupled isotopes (~6%).
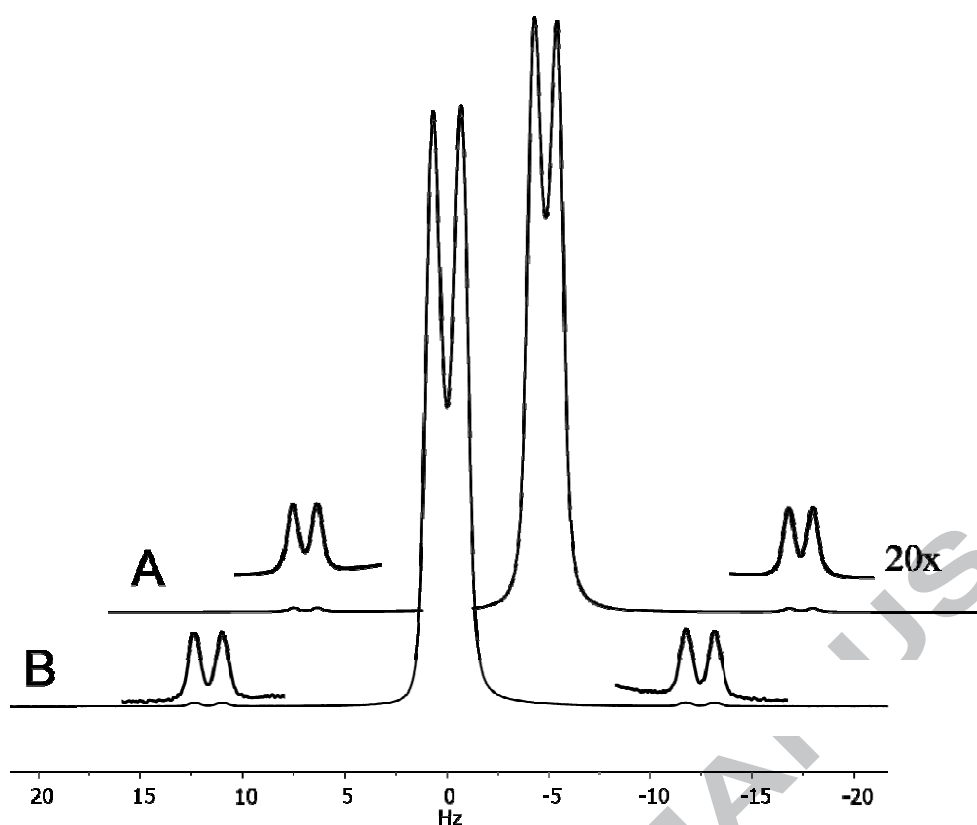
Figure 1. ^{2}H spectra at 153.553 MHz. **A.** neat C_6D_6. **B.** C_6D_6 (3%) diluted in TMS. Spectra were

acquired with a standard single-pulse sequence by using the tuned ^{2}H lock channel and stopping the lock

signal acquisition during the experiment. The low radiofrequency power allowed for in the lock channel

limited the $\pi/2$ pulse to 174.0 µs (1.43 kHz), but this was sufficiently long to uniformly excite the narrow

spectral width in all of the present experiments. Both spectra were obtained by averaging 64 transients

with 32K complex points for an acquisition time of 8.53 s and a recycle delay of 2.0 s. The magnitudes

of the apparent doublets and $\Delta(\Delta\nu)$ are given in Table 1.

1D Spectrum of deuterium at natural abundance in benzene

The deuterium natural abundance is 0.0115 %, and the natural abundance of ^{13}C is 1.07%. To detect this

very small concentration it was necessary to decouple the protons, and to average 23168 free induction

decays (FIDs). The overall acquisition time was ~1 day, and special measures were necessary in order to

maintain a linewidth of ~ 0.5 Hz for such a long experimental time. A ^{2}H lock signal was provided by

5

D_2O contained in a coaxial tube except during the ^2H detected experiment. After a few hundred transients, the natural drift of the magnetic field moved the position of the resonance and degraded the homogeneity of the magnetic field at a level that prevented resolving the quadrupolar doublets. To overcome these problems, an averaged 1D spectrum was obtained by combination of 181 separate experiments of 128 transients each. These experiments were run under the control of a routine that automatically corrected the lock and the field inhomogeneity between one experiment and the next one in the series. In such a way the field homogeneity was preserved during the entire acquisition time and, thereby correcting the resonance drift after acquisition, before adding together the 181 summed FIDs. The summed spectrum is shown in Figure 2.
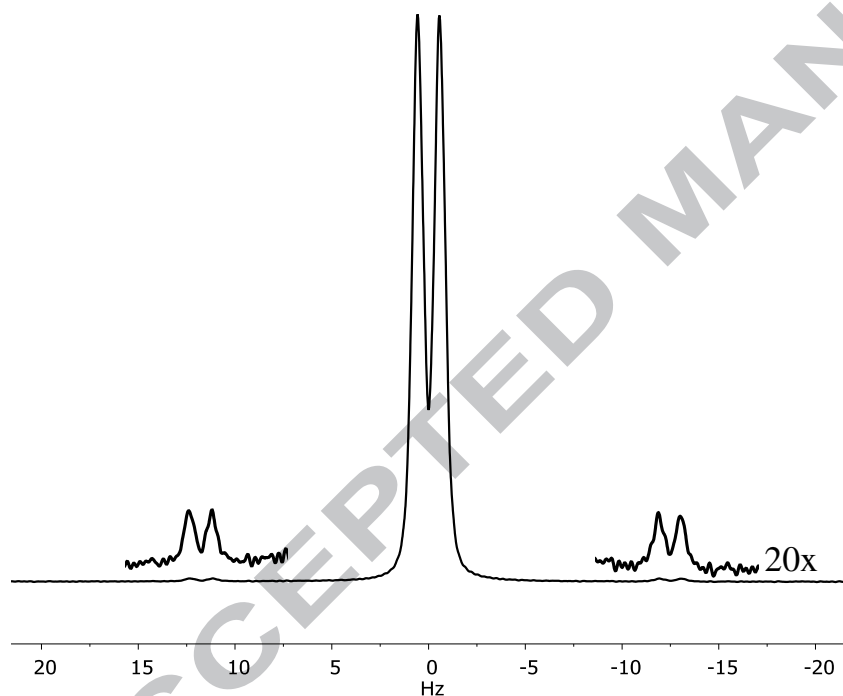

Figure 2. $^2H - \{^1H\}$ spectrum at 153.553 MHz of deuterium nuclei present at natural abundance in neat C_6H_6 obtained by summing 23168 FIDs as described in the text. The spectrum was acquired using the ^2H lock channel by stopping the lock acquisition during the experiment. The ^2H $\pi/2$ pulse was 155.0 µs (1.61 kHz). The acquisition time was 3.2 s, collecting 12288 complex points. During the acquisition time ^1H WALTZ-65 decoupling at 2.77 kHz power was applied. The recycle delay was set to 0.5 s. The magnitudes of the apparent doublets and $\Delta(\Delta\nu)$ are given in Table 1.

The splittings obtained from fitting the spectra in Figures 1 and 2 (see 2.2) are tabulated in Table 1 along with the corresponding $\Delta(\Delta\nu)$ values.

Table 1. Quadrupolar splitting and $\Delta(\Delta\nu)$ for Figures 1 and 2.

spectrum	left satellite doublet (Hz)	center doublet (Hz)	right satellite doublet (Hz)	$\Delta(\Delta\nu)$ (Hz)
Figure 1A	1.16	1.06	1.15	0.10±0.01
Figure 1B	1.39	1.30	1.40	0.10±0.01
Figure 2	1.15	1.14	1.12	-0.02±0.02

2D NMR ^2H – ^{13}C QUASI experiments

The relative sign of $^1J_{CD}$ and $\Delta\nu$ does not appear to have been determined directly by an experiment. While our QUASI-approach has been influenced by methods developed for the similar case of systems of three coupled spin-½ nuclei, such as 2D E-COSY or their heteronuclear analogous versions based on the same principles[2–6], we independently developed the QUASI-HSQC methodology described herein. In the 2D E-COSY two scalar couplings, for example among the spins I-S and I-X, act independently, one splitting the resonance in the direct dimension (for example I-S) and the other acting uniquely in the indirect dimension (for example I-X). The sequence is designed to avoid mixing (during the mixing period) the coherences that have evolved in the indirect dimension. As a result, after the 2D Fourier transform one should observe two peaks composed of the two components that are separated by the J_{IX}-coupling in the indirect dimension and by the J_{IS}-coupling in the direct dimension. Despite the traditional COSY-like experiments, where the cross-peak is composed of four components [(−½ J_{IX}; −½ J_{IS}), (+½ J_{IX}; −½ J_{IS}), (−½ J_{IX}; +½ J_{IS}), (+½ J_{IX}; +½ J_{IS})] in the exclusive-COSY scheme (E-COSY), only two components are observed that are arranged in the positions (−½ J_{IX}; −½ J_{IS}) and (+½ J_{IX}; +½ J_{IS}). Moreover, they are aligned parallel to the diagonal if both the J-coupling constants have the same sign, or parallel to the anti-diagonal if they have opposite sign. Thus, the topology of the 2D map allows

7

one not only to determine the two coupling constants with a resolution that is higher than in the traditional COSY-like experiment, but also to fix the relative sign of the two coupling constants, and that necessarily has to involve three distinct spins. The E-COSY principle has been applied both in homonuclear 2D correlation map[2,3] and in heteronuclear 2D spectra like the HNCA-*J* spectrum[4,5].

We approached the problem of the sign determination of the quadrupolar splitting in an analogous way, finding an E-COSY type of correlation between the quadrupole splitting of the ^{2}H spin and the scalar *J*-coupling between the directly bound ^{2}H and the ^{13}C spins in benzene. For scalar spin-spin coupled spin-½ nuclei, the relative signs can be obtained only when at least 3 coupled nuclei are present. Here only two spins (one ^{2}H and one ^{13}C) are involved, but because of the quadrupolar nature of the spin-1 deuterium, our results can be formally analyzed analogously to three coupled spins[7,8].

Several sequences can be designed to achieve this result by the following QUASI scheme, and two were used which are based on 2D ^{2}H-^{13}C correlation maps analogous to ^{2}H-^{13}C HSQC (Figure 3). Both of these sequences have the ^{13}C acquired in the direct dimension and the ^{2}H in the indirect dimension. In the sequence B, which we call QUASI-HSQC (QUAdrupolar SIgn Heteronuclear Single-Quantum Correlation), the cross-peak in the indirect dimension is composed of two components centered at the frequencies $(v_D - \frac{1}{2}\Delta v)$ and $(v_D - \frac{1}{2}\Delta v)$ around the deuterium chemical shift frequency, where Δv is the quadrupolar splitting. For the sequence A, called QUASI-RESOLVED, the projection in the indirect dimension is analogous to a QUASI-HSQC, the only difference is that inside the sequence the ^{2}H chemical shift evolution is refocused by a πpulse in the middle of the indirect evolution, as a result the two components of the quadrupole doublet have frequencies $(+\frac{1}{2}\Delta v)$ and $(+\frac{1}{2}\Delta v)$ (Figure 4). For both QUASI-RESOLVED and QUASI-HSQC sequences in the direct dimension, the splitting of the ^{13}C peak are observed; but instead of having three lines separated by the J_{CD}-coupling, as in the 1D spectrum, here only the external components of the triplet are seen, since the central line is not

8

transferred by the J_{CD}-coupling Hamiltonian along the magnetization transfer of the sequence scheme. Thus, the projection in the ^{13}C direct dimension shows only two components at frequencies $(\nu_C + J_{CD})$ and $(\nu_C - J_{CD})$ (Figure 4).

The two different splittings, quadrupolar in the indirect dimension and J_{CD}-coupling in the direct dimension, are acting separately to produce the two coherences composing the cross-peak and are not mixed during the magnetization transfer from deuterium to ^{13}C. The result is that these two coherences form two separate peaks in the 2D spectrum at frequency $(\nu_D + \frac{1}{2}\Delta\nu; \nu_C + J_{CD})$ and $(\nu_D - \frac{1}{2}\Delta\nu; \nu_C - J_{CD})$ for the QUASI-HSQC, and $(+ \frac{1}{2}\Delta\nu; \nu_C + J_{CD})$ and $(- \frac{1}{2}\Delta\nu; \nu_C - J_{CD})$ for the QUASI-RESOLVED. These peaks are aligned along the diagonal or the anti-diagonal if the quadrupolar splitting and the J_{CD}-coupling have the same or the opposite sign, respectively (see examples in Figure 4). Knowing the sign of the J_{CD}-coupling (that is analogous to the well-known J_{CH}-coupling) it is thus possible to obtain the sign of the quadrupolar splitting. The 2D methodology employed here was validated using a Product Operator formalism (See SI Section 4).

In both the NMR 2D sequences (Figures 3A and B), the information about the deuterium quadrupolar splitting is encoded in the indirect dimension, while the ^{2}H-^{13}C scalar coupling splitting is observed in the ^{13}C dimension during the direct acquisition. The sequences consist of two INEPT-type building blocks transferring magnetization from ^{13}C to ^{2}H for the indirect evolution and then from ^{2}H to ^{13}C for the direct acquisition. The sequence is conceptually similar to a ^{13}C-^{2}H HSQC where the magnetization is transferred back and forth between ^{13}C and ^{2}H. Alternatively, other schemes can be envisaged, including the reverse approach "^{2}H-^{13}C HSQC" starting from ^{2}H going to ^{13}C and back to ^{2}H, or "HETCOR-type" approaches from ^{2}H to ^{13}C and from ^{13}C to ^{2}H[9–12]. Conversely, all these approaches have the disadvantage that during the ^{2}H to ^{13}C INEPT transfer, the magnetization does not

9

evolve uniquely under the scalar coupling Hamiltonian, but also under the quadrupolar Hamiltonian. This contribution can be refocused only by introducing complicated and less sensitive schemes, and results in a phase distortion that obliges us to acquire the spectrum in the magnitude mode with a consequent reduction in resolution[13,14]. On the contrary, in the ^{13}C-^{2}H approach developed here, during the INEPT magnetization transfer only the ^{13}C spin component of the density matrix is evolving under the scalar coupling interaction, this makes it possible to acquire a 2D spectrum entirely in absorption mode with higher resolution. In the present case this was very important because we aimed to resolve a quadrupolar splitting of only ~1 Hz that required maximizing the resolution. Additionally, since the ^{13}C signal was detected in the direct dimension, the sequence could be designed so as to keep the lock routine active during the recycle delay and just stopping it to pulse on the deuterium channel. This significantly increased the instrumental stability, which was important to achieve the required spectral resolution. Moreover this made it possible to run this sequence on any conventional spectrometer using the lock channel as the deuterium channel without the need to install a lock circuit based on an alternative nucleus (for example, the ^{19}F-lock). Especially for the QUASI-RESOLVED sequence, our acquisition scheme had the advantage that the quadrupolar splitting evolves in the indirect dimension: this makes it possible to refocus both chemical shift and heteronuclear scalar coupling evolution, compensating the line broadening effect due to field inhomogeneity and magnetic field drift. Thus, for a sufficiently long indirect acquisition time, QUASI-RESOLVED showed an even higher resolution of the quadrupolar splitting than what was observed in the direct ^{2}H acquired spectra.
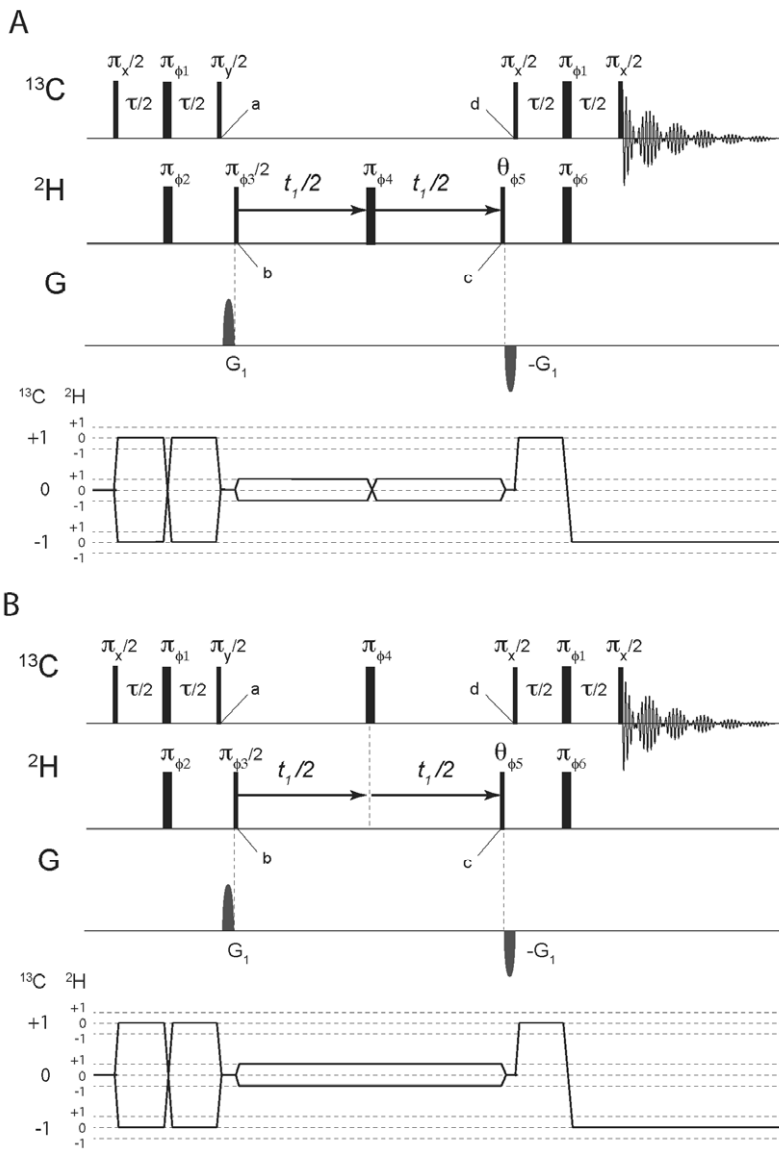
A

^{13}C

$\pi_x/2$ $\pi_{\phi1}$ $\pi_y/2$ $\quad$ $\pi_x/2$ $\pi_{\phi1}$ $\pi_x/2$

$\tau/2$ $\tau/2$ $\quad$ a $\quad$ d $\quad$ $\tau/2$ $\tau/2$

^{2}H

$\pi_{\phi2}$ $\pi_{\phi3}/2$ $t_1/2$ $\pi_{\phi4}$ $t_1/2$ $\theta_{\phi5}$ $\pi_{\phi6}$

G

b $\quad$ c

G_1 $\quad$ $-G_1$

^{13}C ^{2}H

+1 $\quad$ 0 $\quad$ -1

B

^{13}C

$\pi_x/2$ $\pi_{\phi1}$ $\pi_y/2$ $\quad$ $\pi_{\phi4}$ $\quad$ $\pi_x/2$ $\pi_{\phi1}$ $\pi_x/2$

$\tau/2$ $\tau/2$ $\quad$ a $\quad$ d $\quad$ $\tau/2$ $\tau/2$

^{2}H

$\pi_{\phi2}$ $\pi_{\phi3}/2$ $t_1/2$ $t_1/2$ $\theta_{\phi5}$ $\pi_{\phi6}$

G

b $\quad$ c

G_1 $\quad$ $-G_1$

^{13}C ^{2}H

+1 $\quad$ 0 $\quad$ -1

Figure 3. Scheme of the QUASI-pulse sequences used to determine the relative signs of $^1J_{CD}$ and $\Delta\nu$. Both sequences have the ^{13}C in the direct dimension and ^{2}H in the indirect dimension. In the QUASI-RESOLVED (sequence A) only the quadrupolar splitting evolves in the indirect dimension, while in the QUASI-HSQC (sequence B) both quadrupolar coupling and deuterium chemical shift interactions evolve. The INEPT-type delay τ was set in order to have $\tau = 1/(4J_{CD})$, where J_{CD} is the carbon-deuterium scalar coupling constant. For QUASI-RESOLVED the phases of the pulses were set to: $\phi_1 = \phi_2 = \phi_4 = \phi_6 = y, y, y, y,\text{-} y,\text{-} y,\text{-} y,\text{-} y$; $\phi_3 = x,\text{-} x$; $\phi_5 = \text{-} x,\text{-} x, x, x$; the receiver was $\phi_{REC} = x,\text{-} x,\text{-} x, x.$ The indirect dimension was acquired with the States quadrature detection incrementing both ϕ_3 and ϕ_4 by $\pi/2$. For the QUASI-HSQC the phases of the pulses were set to: $\phi_1 = \phi_2 = \phi_6 = y, y, y, y,\text{-} y,\text{-} y,\text{-} y,\text{-} y$; $\phi_3 = x,\text{-} x$; $\phi_5 = \text{-} x,\text{-} x, x, x$; $\phi_4 = y, y, y, y,\text{-} x,\text{-} x,\text{-} x,\text{-} x$; $\text{-} y,\text{-} y,\text{-} y,\text{-} y, x, x, x, x$; the receiver was $\phi_{REC} = x,\text{-} x,\text{-} x, x.$ The indirect dimension was acquired with the States-TPPI[15] quadrature detection incrementing the phase ϕ_3 by $\pi/2$. These sequences were run while temporarily stopping the lock during the acquisition and reactivating the lock and the shim control during the recycle delay.
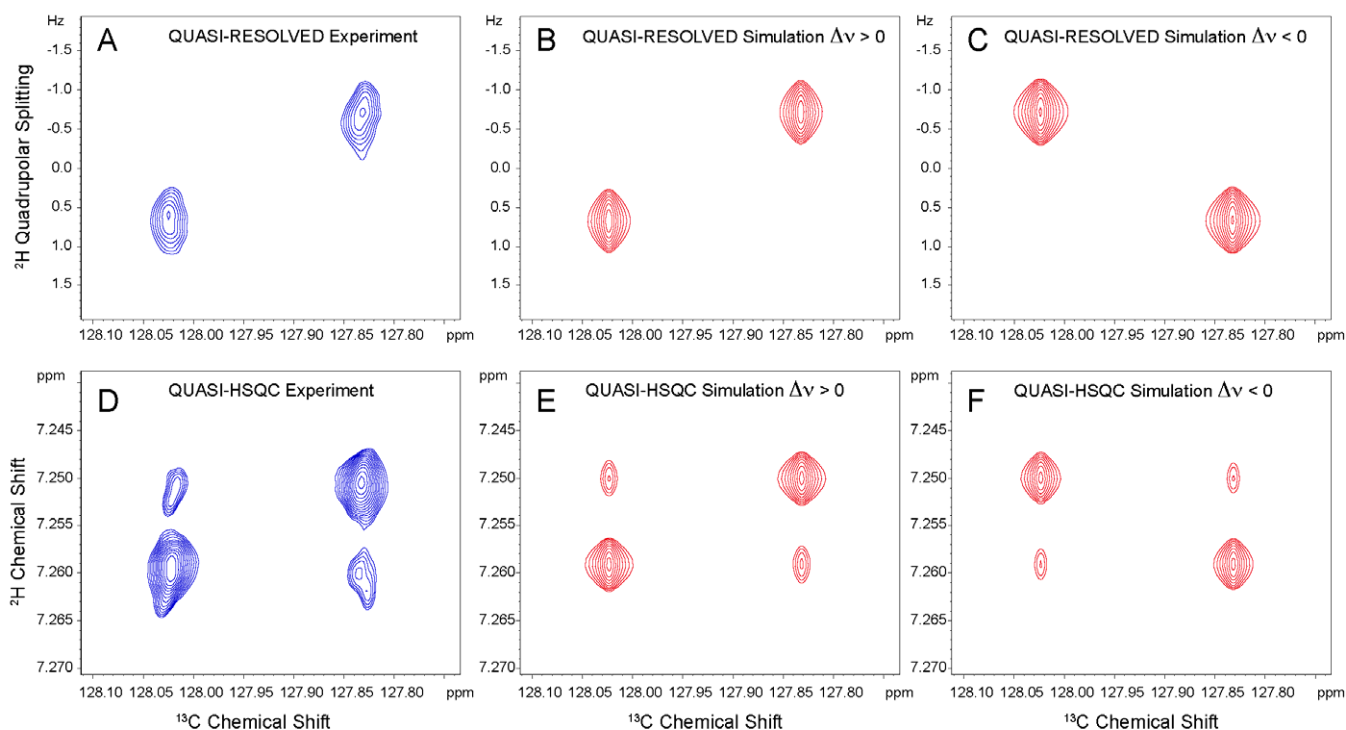
Figure 4. Comparison between experimental and simulated spectra for QUASI-RESOLVED (sequences A) and QUASI-HSQC (sequence B) (Figure 3). The experimental spectra are shown in the panels A and D, for QUASI-RESOLVED and HSQC, respectively, while the simulated spectra are shown in the spectra B,C for QUASI-RESOLVED and E,F for QUASI-HSQC. The experiments were run on the sample of C_6D_6 3% v/v in TMS at 298 K and 23.4 T. For both sequences, the real experiment was acquired with a ^{2}H π pulse of 174.0 μs and a ^{13}C π pulse of 16.3 μs. For the QUASI-HSQC the θ pulse was set to 261.0 μs ($3\pi/4$). For the QUASI-RESOLVED the θ pulse was set to 58.0 μs ($\pi/3$) for the cosine modulated increments in the indirect dimension and 261.0 μs ($3\pi/4$) for the sine modulated increments. In QUASI-RESOLVED the indirect dimension was acquired with States quadrature detection, while for the QUASI-HSQC States-TPPI was used. For the QUASI-HSQC 8192 × 252 complex points were acquired with acquisition times of 1.63 s and 2.10 s in the direct and indirect dimensions, respectively. The spectral window in the indirect dimension was set to 120 Hz, and the recycle delay was 6.37 s in order to have a stable lock during the interscan delay. For the QUASI-RESOLVED 8192 × 96 complex points were acquired with acquisition times of 1.63 s and 3.20 s in the direct and indirect dimensions, respectively. The spectral window in the indirect dimension was set to 30 Hz. The longer acquisition time in the indirect dimension was set to improve the resolution of the quadrupole doublet. For both the sequences the recycle delay was 6.37 s, in order to have a stable lock during the inter-transient delay. The τ delays were set to $\tau = 1/(4J_{CD})$ where $J_{CD} = 24.26$ Hz. The simulated spectra were obtained with the program NMRSIM 5.2.1 using the exact same sequence files used for the experimental pulse sequences A and B; details are reported in SI Section 5. The spectra B and C were simulated using QUASI-RESOLVED on two different spin-systems with quadrupole splitting of $\Delta v = +1.38$ Hz and -1.38 Hz, respectively. Analogously, the spectra E and F were simulated using the QUASI-HSQC on two different spin-systems with quadrupole splitting of $\Delta v = +1.38$ Hz and -1.38 Hz, respectively. The correlation among simulated and experimental spectra unambiguously made it possible to assign the sign of the quadrupole coupling to $\Delta v = +1.38$ Hz. Experimental and simulated spectra were processed with analogous parameters.

12

3.2 The magnitude of a magnetic-field induced deuterium quadrupolar splitting

The observation of a quadrupolar splitting, $\Delta\nu$, for a deuterium in a C D bond implies the presence of molecular orientational order and is described by

$$\Delta\nu = \frac{3}{2}q_{CD}\left[S_{zz} + \frac{1}{3}\eta(S_{xx} - S_{yy})\right], \tag{1}$$

where q_{CD} is the deuterium quadrupolar coupling constant, and is related to the quadrupole moment, eQ, and the electric field gradient tensor (EFG), $e\mathbf{V}$, at the nucleus, via $q_{CD} = eQV_{zz}/h$.

The asymmetry parameter, η is defined as:

$$\eta = (V_{xx} - V_{yy})/V_{zz} \tag{2}$$

For deuterated benzene, z is along the C D bond, y is the benzene ring normal and x is in the ring plane. With this definition of the axes $|V_{zz}| > |V_{xx}| > |V_{yy}|$, and therefore, $\eta > 0$.

The orientational order parameters are defined as,

$$S_{\alpha\alpha} = \tfrac{1}{2}\langle 3\cos^2\theta_\alpha - 1\rangle \tag{3}$$

with θ_α the angle between principal axis α of the molecular fixed x,y,z frame and the applied magnetic field direction.

The magnitudes of the field-induced quadrupolar splitting of deuterium in benzene

The natural abundance deuterium spectrum of neat benzene (Figure 2) has equal quadrupolar splittings on center and satellite lines, as expected for an isolated ^{13}C-^2H spin system, but these splittings differ for a sample of neat C_6D_6, and the magnitudes of this difference in splittings changes when a sample of neat C_6D_6 is diluted by TMS. To understand the origins of these phenomena we start by examining in more detail the relationship between the magnetic field-induced splittings and the orientational order of the molecules. Thus, the magnitude of the quadrupolar splitting, $\Delta\nu$, is given by Eq. (1) and the orientational order matrix for an isolated benzene molecule has principal axes x,y and z fixed by the

13

presence of a C_6 symmetry axis (normal to the six equivalent C—D bonds, and chosen as y). The order

parameters of the in-plane x- and z-axes are simply related to S_{yy}: $S_{zz} = S_{xx} = -\frac{1}{2} S_{yy}$. It follows from Eq.

(1) that the quadrupolar splitting, $\Delta \nu$, of an isolated benzene molecule—at infinite dilution in the

magnetically isotropic solvent TMS—is given by

$$\Delta \nu = -\frac{3}{4} q_{CD} S_{yy} (1+\eta),\qquad (4)$$

where $q_{CD} = 187 \pm 0.4\,\text{kHz}$ is the deuterium quadrupole coupling constant[16] and $\eta = 0.054$ is the

biaxiality of the local EFG tensor at the deuterium nucleus[17].

The observed $\Delta \nu$ derives from the non-zero, average EFG at the deuterium nucleus which, in turn,

stems from the very slight orientational biasing of benzene in the spectrometer magnetic field. That bias

is quantified by the orientational order parameter, $S_{yy} = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$ where θ is the instantaneous

angle between the molecular symmetry axis y and the magnetic field **B**. A value for S_{yy} may be

calculated from the relationship:

$$S_{yy} = \frac{\left\langle \frac{1}{2}(3\cos^2\theta_1 - 1) \times \prod_{i=1}^{N} \exp\left(\frac{1}{2kT}\mathbf{B}\cdot\boldsymbol{\chi}_i\cdot\mathbf{B}\right)\right\rangle_0}{\left\langle \prod_{i=1}^{N} \exp\left(\frac{1}{2kT}\mathbf{B}\cdot\boldsymbol{\chi}_i\cdot\mathbf{B}\right)\right\rangle_0},\qquad (5)$$

where the subscript $_0$ in the angular brackets indicates that the averaging is done with the full (position

and orientation) probability distribution $P_0^N(\omega_1,\mathbf{r}_1;\omega_2,\mathbf{r}_2;\dots\omega_N,\mathbf{r}_N)$ of the N molecules in the liquid, in

the absence of the external magnetic field, with ω_i, $\mathbf{r}_i$ denoting respectively, the orientation (θ_i,φ_i),

relative to the magnetic field direction, and position of molecule $i(=1,2,\dots N)$ in an ensemble of N

molecules. The magnetic energy of the ith molecule in the ensemble is $-\frac{1}{2}\mathbf{B}\cdot\boldsymbol{\chi}_i\cdot\mathbf{B}$, and $\boldsymbol{\chi}_i = \boldsymbol{\chi}_i(a_i)$ is

the traceless diamagnetic anisotropy tensor of the ith molecule. The formal statistical mechanics

definition of S_{yy} (Eq. (5)) can be readily evaluated because at room temperature, for the magnetic field

strengths and the magnetic anisotropies of $\boldsymbol{\chi}_i$ involved, the orientation-dependent magnetic potential

14

energy of a molecule is on the order of $10^{-4} kT$. Expansion of the exponentials in Eq. (5) along with the associated integrations leads to the following expression[18] for the quadrupolar splitting at temperature T in a benzene solution where the mole fraction of C_6D_6 is denoted by x:

$$\Delta \nu(T,x) = \Delta \nu_0(T)(1 + xg(T,x)), \qquad (6)$$

with $\Delta \nu_0(T) = -\frac{3}{4} q_{CD} S_{yy}(1 + \eta)$. The principal order parameter for an *isolated* benzene molecule is given by

$$S_{yy} = \chi_{yy} B^2 / 10 k_B T \qquad (7)$$

The orientational correlations between pairs of benzene molecules in a TMS solution are conveyed by $g(T,x)$, which is defined in terms of the pair correlation function $g(\theta_1, \theta_2; \mathbf{r})$ of the benzene molecules by[18],

$$g(T,x) = \frac{\pi N}{V} \int_0^\infty r^2 dr \int_{-1}^1 d\cos\theta_r \int_{-1}^1 d\cos\theta_{1,2} \left(P_2(\cos\theta_{1,2}) g(r,\theta_r;\theta_{1,2}) \right) \qquad (8)$$

where $\theta_{1,2}$ and θ_r denote the angle of the ring normal of benzene molecule 2 and of the intermolecular vector between molecules 1 and 2, respectively, relative to the ring normal of benzene molecule 1. The temperature and concentration dependence of $g(T,x)$ is a consequence of the fact the pair correlation function $g(r,\theta_r;\theta_{1,2})$ and the density N/V are in principle dependent on the temperature and the concentration.

According to Eq. (6), for vanishing concentration of solute $(x \to 0)$, the measured splitting extrapolates to $\Delta \nu(T, x \to 0) = \Delta \nu_0(T)$, the induced quadrupolar splitting of an isolated benzene molecule in solution and oriented by the spectrometer magnetic field. It is possible to compute a value for $\Delta \nu_0(T)$ at the experimental temperature (298 K) and at the spectrometer field strength $B = 23.4\,\text{T}$, by using a calculated benzene magnetizability tensor with $\chi_{xx} \approx -7.1 \times 10^{-28}\,\text{JT}^{-2}$ (see SI Section 1): we find

15

$S_{yy} = -9.3 \times 10^{-6}$ according to Eq. (7). The calculated value of $\Delta v_0 = 1.38\,\text{Hz}$ is larger than the

observed magnitude of $\Delta v(T, x=1) = 1.15\,\text{Hz}$ for C_6D_6, and this can be attributed to a contribution from

liquid state structure in neat benzene. If pair correlations in the neat liquid constructively reinforce the

magnetic potential energy, the sign of $g(T, x)$ is positive; if those correlations detract from the B-field

alignment, $g(T, x) < 0$. Photinos et al. find that $\Delta v(T, x=1) < \Delta v_0(T)$ in neat benzene at 950 MHz[18]

and that is corroborated at 1 GHz, e.g., contrast the magnitude of the peak splittings in Figures 1A and 3

with those in Figure 1B. The negative value for $g(T, x)$ in neat benzene is due to the dominance of pair

correlations with magnetic-energy-disfavored "T-shaped" dimers (with perpendicular ring planes) that

detract from the magnetic orientational order and lower the value of S_{yy}[18]. For a dilute solution of

C_6D_6 dissolved in TMS (Figure 1B) the magnitude of $|\Delta v| = 1.40\,\text{Hz}$ observed for the satellite doublets

is in good agreement with the calculated value of $\Delta v(T, x=0) = \Delta v_0 = 1.38\,\text{Hz}$. Note, however, that the

difference, $\Delta(\Delta v) = 0.10 \pm 0.01\,\text{Hz}$, between the observed splittings from the ^{13}C satellite doublets and

that of the central doublet is independent of benzene concentration[18] suggesting that its origin is

intramolecular.

3.3 The difference between the observed splittings from the ^{13}C satellite doublets $\Delta v'$ and that of the central doublet Δv in spectra of C_6D_6.

Initially a difference between the coupling constant q_{CD} for deuterium bonded to ^{12}C and ^{13}C, i.e.,

different C—D bond lengths[19–21], was considered to be a potential source of $\Delta(\Delta v)$. We also

considered the effect of a single ^{13}C on the molecular magnetizability tensor and its putative influence

on the molecular order tensor (see SI Section 1). However, this difference vanishes for the proton

decoupled natural abundance ^{2}H NMR spectrum of neat benzene (Figure 2). For this spectrum the

quadrupolar splitting measured from the ^{13}C satellites and from the central doublet were equal within an

16

experimental error of ±0.02 Hz, and the linewidths were equal within the larger error range of ±0.1 Hz

(see Table 2).

Table 2 Resonances of the ^{2}H NMR spectrum of ^{1}H-decoupled C_6H_6.

position (Hz)	width (Hz)	splitting (Hz)
1094.86	0.66	1.15
1093.71	0.64	
1083.11	0.66	1.14
1081.97	0.67	
1070.60	0.69	1.12
1069.48	0.61	

In summary, the difference $\Delta(\Delta\nu)$ in the splittings observed in Figure 1A derived from indirect and

residual dipolar couplings in neat C_6D_6 where the envelope of the unresolved fine structure for the

central doublet led to an apparent difference between the satellite splittings and that of the central

doublet. Fortuitously, the envelope of the fine structure in the satellite doublets was an excellent

approximation to the actual quadrupolar splitting. In the following sections a detailed analysis of the

contributions of these residual interactions to the ^{2}H NMR spectra of benzene as well as a novel 2D

measurement of the sign of $\Delta\nu$ is described.

The simulations of the ^{13}C satellite spectra in the ^{2}H NMR spectrum of C_6D_6 with one ^{13}C in the ring

show that the fine structure of the center peak of the triplet is different for the two sign combinations but

it is masked by the strong doublet of C_6D_6 (See SI Section 2). The splittings of the outer components of

the triplet appear to be the same for the two sign combinations. Thus no confirming information can be

derived from the splittings of the ^{13}C satellite doublets.

3.4 Determination of the relative signs of $^1J_{CD}$ and q_{CD} by a 2D correlation experiment

The ^{2}H-{^{1}H} spectrum of deuterium at natural abundance in C_6H_6 gives unambiguously the magnitude of the field-induced quadrupolar splitting $\left|\Delta \nu^{obs}\right| = 3q_{CD}/2$, but not its sign. The absolute sign of a deuterium splitting is unequivocal for an ordered sample whenever the order parameter S_{CD} is greater than ½. In such a case S_{CD} must be positive, and so too is the deuterium splitting. The sign is in doubt only when $\left|S_{CD}\right| < \frac{1}{2}$. The latter is the case for "probe" molecules partially oriented in deformed polymeric elastomers or gels[22] and the field-induced ordering reported herein. In the former the sign of the residual couplings of the probe is dictated by a combination of transient collision complexes and excluded volume interactions between the probe and the partially oriented polymer. In the latter case of liquid benzene under the biasing influence of the spectrometer magnetic field, its coupling constant signs may be inferred from theory via Eq. (1). However even in this case it is in general better to obtain this important sign information directly from an experiment as subtle intermolecular correlations ("liquid state structure") may overwhelm the anticipated field-induced ordering for an isolated molecule.

The ability to detect the spectrum of the ^{13}C – ^{2}H fragment makes it possible, in theory, to determine the connectivity between the six nuclear spin states. The nuclear spin Hamiltonian, $\hat{H}$, acting on the ^{13}C – ^{2}H spin system is, in units of Hz:

$$\hat{H} = -\nu_D \hat{I}_z - \nu_C \hat{S}_z + J_{CD}\hat{I}_z \hat{S}_z + \Delta\nu\left(3\hat{I}_z^2 - 2/6\right) \qquad (9)$$

This yields six spin energy levels, and adding a constant factor of $\Delta\nu/3$ to each gives

$$E = -m_D \nu_D - m_C \nu_C + \tfrac{1}{2}m_D^2 q_{CD} + m_D m_C J_{CD} \qquad (10)$$
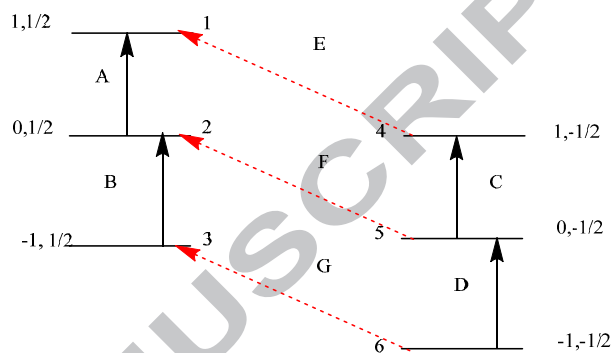
The energy levels are:

Energy levels

	m_D	m_C				
1.	1	½	$-\nu_D$	$-\tfrac{1}{2}\nu_C$	$+\tfrac{1}{2}\Delta\nu$	$+\tfrac{1}{2}J_{CD}$
2.	0	½		$-\tfrac{1}{2}\nu_C$		
3.	-1	½	ν_D	$-\tfrac{1}{2}\nu_C$	$+\tfrac{1}{2}\Delta\nu$	$-\tfrac{1}{2}J_{CD}$

18

4. 1 $-\frac{1}{2}$ $-\nu_D$ $\frac{1}{2}\nu_C$ $+\frac{1}{2}\Delta\nu - \frac{1}{2}J_{CD}$

5. 0 $-\frac{1}{2}$ $\frac{1}{2}\nu_C$

6. -1 $-\frac{1}{2}$ ν_D $\frac{1}{2}\nu_C$ $+\frac{1}{2}\Delta\nu + \frac{1}{2}J_{CD}$
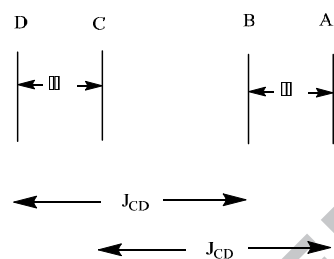
The allowed transitions are:

Transitions

A. $E_2 - E_1$ $\nu_D - \frac{1}{2}\Delta\nu - \frac{1}{2}J_{CD}$

B. $E_3 - E_2$ $\nu_D + \frac{1}{2}\Delta\nu - \frac{1}{2}J_{CD}$

C. $E_5 - E_4$ $\nu_D - \frac{1}{2}\Delta\nu + \frac{1}{2}J_{CD}$

D. $E_6 - E_5$ $\nu_D + \frac{1}{2}\Delta\nu + \frac{1}{2}J_{CD}$

E. $E_4 - E_1$ $\nu_C - J_{CD}$

F. $E_5 - E_2$ ν_C

G. $E_6 - E_3$ $\nu_C + J_{CD}$
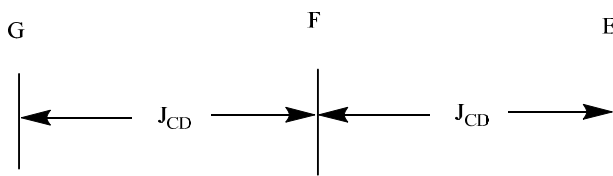
The spectra are:

Deuterium spectrum   Carbon spectrum

The connectivity of the peaks in the ^{13}C and ^{2}H spectra depends on the relative signs of J_{CD} and $\Delta\nu$, and this information has been determined by applying the 2D heteronuclear experiments whose pulse sequences are shown in Figure 3.

The results of applying these pulse sequences to a sample of C_6D_6 at a concentration of 3% v/v in TMS are shown in Figure 4, and it was deduced that the spectra obtained are consistent with $\Delta\nu$ having the same sign, positive, as $^{1}J_{CD}$. This conclusion was tested by applying two validation methods. The first

was to predict the effect of the pulse sequences on the ^{2}H – ^{13}C spin system using the Product Operator method [23] as described in SI Section 4. The second validation process was to simulate the effect on the same spin system using the pulse sequences employed in the experiments with the simulation program NMRSIM.   This produced the simulated 2D QUASI spectra shown in Figure 4 (For details see SI Section 5).

4. Conclusions

The difference between the deuterium quadrupolar splitting observed for the central resonance of benzene-d$_6$ and that derived from the ^{13}C satellite doublets, $\Delta(\Delta\nu)$, is due to unresolved fine structure contributions to the respective resonances. The envelope of the central doublet is distorted and simulations of that envelope yield an apparently smaller splitting than similar fits to the satellite doublet envelope. Efforts to rationalize the observed value of $\Delta(\Delta\nu)$ led to the development of an experiment to observe the induced splitting $\Delta\nu$ free from these distortions. This involved recording the spectra of ^{13}C coupled to ^{2}H nuclei in a sample of benzene, with both nuclei present at natural abundance.   A direct determination of the relative signs of J_{CD} and $\Delta\nu$ by using 2D QUASI-experiments was made, thereby establishing the absolute sign of a deuterium quadrupolar splitting for the first time. The determined positive sign for $\Delta\nu$ is consistent with the magnetic field biasing of an isolated benzene molecule—the magnetic energy of the aromatic ring lowest for configurations where the C$_6$ axis is normal to the field.

Acknowledgements

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Graphical
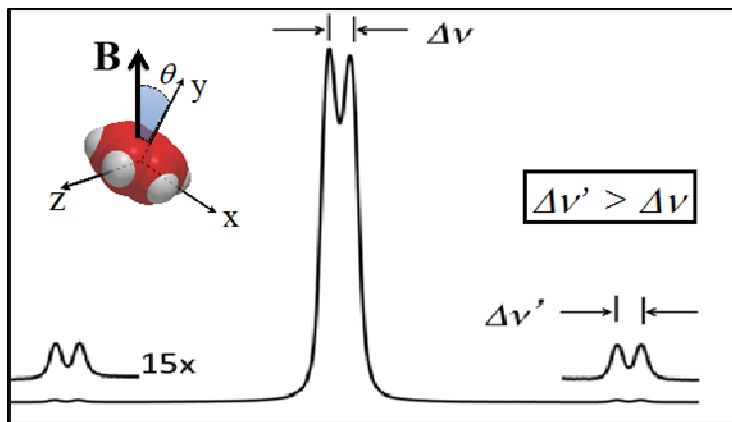
Highlights

- Field-induced deuterium quadrupolar splittings at 1 GHz
- C-13 satellites
- Natural abundance deuterium
- Sign determination of quadrupolar splittings