

A Simple but Accurate Method for Measuring Deuterium Chemical Shifts Relative to the Corresponding Proton Shifts

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The ^2H field/frequency lock commonly found on F.T. n.m.r. spectrometers provides a simple but precise method for the measurement of deuterium chemical shifts relative to the corresponding proton shifts; results are reported for a number of systems, and appreciable isotope effects are observed with non-hydrogen bonded protons.

As expected, ^2H chemical shifts are normally very similar to the corresponding ^1H shifts.^{1†} Most F.T. n.m.r. spectrometers

† Protons involved in strong hydrogen bonds, however, show quite large isotope shifts, which can give valuable information concerning the shape of the hydrogen bond potential function.²

possess a ^2H field/frequency lock, which uses a second fixed and extremely stable radio frequency. This provides a very simple but accurate method for the measurement of $\delta^1\text{H} - \delta^2\text{H}$ ($\Delta\delta$) in a variety of compounds. If the ^2H lock is applied to CD_3COCD_3 (containing a small amount of $\text{CD}_3\text{COCHD}_2$) then the resonance frequency for the centre line of the quin-

tuplet in the ^1H spectrum of $\text{CD}_3\text{COCHD}_2$ can be obtained very precisely, and stored in the spectrometer to provide an arbitrary $\Delta\delta$ value of 0.0000 p.p.m. Subsequent measurement of the ^1H spectrum of (for example) the CHCl_3 present in commercial CDCl_3 , with the spectrometer locked onto the CDCl_3 , will then give $\Delta\delta$ for $\text{CHCl}_3\text{-CDCl}_3$.

Since $\Delta\delta$ is measured on the same sample, any possible bulk susceptibility or solvent effects are eliminated, and the observed shifts (in Hz) are $6.5 \times$ greater than those which would be obtained by direct measurement of the ^2H spectrum. For most samples, the reproducibility of $\Delta\delta$ was $\leq \pm 0.0004$ p.p.m. This technique is, of course, restricted to compounds which give a strong and preferably unsplit ^2H resonance. For molecules containing MD_2 and MD_3 groups, a reasonably high isotopic purity is necessary.

The results obtained are given in Table 1. Appreciable isotope shifts are found with non-hydrogen bonded systems.

Table 1. Results obtained from the measurement of deuterium chemical shifts relative to the corresponding proton shifts.

Deuteriated compound	Proton resonance observed	$\Delta\delta^a$ p.p.m.
CD_3COCD_3	$\text{CD}_3\text{COCHD}_2$	(0.0000)
CD_3COCD_3 (10% v/v in CCl_4)	$\text{CD}_3\text{COCHD}_2$	+0.0011
CD_3COCD_3 (323 K)	$\text{CD}_3\text{COCHD}_2$	-0.0010
CDBr_3	CHBr_3	-0.010
CDCl_3	CHCl_3	+0.0167
CD_3CN (298 K)	CHD_2CN	+0.0109
CD_3OD	CHD_2OD	+0.0021
CD_3OH	CD_3OH	+0.0240
CD_3COOD	CHD_2COOD	+0.0078
CD_3COOH	CD_3COOH	+0.122
$(\text{CD}_3\text{CD}_2)_2\text{O}^b$	$(\text{CHD}_2\text{CD}_2)_2\text{O}$	+0.0016
$(\text{CD}_3\text{CD}_2)_2\text{O}^b$	$(\text{CD}_3\text{CHD})_2\text{O}$	+0.0061
C_6D_6	C_6H_6^c (5% v/v)	-0.0394
C_6D_6 (343 K)	C_6H_6^c (5% v/v)	-0.0411
$\text{C}_6\text{H}_5\text{C}\equiv\text{CD}$	$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	-0.0005
D_2O	HDO	-0.0240
D_2O (323 K)	HDO	-0.0198
D_2O (343 K)	HDO	-0.0150
D_2O (363 K)	HDO	-0.0104

^a At 305 K unless otherwise stated. A positive value of $\Delta\delta$ corresponds to relative shielding of the ^2H resonance. ^b The CD_3 resonance will be a quintuplet, and the CD_2 resonance a heptuplet. However, $J(^1\text{H}^2\text{H})$ will be very small (0.164 Hz). ^c The proton chemical shift of C_6HD_5 is 0.0032 p.p.m. downfield of that of C_6D_6 at 308 K.⁵

As a result of the smaller vibrational amplitude, the effective length of a C–D bond is less than that of the corresponding C–H bond. Long range shielding effects will result in a negative contribution to $\Delta\delta$ in C_6D_6 , but a positive contribution in $\text{C}_6\text{H}_5\text{C}\equiv\text{CD}$. The surprisingly large difference in the $\Delta\delta$ values for CDCl_3 and CDBr_3 may be partly due to deshielding resulting from the magnetic anisotropy of the C–X bonds and/or internal electric field effects.³ These contributions will be greater in CDBr_3 than in CDCl_3 , and will be strongly dependent on the C–H(D) bond length. The negative value of $\Delta\delta$ for D_2O and, in particular, the fact that $\Delta\delta$ becomes markedly less negative on raising the temperature suggest, in agreement with other evidence,⁴ that in this system deuterium bonding is stronger than hydrogen bonding. This has been attributed to the lower librational frequency in D_2O as compared with H_2O .⁴

Measurements were made on Bruker WM-250 and Jeol FX 270 spectrometers. A typical sweep width was 100 Hz, with 16 K data points. The spectrometer was initially zeroed on the ^1H resonance of $\text{CD}_3\text{COCHD}_2$ in 99.5% CD_3COCD_3 . After a number of samples had been run, the $\text{CH}_3\text{COCHD}_2$ was remeasured. For this favourable system, any change in $\Delta\delta$ was normally ≤ 0.0001 p.p.m. The (deoxygenated) samples were commercial deuteriated n.m.r. solvents of isotopic purity >99% [98% for $(\text{CD}_3\text{CD}_2)_2\text{O}$], except for CDBr_3 and $\text{C}_6\text{H}_5\text{C}\equiv\text{CD}$, which were prepared in ca. 80% isotopic purity by exchange with $\text{D}_2\text{O}\text{-Na}_2\text{CO}_3$.

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