

TECH NOTE: 22-004

The Appearance of Solvent and Water Signals in ¹H- and ¹³C-NMR Spectra

Abstract

This tech note describes the appearance, in ¹H- and ¹³C-NMR spectra, of the solvents offered for NMR spectroscopy by ZEOCHEM. Data on residual solvent peaks and residual water peaks are given in a table.

HDO

In deuterated NMR solvents, such as CDCl₃, Acetone-d₆ and DMSO-d₆, trace water is inevitable due to the manufacturing process. The starting point for most deuterated compounds is heavy water, D₂O. The deuterium is incorporated into the target molecule via catalytic exchange or direct synthesis. The deuterated compounds are distilled to give highly pure solvents with low residual water. This residual water can contain both protons and deuterons leading to two species, H₂O and HDO, which are visible via ¹H-NMR spectroscopy. D₂O may also be present but is invisible to ¹H-NMR spectroscopy. This was first described for a dilute solution of H₂O and D₂O in acetone in the 1960s.⁽¹⁾ Two non-overlapping signals are observed when the exchange rate between H₂O and HDO is slow on the NMR timescale. They are typically 0.03 ppm apart. The HDO signal is 1:1:1 triplet that is observed at lower frequency than the H₂O singlet and has a ²J_{HD} coupling constant of approximately 1Hz. The exact appearance of the signal depends on the concentration of H₂O and HDO, the temperature of the measurement, and the magnetic field B₀.^(2,3)

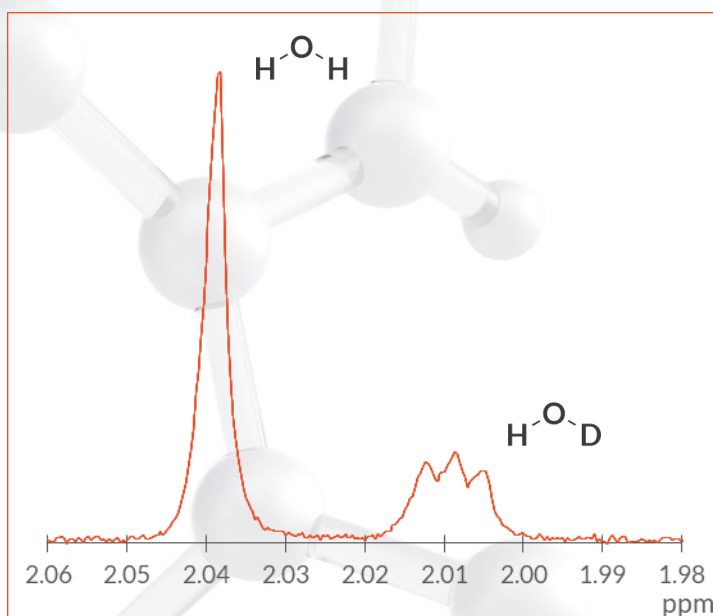


Figure 1: H₂O (left) and HDO (right) peaks in Nitromethane-d₃.

Solvents with Labile Protons/Deuterons

Both acids and alcohols are included in the solvent offering from ZEOCHEM. These contain labile OH/OD moieties which can easily exchange with residual water in the solvent. In practice this means that a separate peak for water is not observed in solvents with a low water content. Additionally, for the acids the chemical shift of the OH/OD will move depending on the concentration, pH, and temperature.

Multiplicity

Deuterium nuclei have a spin of 1. Nuclei coupling to one deuterium nucleus therefore appear as a triplet with an intensity ratio of 1:1:1. Nuclei coupling to two equivalent deuterium nuclei therefore appear as a quintet with an intensity ratio of 1:2:3:2:1. Nuclei coupling to three equivalent deuterium nuclei therefore appear as a septet with an intensity ratio of 1:3:6:7:6:3:1.

References

- (1) J. R. Holmes et al., J. Chem. Phys., 1962, 37, 150-151
- (2) J. Sandström, Dynamic NMR Spectroscopy, Academic Press, 1982
- (3) H.E. Gottlieb et al., J. Org. Chem., 1997, 62, 7512-7515

Solvent		δ - ¹ H (m)	J_{HD}	J_{CH}	δ - ¹ HH ₂ O	δ - ¹ HHDO	δ - ¹³ C (m)	J_{CD}
Acetic Acid-d ₄	CH ₃	2.03 (5)	2.2	128.7			20.04 (7)	19.8
	CO ₂ H	11.59 (1)					178.45 (1)	
Acetone-d ₆	CH ₃	2.05 (5)	2.2	126.1	2.79	2.75	29.84 (7)	19.4
	CO						206.18 (1)	
Acetonitrile-d ₃	CH ₃	1.94 (5)	2.5	133.4	2.11	2.09	1.36 (7)	20.8
	CN						118.34 (1)	
Benzene-d ₆	CH	7.16 (1)		158.3	0.39	0.35	128.04 (3)	24.3
Bromobenzene-d ₅	CBr						122.18	
	CH(2)	7.30 (1)		164.5	1.08	1.05	130.90 (3)	25.3
	CH(3)	6.94 (1)		162.3			129.32 (3)	24.7
	CH(4)	7.02 (1)		164.5			126.14 (3)	24.6
Chlorobenzene-d ₅	CCl						134.21 (1)	
	CH(2)	7.14 (1)		165.2	1.03	1.00	128.27 (3)	25.2
	CH(3)	6.99 (1)		160.9			129.28 (3)	24.7
	CH(4)	6.96 (1)		160.6			125.95 (3)	24.6
Chloroform-d	CH	7.26 (1)		209.4	1.53	1.50	77.02 (3)	31.9
Cyclohexane-d ₁₂	CH ₂	1.38 (b)		124.6	0.84	0.80	26.37 (5)	19.2
Deuterium Oxide	OH	4.76 (1)						
1,2-Dichlorobenzene-d ₄	CCl						132.41 (1)	
	CH(3)	7.19 (1)		138.8	1.35	1.33	130.04 (3)	25.4
	CH(4)	6.94 (1)		145.6			127.20 (3)	24.9
Dichloromethane-d ₂	CH ₂	5.32 (3)	1.0	177.8	1.51	1.48	53.83 (5)	27.2
N,N-Dimethylacetamide-d ₉	CH ₃	1.94 (5)	2.2	126.7			20.76 (5)	19.4
	NCH ₃	2.78 (5)	1.9	138.3	3.52	3.49	33.74 (5)	20.9
	NCH ₃	2.95 (5)	2.0	136.5			36.85 (5)	20.9
	C(O)						170.01 (1)	
N,N-Dimethylformamide-d ₇	NCH ₃	2.74 (5)	1.9	138.6			30.11 (7)	21.0
	NCH ₃	2.91 (5)	1.9	134.8	3.45	3.42	35.21 (7)	20.8
	C(O)H	8.02 (1)		191.5			162.70 (3)	29.3
Dimethyl-d ₆ Sulfoxide	CH ₃	2.50 (5)	1.8	136.8	3.32	3.30	39.43 (7)	21.0
Ethanol-d ₆	CH ₃	1.11 (m)		125.8			17.25 (7)	19.1
	CH ₂	3.55 (b)		140.4	4.49		56.82 (5)	21.5
	OH	5.24 (1)						
1,1,1,3,3,3-Hexafluoro-2-propanol-d ₂ [†]	CH	4.40 (7)		150.5			71.51 (7x3)	22.9
	OH	4.65 (1)						
	CF ₃						128.60 (4)	
Methanol-d ₄	CH ₃	3.31 (5)	1.6	139.7			49.05 (7)	21.4
	OH	4.83 (1)						
Nitromethane-d ₃	CH ₃	4.34 (5)	1.9		2.04	2.01	62.84 (7)	22.4
Pyridine-d ₅	CH(2)	8.73 (1)		177.9			149.92 (3)	27.2
	CH(3)	7.21 (1)		162.1	4.89	4.87	123.52 (3)	29.2
	CH(4)	7.57 (1)		162.2			135.51 (3)	24.8
1,1,2,2-Tetrachloroethane-d ₂	CH	5.98 (1)		181.2	1.58	1.55	73.79 (3)	27.7
Tetrahydrofuran-d ₈	CH ₂	1.72 (b)		131.2	2.44	2.40	25.32 (5)	22.3
	CH ₂ O	3.58 (b)		144.5			67.39 (5)	22.4
Toluene-d ₈	CH ₃	2.09 (5)	2.2	125.5			20.43 (7)	
	CH(1)						137.49 (1)	19.2
	CH(2)	6.98 (1)		155.5	0.37	0.34	128.88 (3)	23.9
	CH(3)	7.09 (1)		157.4			127.98 (3)	24.1
	CH(4)	7.01 (1)		157.8			125.14 (3)	24.3
Trifluoroacetic Acid-d [‡]	CO ₂ H	11.57 (1)					164.31 (4)	
	CF ₃						116.66 (4)	

All spectra were recorded on an Avance III Bruker 300MHz spectrometer at 27°C. All chemical shifts are given in ppm relative to TMS, except deuterium oxide which is relative to TSP-d₄. Observed chemical shifts may change with temperature, concentration, and pH. Complex multiplets are denoted (m), while broad signals are denoted (b). [†]1,1,1,3,3,3-Hexafluoro-2-propanol-d₂ – Coupling to fluorine ³J_{HF} = 5.9Hz, ²J_{CF} = 34.1Hz, and ¹J_{CF} = 281.8Hz.

[‡]Trifluoroacetic Acid-d – Coupling to fluorine, ²J_{CF} = 43.8Hz, and ¹J_{CF} = 283.1Hz.

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