

NMR Solvents

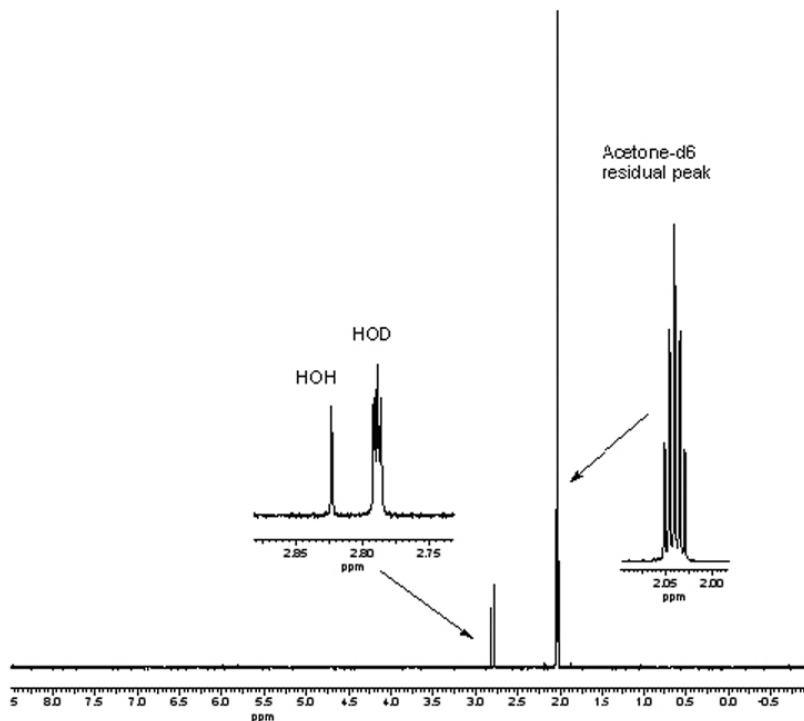
The Observation of "Double Water Peaks" in Deuterated NMR Solvents

Although "double water peaks" in NMR solvents have been observed in proton NMR for decades and it was reported in the NMR literature as early as the 1960s (Holmes et al, J. Chem. Phys., 37, 150,1962), this knowledge is not widely known among all NMR chemists. As a major NMR solvents' producer, Isotec frequently receives questions about "double water peaks" and prepared the following response that summarizes this information.

In deuterated NMR solvents, such as CDCl_3 , Acetone- d_6 , CD_3CN , and $\text{DMSO-}d_6$, trace water is inevitable due to the manufacturing process and solvent storage conditions. Generally speaking, water takes three forms in a deuterated solvent environment: HOH, HOD, and DOD. In the proton NMR spectrum of a pure NMR solvent, both the HOH and HOD peaks are observed, but not the DOD.

In a proton NMR Spectrum, HOH appears as a singlet. However, due to coupling from the ^2D nucleus which has a nuclear spin quantum number $I = 1$, HOD appears as a triplet. The observed splitting $^2J_{\text{HD}}$ of the HOD peak is about 1–2 Hz. The chemical environments of the protons in HOH and HOD are similar, but not identical. Therefore, the HOH and HOD peaks appear to be close in chemical shift, but not overlapped. They are typically 0.03 ppm apart.

Attached is a NMR spectrum shown the HOH and HOD peaks for Acetone- d_6 . The reported chemical shifts and couplings constants are directly measured from the spectrum.



Proton NMR Spectrum of Acetone- d_6 Solvent

NMR Instrument: Varian Mercury 400 MHz.

Acetone- d_6 residual peak appears as a quintet, centered at 2.04 ppm. Peak splitting is due to coupling from two D nuclei with $^2J_{\text{HD}} = 2.11$ Hz. Two carbon- ^{13}C satellite peaks are about 150 Hz apart, barely visible on both sides of Acetone- d_6 residual peak.

H_2O peak appears as a singlet at 2.82 ppm.

HOD peak appears as a triplet at 2.78 ppm. Peak splitting is due to coupling from D nucleus with $^2J_{\text{HD}} = 2.07$ Hz.