

Solid-state NMR of clathrate hydrates at 21.1 T

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Fast developments in NMR instrumentation are of great importance in studies of low- γ , low natural abundance quadrupolar nuclei. Here we report our recent exploration of hydrates with solid-state NMR of nuclei such as ^{131}Xe , ^{83}Kr and ^{33}S at 21.1 T. Until recently these nuclei were completely out of reach for NMR due to their unfavorable properties. We demonstrate that in spite of the experimental difficulties they can be used successfully to sample cavities in inclusion compounds, extending the choice of molecular probes for void spaces.

For nearly 30 years, ^{129}Xe isotope was used extensively as an NMR probe of void space in solids [1,2]. Xenon has a second isotope, ^{131}Xe ($I = 3/2$) that has a promise in providing information on the EFG tensors inside the voids [3]. Figure 1 shows a natural abundance ^{131}Xe NMR spectrum of Xe in dodecasil-3C, an all silica analogue of Str.II hydrate. This phase of DD3C is known to be tetragonal, although the detailed structure is not yet known. The ^{131}Xe NMR spectrum, however, gives direct indication on the cages symmetries. The signal from xenon in the large cage at $\delta_{\text{iso}}=92$ ppm shows no asymmetry due to nearly spherical nature of the large cage. The signal for Xe in the small cage demonstrates a substantial second-order quadrupolar broadening: $C_Q=6.45$ MHz, $\eta_Q=0.30$, $\delta_{\text{iso}}=260$ ppm, indicating significant distortion of the cage from axial symmetry.

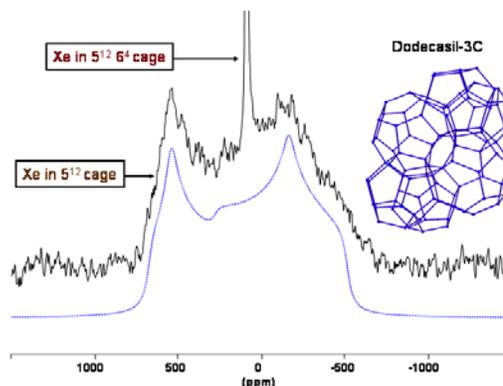


Figure 1: ^{131}Xe NMR of Xe in clathrasil DD3C.

Krypton atom is similar to xenon in size and can form a wide variety of inclusion compounds. Due to its unfavorable NMR properties ^{83}Kr NMR is rarely used [4,5]. Unlike xenon, which is mainly a Str.I hydrate former, krypton forms Str.II hydrates. The ^{83}Kr stationary powder spectra of two Kr hydrates, one is pure hydrate formed by interaction with D_2O ice, and another one is a mixed hydrate prepared by interacting krypton with THF- D_2O hydrate, are shown in Figure 2. In both cases two signals with different relative intensities are observed. The first signal at about 45 ppm shows very little asymmetry, and assigned to Kr residing inside very symmetrical $5^{12}6^4$ cages. The

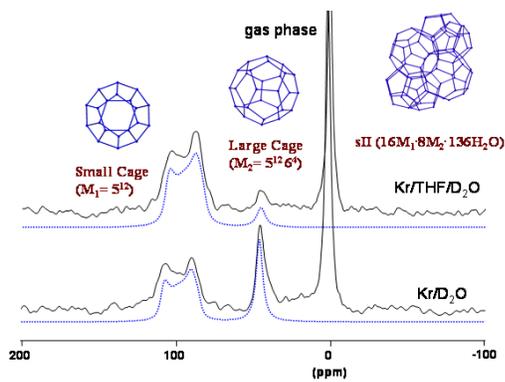


Figure 2: ^{83}Kr NMR spectra of krypton Str.II hydrates obtained at $T=260\text{K}$.

second signal with $\delta_{\text{iso}}=99.5$ ppm demonstrates the lineshape defined by the second order quadrupolar interaction. The signal originates from krypton trapped in the small 5^{12} cage. The coupling constants and quadrupolar asymmetry parameters are identical for both spectra, $C_Q=1.96$ MHz and $\eta_Q=0.17$. The observed non-zero EFG is in agreement with non-spherical symmetry of the small cages, while the value of η_Q indicates a departure of the cage symmetry from the axial characteristic for ideal Str.II hydrate. Overall the obtained ^{83}Kr data show convincingly that in studies of inclusion compounds this nucleus can nicely complement both ^{129}Xe and ^{131}Xe and thus extends the limits of noble gases NMR.

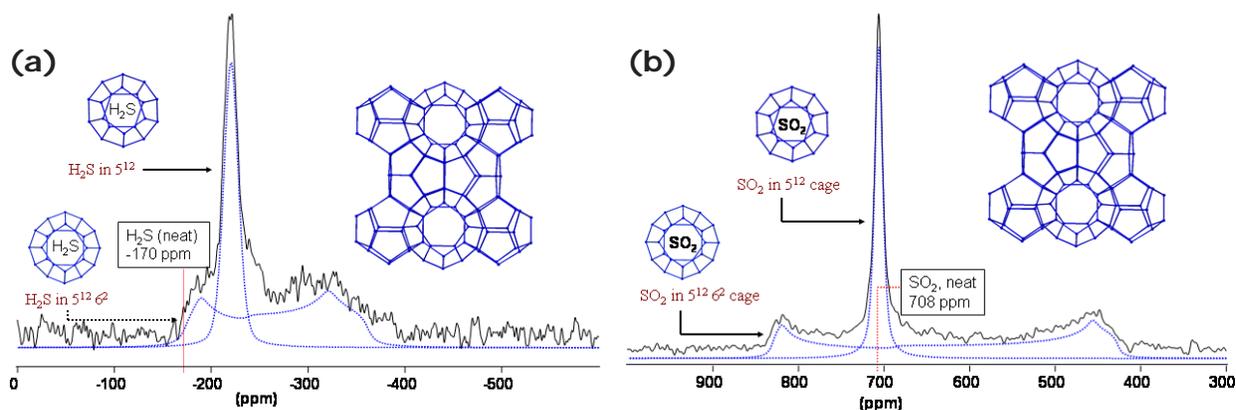


Figure 3: ^{33}S NMR static spectra of Str.I hydrates of H_2S (a) and SO_2 (b) obtained in powder samples at $T=260\text{K}$.

There are no previous reports on ^{33}S NMR in hydrates, which is not surprising given the difficulties of this low- γ , low natural abundance nucleus. Sulfur-containing guests, with H_2S , SO_2 , and SF_6 being the most common, form a broad range of inclusion compounds with potential practical applications. H_2S is a typical Str.I hydrate former, and the stationary solid-state ^{33}S NMR spectrum of the H_2S hydrate shows all the expected features (Figure 3a). The isotropic signal with $\delta_{\text{iso}}=-221$ ppm is assigned to H_2S inside the nearly spherical 5^{12} cages of Str.I hydrate. The second signal features a substantial anisotropy due to a non-zero EFG and corresponds to H_2S in the large $5^{12}6^2$ cages: $\delta_{\text{iso}}=-238$ ppm, $C_Q=2.42$ MHz and $\eta_Q=0.2$. For both cage types we see a significant deviation of δ_{iso} from -170 ppm observed in a pure H_2S . This can be a cage size effect, e.g. as also observed for $^{13}\text{CH}_4$ and ^{129}Xe in large and small cages of Str.I hydrate.

Sulfur dioxide SO_2 is another known Str.I hydrate former. Its ^{33}S spectrum demonstrates the features similar to what was observed for the H_2S hydrate (Figure 3b), with the scaled up quadrupolar interactions in the large cage. The SO_2 in the small cage shows an isotropic signal with $\delta_{\text{iso}}=706$ ppm, which is very close to the chemical shift of 707 ppm in a pure SO_2 . For the SO_2 in the large cage the parameters are $\delta_{\text{iso}}=689$ ppm, $C_Q=3.76$ MHz and $\eta_Q=0.05$. For this hydrate η_Q is indicative of an almost axial symmetry in the large cage. For SO_2 in the large cage it is interesting to see a substantial deviation from the isotropic CS in the free SO_2 . This could be a sign of rather strong interaction between the guest and the water molecules of the host lattice or a strong cage size effect.

We demonstrated that solid-state NMR of low- γ quadrupolar nuclei can be an informative tool in studies of inclusion compounds. Although the experimental approach is not always straightforward, such nuclei as ^{33}S , ^{83}Kr , ^{131}Xe , have a significant potential in clathrate hydrate research. Working at the field of 21.1 T provides a substantial sensitivity boost, and reliable spectra can be often obtained in a reasonable time. The results show convincingly that these previously under-employed nuclei can provide important new information tools to complement more traditional nuclei such as ^1H , ^2H , ^{13}C , ^{19}F , ^{129}Xe and thus extend the limits of NMR in inclusion materials research.

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