

# Solid-State NMR of $(\text{CdSe})_{13}(\text{Propylamine})_{13}$

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## Abstract and Introduction:

Cadmium selenide (CdSe) nanoparticles exhibit unique electrical properties due to quantum confinement of electrons, showing potential for wide-ranging nanomaterial applications [1]. A constituent of these nanoparticles are so-called “magic number clusters” of CdSe, which are stable molecular units that can be synthesized with high purity. It is not known what makes these specifically numbered clusters stable and what the actual structure is. Samples of  $(\text{CdSe})_{13}(n\text{-propylamine})_{13}$ , one of these magic number clusters capped with *n*-propylamine ligands, were synthesized in near-purity and in quantities suitable for NMR spectroscopy by the Buhro lab at Washington University [2]. All NMR studies were performed in Sophia Hayes’s lab.

## Experimental Background:

For this project we focused on the NMR active nuclei  $^{113}\text{Cd}$ .  $^{113}\text{Cd}$  is a very difficult nucleus to find and acquire signal due to a relatively slow precession frequency (9.4 MHz/Tesla), low isotopic abundance (12.26%), a very large chemical shift range (> 3000 ppm), and exceptionally long longitudinal relaxation times ( $T_1$  values over three hours are not uncommon). The other NMR active nuclei in the cluster are  $^{111}\text{Cd}$  and  $^{77}\text{Se}$ , which are both less sensitive than  $^{113}\text{Cd}$ . On average, only one of each NMR active nuclei will be in the nanocluster, which leaves 23 atoms with spin zero. The absence of spin-zero nuclei has the effect of nullifying any strong dipolar interaction within the cluster and lengthening the relaxation time. Further elongating the relaxation time is the lack of a repeating crystal structure with strong phonon modes to mediate spin flips. The lack of repeating crystal orientation is due to each cluster being encapsulated in propylamine ligands. Even with these experimental realities, we were able to acquire high quality  $^{113}\text{Cd}$  NMR data on the  $(\text{CdSe})_{13}(n\text{-propylamine})_{13}$  nanoclusters.

## Experimental Procedure:

All solid-state NMR experiments were performed at room temperature on a 7T (300 MHz) superconducting magnet using a 4 mm MAS Chemagnetics probe tuned to 65.45 and 294.97 MHz for  $^{113}\text{Cd}$  and  $^1\text{H}$ , respectively. A 4 mm zirconium rotor, Tecmag Apollo spectrometer, and 1 kW amplifiers on  $^1\text{H}$  and  $^{113}\text{Cd}$  channels were used universally.

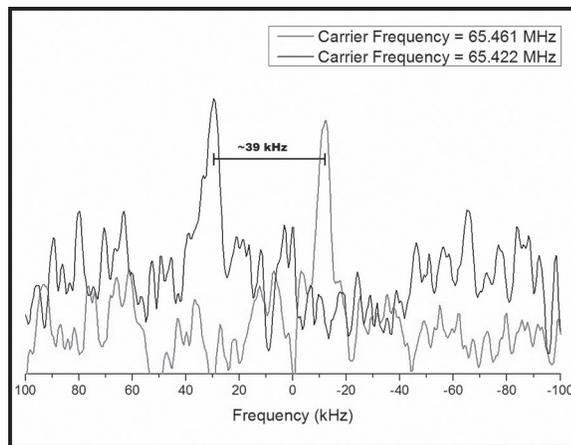


Figure 1:  $^{113}\text{Cd}$  DEFT NMR of  $(\text{CdSe})_{13}(\text{propylamine})_{13}$  at differing carrier frequencies.

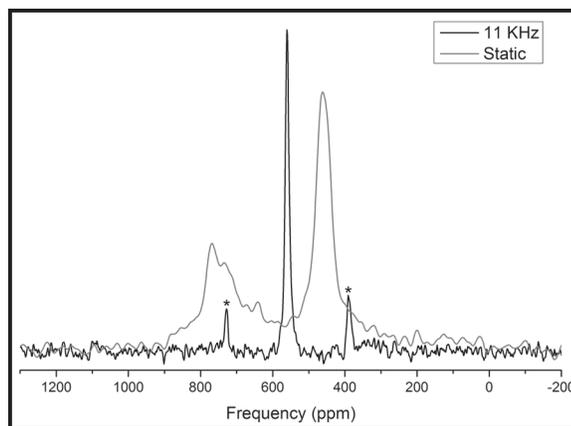


Figure 2: Static CP and 11 kHz CPMAS  $^{113}\text{Cd}$  NMR of  $(\text{CdSe})_{13}(\text{propylamine})_{13}$ .

Three types of NMR pulse sequences were used to excite and observe the  $^{113}\text{Cd}$  spins: “90-acquire,” “Driven Equilibrium Fourier Transform” (DEFT), and “Cross-Polarization Magic Angle Spinning” (CPMAS).

The 90-acquire pulse sequences were used to acquire reference spectra and to optimize equipment. DEFT is a pulse sequence that can reduce the effects of long  $T_1$  relaxation times by realigning nuclear spins back along the main magnetic field after observing the NMR signal. CPMAS is a technique developed by a researcher from Washington University [3] that cross-polarizes the  $^{113}\text{Cd}$  with the  $^1\text{H}$ , which allows the use of the  $^1\text{H}$  relaxation time (typically much faster than  $^{113}\text{Cd}$ ) and results in a large signal enhancement of the  $^{113}\text{Cd}$ . “Magic angle spinning” refers to rapid rotation ( $> 10$  kHz) of the sample about  $54.7^\circ$  relative to the applied magnetic field.

Previous work would indicate that (CdSe) would have a chemical shift that is roughly similar to previous CdSe NMR spectroscopy, such as in the case with Berrettini et al. [1] working with 2 nm CdSe nanoparticles and having a chemical shift of roughly 600 ppm referenced to 0.5M  $\text{Cd}(\text{NO}_3)_2$  solution, so initial signal hunting focused largely on the region from 300-800 ppm from our reference, 0.1M  $\text{Cd}(\text{ClO}_4)_2$ .

After pulse optimization and all reference spectra acquisition, our efforts were focused on finding direct  $^{113}\text{Cd}$  signal using DEFT. Figure 1 shows results from two DEFT experiments with different excitation frequencies which proved the validity of the signal at 458 ppm. This result ensured we had found the  $^{113}\text{Cd}$  signal and told us the frequency range to focus our CPMAS experiments.

### Results and Discussion:

DEFT experiments proved to be too long to acquire acceptable signal to noise and we turned to CPMAS. Our goal was to use the  $^1\text{H}$  magnetization on the propylamine ligands to polarize the  $^{113}\text{Cd}$  and then observe the  $^{113}\text{Cd}$  signal. This worked exceptionally well and the results of this experiment are shown in Figure 2.

As  $^{113}\text{Cd}$  is a spin  $\frac{1}{2}$  nuclei, each unique chemical site should result in only one peak. The CPMAS results while spinning indeed indicate only a single site. It is known that different parts of a powder pattern line CP differently depending on their orientation with respect to the applied magnetic field [4] and this is why the static CPMAS result has two peaks. Longer contact times result in the expected static lineshape of an axially symmetric site.

If the  $(\text{CdSe})_{13}$  cluster has a central Cd, we would expect it to have a different chemical shift than the outer cadmiums. However, the ability for magnetization to transfer from a  $^1\text{H}$  to a central Cd would be severely hampered by distance from surface protons to the center, and spin diffusion through the virtually spin-free nanocluster results in a very weak CPMAS signal. Thus, our conclusion at this juncture in the research is we have, for the first time, successfully observed at least one unique cadmium site and further work, such as  $^{77}\text{Se}$  NMR, needs to be done to complete the NMR study of this material.

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### References:

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