^{133}Cs Nuclear Quadrupole Coupling in $CsOH \cdot H_2O$ Through the 232 K Transition

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The ^{133}Cs NMR has been observed in a pseudosingle crystal of $CsOH \cdot H_2O$ in all three solid state phases. The ^{133}Cs quadrupole coupling constant varies almost linearly with temperature throughout the three phases ($e^2qQ/h = 156 \pm 1$ kHz at 193 K, 101 ± 1 kHz at 295 K, 36.4 ± 0.5 at 410 K). There is also a discontinuous change of (13 ± 2) kHz in the cesium coupling at the monoclinic to Hex β transition. In contrast to previous neutron scattering experiments, which indicate significant atomic motion in the Hex α phase, the temperature dependence of the proton NMR indicates that proton diffusion occurs in the Hex β phase.

Introduction

$CsOH \cdot H_2O$ is known to have at least three different solid state phases [1, 2]. Below 232 K, the structure is strictly monoclinic. However, with respect to cesium and oxygen positions, the monoclinic phase deviates only slightly from a hexagonal crystal structure. Between 232 K and 340 K, the crystal structure is hexagonal and distinct groups of OH^- and H_2O atoms have been identified [1]. This phase will be referred to as Hex β. Above 340 K, the crystal structure remains hexagonal but there is only one unique hydrogen site, and separate OH^- and H_2O groups cannot be distinguished [2]. This phase will be referred to as Hex α. $CsOH \cdot H_2O$ finally melts at 499 K [3].

By observing the ^{133}Cs and ^1H nuclear magnetic resonances (NMR) in these three phases of $CsOH \cdot H_2O$, evidence for significant atomic motion in the monoclinic and Hex β phases was revealed. The results presented here were part of a large NMR study of alkali metal hydroxides [4, 5] and in particular, a study of anhydrous CsOH [6].

Experimental

The ^1H and ^{133}Cs broadline NMR spectra were recorded using a spectrometer of the Torgeson design operating in the non-adiabatic superfast mode [7]. The desired sample temperature was achieved using a gas flow system with a thermocouple temperature controller. Temperature stability was better than ± 1 K. Dry nitrogen gas was used to avoid H_2O and CO_2 contamination. Signal averaging varied from 15 to 60 minutes for each spectrum. Sample containers were made of Teflon.

The samples were taken from a supply of "nominal CsOH" received from ROC/RIC Chemical Company (metal purity 99.9%). Most of this material from ROC/RIC was in the form of large planar pieces averaging in size of about $0.5 \times 2 \times 2$ cm. The initial investigation of the ^{133}Cs NMR of these "as received" samples showed that the resonance was dependent on the angle between the normal of the plane of the sample and the magnetic field, in a manner which was characteristic of a first order quadrupole coupled resonance for a single crystal. Subsequent powder X-ray diffraction analysis yielded a hexagonal structure with $a = 4.5372(2)$ Å and $c = 4.4440(4)$ Å at 295 K which agreed with previous work on $CsOH \cdot H_2O$ [1]. Since the "as received" samples appeared to be polycrystalline, the samples must have been strongly textured. That is, all the grains had their c axes aligned parallel, and the basal planes of each grain were lying in the plane of the sample. Such a strongly textured sample could yield single crystal characteristics in NMR if the asymmetry parameter was zero. A zero asymmetry parameter is consistent the hexagonal symmetry of the ^{133}Cs site at room temperature and thus these samples were referred to as "pseudosingle crystals".

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The samples used for proton NMR were in the form of powder obtained from the same chemical supply.

Results

An NMR spectrum of $^{133}CsOH \cdot H_2O$ at 300 K is shown in Fig. 1 for the c axis parallel to the magnetic field-maximum splitting. For spin $I = 7/2$, seven transitions were expected and all were observed. The maximum splitting, from the (7/2 to 5/2) transition to the ($-5/2$ to $-7/2$) transition, is 42.1 ± 0.4 kHz. A factor of 7/3 is used to obtain the quadrupole coupling constant ($QCC = e^2 q Q/h$) from the maximum splitting for an $I = 7/2$ nucleus [8]. Thus QCC is 98.2 ± 1.0 kHz at 300 K.

The ^{133}Cs spectra were recorded from 180 K to 450 K. The sample was rotated periodically to check that the maximum splitting was being observed. A graph of the ^{133}Cs quadrupole coupling constant is given in Figure 2. Generally, QCC increases almost linearly with decreasing temperature. At 236 K, QCC changes discontinuously by 13 ± 2 kHz. This change marks the Hex β-monoclinic transition which was reported previously to be at 232 K. In the monoclinic phase, QCC continues to increase with decreasing temperature. In addition, much lower r.f. power was necessary to avoid saturation of the NMR spectra. Thus qualitatively, the longitudinal relaxation time T_1, is longer in the monoclinic phase than in the Hex β phase. Below room temperature, the results were completely reproducible with all samples. Above room temperature, QCC decreases with increasing temperature up to about 450 K at which point the splitting of the ^{133}Cs resonance could not be resolved. The samples taken above 400 K did not give reproducible results when measured again at room temperature. This was probably the result of dehydration of the $CsOH \cdot H_2O$ samples. Thus, although the slope of the temperature dependence shown in Fig. 2 appears to change slightly near 340 K, the Hex β to Hex α transition, the lack of confidence in the higher temperature data points limits the significance of this change.

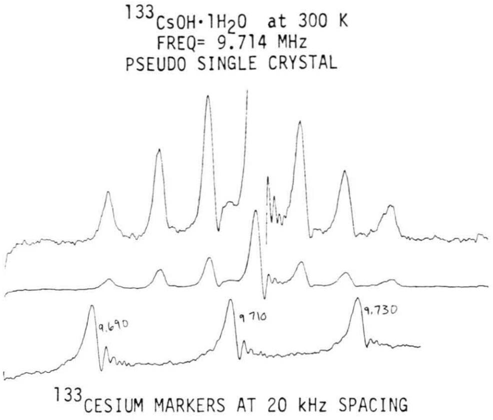

Fig. 1. ^{133}Cs NMR of a pseudosingle crystal of $CsOH \cdot H_2O$ recorded at 9.714 MHz and at 300 K. The c-axes are parallel to the magnetic field.

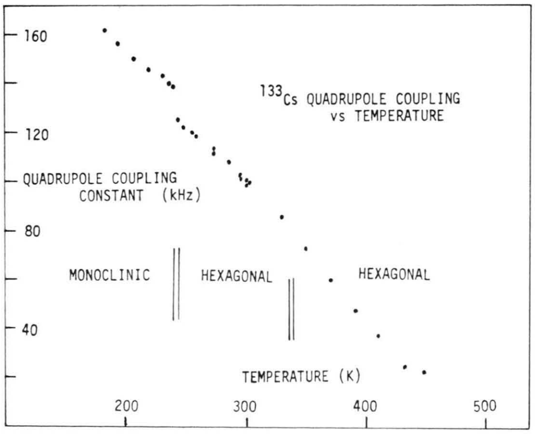

Fig. 2. ^{133}Cs quadrupole coupling constant in the three phases of $CsOH \cdot H_2O$. The coupling constants were determined from first-order quadrupolar perturbed NMR.

The proton NMR of $CsOH \cdot H_2O$ was measured from 77 K to 300 K and the results are presented pictorially in Figure 3. At 300 K, the resonance is narrow and its width is determined by the inhomogeneity of the magnetic field. Generally, the resonance width increases with decreasing temperature. It was difficult to determine whether or not an abrupt change occurs at the Hex β to monoclinic transition near 232 K. Again, qualitatively, the proton NMR T_1 increases significantly with decreasing temperature. At the bottom of Fig. 3, the proton NMR spectrum for $CaSO_4 \cdot 2H_2O$ is given for comparison. This is the spectrum for any rigid, isolated H_2O molecules (Pake pairs).

Discussion

One mechanism that can cause variations in NMR parameters with temperature is atomic motion. It has been reported previously that hydrogen atoms hop between two equivalent sites at lattice vibration rates in the Hex α phase [2]. Also, fixed hydrogen positions, either H_2O or OH^-, have been resolved in the Hex β phase and are presumably present in the monoclinic phase [2]. However, NMR parameters can be affected by atomic motion which is slower than the vibrational rates in the Hex α phase, such as atomic diffusion. For example, the nominally anhydrous alkali metal hydroxides have significant proton conductivity which affects the proton NMR [4, 9] and it is not unreasonable to expect the same for the monohydrates.

Thus it is likely that the decrease in proton linewith and T_1 with increasing temperature is due to motional narrowing caused by proton diffusion. This is probably not the case for the ^{133}Cs NMR. From the proton NMR, the conductivity effects are small below 200 K as the proton NMR changes less rapidly with temperature. Because the magnitude of the ^{133}Cs quadrupole interaction (QCC) is near 150 kHz and the magnitude of the proton interaction (linewidth) is only about 40 kHz at 200 K, the ^{133}Cs NMR is expected to reach its static value at a temperature higher than that for the proton NMR. Yet, at 180 K, the ^{133}Cs QCC still changes at a constant rate with no sign of reaching a static value. Thus, the ^{133}Cs QCC is probably not entirely due to proton diffusion.

Initially, it was surprising that a single crystal pattern for the ^{133}Cs NMR could be observed for the textured samples in the monoclinic phase and that the samples did not noticeably degrade when crossing back and forth through the monoclinic-Hex β transition. This result emphasizes the fact that the monoclinic phase is indeed a minor modification of the Hex β phase and also that the asymmetry parameter must be small (experimentally zero) in the monoclinic phase.

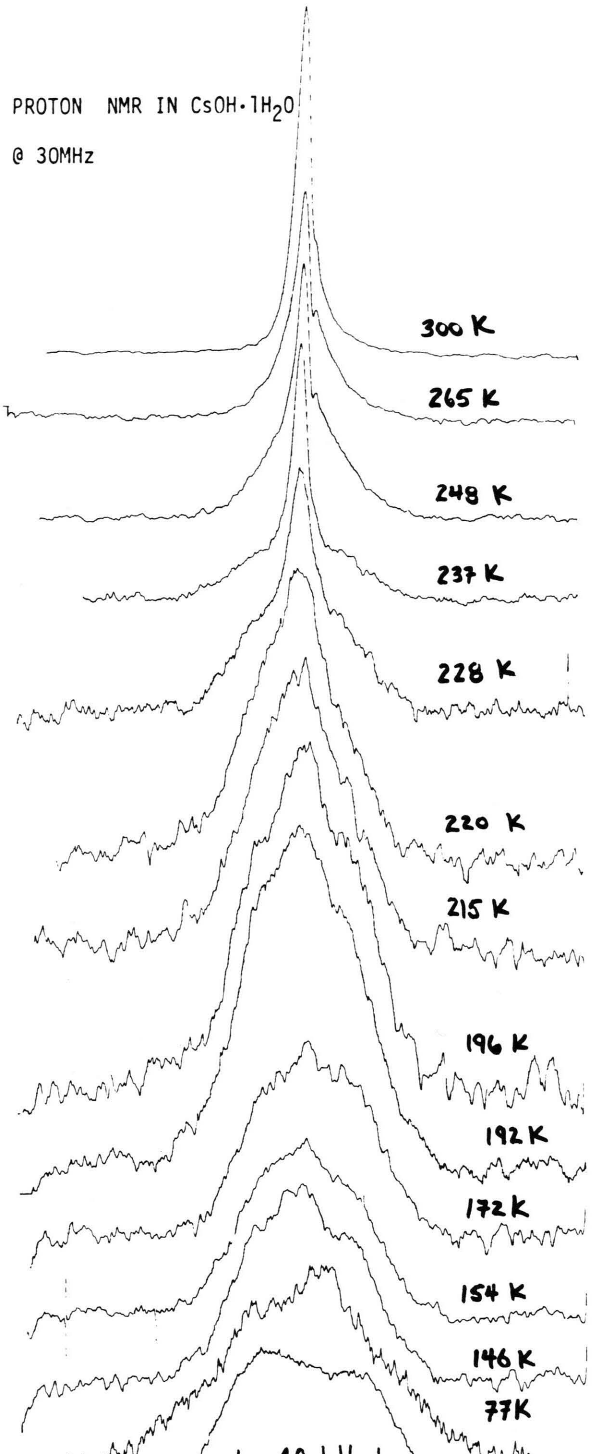

Fig. 3. The temperature dependence of proton NMR in $CsOH \cdot H_2O$ recorded at 30 MHz. For comparison, the spectrum of $CaSO_4 \cdot 2\,H_2O$ shows the characteristic proton NMR for rigid isolated water molecules – a Pake doublet.

An experiment that may answer some of the questions left unanswered by the results presented here, is an NMR study of the deuterium analog $CsOD \cdot D_2O$. This would enable the actual proton (deuteron) sites to be identified by their deuterium quadrupole couplings.

Conclusions

The ^{133}Cs and ^{1}H NMR spectra have been studied as a function of temperature for a pseudo-single crystal of $CsOH \cdot H_2O$. The ^{133}Cs quadrupole coupling decreases with increasing temperature and shows a discontinuity between the monoclinic and Hex β phases. The change in T_1 between these phases indicates an additional relaxation mechanism, such as atomic diffusion, which affects the ^{133}Cs NMR in the Hex β phase. However, the variation of the ^{133}Cs QCC with temperature, which continues down to 180 K, must be due to a different mechanism. The decrease in the proton NMR line-width with increasing temperature is likely due to motional narrowing caused by proton diffusion.

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