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Sodium nuclear quadrupole interactions in sodium hydroxide.

I. The orthorhombic phase

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Using nuclear magnetic resonance techniques the sodium nuclear quadrupole couplings have been observed in anhydrous NaOH and in the monohydrate. They have the values, respectively, of $e^2q_{zz}Q/h = 3.54 \pm 0.08$ MHz, $\eta = 0$ and $e^2q_{zz}Q/h = 2.11 \pm 0.04$ MHz, $\eta = 0.62 \pm 0.03$ at 293 K. The fact that $\eta = 0$ for the anhydrous salt agrees with a lattice gradient calculation although it differs from previous Zeeman quadrupole resonance experiments.

INTRODUCTION

NaOH has three known solid state phases below the melting temperature of 592 K.¹⁻³ Below 514 K the material is orthorhombic: Bmmb $Z = 4$. Although $a = b = 3.401$ Å at room temperature, the crystal lacks a fourfold axis about $c = 11.382$ Å and is therefore pseudotetragonal. At 514 K the material transforms, with practically zero enthalpy change, to a monoclinic structure which is thought to be a ferroelastic structure.⁴ At 566 K, NaOH transforms to a plastic cubic phase⁵ and finally melts at 592 K.

The reasons for the interest in NaOH are twofold⁶; the lower phase transition at 514 K serves as a model for an elastic phase transition with a one-dimensional order parameter. In the monoclinic and cubic phases, the dynamics of the OH⁻ dumbbell are of relevance for the understanding of molecular crystals, plastic crystals and, in general, orientational disorder. This behavior is mimicked by other $M^+(XY)^-$ compounds such as KCN, NaCN, NaSH, and CsSH.

Here we report the interesting symmetry features of the NaOH pseudotetragonal structure and how they relate to the sodium quadrupole coupling. Subsequent reports will discuss the statics and dynamics of the monoclinic and cubic phases.

EXPERIMENTAL

A nuclear magnetic resonance (NMR) spectrometer of the Torgeson design⁷ operating in nonadiabatic superfast passage mode^{8,9} was used with magnetic fields up to 2.1 T. Tailed dewars and dewar pipes were used to achieve 77 K and intermediate temperatures. A Comark copper-constantan electronic thermometer, accurate to 2 K with a thermocouple temperature controller, was used to measure temperatures above and below ambient. X-ray powder diffraction patterns were taken with a Phillips 11.483 cm camera using Cu K α radiation. All powder diffraction patterns were taken at room temperature. Differential thermal analyses were performed using a Dupont 990 DTA in the scanning calorimetry mode.

SAMPLE PREPARATION AND ANALYSIS

The common contaminants of NaOH are water and Na₂CO₃ and efforts were made to either eliminate these or identify remaining levels of contamination. Polycrystalline NaOH samples were prepared from three sources—reagent grade pellet form (low purity), high purity NaOH·H₂O (Alfa

Products), and high purity 50 wt % aqueous solution (Alfa Products). X-ray powder diffraction for the as received monohydrate was in agreement with ASTM Powder Diffraction File Card No. 30-1194 and was used as received.

The anhydrous material was prepared by melting the samples under vacuum. Because of the reaction of molten NaOH with quartz glass, melting was performed in carbon crucibles. The samples were then transferred to sealed quartz, glass, and plastic sample containers. When not in use, the samples were stored in a desiccator over P₂O₅. The water content of the NaOH was monitored by observing the monohydrate x-ray diffraction pattern. Analysis of the samples was performed both before and after the NMR experiments. There was excellent agreement between the x-ray diffraction patterns of our NaOH samples and the ASTM Powder Diffraction File Card No. 1-1183. No differences were noted in the NMR line shape between samples prepared from different sources.

At no time were we able to detect x-ray powder diffraction lines due to Na₂CO₃, even with a four times overexposure of the film. As pointed out by Bleif and Dachs,³ a sensitive way of estimating the carbonate content is through differential thermal analysis. NaOH forms a eutectic mixture with Na₂CO₃ at 22.7 wt. % with a eutectic melting of 554 K.⁸ One can then observe the eutectic melting below both the true melting temperature of 592 K and the monoclinic to cubic transformation temperature of 566 K. The eutectic melting temperature is known to be independent of water content for low concentrations of water.¹⁰ Using temperature scan rates of 5 and 10 deg/min, our best samples agree precisely with the results of Bleif and Dachs with respect to peak height ratios and transition temperatures. The implication of these data are that our carbonate content is less than 0.5% wt. %. Although our thermograms were performed in gold pans and a dried purging gas, it was found that DTA reruns yielded different results for the melting curve, probably due to a lack of equilibrium in the solid. We also observed a small amount of the monohydrate to melt at the appropriate melting temperature of 338 K from which the hydrate content was also estimated to be less than 0.5 wt. %. It is known that Na₂CO₃ contents up to 4.1 wt. % do not affect the transition temperatures in the anhydrous salt.¹⁰

NUCLEAR MAGNETIC RESONANCE RESULTS

When a nucleus suffers a quadrupole coupling, as measured by the constant

$$\nu_Q = e^2 q_{zz} Q (1 + \eta^2/3)^{1/2} / 2h \quad (\text{for } I = 3/2),$$

which is an appreciable fraction of its Zeeman energy given by $\nu_0 = \gamma H$, it can be expected that the central transition ($1/2$ to $-1/2$) will be significantly broadened in a polycrystalline sample. Here, e is the electronic charge, q_{zz} is the principal axis value of the electric field gradient tensor, Q is the nuclear electric quadrupole moment (including the anti-shielding factor), η is the asymmetry parameter in the electric field gradient (efg) equal to $(q_{xx} - q_{yy})/q_{zz}$, γ is the magnetogyric ratio factor divided by 2π , and H is the applied magnetic field. These affects have been well documented in the literature and will not be repeated here.^{11,12}

In Fig. 1(a), we show the ^{23}Na experimental absorption mode line shape for the central transition in NaOH at an operating frequency of 23.5 MHz at room temperature. The second-order broadened polycrystalline line shape is characteristic of $\eta = 0$. This resonance was studied as a function of magnetic field down to 0.45 T in order to confirm that $\eta = 0$ within experimental error. The coupling constant was measured as a function of temperature from 400 to 77 K and the temperature dependence is listed in Table I. We have also observed the first-order shifted satellite transitions which, for an $\eta = 0$ powder pattern, should be located at $\pm \nu_Q/2$ from ν_0 . From their positions, we determine a value of ν_Q to be 1.78 MHz. If there were an asymmetry parameter, the satellite "peaks" would be shifted to a position $\nu_Q(1 - \eta)/2$ from ν_0 .¹³

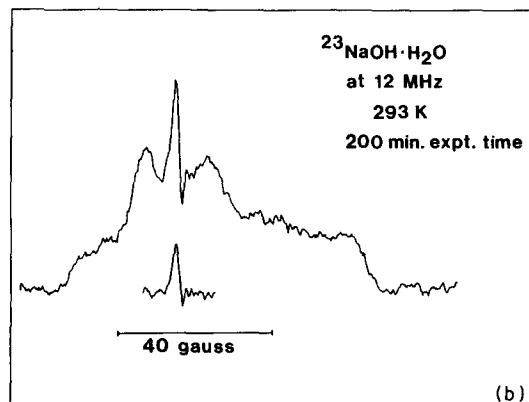
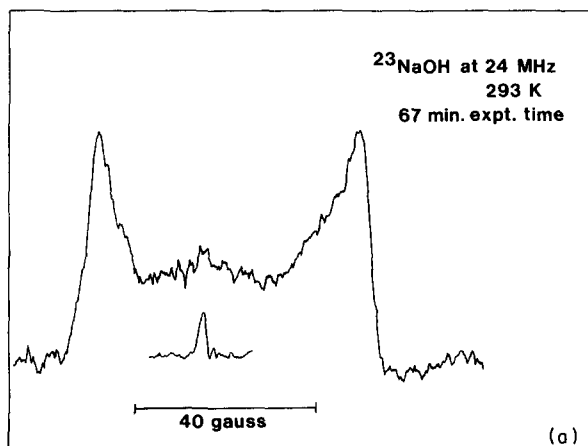


FIG. 1. (a) ^{23}Na central transition line shape in NaOH at $\nu_0 = 23.55$ MHz. Accumulation time was 67 min. (b) ^{23}Na central transition line shape in NaOH·H₂O at $\nu_0 = 11.754$ MHz. Accumulation time was 200 min. Both traces taken at sweep speeds of 50 Hz and $dH/dt = 6$ kG/s, 293 K. Sodium ion markers are at the operating frequency.

TABLE I. Quadrupole coupling constant ($e^2 q_{zz} Q/h$) for $^{23}\text{NaOH}$.

Temperature (K)	Quadrupole coupling constant (MHz)
77	3.84 ± 0.08
151	3.72 ± 0.08
219	3.60 ± 0.08
293	3.54 ± 0.08
369	3.36 ± 0.08
388	3.38 ± 0.08

There have been previous studies of these NMR techniques which estimate the uncertainty in η where it is known from crystal symmetry that η is identically zero.¹⁴ This uncertainty is caused by dipolar broadening of a resonance which masks effects caused by a small η . For the dipolar broadening in the NaOH sodium resonance, an η value of at most 0.04 would escape detection, using just the information from the central resonance as a basis of judgement. On the face of it, the satellites would appear to be the most useful indicator since there, the splitting is affected to first order in η as opposed to second order. However, the characteristic broadening of the satellites is sufficient to give no better limits on the uncertainty in η .

Although our values of the coupling constant and asymmetry parameter determined from first-order and second-order effects are self-consistent, they are in marked disagreement with the values obtained from double resonance by level crossing (DRLC),^{15,16} listed in Table II. Because of this discrepancy, the ^{23}Na resonance in the monohydrate was measured in order to provide another comparison with DRLC data. In Fig. 1(b), we show the monohydrate absorption line shape which is characteristic of a high asymmetry parameter. Comparative measurements are listed in Table II. The peak at ν_0 is due to the sodium ion dissolved in excess water. The excess water is a reassurance of a single phase material since at room temperature all other hydrates of NaOH are fluid.¹⁷ This center peak was not observed at 77 K as expected. The values of the coupling constant and asymmetry parameter for the monohydrate are in reasonable agreement with the DRLC values.

CALCULATION OF THE EFG

The electric field gradient was calculated for the sodium site using a simple point charge model. Despite the or-

TABLE II. Quadrupole coupling data for $^{23}\text{NaOH}$.

Temperature (K)	Quadrupole coupling constant (MHz)	Asymmetry parameter	Reference
293	3.46 ± 0.02	0.4 ± 0.1	16
293	3.54 ± 0.08	< 0.05	This work
77	3.73 ± 0.01	0.4 ± 0.1	15
77	3.84 ± 0.08	< 0.01	This work
Quadrupole coupling data for $^{23}\text{NaOH} \cdot \text{H}_2\text{O}$			
293	2.18 ± 0.01	0.8 ± 0.1	16
293	2.11 ± 0.04	0.62 ± 0.03	This work
77	2.27 ± 0.01	0.6 ± 0.1	15
77	2.11 ± 0.04	0.62 ± 0.03	This work

thorhombic structure, the local symmetry is actually quite high. The structure is composed of two equivalent layers. In each layer the Na, O, and H atoms form linear arrays perpendicular to these layers. Nearest neighbor $M^+(XY)^-$ dipoles are inverted and the dipoles are located on a square array in the ab plane. Considering only a single layer, the Na atoms in that layer possess a fourfold rotation axis and therefore the efg from atoms within that layer would be axially symmetric. The adjacent layers are shifted by half a lattice spacing in the b direction and it is this translation which removes the fourfold axis from the structure. But this plane is 6 Å removed from the original plane so that we can see that the efg will be dominated by contributions from atoms within the plane of the Na atom being considered, giving rise to an axially symmetric efg, and only to a lesser extent affected by the atoms in adjacent planes, which will give rise to a nonaxially symmetric efg.

The lattice constants from Bleif and Dachs³ for the orthorhombic structure at room temperature were used. Charges on the atoms were Na = +1, O = -2, and H = +1. An antishielding factor of -5.1 was used¹⁸ with a quadrupole moment of $Q = 0.12$ b.¹⁹ The result obtained was $\nu_Q = 2.02$ MHz and $\eta = 0.14$ with the principal axis system of the efg along a, b, c (q_{zz} in the c direction) of the so designated Bmmb structure. The fact that ν_Q is close to the experimental value is considered fortuitous, in light of the fact that we have completely neglected dipole and quadrupole polarizabilities of the oxygen atom which are known to make important contributions to the efg.²⁰ The significant factor is that the calculated asymmetry parameter is small.

Furthermore, since the hydrogen atom is located within the ionic radius of the oxygen, it is reasonable to assume that both the oxygen and hydrogen have charges different from -2 and +1, respectively. Changing the oxygen charge to -1.5 and the hydrogen charge to +0.5, lowers ν_Q to 1.15 MHz and η to 0.06. Lastly, convergence was quite rapid. Twenty-seven molecular units (nine molecular units in each of three adjacent planes) yielded a result within 10% of the asymptotic value.

SUMMARY

The ^{23}Na quadrupole coupling has been measured in the orthorhombic phase of NaOH. While its value and temperature dependence are quite reasonable, surprisingly, the asymmetry parameter in the efg is zero within experimental error, despite the orthorhombic structure. Detailed descriptions of the preparation and analyses of the anhydrous material are included to demonstrate the relative ease with which the material can be prepared and maintained and to illustrate the insensitivity of the measurements to the impurity content. The data also includes measurements on the monohydrate so that comparisons with other experiments could be made.

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