Deuterium and Sodium Quadrupole Interactions in Sodium Hydroxide
The Monoclinic Phase*

D. T. Amm and S. L. Segel
Department of Physics, Queen's University, Kingston, Ontario,

T. J. Bastow
CSIRO Clayton, Victoria, Australia

K. R. Jeffrey
Department of Physics, University of Guelph, Guelph, Ontario

Z. Naturforsch. **41 a,** 305–310 (1986); received July 22, 1985

The temperature dependence of the ^{23}NaOH Pure Quadrupole Resonance Frequency has been studied from 77 K to 550 K and shows a change in slope and a discontinuous change in frequency of 6 ± 2 kHz at the orthorhombic to monoclinic phase transition at 505 K. At 292 K the ^{23}Na NQR frequency is 1.778 ± 0.001 MHz, $\eta < 0.04$. The temperature dependence of the deuterium quadrupole coupling was fit to a librating molecule model between 293 K and 570 K ($QCC = 245 \pm 2$ kHz, $\eta = 0.05 \pm 0.01$ at 293 K) and confirms that the frequency of the libration decreases in the high temperature monoclinic phase. X-ray studies indicate that down to 10 K there are no further phase transitions in NaOH. On the other hand, it is now known that NaOD, orthorhombic at room temperature, monoclinic at high temperature, suffers another transition at 160 K to yet another monoclinic phase.

Introduction

Sodium hydroxide is known to form at least three different solid state phases at zero pressure [1, 2] (NaOD has an additional phase transition at 160 K[2]). Below 514 K, NaOH is orthorhombic. Above 514 K, the crystal structure is monoclinic. The transition from the orthorhombic to monoclinic phase is believed to be a ferroelastic transition characterized by a one-dimensional order parameter [3]. At 566 K, NaOH transforms to a cubic phase, where the OH^- ion exhibits orientational disorder. NaOH melts at 592 K.

Little work has been published on the high temperature phases of sodium hydroxide. The initial discovery and characterization of the monoclinic phase was achieved using x-ray and neutron diffraction [1], and these experiments showed that the monoclinic phase is a very minor distortion of the orthorhombic crystal structure. The subtleness of the transition from the orthorhombic to monoclinic phase is shown in the high temperature Raman scattering data where only one Raman active mode, the OH^- libration, differs significantly in these two phases [3]. The enthalpy of transition between the orthorhombic and monoclinic phases is estimated at 20 J/mole. The preliminary results of a ^{23}Na NMR study in the orthorhombic phase of sodium hydroxide has been reported in a previous paper [5]. In a continuation of this study, the results of sodium and deuterium NMR and sodium pure NQR experiments, in both the orthorhombic and monoclinic phases of NaOH, will be presented here.

Experimental

The ^{2}D and ^{23}Na broadline NMR spectra were recorded using an NMR spectrometer operating in the non-adiabatic super-fast passage mode [6]. The sample temperature was stable to ±2 K but at higher temperatures (580 K) the temperature gradient across the sample was typically 5 K. Teflon proved to be a reliable container.

---

* Presented at the VIIIth International Symposium on Nuclear Quadrupole, Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

Reprint requests to Prof. S. Segel, Department of Physics, Queen's Univ., Kingston, K7L3N6 Ontario, Canada.

0340-4811 / 86 / 0100-0305 $ 01.30/0. – Please order a reprint rather than making your own copy.

Deuterium NMR were collected using a pulsed Fourier transform spectrometer with a 6.3 Tesla superconducting magnet. The quadrupolar echo technique was used to reduce the distortion of the spectrum due to a loss of the beginning of the FID because of the receiver dead time. The signal, starting from the peak of the echo, was digitized at 1 μs per point using a Nicolet 1090 digital oscilloscope. Usually, the pulse sequence was repeated every 8 or 16 seconds. The sample temperature was measured using a chromel-alumel thermocouple with an ice bath reference.

The NQR spectrometer used in this work was a special low frequency design of the Robinson marginal oscillator [7]. A zero based sine wave or a half wave rectified sine wave signal was used to provide the magnetic field. The modulation frequency was set at 87 Hz and the signal output from the spectrometer was detected through a lock-in amplifier. The coils were connected to the spectrometer via a coaxial line and enclosed in a metal cell. The cell was placed into a dewar and thermally insulated at the top of the dewar (modulation coils were external to the dewar). Thus by using electrical heaters, liquid nitrogen and/or dry ice baths, the temperature was variable from 77 K to about 550 K. The sample temperature was measured using a copper-constantan thermocouple.

A complete description of the sample preparation and analysis has been given elsewhere [2, 5]. The NaOH material was obtained from Fisher Scientific in a solid form rated at 98.6% purity with 0.6 wt% sodium carbonate. This material was dried in a silver crucible for a minimum of 8 h at 670 K in a stream of dry nitrogen atmosphere. The resulting anhydrous samples of NaOH were estimated to contain < 0.5 wt% H_2O and < 1.0 wt% Na_2CO_3. The NaOD samples were prepared by similarly drying a 40 wt% solution of NaOD in D_2O (99^+ atom% D) received from Aldrich Chemical Company.

Results and Analysis

^{23}NaOH NMR powder lineshape is a second order quadrupole coupled pattern which is parameterized by quadrupole coupling constant (QCC) and an asymmetry parameter, η. At all temperatures below the cubic phase transition, the lineshape shows two distinct "peaks" and has no "shoulder" features, which indicates a zero (or small) asymmetry parameter. In the cubic phase, the ^{23}Na NMR is a single narrow line of a width determined by the magnetic field inhomogeneity.

Using a Robinson oscillator circuit (Robinson, 1982), the pure quadrupole resonances were recorded at temperatures from 77 K to 550 K. The time to sweep through the resonance was about 10 min using a 30 s time constant. The resonances were most intense at low temperatures with decreasing intensity as the temperature increased. Approximately 10 K below the cubic transition, the resonance was too low in intensity to be accurately distinguished from the noise. The estimated error in the peak values of the resonances is 1 to 2 kHz. This is more than an order magnitude more precise than the NMR deduced values. The magnitudes of QCC and $2\nu_Q$ from NMR and NQR are in agreement within experimental error.

The ^{23}Na broadline NMR results of many runs and several different samples are recorded in Figure 1. The QCC decreases monotonically with increasing temperature in the orthorhombic phase, decreases much more rapidly in the monoclinic phase, and drops abruptly to zero in the cubic phase as expected. This change in slope of the temperature dependence of QCC can be correlated to similar changes in the NaOH lattice constants [1]. An ancouraging result of these measurements is that there is very little scatter in the data although a

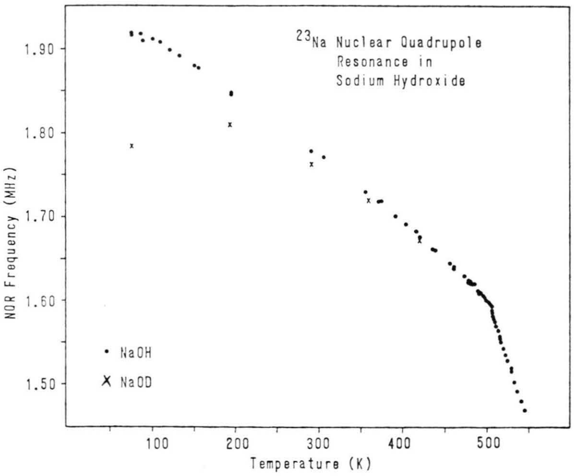

Fig. 1. Sodium NQR frequency in NaOD and NaOH. The change in slope near 500 K marks the transition from the orthorhombic to monoclinic phase.

variety of unsealed samples were used. Our studies indicate that the temperature and enthalpy change of the orthorhombic-monoclinic phase transition is unaffected by up to 30 wt% Na_2CO_3. The change of slope in the temperature dependence of the quadrupole coupling between the orthorhombic and monoclinic phases is better defined in the NQR data than in the NMR data.

The NQR linewidth also varies with temperature. The linewidth decreases monotonically from 20 ± 2 kHz FWHM at 77 K to 8 ± 2 kHz at 475 K. The linewidth then increases abruptly to 13 ± 2 kHz at 506 K and decreases slightly again as the temperature is increased further.

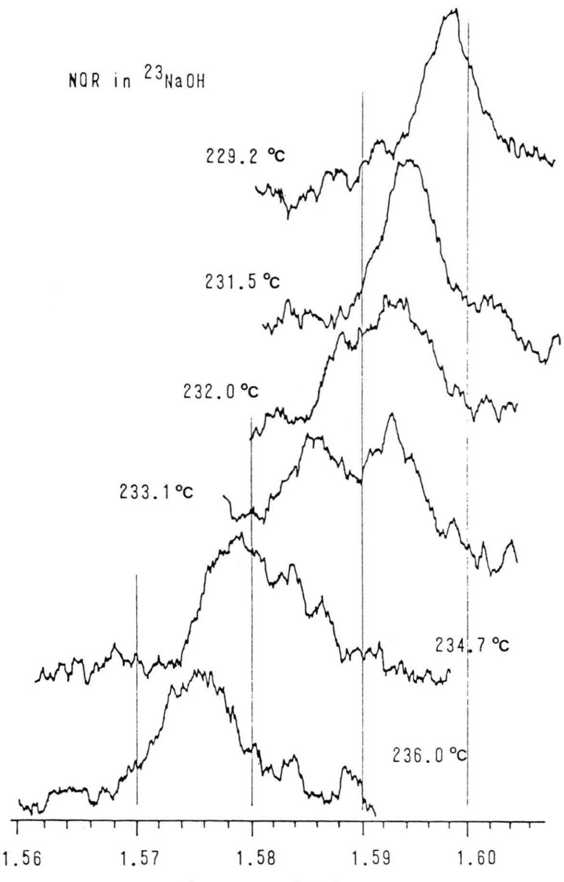

Fig. 2. Sodium NQR lineshapes in NaOH near the orthorhombic-monoclinic phase transition. The resonances at 232.0 K and 233.1 K show a doublet structure which indicates a discontinuous change in the quadrupole coupling at the transition.

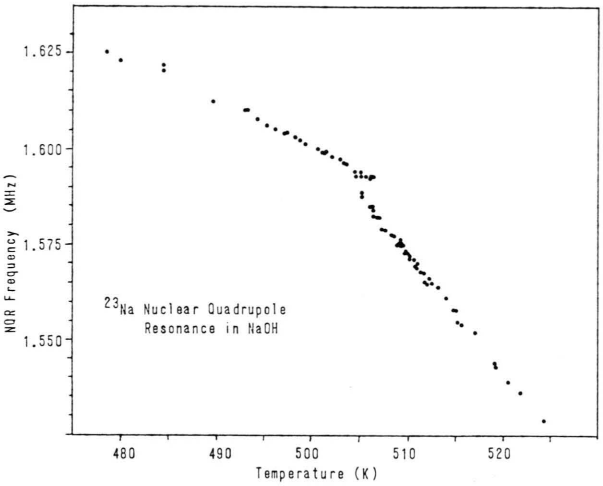

Fig. 3. Sodium NQR transition frequency in NaOH in the vicinity of the orthorhombic-monoclinic transition. The plot shows a discontinuous change of 6 ± 2 kHz at the phase transition.

A detailed study of the ^{23}NaOH NQR in the vicinity of the orthorhombic-monoclinic transition was performed with one sample, always recording the resonance with increasing frequency. Thus, although the absolute error may be as large as ± 3 kHz, the relative error would be reduced to a reading error of ± 1 kHz. A few typical spectra taken in this region are shown in Figure 2. These spectra illustrate the dramatic increase in linewidth at the phase transition. The interpretation of this result was that the broad resonances were actually two slightly overlapping resonances one for each of the orthorhombic and monoclinic phases. Even though the sample was enclosed in an "isothermal" cell, the regions of mixed phase material were believed to be caused by a small temperature gradient across the sample. The results of this detailed NQR study are shown in Figure 3. From the overlapping resonances at the orthorhombic-monoclinic transition, the temperature gradient across the sample was estimated to be about 3 K. The temperature of the transition was about 506 K as determined from the NQR data, compared to 512 K from DTA measurements. This difference was not believed to be significant. However, there is a significant discontinuous change in the value of ν_Q at the transition. The discontinuous change, which was determined to be 6 ± 2 kHz, is consistent with the view that the phase transition is "slightly" first order [1].

A study of the high temperature Raman spectra of NaOH indicates that the frequency of the OH^- libration is the only phonon mode that differs significantly in the orthorhombic and monoclinic phases [3]. As it is well known that torsional oscillations can affect the quadrupole coupling [8], a study of the deuterium NMR in NaOD was undertaken in the hope of obtaining information on the OD^- libration.

Typical pulsed NMR spectra recorded at 41 MHz are shown in Figure 4. These powder spectra are first order quadrupolar coupled with a non-zero (small) asymmetry parameter which is expected for a deuterium site that lacks fourfold rotational symmetry. The deuterium quadrupole coupling parameters derived from the room temperature spectrum were $QCC = 248.1 \pm 1.0$ kHz and $\eta = 0.046 \pm 0.008$.

Previous measurements of the deuterium QCC in mixed NaOH–NaOD (50% H, 50% D) using double resonance techniques yielded $QCC = 247.7 \pm 0.3$ kHz, $\eta = 0.044 \pm 0.003$ at 293 K and $QCC = 279 \pm 1.3$ kHz, $\eta = 0.030 \pm 0.014$ at 77 K [9]. The agreement between the NMR and double resonance determinations of QCC and η at room temperature is excellent. As can be seen from Fig. 4, both the quadrupole coupling constant (the overall resonance width) and the asymmetry parameter (the peak to shoulder splitting) decrease monotonically with increasing temperature. Above 560 K, the quadrupole coupling constant changes abruptly to zero.

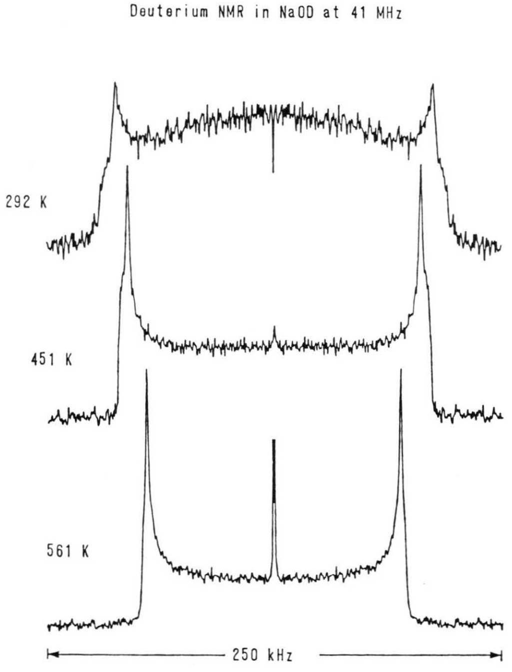

Fig. 4. Deuterium pulsed NMR spectra in NaOD recorded at 41 MHz. The spectrum at 292 K is slightly distorted due to the short delay between pulse sequences and a long deuterium relaxation time.

For the deuterium quadrupole coupling in NaOD, almost all the *efg* at the deuterium site is due to the charges on the oxygen atom and the electron distribution about the OD^- bond. Thus the maximum *efg* is in the direction of the OD^- bond. As the OD^- ion librates, the *efg* changes direction and the measured *efg* will be some average over all these directions. This average value of the quadrupole coupling decreases with increasing libration angles [8]. For a given libration frequency, as the temperature is increased, the average angle of libration will increase. Thus, for a librating OD^- ion, the measured QCC can be expected to decrease with increasing temperature. By modelling the OD^- libration as a simple harmonic oscillator, the temperature dependence can be fitted to a function dependent only on the frequency of libration [8]. To first order perturbation theory and assuming the libration to be axially symmetric, the equations are as follows:

$$q = q_0 [1 - 3 \langle \theta^2 \rangle] , \tag{1}$$

$$\eta = \eta_0 (q/q_0) [1 - \langle \theta^2 \rangle] , \tag{2}$$

$$\langle \theta^2 \rangle = \frac{\hbar}{A\omega} \left\{ \frac{1}{2} + \frac{1}{e^{(\hbar\omega/kT)} - 1} \right\} . \tag{3}$$

$\langle \theta^2 \rangle$ is the average of the square of the libration angle, q_0 and η_0 are static EFG parameters, q and η are the resultant EFG parameters, A is the moment of inertia of the librating molecule and ω is the frequency of libration. Assuming an OD^- bond length of 0.98 Å for the moment of inertia calculation and $QCC = 281$ kHz at zero temperature, the temperature dependence of QCC for different values of libration frequencies were calculated. As a check on the calculations, the temperature dependence for a libration frequency of 300 cm^{-1} calculated in this work was precisely the same as that calculated in the analysis of LiOD deuterium coupling [10].

The results of the calculations and the NMR data, given in Fig. 5, are presented relative to the value at $T = 0$.

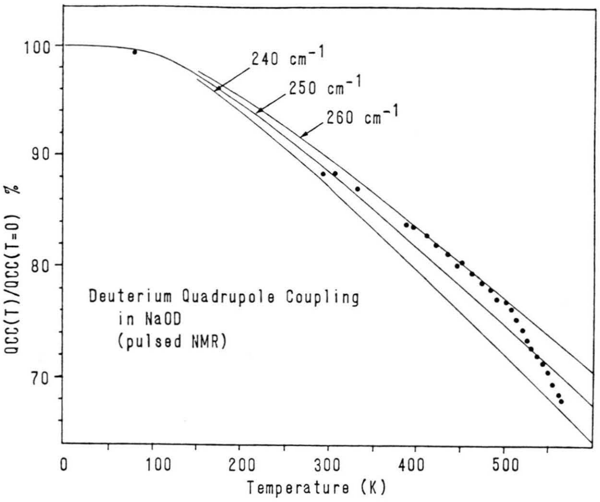

Fig. 5. Quadrupole coupling constant for deuterium in NaOD normalized to 0 K determined from pulsed NMR data at 41 MHz. The QCC at 0 K was assumed to be 281 kHz. The solid lines are the results of the theory for a molecule librating at a given vibrational frequency.

It appears that the libration frequency may increase slightly with increasing temperature in the orthorhombic phase but there is not enough low temperature data to prove this definitely. However, there is clearly a change in the libration frequency for temperatures above 500 K, the orthorhombic to monoclinic transition in NaOD. The NMR data indicates that below 500 K, the libration frequency is 260 ± 3 cm^{-1}. If the force constants for NaOH and NaOD are almost the same, then the libration frequency can be scaled by the square root of the moments of inertia of the OD$^-$ and OH$^-$ ions a factor of 1.372 [11]. From this scaling, the frequency deduced from the deuterium NMR corresponds to about 365 ± 6 cm^{-1} for the OH$^-$ libration which is in reasonable agreement with the average value of 370 cm^{-1} measured over this temperature range by Raman scattering [3].

In the monoclinic phase, the libration frequency starts at 260 cm^{-1} and falls gradually to 240 cm^{-1} with increasing temperatures. Scaling to an OH$^-$ libration, this would correspond to a change from 357 cm^{-1} to 329 cm^{-1}, a difference of almost 30 cm^{-1}. This compares quite favourably with the Raman measurements of the pure libration mode [3].

Discussion

There is some question in the literature as to the nature of the elastic transition from the orthorhombic to monoclinic phase, in particular whether the transition is first or second order. Phonon dispersion measurements in the vicinity of this phase transition indicate that while the appropriate acoustic mode softens, the phonon frequency does not go precisely to zero at the phase transition temperature [12]. The theory of elastic phase transitions reveals that a transverse acoustic phonon mode must soften to identically zero for a second order phase transition [13]. Thus the phonon dispersion measurements indicate a first order transition. However, x-ray diffraction measurements on single crystals did not show any hysteresis when cycling through the transition [1] – a characteristic of a second order transition. This apparent contradiction has been conveyed in the literature by describing the transition as "slightly first order" [14]. Of all the experiments performed in this work, only the ^{23}Na NQR of NaOH was of sufficient precision to resolve a discontinuous change in the quadrupole coupling on crossing the orthorhombic-monoclinic phase transition, giving evidence for a first order transition. Differential thermal analysis results are also indicative of a first order transition with a small enthalpy change [1], of order of 20 J/mole. Thus the evidence is substantial and the nature of the transition is best described as a small enthalpy change, first order transition or a "weak" first order transition.

One of the original goals was to study the nature of the "ferroelastic" orthorhombic to monoclinic transition. Although the transition is clearly visible in the deuterium NMR and in the sodium NMR and NQR, none of these parameters relate to the ferroelastic nature of the transition. These experiments have probed changes in the statics of the structure of NaOH more than dynamics that could be associated with the softening of an acoustic phonon mode. Proton relaxation times might have provided such dynamical information but unfortunately, conductivity mechanisms overwhelmed any other contributions. It may be that NMR relaxation studies of sodium in NaOH would be less dependent on ionic conductivity and perhaps some dynamical information about the ferroelastic transition could be extracted from the data.

Conclusions

NaOH and NaOD have been studied extensively using NMR and NQR. The sodium NMR and NQR show definite differences between the orthorhombic and monoclinic phases. The sodium NQR in NaOH shows a small discontinuity in the quadrupole coupling at the orthorhombic-monoclinic transition, indicating that the transition is first order. The deuterium quadrupole coupling in NaOD indicates that a change in the OD^- libration frequency occurs between the orthorhombic and monoclinic phases. Most of the differences measured between the orthorhombic and monoclinic phases are due to crystal structure changes and do not pertain to the ferroelastic nature of the transition. All NMR and NQR parameters show discontinuous changes at the monoclinic to cubic transition in NaOH.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada and the Commonwealth Scientific and Industrial Research Organization. We would like to thank R. J. C. Brown and R. D. Heyding for helpful discussion.

[1] H. Bleif and H. Dachs, Acta Crystallogr. **A38,** 470 (1982).

[2] D. T. Amm, Ph.D. Thesis, Queen's University, Kingston, Ontario, Canada 1985.

[3] A. Giessler, G. Schaak, and H. Bleif, Phys. Status Solidi **B104,** 151 (1981).

[4] D. T. Amm, S. L. Segel, R. D. Heyding, and B. K. Hunter, J. Chem. Phys. **82,** 2529 (1985).

[5] D. T. Amm and S. L. Segel, J. Chem. Phys. **80,** 4679 (1984).

[6] S. Segel, D. Torgeson, and R. Creel, J. Mol. Struct. **111,** 79 (1983).

[7] F. N. H. Robinson, J. Phys. E, Sci. Instrum. **15,** 814 (1982).

[8] T. P. Das and E. L. Hahn, Solid State Physics, Supplement **1** (1958).

[9] I. J. F. Poplett, J. Magn. Reson. **50,** 382 (1982).

[10] T. Chiba, J. Chem. Phys. **47,** 1592 (erratum 5461) (1967).

[11] H. J. Bleif, Doctoral Thesis, Universität Tübingen, West Germany (1978).

[12] W. I. F. David, J. Phys. C. Solid State Phys. **17,** 385 (1984).

[13] R. Folk, H. Iro, and F. Schwabl, Z. Phys. **B25,** 814 (1982).