restrictions, most of the NOE data came from the two higher field strengths (^{1}H NMR frequencies of 360 and 470 MHz) and most of the T_1 data came from the lower fields (150 and 200 MHz).

Table I demonstrates that normalized correlation times do not differ much from unity, but the differences are highly significant (much greater than +/-2 SDM).[24] All values should be 1.000 (within experimental error) if correlation times and amplitude factors were identical at each ring-carbon position. The table also shows that amplitude factors differ significantly with ring position. The greatest difference in $\langle A(0)A(p)\rangle$ (between carbons 1^g and 3^g) is greater than 6 SDM.

Differences among the amplitude factors are related to flexibility in the molecular structure. The largest amplitude factor (indicating the most restricted vibrational motion) is found at a bridgehead carbon (1^g), and the smallest (i.e., the least restricted motion) is found at the only ring-carbon (3^g) that is separated by two C-C bonds from either a bridgehead or a bulky hydroxymethyl group.

Our data in Table I describe the relative vibrational amplitudes at each of the ring-carbon atoms. Vibrational amplitudes also can be measured in crystallographic diffraction studies. Brown and Levy[15] report thermal amplitudes from a neutron diffraction study of sucrose. Using their data (Table 3 in ref 15), we have calculated a parameter, β_{rms}, which is the square root of the sum of the squares of the thermal factors (β_{11}, β_{22}, and β_{33}) for each ring-carbon atom and for the hydrogen atom bonded directly to it.

Figure 8 shows a plot of $\langle A(0)A(p)\rangle$ vs. β_{rms}. If vibrational motions in the crystal were identical with those in solution, one would expect good correlation between both data sets; indeed, one would expect all points to lie on a smooth curve with a negative slope such as the one suggested by the straight line. Two deviant points (3^f and 4^f) lie well below the others, suggesting that vibrational amplitudes at these two carbons are greater in solution than in the crystal.

Bock and Lemieux[11] studied aqueous sucrose using NMR as well as molecular modeling calculations. They concluded that the conformation of aqueous sucrose is similar to that of the crystal; the major difference in solution is the loss of one intramolecular hydrogen bond which causes increased flexibility in the fructose ring. Our data support their conclusion and show that the increased flexibility is located almost entirely at carbons 3^f and 4^f.

Acknowledgment. The authors thank Dr. C. B. Post for helpful discussions. This research was supported in part by the National Institutes of Health, Division of Research Resources (Grants RR01077 and RR02301). The work was carried out in the Purdue University Biological Magnetic Resonance Laboratory.

Registry No. Sucrose, 57-50-1.

An Analysis of Non-Lorentzian ^{23}Na Line Shapes in Two Model Systems

Laura Lerner and Dennis A. Torchia*

Contribution from the Bone Research Branch, National Institute of Dental Research, National Institutes of Health, Bethesda, Maryland 20892. *Received October 17, 1985*

Abstract: In view of the increasing interest in applications of ^{23}Na NMR to biochemical and biological research, we have investigated the causes of non-Lorentzian ^{23}Na line shapes in two model systems: (a) sodium chloride in an aqueous suspension of sodium laurate; and (b) sodium chloride in glycerin. Analysis of the field and temperature dependence of T_1, T_2, and line shapes leads us to conclude that the non-Lorentzian line shape observed in sodium laurate results from rapid exchange of a small fraction of sodium ions in the slow motion limit with sodium ions in the extreme narrowing region. In contrast, the non-Lorentzian line shape of sodium in glycerin arises from a single population of ions in the slow motion region. In this case, an approximate value of the ^{23}Na quadrupole coupling constant, 1.6 MHz, is derived from the temperature-dependent relaxation data.

Nuclear magnetic resonance spectroscopy (NMR) of quadrupolar nuclei has been used to assess binding of cations to macromolecules such as DNA[1], calmodulin[2], and proteoglycans[3]. Binding of a cation containing a quadrupolar nucleus to a macromolecule is made manifest by the changes in line shape and line width that occur when association with a macromolecule (typical correlation time 10^{-9} s) increases the correlation time of the cation (typical correlation time 10^{-12} s). Binding may also change the electric field gradient at the nucleus.

Non-Lorentzian line shapes have been reported frequently in NMR studies[1,4] of cations having $I \geq 1$ in solutions of macromolecules and in intact tissue. It is therefore important to determine the sources of non-Lorentzian line shapes for these nuclei.

The NMR line shape and relaxation rates of quadrupolar nuclei depend on the value of the product of the Larmor frequency, ω_0, and the rotational correlation time, τ_c. If $(\omega_0\tau_c)^2$ is much less than 1 (extreme narrowing region), then the line shape is Lorentzian and $T_1 = T_2$. T_1 and T_2 are independent of ω_0, and they decrease as τ_c increases.[5] When $(\omega_0\tau_c)^2$ is approximately equal to 1, T_1 is at its minimum. (Actually, relaxation outside the extreme narrowing region is characterized by more than one relaxation time, as described below.)

If $(\omega_0\tau_c)^2$ is greater than 1 (slow motion region), the line shape is non-Lorentzian, and the decays of the longitudinal and transverse magnetizations are described by the sums of exponentials.[6] For nuclei with $I = {}^3/_2$ (for example, ^{23}Na), the line shape consists of two components: 60% of the signal intensity characterized by

(1) Nordenskiold, L.; Chang, D. K.; Anderson, C. F.; Record, M. T., Jr. *Biochemistry* **1984**, *23*, 4309-4317.
(2) Andersson, T.; Drakenberg, T.; Forsen, S.; Thulin, E. *Eur. J. Biochem.* **1982**, *126*, 501-505.
(3) Lerner, L.; Torchia, D. A. *J. Biol. Chem.*, in press.
(4) (a) Berendsen, H. J. C.; Edzes, H. T. *Ann. N.Y. Acad. Sci.* **1973**, *204*, 459-485. (b) Lindman, B. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983; 1, pp 193-231. (c) Detellier, C. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: New York, 1983; Vol. 2, pp 105-151. (d) Lerner, L.; Torchia, D. A., manuscript in preparation.
(5) Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon Press: Oxford, 1961.
(6) Hubbard, P. S. *J. Chem. Phys.* **1970**, *53*, 985-987.

a large line width and 40% of the total signal intensity characterized by a relatively smaller line width. The two components have different Larmor frequencies,[7,8] but this "dynamic frequency shift" is difficult to detect because its value is small relative to the line width of the broad component.[7,8]

In order to measure dynamic frequency shifts and relaxation times in the slow-motion region, Marshall et al.[9] studied an aqueous suspension of sodium chloride in sodium laurate/lauric acid. According to Marshall et al., the non-Lorentzian line shape of ^{23}Na in sodium laurate at 79.39 MHz is caused by a single population of nuclei characterized by $(\omega_0\tau_c) = 5.6$. If this were true, then the ^{23}Na quadrupole coupling constant would have to be on the order of 125 kHz, which is smaller than either the typical values of ^{23}Na coupling constants reported in the literature[10] or the value (1.5 MHz) we measured for ^{23}Na chelated to CDTA (*trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate) in aqueous solution.

This result prompted us to study the sodium laurate/lauric acid system as a function of field strength. Our analysis, reported herein, showed that at least two populations of sodium ions are present and in rapid exchange. In order to observe non-Lorentzian ^{23}Na spectra uncomplicated by exchange effects, while following the changes in line shape and relaxation rates that occur as motion varies from the extreme narrowing region to the slow limit, we also studied ^{23}Na spectra of sodium chloride in glycerin over the temperature range −35 to +40 °C. These measurements enabled us to estimate the ^{23}Na quadrupole coupling constant in glycerin and to assess the difficulties in measuring the broad and narrow spectral components and their spin–lattice relaxation times in the slow-motion region.

Experimental Methods

All compounds used were reagent grade. Sodium chloride and glycerin were obtained from J. T. Baker Chemical Co. (Phillipsburg, NJ). Lauric acid and sodium laurate were obtained from Sigma Chemical Co. (St. Louis, MO). ^2H_2O (99.8% isotopic purity) and CDTA were obtained from Aldrich Chemical Co. (Milwaukee, WI).

^{23}Na spectra were measured at 132.28 MHz on a NIC-500 spectrometer with either a commercial probe containing a saddle-shaped coil (for sodium chloride and sodium laurate samples) or a homebuilt probe containing a solenoidal coil, 5 mm (i.d.) × 7 mm (for glycerin samples). Typical 90° pulse widths were 24 and 6 μs respectively for the saddle-shaped and solenoidal coils. ^{23}Na spectra at 26.45 MHz were obtained on a spectrometer consisting of an Oxford 100-MHz magnet, Nicolet 1180 computer and 293A pulse programmer, EN1 and Heathkit amplifiers, and a Novex transceiver. At 26.45 MHz, the sample was held in a solenoidal coil, 8 mm (i.d.) × 13 mm. A 90° pulse for ^{23}Na in this coil was 9 μs. The same instrument was used to obtain ^{13}C spectra at 25.15 MHz. Line widths at half-height were determined by the Lorentzian linefitting routine included in the Nicolet software for its 1180 and 1280 systems. T_1's were measured by using a $180°_{+x}$–t–$90°_{\pm x}$ pulse sequence (inversion recovery) with alternating addition and subtraction of acquisitions. For all spectra, a delay of at least $10T_1$s was used between acquisitions. The integrated areas of transformed signals of samples were compared with the areas of the transformed signals from aqueous sodium chloride solutions of known concentration. Sample temperature was varied by the flow of nitrogen gas through the probe and measured with a thermocouple placed next to the sample coil. For the 500-MHz spectrometer, static field homogeneity was adjusted by maximizing the ringdown time of either ^2H_2O or ^{23}Na with room temperature shims. The 100-MHz spectrometer was not equipped with room temperature shims. It was necessary to obtain spectra of glycerin samples in plastic tubes, since the signal from ^{23}Na in glass sample tubes (about 5 kHz wide at 132.28 MHz) was significant. In fact, as will be discussed later, the glass Dewar lining the probehead also contributed a less intense, but observable, 8 kHz wide ^{23}Na signal.

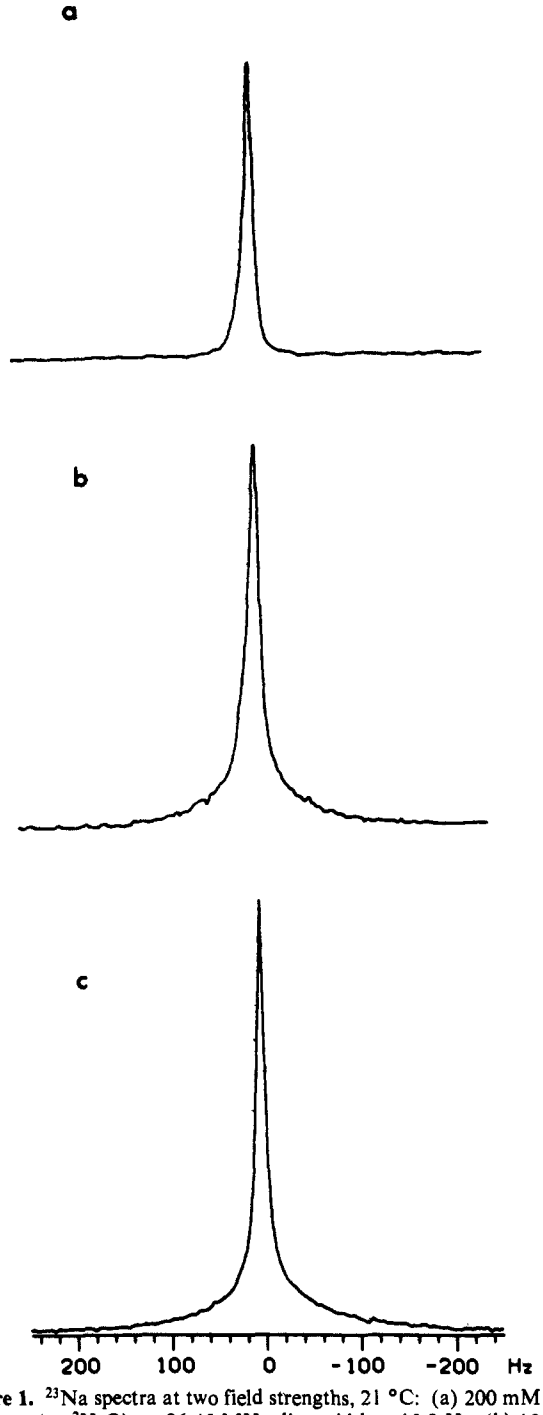

Figure 1. ^{23}Na spectra at two field strengths, 21 °C: (a) 200 mM NaCl in water (no ^2H_2O), at 26.45 MHz, line width = 10.8 Hz; (b) 120 mM NaCl, 20 mM sodium laurate, 5 mM lauric acid (15% ^2H_2O), line width = 21.1 Hz; (c) same sample as in part b, at 132.28 MHz, line width = 15.8 Hz (line width of ^{23}Na in aqueous NaCl at this frequency was 8.6 Hz).

Results and Discussion

Marshall et al. have reported that a two-component non-Lorentzian line shape exhibiting a dynamic frequency shift is observed for ^{23}Na nuclei at 79.39 MHz in a suspension of sodium chloride in sodium laurate/lauric acid micelles.[9] Figure 1 is the ^{23}Na spectra at 26.45 and 132.28 MHz of a sample identical with the one studied by Marshall et al. (120 mM sodium chloride, 20 mM sodium laurate, 5 mM lauric acid, and 15% ^2H_2O). In agreement with ref 9, we find that the lines are non-Lorentzian at both field strengths. Although the observation of a non-Lorentzian line shape suggests that the sodium nucleus may be outside the extreme narrowing region, it is desirable to vary field strength or correlation time to determine whether a quadrupolar nucleus is indeed outside the extreme narrowing region. In the slow-motion region, the

(7) (a) Werbelow, L. G. *J. Chem. Phys.* **1979**, *70*, 5381–5383. (b) Fouques, C. E. M.; Werbelow, L. G. *Can. J. Chem.* **1979**, *57*, 2329–2332.
(8) Werbelow, L. G.; Marshall, A. G. *J. Magn. Reson.* **1981**, *43*, 443–448.
(9) Marshall, A. G.; Wang, T.-C. L.; Cottrell, C. E.; Werbelow, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 7665–7666.
(10) (a) Das, T. P.; Hahn, E. L. In *Solid State Physics*; Seitz, F., Turnbull, D., Eds.; Academic: New York, 1958; pp 181–182. (b) Edmonds, D. T.; Mailer, J. P. G. *J. Magn. Reson.* **1979**, *36*, 411–418. (c) Bonekamp, J.; Eguchi, T.; Jonas, J. *Chem. Phys. Lett.* **1980**, *75*, 360–362. (d) Bastow, T. J. *J. Magn. Reson.*, in press.

longitudinal relaxation times for both the broad and narrow signal components increase with increasing field strength, while the line width of the narrow component decreases with increasing field strength. If $(\omega_0\tau_c)^2$ is much greater than 1 (slow-motion limit), the longitudinal relaxation times increase as the square of the field strength, and the line width of the narrow component decreases as the square of the field strength.

Although, as noted above, the line shapes in Figure 1 are non-Lorentzian at both field strengths, the line widths are only 7 Hz (at 132.28 MHz) or 10 Hz (at 26.45 MHz) wider than the line width of ^{23}Na in 200 mM sodium chloride in H_2O. (The ^{23}Na line width in 200 mM sodium chloride is 10.8 Hz at 26.45 MHz, in the homebuilt solenoid coil, without room temperature shims; and it is 8.6 MHz at 132.28 MHz, in the commercial saddle-shaped coil, with room temperature shims. Since the natural line widths of ^{23}Na, $1/\pi T_2$, is 5.9 Hz, inhomogeneous broadening is negligible.) The field independence of line width suggests that ^{23}Na in sodium laurate is in the extreme narrowing region. A further indication that ^{23}Na in sodium laurate is in the extreme narrowing region comes from T_1 measurements at two different field strengths. If $(\omega_0\tau_c)^2$ is much greater than 1, then ^{23}Na longitudinal relaxation times at 132.28 MHz should be on the order of 25 times longer than at 26.45 MHz, and the line width of the narrow component should be less than at the lower field strength. T_1 for ^{23}Na in the presence of laurate was 40 ms at 26.45 MHz and 36 ms at 132.28 MHz, based on peak heights after a 180°–t–90° or 180°–t–10° pulse sequence.[8] As the T_1's at the two field strengths are nearly equal, within experimental error, this is additional evidence that ^{23}Na in laurate is within the extreme narrowing region. We did not observe different spin–lattice recovery times for the broad and narrow components as reported by Marshall et al.[9] using either a 90° or 10° sampling pulse. The simplest explanation for the non-Lorentzian line shape is that ^{23}Na exists in two states in slow exchange on the NMR time scale: one free in solution and one associated with the negatively charged laurate molecules, with ^{23}Na in the extreme narrowing region in both states. However, this explanation cannot account for the fact that T_2 is ca. 10 times smaller than T_1 for the broad component of the line shape.

The possibility that free and bound sodium ions are in fast exchange is suggested by the observation,[9] confirmed herein at 132.28 MHz, that the experimental line shape is well fit by two Lorentzian lines, with 40% of the total signal intensity in the narrow component (10 Hz line width) and 60% in the broad component (100 Hz line width). The 40:60 intensity ratio of the two components and the relaxation data can be explained by the following model: a small fraction of sodium ions, in the slow-motion limit, are in fast exchange with the major fraction of sodium ions in the extreme narrowing region. Rapid exchange of free and bound sodium ions affects only $1/T_2$ of the $\pm^1/_2 \leftrightarrow \pm^3/_2$ transitions, because in the slow-motion limit $1/T_2$ of these transitions is much larger than $1/T_2$ of the $-^1/_2 \leftrightarrow +^1/_2$ transition and $1/T_1$ of all transitions.[8]

To create a sample in which all ^{23}Na nuclei were likely to be outside the extreme narrowing region, we dissolved sodium chloride in glycerin,[11] which has a viscosity 1500 times that of water at 20 °C. In contrast with the results for sodium laurate, the field dependence of ^{23}Na NMR parameters indicates that ^{23}Na is outside the extreme narrowing region when it is dissolved in glycerin at room temperature. Figure 2 shows the ^{23}Na spectrum of this sample (200 mM sodium chloride) at two field strengths. At 132.28 MHz, the line width at half-height is approximately half its value at 26.45 MHz. This indicates that ^{23}Na is in the neighborhood of the T_1 minimum in this sample. The line shapes are not well-fit by a single Lorentzian function, but it would be difficult to accurately separate narrow and broad components: in part because the two components overlap, and in part because a significant fraction of the broad component is lost as a consequence of spectrometer deadtime. For example, at 132.28 MHz,

(11) Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679–712.

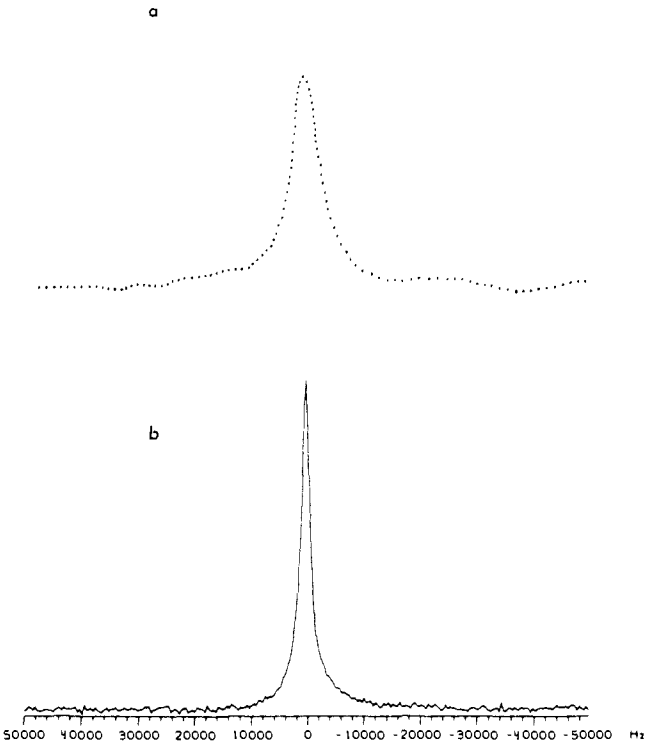

Figure 2. ^{23}Na spectra, at two field strengths, of 200 mM NaCl in glycerin, 21 °C: (a) at 26.45 MHz, line width = 4900 Hz; (b) at 132.28 MHz, line width = 1933 Hz.

if the line width is 10 kHz, over 70% of the signal intensity is lost because of receiver deadtime (30 μs) and $\pi/2$ pulse width (6 μs).

Another way to check whether nuclei are on the slow side of the T_1 minimum is to vary τ_c. For sodium chloride in glycerin, this was accomplished by varying temperature. (For sodium chloride:laurate suspensions, this was not possible since sodium laurate crystallized out of solution at temperatures lower than 21 °C.) If the ^{23}Na nuclei are within the extreme narrowing region, then decreasing temperature should cause the line shape to broaden. If sodium is outside the extreme narrowing region, decreasing temperature (increasing viscosity and increasing τ_c) should decrease the width of the narrow component but increase the width of the broad component.

Figure 3 is a series of ^{23}Na spectra at 132.28 MHz of the same sample as in Figure 2b, as temperature was varied. It appears that ^{23}Na is close to its T_1 minimum at 20 °C, since the width of the narrow component of the line shape decreases at both higher and lower temperatures. At temperatures below −25 °C, there is a broad component that appears to be shifted upfield from the narrow component. This is not the dynamic frequency shifted broad component of sodium chloride, but the ^{23}Na signal from the glass Dewar lining the probe cap. Although we could not discern a dynamic frequency shift, we did observe that the total integrated ^{23}Na signal intensity decreased with decreasing temperature, below about 23 °C, indicating that the signal from the outer transitions ($\pm^1/_2 \leftrightarrow \pm^3/_2$) was getting too broad to be detected.

Longitudinal and transverse relaxation rates calculated[8] for $I = {}^3/_2$ are plotted against correlation time for $\omega_0 = 2\pi(132.28 \times 10^6)$ in Figure 4. The solid curve in Figure 4a is a plot of $1/(\pi T_1)$ against τ_c, according to eq 1. Outside the extreme narrowing region, the recovery of longitudinal magnetization of the narrow component, following a 180°–t–90° pulse sequence, is biexponential and depends upon the value of $(\omega_0\tau_c)^2$. Equation 1 is the expression for the T_1 of the narrow component derived from the initial slope of the recovery curve following a 180°–t–90° pulse sequence.[8] The value of $(e^2qQ/h)(1 + \eta_Q^2/3)^{1/2}$ used in eq 1 (1.31 MHz) was obtained by differentiating eq 1 to find the value of τ_c at which T_1 is a minimum and then solving eq 1 by using the measured value of $T_1 = 0.342 \times 10^{-3}$ s (the apparent T_1 minimum

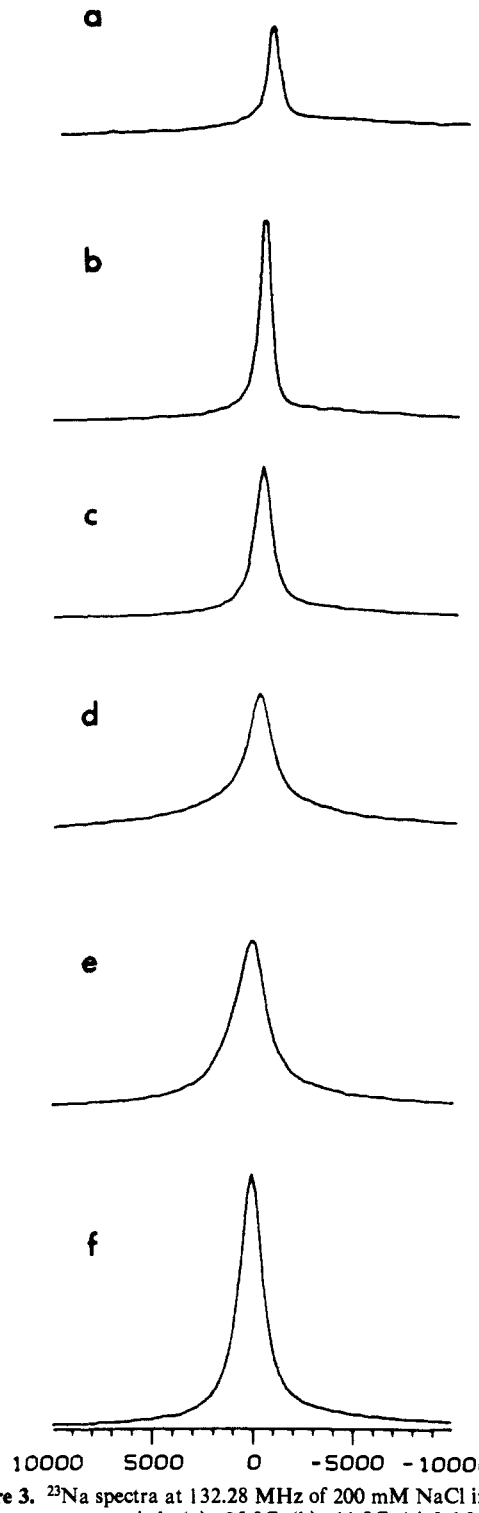

Figure 3. ^{23}Na spectra at 132.28 MHz of 200 mM NaCl in glycerin, as temperature was varied: (a) −25 °C; (b) −11 °C; (c) 0.6 °C; (d) 12 °C; (e) 20 °C; (f) 34 °C. All spectra are plotted to the same scale.

at 23 °C). The value of $(e^2qQ/h)(1 + \eta_Q^2/3)^{1/2}$ used in Figure 4b (1.93 MHz) was similarly obtained by solving eq 2 by using the measured line width of 2 kHz at 23 °C.

These values are close to the value of $(e^2qQ/h)(1 + \eta_Q^2/3)^{1/2}$, 1.5 MHz, that we measured for ^{23}Na chelated to CDTA, under conditions such that virtually all sodium ions are chelated (pH 13, tenfold excess of CDTA).[12] This value was obtained by solving eq 1, in the extreme narrowing limit, after measuring the ^{23}Na T_1 value and determining τ_c from a measurement of the T_1 values

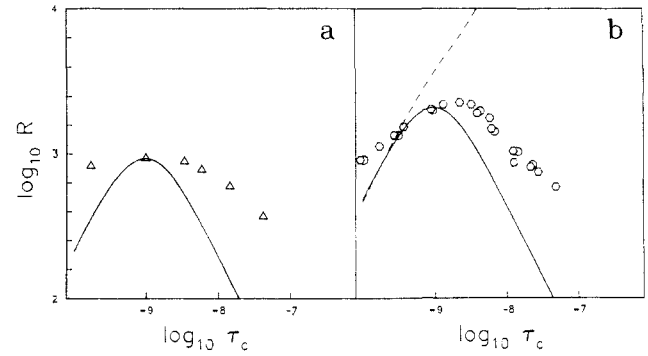

Figure 4. log–log plots of calculated[8] and experimentally obtained ^{23}Na relaxation rates, R, at 132.28 MHz, as functions of the correlation time: (a) longitudinal relaxation, (△) experimental $1/\pi T_1$, obtained from initial slopes of recovery curves following a 180°–t–90° pulse sequence; —, longitudinal relaxation for narrow component, calculated from $R = (1/\pi T_1) = 0.2\pi(e^2qQ/h)^2(1 + \eta_Q^2/3)[\tau_c/(1 + \omega_o^2\tau_c^2) + \tau_c/(1 + 4\omega_o^2\tau_c^2)]$ (1); (b) transverse relaxation, (○) experimental line widths, (—) transverse relaxation for narrow component, calculated from $R = (1/\pi T_2) = 0.2\pi(e^2qQ/h)^2(1 + \eta_Q^2/3)[\tau_c/(1 + \omega_o^2\tau_c^2) + \tau_c/(1 + 4\omega_o^2\tau_c^2)]$ (2), (---) for broad component, calculated from $R = (1/\pi T_2) = (0.2\pi \cdot (e^2qQ/h)^2(1 + \eta_Q^2/3)[\tau_c + \tau_c/(1 + \omega_o^2\tau_c^2)]$ (3). The value of $(e^2qQ/h)(1 + \eta_Q^2/3)^{1/2}$ is 1.31 MHz in (a) and 1.93 MHz in (b).

of the CDTA carbons. The extreme narrowing approximation was confirmed by the observations that the ^{23}Na line shape was Lorentzian and $T_1 = T_2$.

The measured longitudinal relaxation rates $(1/\pi T_1)$ and line widths for ^{23}Na in glycerin are plotted against ^{23}Na correlation times in Figure 4, a and b, respectively. The ^{23}Na correlations times were obtained in the following manner. At 23 °C, the correlation time was set equal to 10^{-9} s because the minimum T_1 was observed at this temperature, and eq 1 shows that $\tau_c = 10^{-9}$ s at the T_1 minimum. The correlation times were obtained at other temperatures by assuming that τ_c was proportional to the ratio of glycerin viscosity to the absolute temperature (η/K)[13]. The viscosity of glycerin at each temperature was estimated by interpolating published values.[14]

The line widths used in Figure 4b were obtained by fitting a single Lorentzian line shape to the experimental spectra. Inhomogeneous broadening contributed no more than 100 Hz to the ^{23}Na line width in glycerin, in spectra obtained at 132.28 MHz in the homebuilt (solenoid coil) probe. Consequently, the line width represented the transverse relaxation rate, at least for the narrow component. Close to the T_1 minimum (at about 20 °C), the experimental line shapes were clearly not well-fit by a single Lorentzian. To the right of the T_1 minimum (increasing τ_c), the fitted line width was actually an average between the broad and narrow components of the spectrum, plus a contribution from ^{23}Na in glass. Even so, the value of the fitted line width at half-height was dominated by the narrow component and was within 5% of the measured width of the line shape at half maximum height.

In spite of errors in determining line width and T_1's, as well as error in estimating viscosity, the general trend of the predicted dependence of relaxation rates on τ_c is evident in the data. The observation of a more shallow dependence of relaxation on η/K than predicted suggest that τ_c is not simply proportional to η/K, or that the motion of sodium is described by a distribution of correlation times.

Equation 2 predicts that the line width of the narrow component decreases, as τ_c increases, in the slow-motion limit. However, we observed a minimum homogeneous line width of ca. 300 Hz at −25 °C, and observed larger line widths at lower temperatures. This behavior was not unexpected because chemical shift anisotropy[5] and the second-order quadrupole coupling[15] broaden the

(12) (a) Schwarzenbach, G.; Flaschka, H. *Complexometric Titrations*, 2nd English ed.; Irving, H. M. M. H., translator; Metheun: London, 1969. (b) Carr, J. D.; Swartzfager, D. G. *Anal. Chem.* **1970**, *42*, 1238–1241.

(13) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry*, W. H. Freeman and Co.: San Francisco, 1980; Part II, Chapter 8.

(14) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 55th ed.; The Chemical Rubber Co.: Cleveland, 1974–1975.

(15) Westlund, P.; Wennerstrom, H. *J. Magn. Reson.* **1982**, *50*, 451–466.

narrow component in the slow-motion limit. Available formulas[5,8,15] predict a minimum line width of 80 Hz for the narrow component at 132.28 MHz assuming isotropic motion with $(e^2qQ/h)(1+\eta_Q^2/3)^{1/2}$ equal to 1.6 MHz and a 100 ppm chemical shift anisotropy. Although the calculated line width is smaller than that observed, the calculated minimum increases if a distribution of correlation times is assumed, or if larger values of the shift anisotropy or quadrupole coupling constant are assumed.

Conclusions

Our purpose was to identify the sources of non-Lorentzian (two component) ^{23}Na line shapes in two simple systems and to ascertain what information about molecular motion and quadrupole coupling constants can be obtained from measurements of relaxation times and line shapes, especially in the slow-motion region. On the basis of our observations of sodium chloride in glycerin and in sodium laurate/lauric acid we conclude that non-Lorentzian line shapes can be interpreted reliably only if one measures T_1, T_2, total signal intensity, and line shape as functions of τ_c and ω_0. The ^{23}Na data presented here for sodium chloride in glycerin (Figure 4) provide a guideline for the relaxation behavior expected if there is a single population of sodium nuclei in the sample. An estimate of $(e^2qQ/h)(1+\eta_Q^2/3)^{1/2}$ can be obtained from relaxation measurements in the neighborhood of the T_1 minimum, while the correlation time and individual spectral densities, $J(\omega_0)$ and $J(2\omega_0)$, can be obtained from analysis of relaxation times and line shapes in the slow-motion region. However, in practice, detection of the broad component will require a spectrometer having a short deadtime, <10 μs, and an intense radio frequency pulse, $\gamma B_1/2\pi$ = 100 kHz. Also, as noted, one must exclude glass from the vicinity of the receiver coil.

The line widths of the $\pm\,^1/_2 \leftrightarrow \pm\,^3/_2$ transitions of bound sodium ions are significantly reduced when the bound ions rapidly exchange with a large population of rapidly tumbling free ions.[16] Although fast exchange greatly reduces the problem of detecting the broad component, the price one pays is the introduction of a large number of unknown parameters that must be determined.[16] Complete analysis of even a simple fast exchange system such as sodium laurate requires the extensive relaxation measurements mentioned earlier.

Acknowledgment. We thank Dr. T. E. Bull for helpful discussions about quadrupolar relaxation.

Registry No. NaCl, 7647-14-5; Na, 7440-23-5; sodium laurate, 629-25-4; glycerin, 56-81-5.

(16) Bull, T. E. *J. Magn. Reson.* **1972**, *8*, 344-353.

Low-Temperature ^{13}C Magnetic Resonance in Solids. 6. Methine Carbons†

Julio C. Facelli, Anita M. Orendt, Mark S. Solum, Gisbert Depke, David M. Grant,* and Josef Michl

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received October 29, 1985*

Abstract: The low-temperature static solid ^{13}C NMR spectra of the methine carbons of bicyclo[1.1.1]pentane, bicyclo[1.1.1]pentanone, norbornadiene, cubane, trimethoxymethane, and isobutane were measured. Calculations of the shielding tensors by the individual gauge localized orbitals (IGLO) method were also performed for these compounds and for tetrahedrane. Assignments of the principal values to the molecular frame were made on the basis of these calculations for cases in which they were not determined by symmetry. The analysis of the IGLO bond contributions either in the principal axis or in the local bond frames was used to obtain some insight into the origin of the chemical shielding.

I. Introduction

Low-temperature ^{13}C NMR spectroscopy in conjunction with quantum mechanical calculation of the shielding tensors[1,2] has been shown to validate the ab initio wave functions which provide information on the electronic structure of small molecules. In previous work the ^{13}C shielding tensors of unsaturated carbon atoms in linear and pseudolinear molecules,[1] of methylene carbons in a variety of compounds,[2] and of unsaturated carbons in a series of alkenes and cycloalkanes[3] have been reported. In this paper the methine ^{13}C shielding tensors in isobutane (**1**), trimethoxymethane (**2**), bicyclo[1.1.1]pentane (**3**), bicyclo[1.1.1]pentanone (**4**), norbornadiene (**5**), and cubane (**6**), measured on natural abundance samples are reported.

Individual gauge for localized orbitals (IGLO)[4,5] calculations of the shielding tensors were performed on these compounds as well as on tetrahedrane (**7**). The calculations of the ^{13}C shielding tensor have provided a basis for the assignment of principal components to the molecular frame in cases for which the orientation cannot be determined by the molecular symmetry. The IGLO results agree with the ordering of the shielding magnitudes found experimentally in all cases in which the orientation can be determined from the experiment except in isobutane where the perpendicular and parallel components differ by only 4 ppm.

† Part 5 of this series: ref 2.

II. Experimental and Computational Methods

The spectra were taken at a temperature of about 20 K with an Air Products displex 202-B refrigeration unit.[3] The spectrum of cubane was also measured at about 6 K with a Heli-tran (Air Products Co.) because the spectrum at 20 K did not exhibit sharp features, suggesting that the molecule may have some degree of movement at this temperature. The 6 K spectrum shows a slightly different broad pattern, but the fitted tensorial values extracted from the spectra obtained at the two temperatures agreed within experimental error. A modest improvement is noted

(1) Beeler, A. J.; Cutts, P.; Orendt, A.; Grant, D. M.; Michl, J.; Zilm, K. W.; Downing, J. W.; Facelli, J. C.; Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1984**, *106*, 7672.
(2) Facelli, J. C.; Orendt, A. M.; Beeler, A. J.; Solum, M. S.; Depke, G.; Malsch, K. D.; Downing, J. W.; Murthy, P. S.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 6749.
(3) Zilm, K. W.; Conlin, R. T.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6672.
(4) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193.
(5) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360.

0002-7863/86/1508-4268$01.50/0