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# $^{23}$Na CHEMICAL SHIFTS OF SOME INORGANIC AND ORGANIC COMPOUNDS IN THE SOLID STATE AS DETERMINED BY THE MAGIC ANGLE SPINNING AND HIGH POWER NMR METHODS

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$^{23}$Na chemical shifts and linewidths of some inorganic and organic salts were examined by magic angle spinning and high power NMR methods. We found that $^{23}$Na linewidths are considerably narrowed when magic angle spinning was employed. Displacements of $^{23}$Na chemical shifts were also discussed.

$^{23}$Na NMR spectroscopy has been extensively utilized in solution state to analyze ion-ion and ion-ligand interactions of chemical and biological interest.$^{1-3)}$ For this purpose, it seems to be very valuable to have data of high resolution chemical shifts free from contribution of solvents employed and rate of chemical exchange. Nevertheless, no such data are available in the solid state except for those by Gauss et al.$^{4)}$ who determined $^{23}$Na chemical shifts by the conventional high power experiments. Generally, line-narrowing of quadrupolar nuclei such as $^{23}$Na (I= 3/2) is not simple as compared with that of spin-1/2 in which magic angle spinning (MAS)$^{5)}$ and/or high power proton-decoupling could be successfully used. However, recent studies$^{6-12)}$ showed that the central $1/2 \rightarrow -1/2$ transition of nuclei with nonintegral spins could be narrowed by magic angle spinning as far as the second-order splitting is negligible owing to smaller quadrupole coupling constant, because this line is not broadened by the first-order quadrupole interaction. Otherwise, rapid sample spinning at rotational axis other than 54°44' is more effective in line-narrowing.$^{12)}$ In the latter case, however, a knowledge of the quadrupole coupling constant is required to deduce the chemical shift values.

Accordingly, we aimed, in this communication, to survey the range of high resolution $^{23}$Na chemical shifts and linewidths of some inorganic and organic salts, to gain an insight into effectiveness of $^{23}$Na NMR spectroscopy in the solid state from chemical point of view. For this purpose, we have recorded $^{23}$Na NMR spectra of twenty samples which do not exhibit the second-order quadrupole splitting.

$^{23}$Na NMR spectra were recorded on a Bruker CXP-300 spectrometer operating at 79.35 MHz with and without MAS. For MAS experiments, samples were contained in an Andrew-Beams rotor machined from Derlin and spun as fast as 1.8-2.7 kHz. High power $^{23}$Na NMR spectra were recorded by placing samples in transverse solenoid coil. Accumulations were usually less than 50 times, but in some instances up to 500 times. 90° pulse was 6 μs and repetition time was 1 s. $^{23}$Na chemical shifts were measured relative to the signal of 1 M NaCl in aqueous solution. Chemicals were mainly from commercial sources and used without further purification.

First, we recorded high power $^{23}$Na NMR spectra to obtain overall spectral feature. In Table 1, we summarize the $^{23}$Na chemical shifts and linewidths of samples which give rise to a single or first-order split line. Hence, we do not discuss $^{23}$Na NMR spectra of NaOH, $NaNO_2$(two lines by

MAS), sodium propane sulfonate, and sodium lauryl sulfate whose spectral features are the second-order or asymmetric. Linewidths of Table 1 are in the range of 1.5 - 7 kHz, depending on variety of chemical structure. Theoretically, this central $1/2 \rightarrow -1/2$ transition is accompanied by the sidebands arising from $3/2 \rightarrow 1/2$ and $-1/2 \rightarrow -3/2$ transitions whose separation being $(3/2)(e^2qQ/h)$.[13,14] We noticed that the quadrupole coupling constant $e^2qQ/h$ is 36.8 and 1.2 kHz for $NaIO_4$ and $NaClO_4$, respectively. In other cases, however, no sidebands were observed.

Figure 1 illustrates typical $^{23}$Na MAS NMR spectra whose linewidths are reduced to values of less than 300 Hz. The extent of the line-narrowing by MAS experiments is more than one tenth except for that of $NaClO_4$, as indicated by the reduction factor of Table 1. This situation is readily understood, because in these cases the quadrupole coupling constants are either virtually zero (face-centered cubic for NaCl, NaBr and NaI) or very small because of symmetric crystal structure (rhombohedral for $NaN_3$ and $NaNO_3$, the quadrupole coupling constant of the latter being 334 kHz;[15] tetragonal for $NaIO_4$ (36.8 kHz) and $NaClO_4$ (1.2 kHz)). The second-order frequency shift of the central line is[13,14]

$$\nu^{(2)} = -\frac{3\nu_Q^2}{12\nu_L}(1-\mu^2)(1-9\mu^2) \quad , \quad \mu = \cos\theta$$

where $\nu_Q = (3/2)(e^2qQ/h)$ and $\nu_L$ stands for Larmor frequency. This frequency correction is less than 1 ppm even for $NaNO_3$ in the present condition of higher Larmor frequency (79.4 MHz) and could be neglected. In the cases of samples with larger linewidths, reduction of the linewidths by MAS is significant (see Table 1). The origin of the residual linewidths (up to 1.5 kHz) is complicated, but arises from dipolar interaction with nearby proton, second-order line-broadening and the presence of asymmetric field-gradients. As to the contribution of the dipolar interaction with proton, we found that proton irradiation results in further narrowing of linewidth in Na(HCOO) (about 50% reduction). This is also true for $Na(CH_3COO)3H_2O$, because removal of $H_2O$ results

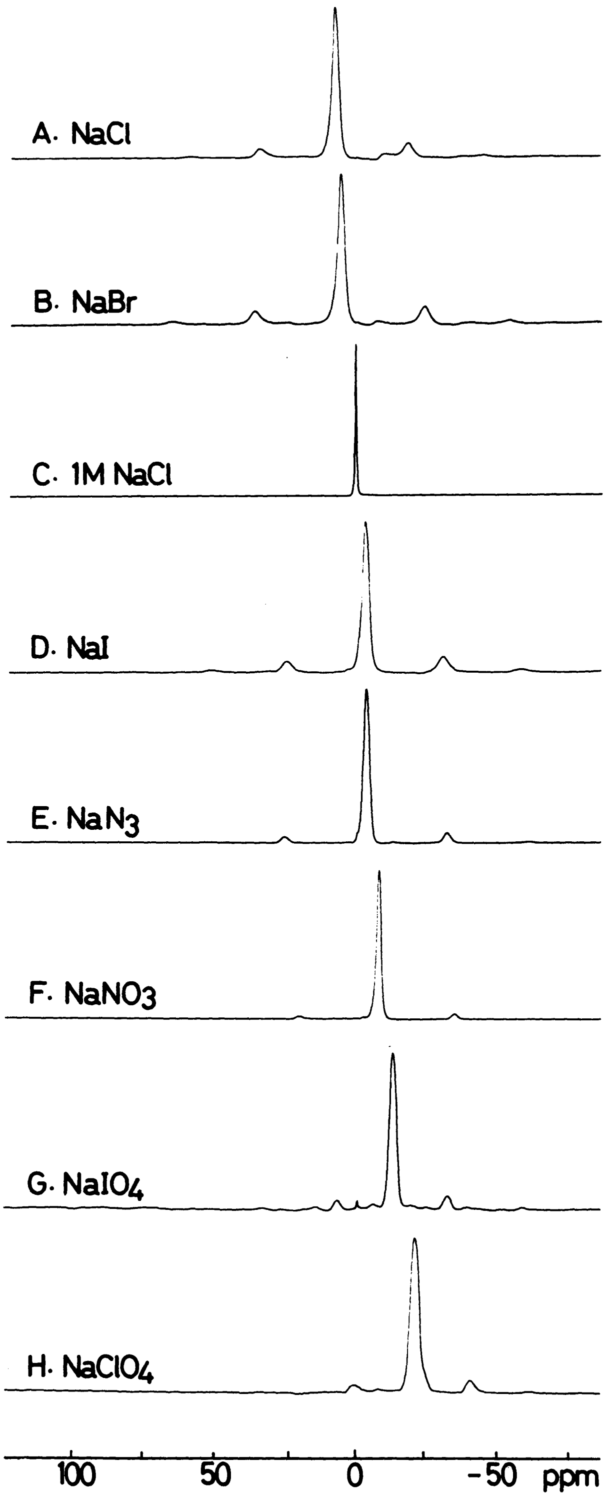

Fig. 1. 79.35 MHz $^{23}$Na MAS NMR spectra of some inorganic salts. Two weak peaks beside the central line are spinning sidebands. Chemical shifts were referred to 1 M NaCl in aqueous solution.

Table 1. $^{23}$Na chemical shifts (ppm) and linewidths (kHz) of some inorganic and organic salts measured by MAS and high-power NMR methods.

| Salts | MAS | | | High-power | | | Crystal structure[c] |
|---|---|---|---|---|---|---|---|
| | Shift[a] | Line-width | Reduction factor by MAS[b] | Shift[a] | Line-width | $e^2qQ/h$ (kHz) | |
| NaF | 7.9 ± 6 | 4.0 | 0.53 | 6 ± 12 | 7.5 | | face-centered cubic |
| NaCl | 7.9 ± 0.3 | 0.17 | 0.063 | 7 ± 4 | 2.7 | | face-centered cubic |
| NaBr | 6.0 ± 0.3 | 0.19 | 0.070 | 6 ± 4 | 2.7 | | face-centered cubic |
| $Na_4P_2O_7\ 10H_2O$ | 1.5 ± 1.7 | 1.1 | 0.20 | 2 ± 9 | 5.6 | | |
| $Na(CH_3COO)\ 3H_2O$ | -0.2 ± 1.7 | 1.1<br>0.7[d] | 0.26<br>0.16 | 0 ± 7 | 4.3 | | |
| Na(HCOO) | -0.2 ± 0.7 | 0.45[e]<br>0.8 | 0.17<br>0.30 | 0 ± 4 | 2.6 | | |
| Na Tartrate | -0.6 ± 1.0 | 0.60 | 0.25 | 0 ± 4 | 2.4 | | |
| Na Benzene sulfonate $xH_2O$ | -1.3 ± 1.0 | 0.58 | 0.18 | -3 ± 5 | 3.2 | | |
| Na Deoxycholate | -2 ± 2 | 1.4 | 0.64 | -2 ± 4 | 2.2 | | |
| NaI | -2.7 ± 0.4 | 0.22 | 0.09 | -3 ± 4 | 2.4 | | face-centered cubic |
| $NaH_2PO_4\ 2H_2O$ | -2.7 ± 1.6 | 1.0 | 0.23 | -1 ± 7 | 4.3 | | |
| $Na_2WO_4\ 2H_2O$ | -2.7 ± 0.8 | 0.50 | 0.11 | 0 ± 7 | 4.6 | | |
| $NaN_3$ | -3.5 ± 0.3 | 0.18 | 0.09 | -3 ± 3 | 2.1 | | rhombohedral |
| $NaHCO_3$ | -5.4 ± 0.6 | 0.36 | 0.11 | -7 ± 5 | 3.2 | | monoclinic |
| $NaNO_3$ | -7.3 ± 0.2 | 0.14 | 0.09 | -7 ± 2 | 1.5 | 334[f] | rhombohedral |
| Na Glutamate | -9 ± 2 | 1.4 | 0.20 | -6 ± 11 | 6.9 | | |
| 3Na Citrate $2H_2O$ | -9 ± 2 | 1.5 | 0.23 | -5 ± 10 | 6.4 | | |
| $NaIO_4$ | -12.5 ± 0.4 | 0.22 | 0.12 | -14 ± 3 | 1.9 | 36.8 | tetragonal |
| 2Na Citrate | -13 ± 3 | 1.6 | 0.23 | -9 ± 11 | 6.9 | | |
| $NaClO_4$ | -20.4 ± 0.5 | 0.30 | 0.20 | -23 ± 2 | 1.5 | 1.2 | tetragonal |

[a] Chemical shifts referred to 1M NaCl aqueous solution. [b] Ratio of the linewidth with MAS to that observed without MAS. [c] Ref. 17 [d] Data observed by proton-decoupling. [e] Data for dehydrated sample. [f] Ref. 15.

in the narrowing from 1.1 kHz to 0.7 kHz. It is found that the MAS experiment is less effective for NaF, because spectral width by the dipolar interaction with $^{19}$F nuclei is too large as compared with the rate of magic angle spinning.

Obviously, the $^{23}$Na chemical shift of NaCl is resonated at lowermost field, whereas that of $NaClO_4$ is at uppermost field. The range of the $^{23}$Na chemical shifts so far observed is about 30 ppm and is significantly small compared with that of other nuclei such as $^{13}$C, $^{15}$N, etc. This is due to the fact that this atom does not have valence p electron which plays important role to the paramagnetic shielding leading to wide-spread chemical shifts.[16] Thus, the local charge at Na atom may be important in determining $^{23}$Na chemical shifts. In this connection, it is expected that displacement of $^{23}$Na chemical shifts is related to the distance of $Na^+X^-$ system, because the extent of the charge transfer from Na to X atoms might be smaller when the distance is increased. In other words, $^{23}$Na nucleus is more shielded when the distance is increased, because higher electron density is created at Na atom. Consistent with this expectation, unit cell dimensions of $NaClO_4$ ($a_0$= 6.48, $b_0$= 7.06, and $c_0$= 7.08 Å) are much longer than those of NaCl ($a_0$= $b_0$= $c_0$= 2.8 Å).[17] The Na-O bond distance of the former is still 5.0 Å even if we assume that Cl-O is colinear with the axis of the unit cell and Cl-O distance is 1.46 Å. It appears that this sort of consideration is applied to interpretation of the $^{23}$Na chemical shifts thus obtained. However, careful analysis taking into account of the electronic nature of X atom is required to achieve more conclusive results. Interestingly, the $^{23}$Na chemical shift of NaI is considerably shifted upfield as compared with that of NaCl and NaBr. Such upfield displacement is partly due to the effect of heavy atoms, as encountered in $^{1}$H and $^{13}$C chemical shifts in a series of $^{1}$H-X[18] and $CH_3$-X,[19] respectively. The effect of heavy atoms was previously explained by a view of spin-polarization by the heavy atoms.[20,21]

It is interesting to note that the $^{23}$Na chemical shifts of organic salts whose Na atoms are bonded to oxygen atoms are very close to the shift of 1 M NaCl aqueous solution. This similarity would be understandable by taking into account that Na atom is solvated with $H_2O$ molecules in aqueous solution. In this connection, dilution shift of $^{23}$Na signal of NaX in solution is explained by the weight-averaged value of the $^{23}$Na chemical shift in the solid state and that it is completely solvated.

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