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^{19}F-NMR solid state investigations of monovalent alkali metal fluorides and tetra-alkylammonium fluorides

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Abstract

The ^{19}F-NMR chemical shifts of the alkali metal fluorides and of monovalent tetra-alkylammonium fluorides were measured under strictly anhydrous conditions. For reducing the line widths of the broad resonance signals, conventional and ultrafast MAS at 32 kHz rotational frequency as well as CRAMPS (combined rotation and multiple-pulse spectroscopy) techniques were used. Averaging the strong homonuclear dipolar interactions of fluorine by MAS, the dependence of line width on the frequency of sample rotation is given for $(CH_3)_4N^+ F^-$. The data obtained are compared with CRAMPS results. The broad distribution in shielding of the fluorine nucleus in the cubic alkali fluorides in the column from LiF to CsF is discussed in terms of cation–anion polarization effects, creating a partial covalent bond. The experimental chemical shift values were correlated with the Allred–Rochow electronegativities and with the polarizabilities of ions in the alkali fluoride crystals. The linear fit of both gave *R*-values better than 0.96. From the latter, a chemical shift of the "free F-ion" at −293 ppm, referred to CCl_3F, was extrapolated. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Prompted by the simple isotropic NaCl-type crystal structure of the alkali metal fluorides, these materials have been the subject of a number of experimental studies and of ab initio calculations on ^{19}F chemical shielding [1–4]. Overviews and literature summaries on ^{19}F magic angle spinning and high resolution F-NMR in solids are given by Harris and Jackson [5] and by Miller [6]. Previous reviews have been given by Gagarinski and Gabuda [7] and by Mason [8].

Isotropic magnetic shielding is expected for fluorine of the cubic structures of alkali fluorides as they are being considered as totally ionic compounds. The differences actually observed in the chemical shifts of up to 210 ppm in going from LiF to CsF are accounted for by the variation of the paramagnetic contribution to the shielding. Conceptually, the paramagnetic part is zero in the spherically symmetric F^- ion. Polarization effects increase the paramagnetic contribution and cause the resonance to be displaced to the lower field. According to Kondo and Yamashita [9], in a crystalline environment, this term is proportional to the overlap integral between the F p-orbital and that of the nearest neighboring ions.

The changes of the ^{19}F chemical shift from LiF to CsF, which indicate a partial deshielding of the fluorine nuclei, are attributed to an electron density transfer from the fluoride ion to the metal ion [2], consistent with partially covalent bonding. Cai et al. [4] have carried out ab initio calculations with the GIAO method for octahedrally coordinated F-clusters and for a more complex cluster in the case of LiF. Their results agree well with the experimental shift data. Attempts of Hayashi and Hayamizu [2] to correlate their measured chemical shift values with structural factors of the alkali fluorides were not successful.

Moreover, efforts were made for reducing the line widths of the generally broad NMR resonances. This is usually done by (i) spinning out the strong dipolar interactions of fluorine with high rotational rates in MAS, (ii) special multiple pulse sequences as REV 8, and (iii) the combination of both as with CRAMPS [10,11]. Smith and Burum [10] reported in their ^{19}F-CRAMPS study good efficiency in line narrowing of resonance signals of CaF_2/F-apatite mixtures. The residual line widths in MAS in the case of homonuclear dipolar interaction is inversely proportional to the rotation rate, a formula describing the relation quantitatively is given in [12]. Its use for the calculation

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of line widths at given spinning rates and at static conditions is reported here.

To the best of the authors' knowledge, ^{19}F-CRAMPS measurements of alkali metal fluorides have not yet been reported. However, the Harris group contributed strongly to this methodology with investigations of other inorganic as well as of organic fluorinated compounds (see, e.g. [5,6]). ^{19}F-NMR data of tetra-alkylammonium fluorides are not mentioned in the literature, except that of the commercially available hydrated tetra-butylammonium fluoride·3H_2O.

2. Results and discussion

2.1. Chemical shifts of alkali metal fluorides

The fluorine chemical shifts of the solid alkali fluorides cover a wide range of shielding from −222 ppm for NaF to −14 ppm in CsF. The MAS spectrum of LiF is presented in Fig. 1 at rotational frequencies of 12 and 32 kHz. Table 1 presents chemical shift values in comparison with data taken from the literature.

The chemical shift data of Table 1, involving the data published by Mortimer et al. [3], Hayashi and Hayamizu [2], and Sears [1] can be regarded as being consistent. In the light of these data, our RbF-value of −124 ppm and also that one of Sears with −119 ppm are suspect, most probably the RbF has become partly hydrated, and therefore, no FWHHs are reported. To elucidate the disagreement of our and the reported RbF-chemical shifts, the dependence of ^{19}F-NMR shifts on water content will be studied separately.

Because of this, our RbF fluoride chemical shift is replaced for the subsequent considerations by the more realistic averaged value of −90 ppm obtained from [2,3,6]. The residual line widths at definite conditions are given as FWHH (full width at half height) in kHz.

Because magnetic shielding, σ, and chemical shift, δ, respectively, are parameters for electron density at the nucleus being investigated, we tried to correlate our experimental data with electronic and structural data of the alkali fluorides as, e.g. electronegativity, EN, and electronic polarizability, α. Electronegativity as a measure for an atom to attract electrons can be described by a function that includes size and charge of the atom. Our experimental ^{19}F chemical shift values correlate quite well with Pauling's electronegativities of the alkali metals (correlation coefficient R, 0.88) and even better with the improved EN approximation by Allred–Rochow (R, 0.960) as shown in Fig. 2.

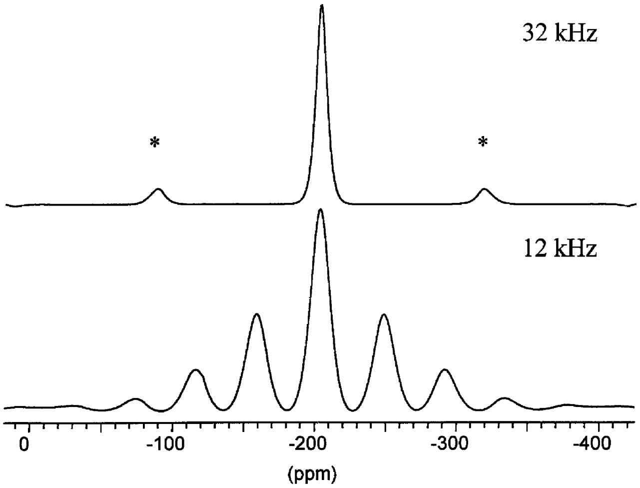

Fig. 1. ^{19}F-MAS spectra of LiF with rotation frequencies of 32 kHz (top) and 12 kHz (bottom) measured at 282 MHz, (∗) rotational sidebands.

Commonly, the ions of the alkali metal fluorides are considered ideally as unperturbed spheres. This assumption holds only as a close approximation to spherically shaped particles. Practically, the geometric size of the ions in the cubic lattice exhibit minor deviations from the spherical arrangement, because of mutual cation–anion polarization effects. This fact is also vividly shown by contour maps of experimental as well as of calculated electron densities of the alkali metal fluorides [13], comparing the hypothetical "pro-molecule" and the bonding state of the ion pairs. The first stage is represented by a nearly symmetric charge distribution at fluorine, while the latter possesses polarized and overlapping electron clouds. In terms of ^{19}F-MAS spectroscopy, this is consistent with deshielding of the fluorine nucleus and contributes to the paramagnetic shielding tensor.

Table 1
^{19}F-NMR chemical shifts δ in ppm of alkali metal fluorides relative to CCl_3F and half line widths FWHH

MF	This work		Mortimer [3] δ	Hayashi [2] δ	Sears [1] δ
	δ (ppm)	FWHH[c] (kHz)			
LiF	−203	2.575[a]	−206	−204	−206
NaF	−221	1.532[b]	−226	−221	−224
KF	−136	0.733[b]	−135	−130	−136
RbF	−124		−93	−88	−119
CsF	−14	1.410[b]	−19	−8	−10

[a] MAS ν_{rot} 32 kHz.
[b] CRAMPS.
[c] Full width at half height.

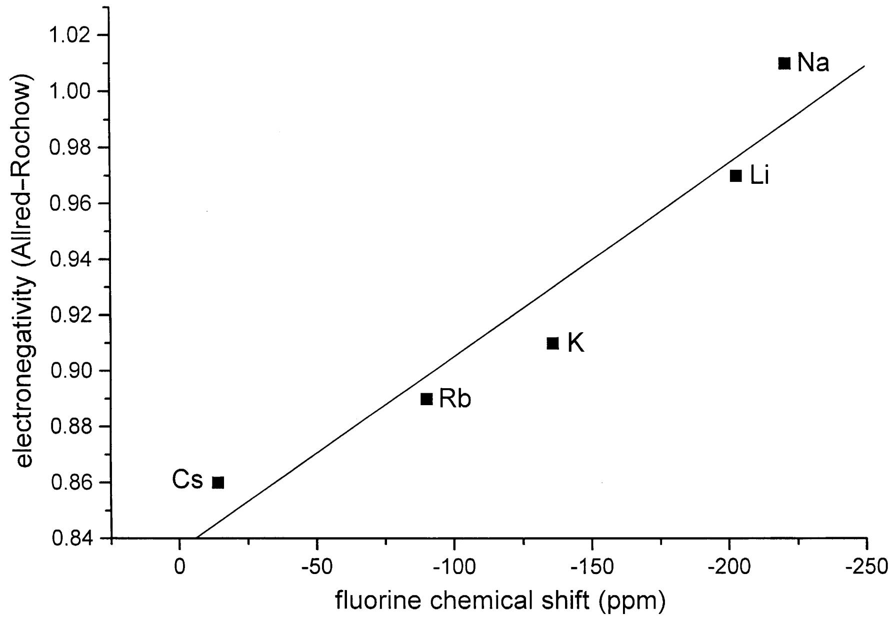

Fig. 2. Allred–Rochow electronegativities of alkali metal fluorides as function of the fluorine chemical shift.

From the metal ion data of α in Table 2 [14] it is obvious that mutual interactions of ion polarization might take place. While Li^+, Na^+ and K^+ may polarize the fluoride ion to a certain extent, conversely, the larger metal ions are polarized by the fluoride ion.

This electronic interaction causes a covalent part of bond in addition to the major ionic bonding in the ionic crystals.

Acknowledging the importance of the degree of covalent bonding in the basically ionic alkali fluorides for the deshielding of the fluorine nuclei, as exemplified in [9], we looked for linear correlation of δ_F with polarizability data. While the polarizabilities of the isolated metal ions gave only poor results, the use of the polarizabilities of the crystalline metal fluorides [15] improved the correlation coefficient to 0.9869 (Fig. 3). Introducing the steric parameter R^{-2} to α, where R is the distance between the two ions, the correlation coefficient of the linear relationship of the function $\alpha R^{-2} = f(\delta_F)$ increased to 0.9967.

The ion pair α-values involve the effect of lattice interactions on the polarizabilities of the component ions in the fluorides: that means, the polarizability of the positive ion is increased in the crystal and that of the fluoride ion is decreased, relative to the values that characterize the free ions [15]. The convincing result of the presentation is that one can see qualitatively the increasing part of covalency in the metal fluorides from LiF to CsF.

It is necessary to note the specific behavior of LiF, where the chemical shift of −203 ppm does not fit well the correlation, as expected. Its position in the graphs has changed with that of NaF, which can be explained by the small size of the Li^+ ion. This small ion exhibits reduced shielding for fluoride in the lattice and makes possible additional fluoride interactions from the second co-ordination sphere. This type of interaction is taken into account for ab initio shielding calculations of [4], where a complex cluster model had to be used that involves a second co-ordination arrangement.

2.2. Chemical shifts of alkylammonium fluorides

While the alkali fluorides are a priori isotropic with their cubic structure, tetra-alkylammonium fluorides possess deviating anisotropic structures. For instance, tetra-methylammonium fluoride (TMAF) occurs in a hexagonal structure [16]. Therefore, the chemical shifts of the different types of compounds cannot be compared with each other. The only reported chemical shift data of tetra-alkylammonium fluorides are that of the water containing tetra-ethyl- and

Table 2
Electronic polarizabilities α of alkali metal ions [14] of fluoride ion [14] and of pairs of ions in alkali metal fluorides [15]

Metal ion	α (10^{-24} cm^3)	Fluoride ion	α (10^{-24} cm^3)	Ion pairs	α (10^{-24} cm^3)
Li^+	0.029	F^-	1.04	LiF	0.927
Na^+	0.179			NaF	1.196
K^+	0.830			KF	2.023
Rb^+	1.40			RbF	2.634
Cs^+	2.42			CsF	3.686

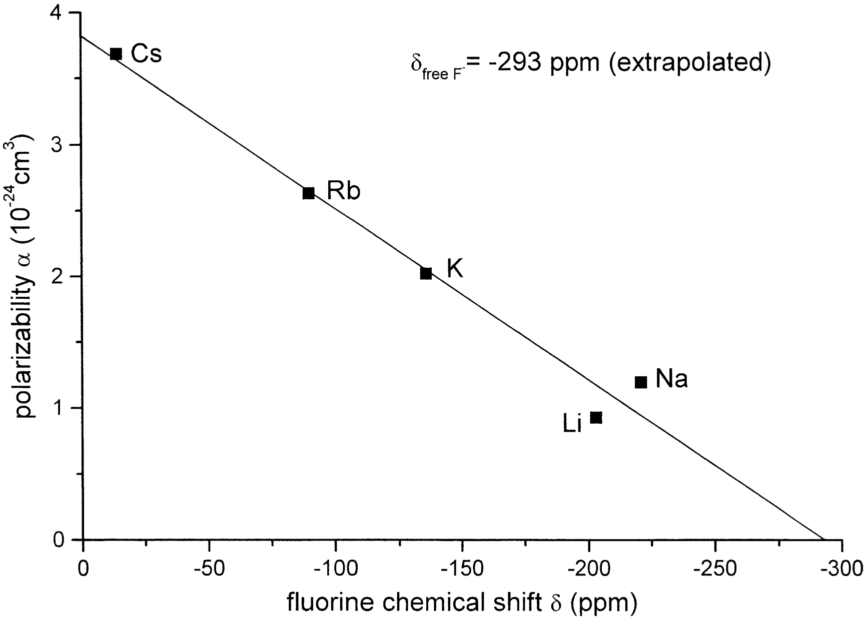

Fig. 3. Variation of the alkali fluoride polarizabilities α with the fluorine chemical shift.

tetra-butylammonium fluorides [17], which we have confirmed in our study.

TMAF with its large cation is used in nonaqueous preparative chemistry as source of a weakly solvated "naked fluoride" with much greater reactivity and especially basicity than the commonly used KF and CsF. The fluorides in Table 3, in addition to TMAF, are trimethyl(neopentyl)ammonium fluoride (TMNPAF), trimethyl(benzyl)ammonium fluoride monohydrate and tetra-(*n*-butyl)ammonium fluoride trihydrate, which were prepared according to standard procedures [16] except the latter, which is a commercial product.

Compounds 3 and 4 are hydrates and cannot be obtained free of water, because of a Hofmann-type destruction when heated in vacuum for removing of residual water. The other two are very sensitive to moisture. The fluorides were measured with the CRAMPS method and with MAS only. The MAS results of TMAF concerning the line width with varying rotational rates from 5 to 8 kHz will be given below.

The δ_F values of these tetra-alkylammonium fluorides are comparatively close, despite fluoride being unsolvated in TMAF and TMNPAF, but hydrated in the others. These findings indicate that in the solid state the fluoride ions in both TMAF and TMNPAF might be interacting strongly with their counterions.

Table 3
Chemical shift data and line widths (FWHH) of tetra-alkylammonium fluorides obtained by the CRAMPS method

No.	Substance	δ (ppm)	FWHH (kHz)
1	$[(CH_3)_4\,N]^+\,F^-$	−98	2.171
2	$[(CH_3)_3CCH_2\,N\,(CH_3)_3]^+\,F^-$	−120	2.888
3	$[C_6H_5CH_2\,N\,(CH_3)_3]^+\,F^-\cdot H_2O$	−129	0.936
4	$[(C_4H_9)_4\,N]^+\,F^-\cdot 3H_2O$	−110	1.438

2.3. Chemical shift of the virtual "free fluoride ion"

As a fluoride ion either in solution or in a solid is inevitably under the influence of its surroundings, the chemical shift of an unperturbed fluoride ion can not be measured directly. The absolute shielding of the free unperturbed fluoride one can obtain only by quantum-chemical calculations describing a species in free space in vibrationless state. This value is calculated to be σ_F^{calc} −480.2 ppm [8,18], which corresponds to a chemical shift δ of −291 ppm according to the equation

$$\delta_{calc}(^{19}F) = \sigma_F^{CFCl_3} - \sigma_F^{calc} \qquad (1)$$

where $\sigma_F^{CFCl_3}$ is the shielding constant of the standard with −189 ppm [18]. Straightforwardly, from the graph in Fig. 3 we found a chemical shift value for the "free" fluoride ion of −293 ppm by extrapolation to zero polarizability. The linear regression of the straight line obeys the equation

$$y = 0.01303x + 3.82414 \qquad (2)$$

When y becomes zero the intercept at x amounts to −293 ppm, the chemical shift of the unperturbed F^- ion.

Independently, our ab initio deshielding calculations by the IGLO-methodology of the fluorine in the C–F-bond of the recently discovered fluorocarbonate ion FCO_2^- [19] gave an undisturbed free fluoride ion chemical shift of −250 ppm corresponding to a 10 Å distance between the two atoms.

2.4. Methodologies for reducing linewidths

Broad resonance lines up to 50 kHz are the inherent characteristics of ^{19}F-solid state NMR. The line shape functions of the signals differ and are of Gaussian, Lorentzian or of a more complex multiple peak type.

Table 4
Magic angle spinning of TMAF with varying rotational frequencies

Spinning speed (kHz)	Line width FWHH (kHz)	Spinning efficiency[a]
0 (static line)	16.650	0.0
5	1.800	9.2
6	1.620	10.2
7	1.260	13.1
8	1.150	14.4

[a] Ratio of static to residual FWHH.

Great efforts have been made to obtain high NMR resolution in solids by reducing the widths of the resonance lines, especially for the very strong dipolar interactions of fluorine and of hydrogen nuclei. The efficiency of averaging dipolar interactions of some principal decoupling methods for selected monovalent fluorides is given below.

2.4.1. Magic angle spinning (MAS)

The influence of rotational speed in the range of 5–8 kHz is shown for dipolar decoupling of the resonances of tetramethylammonium fluoride (Table 4, Fig. 4). It is obvious from the data presented that the spinning efficiency has improved remarkably with increasing speed. The comparable CRAMPS spectrum of TMAF gives a line width of 2.171 kHz, which corresponds to an efficiency of 7.7.

Fig. 4 presents in a graph the linear relationship of the residual line widths of TMAF over a range of the reciprocal spinning speed. From the slope of the curve, the static line width can be calculated for homonuclear coupling, using the Eq. (3) given by Pfeifer and co-workers [12],

$$\nu_{\text{MAS}} = \frac{(\nu_0)^2}{A}\frac{1}{\nu_{\text{rot}}} \qquad (3)$$

where ν_{MAS} is the residual linewidth, ν_0 the static line width, ν_{rot} the rotational frequency, and A a factor concerning the line shape function and crystal lattice.

From Eq. (3) the spinning speed can be calculated which is needed to obtain a definite line width of a resonance signal, e.g. for a 500 Hz residual line in case of TMAF a 18.2 kHz speed is needed, on the other hand a 32 kHz rotational rate will narrow the line to 280 Hz. As factor A we used the number 30 because of the Lorentzian line shape [12], using that value, calculated data are in good agreement with our experimental values. This example is showing the usefulness of Pfeifer's equation in addition to and in combination with the experiment.

Considering our ^{19}F-MAS resonances for the high speed MAS in LiF, the static line width, which is not experimentally available in the literature, is calculated to 49.6 kHz. At a 12 kHz spinning rate the experimental line width is 4176 Hz, and at 32 kHz it amounts to 2575 Hz, which is a spinning efficiency of 19.3.

2.4.2. Cramps

In this study, high-power, phase-alterated sequences such as MREV-8 and multiple pulse combined with rotation were applied to get information concerning their efficiency in line narrowing. The important relationship for effective CRAMPS operation is

$$t_c \ll t_{\text{rot}}$$

where t_c is the time of the pulse sequences and t_{rot} the rotation period. Practically, with pulses much shorter than 100 μs, spinning rates have to be <5 kHz.

The efficiency of decoupling of dipolar interactions is exemplified for NaF. Its static linewidth is 33.9 kHz, and the FWHH at 12.5 kHz spinning rate is 1.91 kHz

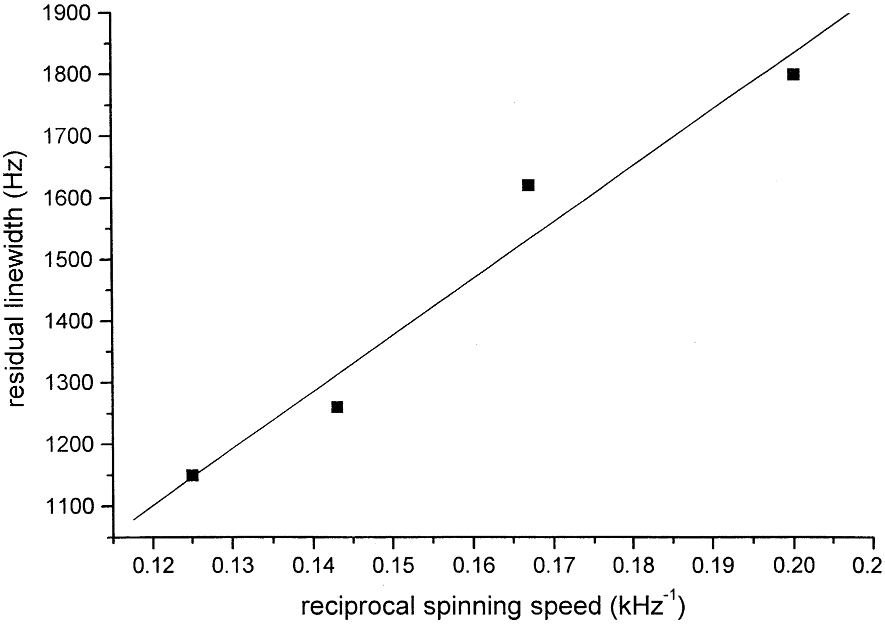

Fig. 4. Residual ^{19}F-NMR linewidth as a function of reciprocal spinning speed for TMAF.

[11], while our experimental CRAMPS value amounts to 1.532 kHz. On the other hand, comparing our line width data for tetra-methylammonium fluoride, TMAF, obtained by the CRAMPS method (Table 3) with that of MAS (Table 4), high speed MAS proved to be more efficient in this case.

3. Conclusions

^{19}F-NMR chemical shifts and respective line widths of solid alkali metal fluorides have been reinvestigated by MAS, and, especially, by the MREV-8 CRAMPS-method. In addition, hitherto unreported solid state ^{19}F-NMR data of some tetra-alkylammonium fluorides have been determined. The chemical shift values, except that of RbF, are in good agreement with data given in the literature, where applicable, and the reduction of line widths is efficient. The ^{19}F chemical shift data of the alkali metal fluorides could be convincingly linearly correlated with physical data of the fluorides, i.e. with metal ion electronegativity and with ion pair electronic polarizabilities, confirming a covalent part of bonding in the ionic fluorides. The free fluoride ion chemical shift with a value of -293 ppm was deduced by extrapolation from the linear graphical presentation.

This study of electron deshielding at fluorine contributes to the overall bonding properties of the alkali metal fluorides, which are not exclusively ionic.

4. Experimental

^{19}F-CRAMPS-spectra were recorded with the solid state NMR spectrometer FKS 176 (ZWG Academy of Sciences, Berlin, Germany) at 56.4 MHz frequency with MREV-8 multiple-pulse sequences and spinning rates of 2–5 kHz, using 4 mm polyethylene-rotors. The maximum error of the shifts are of the order of $\pm$2–4 ppm.

The pulse widths were 1.0–1.2 μs for 90° pulses and τ 4.1 μs for MREV-8, total cycle time 12τ of about 50 μs. Repetition rate 2–10 s, spectral width 250–330 kHz.

The effective scaling factor SF_{eff} was used as criterion for the successful set up of the MREV-8-CRAMPS conditions. In all experiments the deviation from the theoretical scaling factor was <10%. Chemical shifts were measured with respect to external CF_3COOH and referred to the CCl_3F standard.

The LiF MAS-sample was measured with a Bruker AMX-300 at 282,2 MHz and spinning rates of 12 and 32 kHz (pulse width 3 μs, 90°; repetition rate 2 s; spectral width 125 kHz; probe diameter 2.5 mm), while tetra-methylammonium fluoride was studied by MAS using a Varian 400-spectrometer at 376,2 MHz for ^{19}F under static conditions as well as with rotational rates of 5–8 kHz (5 mm rotor) and for comparisons with CRAMPS.

4.1. Preparation of the monovalent fluorides

Commercially available anhydrous alkali metal fluorides were heated for several hours in vacuo under dynamic conditions to about 200–250 °C.

A commonly used method for preparing nonaqueous tetra-alkylammonium fluorides is the neutralization of the corresponding hydroxide with aqueous hydrofluoric acid [16]. For example, a 10% tetra-methylammonium hydroxide solution (Merck) was titrated with an equimolar amount of a diluted aqueous hydrofluoric acid in a polyethylene container. The water was removed in a rotavapor forming a slurry. Evaporation to dryness was continued under good dynamic vacuum at 150 °C with careful control of the heating. The drying process was checked at regular intervals by IR- and NMR-measurements. The endpoint, corresponding to a very high degree of dryness, was confirmed by a single ^{19}F-NMR signal at -72 ppm in acetonitrile solution.

The preparations of trimethyl(neopentyl)ammonium fluoride (TMNPAF) and of trimethyl(benzyl)ammonium fluoride (TMBAF) were carried out principally by the same method. Because of thermal decomposition, the temperature should not exceed 130 °C in case of TMNPAF (δ -72.2 ppm in CH_3CN), and 100 °C for $TMBAF{\cdot}H_2O$ (δ -72.8 ppm; elemental analyses confirmed the chemical formula. Anal. calcd for $C_{10}H_{16}NF{\cdot}H_2O$:C, 64.2; H, 9.6; N, 7.5; F, 10.0. Found: C, 63.7; H, 9.4; N, 7.5; F, 9.9).

Because of their extreme sensitivity to moisture, the fluorides, especially KF, RbF, CsF and alkylammonium fluorides, were handled in a Braun Labmaster 130 drybox, and gas tight rotors were used. As for example: some of the chemical shift values reported by Clark et al. [17] are irreproducible, obviously because of hydrate formation (see [6], p. 268 and 271). All chemical shifts reported are referenced to CCl_3F as standard, with values upfield assigned negative.

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