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Review

Solid-state NMR spectroscopy of the quadrupolar halogens: chlorine-35/37, bromine-79/81, and iodine-127

David L. Bryce* and Gregory D. Sward

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

A thorough review of $^{35/37}$Cl, $^{79/81}$Br, and ^{127}I solid-state nuclear magnetic resonance (SSNMR) data is presented. Isotropic chemical shifts (CS), quadrupolar coupling constants, and other available information on the magnitude and orientation of the CS and electric field gradient (EFG) tensors for chlorine, bromine, and iodine in diverse chemical compounds is tabulated on the basis of over 200 references. Our coverage is through July 2005. Special emphasis is placed on the information available from the study of powdered diamagnetic solids in high magnetic fields. Our survey indicates a recent notable increase in the number of applications of solid-state quadrupolar halogen NMR, particularly ^{35}Cl NMR, as high magnetic fields have become more widely available to solid-state NMR spectroscopists. We conclude with an assessment of possible future directions for research involving $^{35/37}$Cl, $^{79/81}$Br, and ^{127}I solid-state NMR spectroscopy. Copyright © 2006 John Wiley & Sons, Ltd.

INTRODUCTION

Even casual practitioners of solid-state nuclear magnetic resonance (SSNMR) spectroscopy will likely have acquired a free-induction decay for one of the quadrupolar halogens: ^{79}Br in potassium bromide, to set the magic angle, as suggested by Frye and Maciel over twenty years ago.[1] In this review article, we present several other diverse applications of quadrupolar halogen SSNMR spectroscopy.

Approximately two-thirds of the NMR-active nuclei in the periodic table are quadrupolar, i.e. they have nuclear spin quantum numbers (*I*) greater than one-half.[2,3] Of the NMR-active halogen nuclei, ^{19}F, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, and ^{127}I, all are quadrupolar with the exception of ^{19}F ($I = 1/2$). SSNMR spectroscopy of quadrupolar nuclei may pose many challenges,[4,5] the most unique of which stem from the nonzero nuclear electric quadrupole moment, *Q*, which vanishes for spin-1/2 nuclei. Furthermore, there are additional considerations common to all NMR-active nuclei such as the magnetogyric ratio of the nucleus to

be studied and its natural abundance. SSNMR generally offers decreased rates of nuclear spin relaxation compared to solution nuclear magnetic resonance (NMR) of the quadrupolar halogens.

The NMR properties of the quadrupolar halogen nuclei are summarized in Table 1. (We are not aware of any attempts to perform SSNMR on radioactive ^{211}At ($I = 9/2$).[6]) Of these nuclei, only ^{35}Cl and ^{37}Cl may be considered 'low-γ', and even for these only moderately so, as their resonance frequencies are no more than a few percent below ^{15}N. Smith has summarized the recent progress in SSNMR of low-γ nuclei and discussed the experimental challenges associated with observing such nuclei.[7] Both bromine isotopes as well as ^{127}I are well within the standard tuning ranges of commercially available magic-angle spinning (MAS) probes. Why, then, have there been comparatively few SSNMR studies of these nuclei? The answer is not surprising: it is due to the moderately large values of *Q* associated with each of these isotopes, resulting in broad NMR lineshapes for nuclei in all but the most symmetric of environments. There have therefore been two general approaches to performing NMR spectroscopy of the quadrupolar halogens in solid materials. The first relies on choosing compounds where the nucleus sits at a site of high symmetry, resulting in a low electric field gradient (EFG) around the nucleus, so that powdered samples may be studied with relatively standard static echo and possibly MAS experiments. The second option

*Correspondence to: David L. Bryce, Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada.
E-mail: dbryce@uottawa.ca

Table 1. NMR Properties of the quadrupolar halogen nuclides (adapted from Harris *et al.*[2])

	I	N.A./%	$\gamma/10^7$ rad $T^{-1}\,s^{-1}$	Larmor frequency at 11.75 T/MHz	Q/mb[a] (From Pyykkö[8])	Linewidth factor[b] / fm^4	Relative receptivity $D(^1H)$[c,3]	Relative receptivity $D(^{35}Cl)$
^{35}Cl	3/2	75.78	2.624198	49.074	−81.65(80)	89	3.58×10^{-3}	1.0
^{37}Cl	3/2	24.22	2.184368	40.850	−64.35(64)	55	6.59×10^{-4}	0.18
^{79}Br	3/2	50.69	6.725616	125.773	313(3)	1306	4.03×10^{-2}	11.3
^{81}Br	3/2	49.31	7.249776	135.576	261.5(25)	912	4.91×10^{-2}	13.7
^{127}I	5/2	100	5.389573	100.789	−710(10)	1613	9.54×10^{-2}	26.7

[a] 1 mb = 10^{-31} m^2.

[b] Linewidth factor, $l = (2I + 3)Q^2/((I^2)(2I - 1))$.

[c] Receptivity relative to that of ^{1}H, calculated using $D_X^{1H} = \left| \dfrac{\gamma_X^3}{\gamma_{1H}^3} \right| \left(\dfrac{NA(X)}{NA(^1H)} \right) \left(\dfrac{I_X\,(I_X + 1)}{I_{1H}\,(I_{1H} + 1)} \right)$.

is single-crystal NMR, where a sharp resonance is observed for a particular crystal orientation. The latter method has been extensively employed in the solid-state physics literature for studying quadrupolar halogen relaxation times in paramagnetic and ferromagnetic materials. In addition, many such studies are carried out in relatively low applied magnetic fields, where the 'NMR' experiment is effectively Zeeman-perturbed nuclear quadrupole resonance (NQR).

The potential of applying more-or-less 'standard' static-echo and MAS methods to the quadrupolar halogens in various diamagnetic compounds is enticing, given the ubiquity of these elements. All of the isotopes have high natural abundances and relative receptivities. The problem is the linewidth factor arising from the large values of Q. Since the second-order quadrupolar linewidth of the central transition (CT) scales inversely with B_0, particularly high-field magnets may offer new opportunities in the study of the quadrupolar halogens. NMR facilities with high-field and so-called 'ultra-high' field magnets dedicated to the study of solid samples are becoming more widely available to the NMR community. For example, the high-field magnetic resonance facility at Pacific Northwest National Laboratory[9] in Richland (USA), the National High Magnetic Field Laboratory (NHMFL)[10] in Tallahassee (USA), the Center for NMR Spectroscopy and Imaging of Proteins[11] in La Jolla (USA), and the newly-created National Ultra-High Field NMR Facility for Solids[12] in Ottawa (Canada), to name but a few centers, all have 900 MHz instruments available for solid-state NMR experiments. Additionally, the NHMFL has experimental magnets with fields of up to 45 T.

In this review, we limit ourselves to solid-state NMR data. In particular, our focus is on recent studies related to diamagnetic solids, and we have tried to be as thorough as possible in reviewing the literature on this topic. We have also covered the abundance of reports on paramagnetic and ferromagnetic materials, from which mainly relaxation data have been extracted. We have not attempted to cover solution NMR results,[13] zero-field NMR results,[14−16] NQR,[17−20] or Zeeman-NQR results.[21,22] It is certainly recognized that these methods also provide valuable information on the nuclear environments in the form of, for example, quadrupolar coupling tensors and relaxation rate constants. We note,

for example, the detailed review of quadrupolar halogen solution NMR by Lindman and Forsén.[13]

THEORETICAL AND EXPERIMENTAL BACKGROUND

Theoretical

Here, we briefly reiterate some of the methods, concepts, conventions, and terminology associated with our discussion of SSNMR spectroscopy of the quadrupolar halogens.

The relevant Hamiltonian operator for a quadrupolar nucleus in a diamagnetic solid in a magnetic field consists of at least the three following terms:

$$\hat{H} = \hat{H}_Z + \hat{H}_\sigma + \hat{H}_Q \tag{1}$$

The first term represents the Zeeman interaction between the nucleus and the applied magnetic field. The second term represents the nuclear magnetic shielding interaction between the nucleus and the surrounding electrons. The third term represents the nuclear electric quadrupolar interaction between the quadrupole moment and the surrounding EFG. Additional interactions may become important depending on the situation, such as the direct dipolar coupling and the indirect nuclear spin–spin coupling (J) interactions.[23] Aside from the Zeeman interaction, the effects of the quadrupolar interaction are typically dominant in the SSNMR spectroscopy of the quadrupolar halogens.

Nuclear magnetic shielding interaction

The nuclear magnetic shielding (σ) interaction between the nucleus and the surrounding electrons may be decomposed into diamagnetic and paramagnetic terms after Ramsey.[24−28] The σ tensor is, in general, anisotropic and antisymmetric and may therefore be decomposed into isotropic, symmetric, and antisymmetric parts. Experimentally, one measures chemical shifts (CS) (δ) relative to a reference material. The components of the CS tensor are related to those of the magnetic shielding tensor as follows:

$$\delta_{ii} = \frac{\sigma_{ii,\text{ref}} - \sigma_{ii}}{1 - \sigma_{ii,\text{ref}}} \times 10^6 \tag{2}$$

where ii denotes a particular component of the tensor, or the isotropic value. We follow the Maryland conventions[29]

for reporting the magnitude of the σ and δ tensors. The principal components of the tensors are ordered as follows: $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$ and $\delta_{11} \geq \delta_{22} \geq \delta_{33}$. Alternatively it is convenient to use the span, Ω,

$$\Omega = \delta_{11} - \delta_{33} \tag{3}$$

which describes the breadth of the powder pattern associated with the CS tensor, and the skew, κ,

$$\kappa = \frac{3(\delta_{22} - \delta_{iso})}{\Omega} \tag{4}$$

which describes the asymmetry of the CS tensor.

Shown in Fig. 1 are representative solid-state chlorine isotropic chemical shifts for various chlorine compounds including chloride and perchlorate salts. The IUPAC-recommended CS references for the quadrupolar halogens are a 0.1 M solution of NaCl in D_2O, a 0.01 M solution of NaBr in D_2O, and a 0.01 M solution of KI in D_2O, for chlorine, bromine, and iodine, respectively.[2] One should be cautious in substituting a solution prepared in H_2O (instead of D_2O), as large solvent isotope shifts are known to exist. Lauterbur and coworkers[30] have measured the following solvent effects: for a 1–3 M NaCl solution, $\delta(^{35}Cl, H_2O) - \delta(^{35}Cl, D_2O) = 4.7 \pm 0.3$ ppm; for a 0.41–0.82 M RbBr solution, $\delta(^{79/81}Br, H_2O) - \delta(^{79/81}Br, D_2O) = 8.3 \pm 0.3$ ppm; for a 0.45–0.95 M NaI solution, $\delta(^{127}I, H_2O) - \delta(^{127}I, D_2O) = 13.2 \pm 2.5$ ppm.

Often, a solid standard is more convenient for setting up SSNMR experiments. The alkali metal halides are convenient for this purpose, with the potassium salts being somewhat preferred over e.g. sodium or cesium salts, because of the lower magnetogyric ratio of ^{39}K, which results in reduced dipolar broadening of the halogen resonance. Weeding and Veeman[86] have provided measurements of the isotropic ^{35}Cl chemical shifts of solid CsCl (109.4 ppm), NH$_4$Cl (74.0 ppm), RbCl (44.7 ppm), KCl (3.07 ppm), and NaCl (−46.1 ppm) with respect to 'dilute Cl$^-$' (see below and Table 2 for further discussion and ^{37}Cl shifts). The value reported for NaCl is in good agreement with the value of −45.4 ppm obtained with respect to an infinitely dilute NaCl solution in H_2O.[55] In the case of bromine, solid KBr is a suitable standard (and is convenient since it may be used to set the magic angle as well), although other alkali metal bromides have also been used. Solid KI and NaI are useful standards for ^{127}I SSNMR. However, since there has been less work done on bromine and iodine SSNMR compared to chlorine, there is no single

accepted solid CS reference in these cases. It is therefore recommended that any CS referencing scheme be carefully checked against the IUPAC references.

Although to date there have been very few attempts to apply quantum chemical calculations in the interpretation of quadrupolar halogen magnetic shielding/CS parameters derived from SSNMR (*vide infra*), it is imperative to have a reliable absolute magnetic shielding scale for this purpose.[115] Such a scale allows for a proper comparison between experimentally measured chemical shifts and theoretically determined magnetic shielding constants. Gee *et al*. have established an absolute magnetic shielding scale for chlorine.[116] The absolute shielding constant of the chloride ion in infinitely dilute aqueous solution was found to be 974 ± 4 ppm. To our knowledge, absolute shielding scales are not available for bromine or iodine.

Nuclear electric quadrupolar interaction

Quadrupolar nuclei, in addition to being subject to the magnetic shielding interaction, are also influenced by the nuclear electric quadrupolar interaction. Several original articles as well as reviews are available on the nuclear electric quadrupolar interaction in solids.[4,117–123]

As mentioned earlier, the nuclear electric quadrupolar interaction is between Q and the surrounding EFG. The second-rank EFG tensor is traceless and symmetric and may therefore be described by two independent parameters. The nuclear quadrupolar coupling constant, C_Q, is defined as

$$C_Q = \frac{eV_{33}Q}{h} \tag{5}$$

and the asymmetry parameter of the EFG tensor is given as

$$\eta_Q = \frac{V_{11} - V_{22}}{V_{33}} \tag{6}$$

where $|V_{33}| \geq |V_{22}| \geq |V_{11}|$, e is the charge on an electron, and h is Planck's constant. The asymmetry parameter ranges from 0 to 1. Some authors use the so-called quadrupolar product, $P_Q = C_Q(1 + \eta_Q^2/3)^{1/2}$, when there is not enough information to determine C_Q and η_Q independently.

Frequently, interpretation of SSNMR spectra of quadrupolar nuclei relies upon the high-field approximation, where the Larmor frequency (ν_L) is much greater than the quadrupolar frequency, $\nu_Q = 3C_Q/((2I(2I-1))$. When

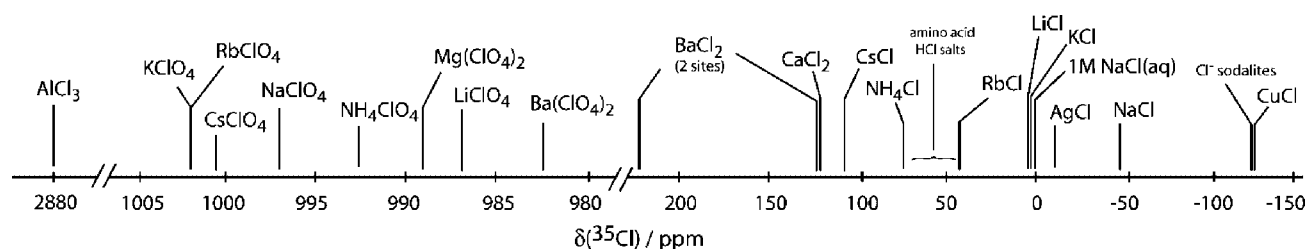**Figure 1.** Representative solid-state chlorine isotropic chemical shifts, shown here on a unified scale with respect to 1 M NaCl(aq) at 0 ppm. Chloride ion chemical shifts are shown at right, from about −150 to 250 ppm; perchlorate ion chemical shifts are shown in the middle, from about 980 to 1005 ppm; AlCl$_3$ shows an anomalously large chemical shift at 2880 ppm.[31] Full data and references are given in Table 2.

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Table 2. Survey of available $^{35/37}$Cl solid-state NMR data[a]

Compound		δ_{iso}/ppm[b]	C_Q/MHz	Additional information[c]	Method[c]	Reference	Year
Amino acid hydrochlorides	L-tyrosine HCl	95 ± 1[f]	2.3 ± 0.1 ($\eta_Q = 0.7 \pm 0.1$)	First-principles calculations of NMR parameters also performed	MAS, static	Gervais et al.[32]	2005
	glycine HCl	117 ± 1[f]	6.5 ± 0.1 ($\eta_Q = 0.6 \pm 0.1$)				
	L-valine HCl	114 ± 1[f]	6.0 ± 0.1 ($\eta_Q = 0.5 \pm 0.1$)				
	L-glutamic acid HCl	104 ± 1[f]	3.7 ± 0.1 ($\eta_Q = 0.6 \pm 0.1$)				
NaCl/cement		~30[d] for solid/adsorbed chloride	–	Signal tentatively assigned to Friedel's salt	MAS	Barberon et al.[33]	2005
Na$_8$[Al$_6$Si$_6$O$_{24}$]Cl$_x$ · (e$^-$)$_{2-x}$ sodalite		–	–	ESR hyperfine coupling constant, $A_0 = 85$ kHz	MAS	Trill et al.[34]	2005
NaClO$_3$		–	–	Frequencies of several single- and multiple-quantum transitions; 17 of 24 possible transitions were observed	Single crystal	Khasawneh et al.[35]	2004
Bis(4-chlorophenyl)sulphone ((ClC$_6$H$_4$)$_2$SO$_2$)		–	68.7 ($\eta_Q = 0.1 \pm 0.03$)	T_1 measurements as a function of temperature; orientation of EFG tensor in crystal axis system	Single crystal	Taye et al.[36-39]	2002, 2004
NaCl/cement		–	–	–	Static	Yun et al.[40]	2004
AlCl$_3$		2880 ± 40[e]	9.4 ± 0.2	–	Static	Sandland et al.[31]	2004
CaCl$_2$		122 ± 5[e]	2.1 ± 0.1	–	MAS	Sandland et al.[31]	2004
NaCl		−46 ± 1[e]	0	–	MAS	Sandland et al.[31]	2004

Compound	Sub-label			Notes	Method	Reference	Year
Several Cl-containing silicate and aluminosilicate glasses	*Silicates*			C_Q was determined with η_Q arbitrarily set to 0.7. Estimated mean values of C_Q could therefore vary up to 15%	MAS	Sandland *et al.*[31]	2004
	NS	-65 ± 5^e	3.3 ± 0.1				
	N2CS	-67 ± 10^e	3.0 ± 0.2				
	CNS	-35 ± 15^e	3.2 ± 0.4				
	C2NS	-20 ± 15^e	3.3 ± 0.3				
	CS	102 ± 22^e	4.4 ± 0.4				
	Aluminosilicates						
	NAS1	-89 ± 11^e	3.0 ± 0.3				
	NAS4	-65 ± 7^e	2.9 ± 0.2				
	CAS1	52 ± 38^e	3.5 ± 0.9				
	CAS3	62 ± 45^e	3.6 ± 1.0				
	CAS4	79 ± 42^e	4.0 ± 0.9				
L-lysine hydrochloride		–	–	A new method, relaxation-assisted separation (RAS), was proposed to resolve different ^{35}Cl sites based on relaxation times	Static QCPMG/RAS	Lupulescu *et al.*[41]	2003
L-ornithine hydrochloride							
$Li_{0.48}(THF)_{0.3}HfNCl$		–	–	Zero Knight shift; temperature dependence of shift measured from 4–150 K	Static oriented powder	Tou *et al.*[42]	2003
$[Al_4(HPO_4)_4(C_2H_5OH)_{12}]Cl_4 \cdot 4 \cdot C_2H_5OH$		76 ± 5^f	5.86 ± 0.05 ($\eta_Q = 0.96 \pm 0.035$)	–	Static and MAS	Azaïs *et al.*[43]	2003
$[Al_2(HC_6H_5PO_2)_2(C_4H_9OH)_8]Cl_4$		76 ± 5^f	7.0 ± 0.15 ($\eta_Q = 0.95 \pm 0.05$)	Two crystallographic sites are simulated with one set of parameters	Static and MAS	Azaïs *et al.*[43]	2003
$[Al_3(\mu_2\text{-}OH)(\mu_3\text{-}C_6H_5PO_3)_2 (C_2H_5OH)_{10}]Cl_4 \cdot H_2O$		Site 1 (Cl2): 76 ± 5^f; Site 2 (Cl1 and Cl4): 70^f; Site 3 (Cl3): 50^f;	Site 1 (Cl2): 5.8 ± 0.15 ($\eta_Q = 0.96 \pm 0.04$) Site 2 (Cl1 and Cl4)7.0 ± 0.15 ($\eta_Q = 0.96 \pm 0.04$) Site 3 (Cl3): 7.8 ± 0.15 ($\eta_Q = 0.96 \pm 0.04$)	Four crystallographic sites are simulated with three sets of parameters	Static and MAS	Azaïs *et al.*[43]	2003

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Table 2. (*Continued*)

Compound	δ_{iso}/ppm[b]	C_Q/MHz	Additional information	Method[c]	Reference	Year
Several n-alkylammonium chlorides	—	1.143 ± 0.001 at 315 K (n-C$_5$H$_{11}$NH$_3$Cl) 1.401 ± 0.001 at 300 K (n-C$_7$H$_{15}$NH$_3$Cl) 1.501 ± 0.001 at 315 K (n-C$_8$H$_{17}$NH$_3$Cl) 1.303 ± 0.002 at 320 K (n-C$_9$H$_{19}$NH$_3$Cl) 1.469 ± 0.001 at 325 K (n-C$_{10}$H$_{21}$NH$_3$Cl) 1.375 ± 0.001 at 300 K (n-C$_7$H$_{15}$ND$_3$Cl) 1.280 ± 0.002 at 320 K (n-C$_9$H$_{19}$ND$_3$Cl) 1.452 ± 0.002 at 325 K (n-C$_{10}$H$_{21}$ND$_3$Cl)	Temperature dependence of C_Q probed; even–odd effect	Static	Honda[44]	2003
Mixed Cl/Br sodalites	-125.4 ± 0.2^e (5% Cl) -125.2 ± 0.2 (18% Cl) -124.7 ± 0.2 (38% Cl) -124.3 ± 0.2 (56% Cl) -124.1 ± 0.2 (62% Cl) -123.8 ± 0.2 (76% Cl) -123.6 ± 0.2 (90% Cl) -123.2 ± 0.2 (100% Cl)	$P_Q{}^g = 0.2 \pm 0.1$ for all Cl percentages from MAS; $P_Q{}^g = 55 \pm 5$ kHz from ^{35}Cl SATRAS spectrum for 100% Cl sodalite	–	MAS, SATRAS	Trill *et al.*[45]	2003
Mixed Cl/I sodalites	-128.2 ± 0.3^e (5% Cl) -128.7 ± 0.3 (6% Cl) -128.4 ± 0.3 (10% Cl) -124.1 ± 0.3 (22% Cl) -123.7 ± 0.3 (89% Cl) -123.8 ± 0.3 (90% Cl) -123.4 ± 0.3 (97% Cl) -123.2 ± 0.3 (100% Cl) -127.6 and -124.6 (50:50 Cl:I), from 3QMAS	$P_Q{}^g = 0.2 \pm 0.1$ for all Cl percentages from MAS	–	MAS, SATRAS, 3QMAS	Trill *et al.*[45]	2003

Compound	δ (ppm)	C_Q / notes	Spectral data	Technique	Reference	Year
$LiAl_2(OH)_6ClO_4 \cdot nH_2O$	997.7^e (at 0% R.H.) 998.3 (at 11% R.H.) 998 (at 51% R.H.) ~999.3 (at 75 and 84% R.H.)	0.7 (and $\eta_Q = 0.1$) at 0% R.H.	Spectra recorded at several relative humidities (R.H.) CS tensor components determined from static spectra: $\delta_\parallel = 1019$ ppm, $\delta_\perp = 987$ ppm at 0% R.H. $\delta_\parallel = 1007$ ppm, $\delta_\perp = 994$ ppm at 11% R.H. $\delta_\parallel = 1004$ ppm, $\delta_\perp = 995$ ppm at 51% R.H.	Static, MAS	Hou and Kirkpatrick[46]	2002
$Mg_3Al(OH)_6ClO_4 \cdot nH_2O$	1001.2^e (at 0% R.H.)	–	Spectra recorded at several relative humidities (R.H.) $\delta_\parallel = 1012$ ppm, $\delta_\perp = 997$ ppm at 0% R.H.	Static, MAS	Hou and Kirkpatrick[46]	2002
$LiAl_2(OH)_6Cl \cdot nH_2O$ ('LiAlCl5'; 'LiAlCl6'; 'LiAlCl8')	9.3^e (at 0% R.H.) 5.3 (at room humidity and temperature, from static spectrum) 11 (at room humidity and temperature, from MAS)	0.9 ($\eta_Q = 0$) (at room humidity and temperature, from MAS)	Spectra recorded at several relative humidities (R.H.) and temperatures $\delta_\parallel = 44$ ppm, $\delta_\perp = -60$ ppm at 0% R.H. $\delta_\parallel = -102$ ppm, $\delta_\perp = 59$ ppm at room humidity and temperature	Static, MAS	Hou et al.[47,48]	2001, 2002
$Na_8(Al_6Si_6O_{24})Cl_2$ (sodalite)	-124 ± 1^e	–	–	MAS	Stebbins and Du[49]	2002
NaCl	-46 ± 1^e	–	–	MAS	Stebbins and Du[49]	2002
CsCl	110 ± 1^e	–	–	MAS	Stebbins and Du[49]	2002
$BaCl_2$	124 ± 5^e (site 1) 219 ± 5^e (site 2)	3.5 ± 0.1 ($\eta_Q = 0.15 \pm 0.05$) (site 1) 3.95 ($\eta_Q = 0.1$) (site 2)	–	MAS	Stebbins and Du[49]	2002

Table 2. (Continued)

Compound	δ_{iso} / ppm[b]	C_Q / MHz	Additional information	Method[c]	Reference	Year
Silicate and aluminosilicate glasses						
Na$_2$Si$_3$O$_7$ + 5 wt% NaCl	-77 ± 10^e	2.4–2.9 (estimated)	–	MAS	Stebbins and Du[49]	2002
Na$_3$AlSi$_6$O$_{15}$ + 5 wt% NaCl	–					
NaAlSi$_3$O$_8$ + 1.5 wt% NaCl	–					
Cs$_2$Si$_4$O$_9$ + 5 wt% CsCl	127 ± 10^e					
95Cs$_2$Si$_4$O$_9$ · 5Al$_2$O$_3$ + 5 wt% CsCl	–					
BaSi$_2$O$_5$ + 5 wt% BaCl$_2$	143 ± 10^e					
NaCl KCl	-49.6^h	–	–	MAS	Saito et al.[50]	2001
CaCl$_2$	–	–	Second-order quadrupolar lineshape observed under MAS	MAS	Saito et al.[50]	2001
Coal A	-49.6^h	–	Peak assigned to NaCl(s)	MAS	Saito et al.[50]	2001
CuCl	–	–	Temperature dependence of T_1 measured	Static	Kanashiro et al.[51]	2001
(CH$_3$)$_4$NCdCl$_3$	–	Phase I (296 K): 13.48 (η_Q = 0.16)[i] Phase I (120 K): 13.64 (η_Q = 0.13) Phase II (115 K, 3 sites): 14.98 (η_Q = 0.12), 14.02 (η_Q = 0.22), 12.64 (η_Q = 0.27) Phase III (98 K, 9 sites): 15.18, 14.72, 14.68, 13.98, 13.90	Data are in agreement with NQR results reported in the same paper. Phase transitions investigated by ^{35}Cl NMR	Single crystal	Mulla-Osman et al.[52–54]	1998, 2000, 2001

Compound	δ_{iso} (ppm)	C_Q (MHz)	η_Q	Additional notes	Method	Reference	Year
		13.86 13.52 13.30 13.04					
L-cysteine ethyl ester hydrochloride	53.2 ± 0.5[j]	3.78 ± 0.02	(η_Q = 0.03 ± 0.03)	Ω = 47 ± 4 ppm; κ = −0.8 ± 0.2	Static, MAS, QCPMG	Bryce et al.[55]	2001
L-tyrosine hydrochloride	49.3 ± 0.5[j]	2.23 ± 0.02	(η_Q = 0.72 ± 0.03)	Ω < 150 ppm; Quantum chemical calculations of NMR parameters were carried out and gave good agreement with experiment	Static, MAS	Bryce et al.[55]	2001
L-cysteine methyl ester hydrochloride	48.2 ± 0.7[j]	2.37 ± 0.01	(η_Q = 0.81 ± 0.03)	Ω = 45 ± 15 ppm	Static, MAS	Bryce et al.[55]	2001
Tris sarcosine CaCl$_2$	14.7 ± 10.0[j]	4.04 ± 0.03	(η_Q = 0.62 ± 0.02)	Ω < 150 ppm	Static (multiple fields, ^{35}Cl and ^{37}Cl)	Bryce et al.[55]	2001
Quinuclidine hydrochloride	9.7 ± 10.0[j]	5.25 ± 0.02	(η_Q = 0.05 ± 0.01)	Ω = 50 ± 20 ppm	Static (multiple fields, ^{35}Cl and ^{37}Cl)	Bryce et al.[55]	2001
Poly[2-(trimethylammonio)ethyl methacrylate chloride]-block-poly(N-(2-hydroxypropyl)methacrylamide) polycation + sodium polyphosphate glasses	–	–		T_1 measurements provided self-diffusion coefficients	MAS	Kříž et al.[56]	2000
Sr$_2$CuO$_2$Cl$_2$	–	–		Temperature dependence of ^{35}Cl relaxation studied	Single crystal	Suh et al.[57,58]	1996; 2000
YBa$_2$Cu$_3$O$_{6.7}$Cl$_{0.2}$ (Cl-doped YBCO)	–	~2	(η_Q = 1)	–	Static	Goren et al.[59]	1999
Several inorganic perchlorates LiClO$_4$	1034.2 ± 0.5[f]; 1034.1 ± 0.5 (^{37}Cl)	1.282 ± 0.008 (^{35}Cl); 1.010 ± 0.012 (^{37}Cl)	(η_Q = 0.34 ± 0.01) (^{35}Cl and ^{37}Cl)	^{35}Cl and ^{37}Cl data are used to assess the ratio of their quadrupole moments	MAS, SATRAS, ^{35}Cl and ^{37}Cl	Skibsted and Jakobsen[60]	1999
LiClO$_4$ · 3H$_2$O	1045.9 ± 0.5[f]	0.695 ± 0.004	(η_Q = 0.00 ± 0.03)				
NaClO$_4$	1044.3 ± 0.5[f]	0.887 ± 0.014	(η_Q = 0.92 ± 0.02)				

(continued overleaf)

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Table 2. (*Continued*)

Compound	δ_{iso}/ppm^b	C_Q/MHz	Additional information	Method^c	Reference	Year
$NaClO_4 \cdot H_2O$	1039.9 ± 0.3^f; 1040.1 ± 0.5 (^{37}Cl)	0.566 ± 0.009 ($\eta_Q = 0.90 \pm 0.02$) (^{35}Cl); 0.459 ± 0.012 ($\eta_Q = 0.91 \pm 0.04$) (^{37}Cl)				
$KClO_4$	1049.2 ± 0.3^f	0.440 ± 0.006 ($\eta_Q = 0.88 \pm 0.02$)				
$RbClO_4$	1049.4 ± 0.3^f; 1049.1 ± 0.3 (^{37}Cl)	0.537 ± 0.015 ($\eta_Q = 0.87 \pm 0.03$) (^{35}Cl); 0.424 ± 0.014 ($\eta_Q = 0.86 \pm 0.02$) (^{37}Cl)				
$CsClO_4$	1047.7 ± 0.3^f	0.585 ± 0.008 ($\eta_Q = 0.86 \pm 0.02$)				
$Mg(ClO_4)_2$	1036.2 ± 0.5^f	2.981 ± 0.007 ($\eta_Q = 0.57 \pm 0.01$)				
$Mg(ClO_4)_2 \cdot 6H_2O$	Site 1: 1046.6 ± 0.3^f 1046.6 ± 0.3 (^{37}Cl) Site 2: 1045.5 ± 0.3^f 1045.5 ± 0.3 (^{37}Cl)	Site 1: 0.309 ± 0.006 ($\eta_Q = 0.00 \pm 0.08$) (^{35}Cl); 0.245 ± 0.005 ($\eta_Q = 0.00 \pm 0.10$) (^{37}Cl) Site 2: 0.475 ± 0.008 ($\eta_Q = 0.00 \pm 0.05$) (^{35}Cl); 0.375 ± 0.003 ($\eta_Q = 0.00 \pm 0.07$) (^{37}Cl)				
$Ba(ClO_4)_2$	1029.6 ± 0.5^f	2.256 ± 0.008 ($\eta_Q = 0.58 \pm 0.01$)				

MRC

Compound			Comments		Reference	Year
Ba(ClO$_4$)$_2$ · 3H$_2$O	1040.6 ± 0.3^f; 1040.5 ± 0.5 (^{37}Cl)	0.383 ± 0.005 (η_Q = 0.00 ± 0.03) (^{35}Cl); 0.299 ± 0.004 (η_Q = 0.01 ± 0.03) (^{37}Cl)		Static	Ono et al.[61]	1999
Cd(ClO$_4$)$_2$ · 6H$_2$O	1044.4 ± 0.3^f	0.328 ± 0.005 (η_Q = 0.00 ± 0.03)				
(CH$_3$)$_4$NClO$_4$	1049.3 ± 0.3^f	0.307 ± 0.004 (η_Q = 0.00 ± 0.03)				
[C$_4$H$_8$NH$_2$]ClO$_4$ [C$_4$H$_8$ND$_2$]ClO$_4$	–	–	Narrow spectra indicated rotation of the perchlorate anion at 315 and 400 K	Static	Kirkpatrick et al.[62]	1999
Hydrotalcite	–	~2.4 (η_Q ≈ 1) (at −97°C); ~1.5 (η_Q ≈ 0) (at −40°C); ~1.2 (at room temperature)	Spectra recorded at several temperatures	Static	Kirkpatrick et al.[62]	1999
Hydrocalumite	30 ± 5^k (at 10−130°C); 26 ± 5^k (<0°C); 3.0 (η_Q = 0.9) (<0°C)	2.87 (η_Q ≈ 0) (at 10°C); 2.22 (η_Q ≈ 0) (at 130°C)	Spectra recorded at several relative humidities (R.H.) and temperatures	Static	Kirkpatrick et al.[62]	1999
Piperidinium perchlorate ([C$_5$H$_{10}$NH$_2$]ClO$_4$)	–	–	Solid−solid phase transitions were investigated	Static	Ono et al.[63]	1997
Poly(ethylene glycol)$_x$ NH$_4$ClO$_4$	–	~25 (low T);	Study of thin films	Static	Binesh and Bhat[64]	1996
CH$_3$NH$_3$GeCl$_3$	–	approaching zero at 500 K	^{35}Cl NMR used to confirm disordered perovskite structure Temperature dependence of T_1 measured ^{35}Cl NMR signal could be detected above 364 K	Static	Yamada et al.[65,66]	1994, 1995
Cocaine hydrochloride	~0^f	5.027 (η_Q = 0.2 ± 0.05)	–	Static; stepped-frequency	Yesinowski et al.[67]	1995

(continued overleaf)

Table 2. (Continued)

Compound	δ_{iso}/ppm[b]	C_Q/MHz	Additional information	Method[c]	Reference	Year
AgCl NaCl	—	—	Temperature dependence of T_1 measured over the range 77–700 K	Static	Michihiro et al.[68]	1995
Betaine calcium chloride dihydrate ((CH_3)$_3$NCH$_2$COO · CaCl$_2$ · 2H$_2$O)	—	4.871 kHz (η_Q = 0.882) (ambient temperature 'N phase') Site 1: 5.667 kHz (η_Q = 0.8) Site 2: 4.875 kHz (η_Q = 0.726) (38 K low-temperature phase)	Very small C_Q values determined from satellite transition frequencies Tensor orientations also determined from single-crystal study	Single crystal	Holzer et al.[69]	1995
NaCl AgCl	—	—	Temperature dependence of T_1 measured	Single crystal	Yamanishi et al.,[70,71] Kanashiro et al.[72]	1994; 1995; 1996
C$_4$H$_9$NH$_3$Cl C$_4$H$_9$ND$_3$Cl	—	~1.2 to 0.85 on heating from 300 to 480 K ($\eta_Q \approx 0$)	Temperature dependence of C_Q and relaxation times are measured	Static; single crystal	Hattori et al.[73]	1994
Guanidinium perchlorate ([C(ND$_2$)$_3$]ClO$_4$)	—	1.785 ± 0.010 (η_Q = 0) (at 78 K) 1.480 ± 0.010 (η_Q = 0) (at 285 K) 0.770 ± 0.005 (η_Q = 0) (at 445 K)	Temperature dependence of C_Q and T_1 measured	Static	Furukawa and Ikeda[74]	1993
Na$_8$Cl$_2$-sodalite Na$_8$Cl$_{0.46}$I$_{1.54}$-sodalite Ag$_8$Cl$_2$-sodalite Ag$_8$Cl$_{0.46}$I$_{1.54}$-sodalite NaCl AgCl	—	—	Peak maxima of −122 (Na$_8$Cl$_2$-sodalite), −125 (Na$_8$Cl$_{0.46}$I$_{1.54}$-sodalite), −310 (Ag$_8$Cl$_2$-sodalite), and −305 ppm (Ag$_8$Cl$_{0.46}$I$_{1.54}$-sodalite) (w.r.t. 0.1 M NaCl) are reported for various chloride levels	MAS	Jelinek et al.[75]	1993
AgCl	−7[l]	—	—	MAS	Jelinek et al.[75]	1993

Compound	δ	C_Q	Notes		Reference	Year
Cl-doped yttrium ceramics (YBCO-Cl)	—	Three sites: 1.2 1.4 1.9	Three resonances are observed and assigned to 'three definite positions in the lattice'	Static	Amitin et al.[76]	1993
VCl$_2$	—	~4 MHz (2 sites) ($\eta_Q = 0$; assumed)	Relaxation rates measured as a function of temperature	Static	Tabak et al.[77]	1993
Alkali metal chlorides LiCl	5.0^e 2.7 (^{37}Cl)	—	Linewidths also given	Static	Lefebvre[78]	1992
NaCl	−47.4^e −45.8 (^{37}Cl)	—				
KCl	3.1^e 3.0 (^{37}Cl)	—				
RbCl	43.2^e 44.0 (^{37}Cl)	—				
CsCl	110.0^e 108.7 (^{37}Cl)	—				
Alkaline earth chlorides MgCl$_2$ · 6H$_2$O	Site 1: 546^e 496 (^{37}Cl) Site 2: −870^e −816 (^{37}Cl)	—	It is likely that the reported 'chemical shifts' refer to peak maxima from two parts of second-order quadrupolar powder patterns rather than true isotropic chemical shifts	Static	Lefebvre[78]	1992
CaCl$_2$ · 2H$_2$O	Site 1: 1050^e 950 (^{37}Cl) Site 2: −1739^e −1527 (^{37}Cl)	—				
SrCl$_2$ · 6H$_2$O	Site 1: 880^e 776 (^{37}Cl) Site 2: −1435^e −1294 (^{37}Cl)	—				
BaCl$_2$ · 2H$_2$O	Site 1: 387^e 357 (^{37}Cl) Site 2: −389^e −322 (^{37}Cl)	—				
SrCl$_2$	140.8^e 142.3 (^{37}Cl)	—				
NH$_4$Cl	73.6^e 72.6 (^{37}Cl)	—	—	Static	Lefebvre[78]	1992

Table 2. (*Continued*)

Compound	δ_{iso}/ppm[b]	C_Q/MHz	Additional information	Method[c]	Reference	Year
CuCl	-127.23 ± 0.05[h] (at 294 K)	–	Linewidths also reported. Temperature dependence of chemical shift also reported: $\delta = (0.092\ \mathrm{ppm\ K^{-1}})(T/K) -154.8$ ppm (over the range 150–400 K)	Static, MAS	Hayashi and Hayamizu[79]	1992
AgCl	-12.82 ± 0.05[h] (at 294 K)	–	Linewidths also reported. Temperature dependence of chemical shift also reported: $\delta = (-0.054\ \mathrm{ppm\ K^{-1}})(T/K) + 2.8$ ppm (over the range 160–320 K)	Static, MAS	Hayashi and Hayamizu[79]	1992
Tris sarcosine calcium chloride	–	4.10 ($\eta_Q = 0.67$); (room temperature); errors in tensor elements are less than 5%	Orientation of EFG tensor reported Temperature dependence of ^{35}Cl signal was studied; quadrupolar frequency varies by 0.75 kHz K^{-1} (120 to 260 K)	Single crystal	Erge et al.,[80–82] Michel et al.[83]	1989, 1990, 1991 and 1994
Tris sarcosine calcium chloride	–	Paraelectric phase: 4.0 ± 0.4 ($\eta_Q = 0.65 \pm 0.05$)	–	Static	Engelke et al.[84]	1990
Alkali metal chlorides LiCl NaCl KCl RbCl CsCl	1.31 ± 0.06[h] -49.73 ± 0.03[h] 0[h] 41.13 ± 0.09[h] 105.96 ± 0.11[h]	–	Linewidths under static and MAS conditions also reported	Static, MAS	Hayashi and Hayamizu[85]	1990
Chloride salts CsCl NH$_4$Cl RbCl	109.4[m] 109.6 (^{37}Cl) 74.0[m] 73.8 (^{37}Cl) 44.7[m] 44.8 (^{37}Cl)	– – –	Correlation between chemical shift and electronegativity/coordination number proposed	MAS	Weeding and Veeman[86]	1989

Compound			Notes	Experiment	Reference	Year
KCl	3.07[m]; 2.8 ([37Cl])	–				
NaCl	−46.1[m]; −42.0 ([37Cl])	–				
NH$_4$ClO$_4$	917.5 ± 0.7[n]	0.6949 ± 0.0005 (η_Q = 0.7552 ± 0.0012)	Orientation of EFG and CS tensors reported. Principal components of the traceless part of the CS tensor reported as −16.7 ± 0.9; 15.3 ± 0.8; 1.4 ± 1.2 ppm	Single crystal	Bastow and Stuart[87]	1989
NH$_4$ClO$_4$	–	0.640 ± 0.040 (η_Q = 0.80 ± 0.10) at 300 K; ±50 kHz at 4.2 K	Temperature dependence of C_Q studied over the range 4–340 K	Single crystal; static	Segel et al.[88]	1988
NH$_4$ClO$_4$ ND$_4$ClO$_4$	930[n]	–	T_1 measured over the range 153–295 K	Static	Bastow et al.[89]	1988
Multimethyl ammonium perchlorates	–	370 kHz (phase III; 303–355 K) (η_Q varies between 0.60 and 1); 318 kHz (phase II; 400–460 K)	Temperature dependence of quadrupolar coupling, T_1, and linewidths probed for the various phases. Activation energies for ClO$_4^-$ reorientation studied	Static, MAS	Jurga et al.[90]	1986
Dimethyl ammonium perchlorate	1003[h] (phase I)	1.120 (η_Q = 0) (phase III); 0.238 (η_Q = 0) (phase II)				
Monomethyl ammonium perchlorate		1.016 (η_Q = 0.75) (phase III); 0.258 (η_Q = 0) (phase II)				
Rb$_2$Mn$_{1-x}$Cr$_x$Cl$_4$	–	–	–	Single crystal	Kubo et al.[91,92]	1986
(C$_3$H$_7$NH$_3$)$_2$MnCl$_4$	–	–	Phase transitions studied	Single crystal	Muralt et al.[93]	1986

Table 2. (*Continued*)

Compound	δ_{iso} / ppm[b]	C_Q/MHz	Additional information	Method[c]	Reference	Year
Na(CN)$_x$Cl$_{1-x}$ glasses	–	–	Temperature dependence of T_1 and linewidth measured	Static	Elschner and Petersson[94]	1986
Calcium chloroapatite	–	0.8	–	–	Yesinowski and Eckert[95]	1985
CuCl	–	–	Chemical shifts measured as a function of temperature	Static	Becker[96]	1978
ClF$_5$	–	–	Relaxation times measured as a function of temperature	Static	Weulersse *et al.*[97]	1975
CoCl$_2 \cdot$ 2H$_2$O	–	At 4.2 K: 9.76 $\pm$ 0.05 (^{35}Cl) 7.70 $\pm$ 0.05 (^{37}Cl)	–	Single crystal (?)	Okada *et al.*[98]	1974
p-Dichlorobenzene	–	73.96; (η_Q = 0.0712 $\pm$ 0.0005)	Principal components of CS tensor reported as 3000 $\pm$ 1000; $-1000 \pm$ 1000; 0 $\pm$ 1000 ppm (assuming the PAS of the EFG and CS tensors are coincident)	Single crystal	Creel *et al.*[99]	1973
GdCl$_3$	–	–	–	–	Hessler[100]	1973
Several alkylchlorosilanes	–	–	–	–	Kreshkov *et al.*[101]	1972
Mn(CO)$_5$Cl	–	36.07 $\pm$ 0.01 (η_Q = 0.050 $\pm$ 0.005) (at 30 °C)	Partial EFG tensor orientation information was obtained.	Single crystal	Spiess and Sheline[102]	1971
CsNiCl$_3$	–	–	–	Single crystal	Clark and Moulton[103]	1971
CsCoCl$_3$	–	14.024 $\pm$ 0.0050 (η_Q = 0.4477 $\pm$ 0.0005) (at 84 K) 13.983 $\pm$ 0.0050 (η_Q = 0.4421 $\pm$ 0.0005) (at 120 K) 13.890 $\pm$ 0.0030 (η_Q = 0.4353 $\pm$ 0.0005) (at 195 K)	Paramagnetic shift tensor components also reported	Single crystal	Rinneberg and Hartmann[104]	1970

Compound		Data	Comments	Method	Reference	Year
CsMgCl$_3$	–	13.75850 ± 0.0002 (η_Q = 0.4293 ± 0.0005) (at 300 K)	–	Single-crystal	Rinneberg and Hartmann[104]	1970
CsMnCl$_3$	–	8.930 ± 0.002 (η_Q = 0.235 ± 0.005) (at 300 K)	Paramagnetic shift tensor components also reported	Single-crystal	Rinneberg and Hartmann[104]	1970
		Site 1: 10.5290 ± 0.0030 (η_Q = 0.2683 ± 0.0004) (at 300 K) Site 2: 18.3670 ± 0.0030 (η_Q = 0.0234 ± 0.0004) (at 300 K)				
CsNiCl$_3$	–	16.698 ± 0.010 (η_Q = 0.387 ± 0.0015) (at 27 °C) 16.978 ± 0.012 (η_Q = 0.387 ± 0.0015) (at 77 K)	Paramagnetic shift tensor components also reported	Single-crystal	Rinneberg et al.[105]	1969
CsCuCl$_3$	–	Site 1: 22.498 ± 0.004 (at 27 °C) 22.832 ± 0.016 (at 77 K) (η_Q = 0.389 ± 0.0005) (at 27 °C and 77 K) Site 2: 21.402 ± 0.010 (at 27 °C) 21.858 ± 0.016 (at 77 K) (η_Q = 0.131 ± 0.0005) (at 27 °C and 77 K)	Paramagnetic shift tensor components also reported	Single-crystal	Rinneberg et al.[105]	1969

(continued overleaf)

MRC

Table 2. (*Continued*)

Compound	δ_{iso}/ppm[b]	C_Q/MHz	Additional information	Method[c]	Reference	Year
$CoCl_2 \cdot 2H_2O$	–	At 76 K (paramagnetic state): 9.866 ± 0.001 (^{35}Cl) ($\eta_Q = 0.44 \pm 0.01$) At 4 K (antiferromagnetic state): 9.855 (^{35}Cl) 7.767 (^{37}Cl)	Information on EFG orientation also obtained	Single crystal	Narath[106]	1965
LiCl NaCl KCl RbCl CsCl	–	–	Trend in chemical shifts, relaxation times, and quadrupolar coupling reported	Static	Yamagata[107]	1964
$NaClO_3$	–	–	$\Omega = 40 \pm 7$ ppm Relaxation times measured; chemical shifts reported for distinct crystal orientations	Single crystal	Kawamori and Itoh[108]	1963
$NaClO_3$	–	–	–	Single crystal	Herzog and Hahn[109]	1956
TlCl CsCl AgCl NaCl	–	–	Early study reported trend in ^{35}Cl solid-state chemical shifts: TlCl > CsCl > AgCl > NaCl	Static	Kanda[110]	1955

NaClO$_3$	–	–		Single crystal	Bloom et al.[111]	1955
NaClO$_3$	–	–	Early study reported anisotropic relaxation studied by spin echoes	Single crystal; static powder	Hahn and Herzog[112]	1954
NaClO$_3$	–	–		Single crystal	Itoh and Kusaka[113]	1954
NaClO$_3$	–	–	Zeeman-perturbed quadrupole resonance	Single crystal	Bloom and Norberg[114]	1954

[a] Results are for ^{35}Cl unless otherwise indicated.
[b] Chemical shift references are specified for each entry as a footnote.
[c] Experiments are performed on powdered samples unless otherwise indicated.
[d] With respect to NaCl(aq) (concentration not specified).
[e] With respect to 1 M NaCl (aq).
[f] With respect to NaCl (s).
[g] $P_Q = C_Q(1 + \eta_Q^2/3)^{1/2}$.
[h] With respect to solid KCl.
[i] Original data in Ref. 52 report the quadrupolar frequency; these data have been doubled to provide the values of C_Q reported here.
[j] With respect to infinitely dilute NaCl(aq).
[k] Chemical shift reference not given.
[l] With respect to 0.1 M NaCl(aq).
[m] With respect to dilute Cl$^-$ (aq).
[n] With respect to NH$_4$Cl(s).

the high-field approximation is valid, the quadrupolar Hamiltonian is given to first-order as

$$\hat{H}_Q = h \frac{C_Q}{8I(2I-1)}(3\hat{I}_z^2 - \hat{I}^2)(3\cos^2\theta - 1 + \eta_Q \sin^2\theta \cos 2\phi) \tag{7}$$

where θ and ϕ are polar angles which define the orientation of B_0 in the principal axis system (PAS) of the EFG tensor. In the case of $^{35/37}$Cl and $^{79/81}$Br, the approximation therefore is valid when $C_Q/2 \ll \nu_L$. For ^{127}I, the condition is $3C_Q/20 \ll \nu_L$. More explicitly, we can write $10\{C_Q/2\} < \nu_L$ and $10\{3C_Q/20\} < \nu_L$, where the approximation is considered to be valid when ν_L is at least an order of magnitude larger than ν_Q. Clearly, larger quadrupolar coupling constants may be interpreted within the high-field approximation for ^{127}I than for $^{35/37}$Cl and $^{79/81}$Br. As an example, consider a SSNMR experiment in a magnetic field of 11.75 T (500 MHz ^{1}H frequency), where $\nu_L(^{35}$Cl$) = 49.1$ MHz, $\nu_L(^{81}$Br$) = 135.6$ MHz, and $\nu_L(^{127}$I$) = 100.8$ MHz. Quadrupolar coupling constants of up to approximately 10 MHz, 27 MHz, and 67 MHz will yield spectral lineshapes which are consistent with the high-field-approximation Hamiltonian. Most reported quadrupolar coupling constants obtained with high-field SSNMR techniques on diamagnetic solids are therefore consistent with the high-field approximation in magnetic fields on the order of at least 10 T. We refer the reader to Bain's detailed presentation of the exact calculation of Zeeman and quadrupolar interactions in any magnetic field.[124]

The breadth of the CT lineshape in a stationary powdered sample due to the quadrupolar interaction is:[123]

$$\Delta\nu_{CT} = \frac{(25 + 22\eta_Q + \eta_Q^2)}{144}\left[\frac{(3C_Q)^2}{((2I)(2I-1))^2}\right]\left[\frac{I(I+1) - 3/4}{\nu_L}\right] \tag{8}$$

As B_0 is increased, therefore, this CT lineshape becomes narrower. When the static linewidth is narrow enough, magic-angle spinning experiments are useful in further narrowing of the CT linewidth by a factor of 3 to 4.[125–127] Samoson[128] and Freude et al.[129] have given expressions that describe how the apparent resonance frequency is modified by the second-order quadrupolar interaction under MAS conditions:

$$\Delta\nu_{+\frac{1}{2}\leftrightarrow-\frac{1}{2}} = -\left(\frac{\nu_Q^2}{30\nu_L}\right)(I(I+1) - 3/4)(1 + \eta^2/3) \tag{9}$$

Here, $\Delta\nu_{+1/2\leftrightarrow-1/2}$ is the difference between the observed center-of-gravity frequency and the frequency corresponding to the true δ_{iso}. It is worth emphasizing that, in general, the center-of-gravity shift (or peak maximum) is therefore *not* equivalent to the true isotropic CS for quadrupolar nuclei. Taulelle[130] has discussed various methods for obtaining the true value of δ_{iso} from the observed lineshape. The most common method is to perform a lineshape simulation to extract δ_{iso}, C_Q, and η_Q. This can be done using software such as WSOLIDS[131] or SIMPSON.[132] Alternatively, if the MAS lineshape is approximately Gaussian with a half width $\Delta\nu_{hw}$, an estimate of the second-order quadrupolar-induced shift is given by:[129]

$$\Delta\nu_{+\frac{1}{2}\leftrightarrow-\frac{1}{2}} = -0.85\Delta\nu_{hw} \tag{10}$$

Residual dipolar coupling

In addition to the magnetic shielding and quadrupolar interactions discussed above, the quadrupolar halogen nuclei are also subject to direct dipolar coupling and indirect nuclear spin–spin coupling (J) interactions;[23] however, such data are relatively scarce in the solid state because of the normally overwhelming influence of the quadrupolar interaction. It is well known that the dipolar coupling between a spin-1/2 nucleus which is coupled to a quadrupolar nucleus is not completely averaged to zero under MAS conditions.[133–142] The residual dipolar coupling, d, is dependent upon the value of C_Q, the effective static dipolar coupling between the two nuclei (R_{eff}), the Larmor frequency of the quadrupolar nucleus (ν_L), and the orientation of the dipolar vector in the PAS of the EFG tensor (α, β):

$$d = -\frac{3C_Q R_{eff}}{20\nu_L}[(3\cos^2\beta - 1) + \eta\sin^2\beta\cos 2\alpha] \tag{11}$$

Therefore, in addition to the J coupling to a quadrupolar nucleus, the appearance of the NMR spectrum of the spin-1/2 nucleus will depend on the value of C_Q for the quadrupolar nucleus as well as the orientation of the EFG tensor. Under favorable conditions, such information may be inferred by simulating the NMR spectrum of the spin-1/2 nucleus.

Experimental

Single-crystal NMR

When single crystals of suitable size can be grown, single-crystal NMR methods offer arguably the best possible characterization of the magnitude and orientation of NMR interaction tensors, e.g. EFG and CS tensors. The specifics pertaining to a detailed analysis of single-crystal NMR data have been presented previously.[143,144] In addition to carrying out single-crystal rotation experiments to map out the orientation dependence of various interactions, single crystals are frequently used in the $^{35/37}$Cl, $^{79/81}$Br, or ^{127}I SSNMR study of paramagnetic and ferromagnetic materials for which static powder lineshapes are simply too broad to be observed using standard NMR methods in commercially available magnetic field strengths.

Powdered samples

A polycrystalline powder yields an NMR spectrum that is reflective of the orientation distribution of the crystallites in such a sample with respect to B_0. For relatively narrow resonances (which will only be the case for the quadrupolar halogens when they sit in a site of high symmetry), a one-pulse experiment may be employed. For powder-patterns that cover several tens or hundreds of kilohertz, it is advantageous to use an echo to circumvent the problems of probe dead time. Short (high-power) pulses are preferable, as they will provide a more uniform excitation of the spectrum. Stepped-frequency methods are also useful in this regard. Smith has summarized the experimental approaches for observing low-frequency nuclei such as $^{35/37}$Cl.[7] A so-called 'whole-echo' acquisition has also been applied,[145,146] which increases the signal-to-noise by $2^{1/2}$.

When the breadth of the powder pattern under static conditions is comparable to achievable MAS rates, MAS

becomes advantageous in removing broadening to first order from the quadrupolar interaction as well as CS anisotropy. As our literature review has shown, it is relatively uncommon to be able to acquire MAS NMR spectra of the quadrupolar halogens, except in special cases, because of the very broad lineshapes under static conditions.

Frydman's multiple-quantum magic-angle-spinning (MQMAS) technique has found widespread use in quadrupolar nucleus (e.g. ^{23}Na, ^{11}B, ^{27}Al) SSNMR for resolving crystallographically distinct sites.[147–149] Although the application of MQMAS is limited to cases where the value of C_Q is sufficiently small to allow for MAS, at least one application to ^{35}Cl has already been reported (*vide infra*). As with other nuclei, the magnitude of C_Q that is feasible to examine by MQMAS depends on various factors including the applied magnetic field strength, the maximum achievable MAS rate, and the maximum power available from the probe. For example, in a magnetic field of 11.75 T, MAS NMR at 15 kHz on a sample containing chlorine sites with values of C_Q(^{35}Cl) of up to approximately 3 MHz results in a CT spectrum with resolved spinning sidebands. Satellite-transition spectroscopy (SATRAS)[128,150,151] is also useful for the quadrupolar halogens when nuclear quadrupolar coupling constants are relatively small.

Various sensitivity enhancement techniques are available for improving the signal-to-noise ratio of spectra of stationary samples and samples undergoing MAS, such as the quadrupolar-Carr–Purcell–Meiboom–Gill (QCPMG) sequence,[152] double-frequency sweeps (DFS),[153] rotor-assisted population transfers (RAPT),[154,155] hyperbolic secant pulses,[156] or combinations thereof.[157] We refer the reader to the recent reviews by Wasylishen and coworkers on these topics.[158,159] These methods have thus far not been widely applied to the quadrupolar halogens.

SURVEY OF EXPERIMENTAL DATA

All SSNMR results for the quadrupolar halogens are tabulated in Tables 2–4. Below, selected examples are discussed, with an emphasis on applications to diamagnetic compounds.

Chlorine-35/37

Chlorine-35/37 SSNMR data and references are summarized in Table 2 (see also Fig. 1).

Over the years, there have been several reports on cubic alkali metal chlorides and related small molecules where the chlorine nucleus sits at a site of symmetry which requires the surrounding EFG to be very close to zero.[31,49,50,68,70,78,79,85,86,96,107,110] Kanda[110] appears to have made the first of such measurements in the mid-1950s, on powdered samples of NaCl, CsCl, AgCl, and TlCl under stationary conditions in magnetic fields of 0.300 and 0.622 T. In 1964, Yamagata[107] reported the trend in alkali metal chloride chemical shifts under stationary conditions as δ(^{35}Cl) CsCl > RbCl > LiCl > KCl > NaCl. The lithium salt does not follow the apparent periodic trend.

Several years later, Weeding and Veeman[86] reported the chlorine chemical shifts under MAS conditions for five cubic chloride salts (CsCl, NH$_4$Cl, RbCl, KCl, NaCl). Sharp lines with no second-order quadrupolar broadening were observed. They reported essentially identical chemical shifts for both chlorine isotopes, indicating a lack of a significant chlorine quadrupolar coupling constant in accord with the cubic structures. These workers also proposed a correlation of the chlorine CS with the interionic separation and Sanderson electronegativity of the cation in these cubic salts. Interestingly, however, no chemical shifts were reported for LiCl.

Shortly thereafter, Hayashi and Hayamizu also reported chlorine CS for powdered samples of the cubic alkali metal chlorides[85] (LiCl, NaCl, KCl, RbCl, CsCl) as well as CuCl and AgCl under static and MAS conditions.[79] They attempted to rationalize the trend in chlorine chemical shifts and proposed an empirical equation that makes use of Yamagata's interpretation[107] of the shifts in terms of nearest-neighbor interactions.

Lefebvre also reported the ^{35}Cl chemical shifts under static conditions for the alkali metal chlorides.[78] An alternative explanation was offered for the apparently anomalous chemical shifts of LiCl, that in fact the hydrated Li(H$_2$O)$_x^+$ ion was the true counterion in solid samples of LiCl observed by ^{35}Cl SSNMR due to the hygroscopic nature of this material. Chlorine 'chemical shifts' reported in this study for various solid alkaline earth chlorides should be interpreted with caution, as it is likely that these 'shifts' actually correspond to singularities from a quadrupolar powder pattern.[78] For example, second-order quadrupolar lineshapes were later observed under MAS conditions for e.g. CaCl$_2$[50] and BaCl$_2$.[49]

The compounds of cubic symmetry discussed above result in an EFG of essentially zero at the chlorine nucleus. In moving to molecules in which chlorine sits at a site of lower symmetry, quadrupolar effects on the solid-state NMR lineshape will be observed. However, in compounds where the symmetry is too low at chlorine, NMR lines will become very broad. In typical magnetic field strengths of 18.8 T or less, ^{35}Cl quadrupolar coupling constants of up to about 10 MHz may be measured feasibly using 'standard' experiments on stationary powder samples. For example, a static spin-echo experiment on AlCl$_3$ at 14.1 T yielded C_Q(^{35}Cl) = 9.4 MHz.[31] Under MAS conditions, C_Q(^{35}Cl) of up to 7.8 MHz have been successfully measured at 14.1 T; however, spinning sidebands are not resolved at this field strength.[43] Cases where the chlorine nuclei sit at sites which possess high symmetry, but which do not typically require that the EFG be exactly zero, occur for chloride ions and perchlorate anions in noncubic materials.

Tris-sarcosine calcium chloride has been a popular choice of compound to study by chlorine SSNMR.[55,80–84] The reason is that it is a model compound for the study of a second-order ferroelectric phase transition. Erge *et al.* reported a single-crystal ^{35}Cl NMR study which gave C_Q(^{35}Cl) = 4.10 MHz and η_Q = 0.67 at room temperature, with errors in the tensor elements of less than 5%.[80,81] A variation in the quadrupolar frequency of -0.75 kHz K^{-1} over the range 120–260 K was also observed. The importance of N–H···Cl hydrogen bonds in determining the EFG was highlighted.[80] The ^{35}Cl NMR signal was also studied in powdered samples as a function of temperature.[84] Bryce *et al.* used static spin-echo NMR

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Table 3. Survey of available $^{79/81}$Br solid-state NMR data[a]

Compound	δ_{iso}/ppm[b]	C_Q/MHz	Additional information	Method[c]	Reference	Year
Fe$_8$Br$_8$	–	–	–	Single crystal	Zipse et al.[160]	2004
Mixed Cl/Br sodalites	−220.6 ± 0.4[d] (0% Cl)	P_Q[e] = 0.7 ± 0.2 (0% Cl)	–	MAS, SATRAS	Trill et al.[45]	2003
	−220.8 ± 0.4 (5% Cl)	P_Q = 0.3 ± 0.2 (5% Cl)				
	−220.5 ± 0.4 (18% Cl)	P_Q = 0.4 ± 0.2 (18−62% Cl)				
	−219.4 ± 0.4 (38% Cl)	P_Q = 0.3 ± 0.2 (76−90% Cl)				
	−218.6 ± 0.4 (56% Cl)					
	−218.3 ± 0.4 (62% Cl)					
	−217.7 ± 0.4 (76% Cl)					
	−217.3 ± 0.4 (90% Cl)					
Mixed Br/I sodalites	−226.4 ± 0.4[d] (6% Br)	P_Q = 0.7 ± 0.2 (6% Br)	–	MAS, SATRAS	Trill et al.[45]	2003
	−225.0 ± 0.4 (25% Br)	P_Q = 1.0 ± 0.2 (25% Br)				
	−223.7 ± 0.4 (46% Br)	P_Q = 0.9 ± 0.2 (46% Br)				
	−223.0 ± 0.4 (65% Br)	P_Q = 0.8 ± 0.2 (65% Br)				
	−222.1 ± 0.4 (77% Br)	P_Q = 0.8 ± 0.2 (77% Br)				
	−222.0 ± 0.4 (86% Br)	P_Q = 0.3 ± 0.2 (86% Br)				
	−221.6 ± 0.4 (91% Br)	P_Q = 0.4 ± 0.2 (91% Br)				
	−220.6 ± 0.4 (100% Br)	P_Q = 0.7 ± 0.2 (100% Br)				
Bromine-containing sodalites	Na$_8$[Al$_6$Si$_6$O$_{24}$]Br$_x$ · (H$_3$O$_2$)$_{2-x}$: −221.0 to −218.0[d] for Br occupancy of 98–0%	P_Q = 0.5–0.8	–	MAS	Trill et al.[161]	2002
	Na$_{6+x}$[Al$_6$Si$_6$O$_{24}$]Br$_x$ · (4H$_2$O)$_{2-x}$: −221.0 to −230.6[d] for Br occupancy of 98–0%	P_Q = 0.5–2.2 for Br occupancy of 98–10%				
	Na$_{6+x}$[Al$_6$Si$_6$O$_{24}$]Br$_x$ · ϕ_{2-x} (ϕ = empty sodalite cage): −221.0 to −237.8[d] for Br occupancy of 98–0%	P_Q = 0.5–1.0				
CuBr	–	–	Temperature dependence of T_1 measured	Static	Kanashiro et al.[51]	2001
YBa$_2$Cu$_3$O$_y$	–	–	^{79}Br and ^{81}Br observed.	Static	Potrepka et al.[162]	1999
BaBr$_2$	–	–	Quadrupole structure not resolved	Static		

Compound			Notes	Method	Reference	Year
CsCoBr₃	—	At 4.2 K 109.2 (^{79}Br) 92.4 (^{81}Br) ($\eta_Q = 0.53$)	—	Single crystal	Uyeda et al.[163]	1998
CsMnBr₃	—	—	T_1 measured as a function of temperature	Single crystal	Xu et al.[164,165] Okada et al.[166]	1996 and 1997
AgBr	—	—	T_1 measured as a function of temperature (77 K to 700 K)	Single crystal	Michihiro et al.[68]	1995
NaBr						
NaBr	—	—	Temperature dependence of T_1 measured; both ^{79}Br and ^{81}Br studied	Single crystal	Yamanishi et al.[70,71], Kanashiro et al.[72]	1994; 1995; 1996
AgBr						
Tris-sarcosine calcium bromide	—	—	Temperature dependence of T_1 measured	Single crystal	Michel et al.[83]	1994
NaBr	−7[f]	—	—	MAS	Jelinek et al.[75]	1993
AgBr	208[f]	—	—	MAS	Jelinek et al.[75]	1993
Various Na$_{8-n-p}$Ag$_n$Br$_{2-p}$-sodalites	—	—	Peak maxima of 214, −219, −220, −550 are reported for various values of n and p. Small quadrupolar broadenings observed	MAS	Jelinek et al.[75]	1993
8{HBr}-Na₅₆(zeolite-Y)	—	—	Broad (~100 kHz) line observed	MAS	Jelinek et al.[75]	1993
CuBr	−134.14 ± 0.20[g] (^{79}Br) (at 294 K)	—	Static linewidth 3.1 kHz or 0.95 kHz at $\nu_r = 3.0$ kHz at 9.4 T Temperature dependence of chemical shift reported: $\delta = (0.165$ ppm K$^{-1})(T/K) - 183.0$ ppm (over the range 160–290 K); $\delta = (0.235$ ppm K$^{-1})(T/K) - 203.7$ ppm (over the range 290–340 K)	Static, MAS	Hayashi and Hayamizu[79]	1992

Table 3. (*Continued*)

Compound		δ_{iso}/ppm[b]	C_Q/MHz	Additional information	Method[c]	Reference	Year
AgBr		169.35 ± 0.07^g (^{79}Br) (at 294 K)	–	Static linewidth 1.4 kHz or 0.40 kHz at ν_r = 3.0 kHz at 9.4 T. Temperature dependence of chemical shift reported: $\delta = (-0.118$ ppm K^{-1})(T/K) $+ 203.9$ ppm (over the range 160–320 K)	Static and MAS	Hayashi and Hayamizu[79]	1992
Deuterated glycyl-L-alanine hydrobromide monohydrate		–	19.750 (η_Q = 0.833)	Orientation of EFG tensor obtained. V_{ZZ} oriented approximately along shortest H···Br hydrogen bond	Single crystal	Kehrer et al.[167]	1992
Tris-sarcosine calcium bromide		–	23.4 (η_Q = 0.64) (errors in tensor elements <5%)	Orientation of EFG tensor PAS also determined.	Single crystal	Erge et al.[81]	1991
Alkali metal bromides	LiBr	64.74 ± 0.12^g	–	Linewidths under static and MAS conditions also reported. Data are for ^{79}Br	Static, MAS	Hayashi and Hayamizu[85]	1990
	NaBr	-52.89 ± 0.08^g					
	KBr	0					
	RbBr	71.66 ± 0.15^g					
	CsBr	227.43 ± 0.08^g					
Doped (Cd, Pb, Ni, Ir, Au) AgBr crystals		–	–	T_1 measurements reported. Attempts to observe ^{79}Br spectra of AgBr$_x$Cl$_{1-x}$ at 4.7 T were unsuccessful	Single crystal	Zumbulyadis and Marchetti[168]	1990
CuBr		–	–	MAS-rate dependence of chemical shift is explored	Static, MAS	Hayashi and Hayamizu[169]	1990

Compound			Comments	Method	Reference	Year
1,4-Didecyl-1,4-diazoniabicyclo[2.2.2]octane dibromide (C$_{10}$-DABCO-C$_{10}$-Br$_2$)	3660^h	—	Temperature dependence of T_1 measured	Static	Nakayama et al.[170]	1989
1,4-Undecyl-1,4-diazoniabicyclo[2.2.2]octane dibromide (C$_{11}$-DABCO-C$_{11}$-Br$_2$)						
1,4-Dodecyl-1,4-diazoniabicyclo[2.2.2]octane dibromide (C$_{12}$-DABCO-C$_{12}$-Br$_2$)						
KBr	—	—	Relaxation times determined	Single crystal	Halstead et al.[171]	1986
Ag$_3$SBr	—	—	No quadrupolar broadening due to symmetry at Br; pressure dependence of phase transition studied	Static; high-pressure NMR	Huber et al.[172]	1986
K$_2$Pt(CN)$_4$Br$_{0.3}$ · 3.2H$_2$O	—	Site 1: ~22–19 over the range 0–300 K ($\eta_Q = 0$ by symmetry); Site 2: ~18–15 over the range 0–300 K ($\eta_Q = 0$ by symmetry)	Experiments done over the range 20–300 K to prove existence of second Br site. Temperature dependence of C_Q and linewidths reported	Single crystal	Brenni et al.,[173] Brinkmann et al.[174]	1982 and 1983
KBr	—	—	^{79}Br signal in KBr established as convenient for setting the magic angle	MAS and single crystal	Frye and Maciel[1]	1982
NaBr	−40^g (^{79}Br)	—	Central signal approximately threefold broader than that of KBr. KBrO$_3$ gave no detectable signal	MAS	Frye and Maciel[1]	1982
(CH$_3$NH$_3$)$_2$Cu(Cl$_{1-x}$Br$_x$)$_4$ (x = 0.25 and 0.50)	—	171 (^{79}Br) 141 (^{81}Br)	–	Single crystal	Kubo et al.[175]	1979

(continued overleaf)

Table 3. (*Continued*)

Compound	δ_{iso}/ppm[b]	C_Q/MHz	Additional information	Method[c]	Reference	Year
CuBr	–	–	Chemical shifts measured as a function of temperature (−150 °C to 600 °C)	Static	Becker[96]	1978
AgBr	–	–	Linewidths measured as a function of temperature	Single crystal	Conti[176]	1976
p-Dibromobenzene	–	–	$\eta_Q = 0.0461 \pm 0.0004$; principal components of CS tensor found to be zero within expt error	Single crystal	Griffin *et al.*[177]	1974
p-Dibromobenzene	–	–	$\eta_Q = 0.0459 \pm 0.0006$	Static	Von Meerwall *et al.*[178]	1973
KBr	–	–	–	Single crystal	Memory and Mathur[179]	1971
Mn(CO)$_5$Br	–	226.7 (^{81}Br) 256.8 (^{79}Br) ($\eta_Q = 0.06$) (at 30 °C)	Preliminary results only EFG tensor orientation information was obtained	Single crystal	Spiess and Sheline[102]	1971
Cu(NH$_4$)$_2$Br$_4$ · 2H$_2$O	–	Paramagnetic phase at 4.2 K: $P_Q = 12.293$ MHz (^{81}Br) ($\eta_Q = 0.928 \pm 0.002$). Ferromagnetic phase at ~1.8 K: $\eta_Q = 0.897 \pm 0.003$.	–	Single crystal	Renard and Velu[180]	1970
AgBr	–	–	–	Static	Conti and D'Alessandro[181]	1970
RbBr	–	–	–	Single crystal	Mehring and Kanert[182]	1969
KBr NaBr	–	–	–	Single crystal	Bonera *et al.*[183,184]	1966 and 1968
LiBr NaBr KBr RbBr CsBr	–	–	Trend in chemical shifts, relaxation times, and quadrupolar coupling reported	Static	Yamagata[107]	1964
CsBr	250 ± 40^i (^{79}Br)	–	T_1 (^{81}Br) $= 0.105$ s $\pm 20\%$	Single crystal	Bloembergen and Sorokin[185]	1958

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Compound		Notes	Method		Reference	Year
KBr	22 ± 30^i (^{79}Br)	–	–	Static	–	Bloembergen and Sorokin[185]	1958
NaBr	-58 ± 30^h (^{79}Br)	–	–	Static	–	Bloembergen and Sorokin[185]	1958
TlBr AgBr LiBr KBr NaBr	–	–	Early study reported trend in Br solid-state chemical shifts: TlBr > AgBr > LiBr > KBr > NaBr	Static	–	Kanda[110]	1955
AgBr LiBr AgBr doped with Cd^{2+}	–	–	–	Single crystal	–	Reif[186]	1955
NaBrO$_3$	–	–	–	Single crystal	–	Itoh and Kusaka[113]	1954
KBr	–	–	Smearing of satellite lines due to EFG at Br suggested to explain unexpected spectral intensities	Single crystal	–	Watkins and Pound[187]	1953
NaBr	–	–	–	Single-crystal	–	Pound[117]	1950

[a] Data are for ^{81}Br unless otherwise indicated.
[b] Chemical shift references are specified for each entry as a footnote.
[c] Results are for a powdered sample unless otherwise indicated.
[d] With respect to 1 M NaBr(aq).
[e] $P_Q = C_Q(1 + \eta_Q^2/3)^{1/2}$.
[f] With respect to 0.1 M NaBr(aq).
[g] With respect to KBr(s).
[h] With respect to NaBr(aq).
[i] With respect to CsBr(aq).
[j] With respect to KBr(aq).

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Table 4. Survey of available ^{127}I solid-state NMR data

Compound	δ_{iso}/ppm[a]	C_Q/MHz	Additional information	Method[b]	Reference	Year
KIO$_4$	–	–	Signal-to-noise enhancements using modified QCPMG pulse sequences are demonstrated	Static QCPMG, DFS-QCPMG, modified-QCPMG	Siegel et al.[159]	2005
Mixed Br/I sodalites	-255.5 ± 0.8[c] (0% Br) -255.5 ± 0.8 (6% Br) -255.2 ± 0.8 (25% Br) -250.4 ± 0.8 (46% Br) -250.0 ± 0.8 (65% Br) -247.6 ± 0.8 (77% Br) -245.5 ± 0.8 (86% Br) -245.0 ± 0.8 (91% Br)	$P_Q = 1.0 \pm 0.5$ (0% Br) $P_Q = 1.1 \pm 0.5$ (6% Br) $P_Q = 1.3 \pm 0.5$ (25% Br) $P_Q = 2.8 \pm 0.5$ (46% Br) $P_Q = 2.6 \pm 0.5$ (65% Br) $P_Q = 2.1 \pm 0.5$ (77% Br) $P_Q = 1.6 \pm 0.5$ (86% Br) $P_Q = 1.8 \pm 0.5$ (91% Br)	–	MAS, SATRAS	Trill et al.[45]	2003
Mixed Cl/I sodalites	-255.5 ± 0.8[c] (0% Cl) -254.6 ± 0.8 (5% Cl) -254.4 ± 0.8 (6% Cl) -253.9 ± 0.8 (10% Cl) -254.8 ± 0.8 (22% Cl) -228.2 ± 0.8 (89% Cl) -227.1 ± 0.8 (90% Cl)	$P_Q = 1.0 \pm 0.5$ (0% Cl) $P_Q = 1.7 \pm 0.5$ (5% Cl) $P_Q = 1.5 \pm 0.5$ (6% Cl) $P_Q = 1.8 \pm 0.5$ (10% Cl) $P_Q = 2.3 \pm 0.5$ (22% Cl) $P_Q = 4.3 \pm 0.5$ (89% Cl) $P_Q = 3.9 \pm 0.5$ (90% Cl)	–	MAS, SATRAS	Trill et al.[45]	2003
NH$_4$IO$_4$ ND$_4$IO$_4$	–	–	Temperature dependence of quadrupole coupling reported; C_Q passes through zero and changes sign for ND$_4$IO$_4$ at 87 K	Static	Segel et al.[188]	2002
Ag$_x$Cu$_{1-x}$I ($x = 0.05$–0.40 and 0.80–0.99)	–	–	Temperature dependence of T_1 studied	Single crystal	Mizuno et al.[189,190]	2001 and 2002
Several scheelite and pseudo-scheelite structures NH$_4$IO$_4$	3960 ± 10[d]	10.00 ± 0.01 ($\eta_Q = 0.0$)	–	Static and MAS; SATRAS; whole-echo	Wu and Dong[146]	2001
RbIO$_4$	3960 ± 10[d]	15.65 ± 0.01 ($\eta_Q = 0.0$)	–			
KIO$_4$	3960 ± 10[d]	20.66 ± 0.01 ($\eta_Q = 0.0$)	–			
NaIO$_4$	3950 ± 10[d]	42.24 ± 0.01 ($\eta_Q = 0.0$)	–			
CsIO$_4$	3972 ± 2[d]	1.00 ± 0.01 ($\eta_Q = 0.0$)	$\delta_{11} = \delta_{22} = 3978$; $\delta_{33} = 3960$			
HIO$_4$	3300 ± 10[d]	43.00 ± 0.01 ($\eta_Q = 0.75$)	–			

Compound			Comments	Method	Reference	Year
CuI	–	–	Temperature dependence of T_1 measured	Static	Kanashiro et al.[51]	2001
LiI/Al$_2$O$_3$ mixtures	–	–	Temperature dependence of iodine T_1 and chemical shift studied	Static; MAS	Ardel et al.[191]	1998
(KI)$_{0.56}$(NH$_4$)$_{0.44}$	–	–	Temperature dependence of T_1 studied; second moment determined	Single crystal; 2D	Hinze et al.[192]	1997
Trimethylethylammonium iodide	–	–	Temperature dependence of T_1 studied	Static	Ishida et al.[193]	1996
HgI$_2$	–	–	–	–	Dzhioev and Kursaev[194]	1996
NaI	–	–	Temperature dependence of T_1 studied	Single crystal	Kanashiro et al.[72]	1996
Glycyl-L-alanine hydroiodide monohydrate	–	At 274.5 K: 74.04 ($\eta_Q = 0.776$) cited from Kehrer et al.[195]	Orientation of iodine EFG tensor determined	Single crystal	Kehrer et al.[167]	1992
CuI	7.7 ± 0.2^e (at 294 K)	–	Temperature dependence of chemical shift: $\delta = $ (0.222 ppm K^{-1})$(T/K) - $65.4 ppm (over the range 200–240 K); $\delta = $ (0.384 ppm K^{-1})$(T/K) - $104.5 ppm (over the range 240–320 K); $\delta = $ (0.446 ppm K^{-1})$(T/K) - $124.4 ppm (over the range 320–400 K)	MAS	Hayashi and Hayamizu[79]	1992
AgI	-230.2 ± 1.0^e (at 294 K)	–	$\delta = $ (0.438 ppm K^{-1})$(T/K) - $360.6 ppm (over the range 160–280 K); $\delta = $ (0.540 ppm K^{-1})$(T/K) - $389.0 ppm (over the range 280–320 K)	–	Hayashi and Hayamizu[79]	1992

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Table 4. (*Continued*)

Compound		δ_{iso}/ppm[a]	C_Q/MHz	Additional information	Method[b]	Reference	Year
Alkali metal iodides	LiI	—	—	$\delta(LiI) = (0.097\ \text{ppm K}^{-1})(T/K) + 185.6$ ppm (over the range 294–400 K)	MAS	Hayashi and Hayamizu[79]	1992
	NaI	—	—	$\delta(NaI) = (0.0008\ \text{ppm K}^{-1})(T/K) + 33.8$ ppm (over the range 294–400 K)			
	KI	—	—	$\delta(KI) = (-0.030\ \text{ppm K}^{-1})(T/K) + 8.7$ ppm (over the range 294–400 K)			
	RbI	—	—	$\delta(RbI) = (-0.056\ \text{ppm K}^{-1})(T/K) + 94.4$ ppm (over the range 294–400 K)			
	CsI	—	—	$\delta(CsI) = (-0.015\ \text{ppm K}^{-1})(T/K) + 374.2$ ppm (over the range 294–400 K)			
KI		—	—	Multipole relaxation times determined	Single crystal	Lee *et al.*[196]	1992
AgI		—	—	Temperature dependence of AgI spectrum studied	MAS	Wagner[197]	1991
KI							
Alkali metal iodides	LiI	215.28 ± 0.35^e	—	Linewidths also reported	Static and MAS	Hayashi and Hayamizu[85]	1990
	NaI	33.53 ± 0.23^e					
	KI	0^e					
	RbI	76.91 ± 0.12^e					
	CsI	368.69 ± 0.12^e					
CuI		—	—	MAS-rate dependence of ^{127}I chemical shift is investigated	–	Hayashi and Hayamizu[169]	1990
$(CH_3)_4AsIO_4$		—	≤ 1.8	Temperature dependence of shift measured	Static	Grommelt and Burkert[198]	1989

Compound		C_Q / range	Comments	Technique	Reference	Year
$(n\text{-}C_4H_9)_4NIO_4$	–	8.07–3.35 (over the range 225–310 K) (η_Q ranges from 0.60–0.77)	Temperature dependence of C_Q and η_Q studied. Several phase transitions studied	Static	Burkert and Grommelt[199]	1988
$(n\text{-}C_4H_9)_4PIO_4$	–	5.98–3.14 (over the range 150–355 K) (η_Q ranges from 0.08–0.30)	Temperature dependence of C_Q and η_Q studied. Several phase transitions studied	Static	Burkert and Grommelt[199]	1988
LiI	–	–	Temperature dependence of T_1 studied	Single crystal	Mali et al.[200]	1988
$(C_2H_5)_4SbIO_4$	–	5.29–5.71 ($\eta_Q = 0.64$–0.38) over the range 217–301 K	Anomalous increase in C_Q with temperature	Static	Klobasa and Burkert[201]	1987
Periodates	$(C_2H_5)_4PIO_4$	6.09–5.87 over the range 177–302 K	Temperature dependence of C_Q studied	Static	Klobasa et al.[202]	1986
	$(C_2H_5)_4AsIO_4$	5.82–5.55 over the range 197–299 K				
Periodates	$(C_6H_5)_4PIO_4$	4.12–5.71 over the range 228–293 K	Phase transitions and temperature dependence of C_Q studied. $\eta_Q \approx 0$ for all three compounds	Static	Burkert and Klobasa;[203] Klobasa et al.[202]	1985 and 1986
	$(C_6H_5)_4AsIO_4$	3.50–7.42 over the range 179–297 K				
	$(C_6H_5)_4SbIO_4$	1.37–2.76 over the range 228–302 K				
$(CH_3)_4NIO_4$	–	$\approx$20–15 over the range 200–300 K	–	Static	Klobasa and Burkert[204]	1984
^{131}I implanted in Fe crystals	–	–	I-131 is a radioactive nucleus with a half life of about 8 days and nuclear spin[205] of 7/2	Single crystal	Visser et al.[206]	1984
CsI	–	–	–	Static	Budde and Richtering[207]	1983
CsI doped with CuI Several scheelites and pseudo-scheelites	NH_4IO_4	1.31–11.59 over the range 145–440 K	–	Static	Burkert[208]	1980
	$RbIO_4$	16.27–14.65 over the range 202–433 K				
	$CsIO_4$	11.45–10.45 over the range 202–294 K; 1.8–1.7 over the range 300–315 K				
	$N(CH_3)_4IO_4$	15.46–9.07 over the range 301–418 K				

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Table 4. (*Continued*)

Compound		$_{iso}$/ppm[a]	C_Q/MHz	Additional information	Method[b]	Reference	Year
Various periodates	NH_4IO_4	3810 ± 50[e]	10.02	$\Omega = 0$ ppm	Static	Segel and Vyas[209]	1980
	KIO_4	6530 ± 200[e]	20.73	$\Omega = 6110$ ppm			
	$AgIO_4$	5410 ± 50[e]	29.66	$\Omega = 980$ ppm			
	$NaIO_4$	-5370 ± 100[e]	42.39	$\Omega = 59\,000$ ppm (see text for discussion)			
Various iodates	$LiIO_3$	—	—	One component of the CS tensor reported as 5000 ± 400 ppm (w.r.t. solid KI)	Static	Segel and Vyas[209]	1980
	$CsIO_3$	—	—	One component of the CS tensor reported as 4400 ± 400 ppm			
	$RbIO_3$	—	—	One component of the CS tensor reported as 4900 ± 400 ppm			
$CsICl_2$		—	—	One component of the CS tensor reported as 3900 ± 200 ppm	Static	Segel and Vyas[209]	1980
IF_7		3040 ± 40[f]	At 77 K: 134.88 ± 0.03 ($\eta_Q = 0.04 \pm 0.004$) (from NQR study in same paper)	Temperature dependence of T_1 studied; new solid–solid phase transition discovered; $J(^{127}I, {}^{19}F) = 2100$ Hz (S_1 phase)	Static	Weulersse et al.[210]	1979
CuI		—	—	Chemical shifts measured as a function of temperature ($-150\,°C$ to $200\,°C$)	Static	Becker[96]	1978
CsI		—	—	Uniaxial stress applied to the crystal produced a broadening of the ^{127}I line; one component of the gradient elastic tensor was determined	Single crystal	Gerhart and Hooper[211]	1974
$Mn(CO)_5I$		—	927 ($\eta_Q = 0.03$) ('preliminary values')	—	—	Spiess and Sheline[102]	1971

Compound	Value		Notes	Technique	Reference	Year
KI	–	–	It was observed that T_2 (satellites) $> T_2$ (CT)	'Fused solid piece'; static	Weisman and Bennett[212]	1969
NaIO$_4$	–	'Very large'	–	Single crystal	Weiss and Weyrich[213]	1969
KI	–	–	Study of spin echoes	Static	Butterworth[214]	1965
Alkali metal iodides: NaI, KI, RbI, CsI	–	–	Trend in chemical shifts reported (KI > NaI > RbI > CsI)	Static	Yamagata[107]	1964
KI	–	–	Study of spin echoes	Single crystal	Solomon[215]	1958
CsI	500 ± 30[g]	–	–	Single crystal	Bloembergen and Sorokin[185]	1958
RbI	170 ± 30[h]	–	–	Single crystal	Bloembergen and Sorokin[185]	1958
NaI	120 ± 30[i]	–	–	Single crystal	Bloembergen and Sorokin[185]	1958
KI	100 ± 30[i]	–	–	Single crystal	Bloembergen and Sorokin[185]	1958
NaI, KI	–	–	Early study reported trend in iodine solid-state chemical shifts: NaI > KI > I$^-$ (aq)	–	Kanda[110]	1955
KI	–	–	Smearing of satellite lines due to EFG at iodine suggested to explain unexpected spectral intensities	Single crystal	Watkins and Pound[187]	1953
KI	–	–	–	Single crystal	Pound[117]	1950

a Chemical shift references are specified for each entry as a footnote.
b Results are for a powdered sample unless otherwise indicated.
c With respect to 1 M NaI(aq).
d With respect to NaI(s).
e With respect to KI(s).
f With respect to 5 M KI(aq).
g With respect to CsI(aq).
h With respect to RbI(aq).
i With respect to NaI(aq).
j With respect to KI(aq).

experiments on powdered tris-sarcosine calcium chloride at 9.4 and 18.8 T, as well as on both chlorine isotopes, and arrived at $C_Q(^{35}Cl) = 4.04 \pm 0.03$ MHz, $\eta_Q = 0.62 \pm 0.02$, and an isotropic CS of 14.7 ± 10 ppm (w.r.t. infinitely dilute NaCl(aq)).[55] These spectra also allowed an upper limit of 150 ppm to be placed on the span of the chlorine CS tensor.

Alkylammonium chlorides are another class of compounds that have received attention.[44,73] For example, Hattori *et al*. measured ^{35}Cl quadrupolar coupling constants in $C_4H_9NH_3Cl$ in the range 1.2 to 0.85 MHz over the temperature range 300 to 480 K.[73] Honda observed an interesting 'even–odd' effect on the ^{35}Cl quadrupolar coupling constants of the highest-temperature solid phases of *n*-alkylammonium chlorides.[44] All values of C_Q were on the order of 1.0–1.5 MHz for the series n-$C_xH_{(2x+1)}NH_3Cl$ ($x = 5$–10); however, for $x = 8$ and 10 ('even'), were significantly larger than for $x = 5, 7, 9$ ('odd'). This observation was rationalized using point-charge EFG calculations and known crystal structures. The author also noted a H/D isotope effect on $C_Q(^{35}Cl)$ by performing experiments on the deuterated analogs n-$C_xH_{(2x+1)}ND_3Cl$; chlorine quadrupolar coupling constants were consistently lower in the deuterated molecules by 20–30 kHz ($\sim2\%$ of C_Q).

The first ^{35}Cl SSNMR studies of the perchlorate anion appear to be those of Jurga *et al*.[90] (see also their associated NQR study[216]). Their work nicely demonstrates the potential of ^{35}Cl MAS NMR in providing well-defined CT second-order quadrupolar lineshapes for perchlorate anions.

Skibsted and Jakobsen performed an impressive study of inorganic perchlorates using static, MAS, and SATRAS methods (Fig. 2).[60] High-quality spectra of the central and satellite transitions under MAS conditions were simulated to extract very precise values of C_Q and η_Q. Isotropic chemical shifts were also determined with high precision; however, no information on the anisotropy of the CS tensor was reported. This report has apparently helped to inspire renewed interest in applying MAS methods to $^{35/37}$Cl in noncubic materials, as there has been a marked increase in the number of such studies since 1999.

A high-field $^{35/37}$Cl SSNMR study of several organic hydrochloride salts also provided several new data on the chlorine EFG tensor (Fig. 3).[55] CT second-order quadrupolar lineshapes were observed under MAS at 18.8 T, and simulations yielded values of C_Q ranging from 2.23 MHz for L-tyrosine hydrochloride to 5.25 MHz for quinuclidine hydrochloride. Marked variations in η_Q were also observed. A potential correlation between the EFG tensor and the hydrogen-bonding environment about chloride was proposed; however, further data will be helpful in establishing the generality of the observations. The QCPMG pulse sequence was also applied to ^{35}Cl for the first time in this study. Importantly, this work also demonstrated that it is possible to extract information on the anisotropy of the chlorine CS tensor from experiments performed on a powdered sample. CS tensor spans on the order of 50 ppm were determined for L-cysteine methyl ester hydrochloride, L-cysteine ethyl ester hydrochloride, and quinuclidine hydrochloride.

Bryce *et al*. also carried out quantum chemical calculations of the chlorine EFG and nuclear magnetic shielding
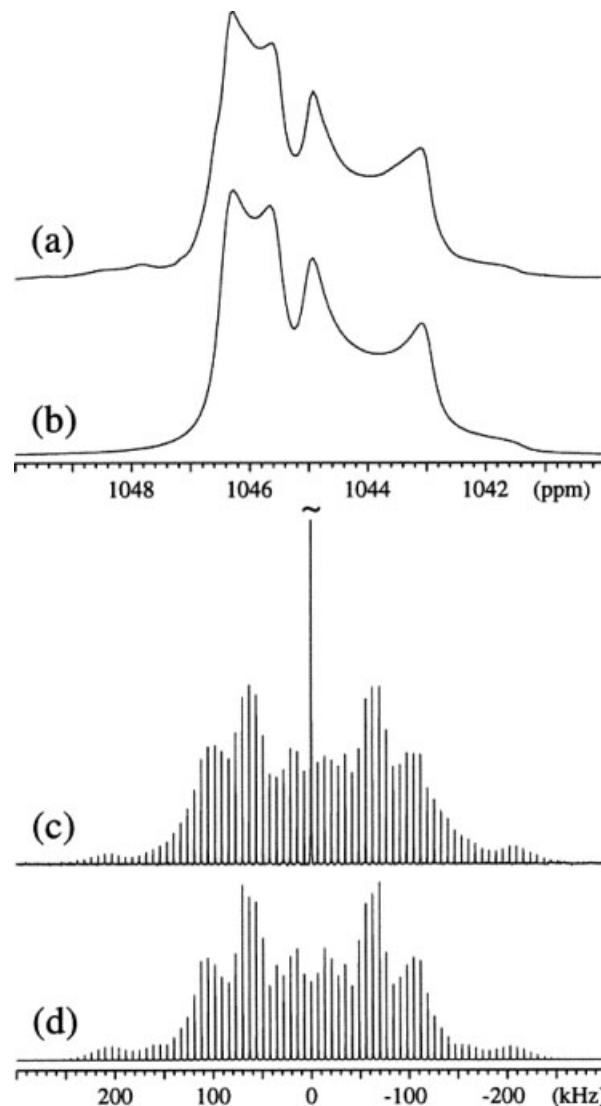
Figure 2. Representative ^{35}Cl NMR spectra of solid powdered perchlorate salts obtained under magic-angle-spinning conditions. The spectra shown here are for $Mg(ClO_4)_2 \cdot 6H_2O$, which has two nonequivalent chlorine sites. Shown in part (a) is the experimental CT part of the spectrum (simulated in (b)); the satellite transitions (SATRAS spectra) are shown in part (c) (simulated in (d)). Reprinted with permission from Skibsted J, Jakobsen HJ. *Inorg. Chem.* 1999; **38**: 1806. Copyright 1999 American Chemical Society.

tensors for L-tyrosine hydrochloride and compared the results with their experimental SSNMR data.[55] The results were in good qualitative agreement and indicate the potential of quantum chemical methods in the prediction and interpretation of halogen NMR interaction tensors. Further improvements between experiment and theory are likely to be obtained by including more of the crystal lattice in the structural model used in the calculations. For direct comparison between the calculated magnetic shielding tensors and the experimental chemical shifts, the chlorine absolute shielding scale of Gee *et al*. was employed.[116]

Gervais *et al*. have recently carried out a thorough experimental and computational study of the NMR parameters of various amino acids and amino acid hydrochloride salts.[32]
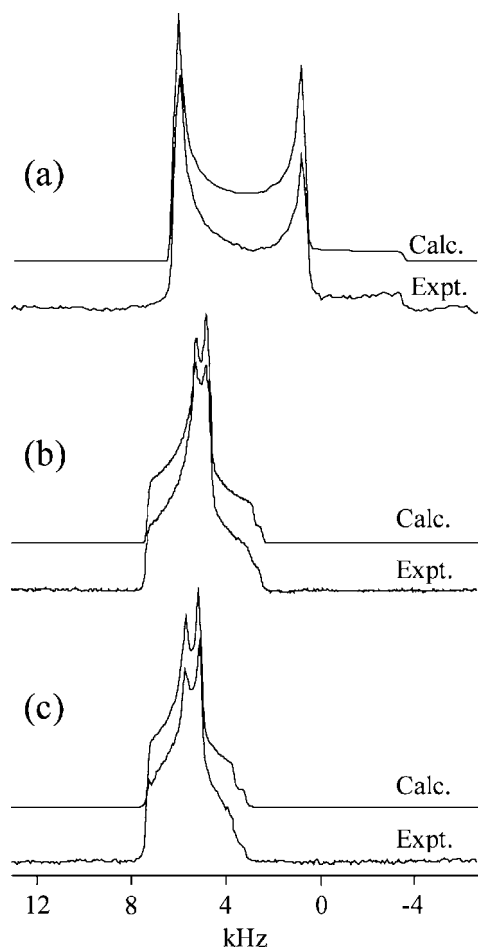
Figure 3. Representative ^{35}Cl NMR spectra of solid powdered amino acid hydrochloride salts obtained under magic-angle-spinning conditions at 18.8 T. Shown are the experimental and calculated CT parts of the spectra for (a) L-cysteine ethyl ester hydrochloride, (b) L-cysteine methyl ester hydrochloride, and (c) L-tyrosine hydrochloride. Reprinted with permission from Bryce DL, Gee M, Wasylishen RE. *J. Phys. Chem. A* 2001; **105**: 10 413. Copyright 2001 American Chemical Society.

In addition to confirming the previously reported results[55] for L-tyrosine hydrochloride, new isotropic chemical shifts, quadrupolar coupling constants, and asymmetry parameters were determined for glycine HCl, L-valine HCl, and L-glutamic acid HCl using static and MAS methods applied to powdered samples at 14.1 T. Furthermore, first-principles calculations provided small CS tensor spans ranging between 78 and 157 ppm. Calculations of the chlorine quadrupolar coupling constants were found to be in fair agreement with experiment; however, a systematic overestimation of experimental values was noted and attributed to the effect of the hydrogen bonding environment around chloride.[32]

Azais *et al.* studied chloride ions in various chlorinated Al–O–P cluster molecules by static and MAS ^{35}Cl SSNMR.[43] Characteristic CT second-order quadrupolar lineshapes were obtained and interpreted to yield quadrupolar coupling constants ranging from 5.8 to 7.8 MHz. The importance of the hydrogen-bonded OH$\cdots$Cl contacts in determining the EFG tensor was also emphasized by these authors.

Recently, Trill *et al.* have applied chlorine MAS NMR to the characterization of various sodalite cages.[34,45] Several mixed-halide (Cl, Br, I) sodalites were prepared and analyzed by ^{27}Al, ^{23}Na, ^{35}Cl, ^{81}Br, and ^{127}I SSNMR spectroscopy. Chlorine-35 quadrupolar products were found to be very small, $P_Q = 0.2 \pm 0.1$ MHz, and constant regardless of the percentage Cl$^-$ in mixed Cl/Br and Cl/I samples (over the range 5–100%). A more precise value ($P_Q = 55 \pm 5$ kHz) for pure chloro-sodalite, Na$_8$[Al$_6$Si$_6$O$_{24}$]Cl$_2$, was determined from a SATRAS spectrum. They have also reported what appears to be the first application of ^{35}Cl triple-quantum MAS (3QMAS), resolving two distinct chloride sites with chemical shifts of -127.6 and -124.6 ppm (w.r.t. 1 M NaCl(aq)) in a mixed Cl/I sodalite.[45] A linear correlation between the ^{35}Cl CS and the sodium–chlorine distance was found (-17 ppm Å^{-1}), suggesting the sensitivity of the CS to the degree of cation–anion overlap.

In a paramagnetic mixed chloride/electrosodalite (Na$_8$ [Al$_6$Si$_6$O$_{24}$]Cl$_x\cdot$(e$^-$)$_{2-x}$) containing 'F-center' electrons, Trill *et al.* observed up to eight resonances in the ^{35}Cl MAS NMR spectrum due to nearest-neighbor interactions with such electrons.[34] A hyperfine coupling constant of $A_0 = 85$ kHz was determined. The paramagnetic shift due to each nearest F-center electron was found to be nonadditive over the range 0 to 8 electrons; this was attributed to the electron exchange interaction.

Hou, Kirkpatrick, and coworkers have applied ^{35}Cl static and MAS NMR methods to study structure and dynamics of chloride and perchlorate anions in interlayered hydroxide materials.[46–48,62] Variable-temperature ^{35}Cl NMR spectra of hydrocalumite revealed well-defined quadrupolar lineshapes characterized by $C_Q(^{35}$Cl$) = 2.87$ MHz at 10 °C and decreasing to 2.22 MHz at 130 °C.[62] Spectra for hydrotalcite were found to be less well defined, and characterized by a dominant chloride site with $C_Q(^{35}$Cl$) = 1.2$–1.5 MHz. The NMR data, in combination with differential scanning calorimetry, were used to probe and characterize phase changes in these materials. In a subsequent report, variable-temperature (up to 1100 °C) ^{35}Cl MAS NMR was used to study LiAl$_2$(OH)$_6$Cl$\cdot n$H$_2$O.[48] The analogous perchlorate material LiAl$_2$(OH)$_6$ClO$_4\cdot n$H$_2$O as well as the magnesium analog Mg$_3$Al(OH)$_6$ClO$_4\cdot n$H$_2$O were also examined.[46] The activation energy for perchlorate reorientation in this latter compound was determined to be 10.7 kJ mol^{-1}. A further detailed study of LiAl$_2$(OH)$_6$Cl$\cdot n$H$_2$O revealed that the hydrated paste form of this material exhibits three distinct chloride resonances, the most interesting of which is dominated by an axially symmetric CS interaction.[47] In dehydrated samples, the principal components of the chlorine CS tensor were reported as $\delta_{11} = \delta_{22} = 44$ ppm and $\delta_{33} = -60$ ppm (w.r.t. 1 M NaCl(aq)). At room temperature and humidity, the span was found to increase; $\delta_{11} = \delta_{22} = 59$ ppm and $\delta_{33} = -102$ ppm. These spans are somewhat large relative to those reported previously for chloride[55] and oxychloro ions.[87,108] It is unclear whether the small quadrupolar interaction (e.g. $C_Q(^{35}$Cl$) = 0.9$ MHz for the room humidity sample) measured under MAS condition was taken into account when extracting the CS tensor components from the spectra of static samples.

Frydman and coworkers have developed a two-dimensional experiment that is applied to stationary powdered samples to resolve different sites on the basis of differential relaxation.[41] Among other examples, that of [35]Cl NMR of a mixture of solid ornithine hydrochloride and lysine hydrochloride was presented. This experiment will likely find use in quadrupolar halogen NMR (in cases where relaxation time constants are sufficiently different for different species/sites) because of the fact that, even with large applied magnetic fields, MAS experiments are unlikely to become routine for the quadrupolar halogens because of the magnitude of the EFG associated with noncubic sites.

Stebbins and coworkers have performed an exemplary [35]Cl MAS NMR study of the chloride ion environment in various silicate and aluminosilicate glasses at 14.1 and 18.8 T.[31,49] They proposed a correlation between the chlorine CS and the cation−chloride ion distance. Additionally, several anhydrous and hydrous samples containing only 0.2 to 0.7 wt% chlorine were analyzed and it was suggested that there is no direct interaction between water and the chloride ion in such glasses, as evidenced by the chlorine EFG. Values of $C_Q(^{35}Cl)$ were found to be essentially constant at ∼3.3 MHz for sodium-aluminosilicate glasses with water contents of up to 5.9%. $C_Q(^{35}Cl)$ increased to ∼4.4 MHz for calcium-aluminosilicate glasses, but this value was also invariant to the level of hydration (up to 5.5 wt% H_2O).[31]

Many early NMR (or Zeeman-perturbed NQR) studies examined the [35]Cl resonance in a single crystal of sodium chlorate.[108,109,111–114] Bain and coworkers have recently revisited the [35]Cl resonance in a single crystal of sodium chlorate to validate their theoretical approach[124] for the exact calculation of combined Zeeman and quadrupolar interactions.[35] The theory is particularly useful as it is valid over the range from quadrupole-perturbed NMR spectroscopy to Zeeman-perturbed NQR. It was shown that nominally multiple-quantum transitions are observable under certain conditions, and experimentally 17 of 24 (6 transitions per [35]Cl; 4 molecules in the unit cell) such transitions were observed in $NaClO_3$.[35] The application of the theory to generate powder patterns may prove to be particularly useful in simulating NMR spectra of the quadrupolar halogens.

Residual dipolar couplings between spin-1/2 nuclei (^{13}C, ^{31}P, [117/119]Sn) and [35/37]Cl have been analyzed to infer information about the chlorine EFG tensor.[217–236] Often, information from other sources (e.g. NQR) is used to provide the necessary EFG tensor information to successfully simulate the NMR spectrum of the spin-1/2 nucleus. Nevertheless, it is possible under favorable circumstances to determine C_Q by simulating the NMR spectrum of the spin-coupled spin-1/2 nucleus. For example, Eichele et al. found $C_Q(^{35}Cl) = -73 \pm 2$ MHz in two closely related chloroketo-sulfones by analyzing the ^{13}C MAS NMR spectrum.[218] The analysis also yielded the first direct measurement of a chlorine−carbon indirect nuclear spin−spin coupling constant, $^1J(^{35/37}Cl, ^{13}C)_{iso} = -20 \pm 5$ Hz. Previous measurements of coupling constants involving the quadrupolar halogens, determined predominantly through relaxation measurements in liquids, have been reviewed.[13,237] Another example

from the solid state is that of bis(acetylacetonato)tin(IV) dichloride, for which the value of $^1J(^{117/119}Sn, ^{35/37}Cl)_{iso}$ was reported as ± 276 Hz and the anisotropy in the J tensor was reported to range between −400 and −800 Hz in this and related compounds.[223]

In principle there is a secondary isotope effect[238] on the CS of a spin-1/2 nucleus, e.g. [13]C, which is coupled to [37]Cl vs [35]Cl (denoted $^1\Delta^{13}C(^{37/35}Cl)$); however, this effect has been measured in solution for some chlorinated hydrocarbons and was found to be on the order of −4 ppb.[239] This value is much too small to be observed in standard ^{13}C CP/MAS NMR experiments and therefore may be neglected in the analysis of residual dipolar coupling. However, separate overlapping subspectra due to different coupling to [35]Cl and to [37]Cl will be present. Proper simulations must therefore take into account the different natural abundances, magnetogyric ratios, and nuclear electric quadrupole moments of the two isotopes (see Table 1).

There have also been numerous [35]Cl NMR studies of chloride ions in solution which are in equilibrium with the solid phase, e.g. in cements[240] or as inclusions in beryl and quartz,[241] or in equilibrium with snow crab meat (to assess 'seafood tastiness'),[242] which we have not reviewed in detail here.

Bromine-79/81

Bromine-79/81 SSNMR data and references are summarized in Table 3.

There are fewer bromine SSNMR reports than there are for chlorine. Despite the higher relative receptivity of both [79]Br and [81]Br compared to [35]Cl and [37]Cl, the substantially larger nuclear electric quadrupole moments for [79]Br and [81]Br result in large linewidth factors, thereby rendering the observation of bromine resonances very difficult in powdered samples which lack high symmetry about bromine (Table 1).

There have been numerous studies of alkali metal bromides and other small molecules where the bromide ions sits at a site of high symmetry.[1,68,75,79,85,96,110,117,168,169,171,176,179,181–187] In fact, studies of such molecules comprise the majority of the bromine solid-state NMR literature, and even more so when we limit ourselves to diamagnetic compounds. In 1953, Watkins and Pound examined the [79]Br and [81]Br resonances in a single crystal of KBr and observed that the expected intensities were only about 40% of what was expected.[187] From these data (and analogous data for [127]I NMR in solid KI) they concluded that the EFG was not perfectly zero at bromine; instead, lattice imperfections in a single crystal result in a small EFG which interacts with the quadrupole moment of the nucleus. This interaction, although small, is enough to broaden (or 'smear') the satellite transitions over a relatively large spectral width, which explained the apparently missing intensity in the observed strong, central resonance. This phenomenon is well known today and forms the basis of the SATRAS experiment.

Under MAS conditions, the extensive manifold of spinning sidebands due to the [79/81]Br satellite transitions in powdered KBr is very sensitive to the setting of the magic

angle. Frye and Maciel proposed that the ^{79}Br resonance of powdered KBr be used to set the magic angle.[1] In addition to the high receptivity of ^{79}Br (allowing its observation in a single scan), the resonance frequency of ^{79}Br is within 1% of that of ^{13}C, making it convenient for setting the angle prior to carrying out ^{13}C CP/MAS experiments without significant retuning of the probe. NaBr was found to be an inferior standard for setting the angle, in part due to the effects of ^{23}Na–^{79}Br dipolar interactions.

Kanda[110] reported the following trend in bromine chemical shifts: TlBr > AgBr > LiBr > KBr > NaBr. Along with their report on chlorine CS of solid alkali metal chlorides (*vide supra*), Hayashi and Hayamizu also updated this early study of Kanda by reporting ^{79}Br chemical shifts for the complete series of alkali metal bromides under MAS.[85] They found that these chemical shifts reproduced the trend observed for the alkali metal chlorides: CsBr > RbBr > LiBr > KBr > NaBr.

Becker[96] reported on the temperature dependence of the bromine CS in CuBr over the range $-150\,°C$ to $600\,°C$. The temperature dependence ($\delta(^{79}$Br$) = (0.165\,\text{ppm K}^{-1})(T/K)$ $-183.0\,\text{ppm}$ (over the range 160–290 K)); $\delta = (0.235\,\text{ppm K}^{-1})(T/K)$ $-203.7\,\text{ppm}$ (over the range 290–340 K)) and MAS-rate dependence of the CS in this same material was studied by Hayashi and Hayamizu.[79,169] The ^{79}Br resonances were observed to shift to higher frequency with an increase in MAS rate, while the $^{63/65}$Cu resonances shift to lower frequencies.[169] After considering various other possible causes for this temperature dependence, they proposed that it is due to the Lorentz force acting on the Cu$^+$ ions.

Zumbulyadis and Marchetti studied the effect of doping AgBr crystals with various metal cations (Cd, Pb, Ni, Ir, Au) on the ^{79}Br SSNMR spectrum and relaxation properties.[168] Interestingly, they were unable to obtain a ^{79}Br SSNMR spectrum of AgBr$_x$Cl$_{1-x}$ or AgBr$_x$I$_{1-x}$ even at chloride or iodide concentrations as low as a few mole percent.

Brenni *et al*.[173] applied ^{81}Br and ^{39}K single-crystal NMR to prove the existence of a second bromine site in the quasi one-dimensional conductor K$_2$Pt(CN)$_4$Br$_{0.3}$·3.2H$_2$O. Bromine-81 quadrupolar coupling constants were measured as a function of temperature and the following results were obtained: $C_Q(^{81}$Br$) \approx 22$–19 MHz (site 1) and 18–15 MHz (site 2) over the range 0–300 K ($\eta_Q = 0$ by symmetry for both sites).

The bromine EFG tensor in tris-sarcosine calcium bromide has been studied by single-crystal ^{81}Br NMR,[81,83] for comparison with the results obtained for the chloride analog (*vide supra*). The two materials are isomorphous. It was found that $C_Q(^{81}$Br$) = 23.4$ MHz ($\eta_Q = 0.64$) (with reported errors in the tensor elements of less than 5%) and that the bromine EFG tensor elements are very similar to those obtained for the chloride salt, within a constant factor, as anticipated because of the isomorphism of the compounds. An activation energy of 28 kJ mol^{-1}, thought to be associated with reorientation of the sarcosine moiety, was deduced from the temperature dependence of $T_1(^{81}$Br$)$.

It is interesting to compare the results of a ^{81}Br single-crystal study of deuterated glycyl-L-alanine hydrobromide monohydrate[167] with existing chlorine quadrupolar parameters for related hydrochloride salts of amino acids. Given that

the environment of the chloride ions in organic hydrochloride salts leads to ^{35}Cl quadrupolar coupling constants ranging from ~1 to 7 MHz (Table 2), we may anticipate that isomorphous bromide salts may be characterized by $C_Q(^{81}$Br$)$ on the order of ~3 to 22 MHz. In the case of glycyl-L-alanine hydrobromide monohydrate, $C_Q(^{81}$Br$)$ was measured as 19.750 MHz, with an asymmetry parameter of 0.833. This magnitude of quadrupolar coupling constant starts to become feasible for observation using fairly standard SSNMR methods at ultra-high field strengths, e.g. 21.1 T. Kehrer *et al*. also noted that the orientation of the bromine EFG tensor may be strongly influenced by the hydrogen-bonding environment about the bromide ion;[167] this is consistent with similar observations in the case of chloride salts (*vide supra*).

Jelinek *et al*. applied ^{81}Br and ^{35}Cl MAS SSNMR to characterize various sodalite semiconductor supralattices (Na$_{8-n-p}$Ag$_n$X$_{2-p}$-sodalites, X = Cl, Br; $0 \leq n \leq 8$; $0 \leq p \leq 2$).[75] Well-resolved second-order quadrupolar lineshapes were generally not observed at 11.7 T; however, asymmetry in the lineshapes was taken as indicative of a distribution of bromide environments. Results for various silver-exchanged samples support the notion that as the silver concentration is increased, a covalent Ag–Br bond is formed, and the bromine resonance disappears because of the resulting large EFG at this nucleus.

Trill *et al*. performed ^{81}Br MAS and SATRAS experiments on various bromide-containing sodalites (Fig. 4).[45,161] Quadrupolar products, P_Q, of 0.5–0.8 MHz were observed for 'basic' Na$_8$[Al$_6$Si$_6$O$_{24}$]Br$_x$·(H$_3$O$_2$)$_{2-x}$; 0.5–2.2 MHz for 'hydro' Na$_{6+x}$[Al$_6$Si$_6$O$_{24}$]Br$_x$·(4H$_2$O)$_{2-x}$; 0.5–1.0 MHz for 'dry' Na$_{6+x}$[Al$_6$Si$_6$O$_{24}$]Br$_x$·ϕ_{2-x} (ϕ = empty sodalite cage), all for Br occupancies of 98 to 10%. A linear correlation between $\delta(^{81}$Br$)$ and the lattice constant of the sodalite cage was observed, with a slope of $-86\,\text{ppm Å}^{-1}$. Studies of mixed Cl/Br and Br/I sodalite systems yielded quadrupolar products of 0.3–0.7 MHz (Cl/Br system) and 0.3–1.0 MHz (Cl/I system). As was observed for ^{35}Cl (*vide supra*), a linear correlation between the ^{81}Br CS and the sodium–bromine distance was found ($-35\,\text{ppm Å}^{-1}$), which was interpreted as being the result of the degree of cation–anion overlap.

Some indirect information on the bromine EFG tensor has been obtained by observing residual dipolar coupling between spin-1/2 nuclei (^{13}C, ^{31}P) coupled to $^{79/81}$Br.[224,225,230,243–247] Secondary isotope effects on the spin-1/2 nucleus chemical shifts, e.g. $^1\Delta^{13}$C$(^{81/79}$Br$)$, are likely on the order of ppb (see discussion for $^{35/37}$Cl, above) and may therefore be neglected. As for chlorine, however, spectral simulations of spin-1/2 NMR spectra must take into account the different natural abundances, magnetogyric ratios, and nuclear electric quadrupole moments of the two bromine isotopes (Table 1).

Iodine-127

Iodine-127 SSNMR data and references are summarized in Table 4.

Iodine-127 has a good NMR receptivity, but its applicability as a useful NMR nucleus is limited because of its large nuclear electric quadrupole moment and resultant
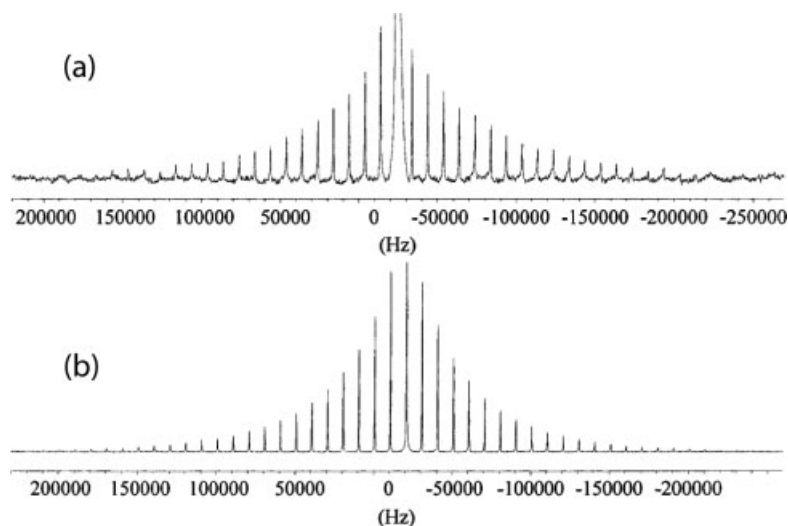
Figure 4. Representative (a) ^{81}Br and (b) ^{127}I SATRAS NMR spectra obtained under magic-angle-spinning conditions for pure bromo and iodo sodalites. The CTs at the center of the two spectra are off-scale to show more clearly the sideband manifolds obtained for the satellite transitions. Reprinted with permission from Trill H, Eckert H, Srdanov VI. *J. Phys. Chem. B* 2003; **107**: 8779. Copyright 2003 American Chemical Society.

linewidth factor (Table 1). I-127 SSNMR studies of diamagnetic solids are, to date, predominantly limited to periodate ($IO_4{}^-$) salts[146,159,188,198,199,201–204,208,209,213] in addition to cubic alkali metal iodides.[79,85,110,117,185,196,200,207,211,212,214,215] The first solid-state ^{127}I NMR study (of a single crystal of KI) seems to be that of Pound in 1950.[117]

Some early studies reported on trends in the solid-state iodine chemical shifts of some of the alkali metal halides.[110,185] The definitive report is that of Hayashi and Hayamizu,[85] who observed the following trend in $\delta(^{127}I)$ under MAS conditions: CsI > LiI > RbI > NaI > KI. This ordering is only somewhat consistent with the trends observed for chlorine and bromine (*vide supra*), and clearly does not follow the trend in ionic radius or electronegativity of the cation.

Segel and Vyas[209] reported on ^{127}I quadrupolar coupling constants and CS tensors for various periodates (NH_4IO_4, KIO_4, $AgIO_4$, $NaIO_4$). Burkert and coworkers[198,199,201–204,208] also reported on ^{127}I quadrupolar coupling constants as a function of temperature in numerous periodates. The ^{127}I nuclear quadrupolar coupling constants for periodates range from 1.31 MHz at 145 K in NH_4IO_4 to about 43 MHz at 300 K in $NaIO_4$.

As discussed by Wu and Dong,[146] the span of the iodine chemical tensor in $NaIO_4$, 59 000 ppm, reported by Segel and Vyas[209] does not seem reasonable for such a symmetric species. Wu and Dong revisited the solid-state ^{127}I NMR of periodates (Fig. 5) and showed that the anisotropy of the iodine CS tensor is essentially negligible (<50 ppm) in the periodates ($NaIO_4$, KIO_4, $RbIO_4$, NH_4IO_4, HIO_4), and a span of only 18 ppm was precisely determined for $CsIO_4$. It is difficult to speculate on the reason that such large spans were reported previously, as no spectra are shown in the paper of Segel and Vyas.[209] To deal with the very broad ^{127}I resonances in stationary powdered samples of $NaIO_4$ ($C_Q = 42.24$ MHz; $\eta_Q = 0.0$) and HIO_4 ($C_Q = 43.00$ MHz; $\eta_Q = 0.75$), Wu and Dong[146] acquired the whole-echo FID and obtained a concomitant signal-to-noise increase of $2^{1/2}$.
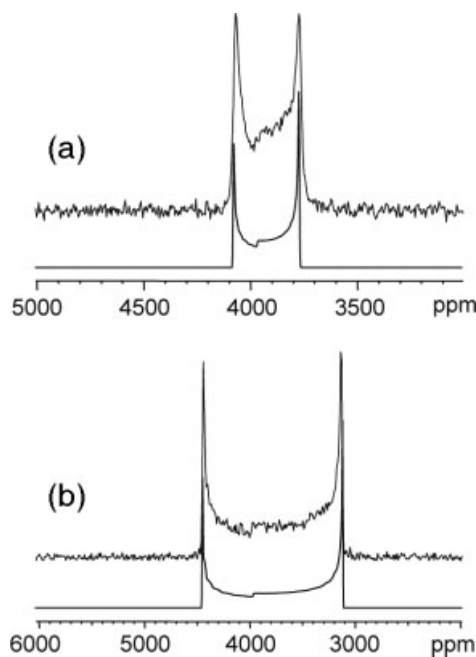

Figure 5. Representative ^{127}I solid-state NMR spectra of periodates obtained under stationary conditions on powdered samples of (a) NH_4IO_4 and (b) KIO_4. Also shown are the results of spectral simulations, from which $C_Q(^{127}I)$ and η_Q were determined (Table 4) and the iodine CSA was shown to be negligible. Reproduced with permission from Wu G, Dong S. *Solid State Nucl. Magn. Reson.* 2001; **20**: 100. Copyright 2001 Elsevier.

A recent report by Wasylishen and coworkers[159] has demonstrated the utility of enhanced-QCPMG methods for the acquisition of ^{127}I NMR specta of periodates, e.g. KIO_4.

Zeeman-perturbed NQR was applied by Kehrer *et al.* to determine the ^{127}I EFG tensor in glycyl-L-alanine hydroiodide monohydrate.[167,195] Although this is not a typical solid-state NMR study, it is interesting to quote the derived magnitude

of the EFG tensor, $C_Q(^{127}I) = 74.04$ MHz and $\eta_Q = 0.776$ (at 274.5 K) since the corresponding hydrobromide salt is isomorphous. The ratio of the ^{127}I and ^{81}Br quadrupolar coupling constants for the two materials (3.75) is somewhat larger than simply taking the ratio of their quadrupole moments (2.72) (although the EFG tensors were determined at different temperatures).

Residual dipolar coupling between iodine-127 and ^{13}C in solid 1,4-diiodobenzene has been observed in the form of a broadened non-Lorenztian ^{13}C lineshape.[224]

CONCLUDING REMARKS

Studies of the quadrupolar halogens have been performed since the early days of NMR spectroscopy. More recently, the availability of higher magnetic field strengths has opened up new opportunities for studying chlorine-35/37, bromine-79/81, and iodine-127 in powdered diamagnetic solids. As we have seen, in most cases, the large nuclear electric quadrupole moments of these nuclei (particularly ^{127}I and $^{79/81}Br$) tend to limit the types of halogen environments that may be studied without resorting to growing a single crystal. The most obvious way to deal with this situation is careful selection of compounds to be studied and to continue to progress toward ever-higher magnetic field strengths. Nevertheless, there is now a steadily growing body of solid-state NMR data, particularly for $^{35/37}Cl$, and it is anticipated that this growth will continue. Importantly, there is no *a priori* reason why $^{35/37}Cl$, $^{79/81}Br$, or ^{127}I SSNMR spectra of powdered organic compounds with covalently bonded halogens cannot be acquired. Two points to be aware of, however, are the expected breadth of the powder patterns (a minimum of hundreds of kHz up to several MHz and higher) and breakdown of the high-field approximation in spectral interpretation. NQR is, in many instances, a viable alternative. Particularly large NMR powder patterns will inevitably require a stepped-frequency piecewise acquisition of the spectrum, which can take several days depending on the system under study. The $C_Q(^{35}Cl)$ of -73 MHz measured indirectly in two chloroketosulfones[218] gives a rough estimate of the order of magnitude one should expect in the case of ^{35}Cl. Anticipated quadrupolar coupling constants for covalently bound ^{81}Br and ^{127}I are larger by factors of roughly 3 and 7.

In conclusion, we summarize a few key points which warrant further investigation in future solid-state NMR studies of the quadrupolar halogens:

1. There have been several mentions in the literature of possible correlations between halogen NMR parameters and the local hydrogen-bonding environment. It would be of interest to perform further studies, most easily on $^{35/37}Cl$, to corroborate and more fully and generally describe such a correlation.

2. There is a dearth of information about the CS tensors of the quadrupolar halogens. Existing information for chlorine indicates that for nuclei that have small enough quadrupolar coupling constants to be observed using powder NMR methods the CS tensor spans are also small (<150 ppm) and therefore difficult to characterize

precisely. Ultra-high magnetic fields will help in this respect. Many single-crystal studies have not accounted for the CS tensor in the analysis of the data. Careful analysis of results for powder and single-crystal data, with a particular emphasis on determining CS tensors is encouraged, where possible.

3. Quantum chemical methods have not been used to their full potential in the characterization of chlorine, bromine, and iodine EFG and CS tensors. Such methods should prove to be particularly valuable when used in concert with experimental data. It would be of interest to study possible trends in chlorine, bromine, and iodine EFG and CS tensors in isomorphous compounds, e.g. perhalogenates and hydrohalide salts. How do relativistic effects influence this trend?

It is clear that among the quadrupolar halogens, chlorine-35/37 NMR studies will continue to be the most widely applicable to different chemical compounds. Because of the large nuclear electric quadrupole moments of $^{79/81}Br$ and ^{127}I, applications involving these nuclei in solid-state NMR will likely remain relatively limited; however, ultra-high field strengths certainly continue to open up new possibilities for all nuclei with large quadrupole moments and/or low resonance frequencies.

REFERENCES

1. Frye JS, Maciel GE. *J. Magn. Reson.* 1982; **48**: 125.
2. Harris RK, Becker ED, Cabral de Menezes SM, Goodfellow R, Granger P. *Pure Appl. Chem.* 2001; **73**: 1795.
3. Harris RK. *NMR and the Periodic Table*, Harris RK, Mann BE (eds). Academic Press: London, 1978; Chapt. 1.
4. Vega AJ. *Encyclopedia of Nuclear Magnetic Resonance*, Grant DM, Harris RK (eds). Wiley: Chichester, 1996; 3869.
5. Frydman L. *Annu. Rev. Phys. Chem.* 2001; **52**: 463.
6. Garvin HL, Green TM, Lipworth E, Nierenberg WA. *Phys. Rev. Lett.* 1958; **1**: 74.
7. Smith ME. *Annu. Rep. NMR Spectrosc.* 2000; **43**: 121.
8. Pyykkö P. *Mol. Phys.* 2001; **99**: 1617.
9. http://www.emsl.pnl.gov/hfmrf/ [2005].
10. http://www.magnet.fsu.edu/ [2005].
11. http://nmrresource.ucsd.edu/index.html [2005].
12. http://www.nmr900.org/ [2005].
13. Lindman B, Forsén S. Chlorine, Bromine, and Iodine NMR. Physico-chemical and biological applications. In *NMR Basic Principles and Progress*, vol. 12, Diehl P, Fluck E, Kosfeld R (eds). Springer-Verlag: Berlin, 1976; 1.
14. Harbison GS, Slokenbergs A, Barbara TM. *J. Chem. Phys.* 1989; **90**: 5292.
15. Liao MY, Harbison GS. *J. Chem. Phys.* 1994; **100**: 1895.
16. Liao MY, Templin R, Harbison GS. *J. Am. Chem. Soc.* 1995; **117**: 9535.
17. Das TP, Hahn EL. Nuclear quadrupole resonance spectroscopy. In *Solid State Physics – Advances in Research and Applications, Supplement 1*, Seitz F, Turnbull D (eds). Academic Press: New York, 1958.

18. Semin GK, Babushkina TA, Yakobson GG. *Nuclear Quadrupole Resonance in Chemistry*. John Wiley & Sons: New York, 1975; (English Translation).

19. Buslaev YA, Kravcenko EA, Kolditz L. *Coord. Chem. Rev.* 1987; **82**: 1.

20. Schempp E, Bray PJ. *Physical Chemistry – An Advanced Treatise, Vol. 4: Molecular Properties*, Henderson D (ed.). Academic Press: New York, 1970; Chapt. 11.

21. Raman KV. *J. Mol. Struct.* 1995; **345**: 31.

22. Ege O, Negita H. *Z. Naturforsch.* 1990; **45a**: 599.

23. Vaara J, Jokisaari J, Wasylishen RE, Bryce DL. *Prog. Nucl. Magn. Reson. Spectrosc.* 2002; **41**: 233.

24. Ramsey NF. *Molecular Beams*. Oxford University Press: London, 1956; 162, 208.

25. Ramsey NF. *Phys. Rev.* 1950; **77**: 567.

26. Ramsey NF. *Phys. Rev.* 1950; **78**: 699.

27. Ramsey NF. *Phys. Rev.* 1951; **83**: 540.

28. Ramsey NF. *Phys. Rev.* 1952; **86**: 243.

29. Mason J. *Solid State Nucl. Magn. Reson.* 1993; **2**: 285.

30. Loewenstein A, Shporer M, Lauterbur PC, Ramirez JE. *J. Chem. Soc., Chem. Commun.* 1968; 214.

31. Sandland TO, Du LS, Stebbins JF, Webster JD. *Geochim. Cosmochim. Acta* 2004; **68**: 5059.

32. Gervais C, Dupree R, Pike KJ, Bonhomme C, Profeta M, Pickard CJ, Mauri F. *J. Phys. Chem. A* 2005; **109**: 6960.

33. Barberon F, Baroghel-Bouny V, Zanni H, Bresson B, d'Espinose de la Caillerie JB, Malosse L, Gan Z. *Magn. Reson. Imaging* 2005; **23**: 267.

34. Trill H, Eckert H, Srdanov VI. *Phys. Rev. B* 2005; **71**: 014 412.

35. Khasawneh M, Hartman JS, Bain AD. *Mol. Phys.* 2004; **102**: 975.

36. Taye A, Michel D. *Phys. Stat. Sol. B* 2002; **233**: 519.

37. Taye A, Michel D, Petersson J. *Phys. Rev. B* 2002; **66**: 174 102.

38. Taye A, Michel D, Petersson J. *Phys. Rev. B* 2004; **69**: 224 206.

39. Taye A, Michel D. *Phys. Stat. Sol. B* 2004; **241**: 1333.

40. Yun H, Patton ME, Garrett JH Jr, Fedder GK, Frederick KM, Hsu JJ, Lowe IJ, Oppenheim IJ, Sides PJ. *Cem. Concr. Res.* 2004; **34**: 379.

41. Lupulescu A, Kotecha M, Frydman L. *J. Am. Chem. Soc.* 2003; **125**: 3376.

42. Tou H, Maniwa Y, Yamanaka S, Sera M. *Physica B* 2003; **329–333**: 1323.

43. Azaïs T, Bonhomme C, Smith ME. *Solid State Nucl. Magn. Reson.* 2003; **23**: 14.

44. Honda H. *Z. Naturforsch.* 2003; **58a**: 623.

45. Trill H, Eckert H, Srdanov VI. *J. Phys. Chem. B* 2003; **107**: 8779.

46. Hou X, Kirkpatrick RJ. *Chem. Mater.* 2002; **14**: 1195.

47. Hou X, Kalinichev AG, Kirkpatrick RJ. *Chem. Mater.* 2002; **14**: 2078.

48. Hou X, Kirkpatrick RJ. *Inorg. Chem.* 2001; **40**: 6397.

49. Stebbins JF, Du LS. *Am. Mineral.* 2002; **87**: 359.

50. Saito K, Kanehashi K, Komaki I. *Annu. Rep. NMR Spectrosc.* 2001; **44**: 23.

51. Kanashiro T, Mahbubar RM, Michihiro Y, Nakamura K, Ohno T, Kishimoto Y. *J. Phys. Soc. Jpn.* 2001; **70**: 3322.

52. Mulla-Osman S, Michel D, Czapla D, Hoffman WD. *J. Phys.: Condens. Matter* 1998; **10**: 2465.

53. Mulla-Osman S, Michel D, Völkel G, Czapla Z. *Phys. Stat. Sol. B* 2000; **219**: 9.

54. Mulla-Osman S, Michel D, Völkel G, Peral I, Madariaga G. *J. Phys.: Condens. Matter* 2001; **13**: 1119.

55. Bryce DL, Gee M, Wasylishen RE. *J. Phys. Chem. A* 2001; **105**: 10 413.

56. Kříž J, Kurková D, Dybal J, Oupický D. *J. Phys. Chem. A* 2000; **104**: 10 972.

57. Suh BJ, Borsa F, Miller LL, Johnston DC, Torgeson DR, Corti M. *J. Appl. Phys.* 1996; **79**: 5084.

58. Suh BJ. *J. Korean Phys. Soc.* 2000; **36**: 387.

59. Goren SD, Ben-Yakar LF, Shames A, Pandyopadhayay B, Korn C, Shaked H, Massiot P, Perrin C, Gallier J, Privalov A. *Physica C* 1999; **313**: 127.

60. Skibsted J, Jakobsen HJ. *Inorg. Chem.* 1999; **38**: 1806.

61. Ono H, Ishimaru S, Ikeda R, Ishida H. *Bull. Chem. Soc. Jpn.* 1999; **72**: 2049.

62. Kirkpatrick RJ, Yu P, Hou X, Kim Y. *Am. Mineral.* 1999; **84**: 1186.

63. Ono H, Ishimaru S, Ikeda R, Ishida H. *Chem. Phys. Lett.* 1997; **275**: 485.

64. Binesh N, Bhat SV. *Solid State Ionics* 1996; **92**: 261.

65. Yamada K, Isobe K, Tsuyama E, Okuda T, Furukawa Y. *Solid State Ionics* 1995; **79**: 152.

66. Yamada K, Isobe K, Okuda T, Furukawa Y. *Z. Naturforsch.* 1994; **49a**: 258.

67. Yesinowski JP, Buess ML, Garroway AN, Ziegeweld M, Pines A. *Anal. Chem.* 1995; **67**: 2256.

68. Michihiro Y, Yamanishi T, Kanashiro T, Kishimoto Y. *Solid State Ionics* 1995; **79**: 40.

69. Holzer KP, Häcker U, Petersson J, Michel D, Kluthe S. *Solid State Commun.* 1995; **94**: 275.

70. Yamanishi T, Kanashiro T, Itabashi A, Michihiro Y, Kishi-moto Y, Ohno T. *J. Phys. Soc. Jpn.* 1994; **63**: 3903.

71. Yamanishi T, Kanashiro T, Michihiro Y, Kishimoto Y, Ohno T. *J. Phys. Soc. Jpn.* 1995; **64**: 643.

72. Kanashiro T, Michihiro Y, Kitahara K, Yamanishi T, Kishi-moto Y, Ohno T. *Solid State Ionics* 1996; **86–88**: 223.

73. Hattori M, Onoda Y, Erata T, Smith ME, Hattori M, Ohki H, Ikeda R. *Z. Naturforsch.* 1994; **49a**: 291.

74. Furukawa Y, Ikeda R. *Ber. Bunsen-Ges. Phys. Chem.* 1993; **97**: 1143.

75. Jelinek R, Stein A, Ozin GA. *J. Am. Chem. Soc.* 1993; **115**: 2390.

76. Amitin EB, Bausck NV, Gromilov SA, Kozlova SG, Moroz NK, Mazalov LN, Naumov VN, Samoilov PP, Slobodjan SA, Starikov MA, Fedorov VE, Frolova GI, Erenburg SB. *Physica C* 1993; **209**: 407.

77. Tabak F, Lascialfari A, Rigamonti A. *J. Phys.: Condens. Matter* 1993; **5**: B31.

78. Lefebvre F. *J. Chim. Phys.* 1992; **89**: 1767.

79. Hayashi S, Hayamizu K. *J. Phys. Chem. Solids* 1992; **53**: 239.

80. Erge Th, Michel D, Petersson J, Windsch W. *Phys. Stat. Sol. A* 1989; **114**: 705.

81. Erge Th, Michel D, Petersson J, Engelke F. *Phys. Stat. Sol. A* 1991; **123**: 325.

82. Erge Th, Engelke F, Michel D, Windsch W, Petersson J. *Ferroelectrics* 1990; **108**: 331.

83. Michel D, Häcker U, Erge Th, Petersson J. *Phys. Stat. Sol. B* 1994; **185**: 257.

84. Engelke F, Michel D, Windsch W, Sarv P, Lippmaa E. *Ferroelectrics* 1990; **108**: 337.

85. Hayashi S, Hayamizu K. *Bull. Chem. Soc. Jpn.* 1990; **63**: 913.

86. Weeding T, Veeman WS. *J. Chem. Soc., Chem. Commun.* 1989; 946.

87. Bastow TJ, Stuart SN. *J. Phys.: Condens. Matter* 1989; **1**: 4649.

88. Segel SL, Maxwell S, Heyding RD, Ingman P, Ylinen E, Punkkinen M. *Solid State Commun.* 1988; **66**: 1039.

89. Bastow TJ, Brown RJC, Segel SL. *J. Chem. Phys.* 1988; **89**: 1203.

90. Jurga S, Harbison GS, Blümich B, Spiess HW, Fujara F, Olinger A. *Ber. Bunsen-Ges. Phys. Chem.* 1986; **90**: 1153.

91. Kubo H, Hamasaki T, Tanimoto M, Katsumata K. *J. Phys. Soc. Jpn.* 1986; **55**: 3301.

92. Kubo H, Hamasaki T, Takeda K, Uryû N, Tanimoto M, Katsumata K. *Technol. Rep. Kyushu Univ.* 1986; **59**: 647.

93. Muralt P, Caravatti P, Kind R, Roos J. *J. Phys. C: Solid State Phys.* 1986; **19**: 1705.

94. Elschner S, Petersson J. *Z. Naturforsch.* 1986; **41a**: 343.

95. (a) Yesinowski JP, Eckert H California Institute of Technology, 1985; Unpublished data; (b) Yesinowski JP, Buess ML, Garroway AN, Ziegeweld M, Pines A. *Anal. Chem.* 1995; **67**: 2256, As cited in ref 67.

96. Becker KD. *J. Chem. Phys.* 1978; **68**: 3785.

97. Weulersse JM, Rigny P, Virlet J. *J. Chem. Phys.* 1975; **63**: 5190.

98. Okada K, Seiwa Y, Hirai A. *J. Phys. Soc. Jpn.* 1974; **37**: 1168.

99. Creel RB, von Meerwall E, Griffin CF, Barnes RG. *J. Chem. Phys.* 1973; **58**: 4930.

100. Hessler JP. *Bull. Am. Phys. Soc.* 1973; **18**: 113.

101. Kreshkov AP, Andronov VF, Drozdov VA. *Zh. Fiz. Khim.* 1972; **46**: 309.
102. Spiess HW, Sheline RK. *J. Chem. Phys.* 1971; **54**: 1099.
103. Clark RH, Moulton WG. *J. Appl. Phys.* 1971; **42**: 1308.
104. Rinneberg H, Hartmann H. *J. Chem. Phys.* 1970; **52**: 5814.
105. Rinneberg H, Haas H, Hartmann H. *J. Chem. Phys.* 1969; **50**: 3064.
106. Narath A. *Phys. Rev.* 1965; **140**: A552.
107. Yamagata Y. *J. Phys. Soc. Jpn.* 1964; **19**: 10.
108. Kawamori A, Itoh J. *J. Phys. Soc. Jpn.* 1963; **18**: 1614.
109. Herzog B, Hahn EL. *Phys. Rev.* 1956; **103**: 148.
110. Kanda T. *J. Phys. Soc. Jpn.* 1955; **10**: 85.
111. Bloom M, Hahn EL, Herzog B. *Phys. Rev.* 1955; **97**: 1699.
112. Hahn EL, Herzog B. *Phys. Rev.* 1954; **93**: 639.
113. Itoh J, Kusaka R. *J. Phys. Soc. Jpn.* 1954; **9**: 434.
114. Bloom M, Norberg RE. *Phys. Rev.* 1954; **93**: 638.
115. Jameson CJ. *Encyclopedia of Nuclear Magnetic Resonance*, Grant DM, Harris RK (eds). Wiley: Chichester, 1996; 1273.
116. Gee M, Wasylishen RE, Laaksonen A. *J. Phys. Chem. A* 1999; **103**: 10 805.
117. Pound RV. *Phys. Rev.* 1950; **79**: 685.
118. Stauss GH. *J. Chem. Phys.* 1964; **40**: 1988.
119. Narita K, Umeda J-I, Kusumoto H. *J. Chem. Phys.* 1966; **44**: 2719.
120. Baugher JF, Taylor PC, Oja T, Bray PJ. *J. Chem. Phys.* 1969; **50**: 4914.
121. Power WP, Wasylishen RE, Mooibroek S, Pettitt BA, Danchura W. *J. Phys. Chem.* 1990; **94**: 591.
122. Taylor PC, Baugher JF, Kriz HM. *Chem. Rev.* 1975; **75**: 203.
123. Amoureux JP, Fernandez C, Granger P. *Multinuclear Magnetic Resonance in Liquids and Solids – Chemical Applications*, *NATO ASI Series C – Vol. 322*, Granger P, Harris RK (eds). Kluwer Academic Publishers: Dordrecht, 1990; Chapt. XXII.
124. Bain AD. *Mol. Phys.* 2003; **101**: 3163.
125. Kundla E, Samoson A, Lippmaa E. *Chem. Phys. Lett.* 1981; **83**: 229.
126. Samoson A, Kundla E, Lippmaa E. *J. Magn. Reson.* 1982; **49**: 350.
127. Behrens HJ, Schnabel B. *Physica* 1982; **114B**: 185.
128. Samoson A. *Chem. Phys. Lett.* 1985; **119**: 29.
129. Freude D, Haase J, Klinowski J, Carpenter TA, Ronikier G. *Chem. Phys. Lett.* 1985; **119**: 365.
130. Taulelle F. *Multinuclear Magnetic Resonance in Liquids and Solids – Chemical Applications*, *NATO ASI Series C – Vol. 322*, Granger P, Harris RK (eds). Kluwer Academic: Dordrecht, 1990; Chapt. XXI.
131. Eichele K, Wasylishen RE. *WSOLIDS NMR Simulation Package, version 1.17.30*. Dalhousie University: Halifax, 2001; http://casgm3.anorg.chemie.uni-tuebingen.de/klaus/soft/.
132. Bak M, Rasmussen JT, Nielsen NC. *J. Magn. Reson.* 2000; **147**: 296, See http://nmr.imsb.au.dk/bionmr/software/simpson.php.
133. Hexem JG, Frey MH, Opella SJ. *J. Chem. Phys.* 1982; **77**: 3847.
134. Olivieri AC, Frydman L, Diaz LE. *J. Magn. Reson.* 1987; **75**: 50.
135. Olivieri A, Frydman L, Grasselli M, Diaz L. *Magn. Reson. Chem.* 1988; **26**: 615.
136. Olivieri AC. *J. Magn. Reson.* 1989; **81**: 201.
137. Grasselli M, Diaz LE, Olivieri AC. *Spectrosc. Lett.* 1991; **24**: 895.
138. Eichele K, Wasylishen RE. *Solid State Nucl. Magn. Reson.* 1992; **1**: 159.
139. Gan Z, Grant DM. *J. Magn. Reson.* 1990; **90**: 522.
140. Harris RK, Olivieri AC. *Prog. NMR Spectrosc.* 1992; **24**: 435.
141. Eichele K, Wasylishen RE. *Inorg. Chem.* 1994; **33**: 2766.
142. Kampermann H, Bain AD, Dumont RS. *J. Chem. Phys.* 2002; **116**: 2464.
143. Kennedy MA, Ellis PD. *Concepts Magn. Reson.* 1989; **1**: 35.
144. Kennedy MA, Ellis PD. *Concepts Magn. Reson.* 1989; **1**: 109.
145. Massiot D, Farnan I, Gautier N, Trumeau D, Trokiner A, Coutures JP. *Solid State Nucl. Magn. Reson.* 1995; **4**: 241.
146. Wu G, Dong S. *Solid State Nucl. Magn. Reson.* 2001; **20**: 100.
147. Frydman L, Harwood JS. *J. Am. Chem. Soc.* 1995; **117**: 5367.
148. Medek A, Harwood JS, Frydman L. *J. Am. Chem. Soc.* 1995; **117**: 12 779.
149. Medek A, Frydman L. *J. Braz. Chem. Soc.* 1999; **10**: 263.
150. Jäger C. *NMR Basic Principles and Progress*, vol. 31, Diehl P, Fluck E, Günther H, Kosfeld R, Seelig J (eds). Springer-Verlag: Berlin, 1994; 133.
151. Skibsted J, Nielsen NC, Bildsøe H, Jakobsen HJ. *J. Magn. Reson.* 1991; **95**: 88.
152. Larsen FH, Jakobsen HJ, Ellis PD, Nielsen NC. *J. Phys. Chem. A* 1997; **101**: 8597.
153. Kentgens APM, Verhagen R. *Chem. Phys. Lett.* 1999; **300**: 435.
154. Yao Z, Kwak HT, Sakellariou D, Emsley L, Grandinetti PJ. *Chem. Phys. Lett.* 2000; **327**: 85.
155. Prasad S, Kwak HT, Clark T, Grandinetti PJ. *J. Am. Chem. Soc.* 2002; **124**: 4964.
156. Siegel R, Nakashima TT, Wasylishen RE. *Chem. Phys. Lett.* 2004; **388**: 441.
157. Schurko RW, Hung I, Widdifield CM. *Chem. Phys. Lett.* 2003; **379**: 1.
158. Siegel R, Nakashima TT, Wasylishen RE. *Concepts Magn. Reson. A* 2005; **26A**: 47.
159. Siegel R, Nakashima TT, Wasylishen RE. *Concepts Magn. Reson. A* 2005; **26A**: 62.
160. Zipse D, Dalal NS, Achey RM, North JM, Hill S, Edwards RS. *Appl. Magn. Reson.* 2004; **27**: 151.
161. Trill H, Eckert H, Srdanov VI. *J. Am. Chem. Soc.* 2002; **124**: 8361.
162. Potrepka DM, Budnick JI, Fenner DB, Hines WA, Balasubramanian M, Moodenbaugh AR. *Phys. Rev. B* 1999; **60**: 10 489.
163. Uyeda M, Kubo T, Chiba M, Ajiro Y, Asano T. *J. Magn. Magn. Mater.* 1998; **177–181**: 833.
164. Xu X, Okada K, Shimamoto T, Chiba M, Fujii M, Ajiro Y. *Physica B* 1997; **239**: 131.
165. Xu X, Okada K, Fujii M, Ajiro Y. *J. Phys.: Condens. Matter* 1996; **8**: L675.
166. Okada K, Xu X, Fujii M. *Czech. J. Phys.* 1996; **46**(Suppl. S4): 2045.
167. Kehrer A, Weiden N, Weiss A. *Z. Phys. Chem.* 1992; **178**: 1.
168. Zumbulyadis N, Marchetti AP. *Colloids Surf.* 1990; **45**: 335.
169. Hayashi S, Hayamizu K. *J. Chem. Phys.* 1990; **92**: 2818.
170. Nakayama H, Eguchi T, Nakamura N, Chihara H, Nogami T, Imamura K, Shirota Y. *Bull. Chem. Soc. Jpn.* 1989; **62**: 399.
171. Halstead TK, Osment PA, Sanctuary BC, Tegenfeldt J, Lowe IJ. *J. Magn. Reson.* 1986; **67**: 267.
172. Huber H, Mali M, Roos J, Brinkmann D. *Solid State Ionics* 1986; **18 & 19**: 1188.
173. Brenni P, Brinkmann D, Huber H, Mali M, Roos J, Arend H. *Solid State Commun.* 1983; **47**: 415.
174. Brinkmann D, Huber H, Mali M, Roos J, Arend H. *Helv. Phys. Acta* 1982; **55**: 568.
175. Kubo H, Suzuki Y, Akitomi T. *J. Phys. Soc. Jpn.* 1979; **47**: 2029.
176. Conti LG. *Gazz. Chim. Ital.* 1976; **106**: 393.
177. Griffin CF, Creel RB, Worth J, von Meerwall E. *J. Phys. Chem. Solids* 1974; **35**: 71.
178. von Meerwall ED, Creel RB, Griffin CF, Segel SL. *J. Chem. Phys.* 1973; **59**: 5350.
179. Memory JD, Mathur J. *Bull. Am. Phys. Soc.* 1971; **16**: 521.
180. Renard JP, Velu E. *Solid State Commun.* 1970; **8**: 1945.
181. Conti LG, D'Alessandro R. *J. Phys. Chem. Solids* 1970; **32**: 1092.
182. Mehring M, Kanert O. *Z. Naturforsch.* 1969; **24a**: 768.
183. Bonera G, Galimberti M. *Solid State Commun.* 1966; **4**: 589.
184. Bonera G, Avogadro A, Borsa F. *Phys. Rev.* 1968; **165**: 391.
185. Bloembergen N, Sorokin PP. *Phys. Rev.* 1958; **110**: 865.
186. Reif F. *Phys. Rev.* 1955; **100**: 1597.
187. Watkins GD, Pound RV. *Phys. Rev.* 1953; **89**: 658.
188. Segel SL, Brown RJC, Ylinen EE, Ingman LP, Bastow TJ. *Z. Naturforsch.* 2002; **57a**: 661.
189. Mizuno M, Hirai A, Matsuzawa H, Endo K, Suhara M. *Phys. Chem. Chem. Phys.* 2001; **3**: 107.
190. Mizuno M, Iijima T, Kimura J, Endo K, Suhara M. *J. Mol. Struct.* 2002; **602–603**: 239.
191. Ardel G, Golodnitsky D, Peled E, Wang Y, Wang G, Bajue S, Greenbaum S. *Solid State Ionics* 1998; **113–115**: 477.
192. Hinze G, Böhmer R, Zalar B, Blinc R. *J. Phys.: Condens. Matter* 1997; **9**: 117.

193. Ishida H, Furukawa Y, Kashino S, Sato S, Ikeda R. *Ber. Bunsen-Ges. Phys. Chem.* 1996; **100**: 433.
194. Dzhioev RI, Kursaev YG. *Fiz. Tverd. Tela* 1996; **38**: 2148, (in Russian).
195. Kehrer A, Dou S-Q, Weiss A. *Z. Naturforsch.* 1989; **47a**: 659.
196. Lee N, Sanctuary BC, Halstead TK. *J. Magn. Reson.* 1992; **98**: 534.
197. Wagner GW. *Solid State Ionics* 1991; **47**: 143.
198. Grommelt M, Burkert PK. *Z. Naturforsch.* 1989; **44b**: 1053.
199. Burkert PK, Grommelt M. *Z. Naturforsch.* 1988; **43b**: 1381.
200. Mali M, Roos J, Brinkmann D, Phipps JB, Skarstad PM. *Solid State Ionics* 1988; **28–30**: 1089.
201. Klobasa DG, Burkert PK. *Z. Naturforsch.* 1987; **42a**: 275.
202. Klobasa DG, Burkert PK, Müller G. *Z. Naturforsch.* 1986; **41a**: 330.
203. Burkert PK, Klobasa DG. *Z. Naturforsch.* 1985; **40a**: 274.
204. Klobasa DG, Burkert P. *Z. Naturforsch.* 1984; **39a**: 1222.
205. Livingston R, Benjamin BM, Cox JT, Gordy W. *Phys. Rev.* 1953; **92**: 1271.
206. Visser D, Niesen L, de Waard H. *J. Phys. F: Met. Phys.* 1984; **14**: 2419.
207. Budde K, Richtering H. *Phys. Stat. Sol. B* 1983; **120**: 595.
208. Burkert PK. *Z. Naturforsch.* 1980; **35b**: 1349.
209. Segel SL, Vyas HM. *J. Chem. Phys.* 1980; **72**: 1406.
210. Weulersse JM, Virlet J, Rigny P. *Mol. Phys.* 1979; **38**: 923.
211. Gerhart GR, Hooper HO. *Phys. Rev. B* 1974; **10**: 4413.
212. Weisman ID, Bennett LH. *Phys. Rev.* 1969; **181**: 1341.
213. Weiss A, Weyrich W. *Z. Naturforsch.* 1969; **24a**: 474.
214. Butterworth J. *Proc. Phys. Soc.* 1965; **86**: 297.
215. Solomon I. *Phys. Rev.* 1958; **110**: 61.
216. Jurga S, Seliger J, Blinc R, Spiess HW. *Phys. Lett. A* 1986; **116**: 295.
217. Olivieri AC, Elguero J, Sobrados I, Cabildo P, Claramunt RM. *J. Phys. Chem.* 1994; **98**: 5207.
218. Eichele K, Wasylishen RE, Grossert JS, Olivieri AC. *J. Phys. Chem.* 1995; **99**: 10 110.
219. Thomas B, Paasch S, Steuernagel S, Eichele K. *Solid State Nucl. Magn. Reson.* 2001; **20**: 108.
220. Alarcón SH, Olivieri AC, Harris RK. *Solid State Nucl. Magn. Reson.* 1993; **2**: 325.
221. Batsanov AS, Cornet SM, Crowe LA, Dillon KB, Harris RK, Hazendonk P, Roden MD. *Eur. J. Inorg. Chem.* 2001; 1729.
222. Harris RK, Sünnetçioğlu MM, Cameron KS, Riddell FG. *Magn. Reson. Chem.* 1993; **31**: 963.
223. Apperley DC, Haiping B, Harris RK. *Mol. Phys.* 1989; **68**: 1277.
224. Aliev AE, Harris KDM, Barrie PJ, Camus S. *J. Chem. Soc., Faraday Trans.* 1994; **90**: 3729.
225. Nagasaka B, Takeda S, Nakamura N. *Chem. Phys. Lett.* 1994; **222**: 486.
226. Alarcon SH, Olivieri AC, Carss SA, Harris RK. *Angew. Chem., Int. Ed. Engl.* 1994; **33**: 1624.
227. Strohmeier M, Orendt AM, Alderman DW, Grant DM. *J. Am. Chem. Soc.* 2001; **123**: 1713.
228. Rentsch D, Hany R, von Philipsborn W. *Magn. Reson. Chem.* 1997; **35**: 832.
229. Alarcón SH, Olivieri AC, Carss SA, Harris RK, Zuriaga MJ, Monti GA. *J. Magn. Reson., Ser. A* 1995; **116**: 244.
230. Harris RK, Sebald A, Furlani D, Tagliavini G. *Organometallics* 1998; **7**: 388.
231. Fleming WW, Fyfe CA, Lyerla JR, Vanni H, Yannoni CS. *Macromolecules* 1980; **13**: 460.
232. Crosby RC, Haw JF. *Macromolecules* 1987; **20**: 2326.
233. Lyčka A, Holeček J, Sebald A, Tkáč I. *J. Organomet. Chem.* 1991; **409**: 331.
234. Harris RK, Root A. *Mol. Phys.* 1989; **66**: 993.
235. Hayashi S, Hayamizu K. *Magn. Reson. Chem.* 1992; **30**: 658.
236. Böhm J, Fenzke D, Pfeifer H. *J. Magn. Reson.* 1983; **55**: 197.
237. Mlynárik V. *Prog. Nucl. Magn. Reson. Spectrosc.* 1986; **18**: 277.
238. Jameson CJ. *Encyclopedia of Nuclear Magnetic Resonance*, Grant DM, Harris RK (eds). Wiley: Chichester, 1996; 2638.
239. Buchner W, Scheutzow D. *Org. Magn. Reson.* 1975; **7**: 615.
240. Yu P, Kirkpatrick RJ. *Cem. Concr. Res.* 2001; **31**: 1479.
241. Sherriff BL, Grundy HD, Hartman JS. *Geochim. Cosmochim. Acta* 1987; **51**: 2233.
242. Nagata T, Chuda Y, Yan X, Suzuki M, Kawasaki K. *J. Sci. Food Agric.* 2000; **80**: 1151.
243. Aubauer C, Engelhardt G, Klapötke TM, Nöth H, Schulz A, Warchhole M. *Eur. J. Inorg. Chem.* 2000; 2245.
244. Alarcón SH, Olivieri AC, Carss SA, Harris RK. *Magn. Reson. Chem.* 1995; **33**: 603.
245. Aliev AE, Elizabé L, Kariuki BM, Kirschnick H, Thomas JM, Epple M, Harris KDM. *Chem. Eur. J.* 2000; **6**: 1120.
246. Aliev AE, Harris KDM, Harris RK, Carss SA, Olivieri AC. *J. Chem. Soc., Faraday Trans.* 1995; **91**: 3167.
247. Luz Z, Olivier L, Poupko R, Müller K, Krieger C, Zimmermann H. *J. Am. Chem. Soc.* 1998; **120**: 5526.