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Solid-state NMR of quadrupolar halogen nuclei

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Abbreviations: Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; CP/MAS, cross-polarization magic-angle spinning; C_Q, quadrupolar coupling constant; CS, chemical shift; CSA, chemical shift anisotropy; CT, central transition; δ_{11}, δ_{22}, δ_{33}, principal components of the chemical shift tensor; EFG, electric field gradient; η_Q, quadrupolar asymmetry parameter; HMS, Haeberlen–Mehring–Spiess; IUPAC, International union of pure and applied chemistry; κ, skew of the magnetic shielding (or chemical shift) tensor; MAS, magic-angle spinning; MQMAS, multiple-quantum magic-angle spinning; NQR, nuclear quadrupole resonance; PAS, principal axis system; Q, nuclear electric quadrupole moment; QCPMG, quadrupolar Carr–Purcell–Meiboom–Gill.

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1. Introduction

Chlorine, bromine, and iodine are elements of importance in a variety of inorganic and organic compounds. For example, chlorine plays an important biological role in vital chloride ion channels [1–4] and all three elements are present in a variety of inorganic catalysts [5,6]. Solid-state nuclear magnetic resonance (SSNMR) spectroscopy of the chlorine-35/37, bromine-79/81, and iodine-127 nuclides is often challenging due to their NMR properties; however, the experiment is an excellent probe of the local halogen environment in many solid compounds and materials because of the technique's sensitivity to the local electronic and structural environments.

Chlorine-35/37 ($I = 3/2$), bromine-79/81 ($I = 3/2$), and iodine-127 ($I = 5/2$) are all NMR-active quadrupolar nuclei that are present in relatively high natural abundances (Table 1). As these nuclei are quadrupoles, the collection of high signal-to-noise (S/N) ratio SSNMR spectra may be difficult, especially for powder samples. In systems where the nucleus does not sit at a site of very high symmetry (e.g., octahedral or tetrahedral), the interaction between the quadrupole moment (Q) of the nucleus and the electric field gradient (EFG) tensor is a significant perturbing interaction to the Zeeman Hamiltonian, which broadens the resulting NMR spectrum of a powder. As halogen atoms do not generally sit at a site of high symmetry in the majority of systems of interest, quadrupolar broadening is generally the dominant contribution to the observed NMR line widths. In these cases, often only the central transition (CT, $m = ½ \leftrightarrow -½$) is observed; even this may be broadened to a significant extent, up to the order of magnitude of MHz in some cases. Further discussion of the NMR properties of the quadrupolar halogen nuclei is given in Section 2.3. Despite the challenges, there have been a number of significant studies using chlorine, bromine,

Table 1
NMR properties of the quadrupolar halogens (chlorine, bromine, and iodine).

	Natural abundance/%	I	$\gamma/10^7$ rad T^{-1} s^{-1}	Ξ^a	Q/mb	$1-\gamma_\infty$[17]	Relative CT line width[b]	IUPAC chemical shift reference[c]
^{35}Cl	75.78	3/2	2.624198	9.797909	−81.65(80)	42.0	1.34	0.1 mol/dm^3 NaCl in D_2O
^{37}Cl	24.22	3/2	2.184368	8.155725	−64.35(64)	42.0	1.00	
^{79}Br	50.69	3/2	6.725616	25.05390	313(3)	80	7.70	0.01 mol/dm^3 NaBr in D_2O
^{81}Br	49.31	3/2	7.249776	27.00658	262(3)	80	5.01	
^{127}I	100.0	5/2	5.389573	20.00748	−696(12)	162	11.44	0.01 mol/dm^3 KI in D_2O

[a] Resonance frequency, in MHz, in a magnetic field where ^1H resonates at exactly 100 MHz.
[b] For a powder sample, based on Eq. (13).
[c] From reference [177].

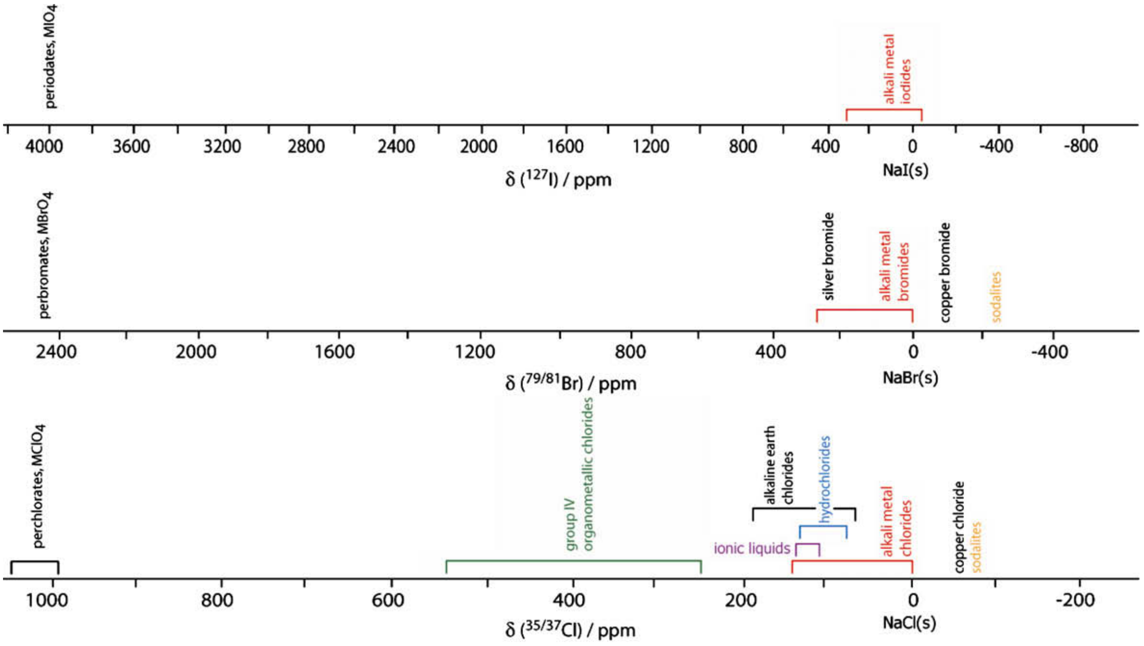

Fig. 1. Approximate chemical shift ranges for chlorine, bromine, and iodine. Scales are with respect to solid NaX (X = Cl, Br, and I) at 0 ppm. Note the different scale for each element.

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