Experimental Gas-phase Halogen Nuclear Quadrupole Coupling Constants; A Review*

Michael H. Palmer
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, UK

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As a prelude to a theoretical study of nuclear quadrupole coupling constants (NQCC), via the electric field gradients at equilibrium, we review the current state of knowledge of gas-phase data for a diverse set of axially symmetric inorganic and organic molecules with symmetries \( C_3v \), \( C_{wm} \), \( D_{an} \) in particular, where the heavy elements are Cl, Br and I with C, Si and Ge hydrides. In most of the cases, the latter elements are in an approximately tetrahedral environment.

1. Introduction

Previously we have reported ab initio studies of a variety of organic and inorganic molecules, containing various quadrupolar nuclei, especially \(^{14}\)N [1], \(^{10,11}\)B [2], \(^{33}\)S [3] and \(^{17}\)O [4]. In the following we continue this survey to cover halogen quadrupole coupling, with particular reference to the stable isotopes of chlorine, bromine and iodine in both inorganic and organic molecules. In the present Paper we consider only axially symmetric molecules, i.e., those with one unique symmetry axis, such that the asymmetry parameter \( \eta \) is zero. In the normal convention for quadrupole coupling constants, \( x_{zz} = x_{yy} \geq x_{xx} \); the further identities with the inertial axis data \( x_{zz} = \chi_{xx} \), \( x_{yy} = \chi_{yy} = x_{bb} = x_{cc} \) occur. For the present molecules, the position of the inertial axes (IA) are determined by symmetry. We review the current state of data for halogen quadrupole coupling in these compounds, since previous reviews are now somewhat out dated [5, 6].

The present set of nuclei has nuclear spin \( I = 3/2 \) (\(^{35}\)Cl, \(^{37}\)Cl, \(^{79}\)Br, and \(^{81}\)Br), \( I = 5/2 \) (\(^{127}\)I), \( I = 9/2 \) (\(^{73}\)Ge). The individual atomic quadrupole coupling constants, with standard deviations in parentheses, for \(^{35}\)Cl (\(-81.65 \text{ mb} \) (80)) and \(^{37}\)Cl (\(-64.35 \text{ mb} \) (64)) [7] are relatively well determined, and their ratio is known with great accuracy (1.268877) [8, 9]. These values, and the less well determined values [10] for the \(^{79}\)Br and \(^{81}\)Br, \(^{127}\)I and \(^{73}\)Ge isotopes have \( Q_{yz} + 331 \) (4), \(+276 \) (4), \(-789 \) and \(-173 \) mb, respectively.

NQR has been widely used for studies of halogenated compounds, but because of the 3/2 and 5/2 nuclear spin, only the resonance frequencies (\( \nu \)) can be determined from polycrystalline samples; the asymmetry parameter (\( \eta \)) requires the use of a single crystal or other techniques [5]. As a typical example, the \(^{35}\)Cl NQR frequency for methyl chloride at 77 K is 34.029 MHz, to be compared with 37.3767 MHz for the vapour by microwave (MW) study at room temperature [11, 12]. The effect is both one of temperature and lattice effects. Indeed, analysis of the NQR frequency and molar heat capacity against temperature lead to the value of \(-2.870 \) (330) MHz as the crystalline contribution to the observed frequency at 0 K [13].

2. Experimental Halogen Nuclear Quadrupole Coupling Constants

In the following text we review the known experimental data for the present group of Cl, Br and I compounds, noting any limitations in the interpretation, and establishing the best values for the most important compounds. In the following Sections, experimental claimed errors are in parentheses. The level of detail in the experimental interpretation of the NQCC of the diatomic and methyl halide species, where considerable interest in relating the NQCC to vibrational states and rotational quantum numbers occurs, is much higher than most NQCC analyses to date. There is little information concerning simple PbH\(_2\)Cl types of molecule. While Sn has no quadrupolar stable isotopes, the \(^{119}\)Sn nucleus is commonly observed in Mössbauer spectroscopy. Some studies of chlorogermane gave no \(^{73}\)Ge isotope (7.8%) quadrupolar splitting [14, 15], but more recent MW studies showed

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Table 1. Experimental nuclear quadrupole coupling constants (MHz).

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<th>Compound</th>
<th>( \chi_{zz} )</th>
<th>Reference</th>
<th>Compound</th>
<th>( \chi_{zz} )</th>
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<td>( ^{35}\text{Cl} )</td>
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<td>[65]</td>
<td>( ^{35}\text{Cl} )</td>
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<td>[52]</td>
<td>( ^{79}\text{Br} )</td>
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<td>( ^{73}\text{Ge} )</td>
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<td>[57]</td>
<td>( ^{73}\text{Ge} )</td>
<td>-93.0320 (152)</td>
<td>[16]</td>
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the natural abundance \( ^{73}\text{Ge} \) splitting as well as the \( ^{35,37}\text{Cl} \) splitting [16].

2.1 The Hydrogen Halides and Interhalogens

Hydrogen chloride has been studied by MW over many years [17], and recently by Doppler resolution FIR study of the deuterium compound [18]. The MW NQCC data, with lower error bounds, for \( ^{35}\text{Cl} \) in \( X={}^1\text{H} \) was \(-67.61893(47) \) MHz and for \( X={}^2\text{H} \) was \(-67.39338(9) \) MHz; the latter deuterium coupling constant is +187.36 (30) kHz. As in the cases shown below, both the NQCC at \( ^{35}\text{Cl} \) and the dipole moment (1.1085(5) D) were fit to power series in \((v +1/2)\). Similar studies to the above, for HBr [19, 20, 21] and DBr [20], yield the \( ^{79}\text{Br} \) coupling in HBr as +532.30590 (24) MHz. In HI the corresponding \( ^{127}\text{I} \) NQCC -1828.059 (51) MHz is obtained by FIR spectroscopy [22].

Various authors have noted the close fit of bond length to NQCC in the interhalogens. The chlorine fluoride NQCC at \( ^{35}\text{Cl} \) is \(-145.87182 (3) \) MHz [23, 24], with values down to \(-85.8 \) MHz for ICl [25, 26]. If we extract the three series FX, BrX and IX (\( X={}^1\text{Cl}, \text{Br}, \text{I} \)), then clearly linear relations emerge. This has led to estimates of about \(-115 \) MHz for the \( ^{35}\text{Cl} \) nucleus [27] in the chlorine molecule, which has not been determined in the gas phase as yet. The advent of FT-MW instruments might allow the small dipole moment of \( ^{35}\text{Cl} \)– \( ^{37}\text{Cl} \) to be used. The NQR value in the \( ^1\text{Cl}_2 \) solid at low temperature, where the environment does not have axial symmetry (\( \eta \) 0.20) is \((-) 108.95 \) MHz [28].

Although these correlations are both useful and important, they clearly only work with molecules with very similar bonding systems. In the interhalogens we have effectively a \( \sigma \)-bond and three lone pairs at each end, staggered with respect to each other; i.e. similar to staggered ethane. If we consider HCl, with bond length 1.27455 Å [29], the NQCC at \( ^{35}\text{Cl} \) based on the interhalogen extrapolated value for this bond length would be about \(-185 \) MHz, three times larger than experiment. Similar results would apply with both HBr and HI. The problem lies with the fact that the halogen NQCC declines with the electronegativity of the attached atom (here halogen), but also with the size. (We note in passing that Mössbauer spectroscopy isomer shifts in covalent \( \text{Fe}^{7}\text{halides} \) show similar linear dependence.) The interhalogen correlations are useful with both the bromine and iodine molecules as well. Laser induced fluorescence on the B to X states gives values for these two molecules of +810.0 (5) \( ^{79}\text{Br} \) [30] and -2452.5837 (16) MHz \( ^{127}\text{I} \) [31, 32, 33]. The NQR values in the solids at various temperatures, again where the environments do not have axial symmetry (\( \eta \) 0.175 and <0.03) are (+) 765.86 and \((-) 2156 \) MHz, respectively [28]. Clearly
there are substantial temperature and condensed phase effects for these molecules. In contrast, some of the heteronuclear interhalogens show much smaller vapour/solid differences, even though the internuclear charge interactions might have been expected to be larger [28].

2.2 The Alkyl and Silyl Halides

The NQCC for chloromethane and its deuterated derivatives have been accurately determined [11, 12] and show a small but linear decrease with extent of deuteration. These are attributed to both (minor) structural changes, CH-CD bond differences being about +0.004 Å, and electronegativity differences, the Me group being less positive relative to Cl in CD/CH isomers. The rotational dependence of the nuclear quadrupole coupling, arising from centrifugal distortion for chloromethane, has been investigated [34]; this led to probably the most accurate values for the ground state quadrupole coupling constants (χ₀) at both 35Cl (−74.7477 (22) MHz) and 37Cl (−58.9060 (61) MHz) centres to date [35, 36].

Rotational dependence of the nuclear quadrupole coupling in chloromethane:

\[ \chi_{J,K} = \chi_0 + J(J+1) (\chi_J + K^2) \chi_K. \]

Similar nuclear quadrupole coupling rotational dependence has been observed for bromo methane [37, 38, 39], with similar analysis to the equation, and the effects of deuteration have been observed [40, 41]. The apparently most accurate data for the two isotopic ground state constants are 79Br: +577.137 (9) MHz and 81Br: +482.13 (14) MHz. Finally, the large quadrupole splitting in the microwave spectrum of iodo-compounds has enabled the magnetic hyperfine structure and nuclear shielding tensors for the 127I nuclear quadrupole coupling constants in iodomethane and its trideutero derivative [42–48] to be intensively investigated. The difference between the 1H3 and 2H(D)3 isotopomers determined under the same conditions is 5.16 MHz [48], and as expected, is much larger than in the chloro-compound. The most accurate value of the NQCC for iodomethane is −1934.13022 (39) MHz [47].

We will discuss a number of typical examples of halogen quadrupole coupling below, but here we note that electronic effects of substituents can lead to surprisingly little effect on the EFG-PA data. For example, in the pair of compounds CX3Cl, with X=H or F, the values of \( \chi_{xx} \) are −74.7477 (22) MHz (CH3Cl) and −77.7902 (30) MHz (CF3Cl) [49, 50].

2.3 The Silyl Halides

The silyl halides have been investigated by MW spectroscopy several times, but in one study all four SiH3X compounds with X=F, Cl, Br, I as well as their partially deuterated compounds were treated by the same methods, thus making the data strictly comparable [51]. Although some of the data was refined later [52, 53, 54], the general conclusions remain, that the ratio of the NQCC in the methyl and silyl halides decreases from Cl to Br to I, with values (C/Si) 1.883:1.722: 1.553. As with CF3Cl and CH3Cl above, the trifluorosilyl halides show almost no differences in the NQCC to the silyl halides [55, 56].

2.4 The Germyl and Stannyl Halides

The germyl and stannyl halides have also been studied by MW spectroscopy. In the germyl series, Krisher et al. [57] obtained 73Ge NQCC in fluorogermane of good precision (−93.03 (10) MHz). This was followed by similar studies of the chloro-compound where both the 35Cl (−46.9500 (26) MHz for the 70Ge isotopomer) and 73Ge (−93.0320 (152) MHz for the 35Cl isotope) were obtained [16]. The bromo- and iodo-compounds gave NQCC similar to the methyl series [58]. At the halogen centres, the germanes behave more closely to the silanes than methanes; thus a factor of 1.5–2.0 occurs in the alkyl/germyl compounds. The SnH3X series with X=Cl, Br, I show NQCC at the major halogen isotope centres of −41.62 (30), +350(6) and −1273 (8) MHz, respectively [59, 60, 62]. These are again more reminiscent of silanes and germanes than methanes [61, 62]. The overall sequence of positions for the halogen NQCC in the alkanes, silanes, germanes and stannanes is: C>Ge>Sn>Si; this has been attributed to p/s-hybridisation differences, Cl>Br>I, together with electronegativity differences C>Ge>Sn>Si.

2.5 The Halogenoacetylenes

The axial symmetry and ready availability of simple acetylenes has led to a number of high resolution FT-MW studies [63]. The difference in 35Cl coupling constants in the halogenoacetylenes relative to the corresponding methanes is small. Further, the effect of electronic substituents at the remote end, such as fluoro- and trifluoromethyl-, lead to reverse effects on the quadrupole coupling; thus we have the magnitude order in chloro-acetylenes, fluoro>hydrogen>trifluoromethyl [64, 65, 66]. In the bromoacetylenes, the remote substituents lead
molecule [27]. The length-NQCC correlation collapses always with the hydrogen halides; so the success is limited to cases with effectively identical modes of bonding, as occurs in the halogens.

Similarly, the pair of CX$_3$ and SiX$_3$ molecules (X=H, F) have almost the same NQCC but significantly different bond lengths; this is generally true for compounds of these types. Thus the coupling relates more to the atoms involved in the local σ-bond than to the length.

### 3.1 Conclusions

Whilst the values for $\chi_{zz}$ in the diverse compounds can be related to various types of physical-organic parameters, such as σ-constants in closely related groups of compounds, and similarly with other parameters such as $\sigma^*$ and the (Swain-Lupton) F/R parameters, these do not help in widely differing types of compounds. Similarly, in the hydrogen halides and interhalogens, the correlations between the $\chi_{zz}$ and bond length are sufficiently satisfactory, to allow the estimation of the $^{35}$Cl quadrupole coupling in the chlorine molecule with some confidence, but the correlation collapses when the nature of the bonding types is changed. For X-Y types of molecule, where X, Y are halogens, the bonding is basically as in ethane, with staggered lone-pairs; in organic molecules, the geometric arrangement of bonding pairs is similar, but the more extensive bonding range defeats the correlation. One reason is that the differing substituent effects of (say) H replacement by F in MX$_3$-halogen, changes the effective electronegativity of M, but does not change the bonding distance M-halogen by the same amount.

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