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

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Z. Naturforsch. **53a,** 615–619 (1998); received January 8, 1998

As a preclude 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}, $C_{\infty v}$, $D_{\infty h}$ 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 (η) is zero. In the normal convention for quadrupole coupling constants, $\chi_{zz} \geq \chi_{yy} \geq \chi_{xx}$; the further identities with the inertial axis data $\chi_{zz} = \chi_{aa}$, $\chi_{yy} = \chi_{xx} = \chi_{bb} = \chi_{cc}$ 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 mb (80)) and ^{37}Cl (–64.35 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_Z+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 (ν) can be determined from polycrystalline samples; the asymmetry parameter (η) 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 data. There is little information concerning simple PbH_3Cl types of molecule. While Sn has no quadrupolar stable isotopes, the ^{119m}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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* Presented at the XIVth International Symposium on Nuclear Quadrupole Interactions, Pisa, Italy, July 20–25, 1997.

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

Compound	χ_{zz}	Reference	Compound	χ_{zz}	Reference
^{35}Cl			^{35}Cl		
ClF_5	–34.63 (6)	[76]	SiH_3Cl	–39.70	[53]
SiF_3Cl	–39.83 (16)	[56]	GeH_3Cl	–46.9500 (26)	[16]
HCl	–67.4605	[15]	MeCl	–74.753	[36]
HC≡CCl	–79.7358	[66]	$CF_3CC≡CCl$	–79.4 (30)	[64]
FC≡CCl	–83.0	[65]	ICl	–85.8	[25, 26]
BrCl	–102.378	[74]	Cl_2	–115.0	[81]
ClF	–145.87182	[24]			
^{79}Br			^{79}Br		
SiH_3Br	+334.981	[52]	GeH_3Br	+384 (2)	[58]
HBr	+532.23977	[21]	MeBr	+577.143	[41]
CF_3Br	+618.2 (3)	[75]	BrC≡CH	+648.113	[67]
BrC≡CF	+672.6	[68]	Br_2	+810.0	[30]
BrCl	+875.078	[74]	BrF	+1086.89197	[80]
^{127}I			^{127}I		
IF_5	–1069.07 (40)	[77]	SiH_3I	–1245.1	[51]
GeH_3I	–1381 (4)	[58]	HI	–1828.059	[78]
MeI	–1934.136	[47]	HC≡CI	–2254.1785	[63]
I_2	–2452.5837	[33]	IBr	–2731.0	[82]
ICl	–2929.0	[25, 26]	IF	–3440.748	[79]
^{73}Ge			^{73}Ge		
GeH_3F	–93.03 (10)	[57]	GeH_3Cl	–93.0320 (152)	[16]

the natural abundance ^{73}Ge splitting as well as the ^{35,37}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 $X^{35}Cl$ in $X={}^1H$ was –67.61893(47) MHz and for $X={}^2H$ 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}Cl and the dipole moment (1.1085(5) D) were fit to power series in $(\nu+1/2)$. Similar studies to the above, for HBr [19, 20, 21] and DBr [20], yield the ^{79}Br coupling in HBr as +532.30590(24) MHz. In HI the corresponding ^{127}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}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=Cl, Br, I), then clearly linear relations emerge. This has led to estimates of about –115 MHz for the ^{35}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 $^{35}Cl-^{37}Cl$ to be used. The NQR value in the Cl_2 solid at low temperature, where the environment does not have axial symmetry (η 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 σ-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}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 Fe^{II} 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}Br) [30] and –2452.5837(16) MHz (^{127}I) [31, 32, 33]. The NQR values in the solids at various temperatures, again where the environments do not have axial symmetry (η 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 (χ_0) at both ^{35}Cl (−74.7477 (22) MHz) and ^{37}Cl (−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 ^{79}Br: +577.137 (9) MHz and ^{81}Br: +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 ^{127}I nuclear quadrupole coupling constants in iodomethane and its trideutero derivative [42–48] to be intensively investigated. The difference between the $^1H_3$ 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 CX_3Cl, with X=H or F, the values of χ_{zz} are −74.7477 (22) MHz (CH_3Cl) and −77.7902 (30) MHz (CF_3Cl) [49, 50].

2.3 The Silyl Halides

The silyl halides have been investigated by MW spectroscopy several times, but in one study all four SiH_3X 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 CF_3Cl and CH_3Cl 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 ^{73}Ge NQCC in fluorogermane of good precision (−93.03 (10) MHz). This was followed by similar studies of the chloro-compound where both the ^{35}Cl (−46.9500 (26) MHz for the ^{70}Ge isotopomer) and ^{73}Ge −93.0320(152) MHz for the ^{35}Cl isotopomer 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 SnH_3X 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 ^{35}Cl 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 chloroacetylenes, fluoro>hydrogen>trifluoromethyl [64, 65, 66]. In the bromoacetylenes, the remote substituents lead to fluoro>hydrogen [67, 68]; the iodoacetylenes have the magnitude order fluoro>hydrogen>chloro [63, 64, 69, 70]. It is not immediately clear what controls these magnitudes, but the first task is to reproduce the trends, and this will be addressed in following Papers.

One type of substitution which leads to unexpected results is replacement of H_3 by F_3 in MX_3Cl (M=C, Si) and related compounds. The fluoro-compound has a slightly higher (negative) NQCC at ^{35}Cl. The two silyl compounds are effectively identical, as observed experimentally. In the comparison of alkyl and silyl halides, the differences cannot be ascribed to d-orbital participation in any meaningful way, since in a following Paper we show that the d-orbitals are purely polarisation functions with low atomic populations.

3. Overall Generalisations with Respect to Structure

The ratios for CH_3X −74.75 (X=^{35}Cl), +577.14 (^{79}Br) and −1934.13 MHz (^{127}I) (i.e. 1:7.72:25.87) are fairly close to the cube of the atomic number ratios (1:8.73:30.30), and of course are a measure of $\langle 1/r^3 \rangle$. If the individual variation in the experimental isotopic quadrupole coupling constants is used to give the weighted ratios (χ_{zz}/Q_Z), then the ratios are 1.00:2.018:2.837, are relatively close to 1:2:3 for ^{35}Cl, ^{79}Br and ^{127}I, respectively.

If we plot the ^{35}Cl NQCC (in MHz) for a series of simple alkyl, silyl and other compounds against Taft σ- or σ^+-constants, the data do not produce any correlation at all; similarly, the Swain and Lupton [71, 72, 73] set of substituent Field Effect data lead to a very poor correlation for the few compounds where the relevant F(R) constants are available. If a set of simple molecules with widely differing bond lengths is plotted against ^{35}Cl NQCC, there is again no correlation; such a procedure was successfully used to predict the ^{35}Cl NQCC for the chlorine 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 χ_{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 σ^+ 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 χ_{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.

Acknowledgements

We thank the SERC (now EPSRC) for purchase of a DEC AXP Alpha 3600 work-station, and Edinburgh University for the generous provision of time on the Cray T3D computer.

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