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A More Reliable Absolute Shielding Scale for Chlorine: Combined Experimental and Theoretical Approach

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Using accurate $^{35/37}$Cl spin−rotation data and the chlorine chemical shift of HCl(g) with respect to the chloride ion in aqueous solution, $\delta = 28 \pm 3$ ppm, a more reliable chlorine absolute shielding scale has been established. The experimental paramagnetic contribution to the chlorine shielding tensor is available from accurate $^{35/37}$Cl spin−rotation data for HCl(g) in the $v = 0$, $J = 1$ state. Combining this with the diamagnetic contribution obtained from molecular orbital calculations yields the absolute chlorine shielding for HCl(g). At the equilibrium geometry and without relativistic corrections, $\sigma_{\text{iso}}(\text{eq}) = 962.3 \pm 0.9$ ppm while $\sigma_{\text{iso}}(298\ \text{K}) = 946.3 \pm 0.9$ ppm. Using these data together with the chemical shift of HCl(g) relative to $\text{Cl}^-(\text{aq})$ leads to $\sigma(298\ \text{K}) = 974 \pm 4$ ppm for the Cl^- ion. The chlorine absolute shielding scale established here is compared with a scale reported in the proceedings of the XIXth Ampere Congress in 1976. Our "experimental" chlorine scale is also compared with a theoretical scale based on a combined ab initio/molecular dynamics (MD) simulation approach. Absolute chlorine shielding tensors deduced from chlorine spin−rotation constants are compared with ab initio calculations. From a basis set dependence study on HCl, Cl_2, and CH_3Cl, it is apparent that large basis sets with polarization functions are essential to approach a quantitative prediction of experimental results. In addition, we have measured accurate values of the $^{35/37}$Cl chemical shifts of liquid chlorine for the first time, $\delta(298\ \text{K}) = 342 \pm 2$ ppm.

Introduction

There are two NMR-active chlorine isotopes, ^{35}Cl (75.53% natural abundance) and ^{37}Cl (24.47% natural abundance), both with spin $^{3}/_{2}$. Chlorine-37 has a slightly smaller quadrupole moment, $Q(^{37}\text{Cl}) = -6.39 \times 10^{-30}\ \text{m}^2$, compared to $Q(^{35}\text{Cl}) = -8.11 \times 10^{-30}\ \text{m}^2$;[1] hence, the line width is narrower by the factor $[Q(^{35}\text{Cl})/Q(^{37}\text{Cl})]^2 = 1.61$. The moderately large quadrupole moments of both isotopes generally result in efficient quadrupolar relaxation and broad NMR lines; for ^{35}Cl, line widths of 15 kHz have been reported for CCl_4(l).[2,3] Gas- and liquid-phase NMR studies are hampered by broad peaks arising from efficient quadrupolar relaxation. Nevertheless, there has been recent interest in chlorine NMR, taking advantage of the increasingly available higher magnetic field spectrometers. Examples include reports of $^{35/37}$Cl chemical shifts in some inorganic chloride salts,[4] small chlorine-containing molecules,[5] and the $^{35/37}$Cl NMR study of inorganic perchlorates in the solid state.[6] The chemical shift range is approximately 1500 ppm as illustrated in Figure 1, which is based on the compilation by Lindman and Forsén of some early data.[7] Working at higher applied magnetic fields reduces the apparent line broadening (in ppm), thus increasing the resolution. Chlorine chemical shielding has also attracted some attention from theoreticians looking for benchmark systems to test computational methods.[5,9,10] Also, there is an increased awareness of the role of relativistic effects on nuclear shielding tensors.[10,11] The result of a recent study of hydrogen halides[10] indicates that for chlorine relativistic corrections are important. Unfortunately, a reliable absolute shielding scale for chlorine is unavailable.[12]

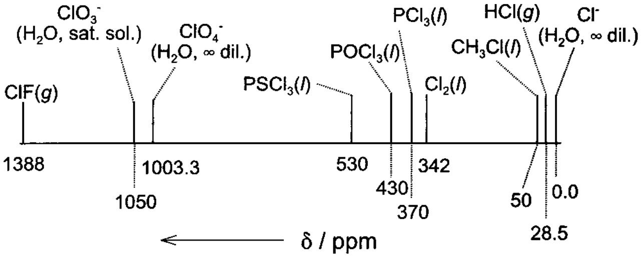

Figure 1. Chlorine chemical shift scale. Data are from ref 7 with the exception of HCl(g), Cl_2(l), CH_3Cl(l) (this work), and ClF(g) (from the chlorine chemical shielding calculated from the chlorine spin−rotation constant[8] and our absolute shielding scale).

To compare experimental and theoretical results, it is necessary to have an absolute shielding scale to convert the experimentally measured chemical shift relative to a primary reference to an absolute chemical shielding constant. If the absolute shielding for one molecule is available and one is able to measure the chemical shielding of the nucleus of interest in this molecule with respect to the primary chemical shift reference, then one can determine the absolute shielding of the reference. All other compounds containing the nucleus of interest can be placed on this shielding scale by measurement of the chemical shift with respect to this primary reference.

An absolute shielding scale for chlorine was reported by Lee and Cornwell in the conference proceedings of the XIXth Ampere Congress in Heidelberg, 1976.[13] The ^{35}Cl chemical shift of HCl(g) was found to be 20 ± 3 ppm with respect to 6.3 M HCl. Using ^{35}Cl nuclear spin−rotation data for HCl(g), the

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authors calculated $\sigma_{iso}(^{35}Cl) = 953$ ppm for HCl. Neglecting vibrational corrections, this led to $\sigma_{iso}(^{35}Cl) = 973 \pm 8$ ppm for the chloride ion (6.3 M HCl). It is remarkable that the authors were able to obtain such accurate data for HCl(g). Unfortunately, experimental details of this investigation have not been reported.

Another absolute shielding scale for chlorine based on the ^{35}Cl spin−rotation data for CH_3Cl(l) was reported in 1977.[14] From molecular beam experiments, Dubrulle et al. found that the perpendicular and parallel components of the ^{35}Cl spin−rotation tensor are 2.70(14) kHz and −7.0(16) kHz, respectively. Unfortunately, the experimental error limits the usefulness of this shielding scale. The absolute shielding constant of the chloride ion derived from their study is 930 ppm with an error of at least ±170 ppm due to the uncertainty in the spin−rotation data.

The purpose of the present investigation is to examine the $^{35/37}$Cl NMR spectra of HCl(g) and to establish a more reliable “experimental” shielding scale for chlorine. In addition, we have obtained accurate values of the ^{37}Cl NMR chemical shift for Cl_2(l). Previous measurements have reported errors of ±75 ppm.[15] The experimental investigations are supplemented by ab initio calculations of chlorine nuclear shielding tensors in these and other small chlorine-containing molecules. For the chloride ion in water, the ab initio methods are combined with molecular dynamics simulations to obtain a theoretical prediction of the chlorine chemical shielding constant. Molecular dynamics simulations in combination with NMR chemical shielding or relaxation studies have been shown to be valuable in previous studies.[16] The dependence of nuclear shielding on the computational method and basis set is examined. In addition, a compilation of chlorine chemical shielding data available in the literature is provided as a challenge for future computational investigations. As a further effort to determine the best basis set and ab initio method required to reproduce experimental results, the chlorine electric field gradient (EFG) tensor is calculated and used to determine the quadrupolar coupling constant, C_Q, for comparison with experimental results from published high-resolution microwave spectroscopy studies.

Theoretical Background

In general, nuclear magnetic shielding is described by a second rank tensor. For the molecules considered in this study, linear or symmetric tops, there are two unique principal components for the shielding tensor. The shielding when the C_∞ or C_3 axis of the molecule is along the direction of the applied magnetic field, B_0, is denoted by $\sigma_{\|}$, while $\sigma_\perp$ is the shielding when this symmetry axis is perpendicular to B_0. The isotropic nuclear magnetic shielding is given by $\sigma_{iso} = (\sigma_{\|} + 2\sigma_\perp)/3$ and the span or anisotropy by $\Omega = \sigma_{\|} - \sigma_\perp$.[17] Each of the unique components may be described by a diamagnetic and paramagnetic part according to the well-known theory of Ramsey:[18]

$$\sigma_i = \sigma_i^{p} + \sigma_i^{d} \tag{1}$$

where i denotes a particular component of the nuclear shielding tensor. For a linear molecule, it has been demonstrated by Ramsey[18,19] and Flygare[20,21] that $\sigma_\perp^{p}$ is intimately related to the spin−rotation constant, $C_\perp$. For a linear molecule, $\sigma_{\|}^{p}$ is zero. At the equilibrium bond length for a diatomic molecule,

$$\sigma_\perp^{p}(\mathrm{eq}) = \frac{-m_p C_\perp(\mathrm{eq})}{2mg_N B_e} - \frac{\mu_0}{4\pi}\frac{e^2}{2m}\left(\frac{Z}{r_e}\right) \tag{2}$$

where m_p and m are the proton and electron masses, g_N is the nuclear g factor (0.547 916 2 for ^{35}Cl)[1] and $B_e = h/(8\pi^2 I_e)$ where I_e is the moment of inertia at the equilibrium bond length, r_e. The atomic number of the other atom in the diatomic molecule is Z. Typically, $C_\perp$ is reported for a particular vibrational and rotational state; hence, it is necessary to correct it to the equilibrium value:[22]

$$C_\perp(\mathrm{eq}) = C_\perp(v,J) - \left(v + \frac{1}{2}\right)\frac{B_e}{\omega_e}\left[\left(\frac{\partial^2 C_\perp}{\partial \xi^2}\right)_{\xi=0} - 3a\left(\frac{\partial C_\perp}{\partial \xi}\right)_{\xi=0}\right] - 4(J^2 + J)\left(\frac{B_e}{\omega_e}\right)^2\left(\frac{\delta C_\perp}{\partial \xi}\right)_{\xi=0} \tag{3}$$

where ω_e is the harmonic vibrational frequency and $\xi = (r - r_e)/r_e$. The cubic force constant, a, is defined as $-[1 + \alpha_e\omega_e/(6B_e^2)]$. The first and second derivatives of $C_\perp$ with respect to ξ can be estimated from ab initio calculations. The diamagnetic component of $\sigma_\perp$, $\sigma_\perp^{d}$(eq), can be obtained accurately from ab initio calculations using r_e, since it is a first-order property, and similarly for $\sigma_{\|}$(eq). Combined with $\sigma_\perp^{p}$(eq) from eq 2, one obtains σ_{iso}(eq). However, to compare the nuclear shielding obtained from $C_\perp$ with the chemical shift obtained at 298 K, one has to perform rovibrational corrections to σ_{iso}(eq):[22]

$$\sigma_{iso}(T) = \sigma_{iso}(\mathrm{eq}) + \frac{B_e}{\omega_e}\left[\left(\frac{\partial^2 \sigma_{iso}}{\partial \xi^2}\right)_{\xi=0} - 3a\left(\frac{\partial \sigma_{iso}}{\partial \xi}\right)_{\xi=0}\right] \times \left[\frac{1}{2} + \frac{\exp[-hc\omega_e/(kT)]}{1 - \exp[-hc\omega_e/(kT)]}\right] + \frac{4kT}{hcB_e}\left(\frac{B_e}{\omega_e}\right)^2\left(\frac{\partial \sigma_{iso}}{\partial \xi}\right)_{\xi=0} \tag{4}$$

The first and second shielding derivatives are estimated from ab initio calculations. Figure 2 summarizes this process for determining $\sigma_{iso}(T)$ from $C_\perp(v,J)$.

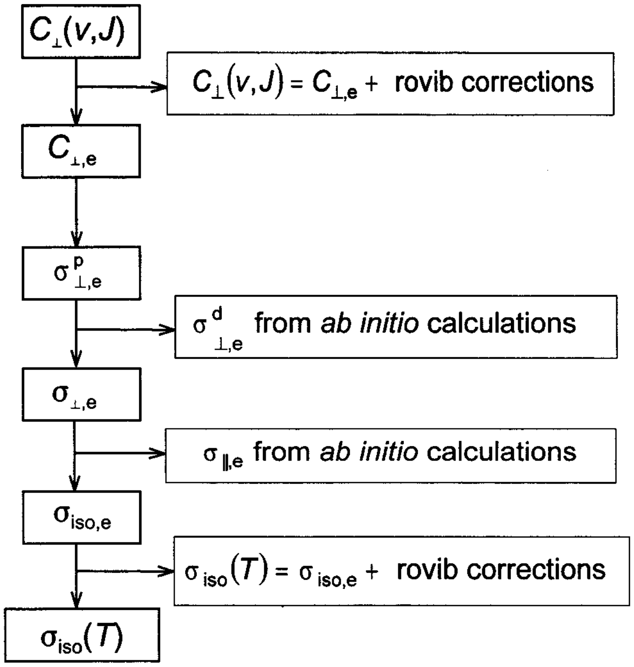

Figure 2. Flowchart showing how $\sigma_{iso}(T)$ is obtained from $C_\perp(v,J)$.

Experimental Section

Sample Preparation. HCl, Cl_2, and CH_3Cl were purchased from Aldrich Chemical Co., Inc. and used without further purification. A sample of HCl(g) was sealed in a thick-walled 7 mm glass tube. Samples of CH_3Cl(l), Cl_2(l), and HCl in chloropentanes were sealed in thick-walled 10 mm glass tubes.

TABLE 1: Geometries Used for Ab Initio Nuclear Shielding and Electric Field Gradient Calculations of Some Chlorine-Containing Linear Molecules

molecule	r_e/Å	notes/ref
HCl	1.274 565 98	23
Cl_2	1.988 5	24
ClF	1.628 332 3	25
HCCCl	1.055 0 (CH)	26 (for $v = 0$)
	1.203 6 (CC)	
	1.636 8 (CCl)	
	1.060 5 (CH)	calculated equilibrium
	1.203 0 (CC)	geometry (ref 27)
	1.635 3 (CCl)	
AlCl	2.130 143 506	28
LiCl	2.020 671	29
KCl	2.666 65	30, 31
NaCl	2.360 79	30, 31
ClCN	1.160 6 (CN)	32
	1.629 0 (CCl)	

TABLE 2: Geometries for Ab Initio Calculations on CH_3Cl

parameter	microwave (1952)[a]	equilibrium (1970)[b]	IR (1973)[c]	optimized (MP2/6-311++G**)
r(CH)/Å	1.113	1.086	1.09	1.0882
r(CCl)/Å	1.781	1.778	1.7854	1.7756
$\angle$(HCH)/deg	110.1	110.66	110.75	109.97
$\angle$(ClCH)/deg	108.1	108.25	108.16	108.97

[a] Reference 33. [b] Reference 34. [c] For the ground vibrational state (ref 35).

For referencing purposes, seven aqueous solutions of NaCl were prepared with concentrations ranging from 0.061 to 6.11 M.

$^{35/37}$Cl NMR. All $^{35/37}$Cl NMR spectra were obtained on a Bruker AMX 400 NMR spectrometer (B_0 = 9.4 T) using a Bruker high-resolution 10 mm multinuclear probe. At this field, the ^{35}Cl NMR frequency is 39.205 MHz and that of ^{37}Cl is 32.634 MHz. Typical pulse widths used were 20 μs with 10 ms recycle delays. For the HCl(g) sample, 600 000 transients were acquired for the ^{37}Cl NMR spectrum. Between 7000 and 20 000 transients were obtained for the remaining samples for both isotopes. To determine the chlorine chemical shift as accurately as possible, all $^{35/37}$Cl NMR spectra were fit using mixed Gaussian−Lorentzian functions.

Computation Details. *Calculation of Chlorine Shielding Tensors*. The geometries used for ab initio calculations on chlorine-containing molecules are summarized in Tables 1 and 2. Ab initio nuclear shielding calculations were performed on an IBM RS/6000 computer using the Gaussian 94[36] and Gaussian 98[37] program suites and DALTON,[38] as well as with Gaussian 98[39] on a 400 MHz Pentium II, with Linux as the operating system. Restricted Hartree−Fock (RHF), second-order Møller−Plesset perturbation (MP2), and density functional theory (DFT) calculations of nuclear shielding tensors were performed using gauge-independent atomic orbitals (GIAO).[40] For the DFT calculations, the Becke three-parameter hybrid method[41] with the correlational functional of Lee, Yang, and Parr[42] (B3LYP) was used. The basis sets chosen for this study are all available in the Gaussian 94/98 program package. The smallest in all cases was the 6-311G** basis set, while the largest basis sets consisted of the 6-311++G(3df,3pd) basis set and the Dunning's correlation consistent quintuple-ζ cc-pV5Z basis set.[43] For CH_3Cl, the experimental geometry[35] used was not for the equilibrium geometry. To better approximate the equilibrium geometry, an optimization at the MP2/6-311++G** level of theory was performed.

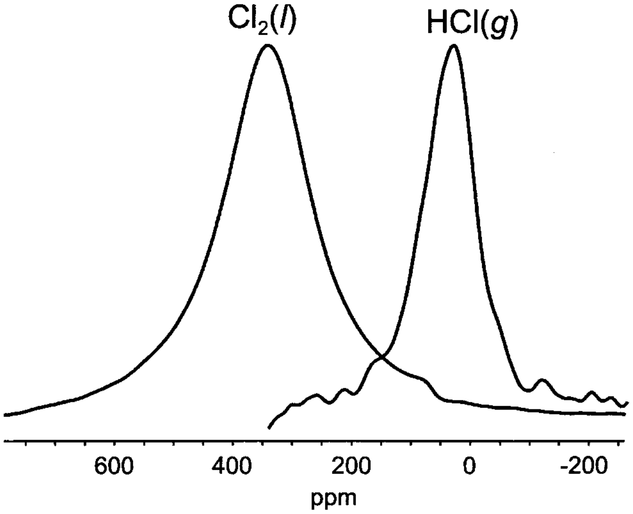

Figure 3. ^{37}Cl NMR spectra of HCl(g) (600 000 transients) and Cl_2(l) (18 000 transients) acquired at 9.4 T. In both cases, a recycle delay of 10 ms was used.

TABLE 3: Experimental $^{35/37}$Cl Chemical Shifts for the Compounds in This Study

sample	nucleus	δ_{iso}/ppm	line width/kHz
HCl(g)	^{35}Cl	28 ± 3	3.8 ± 0.1
	^{37}Cl	28 ± 3	2.6 ± 0.1
HCl in chloropentanes (l)	^{37}Cl	73.4 ± 0.4	1.10 ± 0.03
Cl_2(l)	^{37}Cl	342 ± 2	4.90 ± 0.05
CH_3Cl(l)	^{35}Cl	50 ± 1	3.08 ± 0.07

Hydrated Chloride Ion. The magnetic shielding constants for hydrated chloride ions in aqeuous solution were calculated from the randomly chosen Cl−$(H_2O)_n$ configurations present in an MD simulation of a dilute 0.55 M NaCl solution.[44] The number of water molecules, n, varied from 6 to 10. The hydration shell is extended to the first minimum in the radial distribution function (RDF) for the water oxygen atoms about the chloride ions. The average coordination number from the simulation is 6.9. By use of the HF method with the cc-pV5Z basis set, the calculations took between 7 and 24 days of CPU time, depending on the cluster size.

Calculation of EFG Tensors. Chlorine EFG tensors were calculated at the HF level of theory using the 6-311++G-(3df,3pd) basis set. The principal components of the EFG tensors were converted from atomic units to V m^{-2} using the conversion factor 9.7177 × 10^{21} V m^{-2}/au.[1]

Results and Discussion

$^{35/37}$Cl NMR Spectra. The ^{37}Cl NMR spectra of HCl(g) and Cl_2(l) are shown in Figure 3. All the experimental chemical shifts and line widths for the compounds studied in this work are given in Table 3. Methyl chloride has been investigated a number of times; our results are in agreement with the most recent work.[5] For the HCl(g) sample, pressures in excess of 10 atm were required to overcome the problem of extremely short spin−lattice relaxation times, T_1.[13] To verify the pressure of our sample, the pressure was also determined from the line width of the ^{35}Cl NMR spectrum, making use of the relationship between T_1 and the gas density for HCl.[13] From the van der Waals equation with a = 3.67 and b = 0.408,[45] the pressure of the HCl(g) sample was determined to be 16.6 atm.

The chlorine chemical shift for Cl_2(l) has been reported; at 298 K, δ = 370 ± 75 ppm with a line width of 6.0 ± 0.5 kHz obtained at $\nu_0(^{35}Cl)$ = 5.344 MHz.[15] Our results are more precise; δ = 342 ± 2 ppm and a linewidth of 4.90 ± 0.05 kHz from the ^{37}Cl NMR spectrum. Our attempts to observe the $^{35/37}$Cl NMR spectrum of Cl_2 in the gas phase were unsuccessful. From

TABLE 4: Parameters Used to Determine $\sigma_{iso}(T)$ from $C_\perp(v, J)$ for H^{35}Cl

parameter	value	notes/ref
$C_\perp(v = 0, J = 1)$	53.849 (53) kHz	ref 23
B_e	317.575 611 GHz	calculated from r_e (see Table 1)
ω_e	89 631.6 GHz	ref 25
α_e	9.209 18 GHz	ref 31
a	−2.364 07	calculated from B_e, ω_e, and α_e
$g(^{35}Cl)$	0.547 916 2	ref 1
$(\partial C_\perp/\partial\xi)_{\xi=0}$	129.362 kHz	ab initio calculations of $C_\perp$ for r_e and $r_e \pm 0.01$ Å, at the RHF/6-311G** level
$(\partial^2 C_\perp/\partial\xi^2)_{\xi=0}$	134.835 kHz	from the same data as above
$C_\perp$(eq)	51.972 (53) kHz	from eq 3
$\sigma_\perp^p$(eq)	−285.27 (28) ppm	from eq 2
$\sigma_\perp^d$(eq)	1154.28 ppm	ab initio calculation at RHF/cc-pVQZ level
$\sigma_{\parallel}$(eq)	1148.78 ppm	from the same data as above
σ_{iso}(eq)	962.3 ± 0.9 ppm	
σ_{iso}(298 K)	946.4 ± 0.9 ppm	from eq 4

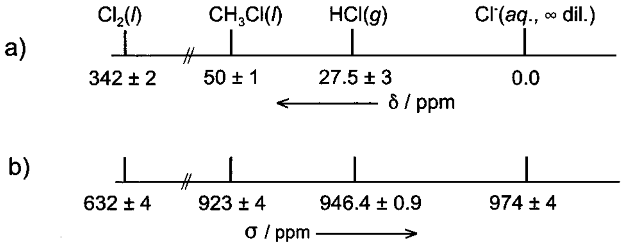

Figure 4. Absolute shielding scale for chlorine based on HCl(g): (a) chlorine chemical shifts (this work); (b) absolute shielding scale for chlorine based on σ_{iso}(298 K) for HCl, calculated from the spin−rotation constant.

the line width, one can determine the correlation time, τ_c, assuming that relaxation is dominated by the quadrupolar relaxation mechanism. Under extreme narrowing conditions and using a quadrupolar coupling constant, C_Q, of 85.890 MHz for ^{37}Cl in Cl_2(l),[46] we obtain $\tau_c = 0.53$ ps. Molecular reorientation of Cl_2 in the neat liquid as a function of temperature has been studied previously.[47]

Absolute Shielding Scale for Chlorine. For HCl(g) at 16.6 atm, the ^{35}Cl and ^{37}Cl isotropic chemical shifts are the same within experimental error, $\delta_{iso} = 28.5 \pm 3.0$ ppm, referenced to the chloride ion in infinitely dilute NaCl(aq). The chlorine chemical shift for the reference at infinite dilution was determined by measuring the ^{35}Cl chemical shift for a series of NaCl aqueous solutions, with concentrations ranging from 0.061 to 6.11 M. By extrapolation, the chlorine chemical shift for the infinitely dilute solutions is −0.51 ppm with respect to 1.2 M NaCl(aq), which was used to reference all the experimental data. In total, a range of 0.81 ppm over these concentrations is observed for Cl^-(aq), in excellent agreement with the results from a previous study.[48] It should be noted that if D_2O is used as a solvent, there is a significant isotope shift of about −5 ppm for Cl^-(aq).[49]

The absolute shielding of chlorine in HCl(g) is obtained using eq 2 from the ^{35}Cl spin−rotation constant for the $v = 0$, $J = 1$ state, $C_\perp = 53.849$ (53) kHz,[23] which is one of the most precisely measured spin−rotation constants for chlorine. In an earlier study,[50] $C_\perp = 53.851$ (42) kHz, which is within the experimental error of the more recent value. All data used to obtain the absolute shielding of chlorine in HCl are given in Table 4. From an ab initio calculation (HF/cc-pVQZ) of chlorine nuclear shielding tensors in HCl, we obtain $\sigma_\perp^d(\text{eq}) = 1154.27$ ppm and $\sigma_\parallel(\text{eq}) = 1148.78$ ppm. At the equilibrium bond length, the absolute shielding of chlorine in HCl(g) is 962.3 ± 0.9 ppm. Applying a vibrational correction of −15.9 ppm (according to eq 4), σ_{iso}(298 K) for chlorine is 946.4 ± 0.9 ppm, where the experimental error is due to the error in $C_\perp$. From our chemical shift data for HCl(g) relative to infinitely dilute NaCl in water, the absolute shielding of chlorine in the reference is

$$\begin{aligned} &\sigma[\text{HCl(g) from } C_\perp] + \delta[\text{HCl(g) relative to NaCl(aq)}] = \\ &946.4 \pm 0.9 \text{ ppm} + 28.5 \pm 3 \text{ ppm} = \\ &\sigma[\text{NaCl(aq)}] \\ &975 \pm 4 \text{ ppm} \end{aligned} \tag{5}$$

Since the HCl(g) sample is of fairly high pressure, the pressure dependence of the chemical shift must be considered. Ideally, one requires experimental data over a range of pressures in order to extrapolate the chemical shift to zero pressure. For HCl(g), the experimental determination of the pressure correction is difficult; experiments at low pressure are hampered by increasing line widths and small sample size, while high-pressure samples represent a serious safety problem. To estimate the pressure correction, the ^{1}H chemical shift data for HCl(g)[51] may be used. The reported ^{1}H chemical shift varies linearly with density, 4.21 ppm g^{-1} cm^3; i.e., shielding increases as density decreases. The ^{1}H chemical shift on going from a density of 0.0266 g cm^{-3} (the density of our sample) to zero pressure is 0.112 ppm. If one assumes the chlorine shielding to be more sensitive to gas density by a factor dependent on their relative shielding derivatives,[52] $-878/-41.6 \approx 21.1$, then our correction is 2.4 ppm. Another estimate of this correction is available from the gas-to-liquid shift. For ^{1}H in HCl, the gas-to-neat liquid shift is 2.05 ppm;[53] for ^{37}Cl the gas-to-liquid (in chloropentanes) shift is 45 ppm, again yielding a correction of 2.4 ppm. A third method for estimating the zero-pressure limit is by ab initio calculations on the HCl dimer. By use of the equilibrium geometry obtained from ab initio methods[54] and by comparison of the change in the chlorine and hydrogen isotropic chemical nuclear shielding for the monomer vs the dimer, a smaller correction for the chlorine shielding, about 0.8 ppm, was obtained. On the basis of these three estimates, it is reasonable to assume that the chlorine nucleus is on the order of 1 ppm more shielded at zero density compared to the density of our sample. This correction is less than the experimental error on the chlorine chemical shift of HCl(g). Applying a correction to δ [HCl(g)], we obtain

$$\sigma[\text{NaCl(aq, } \infty \text{ dil.)}] = 974 \pm 4 \text{ ppm} \tag{6}$$

The chlorine absolute shielding scale based on HCl(g) is illustrated in Figure 4.

From our ab initio/molecular dynamics calculations on the hydrated chloride ion, the average isotropic shielding of the chloride ion in water is 993 ± 14 ppm (HF/cc-pV5Z) with an anisotropy of 33.6 ± 10 ppm. By comparison of the ab initio and experimental results, it is evident that the calculated values are about 19 ppm too shielded; however, given the deviations in shielding calculated for various chloride ion geometries (±14 ppm), this agreement is very good. In addition, geometries with a finite number of H_2O molecules about the chloride ion were used in the ab initio calculations. It is important to recognize that the calculated chemical shift on going from Cl^- (free atom) to Cl^- (H_2O) is significant, 156 ppm (1149 ppm[55] − 993 ppm). Although one might naively think the Cl^- ion in aqueous solution is spherically symmetric, this is clearly not the case. This is reflected in the calculated shielding anisotropy.

Our absolute shielding scale, based on HCl(g), can be compared to the scales reported by Lee and Cornwell,[13] also

TABLE 5: Chlorine Chemical Shielding Tensors for HCl Obtained from Ab Initio Calculations Compared to Experimental Results

method/basis set	σ_{iso}/ppm	Ω/ppm[a]	$\sigma_{\perp}$/ppm	$\sigma_{\parallel}$/ppm
spin−rotation results (exptl, at r_e)	962.3 ± 0.9	279.8	869.0 ± 0.8	1148.8[b]
Flygare (exptl)[c]	951	292	854	1146
Fukui, nonrelativistic[d]	945.6	305.2	843.9	1149.1
Fukui, relativistic[d]	964.4	319.2	858	1177.2
HF/6-311G**	967	273	876	1149
HF/6-311++G**	969	270	879	1149
HF/6-311++G(3df,2p)	959	285	864	1149
HF/6-311G(3df,3pd)	958	286	863	1149
HF/6-311++G(3df,3pd)	958	287	862	1149
HF/cc-pVQZ[e]	963	279	870	1149
HF/cc-pV5Z[f]	951	297	852	1149
MP2/6-311G**	979	254	894	1149
MP2/6-311++G(3df,2p)	980	252	897	1148
MP2/6-311G(3df,3pd)	978	254	894	1148
MP2/6-311++G(3df,3pd)	978	255	893	1148
B3LYP/6-311G**	946	304	844	1148
B3LYP/6-311G(3df,3pd)	942	310	839	1148
B3LYP/6-311++G(3df,3pd)	941	312	837	1148
B3LYP/cc-pV5Z	937	318	831	1149

[a] $\Omega = \sigma_{\parallel} - \sigma_{\perp}$. [b] $\sigma_{\parallel}$ is calculated at the HF/cc-pVQZ level. [c] Reference 57. [d] Reference 10, using a bond length of 1.274 Å with the gauge origin on Cl. The basis set is (15s2p6d/7s2p). Calculations were performed at the HF level, with a Schrödinger−Pauli type two-component perturbation theory treatment of the relativistic effects. [e] Dunning's correlation consistent basis set, which contains 6s,5p,3d,2f,1g on chlorine. [f] Contains 7s,6p,4d,3f,2g,1h on chlorine.

based on HCl(g), and Dubrulle et al.,[14] based on CH_3Cl(l). Lee and Cornwell report an absolute shielding for their reference, 6.3 M HCl, of 973 ± 8 ppm based on their measurement of the chlorine chemical shift of HCl(g) and a chlorine shielding of 953 ppm from $C_{\perp}$. An error of 5 ppm is estimated to account for the neglect of rovibrational corrections. The chlorine chemical shift of 6.3 M HCl is 6.53 ppm less shielded than the chloride ion at infinite dilution in water;[56] hence, the absolute shielding of chlorine in the reference is 979.5 ± 8 ppm on their scale, which is in excellent but most likely fortuitous agreement with our result of 974 ± 4 ppm.

For CH_3Cl, σ_{iso} is 890.5 ppm with an error of ±170 ppm based on the experimental error in the spin−rotation data.[14] By use of $\delta(^{35}Cl) = 50.5 \pm 1$ ppm from our data for CH_3Cl(l), the absolute shielding of the reference is 940.0 ± 170 ppm. Obviously, the large experimental error (about 11% of the total shift range) renders this scale impractical. On our chlorine absolute shielding scale, $\sigma_{iso} = 923 \pm 4$ ppm for CH_3Cl(l).

Chlorine Chemical Shielding for Small Molecules. Ab Initio Calculations. The chlorine chemical shielding data from the literature and from this work are presented in Tables 5−7 for HCl, Cl_2, and CH_3Cl. Since ab initio calculations are performed at the equilibrium geometry, it is necessary to compare the results to the experimentally determined σ_{iso}(eq) rather than to σ_{iso}(298 K).

A study of the basis set dependence of the chlorine nuclear shielding for HCl (Table 5) indicates that for the RHF, MP2, and DFT methods, the 6-311++G(3df,3pd) basis set is nearing the basis set limit. Comparison of the nuclear shielding (for the equilibrium bond length) obtained from the various ab initio methods with this basis set reveals that the chlorine shielding from RHF theory is closest to the experimental values, with the isotropic value being 4.3 ppm less shielded, while MP2 theory predicts a value that is too shielded by about 16 ppm. From DFT, σ_{iso} is calculated to be deshielded by 21 ppm. In all cases, however, relativistic effects have not been considered. The relativistic corrections reported by Fukui et al.[10] do, however, result in an isotropic chemical shielding that is in excellent agreement with the experimental results. The relativistic corrections are significant for both $\sigma_{\perp}$ and $\sigma_{\parallel}$. For $\sigma_{\perp}$, the difference between the relativistic and nonrelativistic values is 14.1 ppm while for $\sigma_{\parallel}$, the difference is 28.1 ppm. In both cases, the calculated nuclear shielding is increased by including the relativistic effects. This agreement between our experimental results and the calculated results of Fukui et al. is fortuitous, since relativistic effects were not considered in deriving our chlorine absolute shielding scale. The relativistic correction to our scale is estimated to be +25 ppm, based on the difference between the free atom shielding of Cl^- calculated using relativistic and nonrelativistic methods.[58]

TABLE 6: Chlorine Chemical Shielding Tensors for Cl_2 Obtained from Ab Initio Calculations Compared to Experimental Results

method/basis set	σ_{iso}/ppm	Ω/ppm	$\sigma_{\perp}$/ppm	$\sigma_{\parallel}$/ppm
exptl results for neat liquid (298 K, this work)	632 ± 4			
exptl results (at r_e, this work)	639 ± 4			
HF/6-311G**	729	640	516	1156
HF/6-311G(3df,3pd)	716	659	497	1156
HF/6-311++G(3df,3pd)	712	666	490	1156
HF/cc-pV5Z	698	687	468	1156
MP2/6-311G**	714	663	493	1156
MP2/6-311G(3df,3pd)	715	661	494	1155
MP2/6-311++G(3df,3pd)	707	671	484	1155
B3LYP/6-311G**	607	823	333	1156
B3LYP/6-311G(3df,3pd)	616	808	347	1155
B3LYP/6-311++G(3df,3pd)	609	819	336	1155
B3LYP/cc-pV5Z	600	834	322	1156

For Cl_2 (Table 6), the experimental value is obtained from our measurements of the chlorine chemical shift and our absolute shielding scale. Unfortunately, there are no spin−rotation data available for Cl_2 in the literature. As well, the experimental data given in Table 6 are for Cl_2(l) rather than for Cl_2(g). By use of eq 4 and ab initio calculations of the shielding derivatives, a rovibrational correction of +7 ppm is applied to the experimental results in order to obtain σ_{iso}(eq) for comparison with the calculated results. Ab initio calculations of the chlorine nuclear magnetic shielding tensor for Cl_2 indicate that, contrary to the HCl results, the 6-311++G(3df,3pd) basis set is not near the basis set limit. In addition, the nuclear magnetic shielding calculated at the MP2 level is less shielded than the results

TABLE 7: Chlorine Chemical Shielding Tensors for CH_3Cl Obtained from Ab Initio Calculations Compared to Experimental Results

geometry/method/ basis set	σ_{iso}/ppm	Ω/ppm	$\sigma_\perp$/ppm	$\sigma_\parallel$/ppm
exptl (298 K, this work)	923 ± 4			
exptl[a]	890 ± 172	277 ± 203	798 ± 18	1075 ± 202
Fedotov et al.[b]	926			
Buckingham et al.[c]	965			
exp/HF/6-311++G**[d]	995	176	936	1112
opt/HF/6-311++G**[e]	996	175	938	1113
opt/HF/6-311G(3df,3pd)	975	197	909	1106
opt/HF/6-311++G(3df,3pd)	979	198	913	1111
opt/HF/cc-pV5Z	977	204	909	1113
opt/MP2/6-311G**	978	197	912	1109
opt/B3LYP/6-311G**	931	247	849	1096
opt/B3LYP/6-311G(3df,3pd)	910	273	819	1092
opt/B3LYP/6-311++G(3df,3pd)	913	277	821	1098
opt/B3LYP/cc-pV5Z	916	277	824	1101

[a] From ref 14. [b] Calculated using the sum-over-states density functional perturbation theory (SOS-DFT). Data from ref 5. [c] From ref 9. [d] exp = the ground-state geometry reported in ref 35. [e] opt = the MP2/6-311++G** optimized geometry.

TABLE 8: Chlorine Spin−Rotation Constants for Some Chlorine-Containing Linear Molecules

molecule	$C_\perp$/kHz	ref
^{35}ClF	21.616 (2)	8
H^{35}Cl	53.849 (53)	23
H^{37}Cl	44.738 (15)	23
HCC^{35}Cl	1.412 (4)	61
HCC^{37}Cl	1.142 (6)	61
K^{35}Cl	0.435 (3)	62
^{7}Li^{35}Cl	1.942 (20)	63
^{205}Tl^{35}Cl	1.37 (5)	64
^{205}Tl^{37}Cl	1.08 (14)	64
^{203}Tl^{35}Cl	1.4 (4)	64
^{35}Cl^{11}BO	0.55 (20)	65, 66

TABLE 9: Chlorine Chemical Shielding Tensors for Chlorine-Containing Linear Molecules Obtained from Ab Initio Calculations Compared to Experimental Results

compound		exptl/ppm	calcd (HF/6-311++G**)/ppm
ClF	σ_{iso}[a]	−413	−344
	$\sigma_\perp$[b]	−1196	−1092
	Ω	2350	2246
AlCl	σ_{iso}	607	649
	$\sigma_\perp$	334	398
	Ω	809	754
LiCl	σ_{iso}	1038	1051
	$\sigma_\perp$	983	1001
	Ω	160	148
NaCl	σ_{iso}	1146	1141
	$\sigma_\perp$	1143	1136
	Ω	8	15
KCl	σ_{iso}	1020	1130
	$\sigma_\perp$	954	1119
	Ω	189	34
HCCCl	σ_{iso}	988	928
	$\sigma_\perp$	904	816
	Ω	251	339

[a] σ_{iso} is determined using $\sigma_\parallel$ from ab initio calculations (HF/6-311++G**). [b] $\sigma_\perp$ is calculated from $C_\perp$ using the approximation $\sigma_\perp \approx -m_pC_\perp/(2mg_NB_e) + \sigma^d$ (free atom) (see refs 18, 20, 21).

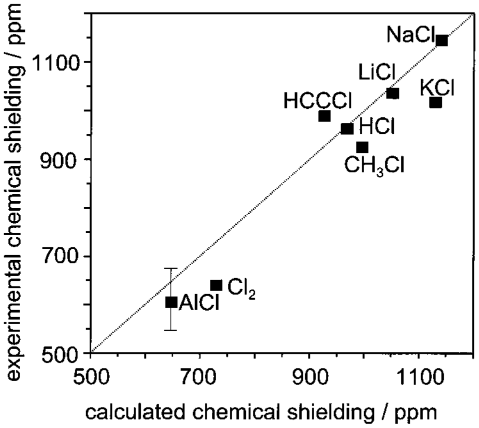

Figure 5. Comparison of the calculated chlorine chemical shielding vs the experimental results for some chlorine-containing molecules. The dotted line, with a slope of 1, represents perfect agreement between the experimental and calculated results.

obtained from HF theory, while the results from DFT are less shielded than the values from MP2.

The calculated chlorine nuclear magnetic shielding tensors for CH_3Cl are summarized in Table 7. The experimental data from this work are for liquid CH_3Cl, while the calculated data are for the isolated molecule; hence, intermolecular contributions to the chlorine chemical shielding are not considered. In addition, rovibrational corrections have not been applied to the experimental results, since eq 4 is not valid for symmetric tops. A calculation at the HF level using the 6-311++G** basis set on the optimized structure gives results that are similar to those calculated using the experimental geometry.[35] At the MP2 level, we are restricted to a relatively small basis set as a result of computer hardware limitations. In this work, the best prediction of the chlorine isotropic chemical shielding for CH_3Cl is obtained from the DFT method. Fedotov et al.,[5] using the sum-over-states density functional perturbation theory (SOS-DFT)[59,60] and the individual gauge for localized orbitals (IGLO) method, report $\sigma_{iso} = 926$ ppm, which is in excellent agreement with our experimental data.

Spin−rotation constants are available for a number of chlorine-containing small molecules. Data with relatively small experimental errors are listed in Table 8. Unfortunately, performing NMR experiments on most of these samples in the gas phase is not practical; hence, we cannot measure their chemical shifts relative to Cl^-(aq). The results of ab initio calculations of the chlorine nuclear shielding tensors for some of these molecules are given in Table 9. The agreement between the experimental and calculated data is quite reasonable at the HF level of theory using the 6-311++G** basis set; however, at the extremely deshielded end of the chlorine scale, represented by ClF, the ab initio methods perform rather poorly. Figure 5 illustrates the agreement between the experimental and calculated results. In many cases, for example, chloroacetylene, the experimental geometry available in the literature is for the ground vibrational state rather than for the equilibrium geometry.

TABLE 10: Experimental and Calculated ^{35}Cl C_Qs for Some Chlorine-Containing Linear Molecules

	C_Q (MHz)		
molecule	exptl	calcd[a]	ref for exptl data
HCl	−67.618 95 (39)	−63.144	23
Cl_2	−108.975 (1)	−108.949 8	46
CH_3Cl	−74.749 6 (13)	−68.034 2	14
HCCCl	−79.733 59 (4)	−78.345 8	61
ClF	−145.871 82 (3)	−144.305 7	8, 69
^{7}LiCl	−3.509 51 (15)	−1.502 4	63
AlCl	−8.829 0 (35)	−8.621 3	70
$ClC^{14}N$	−83.26 (2)	−82.430 4	71

[a] Calculated at the HF level with the 6-311++G(3df,3pd) basis set and $Q = -8.11 \times 10^{-30}$ m^2.

Ab Initio Calculation of Chlorine EFG Tensors. The quadrupolar coupling constant is related to the largest component of the EFG tensor, V_{33}:

$$C_Q = \frac{eQV_{33}}{h} \quad (7)$$

where Q is the nuclear quadrupole moment. Quadrupolar coupling constants are available for many small molecules from high-resolution microwave spectroscopy.[67] The EFG tensor is, in principle, easier to calculate than nuclear shielding using ab initio methods, since it is a first-order property; however, accurate calculations require basis sets of high quality close to the nucleus of interest. The calculation of EFG tensors combined with C_Q values obtained from high-resolution microwave spectroscopy has recently been used to obtain an accurate value of the nuclear quadrupole moment for ^{27}Al.[68]

Table 10 summarizes experimental and calculated chlorine C_Q for some chlorine-containing molecules. All calculations were carried out for the equilibrium structure. At this level of theory (HF with the 6-311++G(3df,3pd) basis set), the calculated C_Q values are in excellent agreement with the experimental results for all the molecules with the exception of CH_3Cl. The discrepancy between the experimental and calculated C_Q may be due to the uncertainty in the structure of CH_3Cl used for the ab initio calculations. Most of the published experimental data are not for the equilibrium geometry; however, the rovibrational corrections are expected to be 1 MHz or less.[68,72] For example, the rovibrational correction to $C_Q(v=0,J=1)$ for HCl is +0.92 MHz, determined using an equation analogous to eq 3. However, for the alkali metal chlorides where the EFG is small, rovibrational effects are significant.[73]

Conclusions

The accurate measurement of the chlorine chemical shift for HCl(g) combined with ab initio methods for the calculation of diamagnetic shielding components has led to a chlorine absolute shielding scale that is more reliable than those proposed previously.[13,14] Using this scale as well as spin−rotation constants available in the literature, we have obtained several experimental chlorine nuclear magnetic shielding constants for comparison with ab initio results obtained from the HF and MP2 levels of theory as well as DFT. For HCl, the best prediction of the experimental results is obtained from the HF method, while DFT seems to perform best for Cl_2 and CH_3Cl. In all cases, it is apparent that relatively large basis sets are required to reach the basis set limit, as is to be expected. As a further test of theoretical methods, we have calculated chlorine C_Qs for some chlorine-containing molecules that are in good agreement with experimental values. We hope that this study will encourage others to compare their calculations with chemical shielding tensors available from spin−rotation data and high-resolution microwave spectroscopy. Such data are ideal for testing theoretical approaches because they are obtained for isolated molecules.

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