Ab initio Study of the Electric Field Gradients in SCl_2

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The electric field gradients (EFG) in SCl_2 have been computed with both self-consistent-field (SCF) and configuration-interaction (CI) methods. The predicted EFG, along with the nuclear quadrupole moment Q_N of ^{35}Cl and ^{37}Cl from other sources, allows us to compare theoretical quadrupole coupling constants with new experimental results. The best values obtained agree with the experiment within 3%. It has been found that the principal axis of the coupling tensor does not coincide with the S–Cl internuclear axis, and the tilt angle has been predicted close to that from experiment.

Key words: Electric field gradient; Nuclear quadrupole coupling constant; SCl_2; ab initio method; Bent chemical bond.

1. Introduction

The nuclear quadrupole coupling constants (NQCC) are useful parameters to calibrate the electronic structure of atoms and molecules. With the advent of Fourier transform microwave spectroscopy [1], these quantities can be determined more accurately, and in some cases information relating to the off-diagonal coupling constants can be obtained. Recently, Merke and Dreizler [2] used waveguide microwave Fourier transform spectroscopy to reinvestigate the quadrupole hyperfine structure of sulfur dichloride. Because of the high resolution of the spectroscopy, the coupling constants obtained are more reliable compared with previous studies [3–5]. Due to some measured transitions with near degeneracy, Merke and Dreizler also obtained a much more accurate off-diagonal coupling constant. The constant they found greatly improved the one reported earlier by Murray et al. [4] who determined the off-diagonal coupling element through analysis with second-order perturbation theory and the assumption of the S–Cl internuclear axis as a principal axis. The knowledge of measured diagonal and off-diagonal coupling constants makes it possible to determine the principal axis system within the molecular geometry frame. They have found that the NQCC prinicpal axis does not coincide with the S–Cl internuclear axis as widely believed before. A tilt angle of about 1.3° is formed between the two. Based on this, Merke and Dreizler concluded that this may provide experimental information on the possibility of bent bonds in SCl_2.

The nuclear quadrupole coupling constant is directly related to the EFG at a nucleus in the system. Given the knowledge of NQCC and the nuclear quadrupole moments from other experimental or theoretical sources, the EFG at the nuclei can be deduced. Therefore, the measurement of NQCC provides direct information on the electronic distribution in the vicinity of the nuclei and can be used in chemical analysis in a similar fashion as nuclear magnetic resonance (NMR) or electron spin resonance (ESR). It may also be useful for verifying theoretical models of eletronic description [6, 7]. On the other hand, the measured NQCC and the EFG calculated with sophisticated theoretical models may provide us with the nuclear quadrupole moments [8–12] which in some cases are quite difficult to determine experimentally. In the present report, we employ ab initio methods to investigate the EFG and NQCC in SCl_2. This work has two purposes: We would like to confirm the above experimental findings from a theoretical point of view and to find the appropriate theoretical treatment of the EFG.

2. Theoretical Model

The EFG on a nucleus N is defined as a 3×3 symmetric traceless tensor [13],

$$q_{N\alpha\beta} = \langle \Phi | \frac{\partial^2 V}{\partial\alpha\, \partial\beta} | \Phi \rangle , \tag{1}$$

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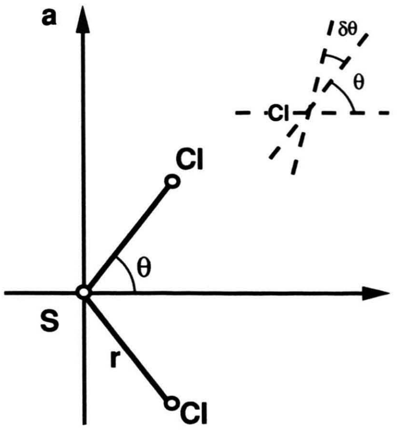

Fig. 1. The experimental geometry of SCl_2.

where $\alpha, \beta = a, b, c$ and Φ is the electronic wavefunction of the system. V is the electrostatic potential operator at the nucleus. Equation (1) may be written in two parts, the nuclear and the electronic terms [14]:

$$q_{N\alpha\beta} = \sum_{K \neq N} Z_K (3\, R_{NK\alpha}\, R_{NK\beta} - R_{NK}^2\, \delta_{\alpha\beta})\, R_{NK}^{-5} - q_{N\alpha\beta}^{\text{el}}\,, \quad (2)$$

$$\begin{aligned} q_{N\alpha\beta}^{\text{el}} &= \langle \Phi \,|\, \sum_k (3\, r_{Nk\alpha}\, r_{Nk\alpha} - r_{Nk}^2\, \delta_{\alpha\beta})\, r_{Nk}^{-5} \,|\, \Phi \rangle \\ &= \sum_{\mu, \nu} P_{\mu\nu} \langle \phi_\mu | (3\, r_{Nk\alpha}\, r_{Nk\beta} - r_{Nk}^2\, \delta_{\alpha\beta})\, r_{Nk}^{-5} \,|\, \Phi_\nu \rangle\,, \quad (3) \end{aligned}$$

where K runs through all the nuclei except the nucleus N, $R_{NK\alpha}$ is the α component of the distance vector R_{NK} between nuclei K and N, Z_K is the nuclear charge of K and $\delta_{\alpha\beta}$ is the Kronecker delta function. k runs through all the electrons in the system and $r_{Nk\alpha}$ is the α component of the distance vector r_{Nk} between electron k and the nucleus N. $P_{\mu,\nu}$ is the one-particle density matrix element expressed in the basis set $\{\phi\}$.

The quadrupole coupling constant tensor χ is simply given by

$$\chi_{N\alpha\beta} = Q_N\, q_{N\alpha\beta}\,, \quad (4)$$

where Q_N is the nuclear quadrupole moment of nucleus N. In (4) and throughout this paper q is given in atomic units and 1 a.u. = 2.3496×10^2 MHz/Barn (note that $q_{N\alpha\beta}$ sometimes is given as $e\,q_{N\alpha\beta}/h$). Q_N is given in units of Barn and χ in MHz.

From microwave spectrum experiments, the $\chi_{N\alpha\beta}$ tensors are given in the principal inertia axis system (a, b, c). When diagonalized, the χ_{Nii}, with $i = x, y, z$ defining the principal EFG axis system, may be obtained. The asymmetry parameter η is defined by

$$\eta = \frac{|\chi_{yy}| - |\chi_{xx}|}{|\chi_{zz}|}\,, \qquad |\chi_{zz}| > |\chi_{yy}| \geq |\chi_{xx}|\,. \quad (5)$$

The electronic term given in (3) has been calculated at both SCF and CI levels by employing the SCF and CI one-density matrices. The geometry used here is the experimental one, $r = 2.01525$ Å, $2\theta = 102.730°$ [5] and is displayed in Fig. 1 with $\delta\theta$ defining the angle between one of the NQCC principal axes (z) and the S–Cl internuclear axis. The cc-PTV basis set by Woon and Dunning [15] was employed. The calculations have been carried out through the Meld program [16] in the MOTECC-90 package.

3. Results and Discussion

In order to assess the basis set effects, the EFG has been calculated with successive increases in the size of the basis sets. Initially, the s and p functions given by Woon and Dunning [15] include 15s and 9p primitives contracted to 5s and 4p. Then, one or two sets of d type polarization functions have been added to the above sp basis sets. Finally, the basis set on each atom is augmented by a set of f functions. The resulting 5s 4p 2d 1f basis set consists of 117 basis functions.

The total energy, predicted EFG in both the principal inertia axis system (a, b, c) and the principal EFG axis system (x, y, z), asymmetry parameter, and dipole moment at the SCF theoretical level are listed in Table 1. The energy is given in Hartree and the dipole moment in atomic units, with 1 a.u. = 2.54177 Debye. Inclusion of polarization functions is found to be important for the energy as well as for other properties. With one set of d polarization functions, the energy decreases by an amount of 0.082964 from that with the 5s 4p basis set. With regard to the EFG, Cl goes through more changes then does the S atom. The addition of the second set of d functions seems to affect properties to a much lesser degree for Cl. However, the S atom shows a steady change. Even by including f polarization, changes in the energy as well as properties are still observed.

Palmer has reported the nuclear quadrupole couplings of ^{14}N and ^{11}B in molecules [10, 11]. Recently, he studied the NQCC of ^{33}S, another element appearing in many biological molecules. With a TZP basis set, the EFG was predicted as $q_{aa} = -3.30286$, $q_{bb} = -1.50011$ and $q_{cc} = 4.80289$, at the SCF level for

Table 1. The total energy, EFG in both the (*a*, *b*, *c*) and (*x*, *y*, *z*) systems, asymmetry parameter, and dipole moment from the SCF calculations.

Basis sets	5s 4p	5s 4p 1d	5s 4p 2d	5s 4p 2d 1f
Energy	−1316.431584	−1316.514548	−1316.546387	−1316.559286
S q_{aa}, q_{yy}	3.4263	3.4438	3.4025	3.3329
q_{bb}, q_{xx}	1.6510	1.5365	1.5086	1.4880
q_{cc}, q_{zz}	−5.0773	−4.9803	−4.9111	−4.8209
η	0.3497	0.3830	0.3856	0.3827
Cl q_{aa}	2.2935	2.1241	2.0972	2.0476
q_{bb}	0.4176	0.3756	0.3822	0.3834
q_{ab}	−3.3255	−3.0122	−2.9620	−2.9107
q_{cc}, q_{yy}	−2.7111	−2.4997	−2.4793	−2.4310
q_{xx}	−2.0997	−1.8867	−1.8439	−1.8118
q_{zz}	4.8108	4.3864	4.3233	4.2428
η	0.1271	0.1398	0.1470	0.1459
Dipole moment	0.3109	0.1909	0.1940	0.1951
$\delta\theta$	1.510	1.727	1.708	1.612

Table 2. The total energy, EFG in both the (*a*, *b*, *c*) and (*x*, *y*, *z*) systems, asymmetry parameter, and dipole moment from the SDCI calculations.

Basis sets	5s 4p*	5s 4p	5s 4p 1d	5s 4p 2d
Energy	−1316.663574	−1316.599137	−1316.857452	−1316.978272
No. CSF	57542	9062	25372	49930
S q_{aa}, q_{yy}	3.2517	3.2265	3.1573	3.2450
q_{bb}, q_{xx}	1.6601	1.6613	1.4817	1.4770
q_{cc}, q_{zz}	−4.9118	−4.8878	−4.6390	−4.7220
η	0.3204	0.3202	0.3612	0.3744
Cl q_{aa}	2.2215	2.2085	2.0971	2.0221
q_{bb}	0.4519	0.4563	0.4047	0.3907
q_{ab}	−3.2112	−3.1913	−2.9704	−2.8448
q_{cc}, q_{yy}	−2.6734	−2.6648	−2.5018	−2.4128
q_{xx}	−1.9942	−1.9770	−1.8377	−1.7530
q_{zz}	4.6676	4.6418	4.3395	4.1658
η	0.1455	0.1482	0.1530	0.1584
Dipole moment	0.2507	0.2440	0.1161	0.1755
$\delta\theta$	1.337	1.311	1.586	1.635

* all electron calculation.

SCl_2. The SCF energy is comparable to the present 5s4p1d calculation at the same theoretical level. But the EFG values are closer to the one from the 5s4p2d1f calculation. No CI calculation for SCl_2 has been reported before.

The energy, the number of configuration state functions (No. CSF) and computed properties are summarized in Table 2. The present CI calculations involve all the single and double excitations (SDCI) with 20 valence electrons except for the one with the 5s4p basis set. In that case, both full electron SDCI and valence electron SDCI have been conducted in order to investigate the effect of the core electron contribution. Upon comparing the first two columns in Table 2, one may conclude that the core electrons have a limited effect on these electronic properties. However, the trend is that with inclusion of the core electrons contribution, the magnitudes of the EFG is increased in contrast to the basis set effect. When the quality of the basis set is improved, the EFG is more likely to decrease in absolute value. The coexistence of counter effects on certain electronic properties has been observed before, such as geometry [17] and spin hyperfine coupling constants [18]. If caution is employed to balance these factors, those electronic properties may be predicted reasonably well without employing heavy CI calculations with very large basis sets.

With the 5s4p2d basis set, the EFG in SCl_2 has been calculated to be, $q_{aa}^{\mathrm{Cl}} = 2.0221$, $q_{ab}^{\mathrm{Cl}} = -2.8448$, and $q_{cc}^{\mathrm{Cl}} = -2.4128$. These EFG's, together with the nuclear quadrupole moments of $^{35}\mathrm{Cl}$ $Q_N = -0.08249$ and $^{37}\mathrm{Cl}$ $Q_N = -0.06493$ [6], produced the NQCC with $\chi_{aa}(^{35}\mathrm{Cl}) = -39.192$ (-38.671), $\chi_{ab}(\mathrm{Cl}) = 55.07$ (53.76) and $\chi_{cc}(^{35}\mathrm{Cl}) = 46.7645$ (47.7945) in $S^{35}Cl_2$, and $\chi_{aa}(^{37}\mathrm{Cl}) = -30.849$ (-31.217), $\chi_{ab}(^{37}\mathrm{Cl}) = -43.350$ (-42.285), and$\chi_{cc}(^{37}\mathrm{Cl}) = 37.5967$ (37.6759) in $S^{35}Cl^{37}Cl$, with the new experimental values given in parenthesis [2]. Thje differences are found to be smaller than 3%.

The EFG on the S atom shows similar trends under electron correlation as reported by Palmer [12] on a series of S-containing compounds. However, the present calculation predicts much larger changes in the value of the EFG. With comparable quality basis sets, changes of about 7% are observed for q_{zz} on S compared with 3% reported in Cl_2SO and Cl_2SO_2 [12]. Based on the above analysis of possible cancellation of errors between electron correlation and basis set effects and the numerical evidence of the NQCC of $^{35}\mathrm{Cl}$ and $^{37}\mathrm{Cl}$, we may assume that the present calculated EFG on S, $q_{aa} = 3.2450$, $q_{bb} = 1.4770$ and $q_{cc} = -4.7220$, inherits similar errors of about 3%. Using the nuclear quadrupole moments of $^{33}\mathrm{S}$ reported by Sundholm and Olsen [6, 8] -0.0678 (which is close to Palmer's derived value of -0.0640 [12]), we predict the NQCC of $^{33}\mathrm{S}$ in SCl_2 to be $\chi_{aa} = -51.69$, $\chi_{bb} = -23.53$ and $\chi_{cc} = 75.22$.

The dipole moment is seen to be quite sensitive to both basis set quality and electron correlation. It changed quite dramatically when the first set of d polarization functions was added. Nevertheless, it appears to be converging at both the SCF and SDCI levels when better basis sets were used. With the 5s4p2d basis set, the SDCI dipole moment is obtained as 0.1755, which is larger than the value 0.14 reported by Murray et al. [4] through fitting of the Stark effect of the $0_0 \rightarrow 1_0$ transition.

The angle between the NQCC principal axis and the S–Cl internuclear direction is small. Nevertheless, it has been predicted quite consistently to be around 1.5° (see Tables 1 and 2). This clearly indicates that the S–Cl bond is not straight in the vicinity of the Cl nuclei.

Even though most chemical bonds are straight, the bent bond model is not a new concept in chemistry [19]. Both x-ray crystallographic experiments [20] and the bond path according to Bader's [21] topological analysis reveal bent bonding in small ring compounds. Actually, in nonlinear molecules, their low symmetry may allow mixing of atomic orbitals of different principal axes. The resulting principal axes of charge density may be turned away from the internuclear direction. For the quadrupole coupling tensor, there are contributions from both nuclei and electrons. The nuclear term is always aligned with the bond axis. However, the electronic term will follow the gradient tensor of the charge density. Therefore, except in the linear molecular case in which all three methods predict the same direction, the bond direction from quadrupole analysis will lie in between the one from the analysis of the charge density itself and the one from its topology.

4. Conclusion

With the extended basis set including two sets of d type functions, the EFG in SCl_2 has been calculated at the CI level to be $q_{aa}^{Cl} = 2.0221$, $q_{bb}^{Cl} = 0.3907$, $q_{ab}^{Cl} = -2.8448$, $q_{cc}^{Cl} = -2.4128$, $q_{aa}^{S} = 1.4770$, $q_{bb}^{S} = 3.2450$, $q_{cc}^{S} = -4.7220$. These EFG's, together with the nuclear quadrupole moments of ^{35}Cl and ^{37}Cl [6], produced the NQCC within 3% errors compared with the new experimental results [2]. The predicted NQCC (with the Q_N given in [8]) of ^{33}S in SCl_2 are given as $\chi_{aa} = -51.69$, $\chi_{bb} = -23.53$, and $\chi_{cc} = 75.22$ with a 3% uncertainty.

The calculated angle between the NQCC principal axis and the S–Cl axis is 1.6°, which is not far off from the experimental one, 1.3°. This leads us to conclude that the S–Cl bond in SCl_2 is actually bent.

Both the basis set and electron correlation play significant roles in the EFG prediction. The augmentation of d and f functions to the basis set changes the EFG value significantly. The electron correlation, mostly that of the valence electrons, contributes largely to the EFG. Nevertheless, as shown here, the EFG can be predicted well because the corrections for basis set quality and electron correlation may cancel for the EFG to a large extent at certain stages.

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