Theoretical Investigation on the Nuclear Quadrupole Interaction of CH$_3$Cl, CH$_2$Cl$_2$ and CHCl$_3$*

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The nuclear quadrupole interaction of $^{35}$Cl in CH$_3$Cl, CH$_2$Cl$_2$ and CHCl$_3$ has been studied theoretically by the Hartree-Fock-Roothaan procedure. The influence of the crystal field on the nuclear quadrupole coupling constant is incorporated by the cluster approach and by using point charges that are consistent with the external potential.

Introduction

The nuclear quadrupole interaction in Cl-substituted methanes CH$_4$-Cl$_n$, $n = 1$ to 3, has been investigated extensively by experimental [1–7] and theoretical [8–10] methods. The nuclear quadrupole coupling constant $v$ (NQCC) is expressed as

$$v = q(eQ/h),$$

where $q$ is the largest component of the electric field gradient (EFG) tensor in the principal axis system at a given nucleus. In the gas phase the NQCC's for CH$_4$-Cl$_n$ are gained from microwave [1, 2] and molecular beam measurements [3], whereas in the solid state the values of $v$ are deduced from NQR and NMR studies [4, 6, 7]. Theoretically, $q$ is calculated for the isolated molecules CH$_2$Cl [8–10] and CHCl$_3$ [9] in the gas phase by ab initio self consistent field (SCF) calculations using Gaussian basis sets [11].

The gas phase value of $v^{(35) \text{Cl}}$ increases from CH$_3$Cl to CHCl$_3$ by about 10%. This trend can be understood simply by considering the electronegativity: with increasing number of Cl atoms each Cl becomes less negatively charged, and therefore the charge around the Cl nucleus becomes more asymmetric. Considering the occupation numbers, the occupation of the 3$p_x$ orbital along the Cl–C bond axis is decreasing with increasing number of Cl atoms, whereas the occupation of the 3$p_y$ and 3$p_z$ orbitals are almost constant. Comparing the experimental EFG at the chlorine site with theoretical results from ab initio SCF calculations, differences of about 1.2–6% for CH$_3$Cl [8–10] and 10% for CHCl$_3$ [9] are found.

In the solid state the compounds crystallize in different structures [12-14] which are displayed in Figure 1. Considering the chlorine nuclei, there is only one crystallographic position in the unit cell of CH$_3$Cl and CH$_2$Cl$_2$, and one resonance line for the chlorine nuclei is found for these compounds [4, 6, 7]. In CHCl$_3$, however, there are two non equivalent chlorine positions labeled $a$ and $b$ in Fig. 1, and two resonance lines for $^{35}$Cl are detected [6, 7]. From the line width analysis and the intensity of the lines it follows that the resonance line for the position $a$ with a lower frequency than for the position $b$ [15].

Comparing the gas phase and solid state data one obtains that the $v^{(35) \text{Cl}}$ in the solid state is between 6% and 9% smaller than in the gas phase. This influence of the surrounding molecules, here called the solid state effect, leads to a decrease of the EFG at the chlorine nucleus. This solid state effect is explained qualitatively by the change of the Cl–C distance on going from the gas phase [16–18] to the solid state, and furthermore by intermolecular Cl–H bonds in the crystal [12, 19].

In the present paper we study the nuclear quadrupole interaction in these compounds by quantum mechanical calculations at the ab initio SCF level. We wanted to find out whether the results of our calculation can verify quantitatively the trends in the $v$'s reported above, and furthermore whether the origin of the trends can be explained in a simple quantum mechanical picture.

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Method

The nuclear quadrupole interaction is characterized by the coupling constant $v$, Eq. (1), and the asymmetry parameter $\eta$,

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}},$$

where $(X, Y, Z)$ is the principal axis system and $q = q_{zz} > q_{yy} > q_{xx}$.

Computationally the EFG tensor is initially obtained in terms of the $x, y, z$ coordinates of the input geometry. For example, the component $q_{zz}$ of the total EFG is the sum of the contribution of the nuclei

$$q_{zz}^{(n)} = \sum Z_i \frac{3z_i^2 - r_i^2}{r_i^2},$$

and the electronic part

$$q_{zz}^{(el)} = -e \int q(r) \frac{3z^2 - r^2}{r^5} \, dr.$$

Here $Z_i$ are the atomic numbers and $q(r)$ is the electron density obtained from the ab initio SCF calculation. Diagonalization of the tensor $q_{ij}$, $i,j = x, y, z$,
gives the components \( q_{XX}, q_{YY}, \) and \( q_{ZZ} \) and the angles between \((x, y, z)\) and \((X, Y, Z)\).

The SCF calculations have been performed using the programs HONDO [20] and GAUSSIAN 90 [21]. It was pointed out in earlier theoretical investigations on the EFG in chlorine compounds [8–10] that one should use extended basis sets including d functions at Cl and C and p functions at H. Additionally we have found that one should have more than one p function at the chlorine site to describe the valence electrons and one should include also one d basis function centered at the hydrogen site. There are several basis sets of this type published in the literature [22]. Using a nuclear quadrupole moment \( Q^{(15}\text{Cl)} = -0.082 \) barn [23] we get the best agreement with the experimental values of the EFG with the following basis set: a \((12s, 9p, 1d)/[6s, 4p, 1d]\) basis [24, 25] for Cl, a \((10s, 5p, 1d)/[3s, 2p, 1d]\) basis [26] for C, and a \((4s, 1p, 1d)/[2s, 1p, 1d]\) basis [27] for H. We have used these basis functions for all calculations of the present paper.

The influence of the surrounding molecules on the electronic states can be investigated by different methods. First, one can perform a band structure calculation using either the Hartree-Fock approximation [28] or the density functional method [29]. Second, within the molecular orbital approach one can calculate the electronic properties for a cluster of several molecules taking the solid state geometry for the atomic positions. Additionally, external point charges can simulate the crystal field of the remaining lattice [30, 31].

As we want to compare the gas phase and the solid state data it is useful to use the same method for both phases. Therefore we have chosen the cluster method for the investigation of the crystal field effect. To study various contributions to the total solid state effect we have performed several model calculations, called model 1 to 4 below. First we have calculated the EFG for a monomer using, however, the geometry found for the solid state instead of the gas phase geometry (model 1). Figure 2a shows the slightly different internal coordinates of \( \text{CH}_2\text{Cl} \) for the solid state [12] and the gas phase [32]. Next we have described the influence of the monomer’s surrounding by point charges (model 2). Third we have performed the molecular SCF calculation for a cluster of three to four molecules (model 3); see Figure 2b for the case of \( \text{CH}_3\text{Cl} \). Finally we have simulated the influence of the rest of the lattice for this cluster again by point charges (model 4). The positions of the point charges are chosen at the atomic positions of the crystal structure.

The values of the charges are chosen in two ways. First we have taken the charges \( q_{\text{Pauli}} \) deduced from the Mulliken population analysis [33]. Second we have used potential-derived charges \( q_{\text{pdc}} \) [34], which describe the multiple moments of the molecules quite well [34]. The \( q_{\text{pdc}} \) are gained from the following least squares fit. From the calculated SCF electron density distribution \( \psi(r) \) of the molecule or cluster the electrostatic potential outside the van der Waals volume of the molecule is calculated on a grid of points. Then those values for the point charges at the atomic positions of the cluster are determined which give the best fit to this potential function.

Furthermore we have deduced \( \psi(r) \) and \( q_{\text{pdc}} \) in a self consistent procedure. We have used the fitted point charges to obtain the external potential of an infinite lattice. This external potential is included in the molecular SCF calculation to recalculate \( \psi(r) \). This procedure is performed until the difference of the charges between the previous run and the actual run has been reached a certain threshold.

### Results and Discussion

The EFG at the chlorine site is calculated for \( \text{CH}_3\text{Cl}, \text{CH}_2\text{Cl}_2 \) and \( \text{CHCl}_3 \) using the basis set given in the previous section. The experimental and theoretical results are summarized in Table 1.

Considering the gas phase results we see from Table 1 that the SCF results describe the trend of the EFG in the series \( \text{CH}_4 \rightarrow \text{Cl}_n \) quite well. The calculated NQCC increases by 1.2 MHz from \( \text{CH}_3\text{Cl} \) to \( \text{CH}_2\text{Cl}_2 \) which agrees with the experimental result. From \( \text{CH}_2\text{Cl}_2 \) to \( \text{CHCl}_3 \) the theory predicts an increase of 5.0 MHz, which is 1.1 MHz larger than the experimental finding. The reason for the increase of the EFG can be seen from the orbital population analysis, see Table 1. The ionicity of the chlorine decreases with increasing \( n \), and according to the Townes-Dailey theory [35] the EFG also increases. However there is no linear dependence of the EFG on the orbital population, or on the occupation of the \( 3p_z \) orbital \( n_{p_z} \); see Figure 3. This can be explained in the following manner. At the chlorine site the valence electron states are described by two s, two p and one d function centered at the chlorine atom. The major contribution to the EFG comes from the two p basis functions given in Table 2. From Table 2 we can see that the function \( f_1 \)
is more localized than the function $f_2$, and therefore the radial integral of the EFG $I_1$,

$$I_1 = \frac{1}{r^2} \int_0^\infty f_1^2(r) r^2 \, dr,$$

is larger than the corresponding integral $I_2$. It follows that the calculated EFG depends on two parameters, on the overall $3p_z$ occupation

$$n_{p_z} = n_{p_z1} + n_{p_z2},$$

and additionally on the ratio $r_{1,2} = \frac{n_{p_z1}}{n_{p_z2}}$ of the partial contributions of the functions $f_1$ and $f_2$. The change of $r_{1,2}$ describes the change of the character of the $3p$ orbital as a function of ionicity of chlorine. For example the normalized $3p$ state for the Cl$^-$ is more diffuse than for Cl$^0$, see Figure 4. In Fig. 3 the calculated EFG is also plotted as function of the partial occupation numbers $n_{p_z1}$ (1) and $n_{p_z2}$ (2) of the function $f_1$ and $f_2$ for the chlorine $3p$ state. We see that the EFG
Table 1. Theoretical and experimental values of the NQCC $v^{(35\text{Cl})}$ and electric field gradient (EFG) at the chlorine site in CH$_3$Cl.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental results</th>
<th>Theoretical results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EFG [a.u.] $v^{(35\text{Cl})}$ [MHz] $\eta$</td>
<td>EFG [a.u.] $v^{(35\text{Cl})}$ [MHz] $q_{\text{mol}}$ $\eta$</td>
</tr>
<tr>
<td>gas phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>$-3.877$ 74.69 [3] 0.000</td>
<td>$-3.869$ 73.76 $-0.199$ 0.000</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>$-3.971$ 76.50 [17] 0.000</td>
<td>$-3.930$ 75.45 $-0.160$ 0.035</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>$-4.173$ 80.39 [1] 0.000</td>
<td>$-4.169$ 80.51 $-0.111$ 0.002</td>
</tr>
<tr>
<td>solid state</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$Cl</td>
<td>$-3.579$ 68.75 [19] 0.000</td>
<td>$-3.614^I$ 69.615 $-0.263^I$ 0.004</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>$-3.762$ 72.49 [15] 0.068</td>
<td>$-3.781^I$ 72.832 $-0.192^I$ 0.046</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>$-4.003$ 77.02 [15] 0.040</td>
<td>$-3.802^II$ 73.237 $-0.183^II$ 0.055</td>
</tr>
</tbody>
</table>

Table 2. The two $3p$ basis functions $f_1$ and $f_2$ of the chlorine basis set [24].

<table>
<thead>
<tr>
<th>$p$ basis function</th>
<th>Exponent</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_1$</td>
<td>0.950083</td>
<td>1.00000</td>
</tr>
<tr>
<td>$f_2$</td>
<td>0.55450</td>
<td>0.31609</td>
</tr>
</tbody>
</table>

depends almost linearly on the occupation of $f_1$ because $f_1$ gives the largest radial contribution to the EFG [36].

Next, differences between the gas phase data and the solid state data will be discussed. The solid state $v$ is always smaller than the gas phase $v$. This trend is also found in our theoretical study. Quantitatively, the calculated shift of $v$ differs by up to 1.5 MHz from the experimental result depending on the chosen model for the solid state effect.

The result are shown in detail in Table 3 and Figure 5. In Table 3 the occupation numbers and the calculated EFG for the different model calculations described above are given. The first line shows again the results for the monomer using the gas phase geometry.

The second line (model 1) gives the results for the monomer, however, using the atomic positions found for the solid state. We see that the change of the geometry has a minor effect on the EFG for CH$_3$Cl, whereas for CH$_2$Cl$_2$ and CHCl$_3$ the change in the geometry causes a distinct decrease of $v$. Furthermore the differences of $v$ for the positions $a$ and $b$ for CHCl$_3$ are larger than the experimental findings [15, 37].

The structure data are from measurements at 77 K. At this temperature the experimental values are $v^{(35\text{Cl})}_a = 76.51$ MHz and $v^{(35\text{Cl})}_b = 76.62$ MHz [15, 37].

In the third line of Table 3 (model 2) we have included the external field of the surrounding molecules within the point charge model using the potential derived charges as external charges. The field of the external charges distinctly influences the EFG and results in a decrease of the EFG in accordance with the experimental finding. We see that the chlorine...
atom becomes slightly more negatively charged in the solid state and therefore the EFG is decreasing. The reason for the small charge transfer to the chlorine can be seen from Fig. 6, in which we have plotted the external potential for an electron along the bonding axis H–C and C–Cl. The potential is negative in the region of the chlorine and positive in the region of the carbon and hydrogen and results in a shift of electronic charge to the chlorine.

Returning to the model calculations given in Fig. 5 and Table 3, we see in the fourth line the results for a cluster calculation (model 3). The cluster used is displayed in Fig. 2b for the case of CH₂Cl. Comparing the monomer with the cluster result we see that the trend is the same as that found on the inclusion of the point charges. However, the change of the EFG and the Mulliken charge at the chlorine site $q_{Mull}$ is smaller than the change found on inclusion of the point charges.

Fig. 4. Radial density $P_{3p}^2(r)$ of a normalized 3p function for the free chlorine atom and anion calculated by the local density approximation.

Fig. 5. Scheme to display the following solid state effects on the nuclear quadrupole interaction in CH₃Cl. (1) Change of the calculated NQCC going from the gas phase geometry to the solid geometry (see Fig. 2a, model 1 in the text); (2) Influence of the external point charges (model 2); (3) Influence of the cluster (model 3); (4) Influence of the point charges on the cluster, (see Figure 2b, model 4).
Theoretical results of the NQCC $\nu(\text{Cl})$, the Mulliken charges $q_{\text{Mull}}$, the potential derived charges $q_{\text{pdc}}$ and the asymmetry parameter $\eta$ at the chlorine in Cl substituted methanes CH$_n$-Cl, $n=1$ to 3. The values are given for the different models discussed in the text, see also Figure 5. In the case of CHCl$_3$ the values are given for both crystallographic sites, see Figure 1.

In the last line of Table 3 (model 4) we have displayed the results using the cluster model and additionally for the rest of the lattice the point charge model. These calculations are extremely time consuming and one sees that the results of model 4 do not differ significantly from the much simpler calculations of model 2. The agreement between theory and experiment is almost the same for both models. Therefore, studying $\nu(\text{Cl})$ in molecular crystal by the Hartree-Fock procedure it seems to be sufficient to use the point charge model for the incorporation of the intermolecular effects. This should be different if correlation effects are included in the calculations.

We also used the Mulliken charges to simulate the external point charges in a self consistent manner. These results differ significantly from those with the potential derived point charges given in Table 3 by about 100–700 kHz. These results are given in Table 4. We see that the trends in the EFG are described much more satisfactorily by the potential derived charges than by the Mulliken charges.

Finally we have investigated the calculated EFG as a function of the position of the hydrogen nuclei. The results are presented in Figure 7. In Fig. 7a the total

Fig. 6. External electrostatic potential for an electron along the H–C and C–Cl direction calculated in CH$_3$Cl from the potential derived charges.
Table 4. Theoretical results of the NQCC \( \nu^{(35}\text{Cl}) \) using the Mulliken charges \( q_{\text{Mull}} \) instead of the potential derived charges (Table 3) to simulate the solid state. The values are given for the different models discussed in the text. In the case of CHCl\(_3\), the values are given for both crystallographic sites, see Figure 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Model</th>
<th>( \nu^{(35}\text{Cl}) ) [MHz]</th>
<th>( q_{\text{Mull}} )</th>
<th>( \eta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)Cl</td>
<td>model 2</td>
<td>69.018</td>
<td>-0.268</td>
<td>0.0039</td>
</tr>
<tr>
<td></td>
<td>model 4</td>
<td>68.691</td>
<td>-0.257</td>
<td>0.0044</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>model 2</td>
<td>72.582</td>
<td>-0.195</td>
<td>0.0503</td>
</tr>
<tr>
<td></td>
<td>model 4</td>
<td>73.610</td>
<td>-0.185</td>
<td>0.0665</td>
</tr>
<tr>
<td>CHCl(_3)Cl(_a)</td>
<td>model 2</td>
<td>78.100</td>
<td>-0.119</td>
<td>0.0189</td>
</tr>
<tr>
<td></td>
<td>model 4</td>
<td>78.340</td>
<td>-0.115</td>
<td>0.0198</td>
</tr>
<tr>
<td>CHCl(_3)Cl(_b)</td>
<td>model 2</td>
<td>78.707</td>
<td>-0.121</td>
<td>0.0087</td>
</tr>
<tr>
<td></td>
<td>model 4</td>
<td>78.361</td>
<td>-0.126</td>
<td>0.0024</td>
</tr>
</tbody>
</table>

in the EFG. However, to study the hydrogen-bonding effect in detail, one has to incorporate correlation effects which could not be included here.

Conclusions

In the present work it is shown that the Hartree-Fock-Roothaan procedure describes the nuclear quadrupole coupling constant of \( ^{35}\text{Cl} \) in the compounds CH\(_4\)–\( n\)Cl\(_n\) quantitatively if one uses large Gaussian basis sets. The intermolecular field of potential derived point charges obtained by a self consistent procedure describes the crystal field effect on the EFG quite well.

In the solid state the chlorine is slightly more negatively charged than in the gas phase. Due to this small charge transfer, a decrease of the NQCC in the solid state compared to the gas phase is observed. This charge transfer can be explained by a small attractive crystal field for the electrons at the chlorine.

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\[6\] R. Livingston, Phys. Rev. 82, 1434 (1951).
\[20\] HONDO-8, M. Dupuis, J. D. Watts, H. O. Villar, and G. J. B. Hurst, Program no. 544, Quantum Chemistry Program Exchange, India University, Bloomington, India.
\[21\] Gaussian 90, M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkly, C. González, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian Inc. Pittsburgh PA, (1990).
\[22\] See e.g. R. Poirier, R. Kari, and J. G. Cizmadia, Handbook of Gaussian basis sets, Elsevier Amsterdam, 1985.
\[36\] See also the discussion in E. A. C. Lucken, Z. Naturforsch. 49a, 133 (1994).