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Ab initio calculations of nuclear quadrupole resonance frequencies in trichloroacetyl halides: a comparison of DFT and experimental data

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Abstract

Ab initio calculations of $^{35}\text{Cl}$ nuclear quadrupole resonance (NQR) frequencies ($\nu_Q$) in trichloroacetyl halides (CCl$_3$COHal, where Hal = F, Cl, Br or I) are performed. The estimated $\nu_Q$ values are compared with experimental values obtained by Gordeev et al \cite{1}. Calculation of the average of $^{35}\text{Cl}$ NQR frequencies in CCl$_3$COCl demonstrated that the difference between the calculated and experimental values are less than 3.1%. This indicates that the density functional theory is a powerful technique that for predicting unknown electronic states before performing experiments. A linear correlation between Hal-C bond length and $\nu_Q$ is observed. This hence provides a scheme to estimate interatomic distances using NQR frequencies.

1. Introduction

Nuclear quadrupole resonance (NQR) is an experimental method that has contributed substantially towards elucidating electronic properties in superconductors \cite{2,3}, heavy fermions \cite{4,5}, organic molecules \cite{6–8}, etc. Nuclear magnetic resonance (NMR) and NQR phenomena are caused by applying radio-frequency wave having energy equivalent to two energy level differences produced by spins with different nuclear spin angular momenta \cite{9}. The energy level difference reflects the electronic state around the nucleus being investigated. Pure NQR uses energy splitting caused by nuclear quadrupole coupling, which is proportional to the electric-field gradient (EFG) at the nucleus, without applying an external magnetic field. As the width of the energy splitting is completely material-specific, unlike in NMR, which is almost proportional to the external magnetic field, the NQR resonance frequency ($\nu_Q$) is also material-specific.

Before an NQR experiment, it is first necessary to find NQR signals. As it is impossible in principle to know resonance frequencies in advance, the following methods have been used: (i) searching around the $\nu_Q$ of materials with a similar crystal (or molecular) structure; (ii) calculating $\nu_Q$ using a point charge model that determines the EFG created at the nucleus to be measured, by placing ions on each atom; (iii) analyzing the shape of the NMR spectrum (line splitting width due to quadrupole coupling). Another method is a first-principles calculation based on the Linearized Augmented Plane Wave (LAPW) developed by Blaha et al \cite{10}. To date, ab initio calculations of EFGs have been performed in heavy electronic systems, superconductors, hcp metals, ferroelectrics, etc and are in good agreement with experimental data \cite{11–17}.

In this study, it is shown that the NQR frequency calculated by the first-principles method agrees well with the experimental value even for molecular materials. The target materials in the present study are the organic solid molecules, i.e. trichloroacetyl halides (CCl$_3$COHal, where Hal is F, Cl, Br or I). The end member, trichloroacetyl chloride (CCl$_3$COCl), is known as a typical example showing a line splitting due to the difference in the intramolecular environment \cite{18,19}. Results of the first-principles calculation when changing Hal are compared with the experimental data obtained by Gordeev et al \cite{1}. As the crystal structure data of molecules other than Hal = Cl are not available, agreement with the experimental data is confirmed by adjusting the Hal-
C intermolecular distance based on the CCl₃COCl crystal structure. This provides a method for estimating the intermolecular distance by NQR.

2. Computational approach

2.1. CCl₃COHal
The crystal structure data used for the calculation is a simulation-based three-dimensional conformer from PubChem [20, 21]. The molecule is placed in the center of a cubic unit cell with a side of 10 Å (figure 1). The molecules can be divided into the CCl₃ group and the COHal segment. The three Cl atoms in CCl₃ group feel different EFG depending on the intramolecular force, and three NQR lines are observed [19]. In this study, prediction of the ν_Q values for these three Cl sites is performed.

2.2. Electric-field gradient
When the nuclear spin is I ≥ 1, the nuclear charge distribution is not spherical. In this case, even without an external magnetic field, the degenerated energy is split according to the direction of the nucleus. This is the condition for NQR. The resonance frequency of NQR (ν_Q) is proportional to the product of the nuclear quadrupole moment Q and principal value of the EFG tensor. The EFG tensor at a nucleus in the three-dimensional Cartesian coordinate system, (x, y, z), is written as follows [22, 23]:

\[ V_{ij} = \frac{\partial^2 V(r)}{\partial x_i \partial x_j} \mid_{r=0} \text{ (} i, j = x, y, z \text{),} \]

where \( V(r) \) is the potential at position \( r \). In other words, EFG is the second derivative of potential at the nucleus. \( r = 0 \) represents the nuclear position. EFG is the traceless symmetric tensor, \( V_{xx} + V_{yy} + V_{zz} = 0 \), where \( V_{xx}, V_{yy}, V_{zz} \) are eigenvalues. When \( |V_{xx}| < |V_{yy}| < |V_{zz}| \), \( V_{zz} \) is the EFG in the principal axis direction.

For Cl, spin \( I = 3/2 \), energy levels splits into two by the quadrupole interaction, and ν_Q is written as

\[ \nu_Q = \frac{e^2 q Q}{2\hbar} \sqrt{1 + \frac{\eta^2}{3}}, \]

where \( e \) is the elementary charge, \( q = V_{zz} \), \( \eta \) is asymmetric parameter \( \eta = (V_{xx} - V_{yy})/V_{zz} \), and \( \hbar \) is Planck constant.

2.3. Ab initio calculation
EFG at the nuclear position is strongly affected by the core electrons close to the nucleus. Therefore, the full-potential ab initio calculation considering all electrons is more accurate than the calculation using a pseudopotential based on plane waves. In the point charge model, the calculation results possibly deviate significantly from the experimental value owing to the effects of modulation of the core orbital (Sternheimer antishielding factor). However, in the full-potential first-principles calculation, the core orbital calculation is originally included, so there is no need to consider the shielding factor separately [24]. In the present study, (L) APW+lo (local orbital) method based on the density functional theory (DFT) implemented in the WIEN2k code.
Table 2. Calculated eigen values and eigen vectors of the EFG tensor in CCl₃COCl for PBE and LDA.

| Calc. No. | Vₓₓ | Vᵧᵧ | Vzz | η  | Vectorₓₓ | Vectorᵧᵧ | Vectorzz |
|-----------|-----|-----|-----|----|---------|---------|---------|
| PBE       | −19.99 | −21.51 | 41.50 | 0.0367 | (−0.0743−0.0673 1.00) | (1.00−0.745 0.124) | (−0.747 1.00 0.0119) |
| 2         | −19.33 | −20.84 | 40.16 | 0.0377 | (1.00−0.639 0.698) | (1.00−0.992 0.525) | (−0.219−0.750 1.00) |
| 3         | −19.16 | −21.17 | 40.33 | 0.0498 | (1.00−0.540−0.6115) | (−0.810 1.00 0.427) | (0.266−0.6397 1.00) |
| LDA       | −20.16 | −21.68 | 41.84 | 0.0363 | (−0.0783−0.7073 1.00) | (1.00−0.7472 0.131) | (−0.749 1.00 0.0116) |
| 2         | −19.44 | −20.10 | 40.41 | 0.0385 | (1.00−0.597 0.671) | (−0.959 1.00 0.539) | (−0.222−0.752 1.00) |
| 3         | −19.26 | −21.35 | 40.61 | 0.0514 | (1.00−0.510−0.597) | (−0.769 1.00 0.434) | (0.269−0.6417 1.00) |

* The calculation number corresponds with the site number in figure 1.

Table 1. Parameters of equation (3) applied to experimental data in [1].

| Hal  | Exp. No. | A₀ (MHz) | A₀ν² (MHz) | α × 10⁻²⁷ |
|------|----------|----------|------------|------------|
| Cl   | 1        | 40.744   | −5.7364    |            |
|      | 2        | 40.577   | 40.522     | −4.4905    |
|      | 3        | 40.243   |            | −5.3867    |
|      | 1        | 40.279   |            | −4.7987    |
|      | 2        | 41.052   | 40.907     | −5.4353    |
|      | 3        | 41.390   |            | −5.0103    |
| F    | 1        | 40.137   |            | −5.5345    |
|      | 2        | 40.434   | 40.450     | −4.5923    |
|      | 3        | 40.779   |            | −5.7804    |
| Br   | 1        | 39.791   |            | −4.2882    |
|      | 2        | 40.105   | 40.238     | −5.0374    |
|      | 3        | 40.819   |            | −5.0223    |

is used [25]. The exchange correlation functional used here is Perdew–Burke–Ernzerhof (PBE) derived from the generalized gradient approximation (GGA) [26]. For comparison, the local density approximation (LDA) is also used for Hal = Cl. The smallest atomic sphere radius multiplied by the largest k vector, RKmax, which controls the number of basis sets, is 5.5. The sampled k-points in a Brillouin zone is 8. The end condition of the iteration of the self-consistent calculation is the energy convergence limit of 10⁻⁶ Ry. In the DFT calculation, the space is divided into a muffin-tin sphere centered around the nucleus and an external interstitial space. The muffin-tin sphere radius for Cl is 1.73 Bohr ≈ 0.915 Å. The obtained EFG is a so-called lattice EFG that includes not only the muffin-tin sphere but also the interstitial region. The quadrupole moment of ³⁵Cl used for the estimation of νQ is \( Q = -0.08249 \times 10^{-24} \text{ cm}^2 \) [27].

The values that can be calculated by \textit{ab initio} calculations are ground state values. As there are no experimental data in the ground state, a value obtained by extrapolating finite temperature data to 0 K is used. The reduced empirical law proposed by Koukoulas and Whitehead [28],

\[
    f(T) = A_0 \exp(\alpha T^2),
\]

is used instead of the polynomial equation used in [1]. The parameters of the fitting are listed in table 1.

### 3. Results and discussion

Table 2 shows the results of the DFT calculation of EFG at three Cl nuclei in the CCl₃ group by GGA and LDA. The calculated νQ based on the EFG tensor is shown in figure 2(a). The number in the figure corresponds to the number labeled at the nucleus in figure 1. Figure 2(b) is the experimental data of [1], with the curve fitted by equation (3). There is one inequivalent molecule in the crystal, and the three spectra obtained are from three inequivalent Cl sites in the molecule [19]. The average value from the calculations is compared with the experimental average value \( A_0 ν² \). The differences are 40.5664 − 40.5215 = 0.045 MHz (0.11%) for PBE and 40.8643 − 40.5215 = 0.343 MHz (0.85%) for LDA. The discrepancy is acceptable considering the reliability of the atomic coordinates and the accuracy of Q. However, it is not clear as to which Cl site each of the three spectra
The estimated value for the core within the muffin-tin sphere is 40.9 V m$^{-2}$. As the p-character ($pp$) contribution for the value is 41.4 V m$^{-2}$, it is thought that anisotropic 3p orbital properties are strongly reflected in EFG. The principal axis direction of the EFG tensor is along the Cl-C bond as shown in the inset of Figure 2 (b).

The results for CCl$_3$COBr are shown in Figure 4. As shown in the figure, the experimental data can be explained as increase in $L$, as the radius of the bromine atom is larger than that of the chlorine atom. The average results indicates that the best value of $L$ is $L = 0.13$ Å.

The atomic radius of the iodine atom (I) is larger than that of the bromine atom (Br). As shown in Figure 5, the experimental data is explained when the I atom is moved by $L = 0.3$ Å.

As discussed above, the correlation between $\nu_Q$ and the C-Hal distance is proportional within the calculated $L$ range. This is because when the Hal atom enters the center of the molecule, a charge transfer occurs in the molecule, and as a result, the charge distribution at the Cl sites approaches spherical symmetry. When the charge distribution becomes spherically symmetric, EFG decreases and $\nu_Q$ also decreases. If the amount of movement of the atom is small, the linear approximation is guaranteed in that range. The movement of atoms with high electronegativity may strongly affect the charge distribution within the molecule. In fact, the slopes of the fitted line are 2.7, 2.0 and 1.7 MHz Å for Hal = F, Br and I, respectively, which is the order of the magnitude of electronegativity.

The average of bond lengths (covalent bonds) between C and Hal are as follows: 1.34, 1.76, 1.93, and 2.13 Å for C-F, C-Cl, C-Br and C-I, respectively [29]. Considering the bond length of Cl-C to be 1.755 Å as used in the structural data for CCl$_3$COCl, the optimal bond lengths determined by the calculations are approximately 1.4,
Figure 3. (a) Dependence of $\nu_Q$ on $L$ in CCl$_3$COF. The dashed purple line shows the results of linear fitting of the average value of the experimental values. $L = -0.33$ Å is the optimal value. (b) Experimental results of CCl$_3$COF from [1] fitted by equation (3).

Figure 4. (a) Dependence of $\nu_Q$ on $L$ in CCl$_3$COBr. The best value of $L$ is $L = 0.13$ Å. (b) Experimental results of CCl$_3$COBr from [1] fitted by equation (3).
1.9 and 2.1 Å, for C-F, C-Br and C-I, respectively. This result is reasonable considering the above literature values.

The values of $\nu_Q$ obtained in the present study for CCl$_3$COCl are in good agreement with the experiments. However, it is not clear whether the experimental data for all the substances agree with the calculation. As the approximation is included even in \textit{ab initio} calculations, when a strong electron-correlation or orbital interaction exists, the calculations may not fully explain the experiment.

The accuracy of the nuclear quadrupole moment affects the precision of the prediction of $\nu_Q$. As discussed above, using the value of $Q = -0.08249 \times 10^{-24}$ cm$^2$, it was confirmed that $\nu_Q$ almost coincided with the experimental value. However, there are some other known values for $Q$, for example $-0.0816 \times 10^{-24}$ cm$^2$ [30] and $-0.0850 \times 10^{-24}$ cm$^2$ [31]. If $Q = -0.0850 \times 10^{-24}$ cm$^2$ is used, the difference between the calculation and experimental values increases to about 6%. The reliability of DFT calculations and $Q$ needs to be confirmed by applying the scheme used in this study to various materials.

### 4. Conclusions

In this study, DFT was applied to calculate the electric-field gradients at the Cl position in trichloroacetyl halides. For Hal = Cl, the difference between the average of the three $\nu_Q$ values and the experimental value was 0.1% to 3.1%. This result shows that this $\nu_Q$ prediction process can be used for similar molecular materials before the actual NQR experiment. This my greatly reduces the time required for the signal search. For Hal = F, Br, and I, \textit{ab initio} calculations were carried out by changing the Cl-Hal distances. In all cases, $\nu_Q$ decreased with the decrease in C-Hal distance $L$ within the calculation range. These results indicate that the charge transfer within the molecule owing to a reduction in Hal-C bond length makes the shape of the charge distribution more spherical. The estimated bond lengths are in good agreement with the values in [29]. The value of $Q = -0.08249 \times 10^{-24}$ cm$^2$ used in the present study is reasonable, although there is concern in the reliability of the value of $Q$. DFT calculations can hence be used to confirm the reliability of $Q$ values.
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