Estimation of the ^{35}Cl NQR Frequencies of Some Organic and Organometallic Molecules Using *ab initio* Calculations at Different Levels and Basis Sets

Dmitry B. Shlyapnikov and Valentin P. Feshin

Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences,
Perm, Russian Federation

Reprint requests to Prof. V. P. F.; Fax: 007-3422-126-237, E-mail: cheminst@mpm.ru

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Ab initio calculations of organic and organometallic molecules at RHF, B3LYP and MP2 levels and 6-31G(d), 6-31+G(d), 6-311G(d) and 6-311+G(d) basis sets were executed. They were used to estimate the ^{35}Cl NQR frequencies of these molecules. A satisfactory agreement between experimental and estimated NQR frequencies was obtained for the populations of the less diffuse 3p-components of the Cl atom valence p-orbitals obtained from the RHF, B3LYP and MP2 calculations with the split valence basis sets 6-31G(d) and 6-31+G(d). An analogous conformity was not obtained using the 6-311G(d) and 6-311+G(d) basis sets.

Key words: Ab initio Calculations; p-orbital Populations; ^{35}Cl NQR Frequency; Chloro-containing Organic and Organometallic Molecules.

1. Introduction

The electronic and spatial structure of organic and organometallic molecules and mechanism of their atomic interactions are fundamental problems of organic and organometallic chemistry. Very efficient methods for the solution of these problems are quantum-chemical calculations and nuclear quadrupole resonance (NQR) measurements. According to the theory of the latter, its main parameters, the NQR frequency (ν) and the asymmetry parameter (η) of the electric field gradient (EFG) at the considered nucleus characterize the electron density distribution at the nucleus. The chlor-containing compounds have often been investigated by this method. The parameters ν and η depend on the populations N_x, N_y and N_z of the Cl-p-orbitals by simple equations, for instance for the ^{35}Cl NQR frequencies [1 - 4] by

$$\nu = (e^2 Q q_{\text{at}}/2h)[-N_z+(N_x+N_y)/2](1+\eta^2/3)^{1/2}. \quad (1)$$

However, the ν and η values estimated using these equations, and the total populations of the Cl atom valence p-orbitals, obtained from semi-empirical or *ab initio* calculations of corresponding molecules, considerably differ from the experimental values (see, e. g., [3]). Apparently this is due to the strong dependence of the EFG at the nucleus on the distance l between it and the charges which create the EFG. This dependence, characterized by the equation [1 - 4]

$$eq_{zz} = -e \int \Psi^* [(3\cos^2\theta - 1)/l^3]\, \Psi \mathrm{d}\, t, \quad (2)$$

is not taken into account in the estimation of ν and η (see, e. g., [2, 3]).

Good agreement between experimental and calculated ν and η values of a great number of organic and organometallic compounds was obtained (see, e. g., [3, 4]) when using the populations of the concentrated 3p-components of the Cl-p-orbitals, but not the total ones obtained from RHF/6-31G(d) calculations of these molecules. It is quite natural that linear correlations between experimental and this way calculated ^{35}Cl NQR parameters are observed [3, 4]. This conformity obtained enables to use these two methods jointly (^{35}Cl NQR and quantum-chemical) for the solution of fundamental problems of organic and

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Table 1. Experimental ^{35}Cl NQR frequencies at 77 K (ν_e) [6] and calculated ones using the populations of 3p-components of the Cl atom valence p-orbitals obtained from RHF/6-31G(d) (ν_{c1}), RHF/6-31+G(d) (ν_{c2}), B3LYP/6-31G(d) (ν_{c3}), B3LYP/6-31+G(d) (ν_{c4}), MP2/6-31G(d) (ν_{c5}) and MP2/6-31+G (d) (ν_{c6}) calculations.

Molecule	ν_e MHz	ν_{c1} MHz	ν_{c2} MHz	ν_{c3} MHz	ν_{c4} MHz	ν_{c5} MHz	ν_{c6} MHz
$ClCH_2CH_3$	32.646	32.116	31.759	33.106	32.786	31.674	31.345
$ClCH=CH_2$	33.411	33.060	33.083	32.395	32.101	32.626	32.665
CH_3COCl	28.963	29.172	29.428	27.702	28.280	29.668	30.012
$ClSi(CH_3)_3$	16.506	15.955	15.637	16.902	16.598	15.703	15.226
trans-$CH_3CH=CHCl$	33.410	32.936	32.939	32.321	32.387	32.464	32.493
$CH_3CCl=CH_2$	32.629	32.509	32.476	31.877	31.948	32.088	32.083
$CH\equiv CCH_2Cl$	35.812	35.761	35.568	36.178	36.096	35.321	35.210
$CH_3CCl=CHCOOH$	34.250	33.528	33.298	32.167	32.109	33.320	33.127
$ClCH_2C\equiv N$	38.122	37.507	37.265	37.775	37.677	37.170	37.006
C_6H_5Cl	34.621	33.857	33.809	32.786	32.872	33.400	33.378
4-ClC_6H_4OH	34.823	33.845	33.783	32.789	32.903	33.354	33.321
$Cl_2C=CHOCH_3$	37.188	36.992	36.809	35.602	35.603	36.298	36.150
	36.904	35.658	35.574	33.782	33.602	35.891	35.883

organometallic chemistry. It allows to check a correctness of quantum-chemical calculations of the electron distribution in molecules by experimental NQR data, and to analyse the latter using quantum-chemical calculations at the RHF/6-31G(d) level [3, 4]. For the use of other quantum-chemical methods and other basis sets it is necessary to establish the conformity between the results of these calculations of organic and organometallic molecules and NQR data of the corresponding compounds.

2. Results and Discussion

For an establishment of such a conformity of ^{35}Cl NQR frequencies we have performed *ab initio* calculations on some organic and organometallic molecules by various quantum-chemical methods for various basis sets. For the molecule calculations the Gaussian 94W program [5] was used. For the calculations molecules where selected as to their size, the presence of ^{35}Cl NQR spectra and the NQR frequency range of them. The experimental ^{35}Cl NQR frequencies presented in [6] were used.

The *ab initio* calculations were executed using Becke's three parameter hybrid method, where the non-local correlation is provided by the Lee, Yang and Parr's gradient-corrected correlation functional (B3LYP) and the Hartree-Fock method followed by a Meller-Plesset correlation energy correction, truncated at second order (MP2). The split valence basis sets 6-31G(d), 6-31+G(d), 6-311G(d) and 6-311+G(d) were used. The molecule calculations were also executed by the restricted Hartree-Fock method using all above basis sets. B3LYP and MP2 are some of the most widely used *ab initio* methods which take into account the electron correlation. In the basis sets 6-31G(d) and 6-31+G(d) each valence orbital represents a combination of two orbitals of different size. In the polarized basis set 6-31G(d), the d-functions for heavy atoms are followed up. In basis set 6-31+G(d) for these atoms diffuse functions were used. In the 6-311G(d) and 6-311+G(d) basis sets each valence orbital was a combination of three orbitals of different sizes [7]. For the estimation of the ^{35}Cl NQR frequencies the total populations of the chlorine atom valence p-orbitals and their components were used. The $e^2Qq_{at}/2h$ values used in these calculations were obtained from Cl_2 molecule calculations at the corresponding level. Satisfactory conformity between experimental and calculated NQR frequencies for the molecules studied was obtained by the use of all above-mentioned quantum-chemical methods and the basis sets 6-31G(d) and 6-31+G(d). However, this conformity was only obtained by use of the populations of the 3p-components of the Cl-p-orbitals (Table 1). Conformity between the experimental and calculated NQR frequencies was not obtained for other components. Using the total populations of the Cl-p-orbitals or their components obtained from calculations by different methods and basis sets 6-311G(d) and 6-311+G(d) does not lead to such conformity neither. Apparently the populations of only the 3p-components of the Cl atom valence p-orbitals in the 6-31G(d) and 6-31+G(d) basis sets describe adequately the Cl atom electron density distribution in organic and organometallic molecules, registered by experimental ^{35}Cl NQR data. The total populations of the Cl atom valence p-orbitals obtained using these basis sets and total populations or their components in the 6-311G(d) and 6-311+G(d) basis sets do not describe this distribution. This is due to the size of these orbitals and their components, which do not correspond to the distance r in (2) at which the contribution of these orbital populations to the EFG is basic.

Quite naturally, the linear correlations between the experimental ^{35}Cl NQR frequencies for the chloro-containing organic and organometallic compounds and those estimated using the 6-31G(d) and 6-31+G(d) basis sets are

$$\nu_c = 0.987(\pm 0.047)\nu_e - 0.071(\pm 1.573),\ r = 0.997,\ \text{(RHF/6-31G(d))}, \quad (3)$$

$$\nu_c = 0.990(\pm 0.057)\nu_e - 0.278(\pm 1.906),\ r = 0.996,\ \text{(RHF/6-31+G(d))}, \quad (4)$$

$$\nu_c = 0.915(\pm 0{,}119)\nu_e + 1.725(\pm 3.970),\ r = 0.981,\ \text{(B3LYP/6-31G(d))}, \quad (5)$$

$$\nu_c = 0.919(\pm 0.114)\nu_e + 1.564(\pm 3.822),\ r = 0.983,\ \text{(B3LYP/6-31+G(d))}, \quad (6)$$

$$\nu_c = 0.974(\pm 0.060)\nu_e + 0.052(\pm 2.002),\ r = 0.996,\ \text{(MP2/6-31G(d))}, \quad (7)$$

$$\nu_c = 0.987(\pm 0.077)\nu_e - 0.440(\pm 2.572),\ r = 0.993,\ \text{(MP2/6-31+G(d))}, \quad (8)$$

Judging from these equations, the best conformity to the experimental ^{35}Cl NQR frequencies is observed for those estimated using the populations of 3p-components of the Cl atom valence p-orbitals, obtained from the RHF/6-31G(d) calculations. In (3) the factor of correlation r is greatest, the factor at ν_e is close to one, and the constant term is close to zero. The use of basis set 6-31+G(d) with diffuse functions does not result in an improvement of the correlation (4) between the experimental and calculated ^{35}Cl NQR frequencies in comparison with basis set 6-31G(d). Despite of the correlation energy correction of B3LYP and MP2 calculations, the ^{35}Cl NQR frequencies estimated using the results (5) - (8) show worse conformity with the experimental ones than that obtained using the RHF method.

The results obtained yield more opportunities for the application of quantum-chemical methods to use them in a comparison with the experimental ^{35}Cl NQR method for the decision of fundamental problems of organic and organometallic chemistry.

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