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Nuclear quadrupole coupling constants from the Gaussian density-functional method

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The reliability of density-functional theory in predicting nuclear quadrupole resonance (NQR) frequencies and nuclear quadrupole coupling constants was tested for a series of straight-chain chloroalkenes (vinyl chloride, 2-chloropropane, *cis*- and *trans*-1-chloropropene, *cis*-dichloroethylene, and tetrachloroethylene). The calculations were performed using the linear combination of Gaussian-type orbitals local-spin-density method and the generalized gradient approximation. The calculated NQR frequencies are in good agreement with experimental data. Less satisfactory agreement is found in the prediction of quadrupole coupling constants. The results show that the calculated NQR frequencies and nuclear quadrupole coupling constants can be used to study the electron distribution in molecular systems. [S1050-2947(96)06905-3]

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I. INTRODUCTION

The determination of the nuclear quadrupole coupling constant (NQCC) and nuclear quadrupole resonance (NQR) frequency, which can be calculated from the NQCC, is a challenge for experimental and theoretical methods. Experimentally the NQCC can be obtained from microwave spectroscopy [1–3]. Since the introduction of pure nuclear quadrupole resonance spectroscopy by Dehmelt and Krüger [4] a direct measurement of NQR frequencies [5–8] is possible too. The comparison of microwave and NQR data yields reliable experimental NQR frequencies. These frequencies are very useful to study experimentally the electron distribution in molecular systems. A relation between the NQR frequencies and the ionicity of chemical bonds has been introduced many years ago [9]. In solid-state chemistry NQR spectroscopy is used to distinguish different atomic environments. Unfortunately, the experimental NQCC and NQR measurements are scarce and were performed more than 20 years ago. So the reported literature is still today state of the art. Theoretical prediction can remedy this lack.

The theoretical calculation of NQR frequencies is based on the calculation of the electric field gradient (EFG) at a nucleus. The electric field gradients are very sensitive to basis set choice and size and often to electron correlation too. For this reason traditional correlated *ab initio* treatments [10] are only possible for systems of modest size. The computation of the EFG quickly becomes prohibitive as the number of atoms increases in the system. Density-functional theory (DFT) has recently emerged as an alternative tool to study electrostatic properties such as electrical moments [11] and electrostatic potentials [12]. The successful calculation of basic electrostatic properties in the DFT framework has motivated us to calculate NQR frequencies with a DFT method. In order to have a reliable reference we have selected a set of chlorinated alkenes, including vinyl chloride, 2-chloropropane, 1-chloropropene (*cis* and *trans* structure), *cis*-dichloroethylene, and tetrachloroethylene, as test molecules. Experimental data for the NQCC And NQR frequencies of ^{35}Cl resonance as well as a systematic discussion of the experimental data for these molecules are available in the literature [6,13].

II. THEORETICAL BASIS

In this paper we will show that DFT methods are able to predict reliable NQR frequencies for ^{35}Cl resonance. All calculations have been performed with the deMon [14] package. The experimental geometries have been used for all chloroalkenes [15]. The local-spin-density (LSD) calculations were performed with the exchange energy functional of the homogeneous electron gas and the corresponding correlation energy functional parametrized by Vosko, Wilk, and Nusair [16]. For the generalized gradient approximation (GGA) calculations the exchange energy functional of Perdew [17] and the correlation energy functional of Perdew and Wang [18] were employed. The basis sets used are the *DZVP* and *TZVP* standard basis sets of deMon [19]. These basis sets were optimized for the local-spin-density approximation and have been shown to perform well also for the generalized gradient approximation. For the fitting of the Coulomb and exchange-correlation contribution during the self-consistent field (SCF) iterations the auxiliary function set *A*2 was used. The orbital basis sets and auxiliary functions (for the notation see Ref. [20]) are

Atom	*DZVP*	*TZVP*	*A*2
C	(621/41/1)	(71111/411/1)	(4,3;4,3)
Cl	(6321/521/1)	(73111/6111/1)	(5,4;5,4)
H	(41)	(41)	(4;4)

The EFG calculations were performed with the recently developed deMon-property package [21]. In this program the components of the EFG tensor are defined over the negative second derivatives of the electrostatic potential $(U(R)$,

$$\left(\frac{\partial \varepsilon_i}{\partial X_j}\right)_{\mathrm{R}} = -\left(\frac{\partial^2 U}{\partial X_i \partial X_j}\right)_{\mathbf{R}} = \sum_{a,b} P_{ab} \langle \mathbf{a} | \hat{A}(\mathbf{1}_i + \mathbf{1}_j) | \mathbf{b} \rangle - \sum_{B} Z_B \frac{3(B_i - R_i)(B_j - R_j) - \delta_{ij} (\mathbf{B} - \mathbf{R})^2}{|\mathbf{B} - \mathbf{R}|}, \tag{1}$$

where we used the notation $\langle \mathbf{a} | \hat{\mathrm{A}}(\mathbf{1}_i + \mathbf{1}_j) | \mathbf{b} \rangle$ for the electric

TABLE I. Comparison of calculated ^{35}Cl NQR frequencies with experimental NQR and microwave data for chloroalkenes. All frequencies are in MHz.

	Method					
	DZVP basis		*TZVP* basis		Experiment[a]	
Molecule	LSD	GGA	LSD	GGA	NQR	Microwave[b]
Vinyl chloride	35.26	35.50	34.32	33.80	33.41	35.19
2-chloropropene	34.74	34.32	33.98	33.38	32.62	34.31
trans-1-chloropropene	35.85	35.19	34.95	34.21	33.42[c]	35.60
cis-1-chloropropene	34.95	34.69	34.10	33.58	33.42[c]	
cis-dichloroethylene	36.53	36.09	35.51	34.94	34.97	
Tetrachloroethylene	39.39	38.85	38.23	37.51	38.53	

[a] From Ref. [6].

[b] Calculated from microwave data of the gas phase quadrupole coupling constants in the C—Cl bond axis system.

[c] NQR frequency for a *cis-trans* mixture.

field gradient integrals over contracted Gaussian-type orbitals. For the calculation of these integrals the algorithm of Obara and Saika [22] is used. The P_{ab} are elements of the density matrix and Z_b is the nuclear charge of atom B. For the calculation of the EFG tensor at a nucleus A in a molecule the second summation in Eq. (1) runs over all atoms of the molecule except A. With these EFG tensor components the traceless EFG tensor V can be constructed.

NQR spectroscopy is based on the magnetic dipole transitions induced between the electric quadrupole energy levels of nuclei located in the inhomogeneous electric field of the molecule. In the principal axis system of the traceless EFG tensor V the nuclear quadrupole coupling Hamiltonian in atomic units is

$$\hat{H}_Q=\frac{Q}{2I(2I-1)}(V_{xx}\hat{I}_x^2+V_{yy}\hat{I}_y^2+V_{zz}\hat{I}_z^2), \tag{2}$$

where Q is the scalar nuclear quadrupole moment (-0.0797 barns for ^{35}Cl), I is the nuclear spin quantum number ($I=\frac{3}{2}$ for chlorine), V_{xx}, V_{yy}, V_{zz} are the eigenvalues of the traceless EFG tensor, and $\hat{I}_x$, $\hat{I}_y$, $\hat{I}_z$ are the components of the nuclear spin operator. From Eq. (2) it is seen that the quadrupole interaction energy is only different from zero if $Q\neq 0$ and the electric field at the nucleus is inhomogeneous. To simplify the description for an arbitrary EFG we now introduce the anisotropy parameter η defined as

$$\eta=\frac{V_{xx}-V_{yy}}{V_{zz}}. \tag{3}$$

With this anisotropy parameter and the eigenvalue equation of the nuclear spin operator, the Hamiltonian for the nuclear quadrupole coupling becomes

$$\hat{H}_Q=\frac{QV_{zz}}{4I(2I-1)}\left[3\hat{I}_z^2-I(I+1)+\frac{\eta}{2}(\hat{I}_+^2+\hat{I}_-^2)\right], \tag{4}$$

where $\hat{I}_+$ and $\hat{I}_-$ are the usual shift operators for spin and angular momentum operators. To obtain a unique orientation of the principal axis system at the atom we use the convention

$$|V_{zz}|>|V_{yy}|\geqslant|V_{xx}| \tag{5}$$

for the eigenvalues of the traceless EFG tensor. This convention also ensures that the anisotropy parameter η lies between zero and one.

For a spin $I=\frac{3}{2}$ nucleus the following two doubly degenerated energy levels for the nuclear quadrupole interaction can be obtained from Eq. (4):

$$E_{\pm 1/2}=-\frac{QV_{zz}}{4}\left(1+\frac{\eta^2}{4}\right)^{1/2}, \quad E_{\pm 3/2}=\frac{QV_{zz}}{4}\left(1+\frac{\eta^2}{3}\right)^{1/2}. \tag{6}$$

The corresponding NQR frequency is then given by

$$\nu=\frac{QV_{zz}}{2}\left(1+\frac{\eta^2}{3}\right)^{1/2}. \tag{7}$$

III. RESULTS AND DISCUSSION

In Table I we give our calculated NQR frequencies with the *DZVP* and *TZVP* basis sets. For both basis sets LSD and GGA calculations were performed. We also have listed in this table experimental solid-state NQR frequencies and calculated frequencies from microwave data. For the calculation of NQR frequencies from microwave data the computed quadrupole coupling constants have to be transformed in the EFG principal axis system. All the reported microwave data were computed under the assumption that the EFG principal axis system coincided with the C—Cl bond axis. This may, or may not, greatly affect the values of the calculated frequencies from microwave data; the magnitude of the resulting error depends upon the geometry of the molecule. The experimental solid-state NQR frequencies of the chloroalkenes show an ordering one expects from the inductive (I) effect. When, therefore, the hydrogen atom on the α carbon

TABLE II. Comparison of calculated nuclear quadrupole coupling constants χ_{xx}, χ_{yy}, χ_{zz} (in MHz) and anisotropy parameter η with microwave data for chloroalkenes.

Molecule	*TZVP* GGA				Microwave[a]			
	χ_{zz}	χ_{yy}	χ_{xx}	η	χ_{zz}	χ_{yy}	χ_{xx}	η
Vinyl chloride	67.37	−38.62	−28.75	0.146	70.16	−40.07	−30.09	0.142
2-chloropropene	66.46	−38.87	−27.59	0.170	68.52	−37.48	−31.04	0.094
trans-1-chloropropene	68.30	−37.97	−30.32	0.112	72.2	−39.6	−31.6	0.113
cis-1-chloropropene	66.90	−38.73	−28.17	0.158	62.38	−31.76	−31.05	0.011
cis-dichloroethylene	69.49	−41.31	−28.18	0.189				
Tetrachloroethylene	74.86	−41.80	−33.06	0.117				

[a] From Ref. [6]. We have changed the signs of the literature values so as to conform with our definitions.

in vinyl chloride is substituted by a methyl group to form 2-chloropropene, the $+I$ effect of the methyl group increases the ionicity of the C—Cl bond. This increased ionicity decreases the NQR frequency. In the case of 1-chloropropene (*cis* and *trans*) a methyl group is substituted for one of the hydrogens on the β carbon of vinyl chloride. The inductive effect is primarily electrostatic and falls off with distance; as a consequence, the reduction of frequency as compared with vinyl chloride is not so pronounced in this case as with 2-chloropropene. For the *trans* isomer the frequency is even increased. Unfortunately the experimental data for these molecules are not very reliable. The microwave data suffer from the high sensitivity of the orientation of the EFG principal axis system and the solid-state NQR frequency is measured for a *cis*-*trans* mixture. In the case of *cis*-dichloroethylene the addition of the electron-with-drawing chlorine on the β carbon in vinyl chloride leads to a $-I$ effect which decreases the ionicity of the C—Cl bond. The increased NQR frequency compared to vinyl chloride reflects this situation. Finally tetrachloroethylene, in which all four hydrogens of vinyl chloride are substituted with chlorine atoms, has the largest $-I$ effect of all the studied molecules and therefore the largest NQR frequency.

The agreement of the calculated NQR frequencies from the *TZVP* GGA with the experimental ones is within the deviation arising from solid-state effects (~0.5 MHz). However, the calculated NQR frequencies include no temperature effects. The reported experimental NQR frequencies were measured at 77 K (for *cis*-dichlorethylene at 20 K). From the comparison of data in the literature we expect that the temperature effect is of the same order as the solid-state effect. The change of the basis set from *DZVP* to *TZVP* results in a downward shift of the NQR frequencies by almost 1 MHz. A test calculation of the NQR frequency of vinyl chloride with a more extended basis set (medium-size polarized basis [23]) showed a downward shift of less than 0.5 MHz compared to the *TZVP* results. Therefore our *TZVP* GGA results are quite reliable for a qualitative comparison with experimental NQR frequencies. Anyway, for the chemical use of these frequencies only the correct prediction of the relative ordering is important and as Table I shows this can be correctly obtained with moderate basis sets from DFT calculations.

One advantage of the theoretical calculation of NQR frequencies is that no assumption for the orientation of the EFG principle axis system is necessary. After the diagonalization of the traceless EFG tensor, using the standard convention for the principal axis orientation [Eq. (5)], the anisotropy parameter η can be directly computed from the principal components of the EFG. In Table II experimental and calculated (*TZVP* GGA) anisotropy parameters and nuclear quadrupole coupling constants for the studied chloroalkenes are reported. At this point it is worth mentioning that the ordering of the calculated anisotropy parameters is almost identical for all presented levels of theory. The comparison of experimental and calculated nuclear quadrupole coupling constants shows qualitative agreement for the main NQCC component (χ_{zz}). Again it should be mentioned that our calculated values include no temperature effects. The other two calculated NQCC components (χ_{xx}, χ_{yy}) differ considerably from the available experimental data. The experimental values for *cis*-1-chloropropene have large errors in the microwave coupling constants [6]. The reason is the high sensitivity of the NQCC to the orientation of the principal axis system. The calculated anisotropy parameter reflects very nicely the anisotropic environment of the chlorine atom in the molecules. The small η value of tetrachloroethylene shows the low anisotropy in this molecule even though it has the largest $-I$ effect. The substitution of one chlorine on the β carbon of vinyl chloride increases mostly the anisotropy at the chlorine atom. For 2-chloropropene the calculated η value is larger as in vinyl chloride. We expected this because the substitution of a hydrogen atom at the α carbon in vinyl chloride by a methyl group should increase the anisotropy of the system. However, the experimental data show the opposite effect. In this case further experimental and theoretical investigations are necessary. The high sensitivity of the anisotropy parameter is demonstrated in the case of the *cis*-*trans* isomers of 1-chloropropene. The increased η value of *cis*-1-chloropropene compared with *trans*-1-chloropropene nicely shows the increased anisotropy in the *cis* isomer. Unfortunately, the experimental data for these molecules are not reliable, as we have already discussed. This example also shows the successful combination of theoretical and experimental data for the interpretation of NQR frequencies.

IV. CONCLUSION

In summary, we have shown that NQR frequencies can be successfully calculated with DFT methods. With the inclusion of GGA corrections a reliable prediction of NQR frequencies for very similar systems, like the discussed chloroalkenes, is possible. The theoretical calculated nuclear quadrupole coupling constants differ considerably from the available experimental data. The reason for this difference is the possible error in the experimental NQCC due to deviation in the principal axis orientation and the neglect of temperature effects in the calculated NQCC. The calculated NQR frequencies and NQCC are very sensitive to the molecular environment and therefore are useful probes for weak interactions. The combination of experimental and theoretical NQR data can be very useful for the analysis of the molecular and electronic structure, as this work demonstrates.

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