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MNDO refinement of the Townes—Dailey theory. Calculation of NQR frequencies of chloro-containing compounds

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Corrections accounting for the effect of the differences in p-electron energies on the electric field gradient are suggested and justified in the framework of Townes—Dailey theory. MNDO calculations of 31 chloro-containing molecules with full geometry optimization were used to evaluate the ^{35}Cl NQR frequencies. The correlational relationships between experimental and calculated NQR frequencies are compared.

Key words: ^{35}Cl NQR; Townes—Dailey theory, chloro-containing compounds; quantum chemical calculations, MNDO method.

The question of how accurate the calculations of the nuclear quadrupole interaction (NQI) constants by means of various semiempirical methods are addressed in several papers.[1,2] Obviously, the accuracy depends both on the abilities of the particular method and on the level of approximation accepted for the evaluation of NQI constants using the corresponding electronic wave functions. The exact calculation of NQI constants involves substantial computational difficulties and can be done only within *ab initio* methods. Almost all semiempirical approaches use the Townes—Dailey approximation,[3–5] in which only the contribution to the electric field gradient (EFG) originating from the valence p-electrons of the resonating atom is taken into account. Hence, the physical meaning of the Townes—Dailey model is quite simple: the EFG at the nucleus of a resonating atom in a molecule is assumed to be equal to that of an individual atom whose electronic distribution is identical to that of the resonating atom. Here we attempt to improve the Townes—Dailey approximation and study the effect of this refinement on the MNDO calculations of ^{35}Cl NQR frequencies.

Using the Townes—Dailey approximation,[3–5] let us consider the EFG created by the valence p-electrons on the nucleus of an individual atom. Their distribution over the orbitals is described by a 3×3 population—bond order matrix. The simplest form of this matrix is the diagonal representation when only the diagonal elements (P_{xx}, P_{yy}, and P_{zz}), which correspond to the electronic populations of p-type atomic orbitals (AOs) are nonvanishing. Using the explicit expressions for the quadrupole interaction operator in the p-AO basis,[6] it is easy to show that the diagonal element of the EFG tensor (eq_{zz}) has the following form

$$eq_{zz} = \frac{4e}{5}\left(\left\langle r_z^{-3}\right\rangle P_{zz} - \frac{\left\langle r_x^{-3}\right\rangle P_{xx} + \left\langle r_y^{-3}\right\rangle P_{yy}}{2}\right), \qquad (1)$$

where $\left\langle r_z^{-3}\right\rangle = \int \frac{\varphi_z^2 dV}{r^3}$ is the average value of the cube of

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the reciprocal of the distance between the nucleus and the electron occupying the p_z-AO. The analogous equations can be written for eq_{xx}, eq_{yy} and $\langle r_x^{-3}\rangle$, $\langle r_y^{-3}\rangle$.

Assuming that all p-AOs are equivalent, the well-known Townes—Dailey equation can be derived from Eq. (1):

$$eq_{zz} = eq_{at}\left(P_{zz} - \frac{P_{xx} + P_{yy}}{2}\right), \qquad (2)$$

where $eq_{at} = \frac{4}{5}e\left\langle r^{-3}\right\rangle$ is an empirical constant equal to the EFG created by a p-electron along the symmetry axis of its AO. This assumption does not take into account changes in $\langle r^{-3}\rangle$ caused by alterations of molecular polarity, which can significantly perturb the electronic distribution on the resonating atom.

Taking into account the different degrees of diffusive character of AOs (*i.e.*, evaluating $\langle r^{-3}\rangle$), requires a knowledge of their analytical representation. Earlier,[7] for calculations of NMR shielding constants, it was suggested that AOs be approximated by Slater-type orbitals for which

$$\left\langle r^{-3}\right\rangle_{lin} = \frac{2\xi^3}{n(n-1)(2n-1)},$$

where n is the principle quantum number and ξ is the exponential of the AO determined by Slater's rules, which is assumed to be the same for all three p-AOs and is a function of the total population of an atom.[6] This dependence written as $\langle r^{-3}\rangle = \lambda_{lin}\xi^3$ with the adjustable empirical parameter λ_{lin} has been used by several authors.[8]

Within this approach the diagonal element eq_{zz} of the EFG tensor at the nucleus of an individual atom with P_{xx}, P_{yy}, and P_{zz} electronic populations of P-AOs obeys the equation

$$eq_{zz} = k\xi^3\left(P_{zz} - \frac{P_{xx} + P_{yy}}{2}\right), \qquad (3)$$

where k is an empirical constant. This approximation does not separate EFG created by the electrons that occupy "chemically-nonequivalent" AOs, such as, for instance, a p-AO lone-pair and the p-AOs of a σ-bond.

There exists, however, an alternative way to account for the dependence of $\langle r^{-3}\rangle$ on the energy of p-electrons, which takes their nonequivalence into consideration. For this, let us evaluate the energy of the electron occupying the φ_μ AO in a molecule using the MNDO approach, *i.e.*, let us try to segregate the one-center contributions from the total electronic energy according to the Townes—Dailey approximation and then calculate the EFG tensor at the nucleus of an individual atom with the same electronic energy distribution as the resonating atom in the molecular environment.

In the SCF MO LCAO method the total electronic energy of a molecule is expressed[10] as

$$E = \sum_\mu \sum_\nu \frac{H_{\mu\nu} + F_{\mu\nu}}{2} P_{\mu\nu},$$

where $H_{\mu\nu}$, $F_{\mu\nu}$, and $P_{\mu\nu}$ are the matrix elements of the core operator, the Fockian, and the population—bond order matrix, respectively. This energy may be expanded into one- (E_A) and two-center (E_{AB}) contributions depending on whether the μ and ν orbital indices refer to the same (A) or different (A, B) atoms. Provided that μ, ν ∈ A and λ, σ ∈ B, we obtain:

$$E = \sum^{A} E_A + \sum^{A}\sum^{B} E_{AB},$$

where

$$E_A = \sum_\mu^A \sum_\nu^A \frac{H_{\mu\nu} + F_{\mu\nu}}{2} P_{\mu\nu}$$

and

$$E_{AB} = \sum_\mu^A \sum_\lambda^B \left(H_{\mu\lambda} + F_{\mu\lambda}\right)P_{\mu\lambda}.$$

In order to clarify the degree to which A and B atoms participate in bonding with one other, the E_{AB} term should be separated into the contributions belonging to the atomic partners. The choice of the criteria for this separation is ambiguous. In the framework of the MNDO approach, the nondiagonal $H_{\mu\lambda}$ and $F_{\mu\lambda}$ matrix elements can be calculated as follows:

$$H_{\mu\lambda} = \frac{1}{2}\left(\beta_\mu^A + \beta_\lambda^B\right)S_{\mu\lambda},$$

$$F_{\mu\lambda} = H_{\mu\lambda} - \frac{1}{2}\sum_\nu^A \sum_\sigma^B P_{\nu\sigma}(\mu\nu,\lambda\sigma),$$

where $S_{\mu\lambda}$ is the overlap integral between the φ_μ and φ_λ AOs, $(\mu\nu,\lambda\sigma)$ are Coulomb two-center integrals, and β_μ^A, β_λ^B are empirical parameters which depend on the nature of the AOs of atoms A and B. Hence, E_{AB} may be expanded into E'_A and E'_B as

$$E_{AB} = E'_A + E'_B = \sum_\mu^A \sum_\lambda^B \left(H_{\mu\lambda} + F_{\mu\lambda}\right)P_{\mu\lambda}\frac{\beta_\mu^A}{\beta_\mu^A + \beta_\lambda^B} + \sum_\mu^A \sum_\lambda^B \left(H_{\mu\lambda} + F_{\mu\lambda}\right)P_{\mu\lambda}\frac{\beta_\lambda^B}{\beta_\mu^A + \beta_\lambda^B}.$$

Then, the model electronic energy of the resonating atom A will be expressed as the double sum

$$\tilde{E}_A = E_A + E'_A = \sum_\mu^A \left[\sum_\nu^A \frac{H_{\mu\nu} + F_{\mu\nu}}{2} P_{\mu\nu} + \sum_\lambda^B \left(H_{\mu\lambda} + F_{\mu\lambda}\right)P_{\mu\lambda}\frac{\beta_\mu^A}{\beta_\mu^A + \beta_\mu^B}\right],$$

where the contributions E_μ connected with the φ_μ AO can be selected. For a resonating atom for which the

population—bond order submatrix of the p-electrons is diagonal,

$$E_\mu = \frac{H_{\mu\mu} + F_{\mu\mu}}{2} P_{\mu\mu} + \sum_\lambda^B \left(H_{\mu\lambda} + F_{\mu\lambda}\right) P_{\mu\lambda} \frac{\beta_\mu^A}{\beta_\mu^A + \beta_\lambda^B} .$$

Following the approach described previously,[7,8] let us approximate the φ_μ AO by Slater functions. The MNDO method uses the following equation

$$H_{\mu\mu} = U_{\mu\mu} + \sum^B V_{\mu\mu,B},$$

where $U_{\mu\mu}$ is a parameter describing the energy of the electron occupying the φ_μ AO in the field of the core of atom A and the term $\sum^B V_{\mu\mu,B}$ accounts for the attraction of this electron to the cores of the other atoms in the molecule. Therefore, calculating the energy E_μ for an individual atom one should assume that $H_{\mu\mu} = U_{\mu\mu}$.

Further, the $F_{\mu\mu}$ matrix element for a molecule is

$$F_{\mu\mu} = U_{\mu\mu} + \sum_\nu^A P_{\mu\nu}\left[(\mu\mu, \nu\nu) - \frac{1}{2}(\mu\nu, \mu\nu)\right] + \sum^B V_{\mu\mu,B} + \sum_\lambda^B \sum_\sigma^B P_{\lambda\sigma}(\mu\mu, \lambda\sigma),$$

where $(\mu\mu,\nu\nu)$, $(\mu\nu,\mu\nu)$ are the one-center Coulomb and exchange integrals, the term $\sum_\lambda^B \sum_\sigma^B P_{\lambda\sigma}(\mu\mu, \lambda\sigma)$ represents the contribution from mutual repulsion between the electron occupying the φ_μ AO and the electrons of atom B. One can suggest that for molecules of low polarity this term is compensated by $\sum^B V_{\mu\mu,B}$ term considered above. Thus, $F_{\mu\mu}$ for the individual atom can be set equal to the corresponding element of the Fockian matrix for the molecule.

Summarizing the considerations given above, we can express the energy of an electron occupying the φ_μ AO in individual atom as

$$E_\mu = \frac{U_{\mu\mu} + F_{\mu\mu}}{2} P_{\mu\mu} + \sum_\lambda^B \left(H_{\mu\lambda} + F_{\mu\lambda}\right) P_{\mu\lambda} \frac{\beta_\mu^A}{\beta_\mu^A + \beta_\lambda^B}.$$

At the same time, the energy of an electron occupying a Slater-type AO with the exponential ξ obeys the equation[9]

$$E = -\xi^2 R,$$

where R is Rydberg's constant. If $P_{\mu\mu} \neq 1$ the equation transforms into

$$E_\mu = -R\xi_\mu^2 P_{\mu\mu}.$$

Equating the two above expressions for E_μ, one can determine the exponential ξ_μ:

$$\xi_\mu = \left[\frac{\frac{U_{\mu\mu} + F_{\mu\mu}}{2} P_{\mu\mu} + \sum_\lambda^B \frac{\left(H_{\mu\lambda} + F_{\mu\lambda}\right) P_{\mu\lambda} \beta_\mu^A}{\beta_\mu^A + \beta_\lambda^B}}{-RP_{\mu\mu}}\right]^{1/2} . \quad (4)$$

In order to check the efficiency of the corrections suggested above, we performed calculation of molecules of chloro-containing substances by the MNDO method with full geometry optimization (Table 1). To avoid the diagonalization of the population-bond order matrix for the 3p-AOs of the Cl atom, the Cl—X bond was directed along the coordinate axis. The ^{35}Cl NQR frequencies were determined by the equation[3]

$$\nu = \frac{e^2 Q q_{zz}}{2h}\left(1 + \frac{\eta^2}{3}\right)^{1/2},$$

Table 1. Experimental (ν_{exp}/MHz) and calculated (ν_1–ν_3/MHz) ^{35}Cl NQR frequencies

Compound	ν_{exp}	ν_1	ν_2	ν_3
FCl **(1)**	70.700	61.881	62.965	68.106
MeOCl **(2)**	57.960	52.802	52.690	56.416
Cl_2 **(3)**	54.247	54.247	54.247	54.247
C_2H_4NCl **(4)***	45.604	46.578	45.730	47.167
$(NO_2)_3CCl$ **(5)**	42.950	51.230	51.509	48.845
CCl_4 **(6)**	40.630	46.871	46.302	43.840
SCl_2 **(7)**	39.342	40.539	39.171	36.907
$CHCl_3$ **(8)**	38.281	44.757	43.892	40.657
SO_2Cl_2 **(9)**	37.720	38.316	36.660	36.569
ICl **(10)**	37.184	42.054	40.524	37.308
PhSCl **(11)**	37.016	39.631	37.994	35.433
$CSCl_2$ **(12)**	36.261	44.739	44.180	40.624
CH_2Cl_2 **(13)**	35.991	42.465	41.294	37.485
S_2Cl_2 **(14)**	35.800	41.542	40.168	38.206
$COCl_2$ **(15)**	35.650	44.030	43.311	40.828
PhCl **(16)**	34.621	44.888	44.060	39.462
MeCl **(17)**	34.029	40.635	39.148	35.303
PCl_5 (eq.) **(18)**	33.750	44.069	43.178	41.427
$CHCl{=}CH_2$ **(19)**	33.411	43.413	42.422	37.543
$SOCl_2$ **(20)**	31.795	32.300	30.427	30.355
Me_3CCl **(21)**	31.065	40.617	39.062	35.991
$MeOCH_2Cl$ **(22)**	30.011	37.673	35.946	35.807
$PSCl_3$ **(23)**	29.723	41.152	40.017	37.884
PCl_5 (ax.) **(24)**	29.250	37.023	35.321	35.141
MeCOCl **(25)**	28.963	38.082	36.337	33.658
$POCl_3$ **(26)**	28.960	40.189	38.925	37.162
PCl_3 **(27)**	26.156	32.891	31.420	28.127
$GeCl_4$ **(28)**	25.661	27.996	26.021	21.368
$SiCl_4$ **(29)**	20.391	30.085	28.192	23.056
Me_3SiCl **(30)**	16.463	25.398	23.297	17.000
$AlCl_4^-$ **(31)****	11.312	23.383	21.524	14.466

Note: ν_1 — calculated by Townes—Dailey equation; ν_2 — calculated with ξ values determined by Slater's rules; ν_3 — calculated by modified Eq. (5).

* *N*-Chloroaziridine. ** $NaAlCl_4$.

where eQ is the nuclear quadrupole moment (in electron charge units) and eq_{zz} is the maximum component of the EFG tensor along the Cl—X bond. When the asymmetry parameters η are small, which is the case for almost all of the molecules under study, one can assume that

$$\nu \approx \frac{e^2 Q q_{zz}}{2h} .$$

In particular, at $\eta = 0.3$ the relative error of this approximation does not exceed 1.5 %.

The NQR frequencies were calculated from the MNDO data in three ways:

1. According to the Townes—Dailey equation (2):

$$\nu_1 = k_1 \left(P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right).$$

2. By Eq. (3):

$$\nu_2 = k_2 \xi^3 \left(P_{zz} - \frac{P_{xx} + P_{yy}}{2} \right),$$

with ξ values determined by Slater's rules,[5] namely, $\xi = (6.1 - 0.35q_{Cl})/3$, where q_{Cl} is the calculated charge on the chlorine atom.

3. By Eq. (5), obtained from Eq.(1) taking into account the dependence of $\langle r_\mu^{-3} \rangle$ on ξ_μ:

$$\nu_3 = k_3 \left(\xi_z^3 P_{zz} - \frac{\xi_x^3 P_{xx} + \xi_y^3 P_{yy}}{2} \right), \qquad (5)$$

where ξ_μ were found from Eq. (4).

In all three approaches k_1, k_2, and k_3 were considered to be empirical parameters. In this work they were calculated from the measured ^{35}Cl frequency according to the general formula $k_i = 54.247/X_i$, where X_i is the value of the corresponding factor in the expressions for ν_i obtained from MNDO calculations of the Cl_2 molecule. Thus, as in the original version of the Townes—Dailey approximation, the chlorine molecule was chosen as a reference point.

The results of the calculations are summarized in Table 1. In order to process the most extended range of experimental frequencies of the Cl atom, we chose compounds that could be treated within the MNDO approximation. This selection of molecules covers ~80 % of the range and is the most representative for this kind of correlation to date.

The following correlations exist between the experimental NQR frequencies and those calculated by different equations:

$$\nu_{exp} = -17.504 + 1.285\nu_1, \; r = 0.925, \; S = 4.413;$$

$$\nu_{exp} = -12.147 + 1.187\nu_2, \; r = 0.924, \; S = 4.424;$$

$$\nu_{exp} = -2.899 + 1.012\nu_3, \; r = 0.956, \; S = 3.388.$$

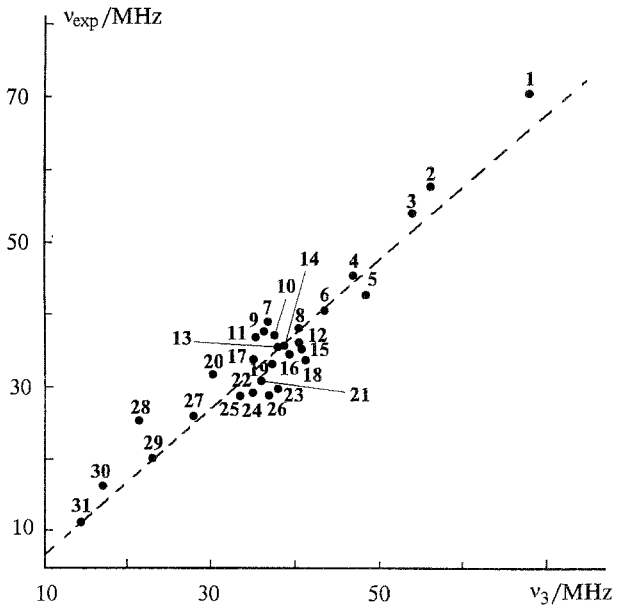

Fig. 1. Correlations between experimental ^{35}Cl NQR frequencies and those calculated taking into account the difference in electronic energies. The numbers correspond to the numbering of compounds in Table 1.

Obviously, in the optimal correlation relationship $y_{exp} = a + by_{calc}$ the constant term (a) should be close to zero, and the tangent (b) should approach unity. Under these conditions the calculated values will be practically coincide with the measured one. Therefore, the above equations reveal that the results of approximation 2 are qualitatively slightly better than those of approximation 1, although the corresponding r and S values are nearly the same. The improved approximation 3 is the best one since in the correlation equation the constant term has the minimum value and tangent factor is close to 1. The corresponding plot is shown in Fig. 1.

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