

Refinement of the Townes–Dailey Theory. MNDO Calculation of ^{35}Cl NQR Frequencies

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Within the framework of the Townes–Dailey theory some corrections have been suggested which make it possible to take account of the effect of differences in the p-electron energy on the electric field gradients and to improve the correlation between the experimental and theoretical NQR frequencies.

The present work is an attempt to account for the effect of p-orbital anisotropy within the framework of the Townes–Dailey theory.

The electric field gradients (EFG) built up by the valent p-electrons of an individual atom are considered in terms of the Townes–Dailey theory.^{1–3} The p-electron distribution on orbitals is described by a population-bond order sub-matrix for p-electrons of an atom in the molecule. The simplest form of the matrix is in its diagonal view where only the P_{xx} , P_{yy} and P_{zz} diagonal elements differ from zero. When the explicit form of the matrix elements of the quadrupole interaction operator for p-electrons is used, the EFG tensor diagonal element eq_{zz} is described by the following expression:⁴

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

where $\langle r_z^{-3} \rangle$ is the mean value of the cubic inverse distance from the nucleus to the electron on the p_z -orbital. From equation (1) the Townes–Dailey equation can readily be derived:

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

The eq_{at} value is supposed to be equal for all atomic orbitals (AO) of all compounds.

It is proposed⁵ to take into account the proportionality between $\langle r_\mu^{-3} \rangle$ and ξ_μ^3 , where ξ_μ is an exponent index for AOs of the Slater type, which remains isotropic for all AOs of the p-type but depends on the charge on the atom.

It is possible to account for $\langle r_\mu^{-3} \rangle$ anisotropy, for example, through the energetic characteristics of electrons. In accordance with the Townes–Dailey theory, EFG on the resonating atom A in the molecule are equal to those on the individual atoms, both atoms being supposed to have identical electronic distribution and energy. The electron energy is defined by the following expression:⁶

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

where $H_{\mu\nu}$, $F_{\mu\nu}$, $P_{\mu\nu}$ are elements of the Hamiltonian, Fockian and population-bond order matrix, respectively. Assuming that diatomic contributions can be divided proportionally between the resonance integrals β_μ^A and β_ν^B of the corresponding atoms, which are the parameters of the MNDO method, one can derive an expression for the electronic energy of atom A with a correction for diatomic interactions ($\mu, \nu \in A$ and $\lambda \in B$ in this case).

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

Since the Townes–Dailey theory operates with only an individual atom, $H_{\mu\mu}$ can be replaced by $U_{\mu\mu}$: a one-centre, one-electron energy in the atomic framework field (also the calculation parameter). Therefore, in the diagonal view of the density matrix the energy of an electron on the ϕ_μ AO in the resonating atom field will be as follows:

$$E_\mu = \frac{U_{\mu\mu} + F_{\mu\mu}}{2} P_{\mu\mu} + \sum_\lambda^B (H_{\mu\lambda} + F_{\mu\lambda}) P_{\mu\lambda} \frac{\beta_\mu^A}{\beta_\mu^A + \beta_\lambda^B} \quad (3)$$

On the other hand, the energy of the electrons with a $P_{\mu\mu}$ population on the ϕ_μ orbital of the Slater type is described as:⁷

$$E_\mu = -R\xi_\mu^2 P_{\mu\mu} \quad (4)$$

where R is the Rydberg constant.

From equations (3) and (4) the ξ_μ exponent index can be derived:

Table 1 Experimental (ν_{exp})³ and theoretical ^{35}Cl NQR frequencies, calculated by equation (2) (ν_1) and (6) (ν_2).

Compound	ν_{exp}	ν_1	ν_2	Compound	ν_{exp}	ν_1	ν_2
FCI	70.700	61.881	68.106	CH ₃ Cl	34.029	40.635	35.303
POCl ₃	28.960	40.189	37.162	PCl ₅ eq.	33.750	44.069	41.427
Cl ₂	54.247	54.247	54.247	CHCl=CH ₂	33.411	43.413	37.543
PCl ₃	26.156	32.891	28.127	SOCl ₂	31.795	32.300	30.355
GeCl ₄	25.661	27.996	21.368	(CH ₃) ₃ CCl	31.065	40.617	35.991
CCl ₄	40.630	46.871	43.840	CH ₃ OCH ₂ Cl	30.011	37.673	35.807
SCl ₂	39.342	40.539	36.907	PSCl ₃	29.723	41.152	37.884
CHCl ₃	38.281	44.757	40.657	PCl ₅ ax.	29.250	37.023	35.141
SO ₂ Cl ₂	37.720	38.316	36.569	CH ₃ COCl	28.963	38.082	33.658
ICl	37.184	42.054	37.308	CH ₃ OCl	57.960	52.802	56.416
SiCl ₄	20.391	30.085	23.056	C ₂ H ₄ NCl ^a	45.604	46.578	47.167
CSCl ₂	36.261	44.739	40.624	(NO ₂) ₃ CCl	42.950	51.230	48.845
CH ₂ Cl ₂	35.991	42.465	37.485	C ₆ H ₅ SCl	37.016	39.631	35.433
S ₂ Cl ₂	35.800	41.542	38.206	(CH ₃) ₃ SiCl	16.463	25.398	17.000
COCl ₂	35.650	44.030	40.828	AlCl ₄ ^{-b}	11.312	23.383	14.466
C ₆ H ₅ Cl	34.621	44.888	39.462				

^a N-Chloroaziridine. ^b NaAlCl₄.

$$\xi_{\mu} = \left(\frac{U_{\mu\mu} + F_{\mu\mu} P_{\mu\mu} + \sum_{\lambda}^B \frac{(H_{\mu\lambda} + F_{\mu\lambda}) P_{\mu\lambda} \beta_{\mu}^A}{\beta_{\mu}^A + \beta_{\lambda}^B}}{-R P_{\mu\mu}} \right)^{\frac{1}{2}} \quad (5)$$

Equation (1) is transformed into equation (6) by use of the $\langle r_{\mu}^{-3} \rangle \sim \xi_{\mu}^3$ dependence and equation (5):

$$v_2 = k_2 \left((\xi_z)^3 P_{zz} - \frac{(\xi_x)^3 P_{xx} + (\xi_y)^3 P_{yy}}{2} \right) \quad (6)$$

To check the efficiency of modified equation (6) calculations of ^{35}Cl NQR frequencies were carried out using both equation (6) (v_2) and Townes–Dailey equation (2) (v_1) (Table 1), with the experimental chlorine NQR frequency (54.247 MHz)³ as the reference point in both cases.

The experimental frequencies correlate well with the calculated values:

$$v_{\text{exp}} = -17.504 + 1.285v_1 \quad r = 0.925 \quad S = 4.413$$

$$v_{\text{exp}} = -2.899 + 1.012v_2 \quad r = 0.956 \quad S = 3.388$$

For the second equation it is worth noting not only the better correlation parameters r and S but also the fact that the free member approaches zero, whereas the slope is closer to the value of unity, which corresponds to the coincidence of

the calculated and experimental data.

Thus, the ^{35}Cl NQR frequencies calculated using the modified Townes–Dailey equation (6) are in better agreement with experimental data.

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