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:

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

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

It is proposed[5] 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 $\beta_\lambda^{\mathrm{B}}$ 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 ($\mu, \nu \in \mathrm{A}$ and $\lambda \in \mathrm{B}$ in this case).

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

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:

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

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
FCl	70.700	61.881	68.106	CH_3Cl	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	$(CH_3)_3CCl$	31.065	40.617	35.991
CCl_4	40.630	46.871	43.840	CH_3OCH_2Cl	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_2Cl_2	37.720	38.316	36.569	CH_3COCl	28.963	38.082	33.658
ICl	37.184	42.054	37.308	CH_3OCl	57.960	52.802	56.416
$SiCl_4$	20.391	30.085	23.056	C_2H_4NCl[a]	45.604	46.578	47.167
$CSCl_2$	36.261	44.739	40.624	$(NO_2)_3CCl$	42.950	51.230	48.845
CH_2Cl_2	35.991	42.465	37.485	C_6H_5SCl	37.016	39.631	35.433
S_2Cl_2	35.800	41.542	38.206	$(CH_3)_3SiCl$	16.463	25.398	17.000
$COCl_2$	35.650	44.030	40.828	$AlCl_4^-$[b]	11.312	23.383	14.466
C_6H_5Cl	34.621	44.888	39.462				

[a] *N*-Chloroaziridine. [b] $NaAlCl_4$.

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

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

$$\nu_2 = k_2 \left((\xi_z)^3 P_{zz} - \frac{(\xi_x)^3 P_{xx} + (\xi_y)^3 P_{yy}}{2} \right) \qquad (6)$$

To check the efficiency of modified equation (6) calculations of ^{35}Cl NQR frequencies were carried out using both equation (6) (ν_2) and Townes–Dailey equation (2) (ν_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:

$$\nu_{\mathrm{exp}} = -17.504 + 1.285\nu_1 \qquad r = 0.925 \quad S = 4.413$$

$$\nu_{\mathrm{exp}} = -2.899 + 1.012\nu_2 \qquad r = 0.956 \quad S = 3.388$$

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.

This work was supported by the Russian Foundation for Fundamental Research (project no. 93-03-5201).

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Received: Moscow, 1st September 1994
Cambridge, 29th September 1994; Com. 4/05385K