An Interpretation of the Nuclear Quadrupole Coupling Constant for the HCl Molecule on the Basis of an “Ab Initio” Calculation

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The results of a LCAO MO SCF calculation of the quadrupole coupling constant of chlorine in the HCl molecule (carried out with a fairly extended set of basic orbitals) are analyzed. Sensible deformations of the internal shells and of the $p_z$-bonding, $p_y$-lone pair and $p_x$ type orbitals of the valence shell of chlorine are evidenced.

Die Ergebnisse einer verhältnismäßig ausgedehnten LCAO-MO-SCF-Rechnung zur Bestimmung der Quadrupolkopplungskonstanten für Chlor in HCl werden untersucht. Die Verzerrungen, die der Rumpf und die verschiedenen Zustände der Valenzschale erleiden, werden dabei gesondert wiedergegeben.

Les résultats d’un calcul LCAO-MO-SCF (avec un jeu d’orbitales assez étendu) de la constante de couplage quadrupolaire du Cl dans la molécule de HCl sont analysés. On trouve que et les couches internes et les orbitales $p_z$ liante, $p_y$ libre et $p_x$ de la couche de valence du chlore sont sensiblement déformées.

The “a priori” evaluation of a variable associated with a one-electron operator, such as the quadrupole coupling constant $e^2Q_A$ in an isolated molecule, requires, beside the knowledge of the nuclear quadrupole moment $eQ_A$ of the nucleus $A$, also a very accurate calculation of the ground state wave function of the molecule, which is necessary to evaluate the electric field gradient $e\mathbf{q}$.

When the electronic wave function is represented by a single Slater’s determinant, in the SCF-LCAO-MO approximation, the expectation value of the field gradient, can be written as:

$$e\mathbf{q} = 2 \text{tr} \mathbf{R} (e\mathbf{q}) - e \sum \chi_\alpha (3 \cos^2 \theta_{Ax} - 1) / r_A^3 ,$$

(1)

where $\mathbf{R} = \mathbf{C} \mathbf{C}^\dagger$, and $\mathbf{C}$ is the rectangular matrix of the coefficients which describe the molecular orbitals as linear combinations of a set of pre-selected basic functions $\chi$; $e\mathbf{q}$ is a matrix with elements:

$$(e\mathbf{q})_{rs} = e \int \chi_\alpha^* (1) [(3 \cos^2 \theta_{1A} - 1) / r_{1A}^3 ] \chi_s (1) \, dx ;$$

$r_A$ and $\theta_{Ax}$ (measured with respect to the $z$ axis), define the position of the generic nucleus $\alpha$, having a charge $Z_{\alpha}$, with respect to the quadrupolar nucleus $A$.

The lack of sufficiently approximate wave functions has led to the assumption of simplifying hypotheses. Therefore, it will be useful to reinterpret the results of a completely “ab initio” calculation using chemical intuition to make evident, as much as possible, the various contributions to the field gradient. To this purpose, the results of a SCF-LCAO-MO calculation will be used, that have been carried
out by the Authors [7] by the direct minimization of the energy through the density matrix $R$, as first proposed by McWeeny [4].

The selected set of basic functions is sufficiently more extended than the necessary minimum and is composed of 19 Slater-type functions, of which the orbital exponents are reported in Tab. 1. It is to note that this set cannot describe the small percent of π bonding that the molecule very probably has [5], and that the energy has not been minimized with respect to the orbital exponents.

In Tab. 4 of ref. [7] the matrices $R$ and $(eq)$, which are necessary for calculating equation (1), are reported. It is found:

$$
eq = (eq)_{el} + (eq)_{nucl} = 2 \text{tr} R (eq) - 2 \frac{e}{r_{\text{HCl}}} = 3.789 + 0.143 = 3.932 \text{ a. u.}
$$

Such a result gives, for the quadrupole coupling constant, the value $e^2qQ = 72.9 \text{ MHz}$, in good agreement with the assumed experimental value*.

To separate the various contributions of the molecular orbitals of the inner shells from those of the valence shell, let us refer to the matrix $C$ reported in Tab. 2.

Such a matrix has been calculated by diagonalizing the Fock's $F$ matrix, which had been obtained from the $R$ matrix of the system. The two orbitals $q^b$ and $q^{nb}$ are the following linear combinations:

$$q^b = 0.473218 q_{4s} + 0.880945 q_{5s}$$

$$q^{nb} = 0.880945 q_{4s} - 0.473218 q_{5s} ,$$

* The quadrupole coupling constant of gaseous HCl suggests that its value is very close to that of gaseous DCP, which amounts to 67.3 MHz [1].