Polarizability of ferrocene derivatives from quantum mechanical delta-function potentials

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The atomic bond and molecular polarizabilities of some ferrocene derivatives have been calculated using variational method and delta-function electronic wave functions. Scales have been presented, where the derivatives are classified in order of their polarization properties. Common trends and patterns of behaviour are recognized and discussed.

Lippincott and Stutman⁶⁴ proposed the use of one-dimensional delta-function potential model to calculate the bond and molecular polarizabilities of simple systems. The model has been successfully applied to larger molecules²⁴. In this note we have applied the method for the determination of bond and molecular polarizabilities of ferrocene and its derivatives and interpreted the results in terms of recent observations of Waite and Papadopoulous and others³⁶. These compounds contain aromatic cyclopentadienyl rings interacting with an Fe atom through their π-electron systems. These rings are staggered (D₅ₛ) and eclipsed (D₅₇) and difference in the electronic structure between the two forms is very small. These systems are of potential interest because they contain transition metal which may offer new properties due to the presence of low lying excited states in many cases. There can be tailoring of the metal-organic ligand interactions in these systems. Organometallics have recently attracted the interest of those who search for novel and efficient non-linear optical materials⁷¹⁰. Moreover the delocalized π-electron of the aromatic moieties in these systems have been shown to be instrumental in the formation of large hyperpolarizabilities.

Polarizability calculations

The average molecular polarizability (αₐ) can be expressed in terms of its principal components αₓₓ, αᵧᵧ, and αzz as,

\[ \alpha_{\text{M}} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \]  

where the principal components of the polarizability tensor are obtainable from the relation P = αE. The molecular polarizability tensor αᵢ is obtained by combining principal components of it for total j-bonds in the molecule, or

\[ \alpha_{ij} = \begin{bmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{bmatrix} \]  

If bonds of molecule have rotational symmetry about their axes, the following assumption is possible⁶¹,

\[ \alpha_{ij} = \alpha_{xx} = \alpha_{zz} \]  

Thus the computation of average molecular polarizability is left with the evaluation of parallel and perpendicular components and hence to sum it overall the bonds to obtain aggregated αₐ values. The concept of parallel and perpendicular components of polarizabilities and even the contribution by the non-bonding electrons to the parallel component is well documented in the delta-function potential technique⁶⁴.

The general expression for molecular polarizability expressed in cartesian coordinate system is given by,

\[ \alpha_{ij} = \frac{2}{3 \sum_{i=0}^{\infty} \frac{(\mu_{ij})^2 + (\mu_{ij})^2 + (\mu_{ij})^2}{E_i - E_0}} \]  

where \[ \langle \psi | \psi \rangle = \sum_{j} C_j | \psi_j \rangle \]  

\( e \) is the electronic charge, \( \psi_0 \) is the ground-state delta-function wave function, and \( E \) denotes the energy. To calculate the molecular polarizabilities for the general class of polyatomic molecules, Lippincott and Stutman⁶⁴ proposed an alternative and simple method than solving through Eq. 5 by the semi-empirical delta-function model of chemical binding⁶¹⁰. Here delta-function model is obtained by replacing the coulomb potentials in the Schrodinger equation of a molecular system with delta-function potentials. The molecular wave functions are obtained from linear combinations of atomic delta-function wave functions.
On the basis of the variational treatment first introduced by Hylleraas and Hasse, the xx component of the polarizability is expressed in the form,

$$\alpha_{xx} = \frac{4nA}{a_0} [(x_1 - x)^2 - (n - 1)(x_1 - x)(x_2 - x)]$$  \ldots (6)

where $x$ is the coordinate of any one of $n$ equivalence class of electrons, which falls in the first equivalence class, $x$ is the average coordinate of any one of these electrons, $A$ is the delta-function strength determined from the reduced electronegativity of the atom, and $a_0$ is the radius of first Bohr orbit. Since delta-function wave function does not allow interaction between the coordinates, $(x_1 - x)(x_2 - x) = 0$. The model with the mean delta-function strength predicts $x = 0$, so Eq. (6) becomes,

$$\alpha_{xx} = \frac{4nA}{a_0} |x|^2$$  \ldots (7)

Molecular polarizability consists of parallel and perpendicular components of the constituents of the bond polarizabilities. The bond parallel component is obtained from the contributions by the bonding and non-bonding electrons of the valence shell. The contribution of the bonding electrons is calculated using a linear combination of atomic delta-function wave functions of the nuclei involved in the bond, i.e. the expectation value of the electronic position squared $<x^2>$ along the bond axis is calculated, and this is used to evaluate the parallel component of bond polarizability $\alpha_{ib}$ from the equation,

$$\alpha_{ib} = \frac{4nA_{ib}}{a_0} <x^2>$$  \ldots (8)

where

$$<x^2> = \frac{R^2}{4} + \frac{1}{2} C_{R^2}$$  and $A_{ib} = (A_{i}A_{j})^{1/2}$  \ldots (9)

$n$ is the bond order and $R$ is the internuclear distance at equilibrium configuration, and $C_{R^2} = (n_1n_2N_1N_2)^{1/4}(A_{i2})^{1/2}$  \ldots (10)

where $n_1$·$n_2$ and $N_1$·$N_2$ stand for the principal quantum number and number of electrons making contribution to the bonding, respectively. For a heteronuclear bond, a polarity correction must be made in the parallel component of the bonding electrons to account for the charge density introduced by the electronegativity difference of the atoms.

The degree of polarity $\rho$ defined by Pauling is given as,

$$\rho = 1 - e^{-\frac{1}{4}(X_1 - X_2)^2}$$  \ldots (11)

The charge density in the bond region then should be related to the percent covalent character,

$$\sigma = e^{-\frac{1}{4}(X_1 - X_2)^2}$$  \ldots (12)

where $X_1$ and $X_2$ are the electronegativities of the atoms 1 and 2 respectively, on the Pauling scale. The corrected value of parallel component of bond polarizability is given by,

$$\alpha_{ip} = \alpha_{ib}$$  \ldots (13)

The contribution of non-bonded electrons is calculated by evaluating the contribution of electrons in the valence shell of each atom not involved in the bonding. Such calculations are made on the basis of octet rule as modified by Linnett in terms of a double quartet of electrons. This can be expressed as,

$$\alpha_{in} = \sum_j f_j \alpha_j$$  \ldots (14)

where $f_j$ is the fraction of valence electrons in the $j$th atom not involved in the bonding and $\alpha_j$ is the atomic polarizability of $j$th atom. The perpendicular component of the bond polarizability was obtained by empirical approach of Lippincott and Stutman, which is expressed as,

$$\Sigma 2\alpha_{ij} = \frac{(3N - 2n_b)}{N} \sum_j \frac{\alpha_j}{x_j^2}$$  \ldots (15)

where $N$ is the number of atoms and $n_b$ is the number of bonds in the molecule. The sum of the perpendicular components of the bond polarizability is given as,

$$\Sigma 2\alpha_{ij} = (3N - 2n_b) \sum_j \frac{\alpha_j}{x_j^2}$$  \ldots (16)

or

$$\sum 2\alpha_{ij} = n_{df} \sum_j \frac{\alpha_j}{x_j^2}$$  \ldots (17)

where $n_{df} = (3N - 2n_b)$, the residual atomic polarizability degrees of freedom obtainable from the consideration of symmetry and geometry of the molecular type. The $n_{df}$ value corresponding to every cyclopentadienyl ring has been taken as 17 and it is assumed that whatever substitutions are made on the ring, the $n_{df}$ value remains constant.
Table 1—Calculated values of molecular polarizabilities of ferrocene and its derivatives (10\(^{-25}\) cm\(^3\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Sigma \alpha_p)</th>
<th>(\Sigma \alpha_m)</th>
<th>(\Sigma 2\alpha_1)</th>
<th>(\alpha_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{C}_5\text{H}_5)_2\text{Fe})</td>
<td>379.173</td>
<td>40.667</td>
<td>180.893</td>
<td>200.244</td>
</tr>
<tr>
<td>(\text{Fe}-\text{NH}_2)</td>
<td>399.385</td>
<td>43.639</td>
<td>170.035</td>
<td>205.686</td>
</tr>
<tr>
<td>(\text{Fe}-\text{CHO})</td>
<td>417.568</td>
<td>44.613</td>
<td>172.52</td>
<td>211.567</td>
</tr>
<tr>
<td>(\text{Fe}-\text{CN})</td>
<td>411.809</td>
<td>43.639</td>
<td>179.692</td>
<td>211.713</td>
</tr>
<tr>
<td>(\text{Fe}-\text{CH}_3)</td>
<td>420.419</td>
<td>40.667</td>
<td>174.494</td>
<td>211.860</td>
</tr>
<tr>
<td>(\text{Fe}-\text{Cl})</td>
<td>404.068</td>
<td>52.564</td>
<td>188.316</td>
<td>214.982</td>
</tr>
<tr>
<td>(\text{Fe}-\text{C} = \text{CH})</td>
<td>431.885</td>
<td>43.639</td>
<td>179.397</td>
<td>217.317</td>
</tr>
<tr>
<td>(\text{Fe}-\text{CHO})</td>
<td>417.568</td>
<td>44.613</td>
<td>174.101</td>
<td>221.567</td>
</tr>
<tr>
<td>(\text{Fe}-\text{CO}-\text{CH}_3)</td>
<td>458.813</td>
<td>44.613</td>
<td>167.826</td>
<td>223.593</td>
</tr>
<tr>
<td>(\text{Fe}-\text{CH} = \text{CH})</td>
<td>448.217</td>
<td>40.667</td>
<td>174.081</td>
<td>220.995</td>
</tr>
<tr>
<td>(\text{CHO}-\text{Fe}-\text{CHO})</td>
<td>455.963</td>
<td>48.559</td>
<td>166.257</td>
<td>223.750</td>
</tr>
<tr>
<td>(\text{Fe}-\text{CH} = \text{CH}-\text{Ar})</td>
<td>655.521</td>
<td>40.667</td>
<td>340.873</td>
<td>345.687</td>
</tr>
<tr>
<td>(\text{CHO} - \text{Fe} - \text{CH} = \text{CH} - \text{Ar})</td>
<td>692.918</td>
<td>44.613</td>
<td>484.841</td>
<td>467.457</td>
</tr>
<tr>
<td>(\text{Ar} - \text{CH} = \text{CH} - \text{Ar})</td>
<td>927.947</td>
<td>40.667</td>
<td>523.210</td>
<td>571.624</td>
</tr>
<tr>
<td>(\text{Fe} - \text{CH} = \text{CH}-\text{Ar}-\text{CH} = \text{CH} - \text{Ar})</td>
<td>1110.330</td>
<td>31.314</td>
<td>523.210</td>
<td>571.624</td>
</tr>
</tbody>
</table>

Now the average molecular polarizability with no bond polarity corrections can be written as,

\[
\alpha_M = \frac{1}{3} \left[ \sum \alpha_{ib} + \sum f_i \alpha_i + \frac{3N - 2n_b}{N} \sum \alpha_j \right] \quad \ldots \quad (18)
\]

and with bond polarity correction it will be,

\[
\alpha_M = \frac{1}{3} \left[ \sum \alpha_p + \sum f_i \alpha_i + n_{df} \sum \frac{x_j^3 \alpha_j}{x_j^2} \right] \quad \ldots \quad (19)
\]

Equation (19) was used in the present calculation of average molecular polarizabilities.

**Results and discussion**

Assuming the isotropic nature of atoms, the atomic polarizabilities along the X-axis (\(\alpha_{xx}\)) were fixed using the delta-function strengths and relation \(\alpha_{xx} = (4/\alpha_0^3) \text{A}^3\). The delta function atomic polarizabilities of hydrogen, carbon and iron are \(5.92 \times 10^{-25}\), \(9.78 \times 10^{-25}\) and \(91.50 \times 10^{-25}\) cm\(^3\) respectively. The \(A\)-values are 1.000, 0.846 and 0.402 in a.u. respectively. The other values of atomic polarizabilities were taken from ref. 1.

The \(\alpha_M\) value for ferrocene is \(189.7 \times 10^{-25}\) cm\(^3\) whereas our theoretical value of \(\alpha_M\) is \(200.244 \times 10^{-25}\) cm\(^3\), which is in close agreement.

A deviation of the order of five per cent with experimental values may be caused due to several reasons of the mechanism of its structural interpretations i.e. the complex mechanisms of distribution of the nine valence electron pairs of ferrocene among 10(C–C) and 10(Fe–C) bonds. The (Fe–C) bonds show very small ionic character and treating the molecule on the basis of electron-neutrality principle, there are many compatible structures\(^\text{i}\). The most favoured structure in which the computed (Fe–C) bond length (2.06 Å) agrees with the experimental value (2.07 ± 0.01 Å) yield (Fe–C) bond number 0.513 and the partial ionic character 0.18.

Thus, considering the cyclopentadienyl ring and the iron atom of ferrocene to be electrically neutral, the available bonds to be treated within delta-function potential framework are 10(C–C), 10(C–H) and only (Fe–C) bonds. These bond components can be transferred from one molecule to another under similar bond environments. The rest two unshared pairs of electrons have also been considered to be effective for the parallel component whose contributions were computed with the help of atomic polarizability of iron and its fraction valence electrons not involved in binding, which is \(40.667 \times 10^{-25}\) cm\(^3\) (carbon and hydrogen have no electrons left in the valence shell).
The calculated values of molecular polarizabilities (in 10^{-25} \text{cm}^3) of ferrocene and its derivatives are given in Table 1. The polarizability is quite sensitive to geometry and therefore it would be better if the geometries be optimised at a common level of theory to avoid geometry effects in predictions. The small differences between experimental values and calculated values may be attributed to the intermolecular interactions and may be related to the loosening effect caused by the slight displacement of protons in the formation of hydrogen bonds between monomers. The more negative differences may be due to van der Waals’ interactions which causes tightening of the electronic system of the molecules.

The order of polarizability of different substituents in ferrocene derivatives is found to be as follows:

\[
\text{NH}_2 < \text{CHO} < \text{CN} < \text{CH}_2 < \text{Cl} < -\text{C} = \text{CH} < -\text{CH} = \text{CH}_2 < -\text{COCH}_3 < \text{CH}_2\text{Cl} < \text{CHCl}_2 < \text{CH}_2\text{I} < \text{CHI}_3,
\]

The trend specified above is a consequence of the important role of the delocalized \( \pi \)-electrons, which is common in these substrates. The main contributions connected with the iron atom and the interactions associated with it are considerably smaller. In the case of ferrocenes, \( \pi \)-electron delocalization through the ferrocene unit is not as effective as we observe in linear conjugated structures.

For most of the molecules, our calculated values are in reasonable agreement with the experimental values. This indicates the wide applicability of the delta-function model of chemical binding to complicated molecular systems and complex metal carbonyls.

**References**