Mobile charge density wave model for third order non-linearity of \( \pi \)-conjugate polymers

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A theoretical one dimensional model based on Hückel’s molecular orbital theory applied to one electron de-localized \( \pi \)-electron Hamiltonian in a conjugate chain of regular polyene (ignoring electron-electron repulsion) is developed. It demonstrates the dependence of third order non-linearity on the following: (a) the chain length, (b) linear correlation plot of \( \nu \) (C=C) versus \( 1/\lambda_{\text{res}} \) (parameters measured from linear spectroscopic technique of Raman and absorption spectroscopy), (c) ratio of the electron velocity to the sound velocity in the chain and (d) deformation potential coupling of the phonons to the on-site electronic charge density.

1 Introduction

The \( \pi \)-conjugate polymeric structures are known to have large values of non-resonant third order non-linearity. This large third order hyper-polarizability has been shown to reflect the effective \( \pi \)-electron conjugation\(^9\). Because of their relatively large non-resonant non-linear optical properties, organic polymers show promise for applications in optical switching and logic operators for optical computing and signal processing\(^9,10\). When an external uniform electric field of strength \( F \) acts upon a molecule of polarizability \( \alpha \), the induced dipole moment deviates from a simple linear dependence on the field and can be written as:

\[
\mu = \alpha F + \frac{1}{2} \beta F^2 + \frac{1}{6} \gamma F^3 + \ldots \quad (1)
\]

The coefficients \( \beta \) and \( \gamma \) (known respectively as the second and third order hyper-polarizability) are associated with the strength of the non-linear response to applied fields in the zero frequency limit. Since \( \beta \) is zero for systems with inversion symmetry, non-linear optical experiments for organic crystals and polymers have usually been devoted to the determination of \( \gamma \).

The first systematic investigation of \( \gamma \) of conjugate systems was carried out by Hermann et al\(^7\). This work generated considerable interest in conjugated structures and spurred theoretical analysis by Rustagi et al\(^11\), who recognised the importance of \( \pi \)-conjugation in determining \( \gamma \). Since then several theoretical studies have been reported\(^13,15\). Interest centres on these theoretical studies on enhancing \( \gamma \) and hence it is of extreme importance to understand the relationship between molecular structure and \( \gamma \) in order to predict structures with large third order process. The interest in the electronic structure of polyenes has grown tremendously after the suggestion that conformational defects such as solitons\(^12\) and polarons\(^13,14\) should account for the unusual transport properties.

In this paper, a theoretical one dimensional model based on Hückel’s molecular orbital theory applied to one electron de-localized \( \pi \)-electron Hamiltonian in a conjugate chain of regular polyene (ignoring electron-electron repulsion) is developed that demonstrates the dependence of third order non-linearity on (a) the chain length, (b) linear correlation plot of \( \nu \) (C=C) versus \( 1/\lambda_{\text{res}} \) (parameters measured from linear spectroscopic technique of Raman and absorption spectroscopy), (c) ratio of the electron velocity to the sound velocity in the chain, and (d) deformation potential coupling of the phonons to the on-site electronic charge density. Earlier attempts to predict \( \gamma \) of organic molecules from linear spectroscopic properties were made by a number of workers\(^8,15,16\).
The presence of an external electric field of strength $\mathbf{F}$, $H_e + H_{ev}$ is written as:

$$
H_e + H_{ev} = \sum_i \sum_k \left[ e'_k(x_i) a_k^+ a_i - J_k(x_i) [a_k^+ a_i, a_k^+ a_i] \right]
$$

Here, $e'_k(x_i) = [\varepsilon_k(x_i) - e\mathbf{F} x_i]$, where $\varepsilon_k(x_i)$ is the on-site molecular orbital energy of the $k^{th}$ molecular orbital assumed to be identical for all carbon atoms.

$-J_k(x_i)$ is the electron transfer integral of the $i^{th}$ C-C bond. $a_k^+ (a_k)$ are the Fermion creation and annihilation operators. $x_i$ is the displacement of the $i^{th}$ C-C bond. $x_i = (U_{i+1} - U_i)$, where $U_i$ is the displacement coordinate of the $i^{th}$ carbon atom. The vibrational Hamiltonian can be written in harmonic approximation as:

$$
H_v = \frac{1}{2} \sum_{i=1}^{N} \left[ \frac{P_i^2}{M} + k(U_{i+1} - U_i)^2 \right]
$$

where $M$ is the reduced mass of the carbon-carbon molecule, $k$ the longitudinal elasticity coefficient and $P_i$ the momentum operator canonically conjugate to the displacement operator $U_i$. The Hamiltonian for the electron-phonon interaction.

$(H_{ev})$ may be written in the simplest case by rewriting both $J_k(x_i)$ and $e'_k(x_i)$ taken as functions of the displacement $x_i$. These can be expanded in Taylor Series as:

$$
e'_k(x_i) = \varepsilon_k + \sum_{i,j} \left( \frac{\partial \varepsilon_k(x_j)}{\partial x_j} \right) \varepsilon_j(0) x_j + .......
$$

$$
J_k(x_i) = J_k + \sum_{i,j} \left( \frac{\partial J_k(x_j)}{\partial x_j} \right) \varepsilon_j(0) x_j + .......
$$

The term $\sum_{i,j} \left( \frac{\partial J_k(x_j)}{\partial x_j} \right)$ for $i \neq j$ is negligible. From Eq. (5), the transfer integral depends upon the separation between adjacent sites. For a dimerized chain (i.e. broken symmetry), the sites move alternatively closer together and further apart. This leads to two types of transfer integrals:
\[ J_i = J_{i-1} - \frac{\Delta_n}{2} \text{ for } U_{i+1} - U_i > 0 \]
\[ J_i = J_{i-1} + \frac{\Delta_n}{2} \text{ for } U_{i+1} - U_i < 0 \] \hspace{1cm} \text{(6)}

For organic compounds, the bandwidth is given by \( 4J_0 = 0.21 \text{eV} \ll 2\Delta_n \) (the band gap = 2.5 eV to 6 eV). Further, C=C is known to be a true measure of conjugation, consequently the transfer integral is effectively taken as that for \( U_{i+1} - U_i < 0 \). Under the above assumptions, \( J = \frac{\Delta_n}{2} \) and
\[ H_{el} = \sum_{i=1}^{N} [\delta \alpha a_i^\dagger a_i + (U_{i+1} - U_i)] \] \hspace{1cm} \text{(7)}

where \( \delta = (X - \epsilon F) \), \( X = \frac{\partial F}{\partial \delta} \) is an non-linear parameter specifying the strength of the deformation potential coupling of the phonons to the on-site electronic charge density and is identical for all carbon-carbon units. One can minimize the average value of \( H \) with respect to the wave function:
\[ |\psi\rangle = \sum_{i} \sum_{k} C_k(\epsilon_i) a_i^\dagger a_i^\dagger 0 \] \hspace{1cm} \text{(8)}

where \( C_k \) is the \( k \)th molecular orbital (MO) coefficient at the \( i \)th carbon atom and satisfy \( \sum_{k} |C_k|^2 = 1 \) \hspace{1cm} \text{(9)}

\( \alpha(t) \) is an operator of the form:
\[ \alpha(t) = -i \hbar \sum_{i} \left[ \beta_i(t) P_i - \Pi_i U_i \right] \] \hspace{1cm} \text{(10)}

where
\[ \langle \psi | \Pi_i | \psi \rangle = \beta_i(t) \text{ and } \langle \psi | P_i | \psi \rangle = \Pi_i(t) \] \hspace{1cm} \text{(11)}

The \( \pi \)-electron density \( \rho \) on the \( i \)th carbon and bond order \( P_i \) of the \( i \)th C-C bond are defined as:
\[ \sum_{i,k} |C_k|^2 = \frac{\rho_i}{2} \text{ and } \sum \text{Re}[C_{i,k}C_{i+1,k}] = \frac{P_i}{2} \] \hspace{1cm} \text{(12)}

where minimization is made over occupied orbitals. Minimization procedure yields the following result:
\[ \langle \psi | H | \psi \rangle = \sum_{i} \sum |C_{i,k}|^2 \frac{\Delta_n}{2} (C_{i,i+1} + C_{i+1,i}) C_{i,k}^* + \delta (\beta_{i+1} - \beta_i) |C_{i,k}|^2 + \frac{1}{2} \left[ \frac{(P_i^2)}{M} + K (\beta_{i+1} - \beta_i)^2 \right] \] \hspace{1cm} \text{(13)}

Eq. (13) in the continuum approximation along with the Hamilton equation of motion is reduced to the nonlinear Schrodinger equation (NLS):
\[ i\hbar \frac{\partial}{\partial t} + \frac{\Delta_n}{2} \frac{\partial^2}{\partial \xi^2} + G |C(\xi, t)|^2 C(\xi, t) = 0 \] \hspace{1cm} \text{(14)}

where \( \Lambda = \epsilon_k - \Delta_n, \xi = \frac{(\lambda - \xi)}{a}, \nu \) is the electron velocity, \( G = \frac{4\delta^2}{(1 - \lambda^2)k} \), \( s = \frac{\nu}{v_n} \), \( v_n^2 = \frac{a^2}{M} \) is the longitudinal sound velocity. Soliton solutions of the NLS Eq. (14) exists for \( s < 1 \), normalized by the condition over the length \( L \) of the chain
\[ \int_0^L |C(\xi, t)|^2 d\xi = 1 \] \hspace{1cm} \text{(15)}

The mobile charge density wave along the conjugate chain is determined by:
\[ |C(\xi, t)|^2 = \frac{\mu \sec h^2 (\mu \xi)}{2} \] \hspace{1cm} \text{(16)}

Now, only the electronic and electron-phonon coupling part of the total Hamiltonian contributes to the non-linear process. Transforming Eq. (13) into continuum approximation for \( t = 0 \) and
\[ \langle \psi | H, + H_{ph} | \psi \rangle = \int_0^L \text{Re}[C^* \left[ \Lambda - \frac{\Delta_n}{2} \frac{\partial^2}{\partial \xi^2} - 2\delta |C|^2 \rho \right] C^* d\xi \] \hspace{1cm} \text{(17)}

One can obtain the total electronic and electronic-visronic coupling energy as:
\[ E = \frac{2}{k_0^2 \Delta_n^2 (1 - s^2)} \left[ N (\frac{2\Delta_n^2}{3\Delta_n}) - K^2 N^2 \right] (\chi - \epsilon F)^b \] \hspace{1cm} \text{(18)}
where $K = \frac{m \omega^2}{\hbar}$, $m$ is the electron mass. In deriving Eq. (18), the following assumptions can be made: for $\mu N < 1$, sech$^2$ $[\mu N] = 1$ and tanh $[\mu N] = (\mu N + \mu N^3/3)$. The energy can be rescaled and set $\varepsilon$ = 0, also $K^2$ is a small quantity and can be neglected. Now according to Hellman-Feynman theorem$^9$:

$$\mu = -\frac{\partial E}{\partial F} = \left( \frac{\partial H}{\partial F} | |H| \langle |\langle |H| | \partial H \rangle \rangle | \langle |H| | \partial F \rangle \rangle \right) \mu$$

...(19)

The first and the third terms on the right hand side of Eq. (19) are zero if $\psi$ is the true wave function. Consequently:

$$\mu = \left( \frac{12e}{k^2 \lambda_0^2 (1 - s^2)} \right) \left( N + \frac{2 N^3}{3} \right) (\chi - eF)^2$$

...(20)

Now, expanding the right side of Eq. (20) and comparing the coefficient of $\chi$ with the right side of Eq. (1), one can obtain the third order hyperpolarizability $\gamma$:

$$\gamma (\text{esu}) = \gamma (S.I.) \times 7.16 \times 10^{31} \text{esu}^3$$

The dependence of the longitudinal elasticity coefficient on the conjugation length can be reproduced by first writing $k$ in terms of the wave number of the C=C Raman mode, since C=C stiffness is a genuine measure of the degree of conjugation through the $\pi$-electron chain$^9$:

$$k = \frac{4 \pi v^2 c^2 M}{v_{\text{rel}}^3 c}$$

...(22)

with $v_{\text{rel}} = 1459 \text{ cm}^{-1} + (720 N') \text{ cm}^{-1}$

...(23)

From $v_{\text{rel}}$ versus $\lambda_{\text{rel}}$ correlation plot, where $N' = N/2$ is the number of double bonds, $M$ is the reduced mass of C=C (9.96 x 10$^{-21}$ kg), $c$ is the velocity of light. The absorption maximum ($\lambda_{\text{max}}$) is taken as the band gap for $\pi \rightarrow \pi^*$ transition. Before proceeding to fit the experimental data to the author’s model (Eq. 21), a rough estimate of $\chi$ would be helpful. In order to obtain the order of magnitude estimate for the level of anharmonicity to be expected in C=C vibrations. The C=C bond is assumed to have the anharmonic potential (about the minimum at $x_o$).

$$U(x) = \frac{kx^2}{2} + bx^4$$

...(24)

Non-linearity enters our model as:

$$H_{\nu} = n \hbar \omega$$

...(25)

where $n$ gives the number of quanta in the C=C bond.

Also $n \hbar \omega = \frac{kx^2}{2}$

...(26)

From Eqs (24)-(26) $\chi = \frac{2 \hbar \omega}{\hbar \omega} \chi_0$ at the minimum of $U(x)$, $a_o$ being the average C=C bond length.

From Eq. (24) $\frac{dU}{dx} |_{x=a_o} = 0$, thus $|\chi| = \frac{k}{4a_o^2}$

...(27)

Finally, one can have $\chi = \frac{\hbar k}{2a_o \hbar \omega} M$

...(28)

Thus from Eq. (28), one can obtain the order estimate for any $N$ as $\chi = 10^{10}$ Newtons.

3 Results and Discussion

The best agreement between this model and the experimental results for $\gamma$ is obtained using $s^2 = 0.95$ and $\chi = 1.14 \times 10^{10}$ Newtons. Table 1 shows experimentally obtained and calculated $\gamma$ values as a function of the number of repeat units. One can see that the agreement between experimental values and those obtained from this model is very good. The present results suggest that, onset of saturation of $\gamma$ of linear polyenes should occur for $N > 24$. The effect of the coupling constant on $\gamma$ is evident from Eq. (21). On increasing the value of $\chi$, the increase of $\gamma$ as a function of chain length is faster and saturation is observed only for large $N$. The influence of $s$ on $\gamma$ is not yet clear and requires further investigation. In the present analysis of the power-law behaviour, the author has used the general equation $\gamma = a N^b$. The parameter
and calculated values (from Eq. 21) of Table 4 repeat units (N)

<table>
<thead>
<tr>
<th>N</th>
<th>( k ) (N/m)</th>
<th>( \Delta_e (\text{eV}) )</th>
<th>( \gamma_{\text{opt}(\text{esu})} )</th>
<th>( \gamma_{\text{nc}(\text{esu})} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1680</td>
<td>4.13</td>
<td>1.32 \times 10^3</td>
<td>1.32 \times 10^3</td>
</tr>
<tr>
<td>4</td>
<td>1171</td>
<td>2.57</td>
<td>7.00 \times 10^3</td>
<td>6.31 \times 10^3</td>
</tr>
<tr>
<td>6</td>
<td>1021</td>
<td>2.06</td>
<td>5.01 \times 10^3</td>
<td>5.01 \times 10^3</td>
</tr>
<tr>
<td>8</td>
<td>951</td>
<td>1.8</td>
<td>1.86 \times 10^3</td>
<td>1.82 \times 10^3</td>
</tr>
<tr>
<td>10</td>
<td>909</td>
<td>1.64</td>
<td>5.01 \times 10^3</td>
<td>5.01 \times 10^3</td>
</tr>
<tr>
<td>12</td>
<td>882</td>
<td>1.54</td>
<td>1.26 \times 10^3</td>
<td>1.00 \times 10^3</td>
</tr>
<tr>
<td>14</td>
<td>863</td>
<td>1.47</td>
<td>2.00 \times 10^3</td>
<td>2.00 \times 10^3</td>
</tr>
<tr>
<td>16</td>
<td>849</td>
<td>1.41</td>
<td>3.09 \times 10^3</td>
<td>3.16 \times 10^3</td>
</tr>
<tr>
<td>18</td>
<td>838</td>
<td>1.37</td>
<td>5.01 \times 10^3</td>
<td>5.01 \times 10^3</td>
</tr>
<tr>
<td>20</td>
<td>830</td>
<td>1.33</td>
<td>7.00 \times 10^3</td>
<td>7.94 \times 10^3</td>
</tr>
<tr>
<td>22</td>
<td>822</td>
<td>1.30</td>
<td>1.12 \times 10^3</td>
<td>1.11 \times 10^3</td>
</tr>
<tr>
<td>24</td>
<td>817</td>
<td>1.28</td>
<td>1.51 \times 10^3</td>
<td>1.51 \times 10^3</td>
</tr>
<tr>
<td>26</td>
<td>812</td>
<td>1.26</td>
<td>2.00 \times 10^3</td>
<td>2.02 \times 10^3</td>
</tr>
</tbody>
</table>

was found to be \( 5.89 \times 10^{-7} \) esu, while \( b \) was estimated to be 3.175 compared to that predicted by free electron model \( b = 5.0 \) [Ref. 11], simple Hückel theory \((b = 5.257 \text{ Ref.20})\), \((b = 4.25 \text{ Ref.5})\) and \((b = 3.2-3.4 \text{ Ref.7})\). The ratio of the bandwidth \( 4 \Delta_e \) to the bandgap \( 2 \Delta_e \) plays the role of coherence length \( \zeta = \frac{2 \Delta_e}{\gamma} \) determines the range of nonlinear excitations. For linear polyenes \( \zeta \ll a \), consequently details on the scale of the lattice spacings are important and different members of the polyene series will exhibit different

This implies that values of \( \chi \) and \( s \) found from the least square fit are less than the true values.

### 4 Conclusions

In this paper, a simple model has been presented which can be used to interpret the non-linear optical behaviour of conjugated structures. The close connection that exists between linear and non-linear properties of conjugated organic molecules has been demonstrated. Such an approach to predict non-linear parameters from linear spectroscopic data will enable the selection of potential conjugate systems from the already existing large amount of linear spectroscopic data for use in non-linear applications. The method can very readily be used to explain the dependence of \( \gamma \) on the chain length by adjusting two parameters: the coupling constant \( (\chi) \) and the ratio of the electron velocity to the velocity of sound \( (s) \). The dependence of \( \gamma \) on \( s \) is a new feature of this model. Despite the gross over simplification, the author is indeed surprised with the excellent agreement found between the values calculated using this model and those experimentally observed.

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### References


