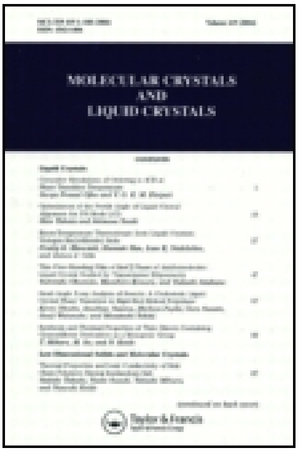

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Optical Response of Linear Polyenes: Extension of the Simple Model for Linear Polyene Electronic Structure

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OPTICAL RESPONSE OF LINEAR POLYENES: EXTENSION OF THE SIMPLE MODEL FOR LINEAR POLYENE ELECTRONIC STRUCTURE

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Abstract A simple model based on Hückel theory that quantitatively accounts for linear polyene 2^1A_g and 1^1B_u excitation energies has been used to predict nonlinear optical response of this class of molecules. The essential elements of the model are the use of alternating resonance integrals to obtain the proper chain-length dependence of the 1^1B_u highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) excitation energy and mixing of the HOMO to LUMO + 1, HOMO-1 to LUMO and HOMO to LUMO double-excitation configurations to describe the 2^1A_g state. Even though one of the appealing features of this model is the ease with which it can be extended to include vibrational levels, this contribution focuses on calculations carried out in a purely electronic basis. Despite the extreme simplicity of the model, it reproduces many of the results of much more elaborate computations including the fact that a higher lying ^1A_g state has substantially larger 2-photon absorptivity than does the 2^1A_g state and the fact that two photon resonance with the 2^1A_g state can provide significant enhancement of the nonlinear optical response of these molecules at wavelengths well below the one-photon absorption edge.

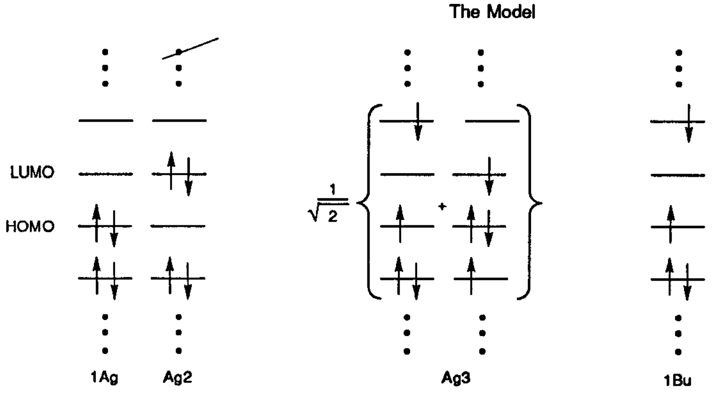
INTRODUCTION

The nonlinear optical response of π-conjugated polymers is of great interest to both experimentalists and theoreticians because of potential use of these systems in optical devices. For example, polydiacetylenes have been shown experimentally to have very large third order nonlinear susceptibilities $\chi^{(3)}$. However, the exact mechanism of the optical nonlinearity remains a matter of controversy. In particular, the contributions of electron-phonon[1,2] and electron-electron[3,4] interactions to the nonlinear optical response are not well understood. In order to properly describe electronic states of systems where electron correlation is known to play a significant role,[5] as it does for the linear polyenes, it is necessary to perform the calculations at least at the double configuration interaction level. For polyenes with three or four double bonds in conjugation the calculations require the use of supercomputers: for longer polyenes they presently cannot be done. Since it has been shown that, at least with respect to the excitation energies of the S_1 and S_2 states, a simple model accurately reproduces experimental results, it is of interest to examine the predictions of this model for nonlinear optical response.

The current status of understanding of linear polyene electronic structure has been recently reviewed from both the theoretical[5] and experimental[6] perspectives. The fact that the π-electrons in linear polyenes are extensively delocalized and highly correlated leads to the expectation that these molecules can have unusually large nonlinear optical responses.[3-5,7] Furthermore, because the lowest energy excited singlet state, the 2^1A_g state, is 1-photon forbidden but allowed for 2-photon absorption,[8] these nonlinear effects can be strongly resonance enhanced at wavelengths well below the 1-photon absorption edge.[9] This has already been demonstrated in the case of the disordered and heterogeneous polymer polyacetylene[10,11] although the interpretation of the observed resonances is still open to discussion. The increasing amount of experimental data has created a need for a simple model which can quickly and reliably relate experimentally measured excitation energies and transition dipoles to microscopic charge distributions in the relevant electronic states. Such a model has already been proposed and has proven itself in explaining experimental trends observed in a series of substituted and unsubstituted linear polyenes.[12] In this paper, we describe the application of the simple model for linear polyene electronic structure to calculations of nonlinear optical response in this class of compounds.

THE MODEL

A detailed description of the model as it applies to the π-electronic structure of the polyenes has already been provided.[12] The inspiration for the model comes from the original Pariser-Parr-Pople (PPP) configuration-interaction calculation of Schulten and Karplus[13] as further elaborated by Ohmine, Karplus and Schulten.[14] Only the four configurations shown in Figure 1, which dominate in the description of the three low-lying singlet states in the more extensive theory, are considered. The 1^1A_g ground state and 1^1B_u second excited singlet state are represented by single configurations. In the former, all bonding molecular orbitals are doubly occupied. The latter is generated from the ground-state configuration by promoting an electron from the HOMO to the LUMO. The 2^1A_g state is a mixture of the doubly excited (promotion of two electrons from the HOMO to the LUMO) and double-jump (promotion of an electron from the HOMO to the LUMO+1 or promotion of an electron from the HOMO-1 to the LUMO) configurations. Because of the particle-hole



1Ag	0	0	0
0	Ag2	A+B/N	0
0	A+B/N	Ag3	0
0	0	0	1Bu

FIGURE 1 The model for linear polyene electronic structure. The left-hand side indicates the four configurations whose energies are calculated by Hückel theory using alternating resonance integrals. The right-hand side shows the configuration interaction Hamiltonian used to compute the energies of the 2^1A_g and 3^1A_g states from those of the Ag2 and Ag3 configurations.

symmetry inherent in these kinds of molecular orbital calculations the double jump configurations always appear as the symmetric linear combination.[15] Because of the fact that these configurations are degenerate, this point can be neglected in calculating the excitation energies but it must be taken into account in the calculation of other properties such as transition dipoles. The energies of the four configurations shown in Figure 1 are calculated by Hückel theory[16] using alternating resonance integrals. The correct order of the excited states, 2^1A_g below the 1^1B_u, is achieved by considering electron-electron repulsion which mixes the states of the same symmetry. In this truncated basis the electron-electron repulsion operator will only have nonzero matrix elements between the A_g configurations. Since the primary effect of this operator will be to mix the nearly degenerate A_g2 and A_g3 configurations, only this mixing is considered. In this model the A_g2-A_g3 configuration mixing matrix element is $<A_g2|H|A_g3> = A + B/N$ where A and B are parameters and N is the number of double bonds in the polyene chain. This form expresses the notion that the perturbation is inversely proportional to the distance between electron pairs which scales with the chain length and that it approaches a finite limit as the chain length increases. With the proper choice of four parameters (the Hückel resonance integral β=-30,305 cm^{-1}, the bond alternation parameter, ξ=0.133, A=12,300 cm^{-1} and B=58,020 cm^{-1}) the 0-0 excitation energies of the 2^1A_g and 1^1B_u states in polyenes with 3 to 8 double bonds in conjugation calculated by the model agree with those determined from high resolution optical experiments within the experimental error (RMS deviation between calculation and experiment of 160 cm^{-1}).[12]

The calculation of optical properties requires, in addition to the excitation energies, the transition dipoles. These were calculated assuming that $<\varphi_i|r|\varphi_j>=r_i\delta_{ij}$ where φ_i is the $2p_x$ orbital on atom i, δ_{ij} is the delta function, and the components of the vector r_i are the Cartesian coordinates for atom i. The C=C and C-C bond lengths were set to 1.34Å and 1.46Å, respectively, and all C=C-C bond angles were set to 120°.

One-Photon Spectra

The excitation energies for the 2^1A_g, 1^1B_u and 3^1A_g states as a function of polyene chain length are plotted in Figure 2. Since the model was parameterized to accurately reproduce the 2^1A_g and 1^1B_u 0-0 excitation energies that have been measured for linear polyenes with from 3 to 8 double bonds in conjugation, the values calculated for the longer polyenes should be viewed more as an extrapolation from experimental data than a theoretical prediction. At this point there are no experimental results on higher lying A_g states so meaning of the 3^1A_g state is somewhat ephemeral. It is not unreasonable to treat it as a kind of effective state whose inclusion is important for describing nonlinear optical response. Work is in progress to experimentally determine the degree to which the nonlinear optical responses predicted by this model correspond to reality.

Absorption from the ground state to the 1^1B_u state is dipole allowed. In addition to the excitation energy, the intensity and polarization of this transition are of interest. The one-photon intensities are conveniently expressed in terms of the dimensionless oscillator strength

$$f = \frac{8\pi^3 m_e \nu}{3h^2e^2}\left|<1^1A_g|\mu|1^1B_u>\right|^2 \qquad (1)$$

The oscillator strength for the 1^1A_g to 1^1B_u transition for polyenes with 2 to 30 double bonds in conjugation are plotted in Figure 3. The angle between the transition dipole and the chain axis (defined such that the angle between the double bonds and the chain axis is

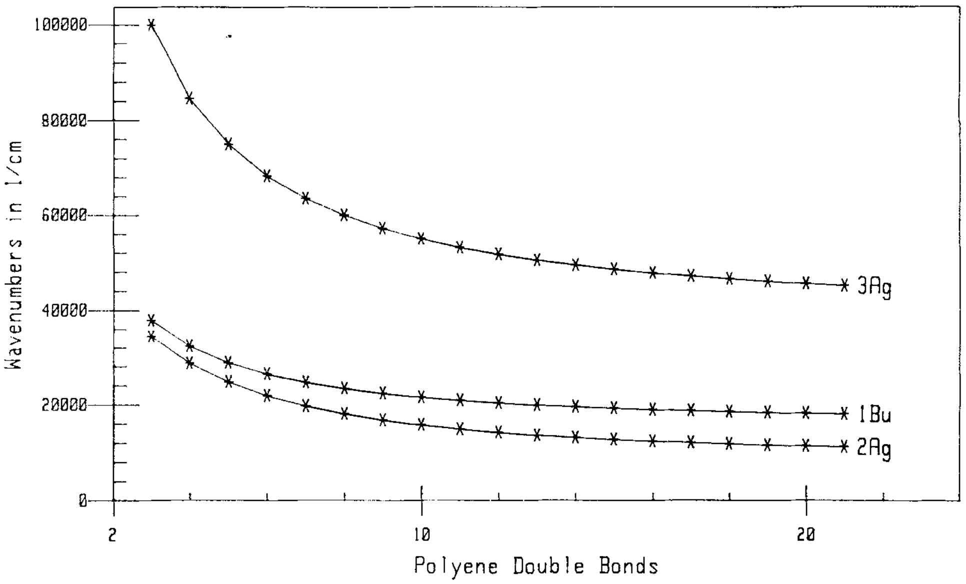


FIGURE 2 Excitation energies of the 2^1A_g (bottom curve), 1^1B_u (middle curve) and 3^1A_g states versus the number of conjugated double bonds.

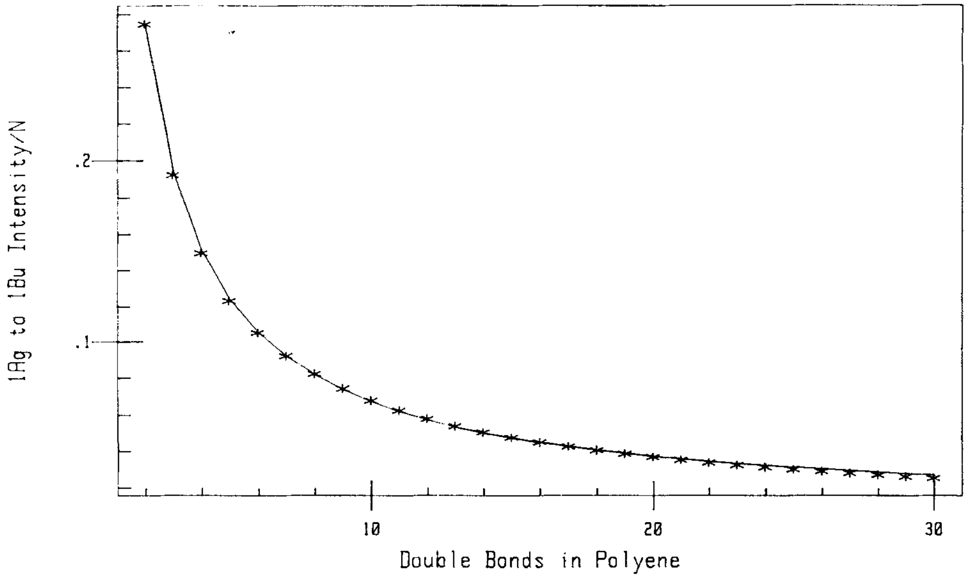


FIGURE 3 Oscillator strength per conjugated double bond of the 1^1A_g-1^1B_u transition versus the number of conjugated double bonds.

ca. 30°) follows a similar curve. As can be seen in Table 1, the calculated transition dipoles for n=4 compare quite favorably to those calculated using much more elaborate theoretical methods[4] and the polarization angle for n=4 is satisfyingly close to that determined by experiment.[17] Of course, the appeal of the simple model is the ease with which it can be

TABLE 1 Comparison of transition dipoles for hexatriene and octatetraene.

N	$<1^1A_g\|\mu\|1^1B_u>$ in debye	Angle from chain axis in degrees	Method
3	7.2853	15.71	exact PPP (ref. 13)
3	6.7737	14.29	simple model
4	8.6941	13.50	exact PPP (ref. 13)
4	8.2398	11.47	simple model
4	— — —	15±1	experiment (ref. 14)

extended to arbitrary chain length. The asymptotic values for the excitation energies of the 2^1A_g, 1^1B_u and 3^1A_g states are 8090 cm^{-1} (1.00eV), 14,450 cm^{-1} (1.79eV), and 37600 cm^{-1} (4.66 eV), respectively. The long chain limit of the 1^1B_u absorption strength per double bond is f/N=0.00076 and the long chain limit of the angle between the 1^1A_g-1^1B_u dipole and the chain axis is 4.1°.

Two-Photon Spectra

The procedure for calculating two photon absorption intensities has been already described in some detail.[18-20] Our method is similar to that of Holneicher and Dick[18,19] where the expression for the two-photon absorption cross section for a transition from the state G to the state F is:

$$\delta^{GF} = \left(\frac{8\pi^3 e^4}{h^2 c^3}\right)\frac{\Gamma_{GF}\,\bar{\upsilon}_1\bar{\upsilon}_2}{(\bar{\upsilon}_{GF}-\bar{\upsilon}_1-\bar{\upsilon}_2)^2+\Gamma^2_{GF}}\left|e_1 \bullet S^{GF} \bullet e_2\right|^2 \qquad (2)$$

where $\bar{\nu}_i$ are the photon wavenumbers, Γ is the damping factor in wavenumbers, the e_i are the unit polarization vectors of the absorbed photons and S^{GF} is the two-photon transition tensor given by:

$$S^{GF} = \left|\sum_A \frac{<G|r|A><A|r|F>}{\bar{\upsilon}_{GF}-\bar{\upsilon}_1-i\Gamma_{GF}} + \frac{<F|r|A><A|r|G>}{\bar{\upsilon}_{GA}-\bar{\upsilon}_2-i\Gamma_{GA}}\right| \qquad (3)$$

We have calculated δ for the special case of a single-color experiment on oriented molecules with both photons linearly polarized along the chain axis using the expression.

$$\delta^{GF} = \left(\frac{32\pi^3 e^4}{h^2 c^3}\right)\frac{\Gamma_{GF}\,\bar{\upsilon}^2}{(\bar{\upsilon}_{GF}-2\bar{\upsilon})^2+\Gamma^2_{GF}} \times \left|\sum_A \frac{<G|z|A><A|z|F>}{\bar{\upsilon}_{GA}-\bar{\upsilon}}\right|^2 \qquad (4)$$

which neglects the very small effects of intermediate state damping.

Of course, the peak values of the 2 photon δ's calculated with eq. 4 directly depend on the width of the resonance Γ_{GF}. In these calculations we have arbitrarily set the damping factors for all three excited states to 100 cm^{-1}: it is straightforward to convert the calculated δ's (in cm^4 s photon^{-1}molecule^{-1}) to values per unit wavenumber interval.

A semi-log plot of the 2 photon absorptivities verses polyene chain length is shown in Figure 4. The 2-photon cross section of the higher lying 3^1A_g state is significantly higher than that of the 2^1A_g state as is the case for the so called m^1A_g state that more detailed theory identifies as the state that dominates the nonlinear optical response. In this model this effect is especially pronounced at short chain length, as is shown in Figure 5. Convergence of the 2-photon cross section is slow enough that extrapolation to the long chain limit is probably not justified.

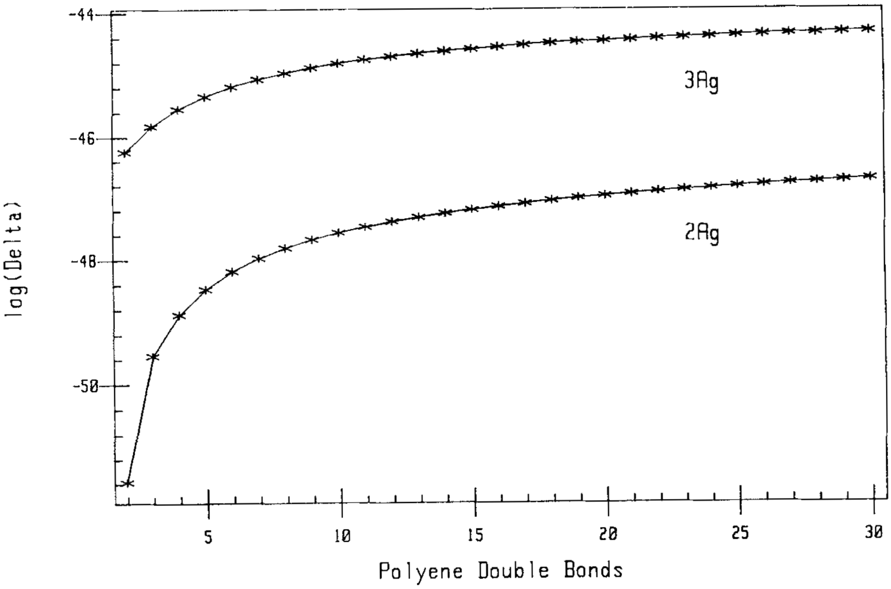


FIGURE 4 Logarithm of the 2-photon absorption intensity in cm^4 s photon^{-1} molecule^{-1} for the 1^1A_g-2^1A_g (lower curve) and 1^1A_g-3^1A_g (upper curve) transitions versus the number of conjugated double bonds.

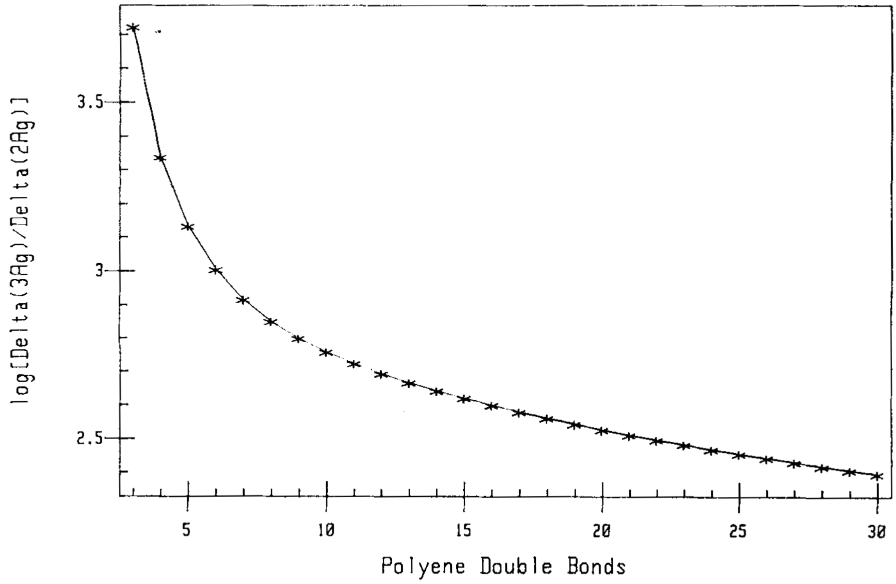


FIGURE 5 Logarithm of the ratio of 1^1A_g-3^1A_g to 1^1A_g-2^1A_g 2-photon intensities versus the number of conjugated double bonds.

Third Order Optical Response

The third order response of linear polyenes that is most frequently treated theoretically is the molecular susceptibility for third harmonic generation. Since most calculations focus on $\gamma_{zzzz}(-3\bar{\nu}, \bar{\nu}, \bar{\nu}, \bar{\nu})$ the tensor component for all fields polarized parallel to the polyene chain axis, we shall consider only this case. Changing from angular frequencies w to wavenumbers $\bar{\nu}$, and adding damping to the expression for γ_{zzzz} worked out by Armstrong, Bloembergen, Ducuing and Pershan[21] leads to

$$\gamma_{zzzz}(-3\bar{\nu}, \bar{\nu}, \bar{\nu}, \bar{\nu}) = \left(\frac{e^4}{24h^3c^3}\right) \sum_{ABC} \langle G|\mu|C\rangle\langle C|\mu|B\rangle\langle B|\mu|A\rangle\langle A|\mu|G\rangle$$
$$\times \left\{ \frac{1}{(\bar{\nu}_{CG}-i\Gamma_{CG}-3\bar{\nu})(\bar{\nu}_{BG}-i\Gamma_{BG}-2\bar{\nu})(\bar{\nu}_{AG}-i\Gamma_{AG}-\bar{\nu})} \right.$$
$$+ \frac{1}{(\bar{\nu}_{CG}-i\Gamma_{CG}+\bar{\nu})(\bar{\nu}_{BG}-i\Gamma_{BG}-2\bar{\nu})(\bar{\nu}_{AG}-i\Gamma_{AG}-\bar{\nu})}$$
$$+ \frac{1}{(\bar{\nu}_{CG}-i\Gamma_{CG}+\bar{\nu})(\bar{\nu}_{BG}-i\Gamma_{BG}+2\bar{\nu})(\bar{\nu}_{AG}-i\Gamma_{AG}-\bar{\nu})} \qquad (5)$$
$$\left. + \frac{1}{(\bar{\nu}_{CG}-i\Gamma_{CG}+\bar{\nu})(\bar{\nu}_{BG}-i\Gamma_{BG}+2\bar{\nu})(\bar{\nu}_{AG}-i\Gamma_{AG}+3\bar{\nu})} \right\}$$

In the case of a centrosymmetric polyene the states A and C must have u symmetry and the states B must have g symmetry. Since there is only one antisymmetric state in this simple model, $A=C=1^1B_u$ and the sum over states only involves summing over the three A_g states, an extremely simple task. The simplicity of this model allows the exploration of many aspects of polyene nonlinear optical response: here we look only at the chain length dependence of $\gamma_{zzzz}(-3\bar{\nu}, \bar{\nu}, \bar{\nu}, \bar{\nu})$ for 2 photon resonance with the 2^1A_g state and 3 photon resonance with the 1^1B_u state. As was the case for 2 photon absorption, it must be born in mind that the calculated values of the resonance enhanced $\gamma_{zzzz}(-3\bar{\nu}, \bar{\nu}, \bar{\nu}, \bar{\nu})$'s depend directly on the damping which we have arbitrarily set to 100 cm^{-1} for all excited states. While it is reasonable to expect the simple calculations reported here to give insight into the relative enhancements, detailed quantitative examination of the absolute magnitudes of the nonlinear susceptibilities only makes sense for calculations where the vibronic structure of the electronic transitions is realistically treated. Calculations that do this within the context of the simple model will be reported in a future paper.

The logarithm of γ_{zzzz} for 2-photon resonance with the 2^1A_g state and γ_{zzzz} for 3-photon resonance with the 1^1B_u state is plotted against the number of conjugated double bonds in Figure 6. For 2 through 4 double bonds in conjugation the two resonance enhanced γ's are similar, the 2^1A_g 2-photon resonance is the more intense for 5 and 6 double bonds in conjugation and the 1^1B_u resonance dominates for chains with 8 to 14 double bonds. The saturation at a chain length of 15 conjugated double bonds is most dramatic. Figure 7 gives some insight into the source of this leveling off: it is a consequence of the crossing of the 3-photon 1^1B_u and 2-photon 2^1A_g resonances. Given the demonstrated accuracy of this model in reproducing 2^1A_g and 1^1B_u excitation energies, there is little doubt that this crossing will occur. Thus, the prediction of a dramatic change

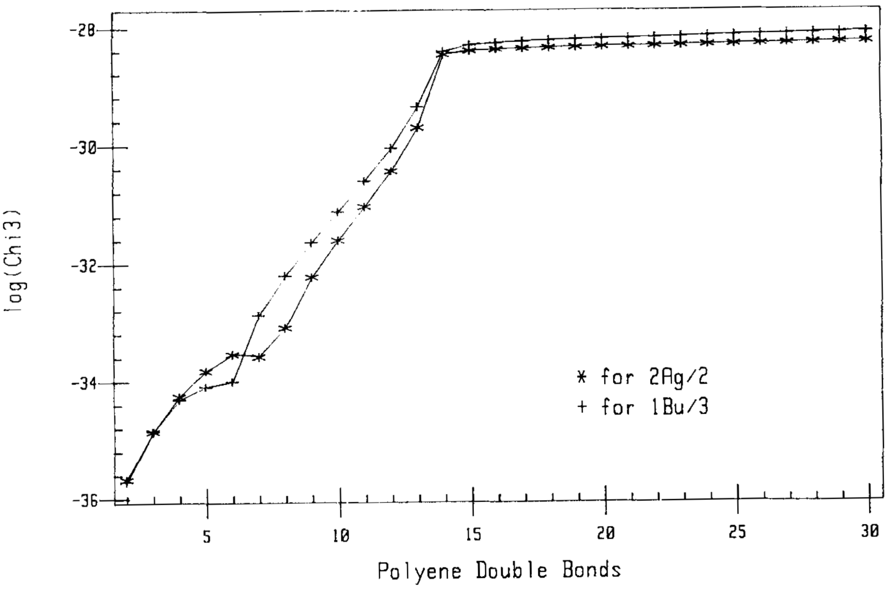


FIGURE 6 Logarithm of $\gamma_{zzzz}(-3\omega,\omega,\omega,\omega)$ in esu versus the number of conjugated double bonds.

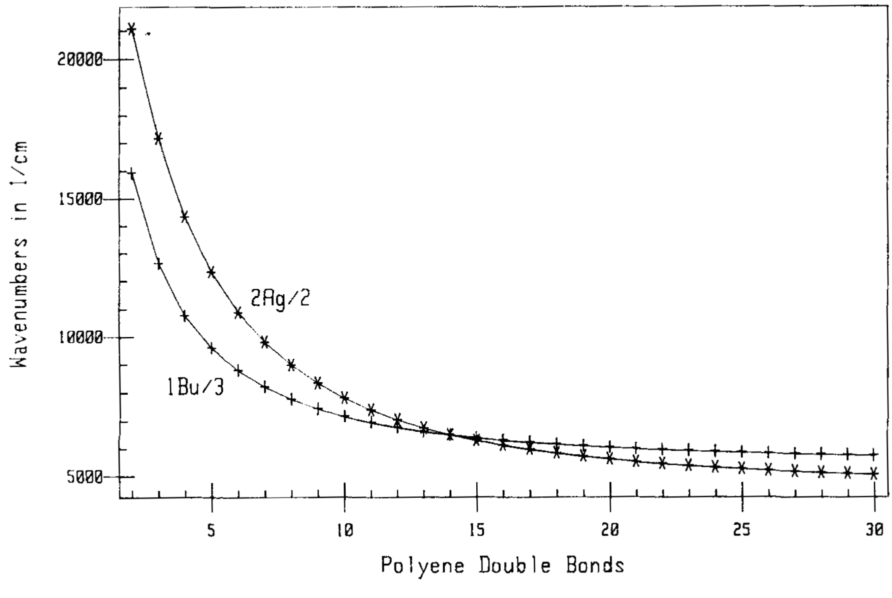


FIGURE 7 Comparison of the energy in wavenumbers for 2^1A_g 2-photon resonance (plotted as *) versus the number of conjugated double bonds to the energy in wavenumbers for 1^1B_u 3-photon resonance versus the number of conjugated double bonds (plotted as +).

Finally, for the resonance enhanced response this model gives little incentive for extending chain length. In strong contrast to the situation for the non-resonant response, the resonance enhanced γ_{zzzz} increases sublinearly with N, the number of double bonds. For chains with less than 15 double bonds the 1^1B_u 3-photon resonance enhanced γ_{zzzz} goes as $N^{0.5}$ while 2^1A_g 2-photon resonant enhanced value goes as $N^{0.6}$: for longer chains the exponents are less than 0.01. This suggests that an optimized material might consist of a short chain oligomer chosen for optimal resonance enhancement. Further, the sensitivity of the expected response to interferences between the contributing states suggests that a careful investigation of the resonance enhanced response as a function of substituents could be most interesting.

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