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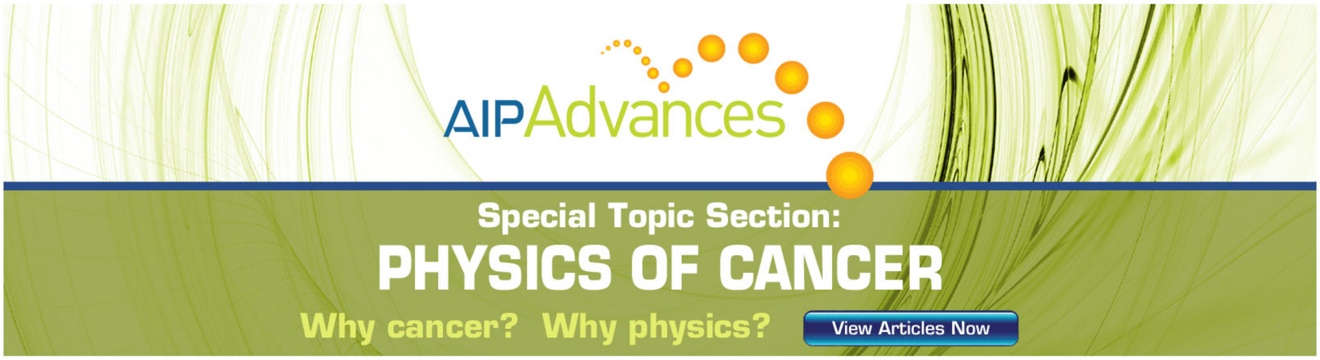

Vibrational contributions to third-order nonlinear optical susceptibilities

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Including vibrational levels in the perturbation theory sum for the third-order nonlinear optical susceptibility γ introduces terms which have a pure vibrational frequency in the denominator. These terms can be rewritten as a sum over Raman amplitudes. Model calculations on a diatomic system with two electronic states show that these terms are negligible, about 3% of the value obtained ignoring vibrations. In polyacetylene, the Herzberg–Teller contribution to the Raman amplitude is much larger than in the diatomic case. Within the tight binding and harmonic oscillator approximations, the sum over Raman amplitudes is 10% of the value for γ obtained ignoring vibrations.

I. INTRODUCTION

The design of materials with large optical nonlinearities is an active and well-reviewed area of research.[1,2] Second-order nonlinearity β results in three-photon processes such as frequency doubling, while the third-order nonlinearity γ results in four-photon processes, such as frequency tripling. The origin of β is reasonably well understood on a microscopic level. To possess a large β, the polarization induced by an electric field pointing along one direction, say up, must be very different from that induced when the electric field points down. Molecules with this property can be designed, a common example being *para*-disubstituted benzenes, which have an electron donor and an electron acceptor at opposite sides of a six-member ring.[3] Designing molecules with a large γ is not as straightforward. What is required here is that the induced polarization be a nonlinear function of the magnitude of the applied electric field. It has been found that highly conjugated organic polymers, such as polyacetylene, polydiacetylene, and polythiophene, have large γ's oriented along the chain.[2] The origin of the large γ in these systems is an area of active theoretical research.[4-10] All studies to date have assumed an electronic origin for γ and have ignored the vibrational motion. That is, only electronic states are included in the perturbation theory summation. If one includes the nuclear motion by summing over both electronic and vibrational states, terms with very small energy denominators are introduced. Thus it appears, at first glance, that the inclusion of vibrational motion may have a large effect on the calculated γ. In this work, we show that these small energy denominator terms do not dominate γ, but in polyacetylene, they can account for about 10% of the total value.

We begin by showing that the sum over terms with small energy denominators can be rewritten as a sum over Raman amplitudes (Sec. II). Experimental values for the absolute nonresonant Raman amplitudes would allow an experimental determination of the importance of the vibrational contributions to γ, however, these are not readily available. Instead, we will estimate the magnitude of the vibrational effects by considering two simple model systems. In Sec. III, we consider a system with two electronic states and one vibrational degree of freedom. The vibrations are described by displaced, one-dimensional harmonic oscillators. In Sec. IV, polyacetylene is examined using the tight binding approximation with harmonic vibrations.

II. EXPRESSING γ IN TERMS OF RAMAN AMPLITUDES

The perturbation theory expression for the nonresonant third order nonlinear optical susceptibility is

$$\gamma=\sum_{n,l,m\neq 0}\frac{\langle 0|\mu|n\rangle\langle n|\mu|l\rangle\langle l|\mu|m\rangle\langle m|\mu|0\rangle}{E_{0,n}E_{0,l}E_{0,m}}-\sum_{n,l\neq 0}\frac{|\langle 0|\mu|n\rangle|^2|\langle 0|\mu|l\rangle|^2}{E^2_{0,n}E_{0,l}},\qquad(1)$$

where $\langle n|\mu|l\rangle$ is the dipole transition amplitude between states n and l, $E_{n,l}$ denotes their energy separation, and $n=0$ refers to the ground state.[11] It will be useful to consider the first and second summations in Eq. (1) separately

$$\gamma=\gamma^+-\gamma^-.\qquad(2)$$

For a centrosymmetric system with only two electronic energy levels, γ^+ is zero. This is because n must be the excited electronic level, but then l can be neither the excited state, since $\langle l|\mu|l\rangle=0$ for a centrosymmetric molecule, nor the ground state, since the summation precludes $l=0$. γ^-, on the other hand, is nonzero for this system and thus γ is strictly negative. If, however, one includes vibrational levels within each electronic state, γ^+ is no longer zero since l can be an excited vibrational level of the ground electronic state. If we include a one-dimensional vibration within the two electronic state model, we have

$$\gamma=\sum_{n,l\neq 0,m}\frac{\langle g;0|\mu|e;n\rangle\langle e;n|\mu|g;l\rangle\langle g;l|\mu|e;m\rangle\langle e;m|\mu|g;0\rangle}{E_{(g;0),(e;n)}E_{(g;0),(g;l)}E_{(g;0),(e;m)}}-\sum_{n,l}\frac{|\langle g;0|\mu|e;n\rangle|^2|\langle g;0|\mu|e;l\rangle|^2}{E^2_{(g;0),(e;n)}E_{(g;0),(e;l)}},\qquad(3)$$

where g and e refer to the ground and excited electronic states, respectively, and n, l, and m are vibrational state labels. Not only is γ^+ nonzero, it appears to have a smaller energy denominator than γ^- due to the presence of a pure vibrational frequency $E_{(g;0),(g;l)}$. The goal of this paper is to determine whether, as a result of this small energy denominator, the inclusion of vibrations will lead to a substantial change in the calculated γ. In our consideration of the two electronic state model, we will examine the ratio of γ^+ to γ^-, since γ^- is the result that would be obtained if vibrations were ignored.

We can rewrite γ^+ as

$$\gamma^+ = \sum_{l\neq 0} \frac{|\mathscr{R}(0\Rightarrow l)|^2}{E_{(g;0),(g;l)}}, \tag{4}$$

where $\mathscr{R}(0\Rightarrow l)$ is the Raman amplitude for a transition to the lth vibrational level of the ground electronic state

$$\mathscr{R}(0\Rightarrow l) = \sum_n \frac{\langle g;0|\mu|e;n\rangle\langle e;n|\mu|g;l\rangle}{E_{(g;0),(e;n)}}. \tag{5}$$

For a system with more than two electronic states, terms which have a pure vibrational energy in the denominator will still occur. The form is similar to that in Eq. (3), however, now there is a sum over excited electronic states e and e',

$$\gamma^+ = \sum_{e,e'} \sum_{n,l\neq 0,m} \frac{\langle g;0|\mu|e;n\rangle\langle e;n|\mu|g;l\rangle\langle g;l|\mu|e';m\rangle\langle e';m|\mu|g;0\rangle}{E_{(g;0),(e;n)}E_{(g;0),(g;l)}E_{(g;0),(e';m)}}. \tag{6}$$

Equation (4) is still a valid resummation of these terms since the Raman amplitude is now

$$\mathscr{R}(0\Rightarrow l) = \sum_e \sum_n \frac{\langle g;0|\mu|e;n\rangle\langle e;n|\mu|g;l\rangle}{E_{(g;0),(e;n)}}. \tag{7}$$

It is important to remember that Eq. (6), and thus Eq. (4), is not the complete expression for γ^+, but contains only those terms which have a pure vibrational frequency in the denominator. This is sufficient for our purposes since we are interested in determining the relative importance of these terms, not in obtaining quantitative values for γ.

III. TWO LEVEL SYSTEM WITH A SINGLE VIBRATIONAL MODE

To get an order of magnitude estimate of the Raman intensities and thus γ, we will first consider a system with only two electronic states and a single vibrational degree of freedom. The vibrational levels of the ground and excited electronic states will be modeled by harmonic oscillators. For simplicity, the oscillators are assumed to have identical frequencies ω, but displaced minima $Q_e^{(g)}$ for the ground electronic state and $Q_e^{(e)}$ for the excited state. The difference in energy between the minima of the two electronic states will be called Δ. The Raman intensity is then

$$\mathscr{R}(0\Rightarrow l) = \sum_n \frac{\langle g;0|\mu|e;n\rangle\langle e;n|\mu|g;l\rangle}{\Delta + n\omega}. \tag{8}$$

Within the Born–Oppenheimer approximation, we can write the electronic transition moment as a function of the vibrational coordinate Q and expand it in a Taylor series about the minimum of the ground electronic state

$$\begin{aligned}\langle g;0|\mu|e;n\rangle &= \langle 0|\mathbf{M}(Q)|\bar{n}\rangle \\ &= \mathbf{M}(Q_e^{(g)})\langle 0|\bar{n}\rangle \\ &\quad + \left(\frac{d\mathbf{M}(Q)}{dQ}\right)_{Q=Q_e^{(g)}} \langle 0|Q|\bar{n}\rangle + \cdots. \end{aligned} \tag{9}$$

The bar over the n in $|\bar{n}\rangle$ indicates that this is a vibrational level of the excited electronic state, $|n\rangle$ being levels of the ground state. The first term in the Taylor expansion is responsible for the Condon contribution to the Raman intensity, while inclusion of the second term leads to the Herzberg–Teller contribution. The Condon term typically dominates resonant Raman amplitudes, with the Herzberg–Teller term becoming dominant far off resonance. We will consider each of these contributions in turn.

A. Condon contribution

The Raman intensity in the Condon approximation is

$$\mathscr{R}(0\Rightarrow l) = |\mathbf{M}(Q_e^{(g)})|^2 \sum_{\bar{n}} \frac{\langle 0|\bar{n}\rangle\langle\bar{n}|l\rangle}{\Delta + \bar{n}\omega}. \tag{10}$$

Since the vibrational frequencies are much smaller than the electronic frequencies, we will expand Eq. (10) in powers of ω/Δ,

$$\begin{aligned}\mathscr{R}(0\Rightarrow l) = \frac{|\mathbf{M}(Q_e^{(g)})|^2}{\Delta} \sum_{\bar{n}} \langle 0|\bar{n}\rangle\langle\bar{n}|l\rangle \Bigg[1 - \bar{n}\frac{\omega}{\Delta} \\ + \bar{n}^2\left(\frac{\omega}{\Delta}\right)^2 + \cdots \Bigg]. \end{aligned} \tag{11}$$

Since the vibrational levels of the excited state $|\bar{n}\rangle$ form a complete set and $l\neq 0$ in Eq. (4) the first term in the series is zero. The summations present in Eq. (11) have been given by Ting.[12] Only the fundamental vibrational transition is allowed to first order in ω/Δ, with the first overtone becoming allowed in second order

$$\begin{aligned}\mathscr{R}(0\Rightarrow 1) = \frac{|\mathbf{M}(Q_e^{(g)})|^2}{\Delta} \Bigg[\frac{\omega}{\Delta}\frac{\delta}{2} \\ - \left(\frac{\omega}{\Delta}\right)^2 \left(\frac{\delta}{2} + \frac{\delta^3}{4}\right) + \mathscr{O}\left(\frac{\omega^3}{\Delta^3}\right) \Bigg], \end{aligned} \tag{12}$$

$$\mathscr{R}(0\Rightarrow 2) = \frac{|\mathbf{M}(Q_e^{(g)})|^2}{\Delta} \left[\left(\frac{\omega}{\Delta}\right)^2 \frac{\delta^2}{2\sqrt{2}} + \mathscr{O}\left(\frac{\omega^3}{\Delta^3}\right) \right]. \tag{13}$$

δ serves as a dimensionless measure of the displacement of the oscillators

$$\delta = \frac{Q_e^{(e)} - Q_e^{(g)}}{\sqrt{\langle 0|Q^2|0\rangle}}. \tag{14}$$

γ^+ [Eq. (4)] is now

$$\gamma^{+} = \frac{|\mathbf{M}(Q_e^{(g)})|^4}{\omega\Delta^2}\Bigg[\left(\frac{\omega}{\Delta}\right)^2 \frac{\delta^2}{4} - \left(\frac{\omega}{\Delta}\right)^3 \left(\frac{\delta^2}{2} + \frac{\delta^4}{4}\right) + \mathscr{O}\left(\frac{\omega^4}{\Delta^4}\right)\Bigg]. \tag{15}$$

Note that the first overtone does not contribute to γ^+ to the order listed. γ^- is nonzero even without inclusion of vibrations, i.e., zeroth order in ω/Δ, and has the value

$$\gamma^{-} = \frac{|\mathbf{M}(Q_e^{(g)})|^4}{\Delta^3}. \tag{16}$$

The ratio of Eqs. (15) to (16) is then

$$\frac{\gamma^+}{\gamma^-} = \frac{\omega}{\Delta}\frac{\delta^2}{4} + \mathscr{O}\left(\frac{\omega^2}{\Delta^2}\right). \tag{17}$$

Below Eq. (3), we commented that the energy denominator in γ^+ appeared smaller than that in γ^- due to the presence of a pure vibrational frequency. However, in Eqs. (15) and (16), the denominator of γ^+ has Δ^4, while γ^- has Δ^3. This is due to the fact that the Raman amplitude does not appear until first order in ω/Δ [see Eq. (12)]. Thus in Eq. (15), the prefactor, $1/\omega\Delta^2$ gets multiplied by an additional $(\omega/\Delta)^2$.

A typical vibrational frequency ω is that of a C═C double bond, about 1500 cm^{-1} or $\frac{3}{16}$ eV. Taking Δ to be the bandgap in polyacetylene, about 1.4 eV, $\omega/\Delta \approx 1/7.5$. The average vibrational amplitude $\sqrt{\langle 0|Q^2|0\rangle}$ for a C═C bond is about 0.043 Å. The calculated change in bond length on excitation of octatetraene is of the same order of magnitude 0.059 Å for the central bonds,[13] so we expect δ to be of order unity. We estimate therefore that $\gamma^+/\gamma^- \approx \frac{1}{30}$. Since γ^- is the result that would be obtained if vibrations were ignored, inclusion of vibrations within the Condon approximation is not expected to have a significant impact on γ.

The Condon contribution to Raman intensities has been investigated more thoroughly by Yeung, Heiling, and Small.[14] They find that allowing the frequencies of the ground and excited states to differ does not affect the fundamental Raman amplitude to first order in ω/Δ. Also, in systems with more than one vibrational degree of freedom, allowing the normal modes of the excited state to differ from those of the ground state, i.e., Duschinsky rotation, does not affect the results to first order.

All of the above is done in a sum over states formalism. A conceptually more appealing means of viewing the Condon contribution to Raman amplitudes is the time-dependent formalism of Lee and Heller.[15] In this formalism, the ground vibrational state wave function is first projected onto the vibrational wave functions of the excited electronic state. Since the potentials of the two states are different, the ground state wave function becomes a Gaussian wave packet on the excited state surface. This wave packet evolves for some length of time and is then projected back onto the ground state wave functions. The evolution time is determined via the uncertainty principle by the energy mismatch between the excited electronic state and the excitation frequency. Since we are interested in nonresonant γ, we consider zero excitation frequency and thus the energy mismatch is Δ. What we have then, is a vibrational wave packet evolving on an electronic time scale. Thus, only very small overlap with the excited vibrational levels of the ground state develops. This is the physical justification for an expansion in powers of ω/Δ.

B. Herzberg–Teller contribution

It will be convenient to introduce a dimensionless measure of the transition moment derivative into Eq. (9)

$$\langle 0|\mathbf{M}(Q)|\bar{n}\rangle = \mathbf{M}(Q_e^{(g)})[\langle 0|\bar{n}\rangle + \lambda\langle 0|Q|\bar{n}\rangle], \tag{18}$$

$$\lambda = \frac{[\partial\mathbf{M}(Q)/\partial Q]_{Q=Q_e^{(g)}}}{\mathbf{M}(Q_e^{(g)})}. \tag{19}$$

The Raman amplitude is then

$$\mathscr{R}(0\Rightarrow l) = \frac{|\mathbf{M}(Q_e^{(g)})|^2}{\Delta}\sum_{\bar{n}}[\langle 0|\bar{n}\rangle + \lambda\langle 0|Q|\bar{n}\rangle] \times [\langle\bar{n}|l\rangle + \lambda\langle\bar{n}|Q|l\rangle]\left(1 - \bar{n}\frac{\omega}{\Delta} + \cdots\right). \tag{20}$$

The lowest order nonzero term is first order in λ and zeroth order in ω/Δ,

$$\begin{aligned}\mathscr{R}(0\Rightarrow l) &= \frac{|\mathbf{M}(Q_e^{(g)})|^2}{\Delta}\lambda\sum_{\bar{n}}(\langle 0|Q|\bar{n}\rangle\langle\bar{n}|l\rangle + \langle 0|\bar{n}\rangle\langle\bar{n}|Q|l\rangle)\\ &= 2\frac{|\mathbf{M}(Q_e^{(g)})|^2}{\Delta}\lambda\langle 0|Q|l\rangle,\end{aligned} \tag{21}$$

where we have used the fact that $|\bar{n}\rangle$ is a complete set. For a harmonic oscillator, $\langle 0|Q|l\rangle$ is zero unless $l = 1$, so at this order, only the fundamental vibrational transition is allowed

$$\mathscr{R}(0\Rightarrow 1) = 2\frac{|\mathbf{M}(Q_e^{(g)})|^2}{\Delta}\lambda\sqrt{\langle 0|Q^2|0\rangle}, \tag{22}$$

where the harmonic oscillator relation $\langle 0|Q|1\rangle = \sqrt{\langle 0|Q^2|0\rangle}$ has been used, γ^+ [Eq. (4)] is now

$$\gamma^{+} = 4\frac{|\mathbf{M}(Q_e^{(g)})|^4}{\omega\Delta^2}(\lambda\sqrt{\langle 0|Q^2|0\rangle})^2 \tag{23}$$

and the ratio to γ^- [Eq. (16)] is

$$\frac{\gamma^+}{\gamma^-} = 4\frac{\Delta}{\omega}(\lambda\sqrt{\langle 0|Q^2|0\rangle})^2. \tag{24}$$

Unlike the Condon contribution, the Herzberg–Teller contribution appears to zeroth order in ω/Δ and thus the energy denominator of γ^+ is $1/\omega\Delta^2$, while that of γ^- is $1/\Delta^3$. This leads to the large ratio $\Delta/\omega \approx 7.5$ in Eq. (24).

In order to estimate the numerical value of λ, we make the following qualitative argument: for a homonuclear diatomic molecule, the ground and first excited electronic states will be of the form

$$\Psi^{(g)} = \frac{1}{\sqrt{2}}(\phi_A + \phi_B); \quad \Psi^{(e)} = \frac{1}{\sqrt{2}}(\phi_A - \phi_B), \tag{25}$$

where ϕ_A and ϕ_B are atomic wave functions centered on atoms A and B. This will also be the form for a pseudodiatomic molecule such as ethylene. The transition moment is then just proportional to the bond length and we find

$$\lambda = 1/Q_e. \tag{26}$$

Using the same parameters for a C=C bond as discussed above and a bond distance of 1.4 Å, we find that $(\lambda\sqrt{\langle 0|Q^2|0\rangle}) \approx \frac{1}{33}$. This more than cancels the energy denominator effect $\Delta/\omega \approx 7.5$, giving $\gamma^+/\gamma^- \approx \frac{1}{35}$. So in this case, inclusion of vibrations has a negligible effect on γ. Of course, this argument is not quantitative, but it indicates that for diatomic or pseudodiatomic systems, the dipole moment derivative λ is in general quite small. Below, we will examine whether this is also true in polymeric systems.

IV. POLYACETYLENE

It is important to consider whether any qualitatively new effects will arise in polymer systems which are not present in the above, single oscillator model. No qualitative differences are expected for the Condon contribution since in the polymer, we will just have a sum over all normal modes of terms of the form of Eq. (15). The displacements $Q_e^{(e)} - Q_e^{(g)}$ will be of roughly the same order of magnitude relative to $\sqrt{\langle 0|Q^2|0\rangle}$ as considered above. A qualitative difference does arise when the normal modes of the excited state differ from those of the ground state. However, the effect of such a "Duschinsky rotation" has been considered by Yeung, Heiling, and Small[14] and found to have little effect on the fundamental Raman intensities.

Qualitative differences between the single oscillator model and polymer systems may arise in the Herzberg–Teller contribution since the derivative of the transition moment with respect to bond distances will be qualitatively different. The homonuclear diatomic molecule model considered above has wave functions [Eq. (25)] which are completely determined by symmetry and are therefore independent of bond length. λ then results strictly from a change in the overall size of the molecule. In polyacetylene, there will also be effects from a direct change in the form of the electronic wave function due to the vibration. The wave functions of polyacetylene reflect the bond alternated geometry arising from a Peierls instability in the "all bonds equal" geometry. Present estimates place the bond alternation at 0.14 Å.[16] This is only three times larger than the expected $\sqrt{\langle 0|Q^2|0\rangle}$ for a C=C bond, so we might expect a rather large λ. Below we will first calculate γ for polyacetylene chains of up to 600 carbons and then consider the infinite chain through the use of band theory.

A. Herzberg–Teller contribution for finite chains

The summation for γ^+ [Eqs. (1) and (2)] is in general rather lengthy, involving sums over all electronic states and normal modes. We expect the major effect of including vibrations arises from those terms in which the intermediate state l is an excited vibrational level of the ground electronic state, since the energy denominator of these terms contains a pure vibrational frequency. In order to estimate the impact of including vibrations in the evaluation of γ, we will consider only these terms, as given by Eqs. (4) and (7).

Since we are only after a qualitative estimate of the effects of including vibrations, we will use periodic boundary conditions for the phonons, even though we are not using periodic boundary conditions for the electronic motion. With periodic boundary conditions for the phonons, only the optical $K = 0$ phonon mode is Raman active. If instead free end boundary conditions were used, the Raman intensity would be spread over many phonon modes, becoming increasingly concentrated in modes near $K = 0$ as the chain length increased.

The development follows along the lines of Eqs. (18)–(22). We again find that only the fundamental vibrational transition is allowed to first order in the transition moment derivatives and zeroth order in ω/Δ. For real transition moments, the Raman intensity is

$$\begin{aligned}\mathscr{R}(0 \Rightarrow 1) &= \sum_e 2\,\frac{|\mathbf{M}_{g,e}(Q_e^{(g)})|^2}{\Delta_{g,e}}\,\lambda_{g,e}\sqrt{\langle 0|Q^2|0\rangle}\\ &= \sum_e 2\,\frac{\mathbf{M}_{g,e}(Q_e^{(g)})}{\Delta_{g,e}}\\ &\quad\times\left(\frac{d\mathbf{M}_{g,e}}{dQ}\right)_{Q=Q_e^{(g)}}\sqrt{\langle 0|Q^2|0\rangle},\end{aligned} \tag{27}$$

where Q refers to the $K = 0$ phonon, $\mathbf{M}_{g,e}$ is the transition moment between the ground and an excited electronic state, and the sum is over all excited electronic states.

The electronic wave functions are calculated using the tight binding, or Hückel model. The transfer integrals β are given by[16]

$$\beta(R) = -Ae^{-R/B}, \tag{28}$$

where R is the distance between the two atoms, $A = 34.56$ eV, and $B = 0.531$ Å. At equilibrium, the single bond distance is $R_1 = 1.47$ Å ($\beta_1 = -2.169$ eV) and the double bond distance is $R_2 = 1.33$ Å ($\beta_2 = -2.824$ eV). The $K = 0$ optical phonon for a chain of $2N$ carbons, i.e, N unit cells, is

$$Q_{K=0} = \frac{1}{\sqrt{2N}}\sum_{a=1}^{N}(d_a^{(1)} - d_a^{(2)}), \tag{29}$$

where $d_a^{(1)}$ is a displacement of the single bond in the ath unit cell and $d_a^{(2)}$ is a displacement of the double bond. The net effect of $Q_{K=0}$ is to increase simultaneously all single bonds while decreasing the double bonds. In the evaluation of the transition moments, we will keep the bond distances fixed[17] and assume that the only effect of the vibrations is to change the β's. Thus we are ignoring that portion of the transition moment derivative which was shown in the single oscillator model to have negligible effects on γ. Since the electronic wave functions are invariant to the transformation $(\beta_1, \beta_2) \Rightarrow (c\beta_1, c\beta_2)$, c being a constant, $\mathbf{M}_{g,e}$ depends only on the ratio

$$\beta_{\text{rat}} = \frac{\beta_1 - \beta_2}{\beta_1 + \beta_2}. \tag{30}$$

We can replace the derivative with respect to Q in Eq. (27) with a derivative with respect to β_{rat},

$$\mathscr{R}(0\Rightarrow1)=2\sqrt{\frac{1}{2N}}\,\frac{1}{B}\left(\frac{4\beta_1\beta_2}{(\beta_1+\beta_2)^2}\right)\sqrt{\langle0|Q^2|0\rangle}\times\sum_e\frac{\mathbf{M}_{g,e}(Q_e^{(g)})}{\Delta_{e,g}}\left(\frac{d\mathbf{M}_{g,e}}{d\beta_{\text{rat}}}\right)_{Q=Q_e^{(g)}}. \tag{31}$$

γ^+ is then

$$\gamma^+=\frac{2}{N}\frac{1}{B^2\omega}\left(\frac{4\beta_1\beta_2}{(\beta_1+\beta_2)^2}\right)^2\langle0|Q^2|0\rangle\times\left[\sum_e\frac{\mathbf{M}_{g,e}(Q_e^{(g)})}{\Delta_{e,g}}\left(\frac{d\mathbf{M}_{g,e}}{d\beta_{\text{rat}}}\right)_{Q=Q_e^{(g)}}\right]^2. \tag{32}$$

Equation (32) was evaluated using the same parameters ($\sqrt{\langle0|Q^2|0\rangle}=0.043$ Å; $\omega=\frac{3}{16}$ eV) as used above for a C=C double bond. The results for $N=3$–300 are shown in Fig. 1. Also shown in Fig. 1 are the results for γ obtained ignoring vibrations, i.e., Eq. (1) with the summation being over all electronic states. The vibrational contribution is 10% of the electronic contribution at long chain lengths and a bit higher (20%) at shorter chain lengths. (The larger relative contribution at short chain lengths may be an artifact of our use of periodic boundary conditions for the phonon modes.) The 10% effect calculated here is a result of the change in the form of the wave function, i.e, the change in the coherence in the charge distribution due to the vibrations. The small contribution due to changes in the bond lengths, the only effect present for the pseudodiatomic case, have been ignored. From this approximate calculation, we see that the vibrational effects do not dominate γ, but that they do have a significant effect.

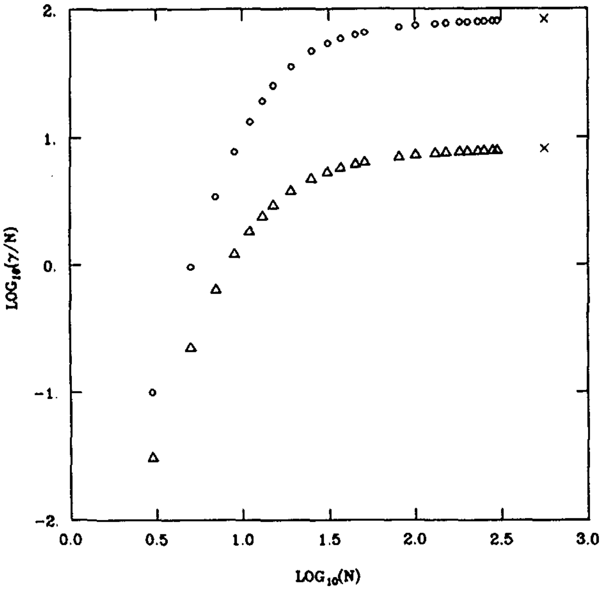

FIG. 1. The third-order nonlinear optical susceptibility γ of polyacetylene is shown as a function of the number of unit cells N. The results obtained ignoring vibrations are shown as circles. When vibrational states are included, terms appear in the perturbation theory expression for γ [Eq. (1)] which have small energy denominators. The contribution of these terms [Eq. (32)] is shown as triangles. The X's are the infinite chain results obtained using band theory [Eqs. (38) and (39)]. For long chains, the vibrational contribution is an order of magnitude smaller than the pure electronic result.

B. Herzberg–Teller contribution for infinitely long chains

The band theory of polyacetylene within the tight binding approximation has been worked out by Cojan, Agrawal, and Flytzanis.[18] The sum over states expression for the polarizability α is

$$\alpha=\sum_n\frac{\langle0|\mu|n\rangle\langle n|\mu|0\rangle}{E_{0,n}}. \tag{33}$$

In the band theory expression, $\langle0|\mu|n\rangle$ is replaced by $\Omega(k)$ and the sum over states is replaced by an integral over all wave vectors k,

$$\alpha=2N\frac{d}{2\pi}\int_{-\pi/d}^{\pi/d}dk\,\frac{|\Omega(k)|^2}{\Delta(k)}, \tag{34}$$

$$\Omega(k)=\frac{1}{d}\int_{\text{u.c.}}dx\,U_k^{c*}(x)\,\frac{\partial}{\partial k}\,U_k^{v}(x) \tag{35}$$

with d the length of a unit cell and u.c. indicating an integral over a unit cell. $U_k^{(c,v)}$ is the periodic part of the Bloch wave function for the conduction or valence band. N appears in Eq. (34), since in the sum over states expressions given up to this point, no normalization for the number of unit cells, usually included in band theory expressions, has been performed. A factor of 2 has been included to account for the double occupation of the orbitals.[11] For polyacetylene, $\Omega(k)$ is given by

$$\Omega(k)=i\frac{d}{4}\frac{\beta_1^2-\beta_2^2}{\beta_1^2+\beta_2^2+2\beta_1\beta_2\cos(kd)}=i\frac{d}{4}\frac{2\beta_{\text{rat}}}{[1+\cos(kd)]+\beta_{\text{rat}}^2[1-\cos(kd)]}. \tag{36}$$

By analogy with the correspondence between Eqs. (33) and (34), we have for the Raman amplitude [Eq. (31)]

$$\mathscr{R}(0\Rightarrow1)=2\sqrt{\frac{1}{2N}}\,\frac{1}{B}\left(\frac{4\beta_1\beta_2}{(\beta_1+\beta_2)^2}\right)\sqrt{\langle0|Q^2|0\rangle}\times\left(2N\frac{d}{2\pi}\int_{-\pi/d}^{\pi/d}dk\,\frac{\Omega(k)^*}{\Delta(k)}\frac{d\Omega(k)}{d\beta_{\text{rat}}}\right), \tag{37}$$

and for γ^+, we find

$$\gamma^+=8N\frac{1}{B^2\omega}\left(\frac{4\beta_1\beta_2}{(\beta_1+\beta_2)^2}\right)^2\langle0|Q^2|0\rangle\times\left(\frac{d}{2\pi}\int_{-\pi/d}^{\pi/d}dk\,\frac{\Omega(k)^*}{\Delta(k)}\frac{d\Omega(k)}{d\beta_{\text{rat}}}\right)^2. \tag{38}$$

The value obtained from Eq. (38) lies at the point extrapolated from the finite chain results (see Fig. 1). Also shown in Fig. 1 is the band theory result for γ obtained using the formula of Flytzanis *et al.*[18]

$$\gamma=2N\frac{d}{2\pi}\int_{-\pi/d}^{\pi/d}dk\left(\frac{1}{\Delta(k)}\frac{\partial[\Omega^*(k)/\Delta(k)]}{\partial k}\times\frac{\partial[\Omega(k)/\Delta(k)]}{\partial k}-\frac{|\Omega(k)|^4}{\Delta(k)^3}\right). \tag{39}$$

Again, the band theory result lies at the point extrapolated from finite length chains. This confirms our conclusions from the finite chain calculations that vibrational effects do not dominate γ, but do have a noticeable effect. It is important to remember that γ^+ of Eq. (4) and thus Eq. (38) contains only those terms of the perturbation theory sum [Eq. (1)] that have a pure vibrational frequency in the denominator.

V. DISCUSSION

Including vibrational levels in the perturbation theory sum for γ introduces terms which have a pure vibrational frequency in the denominator. As a result, these terms may be expected to have a large effect on the calculated γ. By performing calculations on model systems, we have shown that the effect of these terms, while not negligible, does not dominate γ. The sum over terms with small energy denominators was first rewritten as a sum over Raman amplitudes. There are two contributions to the Raman amplitude, the Condon term, and the Herzberg–Teller term.

The importance of the Condon term increases as the excitation frequency approaches resonance, becoming the dominant term in resonant Raman experiments. Since, we have only considered nonresonant γ, the Condon term is quite small. In our treatment of the two level system with one vibrational degree of freedom, we found that the lowest order contribution to the Condon term goes as ω/Δ. This introduces an additional Δ^2 into the denominator of γ, removing the small energy denominator discussed above. This will also occur in systems with many vibrational degrees of freedom, such as polyacetylene, so the Condon contribution to γ is expected to remain negligible. It is important to point out that the above arguments assume the excitation frequency is far off resonance. On resonance, the Condon terms could become significant.

The Herzberg–Teller contribution to the Raman intensity is that typically considered in nonresonant Raman experiments and arises from the dependence of the electronic transition moment on the vibrational displacements. Unlike the Condon term, there is no cancellation of the vibrational frequency in the energy denominator of γ. Instead, the relevant parameter in estimating the importance of the Herzberg–Teller contribution is the degree to which the transition moment depends on the vibrational displacements. In a two level system with diatomic vibrations, this dependence is very weak and the Herzberg–Teller terms have a negligible effect on γ. The situation is more complex in polyacetylene, where the electronic wave functions reflect the alternation in the carbon–carbon bond lengths. Since this alternation 0.14 Å is only about three times larger than the vibrational amplitudes, the vibrations have a large effect on the transition moments. The contribution to γ is between 10% and 20% of the pure electronic value at all chain lengths, and 10% at large chain lengths. (Our calculation of the vibrational effects contains only those terms in the full perturbation theory sum which have a pure vibrational frequency in the denominator, since these terms are expected to dominate.) We find therefore, that inclusion of vibrations in polyacetylene has a small effect on γ.

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