Theory of resonance Raman scattering for finite and infinite polyenes

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We investigate the resonance Raman scattering of finite and infinite polyenes. The connection between the vibronic picture of Raman scattering and the third order perturbation approach normally used in solid state physics for infinite systems is clarified. Starting from the Kramers–Heisenberg–Dirac formula for the Raman scattering, we derive expressions for the Condon and Herzberg–Teller terms for chains from \( N=2 \) (a simple two-level system) to \( N=\infty \) (a two-band system) by using the standard vibronic picture.

Close to resonance the Condon term dominates and converges to the usual solid state result. In the off-resonance region, the Herzberg–Teller term is comparable to the Condon term for both the small molecule and the solid state system. © 1995 American Institute of Physics.

I. INTRODUCTION

Raman scattering is one of the most important methods for probing the microscopic structures of molecules and bulk materials. For instance, it has been used to study the electronic and vibrational properties of such diverse materials as small molecules (e.g., \( I_2 \)), semiconductors (e.g., \( Cu_2O \)), biological chromophores (e.g., bacteriorhodopsin), mixed valence compound (e.g., Wolffram’s red), etc.\(^1-4\) Resonance Raman scattering (RRS) arises when the photon energy of the exciting beam is approximately equal to that of an electronic absorption band. The intensity of the Raman band associated with totally symmetric modes that are coupled to the electronic excited state can then be enhanced by several orders of magnitude. It is unfortunate, however, that the language for the description of Raman scattering in various fields is quite different. In the vibronic approach,\(^5,6\) used conventionally for small molecules or polymers, the Raman cross section is expressed as a sum of the Condon and Herzberg–Teller terms. The parameters of excited states appear explicitly through the Frank–Condon overlap or dependence of transition moment on the normal coordinates in the vibronic picture of Raman scattering. The standard approach used in solid state physics\(^1,2,7\) for the Raman cross section is the third order perturbation theory in the electron–radiation and electron–phonon interaction. The parameters of excited states are hidden in the electron–phonon coupling constant in the solid state picture. Although it is generally believed that these two methods are equivalent to each other, there have been very few attempts to examine the connections between different descriptions.\(^7,8\)

In order to make a connection between the vibronic picture of Raman scattering and the standard third order perturbation theory in solid state physics, we study the chain length dependence of resonance Raman scattering from a simple two level system to a two band system using finite and infinite polyenes as our model systems.\(^8–11\) In polyenes, the vibrations which involve a change of single and double bonds are directly coupled to \( \sigma-\pi^* \) electronic transition and, therefore, are strongly enhanced in RRS. For simplicity, only the delocalized vibrations along dimerization mode are considered in this work. Since RRS is very sensitive to the geometry of the excited state, how the excited state potential surface changes as a function of chain length and the effect on RRS will be discussed at length. The effect of boundary condition on the potential surface and the RRS for finite systems and the relative importance of the Condon and Herzberg–Teller terms in different spectral regions are also discussed. The model we use for polyenes is too simplified for comparison to experiment; it does however illuminate clearly the evolution of the RRS with chain length.

The paper is laid out as follows. In Sec. II, the vibronic approach to Raman scattering is reviewed. In Sec. III, this is applied to the two level system (ethylene) in the Hückel approximation. Both the Condon and Herzberg–Teller terms are calculated. In Sec. IV, finite and infinite polyenes are treated in the same manner and formulas are derived for the Condon and Herzberg–Teller contributions. It is shown that the Condon term dominates in the resonant region due to its stronger resonant terms. Finally, in Sec. V, these results are discussed and compared to earlier work.

II. RAMAN CROSS SECTION

The vibronic approach\(^5\) for Raman scattering starts from the standard second order perturbation theory in the system–radiation interaction. The Raman amplitude from vibronic state \( |G,m\rangle \rightarrow |G,n\rangle \) is given by the Kramers–Heisenberg–Dirac formula

\[
\mathcal{R} = \frac{1}{\hbar} \sum_{E,v} \left( \frac{G,n|\mu|E,v\rangle\langle E,v|\mu|G,m\rangle}{\omega_{Ev,Gm} - \omega_L + i\gamma} + \frac{G,n|\mu|E,v\rangle\langle E,v|\mu|G,m\rangle}{\omega_{Ev,Gm} + \omega_L + i\gamma} \right),
\]

where \( \mu = e \sum \xi_k \) is the dipole operator. Within the Born–Oppenheimer approximation, the vibronic states can be written as products of electronic and vibrational states

\[
|G,m\rangle = |G\rangle|m_G(Q)\rangle, \quad |G,n\rangle = |G\rangle|n_G(Q)\rangle,
\]

\[
|E,v\rangle = |E\rangle|v_E(Q)\rangle,
\]

where \( |G\rangle \) and \( |E\rangle \) are the electronic ground and excited state, respectively, \( |m_G(Q)\rangle \) and \( |n_G(Q)\rangle \) are the initial and
finite vibrational states, and \( |v_E(Q)\rangle \) is the intermediate vibrational state. Transition moments between vibrionic states are given by

\[
\langle G,n|\mu_{E,V}\rangle = \langle n_G(Q)|\mu_{GE}(Q)|v_E(Q)\rangle,
\]
where \( \mu_{GE}(Q) = \langle G(Q)|\mu(E(Q))\rangle \) is the electronic transition moment between adiabatic states \( |G(Q)\rangle \) and \( |E(Q)\rangle \), and \( |m_G\rangle \) and \( |v_E\rangle \) are vibrational states on the ground and excited potential surfaces, respectively. Making a vibronic expansion at the equilibrium geometry of the ground electronic state, we obtain (to lowest order in the vibrational coordinate)

\[
\mu_{EG}(Q) = \mu_{EG}^0(Q_0) + \mu_{EG}'(Q_0)(Q - Q_0),
\]

\( \mu_{EG}^0 \) is the electronic transition moment taken at equilibrium position of the nuclei. Substituting Eq. (4) into Eq. (1), the Raman amplitude \( \mathcal{R} \) becomes a sum of two terms: \( \mathcal{R} = A + B \), which are given by

\[
A = \frac{1}{\hbar} \sum_{E,V} \mu_{EG}^0 \mu_{EG}^0(n_G|v_E\rangle\langle v_E|m_G\rangle) \left( \frac{1}{\omega_{E,G,m} - \omega_L + i\gamma} + \frac{1}{\omega_{E,G,m} + \omega_L + i\gamma} \right)
\]

and

\[
B = \frac{1}{\hbar} \sum_{E,V} \frac{\partial \mu_{GE}}{\partial Q} \left. \langle n_G|v_E\rangle\langle v_E|m_G\rangle \right|_{Q_0} \frac{\partial \mu_{GE}}{\partial Q} \left. \langle m_G|v_E\rangle\langle v_E|n_G\rangle \right|_{Q_0} \times \left( \frac{1}{\omega_{E,G,m} - \omega_L + i\gamma} + \frac{1}{\omega_{E,G,m} + \omega_L + i\gamma} \right),
\]

respectively. If we make a Herzberg–Teller expansion for the excited vibrionic state, the transition moment derivatives in Eq. (4) and (6) can be written in terms of the vibronic coupling matrix elements between different excited states, i.e., \( \langle E'|\partial \mathcal{R}/\partial Q|Q_0\rangle \langle E|\rangle \), while the A terms involve only the diagonal part of excited state vibrionic coupling matrix, i.e., \( \langle E|\partial \mathcal{R}/\partial Q|Q_0\rangle \langle E|\rangle \). Vibronic interactions between ground and excited states, the so-called Albrecht’s C terms, are usually small and will be neglected. In the rest of this paper, we will concentrate on the Raman fundamentals, i.e., terms involving Frank–Condon factors: \( \langle 1_G|v_E\rangle\langle v_E|0_G\rangle \) for Condon contributions and \( \langle 1_G|Q|v_E\rangle\langle v_E|0_G\rangle \) and \( \langle 1_G|v_E\rangle\langle v_E|Q|0_G\rangle \) for the Herzberg–Teller contributions.

III. TWO-LEVEL SYSTEM: ETHYLENE

We first consider the simplest \( \pi \)-electron system: ethylene, which can be described by the Hamiltonian \( \mathcal{H} = f(r) + \beta(r)(c_1^+c_2^+c_1^+c_1^+c_2^+c_2^+) \) in the Hückel approximation where \( \beta(r) \) is the resonance integral between sites 1 and 2 and \( f(r) \) is \( \sigma \)-bond compressional energy. We assume that \( \beta(r) \) is given by the exponential function \( \beta(r) = -A \exp(-r/B) \). Following Kürti and Kuzmany, \( A_b \) and \( B_b \) are given by 234.5 eV and 0.3075 Å, respectively. With the exponential ansatz for the resonance integral and a linear bond-order–bond-length relationship \( r = R_1 - (R_1 - R_2)p(r) \), the \( \sigma \) bond energy, \( f(r) = 2\beta(r)(r - R_1 + B)/(R_1 - R_2) \), can be obtained by the equilibrium condition \( \partial E_{C\beta}/\partial \sigma = 0 \) where \( R_1 = 1.54 \) Å and \( R_2 = 1.33 \) Å are the bond lengths of pure single and double bonds, respectively. Since only one optically allowed singlet state is involved in the Raman scattering, the Hamiltonian can be simplified to a two-level system coupled with a single vibrational degree of freedom:

\[
\mathcal{H} = [f(r) + 2\beta(r)]|G\rangle\langle G| + |f(r)|E\rangle\langle E|. \tag{7}
\]

This implies that the excited electronic state is a pure single bond while the ground state is a pure double bond. Using Kürti and Kuzmany’s parameters for polyenes, we find that the displacement in the excited state for this simplified model is 0.21 Å, which is about 5 times larger than the value in Yaron and Silbey \[\text{[but is close to the change in} \chi(1\Sigma^+_g^+) \rightarrow B(3\Pi_u^+)] \text{of I_2, } ~0.35 \text{ Å (Ref. 3)], and the force constants for the ground and excited state are 15.98 and 8.09 mdyn/Å, respectively. We use the harmonic approximation for the two potential surfaces. The excited state frequency is reduced to almost one-half of the ground state frequency because the excited state has a strong antibonding character in this model of ethylene. A difference in frequency has a stronger effect on \( \langle n_G|v_E\rangle\langle v_E|0_G\rangle \) for the n-even overtones, the effect on the Raman fundamental and odd overtones being absent or very weak. Since we are only interested in Raman fundamentals, the frequency change will be neglected in the following discussion. The difference in energy between the minima of the two electronic states is denoted as \( \Delta \).

A. Condon contribution

The Raman amplitude in the Condon approximation for a two-level system is

\[
A = \frac{|M(Q_0)|^2}{\hbar} \sum_v \langle 1_G|v_E\rangle\langle v_E|0_G\rangle \times \left( \frac{1}{\Delta + \nu \omega_p - \omega_L + i\gamma} + \frac{1}{\Delta + (\nu - 1) \omega_p + \omega_L + i\gamma} \right), \tag{8}
\]
where \( M(Q_0) = \mu_{E_G}^0 \), \( \omega_L \) is the laser frequency and \( \omega_p \) the vibrational frequency. General recursion relations for one-dimensional Franck–Condon overlap has been worked out by Mannebach.\(^{15}\) When the oscillator is displaced in the excited state relative to the ground state, but has the same frequency in the ground and excited state, the Franck–Condon factors for the Raman fundamental are given by

\[
\langle 1_G|v_E|0_G \rangle = \frac{\delta}{\sqrt{2}} \left( \frac{|\langle 0_G|v_E \rangle|^2}{\langle 0_G|v_E \rangle^2} - |\langle 0_G|v - 1_E \rangle|^2 \right), \tag{9}
\]

where we introduce a dimensionless quantity \( \delta = \lambda_E/\sqrt{\langle 0_G|v_E \rangle^2 \langle 0_G|v_E \rangle^2} \) to characterize the size of the displacement of the excited state relative to the ground state with \( \lambda_E \) the displacement for the state \( |E \rangle \). In the normal Raman region, \( \omega_L \approx \Delta + \nu \omega_p \), the summation over all vibrational levels of the excited state can be completed. To the lowest order in \( \omega_p/\Delta \) in Eq. (8), the Condon contribution is given by\(^{14}\)

\[
A = \frac{\omega_p}{\Delta} \left( \frac{M(Q_0)^2}{\Delta} \right) + \left( \frac{\omega_p^2}{\Delta} \right)^2. \tag{10}
\]

Close to resonance, the completeness relation is no longer useful, but we can now approximate only two vibrational states, \( |0_E \rangle \) and \( |1_E \rangle \) are important. Hence, the \( A \) term can be simplified as

\[
A = \frac{\langle M(Q_0) \rangle^2}{\hbar} \left( \frac{\langle 1_G|0_E \rangle \langle 0_E|0_G \rangle}{\Delta - \omega_L + i \gamma} + \frac{\langle 1_G|1_E \rangle \langle 1_E|0_G \rangle}{\Delta + \omega_p - \omega_L + i \gamma} \right), \tag{11}
\]

where only most resonant terms are kept. The Franck–Condon factors in Eq. (11) can be obtained by expanding the vibrational wave functions of the excited states as

\[
|v_E \rangle = e^{-i \frac{P}{\hbar}} |v_G \rangle = |v_G \rangle - i \frac{\lambda_E P}{\hbar} |v_G \rangle \]

\[
- \frac{\lambda_E^2 P^2}{2 \hbar^2} |v_G \rangle + \cdots, \tag{12}
\]

where \( P = (m_s \omega_s \hbar/2)^{1/2} (a - a^\dagger) \) is the displacement generator. Hence, the \( A \) term becomes

\[
A = \frac{1}{\hbar} \lambda_E |M(Q_0)|^2 \langle 1_G | \frac{i P}{\hbar} |0_G \rangle \]

\[
\times \left( \frac{1}{\Delta - \omega_L + i \gamma} + \frac{1}{\Delta + \omega_p - \omega_L + i \gamma} \right). \tag{13}
\]

After some manipulation, we obtain

\[
A = \frac{\delta \omega_p |M(Q_0)|^2}{2 \hbar} \frac{1}{\Delta} \left( \frac{1}{1 - \omega_L/\Delta + i \gamma/\Delta} \right) \left( 1 - \omega_p/\Delta + i \gamma/\Delta \right), \tag{14}
\]

where \( \omega_s = \omega_L - \omega_p \) is the frequency of the Raman (Stokes) lines. In the adiabatic limit \( \omega_p \ll \Delta \), Eq. (14) becomes

\[
A = \frac{\delta \omega_p |M(Q_0)|^2}{2 \hbar} \frac{1}{\Delta} \left( 1 - x \right)^{-2}, \tag{15}
\]

with \( x = \omega_L/\Delta \). We have assumed \( \gamma \to 0 \) in Eq. (15) in order to compare with the result obtained in the solid state limit.

### B. Herzberg–Teller contribution

The Herzberg–Teller contribution for the ethylene is given by \([\langle M(Q) \rangle = \mu_{E_G} \])

\[
B = \frac{2}{\hbar} \left( \frac{|0| \langle Q^2 |0 \rangle \right) \frac{1}{2} M(Q_0) \left( \frac{\partial M(Q)}{\partial Q} \right) Q_0 \]

\[
\times \left( \frac{1}{\Delta - \omega_L + i \gamma} + \frac{1}{\Delta + \omega_L + i \gamma} \right). \tag{16}
\]

The relative dependence of the \( A \) and \( B \) terms depends on the magnitude of \( |M(Q_0)| \) and \( |\langle \partial M(Q)/\partial Q \rangle| \). In the case of ethylene, the transition moment can be approximated as \( Q/2 \). Instead of using the usual Herzberg–Teller expression for the vibronic wave function,\(^{14,16}\) the derivative of the electronic transition moments with respect to the vibrational coordinate can be calculated directly and is equal to \( \frac{1}{2} \) for ethylene, so that the Herzberg–Teller term becomes

\[
B = \frac{2}{\hbar} \left( \frac{|0| \langle Q^2 |0 \rangle \right) \frac{1}{2} M(Q_0) \frac{1}{Q_0} \left( \frac{1}{\Delta - \omega_L} + \frac{1}{\Delta + \omega_L} \right). \tag{17}
\]

In the static limit \( \omega_L = 0 \), the ratio between the \( A \) and \( B \) terms is 1.6. The \( A \) term is more important, but the Herzberg–Teller term is not negligible.\(^{16}\) Close to resonance, the \( B \) term goes like \( (1 - x)^{-1} \), while the \( A \) term goes like \( (1 - x)^{-2} \). Hence, the \( A \) term dominates at resonance.

### IV. FROM FINITE POLYENES TO THE TWO-BAND SYSTEM: POLYACETYLENE

The Hückel Hamiltonian with \( \sigma \)-bond compression is used for polyenes,\(^{8,12,14,17}\)

\[
H = \sum_n \beta(r_n)(c_n^+ c_{n+1} + c_{n+1}^+ c_n) + \sum_n f(r_n). \tag{18}
\]

For a perfect dimerized chain with cyclic boundary condition, the eigenvalue \( \omega_k \) for the one electron orbital \( |k \rangle \) is given by \( \omega_k = [\beta_1^2 + \beta_2^2 + 2 \beta_1 \beta_2 \cos(k a)]^{1/2} \), where \( \beta_1 \) and \( \beta_2 \) are the resonance integrals for the single and double bonds, respectively, and \( a \) is the unit cell length.

The relevant vibrational modes in the resonance Raman scattering are those with large projection on the dimerization mode. In the cyclic chain, the dimerization mode corresponds to the \( K=0 \) mode.\(^{18}\) In the linear open chain, translational symmetry is lost and the \( K=0 \) mode does not exist; thus, Kürmi et al.\(^{8}\) define a \( J_a \) mode for finite linear chains which converges to the \( K=0 \) mode as \( N \to \infty \). For simplicity, we neglect the two-dimensional structure of polyenes, so there is only one optical phonon strongly coupled to electronic degrees of freedom. It is then straightforward to select the \( J_a \) mode of a linear polyene by diagonalizing the Wilson GF matrix.\(^{8}\) The force matrix \( F \) is calculated by taking the second derivative of total energy with respect to the bond length\(^{19}\).
\[
F_{ij} = \left( \frac{\partial^2 E_T(r_1, r_2, \ldots, r_N)}{\partial r_i \partial r_j} \right)_{0}
\]
\[
= \delta_{ij} \left[ \frac{d^2 f(r_j)}{dr_j^2} + 2 \rho_j(r) \frac{d \beta(r_j)}{dr_j^2} \right] + \pi_{ij} \frac{d \beta(r_j)}{dr_j},
\]

where the terms in the large parentheses represent a localized force constant, the second term corresponds to a delocalized force constant, and \(
\pi_{ij} = 2 \partial \rho_j(r)/\partial \beta_j
\) is the bond–bond polarizability. After diagonalizing the GF matrix, we can easily choose the dimerization mode which corresponds to a shortening of the single bond and a lengthening of double bond. This mode is the \(Ja\) mode for a linear chain and the \(K=0\) mode for a cyclic chain. The dimerization modes for the linear and cyclic chain are then given by, respectively,

\[
Q_{Ja} = \sqrt{2/N} \sum_j (-1)^j \sin \frac{j \pi}{N} dr_j,
\]
\[
Q_{K=0} = \sqrt{1/N} \sum_j (-1)^j dr_j.
\]

respectively. Due to the difference between \(K=0\) and \(Ja\) modes, the vibrational spectra of cyclic and linear chains with the same length are different. Even though the equilibrium configuration for the linear chain differs from the cyclic chain only around the boundary layer (usually a few unit cells), and becomes negligible as \(N \to \infty\), the \(Ja\) mode for the linear chain is always different from the \(K=0\) mode of cyclic chain with the same chain length, and, in particular, in the displacement of the \(1B_g\) potential surface. We define the displacement by \(A = Q_{E0} - Q_{G0}\). Within the Huckel model given in Eq. (18), it is straightforward to calculate this displacement as a function of the number of double bonds, along the \(K=0\) mode for cyclic chains and along the \(Ja\) mode for linear chains. We find that, for large \(N\) (\(N > 60\)), these displacements (and, hence, the Franck–Condor factors) have the same functional dependence on \(N\), except for a numerical factor. In Fig. 1, we plot the displacement of the cyclic chain along the \(K=0\) mode, \(\lambda(K=0)\), and the displacement of the linear chain along the \(Ja\) mode, \(\lambda(Ja)\), as functions of \(N\). We find quantitative agreement between the former for \(2N\) with the latter for \(N\). That is, the cyclic chain of length \(2N\) has the same displacement as the linear chain of length \(N\). In addition, for large \(N\), the cyclic chain has essentially the same displacement along the \(K=0\) coordinate as it does along the \(Ja\) coordinate. Since we are interested in large \(N\) we may perform our calculations on cyclic chains with the strongly coupled \(K=0\) modes, and be confident that the same trends apply for linear chains. We will therefore concentrate on the Raman scattering of the cyclic chains in the rest of this paper.

**A. Condon contribution**

In order to calculate the Frank–Condor overlap \(\langle n_G | v_E \rangle\), the excited state potential surfaces are approximated as simple displaced harmonic oscillators.\(^{20,21}\) Hence, the excited state vibrational wave functions can be expanded in terms of the ground vibrational states, i.e., the expansion in Eq. (12). The first term in the expansion gives only elastic scattering, while the second and third terms are responsible for one and two phonon scattering, respectively. In the large \(N\) limit, the displacement \(\lambda_E = \frac{1}{k_G} (\partial \epsilon_{EG}/\partial Q)_{Q_0}\), where \(k_G\) is the force constant for the \(K=0\) mode in the ground (and excited) state and \(\epsilon_{EG}\) is the energy of the excited state relative to the ground state. For polyacetylene, \(\lambda_E \approx N^{-1/2}\), thus in the limit of large chains, only the linear term in \(\lambda_E\) need be considered.\(^{22}\) This is different from the calculation for the two-level system in Sec. III, where a sum over all intermediate vibrational states in the excited state is necessary for normal Raman scattering. The \(A\) term is then given by

\[
A = \frac{1}{\hbar} \sum_{E,v} \mu_{EG} \mu_{EG}^0 \langle 1_G | v_G \rangle \langle v_G | \lambda_E P | \hat{h} | 0_G \rangle
\]
\[
- \langle 1_G | \lambda_E P | \hat{h} | v_G \rangle \langle v_G | 0_G \rangle \left( \frac{1}{\omega_{EG} + v \omega_p - \omega_L + i \gamma} + \frac{1}{\omega_{EG} + (v-1) \omega_p + \omega_L + i \gamma} \right),
\]

where \(\omega_{EG}\) is the energy difference between the two potential minima and \(\omega_p\) is the vibrational frequency. In contrast with our previous results where we replaced \(\lambda_E\) by \(\lambda_0\), the displacement of the LUMO (lowest unoccupied molecular orbital) along the dimerization mode,\(^{10}\) here the lattice displacement in \(|E\rangle\) is evaluated explicitly: \(\lambda_E = \lambda_0 \Delta / \omega_{EG}\) (the derivation is given in Appendix A).\(^{23}\) Using the orthonormal property, \(\langle v_G | m_G \rangle = \delta_{v,m}\), the \(A\) term can be simplified to

![FIG. 1. Displacement \(\lambda\) of excited state \(|d\rangle\) potential surface relative to the ground state along the dimerization coordinate for linear and cyclic polyenes with different chain lengths. Potential surfaces for the linear chains for \(N<29\) are very anharmonic, so their lattice displacements are not shown.](image)
where $\omega_S = \omega_L - \omega_p$ is the scattered light frequency for the Stokes Raman line and $\omega_S = \omega_L + \omega_p$ for the anti-Stokes Raman line. Defining the function $f_A(\omega)$ as

$$f_A(\omega) = \frac{1}{\hbar} \sum_E \frac{\Delta}{\omega_{EG}} \mu_{EG} \mu_{EG} \left( \frac{1}{\omega_{EG} - \omega_S + i\gamma} - \frac{1}{\omega_{EG} + \omega_S + i\gamma} \right),$$

(24)

the Condon term can be written as

$$A = \frac{\lambda_0}{2((0|Q^2|0))^{1/2}} \left[ f_A(\omega_S) - f_A(\omega_L) \right].$$

(26)

Far from resonance, both $\omega_L - \omega_{EG}$ and $\omega_S - \omega_{EG}$ are much larger than the phonon frequency $\omega_p$, and the finite difference in Eq. (26) can be replaced by a derivative with respect to $\omega_l$. Then we find the following expression for the Condon term of the Raman amplitude:

$$A = \frac{\lambda_0 \omega_p}{2((0|Q^2|0))^{1/2}} \left( \frac{df_A(\omega)}{d\omega} \right)_{\omega_l},$$

(27)

which is similar to the results found in the solid state literature.\textsuperscript{2,7} Equation (26) and its approximate, Eq. (27), are generally true for any large system in all dimensions in the nonresonant region.

In the large $N$ limit, $f_A(\omega_L)$ can be replaced by an integral over the first Brillouin zone:\textsuperscript{8,17,28}

$$f_A(\omega_L) = \frac{2N}{\hbar^2 2\pi} \int^\pi_{-\pi} \frac{\Delta}{2\omega_k} \left| \Omega(k) \right|^2 \left( \frac{1}{2\omega_k - \omega_L + i\gamma} - \frac{1}{2\omega_k + \omega_L + i\gamma} \right) dk,$$

(28)

where $N_A(\epsilon)$ is the joint density of states, $\epsilon (= 2\omega_0)$ is the transition energy at $k$, and $\omega_0$ and $x_0$ are defined by $\omega_0 = A \beta e^{-\alpha/2} \beta$ and $x_0 = B \beta^{-1} (r_1 - r_2)/2$, respectively. In deriving Eq. (28) from Eq. (25), we have replaced the summation over many electron wave functions $|E\rangle$ by the summation over single electron wave functions $|k\rangle$ and the transition matrix element $\langle E|\mu|G\rangle$ by $\Omega(k)$, which is given by $\Omega = i\epsilon e^{-\beta^2/2}$. The main contribution to Eq. (28) comes from regions around the critical points in the joint density of states which are defined by the condition $d\epsilon(k)/dk = 0$. For polyacetylene, the critical point is at the Fermi surface (i.e., $k_F = \pi/\alpha$). We make the parabolic approximation around the Fermi surface for the energy band, so that the joint density of states (including spin degeneracy) can be simplified to

$$N_A(\epsilon) = \pi^{-1} (m_e/2)^{1/2} (\epsilon - \Delta)^{-1/2} \Theta(\epsilon/\Delta),$$

where $m_e (= h^2 \sinh \theta_0 x_0 / 2 \epsilon_0)$ is the reduced mass of the interband transition, $\Delta (= 4\alpha \sinh \xi_0)$ is the energy gap, and $\Theta(\epsilon) = \text{Heaviside step function}$. $f_A(\omega)$ can be calculated analytically for $\gamma \rightarrow 0^+$ by extending the upper limit to $\infty$:

$$f_A(\omega) = F(\Delta) \lim_{\gamma \rightarrow 0^+} \frac{1}{\pi} \int_0^\infty d\epsilon \frac{1}{\epsilon} \frac{\Delta}{(\epsilon - \Delta)^{1/2}} \times \left( \frac{1}{\epsilon - \omega_L + i\gamma} - \frac{1}{\epsilon + \omega_L + i\gamma} \right),$$

(29)

$$= F(\Delta) \Delta^{-1/2} \left( \frac{\omega_L}{\Delta} \right)^{1/2},$$

(30)

where

$$F(\Delta) = \frac{2N}{\hbar^2 2\pi} \left( \frac{h v_F}{\Delta} \right)^2 \left( m_e / 2 \right)^{1/2},$$

(31)

$$g(x) = x^{-5} \left( -2 - \frac{3}{4} x^2 - \frac{35}{64} x^4 + (1 - x)^{-1/2} + (1 + x)^{-1/2} \right),$$

(32)

and $v_F (= t_0 a\hbar)$ is the Fermi velocity for undimerized polyacetylene. The signs of the square roots of Eq. (32) are determined by drawing a cut in the complex $\omega$ plane from $\omega = 0$ to $\infty$. From Eq. (27), the Raman amplitude is proportional to the derivative of $f_A(\omega)$ with respect to the laser frequency:

$$\left( \frac{df_A(\omega)}{d\omega} \right)_{\omega_L} = F(\Delta) \Delta^{-3/2} \frac{h}{\Delta} \left( \frac{\omega_L}{\Delta} \right),$$

(33)

where

$$h(x) = x^{-5} \left( 10 x^{-1} + \frac{3}{2} x + \frac{15}{64} x^3 - 5 x^{-1}(1 - x)^{-1/2} - 5 x^{-1}(1 + x)^{-1/2} + \frac{3}{2}(1 - x)^{-3/2} \right).$$

(34)

Substituting Eq. (33) into Eq. (27), we obtain the Condon contribution to the Raman amplitude:

$$A = G(\Delta, \delta_N) h \left( \frac{\omega_L}{\Delta} \right),$$

(35)

where

$$G(\Delta, \delta_N) = \left( \sqrt{2N/2\pi} \right) x_0 \delta_N \frac{h}{\Delta} \frac{\Omega(\Delta)}{\Delta},$$

(36)

the dimensionless measure of the displacement of oscillators is defined here as

$$\delta_N = \sqrt{2N \lambda_0} / \sqrt{(0|Q^2|0)},$$

(37)

and $\Omega(\Delta)$ is the transition moment at band edge. This result is very similar to the result for the two-level system except
for some extra factors, \( \sqrt{2N} \) and \( x_0 \). The factor \( \sqrt{2N} \) keeps the Raman cross section size consistent and the factor \( x_0 \) gives a measure for the bond alternation [see Eqs. (10) and (15)]. For polyacetylene, \( x_0=0.15 \), \( \Delta=1.5 \) eV, \((0|Q^2|0))^{1/2}=0.055 \ \text{Å} \), \( \delta_p=58.2 \), \( \hbar \omega_p=0.21 \) eV, \( \Omega(\Delta)\) =4.70 Å, and \( G/\sqrt{2N}=2.89 \ \text{Å}^2\) eV.

Close to resonance, \( f_A(\omega_L, \Delta)=f_A(\omega_L-\Delta) \); hence, \( df_A(\omega_L)/d\omega_L=\omega_L f_A(\omega_L)/d\omega_L \). The most resonant term of \( f_A \) goes like \( (\Delta-\omega_L)^{1/2} \), so that the singularity for \( df_A(\omega_L)/d\omega_L \) goes like \( (\Delta-\omega_L)^{-3/2} \). This result is consistent with the result from the Green function approach for polyacetylene with infinite chain length.\(^{11}\) If we compare this result with Eq. (15) for the two-level system, there is an extra factor of \((1-x)^{3/2} \) which comes from square root singularity of density of states. Far from resonance, i.e., normal Raman scattering, we have \( h(x)=0.45+\mathcal{C}(x^2) \) as \( x \to 0.\(^{25}\)

B. Herzberg–Teller contribution

The Herzberg–Teller contribution comes from the dependence of the electronic transition moment on the nuclear coordinate. Following a procedure similar to the Condon term, we obtain

\[
B = \frac{2}{\hbar} \left\langle \left| Q^2 \right| \right\rangle^{1/2} \sqrt{2N} \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk \Omega(k) \left( \frac{1}{2\omega_k-\omega_L} + \frac{1}{2\omega_k+\omega_L} \right)
\]

(38)
to the lowest order in \( N \), where

\[
\frac{d\Omega(k)}{dQ} \bigg|_{\omega_b} = -\frac{i}{\hbar} \frac{\Delta^2}{\omega_p^2} \cos(2\omega_0) 2 \sinh(2\omega_0) \frac{e_0^2}{\omega_p^2}.
\]

(39)

A factor of 2 in Eq. (38) comes from the neglect of the phonon frequency \( \omega_p \) relative to the laser frequency for this term. The leading term of the \( (d\Omega(k)/dQ)_{\omega_b} \) as \( \omega \to \infty \) is proportional to \( N^{-1/2} \) which is exactly the same as the asymptotic behavior of \( \lambda \) in the Condon term. Hence, to the lowest order in \( N \), both Condon and Herzberg–Teller terms should be considered. In order to determine which term is dominant in different spectral regions, we must compare the coefficients of these two terms. Changing the integration from \( k \) to \( e \), the \( B \) (Herzberg–Teller) term can be simplified to

\[
B = \frac{2}{\hbar} \left| \left| Q^2 \right| \right|^{1/2} \sqrt{2N} \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} d\epsilon N_d(\epsilon) M(\epsilon) \left( \frac{1}{\epsilon-\omega_L} + \frac{1}{\epsilon+\omega_L} \right),
\]

(40)

where

\[
M(\epsilon) = \frac{a^2}{16B_\beta \epsilon_0} \frac{\Delta^4}{\epsilon^2} \left[ 1 + 2\epsilon_0^2 - 2 \frac{\Delta^2}{\epsilon^2} \right]
\]

(41)
in the small \( x_0 \) limit. The transition element vanishes in the equal bond length limit (i.e., \( x_0=0 \)), as seen from the one band picture for the undimerized polymer, where the selection rule for the interband transition restricts the transition rate to be zero.\(^{26}\) Making a quadratic approximation for the energy band and extending the upper limit for the integration to infinity, the Herzberg–Teller term becomes

\[
B = -2G(\Delta, \delta_N) f_B \left( \frac{\omega_L}{\Delta} \right),
\]

(42)

where

\[
f_B(x) = x^{-4} \left\{ -\frac{1}{2} + 4x^2 + 4x^{-2} + \left( \frac{11}{32} - \frac{2x^2}{90} \right) x^2 
+ \left( 1 + 2x^2 - 2x^{-2} \right) \left[ (1-x)^{-1/2} + (1+x)^{-1/2} \right] \right\}.
\]

(43)

Now, the Raman amplitude from both Condon and Herzberg–Teller terms can be combined into one equation:

\[
\mathcal{R} = G(\Delta, \delta_N) \left[ h \left( \frac{\omega_L}{\Delta} \right) - 2 f_B \left( \frac{\omega_L}{\Delta} \right) \right].
\]

(44)

The resonant term in the Herzberg–Teller contribution goes like \( (\Delta-\omega_L)^{-1/2} \). This singularity is weaker than the Condon term in the resonance region; hence, the Condon terms dominate in the resonance region. Far away from resonance, \( 2 f_B(x) \sim -0.66 + \mathcal{C}(x^2) \) as \( x \to 0 \), which is slightly larger than the contribution from the Condon terms (see Fig. 2). For small molecules far from resonance, the Condon term is larger than the Herzberg–Teller term for totally symmetric modes since the Condon term corresponds to the diagonal element in the vibronic coupling, while the Herzberg–Teller term comes from the off-diagonal coupling between different electronic states.\(^{5}\) In general then, except for nontotally sym-

FIG. 2. Comparison of different contributions to the Raman excitation profile for a polyene of infinite length as a function of laser frequency, \( \epsilon \). The solid line is the Condon contribution, \( h(x) \), [Eq. (34)]. The dotted line is the Herzberg–Teller contribution, \( 2 f_B(x) \). The dotted-dashed line is the sum of the two contributions, \( h(x) + 2 f_B(x) \). The dashed line is the Raman profile calculated by the AMM theory (Ref. 28).
metric modes the Condon (A) term is usually more important than the Herzberg–Teller (B) term. For large molecules, however, if the displacement, x, of the excited state vanishes as \( N \to \infty \), it is then difficult to estimate which term is dominant. In Fig. 2, we plot the various contributions to the Raman amplitude using Eq. (44), as a function of laser frequency, \( x = \omega/\Delta \). Figure 2 shows that the Herzberg–Teller (B) term is slightly larger than the Condon (A) term in the normal Raman region for polyacetylene. This is quantitatively different from the small molecule result in Sec. III.

There are two effects not taken into account in this treatment. Equation (44) implies that the fundamental Raman cross section should be proportional to square of the dimensionless displacement, \( \delta^2 \). However, the interference in the Raman amplitude in a system with more than one vibrational degree of freedom can cause the relative intensity of different lines to vary strongly with the excitation wavelength. In addition, allowing the normal modes of the excited state to differ from those of the ground state, i.e., Duschinsky rotation, will also introduce extra complication for the present theory. As has been shown by Yeung et al.\(^\text{27}\) for small systems, allowing the force constants between ground and excited state to be different and including Duschinsky rotation do not affect the results to first order in \( \omega/\Delta \). In the absence of these two effects, the generalization to the multimode systems is straightforward.

V. RESULTS AND DISCUSSIONS

Thus far, we have discussed \( N=2 \) and \( N=\infty \). In order to discuss intermediate \( N \), we have numerically calculated the A and B terms for finite chains by directly summing over all electronic states. The results are shown in Figs. 3 and 4, where we plot the A (Condon) and B (Herzberg–Teller) terms as a function of \( N \) for three laser frequencies. Both A and B terms are significantly enhanced when the laser frequency is close to band gap. The qualitative behaviors of chain length dependence at different laser frequencies are the same for both the Condon and Herzberg–Teller terms. The chain length dependence of Condon contribution to the pre-resonance Raman scattering (see Fig. 3) shows an interesting trend: instead of approaching to solid state limit from below the B term, it becomes larger than the solid state limit for \( N \sim 30 \) and then approaches the solid state limit from above. Note that \( N \) close to 30 is the region where Duschinsky rotation becomes important. There is another peak at \( N \sim 20 \) in the Condon term which comes from the subtle chain length dependence of the electron-phonon coupling \( \lambda \), which is a maximum around \( N \sim 20 \) and then decreases to zero as \( N \to \infty \). The resonance enhancement of the Condon term for short polyenes is larger than longer polyenes for two reasons: the dimensionless electron-phonon coupling \( \delta_\lambda \) is larger for short chains, and the dimensionless resonant factor \( h(x) \) goes like \( (1-x)^{-2} \) for short chains, but goes like \( (1-x)^{-3/2} \) for long chains.

In general, the Herzberg–Teller contribution is not important in the resonance region for all \( N \), but on the other hand it is not negligible in the off-resonance region as shown in Fig. 5, where we plot the ratio \( |A/B| \) as function of \( N \). For \( N=\infty \) and far from resonance, the contribution of the Herzberg–Teller term to the Raman amplitude becomes slightly larger than that of the Condon terms. The ratio \( |A/B| \) approaches a constant when the chain length reaches about 30 in the off-resonance region. Close to resonance, \( |A/B| \) saturates at a slower rate.

In Table I, we give a comparison of the ratio of the A and B terms for finite polyenes with several different lengths and polyacetylene at four different laser frequencies. Comparing the results in Table I with Fig. 5, we can see the ratio \( A/B \) does converge as \( N \to \infty \). Note that the values of \( N=\infty \) in Table I calculated by \( |h(x)/2 f_B| \) are larger than the results of finite chain calculation because of numerical approximations: we have applied a quadratic approximation and ex-
tended the upper limit of the integration to infinity in evaluating \( h(x) \) and \( f_p(x) \) for \( N=\infty \) [see Eqs. (29) and (42)].

Figure 2 shows the dependence of \( 2|f_p(x)| \) and \( |h(x)| \) on the incident laser frequency in the solid state limit. Close to resonance, the Condon term is much larger than the Herzberg–Teller term due to much stronger singularity for the Condon term, while in the normal nonresonance Raman region, the Condon term is slightly smaller than the Herzberg–Teller term. In order to compare to the solid state results, we also plot the Raman amplitude from the amplitude mode theory (AMM) in Fig. 2. The agreement with the AMM is very good in the resonance region since the single behavior for the Condon term and the AMM theory are the same at resonance. The discrepancy in the off-resonance region comes from the neglect of nonresonant diagrams in the AMM calculation. The effect of finite values of \( \omega_p \) and \( \gamma \) are important in the resonance region. Figure 6 shows the Raman excited profiles from the Condon term alone for different damping factors \( \gamma \). The two peaks correspond to the incoming and outgoing resonances, respectively. The difference between the two peaks is equal to \( \omega_p/\Delta \). The phonon structure in the Fig. 6 is gradually smeared by increasing the damping factor, \( \gamma \).

It has been argued that because the potential surfaces are nearly the same for the ground and excited states for solid and large molecules, the contribution of the A terms to the Raman scattering vanishes because the Franck–Condon overlap between two vibronic states with different vibrational quantum number in the ground and excited electronic states is zero. However, we have shown in this work that the displacement of the potential curves, \( \lambda \), in the A term and the derivative of the transition moment with respect to normal mode \( Q_i \) goes to infinity. The contributions of both terms to the Raman cross section \( (x|A|^2) \) are then proportional to the size of the system in the solid state limit. In other words, both A and B are extensive quantities. Although the size dependence of the two terms are the same, the singular behaviors around and far away from resonance as a function of laser frequency are different. The A term is proportional to the derivative of \( f_A(x) \) with respect to the laser frequency, while the asymptotic behavior of the B term close to the resonance is the same as \( f_A(x) \). Hence, the resonant behavior for the A term is stronger than B term. The higher order Raman scattering terms go like \( (x|A|^2) \) which can be neglected in the thermodynamic limit, so that only first order Raman scattering is important when there is no strong disorder resulting in localization. The connection between the vibronic picture of the Raman scattering and the third order perturbation theory used by solid state physics is now clear. It is the A term which converges to the solid state limit in the resonance region even though the excited state potential surface is displaced only to \( (x|A|^2) \) with respect to the ground state. Therefore, the vibronic picture is more general than the amplitude mode model in the sense that it provides a way to describe Raman scattering for polymers from short chains to infinite chain length.

We only considered the influence of geometry changes along the dimerization mode for linear and cyclic chains with different chain length on the RRS spectrum in the present

<table>
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<th>( \omega E_g )</th>
<th>( N=101 )</th>
<th>( N=499 )</th>
<th>( N=989 )</th>
<th>( N=1969 )</th>
<th>( N=\infty )</th>
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work. However, it is well known that the 1B_u excited state decays to a charged soliton-antisoliton pair in a few femto-
seconds when π electrons are treated by Hückel model.\textsuperscript{29,30} By including electron correlation at single excitation con-
figuration interaction level, we will show in a later paper that the relaxed geometry of the 1B_u excited state is a self-
trapped exciton.\textsuperscript{31} Higher order Raman processes can be in-
duced through interaction with these local distortions. De-
pendence of the excitation profile on the fast relaxation along these direction is currently under study.

Furthermore, the importance of the relative intensities of different modes also been pointed out by Schaffer et al.\textsuperscript{32} in their experiments on the resonance Raman spectra for the oligomers with 3–13 double bonds. As we have mentioned in Sec. III, the interference in the Raman amplitude for the multimode systems can cause the relative intensity of different lines to vary strongly with the excitation wavelength, hence a generalization to the multimode theory which can apply to both small molecules and bulk materials is ex-
tremely complicated.

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APPENDIX A: ELECTRON-PHONON COUPLING

Along the normal coordinate \( Q \), the excited state poten-
tial surface is given by \( E_f(Q) = E_G(Q) + \epsilon_i(Q) \). At equilib-
rium points of ground and excited states, \((\partial E_G/\partial Q)_{Q_0} = (\partial E_f/\partial Q)_{Q_0} = 0\) respectively.

\[
\left( \frac{\partial E_G(Q)}{\partial Q} \right)_{Q_0} - \left( \frac{\partial E_f(Q)}{\partial Q} \right)_{Q_0} = \left( \frac{\partial^2 E_f(Q)}{\partial Q^2} \right)_{Q_0} (Q_{Q_0} - Q_{G_0}). \tag{A1}
\]

Hence, the lattice displacement of the excited state with wave vector \( k \) relative to the ground state is given by

\[
\lambda_k = -k^{-1} \frac{\partial \epsilon_k}{\partial Q} \tag{A2}
\]

\[
= \lambda_0 \frac{\Delta}{2 \omega_k}, \tag{A3}
\]

where \( k = [\partial^2 E_f(Q)/\partial Q^2]_{Q_0} \) and \( \lambda_0 = 4 t_0/k \sqrt{2N} \).

APPENDIX B: COMPARISON WITH PLACZEK’S POLARIZABILITY THEORY

We will show the connection between our approach and the standard polarizability theory\textsuperscript{33,34} in this Appendix. In the off-resonance region, one can define the electronic polar-
izability as

\[
\alpha(Q, \omega) = \frac{1}{\hbar} \sum_{E} \mu_{GE}(Q) \mu_{EG}(Q) \left( \frac{1}{\omega_{EG}(Q) - \omega + i \gamma} + \frac{1}{\omega_{EG}(Q) + \omega + i \gamma} \right). \tag{B1}
\]

The electronic polarizability, \( \alpha(Q, \omega) \), is different from \( f_j(Q) \) in the off-resonance region, but \( \alpha(Q, \omega) - f_j(Q) \) close to resonance since nonresonance terms can be neglected. When we ex-
and \( \alpha(Q, \omega) \) as a function of a normal coordinate,

\[
\alpha(Q, \omega) = \alpha(Q_0, \omega) + \left( \frac{\partial \alpha(Q, \omega)}{\partial Q} \right)_{Q_0} (Q - Q_0) + \frac{1}{2} \left( \frac{\partial^2 \alpha(Q, \omega)}{\partial Q^2} \right)_{Q_0} (Q - Q_0)^2 + \cdots, \tag{B2}
\]

where the first term gives elastic scattering, and the second term causes first-order Raman scattering,

\[
\left( \frac{\partial \alpha(Q, \omega)}{\partial Q} \right)_{Q_0} = \frac{1}{\hbar} \sum_{E} \mu_{GE}^0 \mu_{EG}^0 \left( \frac{1}{(\omega_{EG} - \omega + i \gamma)^2} + \frac{1}{(\omega_{EG} + \omega + i \gamma)^2} \right) \times \left( \frac{d \omega_{EG}}{d Q} \right)_{Q_0} + \frac{1}{\hbar} \sum_{E} \left( \frac{d \mu_{GE}}{d Q} \right)_{Q_0} \mu_{EG}^0 \right) \left( \frac{1}{\omega_{EG} - \omega + i \gamma} + \frac{1}{\omega_{EG} + \omega + i \gamma} \right), \tag{B3}
\]

Equation (50) contains two terms which are similar to the A
and B terms in the vibronic approach. However, from Eqs.
(25) and (27), we get

\[
\left( \frac{df_j(Q)}{d\omega} \right)_{\omega_k} = \sum_{E} \mu_{GE} \mu_{EG}^0 \left( \frac{1}{(\omega_{EG} - \omega + i \gamma)^2} + \frac{1}{(\omega_{EG} + \omega + i \gamma)^2} \right). \tag{B4}
\]

Using the result from Appendix A, \( (d \omega_{EG}/d Q)_{Q_0} \) is exactly \( \lambda_f \). Applying the approximation \( \lambda_f \sim \lambda \), the first term in Eq.
(50) is exactly the Condor term, while the second term corre-
spends to the Herzberg–Teller terms. Equation (50) also
shows different resonant behavior possible in the first and
second terms. With additional powers in \( \omega_{EG} - \omega + i \gamma \), the first term is more strongly resonant than the second term. In one-dimensional systems, the square root singularity in the density of states introduces a \( 1/2 \) factor. Therefore, we get as-
ymptotic behaviors for both the A and B terms close to re-
sonance as in Eqs. (34) and (43). Making a Herzberg–Teller
expansion, the transition moment derivative can be written in
terms of off-diagonal coupling to the other electronic states
which can be in the same or different bands. Hence, Herzberg–Teller terms contribute to both two- and three-
bond Raman processes in the solid state limit for the totally
symmetric modes. For nontotally symmetric modes, we can-

\[
\frac{\partial \alpha(Q, \omega)}{\partial Q} = \frac{1}{\hbar} \sum_{E} \mu_{GE} \mu_{EG}^0 \left( \frac{1}{(\omega_{EG} - \omega + i \gamma)^2} + \frac{1}{(\omega_{EG} + \omega + i \gamma)^2} \right). \tag{B4}
\]
not have Herzberg–Teller coupling in the same band by symmetry, so that only three-band processes are allowed in this case.


5. J. Kürti and H. Kuzmany, Phys. Rev. 102, 8 (1975).


