Albrecht theory of resonance Raman scattering: applied to conjugated polymers in the solid-state limit

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Received 26 February 1992; in final form 26 June 1992

The connection between the vibronic picture of Raman scattering and the third-order perturbation approach in solid-state physics is clarified. Starting from the Kramers–Heisenberg–Dirac formula for Raman scattering, we derive analytical expressions for the Condon and Herzberg–Teller terms for polyacetylene in the solid-state limit. 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, in contrast to the small molecule case.

1. Introduction

Raman scattering is one of the most important methods for probing the microscopic structures of molecules and bulk materials. It is evident that the language for the description of Raman scattering in different fields is quite different. For example, in the vibronic approach [1], used conventionally for molecules or polymers, the Raman cross section is expressed as a sum of Condon and Herzberg–Teller terms. The parameters of excited states appear explicitly in the vibronic picture of Raman scattering. In another approach, used primarily in solid-state physics [2], third-order perturbation theory in the electron–radiation and electron–phonon interaction is used to derive the Raman cross section. The parameters of excited states are hidden in the electron–phonon coupling constant λ_{ep}. 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 [2,3].

By studying the simplest one-dimensional model system – polyacetylene, we show the connection between the vibronic picture of Raman scattering and the standard third-order perturbation approach in solid-state physics. In contrast with the results obtained by Cardona [2] and Kurti and Kuzmany [3], who claim that only Herzberg–Teller terms contribute to the Raman cross section in the solid-state limit (since the potential surface for the excited states and ground state are nearly the same and thus the Frank–Condon overlap for different vibrational states in the Condon term vanishes), we find that both Condon and Herzberg–Teller terms have the same leading behavior in N, the number of unit cells, as N goes to infinity. Higher-order Raman scattering is not important in the solid-state limit since these contributions are of lower order in N. As a function of incident laser frequency however, the most resonant term for the Condon contribution is proportional to $(\omega_L - E_g)^{-3/2}$, which has the same singular behavior near resonance as that found by third-order perturbation theory [4]. The frequency dependence of the most resonant Herzberg–Teller term goes like $(\omega_L - E_g)^{-1/2}$, much smaller than Condon terms in the resonance region. Far from resonance, the Herzberg–Teller term for large N is comparable to the Condon term, which is different from the picture of small molecules.

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2. Raman cross section

The vibronic approach [1] for Raman scattering starts from the standard second-order perturbation theory in the system–radiation interaction. The amplitude from vibronic state $|m_G\rangle$ to $|n_G\rangle$ within the adiabatic approximation is $\mathscr{R}=A+B+\ldots$, A and B are the so-called Condon and Herzberg–Teller terms respectively, which are given by

$$A=\sum_{E,v}\mu^0_{GE}\mu^0_{EG}\langle n_G|v_E\rangle\langle v_E|m_G\rangle\left(\frac{1}{\omega_{Ev,Gm}-\omega_L+i\gamma}+\frac{1}{\omega_{Ev,Gn}+\omega_L+i\gamma}\right), \tag{1}$$

$$B=\sum_{E,v}\left[\mu^0_{GE}\left(\frac{\partial\mu_{EG}}{\partial Q}\right)_{Q_0}\langle n_G|v_E\rangle\langle v_E|Q|m_G\rangle+\left(\frac{\partial\mu_{GE}}{\partial Q}\right)_{Q_0}\mu^0_{EG}\langle n_G|Q|v_E\rangle\langle v_E|m_G\rangle\right]$$
$$\times\left(\frac{1}{\omega_{Ev,Gm}-\omega_L+i\gamma}+\frac{1}{\omega_{Ev,Gn}+\omega_L+i\gamma}\right), \tag{2}$$

where $\mu^0_{GE}=\langle G(Q_0)|\mu|E(Q_0)\rangle$ is the dipole transition moment between crude adiabatic states $|G(Q_0)\rangle$ and $|E(Q_0)\rangle$, and $|m_G\rangle$ and $|v_E\rangle$ are vibrational states on the ground and excited potential surfaces, respectively. In obtaining the separation of the Raman amplitude into the A and B terms, the Herzberg–Teller expansion for the transition moment around the equilibrium configuration of the ground state has been made: $\mu_{EG}(Q)=\mu_{EG}(Q_0)+\mu'_{EG}(Q_0)(Q-Q_0)$.

For simplicity, we neglect the two-dimensional structure for a polymer with $2N$ carbons, then there is only one optical phonon with $K=0$ coupled to electronic degrees of freedom, which is given by $Q_{K=0}=1/\sqrt{2N}\sum_j(d_j^{(1)}-d_j^{(2)})$ and $d_j^{(1)}$ and $d_j^{(2)}$ are the displacements of the single and double bond in jth unit cell, respectively. The subscript $K=0$ will be dropped later without confusion. Generalization to the multimode case is straightforward in the absence of Duschinsky rotation which allows the normal modes of the excited state to differ from those of the ground state [3] [#1].

2.1. Condon contribution

In order to calculate the Frank–Condon overlap, the excited state potential surfaces are approximated as simple displaced harmonic oscillators [#2]. Hence, the vibrational wavefunctions of the excited states can be expressed as

$$|v_E\rangle=\exp(-i\lambda_E P/\hbar)\,|v_G\rangle=|v_G\rangle-i\frac{\lambda_E P}{\hbar}|v_G\rangle-\frac{\lambda_E^2P^2}{2\hbar^2}|v_G\rangle+\ldots, \tag{3}$$

where λ_E is the displacement of the excited $|E(Q)\rangle$ with respect to ground state potential surface along the normal coordinate Q and $P=\sqrt{m_p\omega_p\hbar/2}\,i(a-a^+)$ is the displacement generator. The first term gives only elastic scattering, while second and third terms correspond to one- and two-phonon scattering, respectively. In the large N limit, the displacement $\lambda_E=-k_G^{-1}(\partial E_g/\partial Q)_{Q_0}$, where k_G is the force constant for the $K=0$ mode in the ground (and excited) state and E_g is the energy gap. For polyacetylene, $\lambda_E\propto N^{-1/2}$ [#3]. Since the higher-order Raman scattering is of the order N^{-1}, only the linear term in λ_E needs being considered in this limit. The A term is then given by

[#1] Duschinsky rotation could be important for the linear chain with N close to 25–35 as been observed by Kuzmany.

[#2] We have shown numerically that the excited state potential surfaces of the finite polymer chains are close to simple displaced harmonic oscillators when $N>50$.

[#3] More exactly, $\lambda=-(4t_0/k_gB_\beta)N^{-1/2}$, since the energy gap $E_g=4t_0x_0$ in the small x_0 limit.

$$A=\sum_{E,v}\mu_{GE}^{0}\mu_{EG}^{0}(\langle n_G|v_G\rangle\langle v_G|\mathrm{i}\lambda_E P|m_G\rangle-\langle n_G|\mathrm{i}\lambda_E P|v_G\rangle\langle v_G|m_G\rangle)$$
$$\times\left(\frac{1}{\omega_{EG}+(v-m)\omega_\mathrm{p}-\omega_\mathrm{L}+\mathrm{i}\gamma}+\frac{1}{\omega_{EG}+(v-n)\omega_\mathrm{p}+\omega_\mathrm{L}+\mathrm{i}\gamma}\right), \tag{4}$$

where ω_{EG} is the energy difference between the two potential minima, and ω_p is the vibrational frequency. Since only electrons around Fermi surface most strongly interact with phonons in the large N limit, λ_E can be approximated by the electron–phonon coupling constant, λ, of the LUMO (lowest unoccupied molecular orbital), which is of b_u symmetry [#4]. Using $\lambda_E\sim\lambda$ and the orthonormal property, $\langle v_G|m_G\rangle=\delta_{v,m}$, the A term can be simplified to

$$A=\sum_E\mu_{GE}^{0}\mu_{EG}^{0}\lambda\langle n_G|\mathrm{i}P|m_G\rangle\left(\frac{1}{\omega_{EG}-\omega_\mathrm{S}+\mathrm{i}\gamma}-\frac{1}{\omega_{EG}-\omega_\mathrm{L}+\mathrm{i}\gamma}-\frac{1}{\omega_{EG}+\omega_\mathrm{S}+\mathrm{i}\gamma}+\frac{1}{\omega_{EG}+\omega_\mathrm{L}+\mathrm{i}\gamma}\right), \tag{5}$$

where $\omega_\mathrm{S}=\omega_\mathrm{L}-\omega_\mathrm{p}$ is the scattered light frequency for the Stokes Raman line and $\omega_\mathrm{S}=\omega_\mathrm{L}+\omega_\mathrm{p}$ for the anti-Stokes Raman line. Define the function $f_A(\omega)$ as

$$f_A(\omega)=\sum_E\mu_{GE}^{0}\mu_{EG}^{0}\left(\frac{1}{\omega_{EG}-\omega+\mathrm{i}\gamma}-\frac{1}{\omega_{EG}+\omega+\mathrm{i}\gamma}\right). \tag{6}$$

The Condon term can then be written as

$$A=\lambda\langle n_G|\mathrm{i}P|m_G\rangle[f_A(\omega_\mathrm{S})-f_A(\omega_\mathrm{L})]\,. \tag{7}$$

Far from resonances, both $\omega_\mathrm{L}-\omega_{EG}$ and $\omega_\mathrm{S}-\omega_{EG}$ are much larger than the phonon frequency ω_p, the finite difference in eq. (7) can be replaced by a derivative with respect to ω_L. Then we find the following expression for the Condon term of the Raman amplitude:

$$A=\left(\frac{\mathrm{d}f_A(\omega)}{\mathrm{d}\omega}\right)_{\omega_\mathrm{L}}\lambda\omega_\mathrm{p}\langle n_G|\mathrm{i}P|m_G\rangle\,, \tag{8}$$

which is similar to that found in the solid-state literature [2]. Eq. (7) together with eq. (8) are generally true for any large system in all dimensions.

Consider a polyene of N unit cells with periodic boundary conditions and with the π electronic wavefunctions calculated by the Hückel theory (or the tight-binding approximation [3,5–7]). The resonance integrals are assumed to be an exponential in r: $\beta(r)=A_\beta\exp(-r/B_\beta)$. Diagonalizing the secular equation, we obtain the eigenvalue for the one electron state $|k\rangle$: $\omega_k=(\beta_1^2+\beta_2^2+2\beta_1\beta_2\cos ka)^{1/2}$, where β_1 and β_2 are the resonance integrals for the single and double bond, respectively, and a is the length for a unit cell.

In the large N limit, $f_A(\omega_\mathrm{L})$ can be replaced by an integral over the first Brillouin zone,

$$f_A(\omega_\mathrm{L})=2N\frac{a}{2\pi}\int_{-\pi/a}^{\pi/a}\mathrm{d}k|\Omega(k)|^2\left(\frac{1}{2\omega_k-\omega_\mathrm{L}+\mathrm{i}\gamma}-\frac{1}{2\omega_k+\omega_\mathrm{L}+\mathrm{i}\gamma}\right)$$
$$=2N\frac{a}{2\pi}\int_{4t_0\sinh x_0}^{4t_0\cosh x_0}\mathrm{d}\epsilon\,N_\mathrm{d}(\epsilon)|\Omega(\epsilon)|^2\left(\frac{1}{\epsilon-\omega_\mathrm{L}+\mathrm{i}\gamma}-\frac{1}{\epsilon+\omega_\mathrm{L}+\mathrm{i}\gamma}\right), \tag{9}$$

where $N_\mathrm{d}(\epsilon)$ is the joint density of states, $\epsilon(=2\omega_k)$ is the transition energy at k, and t_0 and x_0 are defined by $t_0=A_\beta\exp(-a/2B_\beta)$ and $x_0=\frac{1}{2}B_\beta^{-1}(r_1-r_2)$, respectively. In deriving eq. (9) from eq. (6), we have replaced

[#4] Due to the square-root singularity of the joint density of state at the Fermi surface for the one-dimensional system, the replacement of λ_E by λ is a good approximation in the large N limit.

the summation over many-electron wavefunctions $|E\rangle$ by the summation over single-electron wavefunctions $|k\rangle$ and the transition matrix element $\langle E|\mu|G\rangle$ by $\Omega(k)$, which is given by $\Omega = \mathrm{i}a\epsilon^{-2}(\beta_1^2-\beta_2^2)$. The main contribution to eq. (9) comes from the critical regions in the joint density of states which are defined by the condition $\mathrm{d}\epsilon(k)/\mathrm{d}k=0$. For polyacetylene, the critical point is at Fermi surface (i.e. $k_F=\pi/a$). We make the parabolic approximation [2] around the Fermi surface for the energy band, so that the joint density of states (including spin degeneracy) can be simplified to $N_d(\epsilon)=\pi^{-1}(\frac{1}{2}m)^{1/2}(\epsilon-E_g)^{-1/2}\Theta(\epsilon/E_g)$, where $m(=\hbar^2\times \sinh x_0/a^2t_0)$ is the reduced mass of the interband transition, $E_g(=4t_0\sinh x_0)$ is the energy gap, and $\Theta(x)$ is the Heaviside step function. $f_A(\omega)$ can be evaluated for $\gamma\to 0^+$:

$$f_A(\omega)=2N\frac{a}{2\pi}\left(\frac{\hbar v_F}{E_g}\right)^2(\tfrac{1}{2}m)^{1/2}E_g^{-1/2}\,g\left(\frac{\omega}{E_g}\right), \tag{10}$$

where

$$g(x)=x^{-4}[-x-\tfrac{5}{8}x^3+(1-x)^{-1/2}-(1+x)^{-1/2}] \tag{11}$$

and v_F $(=t_0a/\hbar)$ is Fermi velocity for undimerized polyacetylene. The signs of the squares roots of eq. (11) are determined by drawing a cut in the complex ω plane from $\omega=0$ to $-\infty$. The Raman amplitude is proportional to the derivative of $f_A(\omega)$ with respect to the laser frequency:

$$\frac{\mathrm{d}f_A(\omega_L)}{\mathrm{d}\omega_L}=2N\frac{a}{2\pi}\left(\frac{\hbar v_F}{E_g}\right)^2(\tfrac{1}{2}m)^{1/2}E_g^{-3/2}\,h\left(\frac{\omega_L}{E_g}\right), \tag{12}$$

where

$$h(x)=x^{-4}[3+\tfrac{5}{8}x-4x^{-1}(1-x)^{-1/2}+4x^{-1}(1+x)^{-1/2}+\tfrac{1}{2}(1-x)^{-3/2}+\tfrac{1}{2}(1+x)^{-3/2}]\,. \tag{13}$$

Close to resonance, $f_A(\omega_L, E_g)=f_A(\omega_L-E_g)$; hence, $\mathrm{d}f_A(\omega_L)/\mathrm{d}\omega_L=-\mathrm{d}f_A(\omega_L)/\mathrm{d}E_g$. The most resonant term of f_A goes like $(E_g-\omega_L)^{-1/2}$, so that the singularity for $\mathrm{d}f_A(\omega_L)/\mathrm{d}\omega_L$ goes like $(E_g-\omega_L)^{-3/2}$. This result is consistent with the Horovitz result from the Green function approach for polyacetylene with infinite chain length (see fig. 1). Far away from resonance, i.e. normal Raman scattering, we have $h(x)\approx 0.49+\mathcal{O}(x^2)$ as $x\to 0$.

2.2. Herzberg–Teller contribution

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

$$B=2\langle n_G|Q|m_G\rangle 2N\frac{a}{2\pi}\int_{-\pi/a}^{\pi/a}\mathrm{d}k\,\Omega(k)\left(\frac{\mathrm{d}\Omega(k)}{\mathrm{d}Q}\right)_{Q_0}\left(\frac{1}{2\omega_k-\omega_L}+\frac{1}{2\omega_k+\omega_L}\right) \tag{14}$$

to the lowest order in N, where

$$\left(\frac{\mathrm{d}\Omega(k)}{\mathrm{d}Q}\right)_{Q_0}=-\frac{\mathrm{i}a}{B_\beta\sqrt{2N}}\frac{t_0^2}{\omega_k^2}\left(\cosh 2x_0-2\sinh^2 2x_0\frac{t_0^2}{\omega_k^2}\right). \tag{15}$$

A factor of 2 in eq. (14) comes from the neglect of the phonon frequency ω_p relative to the laser frequency for this term. The leading term of the $\mathrm{d}\Omega(k)/\mathrm{d}Q$ as $N\to\infty$ is proportional to $N^{-1/2}$, which is exactly the same as the asymptotic behavior of λ in the Condon term. Hence, to the lowest order in N, both Condon and Herzberg–Teller terms should be considered. As to which term is dominant in different spectral regions, we must compare the coefficients of these two terms.

The B term can be simplified to

$$B=-2\frac{\langle n_G|Q|m_G\rangle}{\sqrt{2N}}2N\frac{a}{2\pi}\int_{4t_0\sinh x_0}^{4t_0\cosh x_0}\mathrm{d}\epsilon\, N_d(\epsilon)M(\epsilon)\left(\frac{1}{\epsilon-\omega_L}+\frac{1}{\epsilon+\omega_L}\right), \tag{16}$$

where

$$M(\epsilon)=\frac{a^2}{16B_\beta x_0^3}\frac{E_g^4}{\epsilon^4}\left(1+2x_0^2-2\frac{E_g^2}{\epsilon^2}\right) \tag{17}$$

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 $\delta(ka-k'a\pm\pi/2N)$ for the interband transition restricts the transition rate to be zero. Note that the formula (41) given by Kurti and Kuzmany [3] does not go to zero in this limit. Making a quadratic approximation for the energy band, the Herzberg–Teller term becomes

$$B=-2\frac{\langle n_G|Q|m_G\rangle}{\sqrt{2N}}2N\frac{a}{2\pi}\frac{1}{B_\beta x_0}\left(\frac{\hbar v_F}{E_g}\right)^2(\tfrac{1}{2}m)^{1/2}E_g^{-1}f_B\left(\frac{\omega_L}{E_g}\right), \tag{18}$$

where

$$f_B(x)=x^{-4}\{-\tfrac{1}{2}-4x_0^2+4x^{-2}+(\tfrac{11}{32}-\tfrac{3}{2}x_0^2)x^2+(1+2x_0^2-2x^{-2})[(1-x)^{-1/2}+(1+x)^{-1/2}]\}. \tag{19}$$

The resonant term in the Herzberg–Teller contribution goes like $(E_g-\omega_L)^{-1/2}$. This singularity is weaker than the Condon term in the resonance region, while far off resonance, we have $2f_B(x)\approx-0.66+\mathcal{O}(x^2)$ as $x\to0$, which is slightly larger than the contribution from the Condon term (see fig. 1). For small molecules far from resonance Condon terms are larger than Herzberg–Teller 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 [1]. Except for nontotally symmetric modes, where $\lambda\propto\langle E|(\partial\mathscr{H}(Q)/\partial Q)_{Q_0}|E\rangle$ vanishes exactly, the A term is more important than the B term. However, since the displacement, λ, of the excited state vanishes as $N\to\infty$ in the solid-state limit, is is then hard to estimate which term is dominant. Fig. 1 shows that the B term is slightly larger than the Condon term in the normal

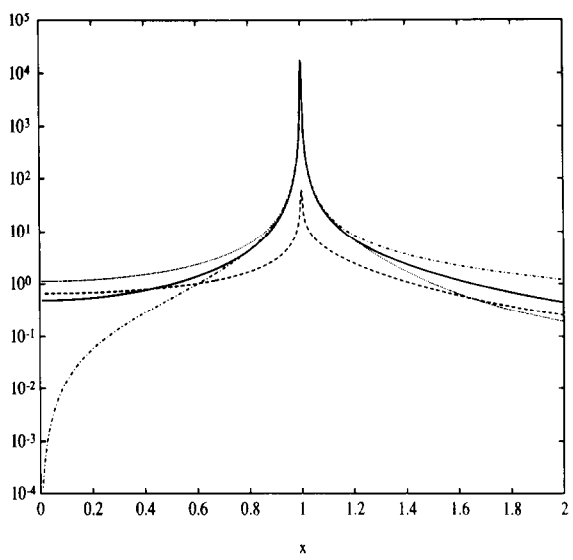

Fig. 1. Comparison of different contributions to the Raman excitation profile for a polyene with infinite chain length. The solid line is the contribution from the Condon term calculated by eq. (13), i.e. $|h(x)|$, the dashed line is from the Herzberg–Teller term, $2|f_B(x)|$, and the dotted line is the sum of Condon and Herzberg–Teller term, $|h(x)-2f_B(x)|$. The dash-dotted line is the Raman profile calculated by the AMM theory [8]. Note that we multiply the Herzberg–Teller term by 2 since the coefficient for the B term is twice of that of the A term except the dimensionless factors $h(x)$ and $f_B(x)$.

Raman region for polyacetylene, i.e. large N, which is different from the small molecule picture.

3. Discussion

Cardona [2] argues that the potential surfaces are nearly the same for the ground and excited states for the solids and large molecules. Therefore, $\langle n_G | v_E \rangle = \delta_{nv}$, and no Raman scattering results from the A terms. But we have shown that the displacement of the potential curves, λ, in the A term and the derivative of the transition moment with normal mode Q, $(\mathrm{d}\Omega/\mathrm{d}Q)_{Q_0}$, in the B term both go as $N^{-1/2}$, as the number of unit cells N goes to infinity. The contributions of both terms to the Raman cross section ($\propto |\mathscr{R}|^2$) 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 is 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 $f_A(\omega)$ with respect to the laser frequency, while the asymptotic behavior of the B term close to the resonance is the same as $f_A(\omega)$. Hence, the resonant behavior for the A term is stronger than for the B term. The higher-order Raman scattering goes like $\mathcal{O}(1)$ which can be neglected in the thermodynamic limit, so that only the first-order Raman scattering is important when there are no impurity centers present. The connection between the vibronic picture of the Raman scattering and the third-order perturbation 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 $\mathcal{O}(N^{-1/2})$ with respect to the ground state. Fig. 1 shows the dependence of $2|f_B(x)|$ and $|h(x)|$ on the incident laser frequency. 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 fig. 1, we also plot the result from the amplitude mode theory (AMM). The agreement with the Horovitz AMM [8] is very good in the resonance region since the singular behavior for the Condon term and AMM theory are the same at resonance. The discrepancy in the off-resonance region comes from the neglect of nonresonant diagrams in the Horovitz calculation. However, the AMM is only valid in the solid-state limit, while the vibronic picture is more general in the sense that it provides a way to describe Raman scattering for polymers from short chains to infinite chain length.

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