



Analytical expressions for the vibrational static second hyperpolarizability of polyacetylene

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ABSTRACT

Analytical results for the vibrational static second hyperpolarizability of polyacetylene are derived. The vibrational second hyperpolarizability of polyacetylene is calculated through the lattice relaxation expression in the solid-state limit. The exact results indicate that the vibrational contribution to the second hyperpolarizabilities of polyacetylene is comparable to the pure electronic contribution. Additionally, the vibrational and electronic second hyperpolarizabilities of polyacetylene under the parabolic approximation for the energy band are also obtained, and they are in excellent qualitative agreement with the exact results. Therefore, the vibrational contribution to the static second hyperpolarizability of polyacetylene is as important as the electronic contribution.

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1. Introduction

The potential for using optical nonlinearities to design optical communication devices leads to a growing interest in third-order nonlinear optics [1]. Nonlinear optical processes are governed by molecular hyperpolarizabilities. These properties can be divided into the electronic contribution originating from the effects of electric fields on electronic motions and the vibrational contribution arising from both the effects of electric fields on nuclear motions and the vibronic coupling. These two kinds of contributions to the linear and nonlinear optical coefficients correspond to electronic and vibrational (hyper)polarizabilities. For some systems, vibrational properties are more important than the electronic ones. Therefore, considerable interest has arisen on calculations for vibrational (hyper)polarizabilities in the past decades [2–11]. From the perturbation theory, the sum-over-state formulas used to calculate vibrational dynamic (hyper)polarizabilities have been derived, and these formulas include corrections for mechanical anharmonic terms in the vibrational potential and electrical anharmonic terms in the dependence of the electronic transition moment on nuclear coordinates [4].

A semiclassical treatment has been proposed to derive explicit analytical expressions (the lattice relaxation expressions) for the vibrational (hyper)polarizabilities in terms of vibrational spectroscopic observables under the mechanical and electrical harmonic approximations [2]. This approach has been widely used to study

the nonlinear optical properties of charge-transfer organic materials in the framework of a simple valence-bond charge-transfer model [12–17].

The purpose of this study is to derive analytical results for the vibrational static second hyperpolarizability of polyacetylene. It is shown that the vibrational contribution to the second hyperpolarizability of polyacetylene is comparable to the electronic contribution. In addition, we calculate the vibrational and electronic second hyperpolarizabilities of polyacetylene under the parabolic approximation for the energy band. The results under the parabolic approximation also show that the vibrational contribution to the second hyperpolarizability of polyacetylene is non-negligible. Therefore, the results under the parabolic approximation are in excellent qualitative agreement with the exact results.

This paper is organized as follows: We begin by briefly introducing vibrational (hyper)polarizabilities in Section 2. In Section 3, analytical results for the vibrational second hyperpolarizability of polyacetylene are derived and the vibrational second hyperpolarizability is compared with the electronic one. In Section 4, the vibrational and electronic second hyperpolarizabilities are calculated under the parabolic approximation. Finally, we make some comments in Section 5.

2. Vibrational polarizabilities and hyperpolarizabilities

If an external electromagnetic field ε interacts with atoms or molecules, the total energy obtained from the perturbation theory is given by

$$E = E_0 + E^{int} = E_0 - \mu\varepsilon - \frac{\alpha}{2!}\varepsilon^2 - \frac{\beta}{3!}\varepsilon^3 - \frac{\gamma}{4!}\varepsilon^4 - \dots,$$

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where E_0 is the energy at zero field, E^{int} is the interaction energy between the system and the field, μ is the dipole moment, α is the polarizability, and β and γ are the first and second hyperpolarizabilities, respectively.

The expressions for the vibrational contributions to the linear and nonlinear optical coefficients have been worked out [2,4]. The formulas for vibrational contributions to (hyper)polarizabilities can be written as explicit analytical expressions in terms of vibrational spectroscopic observables. The diagonal tensor component with only one vibrational mode for the vibrational second hyperpolarizabilities is given by [2,4]

$$\gamma^v = \frac{1}{k_0} \left[4 \left(\frac{\partial \mu}{\partial Q} \right)_0 \left(\frac{\partial \beta}{\partial Q} \right)_0 + 3 \left(\frac{\partial \alpha}{\partial Q} \right)_0 \left(\frac{\partial \alpha}{\partial Q} \right)_0 \right], \quad (1)$$

where 0 denotes the equilibrium geometry of the ground electronic state, k_0 is the force constant of the ground electronic state, and the derivatives are taken with respect to the normal coordinate Q .

3. Vibrational second hyperpolarizability of the infinite polymeric chain

We proceed to calculate the vibrational second hyperpolarizability of the two-band system: polyacetylene. Polyacetylene is examined using the tight-binding approximation with harmonic vibrations. The Longuet-Higgins and Salem's model is used to describe the polyenes [18–21]:

$$H = \sum_n \beta(r_n) (c_n^+ c_{n+1} + c_{n+1}^+ c_n) + \sum_n f(r_n),$$

where $\beta(r)$ is the transfer (resonance) integral and $f(r)$ is σ -bond compressional energy. Following Kürti and Kuzmany [19], we assume that the transfer integral $\beta(r)$ is given by the exponential function, $\beta(r) = -A_\beta \exp(-r/B_\beta)$, where r is the distance between two atoms, $A_\beta = 243.5$ eV, and $B_\beta = 0.3075$ Å. At equilibrium, the single-bond distance is $R_1 = 1.45$ Å and the double-bond distance is $R_2 = 1.36$ Å. For a perfect dimerized chain with periodic boundary condition, the eigenvalue ω_k for the one-electron orbital $|k\rangle$ is given by $\omega_k = [\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(ka)]^{1/2} = \sqrt{2}t_0 \sqrt{\cosh 2x_0 + \cos ka}$, where β_1 and β_2 are the resonance integrals for the single- and double-bonds, a is the unit cell length, and t_0 and x_0 are defined by $t_0 = A_\beta e^{-a/2B_\beta}$ and $x_0 = (r_1 - r_2)/2B_\beta$.

The band theory of polyacetylene within the tight-binding approximation has been developed by Cojan and co-workers [20,21]. In the sum-over-state expression, the electronic polarizability α is given by

$$\alpha = 2 \sum_{i=1}^{\infty} \frac{\mu_{ge_i}^2}{E_{e_i,g}}, \quad (2)$$

where μ_{ge_i} is the electronic transition moment between the ground state and the i th excited state, and $E_{e_i,g}$ denotes their energy separation. In the band theory expression, μ_{ge_i} is replaced by $\Omega(k)$ and the sum over states is replaced by an integral over the first Brillouin zone [19–21]

$$\alpha = 2 \times 2N \frac{a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{|\Omega(k)|^2}{\varepsilon_k} dk, \quad (3)$$

where $\varepsilon_k (= 2\omega_k)$ is the transition energy at k . A factor of 2 has been included to account for the double occupation of the orbitals. Deriving Eq. (3) from Eq. (2), we have replaced the summation over many-electron wave functions with the summation over single-electron wave functions and the transition matrix element μ_{ge_i} with $\Omega(k)$ given by $\Omega(k) = ia(\beta_1^2 - \beta_2^2)/\varepsilon_k^2$.

In polyacetylene chains, the vibrational contribution to the static second hyperpolarizability originates significantly from the second term in Eq. (1), while the first term is two to three orders of

magnitude smaller [7,22,23]. In order to calculate the vibrational second hyperpolarizability, we concentrate on the second term. From Eq. (2), the derivative of the polarizability with respect to the normal coordinate Q can be written as

$$\left(\frac{\partial \alpha}{\partial Q} \right)_0 = A + B, \quad (4)$$

where

$$A = -2 \sum_{i=1}^{\infty} \frac{\mu_{ge_i}^2}{E_{e_i,g}^2} \left(\frac{\partial E_{e_i,g}}{\partial Q} \right)_0 \quad (5)$$

$$B = 2 \sum_{i=1}^{\infty} \left(\frac{1}{E_{e_i,g}} \right)_0 \left[\left(\frac{\partial \mu_{ge_i}}{\partial Q} \right)_0 \mu_{e_i,g} + \mu_{ge_i} \left(\frac{\partial \mu_{e_i,g}}{\partial Q} \right)_0 \right]. \quad (6)$$

Here, A and B are the Condon and Herzberg–Teller terms, respectively. In addition, the Condon contribution involves the electron-phonon coupling, and the Herzberg–Teller contribution arises from the dependence of the electronic transition moment on the nuclear coordinate.

According to Yaron and Silbey's argument [3], we only need to consider the optical $K = 0$ phonon mode. We use periodic boundary conditions for the phonon and treat the electronic motion as an open chain. The $K = 0$ optical phonon for a chain of $2N$ carbons is

$$Q_{K=0} = \frac{1}{\sqrt{2N}} \sum_{j=1}^{2N} (-1)^j dr_j. \quad (7)$$

Since the electronic wave functions are invariant under the transformation $(\beta_1, \beta_2) \Rightarrow (c\beta_1, c\beta_2)$ where c is a constant [3], μ_{ge_i} depends only on the ratio

$$\beta_{rat} = \frac{\beta_1 - \beta_2}{\beta_1 + \beta_2} = -\tanh x_0. \quad (8)$$

Thus, the transition matrix element becomes

$$\Omega(k) = i \frac{a}{4} \frac{2\beta_{rat}}{[(1 + \cos ka) + \beta_{rat}^2(1 - \cos ka)]}. \quad (9)$$

We can replace the derivative with respect to Q in Eq. (6) by a derivative with respect to β_{rat} ,

$$\left(\frac{\partial \mu_{ge_i}}{\partial Q} \right)_0 = \left(\frac{\partial \mu_{ge_i}}{\partial \beta_{rat}} \right)_0 \left(\frac{\partial \beta_{rat}}{\partial Q} \right)_0.$$

In the band theory expression, the derivative of the energy separation between the ground state and the i th excited state with respect to Q , $(\partial E_{e_i,g}/\partial Q)_0$, is replaced by $(\partial \varepsilon_k(Q)/\partial Q)_0$, and the derivative of the transition moment with respect to Q , $(\partial \mu_{ge_i}/\partial Q)_0$, is replaced by $(\partial \Omega(k)/\partial Q)_0$,

$$\begin{aligned} \left(\frac{\partial \Omega(k)}{\partial Q} \right)_0 &= \left(\frac{\partial \Omega(k)}{\partial \beta_{rat}} \right)_0 \left(\frac{\partial \beta_{rat}}{\partial Q} \right)_0 \\ &= i \frac{a}{2} \frac{(1 + \cos ka) - \beta_{rat}^2(1 - \cos ka)}{[(1 + \cos ka) + \beta_{rat}^2(1 - \cos ka)]^2} \times \sqrt{\frac{1}{2N} \frac{1}{B_\beta} \frac{1}{\cosh^2 x_0}}. \end{aligned} \quad (10)$$

Therefore, analytical expressions for the Condon and Herzberg–Teller terms in the solid-state limit become

$$\begin{aligned} A &= 2 \times 2N \times \frac{a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \left(\frac{|\Omega(k)|^2}{\varepsilon_k^2} \right)_0 \left[-\frac{\partial \varepsilon_k(Q)}{\partial Q} \right]_0 dk \\ &= \sqrt{2N} \frac{a^2}{B_\beta t_0} \frac{1}{2\pi} \frac{\sqrt{2}}{8} \times a \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \left(\frac{\beta_{rat}}{(1 + \cos ka) + \beta_{rat}^2(1 - \cos ka)} \right)^2 \\ &\quad \times \frac{\sinh 2x_0}{(\sqrt{\cosh 2x_0 + \cos ka})^3} dk \end{aligned} \quad (11)$$

Table 1

Comparison between the exact analytical results (EAR) and the results under the parabolic approximation (PAR). The Condon and Herzberg–Teller terms are in units of $\sqrt{2Na^2/B_\beta t_0}$. Static second hyperpolarizabilities, γ'' , γ^+ , γ^- , γ^e , and γ' , are in units of $2Na^4/t_0^3$.

	EAR	PAR
A	3.47	3.25
B	4.99	5.12
γ''	7.09	6.95
γ^+	7.19	5.87
γ^-	1.64	1.58
$\gamma^e = \gamma^+ - \gamma^-$	5.55	4.29
$\gamma' = \gamma'' + \gamma^e$	12.64	11.24
γ''/γ'	56%	62%
γ^e/γ'	44%	38%

$$B = 2 \times 2N \times \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} \left(\Omega^*(k) \frac{\partial \Omega(k)}{\partial Q} + \frac{\partial \Omega^*(k)}{\partial Q} \Omega(k) \right) \left[\frac{1}{\varepsilon_k} \right]_0 dk$$

$$= \sqrt{2N} \frac{a^2}{B_\beta t_0} \left(-\frac{1}{2\sqrt{2}} \right) \tanh x_0 \times a \int_{-\pi/a}^{\pi/a} \left(\frac{1}{\sqrt{\cosh 2x_0 + \cos ka}} \right)^3$$

$$\times \frac{(1 + \cos ka) - \beta_{\text{rat}}^2 (1 - \cos ka)}{[(1 + \cos ka) + \beta_{\text{rat}}^2 (1 - \cos ka)]^2} dk. \quad (12)$$

We use Kürti and Kuzmany's parameters for polyacetylene [19]: the force constant of the $K = 0$ phonon mode is 5.390 mdyne/Å. Therefore, we obtain the vibrational second hyperpolarizability γ'' ($= \gamma''/4!$) from Eqs. (1) and (4)

$$\gamma'' = \frac{1}{8k_0} \left(\frac{\partial \alpha}{\partial Q} \right)_0^2 = \frac{1}{8k_0} (A^2 + B^2 + 2AB). \quad (13)$$

On the other hand, we compare the vibrational contribution with the pure electronic contribution to the second hyperpolarizability. The band theory expression for the electronic second hyperpolarizability γ' ($= \gamma'/4!$) is given by $\gamma^e = \gamma^+ - \gamma^-$ [21]. Here, γ^e is divided into two parts

$$\gamma^+ = 2N \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} \frac{1}{\varepsilon_k} \frac{\partial}{\partial k} \left(\frac{\Omega^*(k)}{\varepsilon_k} \right) \frac{\partial}{\partial k} \left(\frac{\Omega(k)}{\varepsilon_k} \right) dk$$

$$= 2N \frac{a^4}{t_0^3} \frac{1}{2\pi} 72 \frac{2^3}{(2\sqrt{2})^{11}} \sinh^2 2x_0 \times a \int_{-\pi/a}^{\pi/a} \frac{\sin^2 ka}{(\sqrt{\cosh 2x_0 + \cos ka})^{11}} dk \quad (14)$$

$$\gamma^- = 2N \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} \frac{|\Omega(k)|^4}{\varepsilon_k^3} dk$$

$$= 2N \frac{a^4}{t_0^3} \frac{1}{2\pi} \frac{2^4}{(2\sqrt{2})^{11}} \sinh^4 2x_0 \times a \int_{-\pi/a}^{\pi/a} \frac{1}{(\sqrt{\cosh 2x_0 + \cos ka})^{11}} dk. \quad (15)$$

The total second hyperpolarizability is the sum of these two kinds of contributions, $\gamma' = \gamma^e + \gamma''$. The relevant results are summarized in Table 1, and it is found that the ratio of these two contributions is $\gamma''/\gamma^e = 1.28$. Thus, the vibrational $K = 0$ phonon mode contributes 56% to the whole second hyperpolarizability. The results indicate that the vibrational contribution is comparable to the electronic contribution.

4. Parabolic approximation

The parabolic approximation is usually used in the solid-state theory [24]. The main contribution to Eqs. (11), (12), (14), and (15) results from the regions around the critical points in the joint density of states defined by the condition $d\varepsilon_k/dk = 0$. For polyacetylene, the critical point is at the Fermi surface (i.e., $k_F = \pi/a$). We will use the parabolic approximation around the Fermi surface

for the energy band to calculate Eqs. (11), (12), (14), and (15), and compare these results with the exact results obtained in the previous section.

From Eq. (11), A term becomes

$$A = \sqrt{2N} \frac{a}{2\pi} \frac{8t_0 a^2}{B_\beta} \Delta \cosh x_0 (\beta_1^2 - \beta_2^2)^2 \int_{-\pi/a}^{\pi/a} \frac{1}{\varepsilon_k^7} dk, \quad (16)$$

where

$$\frac{\partial \varepsilon_k(Q)}{\partial Q} = -\frac{4t_0}{B_\beta} \frac{1}{\sqrt{2N}} \frac{\Delta}{\varepsilon_k} \cosh x_0 \quad (17)$$

has been used and $\Delta (= 4t_0 \sinh x_0)$ is the energy gap. Using the parabolic approximation at $ka = -\pi + x$, we have

$$\varepsilon_k \cong t_0 \left(4 \sinh x_0 + \frac{x^2}{2 \sinh x_0} \right). \quad (18)$$

Substituting Eq. (18) into Eq. (16) gives

$$A \cong \sqrt{2N} \frac{a^2}{B_\beta t_0} 64 \sinh^3 2x_0 \times \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1}{\left(4 \sinh x_0 + \frac{x^2}{2 \sinh x_0} \right)^7} dx. \quad (19)$$

Similarly, B term becomes

$$B = \sqrt{2N} \frac{a}{2\pi} \frac{a^2}{B_\beta} \frac{8\beta_1\beta_2(\beta_1^2 - \beta_2^2)}{(\beta_1 + \beta_2)^2}$$

$$\times \int_{-\pi/a}^{\pi/a} \frac{1}{\varepsilon_k^3} \frac{(1 + \cos ka) - \beta_{\text{rat}}^2 (1 - \cos ka)}{[(1 + \cos ka) + \beta_{\text{rat}}^2 (1 - \cos ka)]^2} dk \quad (20)$$

$$\cong \sqrt{2N} \frac{a^2}{B_\beta t_0} (-8 \tanh x_0) \frac{1}{2\pi}$$

$$\times \int_{-\pi}^{\pi} \frac{1}{\left(4 \sinh x_0 + \frac{x^2}{2 \sinh x_0} \right)^3} \frac{(1 + \beta_{\text{rat}}^2) \frac{x^2}{2} - 2\beta_{\text{rat}}^2}{[(1 - \beta_{\text{rat}}^2) \frac{x^2}{2} + 2\beta_{\text{rat}}^2]^2} dx. \quad (21)$$

Substituting Eqs. (19) and (21) into Eq. (13), we obtain the vibrational second hyperpolarizability under the parabolic approximation. Furthermore, we can determine the pure electronic second hyperpolarizability under the parabolic approximation. From Eqs. (14) and (15), γ^+ and γ^- become

$$\gamma^+ = 2N \frac{a}{2\pi} 72 a^4 (\beta_1^2 - \beta_2^2)^2 \cdot 2\beta_1^2 \beta_2^2 \int_{-\pi/a}^{\pi/a} \frac{\sin^2 ka}{\varepsilon_k^{11}} dk$$

$$\cong 2N \frac{a^4}{t_0^3} 576 \sinh^2 2x_0 \times \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{x^2}{\left(4 \sinh x_0 + \frac{x^2}{2 \sinh x_0} \right)^{11}} dx \quad (22)$$

$$\gamma^- = 2N \frac{a}{2\pi} a^4 (\beta_1^2 - \beta_2^2)^4 \int_{-\pi/a}^{\pi/a} \frac{1}{\varepsilon_k^{11}} dk$$

$$\cong 2N \frac{a^4}{t_0^3} 16 \sinh^4 2x_0 \times \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1}{\left(4 \sinh x_0 + \frac{x^2}{2 \sinh x_0} \right)^{11}} dx. \quad (23)$$

The exact results and the results under the parabolic approximation are summarized in Table 1. Again, the results obtained under the parabolic approximation show that the vibrational contribution is comparable to the electronic contribution. As shown in Table 1, the values of various terms are extremely close, and the results under the parabolic approximation are in excellent qualitative agreement with the exact results.

5. Discussion and concluding remarks

The exact analytical results obtained in Section 3 indicate that the static vibrational second hyperpolarizability of polyacetylene

is larger than the static longitudinal electronic second hyperpolarizability. This conclusion is different from Yaron and Silbey's result derived from the perturbation theory [3]. They adopted a similar model but found that the vibrational contribution amounts to about 10% of the electronic one. In our current model, we followed Kürti and Kuzmany's parameters for the transfer integrals and the force constant k_0 for polyacetylene [19]. In contrast, they used the parameters for a C=C double-bond to approximate the force constant k_0 for polyacetylene. In addition, the vibrational contribution discussed by Yaron and Silbey corresponds to the Herzberg–Teller (*B*) term given by Eqs. (6) and (12). In addition to the Herzberg–Teller term, our method also contains the Condon (*A*) term originating from the electron–phonon coupling given by Eqs. (5) and (11). These two terms both contribute to the vibrational second hyperpolarizabilities through Eq. (13). Therefore, these differences lead to a significant inconsistency between our and their results. Moreover, several studies also implied that the vibrational modes in polyacetylene chains present substantial contributions to the second hyperpolarizability [22,23,7].

Contributions to the linear and nonlinear optical coefficients can be divided into electronic and vibrational parts. Including vibrational levels into the perturbation theory expression leads to the sum-over-state formulas for (hyper)polarizabilities expressed in terms of vibronic energies and dipole moment matrix elements. These expressions for vibrational (hyper)polarizabilities reduce to the lattice relaxation expressions if the anharmonic terms are neglected. In the current study, we obtained the exact analytical results for the vibrational static second hyperpolarizabilities of polyacetylene through the lattice relaxation expressions in the solid-state limit. In addition, the comparison between the vibrational and the electronic contributions indicates that the vibrational contribution is comparable to the electronic one. Furthermore, we also calculated the vibrational and electronic second hyperpolarizabilities of polyacetylene under the parabolic approximation for the energy band. The results under the parabolic approximation are in excellent qualitative agreement with the exact results, and this reaches the same conclusion that the vibrational contribution has a non-negligible effect on the second hyperpolarizability. Therefore, the vibrational contribution is as important as the electronic contribution to the static second hyperpolarizability of polyacetylene.

The current study concentrated on the static vibrational second hyperpolarizability for polyacetylene. In the future, the chain-length dependence of the Condon and Herzberg–Teller contributions deserves further investigation. Furthermore, the current model can be used to analyze dynamic vibrational hyperpolarizabilities and the effects of anharmonicity contributions on the vibrational second hyperpolarizability.

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