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Raman Intensities Induced by Electrostatic Intermolecular Interaction and Related Nonlinear Optical Properties of a Conjugated π-Electron System: A Theoretical Study

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Raman intensities of a charged conjugated π-electron system induced by electrostatic intermolecular interaction are studied theoretically. By using a simple Hamiltonian based on a two-state model, in which the response of the system to an electric field is taken into account, the formulas for the polarizability derivative and related quantities are derived. These formulas are applied to the case of a pentamethine streptocyanine dye, which has a symmetric conjugated chain consisting of four CC bonds with one NC bond on each end. It is shown that a reasonable magnitude of electrostatic interaction with a counterion induces Raman intensities on the order of 10^2 Å^4 amu^{-1} for the modes with large contributions from the vibration along the bond-alternation coordinate of the chain, explaining the appearance of the 1574- and 1207-cm^{-1} bands in the Raman spectrum measured in solution. A slight deformation of the conjugated chain along the bond-alternation coordinate induced by electrostatic interaction and the strong electron−vibration interaction are responsible for these Raman intensities. The formulas derived in this study are then used for evaluating the electronic and vibrational contributions to the first hyperpolarizability. It is concluded that the vibrational contribution is on the same order of magnitude as (but smaller than) the electronic one, at least in the case of typical charged conjugated π-electron systems.

1. Introduction

In our previous study,[1] we have observed the infrared and Raman spectra of a pentamethine streptocyanine dye [(5-dimethylaminopenta-2,4-dienylidene) ammonium perchlorate, alias SC5] in a dimethyl sulfoxide solution and in the polycrystalline state, and we have carried out vibrational analysis by comparing the observed spectra with those calculated by the density functional method. A peculiar finding in that study is that Raman bands with medium intensities appear at 1574 and 1207 cm^{-1} in solution which are not seen in the polycrystalline state. These two Raman bands have also been observed from the "orange-form" crystal, in which the perchlorate ion resides near one end of the conjugated chain of SC5, but not from the "yellow-form" crystal, in which the perchlorate ion is located at a symmetric position.[2] These results indicate that the perchlorate ion is located at a position asymmetric to the chain in solution. From the comparison of the observed and calculated vibrational wavenumbers,[1] it is considered that these Raman bands arise from the same vibrational modes as the strong IR bands observed at 1570 and 1206 cm^{-1}. In these modes, the conjugated chain of SC5 vibrates along the bond-alternation coordinate, or the so-called "effective conjugation coordinate";[3,4] in other words, the adjacent CC bonds in the chain stretch and contract alternately. However, characterization of the vibrational patterns of the relevant vibrational modes alone is not sufficient for elucidating the mechanism which gives rise to these Raman intensities.

In another previous study,[5] two of the present authors (H.T. and M.T.) have considered the mechanism giving rise to strong IR intensities for the vibrations along the bond-alternation coordinate in charged polyenes and other related molecules. By using a simple Hamiltonian based on a two-state model, the electron−vibration interaction involving the bond-alternation coordinate has been formulated theoretically, and the charge flux originating from the electron−vibration interaction has been derived. From the comparison of the prediction based on the model with the result obtained from ab initio molecular orbital (MO) calculations, which is regarded as a solution of a more realistic Hamiltonian, it has been concluded that the model provides a reasonable picture on the role of electron−vibration interaction and changes in electronic structures in generating the charge fluxes and, hence, the strong IR intensities for the vibrations along the bond-alternation coordinate. It is therefore expected that the mechanism inducing the Raman intensities of the 1574- and 1207-cm^{-1} modes of SC5 in solution is elucidated by extending this model.

In the present study, a theoretical formulation is given for the Raman intensities of the vibrations along the bond-alternation coordinate of charged conjugated π-electron systems in general.

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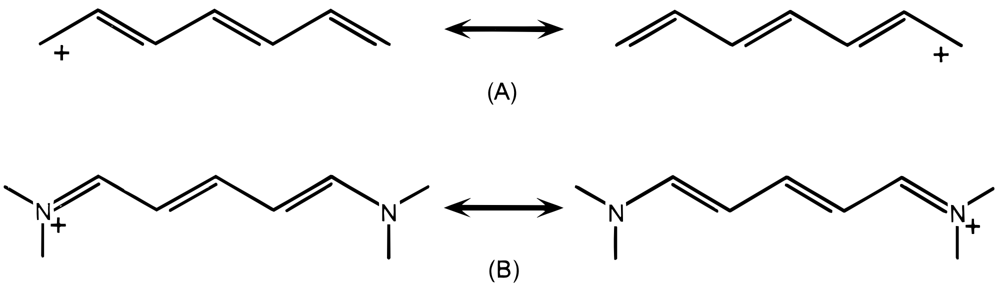

Figure 1. Vibration along the bond-alternation coordinate and the concomitant change in the electronic structure in (A) a charged polyene and (B) a pentamethine cyanine dye.

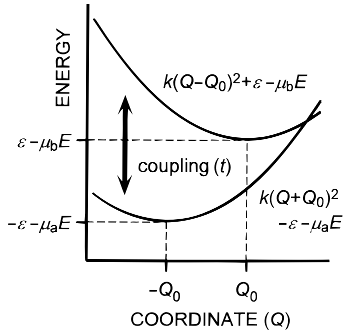

Figure 2. Schematic representation of the model Hamiltonian used in this study.

This formulation is then applied to the case of the 1574- and 1207-cm^{-1} modes of SC5 in solution. It is shown that a slight deformation of the conjugated chain along the bond-alternation coordinate induced by electrostatic interaction with a counterion and the strong electron−vibration interaction give rise to Raman bands with intensities sufficiently large for explaining the feature of the observed Raman spectrum. The relationship between this formulation and those derived in previous studies[6,7] is also examined in relation to the discussion on the electronic and vibrational contributions to the first hyperpolarizability.

2. Theory

We consider electronic basis functions $|a\rangle$ and $|b\rangle$ representing the two resonance structures of a charged conjugated chain, as shown in Figure 1 (A or B), and one vibrational coordinate Q representing the bond-alternation coordinate of the chain. The model given in our previous study[5] is extended by considering the response of the system to an electric field along the direction of the chain. As shown in Figure 2, the diabatic potential energy curves for $|a\rangle$ and $|b\rangle$ of the model Hamiltonian H are assumed to be

$$\langle a|H|a\rangle = k(Q + Q_0)^2 - \epsilon - \mu_a E \tag{1}$$

$$\langle b|H|b\rangle = k(Q - Q_0)^2 + \epsilon - \mu_b E \tag{2}$$

with ϵ, $Q_0 \geq 0$. (In the case of symmetric conjugated chains shown in Figure 1, $\epsilon = 0$.) Here, k (≥ 0) is the force constant, which is assumed to be the same for $|a\rangle$ and $|b\rangle$, ϵ and Q_0 are half the differences in the energies and structures, respectively, between the minima of the two diabatic potential energy curves, E denotes the electric field along the direction of the chain, and μ_a and μ_b stand for the dipole moments of the two basis states. The interaction between $|a\rangle$ and $|b\rangle$ is assumed to be

$$\langle a|H|b\rangle = \langle b|H|a\rangle = -t \tag{3}$$

with $t \geq 0$. The two basis functions are assumed to be orthogonal, i.e., $\langle a|b\rangle = 0$.

The adiabatic potential energy curves for the Hamiltonian are obtained by solving the eigenvalue problem and are expressed as

$$V_\pm = kQ^2 + kQ_0{}^2 - \mu_S E \pm \{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{1/2} \tag{4}$$

with $\mu_S = (\mu_a + \mu_b)/2$ and $\mu_D = (\mu_a - \mu_b)/2$. In this section, we consider only the ground electronic state (V_-).

As shown in ref 8, the dipole moment (μ) and polarizability (α) are calculated as the first and second derivatives of the potential energy with respect to the electric field. Therefore, μ and α are obtained from eq 4 as

$$\mu = -\frac{\partial V_-}{\partial E} = \mu_S - \frac{\mu_D(2kQ_0Q - \epsilon - \mu_D E)}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{1/2}} \tag{5}$$

$$\alpha = \frac{\partial \mu}{\partial E} = \frac{\mu_D{}^2 t^2}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{3/2}} \tag{6}$$

When $E = 0$, eq 6 is consistent with eq 28 of ref 9, in which a model Hamiltonian equivalent to that treated in the present study has been employed. The dipole derivative ($\partial\mu/\partial Q$) and the polarizability derivative ($\partial\alpha/\partial Q$) are obtained from eqs 5 and 6 as

$$\frac{\partial \mu}{\partial Q} = -\frac{2kQ_0\mu_D t^2}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{3/2}} \tag{7}$$

$$\frac{\partial \alpha}{\partial Q} = -\frac{6kQ_0\mu_D{}^2 t^2(2kQ_0Q - \epsilon - \mu_D E)}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{5/2}} \tag{8}$$

When $E = 0$, eqs 7 and 8 are consistent respectively with eqs 6 and 7 of ref 10, which have been obtained by using the formulas given in ref 9. If $|2kQ_0Q| \ll t$ in addition to $E = 0$ is satisfied, eq 7 corresponds to eq 18 of our previous study[5] and to eq 11 of ref 5 when $\epsilon = 0$ is further assumed.

We assume that $|2kQ_0Q|$, $|\mu_D E| \ll t$ is satisfied; i.e., the interaction between $|a\rangle$ and $|b\rangle$ is sufficiently strong. The potential energy minimum is then calculated to be at

$$Q = -\frac{Q_0(\epsilon + \mu_D E)}{(t^2 + \epsilon^2)^{1/2} - 2kQ_0{}^2}\ (\equiv Q_m) \tag{9}$$

by solving the equation of $\partial V_- /\partial Q = 0$.

In the case of symmetric conjugated chains shown in Figure 1, $\epsilon = 0$ and $\mu_S = 0$ are satisfied. Then the quantities given in eqs 5−8 evaluated at $Q = Q_m$ are more concisely expressed as

$$\mu(Q = Q_m) = -\mu_D \frac{x_m}{(1 + x_m^2)^{1/2}} \tag{10}$$

$$\alpha(Q = Q_m) = \frac{\mu_D^2}{t} \frac{1}{(1 + x_m^2)^{3/2}} \tag{11}$$

$$\frac{\partial \mu}{\partial Q}(Q = Q_m) = -\frac{2kQ_0\mu_D}{t} \frac{1}{(1 + x_m^2)^{3/2}} \tag{12}$$

$$\frac{\partial \alpha}{\partial Q}(Q = Q_m) = -\frac{6kQ_0\mu_D^2}{t^2} \frac{x_m}{(1 + x_m^2)^{5/2}} \tag{13}$$

with $x_m = Q_m/Q_0 = -\mu_D E/(t - 2kQ_0^2)$. Equation 13 describes the polarizability derivative (and hence the Raman intensity) induced in a symmetric conjugated chain by an electric field.

3. The Case of the Pentamethine Streptocyanine Dye (SC5)

The theoretical formulation given above is applied to the case of SC5. The conjugated chain of SC5 is symmetric ($\epsilon = 0$) and consists of four CC bonds with one NC bond on each end. Because an end effect is expected to exist, as shown in our previous study,[5] we disregard the NC bonds on the ends of the conjugated chain and take as Q the bond-alternation coordinate for the chain of the four CC bonds.

The values of four physical quantities (μ_D, t, k, and Q_0) are needed to evaluate the polarizability derivative given in eq 13. As shown in ref 5, μ_D is equal to the electronic transition dipole moment, and t is half the electronic excitation energy. These two quantities are estimated as $|\mu_D| \cong 10$ D and $t \cong 2$ eV from ab initio MO calculaitons at the CIS (configuration interaction singles)[11] level with the 6-31G* basis set, which are carried out by using the Gaussian 94 program.[12] By the same reasoning as given in ref 5, we estimate $k \cong 3$ mdyn Å^{-1} and $Q_0 \cong 0.1$ Å. From these values, the dipole derivative (eq 12) at $Q_m = 0$ is calculated[5] to be $|\partial\mu/\partial Q| \cong 20$ D Å^{-1}, in agreement with the result obtained from a density functional calculation (Table 5 of ref 1), $|\partial\mu/\partial Q| = (14.446 + 15.025)/\sqrt{2} = 20.839$ D Å^{-1}. The polarizability at $Q_m = 0$ is calculated from eq 11 to be $\alpha \cong 31$ Å^3. This value is smaller than the chain axis component of the polarizability obtained from the density functional calculation (45 Å^3), probably because the contribution of the four methyl groups in the molecule is not taken into account in the model.

In order for the conjugated chain to deform to the extent of $|Q_m| \cong 0.01$ Å (or $|x_m| \cong 0.1$) by an electric field, $|E|$ should be $\cong 8 \times 10^8$ J C^{-1} m^{-1} or $\cong 0.0015$ au. The electric field of this magnitude is generated (in a vacuum) at $\cong 14$ Å from an elementary charge. It is therefore reasonable that deformation $|Q_m| \cong 0.01$ Å is induced in the conjugated chain of SC5 by the interaction with the perchlorate ion (the counterion). Individual CC bonds deform by 0.005 Å in this case, since there are four CC bonds involved in Q.

When $|x_m| \cong 0.1$, the polarizability derivative is estimated from eq 13 to be $|\partial\alpha/\partial Q| \cong 18$ Å^2. To calculate the Raman activities for the 1574- and 1207-cm^{-1} modes (denoted by q_{1574} and q_{1207}, respectively), the contributions of the bond-alternation coordinate (Q) to these modes are needed. From the density functional calculation carried out in ref 1, they are estimated as $|\partial Q/\partial q_{1574}| \cong 0.37$ amu$^{-1/2}$ and $|\partial Q/\partial q_{1207}| \cong 0.27$ amu$^{-1/2}$. When only one diagonal element is nonzero in a Raman tensor, the Raman activity is given by $12(\partial\alpha/\partial q)^2$. Therefore, the Raman activities of the 1574- and 1207-cm^{-1} modes are calculated to be $\cong$530 and $\cong$280 Å^4 amu^{-1}, respectively. These values are sufficiently large to explain the appearance of these two bands in the Raman spectrum measured in solution. Although the electric field due to the interaction with the counterion is not uniform, the formulas given in this study represent the leading term of the response of the system (apart from the overall electrostatic attraction energy term, which is invariant with Q). It is therefore proposed that a slight deformation of the conjugated chain, which arises from the interaction with the counterion, and the strong electron−vibration interaction are responsible for the experimental result.

4. Remarks on the Previous Formulations of the Polarizability Derivative and Related Nonlinear Optical Properties

For the purpose of examining the vibrational contribution to the first hyperpolarizability, the polarizability derivative has been formulated by Bishop and Kirtman[6] within the framework of the canonical approximation. In this section, we examine the relation between the formulas given in the present study and in ref 6, as well as the validity of the approximation used by Castiglioni et al.[7] in relation to the discussion on the electronic and vibrational contributions to the first hyperpolarizability.

In the canonical approximation, the polarizability of a two-state model is expressed as[6]

$$\alpha = \frac{2\mu_{eg}^2}{V_+ - V_-} \tag{14}$$

where V_- and V_+ are the potential energies of the ground and excited electronic states, respectively, and μ_{eg} is the transition dipole moment between these two states. All these quantities depend on Q. The polarizability derivative is, therefore, expressed as

$$\frac{\partial\alpha}{\partial Q} = \left(\frac{\partial\alpha}{\partial Q}\right)_n + \left(\frac{\partial\alpha}{\partial Q}\right)_d \tag{15}$$

where

$$\left(\frac{\partial\alpha}{\partial Q}\right)_n = \frac{4\mu_{eg}}{V_+ - V_-} \frac{\partial\mu_{eg}}{\partial Q} \tag{16}$$

and

$$\left(\frac{\partial\alpha}{\partial Q}\right)_d = \frac{-2\mu_{eg}^2}{(V_+ - V_-)^2} \frac{\partial(V_+ - V_-)}{\partial Q} \tag{17}$$

correspond to the derivatives of the numerator and denominator, respectively, of eq 14.

We will apply these formulas to the model Hamiltonian used in the present study (eqs 1−3). For this purpose, μ_{eg}, $V_+ - V_-$, and their derivatives with respect to Q have to be evaluated. By generalizing eq 12 of ref 5, which is given for the case of $\epsilon = 0$, $E = 0$, and $|2kQ_0Q| \ll t$, μ_{eg} is expressed as

$$\mu_{eg} = \frac{\mu_D t}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{1/2}} \tag{18}$$

Thus, we obtain

$$\frac{\partial \mu_{eg}}{\partial Q} = -\frac{2kQ_0\mu_D t(2kQ_0Q - \epsilon - \mu_D E)}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{3/2}} \tag{19}$$

From eq 4, we obtain

$$V_+ - V_- = 2\,\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{1/2} \tag{20}$$

$$\frac{\partial (V_+ - V_-)}{\partial Q} = \frac{4kQ_0(2kQ_0Q - \epsilon - \mu_D E)}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{1/2}} \tag{21}$$

By using these equations, $(\partial\alpha/\partial Q)_n$ and $(\partial\alpha/\partial Q)_d$ are calculated as

$$\left(\frac{\partial \alpha}{\partial Q}\right)_n = -\frac{4kQ_0{\mu_D}^2 t^2(2kQ_0Q - \epsilon - \mu_D E)}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{5/2}} \tag{22}$$

$$\left(\frac{\partial \alpha}{\partial Q}\right)_d = -\frac{2kQ_0{\mu_D}^2 t^2(2kQ_0Q - \epsilon - \mu_D E)}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{5/2}} \tag{23}$$

It is clear from these equations that $(\partial\alpha/\partial Q)_n$ and $(\partial\alpha/\partial Q)_d$ are 2:1 in magnitude, and the sum of these two is exactly equal to eq 8. The formulas given in section 2 of the present study and those given in ref 6 are, therefore, consistent with each other. The 2:1 ratio arises from the specific forms of μ_{eg} and $V_+ - V_-$ given in eqs 18 and 20. By substituting these equations into eq 14, it is clear that α is inversely proportional to $(V_+ - V_-)^3$ instead of $V_+ - V_-$. As a result, $\partial\alpha/\partial Q$ is 3 times larger than $(\partial\alpha/\partial Q)_d$.

Castiglioni et al.[7] have discussed the relationship between the electronic and vibrational contributions to the first hyperpolarizability (denoted by β_{el} and β_{vib}, respectively), which are expressed as

$$\beta_{el} = \frac{6\Delta\mu_{e-g}{\mu_{eg}}^2}{(V_+ - V_-)^2} \tag{24}$$

$$\beta_{vib} = \frac{3}{2k}\frac{\partial \alpha}{\partial Q}\frac{\partial \mu}{\partial Q} \tag{25}$$

where $\Delta\mu_{e-g}$ is the difference between the dipole moments of the ground and excited electronic states. They have shown that these two quantities are closely related to each other and are determined by the same set of molecular parameters.[7] In their discussion, they treated $(\partial\alpha/\partial Q)$ in eq 25 as being equal to $(\partial\alpha/\partial Q)_d$. However, $(\partial\alpha/\partial Q)_n$ is more important than $(\partial\alpha/\partial Q)_d$, at least in the case of charged conjugated π-electron systems, since the former is twice as large as the latter as shown above in eqs 22 and 23. This conclusion is consistent with that obtained by Bishop and Kirtman.[6] In the present study, we have clarified this point quantitatively by using a model Hamiltonian which includes the response of the system to an electric field.

We will evaluate β_{el} and β_{vib} by using the formulas derived in this study. By substituting eqs 7, 8, 18, 20, and the following equation,

$$\Delta\mu_{e-g} = -\frac{\partial (V_+ - V_-)}{\partial E} = \frac{2\mu_D\,(2kQ_0Q - \epsilon - \mu_D E)}{\{(2kQ_0Q - \epsilon - \mu_D E)^2 + t^2\}^{1/2}} \tag{26}$$

into eqs 24 and 25, we obtain for the case of $E = 0$

$$\beta_{el} = \frac{3{\mu_D}^3 t^2(2kQ_0Q - \epsilon)}{\{(2kQ_0Q - \epsilon)^2 + t^2\}^{5/2}} \tag{27}$$

$$\beta_{vib} = \frac{18k{Q_0}^2{\mu_D}^3 t^4(2kQ_0Q - \epsilon)}{\{(2kQ_0Q - \epsilon)^2 + t^2\}^{4}} \tag{28}$$

As suggested by Castiglioni et al.,[7] β_{el} and β_{vib} are determined by the same set of molecular parameters. The ratio of β_{vib} to β_{el} is

$$\frac{\beta_{vib}}{\beta_{el}} = \frac{6k{Q_0}^2 t^2}{\{(2kQ_0Q - \epsilon)^2 + t^2\}^{3/2}} \lesssim \frac{6k{Q_0}^2}{t} \tag{29}$$

If we substitute into eq 29 the values of t, k, and Q_0 estimated for SC5 in section 3, which are considered to be typical for charged conjugated π-electron systems, we obtain

$$\frac{\beta_{vib}}{\beta_{el}} \lesssim 0.5 \tag{30}$$

This result shows that the vibrational contribution to the first hyperpolarizability is on the same order of magnitude as (but smaller than) the electronic one.

5. Concluding Remarks

It has been shown in the present study that a reasonable magnitude of electrostatic intermolecular interaction induces Raman bands with intensities sufficiently large for explaining the appearance of the 1574- and 1207-cm^{-1} bands in the Raman spectrum of SC5 measured in solution.[1] A slight deformation of the conjugated chain along the bond-alternation coordinate and the strong electron−vibration interaction are responsible for the Raman intensities of these bands. Because of the strong electron−vibration interaction, the vibrational contribution to the first hyperpolarizability, which arises from the dipole and polarizability derivatives, is on the same order of magnitude as the electronic one. The results of the present study show intimate relations between the electronic and vibrational properties of conjugated π-electron systems, which deserve further theoretical and experimental investigation.

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