



Theoretical treatment of anharmonic effect on molecular absorption, fluorescence spectra, and electron transfer

Chaoyuan Zhu^{a,*}, Kuo Kan Liang^b, Michitoshi Hayashi^c, Sheng Hsien Lin^{a,b,d}

^a Department of Applied Chemistry, Institute of Molecular Science and Center for Interdisciplinary Molecular Science, National Chiao-Tung University, 1001 Ta-Hseuh Rd., Hsinchu 300, Taiwan

^b Division of Mechanics, Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan

^c Center for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan

^d Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 106, Taiwan

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ABSTRACT

It is well-known that the mirror image between absorption and fluorescence spectra is held for the displaced harmonic-oscillator system, and also this mirror image is independent to the chiral symmetry in which the excited-state potential energy surface is right-handed or left-handed with respect to the ground-state potential energy surface. As the first-order approximation of anharmonic correction is added into the displaced harmonic oscillator, this mirror image is broken down, and then the spectra can be depended on the chiral symmetry mentioned above. Both absorption and fluorescence coefficients are derived analytically within the first-order anharmonic approximation and numerical test is carried out to demonstrate the breaking down of the mirror image. Based on the same analysis, the electron transfer rate is derived analytically within the first-order anharmonic approximation. This rate might take the form of Arrhenius's equation but not form of Marcus's equation. Furthermore, it is found that this rate is also depending on the chiral symmetry.

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1. Introduction

Within Born–Oppenheimer approximation, the Franck–Condon overlap integrals between vibrational wave functions which belong to two different electronic states are very important quantity in theoretical treatment of molecular processes. The Franck–Condon overlap integrals are extensively utilized for the interpretations and theoretical modeling not only for the vibronic structure of electronic spectra like UV absorption, fluorescence, and other nonlinear optical spectra of molecules, but also some nonradiative processes like electronic transfer, relaxation, photodissociation, and reactive scattering. If the vibrational normal modes for the two electronic states are the same, these integrals can be separated into a product of individual mode oscillators within the harmonic-oscillator approximation. This is called displaced oscillators. If the vibrational normal modes for the two electronic states are different, these separations are no longer possible in general. This is called distorted oscillators. If couplings among vibrational normal modes are taken into account, the theoretical treatment becomes very complicated, for example, the mode-mixing is kind of mode couplings that are called Duschinsky's effect. Within harmonic-

oscillator approximation, there are many well-developed theoretical methods [1–13]. The molecular vibration is harmonic only in the low energy range (in the relative sense) of the potential surface and as the energy increases and/or the energy gap between two electronic states becomes large, the anharmonicity becomes significant. This is especially true for low frequency modes, for example, intermolecular modes or bending modes. Anharmonicity can be treated as kind of perturbation in harmonic treatment framework, and this is also rapidly developing area [14–22].

It is the purpose for this paper to examine the effect of anharmonicity on molecular spectroscopy in a preliminary manner, and that means to focus on the displaced oscillators. In order to describe the anharmonic effect, the Morse potential is commonly used in literature [16,23], the potential for each vibrational mode is given by

$$V_j(Q_j) = D_j(1 - e^{-a_j Q_j})^2. \quad (1.1)$$

The solution of the Schrödinger equation for the Morse oscillator yields energy levels as

$$\varepsilon_{v_j} = \hbar\omega_j \left(v_j + \frac{1}{2} \right) - x_j \hbar\omega_j \left(v_j + \frac{1}{2} \right)^2. \quad (1.2)$$

One feature of the Morse oscillator is that there exists a maximal value of the eigenenergy ε_{v_j} . For small quantum number v_j , the

* Corresponding author. Tel.: +886 3 5131224; fax: +886 3 5723764.

E-mail addresses: cyzhu@mail.nctu.edu.tw (C. Zhu), kkliang@sinica.edu.tw (K.K. Liang).

eigenenergy increases with v_j until it reaches the maximal value. Beyond that, the eigenenergy decreases with further increase in v_j . It is a common practice to truncate the possible values of v_j up to a maximum corresponding to the maximal energy value. Thus, at high temperature the partition function of a Morse's oscillator reaches a constant value determined by the maximal v_j , while the partition function of a harmonic oscillator increases indefinitely with temperature. Another feature is that the vibrational energy level spacing is no longer constant. In the present work, we demonstrate the basic effects of anharmonicity on molecular spectroscopy and investigate the leading-order anharmonic correction to harmonic oscillator. Therefore, we shall use the perturbation method to express the anharmonic potential in the polynomial form

$$V_j(Q) = a_{j2}Q_j^2 + \lambda a_{j3}Q_j^3 + \lambda^2 a_{j4}Q_j^4 + \dots \quad (1.3)$$

in which λ is a small perturbation parameter. It is well understood when the vibrational energy level spacing is similar for the ground and electronically excited states, which results in a fluorescence spectrum that strongly resembles the mirror image of the absorption spectrum. This is due to the fact that the same transitions are most favorable for both absorption and fluorescence. Even when solvent effects are included, the mirror image still preserves as the fluorescence and absorption spectra are broaden. However, we demonstrate in this paper when anharmonicity is taken into account, the mirror image breaks down even for displaced oscillators where energy level spacing is still exactly same for the ground and electronically excited states.

The anharmonic-oscillator model of molecular spectrum is formulated by following method in Ref. [1] (and references therein) in which the harmonic-oscillator model is employed in calculating the Franck–Condon overlap integrals. The present paper is organized as follows. In Section 2, the molecular theory for absorption and fluorescence spectroscopy is briefly presented which will be followed by the derivation of the quantum mechanical expression of molecular absorption coefficient using the cumulant method. Section 3 is concerned with the treatment of anharmonic effect on absorption and fluorescence spectra. For this purpose, the perturbation method will be used; that is, the harmonic wavefunction will be used as the basis set and the anharmonicity is treated as a perturbation. The numerical results to demonstrate the anharmonic effect on absorption and fluorescence spectra will be presented in Section 4 and concluding remark will be given in Section 5 along with analytical discussion of unharmonic effect for absorption and fluorescence spectroscopy as well as electron transfer rate.

2. General theory

By using the time-dependent perturbation method and dipole approximation with assumption that molecular systems in the dense media are randomly oriented, we can write down the absorption coefficient of the electronic transition from adiabatic state a to b [1]

$$\alpha(\omega) = \frac{4\pi^2\omega}{3ach} |\bar{\mu}_{ba}|^2 \sum_{\bar{v}} \sum_{\bar{v}'} P_{a\bar{v}} |\langle \Theta_{b\bar{v}'} | \Theta_{a\bar{v}} \rangle|^2 \delta(\omega_{b\bar{v}',a\bar{v}} - \omega), \quad (2.1)$$

where $\bar{\mu}_{ba}$ is the electronic transition dipole moment, $P_{a\bar{v}}$ is the Boltzmann factor and $|\langle \Theta_{b\bar{v}'} | \Theta_{a\bar{v}} \rangle|^2$ is the Franck–Condon factor. The factor a in denominator of Eq. (2.1) that stands for a function of refractive index is introduced to take into account the solvent effect.

With further assumption of the independent oscillators we can expand wave function into simple product of each vibration mode

$$\Theta_{a\bar{v}}(\vec{Q}) = \prod_j \chi_{av_j}(Q_j) \quad (2.2a)$$

and

$$\Theta_{b\bar{v}'}(\vec{Q}') = \prod_j \chi_{bv'_j}(Q'_j) \quad (2.2b)$$

in which Eq. (2.2a) denotes the wave function of an initial electronic state a and Eq. (2.2b) denotes the wave function of a final electronic state b . For absorption process as shown in Fig. 1a, a (b) represents ground (excited) state. For fluorescence process as shown in Fig. 1b, a (b) represents excited (ground) state. In the harmonic-oscillator approximation, there is no observable effect in either absorption or fluorescence spectrum whether the PES of the excited state in Fig. 1 shifts to the right-handed side or the left-handed side with respect to the PES of the ground state. We define this symmetry as a chiral symmetry of the potential energy surfaces. This is nothing to do with conventional definition of chiral symmetry of molecule itself. Throughout this paper, the chiral symmetry means symmetry of the potential energy surfaces. We can easily understand this chiral symmetry from the Franck–Condon overlap integrals; these integrals are invariant with the chiral transformation for displaced harmonical oscillators and one of consequences is leading to the mirror image between absorption and fluorescence spectra. However, the spectra of the mirror image are obviously broken down when anharmonic effects are taken into account because the Franck–Condon overlap integrals are no longer invariant.

Based on the independent oscillator approximation of Eqs. (2.2a and 2.2b), Eq. (2.1) can be derived as [1]

$$\alpha(\omega) = \frac{2\pi\omega}{3ach} |\bar{\mu}_{ba}|^2 \int_{-\infty}^{\infty} dt \exp[it(\omega_{ba} - \omega)] \prod_j G_j(t), \quad (2.3)$$

where

$$G_j(t) = \sum_{v_j} \sum_{v'_j} P_{av_j} |\langle \chi_{bv'_j} | \chi_{av_j} \rangle|^2 \exp\left[\frac{it}{\hbar}(\epsilon_{v'_j} - \epsilon_{v_j})\right]. \quad (2.4)$$

The time correlation function (TCF) $G_j(t)$ can be rewritten as

$$G_j(t) = \sum_{v_j} P_{av_j} \langle \chi_{av_j} | e^{it\hat{H}_{bj}/\hbar} e^{-it\hat{H}_{aj}/\hbar} | \chi_{av_j} \rangle = \langle \langle e^{it\hat{H}_{bj}/\hbar} e^{-it\hat{H}_{aj}/\hbar} \rangle \rangle, \quad (2.5)$$

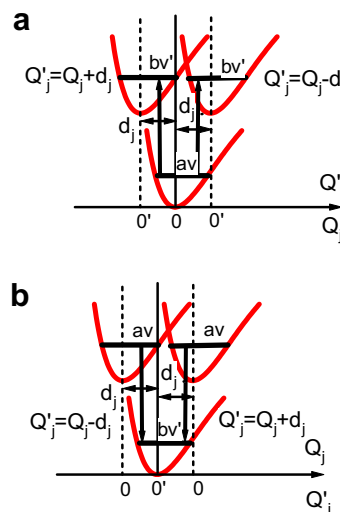


Fig. 1. As anharmonic effect is taken into account, absorption and fluorescence spectra can depend on direction of shift of excited electronically state with respect ground electronically state. (a) Potential energy surfaces for absorption. (b) Potential energy surfaces for fluorescence.

where \hat{H}_{aj} and \hat{H}_{bj} represent the vibrational Hamiltonians corresponding to the a and b electronic states, respectively. The angular brackets in Eq. (2.5) denote an equilibrium ensemble average over the initial vibronic states. If a particular vibronic transition (say, corresponding to the Q_ℓ mode) is resolved, it is more convenient to write Eq. (2.3) as

$$\alpha(\omega) = \frac{2\pi\omega}{3ac\hbar} |\bar{\mu}_{ba}|^2 \sum_{v_\ell} \sum_{v'_\ell} P_{av_\ell} |\langle \chi_{bv'_\ell} | \chi_{av_\ell} \rangle|^2 \times \int_{-\infty}^{\infty} dt \exp \left[it(\omega_{bv'_\ell av_\ell} - \omega) \right] \prod_j^{j \neq \ell} G_j(t), \quad (2.6)$$

where

$$\omega_{bv'_\ell av_\ell} = \omega_{ba} + \frac{1}{\hbar} (\varepsilon_{v'_\ell} - \varepsilon_{v_\ell}) \quad (2.7)$$

in which $\omega_{ba} = \frac{1}{\hbar} (E_b - E_a)$ and E_b (E_a) is electronic energy at the equilibrium geometry of the electronic state b (a). As is shown from the above discussion, the central problem for deriving $\alpha(\omega)$ is the calculation of TCF $G_j(t)$. In this paper, we shall calculate $G_j(t)$ by applying the cumulant expansion method [24] to the second-order, and then we find

$$G_j(t) = \exp \left[\frac{it}{\hbar} \langle \langle \hat{U}_j \rangle \rangle + \left(\frac{i}{\hbar} \right)^2 \int_0^t d\tau (t - \tau) \langle \langle \hat{U}_j(0) \hat{U}_j(\tau) \rangle \rangle_c \right], \quad (2.8)$$

where

$$\hat{U}_j(t) = \exp \left(\frac{it}{\hbar} \hat{H}_{aj} \right) (\hat{H}_{bj} - \hat{H}_{aj}) \exp \left(-\frac{it}{\hbar} \hat{H}_{aj} \right), \quad (2.9)$$

$$\langle \langle \hat{U}_j(0) \hat{U}_j(t) \rangle \rangle_c = \langle \langle \hat{U}_j(0) \hat{U}_j(t) \rangle \rangle - \langle \langle \hat{U}_j \rangle \rangle^2. \quad (2.10)$$

In the short-time approximation, $\alpha(\omega)$ can be expressed as

$$\alpha(\omega) = \frac{2\pi\omega}{3ac\hbar} |\bar{\mu}_{ba}|^2 \left(\frac{2\pi\hbar^2}{\sigma_u^2} \right)^{1/2} \times \exp \left[-\frac{(E_b - E_a - \hbar\omega + \langle \langle \hat{U} \rangle \rangle)^2}{2\sigma_u^2} \right], \quad (2.11)$$

where

$$\langle \langle \hat{U} \rangle \rangle = \sum_j \langle \langle \hat{U}_j \rangle \rangle \quad (2.12)$$

and

$$\sigma_u^2 = \sum_j \left(\langle \langle \hat{U}_j^2 \rangle \rangle - \langle \langle \hat{U}_j \rangle \rangle^2 \right) = \langle \langle \hat{U}^2 \rangle \rangle - \langle \langle \hat{U} \rangle \rangle^2, \quad (2.13)$$

where

$$\langle \langle \hat{U}^2 \rangle \rangle = \sum_j \langle \langle \hat{U}_j^2 \rangle \rangle. \quad (2.14)$$

It should be noted that using the vibrational basis set of the electronic state a , we can find

$$G_j(t) = \exp \left[\frac{it}{\hbar} \langle \langle \hat{U}_j \rangle \rangle + \frac{1}{2} \left(\frac{it}{\hbar} \right)^2 \left(\sum_{v_j} P_{av_j} |\langle \chi_{av_j} | \hat{U}_j | \chi_{av_j} \rangle|^2 - \langle \langle \hat{U}_j \rangle \rangle^2 \right) + \left(\frac{i}{\hbar} \right)^2 \sum_{v_j} \sum_{u_j} P_{av_j} \frac{|\langle \chi_{au_j} | \hat{U}_j | \chi_{av_j} \rangle|^2}{\omega_{u_j v_j}^2} \left(1 + it\omega_{u_j v_j} - e^{it\omega_{u_j v_j}} \right) \right]. \quad (2.15)$$

In the double summations of Eq. (2.15), $u_j \neq v_j$.

3. Anharmonic potential

In this section we shall present how the anharmonic effect can be introduced into the calculations of the absorption and fluorescence spectra by using the cumulant expansion of the TCF.

3.1. Absorption coefficient

Although the Schrödinger equation of the Morse oscillator can be solved exactly and analytically, it is difficult to use its wavefunctions and energies to compute the TCF $G(t)$ involved in absorption and fluorescence spectra as we mentioned in Section 1. Therefore, we consider the perturbation expansion of vibration- j -mode potential as

$$V_j(Q) = a_{j2} Q_j^2 + \lambda a_{j3} Q_j^3 + \lambda^2 a_{j4} Q_j^4 + \dots = V_{j2}(Q_j) + V_{j3}(Q_j) + V_{j4}(Q_j) + \dots \quad (3.1)$$

in which λ is chosen as the perturbation parameter. In case of the Morse potential, we can find coefficient relations as

$$a_{j2} = D_j a_j^2, \quad \lambda a_{j3} = -D_j a_j^3, \quad \lambda^2 a_{j4} = \frac{7}{12} D_j a_j^4, \dots \quad (3.2)$$

Based on the standard perturbation method, we use the harmonic basis set as the zero-order approximation and expand the energy level and wave function for vibration mode - v_j as

$$\varepsilon_{v_j} = \varepsilon_{v_j}^{(0)} + \lambda \varepsilon_{v_j}^{(1)} + \lambda^2 \varepsilon_{v_j}^{(2)} + \dots \quad (3.3)$$

and

$$\chi_{v_j}(Q_j) = \chi_{v_j}^{(0)}(Q_j) + \lambda \chi_{v_j}^{(1)}(Q_j) + \lambda^2 \chi_{v_j}^{(2)}(Q_j) + \dots, \quad (3.4)$$

where $\chi_{v_j}^{(0)}(Q_j)$ denote the harmonic basis set. Using Appendix A, we obtain

$$\varepsilon_{v_j}^{(0)} = \hbar\omega_j \left(v_j + \frac{1}{2} \right) \quad (3.5a)$$

$$\varepsilon_{v_j}^{(1)} = 0 \quad (3.5b)$$

and

$$\varepsilon_{v_j}^{(2)} = 6a_{j4} \left(\frac{\hbar}{2\omega_j} \right)^2 \left[\left(v_j + \frac{1}{2} \right)^2 + \frac{1}{4} \right] - \frac{30a_{j3}^2}{\hbar\omega_j} \left(\frac{\hbar}{2\omega_j} \right)^3 \left[\left(v_j + \frac{1}{2} \right)^2 + \frac{7}{60} \right]. \quad (3.6)$$

The first-order correction to wave function turns to be

$$\chi_{v_j}^{(1)}(Q_j) = -\frac{a_{j3}}{\hbar\omega_j} \left(\frac{\hbar}{2\omega_j} \right)^{3/2} \left\{ 3 \left[\sqrt{(v_j+1)^3} \chi_{v_j+1}^{(0)}(Q_j) - \sqrt{v_j^3} \chi_{v_j-1}^{(0)}(Q_j) \right] + \frac{1}{3} \left[\sqrt{(v_j+1)(v_j+2)(v_j+3)} \chi_{v_j+3}^{(0)}(Q_j) - \sqrt{v_j(v_j-1)(v_j-2)} \chi_{v_j-3}^{(0)}(Q_j) \right] \right\}. \quad (3.7)$$

The first-order correction is zero for energy but is nonzero for wave function. As the present discussion focuses on the first-order correction of the anharmonicity that is actually the leading term correction, we neglect all contributions of the second-order anharmonicity in terms of λ^2 from now on.

Next we consider \hat{U}_j in Eq. (2.9) up to the first-order correction of anharmonicity. In principle, the difference of Hamiltonian in Eq. (2.9) can be written as

$$\hat{H}_{bj} - \hat{H}_{aj} = V_{bj}(Q'_j) - V_{aj}(Q_j). \quad (3.8)$$

For displaced oscillator surfaces, we have

$$\hat{U}_j = \hat{U}_{j2} + \hat{U}_{j3} + \dots, \quad (3.9)$$

where

$$\hat{U}_{j2} = D_j a_j^2 (Q_j^2 - Q_j^2) = a_{j2} (2Q_j d_j + d_j^2), \quad (3.10)$$

$$\hat{U}_{j3} = -D_j a_j^3 (Q_j^3 - Q_j^3) = \lambda a_{j3} (3Q_j^2 d_j + 3Q_j d_j^2 + d_j^3), \quad (3.11)$$

where $Q_j' = Q_j + d_j$ that corresponds to left-handed shift with respect to ground electronic state as shown in Fig. 1a. We can easily calculate

$$\langle \chi_{v_j} | \hat{U}_{j2} | \chi_{v_j} \rangle = a_{j2} d_j^2 - \lambda \frac{6a_{j2} a_{j3} \hbar d_j}{\omega_j^3} \left(v_j + \frac{1}{2} \right) + O(\lambda^2), \quad (3.12)$$

$$\langle \chi_{v_j} | \hat{U}_{j3} | \chi_{v_j} \rangle = \lambda a_{j3} d_j \left[d_j^2 + \frac{3\hbar}{\omega_j} \left(v_j + \frac{1}{2} \right) \right] + O(\lambda^2) \quad (3.13)$$

and

$$\langle \chi_{v_j} | \hat{U}_j | \chi_{v_j} \rangle = \langle \chi_{v_j} | \hat{U}_{j2} + \hat{U}_{j3} | \chi_{v_j} \rangle = a_{j2} d_j^2 \left(1 + \lambda \frac{a_{j3}}{a_{j2}} d_j \right) + O(\lambda^2) \quad (3.14)$$

or $\langle \langle \hat{U}_j \rangle \rangle = a_{j2} d_j^2 \left(1 + \lambda \frac{a_{j3}}{a_{j2}} d_j \right) + O(\lambda^2)$. Thus, we obtain

$$\sum_{v_j} P_{av_j} \left| \langle \chi_{av_j} | \hat{U}_j | \chi_{av_j} \rangle \right|^2 - \langle \langle \hat{U}_j \rangle \rangle^2 = O(\lambda^2). \quad (3.15)$$

Inserting the above equations into Eq. (2.15) leads to

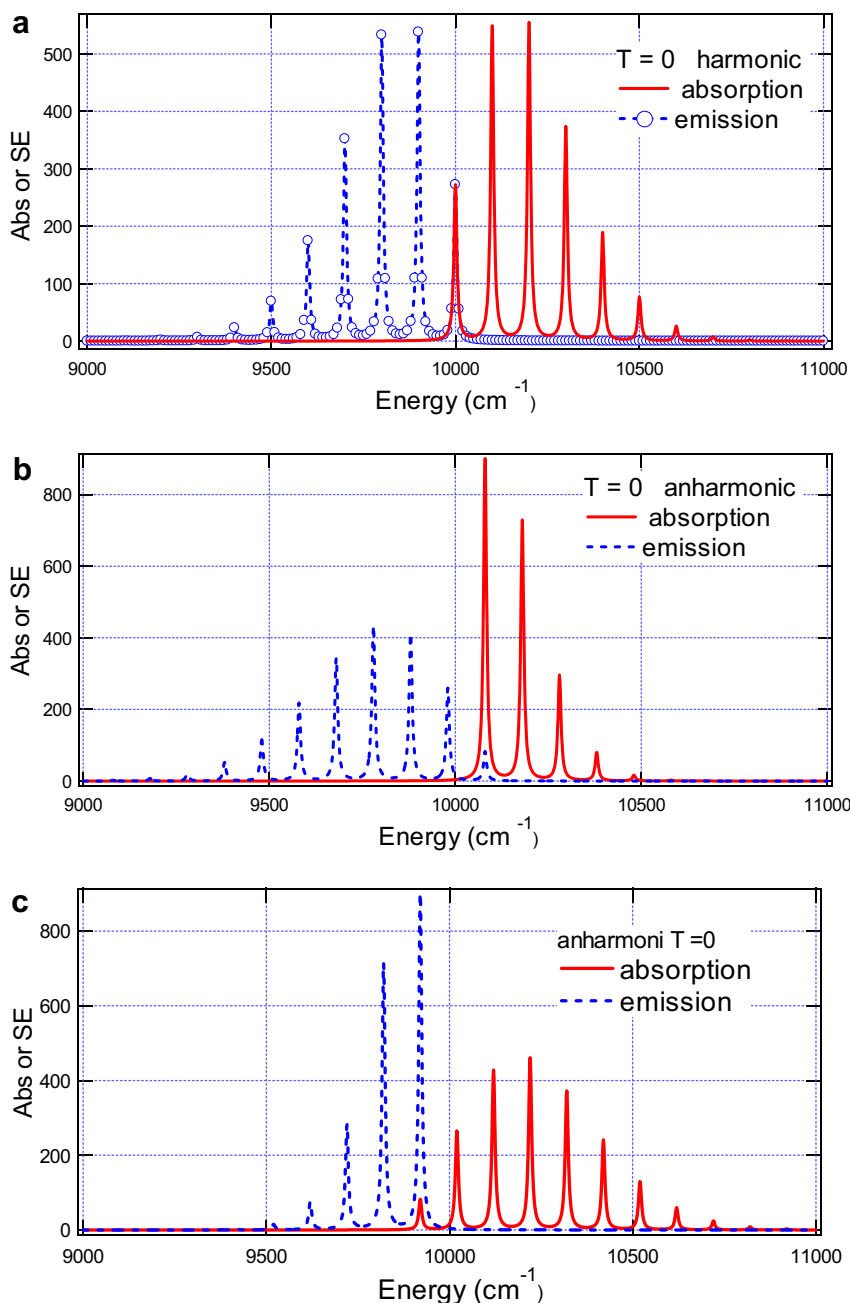


Fig. 2. Comparison of absorption and fluorescence spectra for the case of $\omega_{ba} = 10,000 \text{ cm}^{-1}$, $S_1 = 2.0$, $\omega_1 = 100 \text{ cm}^{-1}$ and $a_{13}d_1/a_{12} = a_n$ for temperature $T = 0 \text{ K}$. Dashed lines stand for fluorescence spectra and solid lines stand for absorption spectra. (a) $a_n = 0$ corresponds to the harmonic case. (b) $a_n = 0.2$ corresponds to Fig. 1 in which the electronically excited-state shifts to the right-handed with respect to electronically ground state. (c) $a_n = 0.2$ corresponds to Fig. 1 in which electronically excited-state shifts to the left-handed with respect to electronically ground state (absorption and fluorescence spectra are computed by Eqs. (3.22) and (3.24), respectively with setting up unit of $\frac{2\pi\omega}{3ach} |\bar{\mu}_{ba}|^2 = 1$. All the following Figs. 3–5 are computed by the same equations).

$$G_j(t) = \exp \left[itS_j\omega_j \left(1 + \frac{\lambda a_{j3}}{a_{j2}} d_j \right) + \left(\frac{i}{\hbar} \right)^2 \sum_{v_j} \sum_{u_j} P_{av_j} \frac{|\langle \chi_{av_j} | \hat{U}_j | \chi_{av_j} \rangle|^2}{\omega_{u_j v_j}^2} \left(1 + it\omega_{u_j v_j} - e^{it\omega_{u_j v_j}} \right) \right], \quad (3.16)$$

where $S_j = \frac{1}{2\hbar} \omega_j d_j^2$ is defined as the Huang–Rhys factor, and note that $\omega_j = \sqrt{2a_{j2}}$. In order to evaluate non-zero terms in the summation of Eq. (3.16), we need to calculate the following non-zero terms as

$$|\langle \chi_{av_{j+1}} | \hat{U}_j | \chi_{av_j} \rangle|^2 = S_j (\hbar\omega_j)^2 (v_j + 1) \left(1 + 3\lambda \frac{a_{j3}}{a_{j2}} d_j \right) + O(\lambda^2) \quad (3.17)$$

and

$$|\langle \chi_{av_{j-1}} | \hat{U}_j | \chi_{av_j} \rangle|^2 = S_j (\hbar\omega_j)^2 v_j \left(1 + 3\lambda \frac{a_{j3}}{a_{j2}} d_j \right) + O(\lambda^2). \quad (3.18)$$

Actually we have

$$|\langle \chi_{av_{j+2}} | \hat{U}_j | \chi_{av_j} \rangle|^2 = O(\lambda^2), \quad (3.19)$$

and

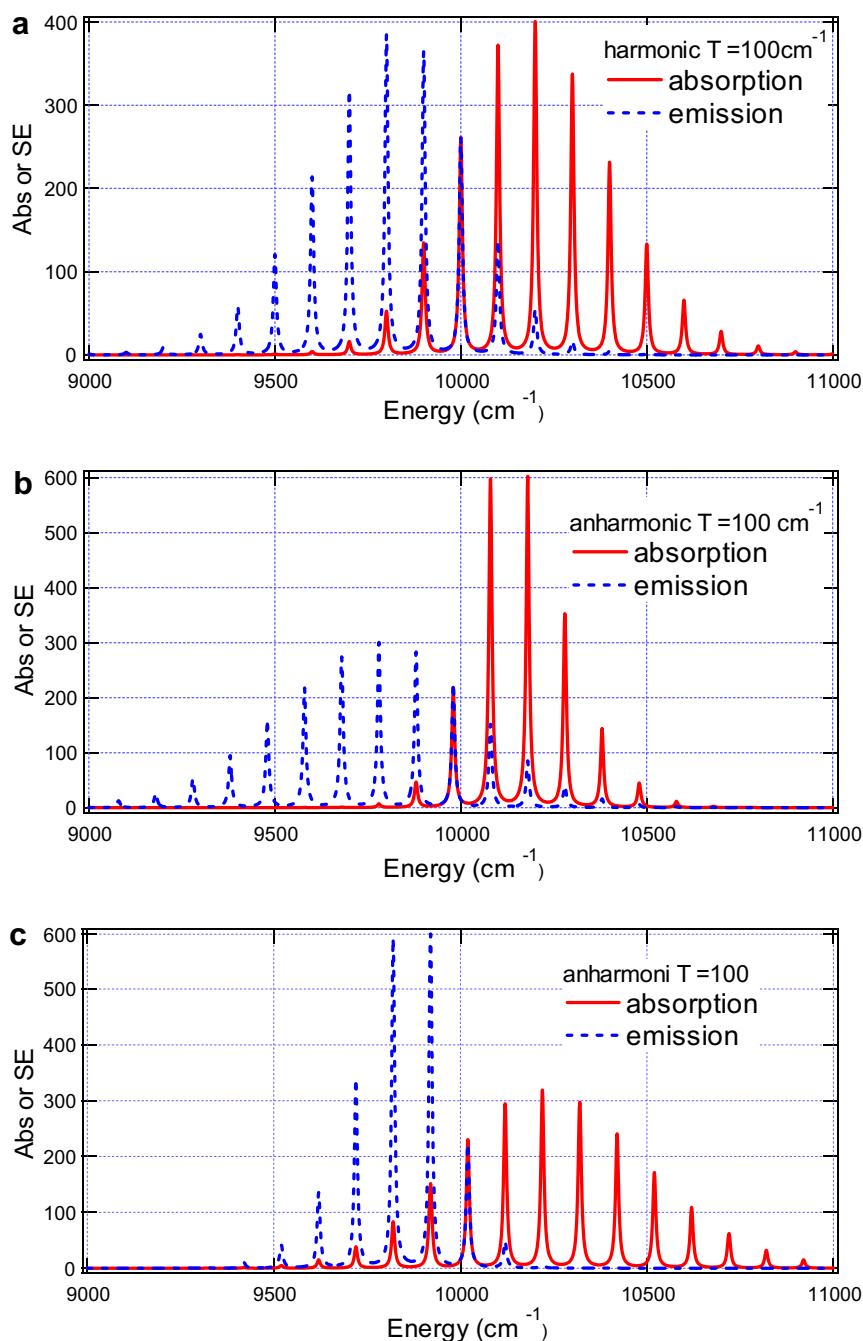


Fig. 3. The same as Fig. 2, but for temperature $T = 100 \text{ cm}^{-1}$.

$$|\langle \chi_{av_j-2} | \hat{U}_j | \chi_{av_j} \rangle|^2 = O(\lambda^2).$$

Within first-order approximation, we finally have

$$G_j(t) = \exp \left[(2itS_j\omega_j) \left(-\frac{a_{j3}}{a_{j2}} d_j \right) \right] \exp \left[-S_j \left(1 + 3 \frac{a_{j3}}{a_{j2}} d_j \right) \{ 2\bar{v}_j + 1 - (\bar{v}_j + 1)e^{it\omega_j} - \bar{v}_j e^{-it\omega_j} \} \right] + 1 - (\bar{v}_j + 1)e^{it\omega_j} - \bar{v}_j e^{-it\omega_j} \}. \quad (3.21)$$

It follows that

$$\alpha(\omega) = \frac{2\pi\omega}{3ac\hbar} |\bar{\mu}_{ba}|^2 \int_{-\infty}^{\infty} dt e^{it[(\omega_{ba}-\omega)-2\sum_j S_j\omega_j a_{j3}d_j/a_{j2}]} \times \exp \left[-\sum_j S_j \left(1 + 3 \frac{a_{j3}}{a_{j2}} d_j \right) \{ 2\bar{v}_j + 1 - (\bar{v}_j + 1)e^{it\omega_j} - \bar{v}_j e^{-it\omega_j} \} \right], \quad (3.22)$$

where $\bar{v}_j = \left(\exp \left(\frac{\hbar\omega_j}{k_B T} \right) - 1 \right)^{-1}$ is phonon distribution and $\omega_{ba} = (E_b - E_a)/\hbar > 0$.

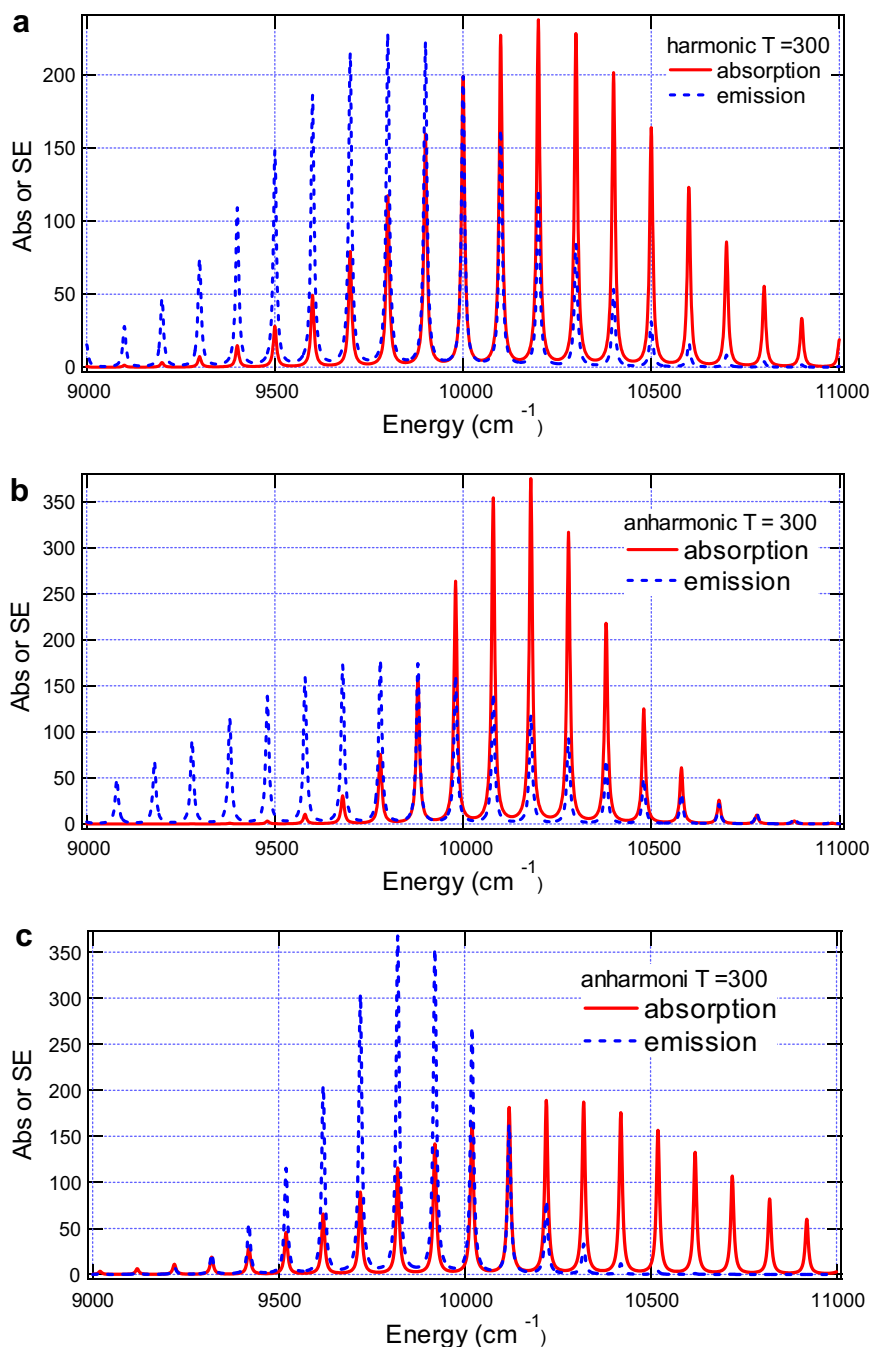


Fig. 4. The same as Fig. 2, but for temperature $T = 300 \text{ cm}^{-1}$.

3.2. Fluorescence coefficient

The molecular fluorescence coefficient for the electronic transition $a \rightarrow b$ as shown in Fig. 1b is defined as

$$I(\omega) = \frac{4\pi^2\omega}{3ac\hbar} |\bar{\mu}_{ba}|^2 \sum_{\bar{v}} \sum_{\bar{v}'} P_{b\bar{v}'} |\langle \Theta_{a\bar{v}} | \Theta_{b\bar{v}'} \rangle|^2 \delta(\omega_{a\bar{v},b\bar{v}'} + \omega). \quad (3.23)$$

Applying the similar procedure as above to calculate absorption coefficient, within the first-order approximation of anharmonicity we can derive

$$I(\omega) = \frac{2\pi\omega}{3ac\hbar} |\bar{\mu}_{ba}|^2 \int_{-\infty}^{\infty} dt e^{it[(\omega_{ba} + \omega) + 2\sum_j S_j \omega_j a_{j3} d_j / a_{j2}]} \times \exp \left[- \sum_j S_j \left(1 - 3 \frac{a_{j3}}{a_{j2}} d_j \right) \{ 2\bar{v}_j + 1 - (\bar{v}_j + 1) e^{it\omega_j} - \bar{v}_j e^{-it\omega_j} \} \right] \quad (3.24)$$

where $\omega_{ba} = (E_b - E_a)/\hbar < 0$. It should be noticed that $Q'_j = Q_j - d_j$ for fluorescence in Fig. 1b corresponds to $Q'_j = Q_j + d_j$ for absorption in Fig. 1a. As sign in d_j enters absorption coefficient in Eq. (3.22) and fluorescence coefficient in Eq. (3.24), we can conclude that the breaking down of mirror image between absorption and

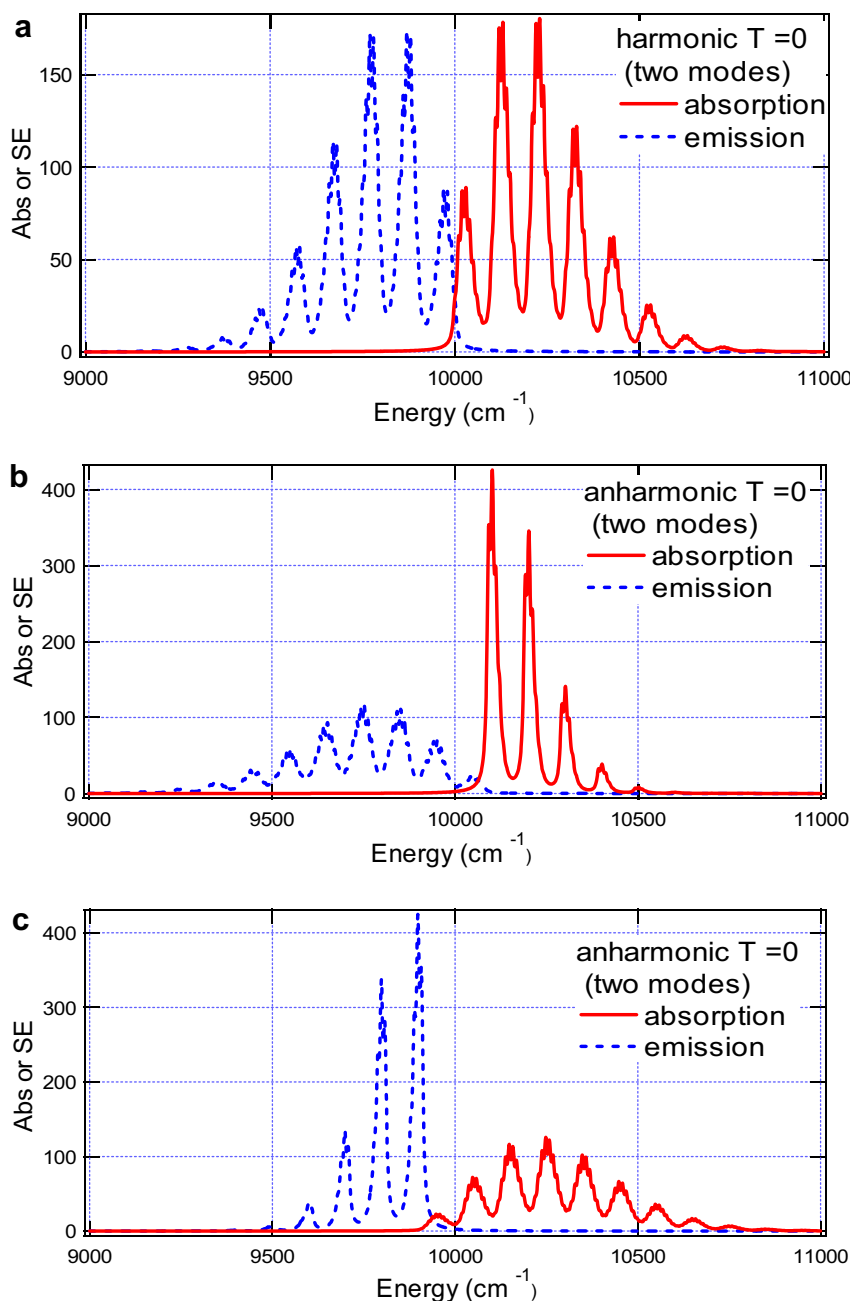


Fig. 5. Comparison of absorption and fluorescence spectra for the two-mode case of $\omega_{ba} = 10,000 \text{ cm}^{-1}$, $(S_1, S_2) = (2.0, 3.0)$, $(\omega_1, \omega_2) = (100 \text{ cm}^{-1}, 10 \text{ cm}^{-1})$ and $(a_{13}d_1/a_{12}, a_{23}d_2/a_{22}) = (an_1, an_2)$ for temperature $T = 0 \text{ K}$. Dashed lines stand for fluorescence spectrum and solid lines stands for absorption spectrum. (a) $an_1 = an_2 = 0$ corresponds to the harmonic case. (b) $an_1 = an_2 = -0.2$ corresponds to Fig. 1 in which the electronically excited-state shifts at the right-handed with respect to electronically ground state. (c) $an_1 = an_2 = 0.2$ corresponds to Fig. 1 in which electronically excited-state shifts at the left-handed with respect to electronically ground state.

fluorescence spectroscopy comes from the anharmonic effects within the first-order approximation to harmonic displaced oscillators. If we return to displaced harmonic case in Eqs. (3.22) and (3.24) with $a_{j3} = 0$, the both absorption and fluorescence coefficients agree with the formula for harmonic oscillators in which the mirror image holds.

4. Numerical calculations

Numerical calculations for absorption and fluorescence spectra are carried out with numerically integrating out Eqs. (3.22) and (3.24), respectively. We first consider the absorption and fluorescence spectra at temperature $T = 0$ K. The results are presented in Fig. 2. The mirror image relation of the spectrum is held perfectly in the harmonic case as shown in Fig. 2a. In contrast, the mirror image breaks down in Fig. 2b and c as the anharmonic effect is turned on. The spectra in Fig. 2b (Fig. 2c) correspond to the case in which the excited-state potential energy surface shifts at the right-handed (left-handed) side with respect to the ground-state potential energy surface. Obviously, the effects of the right-handed or left-handed shifts are distinguishable. This distinction is not observed in the case of harmonic oscillator. Actually we can interpret the mirror image relation as a consequence of the chiral symmetry of the excited-state potential energy surface with respect to the ground-state energy surface. The more interesting effect is that when this shift between the right-handed and left-handed is symmetric, the absorption (fluorescence) spectra in Fig. 2b form mirror image with respect to the fluorescence (absorption) spectra in Fig. 2c, but it should be emphasized that this mirror image is happened to two different systems that show chiral symmetry on their excited-state potential energy surfaces. We conclude that when molecule has the chiral symmetry of potential surfaces, the right-handed or left-handed the excited-state potential energy surface is indistinguishable from harmonic-oscillator spectra, but can be distinguishable when the first-order anharmonic effect is turned on. Figs. 3 and 4 demonstrate the absorption and fluorescence spectra at temperature $T = 100$ and 300 cm⁻¹, respectively. The same conclusion is held as it is shown at $T = 0$ K, except that the absorption and fluorescence spectra become more overlapped and are broader. However, at non-zero temperature the numerical integration of Eq. (3.22) for absorption coefficient and Eq. (3.24) for the fluorescence coefficient requires great caution for convergence at dips of spectra. In order to further confirm our conclusion, we carry out two-mode calculation, and the results are shown in Fig. 5, in which the above analysis about the chiral system is still held except the spectra are getting broader and more structured.

5. Concluding remarks

We have demonstrated numerical calculations for breaking down of mirror image between the absorption and fluorescence spectroscopy in the Section 4. Actually, we can use the short-time approximation to demonstrate it analytically. By assuming strong vibronic coupling, i.e., $\sum_j S_j \gg 1$ and

$$\exp(\pm it\omega_j) = 1 \pm it\omega_j - \frac{\omega_j^2 t^2}{2} + \dots \quad (5.1)$$

we can integral out Eq. (3.24) for absorption coefficient

$$\alpha(\omega) = \frac{2\pi\omega}{3ach} |\bar{\mu}_{ba}|^2 \sqrt{\frac{\pi}{\sum_j S_j \omega_j^2 (\bar{\nu}_j + \frac{1}{2}) (1 + 3 \frac{a_{j3}}{a_{j2}} d_j)}} \times \exp \left[-\frac{[E_b - E_a - h\omega + \sum_j S_j h\omega_j (1 + \frac{a_{j3}}{a_{j2}} d_j)]^2}{\sum_j S_j (h\omega_j)^2 (\bar{\nu}_j + \frac{1}{2}) (4 + 12 \frac{a_{j3}}{a_{j2}} d_j)} \right] \quad (5.2)$$

and for fluorescence coefficient

$$I(\omega) = \frac{2\pi\omega}{3ach} |\bar{\mu}_{ba}|^2 \sqrt{\frac{\pi}{\sum_j S_j \omega_j^2 (\bar{\nu}_j + \frac{1}{2}) (1 - 3 \frac{a_{j3}}{a_{j2}} d_j)}} \times \exp \left[-\frac{[E_b - E_a + h\omega - \sum_j S_j h\omega_j (1 + \frac{a_{j3}}{a_{j2}} d_j)]^2}{\sum_j S_j (h\omega_j)^2 (\bar{\nu}_j + \frac{1}{2}) (4 - 12 \frac{a_{j3}}{a_{j2}} d_j)} \right] \quad (5.3)$$

Both Eqs. (5.2) and (5.3) imply the Gaussian form of the band shape function with the maxima shift with respect to the harmonic-oscillator case, while the temperature dependence is still preserved. It is easy to see from Eqs. (5.2) and (5.3) that the mirror image is broken down as the first-order anharmonicity $a_{j3} \neq 0$ and the sign of displacement d_j is now observable quantity in the spectra as well. Let us see another limit at absolute zero temperature $T = 0$ K, Eq. (3.22) for the absorption coefficient is reduced to

$$\alpha(\omega) = \frac{2\pi\omega}{3ach} |\bar{\mu}_{ba}|^2 \int_{-\infty}^{\infty} dt e^{it[(\omega_{ba} - \omega) - 2 \sum_j S_j \omega_j a_{j3} d_j / a_{j2}]} \times \exp \left[-\sum_j S_j \left(1 + 3 \frac{a_{j3}}{a_{j2}} d_j \right) (1 - e^{it\omega_j}) \right] \quad (5.4)$$

and for fluorescence coefficient Eq. (3.24) turns to be

$$I(\omega) = \frac{2\pi\omega}{3ach} |\bar{\mu}_{ba}|^2 \int_{-\infty}^{\infty} dt e^{it[(\omega_{ba} + \omega) + 2 \sum_j S_j \omega_j a_{j3} d_j / a_{j2}]} \times \exp[-\sum_j S_j (1 - 3 \frac{a_{j3}}{a_{j2}} d_j) (1 - e^{it\omega_j})] \quad (5.5)$$

By introducing the average frequency $\bar{\omega}$ in $e^{it\omega_j}$, further simplification can be carried out and we can derive the following simple expression for absorption coefficient

$$\alpha(\omega) = \frac{4\pi^2\omega}{3ach^2\bar{\omega}} |\bar{\mu}_{ba}|^2 \frac{S^n e^{-S}}{n!}, \quad (5.6)$$

where

$$n = \frac{|\omega_{ba} - \omega - 2 \sum_j S_j \omega_j (\frac{a_{j3}}{a_{j2}} d_j)|}{\bar{\omega}} \quad (5.7)$$

and

$$S' = \sum_j S_j (1 + 3 \frac{a_{j3}}{a_{j2}} d_j). \quad (5.8)$$

The derivation of Eq. (5.6) is given in Appendix B. Similarly, we can derive the simple expression for fluorescence coefficient

$$I(\omega) = \frac{4\pi^2\omega}{3ach^2\bar{\omega}} |\bar{\mu}_{ba}|^2 \frac{S'' e^{-S''}}{n!}, \quad (5.9)$$

where

$$S'' = \sum_j S_j \left(1 - 3 \frac{a_{j3}}{a_{j2}} d_j \right). \quad (5.10)$$

The band origin (or the 0–0 transition) for $\alpha(\omega)$ and $I(\omega)$ are the same, but their intensities are different since $\alpha(\omega)$ is proportional to e^{-S} in Eq. (5.8), while $I(\omega)$ is proportional to $e^{-S''}$ in Eq. (5.10). As $S' \neq S''$, the mirror image relation between $\alpha(\omega)$ and $I(\omega)$ are no longer exist even at zero temperature. All these analytical observations are confirmed from numerical demonstrations in Section 4.

In order to make the current theory as self-completed simulation method on the same level of anharmonic approximation, we further demonstrate this anharmonic effect on photo-induced electron transfer and we will see the rate constant is depending on the sign of displacement as well. In the Condon approximation, the electron transfer (ET) rate W can be expressed as [1]

$$W = \frac{2\pi}{\hbar^2} |T_{ba}|^2 \sum_{\bar{v}} \sum_{\bar{v}'} P_{a\bar{v}'} |\langle \Theta_{b\bar{v}'} | \Theta_{a\bar{v}} \rangle|^2 \delta(\omega_{b\bar{v}'} - \omega_{a\bar{v}}), \quad (5.11)$$

where T_{ba} denotes the electronic coupling matrix element. As the derivation is quite similar to those for absorption coefficient and stimulated fluorescence coefficient given in the previous sections, we would like just to present the results here. The rate W in the displaced oscillator approximation with including the first-order anharmonic contribution takes the following form

$$= \frac{|T_{ba}|^2}{\hbar^2} \int_{-\infty}^{\infty} dt \exp \left[it \left(\omega_{ba} - 2 \sum_j S_j \omega_j \left(\frac{a_{j3}}{a_{j2}} d_j \right) \right) \right] \times \exp \left[- \sum_j S_j \left(1 + 3 \frac{a_{j3}}{a_{j2}} d_j \right) \{ 2\bar{v}_j + 1 - (\bar{v}_j + 1) e^{it\omega_j} - \bar{v}_j e^{-it\omega_j} \} \right] \quad (5.12)$$

for the case in which the relation between the ground-state excited-state PESs is described by Fig. 1a, and

$$W = \frac{|T_{ba}|^2}{\hbar^2} \int_{-\infty}^{\infty} dt \exp \left[it \left(\omega_{ba} + 2 \sum_j S_j \omega_j \left(\frac{a_{j3}}{a_{j2}} d_j \right) \right) \right] \times \exp \left[- \sum_j S_j \left(1 - 3 \frac{a_{j3}}{a_{j2}} d_j \right) \{ 2\bar{v}_j + 1 - (\bar{v}_j + 1) e^{it\omega_j} - \bar{v}_j e^{-it\omega_j} \} \right] \quad (5.13)$$

for the case in which the relation between the excited-state and ground-state PESs is described by Fig. 1b. By applying the short-time approximation mentioned above, Eqs. (5.12) and (5.13) are reduced to

$$W = \frac{|T_{ba}|^2}{\hbar^2} \sqrt{\frac{\pi}{\sum_j S_j \omega_j^2 (\bar{v}_j + \frac{1}{2}) (1 \pm 3 \frac{a_{j3}}{a_{j2}} d_j)}} \times \exp \left[- \frac{\{ E_b - E_a + \sum_j S_j \hbar \omega_j (1 \pm \frac{a_{j3}}{a_{j2}} d_j) \}^2}{4 \sum_j S_j (\hbar \omega_j)^2 (\bar{v}_j + \frac{1}{2}) (1 \pm 3 \frac{a_{j3}}{a_{j2}} d_j)} \right], \quad (5.14)$$

where the upper plus sign corresponds to Eq. (5.12) and the lower minus sign corresponds to Eq. (5.13). In the classical region (i.e., $\hbar \omega_j / k_B T \ll 1$), we obtain

$$W = \frac{|T_{ba}|^2}{\hbar^2} \sqrt{\frac{\pi \hbar}{\lambda'' k_B T}} \exp \left[- \frac{(\Delta G_{ba} + \lambda')^2}{4 \lambda'' k_B T} \right], \quad (5.15)$$

where $\Delta G_{ba} = E_b - E_a$,

$$\lambda'' = \sum_j S_j \hbar \omega_j \left(1 \pm 3 \frac{a_{j3}}{a_{j2}} d_j \right); \quad \lambda' = \sum_j S_j \hbar \omega_j \left(1 \pm \frac{a_{j3}}{a_{j2}} d_j \right). \quad (5.16)$$

Since $\lambda'' \neq \lambda'$, the rate constant W given by Eq. (5.15) does not take the form of Marcus's equation. In other words, it is found that if the anharmonic effect is significant, the conventional Marcus's equation for electron transfer is no longer valid. Furthermore, in the case of an anharmonic displaced oscillator, the ET rate depends not only on whether the transfer takes place from upper to lower or lower to upper PES, but also whether the excited-state PES shifts at the right-handed or the left-handed with respect to the ground-state PES.

In brief, we would like to point out that in this work only the displaced oscillator surfaces have been studied and the anharmonic effect is examined only to the first-order approximation. The chiral symmetry of potential energy surfaces can produce observable effects for absorption spectra, stimulated fluorescence spectra and electron transfer process within the first-order anharmonic effect. In the near future, we will investigate the general the

displaced-distorted oscillators and the Duschinsky effect due to normal-mode mixing of two electronic states including the first-order as well as the higher order anharmonic corrections. The main complicity of the Duschinsky effect is involved in dealing with non-separable Franck–Condon overlap integrals in Eqs. (2.1), (3.23), and (5.11),

$$\langle \Theta_{b\bar{v}'}(\vec{Q}') | \Theta_{a\bar{v}}(\vec{Q}) \rangle = \langle \chi_{bv'_1}(Q'_1) \chi_{bv'_2}(Q'_2) \cdots \chi_{bv'_N}(Q'_N) | \chi_{av_1}(Q_1) \chi_{av_2}(Q_2) \cdots \chi_{av_N}(Q_N) \rangle \quad (5.17)$$

in the case of displaced harmonic oscillator and displaced anharmonic oscillator with just the first-order correction, Eq. (5.17) can be factored out into a product of individual mode overlap integrals as we have done in the present work. Eq. (5.17) has been integrated out analytically for the harmonic oscillators including the Duschinsky effect [25]. We can generalize the method in Ref. [25] with applying the first-order correction of wave function in Eqs. (3.7)–(3.9), (3.12)–(3.24), (5.1)–(5.17). For the higher order anharmonic correction, even the second-order correction can induce a different kind of mode mixing [26] that (differs from the Duschinsky effect) can mix wavefunctions within the same electronic state accompanying energy flow among vibrational modes. It is also very interesting question that how the two kinds of mode mixings are distinguished in the experimental observations. Finally, we conclude that anharmonic effects should be very important in dealing with unimolecular decomposition of molecular clusters, especially the effect from the intermolecular modes.

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Appendix A. The first- and second-order energy corrections for cubic and quartic anharmonic oscillator

In this appendix we use general perturbation theory to solve the first- and second-order energy corrections for anharmonic oscillator with the following potential form

$$V(Q) = a_2 Q^2 + \lambda a_3 Q^3 + \lambda^2 a_4 Q^4 = V_2(Q) + V_3(Q) + V_4(Q) \quad (A1)$$

in which Q is mass-weighted normal-mode coordinate, and λ is chosen to be a small quantity such that cubic term $V_3(Q)$ and quartic term $V_4(Q)$ represent the first-order and second-order corrections to harmonic potential, respectively. With $\lambda = 0$, we have the zero-order wave function $\chi_v^{(0)}(Q) \equiv |v\rangle$ with the zero-order energy level

$$E_v^{(0)} = \hbar \omega \left(v + \frac{1}{2} \right), \quad v = 0, 1, 2, \dots, \quad (A2)$$

where $\omega = \sqrt{2a_2}$. By employing general perturbation theory, we have the first-order energy correction in terms of the anharmonic terms in Eq. (A1)

$$E_v^{(1)} = \langle v | V_3(Q) + V_4(Q) | v \rangle = \lambda a_3 \langle v | Q^3 | v \rangle + \lambda^2 a_4 \langle v | Q^4 | v \rangle. \quad (A3)$$

It can be easily shown that

$$\langle v | Q^3 | v \rangle = 0 \quad (A4)$$

and

$$\langle v | Q^4 | v \rangle = 6 \left(\frac{\hbar}{2\omega} \right)^2 \left[\left(v + \frac{1}{2} \right)^2 + \frac{1}{4} \right]. \quad (A5)$$

The second-order energy correction in terms of the anharmonic terms in Eq. (A1) can be expressed as

$$E_v^{(2)} = \sum_{\mu \neq v} \frac{|\langle v|V_3(Q) + V_4(Q)|\mu\rangle|^2}{E_v^{(0)} - E_\mu^{(0)}} \\ = \lambda^2 a_3^2 \sum_{\mu \neq v} \frac{|\langle v|Q^3|\mu\rangle|^2}{E_v^{(0)} - E_\mu^{(0)}} + \lambda^4 a_4^2 \sum_{\mu \neq v} \frac{|\langle v|Q^4|\mu\rangle|^2}{E_v^{(0)} - E_\mu^{(0)}} \quad (\text{A6})$$

in which the cross term can be easily proved to be zero. After tedious but not difficult derivation, we can evaluate the first term in Eq. (A6) as

$$\sum_{\mu \neq v} \frac{|\langle v|Q^3|\mu\rangle|^2}{E_v^{(0)} - E_\mu^{(0)}} = \frac{|\langle v|Q^3|v+3\rangle|^2}{E_v^{(0)} - E_{v+3}^{(0)}} + \frac{|\langle v|Q^3|v+1\rangle|^2}{E_v^{(0)} - E_{v+1}^{(0)}} \\ + \frac{|\langle v|Q^3|v-1\rangle|^2}{E_v^{(0)} - E_{v-1}^{(0)}} + \frac{|\langle v|Q^3|v-3\rangle|^2}{E_v^{(0)} - E_{v-3}^{(0)}}, \quad (\text{A7})$$

and finally

$$\sum_{\mu \neq v} \frac{|\langle v|Q^3|\mu\rangle|^2}{E_v^{(0)} - E_\mu^{(0)}} = -\frac{1}{\hbar\omega} \left(\frac{\hbar}{2\omega}\right)^3 (30v^2 + 30v + 11) \\ = -\frac{30}{\hbar\omega} \left(\frac{\hbar}{2\omega}\right)^3 \left[\left(v + \frac{1}{2}\right)^2 + \frac{7}{60}\right]. \quad (\text{A8})$$

For the present purpose, we do not have to evaluate the second term in Eq. (A6) as it turns to be in the order of λ^4 . All above derivations are repeated by using the following recurrence relation

$$Q|v\rangle = \sqrt{\frac{\hbar}{2\omega}} \left\{ \sqrt{v+1}|v+1\rangle + \sqrt{v}|v-1\rangle \right\}. \quad (\text{A9})$$

Next, we consider the first-order correction to wave function $\chi_v^{(0)}(Q) \equiv |v\rangle$ by general perturbation theory

$$\chi_v^{(1)}(Q) = \sum_{\mu \neq v} \frac{\langle v|V_3(Q) + V_4(Q)|\mu\rangle}{E_v^{(0)} - E_\mu^{(0)}} \chi_v^{(0)}(Q) \\ = \lambda a_3 \sum_{\mu \neq v} \frac{\langle v|Q^3|\mu\rangle}{E_v^{(0)} - E_\mu^{(0)}} \chi_v^{(0)}(Q) + \lambda^2 a_4 \sum_{\mu \neq v} \frac{\langle v|Q^4|\mu\rangle}{E_v^{(0)} - E_\mu^{(0)}} \chi_v^{(0)}(Q). \quad (\text{A10})$$

The first term in Eq. (A10) can be evaluated as

$$\sum_{\mu \neq v} \frac{\langle v|Q^3|\mu\rangle}{E_v^{(0)} - E_\mu^{(0)}} \chi_v^{(0)}(Q) = -\frac{3}{\hbar\omega} \left(\frac{\hbar}{2\omega}\right)^{3/2} \\ \times \left[\sqrt{(v+1)^3} \chi_{v+1}^{(0)}(Q) - \sqrt{v^3} \chi_{v-1}^{(0)}(Q) \right] \\ - \frac{1}{3\hbar\omega} \left(\frac{\hbar}{2\omega}\right)^{3/2} \\ \times \left[\sqrt{(v+1)(v+2)(v+3)} \chi_{v+3}^{(0)}(Q) \right. \\ \left. - \sqrt{v(v-1)(v-2)} \chi_{v-3}^{(0)}(Q) \right]. \quad (\text{A11})$$

The second-term in Eq. (A10) is not necessarily derived here it turns to be in the order of λ^2 . In summary, the energy level for anharmonic oscillator can be rewritten as

$$E_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)} = \varepsilon_v^{(0)} + \lambda \varepsilon_v^{(1)} + \lambda^2 \varepsilon_v^{(2)} + \dots, \quad (\text{A12})$$

where the second equality rearranges the order of perturbation in terms of λ , and they are easily evaluated as follows:

$$\varepsilon_v^{(0)} = \hbar\omega \left(v + \frac{1}{2}\right), \quad (\text{A13})$$

and the first-order correction to the energy is zero

$$\varepsilon_v^{(1)} = 0 \quad (\text{A14})$$

and the second-order is given by

$$\varepsilon_v^{(2)} = 6a_4 \left(\frac{\hbar}{2\omega}\right)^2 \left[\left(v + \frac{1}{2}\right)^2 + \frac{1}{4} \right] \\ - \frac{30a_3^2}{\hbar\omega} \left(\frac{\hbar}{2\omega}\right)^3 \left[\left(v + \frac{1}{2}\right)^2 + \frac{7}{60} \right]. \quad (\text{A15})$$

The first-order correction to wave function in terms of λ turns to be

$$\chi_v^{(1)}(Q) = -\frac{3\lambda a_3}{\hbar\omega} \left(\frac{\hbar}{2\omega}\right)^{3/2} \left[\sqrt{(v+1)^3} \chi_{v+1}^{(0)}(Q) - \sqrt{v^3} \chi_{v-1}^{(0)}(Q) \right] \\ - \frac{\lambda a_3}{3\hbar\omega} \left(\frac{\hbar}{2\omega}\right)^{3/2} \left[\sqrt{(v+1)(v+2)(v+3)} \chi_{v+3}^{(0)}(Q) \right. \\ \left. - \sqrt{v(v-1)(v-2)} \chi_{v-3}^{(0)}(Q) \right]. \quad (\text{A16})$$

In this way, we have a consistent order correction with anharmonic potential in Eq. (A1). It should be noted that up to the first-order correction to harmonic potential in terms of λ , the energy correction is zero but wave function correction is not.

Appendix B. The derivation Eq. (5.6)

By replacing $(1 - e^{it\omega_j})$ with $(1 - e^{it\bar{\omega}})$ by average frequency $\bar{\omega}$ in Eq. (5.4), we turn out to deal with the following integration

$$A = \int_{-\infty}^{\infty} dt e^{itA} \times \exp[-B(1 - e^{it\bar{\omega}})] \\ = e^{-B} \int_{-\infty}^{\infty} dt e^{itA} \times \exp[Be^{it\bar{\omega}}] \quad (\text{B1})$$

in which A and B are constants. By expanding the second exponential function in power series form $\exp[Be^{it\bar{\omega}}] = \sum_{n=0}^{\infty} \frac{B^n}{n!} e^{in\bar{\omega}t}$, we obtain

$$A = e^{-B} \sum_{n=0}^{\infty} \frac{B^n}{n!} \int_{-\infty}^{\infty} dt e^{it(A+n\bar{\omega})} = e^{-B} \sum_{n=0}^{\infty} \frac{B^n}{n!} 2\pi \delta(A+n\bar{\omega}) = 2\pi e^{-B} \frac{B^n}{n!} \Big|_{n=|A/\bar{\omega}|}. \quad (\text{B2})$$

Note that δ -function is even function.

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