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Harmonic Theory of Thermal Two-Photon Absorption in Benzene

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A correlation function formalism is applied to compute the two-photon absorption spectrum of benzene. Using harmonic Hamiltonians for the ground and excited electronic states, we find that the theory agrees qualitatively with the experimentally observed sparsity of the thermal two-photon absorption spectrum as compared with the single-photon absorption spectrum. An expression for the average vibrational energy in the excited state is derived. We find that cooling of the nascent vibrational energy in the electronically excited state is not as extensive in the two-photon absorption process as compared to the single-photon case.

I. Introduction

The transition probability for two-photon absorption (TPA) was first considered ca. 70 years ago by Goppert-Mayer using second-order perturbation theory.[1] Even today, the topic remains of interest.[2−4] Applying TPA to explore inorganic and organic materials[3,4] is attractive because the selection rule followed by TPA is different from that of the one-photon transition; therefore, they complement each other by reaching different vibronic states.

In principle, the theory of TPA is well-understood. Theoretical studies have shown how to calculate the TPA cross-section as well as the transition moments needed as input.[5−11] A very convenient method for computing the transition probability is by use of correlation functions[12−14] because it avoids the rather complicated multicenter integrals needed when applying a wave function approach.[12,13]

The first objective of the present work is to apply the correlation function method to compute the TPA spectrum in the benzene molecule. As long as one limits oneself to harmonic Hamiltonians, one may derive analytic expressions for the four-point dipole correlation function *Q*. The TPA spectrum is then obtained as a special three-dimensional Fourier transform of this correlation function. We are not aware of any previous attempts at computation of a thermal TPA spectrum of a polyatomic molecule as big as benzene using this methodology.

Our interest in the theory of TPA stems also from recent studies on the photoinduced cooling of the nascent vibrational population in electronically excited states.[15−20] We found that in single-photon excitation the vibrational distribution in the excited electronic state may be significantly cooled relative to the ground-state thermal population. This happens when the ground-state molecular Hamiltonian does not differ too much from the excited-state molecular Hamiltonian. Because frequencies in the excited electronic state are usually somewhat lower than in the ground state, cooling may be found in the vicinity of the 0−0 transition frequency and to the red of it.[16] The question we posed to ourselves in this paper is whether there is any difference between single-photon and two-photon absorption in this respect. Extensive cooling was found in the single-photon excitation of benzene,[18] and so we chose this same molecule to try and understand what happens in TPA. In addition to computing the TPA spectrum, we also demonstrate how one may compute the average energy in the excited electronic state from the four-point correlation function. The major finding of this study is that, at least for the harmonic benzene model considered here, TPA does not lead to extensive cooling in the excited state.

In section II, we review the theory of two-photon absorption and derive an explicit expression for the frequency dependence of the nascent average vibrational energy in the electronically excited state. This formulation is then applied to the benzene molecule in section III. Finally, in section IV, we present a brief summary and indicate how to apply the same methodology to calculate Raman scattering and third- or higher-order susceptibility.

II. The Two-Photon Absorption Spectrum and Average Vibrational Energy in the Electronically Excited State

A. Harmonic Approximation. A molecule is characterized by its electronic, vibrational, rotational, and translational states. At room temperature or lower, typical of most spectroscopy experiments, the velocity of the molecules does not give rise to a strong Doppler effect and so may be neglected. Rotation−vibration coupling affects selection rules; the rotational structure of the TPA spectrum can be clearly seen in high-resolution experiments.[21,22] However, they are a finer effect than the change in the vibrational states. We will neglect the influence of the rotational states on the TPA process.

With these assumptions, the state of a molecule $|A\rangle$ is a direct product of its electronic state $|A_{\mathrm{el}}\rangle$ and its vibrational state $|A_{\mathrm{v}}\rangle$; $|A\rangle = |A_{\mathrm{el}}\rangle\,|A_{\mathrm{v}}\rangle$. The electron-vibration coupling realizes itself through the vibrational coordinate dependence of the transition moments. The harmonic Hamiltonians of the ground and excited electronic states are assumed to be harmonic

$$H_{\mathrm{g}} = \frac{1}{2}\sum_{\alpha=1}^{M}(p_\alpha^2 + \omega_\alpha^{\mathrm{g}2} q_\alpha^2)$$

$$H_{\mathrm{e}} = \frac{1}{2}\sum_{\alpha=1}^{M}[p_\alpha^2 + \omega_\alpha^{\mathrm{e}2}(q_\alpha - q_{\alpha0})^2] + \Delta E \qquad (2.1)$$

Here, q_α and p_α are the mass-weighted coordinate and momentum operators of the αth normal mode and *M* is the number of

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normal modes. The equilibrium point of the αth normal mode in the electronically excited states is shifted by $q_{\alpha 0}$ relative to the ground state. We ignore Duschinskii rotations;[23] they are not very important for the benzene molecule.[18] The initial state of the molecule is thus characterized as $|\mathrm{el_g}\rangle\ |n_1^{\mathrm{g}}(i)\cdots n_M^{\mathrm{g}}(i)\rangle$; its energy is $E_i = \sum_{\alpha=1}^{M} (n_\alpha^{\mathrm{g}}(i) + (^1/_2))\hbar\omega_\alpha^{\mathrm{g}}$. It depends on $n_1^{\mathrm{g}}(i), \cdots, n_M^{\mathrm{g}}(i)$ the occupation numbers for each of the normal modes. The ground-state energy is $Y_{\mathrm{g}} = \sum_{\alpha=1}^{M}(^1/_2)\hbar\omega_\alpha^{\mathrm{g}}$. Similarly, the final state is characterized by $|\mathrm{el_e}\rangle\ |n_1^{\mathrm{e}}(j)\cdots n_M^{\mathrm{e}}(j)\rangle$, its energy $E_j = \sum_{\alpha=1}^{M}(n_\alpha^{\mathrm{e}}(j) + (^1/_2))\hbar\omega_\alpha^{\mathrm{e}} + \Delta E$ measured relative to the energy zero of the ground state, and $n_1^{\mathrm{e}}(j),\cdots, n_M^{\mathrm{e}}(j)$ are the occupation numbers of each normal mode in the electronically excited state. The ground-state energy is $Y_{\mathrm{e}} \equiv \sum_{\alpha=1}^{M}(^1/_2)\hbar\omega_\alpha^{\mathrm{e}} + \Delta E$. The 0−0 transition frequency is defined as $\hbar\omega_{00} = Y_{\mathrm{e}} - Y_{\mathrm{g}}$.

The harmonic approximation is appropriate when considering the thermal absorption spectrum of a molecule such as benzene at room temperature. However, when considering two-photon absorption, in which the first photon induces an excitation to a high-lying vibrational state, the harmonic approximation for the intermediate states is expected to fail, at least quantitatively. However, it is impossible to compute the TPA spectrum when the ground-state Hamiltonian is anharmonic; moreover, the anharmonicity of the ground state at the high energies involved is not that easily accessible even with present-day ab initio techniques. We therefore make do with a strictly harmonic approach. With these assumptions, an explicit expression for the four-point dipole thermal correlation function is derived in Appendix A. Here, we note that a novel element in the derivation is the simplification due to the use of a generating function approach.

B. The Two-Photon Absorption Spectrum. In the harmonic approximation stated in the previous section, the initial state $|A\rangle$ of the molecule is one of the vibrational states $|n_1^{\mathrm{g}}(A)\cdots n_M^{\mathrm{g}}(A)\rangle$ in the electronic ground state $|\mathrm{el}_g\rangle$. For a thermal distribution of molecules at temperature T, the probability that the molecule is in state $|\mathrm{el_g}\rangle\ |n_1^{\mathrm{g}}(A)\cdots n_M^{\mathrm{g}}(A)\rangle$ is given by the Boltzmann factor $p_A = (\mathrm{e}^{-\beta E}A)/[Z_{\mathrm{g}}(\beta)]$; the partition function for the harmonic Hamiltonian is well-known[12]

$$Z_{\mathrm{g}}(\beta) = \sum_i \mathrm{e}^{-\beta E_i} = \prod_{\alpha=1}^{M} \frac{1}{2\sinh\left(\dfrac{\beta\hbar\omega_\alpha^{\mathrm{g}}}{2}\right)} \tag{2.2}$$

The TPA process involves two photons characterized respectively by the modes $(\vec{k}, \delta)$ and $(\vec{k}', \delta')$ with associated frequencies $\omega = c|\vec{k}|$ and $\omega' = c|\vec{k}'|$, where $\vec{k}$ and δ are the wave vector and polarization direction of the photon and c is the speed of light. The thermal transition probability per unit time from the ground state to an electronically excited state $|B\rangle$ is[24] $\sum_A(|c_{BA}^{(2)}(t)|^2/tII')p_A$, where $c_{BA}^{(2)}(t)$ is the second-order transition amplitude from state $|A\rangle$ to state $|B\rangle$, t is the time during which the molecule is irradiated by the electromagnetic field, and I is the intensity of the incident light for the mode $(\vec{k}, \alpha)$, and it is related to the occupation number $n_{k\alpha}$ by $I_{k\alpha} = c\hbar\omega_k n_{k\alpha}/V$. V is the normalization volume in a discrete description of the field.

The total absorption probability is obtained by summation over all possible final states. Because we will be interested only in the relative absorption intensities among different excitation frequencies, a constant factor $[(2\pi)^3/\hbar^2]\alpha^2$ is dropped out, where $\alpha = (e^2/4\pi\epsilon_0\hbar c)$ is the fine structure constant. The relative probability that the molecule absorbs two photons with respective frequencies ω and ω' is[24,25]

$$g(\omega, \omega', \beta) = \sum_{\delta'\delta''\delta'''} e_\delta^{k'\alpha'}\, e_{\delta'}^{k\alpha}\, e_{\delta''}^{k'\alpha' *}\, e_{\delta'''}^{k\alpha *}\, D^{(2)}_{\delta\delta'\delta''\delta'''} \tag{2.3}$$

where $e_{\delta'}^{k\alpha}$ is the δ'th Cartesian component of the polarization vector $\vec{e}_{k\alpha}$. The coefficient is given by the expression

$$\begin{aligned} D^{(2)}_{\delta\delta'\delta''\delta'''} = {} & \sum_{BA} \delta(\omega_{BA} - \omega - \omega')p_A \sum_{RR'} \\ & \left[\frac{\langle B_{\mathrm{v}}|\mu_\delta^{BR}|R_{\mathrm{v}}\rangle\langle R_{\mathrm{v}}|\mu_{\delta'}^{RA}|A_{\mathrm{v}}\rangle}{\omega_{RA} - \omega} + \frac{\langle B_{\mathrm{v}}|\mu_{\delta'}^{BR}|R_{\mathrm{v}}\rangle\langle R_{\mathrm{v}}|\mu_\delta^{RA}|A_{\mathrm{v}}\rangle}{\omega_{RA} - \omega'}\right] \times \\ & \left[\frac{\langle A_v|\mu_{\delta'''}^{AR'}|R'_{\mathrm{v}}\rangle\langle R'_{\mathrm{v}}|\mu_{\delta''}^{R'B}|B_{\mathrm{v}}\rangle}{\omega_{R'A} - \omega} + \frac{\langle A_{\mathrm{v}}|\mu_{\delta''}^{AR'}|R'_{\mathrm{v}}\rangle\langle R'_{\mathrm{v}}|\mu_{\delta'''}^{R'B}|B_{\mathrm{v}}\rangle}{\omega_{R'A} - \omega'}\right] \end{aligned} \tag{2.4}$$

where R and R' are the indices of the intermediate states and the transition frequencies are defined as $\omega_{RA} = (E_R - E_A)/\hbar$ and $\omega_{BA} = (E_B - E_A)/\hbar$. E_B, E_R, and E_A are the energies of the respective states $|B\rangle$, $|R\rangle$, and $|A\rangle$. μ_δ^{BR} is the δth Cartesian component of the dipole operator $\hat{\vec{\mu}}_{BR} = \langle B_{\mathrm{el}}|\sum_j \vec{x}_j\ |R_{\mathrm{el}}\rangle$, $\mu_{\delta'}^{RA}$ is the δ'th Cartesian component of the dipole operator $\hat{\vec{\mu}}_{RA} = \langle R_{\mathrm{el}}|\sum_j \vec{x}_j\ |A_{\mathrm{el}}\rangle$, and $\vec{x}_j$ is the coordinate of the jth electron. The electronic wave functions $|A_{\mathrm{el}}\rangle$, $|R_{\mathrm{el}}\rangle$, and $|B_{\mathrm{el}}\rangle$ include the nuclear coordinates so that $\hat{\vec{\mu}}_{BR}$ and $\hat{\vec{\mu}}_{RA}$ are functions of the nuclear coordinates and are operators operating on the vibrational states $|A_{\mathrm{v}}\rangle$, $|R_{\mathrm{v}}\rangle$, and $|B_{\mathrm{v}}\rangle$.

The four-point dipole correlation function is defined as

$$\begin{aligned} Q_{\alpha\alpha'\alpha''\alpha'''}(s, \tau, \tau_1, \beta) = {} & \frac{1}{Z_{\mathrm{g}}(\beta)} Tr[\exp(-isH_B/\hbar)\, \mu_\alpha^{BR} \\ & \exp(i\tau H_R/\hbar)\, \mu_{\alpha'}^{RA} \exp[(is - i\tau - i\tau_1)H_A/\hbar - \beta H_A]\, \mu_{\alpha''}^{AR'} \\ & \exp(iH_{R'}\tau_1/\hbar)\, \mu_{\alpha'''}^{R'B}] \end{aligned} \tag{2.5}$$

where H_B, H_R, and H_A are the vibrational Hamiltonians in the electronic states $|B_{\mathrm{el}}\rangle$, $|R_{\mathrm{el}}\rangle$, and $|A_{\mathrm{el}}\rangle$. The relative absorption strength, eq 2.3, can be expressed as a special 3-fold Fourier integral of the four-point dipole correlation function.[12] By using the identities

$$\delta(\omega_{BA} - \omega - \omega') = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}s\, \exp[-is(\omega_{\mathrm{BA}} - \omega - \omega')] \tag{2.6}$$

and

$$\begin{aligned} \frac{1}{\omega_{RA} - \omega - i\lambda} = {} & i\int_{-\infty}^{0} \mathrm{d}\tau\, \exp[i\tau(\omega_{RA} - \omega - i\lambda)],\ \frac{1}{\omega_{R'A} - \omega + i\lambda} = \\ & -i\int_{0}^{\infty} \mathrm{d}\tau\, \exp[i\tau(\omega_{R'A} - \omega + i\lambda)],\ \lambda \to 0^+ \end{aligned} \tag{2.7}$$

one finds that eq 2.4 is rewritten as

$$\begin{aligned} D^{(2)}_{\delta\delta'\delta''\delta'''} = {} & \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}s \exp[is(\omega+\omega')] \\ & \exp(-is\Delta E/\hbar)\int_{-\infty}^{0}\mathrm{d}\tau \exp(-\mathrm{i}\tau\omega+\lambda\tau)\int_{0}^{\infty}\mathrm{d}\tau' \\ & \exp(-i\tau'\omega-\lambda\tau')Q_{\delta\delta'\delta'''\delta''}(s,\tau,\tau',\beta) + \\ & \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}s \exp[is(\omega+\omega')]\exp(-is\Delta E/\hbar)\int_{-\infty}^{0}\mathrm{d}\tau \\ & \exp(-i\tau\omega+\lambda\tau)\int_{0}^{\infty}\mathrm{d}\tau' \\ & \exp(-i\tau'\omega'-\lambda\tau')Q_{\delta\delta'\delta''\delta'''}(s,\tau,\tau',\beta) + \\ & \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}s \exp[is(\omega+\omega')]\exp(-is\Delta E/\hbar)\int_{-\infty}^{0}\mathrm{d}\tau \\ & \exp(-i\tau\omega'+\lambda\tau)\int_{0}^{\infty}\mathrm{d}\tau' \\ & \exp(-i\tau'\omega-\lambda\tau')Q_{\delta'\delta\delta'''\delta''}(s,\tau,\tau',\beta) + \\ & \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}s \exp[is(\omega+\omega')]\exp(-is\Delta E/\hbar)\int_{-\infty}^{0}\mathrm{d}\tau \\ & \exp(-i\tau\omega'+\lambda\tau)\int_{0}^{\infty}\mathrm{d}\tau' \\ & \exp(-\mathrm{i}\tau'\omega'-\lambda\tau')Q_{\delta'\delta\delta''\delta'''}(s,\tau,\tau',\beta) \end{aligned} \quad (2.8)$$

For a realistic molecule, the intermediate states and the final states are quasidiscrete, and the four integrands in eq 2.8 decay sufficiently rapidly with time so that the integral converges. However, the integrands calculated from the harmonic energy surfaces are quasiperiodic functions. In eq 2.3, the two photons are plane wave states ($\vec{k}$, α) and ($\vec{k}'$, α′) which are infinite in the space and time domains, so that, strictly speaking, all four integrals in eq 2.8 diverge.

This difficulty is avoided when using photon pulses. For the sake of analytical simplicity, we will use Gaussian pulses centered at ω_0 and with variance Δ. Averaging eq 2.3 over the Gaussian incident pulses leads to our final expression for the TPA spectrum

$$\begin{aligned} g(\omega_0,\Delta,\beta) & = \int_{-\infty}^{\infty}\mathrm{d}\omega \frac{\exp\left\{-\frac{(\omega-\omega_0)^2}{2\Delta^2}\right\}}{\Delta\sqrt{2\pi}}\int_{-\infty}^{\infty}\mathrm{d}\omega' \frac{\exp\left\{-\frac{(\omega'-\omega_0)^2}{2\Delta^2}\right\}}{\Delta\sqrt{2\pi}} \\ & \qquad g(\omega,\omega',\beta) \quad (2.9) \\ & = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}s\int_{-\infty}^{0}\mathrm{d}\tau\int_{0}^{\infty}\mathrm{d}\tau' \exp[i\omega_0(2s-\tau-\tau')] \\ & \quad \exp(-is\Delta E/\hbar)[\sum_{\delta\delta'\delta''\delta'''} e_{\delta}^{k'\alpha'} e_{\delta'}^{k\alpha} e_{\delta''}^{k'\alpha'*} e_{\delta'''}^{k\alpha*} M_{\delta\delta'\delta''\delta'''}(s,\tau,\tau',\beta)] \end{aligned} \quad (2.10)$$

where

$$\begin{aligned} M_{\delta\delta'\delta''\delta'''}(s,\tau,\tau',\beta) = {} & [F_{\delta\delta'\delta''\delta'''}(s,\tau,\tau',\beta) + \\ & G_{\delta\delta'\delta''\delta'''}(s,\tau,\tau',\beta)] \end{aligned} \quad (2.11)$$

$$\begin{aligned} F_{\delta\delta'\delta''\delta'''}(s,\tau,\tau',\beta) = {} & \exp[-(\Delta^2/2)s^2] \\ & \exp[-(\Delta^2/2)(s-\tau-\tau')^2](Q_{\delta\delta'\delta'''\delta''} + Q_{\delta'\delta\delta''\delta'''}) \end{aligned} \quad (2.12)$$

and

$$\begin{aligned} G_{\delta\delta'\delta''\delta'''}(s,\tau,\tau',\beta) = {} & \exp[-(\Delta^2/2)(s-\tau)^2] \\ & \exp[-(\Delta^2/2)(s-\tau')^2](Q_{\delta\delta'\delta''\delta'''} + Q_{\delta'\delta\delta''\delta'''}) \end{aligned} \quad (2.13)$$

Because of the exponential decay factors in eqs 2.12 and 2.13, the integral in eq 2.10 is convergent.

C. Averaging Over the Molecular Orientations. If a molecule is fixed in space, as would be the case, for example, in a crystal, the incident direction of light is fixed relative to the orientation of the molecule. The absorption spectrum is determined by one term in eq 2.10 supplemented with some rotational state which specifies the molecule's orientation. In the gas phase, molecules are freely rotating in space relative to the laboratory coordinate system, and this free rotation must be accounted for.

For elliptically polarized light incident in the *x* direction, the polarization vector is written as

$$\vec{e} = b_1\vec{e}^{(+)} + b_2\vec{e}^{(-)}, \quad E_y = b_1\cos(\omega t - \vec{k}\cdot\vec{r} + \alpha), \quad E_z = b_2\sin(\omega t - \vec{k}\cdot\vec{r} + \alpha)$$

b_1 and b_2 are two real numbers; E_y and E_z are the electric field components along the *y* and *z* axes. The two elliptical polarization vectors $\vec{e}^{(+)}$ and $\vec{e}^{(-)}$can be expressed in terms of the linear polarization vectors $\vec{e}^{(\xi)}$and $\vec{e}^{(\eta)}$as

$$\vec{e}^{(+)} = \frac{-i}{\sqrt{2}}(\vec{e}^{(\xi)} + i\vec{e}^{(\eta)}), \quad \vec{e}^{(-)} = \frac{-i}{\sqrt{2}}(\vec{e}^{(\xi)} - i\vec{e}^{(\eta)})$$

Because the orientation of the molecule in the final state is not detected and the molecule in the initial state is freely rotating, one must sum over all the orientations in the final state and average over the orientations in the initial state.[25] This is effected by summation over the rotational quantum number of the final states and averaging over the rotational quantum number of the initial states, similar to the famous Placzek treatment for scattering.[26] The square bracket in eq 2.10 is changed into

$$\begin{aligned} [] = {} & A^0|\vec{e}\cdot\vec{e}'|^2 + \frac{1}{10}A^s\left(\left|\vec{e}'\cdot\vec{e}*\right|^2 + 1 - \frac{2}{3}\left|\vec{e}\cdot\vec{e}'\right|^2\right) + \\ & \frac{1}{6}A^a(|\vec{e}'\cdot\vec{e}*|^2 - 1) \end{aligned} \quad (2.14)$$

where

$$A^0 = \frac{1}{9}\sum_{\alpha\alpha'} M_{\alpha\alpha\alpha'\alpha'}(s,\tau,\tau',\beta) \quad (2.15)$$

$$A^s = \frac{1}{2}\sum_{\alpha\alpha'}(M_{\alpha\alpha'\alpha'\alpha} + M_{\alpha\alpha'\alpha\alpha'}) - \frac{1}{3}M_{\alpha\alpha\alpha'\alpha'} \quad (2.16)$$

$$A^a = \frac{1}{2}\sum_{\alpha\alpha'}(M_{\alpha\alpha'\alpha'\alpha} - M_{\alpha\alpha'\alpha\alpha'})$$

For unpolarized light, the square bracket in eq 2.10 is

$$[] = \frac{1}{9}(3A^0 + A^s - A^a)$$

for elliptically polarized light, the square bracket in eq 2.10 is

$$\begin{aligned} [] = {} & A^0(2b_1b_2)^2 + \frac{1}{10}A^s\left[(b_1^2 + b_2^2)^2 + 1 - \frac{2}{3}(2b_1b_2)^2\right] + \\ & \frac{1}{6}A^a[(b_1^2 + b_2^2)^2 - 1] \end{aligned}$$

and for linearly polarized light, the square bracket in eq 2.10 is (1/5)A^s.

D. The Average Energy in the Electronically Excited State after TPA. The average vibrational energy E_{v}^{e} in the electronically excited state after absorbing two photons with frequency (ω, ω') is

$$E_{\mathrm{v}}^{e}(\omega, \omega') = \frac{\sum_{j} E_{ej}\left[\sum_{i} \frac{|c_{ji}^{(2)}|^2}{tII'} p_i\right]}{\sum_{j}\left[\sum_{i} \frac{|c_{ji}^{(2)}|^2}{tII'} p_i\right]} \tag{2.17}$$

The expression in square brackets in the numerator is proportional to the probability of reaching the final state j from the initial state i. As shown in Appendix B, using a similar procedure as in subsection II.B, and following the derivation of the expression for the average energy in the single-photon excitation,[15,16] one finds that after averaging over a Gaussian incident pulse the average energy in the excited state is given by the expression

$$\begin{aligned} E_{\mathrm{v}}^{e}(\omega_0, \Delta, \beta) = 2\hbar\omega_0 - \Delta E - \frac{\partial \ln g(\omega_0, \Delta, \beta)}{\partial \beta} + \langle E_g \rangle + \\ \frac{i\hbar\Delta^2}{g(\omega_0, \Delta, \beta)} \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}s \int_{-\infty}^{0} \mathrm{d}\tau \int_{0}^{\infty} \mathrm{d}\tau' \\ \exp[i\omega_0(2s - \tau - \tau')] \exp(-is\Delta E/\hbar)(2s - \tau - \tau') \\ [\sum_{\delta\delta'\delta''\delta'''} e_{\delta}^{k'\alpha'} e_{\delta'}^{k\alpha} e_{\delta''}^{k'\alpha'*} e_{\delta'''}^{k\alpha*} M_{\delta\delta'\delta''\delta'''}(s, \tau, \tau', \beta)] \end{aligned} \tag{2.18}$$

where the last term on the right-hand side results from the Gaussian pulse shape. It vanishes in the limit of a continuous wave laser for which $\Delta = 0$. We stress that the use of a Gaussian pulse shape is only for numerical simplicity. It is straightforward to derive a similar epxression for an arbitrary pulse shape.

III. Harmonic Theory of TPA for Benzene

For benzene, the static transition moments $\mu_{\alpha'''0}^{\mathrm{ge}}$ and $\mu_{\alpha'0}^{\mathrm{gg}}$ equal zero for all 30 modes. Only a few coefficients $\mu_{\alpha'''j}^{\mathrm{ge}}$ ($\mu_{\alpha'j}^{\mathrm{gg}}$) of the vibration-induced moment $\sum_{j=1}^{M} \mu_{\alpha'''j}^{\mathrm{ge}} q_j$ ($\sum_{j=1}^{M} \mu_{\alpha'j}^{\mathrm{gg}} q_j$) are nonzero. The Cartesian components of the coefficients $\mu_{\alpha'''j}^{\mathrm{ge}}$ of the transition moment[27] and the coefficients $\mu_{\alpha'j}^{\mathrm{gg}}$ of the induced dipole moment,[28] which are needed for determining the TPA spectrum, are not available from the literature; only their absolute values are known. We therefore neglected any differences between different components and equated any $\mu_{\delta j}^{\mathrm{ge}}$($\mu_{\delta j}^{\mathrm{gg}}$; $\delta = x, y, z$) with its absolute value d_j^{ge} (d_j^{gg}) although we are aware that for a planar molecule such as benzene this is not a really good approximation.

The correlation function in eq A.29 (see Appendix A) is a product of many sine or cosine functions and is highly oscillatory. To carry out the integral in eq 2.10 with appropriate precision, we used the fast Fourier transform (FFT) method. The highest frequency in benzene is $\nu_{\max} = 3187$ cm^{-1}; the largest time interval which may be used that can still reflect the time variation of the four-point correlation function will thus be $\mathrm{d}t \approx (1/c\nu_{\max}) \approx 1 \times 10^{-14}$ sec. For a frequency resolution of $\mathrm{d}\omega = 20$ cm^{-1} in the spectrum, the number of time steps N_t's has to be larger than 10^3 to satisfy the FFT requirement $\mathrm{d}t\,\mathrm{d}\omega = (2\pi/N_t)$, where $N_t = 2^n$ with n a nonnegative integer. This implies that we must choose $n \geq 10$; in all computations, we used $n = 10$. A stringent check for the convergence of the numerics is that indeed the computed TPA spectrum is positive. When using a grid spacing which is too large, one finds negative absorption probabilities.

TABLE 1: Input Data for Benzene

mode	ν_g^a(cm^{-1})	ν_e^a(cm^{-1})	q_0	$d^{eg\ a}$	$d^{gg\ b}$(D/Å)
a_{1g}	3187	3204	0.415	0.000	0.000
a_{1g}	979	902	1.710	0.000	0.000
a_{2g}	1353	1323	0.000	0.000	0.000
e_{2g}	3155	3174	0.000	0.065	0.000
e_{2g}	1611	1560	0.000	0.257	0.000
e_{2g}	1173	1151	0.000	0.088	0.000
e_{2g}	592	529	0.000	0.217	0.000
b_{1u}	3145	3165	0.000	0.000	0.000
b_{1u}	998	963	0.000	0.000	0.000
b_{2u}	1342	1739	0.000	0.000	0.000
b_{2u}	1163	1149	0.000	0.000	0.000
e_{1u}	3173	3189	0.000	0.000	−0.780
e_{1u}	1479	1400	0.000	0.000	−0.320
e_{1u}	1023	916	0.000	0.000	−0.510
b_{2g}	916	641	0.000	0.000	0.000
b_{2g}	650	434	0.000	0.000	0.000
e_{1g}	781	548	0.000	0.000	0.000
a_{2u}	631	480	0.000	0.000	−1.430
e_{2u}	891	628	0.000	0.000	0.000
e_{2u}	383	262	0.000	0.000	0.000

[a] ν_{gj}, ν_{ej}, q_{0j}, and d_j^{eg} are taken from ref 18; q_{0j} is dimensionless, given in units of $\sqrt{(\hbar/m_p\omega_j^e)}$; d_j^{eg} is dimensionless. [b] d_j^{gg} is adapted from ref 27.

For benzene, $\omega_{00} = 38\,086$ cm^{-1}.[29] Apart from the ambiguity in the choice of the Cartesian components of the induced transition moment, all other input is known from either experiment or ab initio computations, as detailed in ref 18. The input parameters are listed in Table 1: they are the vibrational frequencies $\tilde{\nu}_j^{\mathrm{g}}$ and $\tilde{\nu}_j^{\mathrm{e}}$ in the electronic ground and excited states, respectively, the displacement q_{0j} of the equilibrium point of each normal mode in the excited state, the coefficient d_j^{eg} of the induced transition moment between the electronic ground state and excited state, and the coefficient d_j^{gg} of the induced average dipole moment in the ground state.

The TPA spectrum as calculated from eqs 2.10 and A.29, with $\omega = \omega'$, is shown in Figure 1 for two different temperatures. The qualitative features are consistent with the experimentally measured TPA spectra in the gas[29] and crystalline phases.[30,31] Comparing the theoretical TPA spectrum with the single-photon spectrum,[18] we note that the TPA spectrum is much sparser, in agreement with the experimental observations. In the calculated spectrum, some experimental absorption lines do not appear because of the use of the harmonic ground electronic state Hamiltonian also for the intermediate states. The hot bands[32] do appear and are presented more clearly in Figure 2 where the theoretical spectrum is displayed on a logarithmic scale. Differences between 300 and 400 K are minor; the higher temperature broadens the spectrum somewhat and increases the amplitude of the hot bands.

The average energy in the excited state is displayed in Figure 3. The dotted line in the figure denotes what the average vibrational energy in the excited state would be if the nascent temperature were identical to the ground-state vibrational temperature. It is evident that although there is a bit of cooling in the hot band region of the spectrum at $37\,530$ cm^{-1} (corresponding to the transition $14_1^0 16_1^1\, 1_0^1$,[32] which is to the red of the ω_{00} transition frequency), the overall cooling effect is much smaller than that found in the single-photon absorption of benzene. As also found for single-photon absorption, cooling does become more pronounced as the temperature is increased.

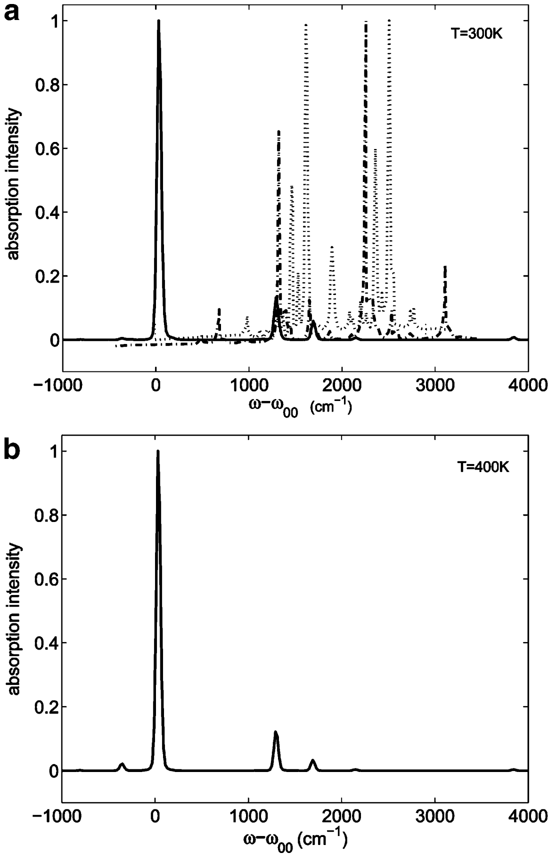

Figure 1. The thermal TPA absorption spectrum. In panels a and b, the solid line is the result computed from the harmonic theory of this paper (with frequency interval $d\omega = 20$ cm^{-1} and excitation pulse width $\Delta = 20$ cm^{-1}). Other data are taken from Table 1. The dashed−dotted line is the gas-phase experimental TPA spectrum taken from ref 29; the dotted line is the crystalline experimental TPA spectrum of refs 30−31. The calculated absorption spectrum $g(\omega_0, \Delta, \beta)$ is normalized to unity by its maximum value in the entire range of frequency. Panels a and b are for ground-state temperatures $T = 300$ and 400 K, respectively.

We also note that the average energy is approximately a linear function of the excitation frequency; the slope is roughly 2 as expected for TPA with photons of equal frequency.

IV. Summary and Discussion

The absorption spectrum and the average energy in the excited state for the case of two-photon excitation are expressed as a special Fourier integral (eqs 2.10 and 2.18) of the four-point dipole correlation function. For harmonic potential energy surfaces, the correlation function can be obtained analytically as in eq A.29. Introducing generating functions as in Appendix eqs A.2 and A.3 saves some heavy labor as compared with a direct calculation of the correlation function.

Applying this formulation to benzene, we find a thermal two-photon absorption spectrum which agrees roughly with experiment. There are two major sources of error in our computation: (1) The intermediate states, which are the highly excited vibrational states in the electronic ground state, are not accurately accounted for with a harmonic potential energy surface. (2) The relative absorption strength is much more sensitive to the orientation of the molecule and the polarization of the incident radiation. Although we worked out the formalism in subsection II.C, we had to resort to a more approximate calculation because of the lack of information on the Cartesian components of the coefficients of the induced transition moments.

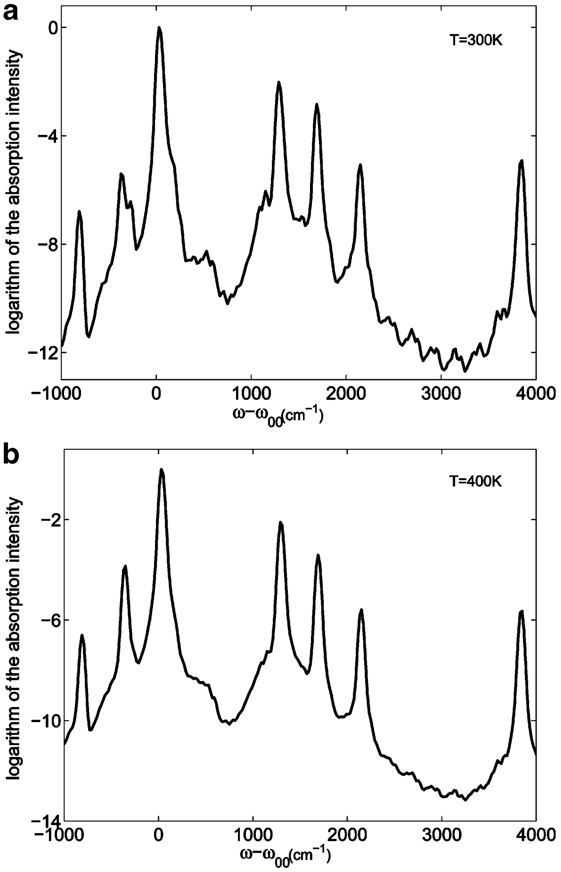

Figure 2. Natural logarithm of the TPA absorption intensity at two different temperatures. The hot band absorption is clearly displayed. Other details are as in Figure 1.

Even with these limitations, the results presented here are a step forward. Computation of the triple Fourier transform needed for the spectrum is not trivial and would not have been possible without the significant advances of present-day computers in terms of storage space and processor speed. Still, we had to resort to a frequency resolution of 20 cm^{-1}. The computation of a single spectrum took a few weeks on a multiprocessor PC farm. We are not aware of any previous attempt to compute the TPA spectrum for a molecule with the size of benzene.

A second result of this study is the computation of the nascent average vibrational energy in the excited state following TPA. Interestingly, we found that vibrational cooling is much less important in TPA than in the single-photon absorption experiment. The cooling effect for TPA is determined by the transition moments μ^{ge} and μ^{gg} for each mode and the selection rule (i.e., the symmetry of a specific molecule). Only states whose energy is close to the vibrational ground state of the ground electronic state are well-populated; therefore, many strong peaks in the vicinity of the 0−0 transition are needed for strong cooling. For benzene, because of the selection rules, the TPA peaks are too few and weak near the 0−0 transition frequency. This is the probable reason for the lack of a cooling effect. This does not preclude the possibility that for larger more structured molecules the cooling effect in TPA would become more important.

The present study was limited to the use of two photons of equal frequency. It would be of interest to probe the full two-dimensional TPA absorption spectrum as a function of different photon frequencies. The formalism presented in this paper makes this possible, albeit with a substantial investment in computational resources. Such a study would also shed more light on

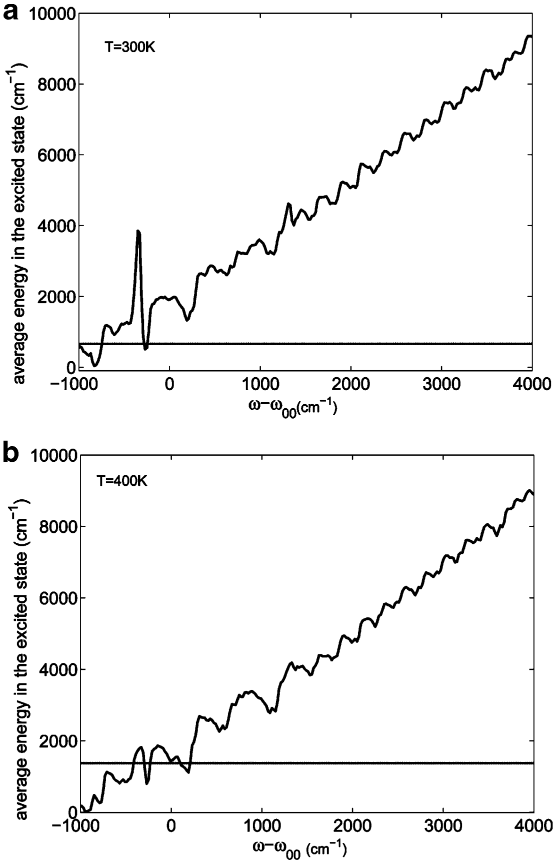

Figure 3. The average energy in the excited state following TPA excitation at two different temperatures. The dotted line shows the value of the excited-state average energy at the ground-state temperature. Note that only the hot band absorption displays cooling. Other details are as in Figure 1.

the possibility of controlling the nascent vibrational energy in the excited electronic state using TPA.

As is well-known, the theories for the Raman scattering spectrum and the third- or higher-order susceptibility have a structure which is similar to that of eqs 2.3 and 2.4. By making use of eq 2.7, these quantities can be changed into a multidimensional Fourier transform of a multidipole correlation function. Assuming a harmonic Hamiltonian would then allow evaluation by following a procedure similar to the one detailed in the Appendix.

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Appendix A: An Analytic Expression for the Four-Point Dipole Correlation Function

The four-point dipole correlation function is defined as

$$Q(s, \tau, \tau', \beta) = Tr\{\mu^{\mathrm{ge}}_{\alpha'''} \exp(-isH_{\mathrm{e}}/\hbar)\mu^{\mathrm{eg}}_{\alpha} \exp(i\tau H_{\mathrm{g}}/\hbar)\mu^{\mathrm{gg}}_{\alpha'} \exp[(is - i\tau - i\tau')H_{\mathrm{g}}/\hbar - \beta H_{\mathrm{g}}]\mu^{\mathrm{gg}}_{\alpha''} \exp(iH_{\mathrm{g}}\tau'\hbar)\} \quad (\mathrm{A.1})$$

It is possible to calculate it directly for harmonic Hamiltonians; however, this would be very lengthy. A more elegant route is by using a generating function G for the correlation function

$$G(s, \tau, \tau', \beta) = Tr\{\exp(\phi_1\mu^{\mathrm{ge}}_{\alpha'''}) \exp(-isH_{\mathrm{e}}/\hbar) \exp(\phi_2\mu^{\mathrm{eg}}_{\alpha}) \exp(i\tau H_{\mathrm{g}}/\hbar) \exp(\phi_3\mu^{\mathrm{gg}}_{\alpha'}) \exp[(is - i\tau - i\tau')H_{\mathrm{g}}/\hbar - \beta H_{\mathrm{g}}] \exp(\phi_4\mu^{\mathrm{gg}}_{\alpha''}) \exp(iH_{\mathrm{g}}\tau'\hbar)\} \quad (\mathrm{A.2})$$

where ϕ_1, ϕ_2, ϕ_3, and ϕ_4 are four real parameters. Then, the correlation function Q can be deduced from G by noting that

$$Q = \frac{\partial}{\partial\phi_1}\frac{\partial}{\partial\phi_2}\frac{\partial}{\partial\phi_3}\frac{\partial}{\partial\phi_4}G|_{\phi_1=\phi_2=\phi_3=\phi_4=0} \quad (\mathrm{A.3})$$

Before deriving the expression for G, we introduce the Herzberg−Teller approximation for the dipole moment operators in eq A.1. For the transition moment between the intermediate state and the excited state, $\mu^{\mathrm{ge}}_{\alpha'''}$ and $\mu^{\mathrm{eg}}_{\alpha}$,[33] we use

$$\mu^{\mathrm{ge}}_{\alpha'''} = \mu^{\mathrm{ge}}_{\alpha'''0} + \sum_{j=1}^{M}\mu^{\mathrm{ge}}_{\alpha'''j}q_j, \quad \mu^{\mathrm{eg}}_{\alpha} = \mu^{\mathrm{eg}}_{\alpha 0} + \sum_{j=1}^{M}\mu^{\mathrm{eg}}_{\alpha j}q_j, \quad \alpha''', \alpha = x, y, z \quad (\mathrm{A.4})$$

The constant term in each expression is the static value of the transition moment; the second term is the contribution induced by the various vibrational modes in both the excited and ground electronic states.[27]

Because the intermediate states are in the electronic ground state, the transition moment μ^{gg} between the intermediate state and the ground state is the average dipole operator in the electronic ground state:

$$\mu^{\mathrm{gg}}_{\alpha'} = \mu^{\mathrm{gg}}_{\alpha'0} + \sum_{j=1}^{M}\mu^{\mathrm{gg}}_{\alpha'j}q_j, \quad \mu^{\mathrm{gg}}_{\alpha''} = \mu^{\mathrm{gg}}_{\alpha''0} + \sum_{j=1}^{M}\mu^{\mathrm{gg}}_{\alpha''j}q_j, \quad \alpha',\alpha'' = x, y, z \quad (\mathrm{A.5})$$

The constant term is the static value of the dipole; the additional terms are the vibrationally induced dipole moments.

The harmonic Hamiltonians and the Herzberg−Teller approximation are separable (see eqs 2.1, A.4, and A.5), so that the generating function G may be factored into a product of mode-generating functions:

$$G = \exp(\phi_1\mu^{\mathrm{ge}}_{\alpha'''0} + \phi\mu^{\mathrm{eg}}_{2\alpha 0} + \phi_3\mu^{\mathrm{gg}}_{\alpha'0} + \phi_4\mu^{\mathrm{gg}}_{\alpha''0})\prod_{j=1}^{M}G_j \quad (\mathrm{A.6})$$

where the single mode-generating functions take the form

$$G_j = Tr[\exp(\phi_1\mu^{\mathrm{ge}}_{\alpha'''j}q_j) \exp(-isH^j_{\mathrm{e}}/\hbar) \exp(\phi_2\mu^{\mathrm{eg}}_{\alpha j}q_j) \exp(i\tau H^j_{\mathrm{g}}/\hbar) \exp(\phi_3\mu^{\mathrm{gg}}_{\alpha'j}q_j) \exp[(is - i\tau - i\tau')H^j_{\mathrm{g}}/\hbar - \beta H^j_{\mathrm{g}}] \exp(\phi_4\mu^{\mathrm{gg}}_{\alpha''j}q_j) \exp(iH^j_{\mathrm{g}}\tau'\hbar)] \quad (\mathrm{A.7})$$

In the coordinate representation G_j becomes a 4-fold Gaussian integral about coordinates by applying the well-known expression for the harmonic oscillator propagator for each evolution operator whether with real or complex time. The Gaussian integrals are readily carried out. After substituting G_j into eq A.6 and some rearrangement, the generating function G can be written as

$$G = \exp\{\phi_1^2\psi_1 + \phi_2^2\psi_2 + \phi_3^2\psi_3 + \phi_4^2\psi_4 + 2\phi_1\phi_2\psi_5 + 2\phi_1\phi_3\psi_6 + 2\phi_1\phi_4\psi_7 + 2\phi_2\phi_3\psi_8 + 2\phi_2\phi_4\psi_9 + 2\phi_3\phi_4\psi_{10} + 2\phi_1\psi_{11} + 2\phi_2\psi_{12} + 2\phi_3\psi_{13} + 2\phi_4\psi_{14}\}\prod_{j=1}^{M}\chi_{j0}(s,\beta) \quad \text{(A.8)}$$

where

$$\chi_{j0}(s,\beta) = \left[\frac{a_{\mathrm{g}j}a_{\mathrm{e}j}}{(b_{\mathrm{g}j} + b_{\mathrm{e}j})^2 - (a_{\mathrm{g}j} + a_{\mathrm{e}j})^2}\right]^{1/2} \exp\left\{\frac{imq_{0j}^2}{\hbar}\frac{(b_{\mathrm{g}j} - a_{\mathrm{g}j})(b_{\mathrm{e}j} - a_{\mathrm{e}j})}{b_{\mathrm{e}j} - a_{\mathrm{e}j} + b_{\mathrm{g}j} - a_{\mathrm{g}j}}\right\} \quad \text{(A.9)}$$

is just the dipole correlation function of the jth mode needed for computation of the single-photon absorption within the Condon approximation.[16] It is interesting to note that

$$G|_{\phi_1=\phi_2=\phi_3=\phi_4=0} = Tr\, \exp(-isH_{\mathrm{e}}/\hbar)\exp(isH_{\mathrm{g}}/\hbar - \beta H_{\mathrm{g}}) = \prod_{j=1}^{M}\chi_{j0}(s,\beta) \quad \text{(A.10)}$$

The notations appearing in eq A.9 are the same as in ref 18

$$a_{\mathrm{g}j} = \frac{\omega_j^{\mathrm{g}}}{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}, \quad b_{\mathrm{g}j} = \frac{\omega_j^{\mathrm{g}}\cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}, \quad \tau_{\mathrm{c}} = -s - i\beta\hbar \quad \text{(A.11)}$$

$$a_{\mathrm{e}j} = \frac{\omega_j^{\mathrm{e}}}{\sin(\omega_j^{\mathrm{e}}s)}, \quad b_{\mathrm{e}j} = \frac{\omega_j^{\mathrm{e}}\cos(\omega_j^{\mathrm{e}}s)}{\sin(\omega_j^{\mathrm{e}}s)} \quad \text{(A.12)}$$

The 14 coefficients $\psi_i (i = 1, ..., 14)$ in the generating function eq A.8 are

$$\psi_1 = \sum_{j=1}^{N}\left(\frac{\mu_{\alpha'''j}^{\mathrm{ge}}}{2}\right)^2 \frac{2\hbar}{im}\frac{(b_{\mathrm{g}j} + b_{\mathrm{e}j})}{(a_{\mathrm{g}j} + a_{\mathrm{e}j})^2 - (b_{\mathrm{g}j} + b_{\mathrm{e}j})^2} \quad \text{(A.13)}$$

$$\psi_2 = \sum_{j=1}^{N}\left(\frac{\mu_{\alpha j}^{\mathrm{eg}}}{2}\right)^2 \frac{2\hbar}{im}\frac{(b_{\mathrm{g}j} + b_{\mathrm{e}g})}{(a_{\mathrm{g}j} + a_{\mathrm{e}g})^2 - (b_{\mathrm{g}j} + b_{\mathrm{e}j})^2} \quad \text{(A.14)}$$

$$\psi_3 = \sum_{j=1}^{N}\frac{\left(\frac{\mu_{\alpha'j}^{\mathrm{gg}}}{2}\right)^2 2\hbar}{im(a_{\mathrm{g}j}^{\tau})^2}\left[\frac{(b_{\mathrm{g}j} + b_{\mathrm{e}j})[(b_{\mathrm{g}j} + b_{\mathrm{g}j}^{\tau})^2 + a_{\mathrm{g}j}{}^2] - 2(a_{\mathrm{g}j} + a_{\mathrm{e}j})a_{\mathrm{g}j}(b_{\mathrm{g}j} + b_{\mathrm{g}j}^{\tau})}{(a_{\mathrm{g}j} + a_{\mathrm{e}j})^2 - (b_{\mathrm{g}j} + b_{\mathrm{e}j})^2} + (b_{\mathrm{g}j} + b_{\mathrm{g}j}^{\tau})\right] \quad \text{(A.15)}$$

where

$$a_{\mathrm{g}j}^{\tau} = \frac{\omega_j^{\mathrm{g}}}{\sin(\omega_j^{\mathrm{g}}\tau)}, \quad b_{\mathrm{g}j}^{\tau} = \frac{\omega_j^{\mathrm{g}}\cos(\omega_j^{\mathrm{g}}\tau)}{\sin(\omega_j^{\mathrm{g}}\tau)} \quad \text{(A.16)}$$

$$\psi_4 = \sum_{j=1}^{N}\frac{\left(\frac{\mu_{\alpha''j}^{\mathrm{gg}}}{2}\right)^2 2\hbar}{im(a_{\mathrm{g}j}^{\tau'})^2}\left[\frac{(b_{\mathrm{g}j} + b_{\mathrm{e}j})[(b_{\mathrm{g}j} + b_{\mathrm{g}j}^{\tau'})^2 + a_{\mathrm{g}j}^2] - 2a_{\mathrm{g}j}(a_{\mathrm{g}j} + a_{\mathrm{e}j})(b_{\mathrm{g}j} + b_{\mathrm{g}j}^{\tau'})}{(a_{\mathrm{g}j} + a_{\mathrm{e}j})^2 - (b_{\mathrm{g}j} + b_{\mathrm{e}j})^2} + (b_{\mathrm{g}j} + b_{\mathrm{g}j}^{\tau'})\right] \quad \text{(A.17)}$$

where

$$a_{\mathrm{g}}^{\tau'} = \frac{\omega_j^{\mathrm{g}}}{\sin(\omega_j^{\mathrm{g}}\tau')}, \quad b_{\mathrm{g}}^{\tau'} = \frac{\omega_j^{\mathrm{g}}\cos(\omega_j^{\mathrm{g}}\tau')}{\sin(\omega_j^{\mathrm{g}}\tau')} \tag{A.18}$$

$$\psi_5 = \sum_{j=1}^{N} \frac{\mu_{\alpha'''j}^{\mathrm{ge}}}{2}\frac{\mu_{\alpha j}^{\mathrm{eg}}}{2}\frac{2\hbar}{im}\frac{\dfrac{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}{\omega_j^{\mathrm{g}}} + \dfrac{\sin(\omega_j^{\mathrm{e}}s)}{\omega_j^{\mathrm{e}}}}{\left(\dfrac{\omega_j^{\mathrm{g}}}{\omega_j^{\mathrm{e}}} + \dfrac{\omega_j^{\mathrm{e}}}{\omega_j^{\mathrm{g}}}\right)\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{e}}s) + 2[1 - \cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\cos(\omega_j^{\mathrm{e}}s)]} \tag{A.19}$$

$$\psi_6 = \sum_{j=1}^{N} \frac{\mu_{\alpha'''j}^{\mathrm{ge}}}{2}\frac{\mu_{\alpha'j}^{\mathrm{gg}}}{2}\frac{2\hbar}{im}\frac{\left(\dfrac{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}{\omega_j^{\mathrm{g}}} + \dfrac{\sin(\omega_j^{\mathrm{e}}s)}{\omega_j^{\mathrm{e}}}\right)\cos(\omega_j^{\mathrm{g}}\tau) + \dfrac{\sin(\omega_j^{\mathrm{g}}\tau)}{\omega_j^{\mathrm{g}}}[\cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}}) - \cos(\omega_j^{\mathrm{e}}s)]}{\left(\dfrac{\omega_j^{\mathrm{g}}}{\omega_j^{\mathrm{e}}} + \dfrac{\omega_j^{\mathrm{e}}}{\omega_j^{\mathrm{g}}}\right)\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{e}}s) + 2[1 - \cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\cos(\omega_j^{\mathrm{e}}s)]} \tag{A.20}$$

$$\begin{aligned}\psi_7 = \sum_{j=1}^{N} \frac{\mu_{\alpha'''j}^{\mathrm{ge}}}{2}\frac{\mu_{\alpha''j}^{\mathrm{gg}}}{2}\frac{2\hbar}{im}\Bigg\{&\frac{(-)\left(\dfrac{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}{\omega_j^{\mathrm{g}}} + \dfrac{\sin(\omega_j^{\mathrm{e}}s)}{\omega_j^{\mathrm{e}}}\right)\dfrac{\sin(\omega_j^{\mathrm{g}}\tau')}{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}}{\left(\dfrac{\omega_j^{\mathrm{g}}}{\omega_j^{\mathrm{e}}} + \dfrac{\omega_j^{\mathrm{e}}}{\omega_j^{\mathrm{g}}}\right)\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{e}s) + 2[1 - \cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\cos(\omega_j^{\mathrm{e}}s)]} + {}\\ &\frac{\left(\dfrac{\cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{e}}s)}{\omega_j^{\mathrm{e}}} + \dfrac{\cos(\omega_j^{\mathrm{e}}s)\sin(\omega_j^{g}\tau_{\mathrm{c}})}{\omega_j^{\mathrm{g}}}\right)\left[\dfrac{\cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{g}}\tau')}{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})} + \cos(\omega_j^{\mathrm{g}}\tau')\right]}{\left(\dfrac{\omega_j^{\mathrm{g}}}{\omega_j^{\mathrm{e}}} + \dfrac{\omega_j^{\mathrm{e}}}{\omega_j^{\mathrm{g}}}\right)\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{e}}s) + 2[1 - \cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\cos(\omega_j^{\mathrm{e}}s)]}\Bigg\}\end{aligned} \tag{A.21}$$

$$\begin{aligned}\psi_8 = \sum_{j=1}^{N} \frac{\mu_{\alpha'j}^{\mathrm{gg}}}{2}\frac{\mu_{\alpha j}^{\mathrm{eg}}}{2}\frac{2\hbar}{im}\Bigg\{&\frac{(-)\left(\dfrac{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}{\omega_j^{g}} + \dfrac{\sin(\omega_j^{\mathrm{e}}s)}{\omega_j^{\mathrm{e}}}\right)\dfrac{\sin(\omega_j^{\mathrm{g}}\tau)}{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}}{\left(\dfrac{\omega_j^{\mathrm{g}}}{\omega_j^{\mathrm{e}}} + \dfrac{\omega_j^{\mathrm{e}}}{\omega_j^{\mathrm{g}}}\right)\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{e}}s) + 2[1 - \cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\cos(\omega_j^{\mathrm{e}}s)]} + {}\\ &\frac{\left(\dfrac{\cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{e}}s)}{\omega_j^{\mathrm{e}}} + \dfrac{\cos(\omega_j^{e}s)\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}{\omega_j^{\mathrm{g}}}\right)\left[\dfrac{\cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{g}}\tau)}{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})} + \cos(\omega_j^{\mathrm{g}}\tau)\right]}{\left(\dfrac{\omega_j^{\mathrm{g}}}{\omega_j^{\mathrm{e}}} + \dfrac{\omega_j^{\mathrm{e}}}{\omega_j^{\mathrm{g}}}\right)\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{e}}s) + 2[1 - \cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\cos(\omega_j^{\mathrm{e}}s)]}\Bigg\},\end{aligned} \tag{A.22}$$

$$\psi_9 = \sum_{j=1}^{N} \frac{\mu_{\alpha''j}^{\mathrm{gg}}}{2}\frac{\mu_{\alpha j}^{\mathrm{eg}}}{2}\frac{2\hbar}{im}\frac{\left(\dfrac{\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})}{\omega_j^{\mathrm{g}}} + \dfrac{\sin(\omega_j^{\mathrm{e}}s)}{\omega_j^{\mathrm{e}}}\right)\cos(\omega_j^{\mathrm{g}}\tau') + \dfrac{\sin(\omega_j^{\mathrm{g}}\tau')}{\omega_j^{\mathrm{g}}}[\cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}}) - \cos(\omega_j^{\mathrm{e}}s)]}{\left(\dfrac{\omega_j^{\mathrm{g}}}{\omega_j^{\mathrm{e}}} + \dfrac{\omega_j^{\mathrm{e}}}{\omega_j^{\mathrm{g}}}\right)\sin(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\sin(\omega_j^{\mathrm{e}}s) + 2[1 - \cos(\omega_j^{\mathrm{g}}\tau_{\mathrm{c}})\cos(\omega_j^{\mathrm{e}}s)]} \tag{A.23}$$

$$\begin{aligned}\psi_{10} = {} & \sum_{j=1}^{N} \frac{\mu^{\mathrm{gg}}_{\alpha''j}}{2}\frac{\mu^{\mathrm{gg}}_{\alpha'j}}{2}\frac{2\hbar}{im}\frac{\left(\dfrac{\cos(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})\sin(\omega^{\mathrm{e}}_j s)}{\omega^{\mathrm{e}}_j}+\dfrac{\cos(\omega^{\mathrm{e}}_j s)\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}{\omega^{\mathrm{g}}_j}\right)}{\left(\dfrac{\omega^{\mathrm{g}}_j}{\omega^{\mathrm{e}}_j}+\dfrac{\omega^{\mathrm{e}}_j}{\omega^{\mathrm{g}}_j}\right)\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})\sin(\omega^{\mathrm{e}}_j s)+2[1-\cos(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})\cos(\omega^{\mathrm{e}}_j s)]}\times \\
& \left\{\frac{[\omega^{\mathrm{g}}_j\sin(\omega^{\mathrm{e}}_j s)+\omega^{\mathrm{e}}_j\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})]}{\omega^{\mathrm{g}}_j\cos(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})\sin(\omega^{\mathrm{e}}_j s)+\omega^{\mathrm{e}}_j\cos(\omega^{\mathrm{e}}_j s)\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\times\left[\frac{\cos(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\sin(\omega^{\mathrm{g}}_j\tau')+\cos(\omega^{\mathrm{g}}_j\tau')\right]\left[\frac{\cos(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\sin(\omega^{\mathrm{g}}_j\tau)+\cos(\omega^{\mathrm{g}}_j\tau)\right]-\right. \\
& \left.\frac{\sin(\omega^{\mathrm{g}}_j\tau')}{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\left[\frac{\cos(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\sin(\omega^{\mathrm{g}}_j\tau)+\cos(\omega^{\mathrm{g}}_j\tau)\right]-\frac{\sin(\omega^{\mathrm{g}}_j\tau)}{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\left[\frac{\cos(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\sin(\omega^{\mathrm{g}}_j\tau')+\cos(\omega^{\mathrm{g}}_j\tau')\right]\right\}+ \\
& \sum_{j=1}^{N} \frac{\mu^{\mathrm{gg}}_{\alpha''j}}{2}\frac{\mu^{\mathrm{gg}}_{\alpha'j}}{2}\frac{2\hbar}{im}\left\{\frac{\left(\dfrac{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}{\omega^{\mathrm{g}}_j}+\dfrac{\sin(\omega^{\mathrm{e}}_j s)}{\omega^{\mathrm{e}}_j}\right)\left[\dfrac{\sin(\omega^{\mathrm{g}}_j\tau)}{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\dfrac{\sin(\omega^{\mathrm{g}}_j\tau')}{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\right]}{\left(\dfrac{\omega^{\mathrm{g}}_j}{\omega^{\mathrm{e}}_j}+\dfrac{\omega^{\mathrm{e}}_j}{\omega^{\mathrm{g}}_j}\right)\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})\sin(\omega^{\mathrm{e}}_j s)+2[1-\cos(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})\cos(\omega^{\mathrm{e}}_j s)]}-\frac{\sin(\omega^{\mathrm{g}}_j\tau)}{\omega^{\mathrm{g}}_j}\frac{\sin(\omega^{\mathrm{g}}_j\tau')}{\sin(\omega^{\mathrm{g}}_j\tau_{\mathrm{c}})}\right\}\end{aligned} \tag{A.24}$$

$$\psi_{11} = \frac{\mu^{\mathrm{ge}}_{\alpha'''0}}{2}+\sum_{j=1}^{N}\frac{\mu^{\mathrm{ge}}_{\alpha'''j}q_{0j}}{2}\frac{\sin\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)}{\sin\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)+\dfrac{\omega^{\mathrm{g}}_j}{\omega^{\mathrm{e}}_j}\tan\left(\dfrac{\omega^{\mathrm{g}}_j\tau_{\mathrm{c}}}{2}\right)\cos\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)} \tag{A.25}$$

$$\psi_{12} = \frac{\mu^{\mathrm{eg}}_{\alpha 0}}{2}+\sum_{j=1}^{N}\frac{\mu^{\mathrm{eg}}_{\alpha j}q_{0j}}{2}\frac{\sin\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)}{\sin\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)+\dfrac{\omega^{\mathrm{g}}_j}{\omega^{\mathrm{e}}_j}\tan\left(\dfrac{\omega^{\mathrm{g}}_j\tau_{\mathrm{c}}}{2}\right)\cos\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)} \tag{A.26}$$

$$\psi_{13} = \frac{\mu^{\mathrm{gg}}_{\alpha'0}}{2}+\sum_{j=1}^{N}\frac{\mu^{\mathrm{gg}}_{\alpha'j}q_{0j}}{2}\frac{\omega^{\mathrm{e}}_j\sin\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)\left[\cos(\omega^{\mathrm{g}}_j\tau)-\sin(\omega^{\mathrm{g}}_j\tau)\tan\left(\dfrac{\omega^{\mathrm{g}}_j\tau_{\mathrm{c}}}{2}\right)\right]}{\omega^{\mathrm{g}}_j\cos\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)\tan\left(\dfrac{\omega^{\mathrm{g}}_j\tau_{\mathrm{c}}}{2}\right)+\omega^{\mathrm{e}}_j\sin\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)} \tag{A.27}$$

$$\psi_{14} = \frac{\mu^{\mathrm{gg}}_{\alpha''0}}{2}+\sum_{j=1}^{N}\frac{\mu^{\mathrm{gg}}_{\alpha''j}q_{0j}}{2}\frac{\omega^{\mathrm{e}}_j\sin\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)\left[\cos(\omega^{\mathrm{g}}_j\tau')-\sin(\omega^{\mathrm{g}}_j\tau')\tan\left(\dfrac{\omega^{\mathrm{g}}_j\tau_{\mathrm{c}}}{2}\right)\right]}{\omega^{\mathrm{g}}_j\cos\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)\tan\left(\dfrac{\omega^{\mathrm{g}}_j\tau_{\mathrm{c}}}{2}\right)+\omega^{\mathrm{e}}_j\sin\left(\dfrac{\omega^{\mathrm{e}}_j s}{2}\right)} \tag{A.28}$$

These functions have some notable symmetries. The pairs of functions (ψ_3, ψ_4), (ψ_7, ψ_8), (ψ_6, ψ_9), and (ψ_{13}, ψ_{14}), which are functions of the time variables (s, τ, τ'), are symmetric with respect to exchanging τ' and τ. ψ_{10} is also symmetric with respect to exchanging the time variables τ and τ'.

The correlation function Q is now found from eq A.3 to be

$$\begin{aligned}Q(s,\tau,\tau',\beta) = {} & [(2\psi_5)(2\psi_{10})+(2\psi_5)(2\psi_{13})(2\psi_{14})+(2\psi_{10})(2\psi_{11})(2\psi_{12})+(2\psi_6)(2\psi_9)+(2\psi_6)(2\psi_{12})(2\psi_{14})+ \\
& (2\psi_9)(2\psi_{11})(2\psi_{13})+(2\psi_7)(2\psi_8)+(2\psi_7)(2\psi_{12})(2\psi_{13})+(2\psi_8)(2\psi_{11})(2\psi_{14})+(2\psi_{11})(2\psi_{12})(2\psi_{13})(2\psi_{14})]\chi_0(s,\beta)\end{aligned} \tag{A.29}$$

ψ_1, ψ_2, ψ_3, and ψ_4 do not appear in this final result.

Appendix B: An Expression for the Average Energy in the Excited Electronic State

In this Appendix, we detail the derivation of eq 2.18 for the average energy in the excited state. By definition, the average energy in the excited state is obtained by averaging the transition probability per unit of time ($|c_{BA}^{(2)}(t)|^2/tII'$) over all initial states but summing over all final states weighted by their energy as defined in eq 2.17. Following the same derivation as for the spectrum, we can write the numerator of eq 2.17 as

$$\sum_{\delta\delta'\delta''\delta'''} e_{\delta}^{k'\alpha'}\, e_{\delta'}^{k\alpha}\, e_{\delta''}^{k'\alpha'*}\, e_{\delta'''}^{k\alpha*}\, E_{\delta\delta'\delta''\delta'''}^{(2)}$$

where

$$E_{\delta\delta'\delta''\delta'''}^{(2)} = \sum_{BA} E_B \delta(\omega_{BA} - \omega - \omega')p_A \sum_{RR'} \left[\frac{\langle B_{\mathrm{v}}|\mu_{\delta}^{BR}|R_{\mathrm{v}}\rangle\langle R_{\mathrm{v}}|\mu_{\delta'}^{RA}|A_{\mathrm{v}}\rangle}{\omega_{RA} - \omega} + \frac{\langle B_{\mathrm{v}}|\mu_{\delta'}^{BR}|R_{\mathrm{v}}\rangle\langle R_{\mathrm{v}}|\mu_{\delta}^{RA}|A_{\mathrm{v}}\rangle}{\omega_{RA} - \omega'}\right] \times \left[\frac{\langle A_{\mathrm{v}}|\mu_{\delta'''}^{AR}|R'_{\mathrm{v}}\rangle\langle R'_{\mathrm{v}}|\mu_{\delta''}^{R'}|B_{\mathrm{v}}\rangle}{\omega_{R'A} - \omega} + \frac{\langle A_{\mathrm{v}}|\mu_{\delta''}^{AR}|R'_{\mathrm{v}}\rangle\langle R'_{\mathrm{v}}|\mu_{\delta'''}^{R'}|B_{\mathrm{v}}\rangle}{\omega_{R'A} - \omega'}\right] \quad \text{(B.1)}$$

Comparing with eq 2.4, we note that only an additional factor E_B, the energy of the final state B, appears inside the summation over final states B's.

Relative to the bottom of the potential well of the ground state, the energy E_B of a given vibrational state in the electronic excited state is defined as $E_B = E_{\mathrm{v}}^{\mathrm{e}} + \Delta E$, where $E_{\mathrm{v}}^{\mathrm{e}}$ is the corresponding eigenvalue of H_{e} minus ΔE (cf. eq 1). By following the same procedure for deriving eq 2.8, $E_{\delta\delta'\delta''\delta'''}^{(2)}$ is rewritten as

$$\begin{aligned} E_{\delta\delta'\delta''\delta'''}^{(2)} = {} & \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}s\, \mathrm{e}^{is(\omega+\omega')}\, \mathrm{e}^{-is\Delta E/\hbar} \int_{-\infty}^{0} \mathrm{d}\tau\, \mathrm{e}^{-i\tau\omega+\lambda\tau} \int_{0}^{\infty} \mathrm{d}\tau'\, \mathrm{e}^{-i\tau'\omega-\lambda\tau'}\left(i\hbar\frac{\partial}{\partial s} - \frac{\partial}{\partial\beta}\right)Q_{\delta\delta'\delta'''\delta''}(s, \tau, \tau', \beta) + \\ & \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}s\, \mathrm{e}^{is(\omega+\omega')}\, \mathrm{e}^{-is\Delta E/\hbar} \int_{-\infty}^{0} \mathrm{d}\tau\, \mathrm{e}^{-i\tau\omega+\lambda\tau} \int_{0}^{\infty} \mathrm{d}\tau'\, \mathrm{e}^{-i\tau'\omega'-\lambda\tau'}\left(i\hbar\frac{\partial}{\partial s} - \frac{\partial}{\partial\beta}\right)Q_{\delta\delta'\delta''\delta'''}(s, \tau, \tau', \beta) + \\ & \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}s\, \mathrm{e}^{is(\omega+\omega')}\, \mathrm{e}^{-is\Delta E/\hbar} \int_{-\infty}^{0} \mathrm{d}\tau\, \mathrm{e}^{-i\tau\omega'+\lambda\tau} \int_{0}^{\infty} \mathrm{d}\tau'\, \mathrm{e}^{-i\tau'\omega-\lambda\tau'}\left(i\hbar\frac{\partial}{\partial s} - \frac{\partial}{\partial\beta}\right)Q_{\delta'\delta\delta'''\delta''}(s, \tau, \tau', \beta) + \\ & \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}s\, \mathrm{e}^{is(\omega+\omega')}\, \mathrm{e}^{-is\Delta E/\hbar} \int_{-\infty}^{0} \mathrm{d}\tau\, \mathrm{e}^{-i\tau\omega'+\lambda\tau} \int_{0}^{\infty} \mathrm{d}\tau'\, \mathrm{e}^{-i\tau'\omega'-\lambda\tau'}\left(i\hbar\frac{\partial}{\partial s} - \frac{\partial}{\partial\beta}\right)Q_{\delta'\delta\delta''\delta'''}(s, \tau, \tau', \beta) + \\ & \langle E_{\mathrm{g}}\rangle \times \text{denominator of eq 2.17} \quad \text{(B.2)} \end{aligned}$$

where

$$\langle E_{\mathrm{g}}\rangle = \frac{-1}{Z_{\mathrm{g}}(\beta)}\frac{\partial Z_{\mathrm{g}}(\beta)}{\partial\beta} \quad \text{(B.3)}$$

is the average energy of the ground state.

We average the numerator and denominator of eq 2.17 over two Gaussian pulses separately

$$E_{\mathrm{v}}^{\mathrm{e}}(\omega_0, \Delta, \beta) = \frac{\displaystyle\int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\exp\left\{-\dfrac{(\omega-\omega_0)^2}{2\Delta^2}\right\}}{\Delta\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\exp\left\{-\dfrac{(\omega'-\omega_0)^2}{2\Delta^2}\right\}}{\Delta\sqrt{2\pi}} \sum_j E_{\mathrm{e}j}\left[\sum_i \frac{|c_{ji}^{(2)}|^2}{tII'}p_i\right]}{\displaystyle\int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\exp\left\{-\dfrac{(\omega-\omega_0)^2}{2\Delta^2}\right\}}{\Delta\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\omega' \frac{\exp\left\{-\dfrac{(\omega'-\omega_0)^2}{2\Delta^2}\right\}}{\Delta\sqrt{2\pi}} \sum_j \left[\sum_i \frac{|c_{ji}^{(2)}|^2}{tII'}p_i\right]} \quad \text{(B.4)}$$

The denominator of eq B.4 is just $g(\omega_0, \Delta, \beta)$ (cf. eq 2.10), while the numerator of eq B.4 becomes

$$\begin{aligned} & \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}s \int_{-\infty}^{0} \mathrm{d}\tau \int_{0}^{\infty} \mathrm{d}\tau' \exp[i\omega_0(2s - \tau - \tau') - \\ & \quad is\Delta E/\hbar]\Big\{\exp[-(\Delta^2/2)(s - \tau - \tau')^2 - (\Delta^2/2)s^2]\left(i\hbar\frac{\partial}{\partial s} - \frac{\partial}{\partial\beta}\right)[Q_{\delta\delta'\delta'''\delta''}(s, \tau, \tau', \beta) + Q_{\delta'\delta\delta''\delta'''}(s, \tau, \tau', \beta)] + \\ & \quad \exp[-(\Delta^2/2)(s - \tau)^2 - (\Delta^2/2)(s - \tau')^2]\left(i\hbar\frac{\partial}{\partial s} - \frac{\partial}{\partial\beta}\right)[Q_{\delta\delta'\delta''\delta'''}(s, \tau, \tau', \beta) + Q_{\delta'\delta\delta'''\delta''}(s, \tau, \tau', \beta)]\Big\} + \\ & \quad \langle E_{\mathrm{g}}\rangle \times g(\omega_0, \Delta, \beta) \quad \text{(B.5)} \end{aligned}$$

The $(\partial/\partial\beta)$ terms will produce the third term of eq 2.18. By integrating by parts, the $i\hbar(\partial/\partial s)$ terms produce the first, second, and last terms of eq 2.18.

References and Notes

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