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Density Matrix Method Application to Resonance Raman Scattering

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A projection operator method and density matrix formalism to calculate the rate (transition probability per unit time) of the two-photon process in which the damping effect originating from the molecule-heat bath interaction is properly taken into account and applied this method to resonance Raman scattering.

Key Words: Density matrix, Damping effect, Two-photon and Multiphoton process

INTRODUCTION

The density matrix method is useful in treating relaxation processes, linear and non-linear laser spectroscopies and non-equilibrium statistical mechanics.

Expressions for the transition probabilities of multiphoton and ionization processes have been derived by several theoretical methods. The time-dependent perturbation has been used to calculate the rate constant of multiphoton and various relaxation processes[1, 2]. A systematic formulation of theory of multiphoton processes has been presented based on the Green's function method[1]. Assuming the hot bands with molecules initially at the *j*th vibrational level, the Green's function approach has been used to derive the expression for Raman scattering cross-section[3]. To derive a general expression for the relaxation process, Fujimura and Lin[4] have utilized the Liouville operator technique for the time evolution of the density matrix of the total system by Nakajima[5] and Zwanzig[6]. Within this density matrix formalism both steady-state and transient optical phenomena can be studied[4, 7–9].

In this paper, we shall consider a dynamical system consisting of molecules which interact with a heat bath (or reservoir) and the weak monochromatic radiation field. It is assumed that interaction between the molecular system and the heat bath is responsible for the energy damping of the vibronic levels of the molecules. In this paper, we shall show that the density matrix method can directly provide the dynamic information of both population and coherence (or phase).

We shall use the projection operator and the density matrix method to obtain an expression for transition probabilities of two-photon scattering. We first derive the master equation that describes how one state relaxes into other states and how other states populate it. It is notable that one of the important applications of the master equation arises in the investigation of damping when light interacts with matter. This derivation is performed in two steps by the projection operator method. In one step, we shall omit all of the heat bath variables, and in the other, all of the radiation field variables. The expressions for two-photon transition probability are then obtained by using the derived master equation. In this method, the Markov approximation is used. It is assumed that the coupling between the dynamical system and the radiation field is sufficiently weak so that the molecule-radiation field interaction time is instantaneously short compared with the time of the change of the molecular system density matrix and finally the derived expression of the two-photon transition probability to Raman scattering will be applied.

General Theory

Consider a quantum system whose state is represented by a wavefunction $|\psi(t)\rangle$. Using an arbitrary basis set, $\{|m\rangle\}$, the wavefunction can be expanded as

$$|\psi(t)\rangle = \sum_{m} a_m(t)|m\rangle \tag{1}$$

As this point the density operator may be defined as $\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$. In the basis set, it can be written as:

$$\hat{\rho}(t) = \sum_{m,n} \rho_{mn}(t)|m\rangle\langle n| \tag{2}$$

Here $\rho_{mn}(t) = a_m(t)a_n^*(t)$ is the density operator matrix element.

For investigating the time evolution of the density operator and derive its equation of motion, we start from time derivative of the density operator.

$$\frac{\partial\hat{\rho}}{\partial t} = \left(\frac{\partial}{\partial t}|\psi(t)\rangle\right)\langle\psi(t)| + |\psi(t)\rangle\left(\frac{\partial}{\partial t}\langle\psi(t)|\right) \tag{3}$$

Using the time dependent of Schrödinger equation $\partial|\psi\rangle/\partial t = -(i/\eta)\hat{H}|\psi(t)\rangle$ and its Hermitian conjugate, we get

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{i}{\eta}[\hat{H}, \hat{\rho}] \tag{4}$$

This equation shows time evolution of the density operator and is called the quantum Liouville equation. The jk matrix element of Eq. (4) is as

$$\frac{d\rho_{jk}}{dt} = -\frac{i}{\eta}\sum_{m}[H_{jm}\rho_{mk} - \rho_{jm}H_{mk}] \tag{5}$$

This can be rearranged in the following form:

$$\frac{d\rho_{jk}}{dt} = -i\sum_{m,n} L_{jk,mn}\rho_{mn} \tag{6}$$

Upon the comparison of Eqs. (5) and (6), we have

$$L_{jk,mn} = \frac{1}{\eta}(H_{jm}\delta_{kn} - H_{kn}^{*}\delta_{jm}) = \frac{1}{\eta}(H_{jm}\delta_{kn} - H_{nk}\delta_{jm}) \tag{7}$$

The Liouville equation that describes the motion of the density matrix for the system is given by

$$\frac{\partial\hat{\rho}}{\partial t} = -i\hat{L}\hat{\rho} \tag{8}$$

where $\hat{L}$ is called the Liouville operator (or Liouvillian) and $\hat{L}$ denotes a super operator .

Calculation of the Rate of Two-Photon Process

Considering a total system consisting of the molecular system, heat bath and radiation field. In the equation (8), Liouville operator $\hat{L}$ is

$$\hat{L} = \hat{L}_S^0 + \hat{L}_R^0 + \hat{L}_B^0 + \hat{L}'_{SB} + \hat{L}'_{SR} \tag{9}$$

here $\hat{L}_S^0$, $\hat{L}_R^0$, $\hat{L}_B^0$, $\hat{L}'_{SB}$, $\hat{L}'_{SR}$ are Liouville operators of the system molecular, the heat bath, the radiation field, the interaction Liouville operators between the system molecular and the heat bath, and the radiation field, respectively. Hamiltonian $\hat{H}$ of the total system has the form

$$\hat{H} = \hat{H}_0 + \hat{H}' \tag{10}$$

with $\hat{H}_0 = \hat{H}_S + \hat{H}_B + \hat{H}_R$ and $\hat{H}' = \hat{H}'_{SB} + \hat{H}'_{SR}$. Here $\hat{H}_S$, $\hat{H}_B$, $\hat{H}_R$, $\hat{H}'_{SB}$ and $\hat{H}'_{SR}$ are Hamiltonian operators of the system molecular, the heat bath, the radiation field, the interaction Hamiltonian between the system molecular and the heat bath, and the radiation field, respectively. We are concerned only with the time-dependent behavior of the system, which is described by the reduced density matrix obtained by eliminating the heat bath and radiation field variables, respectively. For this purpose, in first step, it is necessary to eliminate heat bath variables; reduced density operator $\hat{\rho}^{(SR)}$, where $\hat{\rho}^{(SR)} = Tr_B\rho$ has been introduced. Tr_B represents the operation of carrying out a trace over the quantum states of the heat bath. In the second step, radiation field variables by introducing system reduced density operator, $\hat{\rho}^{(S)}$, where $\hat{\rho}^{(S)} = Tr_R\rho^{(SR)}$ has been eliminated. Tr_R represents the operation of carrying out a trace over the quantum states of the radiation field. Thus to obtain the system reduced density matrix $\hat{\rho}^{(S)}$ it is necessary to know the matrix elements of ρ and $\rho^{(SR)}$ are denoted by $\rho_{m_s m_b m_r,\, n_s m_b n_r}$ and $\rho^{(SR)}_{m_s m_r,\, n_s m_r}$ where indices (n_s, m_s), (n_b, m_b), (n_r, m_r) describe the molecular system, heat bath and radiation field variables respectively.

For eliminating the heat bath variables, the projection operator $\hat{P}_B$ has been introduced such that

$$\hat{P}_B\hat{\rho} = \hat{\rho}_1, \quad (1-\hat{P}_B)\hat{\rho} = \hat{\rho}_2, \quad \hat{\rho}_1 + \hat{\rho}_2 = \hat{\rho} \tag{11}$$

and its matrix elements can be written by

$$[\hat{\rho}_1]_{m_s m_b m_r,\, n_s n_b n_r} = \rho_{m_s m_b m_r,\, n_s n_b n_r}\delta_{m_b n_b} \tag{12}$$

$$\lfloor(1-\hat{P}_B)\hat{\rho}\rfloor_{m_sm_bm_r,\,n_sn_bn_r}=(1-\delta_{m_bn_b})\rho_{m_sm_bm_r,\,n_sn_bn_r} \tag{13}$$

Applying the Laplace transform method to Eq. (8) yields

$$p\hat{\rho}(p)-\hat{\rho}(0)=-i\hat{L}\hat{\rho}(p) \tag{14}$$

where $\hat{\rho}(p)$ denotes the Laplace transform of $\hat{\rho}(t)$ and $\hat{\rho}(0)$ is the density matrix of the total system at $t = 0$.

$$\hat{\rho}(0)=\hat{\rho}^{(S)}(0)\hat{\rho}^{(B)}(0)\hat{\rho}^{(R)}(0) \tag{15}$$

Here $\hat{\rho}^{(S)}(0)$, $\hat{\rho}^{(B)}(0)$, $\hat{\rho}^{(R)}(0)$ are the density operator of molecular system, heat bath and radiation field in equilibrium condition, respectively.

Apply $\hat{P}_B$ and $(1-\hat{P}_B)$ to Eq. (14) and use the Eq. (11), result

$$p\hat{\rho}_1(p)-\hat{\rho}_1(0)=-i\hat{P}_B\hat{L}\,\hat{\rho}_1(p)-i\hat{P}_B\hat{L}\,\hat{\rho}_2(p) \tag{16}$$

$$p\hat{\rho}_2(p)-\hat{\rho}_2(0)=-i(1-\hat{P}_B)\hat{L}\,\hat{\rho}_1(p)-i(1-\hat{P}_B)\hat{L}\,\hat{\rho}_2(p) \tag{17}$$

From Eq. (17), substituting $\hat{\rho}_2(p)$ in Eq. (16) yields

$$p\hat{\rho}_1(p)-\hat{\rho}_1(0)=-i\hat{P}_B\hat{L}\,\hat{\rho}_1(p)-i\hat{P}_B\hat{L}\frac{1}{p+i(1-\hat{P}_B)\hat{L}}\hat{\rho}_2(0)-\hat{M}(p)\hat{\rho}_1(p) \tag{18}$$

where $$\hat{M}(p)=\hat{P}_B\hat{L}\frac{1}{p+i(1-\hat{P}_B)\hat{L}}(1-\hat{P}_B)\hat{L} \tag{19}$$

We can trace over the heat bath variables (Tr_B) to Eq. (18).

$$p\hat{\rho}^{(SR)}(p)-\hat{\rho}^{(SR)}(0)=-i\overline{L}\,\hat{\rho}^{(SR)}(p)-\overline{M}(p)\hat{\rho}^{(SR)}(p) \tag{20}$$

where $$\overline{L}=Tr_B\lfloor\hat{P}_B\hat{L}\,\hat{\rho}^{(B)}(0)\rfloor=\hat{L}_S+\hat{L}_R^0+Tr_B\hat{L}'_{SB}\,\hat{\rho}^{(B)}(0) \tag{21}$$

$$\overline{M}(p)=Tr_B[\hat{M}(p)\hat{\rho}^{(B)}(0)]=\hat{L}'_{SB}\,(1-\hat{P}_B)\left(\frac{1}{P+i\hat{L}}\right)(1-\hat{P}_B)\hat{L}'_{SB}\,\hat{\rho}^{(B)}(0) \tag{22}$$

Applying $Tr_B\rho=\rho^{(SR)}$, $\hat{\rho}_1=\hat{\rho}^{(SR)}\hat{\rho}^{(B)}(0)$, in equilibrium condition of heat bath ($t = 0$) where $\rho_2^{(B)}=0$ and eliminating heat bath variables, we get

$$\lfloor p+i\hat{L}_S+i\hat{L}_R^0+\langle\Sigma(p)\rangle_B\rfloor\hat{\rho}^{(SR)}(p)=\hat{\rho}^{(SR)}(0) \tag{23}$$

where $$\langle\Sigma(p)\rangle_B=Tr_B\,\Sigma(p)\rho^{(B)}(0) \tag{24}$$

$$\Sigma(p)=i\hat{L}'_{SB}+\hat{L}'_{SB}\,(1-\hat{P}_B)(p+i\hat{L})^{-1}(1-\hat{P}_B)\hat{L}'_{SB} \tag{25}$$

Projection operator $\hat{P}_R$ will be applied to eliminate radiation field variables. Operator $\hat{P}_R$ is defined as

$$\hat{P}_R\hat{\rho}^{(SR)}=\hat{\rho}_1^{(SR)},\quad(1-\hat{P}_R)\hat{\rho}^{(SR)}=\hat{\rho}_2^{(SR)},\quad\hat{\rho}_1^{(SR)}+\hat{\rho}_2^{(SR)}=\hat{\rho}^{(SR)} \tag{26}$$

and its matrix elements can be written by

$$[\rho_1^{(SR)}]_{m_sm_r,\,n_sn_r}=\rho^{(SR)}_{m_sm_r,\,n_sn_r}\delta_{m_rn_r},\ \lfloor(1-\hat{P}_R)\hat{\rho}^{(SR)}\rfloor_{m_sm_r,\,n_sn_r}=(1-\delta_{m_rn_r})\rho^{(SR)}_{m_sm_rn_sn_r} \tag{27}$$

Applying operators $\hat{P}_R$ and $(1-\hat{P}_R)$ to Eq. (23), substitute $\hat{L}_S = \hat{L}_S^0 + \hat{L}'_{SR}$, and use Eq. (26) and Eq. (27), to give

$$\begin{aligned} & p\hat{\rho}_1^{(SR)}(p) + i\hat{L}_S^0\,\hat{\rho}_1^{(SR)}(p) + i\hat{P}_R\hat{L}'_{SR}\;\hat{\rho}_1^{(SR)}(p) + i\hat{P}_R\hat{L}'_{SR}\;\hat{\rho}_2^{(SR)}(p) \\ & \quad + \hat{P}_R\langle\Sigma(p)\rangle_B\hat{\rho}_1^{(SR)}(p) + \hat{P}_R\langle\Sigma(p)\rangle_B\hat{\rho}_2^{(SR)}(p) = \hat{\rho}_1^{(SR)}(0) \end{aligned} \tag{28}$$

$$\begin{aligned} & p\hat{\rho}_2^{(SR)}(p) + i\hat{L}_S^0\hat{\rho}_2^{(SR)}(p) + i(1-\hat{P}_R)\hat{L}'_{SR}\;\hat{\rho}_1^{(SR)}(p) + i(1-\hat{P}_R)\hat{L}'_{SR}\;\hat{\rho}_2^{(SR)}(p) \\ & \quad + i\hat{L}_R^0\hat{\rho}_2^{(SR)}(p) + (1-\hat{P}_R)\langle\Sigma(p)\rangle_B\hat{\rho}_1^{(SR)}(p) + (1-\hat{P}_R)\langle\Sigma(p)\rangle_B\hat{\rho}_2^{(SR)}(p) = 0 \end{aligned} \tag{29}$$

From Eq. (29) for $\hat{\rho}_2^{(SR)}(p)$ can be solved by substituting it in Eq. (28) and trace over the radiation field variables (TrR), to yield

$$\begin{aligned} & p\hat{\rho}^{(S)}(p) + i\hat{L}_S^0(p) + \mathrm{Tr}_R\lfloor(i\hat{L}'_{SR} + \langle\Sigma(p)\rangle_B)\hat{\rho}_1^{(SR)}(p)\rfloor - \mathrm{Tr}_R\{\lfloor i\hat{L}'_{SR} + \langle\Sigma(p)\rangle_B\rfloor \\ & \times[(1-\hat{P}_R)(p + i\hat{L}_S^0 + i\hat{L}_R^0 + i\hat{L}'_{SR} + \langle\Sigma(p)\rangle_B)(1-\hat{P}_R)]^{-1}[i\hat{L}'_{SR} + \langle\Sigma(p)\rangle_B]\rho_1^{(SR)}(p)\} \\ & = \hat{\rho}^{(S)}(0) \end{aligned} \tag{30}$$

where $\rho^{(S)}(p) = \mathrm{Tr}_R\hat{\rho}^{(SR)}(p)$. It is easy to show that

$$\hat{\rho}^{(SR)} = \hat{\rho}^{(S)}\rho^{(R)}(0) \tag{31}$$

Here $\rho^{(R)}(0)$ is equilibrium distribution of radiation field. In the equilibrium

$$\rho^{(R)}_{m_{\gamma}, m_{\gamma'}} = 0 \quad \text{and} \quad \Sigma_{m_{\gamma}}\, \rho^{(R)}_{m_{\gamma}, m_{\gamma}} = 1$$

Substituting Eq. (31) to Eq. (30) yields

$$\lfloor p + i\hat{L}_S^0 + \{\hat{M}(p)\}\rfloor\hat{\rho}^{(S)}(p) = \hat{\rho}^{(S)}(0) \tag{32}$$

where $\hat{M}(p)$ is the transition operator

$$\hat{M}(p) = i\hat{L}'_{SR} + \langle\Sigma(p)\rangle_B - \lfloor i\hat{L}'_{SR} + \langle\Sigma(p)\rangle_B\rfloor(1-\hat{P}_R)\hat{V}(1-\hat{P}_R)\lfloor i\hat{L}'_{SR} + \langle\Sigma(p)\rangle_B\rfloor \tag{33}$$

where
$$\hat{V} = \frac{1}{p + i\hat{L}_S^0 + i\hat{L}_R^0 + i\hat{L}'_{SR} + \langle\Sigma\,(p)\rangle_B} \tag{34}$$

Carrying out the inverse Laplace transformation of Eq. (32), the equation for the reduced density matrix $\hat{\rho}^{(S)}(t)$ is obtained as

$$\frac{d\rho^{(S)}}{dt} = -i\hat{L}_S^0\hat{\rho}^{(S)}(t) - \int_0^t dt\,\{\hat{M}(\tau)\}\hat{\rho}^{(S)}(t-\tau) \tag{35}$$

where
$$\{\hat{M}(\tau)\} = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} dp\{\hat{M}(p)\}\exp(p\tau) \tag{36}$$

This integral is called the Bromwich integral and is evaluated along the vertical line x = c and the complex plane p. In obtaining Eq. (35), the convolution theorem has been used. This equation can be written as

$$\frac{d\hat{\rho}^{(S)}}{dt} = -i\hat{L}_S^0\hat{\rho}^{(S)}(t) - \int_0^t d\tau\{\hat{M}(\tau)\}\exp(i\hat{L}_S^0\tau)\hat{\rho}^{(S)}(t) \tag{37}$$

Here the expansion $\hat{\rho}^{(S)}(t-\tau)$ along $\tau = 0$,

$$\hat{\rho}^{(S)}(t-\tau) = \sum_{n=0}^{+\infty} \frac{(-\tau)^n d^n}{n!} \frac{d^n}{dt^n} \hat{\rho}^{(S)}(t) = \exp(-\tau\, d/dt)\hat{\rho}^{(S)}(t) \qquad (38)$$

and the approximation of replacing d/dt in Eq. (38) by $-i\hat{L}_S^0$ have been used. Eq. (37) is called the generalized master equation (GME), which can yield both the diagonal and off diagonal matrix elements of the density matrix of the system. While the diagonal matrix elements of $\hat{\rho}^{(S)}(t)$ describe the time evolution of the population of the system, the off-diagonal matrix elements of $\hat{\rho}^{(S)}(t)$ provide the phase information of the system and determine the Lorentzian bandwidths and the band shifts of optical spectra.

For defining the rate constant, the Markov approximation is applied, *i.e.*, the molecule-radiation field interaction time is instantaneously short compared with the time of the change of the molecular system density matrix. This means that the future development of a Markovian system is determined entirely by the most recent state whereas the past history of the system has no influence on its future behaviour. In this approximation Eq. (37) can be written as

$$\frac{d\hat{\rho}^{(S)}(t)}{dt} = (-i\hat{L}_S^0 - \hat{k})\hat{\rho}^{(S)}(t) \qquad (39)$$

where

$$\hat{k} = \lim_{t \to \infty} \int_0^t d\tau \{\hat{M}(\tau)\} \exp(i\hat{L}_S^0 \tau) \qquad (40)$$

Equation (39) is the master equation for the multiphoton processes of the molecular system in the presence of the heat bath and radiation field.

For multiphoton processes, we should calculate the transition operator $\hat{M}(p)$ from Eq. (33). This involves solving Eq. (34). The term V in this equation can be written as

$$\hat{V} = \hat{G}(p) + \hat{G}(p)(-i\hat{L}'_{SR})\hat{V} \qquad (41)$$

where

$$\hat{G}(p) = \frac{1}{p + i\hat{L}_S^0 + i\hat{L}_R^0 + \langle \Sigma(p) \rangle_B} \qquad (42)$$

Eq. (41) solved by iterative method, yields

$$\hat{V} = \hat{G}(p) + \hat{G}(p)(-i\hat{L}'_{SR})\hat{G}(p) + \hat{G}(p)(-i\hat{L}'_{SR})\hat{G}(p)(-i\hat{L}'_{SR})\hat{G}(p)$$
$$+ \hat{G}(p)(-i\hat{L}'_{SR})\hat{G}(p)(-i\hat{L}'_{SR})\hat{G}(p)(-i\hat{L}'_{SR})\hat{G}(p) + \ldots \qquad (43)$$

Substituting Eq. (43) to Eq. (33) gives

$$\hat{M}(p) = i\hat{L}'_{SR} + \langle \Sigma(p) \rangle_B - (i\hat{L}'_{SR} + \langle \Sigma(p) \rangle_B)(1 - \hat{P}_R) \lfloor \hat{G}(p)$$
$$+ \hat{G}(p)(-i\hat{L}'_{SR})\hat{G}(p) + \hat{G}(p)(-i\hat{L}'_{SR})\hat{G}(p)(-i\hat{L}'_{SR})\hat{G}(p) + \ldots]$$
$$(1 - \hat{P}_R)(i\hat{L}'_{SR} + \langle \Sigma(p) \rangle_B) \qquad (44)$$

Then the transition operator $\hat{M}(p)$ can be expanded as

$$\{\hat{M}(p)\} = \{\hat{M}^{(0)}(p)\} + \{\hat{M}^{(1)}(p)\} + \{\hat{M}^{(2)}(p)\} + \{\hat{M}^{(3)}(p)\} + \ldots \tag{45}$$

where the transition operators with superscripts related to the photon number involved in the processes for example radiationless, one-, two-, three-, . . . photon processes, respectively.

The two-photon transition probabilities are defined as

$$W^{(2)} = \sum_{m_s} \lim_{t \to \infty} \frac{d\rho^{(S)}_{m_s m_s}(t)}{dt} \tag{46}$$

Substituting Eq. (36) and Eq. (40) into Eq. (39) and using diagonal matrix elements of density operator, transition probability is given by

$$W^{(2)} = -\lim_{t \to +\infty} \sum_{m_s, n_s} \int_0^t d\tau \left(\frac{1}{2\pi i}\right) \int_{-i\infty + c}^{+i\infty + c} dp \exp(p\tau) \{\hat{M}^{(2)}(p)\}^{n_s n_s}_{m_s m_s} \rho^{(S)}_{n_s n_s}(0) \tag{47}$$

where
$$\{\hat{M}^{(2)}(p)\}^{n_s n_r}_{m_s m_r} = \sum_{m_r n_r} \rho^{(R)}_{n_r n_r}(0) [\hat{M}^{(2)}(p)]^{n_s n_r,\, n_s n_r}_{m_s m_r,\, m_s m_r} \tag{48}$$

$$\lfloor \hat{M}^{(2)}(p) \rfloor^{n_s n_r,\, n_s n_r}_{m_s m_r,\, m_s m_r} = -\lfloor \hat{L}'_{SR} \hat{G}(p) \hat{L}'_{SR} \hat{G}(p) \hat{L}'_{SR} \hat{G}(p) \hat{L}'_{SR} \rfloor^{n_s n_r,\, n_s n_r}_{m_s m_r,\, m_s m_r} \tag{49}$$

The matrix element of the transition operator is given by

$$\hat{M}^{(2)}(p)^{NN}_{MM} = -\sum_{\substack{LL' \\ AA' \\ II'}} [\hat{L}'_{SR}]^{AA'}_{MM} [\hat{G}^{(0)}(p)]^{AA'}_{AA'} [\hat{L}'_{SR}]^{II'}_{AA'} [\hat{G}^{(0)}(p)]^{II'}_{II'} [\hat{L}'_{SR}]^{LL'}_{II'} [\hat{G}^{(0)}(p)]^{LL'}_{LL'}$$

$$[\hat{L}'_{SR}]^{NN}_{LL'}$$

$$= -\frac{1}{\eta^4} \sum_{\substack{LL' \\ AA' \\ II'}} (H'_{MA}\delta_{A'M} - H'_{A'M}\delta_{AM}) [G^{(0)}(p)]^{AA'}_{AA'} (H'_{AI}\delta_{A'I'} - H_{I'A'}\delta_{AI}) [G^{(0)}(p)]^{AA'}_{AA'}$$

$$(H'_{LI}\delta_{I'L'} - H'_{LI'}\delta_{LI}) [G^{(0)}(p)]^{AA'}_{AA'} (H'_{LN}\delta_{L'N} - H'_{NL'}\delta_{NL}) \tag{50}$$

$$= -\frac{2}{\eta^4} \mathrm{Re} \sum_A \sum_L H'_{NL} H'_{LM} H'_{MA} H'_{AN} \{G^{(0)}(p)_{AM} G^{(0)}(p)_{NL} G^{(0)}(p)_{NM}$$

$$+ G^{(0)}(p)_{AM} G^{(0)}(p)_{AL} (G^{(0)}(p)_{NL} + G^{(0)}(p)_{AN})\}$$

where $\hat{H}' = \hat{H}'_{SR}$, $N = n_s n_r$, $M = m_s m_r$, and so on. Here the effect of the radiation field-molecule interaction in $\hat{G}(p)$ has been neglected.

$$\hat{G}(p) \cong \hat{G}^{(0)}(p) = [p + i\hat{L}^0_S + i\hat{L}^0_R + \langle \Sigma^{(0)}(p) \rangle_B]^{-1} \tag{51}$$

with
$$\langle \Sigma^{(0)}(p) \rangle_B = \langle \hat{L}'_{SB} (p + i\hat{L}^0_S + i\hat{L}^0_B)^{-1} \hat{L}'_{SB} \rangle \tag{52}$$

where
$$G^{(0)}(p)_{MN} = \hat{G}^{(0)}(p)^{MN}_{MN} = (p + i\omega_{m_s m_r,\, n_s n_r} + \Gamma_{m_s n_s})^{-1}$$

Here $\Gamma_{m_s n_s} = \langle \Sigma^{(0)}(p) \rangle_{m_s n_s}$ is the dephasing rate constant relevant to the m and n molecular states.

We can simplify Eq. (50) using the relations

$$
\begin{aligned}
&G^{(0)}(p)_{AM}G^{(0)}(p)_{NL}G^{(0)}(p)_{NM}\\
&\quad = G^{(0)}(p)_{AN}G^{(0)}(p)_{NL}G^{(0)}(p)_{NM} + G^{(0)}(p)_{NL}G^{(0)}(p)_{NM}[G^{(0)}(p)_{AM} - G^{(0)}(p)_{AN}]\\
&\quad = G^{(0)}(p)_{AN}G^{(0)}(p)_{NL}G^{(0)}(p)_{NM} + [-1 + (\Gamma_{AN} - \Gamma_{AM} + \Gamma_{NM})G^{(0)}(p)_{NM}]\\
&\quad\quad \times G^{(0)}(p)_{AM}G^{(0)}(p)_{AN}G^{(0)}(p)_{NL} \qquad (54)
\end{aligned}
$$

$$
\begin{aligned}
&G^{(0)}(p)_{AM}G^{(0)}(p)_{AL}(G^{(0)}(p)_{NL} + G^{(0)}(p)_{AN})\\
&\quad = (1 + (\Gamma_{NL} + \Gamma_{AN} - \Gamma_{AL})G^{(0)}(p)_{AL})\ G^{(0)}(p)_{AM}G^{(0)}(p)_{NL}G^{(0)}(p)_{AN} \qquad (55)
\end{aligned}
$$

Substituting Eq. (54) and Eq. (55) into Eq. (50) gives

$$
M^{(2)}(p)_{MM}^{NN} = M_{sim}^{(2)}(p)_{MM}^{NN} + M_{seq}^{(2)}(p)_{MM}^{NN} + M_{mix}^{(2)}(p)_{MM}^{NN} \qquad (56)
$$

with

$$
\begin{aligned}
M_{sim}^{(2)}(p) &= -\frac{2}{\eta^4}\,\mathrm{Re}\sum_{A}\sum_{L} H'_{NL}H'_{LM}H'_{MA}H'_{AN}G^{(0)}(p)_{NM}G^{(0)}(p)_{AN}G^{(0)}(p)_{NL} \qquad (57)\\
&= -\frac{2}{\eta^4}\,\mathrm{Re}\,G^{(0)}(p)_{NM}\,\Big|\sum_{A} H'_{MA}G^{(0)}(P)_{AN}H'_{AN}\Big|^2\\
M_{seq}^{(2)}(p) &= -\frac{2}{\eta^4}\,\mathrm{Re}\sum_{A}\sum_{L}(\Gamma_{AN} + \Gamma_{AL} + \Gamma_{NL})H'_{NL}H'_{LM}H'_{MA}H'_{AN}\\
&\quad \times G^{(0)}(p)_{AM}G^{(0)}(P)_{NL}G^{(0)}(p)_{AL}G^{(0)}(p)_{AN} \qquad (58)\\
M_{mix}^{(2)}(p)_{MM}^{NN} &= -\frac{2}{\eta^4}\,\mathrm{Re}\sum_{A}\sum_{L}(\Gamma_{AN} - \Gamma_{AM} + \Gamma_{NM})H'_{NL}H'_{LM}H'_{MA}H'_{AN}\\
&\quad \times G^{(0)}(p)_{NM}G^{(0)}(P)_{AM}G^{(0)}(p)_{AN}G^{(0)}(p)_{NL} \qquad (59)
\end{aligned}
$$

Substituting Eq. (56) into Eq. (47), in terms of the simultaneous, sequential, and mixed processes, the two-photon transition probability becomes

$$
\begin{aligned}
W^{(2)} &= -\lim_{t\to\infty}\sum_{M}\sum_{N}\rho_{n_sn_s}^{(S)}(0)\int_0^t d\tau\left(\frac{1}{2\pi i}\right)\int_{c-i\infty}^{c+i\infty} dp\,\exp(p\tau)[M_{sim}^{(2)}(p)_{MM}^{NN}\\
&\quad + M_{seq}^{(2)}(p)_{MM}^{NN} + M_{mix}^{(2)}(p)_{MM}^{NN}]\\
&= W_{sim}^{(2)} + W_{seq}^{(2)} + W_{mix}^{(2)} \qquad (60)
\end{aligned}
$$

In Eq. (60), first integrals over p are carried out by the method of Coushi integral, and then time integrals are evaluated. We have

$$
\begin{aligned}
W_{sim}^{(2)} &= \frac{2}{\eta^4}\sum_{M}\sum_{N}\rho_{n_sn_s}^{(S)}\,\rho_{n_rn_r}^{(R)}(0)\,\mathrm{Re}\sum_{A}\sum_{L} H'_{MA}H'_{AN}H'_{LM}H'_{NL}\\
&\quad \times \frac{1}{(i\omega_{NM} + \Gamma_{NM})(i\omega_{NM} + \Gamma_{NM})(i\omega_{NM} + \Gamma_{NM})} \qquad (61)\\
&= \frac{2}{\eta^4}\sum_{M}\sum_{N}\rho_{n_sn_s}^{(S)}\,\rho_{n_rn_r}^{(R)}(0)\,\mathrm{Re}\frac{1}{(i\omega_{NM} + \Gamma_{NM})}\left|\sum_{A}\frac{H'_{MA}H'_{AN}}{i\omega_{AN} + \Gamma_{AN}}\right|^2
\end{aligned}
$$

$$= \frac{2}{\eta^4} \sum_{m_s} \sum_{n_s} \sum_{m_r} \sum_{n_r} \rho^{(S)}_{n_s n_s} \rho^{(R)}_{n_r n_r}(0) \frac{\Gamma_{NM}}{(\omega^2_{NM} + \Gamma^2_{NM})} \left| \sum_A \frac{H'_{MA} H'_{AN}}{\omega_{AN} + i\Gamma_{AN}} \right|^2$$

Here we have used $\mathrm{Re}\left[\frac{1}{(i\omega_{NM} + \Gamma_{NM})}\right] = \frac{\Gamma_{NM}}{(\Gamma^2_{NM} + \omega^2_{NM})}$.

For the sequential and the mixed process, respectively, we have

$$W^{(2)}_{seq} = \frac{2}{\eta^4} \mathrm{Re} \sum_{m_s} \sum_{n_s} \sum_{m_r} \sum_{n_r} \rho^{(S)}_{n_s n_s} \rho^{(R)}_{n_r n_r}(0) \sum_A \sum_L (\Gamma_{AN} - \Gamma_{AL} + \Gamma_{NL})$$

$$\times \frac{H'_{NL} H'_{LM} H'_{MA} H'_{AN}}{(\omega_{AM} - i\Gamma_{AM})(\omega_{NL} - i\Gamma_{NL})(\omega_{AN} - i\Gamma_{AN})(\omega_{AL} - i\Gamma_{AL})} \tag{62}$$

$$W^{(2)}_{mix} = \frac{2}{\eta^4} \mathrm{Re} \sum_{m_s} \sum_{n_s} \sum_{m_r} \sum_{n_r} \rho^{(S)}_{n_s n_s} \rho^{(R)}_{n_r n_r}(0) \sum_A \sum_L (\Gamma_{AN} - \Gamma_{AM} + \Gamma_{NM})$$

$$\times \frac{H'_{NL} H'_{LM} H'_{MA} H'_{AN}}{(\omega_{NM} - i\Gamma_{AM})(\omega_{AM} - i\Gamma_{AM})(\omega_{AN} - i\Gamma_{AN})(\omega_{NL} - i\Gamma_{NL})} \tag{63}$$

where the subscripts in capital letters specify both the molecular state and radiation fields.

Calculation of transition probability in resonance Raman scattering

Two-photon processes, including scattering, two-photon emission and two-photon absorption may occur in two sequential one-photon steps or in two simultaneous steps. In the former, an atom may absorb or emit a single photon, then during the lifetime of its excited state, it may absorb or emit another photon to reach a new state. In the latter, two-photons are simultaneously absorbed and emitted, as only the beginning and end of the process are observable but intermediate states are not observable experimentally. Raman scattering process is a two-photon process that cannot be decomposed into individual steps; intermediate states are not separable in time and are not detectable. We will evaluate two-photon transition probability of resonance Raman scattering. A simultaneous process makes a dominant contribution to this process and transition probability can be calculated by Eq. (61).

Similar to the method described in the previous section, we can derive the master equations for a system coupled in a heat bath and describe the proper time dependent behaviour of both diagonal and off-diagonal portios of the density matrix.

We find that
$$\Gamma_{MN} = \Gamma_{MN}(r) + i\Gamma_{MN}(i) \tag{64}$$

$$\Gamma_{MN}(r) = \frac{1}{2}(\Gamma_{MM} + \Gamma_{NN}) + \Gamma^{(d)}_{MN} \tag{65}$$

Here $M \equiv m_s m_b$, $N \equiv n_s n_b$. The term $\Gamma_{MN}(r)$ is called the dephasing rate constant where $\Gamma_{MM} = \Gamma^{m_s m_s}_{m_s m_s}$ and $\Gamma_{NN} = \Gamma^{n_s n_s}_{n_s n_s}$ are known as population decay constant which are related to the life times of the states $|m_s\rangle$ and $|n_s\rangle$ by $\tau_m = \pi/\Gamma_{m_s m_s}$ and

$\tau_n = \pi/\Gamma_{n_s n_s}$, respectively. $\Gamma^{(d)}$ is known as a pure dephasing constant. It is a constant associated with an elastic process which disturbs the phase of the wave function but do not disturb the populations of states because the system does not change energy in the pure dephasing process. Its contribution is significant in the presence of additional damping mechanism such as collision processes, phonon interactions, intramolecular processes, lattice interactions and various other processes. The term $\Gamma_{MN}(i) = \Gamma^{m_s n_s}_{m_s n_s}(i)$ represents the energy level shift of the system due to its interaction with the heat bath.

An expression for rate of resonance Raman scattering process by using Eq. (60) can be obtained. In two-photon scattering the effects of pure dephasing are negligibly small compared with the population decay constants of the intermediate and/or final states the simultaneous process makes a dominant contribution to the two-photon process and transition probability is given by Eq. (61). Raman scattering can be described with basis set consisting of the initial state $(|N\rangle = |n_s, n_{\lambda\mu}, n_{\lambda^\square}\mu^\square\rangle)$, final state $(|M\rangle = |m_s,\ n_{\lambda\mu} - 1\ n_{\lambda^\square}{}_{\mu^\square} + 1)$ and intermediate states $(|A\rangle = |a_s, n_{\lambda\mu}, n_{\lambda^\square}\mu^\square + 1\rangle$, $(|A\rangle = |a_s, n_{\lambda\mu} - 1, n_{\lambda^\square}\ \mu^\square\rangle)$.

Assuming that the radiation field can be expressed in terms of monochromatic plane wave in the radiation cavity with volume V, so that the density matrix of radiation field at t = 0 is $\rho^{(R)}(0) = |n_{\lambda\mu} n_{\lambda'\mu'}\rangle\langle n_{\lambda\mu} n_{\lambda'\mu'}|$, in the dipole approximation, and the low temperature $(\rho^{(S)} = 1)$, the transition probability per unit time of two-photon resonance Raman scattering is given by

$$W_{n_s m_s} = \frac{(2\pi)^3}{\eta^2 c^4}\,\omega_\lambda \omega_{\lambda'} n_{\lambda\mu}(n_{\lambda'}\mu' + 1)\left|\sum_{\substack{\lambda'\mu' \\ a_s \neq n_s}}\left\{\frac{(\varepsilon_{\lambda\mu} M_{a_s n_s})(\varepsilon_{\lambda'\mu'} M_{m_s a_s})}{\omega_{a_s n_s} - \omega_0 - i\Gamma_{a_s}}\right.\right.$$
$$\left.\left. + \frac{(\varepsilon_{\lambda\mu} M_{m_s a_s})(\varepsilon_{\lambda'\mu'} M_{a_s n_s})}{\omega_{a_s m_s} + \omega_\lambda + i\Gamma_{a_s}}\right\}\right|^2 \delta(\omega_{m_s n_s} - \omega_\lambda + \omega_{\lambda'}) \qquad (66)$$

where $\omega_{\lambda\mu}$ and $\omega_{\lambda'\mu'}$ are incident and scattered photon frequency, $\omega_{a_s n_s}$ and $\omega_{a_s m_s}$ are the vibronic energy gaps, $\varepsilon_{\lambda\mu}(\varepsilon_{\lambda'\mu'})$ is the polarization direction of the incident (scattered) laser and $M_{a_s m_s}$, $M_{n_s a_s}$ are transition dipole moments.

RESULTS AND DISCUSSION

In the perturbation method, transition probability two-photon is given by

$$W^{(2)}_{N \to M} = \frac{2\pi}{\eta}\left|\sum_{A} \frac{H'_{MA} H'_{AN}}{\omega_{AN}}\right|^2 \delta(\omega_{MN}) \qquad (67)$$

where indices in capital letters specify both the molecular state and radiation field. Comparing this relation with Eq. (60) which is obtained by density matrix method, it may be shown that

(a) Derived probabilities by using density matrix method involve not only those of simultaneous processes, but also those of sequential and mixed that cannot be obtained by using the conventional time dependent perturbation.

(b) Within the density matrix method, we can take into account the effect of dephasing that from originating the molecule heat bath interaction.

In the perturbation method and in the dipole approximation, expression of transition probability of Raman scattering is similar to above Eq. (66) except without damping constant, but in the resonance conditions $\omega_{m_s n_s} \approx \omega_\lambda$, the damping instant Γ_{m_s} is introduced by phenomenological to avoid singularities.

Conclusion

A molecule can lose its energy by making non-radiation transitions such as collisions and interaction with other molecules when it is coupled to the environment. The process whereby a dynamical system such as a molecule progresses toward equilibrium (steady state) with its heat bath is known as relaxation or damping. The use of ordinary perturbation method cannot take into account the damping effect. Without a complete quantum mechanical treatment, we cannot hope to account for the non-radiative transition rate (damping constant) except in a phenomenological way.

The temporal behaviour of the density operator is of central importance in the time development of a physical system under the influence of various interactions. Density matrix formalism is a convenient way to describe relaxation dynamics of a molecule when it can interact with its surrounding, often referred to as the bath. One of the merits of applying the density matrix method to two photon processes is that one can take into account the effects of dephasings that originate from the molecule-heat bath interaction. The derived transition probabilities involved not only those of simultaneous processes but also those of sequential ones that cannot be obtained by using the conventional time dependent perturbation.

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