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Relation between the Vibrational Wavepacket Propagation Formalism and the Time-Correlation Function Formalism for Absorption and Raman Scattering

Soo-Y. Lee
Department of Chemistry, National University of Singapore, Kent Ridge, S. 0511, Singapore
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By a proper choice of the system Hamiltonian and the dipole or polarizability operators, we show that the widely used wavepacket propagation formalism for optical absorption presented by Heller (*J. Chem. Phys.*, **68**, 2066 (1978)) and vibrational Raman scattering by Lee and Heller (*J. Chem. Phys.*, **71**, 4777 (1979)) can be derived from the dipole and polarizability correlation function formalisms, respectively, presented by Gordon (*Adv. Magn. Reson.*, 3, 1 (1968)). Gordon focused on processes in the ground electronic state, whereas Heller et al. dealt with optical processs involving excited electronic states. The cases of an isolated molecule and of a molecule in a bath where only pure electronic dephasing occurs are both considered in this paper.

The time-correlation function formalism of Gordon1) preceeded the vibrational wavepacket propagation picture for optical absorption by Heller2) and for vibrational Raman scattering by Lee and Heller.3) Gordon1) focused on deriving information about molecular rotation in the ground electronic state from infrared and rotational Raman spectra, whereas Heller et al.2–4) studied the relationship between vibrational dynamics in the excited electronic states and optical absorption and vibrational Raman spectra. The connection between Gordon's approach and the work of Heller et al. has not previously been discussed in depth. Here, it is shown that the vibrational wavepacket propagation picture, by an isolated molecule or by a molecule in a bath with pure electronic dephasing only, can be derived from the time-correlation function formalism.

Absorption. Gordon1) has shown that the normalized lineshape function $I(\omega)$ is given by the Fourier transform of the dipole correlation function,

$$I(\omega)=(1/2\pi)\int_{-\infty}^{\infty} \mathrm{d}t\ \mathrm{e}^{-i\omega t}\langle\vec{\mu}(0)\cdot\vec{\mu}(t)\rangle, \tag{2.1}$$

where ω is the light frequency, and the time-dependent Heisenberg operator $\vec{\mu}(t)$ for the dipole at time t is defined by,

$$\vec{\mu}(t)=\mathrm{e}^{iHt/\hbar}\vec{\mu}(0)\,\mathrm{e}^{-iHt/\hbar}, \tag{2.2}$$

with H as the system Hamiltonian. Since the lineshape function is real, $I(\omega)$ can also be written as,

$$I(\omega)=(1/\pi)\mathrm{Re}\int_{0}^{\infty} \mathrm{d}t\ \mathrm{e}^{i\omega t}\langle\vec{\mu}(0)\cdot\vec{\mu}^*(t)\rangle, \tag{2.3}$$

where Re denotes taking the real part.

Equation 2.1 or 2.3 is a general expression for the absorption lineshape function, and is true for an ensemble of interacting molecules as well as a single molecule. Gordon1) applied the inverse of Eq. 2.1 to obtain and interpret the dipole correlation function from the rotation–vibration bands in the near infrared. In this case, $\vec{\mu}$ is the vibrational transition dipole moment of the absorbing molecules in the ground electronic state; and H is the Hamiltonian for the rotation–translation motion with the neglect of vibrational perturbations.

Our focus here is on optical transitions, first, for a single molecule. We assume the Born–Oppenheimer approximation and consider the molecule to have two electronic states; a ground electronic state $|\mathrm{e}_1\rangle$ and an optically bright excited electronic state $|\mathrm{e}_2\rangle$. In the spinor representation, the Hamiltonian H for the molecule can be written as,

$$H=h_1(\mathbf{Q})|\mathrm{e}_1\rangle\langle\mathrm{e}_1|+(h_2(\mathbf{Q})-i\hbar\gamma)|\mathrm{e}_2\rangle\langle\mathrm{e}_2|, \tag{2.4}$$

where $h_1(\mathbf{Q})$ and $h_2(\mathbf{Q})$ are the vibrational Hamiltonians in electronic states $|\mathrm{e}_1\rangle$ and $|\mathrm{e}_2\rangle$, respectively, and γ^{-1} is the lifetime in the excited electronic state. The dipole operator for an electronic transition between the two states in the Franck–Condon approximation is given by,

$$\vec{\mu}(0)=\vec{\mu}_{12}(\mathbf{Q})|\mathrm{e}_1\rangle\langle\mathrm{e}_2|+\vec{\mu}_{21}(\mathbf{Q})|\mathrm{e}_2\rangle\langle\mathrm{e}_1|, \tag{2.5}$$

where $\vec{\mu}_{12}(\mathbf{Q})$ and $\vec{\mu}_{21}(\mathbf{Q})$ are electronic transition dipole moments which may depend on the vibrational coordinates. Let us further assume that the molecule is initially in electronic state $|\mathrm{e}_1\rangle$ with vibrational distribution represented by the density matrix $\rho_{\mathbf{Q}}$. The absorption lineshape function then takes the form,

$$I(\omega)=(1/\pi)\mathrm{Re}\int_{0}^{\infty}\mathrm{d}t\ \mathrm{e}^{i\omega t}\mathrm{Tr}_{\mathbf{Q}}\left\{\rho_{\mathbf{Q}}\langle\mathrm{e}_1|\vec{\mu}(0)\cdot\mathrm{e}^{-iHt/\hbar}\vec{\mu}(0)\mathrm{e}^{iHt/\hbar}|\mathrm{e}_1\rangle\right\} \tag{2.6a}$$

$$=(1/\pi)\mathrm{Re}\int_{0}^{\infty}\mathrm{d}t\ \mathrm{e}^{i\omega t-\gamma t}\mathrm{Tr}_{\mathbf{Q}}\left\{\rho_{\mathbf{Q}}\vec{\mu}_{12}\cdot\mathrm{e}^{-ih_2t/\hbar}\vec{\mu}_{21}\mathrm{e}^{ih_1t/\hbar}\right\}, \tag{2.6b}$$

where we have integrated over the electronic states in Eq. 2.6b. If the molecule is in a pure vibrational state $|\chi_i\rangle$ then,

$$\rho(\mathbf{Q})=|\chi_i\rangle\langle\chi_i|, \tag{2.7}$$

and furthermore if $|\chi_i\rangle$ satisfies,

$$h_1|\chi_i\rangle=\hbar\omega_i|\chi_i\rangle, \tag{2.8}$$

then Eq. 2.6b yields,

$$I(\omega)=(1/\pi)\mathrm{Re}\int_0^\infty \mathrm{d}t\ \mathrm{e}^{i\omega t-\gamma t}<\chi_i|\vec{\mu}_{12}\cdot\mathrm{e}^{-ih_2t/\hbar}\vec{\mu}_{21}\mathrm{e}^{ih_1t/\hbar}|\chi_i> \tag{2.9a}$$

$$=(1/\pi)\mathrm{Re}\int_0^\infty \mathrm{d}t\ \mathrm{e}^{i\tilde{\omega}t-\gamma t}<\chi_i|\vec{\mu}_{12}\cdot\mathrm{e}^{-ih_2t/\hbar}\vec{\mu}_{21}|\chi_i>, \tag{2.9b}$$

$$=<\chi_i|\vec{\mu}_{12}\cdot(1/\pi)\ \mathrm{Re}\left\{\int_0^\infty \mathrm{d}t\ \mathrm{e}^{i\tilde{\omega}t-\gamma t}\mathrm{e}^{-ih_2t/\hbar}\vec{\mu}_{21}|\chi_i>\right\}. \tag{2.9c}$$

where $\tilde{\omega}=\omega+\omega_i$. Only when ($h_2=h_1$+constant) can Eq. 2.9a be interpreted as an electronic transition dipole correlation function; in most cases this condition is not satisfied. A more useful interpretation is Heller's time-dependent vibrational wavepacket propagation picture of photoabsorption[2] based on Eq. 2.9b.

There has been some controversy[5–8] as to whether the optical absorption lineshape function $I(\omega)$ is due to a δ-function pulse or a continuous wave (cw) source. Equation 2.9b seems to suggest that it holds for a δ-function pulse. Such a pulse would instantaneously prepare a wavepacket $\vec{\mu}_{21}|\chi_i>$ in the excited electronic state $|e_2>$, whose subsequent evolution is given by the operation with the propagator $\exp(-ih_2t/\hbar)$. A final Fourier transform of the autocorrelation function, scaled by the lifetime factor $\exp(-\gamma t)$ in the excited electronic state, is then required to give the absorption lineshape because the δ-function pulse spectrum is infinitely wide. On the other hand, the equivalent expression Eq. 2.9c seems to suggest that it holds for a continuous wave (cw) light source. Such a source prepares a Raman wavefunction[4] in the excited electronic state, as given by the bracketted term in Eq. 2.9c. A final Franck–Condon overlap gives the absorption lineshape, without the need for a further Fourier transform because the cw source is monochromatic. However, it can be shown[9] that the expression for $I(\omega)$, which is given by the ratio of the Fourier transform of the induced first order polarization of the system to the pulse spectrum, is actually *independent of the pulse shape*. Thus, it is the simplicity of the pulse shape and associated pulse spectrum that deceives the spectroscopist into reading a δ-function pulse or a cw source in the optical absorption lineshape function $I(\omega)$!

The case of a single molecule in a bath where the bath modes **X** are *independent* of **Q** can be similarly treated. The system Hamiltonian in this case can be written as,

$$H=(h_{1b}(\mathbf{X})+h_1(\mathbf{Q}))|1><1| \\ +(h_{2b}(\mathbf{X})+h_2(\mathbf{Q})-i\hbar\gamma)|2><2|, \tag{2.10}$$

where $h_{1b}(\mathbf{X})$ and $h_{2b}(\mathbf{X})$ are the vibrational Hamiltonians for the bath. Such a model can only give rise to pure electronic dephasing. Assuming the same expression for the transition dipole operator as Eq. 2.5, the extension of Eq. 2.6b for the absorption lineshape function is simply given by,

$$I(\omega)=(1/\pi)\mathrm{Re}\int_0^\infty \mathrm{d}t\ \mathrm{e}^{i\omega t-\gamma t}\mathrm{Tr}_\mathrm{Q}\left\{\rho_\mathrm{Q}\ \vec{\mu}_{12}\cdot\mathrm{e}^{-ih_2t/\hbar}\vec{\mu}_{21}\mathrm{e}^{ih_1t/h}\right\} \\ \times\mathrm{Tr}_\mathrm{X}\left\{\rho_\mathrm{X}\ \mathrm{e}^{-ih_{2b}t/h}\mathrm{e}^{ih_{1b}t/h}\right\} \tag{2.11a}$$

$$=(1/\pi)\mathrm{Re}\int_0^\infty \mathrm{d}t\ \mathrm{e}^{i\tilde{\omega}t-\gamma t}<\chi_i|\vec{\mu}_{12}\cdot\mathrm{e}^{-ih_2t/\hbar}\vec{\mu}_{21}|\chi_i>\Phi_\mathrm{b}(t), \tag{2.11b}$$

where ρ_X is the density matrix for the initial vibrational distribution of the bath in electronic state $|e_1>$. In Eq. 2.11b we have assumed that the molecule is initially in a pure state $|\chi_i>$ satisfying Eq. 2.8. The difference from the isolated molecule case, Eq. 2.9b, is the introduction of the bath correlation funtion $\Phi_\mathrm{b}(t)$ defined as,

$$\Phi_\mathrm{b}(t)=\mathrm{Tr}_\mathrm{X}\left\{\rho_\mathrm{X}\ \mathrm{e}^{-ih_{2b}t/\hbar}\mathrm{e}^{ih_{1b}t/\hbar}\right\} \tag{2.12}$$

A similar result has been derived by Harris et al.[10] using the Fermi golden rule, and various models for the bath correlation function have also been discussed.

Raman Scattering. Gordon[1] has shown that the differential scattering cross section (i.e. scattered power/incident intensity) for scattering into a frequency range $\mathrm{d}\omega$ and a solid angle element $\mathrm{d}\Omega$ is given by the Fourier transform of the polarizability correlation function,

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_\mathrm{S}}=\left(\frac{\omega_\mathrm{S}}{c}\right)^4(1/2\pi)\int_{-\infty}^{\infty}\mathrm{d}t\ \mathrm{e}^{-i\omega t}<\alpha_\mathrm{SI}^\dagger(0)\alpha_\mathrm{SI}(t)>, \tag{3.1}$$

where ω_S is the scattered frequency; α_SI is the polarizability tensor (operator) projected along the direction of the electric vectors $\hat{\varepsilon}_\mathrm{I}$ and $\hat{\varepsilon}_\mathrm{S}$ in the incident (I) and scattered (S) radiation, respectively; and the transform frequency $\omega=\omega_\mathrm{I}-\omega_\mathrm{S}$ where ω_I is the incident frequency. The time-dependent Heisenberg operator $\alpha(t)$ for the polarizability tensor (operator) at time t is defined by,

$$\alpha(t)=\mathrm{e}^{iHt/\hbar}\alpha(0)\mathrm{e}^{-iHt/\hbar}. \tag{3.2}$$

In the rotational Raman application of Gordon,[1] α_SI is simply a polarizability tensor,[11] which depends on the vibrational quantum number of the band, and H is the Hamiltonian for rotation–translation motion.

Our focus here is on vibrational Raman scattering, and α_SI is a polarizability tensor operator which has a dependence on the vibrational Hamiltonians of the excited electronic states.[3] Equation 3.1 applies to an ensemble of interacting molecules is well as a single molecule. For the latter case, we take H to be given by Eq. 2.4 and assume that the molecule is initially in electronic state $|e_1>$ with a vibrational distribution represented by the density matrix ρ_Q. Then Eq. 3.1 can be written as,

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_\mathrm{S}}=\left(\frac{\omega_\mathrm{S}}{c}\right)^4(1/2\pi)\int_{-\infty}^{\infty}\mathrm{d}t\ \mathrm{e}^{-i\omega t}\mathrm{Tr}_\mathrm{Q}\left\{\rho_\mathrm{Q}<e_1|\alpha_\mathrm{SI}^\dagger(0) \\ \times\mathrm{e}^{iHt/\hbar}\alpha_\mathrm{SI}(0)\mathrm{e}^{-iHt/\hbar}|e_1>\right\}. \tag{3.3}$$

In the case of a state-to-state vibrational Raman scattering, we start with an initial pure state where ρ_Q is given by Eq. 2.7, and insert a complete set of vibrational states $(\sum_f|\chi_f><\chi_f|=1)$ for electronic state $|e_1>$ in Eq. 3.3 to give,

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega_\mathrm{S}}=\sum_f\left(\frac{\omega_\mathrm{S}}{c}\right)^4(1/2\pi)\int_{-\infty}^{\infty}\mathrm{d}t\ \mathrm{e}^{-i(\omega-\omega_f+\omega_i)t}<\chi_i|\left(<e_1|\alpha_\mathrm{SI}^\dagger(0)|e_1>\right)|\chi_f> \\ \times<\chi_f|\left(<e_1|\alpha_\mathrm{SI}(0)|e_1>\right)|\chi_i> \tag{3.4a}$$

$$=\sum_f\left(\frac{\omega_\mathrm{S}}{c}\right)^4\left|<\chi_f|\left(<\mathrm{e}_1|\alpha_\mathrm{SI}(0)|\mathrm{e}_1>\right)|\chi_i>\right|^2\delta(\omega-\omega_f+\omega_i). \tag{3.4b}$$

Equation 3.4b gives the Schrödinger representation (Fermi golden rule) of the differential scattering cross section from an initial state $|\chi_i>$ to all the resolved final states $|\chi_f>$ of electronic state $|\mathrm{e}_1>$. This was the starting point of Gordon's work.1) An observable is given by integrating over the scattered frequency ω_S; the differential scattering cross section from $|\chi_i>$ to $|\chi_f>$ in a solid angle element $\mathrm{d}\Omega$ and a fixed incident frequency ω_I is then given by,

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{i\to f}=\left(\frac{\overline{\omega}_\mathrm{S}}{c}\right)^4\left|<\chi_f|\left(<\mathrm{e}_1|\alpha_\mathrm{SI}(0)|\mathrm{e}_1>\right)|\chi_i>\right|^2, \tag{3.5}$$

where by the conservation of energy,

$$\overline{\omega}_\mathrm{S}=\omega_\mathrm{I}-\omega_f+\omega_i. \tag{3.6}$$

Quantum-mechanically, the effect of the polarizability tensor operator for electronic state $|\mathrm{e}_1>$ is given by a sum of a resonant and anti-resonant term,12)

$$\begin{aligned}&\left(<\mathrm{e}_1|\alpha_\mathrm{SI}(0)|\mathrm{e}_1>\right)|\chi_i>\\&\quad=\left(<\mathrm{e}_1|(\vec{\mu}(0)\cdot\hat{\varepsilon}_\mathrm{S})\frac{1}{H-\hbar(\omega_i+\omega_\mathrm{I})}(\vec{\mu}(0)\cdot\hat{\varepsilon}_\mathrm{I})|\mathrm{e}_1>\right)|\chi_i>\\&\quad+\left(<\mathrm{e}_1|(\vec{\mu}(0)\cdot\hat{\varepsilon}_\mathrm{I})\frac{1}{H-\hbar(\omega_i-\omega_\mathrm{S})}(\vec{\mu}(0)\cdot\hat{\varepsilon}_\mathrm{S})|\mathrm{e}_1>\right)|\chi_i>\end{aligned} \tag{3.7a}$$

$$\begin{aligned}&=\left((\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{S})\frac{1}{h_2-i\hbar\gamma-\hbar(\omega_i+\omega_\mathrm{I})}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{I})\right)|\chi_i>\\&+\left((\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{I})\frac{1}{h_2-i\hbar\gamma-\hbar(\omega_i-\omega_\mathrm{S})}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{S})\right)|\chi_i>\end{aligned} \tag{3.7b}$$

$$\begin{aligned}&=(\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{S})(i/\hbar)\int_0^\infty\mathrm{d}t\ \mathrm{e}^{i\widetilde{\omega}_\mathrm{I}t-\gamma t}\mathrm{e}^{-ih_2t/h}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{I})|\chi_i>\\&+(\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{I})(i/\hbar)\int_0^\infty\mathrm{d}t\ \mathrm{e}^{-i\widetilde{\omega}_\mathrm{S}t--\gamma t}\mathrm{e}^{-ih_2t/\hbar}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{S})|\chi_i>.\end{aligned} \tag{3.7c}$$

The dipole moment in Eq. 3.7a is given by Eq. 2.5 and the energy denominator in Eq. 3.7b is written as a Laplace-Fourier transform in Eq. 3.7c to give the Heisenberg picture. The integrals in Eq. 3.7c correspond to Raman wavefunctions,4) and we have defined $\widetilde{\omega}_\mathrm{I}=\omega_\mathrm{I}+\omega_i$ and $\widetilde{\omega}_\mathrm{S}=\omega_\mathrm{S}-\omega_i$. Inserting Eq. 3.7c into Eq. 3.5, we obtain,

$$\begin{aligned}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{i\to f}=\frac{1}{\hbar^2}\left(\frac{\overline{\omega}_\mathrm{S}}{c}\right)^4\Bigg|&\int_0^\infty\mathrm{d}t\ \mathrm{e}^{i\widetilde{\omega}_\mathrm{I}t-\gamma t}<\chi_f|(\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{S})\ \mathrm{e}^{-ih_2t/\hbar}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{I})|\chi_i>\\&+\int_0^\infty\mathrm{d}t\ \mathrm{e}^{-i\widetilde{\omega}_\mathrm{S}t-\gamma t}<\chi_f|(\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{I})\ \mathrm{e}^{-ih_2t/\hbar}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{S})|\chi_i>\Bigg|^2.\end{aligned} \tag{3.8}$$

This result is identical to the time-frame formulation of vibrational Raman scattering derived by Lee and Heller3) where the second-order time-dependent perturbation theory was used as the starting point. The physical interpretation of Eq. 3.8 in terms of vibrational wavepacket propagation on the excited state surface has previously been given.3)

The case of a single molecule in a bath, with the same assumptions as in Absorption section, leads to an extension of Eq. 3.3,

$$\begin{aligned}\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\ \mathrm{d}\omega_\mathrm{S}}=\left(\frac{\omega_\mathrm{S}}{c}\right)^4(1/2\pi)\int_{-\infty}^\infty\mathrm{d}t\ \mathrm{e}^{-i\omega t}\mathrm{Tr_X Tr_Q}\Big\{&\rho_\mathrm{X}\rho_\mathrm{Q}<\mathrm{e}_1|\alpha^\dagger_\mathrm{SI}(0)\\&\times\mathrm{e}^{iHt/\hbar}\alpha_\mathrm{SI}(0)\mathrm{e}^{-iHt/\hbar}|\mathrm{e}_1>\Big\}.\end{aligned} \tag{3.9}$$

By inserting the complete set of bath states $(\sum_n|\xi_{\mathrm{b}n}><\xi_{\mathrm{b}n}|)$ where $h_{1\mathrm{b}}|\xi_{\mathrm{b}n}>=\hbar\omega_{\mathrm{b}n}|\xi_{\mathrm{b}n}>$ at the appropriate places, the differential scattering cross section from $|\chi_i>$ to $|\chi_f>$ over all scattered frequencies is easily shown to be given by,

$$\begin{aligned}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{i\to f}=\frac{1}{c^4}\sum_m\sum_n\mathrm{Tr_X}\Big\{&\rho_\mathrm{X}<\chi_i|\left(<\mathrm{e}_1|\alpha^\dagger_\mathrm{SI}(0)|\mathrm{e}_1>\right)|\chi_f>|\xi_{\mathrm{b}n}><\xi_{\mathrm{b}n}|\\&\times<\chi_f|\left(<\mathrm{e}_1|\alpha_\mathrm{SI}(0)|\mathrm{e}_1>\right)|\chi_i>|\xi_{\mathrm{b}m}><\xi_{\mathrm{b}m}|\Big\}\\&\times(\omega_\mathrm{I}+\omega_i+\omega_{\mathrm{b}m}-\omega_f-\omega_{\mathrm{b}n})^4.\end{aligned} \tag{3.10}$$

By an extension of Eqs. 3.7a—c, the effect of the polarizabiliy tensor operator in the Heisenberg picture is given by,

$$\begin{aligned}&\left(<\mathrm{e}_1|\alpha_\mathrm{SI}(0)|\mathrm{e}_1>\right)|\chi_i>|\xi_{\mathrm{b}m}>=\\&\left(<\mathrm{e}_1|(\vec{\mu}(0)\cdot\hat{\varepsilon}_\mathrm{S})\frac{1}{H-\hbar(\omega_i+\omega_{\mathrm{b}m}+\omega_\mathrm{I})}(\vec{\mu}(0)\cdot\hat{\varepsilon}_\mathrm{I})|\mathrm{e}_1>\right)|\chi_i>|\xi_{\mathrm{b}m}>\\&+\left(<\mathrm{e}_1|(\vec{\mu}(0)\cdot\hat{\varepsilon}_\mathrm{I})\frac{1}{H-\hbar(\omega_i+\omega_{\mathrm{b}m}-\omega_\mathrm{S})}(\vec{\mu}(0)\cdot\hat{\varepsilon}_\mathrm{S})|\mathrm{e}_1>\right)|\chi_i>|\xi_{\mathrm{b}m}>\\&=\Big\{(\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{S})(i/\hbar)\int_0^\infty\mathrm{d}t\ \mathrm{e}^{i\widetilde{\omega}_\mathrm{I}t-\gamma t}\mathrm{e}^{-ih_2t/\hbar}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{I})|\chi_i>\\&+\ (\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{I})(i/\hbar)\int_0^\infty\mathrm{d}t\ \mathrm{e}^{-i\widetilde{\omega}_\mathrm{S}t-\gamma t}\mathrm{e}^{-ih_2t/\hbar}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{S})|\chi_i>\Big\}\\&\times\mathrm{e}^{-ih_{2\mathrm{b}}t/\hbar}\mathrm{e}^{ih_{1\mathrm{b}}t/\hbar}|\xi_{\mathrm{b}m}>.\end{aligned} \tag{3.11b}$$

The state-to-state differential scattering cross section in the time-dependent form is then given by,

$$\begin{aligned}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{i\to f}=\frac{1}{c^4\hbar^2}\int_0^\infty\mathrm{d}t'\int_0^\infty\mathrm{d}t\ &A^*(t')A(t)\\&\times\mathrm{Tr_X}\Big\{\rho_\mathrm{X}\mathrm{e}^{-ih_{1\mathrm{b}}t'/h}\mathrm{e}^{ih_{2\mathrm{b}}t'/h}\sum_n|\xi_{\mathrm{b}n}><\xi_{\mathrm{b}n}|\\&\times\mathrm{e}^{-ih_{2\mathrm{b}}t/h}\mathrm{e}^{ih_{1\mathrm{b}}t/h}\sum_m|\xi_{\mathrm{b}m}><\xi_{\mathrm{b}m}|\Big\}\\&\times(\omega_\mathrm{I}+\omega_i+\omega_{\mathrm{b}m}-\omega_f-\omega_{\mathrm{b}n})^4,\end{aligned} \tag{3.12}$$

where we define the vibrational correlation function $A(t)$ for the molecule to be,

$$\begin{aligned}A(t)=&\mathrm{e}^{i\widetilde{\omega}_\mathrm{I}t-\gamma t}<\chi_f|(\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{S})\ \mathrm{e}^{-ih_2t/h}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{I})|\chi_i>\\&+\mathrm{e}^{-i\widetilde{\omega}_\mathrm{S}t-\gamma t}<\chi_f|(\vec{\mu}_{12}\cdot\hat{\varepsilon}_\mathrm{I})\ \mathrm{e}^{-ih_2t/h}(\vec{\mu}_{21}\cdot\hat{\varepsilon}_\mathrm{S})|\chi_i>.\end{aligned} \tag{3.13}$$

In the absence of the bath, Eq.3.12 reduces to Eq. 3.8 for an isolated molecule. If in the scattering process, the change in the bath modes can only occur between nearly degenerate states, i.e. $|\omega_{\mathrm{b}m}-\omega_{\mathrm{b}n}|\ll(\omega_\mathrm{I}+\omega_i-\omega_f)$, the quartic frequency term becomes $\overline{\omega}_\mathrm{S}^4$, where $\overline{\omega}_\mathrm{S}$ is defined by Eq. 3.6, and by closure over the bath states, Eq. 3.12 gives the simpler looking result,

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{i\to f}\cong\frac{\overline{\omega}_\mathrm{S}^4}{c^4\hbar^2}\int_0^\infty\mathrm{d}t'\int_0^\infty\mathrm{d}t\ A^*(t')A(t)\Phi_\mathrm{b}(t'-t). \tag{3.14}$$

Here the bath correlation function $\Phi_b(t'-t)$ which depends only on the difference in the two times is defined the same as Eq. 2.12 for absorption. This is similar to the equation derived by Harris et al.[10] for Raman scattering with pure dephasing, but we have also shown that the quartic frequency dependence in the differential cross section makes it necessary to make the additional assumption that the change in energy of the bath modes in Raman scattering is much less than the energy of the scattered light.

Conclusion. The general formulation for absorption and Raman scattering in the Heisenberg representation is in terms of the dipole and polarizability correlation functions. It is clear from Gordon's work[1] that (a) the absorption lineshape for an infrared spectrum is given by a Fourier transform of the vibrational transition dipole correlation function of the absorbing molecules in the ground electronic state, and (b) the differential cross section for rotational Raman scattering is given by a Fourier transform of the polarizability tensor correlation function of the molecule. However, for optical absorption and vibrational Raman scattering, it is more useful to phrase the Heisenberg representation in terms of vibrational wavepacket propagation on the excited electronic state surface(s).[2–4] We have shown that this viewpoint can be derived directly from the correlation function formalism by an appropriate choice of the system Hamiltonian and the dipole and polarizability operators.

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