Eigenstate-free, Green function, calculation of molecular absorption and fluorescence line shapes

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Green function techniques are used to develop a simple and efficient method towards the calculation of optical absorption, excitation, and dispersed fluorescence spectra of large harmonic polyatomic molecules. The molecular line shapes are expressed in terms of Fourier transforms of appropriate correlation functions which may be explicitly evaluated. Closed expressions are derived for a general harmonic molecule with two electronic states including equilibrium displacements, frequency changes, and Dushinsky rotation, within the Condon approximation. A simple method for extracting the complete set of parameters characterizing the ground and the electronically excited states from supersonic beam absorption and emission spectra is presented. Detailed calculations are performed for a model system with ten vibrational modes, and the sensitivity of the various experimental observables to Dushinsky rotation is analyzed.

I. INTRODUCTION

Recent progress in molecular spectroscopic techniques creates the need for developing theoretical approaches suitable for calculating spectral line shapes of large polyatomic molecules. In this article we utilize Green function techniques to calculate electronic spectra of isolated polyatomic molecules. Our results are particularly useful for the spectroscopy of ultracold molecules in supersonic beams. Moreover, they may be conveniently extended to calculate the spectra of such molecules in condensed phases (solutions, solid matrices) by properly incorporating external broadening mechanisms. The calculation of molecular nonlinear susceptibilities and coherent Raman line shapes (CARS) of large polyatomic molecules may also be carried out using these methods. We consider a polyatomic molecule with two electronic states, \( |g\rangle \) and \( |e\rangle \), and \( N \) vibrational degrees of freedom. Within the adiabatic approximation the molecular Hamiltonian is given by

\[
H = |g\rangle H_g \langle g| + |e\rangle \langle e| (\omega_{eg} + H_e - i\gamma/2) |e\rangle,
\]

where

\[
H_g = - \sum_{j=1}^{N} \frac{\hbar^2}{2m_j} \frac{\partial^2}{\partial Q_j^2} + V_g(Q_1,\ldots,Q_N)
\]

and

\[
H_e = - \sum_{j=1}^{N} \frac{\hbar^2}{2m_j} \frac{\partial^2}{\partial Q_j^2} + V_e(Q_1,\ldots,Q_N).
\]

Here \( m_j \) and \( Q_j \) are the mass and Cartesian coordinate of the \( j \)th nucleus, \( \omega_{eg} \) is the electronic transition frequency between the lowest vibronic states of \( |g\rangle \) and \( |e\rangle \) (0-0 transition), and \( \gamma \) denotes the inverse lifetime of the electronically excited vibronic states. In this article, we shall be interested in calculating the absorption, the excitation, and the dispersed fluorescence line shapes of the polyatomic molecule represented by the Hamiltonian Eq. (1) (Fig. 1). The interaction of the molecule with the electromagnetic field \( E(t) \) is given by

\[
H_{\text{int}} = - \mu E(t),
\]

where the dipole operator \( \mu \) is

\[
\mu = \mu(Q) (|g\rangle \langle e| + |e\rangle \langle g|).
\]

The absorption line shape of an \( \omega_L \) photon \( \sigma(\omega_L) \) is given by

\[
\sigma(\omega_L) = \sum_{n,k} P(n) |\mu_{sk}|^2 \frac{\gamma/2}{(\omega_L - \omega_{eg} + \epsilon_n - \epsilon_k)^2 + \gamma^2/4}.
\]

The steady-state fluorescence rate, whereby the molecule absorbs an \( \omega_L \) photon and emits an \( \omega_S \) photon, is given by the Kramers–Heisenberg expression:

\[
\text{FIG. 1. The level scheme for a fluorescence process. } |n\rangle \text{ and } |m\rangle \text{ are vibronic states corresponding to the ground electronic state } |g\rangle. |k\rangle \text{ and } |j\rangle \text{ are vibronic states corresponding to the excited electronic state } |e\rangle. \omega_{eg} \text{ is the fundamental (0-0) transition frequency.}
\]

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\[ \hat{T}(\omega_L, \omega_S) = 2\pi \sum_{n,m} P(n) \left( \sum_k \frac{\mu_{mk} \mu_{kn}}{\omega_L - \omega_{eq} + \epsilon_n - \epsilon_k + i\gamma/2} \right)^2 \times \delta(\omega_S - \omega_L - \epsilon_n + \epsilon_m) \]  

(4b)

where \( I_{mn}(\omega_L) \) is the Raman excitation profile for the transition from state \(|n\rangle\) to state \(|m\rangle\):

\[ I_{mn}(\omega_L) = 2\pi \left( \sum_k \frac{\mu_{mk} \mu_{kn}}{\omega_L - \omega_{eq} + \epsilon_n - \epsilon_k + i\gamma/2} \right)^2. \]  

(4c)

Here \(|n\rangle\) and \(|m\rangle\) represent vibrational eigenstates of \( H_g \), whereas \(|k\rangle\) are the vibrational eigenstates of \( H_s \), i.e.,

\[ H_g |n\rangle = \hbar \epsilon_n |n\rangle, \]  

(5a)

\[ H_s |m\rangle = \hbar \epsilon_m |m\rangle, \]  

(5b)

and

\[ H_s |k\rangle = \hbar \epsilon_k |k\rangle. \]  

(5c)

Hereafter, we shall set \( \hbar = 1 \). The molecule is assumed to be initially in the \(|g\rangle\) electronic state, and \( P(n) \) is the equilibrium population of \(|n\rangle\). Equations (4) may be used to calculate the molecular absorption and emission line shapes provided all the vibrational eigenstates and their dipole matrix elements can be evaluated and provided the necessary summations can be carried out. Both of these steps become extremely tedious as the molecular size increases. This is the motivation for developing the Green function eigenstate-free techniques which provide a convenient way for overcoming these difficulties. Correlation function time domain techniques are commonly used in macroscopic theories of spectral line shapes. The basic idea is to start with a formal expression for the experimental observable and develop an approximate method towards its direct calculation. A successful application of these techniques may allow us to avoid the necessity of calculating the entire spectrum of eigenvalues and eigenvectors of a complex system. Green functions play an important role in utilizing these techniques. The simplicity of the Green functions for harmonic systems in the coordinate representation has been extensively used in semiclassical theories of quantum propagators, spectra of impurities in solids, radiationless transitions, and molecular line shapes. In the present article, we develop exact expressions for absorption, excitation, and dispersed fluorescence spectra of isolated harmonic polyatomic molecules. We shall now introduce the excited state Green function, 

\[ G(E) = (E - H_e + i\gamma/2)^{-1} \]  

(6a)

the ground state Green function, 

\[ \bar{G}(E) = (E - H_g + i\gamma/2)^{-1} \]  

(6b)

and the corresponding operators (the \( T \) matrix)

\[ T(E) = iG(E)\mu \]  

(7a)

and

\[ \bar{T}(E) = i\bar{G}(E)\mu. \]  

(7b)

Equation (4) may then be recast in the form

\[ \sigma(\omega_L) = -\sum_n P(n) \text{Im} T_{nn}(\omega_L - \omega_{eq} + \epsilon_n), \]  

(8a)

\[ \hat{T}(\omega_L, \omega_S) = \sum_{n,m} P(n) I_{mn}(\omega_L) \delta(\omega_S - \omega_L - \epsilon_n + \epsilon_m), \]  

(8b)

and

\[ I_{mn}(\omega_L) = 2\pi |T_{mn}(\omega_L - \omega_{eq} + \epsilon_n)|^2. \]  

(8c)

Emission spectra of ultracold molecules in supersonic beams are usually obtained by tuning the incident frequency to be on resonance with a single doorway state \(|k\rangle\), i.e., \( \epsilon_n + \omega_L = \omega_{eq} + \epsilon_k \). If this doorway state is well separated from all other molecular states, we may simplify Eq. (8b) and recast it in a form which does not include any summations over vibronic eigenstates. The derivation is given in Appendix A, and the dispersed fluorescence, denoted \( S_x(\omega_S) \), is in this case given by

\[ S_x(\omega_S) = -\text{Im} \bar{T}_{xx}(\epsilon_x - \omega_S + \omega_{eq}). \]  

(9)

The calculation of the absorption, the fluorescence line shapes, and the Raman profile reduces therefore to evaluating the appropriate matrix elements of \( T(E) \) and \( \bar{T}(E) \). Hereafter for simplicity, we shall invoke the Condon approximation and assume that \( \mu(Q) \) is independent of \( Q \). We then get

\[ \mu_{nk} = \mu_{eq} \langle n | k \rangle. \]  

(10)

Equations (8) and (9) can then be written in the form

\[ \sigma(\omega_L) = -|\mu_{eq}|^2 \sum_n P(n) \text{Im} G_{nn}(\omega_L - \omega_{eq} + \epsilon_n), \]  

(11a)

\[ \hat{T}(\omega_L, \omega_S) = \sum_{n,m} P(n) I_{mn}(\omega_L) \delta(\omega_S - \omega_L - \epsilon_n + \epsilon_m), \]  

(11b)

\[ I_{mn}(\omega_L) = 2\pi |\mu_{eq}|^2 |G_{mn}(\omega_L - \omega_{eq} + \epsilon_n)|^2, \]  

(11c)

and

\[ S_x(\omega_S) = -|\mu_{eq}|^2 \text{Im} \bar{G}_{xx}(\epsilon_x - \omega_S + \omega_{eq}). \]  

(11d)

We have, thus, reduced the theoretical calculation of the spectral line shapes of our molecule [Eq. (1)] to calculating the appropriate matrix elements of the Green function [Eq. (6)]. The latter may be conveniently calculated in the time domain by defining

\[ G(t) = \exp(-iH_s t), \]  

(12a)

and

\[ \bar{G}(t) = \exp(-iH_g t), \]  

(12b)

so that

\[ G(E) = -i \int_0^\infty dt \exp(iEt - \gamma t/2) G(t). \]  

(12c)
\[
\mathcal{G}(E) = -i \int_0^\infty dt \exp(iEt - \gamma t/2)\mathcal{G}(t). \tag{12d}
\]

Equations (11) and (12) will be explicitly evaluated in the coming sections for a general model of harmonic molecules. A Gaussian wave packet method was proposed towards the calculation of the time evolution operator [Eq. (12a)]. The method provides a numerical algorithm for computing the matrix elements \(G_{20}(t)\), where the initial state is the ground vibrational state \(|0\rangle\). The present Green function approach provides analytical closed form expressions for the general matrix element \(G_{mn}(t)\) and allows the calculation of the absorption, the dispersed fluorescence, and the excitation profiles.

II. THE GREEN FUNCTION FOR A GENERAL HARMONIC MOLECULE

We shall now specialize to harmonic molecules, whereby \(V_r\) and \(V_s\) are quadratic functions of \(Q_s\). The most general harmonic polyatomic molecule may be represented by the Hamiltonian

\[
H = |g\rangle H_g \langle g| + |e\rangle (\omega_{eg} + H_e - i\gamma/2) \langle e|, \tag{13}
\]

with

\[
H_g = 1/2 \sum_{j=1}^N \omega_j^g (p_j^g)^2 + q_j^g - 1, \tag{14a}
\]

\[
H_e = 1/2 \sum_{j=1}^N \omega_j^e (p_j^e)^2 + q_j^e - 1, \tag{14b}
\]

and where

\[
q' = Sq^* + D. \tag{15}
\]

Here \(\omega_{eg}\) is the fundamental \((0-0)\) transition frequency and we have adopted the common spectroscopic notation, whereby we label ground-state quantities by a double prime and excited state quantities by a single prime. \(p'\) and \(q'\) denote the dimensionless momentum and coordinate vectors, whose elements correspond to the normal modes:

\[
p_j' = \left(\frac{1}{m_j\omega_j^g}\right)^{1/2}p_j^g, \tag{16a}
\]

\[
q_j' = \left(\frac{m_j\omega_j^e}{\hbar}\right)^{1/2}Q_j^e. \tag{16b}
\]

\(p'\) and \(Q'\) being the conjugate momentum and the normal coordinate, respectively, of the \(j\)th mode of the excited state. A similar transformation between \(p_{j'}^g\), \(q_{j'}^g\) and \(P_{j'}^e\), \(Q_{j'}^e\) is defined by changing all ' indexes in Eqs. (16) to . \(S\) is the Dushinsky rotation matrix \(^{32}\) which allows the ground-state and the excited-state normal modes to be different. \(S\) denotes the transformation for the dimensionless coordinates \(q\). The matrix \(S\) representing the transformation between the normal modes is orthogonal:

\[
Q' = S Q^* + D, \tag{17}
\]

\[
S^T S = I, \tag{18a}
\]

where \(S^T\) denotes the transpose of \(S\), i.e., \((S^T)_y^* = S_y^*\). \(S\) is related to \(\mathcal{S}\) by

\[
S_y = (\omega'_y/\omega_y^0)^{1/2}\mathcal{S}_y. \tag{18b}
\]

\(D\) is the dimensionless displacement between the equilibrium configuration of the two electronic states. Its components \(D_{ij}\) are related to \(\mathcal{D}_{ij}\) by

\[
D_{ij} = \left(\frac{m_i\omega_j^0}{\hbar}\right)^{1/2} \mathcal{D}_{ij}. \tag{19}
\]

We shall be interested in calculating the matrix elements of \(G\) and \(\mathcal{G}\) [Eqs. (12)]. Their calculation is formally very similar and the expressions for \(G_{mn}(t)\) may be applied to calculate the matrix element \(G_{kj}(t)\) as well, by simply changing \(D\) to \(-S^{-1}D, S\) to \(S^{-1}\), and exchanging \(\omega_j^g\) and \(\omega_j^e\). We shall, therefore, focus on the evaluation of \(G_{mn}(t)\). The matrix element \(G_{mn}(t)\) may be written as the form

\[
G_{mn}(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq^* dq^m \psi_m(q^*) \psi_n(q^m) \exp(-iH_2t|q^m|), \tag{20}
\]

where

\[
\psi_m(q) = \prod_{j=1}^N \psi_{m_j}(q_j), \tag{21a}
\]

and

\[
\psi_{m_j}(q_j) = \pi^{-1/4}(m_j2^{m_j})^{-1/2} \exp(-1/2q_j^2) H_{m_j}(q_j). \tag{21b}
\]

is the \(m_j\)th eigenfunction of the \(j\)th mode and \(H_{m_j}(q_j)\) is the \(m_j\)th Hermite polynomial. The Green function in the \(q^*\) representation \(\langle q^m|\exp(-iH_2t)|q^m\rangle\) is Gaussian.\(^{11,24,25}\) By using the generating function of Hermite polynomials and performing a Gaussian integration, we have derived explicit expressions for the absorption spectrum \(\sigma(\omega_L)\) and the general Green function matrix element \(G_{mn}(t)\), i.e.,

\[
\sigma(\omega_L) = |\mu_{eg}|^2 \text{Re} \int_0^\infty dt \exp[i(\omega_L - \omega_{eg})t] \sigma(t) \tag{22a}
\]

and

\[
G_{mn}(t) = G_{00}(t) W_{mn}(t) = \sigma(t) W_{mn}(t). \tag{22b}
\]

The most general expression for \(G_{mn}(t)\) is presented in Appendix B, and its detailed derivation is given in Appendix C. \(\sigma(t)\) is given in Appendix D. \(\sigma_0(t)\) is the zero temperature limit of \(\sigma(t)\). In Appendix E we present a simplified expression for \(\sigma_0(t)\) in the absence of Dashinsky rotation. Several limiting cases of our general expression will be considered in the coming sections.

III. ELECTRONIC SPECTRA OF HARMONIC MOLECULES IN THE ABSENCE OF DUSHINSKY ROTATION

The final expressions of Sec. II, Eqs. (22) together with Appendices B and D, are greatly simplified when the normal modes in the ground and the electronically excited states are identical and the Dushinsky transformation matrix is diagonal, i.e.,

\[
S_y = (\omega'_y/\omega_y^0)^{1/2}S_y. \tag{23}
\]

We shall therefore focus on this case first. Making use of Eq. (23), all the matrices defined in Sec. II are diagonal and \(G_{mn}(t)\) may be factorized as
Equation (25b) then assumes the form
\[ \sigma_0(t) = \exp(-D^2/2) \exp[D^2/2 \exp(-i\omega t)] \]
and Eq. (29a) reduces to \[^{14,16}\]
\[ W_{\text{\scriptsize m}0}(t) = (m!2^n)^{-1/2} D^m \exp(-i\omega t) - 1)^m. \]

The absorption kernel \( \sigma(t) \) of Eq. (22a) at temperature \( T \) is given by substitution of Eq. (23) in Eqs. (D8), resulting in
\[ \sigma(t) = [\psi_T(t)]^{-1/2} \exp[D^2 f_T(t)] \]
with
\[ \psi_T(t) = \frac{1}{4\omega^* \omega} \left( \frac{\omega^* C^+_A \omega^* C^- A}{} \times \right) \]
\[ \times (\omega^* C^+_A + \omega^* C^- A) \]
and
\[ f_T(t) = -\frac{\omega^* C^- A}{\omega^* C^+_A + \omega^* C^- A} \]
where
\[ C = \pm 1 \pm \exp(-i\omega t), \]
\[ A = (\bar{n} + 1) \pm \bar{n} \exp(i\omega^* t), \]
\[ \bar{n} = \exp[(i\omega^* / kT) - 1]^* \].

When \( T = 0 \), \( \bar{n} = 0 \) and \( A = 1 \), we have \( \sigma(t) = \sigma_0(t) \) and Eqs. (32b) and (32c) reduce to Eqs. (26a) and (26b), respectively. When \( \omega = \omega^* = \omega \), \( \psi_T(t) = 1 \), \( f_T = -1/2 C_A \), and Eq. (32a) reduces to \[^{8,11,26}\]
\[ \sigma(t) = \exp[D^2 (\bar{n} + 1) \exp(-i\omega^* t)] \]
\[ + iD^2 \bar{n} \exp(i\omega^* t) - 1 \].

**IV. SPECTRA OF SUPERCOOLED MOLECULES**

In this section we shall consider the absorption and the fluorescence or Raman line shapes of supercooled molecules at zero temperature (\( T = 0 \)) including the Dushinsky rotation within the Condon approximation. This calculation applies to molecular line shapes in supersonic beams. In this case Eqs. (11) assume the form
\[ \sigma(\omega_L) = -|\mu_{eg}|^2 \text{Im} G_{\text{\scriptsize m}0}(\omega_L - \omega_{eg}), \]
\[ \tilde{I}(\omega_L, \omega_S) = \sum_m I_{\text{\scriptsize m}0}(\omega_L) \delta(\omega_S - \omega_L + \epsilon_m), \]
and
\[ I_{\text{\scriptsize m}0}(\omega_L) = 2\pi |\mu_{eg}|^2 |G_{\text{\scriptsize m}0}(\omega_L - \omega_{eg})|^2. \]

The only relevant matrix elements in this case are \( G_{\text{\scriptsize m}0} \). From Eqs. (B1)-(B4), we have
\[ G_{\text{\scriptsize m}0}(t) = \sigma_0(t) W_{\text{\scriptsize m}0}(t), \]
where
\[ \sigma_0(t) = \sigma_0(t) W_{\text{\scriptsize m}0}(t), \]
and
\[ \sigma_0(t) = \psi(t) \left| \psi(t) \right| \exp[D^2 f(t)] \]
with
\[ W_{\text{\scriptsize m}0}(t) = (m!2^n)^{-1/2} D^m \exp(-i\omega t - 1). \]

The quantities appearing in Eqs. (36) are defined in Appendix B. \( G_{\text{\scriptsize m}0}(t) = \sigma_0(t) \) is the absorption part and its Fourier transform gives the zero temperature absorption line.
shape \[ \text{[Eq. (35a)]} \]. The size of the \( S, l(t), \phi, \) and \( \Phi \) matrices in Eq. (36) is equal to the number of vibrational degrees of freedom \( N \). However, if we consider combination bands involving only \( N' \) modes \( (N' < N) \) (i.e., all \( m_j = 0 \), except for \( N' \) modes), then the actual size of these matrices reduces to \( N' \). Equations (36c) may be further simplified for excitations involving only one mode, i.e., \( |m\rangle = |0 \cdots 0 \cdots 0 \rangle \).

Equation (36c) then becomes
\[
W_{m0} = (m!)^{1/2} \frac{\partial^m}{\partial \mu^m} \exp \left[ - (\Phi_1)_{\mu \nu}^2 + 2 \zeta(t) \mu \right] |m = 0 \rangle
\]
\[= (m!)^{1/2} (\Phi_1)_{\mu \nu}^m H_m \left[ \zeta(t)/(\Phi_1)_{\mu \nu} \right] \]
\[(37)\]
where
\[\zeta(t) = [S^T(t)D]_i \]
\[(38)\]
and \( \Phi \) is given by Eq. (B6a). In particular we have
\[W_{10} = 2^{1/2} \zeta(t) \]
\[(39)\]
In the absence of Dushinsky rotation, \( G_{m0}(t) \) factorizes into a product of contributions from individual modes, and Eqs. (37) and (39) then reduced to Eqs. (29a) and (29c), respectively.

In concluding this section, we shall examine the absorption spectrum in more detail. In the case of a single mode, \( \sigma_0(t) \) [Eq. (25b)] may be expanded in a power series in \( \omega - \omega_\alpha \exp(-i\omega t) \). It can then be rearranged as
\[\sigma_0(t) = \frac{2(\omega \omega')^{1/2}}{\omega +} \exp(-D^2 \omega''/\omega+) \exp(-i\omega t) \]
\[\times \sum_{m=0}^{\infty} c_m (\omega - \omega_\alpha)^m \exp(-im\omega t) \]
\[(40a)\]
where the coefficients \( c_m \) are defined in Appendix D. When the upper and lower frequencies are the same \( (\omega = \omega' = \omega''), \) Eq. (40a) reduces to
\[\sigma_0(t) = \exp(-D^2/2) \sum_{m=0}^{\infty} 1/m!(D^2/2)^m \exp(-im\omega t) \]
\[(40b)\]
This is identical with Eq. (31a). Upon the substitution of Eq. (40a) into Eq. (22a), the absorption spectrum for a single mode assumes the form
\[\sigma(\omega_\alpha) = \pi |u_{\alpha \alpha}|^2 \frac{2(\omega \omega')^{1/2}}{\omega +} \exp(-D^2 \omega''/\omega+) \]
\[\times \sum_{m=0}^{\infty} c_m (\omega - \omega_\alpha)^m \delta(\omega_\alpha - \omega_m) \]
\[(41)\]
For multimode, harmonic molecules without Dushinsky rotation, the absorption line shape can be calculated as a convolution of the single mode line shape functions, i.e.,
\[\sigma(\omega_\alpha) = \int d\omega_1 \cdots \int d\omega_{N-1} \]
\[\times \sigma_1(\omega_\alpha - \omega_1) \sigma_2(\omega_1 - \omega_2) \cdots \sigma_{N-1}(\omega_{N-1}) \]
\[(42)\]
where \( \sigma_j(\omega_\alpha) \) is given by Eq. (41). Equations (40)–(42) may be used to extract the displacement parameter \( D_j \) from the absorption spectra of ultracold molecules in supersonic beams.\(^{26,30}\) To that end we introduce the quantity \( R(\omega) \) which denotes the ratio of the intensity of the absorption line at \( \omega_\alpha = \omega_{\alpha 0} + \omega \) to the fundamental \( 0 \rightarrow 0 \) transition. By definition \( R(0) = 1 \). We further denote
\[R_j \equiv R(\omega_j') \]
\[(43a)\]
and
\[Y_j \equiv \frac{R(\omega_j' + \omega_j')}{R(\omega_j' + \omega_j') + R(\omega_j')R(\omega_j')} \]
\[(43b)\]
In the absence of Dushinsky mixing, we have
\[D_j^2 = \begin{pmatrix} \omega_j' + \omega_j' \\ 2\omega_j'' \end{pmatrix}^2 2R_j \]
\[(44a)\]
and
\[Y_j = 0.5, \quad i \neq j. \]
\[(44b)\]
In deriving Eqs. (44), we have assumed that no Fermi resonance (i.e., no accidental degeneracy) occurs at the fundamental frequency \( \omega' \) and at the combination frequency \( \omega'_i + \omega'_j \).

In the case of an isolated single doorway state (see Appendix A), the \( 0_0' \) dispersed fluorescence is governed by the imaginary part of the matrix element \( G_{00}^0(\omega_{\alpha 0} - \omega_S) \). In analogy with \( R(\omega) \), we now introduce \( \overline{R}(\omega) \) to denote the ratio of the intensity of the emission line at \( \omega_S = \omega_{\alpha 0} - \omega \) to the fundamental \( (\omega = 0) \) emission line, following a \( 0_0' \) excitation. By definition \( \overline{R}(0) = 1 \). We further denote
\[\overline{R}_j = \overline{R}(\omega_j') \]
\[(45a)\]
and
\[\overline{Y}_j = \frac{\overline{R}(\omega_j' + \omega_j')}{\overline{R}(\omega_j' + \omega_j') + \overline{R}(\omega_j')\overline{R}(\omega_j')} \]
\[(45b)\]
In the absence of Dushinsky mixing and Fermi resonances, we obtain a relation similar to Eq. (44), i.e.,
\[D_j^2 = \frac{(\omega_j' + \omega_j')^2}{4\omega_j''\omega_j'} \cdot 2\overline{R}_j \]
\[(46a)\]
and
\[\overline{Y}_j = 0.5, \quad i \neq j. \]
\[(46b)\]
Equations (44) or (46) may be used to extract the displacement parameters \( D_j \) from the experimental absorption or the \( 0_0' \) emission spectra, respectively. In the absence of Dushinsky mixing, the \( D_j \) obtained from absorption [Eq. (44a)] and emission [Eq. (46a)] should be identical and also \( Y_j = \overline{Y}_j = 0.5 \) [Eqs. (44b) and (46b)]. When the \( D_j \) obtained from absorption and emission do not agree or when Eq. (44b) or (46b) do not hold, this may be an indication for the presence of Dushinsky rotation or Fermi resonances involving anharmonicities. In that case, a careful examination of \( Y_j \) and \( \overline{Y}_j \) may allow us to extract the complete Dushinsky rotation matrix \( S \) from the experimental absorption and \( 0_0' \) dispersed fluorescence. For an \( N \) mode system a complete knowledge of \( \overline{Y}_{ij} \) \((i, j = 1, \ldots, N)\) or \( Y_{ij} \) \((i, j = 1, \ldots, N)\) is sufficient to determine all the Dushinsky rotation matrix elements \( S_{ij} \).
TABLE I. Frequencies and displacements of the model system.

<table>
<thead>
<tr>
<th>mode j</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega_j^c) (cm(^{-1}))</td>
<td>755</td>
<td>1015</td>
<td>220</td>
<td>300</td>
<td>380</td>
<td>520</td>
<td>860</td>
<td>1180</td>
<td>1280</td>
<td>1340</td>
</tr>
<tr>
<td>(\omega_j^s) (cm(^{-1}))</td>
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<td>985</td>
<td>200</td>
<td>280</td>
<td>380</td>
<td>540</td>
<td>840</td>
<td>1160</td>
<td>1260</td>
<td>1320</td>
</tr>
<tr>
<td>(D_j)</td>
<td>1.5</td>
<td>1.2</td>
<td>0.5</td>
<td>0.3</td>
<td>1.0</td>
<td>0.5</td>
<td>1.0</td>
<td>0.7</td>
<td>0.35</td>
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</table>

V. MODEL CALCULATIONS

In the previous sections we derived the general expression for matrix elements of the excited state Green function \(G_{mn}(t)\) [Eqs. (25) and Appendix B]. The time evolution of this Green function is governed by the excited level Hamiltonian \(H_e\), while the states \(|m\rangle\) and \(|n\rangle\) are the vibronic states of \(H_e\). All the equations derived in this article for \(G_{mn}(t)\) may be applied to calculate the matrix elements of the ground state Green function \(\mathcal{G}_{nl}(t)\) as indicated in Sec. I. Such matrix elements are very useful in the calculation of absorption spectra, Raman profiles, the dispersed fluorescence, and in many other applications as well.\(^{11,16,17}\)

In this section we shall apply our results to calculate the absorption spectrum [Eq. (22a)], the single doorway state dispersed fluorescence [Eq. (11d)], and the Raman profiles [Eq. (11c)] of the model harmonic molecule with ten vibrational modes given in Table I. In order to examine the effect of the Dushinsky rotation, the first two modes in Table I were assumed to be mixed by a Dushinsky transformation with \(\Sigma_{13} = \sin \theta \left(-\pi/2 < \theta < \pi/2\right)\). In this case, the total Green function in the time domain may be factorized in the form\(^6\)

\[
G_{mn}(t) = G_{m'n'}(t) \prod_{j=1}^{10} G_{mpj}(t),
\]

(47)

where \(m' = (m_1, m_2)\) and \(n' = (n_1, n_2)\). A similar factorization holds for \(\mathcal{G}_{nl}(t)\) and \(\sigma(t)\) as well. The calculation of \(\sigma(\omega_e, I_{mn}(\omega_e)), S_e(\omega_e)\) involves a single Fourier transform [Eqs. (22a), (11), and (12)]. The time domain Green function was calculated at \(M = 8192\) points with a time interval \(\Delta t = 2\pi/(M \times \Delta\omega)\), where \(\Delta\omega = 5 \text{ cm}^{-1}\) is the spectral resolution of our calculation. A standard fast Fourier transform program was then used to calculate \(G_{nn}(\omega)\) or \(\sigma(\omega_e)\). The CPU time in PDP/11 is about 1 min for each of the spectra shown in Figs. 5–13. The following comments

FIG. 2. Absorption spectra of our ten mode model molecule (Table I) at \(T = 0\) K. Equation (36a) and its Fourier transform were used. The lower and upper spectra are for a Dushinsky rotation \(\theta = 0\) and \(\theta = -\pi/3\), respectively, defined in Sec. V and Eqs. (17) and (18). \(\gamma = 10 \text{ cm}^{-1}\).

FIG. 3. The \(\sigma^0_0\) dispersed fluorescence of the model molecule. Equations (11d) and (36a) have been used. From the bottom to the top the corresponding Dushinsky rotation angle, which is defined in Sec. V and Eq. (17), is \(-\pi/3, -\pi/6, 0, \pi/6, \pi/3, \pi/2\), respectively. The relative intensities of the strongest line in each spectra are 0.84, 1, 0.58, 0.68, 0.74, and 0.49, respectively.
need to be made regarding the choice of parameters used in the fast Fourier transform. $\Delta \omega$ is the desired spectral resolution. For the sake of a better numerical accuracy, we found it desirable to round off all the frequencies $\omega'$ and $\omega''$ to be integer multiples of the chosen spectral resolution $\Delta \omega$. The resulting Green function is obtained in the frequency range $-M\Delta \omega/2 < \omega < M\Delta \omega/2$. $M$ and $\Delta \omega$ are, thus, determined by the desired spectral resolution and spectral range of the calculation.

Figure 2 displays the absorption spectrum of our model molecule at zero temperature. The calculations were made using Eqs. (35a) and (36b). The lower curve is calculated in the absence of Dushinsky rotation, whereas in the upper curve we have assumed that modes 1 and 2 are mixed by a Dushinsky rotation angle of $\theta = -\pi/3$. Figure 3 shows the $0^0_s$ dispersed fluorescence spectrum calculated using Eqs. (11d) and (36b). The figure demonstrates a dramatic change in the spectra as $\theta$ is varied. In Fig. 4(A) we examine the effect of the Dushinsky rotation on the relative intensity of the fundamental lines. Shown are $R_1, R_2, R_1'$, and $R_2'$ [Eqs. (43a) and (45a)] as a function of the Dushinsky rotation angle. The intensity flow between the Dushinsky mixed modes is clearly seen. In Fig. 4(B) we examined the effects of the Dushinsky rotation on the combination bands. Shown are $Y_{12}$ and $\bar{Y}_{12}$ [Eqs. (43b) and (45b)] as a function of the Dushinsky rotation angle. The abrupt changes of $Y_{12}$ around $\theta = 0.28\pi$ and $-0.22\pi$ may be attributed to the constructive interference effect of the displacement and Dushinsky rotation. Figures 5 and 6 show the dispersed fluorescence corresponding to $1^1_0$ and $2^0_0$ excitation, respectively. The spectra were calculated using Eqs. (11d), (36b), and (F7). Most remarkable is the Dushinsky effect on the Raman profiles [Eq. (11c)] shown in Figs. 7–12. Hereafter we introduce $I^{(n)}_{10}(\omega_L)$ to denote the Raman profile when only mode 1 changes its quantum number from $n$ to $m$ in the Raman process, while all the other modes remain at zero temperature. Figures 7, 8, 10, and 11 show the Raman profiles of $I^{(1)}_{10}, I^{(2)}_{10}, I^{(3)}_{10}$, and $I^{(4)}_{10}$, respectively, for positive detuning, i.e., $\omega_L > \omega_{eg}$. A close examination of Figs. 7 and 8 reveals a similarity of the Raman profile $I^{(1)}_{10}(\omega_L)$ at $\theta$ and the profile $I^{(2)}_{10}(\omega_L)$ at $-\theta$; for example, the bottom panel ($\theta = -\pi/3$) of Fig. 7 and the second from top panel ($\theta = \pi/3$) of Fig. 8. The similarity between the Raman profile $I^{(1)}_{10}(\omega_L)$ with $\theta = 0$ and the profile $I^{(3)}_{10}(\omega_L)$ with $\theta = \pi/2$ may be understood by recognizing that a $\theta = \pi/2$ transformation amounts simply to interchanging $\omega'_1$ and $\omega'_2$. The same behavior is observed in $I^{(1)}_{11}(\omega_L)$ (Fig. 10) and $I^{(4)}_{11}(\omega_L)$ (Fig. 11) as well. In Fig. 9 we plot log $I^{(10)}_{10}(\omega_L)$ (lower panel) and log $I^{(11)}_{10}(\omega_L)$ (upper panel) for negative detunings

![FIG. 4. (A) Study of the Dushinsky effect on the relative intensity of fundamental lines $R_1$ and $R_2$ of the $T = 0$ K absorption spectra (solid lines) of Fig. 2 and $\bar{R}_1$ and $\bar{R}_2$ of the $0^0_s$ dispersed fluorescence (dashed lines) of Fig. 3. $R_1$ and $\bar{R}_1$ are defined by Eqs. (43a) and (45a), respectively. (B) Same as (A) but we make a plot of $Y_{12}$ (solid line) and $\bar{Y}_{12}$ (dashed line) vs $\theta$. $Y_{12}$ and $\bar{Y}_{12}$ are defined by Eqs. (43b) and (45b), respectively. When $\theta = 0$, Eqs. (44) and (46) hold.]

![FIG. 5. The same as Fig. 3 but for the $1^1_0$ dispersed fluorescence, in which one quantum of mode 1 has been excited. Equations (11d) and (F7) have been used. The relative scaling factors from bottom to top are 0.98, 0.88, 0.82, 0.85, 0.93, and 1, respectively.]
FIG. 6. The same as Fig. 5 but for $2^1_0$ dispersed fluorescence, i.e., the mode 2 being excited. The relative scaling factors are 0.92, 1, 0.59, 0.61, 0.77, and 0.54.

FIG. 7. Raman excitation profiles $I^{(1)}_{10}$ in which the system starts from $n = 0$ and ends at $m = 1$ of mode 1. From bottom to top, the corresponding Dushinsky rotation angle $\theta$ is $-\pi/3$, $-\pi/6, 0, \pi/6, \pi/3$, and $\pi/2$, and the relative scaling factors are 0.81, 1, 0.52, 0.28, 0.38, and 0.63, respectively. Equations (11c) and (F7) are involved in the calculation.

$(\omega_L - \omega_{eg} < 0)$. These figures also demonstrate the flow of intensity with the Dushinsky rotation. In Fig. 12 we show the Raman profile for the two-mode Raman transition from $n_i = 1, n_j = 0$ ($j \neq 1$) to the state $m_i = 1, m_j = 0$ ($j \neq 2$). These calculations were made using Eqs. (11c) and (B1). Finally, we have calculated the absorption spectrum of our model molecule with $\theta = \pi/4$ at finite temperatures using Eq. (D8). These calculations are displayed in Figs. 13 and 14. Figure 14 shows the same spectra of Fig. 13 but with a better resolution. The growing complexity of the spectrum with temperature due to sequence congestion is apparent. The present calculations demonstrate the efficiency and simplicity in utilizing Green function time-domain techniques towards the calculation of complex molecular spectra. The Condon approximation was invoked in this article for the sake of clarity. The methodology developed here may be extended towards the calculation of molecular line shapes, when the dipole operator depends explicitly on the nuclear coordinates. In this case, we should start with Eqs. (8) and (9) rather than Eq. (11), and the calculation can be done along the same lines, thereby relaxing the Condon approximation. The exact solution for harmonic isolated molecules may serve as a convenient starting point for constructing approximate theories for more complex situations. Anharmonicities may be introduced perturbatively. Effects of solvation and line broadening in condensed phases may be introduced using a stochastic formulation$^{11,20}$ which may allow us to relate the line broadening to the macroscopic properties of the solvent, such as viscosity and dielectric relaxation properties.

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APPENDIX A: DISPERSED FLUORESCENCE WITH A SINGLE DOORWAY STATE. DERIVATION OF EQ. (9)

When the incident frequency $\omega_L$ is resonant with an intermediate state $|\kappa\rangle$, we have

$$\omega_L - \omega_{eg} + \epsilon_n - \epsilon_k = 0. \quad (A1)$$

If the state $|\kappa\rangle$ is well separated from the other states, i.e., $\Delta \epsilon \gg \gamma$, the summation over $k$ inside the absolute value sign of Eq. (4b) reduces to only one term


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FIG. 8. The same as Fig. 7 but for Raman excitation profiles $I^{(2)}_{10}$ in which the system starts from $n = 0$ and ends at $m = 1$ of mode 2. The relative scaling factors are 0.57, 0.54, 0.76, 0.98, 1, and 0.75.

\[ T_{mn}(\omega_L - \omega_{eg} + \epsilon_n) = \sum_k \frac{\mu_{mk} \mu_{kn}}{\omega_L - \omega_{eg} + \epsilon_n - \epsilon_k + i\gamma/2} \approx \frac{2}{i\gamma} \mu_{me} \mu_{sn}. \]  

(A2)

Substituting Eqs. (A1) and (A2) into Eq. (4b), we get the line shape of scattered photon $\omega_S$,

\[ S_\nu(\omega_s) = A_\nu \sum_m |\mu_{me}|^2 \delta(\omega_S - \omega_{eg} + \epsilon_m - \epsilon_v), \]  

(A3)

where

\[ A_\nu = \frac{8\pi}{\gamma^2} \sum_n P(n)|\mu_{sn}|^2 \]

is a constant for the specific excitation to |$\nu$>. The $\delta$ function in Eq. (A3) may more properly be replaced by a Lorentzian to account for the phenomenological lifetime of state |$\nu$>. Except for the normalization constant, the dispersed fluorescence of emitting photon $\omega_S$ is now given by

\[ S_\nu(\omega_s) = \sum_m |\mu_{me}|^2 \frac{\gamma/2}{(\omega_S - \omega_{eg} + \epsilon_m - \epsilon_e)^2 + (\gamma/2)^2} \]

where we have used Eq. (6b). Equation (A4) is the same as Eq. (9).

**APPENDIX B: THE GREEN FUNCTION FOR GENERAL HARMONIC MOLECULES**

In this Appendix we present the final result for the Green function of the general harmonic polyatomic molecule whose Hamiltonian is given by Eqs. (13)–(15). The detailed derivation is given in Appendix C. The general expression for the matrix elements of the Green function is

\[ G_{mn}(t) = \sigma_0(t) W_{mn}(t), \]  

(B1)

where

\[ \sigma_0(t) \equiv G_{oo}(t) = |\psi(t)|^{-1/2} \exp[D^T f(t) D], \]

(B2)

\[ W_{mn}(t) = (\text{min} |l^m + n|)^{-1/2} \frac{\partial^{m+l}}{\partial u^m \partial \bar{u}^l} Z(t, u, \bar{u})|_{\nu = 0} \]  

(B3)

with

\[ Z(t, u, \bar{u}) = \exp[-u^T \Phi u - \bar{u}^T \Phi \bar{u} - 2u^T \Phi \bar{u}] \]

(B4)

\[ \psi(t) = 1/4U^{-1}v^{-1}, \]

(B5a)

\[ f(t) = -S'Uc, \]

(B5b)
and

\[ \Phi_1 = 1 - UC_+S' - VC_+S', \quad (B6a) \]
\[ \Phi_2 = VC_-S' - UC_+S', \quad (B6b) \]

where

\[ U = (C_+S' + C_-S)^{-1}, \quad (B7a) \]
\[ V = (C_+S + C_-S')^{-1}, \quad (B7b) \]
\[ C_\pm = 1 \pm \exp(-i\omega't), \quad (B8) \]
\[ S' = (S^{-1})^T, \quad (B9) \]
\[ \omega'_y = \omega'_1 \delta_y, \quad (B10) \]

and \(|\psi|\) denotes the determinant of the \(\psi\) matrix.

### APPENDIX C: THE FLUORESCENCE SPECTRUM OF A GENERAL HARMONIC MOLECULE. DERIVATION OF EQ. (22)

The Green function in the \(q'\) representation is Gaussian and assumes the form

\[ \langle q'| \exp(-iHt)|q'\rangle = |2\pi i \sin \omega't|^{-1/2} \exp\{-1/4(q'+q')^T C(q'+q') \]
\[ - 1/4(q'-q')^T C^{-1}(q'-q')\}. \quad (C1) \]

Upon substituting Eq. (14a) in Eq (C1) and changing the representation to \(q^*\), we get\(^{11(b)}\) the Green function of Eq. (20),

\[ \langle q^*| \exp(-iHt)|q^*\rangle = \frac{|\lambda| \exp(-D^T CD)}{|2\pi i \sin \omega't|^{1/2}} \times \exp\{-1/4(q^* + q^*)^T S^T C S(q^* + q^*) \]
\[ - 1/4(q^* - q^*)^T S^T C^{-1} S(q^* - q^*) \]
\[ - (q^* + q^*)^T S^T CD\}, \quad (C2) \]

where

\[ C = i \tan (1/2\omega't), \quad (C3a) \]
\[ \lambda_y = (\omega'_1 / \omega'_y)^{1/2} \delta_y, \quad (C3b) \]
\[ |\lambda| = \det \lambda, \quad (C3c) \]

and \(\omega'\) is defined in Eq. (B10). Substituting Eqs. (21) and (22) into Eq. (20), we get

\[ G_{mm}(t) = \theta(t) (m!n!2^{m+n})^{-1/2} Y_{mm}(t), \quad (C4) \]
where

\[ \theta(t) = \left| \frac{\lambda}{2i \sigma^2 \sin \omega't} \right|^{1/2}, \]

\[ \text{mln}2^{m+n} = n \prod_{j=1}^{N} (m_j n_j) 2^{m_j + n_j}, \]

and

\[ Y_{mn}(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dq \, d\bar{q} \exp \left[ -1/2(q^T \bar{q} + \bar{q}^T \bar{q}) \right. \]

\[ - 1/4(q + \bar{q})^T S^2 C S(q + \bar{q}) \]

\[ - 1/4(q - \bar{q})^T S^2 C^{-1} S(q - \bar{q}) \]

\[ - (q + \bar{q})^T S^2 CD ] H_m(q) H_n(\bar{q}). \]  \hspace{1cm} (C5)

Making use of the generating function of the Hermite polynomials, \(^{33}\)

\[ H_m(q) = \frac{\partial^m}{\partial u^m} \exp(2qu - u^T u) |_{u=0}, \]

we define the auxiliary quantity

\[ \bar{Z}(t; u, \bar{u}) = \int \int dq \, d\bar{q} \exp \left[ -1/2(q^T \bar{q} + \bar{q}^T \bar{q}) \right. \]

\[ - 1/4(q + \bar{q})^T S^2 C S(q + \bar{q}) \]

\[ - 1/4(q - \bar{q})^T S^2 C^{-1} S(q - \bar{q}) \]

\[ - (q + \bar{q})^T S^2 CD + 2q^T u + 2\bar{q}^T \bar{u} - u^T u - \bar{u}^T \bar{u}]. \]  \hspace{1cm} (C7)

Equations (C5)–(C7) result in

\[ Y_{mn}(t) = \frac{\partial^m}{\partial u^m} \frac{\partial^n}{\partial \bar{u}^n} \bar{Z}(t; u, \bar{u}) \bigg|_{u=0, \bar{u}=0}. \]  \hspace{1cm} (C8)

Equation (C7) can be easily integrated since the integrand is Gaussian. We then have

\[ \bar{Z}(t; u, \bar{u}) = \frac{(4\pi)^N}{(\det R)^{1/2}} \exp(-u^T u - \bar{u}^T \bar{u}) \exp(B^T R^{-1} B), \]  \hspace{1cm} (C9)

where

\[ R = \begin{bmatrix} R_1 \, R_2 \\ R_2 \, R_1 \end{bmatrix}. \]  \hspace{1cm} (C10a)
Equation (C9) can now be rewritten in the form
\[ \tilde{Z}(t; u, \bar{u}) = \frac{(4\pi)^N}{|R|^{1/2}} \exp\left[2D^T CS(\bar{R}_1 + \bar{R}_2)S^T CD\right] Z(t; u, \bar{u}), \]
(C15)
where \( u \) and \( \bar{u} \) dependence occurs only in
\[ Z(t; u, \bar{u}) = \exp\left[-u^T \Phi u - \bar{u}^T \bar{\Phi} \bar{u} \right. \]
\[ 
- 2u^T \Phi_2 \bar{u} - 2(u + \bar{u})^T(1 + S^T CS)^{-1} S^T CD \]
(C16a)
with
\[ Z(t; 0, 0) = 1 \]
(C16b)
and
\[ \Phi_1 = 1 - 4\bar{R}_1 = 1 - (1 + S^T CS)^{-1} - (1 + S^T C^{-1} S)^{-1}, \]
(C16c)
\[ \Phi_2 = -4\bar{R}_2 = (1 + S^T C^{-1} S)^{-1} - (1 + S^T CS)^{-1}, \]
(C16d)
Upon the substitution of Eqs. (C15) and (C8) into Eq. (C4) and using the relation (C16b), we get Eq. (22), i.e.,
\[ G_{ma}(t) = G_{00}(t) W_{ma}(t) = \sigma_0(t) W_{mn}(t), \]
(C17)
where
\[ W_{ma} = (\min(2m + n)^{-1/2} \frac{\partial m}{\partial u} \frac{\partial n}{\partial \bar{u}} Z(t; u, \bar{u})|_{u = 0, \bar{u} = 0} \]
(C18)
and \( G_{00}(t) = \sigma_0(t) \) whose Fourier transform gives the absorption spectrum \( \sigma(t) \) at \( T = 0 \) K [Eq. (F2)]. Its derivation is given in Appendix D. Since there are singular points in \( C \) and \( C^{-1} \) whenever \( \omega(t) = \pi \), Eqs. (C16) and (C18) are not suitable for direct computation. By introducing \( C_{\pm} = 1 \pm \exp(-i\omega t) \), we have
\[ C = C_{\pm}^{-1} = C_{\pm} C_{\pm}^{-1}, \]
(C19a)
\[ (1 + S^T CS)^{-1} = [S^T C_{\pm}^{-1}(C_{\pm} S + C_{\pm} S) - C_{\pm} S]^{-1} \]
(C19b)
and
\[ (1 + S^T C^{-1} S)^{-1} = (C_{\pm} S + C_{\pm} S')^{-1} C_{\pm} S'. \]
(C19c)
Substitution of Eqs. (C16) and (C19) into (C18) gives the final expression for \( W_{ma} \) which, together with the final expression for \( \sigma_0(t) \), is presented in Appendix B.

The Fourier transform of \( \sigma_0(t) \) gives the absorption spectrum of the molecule initially at \( T = 0 \) K. Except for a frequency shift due to a different definition of \( \omega_m \), Eq. (B2) is identical to Eq. (36) of Ref. 11(b). The expression for \( W_{ma}(t) \) is the main accomplishment of this paper. From Eq. (C17) and also from Eqs. (C16b) and (C18) we have \( W_{00}(t) = 1 \). The quantity \( W_{ma}(t) \) can be calculated systematically as follows.

In general the exponential term in Eq. (C16) contains the following \( 2N \times 2N \) matrix:
\[ \begin{bmatrix} \Phi_1 & \Phi_2 \\ \Phi_2 & \Phi_1 \end{bmatrix}, \]
(C20)
where \( \Phi_1 \) and \( \Phi_2 \) are defined in Eqs. (C16c) and (C16d). However in realistic calculations of \( W_{ma}(t) \), many of the elements \( m_j \)'s in \( |m\rangle = |m_1...m_N\rangle \) or \( n_j \)'s in \( |n\rangle = |n_1...n_N\rangle \)
are often zero; in other words only a small fraction of the \(N\) modes are excited and the size of the matrix involved in the calculation of \(W_{mn}(t)\) can be greatly reduced. If the number of nonzero indexes is \(|m| = N_m\) and the number of nonzero indexes in \(|n| = N_n\), then the size of the matrix involved in the calculation of \(W_{mn}(t)\) is only \(N_r \times N_r\), where \(N_r = N_m + N_n\). This \(N_r \times N_r\) matrix is obtained by simply setting those \(u_j\)'s and \(\bar{u}_j\)'s equal to zero in Eq. (C16a), since the associated indexes \(m_j\)'s and \(n_j\)'s are zero (cf. Eq. C18). This \(N_r \times N_r\) matrix is symmetric and it may be easily diagonalized. We can now use Eqs. (C18) and (C6) and finally get an expression for \(W_{mn}(t)\) which is a combination of terms such as

\[
H_{r_1}(z_1)H_{r_2}(z_2)\cdots H_{r_N}(z_N),
\]

where

\[
0 < r < R_r, \quad i = 1, \ldots, N_r
\]

and

\[
\sum_{i=1}^{N_r} n_i = m + n.
\]

Such a procedure will be demonstrated in detail in Secs. III, IV, and Appendix F for several levels of sophistication of the harmonic model.

**APPENDIX D: ELECTRONIC ABSORPTION SPECTRA OF GENERAL HARMONIC MOLECULES**

In this Appendix we shall calculate the absorption line shape of our harmonic molecule described by the Hamiltonian given by Eq. (13) at temperature \(T\) [Eq. (11a)]. Within the Condon approximation, we have

\[
\sigma(\omega_L) = -|u_{ex}|^2 \sum_n P(n) \text{Im} G_{mn}(\omega_L - \omega_{ex} + \epsilon_n)
\]

\[
= |u_{ex}|^2 \text{Re} \int_0^\infty dt \exp[i(\omega_L - \omega_{ex})t] \sigma(t).
\]

We have already derived an expression for \(\sigma(t)\) in Ref. 11(b). It should be noted that \(\omega_{ex}\) in this article is slightly different than in Ref. 11(b). This expression will now be given here using the present notation:

\[
\sigma(t) = \frac{1}{2} \psi_\tau(t)^{-1/2} \exp[D^T f_\tau(t) D],
\]

where

\[
\psi_\tau = [\bar{W} \bar{V} \bar{G}]
\]

\[
f_\tau(t) = S' A [\bar{W}^{-1} - A^{-1}] A S^{-1},
\]

with

\[
\bar{W} = A + S'TCS,
\]

\[
\bar{V} = C^{-1} + (SAS^T)^{-1},
\]

\[
\bar{G} = 1/4 A_+ A_- C_+ C_-,
\]

\[
S' = (S^{-1})^T,
\]

and

\[
A_\pm = (\bar{n} + 1) \pm \bar{n} \exp(\pm i\omega t),
\]

\[
C_\pm = 1 \pm \exp(\pm i\omega t),
\]

\[
\bar{n} = \exp(\pm i\omega t / \kappa T) - 1^{-1},
\]

\[
A = A_+ A_- = A_- A_+^{-1},
\]

\[
C = i \tan(\omega t / 2) = C_+ C_- = C_- C_+^{-1},
\]

\[
\bar{W}^\prime = \omega_{ex} \delta_\prime
\]

\[
\bar{W}^\prime = \omega_{ex} \delta_\prime
\]

The above formulas (D3) to (D5) are not suitable for direct computation, since there are singular points in \(C\) and \(C^{-1}\), whenever \(\omega_{ex} t = \pi n\). In order to eliminate this singularity, we rearrange Eq. (D3a) as follows. We define

\[
\bar{W} = A + S'TCS
\]

\[
= A_+ A_-^{-1} + S'TC_- C_+ S
\]

\[
= S'TC_+^{-1} (C_+ S'A_- + C_- SA_+) A_+^{-1}
\]

\[
\bar{V} = C_+^{-1} (SAS^T)^{-1}
\]

\[
= C_+^{-1} C_+ + S'A_+ A_-^{-1} S^{-1}
\]

\[
= C_+^{-1} (C_+ S'A_- + C_- S'A_+) A_+^{-1} S^{-1}.
\]

Substitution of Eqs. (D4c), (D6a), and (D6b) in Eq. (D3a) results in

\[
|\psi_\tau(t)| = \frac{1}{2} \sqrt{\bar{W} \bar{V} \bar{G}}
\]

\[
= \frac{1}{4} (C_+ S'A_- + C_- SA_+)
\]

\[
\times (C_+ S'A_- + C_- S'A_+).\]

The \(f_\tau(t)\) of Eq. (3b) can also be rearranged in a similar way. Finally we have

\[
\sigma(\omega_L) = |u_{ex}|^2 \text{Re} \int_0^\infty dt \exp[i(\omega_L - \omega_{ex})t] \sigma(t),
\]

\[
\sigma(t) = |\psi_\tau(t)|^{-1/2} \exp[D^T f_\tau(t) D],
\]

where

\[
\psi_\tau(t) = 1/4 (C_+ S'A_- + C_- SA_+)
\]

\[
\times (C_+ S'A_- + C_- S'A_+),
\]

and

\[
f_\tau(t) = -S'A_- (C_+ S'A_- + C_- SA_+) A^{-1} C_-.
\]

Equation (D8) is our final expression for absorption at the finite temperature. Note that at zero temperature, Eq. (D1) reduces to

\[
\sigma(\omega_L) = |u_{ex}|^2 \text{Im} G_{00}(\omega_L - \omega_{ex})
\]

\[
= |u_{ex}|^2 \text{Re} \int_0^\infty dt \exp[i(\omega_L - \omega_{ex})t] \sigma_0(t)
\]

with \(\sigma_0(t) = G_{00}(t)\).

In this case, we have \(\bar{n} = 0\) and \(A_\pm = 1\). Equations (D8b), (D8c), and (D8d) reduces to Eqs. (B2), (B5a), and (B5b), respectively. In the absence of Dushinsky mixing, then Eq. (24) holds. In this case we need only consider a single mode. Equations (D8) reduce to Eqs. (32).
APPENDIX E: ABSORPTION SPECTRA OF SUPERCOOLED HARMONIC MOLECULES

In this Appendix we derive Eqs. (40) and (41), which explicitly give the absorption line shape of supercooled molecules in the absence of Dushinsky rotation. The following derivation is based on Eqs. (25b), (26a), and (26b). We start in the special case, whereby \( \omega' = \omega'' = \omega \), i.e., \( \omega_+ = 0 \). In this case, we have

\[
\psi(t) = 1, \quad f(t) = -1/2[1 - \exp(-i\omega t)], \quad \sigma_0(t) = \exp\left(-\frac{D^2}{2} \right) \quad \text{[E1]}
\]

\[
= \exp\left(-\frac{D^2}{2}\right) \exp\left(\frac{D^2}{2} \exp(-i\omega t)\right) \quad \text{[E2]}
\]

\[
= \exp\left(-\frac{D^2}{2}\right) \sum_{m=0}^{\infty} \frac{1}{m!} \left(\frac{D^2}{2}\right)^m \exp(-im\omega t). \quad \text{[E3]}
\]

Equation (E3) is identical to Eq. (40b). The ratio of intensities, \( R(\omega) \), of the Raman fundamental to the 0-0 transition is then related to the displacement by [cf. Eq. (44a)]

\[
D^2 = 2R(\omega). \quad \text{(E4)}
\]

When \( \omega' \neq \omega'' \), using the Taylor expansion

\[(1 - z)^{-1/2} = 1 + 1/2z + 3/8z^2 + \cdots = \sum_{n=0}^{\infty} a_n z^n, \quad |z| < 1, \quad \text{[E5]}
\]

for Eq. (26a) we get

\[
[\psi(t)]^{-1/2} = \frac{2(\omega''/\omega_+)^{1/2}}{\omega_+} \sum_{n=0}^{\infty} a_n (\omega_-/\omega_+)^n \exp(-i2n\omega_0 t) \quad \text{[E6]}
\]

with \( a_n \) defined in Eq. (E5).

Similarly, upon expanding Eq. (26b), we get

\[
f(t) = -\frac{\omega''[1 - \exp(-i\omega_0 t)]}{\omega_+ [1 - (\omega_-/\omega_+)^2 \exp(i\omega_0 t)]} \quad \text{[E7]}
\]

\[
= -\frac{(\omega''/\omega_+)[1 - \exp(-i\omega_0 t)]}{\omega_-} \sum_{n=0}^{\infty} (\omega_-/\omega_+)^n \exp(-in\omega_0 t) \quad \text{[E8]}
\]

so that

\[
\exp[D^2 f(t)] = \exp(-D^2 \omega''/\omega_+) \sum_{m=0}^{\infty} \frac{1}{m!} A^m \left[ \sum_{n=1}^{\infty} (\omega_-/\omega_+)^n \exp(-in\omega_0 t) \right]^m \quad \text{[E9]}
\]

where

\[
A = \frac{2\omega''^2 D^2}{\omega_+ \omega_-} \quad \text{[E10]}
\]

and

\[
b_0 = 1, \quad b_q = \sum_{k=1}^{q} \frac{1}{k!} A^k B(k, q) \quad \text{[E11]}
\]

and

\[
B(k, q) = k! \sum_{\alpha_1, \alpha_2, \ldots, \alpha_q} (\alpha_1, \alpha_2, \ldots, \alpha_q)^{-1}. \quad \text{[E12]}
\]

\( \alpha_q \) are nonnegative integers, and the summation is done over all possible \( \alpha_j = 0, 1, 2, \ldots \) satisfying the constraints \( \alpha_1 + \alpha_2 + \cdots + \alpha_q = k \) and \( \alpha_1 + 2\alpha_2 + \cdots + q\alpha_q = q \).

Using Eqs. (E6) and (E8), we get Eq. (40a) with

\[
c_m = \sum_{\alpha_q=0}^{m} a_\alpha b_q \quad \text{[E13]}
\]

where \( a_\alpha \) is defined by Eq. (E5) as the \( \alpha \)th coefficient of the Taylor expansion of \( (1 - z)^{-1/2} \), and \( b_q \) is defined by Eq. (E10). In particular, we have

\[
c_0 = a_0 b_0 = 1, \quad c_1 = a_0 b_1 = \frac{2\omega''^2}{\omega_+ \omega_-} D^2. \quad \text{[E14]}
\]

so that

\[
R(\omega') = (c_1/c_0)(\omega_-/\omega_+) = 2D^2 \omega''^2/\omega_+^2. \quad \text{[E15]}
\]

Equation (E15) is identical to Eq. (44a). When \( \omega_+ = 2\omega'' \) or \( \omega_- = 0 \), Eq. (E15) reduces to Eq. (E4).

APPENDIX F: A SINGLE MODE EXCITATION SPECTRUM

A particularly simple case is when \( |m| = |0, \ldots, m, \ldots, 0| \) and \( |n| = |0, \ldots, n, \ldots, 0| \). In the present paper we refer to this case as the single mode excitation in which the \( j \)th mode changes from state \( n \) to \( m \), all the other modes remaining in the ground state.
In this case, we can set all $u_j$ and $\tilde{u}_j$ to zero except $u_j = u$ and $\tilde{u}_j = \tilde{u}$ in Eq. (B4). Under this simplification, Eq. (B3) can be rewritten as

$$W_m(t) = (mn!2^{m+n})^{-1/2} \frac{\partial^m}{\partial u^m} \frac{\partial^n}{\partial \tilde{u}^n} Z(t,u,\tilde{u})\bigg|_{u=0,\tilde{u}=0},$$  \hspace{1cm} (F1a)

where

$$Z(t,u,\tilde{u}) = \exp\left[ -(\Phi_1)_{ij}(u^2 + \tilde{u}^2) - 2z(\Phi_2)_{ij} u \tilde{u} + 2\xi(t)(u + \tilde{u}) \right]$$

and

$$\xi(t) = [S^T(t)D]_j.$$  \hspace{1cm} (F1b)

We now make the following transformation:

$$\begin{bmatrix} u \\ \tilde{u} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

and using

$$\frac{\partial}{\partial u} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ -1 & -1 \end{bmatrix} \frac{\partial}{\partial x},$$

we get

$$\frac{\partial^m}{\partial u^m} Z(t,u,\tilde{u})\bigg|_{u=0,\tilde{u}=0} = 2^{-(m+n)/2} \left( \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \right)^m \left( \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right)^n \times Z(t,x,y)\bigg|_{x=0,y=0},$$  \hspace{1cm} (F2a)

where

$$Z(t,x,y) = \exp\left[ -(\Phi_1 + \Phi_2)_{ij} x^2 -(\Phi_1 - \Phi_2)_{ij} y^2 + 2\sqrt{2} \xi(t)x \right]$$

$$\equiv \exp\left[ -2\alpha^2(t)x^2 - 2\overline{\alpha}^2(t)y^2 + 2\sqrt{2} \xi(t)x \right]$$  \hspace{1cm} (F2b)

with

$$\alpha(t) = \left[ 1/2(\Phi_1 + \Phi_2)_{ij} \right]^{1/2} = \left[ 1/2 - \left[ U_{SC}S \right]_{ij} \right]^{1/2},$$  \hspace{1cm} (F3a)

$$\overline{\alpha}(t) = \left[ 1/2(\Phi_1 - \Phi_2)_{ij} \right]^{1/2} = \left[ 1/2 - \left[ U_{SC}S \right]_{ij} \right]^{1/2},$$  \hspace{1cm} (F3b)

and

$$\xi(t) = [S^T(t)D]_j.$$  \hspace{1cm} (F3c)

Using the binomial expansion, we have

$$\left( \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \right)^m \left( \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right)^n = \sum_{p=0}^{m} \sum_{q=0}^{n} (-1)^p \binom{m}{p} \binom{n}{q} \frac{\partial^m}{\partial x^{m-p-q}} \frac{\partial^n}{\partial y^{n-p-q}} \frac{\partial^{m+p+q}}{\partial x^{m-p-q} \partial y^{n-p-q} \partial x^{p+q}}.$$  \hspace{1cm} (F4)

Substituting Eq. (F4) into Eq. (F2), we have

$$W_m(t) = (mn!2^{m+n})^{-1/2} \times \sum_{p=0}^{m} \sum_{q=0}^{n} (-1)^p \binom{m}{p} \binom{n}{q} [\alpha(t)]^{m-n-p-q} \times [\overline{\alpha}(t)]^p + 4H_{m+n-p-q} [\xi(t)/\alpha(t)] H_{p+q}(0).$$  \hspace{1cm} (F5)

Here $H_n(q)$ denotes the Hermite polynomial. At $q = 0$, $H_n(q)$ assumes the form

$$H_n(0) = \begin{cases} 0 & \text{for odd } n \\ \text{for even } n \end{cases}$$  \hspace{1cm} (F6)

Making use of Eq. (F6), we may recast Eq. (F5) in the form

$$W_m(t) = (mn!2^{m+n})^{-1/2} [\alpha(t)]^m [\overline{\alpha}(t)]^n \times \sum_{k=0}^{\frac{n}{2}} \binom{\frac{n}{2}}{k} \sum_{q=0}^{\frac{n}{2}} \binom{\frac{n}{2}}{q} \eta_{mk} \gamma(t)^k \times H_{m+n-2k} [\xi(t)/\alpha(t)],$$  \hspace{1cm} (F7)

where

$$\gamma(t) = - \frac{[\overline{\alpha}(t)/\alpha(t)]^2}{1 - 2[U_{SC}S]_{ij}^2},$$  \hspace{1cm} (F8)

$$\eta_{mk} = \sum_{\ell=0}^{2k} (-1)^\ell \binom{m}{2k-\ell} \binom{n}{q}.$$  \hspace{1cm} (F9a)

We have further defined

$$\binom{m}{q} = \begin{cases} \frac{m!}{(m-q)!} & \text{when } m>q \\ 0 & \text{when } m<q \end{cases}$$  \hspace{1cm} (F9b)

and $k^*$ is the integer part of $(m+n)/2$.  

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