

LETTERS

Generating Function for Electronic Spectra of Polyatomic Molecules

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An exact zero-temperature reduced equation of motion is derived for a generating function $P(q,t;q')$ which allows the calculation of electronic absorption spectra of anharmonic polyatomic molecules. The present theory is an extension of our previous study of vibrational spectra. It allows the direct calculation of quantum electronic spectra without solving for the vibronic eigenstates. An easily calculable expression for the absorption spectrum of a molecule with harmonic potential surfaces including equilibrium shifts, frequency shifts, and Dushinsky rotations is derived.

Generating Function for Electronic Spectra

The calculation of electronic absorption and fluorescence spectra of isolated large polyatomic molecules is one of the most challenging problems in molecular dynamics. One reason for the recent interest in this problem is the developments in supersonic beam spectroscopic techniques of ultracold molecules.¹⁻⁴ These create the need for a simple method to calculate spectra and fit them to experimental data. We have recently developed a generating function for the calculation of vibrational spectra of anharmonic molecules.⁵ In this letter, we extend our derivation to electronic spectra involving two potential surfaces. The generating function contains the information relevant for the spectrum and allows us to develop approximate methods toward its calculation, which are not based on the explicit calculation of the vibronic eigenstates. A simple expression for the absorption spectrum of harmonic molecules is also derived from the generating function. This expression (eq 36) is very convenient for numerical computations and for extracting information on the potential surfaces from experimental spectra. Moreover, this will serve as a starting point

for mode coupling calculations of the generating function in the anharmonic case.

We consider a molecule with two electronic adiabatic states $|a\rangle$ and $|b\rangle$ and N vibrational degrees of freedom characterized by the Born-Oppenheimer Hamiltonian

$$H = |a\rangle H_a \langle a| + |b\rangle (\omega_{ba} + H_b) \langle b| \quad (1)$$

where

$$H_a = \sum_{j=1}^N -\frac{\hbar^2}{2m_j} \frac{\partial^2}{\partial Q_j^2} + V_a(Q_1 \dots Q_N) \quad (1a)$$

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and

$$H_b = \sum_{j=1}^N -\frac{\hbar^2}{2m_j} \frac{\partial^2}{\partial Q_j^2} + V_b(Q_1 \dots Q_N) \quad (1b)$$

Here m_j and Q_j are the mass and Cartesian displacement of the j th nucleus and ω_{ba} is the electronic transition frequency. The dipole operator representing the interaction of the molecule with the radiation field is given by

$$\hat{\mu}(\mathbf{Q}) = \mu(\mathbf{Q})(|a\rangle\langle b| + |b\rangle\langle a|) \quad (2)$$

We shall be interested in calculating the dipole correlation function

$$I(t) \equiv \langle \hat{\mu}(t) \hat{\mu}(0) \rangle \equiv \text{Tr} [\exp(iH_a t) \mu \exp(-iH_b t) \mu \rho_a] \quad (3)$$

and the absorption spectrum

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp[i(\omega - \omega_{ba})t] I(t) \quad (4)$$

Here ρ_a is the canonical equilibrium density matrix of the molecule in the $|a\rangle$ state, i.e.

$$\rho_a = \exp(-H_a/kT) / \text{Tr} [\exp(-H_a/kT)] \quad (5)$$

In analogy with our previous expansion,⁵ let us introduce the electronic generating function

$$P(\mathbf{q}, t; \mathbf{q}') = \text{Tr} [\exp(iH_a t) \delta(\mathbf{q} - \mathbf{Q}) \exp(-iH_b t) \delta(\mathbf{q}' - \mathbf{Q}) \rho_a] \quad (6)$$

Using eq 3 and 6, we immediately get

$$I(t) = \int \int d\mathbf{q} d\mathbf{q}' \mu(\mathbf{q}) \mu(\mathbf{q}') P(\mathbf{q}, t; \mathbf{q}') \quad (7)$$

The generating function therefore plays the role of a joint probability for the coordinates to assume the values \mathbf{q}' at $t = 0$ and \mathbf{q} at time t . It should be pointed out that P is a complex quantity and is not a probability. The important property of P is, however, eq 7; i.e., P serves as a generating function for molecular electronic spectra.

We shall now derive an equation of motion for P , specializing at supercooled molecules at zero temperature. This case is of considerable current interest, in particular for supersonic beam spectra.¹⁻⁴ At zero temperature we have

$$\rho_a = |\Psi_0\rangle\langle\Psi_0| \quad (8a)$$

$|\Psi_0\rangle$ being the ground vibronic eigenstate of H_a , i.e.

$$H_a |\Psi_0\rangle = E_0 |\Psi_0\rangle \quad (8b)$$

Upon the substitution of eq 8 in eq 6, we get

$$P(\mathbf{q}, t; \mathbf{q}') = \Psi_0(\mathbf{q}) \langle \mathbf{q} | \exp[-i(H_b - E_0)t] \delta(\mathbf{q}' - \mathbf{Q}) | \Psi_0 \rangle \quad (9)$$

so that

$$\partial P / \partial t = -i \Psi_0(\mathbf{q}) \langle \mathbf{q} | (H_b - E_0) \exp[-i(H_b - E_0)t] \delta(\mathbf{q}' - \mathbf{Q}) | \Psi_0 \rangle \quad (10)$$

$$= -i \Psi_0(\mathbf{q}) \int d\mathbf{q}'' \langle \mathbf{q} | (H_b - E_0) | \mathbf{q}'' \rangle \times \langle \mathbf{q}'' | \exp[-i(H_b - E_0)t] \delta(\mathbf{q}' - \mathbf{Q}) | \Psi_0 \rangle$$

The second factor inside the integration in eq 10 is equal to $P(\mathbf{q}'', t; \mathbf{q}') / \Psi_0(\mathbf{q}'')$. If we write H_b in the conventional differential form, we get

$$\frac{\partial P}{\partial t} = -i \Psi_0(\mathbf{q}) \left[H_b \left(-i \frac{\partial}{\partial \mathbf{q}}, \mathbf{q} \right) - E_0 \right] P(\mathbf{q}, t; \mathbf{q}') / \Psi_0(\mathbf{q}) \quad (11)$$

We now introduce the ground-state distribution function

$$g(\mathbf{q}) \equiv |\Psi_0(\mathbf{q})|^2 \quad (12)$$

and rearrange eq 11 in the form

$$\frac{\partial P(\mathbf{q}, t; \mathbf{q}')}{\partial t} = -i \Psi_0(\mathbf{q}) [H_b \Psi_0 - (H_a \Psi_0)] P(\mathbf{q}, t; \mathbf{q}') / g(\mathbf{q}) \quad (13)$$

Equation 13, for $H_a = H_b$, was derived in Appendix C in ref 5b.

Upon substituting eq 1 in eq 13 and rearranging, we finally get

$$\frac{\partial P}{\partial t} = \frac{i\hbar}{2} \sum_j \frac{1}{m_j} \frac{\partial}{\partial q_j} g(\mathbf{q}) \frac{\partial}{\partial q_j} [P/g(\mathbf{q})] - \frac{i}{\hbar} U P \quad (14)$$

or alternatively

$$\frac{\partial P}{\partial t} = \sum_j \left[\frac{i\hbar}{2m_j} \frac{\partial^2 P}{\partial q_j^2} + \frac{i\hbar}{2m_j} \frac{\partial}{\partial q_j} u_j(\mathbf{q}) P \right] - \frac{i}{\hbar} U P \quad (15)$$

where the driving force u_j is given by

$$u_j(\mathbf{q}) = -\frac{\partial \ln g(\mathbf{q})}{\partial q_j} \quad (16a)$$

and

$$U(\mathbf{q}) \equiv V_b(\mathbf{q}) - V_a(\mathbf{q}) \quad (16b)$$

Equation 14 or 15 together with the initial condition

$$P(\mathbf{q}, 0; \mathbf{q}') = g(\mathbf{q}) \delta(\mathbf{q} - \mathbf{q}') \quad (17)$$

is our final reduced equation of motion for P . Within the present algorithm we calculate the spectrum in three stages: (i) solve eq 15 together with eq 17 for P , (ii) calculate the correlation function $I(t)$ via eq 7, and (iii) calculate the spectrum via the Fourier transform (eq 4). Equation 15, which is purely quantum mechanical, is strikingly similar to the Fokker-Planck equations which appear in classical nonlinear dynamics⁵ and is reminiscent of the stochastic (hidden variable) formulation of quantum mechanics.⁶

In concluding this section, we note the following: (1) For $U = 0$, eq 14 or 15 reduces to our previous equations for the generating function of vibrational spectra.⁵ (2) Our reduced equation of motion, eq 14 or 15, holds not only at zero temperature but whenever the molecule is initially in a pure state. Thus, $|\Psi_0\rangle$ in eq 8a can be any vibronic eigenstate of the $|a\rangle$ electronic state. In practice, this limit occurs naturally at zero temperature. (3) If we expand the solution of eq 15 perturbatively in U , we get the conventional cumulant expansion.⁷ In general, we wish to derive a nonperturbative self-consistent solution of eq 15. This can be done by use of the mode coupling formalism, as was done in ref 5 for the vibrational generating function.

The Harmonic Limit

We shall now consider the most general case of a harmonic molecule with two electronic states including linear displacements of the equilibrium positions, frequency changes, and Dushinsky rotations. This model has been extensively studied in the past in the context of various solid-state and molecular dynamics problems.⁸⁻¹⁴ The exact state to state Franck-Condon factors are calculable but are quite cumbersome.^{13,14} The calculation becomes much simpler, however, if we work in the time domain. Making use of the generating function, we shall derive simple expressions for the absorption spectra of polyatomic molecules involving matrices whose size is the number of the molecular degree of freedom. This form is particularly suited for numerical calculations and for fitting potential surfaces to experimental spectra. In addition, the present expression for the harmonic generating function may serve as a convenient starting point for expanding the generating function in the anharmonic case, by use of the mode coupling formalism, as was done in ref 5 for vibrational spectra.

We consider a harmonic molecule with two electronic states: a ground state $|a\rangle$ and an excited state $|b\rangle$. The corresponding

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Born-Oppenheimer Hamiltonians are

$$H_a = \frac{1}{2} \sum_{j=1}^N \hbar \omega_j'' [p_j''^2 + q_j''^2] \quad (18a)$$

$$H_b = \frac{1}{2} \sum_{j=1}^N \hbar \omega_j' [p_j'^2 + q_j'^2] \quad (18b)$$

We adopt the common spectroscopic notation, whereby we label ground-state quantities by a double prime and excited-state quantities by a single prime. p_j and q_j are the dimensionless momenta and coordinates corresponding to the normal modes

$$p_j = \frac{1}{(m_j \omega_j \hbar)^{1/2}} P_j \quad (19a)$$

$$q_j = \left(\frac{m_j \omega_j}{\hbar} \right)^{1/2} Q_j \quad (19b)$$

P_j and Q_j being the conjugate momenta and normal coordinates, respectively. We further assume that the normal modes \mathbf{q}' and \mathbf{q}'' are related by the following transformation:

$$\mathbf{q}' = \mathbf{S} \mathbf{q}'' + \mathbf{D} \quad (20)$$

Here \mathbf{D} , \mathbf{q}' , and \mathbf{q}'' are vectors. \mathbf{D} stands for a linear displacement of the equilibrium configuration in the two electronic states, whereas \mathbf{S} is the Dushinsky rotation matrix. Note that \mathbf{S} is not unitary since

$$S_{jk} = (\omega_j' / \omega_k'')^{1/2} \tilde{S}_{jk} \quad (21)$$

where \tilde{S} is the unitary matrix of transformation of the Cartesian coordinates, i.e. $\mathbf{Q}' = \tilde{S} \mathbf{Q}'' + \mathbf{D}$. In the absence of Dushinsky rotation, \mathbf{S} is diagonal, i.e.

$$S_{jk} = (\omega_j' / \omega_j'')^{1/2} \delta_{j,k} \quad (22)$$

The generating function (eq 6) can be written in the form

$$P(\mathbf{q}'', t; \bar{\mathbf{q}}'') = Z^{-1} \langle \mathbf{q}'' | \exp(-iH_b \tau) | \bar{\mathbf{q}}'' \rangle \langle \bar{\mathbf{q}}'' | \exp(iH_a \tau) | \mathbf{q}'' \rangle \quad (23)$$

where

$$\tau = t + i\hbar/kT \quad (24)$$

Z is the ground-state partition function

$$Z = \prod_{j=1}^N [\bar{n}_j (\bar{n}_j + 1)]^{1/2} \quad (25)$$

with \bar{n}_j the mean occupation number of the j th mode, i.e.

$$\bar{n}_j = [\exp(\hbar \omega_j'' / kT) - 1]^{-1} \quad (26)$$

The matrix elements in eq 23 may be easily evaluated from the relation¹⁵

$$\begin{aligned} \langle \bar{q} | \exp(-\Lambda H) | q \rangle &= \sum_{n=0}^{\infty} \frac{\exp[-(n + 1/2)\omega\Lambda]}{\pi^{1/2} 2^n n!} H_n(q) H_n(\bar{q}) \exp[-1/2(q^2 + \bar{q}^2)] \\ &= (2\pi \sinh \omega\Lambda)^{-1/2} \exp\{-1/4(\tanh 1/2\omega\Lambda) \times \\ &\quad (q + \bar{q})^2 - 1/4(\coth 1/2\omega\Lambda)(q - \bar{q})^2\} \end{aligned} \quad (27)$$

H_n being the Hermite polynomials and Λ is a complex number. The first matrix element in eq 23 is obtained from eq 27 by taking Λ as it and $q = q'$. The second matrix element is obtained by taking $\Lambda = -it + \hbar/kT$ and $q = q''$. When these are substituted in eq 23, we get

$$\begin{aligned} P(\mathbf{q}'', t; \bar{\mathbf{q}}'') &= \frac{|\rho|^{-1/2}}{Z \prod_{j=1}^N \Psi_j(t)} \times \\ &\quad \exp\{-1/4(\mathbf{q}' + \bar{\mathbf{q}}') \mathbf{C} (\mathbf{q}' + \bar{\mathbf{q}}') - 1/4(\mathbf{q}' - \bar{\mathbf{q}}') \mathbf{C}^{-1} (\mathbf{q}' - \bar{\mathbf{q}}')\} \times \\ &\quad \exp\{-1/4(\mathbf{q}'' + \bar{\mathbf{q}}'') \mathbf{A} (\mathbf{q}'' + \bar{\mathbf{q}}'') - 1/4(\mathbf{q}'' - \bar{\mathbf{q}}'') \mathbf{A}^{-1} (\mathbf{q}'' - \bar{\mathbf{q}}'')\} \quad (28) \end{aligned}$$

\mathbf{q}' and $\bar{\mathbf{q}}'$ on the right-hand side are related to \mathbf{q}'' and $\bar{\mathbf{q}}''$ via the transformation

$$\mathbf{q}' = \mathbf{S} \mathbf{q}'' + \mathbf{D} \quad (29a)$$

$$\bar{\mathbf{q}}' = \mathbf{S} \bar{\mathbf{q}}'' + \mathbf{D} \quad (29b)$$

\mathbf{A} and \mathbf{C} are diagonal matrices

$$A_{jj} = \tanh [1/2(\hbar \omega_j'' / kT - i\omega_j'' t)] \quad (30a)$$

$$C_{jj} = \tanh (1/2 i\omega_j' t) \quad (30b)$$

and

$$\begin{aligned} \psi_j(t) &= \pi \left\{ \frac{\bar{n}_j + 1}{\bar{n}_j} [\exp(i\omega_j^- t) - \exp(-i\omega_j^+ t)] + \right. \\ &\quad \left. \frac{\bar{n}_j}{\bar{n}_j + 1} [\exp(-i\omega_j^- t) - \exp(i\omega_j^+ t)] \right\}^{1/2} \quad (31) \end{aligned}$$

where

$$\omega_j^+ = \omega_j' + \omega_j'' \quad (31a)$$

$$\omega_j^- = \omega_j' - \omega_j'' \quad (31b)$$

ρ is a diagonal matrix

$$\rho_{jj} = \omega_j'' / \omega_j' \quad (32)$$

and $|\rho|$ is its determinant

$$|\rho| = \prod_{j=1}^N (\omega_j'' / \omega_j') \quad (33)$$

The $|\rho|$ factor comes from the transformation from Cartesian to dimensionless coordinates.

Equation 28 is our final result for the generating function for harmonic molecules. We shall now use this result to calculate the dipole correlation function $I(t)$ for the special case whereby μ does not depend on \mathbf{Q} , i.e., $\mu(\mathbf{Q}) = 1$ in eq 7. We then have

$$I(t) = \int \int d\mathbf{q}'' d\bar{\mathbf{q}}'' P(\mathbf{q}'', t; \bar{\mathbf{q}}'') \quad (34)$$

To that end we first make use of eq 29 to transform \mathbf{q}' and $\bar{\mathbf{q}}'$ to \mathbf{q}'' and $\bar{\mathbf{q}}''$ and then change variables to $\mathbf{q}'' + \bar{\mathbf{q}}''$ and $\mathbf{q}'' - \bar{\mathbf{q}}''$ and make use of the Gaussian integration formula¹⁵

$$\int d\mathbf{X} \exp\{-\mathbf{X}^T \mathbf{P} \mathbf{X} + 2\mathbf{X}^T \mathbf{q}\} = \frac{\pi^{N/2}}{|\mathbf{P}|^{1/2}} \exp\{\mathbf{q}^T \mathbf{P}^{-1} \mathbf{q}\} \quad (35)$$

Here \mathbf{X} and \mathbf{q} are N -component vectors, \mathbf{X}^T and \mathbf{q}^T are their transpose, and \mathbf{P} is an $N \times N$ matrix. This results in a closed expression for $I(t)$, in terms of \mathbf{A} , \mathbf{C} , ρ , and Ψ (eq 30-32).

$$I(t) = |\chi(t)|^{-1/2} \exp[F(t)] \quad (36)$$

where

$$\chi(t) = \mathbf{W} \mathbf{V} \mathbf{G} \quad (36a)$$

$$F(t) = \tilde{\mathbf{D}}^T [\mathbf{W}^{-1} - \mathbf{A}^{-1}] \tilde{\mathbf{D}} \quad (36b)$$

$|\chi|$ stands for the determinant of χ , and $\tilde{\mathbf{D}}^T$ and \mathbf{S}^T are the transpose of $\tilde{\mathbf{D}}$ and \mathbf{S} , respectively. The other matrices appearing in eq 36 are

$$\begin{aligned} G_{jk} &= 1/4(\bar{n}_j + 1)^2 [\exp(i\omega_j^- t) - \exp(-i\omega_j^+ t)] + \\ &\quad \bar{n}_j^2 [\exp(-i\omega_j^- t) - \exp(i\omega_j^+ t)] \delta_{jk} \quad (37a) \end{aligned}$$

$$\mathbf{W} = \mathbf{A} + \mathbf{S}^T \mathbf{C} \mathbf{S} \quad (37b)$$

$$\mathbf{V} = (\mathbf{S} \mathbf{A} \mathbf{S}^T)^{-1} + \mathbf{C}^{-1} \quad (37c)$$

$$\tilde{\mathbf{D}} = \mathbf{A} \mathbf{S}^{-1} \mathbf{D} \quad (37d)$$

Equation 4 together with eq 36 is our final result for the absorption line shape. Note that the calculation involves multiplying and inverting $N \times N$ matrices, where N is the number of degrees of freedom, and we do not need to perform summations over individual vibronic eigenstates. Evaluating the spectrum in the time

domain is much more convenient than performing summations over individual Franck-Condon factors¹⁴ and provides the most straightforward means of fitting structural factors to experimental spectra. Equation 36 can be alternatively written in the form

$$I(t) = \exp[F(t) - \frac{1}{2} \text{Tr}(\ln \chi)] \quad (38)$$

In this form, the connection with the spectral density formalism¹⁶ is more transparent. In the absence of Dushinsky rotation, i.e. when eq 22 holds, all the matrices involved are diagonal and $I(t)$ is factorizable in the form

$$I(t) = \prod_{j=1}^N I_j(t) \quad (39)$$

where

$$I_j(t) = \chi_j(t)^{-1/2} \exp[F_j(t)] \quad (39a)$$

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χ_j and F_j being the diagonal elements χ_{jj} and F_{jj} , respectively. If in addition the molecule is initially cold ($T = 0$), we further have

$$\chi_j(t) = \frac{(\omega_j^+)^2 \exp(i\omega_j^- t) - (\omega_j^-)^2 \exp(-i\omega_j^+ t)}{4\omega_j^+ \omega_j^-} \quad (40a)$$

and

$$F_j(t) = -\frac{\omega_j'' [\exp(i\omega_j^+ t) - 1]}{\omega_j^+ \exp(i\omega_j^+ t) - \omega_j^-} D_j^2 \quad (40b)$$

Equations 38-40 may be used to conveniently calculate spectra of supercooled polyatomic molecules. Equation 28 forms the basis for a mode coupling solution of eq 14 for anharmonic molecules.⁵

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Evaluation of the Dipolar Contribution to Lanthanide Shift Reagent Induced Isotropic Shifts

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A method is outlined to determine the dipolar contribution to the isotropic chemical shift for substrates attached to a lanthanide shift reagent. The procedure is illustrated for $\text{Ln}(\text{dpm})_3(\text{py})_2$ complexes, with $\text{Ln} = \text{Ho}, \text{Tb}$. The difference between the calculated dipolar contribution to the shift and the experimental shift is about 10%. The discrepancy can be accounted for by small nondipolar shift contributions and/or assumptions concerning the molecular structure.

Introduction

Since Hinckley's first report¹ of the use of lanthanide shift reagents (LSR), the chemical shifts induced in isotropic solution by LSR have been exploited extensively to determine magnetic susceptibilities and/or structure parameters of the complexes involved.²⁻⁴ However, uncertainties in the interpretation of the results arise from assumptions made, for example that the Fermi contact contribution to the observed shift is negligible or that the magnetic susceptibility tensor χ of the complex is axially symmetric.

Two possible experimental ways of separating the dipolar and Fermi contact contributions to the observed shifts are to study the temperature dependence of the shift⁵ or to measure χ of the complex by solid-state⁶ or liquid-state⁷ methods. Theories for

separating the contributions have been developed,^{8,9} but they have often involved the assumption of an axially symmetric χ , an assumption which is invalid in most cases.^{3,6,9-11} In this letter a method is presented to evaluate the dipolar contribution to the shift without knowledge of molecular angles and susceptibility components, but taking into account the nonaxial character of χ . The dipolar contribution to the LSR-induced shifts is related, via the magnetic susceptibility tensor, to the electric quadrupolar or magnetic dipolar splittings which occur in the high-field NMR spectra of such complexes.⁷ The method may be demonstrated by a study of shifts and quadrupolar splittings of the para deuteron in complexes of pyridine-*d*₅ with $\text{Tb}(\text{dpm})_3$ and $\text{Ho}(\text{dpm})_3$, where $\text{dpm} = \text{dipivalomethanato}$. It is well established^{2,3} that, in the presence of excess pyridine, the $\text{Ln}(\text{dpm})_3$ -pyridine complex is completely in the form $\text{Ln}(\text{dpm})_3(\text{py})_2$ and that free and bound pyridine are in rapid exchange. Under these circumstances the observed shifts δ and the quadrupolar splittings ν are given by

$$\delta = x_f \delta_f + x_b \delta_b \quad (1b)$$

$$\nu = x_f \nu_f + x_b \nu_b \quad (1b)$$

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