# Continuum limit theory of absorption in the presence of dissipation

Reuven Ianconescu, Mikhail G. Brik and Eli Pollak

Chemical Physics Department, Weizmann Institute of Science, 76100 Rehovot, Israel (September 14, 2004)

# Abstract

A second order cumulant expansion is used to derive continuum limit expressions for the electronic absorption spectrum of a polyatomic molecule interacting with a bath, within the Condon approximation and weak fields. The small expansion parameter is the difference between the vibrational Hamiltonians in the ground and excited electronic states. The second order cumulant expansion is shown to be a good approximation for a reasonable model of a polyatomic molecule with 45 degrees of freedom. Friction tends to shift the maximum in the absorption peak to the blue. When the vibrational frequencies in the excited electronic state are lower than those in the ground electronic state, one finds a stochastic resonance feature. Friction first narrows the peak and then broadens it. This narrowing is absent when one only shifts the equilibrium positions in the excited state relative to the ground state.

### I. INTRODUCTION

It is today well understood that the Langevin equation describing friction and fluctuations and which gives the basic description of Brownian motion may be derived from a Hamiltonian. In this "dissipative" Hamiltonian, the test particle, which may be moving under the influence of a force field, is also bilinearly coupled to a bath of harmonic oscillators. This bath is characterized by a spectral density, which in the continuum limit would be identical to the spectral density underlying the Langevin equation [1,2].

The Hamiltonian representation has many attractive features. In some instances it provides a microscopic basis for understanding and describing the frictional forces felt by the particle. This is the case for example for impurities in solids at low temperatures, and atomic or molecular diffusion on surfaces [3,4]. Although liquids in general cannot be considered to provide harmonic baths, the harmonic bath approximation may be considered to be in many cases a semi-quantitative approximation [5,6]. Perhaps though the most important aspect of the Hamiltonian representation is that it provides a quantum mechanical framework for friction [2,7]. Thus a quantum mechanical dissipative system is one whose classical Hamiltonian leads in the continuum limit to the generalized Langevin equation.

One of the major challenges in recent years has been to develop methods and theories for quantum dissipation [8]. In this paper we present the application of this strategy to the time dependent photoabsorption spectrum of polyatomic molecules, within the weak field Condon approximation. It is well known that the spectrum is given as a Fourier transform of a correlation function of the propagator on the ground and electronically excited states [9–11]. If the corresponding molecular Hamiltonians are harmonic, then at least in principle one can write down an analytic expression for the correlation function and the Fourier transform is then effected numerically. This has been carried out in a recent series of papers by Berne and coworkers [12–14]. They however could not derive an expression in the continuum limit, rather they were limited to studying numerically a finite number of bath oscillators.

In this paper we show how one can derive continuum limit expressions for the spectrum by using a perturbation theory approach. Our recent studies of photoabsorption spectra of polyatomics have shown that frequently, the differences between the frequencies and equilibrium points in the ground and excited states of polyatomic molecules are not very big [15–17]. This suggests that one could use a perturbation theory in which the difference between the vibrational Hamiltonian in the ground and excited states is "the small parameter". We will show, that indeed, using a second order cumulant expansion, such an approximation can be rather accurate. We then apply it to the case when the molecule is in contact with a dissipative bath. All results are now readily derived in the continuum limit.

In Section II we provide the necessary theoretical framework, paying special attention to the spectral density of normal modes. Then in Section III we consider a model numerical example of a polyatomic molecule with 45 degrees of freedom. We find a stochastic resonance in the width of the absorption spectrum. At first increasing the friction causes a narrowing of the absorption spectrum while further increase then leads to a broadening of the spectrum. We find that the friction also causes a blue shift in the location of the maximum absorption peak. We end with a discussion, noting that the present theory can also be further developed to provide information on the time dependence of the energy distribution in the excited state and how it is affected by coupling to a dissipative bath.

# II. THE ABSORPTION SPECTRUM IN THE PRESENCE OF DISSIPATION

#### A. Formalism

We assume that we are dealing with two different orthogonal electronic states representing the ground state ( $|g\rangle$ ) and the excited state ( $|e\rangle$ ). The nuclear Hamiltonians for the two electronic states will be denoted  $H_g$ ,  $H_e$  respectively. The full Hamiltonian (H) of the system is composed of two parts:

$$H = H_0 + V(t) \tag{2.1}$$

where  $H_0$  is diagonal in the two electronic states:

$$H_0 = |g > H_q < g| + |e > H_e < e|.$$
(2.2)

V(t) is the laser field that induces the excitation from the ground state to the excited state:

$$V(t) = \mu E(t) \cos(\omega t) |e| < g| + \mu^* E^*(t) \cos(\omega t) |g| < e|$$
(2.3)

where  $\mu$  is the dipole operator which may depend on the nuclear coordinates and E(t) is the time profile of the optical field whose central frequency is  $\omega$ .

In the weak field limit, it is well known (see for example Ref. [18]) that to leading order in  $\mu^2$  the time dependent population of the excited donor state, assuming that the field is turned on at time  $t_0$  is given by the expression:

$$P_e(t,\omega;\beta) = \frac{2}{\hbar^2 Z_g} Re\left(Tre^{-\beta H_g} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \tilde{V}^{\dagger}(t') \tilde{V}(t'')\right)$$
(2.4)

where  $\beta \equiv \frac{1}{k_B T}$  and  $Z_g$  is the partition function of the ground state nuclear Hamiltonian at the inverse temperature  $\beta$ :

$$Z_g = Tre^{-\beta h_g}.$$
(2.5)

 $\tilde{V}$  comes from the representation of the field Hamiltonian in the interaction picture with respect to the zero-th order Hamiltonian [19]:

$$\tilde{V}(t) = e^{iH_e(t-t_0)/\hbar} \mu e^{-iH_g(t-t_0)/\hbar} E(t) \cos(\omega t)$$
(2.6)

We assume that the field has been turned on in the infinite past  $(t_0 \rightarrow -\infty)$ . One then readily finds (within the Condon approximation where the dipole operator  $\mu$  is taken to be a constant) that the time dependent population in the locally excited donor state (Eq. 2.4), at the central excitation frequency  $\omega$  is:

$$P_e(t,\omega;\beta) = \frac{|\mu|^2}{\hbar^2} Re\left(\int_0^\infty dt'' \chi(t'';\beta)\eta(t,t'';\omega)\right)$$
(2.7)

where the thermal correlation function is

$$\chi(t,\beta) = \frac{Tr\left[e^{-\left(\beta - i\frac{t}{\hbar}\right)H_g}e^{-i\frac{t}{\hbar}H_e}\right]}{Z_g}$$
(2.8)

The field function  $\eta(t, t''; \omega)$  is:

$$\eta(t, t''; \omega) = \int_{-\infty}^{t} dt' E^*(t') E(t' - t'') \cos(\omega t') \cos(\omega (t' - t''))$$
(2.9)

Computation of the time and frequency dependent population in the locally excited donor state is thus reduced to two quadratures. If the temporal profile of the field (E(t)) is a Gaussian, than an analytic expression is readily obtained for the field function  $\eta$  and one remains with a single quadrature. Since we will assume that the energy difference between the two electronic surfaces is large and we will not be using ultrashort pulses, we can further simplify by using the rotating wave approximation, that is

$$\eta(t, t''; \omega) \simeq e^{i\omega t''} \int_{-\infty}^{t} dt' E^*(t') E(t' - t'').$$
(2.10)

The normalized absorption spectrum is then defined via the infinite time limit of the time dependent population in the excited state, that is:

$$S_e(\omega;\beta) = \frac{\int_{-\infty}^{\infty} dt \eta(\infty,t;\omega) \chi(t,\beta)}{2\pi\eta(\infty,0;0)}$$
(2.11)

#### **B.** Dissipation

We will assume that the ground and excited system Hamiltonians are well approximated as harmonic and without Duschinskii rotations. If the molecule being excited has N vibrational degrees of freedom, then the system Hamiltonians in mass weighted coordinates and momenta are:

$$H_{g,s} = \sum_{j=1}^{N} h_{g_j} = \frac{1}{2} \sum_{j=1}^{N} \left[ p_{q_j}^2 + \omega_{g_j}^2 q_j^2 \right]$$
(2.12)

$$H_{e,s} = \sum_{j=1}^{N} h_{e_j} + \Delta E = \frac{1}{2} \sum_{j=1}^{N} \left[ p_{q_j}^2 + \omega_{e_j}^2 (q_j - q_{j0})^2 \right] + \Delta E.$$
(2.13)

Dissipation is introduced by coupling each one of the ground and excited state vibrational modes to a dissipative bath. Classically this would imply that the equation of motion of each of the modes is that of a generalized Langevin equation:

$$\ddot{q}_{j} + \omega_{j}^{2} q_{j} + \int_{0}^{t} d\tau \gamma(t - \tau) \dot{q}_{j}(\tau) = F_{j}(t)$$
(2.14)

where we have expressly assumed that the friction function is the same for all modes, both in the ground and in the excited states. These are reasonable assumptions, since (a) the bath influencing all modes is the same bath, and (b) we will assume below that the differences between the ground and excited state system Hamiltonians is small.  $F_j(t)$  is the Gaussian random force exerted on the *j*-th mode, it has zero mean and obeys the fluctuation dissipation relation

$$\langle F_j(t)F_j(\tau)\rangle = \frac{1}{\beta}\gamma(t-\tau)$$
 (2.15)

where  $\gamma(t)$  is the time dependent friction function and the dot in Eq. 2.14 denotes differentiation with respect to the time.

It is well known [2,7] that a Langevin equation of this form is the continuum limit of a Hamiltonian

$$H_{(g,e)_j} = h_{(g,e)_j} + \sum_{k=1}^{M} \left[ \frac{p_{x_k}^2}{2} + \frac{1}{2} \left( \omega_k x_k - \frac{c_k}{\omega_k} q_j \right)^2 \right].$$
 (2.16)

The k-th harmonic bath mode is characterized by the mass weighted coordinate  $x_k$ , momentum  $p_{x_k}$  and frequency  $\omega_k$ . The solution of Hamilton's equations of motion for the bath modes is expressed in terms of the system coordinate  $q_j$  and the initial conditions, and then introduced into the equation of motion for the system variables  $q_j$ ,  $p_{q_j}$  [7]. This leads to the Langevin equation (2.14) with the identification for the friction function

$$\gamma(t) = \sum_{k=1}^{M} \frac{c_k^2}{\omega_k^2} \cos\left(\omega_k t\right).$$
(2.17)

and the Gaussian random force

$$F_{j}(t) = \sum_{k=1}^{M} c_{k} \left[ \left( x_{k}(0) - \frac{c_{k}}{\omega_{k}^{2}} q_{j}(0) \right) \cos\left(\omega_{k}t\right) + \frac{p_{k}(0)}{\omega_{k}^{2}} \sin\left(\omega_{k}t\right) \right].$$
(2.18)

Averaging over the initial conditions of the bath with the thermal distribution  $e^{-\beta H_j}$  gives a zero mean and the fluctuation dissipation relation of Eq. 2.15. The continuum limit in the Hamiltonian formalism is achieved by defining the spectral density [2]

$$J(\omega) = \frac{\pi}{2} \sum_{k=1}^{M} \frac{c_k^2}{\omega_k} [\delta(\omega - \omega_k) - \delta(\omega + \omega_k)].$$
(2.19)

The Hamiltonian formulation presents some advantages over the phenomenological Langevin formulation: first of all, Ohmic and memory friction are treated in the same way, and the results obtained can be extended to any kind of friction function obeying the fluctuation dissipation relation. Second, as already mentioned in the Introduction, the quantum treatment is straightforward. Instead of a classical Langevin equation for each mode, we describe the dissipation on each molecular mode through the system bath Hamiltonian operator as in Eq. 2.16 [7].

The correlation function  $\chi(t,\beta)$  can now be represented as a product of mode correlation functions, that is

$$\chi(t,\beta) = \prod_{j=1}^{N} \chi_j(t,\beta) = \prod_{j=1}^{N} \frac{Tr\left[e^{-\left(\beta - i\frac{t}{\hbar}\right)H_{g_j}}e^{-i\frac{t}{\hbar}H_{e_j}}\right]}{Z_{g_j}}$$
(2.20)

#### C. Perturbation theory

In principle, the *j*-th correlation function can be evaluated exactly in terms of the system excited and ground state frequencies, equilibrium shift of the excited state and the frequencies and coupling constants of the harmonic bath. This has been carried out in Refs. [12,13]. However, the resulting formulae are not given in the continuum limit. The central aim of this paper, is to derive an expression for the absorption spectrum and the nascent energy in the excited state in the continuum limit. For this purpose, we note that in many molecules, the differences between the vibrational Hamiltonians in the ground and excited states are not very big. Typically, vibrational frequencies in the excited electronic state are a few percent lower than in the ground state and the equilibrium position shifts in the excited state are small. This means that a good approximation may be obtained by considering the Hamiltonian difference operator

$$\Delta H = H_e - \Delta E - H_g = \sum_{j=1}^{N} \Delta h_j \tag{2.21}$$

as the 'small parameter' and then expanding with respect to it. Using the standard cumulant expansion to second order, this then means that our approximation to the j-th correlation function takes the form:

$$\chi_j(t,\beta) = \frac{Tr\left[e^{-\beta_c H_{g_j}}e^{-\beta_{im} H_{e_j}}\right]}{Z_{g_j}} \simeq \exp\left(-\frac{i}{\hbar}\left\langle\Delta h_j\right\rangle t - \int_0^t dt'(t-t')\left(\left\langle\Delta h_j(t')\Delta h_j\right\rangle - \left\langle\Delta h_j\right\rangle^2\right)\right)$$
(2.22)

with

$$\beta_c = \beta - \frac{i}{\hbar}t, \quad \beta_{im} = \frac{i}{\hbar}t.$$
(2.23)

The averages in Eq. 2.22 come from the interaction picture, that is:

$$\left\langle \Delta h_j^n \right\rangle = \frac{1}{Z_{g_j}} Tr \left[ e^{-\beta H_{g_j}} \Delta h_j^n \right]$$
(2.24)

and

$$\left\langle \Delta h_j(t) \Delta h_j \right\rangle = \frac{1}{Z_{g_j}} Tr \left[ e^{-\beta H_{g_j}} e^{\frac{i}{\hbar} H_{g_j} t} \Delta h_j e^{-\frac{i}{\hbar} H_{g_j} t} \Delta h_j \right].$$
(2.25)

Since henceforth we will be only using the ground state Hamiltonian and the difference operator, we will use the simpler notation  $H_j$  instead of  $H_{g_j}$ .

#### D. The normal mode transformation

The j-th mode Hamiltonian  $H_j$  is harmonic and so may be separated via a normal mode transformation [20–22]. The normal mode form is

$$H_j = \sum_{k=0}^{M} \left( \frac{p_{y_k}^2}{2} + \frac{1}{2} \lambda_k^2 y_k^2 \right)$$
(2.26)

where the normal mode coordinates  $y_k$ , are related to the *j*-th vibrational coordinate  $q_j$  and the bath modes  $x_k$  by an orthogonal transformation matrix  $\mathbf{U}^{(j)}$  such that

$$q_j = \sum_{k=0}^{M} u_{k0}^{(j)} y_k, \tag{2.27}$$

$$x_l = \sum_{k=0}^{M} u_{kl}^{(j)} y_k, \qquad l = 1, ..., N.$$
(2.28)

It should be clear, that the normal mode transformation is different for each vibrational mode of the molecule, since it depends (see also below) on the system frequency. To simplify the notation, we will below sometimes suppress the (j) superscript, which should also have been added (but was omitted for the sake of brevity) to each of the normal mode frequencies  $\lambda_k$ and coordinates  $y_k$  which are also different for different vibrational modes.

The matrix elements of the j-th normal mode transformation are given in terms of the coupling coefficients and original bath frequencies as [22]:

$$u_{l0}^{2} = \frac{1}{1 + \sum_{k=1}^{M} \frac{c_{k}^{2}}{(\omega_{k}^{2} - \lambda_{l}^{2})^{2}}}, \quad l = 0, ..., M$$
(2.29)

$$u_{lm} = \frac{c_m}{\lambda_l^2 - \omega_m^2} u_{l0}, \quad m = 1, ..., M$$
(2.30)

The normal mode frequencies are then expressed as:

$$\lambda_l^2 = \frac{\omega^2}{1 + \sum_{m=1}^M \frac{c_m^2}{\omega_m^2(\omega_m^2 - \lambda_l^2)}}, \quad l = 0, ..., M$$
(2.31)

where  $\omega$  stands for  $\omega_j$ , j = 1, ..., N, that is for each of the N vibrational modes of the ground state, we have M + 1 normal modes.

To obtain the continuum limit, we define a normal mode friction function [23,24]

$$K(t) = \sum_{l=0}^{M} u_{l0}^{2} \cos(\lambda_{l} t).$$
(2.32)

and a normal mode spectral density

$$\Upsilon(\lambda) = \frac{\pi}{2} \sum_{l=0}^{M} \frac{u_{l0}^2}{\lambda_l} [\delta(\lambda - \lambda_l) - \delta(\lambda + \lambda_l)]$$
(2.33)

The normal mode transformation has the important property that for any s [24],

$$\sum_{l=0}^{M} \frac{u_{l0}^2}{s^2 + \lambda_l^2} = \frac{1}{s^2 + s\hat{\gamma}(s) + \omega^2},$$
(2.34)

where  $\hat{\gamma}(s)$  is the Laplace transform of the friction function. From this relationship, using the Fourier decomposition of the Dirac delta function, one can deduce the continuum limit for the *j*-th normal mode spectral density:

$$\lambda \Upsilon_j(\lambda) = Re\left[\hat{K}_j(i\lambda)\right] = Re\left[\frac{i\lambda}{\omega_j^2 - \lambda^2 + i\lambda\hat{\gamma}(i\lambda)}\right], \quad j = 1, ..., N$$
(2.35)

and here we have explicitly reintroduced the j subscript, to remind ourselves that we are dealing with the j-th vibrational mode of the ground electronic state.

To show the usefulness of this representation we consider for example the velocity autocorrelation function  $C_v(t) \equiv \langle v(t)v(0) \rangle$ . In normal mode coordinates one has

$$C_{v}(t) = \left\langle \left( \sum_{l=0}^{M} u_{l0} p_{y_{l}}(t) \right) \cdot \left( \sum_{l=0}^{M} u_{l0} p_{y_{l}}(0) \right) \right\rangle.$$

$$(2.36)$$

The equations of motion for the normal modes  $y_l$  are those of a harmonic oscillator with frequency  $\lambda_l$ , so that

$$y_l(t) = y_l(0)\cos(\lambda_l t) + \frac{p_{y_l}(0)}{\lambda_l}\sin(\lambda_l t), \quad l = 0, ..., M.$$
(2.37)

The initial positions  $y_l(0)$  and velocities  $p_{y_l}(0)$  of the bath modes are distributed thermally, i.e.,

$$\langle \lambda_l^2 y_l^2(0) \rangle = \langle p_{y_l}^2(0) \rangle = \frac{\hbar}{2} \lambda_l \coth\left(\hbar\beta\lambda_l/2\right).$$
(2.38)

One thus finds that the quantum mechanical expressions for the position and momentum correlation functions are

$$Re[C_{q,j}(t)] = \sum_{l=0}^{M} u_{l0}^{2} \langle y_{l}^{2}(0) \rangle \cos(\lambda_{l} t) = \frac{\hbar}{\pi} \int_{0}^{\infty} d\lambda \Upsilon_{j}(\lambda) \coth(\hbar\beta\lambda/2) \cos(\lambda t)$$
(2.39)

$$Re[C_{v,j}(t)] = \sum_{l=0}^{M} u_{l0}^2 \langle p_{y_l}^2(0) \rangle \cos\left(\lambda_l t\right) = \frac{\hbar}{\pi} \int_0^\infty d\lambda \lambda^2 \Upsilon_j(\lambda) \coth\left(\hbar\beta\lambda/2\right) \cos\left(\lambda t\right)$$
(2.40)

where we have used the definition of the spectral density of the normal modes as given in Eq. (2.33).

# **E.** The correlation function $\chi_j(t,\beta)$ .

The partition function for the Hamiltonian of the j-th vibrational mode is

$$Z_{\beta,j} = \prod_{l=0}^{M} Z_{\beta_{jl}} = \prod_{l=0}^{M} \left( 2 \sinh\left(\frac{\hbar\beta\lambda_l^{(j)}}{2}\right) \right)^{-1}$$
(2.41)

and henceforth we will again suppress the (j) superscript. For the l-th normal mode, the harmonic oscillator propagator matrix element is well known to be:

$$\left\langle y_{l}^{\prime} \left| e^{-\beta_{c}h_{l}} \right| y_{l} \right\rangle = \frac{Z_{\beta_{c,l}}}{\sqrt{2\pi \left\langle y_{l}^{2} \right\rangle_{\beta_{c}}}} \exp\left(-\frac{1}{2} \left(\frac{\left(y_{l} - y_{l}^{\prime}\right)^{2} \left\langle p_{y_{l}}^{2} \right\rangle_{\beta_{c}}}{\hbar^{2}} + \frac{\left(\frac{y_{l} + y_{l}^{\prime}}{2}\right)^{2}}{\left\langle y_{l}^{2} \right\rangle_{\beta_{c}}}\right)\right)$$
(2.42)

where the second moments of the coordinate and momentum are given in Eqs. 2.38. One then readily finds that

$$\left\langle \Delta h \right\rangle_{\beta} = \frac{1}{2} \left( \omega_e^2 - \omega_g^2 \right) \left\langle q^2 \right\rangle_{\beta} + \frac{1}{2} \omega_e^2 q_0^2 \tag{2.43}$$

where in the continuum limit, the second moment of the coordinate is

$$\left\langle q^2 \right\rangle_{\beta} = \sum_{l=0}^{M} u_{l0}^2 \left\langle y_l^2 \right\rangle_{\beta} = \hbar \sum_{l=0}^{M} \frac{u_{l0}^2}{2\lambda_l \tanh\left(\frac{\hbar\beta\lambda_l}{2}\right)} = \frac{1}{\pi\hbar} \int_0^\infty d\lambda \frac{\Upsilon(\lambda)}{\tanh\left(\frac{\hbar\beta\lambda}{2}\right)}.$$
 (2.44)

Using the known expression for the matrix element of the harmonic propagator as in Eq. 2.42 one finds after performing the necessary Gaussian integrals (see the Appendix) that

$$\left\langle \Delta h_j(t) \Delta h_j \right\rangle - \left\langle \Delta h_j \right\rangle^2 = \frac{\left(\omega_{e_j}^2 - \omega_{g_j}^2\right)^2}{8} g_j^2(\beta, t) + \frac{1}{2} \omega_e^4 q_0^2 g_j(\beta, t) \tag{2.45}$$

where

$$g_j(\beta, t) = \hbar \sum_{l=0}^{M} \frac{u_{l0}^2 \cosh\left(\frac{\hbar\beta\lambda_l}{2} - i\lambda_l t\right)}{\lambda_l \sinh\left(\frac{\hbar\beta\lambda_l}{2}\right)} = \frac{2\hbar}{\pi} \int_0^\infty d\lambda \Upsilon_j(\lambda) \frac{\cosh\left(\frac{\hbar\beta\lambda}{2} - i\lambda t\right)}{\sinh\left(\frac{\hbar\beta\lambda}{2}\right)}$$
(2.46)

As noted in the Appendix, one can also perform the time integration in Eq. 2.22. The time dependent absorption spectrum is then obtained by appropriate integration over the time weighted spectral densities of normal modes and subsequent Fourier transformation of the product of all N correlation functions, thus completing the continuum limit theory of the harmonic absorption spectrum.

#### III. NUMERICAL MODEL

#### A. Perturbation theory without dissipation

Our model polyatomic molecule will be the same as used in previous studies. The molecule will have 45 degrees of freedom, divided into three groups: low, medium and high

frequencies. The low frequency group ranges from 50 to 470  $cm^{-1}$  with an equal spacing of 30  $cm^{-1}$ , the medium frequency group ranges from 800 to 1220  $cm^{-1}$  with the same spacing, and the high frequency group ranges from 2000 to 2700  $cm^{-1}$  with an equal spacing of 50  $cm^{-1}$ . These three groups mimic a typical frequency distribution of a polyatomic molecule.

For the excited state Hamiltonian, we assume the same groupings of frequencies as for the ground state. However the low frequency group frequencies are reduced by 5%, the medium group frequencies by 2% and the high frequency group by 1%. At this point, we will also assume that there are no equilibrium position shifts in the excited state.

If the equilibrium positions and frequencies in the excited electronic state are the same as in the ground state the absorption spectrum is a " $\delta$ " function centered at the  $\omega_{00}$  transition frequency, defined more generally as

$$\omega_{00} \equiv \frac{1}{2} \sum_{j=1}^{N} (\omega_{e_j} - \omega_{g_j}) + \frac{\Delta E}{\hbar}.$$
(3.1)

The average energy in the excited state is then identical to the average energy in the ground state, there is no cooling or heating. The energy gap  $\Delta E$  between the ground and excited electronic states is unimportant, it simply sets the scale of frequencies for the photoexcitation laser, so it will be set to 0.

The first test will be to show that indeed the second order cumulant expansion presented in the previous section is quite good. In the absence of dissipation, the exact correlation function is well known, for explicit formulae, see for example Refs. [17,25]. In Fig. 1 we plot the numerically exact absorption spectrum and compare it with the second cumulant expansion result as obtained from Eq. 2.22. The good agreement, indicates that also the results in the presence of dissipation will be rather accurate, since the dissipative bath is treated exactly, it is only the difference in the ground and excited state Hamiltonians which is treated perturbatively and this difference is small independent of the dissipative bath.

#### B. The effect of dissipation

As is well known, quantum dissipation cannot be usually treated with Ohmic friction, due to the divergence of the variance of the momentum. In the present analysis though, the hamiltonian difference operator is a function only of the system coordinates for which the variance does not diverge. Therefore results may be obtained also for Ohmic friction

$$\gamma(t) = 2\gamma\delta(t) \tag{3.2}$$

where  $\gamma$  is the friction strength parameter and  $\delta(t)$  is the Dirac  $\delta$  function. From Eq. 2.35 it follows that the spectral density of the normal modes for the *j*-th mode with frequency  $\omega_j$  is:

$$\Upsilon_j(\lambda) = \frac{\gamma\lambda}{(\omega_j^2 - \lambda^2)^2 + \gamma^2\lambda^2}.$$
(3.3)

In Fig. 2 we plot the resulting absorption spectrum for five different values of the friction strength ( $\gamma = 50, 100, 200, 350, \text{ and } 500 \text{ cm}^{-1}$ ) at the temperature T = 300K. We note that increasing the friction causes a blue shift of the spectrum. This is shown in more detail in Fig. 3 where we plot the location of the maximal absorption as a function of the friction strength. Note that the friction induced shift comes mainly from the first order term in  $\Delta h$ , as given by Eq. 2.43. The contribution from the first order term to the shift is shown as the green line in Fig. 3. The contribution of the second order term is small and almost independent of the magnitude of the friction. This is another indication that the second order cumulant expansion suffices for an accurate representation of the absorption spectrum.

Perhaps of greater interest is the fact that the full width at half height, which is a measure of the dephasing rate of the spectrum [26] is not a monotonic function of the friction strength. As shown in Fig. 4 increasing the friction first causes a narrowing of the peak and only for sufficiently large friction strength does the spectrum again broaden. This narrowing may be considered as a manifestation of stochastic resonance, its maximum occurs for friction values that are approximately twice as large as the red shift of the spectrum at zero friction.

Interestingly, this stochastic resonance disappears if the frequencies in the ground and excited states are the same and the only difference comes from equilibrium position shifts. In Fig. 5, we plot the spectrum as a function of the friction strength for the same ground state Hamiltonian as before but with the *same* vibrational frequencies in the excited state. However, now we introduce reduced equilibrium position shifts for the low frequency set of 15 modes, such that  $\delta_j = \sqrt{\frac{\omega_j}{\hbar}}q_j = 0.2$ . As is well understood, the spectrum now is more structured, with a broader wing to the blue of  $\omega_{00}$ . As shown in Fig. 6, friction causes a small blue shift of the maximum of the spectrum, but the most important effect is the broadening, (shown in Fig. 7) which smears the spectrum, ultimately giving a broad bell shaped function, slightly shifted to the blue of  $\omega_{00}$ . The width increases monotonically with the friction, the stochastic resonance results from frequency shifts only.

# **IV. DISCUSSION**

This is the first study of the effect of friction on a model polyatomic molecule with 45 degrees of freedom. Previous numerical results obtained by Berne and coworkers [12–14] were limited to a single mode coupled to a harmonic bath, modeling the absorption spectrum of a diatomic molecule coupled to a bath. The use of perturbation theory was justified by showing that the exact spectrum and the one obtained using the second order cumulant expansion were rather close to each other. As found for example for benzene [16], naphthalene [17] or stilbene [15,27], the differences between the excited and ground state vibrational Hamiltonians is rather small, justifying the use of the Hamiltonian difference operator as a small parameter.

The use of perturbation theory enabled us to derive continuum limit formulae for the time dependent population in the excited states as a function of the excitation frequency. In this paper we presented results for the infinite time population in the excited state, that is, the absorption spectrum. We found that friction has two major effects. One is a blue shift of the spectrum with increasing friction. The second more interesting result is a stochastic resonance like narrowing of the peak followed by a broadening as the friction becomes very large. The maximal narrowing is found in a range of friction values which are of the order of the red shift in the absorption spectrum at zero friction. This stochastic resonance was shown to be caused by the frequency shifts between the ground and excited state Hamiltonians, the position shifts lead only to a monotonically increasing width of the spectrum with friction.

Although the results presented here were for Ohmic friction, we also performed some computations with exponential memory friction, these did not show any qualitative differences as compared to the Ohmic limit.

An interesting related question has to do with the effect of friction on the nascent vibrational energy distribution in the excited state. In the strong friction limit, one would expect an almost instant thermalization of the distribution leading to the broad absorption spectrum in this limit. However, for weak friction, the slow relaxation of the distribution can lead to a stronger overlap with the ground state and thus a larger absorption and a narrower distribution. We suspect that this is the dynamics underlying the stochastic resonance phenomenon found in the present work.

# ACKNOWLEDGMENTS

This work has been supported by grants from the Israel Science Foundation and the US-Israel Binational Science Foundation.

# Appendix A The Hamiltonian difference correlation function

In this Appendix we will outline the derivation of the Hamiltonian difference correlation function defined in Eq. 2.25. Because of the separability of the molecular modes, it is sufficient to consider only a single molecular mode and then attach to it the appropriate index. Henceforth we will do away with the index j for the molecular mode.

The energy difference operator for a single mode is readily seen to be

$$\Delta h = \frac{1}{2} \left( \omega_e^2 - \omega_g^2 \right) q^2 + \frac{1}{2} \omega_e^2 \left( q_0^2 - 2qq_0 \right)$$
(A.1)

Consider first that part of the energy difference operator which depends only on the system coordinate q. One then readily finds that:

$$Z_{g_{j}} \left\langle \Delta h(t) \Delta h \right\rangle = Tr \left[ e^{-\beta H_{g}} e^{\frac{i}{\hbar} H_{g}t} \Delta h e^{-\frac{i}{\hbar} H_{g}t} \Delta h \right]$$
$$= \int_{-\infty}^{\infty} d\underline{y} d\underline{y}' \Delta h \left( \sum_{l=0}^{M} u_{l0} y_{l} \right) \Delta h \left( \sum_{l=0}^{M} u_{l0} y_{l}' \right) \left\langle \underline{y} \left| e^{-(\beta - \frac{i}{\hbar} t) H_{g}} \right| \underline{y}' \right\rangle \left\langle \underline{y}' \left| e^{-\frac{i}{\hbar} t H_{g}} \right| \underline{y} \right\rangle.$$
(A.2)

Introducing the unity function as  $\int_{-\infty}^{\infty} dq dq' \delta\left(q - \sum_{l=0}^{M} u_{l0} y_l\right) \delta\left(q' - \sum_{l=0}^{M} u_{l0} y'_l\right)$ , using the Fourier decomposition of the Dirac delta function  $\left(\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{ikx}\right)$ , performing the Gaussian integrals over all the modes  $y_j, y'_j$  as well as the Fourier variables k, k' leads to the result:

$$\langle \Delta h(t)\Delta h \rangle = \frac{1}{2\pi} \frac{1}{\sqrt{\alpha_c \alpha_s}} \int_{-\infty}^{\infty} dq dq' \Delta h(q) \Delta h(q') e^{-\frac{(q+q')^2}{2a_c} - \frac{(q-q')^2}{8a_s}}$$
(A.3)

where the 'variances'  $\alpha_c$  and  $\alpha_s$  are

$$\alpha_c = 2\hbar \sum_{l=0}^{M} \frac{u_{l0}^2}{\lambda_l} \left( \frac{\cosh\left(\frac{\hbar\beta_c\lambda_l}{2}\right)\cos\left(\frac{\lambda_l t}{2}\right)}{\sinh\left(\frac{\hbar\beta\lambda_l}{2}\right)} \right) = \frac{4\hbar}{\pi} \int_0^\infty d\lambda \Upsilon(\lambda) \frac{\cosh\left(\frac{\hbar\beta_c\lambda}{2}\right)\cos\left(\frac{\lambda t}{2}\right)}{\sinh\left(\frac{\hbar\beta\lambda_l}{2}\right)} \tag{A.4}$$

$$\alpha_s = \frac{i\hbar}{2} \sum_{l=0}^{M} \frac{u_{l0}^2}{\lambda_l} \left( \frac{\sinh\left(\frac{\hbar\beta_c \lambda_l}{2}\right) \sin\left(\frac{\lambda_l t}{2}\right)}{\sinh\left(\frac{\hbar\beta\lambda_l}{2}\right)} \right) = \frac{i\hbar}{\pi} \int_0^\infty d\lambda \Upsilon(\lambda) \frac{\sinh\left(\frac{\hbar\beta_c \lambda}{2}\right) \sin\left(\frac{\lambda t}{2}\right)}{\sinh\left(\frac{\hbar\beta\lambda_l}{2}\right)}.$$
 (A.5)

with  $\beta_c = \beta - \frac{i}{\hbar}t$ . The continuum form of these functions in terms of the spectral density of the normal modes is obtained from the definition of the spectral density (see Eq. 2.35). Defining

$$g(\beta, t) \equiv \frac{\alpha_c}{2} - 2\alpha_s = \frac{2\hbar}{\pi} \int_0^\infty d\lambda \Upsilon(\lambda) \frac{\cosh\left(\frac{\hbar\beta\lambda}{2} - i\lambda t\right)}{\sinh\left(\frac{\hbar\beta\lambda}{2}\right)},\tag{A.6}$$

noting that

$$\langle \Delta h \rangle = \frac{1}{2} \left( \omega_e^2 - \omega_g^2 \right) \left( \frac{\alpha_c}{4} + \alpha_s \right) + \frac{1}{2} \omega_e^2 q_0^2 \tag{A.7}$$

one readily finds that

$$\langle \Delta h(t)\Delta h \rangle - \langle \Delta h \rangle^2 = \frac{\left(\omega_e^2 - \omega_g^2\right)^2}{8} g^2(\beta, t) + \frac{1}{2} \omega_e^4 q_0^2 g(\beta, t) \tag{A.8}$$

as given in Eq. 2.45.

Finally we note that the time integral in Eq. 2.22 can also be carried out analytically, that is:

$$\int_{0}^{t} dt'(t-t')g(\beta,t') = \frac{4i\hbar}{\pi} \int_{0}^{\infty} d\lambda \frac{\Upsilon(\lambda)}{\lambda^{2}} \left(\frac{\sinh\left(\frac{\lambda(\hbar\beta-it)}{2}\right)\sin\left(\frac{\lambda t}{2}\right)}{\sinh\left(\frac{\hbar\beta\lambda}{2}\right)} - \frac{\lambda t}{2}\right)$$
(A.9)

and similarly

$$\int_{0}^{t} dt'(t-t')g^{2}(\beta,t') = \frac{4\hbar^{2}}{\pi^{2}} \int_{0}^{\infty} d\lambda d\lambda' \frac{\Upsilon(\lambda)\Upsilon(\lambda')}{\sinh\left(\frac{\hbar\beta\lambda}{2}\right)\sinh\left(\frac{\hbar\beta\lambda'}{2}\right)} F(\lambda,\lambda',t;\beta)$$
(A.10)

where

$$F(\lambda,\lambda',t;\beta) \equiv \int_{0}^{t} dt'(t-t') \cosh\left(\frac{\hbar\beta\lambda}{2} - i\lambda t'\right) \cosh\left(\frac{\hbar\beta\lambda'}{2} - i\lambda't'\right) = i\left[\frac{\sinh\left(\frac{\hbar\beta(\lambda+\lambda')-i(\lambda+\lambda')t}{2}\right) \sin\left(\frac{(\lambda+\lambda')t}{2}\right)}{(\lambda+\lambda')^{2}} + \frac{\sinh\left(\frac{\hbar\beta(\lambda-\lambda')-i(\lambda-\lambda')t}{2}\right) \sin\left(\frac{(\lambda-\lambda')t}{2}\right)}{(\lambda-\lambda')^{2}}\right] - i\frac{t}{2}\left[\frac{\sinh\left(\frac{\hbar\beta(\lambda+\lambda')}{2}\right)}{(\lambda+\lambda')} + \frac{\sinh\left(\frac{\hbar\beta(\lambda-\lambda')}{2}\right)}{(\lambda-\lambda')}\right].$$
(A.11)

# REFERENCES

- [1] R. Zwanzig, J. Stat. Phys. 9, 215 (1973).
- [2] A. O. Caldeira and A. J. Leggett, Ann. Phys. **149**, 374 (1983).
- [3] J. C. Tully, Annu. Rev. Phys. Chem. **31**, 319 (1980).
- [4] J. D. Doll and A. F. Voter, Annu. Rev. Phys. Chem. 38, 413 (1987).
- [5] J. P. Bergsma, B. J. Gertner, K. R. Wilson and J. T. Hynes, J. Chem. Phys. 86, 1356 (1987).
- [6] J. E. Straub, B. J. Berne and B. Roux, J. Chem. Phys. **93**, 6804 (1990).
- [7] E. Cortés, B. J. West and K. Lindenberg, J. Chem. Phys. 82, 2708 (1985).
- [8] E. Pollak, in Theoretical Methods in Condensed Phase Chemistry, edited by S. D.
   Schwartz (Kluwer Academic Publishers, The Netherlands, 2000) pp. 1-46.
- [9] R. G. Gordon, Adv. Magn. Res. 3, 1 (1968).
- [10] S. Mukamel, Principles of Nonlinear Optical Spectroscopy (Oxford University Press, Oxford, 1995).
- [11] V. May and O. Kühn, Charge and Energy Transfer Dynamics in Molecular Systems (Wiley-VCH, Berlin, 2000).
- [12] S. A. Egorov, E. Gallicchio and B. J. Berne, J. Chem. Phys. 107, 9312 (1997).
- [13] S. A. Egorov, E. Rabani and B. J. Berne, J. Chem. Phys. 108, 1407 (1998).
- [14] S. A. Egorov, E. Rabani and B. J. Berne, J. Chem. Phys. 110, 5238 (1999).
- [15] H. Wadi and E. Pollak, J. Chem. Phys. **110**, 11890 (1999).
- [16] Y. He and E. Pollak, J. Phys. Chem. A **105**, 10961 (2001).
- [17] Y. He and E. Pollak, J. Chem. Phys. **116**, 6088 (2002).

- [18] M. Cho and R. J. Silbey, J. Chem. Phys. **103**, 595 (1995).
- [19] Note the typographical error in Eqs. 6 of Ref. [18]. The correct version of the first equation is  $\tilde{V} = \tilde{V}_1(t)|e\rangle \langle g| + \tilde{V}_1^{\dagger}(t)|g\rangle \langle e|$  where  $\tilde{V}_1(t)|e\rangle \langle g|$  is as defined in Eq. 2.6.
- [20] F. Haake and R. Reibold, Phys. Rev. A **32**, 2462 (1984).
- [21] (a) E. Pollak, J. Chem. Phys. 85, 865 (1986); (b) E. Pollak, Phys. Rev. A 33, 4244 (1986).
- [22] A. M. Levine, M. Shapiro and E. Pollak, J. Chem. Phys. 88, 1959 (1988).
- [23] I. Rips and E. Pollak, Phys. Rev. A 41, 5366 (1990).
- [24] E. Pollak in *Dynamics of Molecules and Chemical Reactions*, 1996, R. E. Wyatt and J. Z. H. Zhang eds., Marcel Dekker, New York.
- [25] Y. J. Yan and S. Mukamel, J. Chem. Phys. 85, 5908 (1986).
- [26] J. L. Skinner and D. Hsu, J. Phys. Chem. **90**, 4931 (1986).
- [27] G. Gershinsky and E. Pollak, J. Chem. Phys. **107**, 812 (1997).

# FIGURE CAPTIONS

- Absorption spectrum in the absence of dissipation. The red (asymmetric) line is the exact absorption spectrum for the model Hamiltonians without equilibrium position shifts. The green line is its approximation using the second order cumulant expansion.
- 2. The effect of dissipation on the absorption spectrum with shifted frequencies but no equilibirum position shifts in the excited state.
- 3. The blue shift of the peak (with shifted frequencies) induced by friction. The red line shows the shift of the maximum of the absorption spectrum with increasing friction. The green line shows the approximate shift as predicted when using only the first order cumulant expansion.
- 4. Stochastic resonance in the absorption spectrum. The width of the absorption spectrum (with shifted frequencies but no position shifts) is plotted vs. the friction. Note the maximal narrowing of the peak for  $\gamma \sim 140 \text{ cm}^{-1}$ .
- 5. The absorption spectrum with equilibrium position shifts but no frequency shifts. Note the structure of the spectrum at low friction and its smearing as the friction is increased. For further details, see the text.
- 6. The blue shift of the peak (with shifted equilibrium positions) induced by friction.
- 7. Broadening of the peak as a function of the friction, for the model with equilibirum position shifts but without frequency shifts. Here, the friction induces a monotonic broadening, there is no stochastic resonance feature.









Figure 3



Figure 4











