On the derivation of rate equations for collisionless molecular multiphoton processes

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Starting with the complete molecular Liouville equation and making use of the Mori–Zwanzig projection operator formalism we derive generalized rate equations which describe the collisionless dynamics of level populations in the quasicontinuum of molecular multiphoton processes. We define precisely the complete molecular information required for the description of these processes which is expressed in the form of a hierarchy of intramolecular dipole correlation functions. We then discuss the general conditions under which the equations attain the form of simple rate equations and show how the complete molecular information reduces considerably in this case to three relevant quantities per transition: an integrated Rabi frequency, a dephasing time and *ratios* of statistical weights of the levels.

I. INTRODUCTION

The feasibility of pumping large amounts (few eV) of energy into collision-free polyatomic molecules via the absorption of many infrared photons has triggered the attention of numerous experimental and theoretical groups.[1,2] One reason for the broad interest in these studies of molecular multiphoton processes (MMP) is their potential usefulness as a probe for the dynamics of highly vibrationally excited polyatomics, which in turn is a key problem in the theories of chemical reactions. Another appealing aspect of these studies is the possibility of achieving laser-induced and controlled chemistry, provided the energy-pumping process is proved to be selective and capable of competing with the intramolecular redistribution of energy. The currently available experimental information regarding MMP includes absolute cross sections for energy absorption,[3] translational[4] and vibrational[5] distribution of the products of unimolecular decomposition following infrared pumping, total reaction yields and branching ratios of various channels as a function of laser frequency, intensity and fluence,[6] infrared[7] and visible[8] emission characteristics of the excited molecules, double resonance experiments[9] (both frequency and time resolved), etc.

Regarding the theoretical aspects of these studies,[10–12] it is clear that a complete dynamical description of MMP incorporating explicitly all the molecular states involved is neither feasible nor desirable. Due to the enormously high density of states of vibrationally excited polyatomic molecules, such a description will require a huge amount of (unavailable) information regarding the molecule for the calculation of few experimentally relevant meaningful quantities. An inevitable conclusion from these considerations is the necessity to develop a mesoscopic (i.e., partially statistical, partially dynamical) level of theoretical description which will enable us to evaluate the experimental observables using only partial (reduced) information regarding the molecule, thus matching the level of the theoretical description to the level of the available (or potentially available) experimental observables.

It has been suggested phenomenologically[13,3(a)] and demonstrated in several cases[1,2] that a simple description of the multiphoton excitation process in terms of ordinary rate equations may be quite adequate (at least for highly excited molecules in the so-called "quasicontinuum" region). A basic prediction of this postulate[3(a)] which was experimentally verified, in particular by the recent very nice low power ICR experiments,[2(b)] is the dependence of the dissociation yield on the total fluence (and not on the laser power, once it is above threshold). The major problem with the phenomenological approach is that, apart from a convenient way of fitting experimental data,[4] it does not give us any microscopic interpretation of the observed rate constants.

Early attempts[14,15] to derive reduced equations of motion (REM) for MMP (which may lead to rate equations in some limits) relied on separating the molecular degrees of freedom into a "system" and a "bath" with weak interaction between them. The few molecular normal modes which interact with the radiation field are taken to be the system whereas the rest are the bath. This approach is in the spirit of conventional theories of line broadening.[16,17] It is, however, fraught with some difficulties since the dynamics of highly vibrationally excited polyatomic molecules is not expected to be properly described using a perturbative approach in anharmonicities.[18] Moreover, perturbative treatments in anharmonicities necessarily become less adequate with the degree of molecular excitation.

A different type of approach is based on the usage of a basis set of the true molecular states, which enables us to formulate the problem in a form free of perturbative arguments in any intramolecular interactions.[19–21] Quack[20] has recently demonstrated for some simple molecular models how ordinary rate equations may emerge out of the complexity of the detailed dynamics, once we ask for a coarse-grained type of information. We have recently applied the projection operator formalism of Zwanzig and Mori[22,23] combined with the usage of the representation of the true molecular states to develop a microscopic systematic reduction scheme for MMP. The main steps in this "hydrodynamic-like" approach[21] are (1) the choice of a few molecular operators whose expectation values are the important variables for the dynamics of MMP; (2) the definition of an appropriate Mori projection operator onto the space spanned by these operators; and (3) the derivation of reduced equa-

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tions of motion (REM) for the time evolution of these variables.

This procedure is completely general, and formally the choice of the number and type of variables is arbitrary. However, the complexity and usefulness of the resulting REM depend crucially upon a successful choice of variables.

In the recent application of the projection operator formalism to MMP,[21] we have defined a set of operators corresponding to populations and coherences. We were then able to derive REM which interpolate smoothly all the way from the early stages of the molecular coherent driving (Region "I") up to the complete incoherent driving where the density of molecular states is sufficiently high (i.e., the quasicontinuum). Within this approach, intramolecular relaxation of populations (T_1 processes) need not be considered at all (since they are "buried" in our choice of basis set). The intramolecular dephasing processes (T_2) however are playing a major role in the continuous transition of the driving from coherent to totally incoherent. It should be pointed out that no perturbative arguments in intramolecular couplings need to be made in order to give a precise definition to the dephasing rates since they are associated solely with our reduction scheme (i.e., choice of variables).[21,24]

The explicit inclusion of molecular variables corresponding to coherences in our REM[21] is important for the sake of getting a unified description all the way from Region I (where they are important) to the quasicontinuum. Furthermore, in intramolecular line broadening measurements, as well as in combination of infrared pumping and coherent transient spectroscopy, the coherences are directly related to the experimental observables and should be therefore included explicitly in the REM. In the present work, we focus our attention on the dynamics of energy pumping into the molecule in the quasicontinuum with the main objectives of defining precisely the molecular information which may be extracted from these experiments and providing the most general conditions for the applicability of simple rate equations as well as microscopic expressions for the rate constants. To that end, we adopt a simpler approach than used previously[21] and consider explicitly only variables corresponding to populations.

In Sec. II, we define the molecular Hamiltonian and the reduced variables corresponding to populations of the various levels. We then derive our REM for these variables. We are able to give closed formal expressions for the complete information that is contained in any multiphoton experiment involving populations only. This information is a hierarchy of k-time intramolecular dipole correlation functions where $k=2, 4, 6, \ldots$ [Eq. (19)]. In Sec. III, we expand the REM to second order in the field and show how under quite general conditions (the Markovian limit,[17,22,23] where the integrated Rabi frequency is small compared to the energetic spread of the states within the levels) they reduce to simple rate equations. In Sec. IV, we consider higher order terms in the expansion of the REM and define an expansion parameter which shows that in the Markovian limit the higher order correlation functions are not important. The conclusion from Secs. III and IV is that, in the Markovian limit, simple rate equations apply, and most of the molecular information contained in the complete set of correlation functions (19) is redundant and is reduced to two numbers per transition. These are the integrated Rabi frequency and a dephasing rate given in terms of the time integral over a two-time dipole correlation function. (In addition, the REM depend on *ratios* of the statistical weights of the various levels.) Finally, in Sec. V, we summarize the assumptions and results of the present paper and discuss their relation to the currently available experimental information.

II. THE REDUCTION SCHEME

We consider a collision-free polyatomic molecule interacting with a monochromatic infrared laser beam whose frequency is ω_L. We assume that the Schrödinger equation for the isolated molecule (in the absence of the field) has been solved. As a result, we know the complete set of molecular eigenvalues as well as the dipole matrix elements between them. Assuming that the molecule is initially cold ($kT \ll \hbar\omega_L$), then only states with energies around $n\omega_L$, $n=0, 1, 2, \ldots$, are important for the multiphoton excitation process and need to be considered. We shall therefore group the relevant molecular states into levels and denote them as $\{|n\alpha\rangle\}$ with eigenvalues $E^0_{n\alpha}$, where n stands for the level and α runs over the states within the nth level. Invoking the rotating wave approximation (RWA),[10-12] which is very reasonable for MMP with infrared photons, we can thus write the combined Hamiltonian for the molecule and the field in the time independent form[20,21]:

$$H = H_0 + H' , \tag{1}$$

where

$$H_0 = \sum_{n,\,\alpha} |n\alpha\rangle E_{n\alpha}\langle n\alpha| , \tag{1a}$$

and

$$H' = \epsilon \sum_{\substack{n\alpha \\ m\beta \\ m=n\pm1}} |n\alpha\rangle \mu^{\alpha\beta}_{nm}\langle m\beta| . \tag{1b}$$

Here the molecular states within the nth level have absorbed n infrared quanta from the field, and $E_{n\alpha} = E^0_{n\alpha} - n\omega_L$ is the energy of the $|n\alpha\rangle$ state dressed (to zero order) by the field. $\mu^{\alpha\beta}_{nm} = \langle m\beta|\,\mu\,|n\alpha\rangle$ is the transition dipole between the $|n\alpha\rangle$ and $|m\beta\rangle$ states and ϵ is the laser field amplitude. The molecular level and coupling scheme is presented in Fig. 1.

The state of the molecule at time t is described by the complete molecular density matrix $\rho(t)$, which satisfies the Liouville equation

$$d\rho/dt = -i[H, \rho] = -iL\rho , \tag{2}$$

where $L(L_0, L')$ is the Liouville (tetradic) operator corresponding to $H(H_0, H')$, i.e.,[25]

$$L_{ab,cd} = H_{ac}\delta_{b,d} - H^*_{bd}\delta_{a,c} . \tag{3}$$

The density matrix $\rho(t)$ contains the complete information regarding the state of the molecule at time t.

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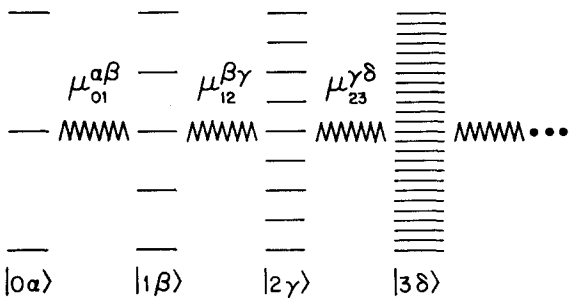

FIG. 1. The coupling scheme for molecular multiphoton processes. The true molecular states are grouped into levels where the nth level includes states $|n\phi\rangle$ which absorbed n photons from the field. μ is the radiative dipole coupling.

Most of this information, however, is redundant and we shall be interested only in some projections of the molecular density matrix on few "relevant" operators whose nature is determined by the initial conditions and the type of experiments considered. In a molecular multiphoton excitation experiment, the quantities that are of primary interest to us are the populations of the various levels [the probability $P_n(t)$ for the molecule to absorb n photons at time t]. In order to derive REM for these populations, we shall now introduce the following set of molecular operators[21]:

$$A_{nn} = \frac{1}{\sqrt{d_n}} \sum_{\alpha} |n\alpha\rangle\langle n\alpha| \quad , \quad n = 0, 1, \ldots, N-1, \tag{4}$$

d_n being the number of states within the nth level (the statistical weight of that level) and N is the total number of levels considered. It should be noted that the choice of d_n is important as it affects the resulting REM [Eqs. (33)], and therefore it should be based on physical grounds [only states that are expected to participate in the molecular excitation in the experimentally relevant time scale should be incorporated in Eq. (4)].

The operators A_{nn} were constructed to be orthonormal, i.e.,

$$\langle A_{nn}, A_{kk}\rangle \equiv \mathrm{Tr}\,(A_{nn}^{\dagger} A_{kk}) = \delta_{n,k} \quad . \tag{5}$$

We shall now expand the molecular density matrix ρ as follows:

$$\rho(t) = \sum_n \sigma_n(t) A_{nn} + \rho' \quad , \tag{6}$$

where $\sigma_n(t)$ are c numbers and where ρ', by construction, is orthogonal to A_{nn}, i.e.,

$$\langle \rho', A_{nn}\rangle = 0 \quad . \tag{7}$$

The populations of the various levels, P_n, are given by

$$P_n = \sqrt{d_n}\,\mathrm{Tr}[A_{nn}^{\dagger}\rho(t)] = \sqrt{d_n}\,\sigma_n(t) \quad . \tag{8}$$

Using the Zwanzig–Mori projection operator technique,[22,23] we can now derive reduced equations of motion for $\sigma_n(t)$. To that end, we define the vector σ whose components are $\sigma_0, \sigma_1, \ldots, \sigma_{N-1}$. We further introduce the Mori projection operator

$$PB \equiv \sum_n A_{nn}\langle A_{nn}, B\rangle \quad , \tag{9a}$$

and the complementary projection

$$Q = 1 - P \quad . \tag{9b}$$

Utilizing Eqs. (6), (7), and (9), we have

$$P\rho(t) = \sum_n \sigma_n(t) A_{nn} \quad . \tag{10}$$

The Mori–Zwanzig projection operator formalism[22,23] enables us to write the following *exact* closed REM for σ:

$$\frac{d\sigma}{dt} = -i\langle L\rangle\sigma - \int_0^t d\tau \langle R(t-\tau)\rangle\,\sigma(\tau) \quad , \tag{11}$$

where $R(t-\tau)$ is the tetradic operator

$$R(t-\tau) = L \exp[-iQL(t-\tau)]\,QL \quad . \tag{12}$$

Here, $\langle\cdots\rangle$ denotes a projection onto the P space, i.e.,

$$\langle L\rangle_{nn,mm} = (PLP)_{nn,mm} = \mathrm{Tr}(A_{nn}^{\dagger} L A_{mm}) \quad , \tag{13a}$$

and

$$\langle R(t-\tau)\rangle_{nn,mm} = [PR(t-\tau)P]_{nn,mm} = \mathrm{Tr}[A_{nn}^{\dagger} R(t-\tau) A_{mm}]. \tag{13b}$$

Equation (11) is general and gives a closed REM for *any* choice of the projection operator P. For our particular choice (9a) with Eq. (4), we have

$$PLP = 0 \quad , \tag{14a}$$

and

$$PL_0 = L_0 P = 0 \quad . \tag{14b}$$

Equation (14b) results in

$$QL = (1-P)(L_0 + L') = L_0 + QL' \quad . \tag{14c}$$

Making use of the integral relation

$$\exp(-iQLt) = \exp(-iL_0 t) - i\int_0^t d\tau \exp[-iL_0(t-\tau)]QL' \exp(-iQL\tau), \tag{15}$$

which is a direct consequence of Eq. (14c), we can now expand $\exp(-iQLt)$ and consequently also the memory kernel R [Eq. (12)] in a power series in QL'. We note in addition that, due to the nature of our P and L', only even powers in QL' will contribute to PRP. We thus have

$$\frac{d\sigma}{dt} = -\int_0^t d\tau \langle R(t-\tau)\rangle\,\sigma(\tau) \quad , \tag{16}$$

where

$$\langle R(t-\tau)\rangle = \langle R^{(2)}(t-\tau)\rangle + \langle R^{(4)}(t-\tau)\rangle + \langle R^{(6)}(t-\tau)\rangle + \cdots \quad , \tag{16a}$$

and where

$$\langle R^{(2)}(t-\tau)\rangle = \theta_2(t-\tau, 0) \quad , \tag{16b}$$

$$\langle R^{(4)}(t-\tau)\rangle = \int_0^{t-\tau} d\tau_1 \int_0^{\tau_1} d\tau_2\, \theta_4(t-\tau, \tau_1, \tau_2, 0) \quad , \tag{16c}$$

$$\langle R^{(6)}(t-\tau)\rangle = \int_0^{t-\tau} d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \times \theta_6(t-\tau, \tau_1, \tau_2, \tau_3, \tau_4, 0) \quad , \tag{16d}$$

and

$$\langle R^{(2k)}(t-\tau)\rangle = \int_0^{t-\tau} d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{2k-3}} d\tau_{2k-2} \times \theta_{2k}(t-\tau, \tau_1, \tau_2, \ldots, \tau_{2k-2}, 0) \quad . \tag{16e}$$

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Here,

$$\theta_{2k}(\tau_1, \tau_2, \ldots, \tau_{2k}) = (-1)^{k+1}\langle L'(\tau_1)L'(\tau_2)(1-P)L'(\tau_3)L'(\tau_4) \times (1-P)\cdots(1-P)L'(\tau_{2k-1})L'(\tau_{2k})\rangle , \quad (17)$$

where

$$L'(\tau) = \exp(iL_0\tau)L'\exp(-iL_0\tau) . \quad (18)$$

Let us introduce further the kth moment of L' as the k-time correlation functions

$$M_k(\tau_1, \tau_2, \ldots, \tau_k) = \langle L'(\tau_1)L'(\tau_2)\cdots L'(\tau_k)\rangle , \quad (19)$$

in terms of which we may rewrite Eq. (17) in the form

$$\theta_2(\tau_1, \tau_2) = M_2(\tau_1, \tau_2) , \quad (20a)$$

$$\theta_4(\tau_1, \tau_2, \tau_3, \tau_4) = -[M_4(\tau_1, \tau_2, \tau_3, \tau_4) - M_2(\tau_1, \tau_2)M_2(\tau_3, \tau_4)] , \quad (20b)$$

etc.

Equations (16) together with Eqs. (17)–(20) constitute our basic reduction scheme. They enable us to derive closed REM for the N populations of the various levels ($P_n = \sqrt{d_n}\,\sigma_n$, $n = 0, 1, \ldots, N-1$) in terms of the tetradic $N\times N$ R matrix. Evaluation of the latter requires the calculation of the intramolecular dipole correlation functions M_k [Eq. (19)] [or θ_k, Eq. (20)], $k = 2, 4, \ldots$, which provide us with the complete molecular information needed for the description of all MMP whenever the experimental observables are connected with populations only.

III. EXPANSION OF THE REM TO SECOND ORDER IN THE FIELD

To second order in the applied field (H'), we set

$$\langle R(t-\tau)\rangle \cong \langle R^{(2)}(t-\tau)\rangle . \quad (21)$$

Substitution of Eq. (1) in (16b) results in the following nonzero matrix elements of R:

$$\langle R_{nn,mm}(t-\tau)\rangle = -\frac{1}{\sqrt{d_n d_m}} \times \sum_{\alpha\beta} [L'^{\alpha\alpha,\alpha\beta}_{nn,nm}(t-\tau)L'^{\alpha\beta,\beta\beta}_{nm,mm}(0) + \text{c.c.}], \quad m = n\pm 1, \quad (22a)$$

and

$$\langle R_{nn,nn}(t-\tau)\rangle = \frac{1}{d_n} \times \sum_{\substack{\alpha,\beta \\ m=n\pm1}} [L'^{\alpha\alpha,\alpha\beta}_{nn,nm}(t-\tau)L'^{\alpha\beta,\alpha\alpha}_{nm,nn}(0) + \text{c.c.}] . \quad (22b)$$

Here,

$$L'^{\alpha\beta,\gamma\delta}_{ij,kl} \equiv \langle\langle i\alpha, j\beta | L' | k\gamma, l\delta\rangle\rangle , \quad (23)$$

comes for the tetradic matrix element of L' (we are using here the double bracket notation[25] whereby the tetradic state corresponding to $|a\rangle\langle b|$ is denoted $|ab\rangle\rangle$). In Eqs. (22), we have made use of the Liouville conjugation symmetry

$$L'_{ab,cd} = -L'^{*}_{ba,dc} , \quad (24)$$

which is valid for any tetradic operator[25] and may be easily verified using Eq. (3).

We shall now define the two-time intramolecular dipole correlation function for the nm transition:

$$I_{nm}(t) = \mathrm{Re}\,\tilde{I}_{nm}(t) , \quad (25a)$$

where

$$\tilde{I}_{nm}(t) = \langle\mu_{nm}(t)\mu_{mn}(0)\rangle / \langle\mu_{nm}(0)\mu_{mn}(0)\rangle = \frac{1}{\gamma^2_{nm}} \sum_{\alpha,\beta} |\mu^{\alpha\beta}_{nm}|^2 \exp(i\omega_{n\alpha,m\beta}t) . \quad (25b)$$

Here,

$$\mu_{nm}(t) = \exp(iH_0 t)\,\mu_{nm}\exp(-iH_0 t) , \quad (26)$$

$$\gamma^2_{nm} = \langle\mu_{nm}(0)\,\mu_{mn}(0)\rangle = \sum_{\alpha,\beta} |\mu^{\alpha\beta}_{nm}|^2 , \quad (27)$$

and

$$\hbar\omega_{n\alpha,m\beta} = E_{n\alpha} - E_{m\beta} . \quad (28)$$

We further define two quantities which are related to the integrated Rabi frequency for the nm transition

$$\Omega_{nm} = \sqrt{2}\epsilon\,\gamma_{nm} , \quad (29)$$

and

$$\bar{\Omega}^2_{nm} = \Omega^2_{nm}/\sqrt{d_n d_m} = 2\epsilon^2 \sum_{\alpha,\beta} |\mu^{\alpha\beta}_{nm}|^2/\sqrt{d_n d_m} . \quad (30)$$

Making use of the quantities (25)–(29), we can express the matrix elements of $\langle R\rangle$ [Eqs. (22)] as follows:

$$\langle R^{(2)}_{nn,mm}(t-\tau)\rangle = -\frac{\Omega^2_{nm}}{\sqrt{d_n d_m}} I_{nm}(t-\tau) \quad (31a)$$

and

$$\langle R^{(2)}_{nn,nn}(t-\tau)\rangle = \sum_{m=n\pm1} \frac{\Omega^2_{nm}}{d_n} I_{nm}(t-\tau) . \quad (31b)$$

Upon substitution of Eqs. (31) in (11) and putting $P_n = \sqrt{d_n}\,\sigma_n$, we finally get

$$\frac{dP_n}{dt} = \sum_{m=n\pm1} \Omega^2_{nm} \int_0^t d\tau I_{nm}(t-\tau) \times [P_m(\tau)/d_m - P_n(\tau)/d_n] , \quad (32)$$

or alternatively

$$\frac{dP_n}{dt} = \sum_{m=n\pm1} \bar{\Omega}^2_{nm} \int_0^t d\tau I_{nm}(t-\tau) \times \left[P_m(\tau)\sqrt{\frac{d_n}{d_m}} - P_n(\tau)\sqrt{\frac{d_m}{d_n}}\right] . \quad (33)$$

Equations (32) and (33) reduce to simple rate equations under one, very general type of condition. If $I_{nm}(t-\tau)$ has a characteristic time scale $\tau_c = \Gamma^{-1}_{nm}$ such that

$$\bar{\Omega}_{nm} \ll \Gamma_{nm} , \quad (34)$$

then we expect $P_n(t)$ to vary on a time scale considerably longer than Γ^{-1}_{nm} (this expectation will be verified later). In this case, $I_{nm}(t-\tau)$ acts like a δ function inside the integrals of Eqs. (32) or (33). We thus have

$$I_{nm}(t-\tau) = \Gamma^{-1}_{nm}\,\delta(t-\tau) , \quad (35)$$

where

$$\tau_c \equiv \Gamma^{-1}_{nm} = \int_0^\infty d\tau I_{nm}(\tau) . \quad (36)$$

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[We note that $I_{nm}(\tau)$ is dimensionless and $I_{nm}(0)=1$ so that $\int_0^\infty d\tau I_{nm}(\tau)$ is actually the typical time scale of $I_{nm}(\tau)$.] Substitution of Eq. (35) in (33) results in the simple rate equations

$$\frac{dP_n}{dt}=\sum_{m=n\pm1} W_{nm}^{(2)}\left(P_m\sqrt{\frac{d_n}{d_m}}-P_n\sqrt{\frac{d_m}{d_n}}\right), \tag{37}$$

where

$$W_{nm}^{(2)}=\bar{\Omega}_{nm}^2/\Gamma_{nm}\ . \tag{37a}$$

Equation (37) may be recast in the form

$$\frac{dP_n}{dt}=\sum_{m=n\pm1} K_{nm}^{(2)}P_m(t)-K_{nn}^{(2)}P_n(t)\ , \tag{38}$$

where

$$K_{nm}^{(2)}=\frac{\Omega_{nm}^2}{d_m\Gamma_{nm}}, \tag{38a}$$

and

$$K_{nn}^{(2)}=\sum_{m=n\pm1} K_{mn}^{(2)}\ . \tag{38b}$$

The superscript (2) in Eqs. (37) and (38) signifies that $W^{(2)}$ and $K^{(2)}$ are evaluated to second order in $H'(\mu)$. Utilizing Eqs. (38a) and (37a), we have

$$W_{nm}^{(2)}=\sqrt{K_{nm}^{(2)}K_{mn}^{(2)}}\ . \tag{38c}$$

Condition (34) is called the *Markovian limit*[22,23,25] and implies that a separation of time scales exists in our problem such that our chosen set of variables is slowly varying compared to all the rest. *A posteriori* we can now justify the substitution (35). Using Eqs. (37), we note that the characteristic rate of change of P_n is $W_{nm}=\bar{\Omega}_{nm}^2/\Gamma_{nm}$. Condition (34) thus implies also that $W_{nm}\ll\Gamma_{nm}$, which provides a consistency check to our assumption that P_n are varying on a much slower time scale than Γ_{nm}^{-1} [which led to Eq. (35)].

For the sake of illustration, we shall consider now a simple model whereby $|\mu_{nm}^{\alpha\beta}|^2$ is constant, independent on α and β, i.e.,

$$|\mu_{nm}^{\alpha\beta}|^2=\begin{cases}|V|^2, & -\Delta<E_{n\alpha},\ E_{m\beta}<\Delta\ ,\\ 0, & \text{elsewhere}\ .\end{cases} \tag{39}$$

Assuming that the number of states d_n and d_m is sufficiently large and that they are uniformly distributed throughout the n, m manifolds, we can replace the summation (25) by integration, resulting in

$$I_{nm}(t)=\frac{\sin^2(\Delta t)}{(\Delta t)^2}\ , \tag{40a}$$

$$\Omega_{nm}^2=2\epsilon^2|V|^2 d_n d_m\ , \tag{40b}$$

and

$$\bar{\Omega}_{nm}^2=2\epsilon^2|V|^2\sqrt{d_n d_m}\ ; \tag{40c}$$

The characteristic time scale of $I_{nm}(t)$ is thus Δ^{-1}. Assuming that Δ is sufficiently large such that

$$\bar{\Omega}_{nm}\ll\Delta\ , \tag{41}$$

we are in the Markovian limit whereby

$$\Gamma_{nm}^{-1}=\int_0^\infty d\tau I_{nm}(\tau)=\frac{\pi}{2\Delta}\ . \tag{42}$$

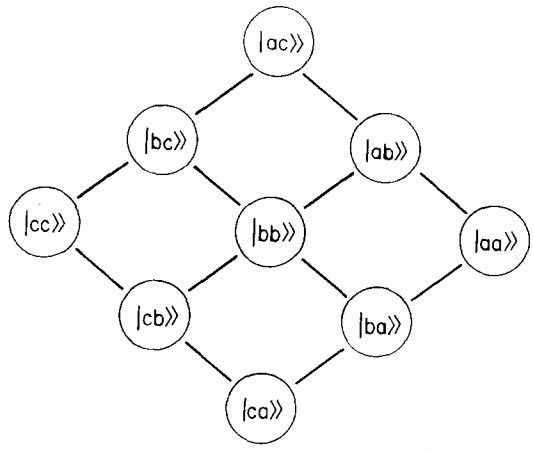

FIG. 2. Diagrammatic representation of the Liouville space terms contributing to M_4. Note that there are six pathways to go from $|aa\gg$ to $|cc\gg$ in fourth order.

We thus obtain, utilizing Eq. (41), the simple rate equation (38) where

$$K_{nm}^{(2)}=\frac{\Omega_{nm}^2}{\Gamma_{nm}d_m}=2\pi\epsilon^2|V|^2\rho_n\ , \tag{43}$$

and where

$$\rho_n=d_n/2\Delta \tag{44}$$

is the density of states in the $|n\alpha\rangle$ manifold. Equation (43) is the familiar golden rule type expression.

IV. EVALUATION OF THE HIGHER ORDER CORRELATION FUNCTIONS

In order to get an estimate of the approximations involved in the expansion of the REM to second order in H' (as was done in Sec. III), we shall now proceed to the evaluation of the fourth order contribution to $\langle R\rangle$. This will enable us to define a dimensionless expansion parameter for the series (16a) and as a result to define precisely the general conditions for its truncation.

We shall consider first $M_4(t-\tau,\tau_1,\tau_2,0)$ which is required for the evaluation of $\langle R^{(4)}(t-\tau)\rangle_{mm,nn}$, where $m=n$, $n\pm2$. To that end, we take three consecutive levels n, l, and m. For abbreviating the notation, we shall throughout the present section substitute a, b, b', and c for $n\alpha$, $l\beta$, $l\beta'$, and $m\gamma$, respectively. Similarly, $\sum_a$ will substitute for $\sum_\alpha$, etc. Figure 2 presents diagrammatically the coupling scheme required for the evaluation of $(M_4)_{cc,aa}$. Using Fig. 2, we notice that there are six pathways which lead from $|aa\rangle\rangle$ to $|cc\rangle\rangle$ in fourth order. However, by virtue of the Liouville conjugation symmetry [Eq. (24)], we need consider only three independent paths and the other three have a contribution which is simply their complex conjugate. We thus have

$$M_4(t-\tau,\tau_1,\tau_2,0)_{cc,aa}=\text{(I)}+\text{(II)}+\text{(III)}+\text{c.c.}, \tag{45}$$

where

$$\text{(I)}=\frac{1}{\sqrt{d_a d_c}}\sum_{\substack{ab\\b'c}} L'_{cc,b'c}(t-\tau)L'_{b'c,ac}(\tau_1)L'_{ac,ab}(\tau_2)L'_{ab,aa}(0)$$

$$=\frac{1}{\sqrt{d_a d_c}}\sum_{\substack{ab\\b'c}}\mu_{b'a}\mu_{ab}\mu_{bc}\mu_{cb'}$$

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$$\times\exp[i\omega_{cb'}(t-\tau)+i\omega_{b'a}\tau_1+i\omega_{bc}\tau_2]\ , \tag{45a}$$

$$\text{(II)}=\frac{1}{\sqrt{d_a d_c}}\sum_{\substack{ab\\b'c}} L'_{cc,b'c}(t-\tau)L'_{b'c,b'b}(\tau_1)L'_{b'b,ab}(\tau_2)L'_{ab,aa}(0)$$

$$=\frac{1}{\sqrt{d_a d_c}}\sum_{\substack{ab\\b'c}}\mu_{b'a}\mu_{ab}\mu_{bc}\mu_{cb'}$$

$$\times\exp[i\omega_{cb'}(t-\tau)+i\omega_{bc}\tau_1+i\omega_{b'a}\tau_2]\ , \tag{45b}$$

and

$$\text{(III)}=\frac{1}{\sqrt{d_a d_c}}\sum_{\substack{ab\\b'c}} L'_{cc,cb}(t-\tau)\,L'_{cb,b'b}(\tau_1)\,L'_{b'b,ab}(\tau_2)\,L'_{ab,aa}(0)$$

$$=\frac{1}{\sqrt{d_a d_c}}\sum_{\substack{ab\\b'c}}\mu_{b'a}\mu_{ab}\mu_{bc}\mu_{cb'}$$

$$\times\exp[i\omega_{bc}(t-\tau)+i\omega_{cb'}\tau_1+i\omega_{b'a}\tau_2]\ . \tag{45c}$$

At this stage, we introduce a simplifying assumption which makes use of the complexity of our system. The various μ's are expected to vary randomly and have an arbitrary phase. As a result, we anticipate that

$$\sum_a \mu_{b'a}\mu_{ab}\cong\sum_a|\mu_{ab}|^2\delta_{b,b'}\ , \tag{46}$$

and

$$\sum_c \mu_{bc}\mu_{cb'}\cong\sum_c|\mu_{bc}|^2\delta_{bb'}\ . \tag{47}$$

This is a form of the statistical random phase approximation (RPA). Making use of this assumption, we can omit the b' summation in Eqs. (45) and set $b=b'$. It is now clear that when Eq. (46) holds, then diagrams (II) and (III) do not contribute at all to θ_4 (17) (and to $R^{(4)}$). This arises since they both pass through $A_{bb}=(1/\sqrt{d_l}\times\sum_\beta|l\beta\rangle\langle l\beta|$, and by construction of the P projection (9a), we have

$$(1-P)A_{bb}=0\ . \tag{48}$$

An alternative way to see this is by looking at Eq. (20b). We then note that the contribution to $M_4(t-\tau,\tau_1,\tau_2,0)$ from these diagrams exactly equals that of $M_2(t-\tau,\tau_1)M_2(\tau_2,0)$ and as a result their net contribution to θ_4 vanishes. Using Eqs. (20), (45), and (46), we thus have

$$\theta_4(t-\tau,\tau_1,\tau_2,0)=-(\text{(I)}+\text{c.c.})$$

$$=\frac{-1}{\sqrt{d_a d_c}}\sum_{\substack{a,b\\c}}|\mu_{ab}|^2|\mu_{bc}|^2$$

$$\times\exp[i\omega_{cb}(t-\tau-\tau_2)+i\omega_{ba}\tau_1]+\text{c.c.} \tag{49}$$

Within the random phase approximation, we do not expect $|\mu_{ab}|^2$ and $|\mu_{bc}|^2$ to be correlated. It is thus reasonable to assume that Eq. (49) may be further factorized in the form

$$\theta_4=\frac{-1}{\sqrt{d_a d_c d_b^2}}\left\{\sum_{ab}|\mu_{ab}|^2\exp(i\omega_{ba}\tau_1)\right.$$

$$\left.\times\sum_{bc}|\mu_{bc}|^2\exp[i\omega_{cb}(t-\tau-\tau_2)]+\text{c.c.}\right\}\ , \tag{50}$$

i.e.,

$$\theta_4(t-\tau,\tau_1,\tau_2,0)=-\bar{\Omega}_{ab}^2\bar{\Omega}_{bc}^2\,\mathrm{Re}[\tilde{I}_{ab}(\tau_1)\tilde{I}_{bc}(t-\tau-\tau_2)]\ . \tag{51}$$

The factorization (50) implies a statistically uniform distribution of oscillator strength whereby there are no special states within the a, b, and c manifolds that are more strongly radiatively coupled than the others. Moreover, even if Eq. (50) does not strictly hold, this will not change the order of magnitude estimates of the present section. We are now in a position to evaluate $\langle R^{(4)}\rangle$:

$$\langle R^{(4)}_{cc,aa}(t-\tau)\rangle=\int_0^{t-\tau}d\tau_1\int_0^{\tau_1}d\tau_2\,\theta_4(t-\tau,\tau_1,\tau_2,0)\ . \tag{52}$$

From the definition (25), we expect $\tilde{I}(\tau)$ to be finite only over a limited time scale $\tau\lesssim\tau_c=\Gamma^{-1}$, where Γ is a measure of the energy spread of the levels involved. Using Eq. (51), it is clear that θ_4 {and consequently also $\langle R^{(4)}_{cc,aa}(t-\tau)\rangle$ [Eq. (16c)]} vanishes when $t-\tau\gtrsim\tau_c$. Thus, the characteristic time scale of R is equal to that of $\tilde{I}$. Usually, we are interested in the time evolution of P_n which occurs on a much longer time scale than Γ^{-1}. This is again a manifestation of the Markovian assumption (34). We can thus substitute in Eq. (16):

$$\langle R^{(4)}(t-\tau)\rangle=-W^{(4)}\delta(t-\tau)\ , \tag{53}$$

where

$$W^{(4)}_{cc,aa}=-\int_0^\infty dt\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\,\theta_4(t,\tau_1,\tau_2,0)$$

$$=\bar{\Omega}_{ab}^2\bar{\Omega}_{bc}^2\int_0^\infty dt\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\,\mathrm{Re}[\tilde{I}_{ab}(\tau_1)\tilde{I}_{bc}(t-\tau-\tau_2)]. \tag{54}$$

Equation (53) together with Eqs. (35) and (16) result in the following rate equations:

$$\frac{dP_n}{dt}=\sum_{m=n\pm1}W^{(2)}_{nm}\left(P_m\sqrt{\frac{d_n}{d_m}}-P_n\sqrt{\frac{d_m}{d_n}}\right)$$

$$+\sum_{m=n\pm2}W^{(4)}_{nm}\left(P_m\sqrt{\frac{d_n}{d_m}}-P_n\sqrt{\frac{d_m}{d_n}}\right). \tag{55}$$

We shall now turn to an order of magnitude estimate of $W^{(4)}$. From the previous arguments, it is clear that the only contribution to the integral (52) comes from the region

$$0<\tau_1,\ \tau_2,\ t<\tau_c=\Gamma^{-1}\ , \tag{56}$$

since otherwise the integrand vanishes. We thus expect that

$$W^{(4)}\cong\bar{\Omega}_{ab}^2\bar{\Omega}_{bc}^2/\Gamma^3\ . \tag{57}$$

For the sake of illustration, let us take

$$\tilde{I}(\tau)=\exp(-\Gamma\tau)\ , \tag{58}$$

which yields

$$\langle R^{(4)}(t-\tau)\rangle=\bar{\Omega}_{ab}^2\bar{\Omega}_{bc}^2\int_0^{t-\tau}d\tau_1\int_0^{\tau_1}d\tau_2$$

$$\times\exp(-\Gamma\tau_1)\exp[-\Gamma(t-\tau-\tau_2)]\ , \tag{59}$$

resulting in

$$\langle R^{(4)}(t-\tau)\rangle_{cc,aa}=\frac{\bar{\Omega}_{ab}^2\bar{\Omega}_{bc}^2}{\Gamma^2}\exp[-\Gamma(t-\tau)]$$

$$\times\{\exp[-\Gamma(t-\tau)]+\Gamma(t-\tau)-1\} \tag{60a}$$

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and

$$W^{(4)}_{cc,aa} = -\int_0^\infty dt\,\langle R^{(4)}(t)\rangle_{cc,aa} = \frac{1}{2}\frac{\bar{\Omega}^2_{ab}\bar{\Omega}^2_{bc}}{\Gamma^3} \,. \tag{60b}$$

Equations (60) demonstrate the validity of our general argument leading to Eq. (57), which is not restricted to the particular form (58). Assuming that $\bar{\Omega}_{ab} \cong \bar{\Omega}_{bc} = \bar{\Omega}$, we recall from Eq. (37a) that

$$W^{(2)} = \bar{\Omega}^2/\Gamma \,. \tag{61}$$

We thus get, using Eqs. (57) and (61),

$$W^{(4)}/W^{(2)} = K^{(4)}/K^{(2)} = (\bar{\Omega}/\Gamma)^2 = W^{(2)}/\Gamma \,, \tag{62}$$

which shows that the expansion parameter for the series

$$W = W^{(2)} + W^{(4)} + \cdots \tag{63}$$

is

$$\eta = (\bar{\Omega}/\Gamma)^2 = W^{(2)}/\Gamma \,. \tag{64}$$

Thus,

$$W^{(2k+2)} \cong W^{(2)}\,\eta^k \,. \tag{65}$$

We further note that the condition for the validity of the Markovian limit [i.e., Eq. (34)] is $\eta \ll 1$, which implies that in this limit the higher order terms in the expansion (63) become unimportant!

In concluding this section, we shall consider now another model (i.e., a constant coupling model) for $\mu^{\alpha\beta}_{nm}$.[26-30] This model is physically unrealistic for MMP; however, comparison of its results with the present model where we have invoked the random phase approximation (46) and (47) will enable us to gain a better insight on the dynamics of MMP. In the constant coupling model, we take $\mu^{\alpha\beta}_{nm}$ to be independent on α and β (no randomness in phase). We thus assume

$$\mu^{\alpha\beta}_{nm} = \begin{cases} V, & -\Gamma < E_{n\alpha},\, E_{m\beta} < \Gamma \,, \\ 0, & \text{elsewhere} \,, \end{cases} \tag{66}$$

We further assume that Γ^{-1} is much faster than our relevant time scale for P_n (the Markovian assumption) and that $d \gg 1$. The latter implies that $\theta_4 \cong -M_4 + O(1/d)$. $W^{(4)}$ will now have three contributions corresponding to the diagrams (I), (II), and (III) of Eq. (45):

$$W^{(4)}_{cc,aa} = \text{(I)} + \text{(II)} + \text{(III)} \,. \tag{67}$$

Let us take, for example, the contribution of (III):

$$\text{(III)} = \bar{\Omega}^2_{ab}\bar{\Omega}^2_{bc}\,d_b \int_0^\infty dt \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \times \frac{\sin\Gamma t}{\Gamma t}\,\frac{\sin\Gamma(t-\tau_1)}{\Gamma(t-\tau_1)}\,\frac{\sin\Gamma(\tau_1-\tau_2)}{\Gamma(\tau_1-\tau_2)}\,\frac{\sin\Gamma\tau_2}{\Gamma\tau_2} \,. \tag{68}$$

It is again clear that the only region contributing to the integrals (68) is

$$0 < t,\ \tau_1,\ \tau_2 < \Gamma^{-1} \,, \tag{69}$$

which means that the value of the integral is $0(\Gamma^{-3})$; we thus get

$$\text{(III)} \cong \frac{\bar{\Omega}^2_{ab}\bar{\Omega}^2_{bc}}{\Gamma^3}\,d_b \,. \tag{70}$$

(I) and (II) are given by an expression similar to Eq. (68) with the replacement of the time argumentus t, $t-\tau_1$, $\tau_1-\tau_2$, and τ_2 in the integrand, by $t-\tau_2$, τ_2, τ_1, and $t-\tau_1$, and by $t-\tau_2$, τ_1, $t-\tau_1$, and τ_2, respectively. It is then clear that condition (69) applies for (I) and (II) as well so that (I) and (II) will be of the same order of magnitude as (III) [Eq. (70)]. We thus have

$$W^{(4)}_{cc,aa} \cong \frac{\bar{\Omega}^4}{\Gamma^3}\,d_b \,, \tag{71}$$

which implies

$$\eta \equiv W^{(4)}/W^{(2)} = \left(\frac{\bar{\Omega}}{\Gamma}\right)^2 d_b = \frac{W^{(2)}}{\Gamma}\,d_b \,. \tag{72}$$

By comparing $W^{(4)}$ or η for the present, constant coupling (CCP) model [Eqs. (71) and (72)] with the same quantities calculated for the previous model involving the random phase approximation (RPA) [Eqs. (62) or (64)], we note that the former are larger by a factor of d_b. In fact, within the Markovian limit with the RPA, the resulting rate equations do not depend at all on the number of states involved (d) but rather only on $\bar{\Omega}$, Γ, and *ratios* of statistical weights d_a/d_b. In contrast, the present CCP equations do depend explicitly on d. We thus have for both models

$$W^{(2k+2)} = W^{(2)}\,\eta^k \,, \tag{73}$$

where

$$\eta^{(\mathrm{RPA})} = (\bar{\Omega}/\Gamma)^2 \,, \tag{73a}$$

and

$$\eta^{(\mathrm{CCP})} \cong (\bar{\Omega}/\Gamma)^2 d \,. \tag{73b}$$

This may be rationalized as follows (we shall consider $W^{(4)}$ but the argument holds for any $W^{(2k+2)}$): In both cases, the correlation time is related to the energy spread of the states and is the same Γ^{-1}. We thus have

$$W^{(4)} \cong M_4(0,0,0,0)/\Gamma^3 \,, \tag{74}$$

where

$$M_4(0,0,0,0) = \frac{1}{\sqrt{d_a d_c}} \sum_{\substack{ab \\ b'c}} \mu_{b'a}\,\mu_{ab}\,\mu_{bc}\,\mu_{cb'} \,. \tag{75}$$

The statistical weight of this sum (the number of pathways to go from a to c) is $d_a d_c d_b^2$ for the CCP model and is only $d_a d_b d_c$ for the RPA (since $b = b'$). This is the reason for the extra d_b factor multiplying the former. We thus have

$$M_4^{(\mathrm{CCP})}(0,0,0,0) = |V|^4 \sqrt{d_a d_c}\; d_b^2 = \bar{\Omega}^4\,d_b \,, \tag{76a}$$

$$M_4^{(\mathrm{RPA})}(0,0,0,0) = |V|^4 \sqrt{d_a d_c}\; d_b = \bar{\Omega}^4 \tag{76b}$$

We shall return to this model briefly in the next section.

V. SUMMARY AND DISCUSSION

In this paper, we have presented a general framework for the theoretical description of the multiphoton absorption processes in the quasicontinuum of polyatomic molecules. This is done by the derivation of an appropriate set of REM. Within the present formalism, we are able to define precisely the complete molecular information which is relevant for these processes and to see how this information is reduced considerably in the

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Markovian limit leading to simple rate equations. We shall now summarize our basic assumptions and the various forms of the REM and discuss the validity of the Markovian limit for typical molecular multiphoton experiments. Our general derivation of the rate equations goes as follows:

(1) We have grouped the molecular states relevant for the dynamics of MMP into levels, and making use of the Mori–Zwanzig projection operator formalism, we have derived our most general set of REM (16) for the population of these levels. The complete molecular information that is required for our REM is a hierarchy of k-time intramolecular dipole correlation functions M_k[Eqs. (19)], where $k=2,4,6,\ldots$.

(2) The two-time correlation functions $M_2(t-\tau,0)$ are factorized in the form

$$M_2(t-\tau,0)_{nn,mm}=\bar{\Omega}_{nm}^2 I_{nm}(t-\tau), \tag{77}$$

where $\bar{\Omega}_{nm}^2=M_2(0,0)$ is the square of the integrated Rabi frequency for the nm transition and is proportional to the incoming laser intensity. $I_{nm}(t-\tau)$ is a dimensionless correlation function which decays from one to zero on a characteristic correlation time $\tau_c=\Gamma_{nm}^{-1}$ which has to do with the energy spread of the states within the n and m levels. The significance of $\bar{\Omega}_{nm}$ as defined in Eq. (30) lies in the reasonable assumption[21] that, for large molecules where only few degrees of freedom are coupled with the radiation field, $\bar{\Omega}_{nm}$ will be approximately independent of the number of states involved (i.e., d_n and d_m). This is expected since any quantity of the form

$$\sum_{\alpha\beta}\frac{1}{d_n}|\langle n\alpha|\mu|m\beta\rangle|^2=|\mu_{nm}|^2 \tag{78a}$$

or

$$\sum_{\alpha\beta}\frac{1}{d_m}|\langle n\alpha|\mu|m\beta\rangle|^2=|\mu_{nm}|^2 \tag{78b}$$

is independent on the addition of degrees of freedom which do not couple with μ. The dipole sum rule (78a) implies $\bar{\Omega}_{nm}^2\propto d_n$ and Eq. (78b) implies $\bar{\Omega}_{nm}^2\propto d_m$. It is thus fair to assume that $\bar{\Omega}_{nm}^2$ is proportional to $\sqrt{d_n d_m}$, which implies that $\bar{\Omega}_{nm}$ is independent of d_n and d_m.

(3) The Markovian limit is defined whenever

$$\sqrt{\eta}=\bar{\Omega}/\Gamma_{nm}\ll 1. \tag{79}$$

For a typical infrared transition dipole (0.1 D) and taking an intense laser field of 10 MW/cm^2, we have $\bar{\Omega}\sim 1$ cm^{-1}. Γ_{nm} may be estimated from the observed multiphoton cross sections for energy absorption.[1,21] and it is typically around 10–100 cm^{-1} for highly vibrationally excited polyatomic molecules. Thus, condition (79) is expected usually to hold for real life MMP even for very intense laser fields. In this limit, we have the following:

(i) On the relevant time scale for the evolution of populations, we may write

$$I_{nm}(t-\tau)=\Gamma_{nm}\delta(t-\tau), \tag{80}$$

where

$$\Gamma_{nm}^{-1}=\int_0^\infty d\tau I_{nm}(\tau) \tag{81}$$

and the REM reduce to simple rate equations of the form (55) with the rate matrix

$$W=W^{(2)}+W^{(4)}+W^{(6)}+\ldots . \tag{82}$$

(ii) The higher order terms in the expansion (82) are much smaller than $W^{(2)}$. In fact,

$$W^{(2k+2)}\cong W^{(2)}\eta^k . \tag{83}$$

(4) In the Markovian limit the molecular information that is required for a proper description of the multiphoton excitation process is greatly reduced. Not only that the high order correlation functions M_{2k}, $k=2,3,\ldots$, are not important, but even M_2 enters only via $\bar{\Omega}_{nm}$ and $\Gamma_{nm}^{-1}=\int_0^\infty d\tau I_{nm}(\tau)$. Thus, even the details of the two-time correlation functions $I_{nm}(\tau)$ [Eq. (25)] are also irrelevant for the dynamics of the MMP. The only molecular information that enters the rate equations is thus (i) $\bar{\Omega}_{nm}$, the integrated dipole for the nm transition times the field amplitude; (ii) Γ_{nm}, the inverse correlation time which is connected to the energetic spread of the states within the nm molecular levels; and (iii) *ratios* of statistical weights of the levels d_n/d_m. The relevant molecular information thus reduces essentially to two numbers ($\bar{\Omega}_{nm}^2/\Gamma_{nm}$ and d_n/d_m) per transition in the Markovian limit where rate equations apply.

(5) Finally, we would like to make a few comments regarding the constant coupling (CCP) model which was extensively studied in the past in connection with other molecular relaxation problems.[26–29] For the sake of concurring with previous notation[26–29] we shall introduce the quantities $\rho=d/\Gamma$ and $|V|^2=|\Omega|^2/d$, which are the density of states and the mean square coupling (per state, respectively). (The model may thus be characterized by ρ, $|V|^2$, and d instead of $\bar{\Omega}$, Γ, and d.) We now have

$$W_{(\mathrm{CCP})}^{(2)}=W_{(\mathrm{RPA})}^{(2)}\cong\bar{\Omega}^2/\Gamma\cong|V|^2\rho, \tag{84}$$

$$W_{(\mathrm{RPA})}^{(4)}\cong\frac{\bar{\Omega}^4}{\Gamma^3}\cong W^{(2)}\left(\frac{\bar{\Omega}}{\Gamma}\right)^2\cong W^{(2)}\frac{|V|^2 d}{\Gamma^2}, \tag{85a}$$

$$W_{(\mathrm{CCP})}^{(4)}\cong\frac{\bar{\Omega}^4}{\Gamma^3}d\cong W^{(2)}\left(\frac{\bar{\Omega}}{\Gamma}\right)^2 d\cong W^{(2)}|V|^2\rho^2, \tag{85b}$$

i.e.,

$$W_{(\mathrm{CCP})}^{(4)}\cong d\,W_{(\mathrm{RPA})}^{(4)}. \tag{86}$$

For real life MMP, $(\bar{\Omega}/\Gamma)^2$ is a small parameter $\sim 10^{-2}$–10^{-4} [see (3) above], whereas $(\bar{\Omega}/\Gamma)^2 d$ need not be small. When $(\bar{\Omega}/\Gamma)^2 d\gg 1$, then our expansion (82) does not converge and a renormalization procedure is required.[30] The resulting time evolution is then very different than that predicted by the simple rate equations (37).[26–30] A detailed discussion of the solution of the CCP model in this case was given recently by Carmeli and Nitzan.[30] We note, however, that the RPA is a much more physically realistic model for MMP than the CCP. This is indeed verified by the applicability of the simple RPA rate equations to actual MMP experiments.[1,2] We found it convenient to consider the quantities $\bar{\Omega}$ and Γ rather than $|V|^2$ and ρ since $\bar{\Omega}$ and Γ are the two actual time scales of the problem and their relative magnitude determines the validity of the Markovian assumption. Also, when adding more modes to the molecule which do not couple with the radiation field, then ρ

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is changing and $|V|^2$ will depend strongly on ρ. Thus, $|V|^2$ and ρ are not the natural independent parameters for the problem of MMP. $\bar{\Omega}$ and Γ, however, may be considered independent.

(6) The present REM which contain no coherence variables are useful for any MMP experiment where only populations are observed. For line shape studies (intramolecular dephasing) or for Region I, it is desirable to include the coherence variables and use a "less reduced" set of REM.[21]

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[1] See papers in (a) *Tunable Lasers and Applications*, edited by A. Mooradian, T. Jaeger, and P. Stokseth (Springer, New York, 1976); (b) *Multiphoton Processes*, edited by J. H. Eberly and P. Lambropolous (Wiley, New York, 1978); (c) Proceedings of the Laser Chemistry Conference, Israel (1978), edited by J. Jortner and R. D. Levine, Adv. Chem. Phys. (to appear).

[2] For recent reviews, see (a) C. D. Cantrell, S. M. Freund, and J. L. Lyman, "Laser Induced Chemical Reactions and Isotope Separation," in *Laser Handbook*, edited by M. L. Stitch (North-Holland, to be published), Vol. IIIb; (b) R. L. Woodin, D. S. Bomse, and J. L. Beauchamp, in *Chemical and Biochemical Applications of Lasers*, edited by C. B. Moore (Academic, New York, 1979), Vol. IV.

[3] (a) J. G. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, Phys. Rev. Lett. **38**, 1131 (1977); (b) K. L. Kompa, in Ref. 1(c).

[4] (a) M. J. Coggiola, P. A. Schultz, Y. T. Lee, and Y. R. Shen, Phys. Rev. Lett. **38**, 17 (1977); (b) E. R. Grant, P. A. Schultz, As. S. Sudbo, Y. R. Shen, and Y. T. Lee, Phys. Rev. Lett. **40**, 115 (1978).

[5] (a) D. J. King and J. C. Stephenson, Chem. Phys. Lett. **51**, 48 (1977); (b) J. C. Stephenson and D. J. King, J. Chem. Phys. **69**, 1485 (1978).

[6] (a) R. V. Ambartsumyan, in Ref. 1(a); (b) R. B. Hall and A. Kaldor, J. Chem. Phys. **70**, 4027 (1979).

[7] J. D. McDonald (private communication).

[8] (a) D. F. Heller and J. T. Yardley, Proceedings of the International Quantum Electronics Conference Xth, Atlanta, Georgia (May 1978); (b) Z. Karny, A. Gupta, R. N. Zare, S. T. Lin, J. Nieman, and A. M. Ronn (to be published); (c) I. Burak, T. J. Quelly, and J. I. Steinfeld, J. Chem. Phys. **70**, 334 (1979).

[9] (a) D. S. Frankel, J. Chem. Phys. **65**, 1696 (1976); (b) see papers by E. Yablonovitch and by K. L. Kompa, in Ref. 1(c).

[10] N. Bloembergen, C. D. Cantrell, and D. M. Larsen, in Ref. 1(a).

[11] M. F. Goodman, J. Stone, and D. A. Dows, J. Chem. Phys. **65**, 5052 (1976).

[12] S. Mukamel and J. Jortner, J. Chem. Phys. **65**, 5204 (1976).

[13] J. L. Lyman, J. Chem. Phys. **67**, 1868 (1977).

[14] D. P. Hodgkinson and J. S. Briggs, Chem. Phys. Lett. **43**, 451 (1976); J. Phys. B **10**, 2583 (1977).

[15] (a) C. D. Cantrell, in *Laser Spectroscopy II*, edited by J. L. Hall and J. L. Carlsten (Springer, New York, 1977), p. 109; (b) C. D. Cantrell, H. W. Galbraith, and J. R. Ackerhalt, in Ref. 1(b).

[16] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).

[17] (a) R. Kubo, in *Fluctuation Relaxation and Resonance in Magnetic Systems*, edited by D. Ter Haar (Oliver and Boyd, Edinburgh, 1962); (b) R. Kubo, Adv. Chem. Phys. 15, 101 (1969).

[18] S. A. Rice, in *Excited States*, edited by E. C. Lim (Academic, New York, 1975), Vol. 2.

[19] J. Jortner, Adv. Laser Spectrosc. **113**, 88 (1977).

[20] M. Quack, J. Chem. Phys. **69**, 1282 (1978).

[21] S. Mukamel, Phys. Rev. Lett. **42**, 168 (1979); J. Chem. Phys. **70**, 2479 (1979).

[22] R. Zwanzig, Physica (Utrecht) **30**, 1109 (1964).

[23] (a) H. Mori, Prog. Theor. Phys. **33**, 423 (1965); (b) M. Tokuyama and H. Mori, *ibid.* **55**, 411 (1976).

[24] S. Mukamel, Chem. Phys. **31**, 327 (1978).

[25] A. Ben-Reuven, Adv. Chem. Phys. **33**, 235 (1975).

[26] R. Lefebvre and J. A. Beswick, Mol. Phys. **33**, 1223 (1972).

[27] A. Nitzan, J. Jortner, and B. Berne, Mol. Phys. **26**, 281 (1973).

[28] E. J. Heller and S. A. Rice, J. Chem. Phys. **61**, 936 (1974).

[29] S. Mukamel and J. Jortner, J. Chem. Phys. **65**, 3735 (1976).

[30] (a) B. Carmeli and A. Nitzan, Chem. Phys. Lett. **58**, 310 (1978); (b) B. Carmeli and A. Nitzan (preprint).

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