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REDUCED EQUATIONS OF MOTION FOR COLLISIONLESS MOLECULAR MULTIPHOTON PROCESSES

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CONTENTS

I. INTRODUCTION

The discovery[1-3] that polyatomic molecules under collision-free conditions may absorb many infrared quanta from a powerful laser and acquire energies of chemical interest (few eV), had triggered considerable experimental and theoretical efforts in recent years.[1-19] The currently available experimental information regarding molecular multiphoton processes (MMP) includes absolute cross-sections for energy absorption,[6] translational,[7] and vibrational[8] 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,[9] infrared,[10] and visible[11] emission characteristics of the excited molecules, double resonance experiments[12] (both frequency and time resolved), etc.

The following qualitative picture[13-19] has emerged out of the numerous experimental and theoretical studies: The molecular energy levels are separated into three regions. In the lowest energy range (region I) the density of molecular states is very low and the laser field is interacting with isolated molecular states (coherent driving). In this region the laser power is required to overcome the molecular anharmonicities and phenomena such as threshold power, saturation behavior, isotopic selectivity, and multiphoton resonances are accounted for in terms of the molecular level-scheme of region I. After the molecule has absorbed few quanta, the density of molecular states becomes very large, and we can no longer describe the time evolution in terms of few isolated molecular states. This region is denoted region II or the quasicontinuum and a proper description of the molecular time evolution in this range requires a quantitative understanding of the mechanisms of intramolecular energy transfer and line broadening (dephasing)[20] of highly vibrationally excited polyatomic molecules, of which very little is known at present. (We should note, however, that recent developments in overtone spectroscopy,[21, 22] coherent transients,[23] and high-resolution optical spectroscopy[24] are currently yielding novel information regarding intramolecular line broadening.) Finally, when the molecule acquires enough energy for dissociation, it enters region III, where, in addition to all the complications of region II, we have to incorporate also the dynamics of unimolecular decomposition.

Some of the theoretical problems which are underlying the current studies of molecular multiphoton processes are as follows: (1) How much energy is absorbed by a polyatomic molecule interacting with a strong infrared laser, and what is the *intermolecular* distribution of energy as a function of the molecular and laser parameters (molecular size, frequencies, anharmonicities, laser frequency, intensity, and duration)? (2) What is the *intramolecular* energy redistribution rate? How much time does it take for the absorbed energy to flow among the various degrees of freedom? Does the energy randomize, and at what time scales? (i.e., does the molecule exhibit an ergodic behavior?)[25] These questions are essential for the observation of laser-specific nonthermal effects in chemical reactions. (3) Can we use the information extracted from studies of molecular multiphoton processes to study the dynamics of unimolecular reactions and, in particular, to test the validity of the various statistical approaches that are extensively used to predict reaction rates and branching ratios?[26]

It is clear that a complete quantum-mechanical treatment of these problems is extremely complicated and is impractical. The density of molecular states is very rapidly increasing with energy. (For SF_6, e.g., it is $10^3/\text{cm}^{-1}$, $2\times10^8/\text{cm}^{-1}$, and $3\times10^{11}/\text{cm}^{-1}$ at energies of 5000 cm^{-1}, 10,000 cm^{-1}, and 19,000 cm^{-1}, respectively.) Due to the lack of structural information (i.e., potential surfaces) on highly excited polyatomic molecules, we do not know the exact nature and coupling strengths of these states even for a single polyatomic molecule. Moreover, even if we had this structural (static) information, it would have been impossible to solve for the dynamics of about 10^{10} states interacting with a strong laser field. On the other hand, we should bear in mind that the information that is of real interest for us is much less detailed than the knowledge of the complete molecular density matrix, including the amplitudes and phases of all molecular states. In practice we are interested only in a few molecular observables and their time evolution on a coarse-grained time scale ($\sim10^{-9}$ sec) which is much longer than the molecular frequencies (i.e., 10^{-13}–10^{-14} sec). *A complete dynamical treatment of the problem is thus neither feasible nor desirable.*

The current theories of unimolecular reactions[26] avoid these complications by assuming a complete microcanonical redistribution of energy prior to the reaction. This assumption makes it feasible to evaluate reaction rates using equilibrium statistical mechanics. The relative success of these theories in predicting reaction rates does not, however, prove the validity of their basic assumptions, which were very seriously challenged[25] by a variety of recent experimental[27] and theoretical[28] studies.

An inevitable conclusion from the foregoing discussion is that we should adopt a *mesoscopic* level of theoretical description, which is intermediate between the fully dynamical and completely statistical approaches.[29] The basic idea of the mesoscopic level of description is to find some few key molecular variables and to adopt a reduction scheme that will enable us to derive closed reduced equations of motion (REM) describing the approximate time evolution of these variables in the presence of the rest. Formally this is one of the most important problems in irreversible statistical mechanics,[30] and there are many methods for constructing REM, for example, the Langevin approach,[31-33] the stochastic Liouville approach,[34] and projection operator techniques.[35, 36]

It has been suggested phenomenologically[16, 6] and demonstrated in several cases[4, 5] 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 quasicontinuum region). A basic prediction of this postulate,[6] which was experimentally verified, in particular by the recent low-power ICR experiments,[5b] 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,[7] it does not give us any microscopic interpretation of the observed rate constants.

Early attempts[17, 18] 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 that 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.[34, 35, 37–39] 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.[25] Moreover, perturbative treatments in anharmonicities necessarily become less adequate with the degree of molecular excitation.

In this review we develop a new approach toward the derivation of REM for MMP,[19] which is based on the projection operator formalism of Zwanzig[36] and Mori[40] combined with the representation of the true molecular states. The latter enables us to formulate the problem in a form free of perturbative arguments in any intramolecular interactions.[19, 41, 42] The main steps in this "hydrodynamic-like" approach[19] 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 equations 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 Section II we present the general systematic reduction scheme, which allows us to construct a closed set of equations of motion for *any* chosen set of molecular variables, starting from the complete Liouville equation. We present two formally different schemes based on different choices of time ordering.[34, 43, 44] In Section III we construct the molecular Hamiltonian for MMP using molecular states "dressed" by the radiation field[15, 19, 45] and define a "minimal set" of reduced variables corresponding to the 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 $k=2,4,6,\ldots$ (29). In Section IV we expand the REM to second-order in the field and show how under quite general conditions (the Markovian limit,[34, 36, 40] 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 Section V 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 Sections IV and V is that in the Markovian limit simple rate equations apply, and most of the molecular information contained in the complete set of correlation functions (29) 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.) In Section VI we derive a different set of REM for the populations and the coherence variables. The explicit inclusion of molecular variables corresponding to coherences in our REM is important for the sake of getting a unified description all the way from region I (where they are important) to the quasicontinuum, for establishing the connection between MMP and other spectroscopic techniques, and for getting a better insight on the dynamics of MMP. Intramolecular relaxation of populations (T_1 processes) need not be considered at all in these REM (unlike phenomenological Bloch equations) 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).[19, 20] We finally show how in the limit of fast dephasing these REM reduce to the same rate equations obtained in Section IV. This alternative derivation of the simple rate equations gives us a better understanding regarding the "loss of relevant information," which occurs when the REM reduce to simple rate equations. Finally in Section VIII we present a microscopic model for the intramolecular two-time dipole correlation functions which enables us to calculate the dephasing rates appearing in our REM and to compare with existing experimental data.

II. THE SYSTEMATIC REDUCTION SCHEME

We consider a large system with many degrees of freedom characterized by a Hamiltonian H and a density matrix ρ. The time evolution of ρ is given by the Liouville equation:

$$\frac{d\rho}{dt} = -i[H, \rho] \equiv -iL\rho \tag{1}$$

where L is the Liouville (tetradic) operator corresponding to H, i.e.,

$$\frac{d\rho_{ab}}{dt} = -i\sum_{cd} L_{ab,cd}\rho_{cd} \tag{2}$$

and

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

The density matrix $\rho(t)$ contains the complete information regarding the state of the system at time t. In practice, however, much of this information is redundant and we shall be interested only in some projections of $\rho(t)$ on few "relevant" operators A_μ whose nature is determined by the initial conditions and the type of experiments considered. We are thus interested in deriving reduced equations of motion (REM) which will provide us directly with the time evolution of the expectation values of A_μ.

The appropriate formalism to achieve that goal is the projection operator technique of Zwanzig[36] and Mori.[40] The procedure goes as follows: We first have to define the set of molecular operators of interest, A_μ. We then define a scalar product of two operators as

$$(A_\mu, A_\nu) \equiv \mathrm{Tr}(A^\dagger_\mu A_\nu) \tag{4}$$

Throughout the present work we shall assume that the chosen operators A_μ are orthonormal with respect to the scalar product (4), that is,

$$S_{\mu\nu} \equiv (A_\mu, A_\nu) = \delta_{\mu,\nu} \tag{5}$$

although the general reduction procedure does not rely on this property and it could be easily generalized to include a general overlap matrix $S_{\mu\nu}$, as well as a more general definition of the scalar product.[40]

We now define a Mori projection P which projects onto the subspace spanned by our relevant operators A_μ:

$$PB = \sum_\mu (B, A_\mu)A_\mu \tag{6}$$

and the complementary projection

$$Q \equiv 1 - P \tag{6b}$$

Our quantities of interest are the expectation values of A_μ at time t, that is,

$$\sigma_\mu(t) \equiv (A_\mu, \rho(t)) \tag{7}$$

and using the definition (6) it is clear that all our relevant information is contained in the projection $P\rho(t)$, that is,

$$\sigma_\mu(t) = (A_\mu, P\rho(t)) \tag{8}$$

Making use of the Zwanzig[36]–Mori[40] technique we can now derive REM for $P\rho(t)$ and project it on the variables A_μ resulting in the following REM for σ_ν:

$$\frac{d\sigma_\nu}{dt} = -i\sum_\mu \langle L\rangle_{\nu\mu}\sigma_\mu(t) - \int_0^t d\tau \sum_\mu \langle R(t-\tau)\rangle_{\nu\mu}\sigma_\mu(\tau) - i\langle F(t)\rangle_\nu \tag{9}$$

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

$$R(t-\tau) \equiv L\exp[-iQL(t-\tau)]QL \tag{10}$$

and the tetradic matrix elements $\langle L\rangle_{\nu\mu}$ and $\langle R\rangle_{\nu\mu}$ are defined as

$$\langle Y\rangle_{\nu\mu} \equiv \mathrm{Tr}(A_\nu^\dagger Y A_\mu) \qquad Y = R, L \tag{11}$$

$\langle F\rangle$ is the vector:

$$\langle F(t)\rangle_\nu \equiv \mathrm{Tr}[A_\nu^\dagger L\exp(-iQLt)Q\rho(0)] \tag{12}$$

$\rho(0)$ being the density matrix at time $t=0$. Equations 9 are exact and are valid for an arbitrary choice of dynamical operators A_μ. In practice, however, the memory kernel $\langle R\rangle$ and the vector $\langle F\rangle$ are usually evaluated in some approximate manner using an expansion in a properly chosen parameter. To that end it is sometimes advantageous to use a different form of the REM,[19] that is,

$$\frac{d\sigma_\nu}{dt} = -i\sum_\nu \langle L\rangle_{\nu\mu}\sigma_\nu(t) - \sum_\nu \langle K(t)\rangle_{\nu\mu}\sigma_\mu(t) - i\langle G(t)\rangle_\nu \tag{13}$$

where

$$\langle K(t)\rangle_{\nu\mu} = \sum_{\nu'} W(t)_{\nu\nu'} V_{\nu'\mu}^{-1}(t) \tag{14}$$

$$W_{\nu\nu'}(t) = \mathrm{Tr}[A_\nu^\dagger LQ\exp(-iLt)A_{\nu'}] \tag{15}$$

$$V_{\nu'\mu} = \mathrm{Tr}[A_{\nu'}^\dagger \exp(-iLt)A_\mu] \tag{16}$$

and

$$\langle G(t)\rangle_\mu = \mathrm{Tr}\left[A_\nu^\dagger L\exp(-iLt)Q\rho(0)\right] \tag{17}$$

The form (9) arises naturally when keeping the complete time ordering of the various operators and will be referred to as the COP (chronological ordering prescription). The form (13) uses only partial time ordering and will be referred to as the POP (partial ordering prescription). Equation 13, like (9), is also exact. However, once an expansion is made both equations may have very different predictions. A comparison of the two forms for general-relaxation and line-shape problems was made recently.[43, 44, 46] In the next section we shall perform a formal expansion of both REM for a particular choice of variables for the multiphoton problem, and this will enable us to point out more precisely the differences between the two.

III. THE MODEL HAMILTONIAN FOR MOLECULAR MULTIPHOTON PROCESSES—REM FOR THE POPULATIONS

We consider a polyatomic molecule interacting with a monochromatic infrared laser beam whose frequency is ω_L, under collision-free conditions. We assume that the Schrödinger equation for the isolated molecule (in the absence of the field) has been solved and that we have 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 these relevant molecular states into levels and denote them as $\{|n\alpha\rangle\}$ with eigenvalues $E^\circ_{n\alpha}$, where n stands for the level and α runs over the states within the nth level. We further invoke the rotating wave approximation (RWA),[13–15, 45] which is very reasonable for MMP with infrared photons and which amounts to neglecting high-frequency terms in the Hamiltonian, which are not expected to contribute significantly to the molecular time evolution. We can thus write the combined Hamiltonian for the molecule and the field in the time-independent form:[19]

$$H = H_0 + H' \tag{18}$$

where

$$H_0 = \sum_{n,\alpha} |n\alpha\rangle E_{n\alpha}\langle n\alpha| \tag{18a}$$

and

$$H' = \epsilon \sum_{\substack{n\alpha \\ m\beta \\ m=n\pm 1}} |n\alpha\rangle \mu_{nm}^{\alpha\beta} \langle m\beta| \tag{18b}$$

Here the molecular states within the nth level have absorbed n infrared quanta from the field, and $E_{n\alpha} = E_{n\alpha}^{\circ} - n\omega_{\mathrm{L}}$ is the energy of the $|n\alpha\rangle$ state dressed (to zero order) by the field. $\mu_{nm}^{\alpha\beta} = \langle m\beta|\mu|n\alpha\rangle$ 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.

We shall now turn to the construction of the set of relevant operators. 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). It is thus clear that a minimal set of relevant variables should include these populations. In order to derive REM for $P_n(t)$ we shall now introduce the following set of molecular operators:[19]

$$A_{nn} = \frac{1}{\sqrt{d_n}} \sum_{\alpha} |n\alpha\rangle\langle n\alpha| \qquad n = 0, 1, \ldots, N-1 \tag{19}$$

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. The choice of the states included in A_{nn} (and consequently of d_n) is important since the ratios d_n/d_m enter explicitly in the resulting REM (48). It should thus be made with physical insight and only states that are expected to participate in the dynamics of the MMP in the experimentally relevant time scale should be included in the summation (19). The A_{nn} operators (19) are

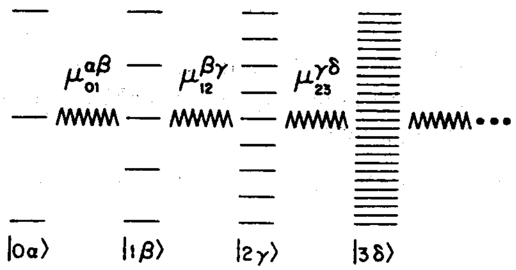

Fig. 1. The coupling scheme for molecular multiphoton processes. The true molecular states are grouped into levels where the nth level includes states $|n\phi\rangle$ which absorbed n photons from the field. μ is the radiative dipole coupling.

orthonormal, that is,

$$(A_{nn}, A_{kk}) = \delta_{n,k} \tag{20}$$

and the populations of the various levels are

$$P_n(t) = \sqrt{d_n}\,(A_{nn}, \rho(t)) = \sqrt{d_n}\,\sigma_n(t) \tag{21}$$

From the definitions (6), (19), and (18) it is clear that for our particular choice of P [(6) with (19)] we have

$$PLP = 0 \tag{22a}$$

and

$$PL_0 = L_0 P = 0 \tag{22b}$$

Here L, L_0 and L' denote the Liouville operators corresponding to H, H_0 and H', respectively. We shall further assume that initially at $t=0$ all the population is in the zeroth level so that

$$\rho(0) = \frac{1}{\sqrt{d_0}} A_{00} \tag{23a}$$

which implies that

$$Q\rho(0) = 0 \tag{23b}$$

Substitution of (23b) in (12) and (17) shows that for this type of initial condition we have

$$\langle F \rangle = \langle G \rangle = 0 \tag{23c}$$

that is, the inhomogeneous part of the REM vanishes.

We shall turn now to the expansion of the REM in a power series of L' using both time-ordering prescriptions.

A. The COP Reduced Equations of Motion

Using (6), (19), and (18) we note that

$$QL = (1-P)(L_0 + L') = L_0 + QL' \tag{24}$$

which enables us to expand $\exp(-iQLt)$ and the memory kernel R eq (10) in a power series in QL', that is,

$$\exp(-iQLt)=\exp(-iL_0t)-i\int_0^t d\tau \exp[-iL_0(t-\tau)]QL'\exp(-iQL\tau) \tag{25}$$

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

$$\frac{d\sigma_\nu}{dt}=-\int_0^t d\tau \sum_\mu \langle R(t-\tau)\rangle_{\nu\mu}\sigma_\mu(\tau) \tag{26}$$

where

$$\langle R(t-\tau)\rangle=\langle R^{(2)}(t-\tau)\rangle+\langle R^{(4)}(t-\tau)\rangle+\langle R^{(6)}(t-\tau)\rangle+\cdots \tag{26a}$$

and where

$$\langle R^{(2)}(t-\tau)\rangle=\theta_2(t-\tau,0) \tag{26b}$$

$$\langle R^{(4)}(t-\tau)\rangle=\int_0^{t-\tau}d\tau_1\int_0^{\tau_1}d\tau_2\,\theta_4(t-\tau,\tau_1,\tau_2,0) \tag{26c}$$

$$\langle R^{(6)}(t-\tau)\rangle=\int_0^{t-\tau}d\tau_1\int_0^{\tau_1}d\tau_2\int_0^{\tau_2}d\tau_3\int_0^{\tau_3}d\tau_4\,\theta_6(t-\tau,\tau_1,\tau_2,\tau_3,\tau_4,0) \tag{26d}$$

and

$$\langle R^{(2k)}(t-\tau)\rangle=\int_0^{t-\tau}d\tau_1\int_0^{\tau_1}d\tau_2\cdots \times\int_0^{\tau_{2k-3}}d\tau_{2k-2}\,\theta_{2k}(t-\tau,\tau_1,\tau_2,\dots,\tau_{2k-2},0) \tag{26e}$$

Here

$$\theta_{2k}(\tau_1,\tau_2,\dots,\tau_{2k})=(-1)^{k+1}\langle L'(\tau_1)L'(\tau_2)(1-P)L'(\tau_3)L'(\tau_4)(1-P)\dots(1-P)L'(\tau_{2k-1})L'(\tau_{2k})\rangle \tag{27}$$

where

$$L'(\tau)=\exp(iL_0\tau)L'\exp(-iL_0\tau) \tag{28}$$

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

$$M_k(\tau_1, \tau_2 \ldots \tau_k) = \langle L'(\tau_1) L'(\tau_2) \ldots L'(\tau_k) \rangle \tag{29}$$

in terms of which we may rewrite (27) in the form:

$$\theta_2(\tau_1, \tau_2) = M_2(\tau_1, \tau_2) \tag{30a}$$

$$\theta_4(\tau_1, \tau_2, \tau_3, \tau_4) = -\left[M_4(\tau_1, \tau_2, \tau_3, \tau_4) - M_2(\tau_1, \tau_2) M_2(\tau_3, \tau_4) \right] \tag{30b}$$

$$\vdots$$

etc.

The $\langle \ldots \rangle$ in (26)–(30) denotes a tetradic matrix element as defined by eq (11).

Equations 26 together with (27)–(30) constitute our COP 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 (29) [or θ_k, (30)], $k = 2, 4, \ldots$ which provide us with the complete molecular information needed for the description of all MMP whenever the experimental observables are connected with populations only.

B. The POP Reduced Equations of Motion

Turning now to the POP reduction scheme for our particular choice of P [(6) with (19)], we may use the relation

$$\exp(-iLt) = \exp(-iL_0 t) - i\int_0^t d\tau \exp(-iL(t-\tau)) L' \exp(-iL_0 \tau) \tag{31}$$

to expand $\langle K(t) \rangle$ (14) in a power series in L', that is,

$$\langle K(t) \rangle = \langle L'Q(1 - i\int_0^t d\tau \exp(-iL(t-\tau)) L' \rangle$$
$$\times \left[1 - i\int_0^t d\tau \langle \exp(-iL(t-\tau)) L' \rangle \right]^{-1} \tag{32}$$

resulting in[19]

$$\frac{d\sigma_\nu}{dt} = -\sum_\mu \langle K(t) \rangle_{\nu\mu} \sigma_\nu(t) \tag{33}$$

where

$$\langle K(t)\rangle = \langle K^{(2)}(t)\rangle + \langle K^{(4)}(t)\rangle + \cdots \tag{33a}$$

and where

$$\langle K^{(2)}(t)\rangle = \int_0^t d\tau\, M_2(t-\tau,0) \tag{33b}$$

$$\begin{aligned}\langle K^{(4)}(t)\rangle &= -\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3\, M_4(t,\tau_1,\tau_2,\tau_3) + \int_0^t d\tau_1 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_3 \\ &\quad \times M_2(t,\tau_1) M_2(\tau_2,\tau_3) \\ &= -\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \big[M_4(t,\tau_1,\tau_2,\tau_3) - M_2(t,\tau_1)M_2(\tau_2,\tau_3) \\ &\quad - M_2(t,\tau_2)M_2(\tau_1,\tau_3) - M_2(t,\tau_3)M_2(\tau,\tau_2)\big] \end{aligned} \tag{33c}$$

$$\vdots$$

The complete molecular information that enters into the POP equations (33) is identical to that used for the COP (26); that is, it consists of the entire set of intramolecular correlation functions M_k (29). However, these correlation functions enter in a different way in each reduction scheme. The expansions (26) and (33) enable us to point out more precisely the differences between the two prescriptions. In principle they are both exact.[43, 44] However, if we truncate the REM at second order, this amounts to setting $\langle R^{(4)}\rangle = \langle R^{(6)}\rangle = \cdots = 0$ in the COP (26) and $\langle K^{(4)}\rangle = \langle K^{(6)}\rangle = \cdots = 0$ in the POP (33). $\langle R^{(4)}\rangle = 0$ implies

$$M_4(\tau_1,\tau_2,\tau_3,\tau_4) = M_2(\tau_1,\tau_2)M_2(\tau_3,\tau_4) \tag{34}$$

whereas $\langle K^{(4)}\rangle = 0$ implies

$$\begin{aligned} M_4(\tau_1,\tau_2,\tau_3,\tau_4) &= M_2(\tau_1,\tau_2)M_2(\tau_3,\tau_4) + M_2(\tau_1,\tau_3)M_2(\tau_2,\tau_4) \\ &\quad + M_2(\tau_1,\tau_4)M_2(\tau_2,\tau_3) \end{aligned} \tag{35}$$

Thus, the two expansions correspond to different statistical properties of the dipole operator. These points and their implications were discussed recently in detail for other line-shape problems.[43, 44]

Finally, we should point out that there is one general type of condition in which both equations reduce to the same form. This is the *Markovian limit* where a separation of time scales exists between the relevant operators A_μ and the dipole correlation functions, whereupon the latter decay on a time scale τ_c which is much more rapid than the evolution of the former. In this case the higher order terms M_4, M_6 have a contribution which is higher order in τ_c compared to that of M_2 and may be neglected, and both REM [(26) and (33)] reduce, on a coarse-grained time scale $t > \tau_c$, to the form:

$$\frac{d\sigma_\nu}{dt} = -\sum_\mu W_{\nu\mu}\sigma_\nu(t) \tag{36}$$

where

$$W = \langle K^{(2)}(\infty)\rangle = \int_0^\infty d\tau \langle R^{(2)}(\tau)\rangle = \int_0^\infty d\tau \langle L'(\tau)L'(0)\rangle \tag{36a}$$

In this case the resulting REM (36) attain a very simple time-independent form and the amount of molecular information necessary for the description of the MMP is considerably reduced [we need consider only W (36a) instead of the complete set of correlation functions M_k (29)]. In the coming sections we shall make use extensively of the Markovian limit condition after justifying it from microscopic considerations for MMP.

IV. EXPANSION OF THE REM TO SECOND-ORDER IN THE FIELD

We shall now apply the formal results of Section III to derive explicit expressions for the REM, to second order in the applied field (H'). We shall adopt here the COP formulation. We should bear in mind, however, that the final rate equations derived here (52) are in the Markovian limit where the POP equations coincide with the COP as implied by (36).

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

$$\langle R(t-\tau)\rangle \cong \langle R^{(2)}(t-\tau)\rangle \tag{37}$$

in (26). Substitution of (18) in (26b) results in the following nonzero matrix elements of R:

$$\langle R_{nn,mm}(t-\tau)\rangle = \frac{1}{(d_n d_m)^{1/2}} \sum_{\alpha\beta} \left(L'^{\alpha\alpha,\alpha\beta}_{nn,nm}(t-\tau) L'^{\alpha\beta,\beta\beta}_{nm,mm}(0) + \text{c.c.}\right)$$
$$m = n \pm 1 \tag{38a}$$

and

$$\langle R_{nn,nn}(t-\tau)\rangle = \frac{1}{d_n} \sum_{\substack{\alpha,\beta \\ m=n\pm 1}} \left(L'^{\alpha\alpha,\alpha\beta}_{nn,nm}(t-\tau) L'^{\alpha\beta,\alpha\alpha}_{nm,nn}(0) + \text{c.c.}\right) \tag{38b}$$

Here

$$L'^{\alpha\beta,\gamma\delta}_{ij,kl} = \langle\langle i\alpha, j\beta | L' | k\gamma, l\delta \rangle\rangle \tag{39}$$

comes for the tetradic matrix element of L' (we are using here the double bracket notation[39] whereby the tetradic state corresponding to $|a\rangle\langle b|$ is denoted $|ab\rangle\rangle$). In (38) we have made use of the Liouville conjugation symmetry

$$L'_{ab,cd} = -L'^{*}_{ba,dc} \tag{40}$$

which is valid for any tetradic operator[39] and may be easily verified using (3).

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

$$I_{nm}(t) = \operatorname{Re} \tilde{I}_{nm}(t) \tag{41a}$$

where

$$\tilde{I}_{nm}(t) = \frac{\langle \mu_{nm}(0)\mu_{mn}(t)\rangle}{\langle \mu_{nm}(0)\mu_{mn}(0)\rangle} = \frac{1}{\gamma_{nm}^{2}} \sum_{\alpha,\beta} |\mu_{nm}^{\alpha\beta}|^{2} \exp(-i\omega_{n\alpha,m\beta}t) \tag{41b}$$

Here

$$\mu_{nm}(t) = \exp(iH_0 t)\mu_{nm}\exp(-iH_0 t) \tag{42}$$

$$\gamma_{nm}^{2} = \langle \mu_{nm}(0)\mu_{mn}(0)\rangle = \sum_{\alpha,\beta} |\mu_{nm}^{\alpha\beta}|^{2} \tag{43}$$

and

$$\hbar\omega_{n\alpha,m\beta} = E_{n\alpha} - E_{m\beta} \tag{44}$$

We further define the integrated Rabi frequency for the nm transition

$$\bar{\Omega}_{nm}^{2} \equiv 2\epsilon^{2} \sum_{\alpha,\beta} \frac{|\mu_{nm}^{\alpha\beta}|^{2}}{(d_n d_m)^{1/2}} \tag{45}$$

Making use of the quantities (41)–(45) we can express the matrix elements of $\langle R\rangle$ (38) as follows:

$$\langle R^{(2)}_{nn,mm}(t-\tau)\rangle = -\bar{\Omega}_{nm}^{2} I_{nm}(t-\tau) \tag{46a}$$

and

$$\langle R^{(2)}_{nn,nn}(t-\tau)\rangle = \sum_{m=n\pm1} \bar{\Omega}^2_{nm}\left(\frac{d_n}{d_m}\right)^{1/2} I_{nm}(t-\tau) \tag{46b}$$

Upon substitution of (46) in (9) and putting $P_n=(d_n)^{1/2}\sigma_n$, we finally get:

$$\frac{dP_n}{dt} = \sum_{m=n\pm1} \bar{\Omega}^2_{nm}(d_n d_m)^{1/2}\int_0^t d\tau\, I_{nm}(t-\tau)\left[\frac{P_m(\tau)}{d_m}-\frac{P_n(\tau)}{d_n}\right] \tag{47}$$

or, alternatively,

$$\frac{dP_n}{dt} = \sum_{m=n\pm1} \bar{\Omega}^2_{nm}\int_0^t d\tau\, I_{nm}(t-\tau)\left[P_m(\tau)\left(\frac{d_n}{d_m}\right)^{1/2}-P_n(\tau)\left(\frac{d_m}{d_n}\right)^{1/2}\right] \tag{48}$$

Equations (47) or (48) reduce to simple rate equations in the following limit: If $I_{nm}(t-\tau)$ has a characteristic time scale $\tau_c=\Gamma^{-1}_{nm}$ such that

$$\bar{\Omega}_{nm}\gg\Gamma_{nm} \tag{49}$$

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 (47) or (48). We thus have:

$$I_{nm}(t-\tau)=\Gamma^{-1}_{nm}\delta(t-\tau) \tag{50}$$

where

$$\tau_c\equiv\Gamma^{-1}_{nm}=\int_0^\infty d\tau\, I_{nm}(\tau) \tag{51}$$

Substitution of (50) in (48) results in the simple rate equations:

$$\frac{dP_n}{dt} = \sum_{m=n\pm1} W^{(2)}_{nm}\left[P_m\left(\frac{d_n}{d_m}\right)^{1/2}-P_n\left(\frac{d_m}{d_n}\right)^{1/2}\right] \tag{52}$$

where

$$W^{(2)}_{nm}=\frac{\bar{\Omega}^2_{nm}}{\Gamma_{nm}} \tag{52a}$$

Equation 52 may be recast in the form:

$$\frac{dP_n}{dt} = \sum_{m=n\pm1} \mathrm{K}^{(2)}_{nm}P_m(t)-\mathrm{K}^{(2)}_{nn}P_n(t) \tag{53}$$

where

$$K^{(2)}_{nm} = \left(\frac{d_n}{d_m}\right)^{1/2} \frac{\bar{\Omega}^2_{nm}}{\Gamma_{nm}} \tag{53a}$$

and

$$K^{(2)}_{nn} = \sum_{m=n\pm1} K^{(2)}_{mn} \tag{53b}$$

We note that K_{nm} satisfies the detailed balance relation

$$\frac{K_{nm}}{K_{mn}} = \frac{d_n}{d_m} \tag{53c}$$

which implies that the radiation field is tending to establish a distribution of molecular states where all radiatively coupled states are equally populated. Thus the ratio (53c) is equal to the ratio of the number of effectively coupled states in each level. The superscript (2) in (52) and (53) signifies that $W^{(2)}$ and $K^{(2)}$ are evaluated to second order in $H'(\mu)$. Utilizing (53a) and (52a) we have

$$W^{(2)}_{nm} = (K^{(2)}_{nm} K^{(2)}_{mn})^{1/2} \tag{54}$$

Condition (49) is the *Markovian limit*[34-36, 40, 19] and implies that a separation of time scales exists in our problem such that our chosen set of variables (i.e., the P space) is slowly varying compared to the other variables (the Q space). Equations 52 could have been obtained directly from (36) where we have derived the Markovian form in a formal way. A posteriori we can now justify the substitution (50). Using (52) we notice that the characteristic rate of change of P_n is $W_{nm} = \bar{\Omega}^2_{nm}/\Gamma_{nm}$. Condition (49) 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^{-1}_{nm} [which led to (50)].

We note that the only molecular information that enters the rate equations (53) is

1. $\bar{\Omega}_{nm}$, the integrated dipole for the nm transition times the field amplitude;
2. Γ_{nm}, inverse correlation time (i.e. a dephasing rate); and
3. *Ratios* of statistical weights of the levels d_n/d_m.

The relevant molecular information thus reduces essentially to two numbers ($\bar{\Omega}^2_{nm}/\Gamma_{nm}$ and d_n/d_m) per transition in the Markovian limit where rate equations apply.

The significance of $\bar{\Omega}_{nm}$ as defined in (45) lies in the reasonable assumption[19] 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

$$\sum_{\alpha\beta}\frac{1}{d_n}|\langle n\alpha|\mu|m\beta\rangle|^2=|\mu_{nm}|^2 \tag{55a}$$

or

$$\sum_{\alpha\beta}\frac{1}{d_m}|\langle n\alpha|\mu|m\beta\rangle|^2=|\mu_{nm}|^2 \tag{55b}$$

is independent on the addition of degrees of freedom that do not couple with μ. The dipole sum rule (55a) implies $\Omega^2_{nm}\equiv\Sigma_{\alpha\beta}|\langle n\alpha|\mu|m\beta\rangle|^2\propto d_n$ and (55b) implies $\Omega^2_{nm}\propto d_m$. It is thus fair to assume that Ω^2_{nm} is proportional to $(d_n d_m)^{1/2}$, which implies that $\bar{\Omega}_{nm}$ is independent of d_n and d_m. Regarding the dephasing rate Γ_{nm} it is clear from its definition (51) that it is associated with the energetic spread of the states within the n and m molecular levels. For the sake of illustration, we shall consider now a simple model whereby $|\mu^{\alpha\beta}_{nm}|^2$ is constant, independent on α and β, that is,

$$|\mu^{\alpha\beta}_{nm}|^2=\begin{cases}|V|^2 & -\Delta<E_{n\alpha},\,E_{m\beta}<\Delta\\ 0 & \text{else}\end{cases} \tag{56}$$

Assuming that the number of states d_n, d_m is sufficiently large and that they are uniformly distributed throughout the n, m manifolds, we can replace the summation (41) by an integration, resulting in

$$I_{nm}(t)=\frac{\sin^2(\Delta t)}{(\Delta t)^2} \tag{57a}$$

and

$$\bar{\Omega}^2_{nm}=2\epsilon^2|V|^2(d_n d_m)^{1/2} \tag{57b}$$

The characteristic time scale of $I_{nm}(t)$ is thus Δ^{-1}. The condition for the

Markovian limit (49) is then equivalent to

$$\bar{\Omega}_{nm} \ll \Delta \tag{58}$$

and we have

$$\Gamma_{nm}^{-1} = \int_0^{\infty} d\tau I_{nm}(\tau) = \frac{\pi}{2\Delta} \tag{59}$$

Finally, it should be pointed out that the molecular driving rates $K_{nm}^{(2)}$ may be recast in the form

$$K_{nm}^{(2)} = \frac{\bar{\Omega}_{nm}^2}{\Gamma_{nm}} \left(\frac{d_n}{d_m} \right)^{1/2} = 2\pi\epsilon^2 |V|^2 \rho_n \tag{60}$$

where

$$\rho_n = \frac{d_n}{2\Delta} \tag{61}$$

is the density of states in the $|n\alpha\rangle$ manifold. Equation 60 is the familiar golden-rule-type expression. We found it convenient to express the REM in terms of the quantities $\bar{\Omega}_{nm}$ and Γ_{nm} rather than $|V_{nm}|^2$ and ρ_n, since $\bar{\Omega}_{nm}$ and Γ_{nm} 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_n is changing and $|V_{nm}|^2$ will depend strongly on ρ_n and ρ_m. Thus $|V_{nm}|^2$ and ρ_n are not the natural independent parameters for the problem for MMP. $\bar{\Omega}_{nm}$ and Γ_{nm}, however, may be considered independent.

V. 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 Section IV), 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 (26a) 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

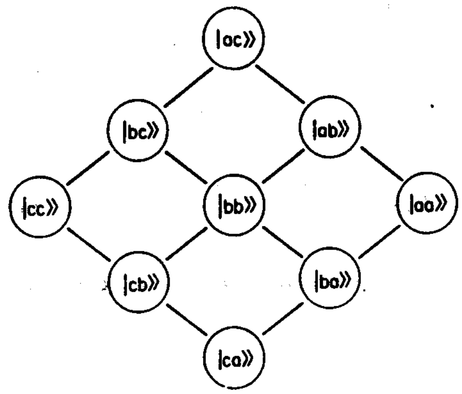

Fig. 2. Diagrammatic representation of the Liouville space terms contributing to M_4. Note that there are six pathways to go from $|aa\rangle\rangle$ to $|cc\rangle\rangle$ in fourther order.

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 Σ_a will substitute Σ_α, 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 (40) we need consider only three independent paths and the other three have a contribution which is simply their complex conjugate. We thus have:

$$M_4(t-\tau,\tau_1,\tau_2,0)_{cc,aa}=\textcircled{I}+\textcircled{II}+\textcircled{III}+\text{c.c.} \tag{62}$$

where

$$\begin{aligned}\textcircled{I}&=\frac{1}{(d_a d_c)^{1/2}}\sum_{\substack{ab\\b'c}}L'_{cc,b'c}(t-\tau)L'_{b'c,ac}(\tau_1)L'_{ac,ab}(\tau_2)L'_{ab,aa}(0)\\&=\frac{1}{(d_a d_c)^{1/2}}\sum_{\substack{ab\\b'c}}\mu_{b'a}\mu_{ab}\mu_{bc}\mu_{cb'}\exp[i\omega_{cb'}(t-\tau)+i\omega_{b'a}\tau_1+i\omega_{bc}\tau_2]\end{aligned} \tag{62a}$$

$$\begin{aligned}\textcircled{II}&=\frac{1}{(d_a d_c)^{1/2}}\sum_{\substack{ab\\b'c}}L'_{cc,b'c}(t-\tau)L'_{b'c,b'b}(\tau_1)L'_{b'b,ab}(\tau_2)L'_{ab,aa}(0)\\&=\frac{1}{(d_a d_c)^{1/2}}\sum_{\substack{ab\\b'c}}\mu_{b'a}\mu_{ab}\mu_{bc}\mu_{cb'}\exp[i\omega_{cb'}(t-\tau)+i\omega_{bc}\tau_1+i\omega_{b'a}\tau_2]\end{aligned} \tag{62b}$$

and

$$\textcircled{\scriptsize III}=\frac{1}{(d_a d_c)^{1/2}}\sum_{\substack{ab\\b'c}} L'_{cc,cb}(t-\tau)L'_{cb,b'b}(\tau_1)L'_{b'b,ab}(\tau_2)L'_{ab,aa}(0)$$

$$=\frac{1}{(d_a d_c)^{1/2}}\sum_{\substack{ab\\b'c}} \mu_{b'a}\mu_{ab}\mu_{bc}\mu_{cb'}\exp[i\omega_{bc}(t-\tau)+i\omega_{cb'}\tau_1+i\omega_{b'a}\tau_2]$$

(62c)

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

$$\sum_a \mu_{b'a}\mu_{ab}\cong\sum_a |\mu_{ab}|^2\delta_{b,b'} \tag{63a}$$

and

$$\sum_c \mu_{bc}\mu_{cb'}\cong\sum_c |\mu_{bc}|^2\delta_{bb'} \tag{63b}$$

This is a form of the statistical random phase approximation (RPA). Making use of this assumption we can omit the b' summation in (62) and set $b=b'$. It is now clear that when (62) holds, then diagrams $\textcircled{\scriptsize II}$ and $\textcircled{\scriptsize III}$ do not contribute at all to θ_4 (27) (and to $R^{(4)}$). This arises since they both pass through $A_{bb}=(1/\sqrt{d_l})\Sigma_\beta|l\beta\rangle\langle l\beta|$, and by construction of the P projection (6) we have

$$(1-P)A_{bb}=0 \tag{64}$$

An alternative way to see this is by looking at (30b). 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 (30), (62), and (63) we thus have:

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

$$=\frac{-1}{(d_a d_c)^{1/2}}\sum_{\substack{a,b\\c}}|\mu_{ab}|^2|\mu_{bc}|^2\exp[i\omega_{cb}(t-\tau-\tau_2)+i\omega_{ba}\tau_1]+\text{c.c.}$$

(65)

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 (65) may be further factorized in the form

$$\theta_4 = \frac{-1}{(d_a d_c d_b^2)^{1/2}} \left[\sum_{ab} |\mu_{ab}|^2 \exp(i\omega_{ba}\tau_1) \sum_{bc} |\mu_{bc}|^2 \exp(i\omega_{cb}(t-\tau-\tau_2)) + \text{c.c.} \right] \tag{66}$$

i.e.

$$\theta_4(t-\tau, \tau_1, \tau_2, 0) = -\bar{\Omega}_{ab}^2 \bar{\Omega}_{bc}^2 \cdot \mathrm{Re}\left[\tilde{I}_{ab}(\tau_1) \tilde{I}_{bc}(t-\tau-\tau_2) \right] \tag{67}$$

We are now in a position to evaluate $\langle R^{(4)} \rangle$,

$$\langle R^{(4)}_{cc,aa}(t-\tau) \rangle = \int_0^{t-\tau} d\tau_1 \int_0^{\tau_1} d\tau_2\, \theta_4(t-\tau, \tau_1, \tau_2, 0) \tag{68}$$

From the definition (41) 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 (67) it is clear that θ_4 (and consequently also $\langle R^{(4)}_{cc,aa}(t-\tau) \rangle$ (26c)) 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 (49). We can thus substitute in (26)

$$R^{(4)}(t-\tau) = -W^{(4)} \delta(t-\tau) \tag{69}$$

where

$$\begin{aligned} W^{(4)}_{cc,aa} &= -\int_0^\infty dt \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2\, \theta_4(t, \tau_1, \tau_2, 0) \\ &= \bar{\Omega}_{ab}^2 \bar{\Omega}_{bc}^2 \int_0^\infty dt \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2\, \mathrm{Re}\left[\tilde{I}_{ab}(\tau_1) \tilde{I}_{bc}(t-\tau-\tau_2) \right] \end{aligned} \tag{70}$$

Equation (69) together with (50) and (26) result in the following rate equations:

$$\begin{aligned} \frac{dP_n}{dt} = &\sum_{m=n\pm 1} W^{(2)}_{nm} \left[P_m \left(\frac{d_n}{d_m} \right)^{1/2} - P_n \left(\frac{d_m}{d_n} \right)^{1/2} \right] \\ &+ \sum_{\substack{m=n\pm 1 \\ n\pm 2}} W^{(4)}_{nm} \left[P_m \left(\frac{d_n}{d_m} \right)^{1/2} - P_n \left(\frac{d_m}{d_n} \right)^{1/2} \right] \end{aligned} \tag{71}$$

The evaluation of $W^{(4)}_{nm}$ where $m=n\pm 1$ proceeds along the same lines and the results are similar to (70). For brevity we shall not consider these terms here.

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 (68) comes from the region:

$$0<\tau_1,\tau_2,t<\tau_c\doteq\Gamma^{-1} \tag{72}$$

since otherwise the integrand vanishes. We thus expect that

$$W^{(4)}\simeq\frac{\bar{\Omega}^2_{ab}\bar{\Omega}^2_{bc}}{\Gamma^3} \tag{73}$$

For the sake of illustration, let us take

$$\tilde{I}(\tau)=\exp(-\Gamma\tau) \tag{74}$$

which yields

$$\langle R^{(4)}(t-\tau)\rangle=\bar{\Omega}^2_{ab}\bar{\Omega}^2_{bc}\int_0^{t-\tau}d\tau_1\int_0^{\tau_1}d\tau_2\exp(-\Gamma\tau_1)\exp[-\Gamma(t-\tau-\tau_2)] \tag{75}$$

resulting in

$$\langle R^{(4)}(t-\tau)\rangle_{cc,aa}=\frac{\bar{\Omega}^2_{ab}\bar{\Omega}^2_{bc}}{\Gamma^2}\exp[-\Gamma(t-\tau)]\{\exp[-\Gamma(t-\tau)]+\Gamma(t-\tau)-1\} \tag{76a}$$

and

$$W^{(4)}_{cc,aa}=-\int_0^{\infty}dt\,R^{(4)}(t)_{cc,aa}=\frac{1}{2}\frac{\bar{\Omega}^2_{ab}\bar{\Omega}^2_{bc}}{\Gamma^3} \tag{76b}$$

Equations (76) demonstrate the validity of our general argument leading to (73), which is not restricted to the particular form (74). Assuming that $\bar{\Omega}_{ab}\simeq\bar{\Omega}_{bc}=\bar{\Omega}$ we recall from (52a) that

$$W^{(2)}=\frac{\bar{\Omega}^2}{\Gamma} \tag{77}$$

We thus get, using (73) and (77)

$$\frac{W^{(4)}}{W^{(2)}}=\frac{K^{(4)}}{K^{(2)}}=(\bar{\Omega}/\Gamma)^2=\frac{W^{(2)}}{\Gamma} \tag{78}$$

which shows that the expansion parameter for the series

$$W=W^{(2)}+W^{(4)}+\dots \tag{79}$$

is

$$\eta=\left(\frac{\bar{\Omega}}{\Gamma}\right)^2=\frac{W^{(2)}}{\Gamma} \tag{80}$$

Thus

$$W^{(2k+2)}\cong W^{(2)}\eta^k \tag{81}$$

We further note that the condition for the validity of the Markovian limit [i.e., (49)] is $\eta \ll 1$, which implies that *in this limit the higher order terms in the expansion* (79) *become unimportant*!

In concluding this section we note that using the present formalism we were able to define precisely the complete molecular information that is relevant for MMP and to see how this information is reduced considerably in the *Markovian limit* leading to simple rate equations. We shall now summarize the basic steps leading to the rate equations 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[36, 40] projection operator formalism we have derived our most general set of REM [(26) or (33)] for the populations 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 where $k=2,4,6,\dots$.
2. The two-time correlation functions $M_2(t-\tau,0)$ are factorized in the form

$$M_2(t-\tau,0)_{nn,mm}=-\bar{\Omega}^2_{nm}I_{nm}(t-\tau) \tag{82}$$

where $\bar{\Omega}^2_{nm}=M_2(0,0)$ is the square of the integrated Rabi frequency for the nm transition, is proportional to the incoming laser intensity, and is roughly independent of the addition of molecular degrees of freedom that do not couple directly with the radiation field. $I_{nm}(t-\tau)$ is a dimensionless correlation function that 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.

3. The Markovian limit is defined whenever

$$\sqrt{\eta}=\frac{\bar{\Omega}}{\Gamma_{nm}}\ll 1 \tag{83}$$

For a typical infrared transition dipole (0.1 Debye) 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[4, 5] and it is typically around 10–100 cm^{-1} for highly vibrationally excited polyatomic molecules (see Section VIII). Thus condition (83) 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

$$I_{nm}(t-\tau)=\Gamma_{nm}\delta(t-\tau) \tag{84}$$

where

$$\Gamma_{nm}^{-1}=\int_0^{\infty}d\tau\, I_{nm}(\tau) \tag{85}$$

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

$$W=W^{(2)}+W^{(4)}+W^{(6)}+\dots \tag{86}$$

ii. The higher order terms in the expansion (86) are much smaller than $W^{(2)}$. In fact

$$W^{(2k+2)}\simeq W^{(2)}\eta^{k}\ll W^{(2)} \tag{87}$$

iii. 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}, $k=2,3,\dots$ are not important, but even M_2 enters only via Ω_{nm} and $\Gamma_{nm}^{-1}=\int_0^{\infty}d\tau I_{nm}(\tau)$. Thus even the details of the two-time correlation functions $I_{nm}(\tau)$ (41) are also irrelevant for the dynamics of the MMP. The rate equations thus depend only on $\bar{\Omega}_{nm}$, Γ_{nm} and *ratios* of the statistical weights of the levels d_n/d_m.

iv. The COP and POP equations are the same and the present analysis justifies the formal derivation of (36), which is equivalent to (52).

4. Finally, we would like to make a few comments regarding a constant coupling model, since it was extensively studied in the past in connection with other molecular relaxation problems,[47, 48] although this model is physically unrealistic for MMP. In the constant coupling model we take $\mu_{nm}^{\alpha\beta}$ to be independent of α and β (no randomness in phase). We thus assume:

$$\mu_{nm}^{\alpha\beta} = \begin{cases} V & -\Gamma < E_{n\alpha} - E_{m\beta} < \Gamma \\ 0 & \text{else} \end{cases} \tag{88}$$

We further assume that Γ^{-1} is much faster than our relevant time scale for P_n (the Markovian assumption) and that $d \gg 1$. For this model the REM will assume the same form [i.e., (71)] as for the previous coupling model (56) with the random phase approximations, and $W_{ab}^{(2)}$ attains the same value, that is,

$$\tilde{W}_{ab}^{(2)} = W_{ab}^{(2)} = \frac{\bar{\Omega}_{ab}^2}{\Gamma_{ab}} = 2\pi\epsilon^2 |V|^2 \sqrt{\rho_a \rho_b} \tag{89a}$$

where

$$\rho_i = \frac{d_i}{2\Gamma} \qquad i = a, b \tag{89b}$$

(We add $\tilde{}$ to quantities corresponding to the present, constant coupling, model to distinguish them from the previous quantities corresponding to (56) with the random phase assumption.) $\tilde{W}^{(4)}$, however, will be much larger than $W^{(4)}$ (73), and simple insertion of (88) in (62) yields

$$\tilde{W}_{cc,aa}^{(4)} = \frac{\bar{\Omega}_{ab}^2 \bar{\Omega}_{bc}^2}{\Gamma^3} d_b = W_{cc,aa}^{(4)} d_b \tag{89c}$$

Thus, for the constant coupling model we have $\tilde{\eta} \equiv \tilde{W}^{(4)}/\tilde{W}^{(2)} = (\bar{\Omega}/\Gamma)^2 d$ whereas for our random phase model we had $\eta = W^{(4)}/W^{(2)} = (\bar{\Omega}/\Gamma)^2$ (78). This arises simply, since the effective number of pathways to go from

$|aa\rangle\rangle$ to $|cc\rangle\rangle$ is d times larger for $\tilde{W}^{(4)}$.[19] 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 (86) does not converge and the resulting time evolution is then very different from that predicted by the simple rate equations (52).[47, 49] We should bear in mind, however, that the random phase assumptions (63), (66), and (67) are much more physically realistic for MMP than the constant coupling (88). This is indeed verified by the applicability of the simple rate equations (52) to actual MMP experiments.[4, 5]

VI. REM FOR POPULATIONS AND COHERENCES

In Sections III–V we have derived REM for the populations in MMP and showed how in the Markovian limit they reduce to simple rate equations. The basic reduction procedure of Section II is, however, more general and enables us to derive a closed set of REM for *any* arbitrary set of chosen variables. As we have already pointed out, the choice of the right number and kind of variables is a crucial step in the derivation of the REM since their simplicity and applicability depend on a successful choice. In particular it is desirable (if possible) to choose a complete set of slow variables whose evolution occurs on a much longer time scale compared to the rest, since then the REM attain a simple time-independent form [the Markovian limit (36)].[19] Thus a non-Markovian equation may become Markovian with the addition of a few more variables.[31] On the other hand, if we consider also fast variables, this will complicate the REM, may force us to make unnecessary simplifying assumptions; and we may end up with less accurate and oversimplified equations. Thus the flexibility of the general formulation of Section II should be utilized to match the number of variables to the problem.

In this section we shall construct and analyze a different set of REM for MMP by the addition of more variables corresponding to coherences. This is done due to several reasons:

1. It is clear that at the early stages of the molecular driving (region I), the expansion of $\langle R \rangle$ to second-order in the field (37) and the Markovian limit of (49) do not hold and we should in fact solve the exact Schrödinger equation with few states and coherent driving. Although we can in principle retain the populations as our only variables and expand the evolution operator $\langle R \rangle$ in higher powers in the field, it is much better to add few variables corresponding to coherences and get a simple Markovian equation, which will be in the form of a general (multilevel) Bloch equation.[50] Thus the explicit

inclusion of coherences as variables in region I results in a considerable simplification of the description in this region.

2. Studies of multilevel systems in contact with a bath and subject to coherent driving are usually carried out by introducing a Zwanzig projection operator which projects out the bath degrees of freedom and results in a set of variables consisting of a complete set of system operators.[32, 33] It is thus of interest to see the connection between the present and the more common formulations. We shall be able to show how in the case of a weak coupling of a system and a bath, our REM reduce to the familiar line broadening formulations.
3. In spectroscopic studies other than multiphoton excitations (ordinary line shapes,[34, 44] double resonance,[12] coherent transients,[23] resonance fluorescence[51]) the experimentalist usually probes directly the time evolution of coherences and their damping (dephasing) rates (e.g., an ordinary line shape is the Fourier transform of the correlation function of the molecular coherence).[34] In the present REM for the populations, the dephasing rates are "buried" inside the kernel $\langle R \rangle$ (or $\langle K \rangle$). By using a less-reduced description including coherences, we are able to see clearly the role of coherences in the dynamics of MMP and we can use the results of other spectroscopic experiments to evaluate the parameters appearing in our REM.
4. Conceptually, the addition of coherences enables us to look at MMP from a different viewpoint and to gain a better insight into the meaning of the Markovian limit and the "reduction of information" that occurs there. We shall be able to provide an alternative derivation to the rate equations (52), which will demonstrate how the explicit inclusion of coherence variables becomes redundant in this case.

We shall now turn to the construction of the relevant set of variables for our new REM. The first group of variables consists of the population variables A_{nn}, which were introduced in (19). These variables should, of course, be included in any REM for MMP, since they contain the significant information which is of primary interest to us, that is, the intermolecular distribution of energy as a function of time. We next define a set of operators which correspond to the time derivatives of A_{nn}, i.e., $[H', A_{nn}]$ [H' was defined in (18b)]. We thus introduce the operators corresponding to single quantum coherences:

$$A_{nm} = \frac{1}{\gamma_{nm}} \sum_{\alpha\beta} |n\alpha\rangle \mu^{nm}_{\alpha\beta} \langle m\beta| \tag{90}$$

where γ_{nm} was introduced in (43). We can now continue the process of constructing new variables by adding operators of the form $[H',[H',A_{nn}]]$, $[H',[H',[H',A_{nn}]]]$, etc. which correspond to the second, third, etc. time derivatives of A_{nn}. We thus get the following set of N^2 operators corresponding to populations (A_{nn}) and multiquantum coherences defined as follows:

$$A_{nm}=\frac{1}{\gamma_{nm}}\sum_{\alpha\beta}\nu_{\alpha\beta}^{nm}|n\alpha\rangle\langle m\beta| \qquad n,m=0,1,\ldots,N-1 \tag{91}$$

where (taking $m>n$)

$$\nu_{\alpha\beta}^{nm}=\sum_{\substack{\gamma,\delta\ldots\\ \beta'}}\mu_{\alpha\gamma}^{n,n+1}\mu_{\gamma,\delta\ldots}^{n+1,n+2}\mu_{\beta'\beta}^{m-1,m} \tag{91a}$$

and

$$\gamma_{nm}^{2}=\sum_{\alpha\beta}\left|\mu_{\alpha\beta}^{nm}\right|^{2} \tag{91b}$$

(For $m<n$ we have $A_{nm}=A_{mn}^{\dagger}$.) When $|n-m|=1$, the definition (91) coincides with (90). We should note at this point that the set (91) contains only certain projections of the high order derivatives of A_{nm}. Also the truncation at $N-1$ is arbitrary and the level of theoretical description may be easily varied within the present formulation by changing the number of relevant operators. The attempts[14, 17, 18] to provide a phenomenological description for MMP in terms of $N^2\times N^2$ generalized Bloch equations (for an N-level system) are intimately related to the picture of a system and a bath that are *weakly* interacting (since N^2 is the size of a complete set of "system" operators) (see Section VII). From the present approach, however, it is clear that the number N^2 does not play any special role. A complete description of the molecular density matrix requires much more than N^2 operators, but in practice we may construct a convenient set of REM whereby the number of variables is significantly smaller than N^2; for example, it may turn out that only single-quantum coherences are sufficient for a complete simple description of the molecular evolution all the way up to dissociation, and that we could ignore the effects of multiquantum coherences. Using the set of relevant operators (19) and (91) we may now evaluate the REM making use of the formulation of Section II. This was done in detail in Ref. 19b, making use of the POP formulation. (We note that for this choice of operators the Mori projection P does not commute with L_0 and $PL_0\neq 0$. As a result the expansion of $\exp(-iLt)$ in

powers of L' becomes more convenient than the expansion of $\exp(-iQLt)$, and this is the reason for the adoption of the POP formulation in this case.) The resulting equations, to first-order in H' and after invoking some simplifying assumptions, are[19b]

$$\frac{dP_n}{dt}=\frac{-i\bar{\Omega}_{n,n+1}}{\sqrt{2}}(\sigma'_{n+1,n}-\sigma'_{n,n+1})-\frac{i\bar{\Omega}_{n,n-1}}{\sqrt{2}}(\sigma'_{n-1,n}-\sigma'_{n,n-1}) \tag{92a}$$

$$\begin{aligned}\frac{d\sigma'_{n,n+1}}{dt}={}&\left[-i\bar{\omega}_{n,n+1}-\bar{\Gamma}_{n,n+1}\right]\sigma'_{n,n+1}-\frac{i\bar{\Omega}_{n,n+1}}{\sqrt{2}}\\&\times\left[P_{n+1}\left(\frac{d_n}{d_{n+1}}\right)^{1/2}-P_n\left(\frac{d_{n+1}}{d_n}\right)^{1/2}\right]\\&+\frac{i\bar{\Omega}_{n+1,n+2}}{\sqrt{2}}\sigma'_{n,n+2}-\frac{i\bar{\Omega}_{n,n-1}}{\sqrt{2}}\sigma'_{n-1,n+1}\end{aligned} \tag{92b}$$

$$\begin{aligned}\frac{d\sigma'_{nm}}{dt}={}&\left[-i\bar{\omega}_{nm}-\bar{\Gamma}_{nm}\right]\sigma'_{nm}+\frac{i\bar{\Omega}_{m,m+1}}{\sqrt{2}}\sigma'_{n,m+1}\\&+\frac{i\bar{\Omega}_{m,m-1}}{\sqrt{2}}\theta^{n}_{m,m-1}\left(\frac{d_m}{d_{m-1}}\right)^{1/2}\sigma'_{n,m-1}\\&-\frac{i\bar{\Omega}_{n,n+1}}{\sqrt{2}}\theta^{m}_{n,n+1}\left(\frac{d_n}{d_{n+1}}\right)^{1/2}\sigma'_{n+1,m}\\&-\frac{i\bar{\Omega}_{n,n-1}}{\sqrt{2}}\sigma'_{n-1,m}\qquad(m>n+1)\end{aligned} \tag{92c}$$

[In (92c) we have taken $m>n+1$. The REM for $\sigma'_{nm}(m<n-1)$ and for $\sigma'_{n+1,n}$ are simply the complex conjugates of (92c) and (92b).] Here

$$\sigma'_{nm}=\left(d_n d_{n+1}^2 d_{n+2}^2\cdots d_{m-1}^2 d_m\right)^{1/4}\sigma_{nm} \tag{92d}$$

σ_{nm} being the expectation value of the coherence operator A_{nm}, that is,

$$\sigma_{nm}(t)=(A_{nm},\rho(t)) \tag{93}$$

The quantity inside the parentheses in (92d), which scales the coherences σ'_{nm}, is the *statistical weight* of the *nm* coherence (the number of possible pathways to go from n to m). The θ^c_{ab} factors are defined as

$$\theta^c_{ab} = \frac{\bar{\Gamma}_{ac} - \bar{\Gamma}_{bc} + i\bar{\omega}_{ab}}{\bar{\Gamma}_{ab} + i\bar{\omega}_{ab}} \tag{94}$$

$\bar{\omega}_{nm}$ and $\bar{\Gamma}_{nm}$ are the off-resonant frequency and the dephasing rate of the *nm* coherence and are defined in terms of the asymptotic behavior of the two-time dipole correlation function $\tilde{I}_{nm}(t)$ (41), that is,

$$-i\bar{\omega}_{nm} - \bar{\Gamma}_{nm} = \lim_{t\to\infty} \frac{1}{\tilde{I}_{nm}} \frac{d\tilde{I}_{nm}}{dt} = \lim_{t\to\infty} \frac{d}{dt} \ln \tilde{I}_{nm}(t) \tag{95}$$

$\bar{\Omega}_{nm}$ and d_n were defined in Section III. The more general equations derived in Ref. 19b have the same form as (92); however, $\bar{\Gamma}_{nm}$ and $\bar{\omega}_{nm}$ are defined by (95) without the limit $t\to\infty$ and are thus time-dependent. Also the $\bar{\Omega}_{nm}$ factors in (92b) and (92c) are replaced by more complicated time-dependent factors, which include also higher order (three-time) dipole correlation functions, which are direct generalizations of $\tilde{I}_{nm}$, that is,

$$J_{abc}(\tau_1, \tau_2) = \langle v_{ab}(\tau_1) v_{ba}(0) v_{ac}(0) v_{ca}(\tau_2) \rangle \tag{96}$$

In order to get the form (92) we have assumed[19b] that $\tilde{I}_{nm}(t)$ has a time scale τ_c much shorter than that of our variables P_n. This is the Markovian limit of the present REM. In Section VIII we shall demonstrate that τ_c^{-1} is of the order of the molecular frequencies that are much larger than the multiphoton rates and that provide a justification to the Markov assumption. (We recall that the Markovian limit actually means separation of time scales between the P and Q variables, and it has a different meaning when we change the definition of P. Thus invoking the Markov assumption in the present equations is not equivalent to the Markov assumption in the previous REM.) Furthermore, we have assumed that asymptotically for long times $\tilde{I}_{nm}(t)$ exhibits an exponential behavior,

$$\tilde{I}_{nm}(t) \sim \exp(-i\bar{\omega}_{nm}t - \bar{\Gamma}_{nm}t) \tag{97}$$

This type of behavior is reasonable for dipole correlation functions as verified by some solvable models corresponding, for example, to impurities in solids[52] and pressure broadening[53] (see also Section VIII). In addition we have factorized the three-time correlation functions in the form

$$J_{abc} = \langle v_{ab}(\tau_1) v_{ba}(0) v_{ac}(0) v_{ca}(\tau_2) \rangle \simeq \frac{\langle v_{ab}(\tau_1) v_{ba}(0) \rangle \langle v_{ac}(0) v_{ca}(\tau_2) \rangle}{d_a} \tag{98}$$

This factorization is consistent with a random-phase approximation which is expected to hold in the quasicontinuum. In the next section we shall discuss (92) and their connection with the previous REM (52).

VII. THE ROLE OF COHERENCES AND INTRAMOLECULAR DEPHASING

Our general REM (92) provide a unified description for MMP, which is valid for weak and strong driving fields and interpolate continuously all the way from the coherent to the totally incoherent limits of the molecular driving. They may be thus used to describe the evolution of a polyatomic molecule starting in region I up to the dissociation. We note that due to our adoption of a basis set of true molecular states, all the anharmonicities are properly (nonperturbatively) incorporated in our REM (92). As a result, no relaxation of population (T_1 type) terms need to be considered. The T_1 terms which appear in the perturbative approaches[50, 17, 18] couple different zero-order states and allow for energy exchange between the "system" and the "bath." In the present formulation they are included in the dephasing operators. The equivalence of T_1 and T_2, depending on the choice of a basis set, was discussed recently for intra- and intermolecular interactions.[20, 54]

In this section we shall analyze the behavior of the REM (92) throughout the multiphoton pumping process.

A. The Early Stages of Region I-Coherent Driving

At the early stages of the molecular excitation there is no reduction and each level contains only one state. We thus have $\bar{I}_{nm}(t) = \exp(-i\bar{\omega}_{nm}t)$ so that $\bar{\Gamma}_{nm} = 0$, there is no dephasing and (92) become equivalent to the complete Schrödinger equation for the driven molecule (coherent driving). This behavior demonstrates how, within the present formulation, the dephasing is a direct consequence of our *reduced description* of the molecular dynamics in terms of few variables.[20] The dephasing rates in our REM $\bar{\Gamma}_{nm}$ (95) are expressed in terms of microscopic intramolecular dipole correlation functions. They are independent of the dipole strength but rather depend merely on the *functional form* of the dipole operator. *No perturbative arguments regarding intramolecular interactions are required in* *order to give a precise definition of these terms*. Thus intramolecular interactions are rigorously treated by using the true molecular basis set. This state of affairs is in contrast to ordinary line-broadening formulations[35, 38, 39] where the dephasing is treated perturbatively in the system-bath interactions (see Section VII.B).

B. The Perturbative Line-Broadening Limit: Weak Coupling of a "System" and a "Bath"

As the molecule absorbs more photons, the density of molecular states rapidly increases and the reduction starts to play a role. But as long as the total molecular energy is not too high, the normal mode picture for the molecule is quite adequate and the anharmonicities may be treated as weak perturbations. In this case the dephasing operator assumes the well-known form from perturbative line-broadening theories.[35, 38, 39] We shall now analyze the behavior of the REM in the weak intramolecular interaction limit. To that purpose we assume separation of our degrees of freedom into "system" and "bath." We further assume that only one "system" degree of freedom interacts directly with the radiation field. However, it is coupled to the bath by a weak perturbation V. The molecular Hamiltonian (18) thus assumes the form

$$H=\sum_{m}|m\rangle E_m\langle m|+\sum_{\alpha}|\alpha\rangle E_\alpha\langle\alpha| \sum_{\substack{m,\alpha,\beta\\ \beta\neq\alpha}}|m\alpha\rangle V_{m\alpha,m\beta}\langle m\beta| \tag{99}$$

Here m is the system quantum number, whereas α comes for the collection of all bath quantum numbers. As in (18), $|m\alpha\rangle$ are molecular states "dressed" by the radiation field (m photons were absorbed at $|m\alpha\rangle$). Therefore the intramolecular coupling cannot connect molecular states with different $|m\rangle$

$$V_{n\alpha,m\beta}=V_{n\alpha,n\beta}\delta_{m,n} \tag{100}$$

The radiation field is assumed to interact only with the system thus

$$\langle n\alpha|\mu|m\beta\rangle=\mu_{nm}\delta_{\alpha,\beta} \tag{101}$$

In order to evaluate the dephasing terms in our REM perturbatively in V, let us first diagonalize the molecular states to first-order in V. We thus get

$$|m\beta^+\rangle=|m\beta\rangle+\sum_{\alpha\neq\beta}\frac{V_{m\beta,m\alpha}}{\omega_{\beta\alpha}+i\eta}|m\alpha\rangle \tag{102a}$$

and

$$\langle n\alpha^+| = \langle n\alpha| + \sum_{\alpha\neq\beta} \langle n\beta| \frac{V_{n\beta,n\alpha}}{\omega_{\alpha\beta} - i\eta} \tag{102b}$$

Substitution of (102) in (101) results in

$$\langle n\alpha^+|\mu|m\beta^+\rangle = \mu_{nm}\left[\delta_{\alpha,\beta} + \frac{\Delta V^{mn}_{\beta\alpha}}{\omega_{\beta\alpha} + i\eta}(1-\delta_{\alpha\beta})\right] \tag{103}$$

where we have defined

$$\Delta V^{mn}_{\beta\alpha} \equiv V_{m\beta,m\alpha} - V_{n\beta,n\alpha} \tag{104}$$

Substitution of (103) into (41) results in (where for the sake of simplicity we take $\Delta V^{mn}_{\alpha\alpha} = 0$)

$$\begin{aligned} \bar{I}_{nm}(t) &= \frac{1}{\gamma^2_{nm}} \sum_{\alpha\beta} |\langle n\alpha^+|\mu|m\beta^+\rangle|^2 \exp(-i\omega_{\alpha\beta}t) \\ &= |\mu_{nm}|^2 \left[\sum_{\alpha} 1 + \sum_{\alpha\neq\beta} \frac{|\Delta V^{mn}_{\beta\alpha}|^2}{\omega^2_{\alpha\beta}} \exp(-i\omega_{\alpha\beta}t)\right] \end{aligned} \tag{105a}$$

From (95) and (105) we thus get, to second order in V:

$$G_{nm}(t) \equiv -\frac{1}{\bar{I}_{nm}} \frac{d\bar{I}_{nm}}{dt} = \frac{i}{d} \sum_{\alpha\neq\beta} \frac{|\Delta V^{mn}_{\beta\alpha}|^2}{\omega_{\alpha\beta}} \exp(-i\omega_{\alpha\beta}t) \tag{106}$$

where d is the number of relevant bath states. Since $G_{nm}(0) = 0$, (106) can be recast in the form

$$G_{nm}(t) = \int_0^t d\tau\, \chi_{nm}(\tau) \tag{107}$$

Where $\chi_{nm}(\tau)$ is a dynamical line-width function

$$\chi_{nm}(\tau) = \frac{1}{d} \sum_{\alpha,\beta} |\Delta V^{nm}_{\beta\alpha}|^2 \cos \omega_{\alpha\beta}\tau \tag{108}$$

and we have

$$\bar{\Gamma}_{nm} = G_{nm}(\infty) \tag{109}$$

These are the familiar expressions from the theories of line broadening.[35, 38, 39]

In conclusion we note the following:

1. *Ordinary Line Shapes*

In ordinary line-shape studies, the driving field is weak and is switched adiabatically. If the molecule is initially at the *n*th level, then the line shape predicted by our REM is the Fourier transform of the molecular coherence correlation function, which is the solution of our REM for $\sigma'_{nm}(t)$ with $\bar{\Omega}=0$ and $\sigma'_{nm}(0)=1$.[34] We thus get for the absorption line shape

$$\Phi_{nm}(\omega_0)=\int_0^{\infty}d\tau\cos(\omega_{nm}\tau)\exp\left[-\int_0^{t}d\tau(t-\tau)\chi_{nm}(\tau)\right] \tag{110}$$

[In the derivation of (110) we have used the non-Markovian version of (92), which in the perturbative limit simply amounts to replacing $i\bar{\omega}_{nm}+\bar{\Gamma}_{nm}$ by $G_{nm}(t)$.[19] Only in the Markovian limit we have $G_{nm}(t)\cong G_{nm}(\infty)$, $\int_0^t d\tau(t-\tau)\chi_{nm}(\tau)\rightarrow t\int_0^{\infty}d\tau\,\chi_{nm}(\tau)$, and the line shape (110) assumes a simple Lorentzian form with a width of $\int_0^{\infty}d\tau\,\chi_{nm}(\tau)$.][19, 34]

2. *Absence of Energy Redistribution*

In the weak perturbation limit, the system mode is being pumped by the radiation field, and the bath merely causes a dephasing but does not induce any relaxation of population (T_1) in the system (all energy absorbed from the field remains in the pumped mode). This arises since in our "dressed" picture the bath cannot couple states which belong to different levels (100) and in the perturbative limit each level is associated with a definite state of the system. We could take account for T_1 within a perturbative approach by adding more variables (each level could be split into several groups with the same total energy but with different energy in the pumped mode). This will result in a large increase in the number of variables.[17, 18]

3. *Limitations of the Perturbative Approach*

The usage of a zero-order (harmonic or local-mode)[22, 55, 56] basis set with intramolecular couplings may be advantageous provided we can get along with few states (say, when only one state in each level is carrying oscillator strength to the previous level). In such a case we can, in the Markovian limit, attribute a width of $2\pi|V|^2\rho_f$ to the various levels (where ρ_f is the density of final molecular states), and this provides a very convenient framework for the description of molecular radiative phenomena.[57] This is the case in ordinary optical line-shape[24] and transient experiments[23] in electronically excited states of polyatomic molecules where it is possible to find a well-defined "doorway state."[57] Another type of related experiments where such a zero-order basis set was proved useful is the novel gas-phase CH stretch overtone spectroscopy in benzene done by Bray and Berry.[21, 22] For these experiments, by adopting a local mode picture we may again consider a single (local-mode) doorway state and perform a dynamical line-shape analysis by considering its coupling to the rest of the modes.[22] This is not the case, however, for MMP in the quasicontinuum where we do not expect a perturbative treatment in intramolecular interactions to hold. This is why in the present work we have chosen a basis set ($|n\alpha\rangle$) of the true molecular states for the description of the highly excited molecules.

C. The Quasicontinuum

At high degrees of excitation we expect the Markovian limit [which led to (92)] to hold very early (see Section VIII) so that we are left with the general REM (92) where each transition is characterized by a frequency $\bar{\omega}_{nm}$, integrated Rabi frequency $\bar{\Omega}_{nm}$ (which is roughly independent on the molecular size) and a dephasing rate $\bar{\Gamma}_{nm}$ given by the asymptotic behavior of the logarithmic derivative of $\tilde{I}_{nm}(t)$. [The perturbative expression (109) no longer holds.] In addition the REM (92) include *ratios* of statistical weights (d_n/d_m) of the various levels.

D. The Complete Incoherent Driving—Rate Equations Revisited

If the dephasing rates $\bar{\Gamma}_{nm}$ are fast compared to the driving $\bar{\Omega}_{nm}$, we may invoke a steady state assumption for the coherences, (i.e. set $d\sigma'_{nm}/dt=0$ in (92)), solve for σ'_{nm} and substitute back into the equations for the populations. As a result our REM assume the form of simple rate equations corresponding to incoherent driving[58]

$$\frac{dP_n}{dt} = \sum_{m\neq n} \mathrm{K}_{nm}P_m - \mathrm{K}_{nn}P_n \tag{111}$$

If we consider only single quantum coherences (i.e., set $\sigma'_{nm}=0$ for $|n-m|>1$) we have

$$\sigma'_{n,n+1} = \frac{-i\bar{\Omega}_{n,n+1}}{\sqrt{2}\left(i\bar{\omega}_{n,n+1}+\bar{\Gamma}_{n,n+1}\right)} \times\left[P_{n+1}\left(\frac{d_n}{d_{n+1}}\right)^{1/2} - P_n\left(\frac{d_{n+1}}{d_n}\right)^{1/2}\right] \tag{112}$$

which when substituted back into (92a) results in

$$\frac{dP_n}{dt}=\sum_{m=n\pm 1}\frac{\bar{\Gamma}_{nm}\bar{\Omega}^2_{nm}}{\bar{\Gamma}^2_{nm}+\bar{\omega}^2_{nm}}\left[P_m\left(\frac{d_n}{d_m}\right)^{1/2}-P_n\left(\frac{d_m}{d_n}\right)^{1/2}\right] \tag{113}$$

We recall that in the derivation of (92) we have assumed

$$\bar{I}_{nm}(t)=\exp\left(-i\bar{\omega}_{nm}t-\bar{\Gamma}_{nm}t\right) \tag{114}$$

Substitution of (114) in (51) results in

$$\Gamma^{-1}_{nm}=\mathrm{Re}\int_0^{\infty}d\tau\,\bar{I}_{nm}(\tau)=\frac{\bar{\Gamma}_{nm}}{\bar{\omega}^2_{nm}+\bar{\Gamma}^2_{nm}} \tag{115}$$

which shows that *the simple rate equations* (113) *derived from our new REM* (92) *are identical with* (52) *derived from the previous REM* (48).

The present alternative derivation of (52) provides us with a new insight regarding the significance of the simple rate equations. As is clearly seen from (92), the dynamics of molecular multiphoton processes is governed by the competition between the driving terms $\bar{\Omega}_{nm}$, which tend to build higher coherences and the dephasing rates $\bar{\Gamma}_{nm}$, which tend to destroy them. If

$$\beta\equiv\frac{\bar{\Omega}^2}{\bar{\omega}^2+\bar{\Gamma}^2}\ll 1 \tag{116}$$

we can solve iteratively for the steady state of (92), that is, we can substitute $\sigma'_{n,n+1}$(112) in (92c) to generate $\sigma'_{n,n+2}$, etc. This simple solution of (92) (perturbative in β) reveals that we have a hierarchy of multiquantum coherences where $\sigma'_{n,n+k}=O(\beta^{k/2})$, $k>0$. The contribution of $\sigma'_{n,n+k}$ to the rate equation (111) for the populations will be $O(\beta^k)$. Equations (112) and (113) are the simplest demonstration of this where for $k=1$, $\sigma'_{n,n+1}=O(\beta^{1/2})$ and $K_{n,n+1}=O(\beta)$. When $\beta\ll 1$ this means that the steady-state values of the high-order coherences will be very small, and when we ignore all $\sigma'_{n,n+k}$ except for $k=1$, we get our simple rate equations (113). These arguments show how most of the information regarding the molecular dynamics (i.e., the dynamics of the higher order coherences $k>1$) becomes irrelevant for the dynamics of MMP in the Markovian limit $\beta\ll 1$ where simple rate equations apply. In the previous derivation of (52) from (48) all the extra dynamical information was hidden in the higher order correlation functions contributing to $\langle R\rangle$.

It is obvious from the comparison of the two derivations of the REM (52) and (92) that the k quantum coherences in the latter $\sigma'_{n,n+k}$ play the role of $W^{(2k)}$ in the former. If we take, for example, $W^{(4)}_{cc,aa}$, we can see from Fig. 2 that it corresponds to the path $|cc\rangle\rangle - |bc\rangle\rangle - |ac\rangle\rangle - |ab\rangle\rangle - |aa\rangle\rangle$, which leads from $|aa\rangle\rangle$ to $|cc\rangle\rangle$ via the two quantum coherences $|ac\rangle\rangle$. The neglect of $W^{(4)}$ in (79) is thus equivalent to ignoring $\sigma'_{n,n+2}$ in (92). The same rate equations thus result from the neglect of all higher order coherences in (92) or of all higher order correlation functions in (48). Furthermore, the expansion parameter β (116) corresponds to η (80) (from (115) we see that if $\bar{\omega}=0$ then $\eta=\beta$).

VIII. A MODEL FOR THE INTRAMOLECULAR DIPOLE CORRELATION FUNCTIONS

In the preceding sections we have developed a complete theory for MMP where in the Markovian limit the resulting REM (52) or (92) are expressed in terms of the two-time intramolecular dipole correlation functions $\tilde{I}_{nm}(t)$ (41).

In this section we shall develop a simple microscopic model for $\tilde{I}_{nm}(t)$, which will enable us to relate the dephasing times (and the whole dynamics of MMP) to real molecular parameters (size, frequencies, anharmonicities, masses, etc.). We start with the molecular Hamiltonian

$$H_M = \sum_{\nu} H_{0\nu}(q_\nu) + H' \tag{117}$$

where $H_{0\nu}(q_\nu)$ is a harmonic Hamiltonian for the νth normal mode and q_ν is its dimensionless coordinate. H' is the anharmonic part of the Hamiltonian and includes terms cubic and higher in $\mathbf{q}$. Our expressions for the dephasing rates are given in terms of the true molecular states. We thus need a way for obtaining a reasonable approximation for these states. In fact, since the dephasing is essentially a spreading process of a wavepacket of molecular states on the energy shell, we need to have a "mean field" Hamiltonian that will describe correctly the motion only on the energy shell. The simplest way to achieve that is to expand H' to linear terms in q_ν, that is,

$$H' = \sum_{\nu} F_\nu(\mathbf{q}) q_\nu \tag{118}$$

and to replace each $F_\nu(\mathbf{q})$ by its microcanonial average at energy E, that is,

$$\Delta_\nu(E) \equiv \langle F_\nu \rangle_E = \frac{\mathrm{Tr}[F_\nu \delta(E-H)]}{\mathrm{Tr}\,\delta(E-H)} \tag{119}$$

We thus get

$$H(E) = \sum_{\nu} H_{0\nu}(q_\nu) + \sum_{\nu} \Delta_\nu(E) q_\nu \tag{120}$$

(Note that Δ_ν and q_ν are dimensionless.) We have thus established a simple picture of a collection of harmonic oscillators whose equilibrium position is being shifted as a function of the molecular energy. At $E = 0$, $\langle q_\nu \rangle = 0$ and we recover the normal-mode Hamiltonian. $\Delta_\nu(E)$ are related to the anharmonicities to lowest order as

$$\Delta_\nu(E) = \sum_{\nu'} \alpha_{\nu\nu'\nu'} \langle q_{\nu'}^2 \rangle_E \tag{121}$$

where $\alpha_{\nu\nu'\nu'}$ are cubic anharmonicities and $\langle q_{\nu'}^2 \rangle_E$ is the microcanonial mean square displacement of the νth mode.

Let us consider now the following *microcanonial* correlation function

$$\tilde{I}_{nm}(E, t) = \frac{1}{\gamma_{nm}^2 W(E)} \sum_{\alpha,\beta} |\mu_{nm}^{\alpha\beta}|^2 \exp(-i\omega_{n\alpha,m\beta} t) \delta(E_{n\alpha} - E) \tag{122}$$

where $W(E)$ is the density of molecular states at energy E. In terms of this correlation function we have

$$\tilde{I}_{nm}(t) = \tilde{I}_{nm}(\bar{E}_n, t) \tag{122a}$$

where $\bar{E}_n$ is the mean energy of the nth level. We further assume that the dipole operator is coupled only with one normal mode (ν_s)

$$\mu = \bar{\mu} q_s \tag{123}$$

The quantity that may be easily evaluated is, however, the *canonial* correlation function[59–62]

$$\hat{I}_{nm}(\beta, t) = \frac{1}{Q(\beta)} \int_0^\infty dE\, \tilde{I}_{nm}(E, t) W(E) \exp(-\beta E) \tag{124}$$

where $Q(\beta)$ is the partition function

$$Q(\beta) = \int_0^\infty dE\, W(E) \exp(-\beta E) \tag{125}$$

$I_{nm}(E,t)$ may then be evaluated by the inverse Laplace transform[49, 50]

$$\tilde{I}_{nm}(E,t)=\frac{\int_{\lambda-i\infty}^{\lambda+i\infty} d\beta \exp(\beta E)Q(\beta)\hat{I}_{nm}(\beta,t)}{\int_{\lambda-i\infty}^{\lambda+i\infty} d\beta \exp(\beta E)Q(\beta)} \tag{126}$$

The anharmonicity of q_s, $\Delta_s(E)$ has a special role in determining $\bar{\omega}_{nm}$ (the mean frequencies of the transitions); however, for the dephasing it contributes just as any other mode. For the sake of simplicity we shall assume $\Delta_s=0$. (Incorporating Δ_s will not affect substantially our final expressions.) We then get[59-62]

$$\hat{I}_{nm}(\beta,t)=\exp[-S(\beta)]\exp[S_+(\beta,t)+S_-(\beta,t)] \tag{127}$$

where

$$S_+(\beta,t)=\sum_\nu \tfrac{1}{2}|\Delta_\nu^{(nm)}|^2(\bar{n}_\nu+1)\exp(i\omega_\nu t) \tag{127a}$$

$$S_-(\beta,t)=\sum_\nu \tfrac{1}{2}|\Delta_\nu^{nm}|^2\bar{n}_\nu\exp(-i\omega_\nu t) \tag{127b}$$

and

$$S(\beta)=S_+(\beta,0)+S_-(\beta,0)=\sum_\nu \tfrac{1}{2}|\Delta_\nu^{nm}|^2(2\bar{n}_\nu+1) \tag{127c}$$

Here

$$\Delta_\nu^{(nm)}=\Delta_\nu(E_n)-\Delta_\nu(E_m) \tag{128}$$

and $\bar{n}_\nu$ is the mean occupation number of the νth oscillator at temperature $\beta^{-1}=kT$, that is,

$$\bar{n}_\nu=[\exp(\beta\hbar\omega_\nu)-1]^{-1} \tag{129}$$

Evaluation of the inverse Laplace transform (126) should now be made in order to evaluate $\tilde{I}_{nm}(E,t)$. We recall that under quite general conditions[62, 63] the inversion may be achieved by using the saddle-point method. This results in the extremely simple relation

$$\tilde{I}(E,t)\simeq\hat{I}(\beta^*,t) \tag{130}$$

where β^* is the saddle point, obtained from the solution of

$$\sum_{\nu} \bar{n}_{\nu}(\beta^*)\hbar\omega_{\nu} = E \tag{131}$$

Using this result we get

$$\tilde{I}(E,t) = \exp(-S(\beta^*))\exp[S_+(\beta^*,t) + S_-(\beta^*,t)] \tag{132}$$

The exact equation (122) satisfies $\tilde{I}_{nm}(t) = \tilde{I}^*_{mn}$. This is no longer the case due to our use of the saddle point; we thus take

$$\tilde{I}_{nm}(t) = \tilde{I}_{nm}\left(\frac{\bar{E}_n + \bar{E}_m}{2}, t\right) \tag{132a}$$

Substituting (132) in (106) we get

$$\begin{aligned} G_{nm}(t) &= -\frac{1}{\tilde{I}_{nm}}\frac{d\tilde{I}_{nm}}{dt} = -\frac{d}{dt}[S_+(\beta^*,t) + S_-(\beta^*,t)] \\ &= -\frac{d}{dt}S(\beta^*,t)\bigg|_{t=0} + \int_0^t d\tau\, \chi_{nm}(\tau) \end{aligned} \tag{133}$$

where

$$\chi_{nm}(\tau) = \chi'_{nm}(\tau) + i\chi''_{nm}(\tau) \tag{134}$$

$$\chi'_{nm}(\tau) = \sum_{\nu} \frac{|\Delta_{\nu}^{mn}|^2}{2}\omega_{\nu}^2(2\bar{n}_{\nu}+1)\cos\omega_{\nu}t \tag{135a}$$

$$\chi''_{nm}(\tau) = \sum_{\nu} \frac{|\Delta_{\nu}^{nm}|^2}{2}\omega_{\nu}^2\sin\omega_{\nu}t \tag{135b}$$

$$\frac{d}{dt}S(\beta^*,t)\bigg|_{t=0} = i\sum_{\nu} \frac{|\Delta_{\nu}^{nm}|^2}{2}(2\bar{n}_{\nu}+1)\omega_{\nu} \tag{135c}$$

And the dephasing rate Γ_{nm} in the Markovian limit (95) assumes the form

$$\bar{\Gamma}_{nm} = \tfrac{1}{2}\int_0^{\infty} d\tau \sum_{\nu} |\Delta_{\nu}^{nm}|^2(2\bar{n}_{\nu}+1)\omega_{\nu}^2\cos\omega_{\nu}\tau \tag{136}$$

which corresponds to a Lorentzian line profile.

Let us now have a rough estimate of Γ_{nm}. The integral (136) in the high-temperature limit is over a wavepacket whose frequency width is the spread in molecular frequencies that is of the same magnitude as the molecular frequencies. We thus have

$$\Delta_v^{nm}(E) \sim \frac{\alpha}{2} \frac{\omega_0}{\langle \omega \rangle} \tag{137a}$$

and

$$\bar{\Gamma}_{nm} \sim \frac{1}{2} |\Delta|^2 (2\bar{n}+1) \frac{\langle \omega \rangle^2}{\langle \omega \rangle} = \frac{1}{2} \left(\frac{\alpha}{2} \right)^2 (2\bar{n}+1) \omega_0 \tag{137b}$$

Here $\langle \omega \rangle$ is a typical molecular frequency, ω_0 is the laser frequency, and $\bar{n}$ is the total number of absorbed quanta. α is a dimensionless cubic anharmonicity and is typically $\alpha \sim 10^{-1} - 10^{-2}$.

Taking the typical values $\bar{n} = 40$ and $\omega_0 = 1000\ \mathrm{cm}^{-1}$, we get $\bar{\Gamma}_{nm} = 1\ \mathrm{cm}^{-1}$ assuming $\alpha = 10^{-2}$ and $\bar{\Gamma}_{nm} = 100\ \mathrm{cm}^{-1}$ assuming $\alpha = 10^{-1}$. These are very reasonable values for MMP. If we consider the experimental data of SF_6, the absorption cross-sections were fitted to experiment assuming a rate equation (113),[6, 4] resulting in a cross-section of $\sigma \sim 2 \times 10^{-20}\ \mathrm{cm}^2$ at $\bar{n} = 40$. Using (113) the cross-section is given by

$$\frac{\sigma \Phi}{\hbar \omega_0} = \frac{\bar{\Omega}_{nm}^2}{\bar{\Gamma}_{nm}} \tag{138}$$

where Φ is the incoming laser flux and we have taken $\bar{\omega}_{nm} = 0$. Assuming a diluted oscillator strength of $\mu \sim 0.03 - 0.1$ Debye we get $\Gamma_{nm} \sim 15 - 150\ \mathrm{cm}^{-1}$, which agrees very nicely with the above estimates.

Furthermore, the multiphoton absorption data[7] indicate that the effective multiphoton absorption cross section defined as $d\bar{n}/dI$ is decreasing with Φ (and hence with the degree of excitation). This type of behavior is predicted by our REM due to the roughly linear increase of $\bar{\Gamma}_{nm}$ with $\langle n \rangle$ (137) and the dilution of $\bar{\Omega}_{nm}$, which result in a gradual decrease of the effective absorption cross-section with $\bar{n}$. From these estimates we can also verify the validity of the Markovian assumption leading to (136) as the relation $\Gamma \ll \tau_c^{-1} \sim \langle \omega \rangle$ is equivalent to (49). Rate equations of the form (111) and (113) were used by several authors to fit experimental data.[5c, 6, 7, 16] We should bear in mind, however, that these equations are only the final stage in the reduction hierarchy described in this work and only at the higher energy part of the quasicontinuum are we allowed to use the simple rate equation (113).

Furthermore, in the actual calculations[7] it was assumed that

$$\frac{K_{nm}}{K_{mn}} = \frac{\rho_n}{\rho_m} \tag{139}$$

where ρ is the density of molecular states. From the present derivation it is clear that ρ_n/ρ_m should be actually d_n/d_m, that is, the ratio of effectively radiatively coupled states, which may be very different. This may crucially affect the intermolecular energy distributions and the conclusions drawn by Grant et al.[7] should be thus treated with caution. Fitting of the present REM with experimental data may thus provide a clue for understanding the dynamics of highly excited polyatomic molecules, by providing us with $\bar{\Omega}_{nm}$ and $\bar{I}_{nm}(t)$ as a function of the molecular degree of excitation. The experimental data available at present are not sufficiently detailed to allow for an unambiguous quantitative study, and this is the reason that different authors are able to fit their data using completely different assumptions.[46] For that reason it is necessary to use data from other types of experiments, especially regarding the intramolecular dephasing times, which will eliminate the number of unknown parameters in the REM. Great progress has been recently achieved in that direction by various techniques.[21-24]

Finally we should note that although M_k were defined in Section III using the true molecular eigenstates, their microscopic evaluation does not necessarily require the complete knowledge of the molecular eigenstates. It is possible to calculate M_k semiclassically directly from the Hamiltonian and to avoid the reference to the molecular eigenstates altogether. Such semiclassical methods were recently developed for absorption and fluorescence spectra[64] (i.e. one and two photon processed, M_2 and M_4) and they may be easily extended towards the evaluation of any intramolecular dipole correlation function M_k.

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