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Theory of Collisionless Molecular Multiphoton Processes

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ABSTRACT

We derive reduced equations of motion (REM) which describe the dynamics of polyatomic molecules in the presence of strong infrared lasers. The derivation is made starting from the complete molecular Liouville equation and making use of the Zwanzig-Mori projection operator formalism. The complete molecular information relevant for the dynamics of molecular multiphoton processes (MMP) is expressed in terms of a hierarchy of intramolecular dipole correlation functions. We show how by invoking simple statistical assumptions (the random phase approximation and separation of time scales) this information is considerably reduced to essentially four quantities per transition: An integrated Rabi frequency $\bar{\Omega}_{nm}$, a dephasing rate Γ_{nm}, a detuning $\bar{\omega}_{nm}$ and ratios of statistical weights of the levels d_n/d_m. Depending on our choice of reduction scheme we may obtain either generalized Bloch equations or simple rate equations. The interrelation between the two and their limits of validity are precisely specified. The present formulation enables us to describe the dynamics of MMP all the way from "region I" via the quasicontinuum and up to the dissociation. Finally we present novel spectroscopic results done in supersonic beams which provide us directly with the intramolecular dephasing rates which are the key dynamical quantities in MMP.

I. Introduction

Our understanding of the dynamics of highly vibrationally excited polyatomic molecules has improved dramatically in recent years due to the development of novel spectroscopic techniques such as overtone spectroscopy [1,2], spectroscopy of supercooled molecules in beams [3,4], picosecond spectroscopy [5] etc. Of special interest are studies of molecular multiphoton processes (MMP) which are based on pumping few e.V. (30-40 photons) of energy into isolated (collision-free) polyatomic molecules via the interaction with strong infrared laser pulses in the power range of 10M watt/cm^2[6,7]. Some of the main reasons for the enormous theoretical and experimental activity in this field are:(i) This is a relatively clean and convenient way of pumping energies of chemical interest to large molecules in short times (0.5nsec-100 nsec). The excitation conditions are easily controllable by varying the laser frequency, power, fluence, using several lasers (multicolour experiments) etc. (ii) The excitation may in principle be made bond selective since the oscillator strength is not evenly distributed among the various molecular vibrational degrees of freedom. This opens the fascinating possibility of achieving laser-induced and laser controlled chemical reactions by putting the right amount of energy in the region of interest. This depends of course on the relative rates of pumping the energy to the intramolecular redistribution of energy which tends to destroy any selectivity. (iii) Unimolecular disso-

ciation following MMP turned out to be highly isotopically selective in several cases. (iv) Understanding the mechanism of the multiphoton pumping processes provides us with a clue for monitoring the dynamics of highly vibrationally excited polyatomic molecules. This is connected to the new field of intramolecular line broadening (dephasing) and may help us clarify the validity of the existing statistical theories of unimolecular reactions [8].

The following qualitative picture [6] 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 quasi-continuum and a proper description of the molecular time evolution in this range requires a quantitative understanding of the mechanism of intramolecular energy transfer and line broadening (dephasing) of highly vibrationally excited polyatomic molecules, of which very little is known at present. 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. Since numerous reviews were written recently on this subject [6,7], we shall not give here an extensive survey of the current experimental status. We shall rather try to develop a general unified framework for the theoretical description of these processes. It is clear that a complete microscopic treatment of MMP (i.e.the calculation of the entire molecular density matrix ρ) is neither feasible nor desirable. Due to the huge number of molecular states involved (10^{10} or more) such a treatment will require an enormous amount of (unavailable) information for the calculation of a density matrix whose most parts are irrelevant and redundant. The present approach [9] is based on the projection operator formalism of Zwanzig [10] and Mori [11] 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. The main steps in this "hydrodynamic-like" approach [9] 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.

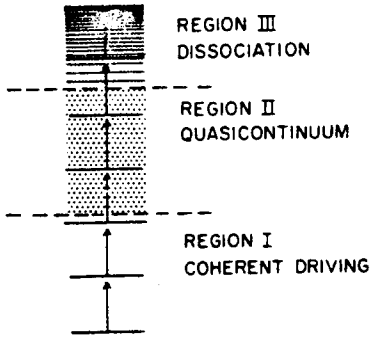

Fig.1 Energy regions for molecular multiphoton processes.

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 which should be adjusted to the desired level of description. In Section II we present the basic reduction formalism which is based on the projection operator techniques of Mori and Zwanzig. In Section III we present the Hamiltonian for MMP and formally derive the REM for a specific choice of variables corresponding to level populations. These REM are then expanded in Section IV and the conditions under which they further reduce to simple rate equations in the quasi-continuum are analysed. In Section V we add more variables corresponding to coherences and derive another REM (generalized Bloch equations) which are valid also in region I of coherent driving. An alternative derivation of the simple rate equations is also obtained as a limiting case of these new REM. Finally in Section VI we discuss and summarize our results.

II. The basic reduction formalism

We consider a complicated system with many degrees of freedom characterized by a Hamiltonian H and a density matrix ρ whose time evolution 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. Due to the complexity of the system, the information contained in the complete density matrix ρ is too detailed and its evaluation is impractical. Consequently we shall be interested only in a few quantities $\sigma_\mu(t)$ which are the expectation values of a small set of dynamical operators A_μ, i.e.

$$\sigma_\mu(t) \equiv (A_\mu,\rho(t)) \tag{2}$$

where we have defined the scalar product $S_{\mu\nu}$ of two operators as

$$S_{\mu\nu} \equiv (A_\mu,A_\nu) \equiv Tr(A_\mu^+ A_\nu) \ . \tag{3}$$

Without loss of generality we may assume that our relevant operators are orthonormal, i.e. $S_{\mu\nu}=\delta_{\mu\nu}$. The Mori-Zwanzig [10,11] projection operator technique enables us to derive reduced equations of motion (REM) which yield $\sigma_\mu(t)$ directly without having to calculate ρ. To that end we define a Mori projection P which projects onto the subspace spanned by our relevant operators A_μ:

$$PB = \sum_\mu (B,A_\mu)A_\mu \ , \tag{4}$$

and the complementary projection Q≡1-P. We shall further assume that $\rho(0)=P\rho(0)$ so that $Q\rho(0)=0$. Making use of these definitions the REM may be written in the form [9]

$$\frac{d\sigma_\nu}{dt} = -i \sum_\mu \langle L\rangle_{\nu\mu} \sigma_\mu(t) - \int_0^t d\tau \sum_\mu \langle R(t-\tau)\rangle_{\nu\mu} \sigma_\mu(\tau) \ , \tag{5}$$

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

$$R(t-\tau) \equiv L \exp(-iQL(t-\tau))\, Q L \ , \tag{6}$$

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

$$\langle Y\rangle_{\nu\mu} \equiv \mathrm{Tr}(A_\nu^\dagger\, Y\, A_\mu) \quad , \quad Y=R,L \ . \tag{7}$$

Equations (5) are exact and are valid for an arbitrary choice of dynamical operators A_μ. In practice, however, the memory kernel $\langle R\rangle$ is 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 [9], i.e.,

$$\frac{d\sigma_\nu}{dt} = -i \sum_\nu \langle L\rangle_{\nu\mu}\, \sigma_\nu(t) - \sum_\nu \langle \tilde{R}(t)\rangle_{\nu\mu}\, \sigma_\mu(t) \tag{8}$$

where

$$\langle \tilde{R}(t)\rangle_{\nu\mu} = \sum_{\nu'} W(t)_{\nu\nu'}\, V^{-1}_{\nu'\mu}(t) \quad , \tag{9}$$

$$W_{\nu\nu'}(t) = \mathrm{Tr}(A_\nu^\dagger\, LQ\, \exp(-iLt) A_{\nu'}) \ , \tag{9a}$$

$$V_{\nu'\mu} = \mathrm{Tr}(A^\dagger_{\nu'}\, \exp(-iLt) A_\mu) \quad . \tag{9b}$$

Equations (5) or (8) constitute the basic reduction scheme to be used throughout the present lecture. The form (5) 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 (8) uses only partial time ordering and will be referred to as the POP (partial ordering prescription). Equation (8), like (5), is also exact. However, once an expansion is made both equations may have very different predictions [12,9]. Furthermore, it may turn out that depending on the choice of variables one form could become advantageous. This is indeed the case for the present problem of MMP. When we try to derive simple rate equations (Sections III and IV) then the COP form (Eq. (5)) is most convenient. When we add more variables corresponding to coherences (Section V), the expansion of the COP equations becomes extremely tedious and the POP approach (Eq. (8)) is the natural way to proceed. A comparison of the two forms for general relaxation and line shape problems was made recently [12].

III. Reduced equations of motion involving populations only

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 ($kT \ll h\omega_L$), 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 n'th level. We further invoke the rotating wave approximation (RWA) [13] 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[9]:

$$H = H_0 + H' \ , \tag{10}$$

where

$$H_0 = \sum_{n,\alpha} |n\alpha\rangle E_{n\alpha} \langle n\alpha| \quad , \tag{10a}$$

and

$$H' = \varepsilon \sum_{\substack{n\alpha \\ m\beta \\ m=n\pm 1}} |n\alpha\rangle \ \mu_{nm}^{\alpha\beta} \langle m\beta| . \tag{10b}$$

Here the molecular states within the n'th level have absorbed n infrared quanta from the field, and $E_{n\alpha}=E^{o}_{n\alpha}-n\omega_L$ 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. 2.

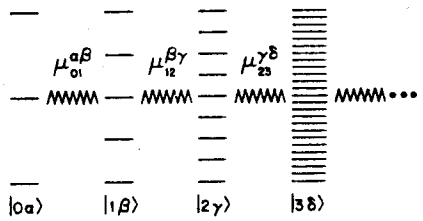

Fig.2 The coupling scheme for molecular multiphoton processes.

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 [9]:

$$A_{nn} = \frac{1}{\sqrt{d_n}} \sum_{\alpha} |n\alpha\rangle \langle n\alpha| \quad , \qquad n=0,1,\ldots,N-1 \tag{11}$$

d_n being the number of states within the n'th 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 (Eqs. (33) or (47)). 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 [11]. The A_{nn} operators are orthonormal (with respect to their scalar product) and the populations of the various levels are

$$P_n(t) = \sqrt{d_n}\ (A_{nn},\rho(t)) = \sqrt{d_n}\ \sigma_n(t) \quad . \tag{12}$$

At time t=0 we assume that all the molecules are in the zeroth level so that $\rho(0)=P\rho(0)=1/\sqrt{d_0}\ A_{00}$. For the present set of operators we have the convenient relation $PL_0=0$ (L_0 and L' are the Liouville operators corresponding to H_0 and H' respectively). This implies that

$$QL = (1-P)(L_0+L') = L_0 + QL' \ , \tag{13}$$

which enables us to expand $\exp(-QL\tau)$ in a power series in QL' and makes

the formal evaluation of the COP operator $\langle R(T-\tau)\rangle$ straightforward resulting in [9]:

$$\frac{d\sigma_\nu}{dt} = -\int_0^t d\tau \sum_\mu \langle R(t-\tau)\rangle_{\nu\mu}\, \sigma_\mu(\tau) \quad , \tag{14}$$

where

$$\langle R(t-\tau)\rangle = \langle R^{(2)}(t-\tau)\rangle + \langle R^{(4)}(t-\tau)\rangle + \langle R^{(6)}(t-\tau)\rangle + \ldots \quad , \tag{14a}$$

$$\langle R^{(2)}(t-\tau)\rangle = K^{(2)}(t-\tau,0) \quad , \tag{14b}$$

and

$$\langle R^{(2n)}(t-\tau)\rangle = \int_0^{t-\tau} d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{2n-3}} d\tau_{2n-2}\, K^{(2n)}(t-\tau,\tau_1,\tau_2,\ldots,\tau_{2n-2},0) \tag{15}$$

Here

$$K^{(2n)}(\tau_1,\tau_2,\ldots,\tau_{2n}) = (-1)^{n+1}\langle L'(\tau_1)L'(\tau_2)(1-P)L'(\tau_3)L'(\tau_4) \tag{16}$$

$$(1-P)\ldots(1-P)L'(\tau_{2n-1})L'(\tau_{2n})\rangle \quad ,$$

where

$$L'(\tau) = \exp(iL_0\tau)L' \exp(-iL_0\tau) \quad . \tag{17}$$

Let us introduce further the n'th moment of L' as the n-time correlation function

$$M^{(n)}(\tau_1,\tau_2\ldots\tau_n) = \langle L'(\tau_1)L'(\tau_2)\ldots L'(\tau_n)\rangle \quad , \tag{18}$$

in terms of which we may rewrite Eq. (16) in the form:

$$K^{(2)}(\tau_1,\tau_2) = M^{(2)}(\tau_1,\tau_2) \quad , \tag{19a}$$

$$K^{(4)}(\tau_1,\tau_2,\tau_3,\tau_4) = -[M^{(4)}(\tau_1,\tau_2,\tau_3,\tau_4) - M^{(2)}(\tau_1,\tau_2)M^{(2)}(\tau_3,\tau_4)] \tag{19b}$$

etc. The $\langle\cdots\cdot\rangle$ in Eqs. (14)-(19) denotes a tetradic matrix element as defined by Eq. (7).

Equations (14) together with (15)-(19) enable us to derive closed REM for the N populations of the various levels (P_n) in terms of the tetradic NxN R matrix. Evaluation of the latter requires the calculation of the intramolecular dipole correlation functions $M^{(n)}$ (Eq. (18)) (or $K^{(n)}$ (Eq. (19)), n=2,4,... which provide us with the complete molecular information needed for the description of all MMP whenever the experimental observables are connected with populations only.

IV. Expansion of the REM - the derivation of simple rate equations

We shall now utilize the formalism of Section III to derive explicit expression for the relaxation operator $\langle R\rangle$. To that purpose we make use of the property [10]

$$\sum_n \sqrt{d_n/d_m}\langle R(\tau)\rangle_{nn,mm} = 0 \quad , \tag{20}$$

which is a direct consequence of the conservation of probability, to rewrite Eq. (14) (to fourth order in ε) in the form.

$$\frac{dP_n}{dt} = \varepsilon^2 \sum_{m=n\pm1} \int_0^t d\tau \langle R^{(2)}(t-\tau)\rangle_{nn,mm}$$

$$[P_m(\tau)\sqrt{d_n/d_m} - P_n(\tau)\sqrt{d_m/d_n}] \qquad (21)$$

$$+ \varepsilon^4 \sum_{\substack{m=n\pm2 \\ n\pm1}} \int_0^t d\tau \langle R^{(4)}(t-\tau)\rangle_{nn,mm}$$

$$[P_m(\tau)\sqrt{d_n/d_m} - P_n(\tau)\sqrt{d_m/d_n}] \ ,$$

where

$$\langle R^{(2)}(t-\tau)\rangle_{bb,aa} = (d_a d_b)^{-1/2} \langle \mu_{ab}(t-\tau)\mu_{ba}(0)\rangle + \text{c.c.} \qquad (22a)$$

$$\langle R^{(4)}(t-\tau)\rangle_{cc,aa} = (d_a d_c)^{-1/2} \int_0^{t-\tau} d\tau_1 \int_0^{\tau_1} d\tau_2 \, K^{(4)}_{cba}(t-\tau,\tau_1,\tau_2,0) + \text{c.c.} \qquad (22b)$$

$$K^{(4)}_{cba} = I + II + III \qquad (23)$$

$$I = \langle \mu_{ab}(0)\mu_{bc}(t-\tau)\mu_{cb}(\tau_1)\mu_{ba}(\tau_2)\rangle$$

$$- \frac{1}{d_b} \langle \mu_{bc}(t-\tau)\mu_{cb}(\tau_1)\rangle \langle \mu_{ab}(0)\mu_{ba}(\tau_2)\rangle \ ,$$

$$II = \langle \mu_{ab}(0)\mu_{bc}(\tau_1)\mu_{cb}(t-\tau)\mu_{ba}(\tau_2)\rangle$$

$$- \frac{1}{d_b} \langle \mu_{bc}(\tau_1)\mu_{cb}(t-\tau)\rangle \langle \mu_{ab}(0)\mu_{ba}(\tau_2)\rangle \ ,$$

$$III = \langle \mu_{ab}(0)\mu_{bc}(\tau_2)\mu_{cb}(t-\tau)\mu_{ba}(\tau_1)\rangle \ ,$$

and where we consider only $c=a\pm2$ (the $a\pm1$ terms are similar), i.e.

$$a=n, \quad b=n\pm1, \quad c=n\pm2 \ . \qquad (24)$$

The correlation functions $\langle\cdots\cdot\rangle$ are defined as the trace of the product of operators and

$$\mu_{ab}(\tau) = \exp(iH_0\tau)\mu_{ab}\exp(-iH_0\tau) \qquad (25)$$

$$= \sum_{\alpha\beta} |a\alpha\rangle \mu^{\alpha\beta}_{ab} \langle b\beta| \exp(i\omega_{\alpha\beta}\tau)$$

In Fig.3 we have a diagrammatic representation of $\langle R^{(4)}\rangle$. We note that there are six pathways leading from $|aa\rangle\rangle$ to $|cc\rangle\rangle$ in fourth order. Four of them (I , II and their c.c.) are passing via $|bb\rangle\rangle$ and the other two (III and its c.c.) are passing via $|ac\rangle\rangle$ or $|ca\rangle\rangle$. These two types of pathways are often called incoherent and coherent pathways, respectively. For the sub-

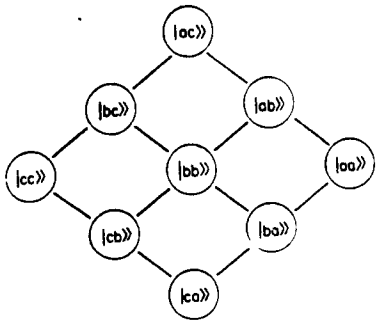

Fig.3 Diagrammatic representation of the Liouville space terms contributing to $R^{(4)}$ showing the six pathways to go from |aa>> to |cc>> in fourth order.

sequent manipulations we shall now introduce the integrated Rabi frequency for the ab transition, i.e.

$$\bar{\Omega}_{ab}^2 = \langle R^{(2)}_{aa,bb}(0)\rangle = 2\varepsilon^2 \sum_{\alpha\beta} |\mu_{ab}^{\alpha\beta}|^2/\sqrt{d_a d_b} \quad , \tag{26}$$

and the dimensionless correlation function

$$\tilde{I}_{ab}(\tau) = \langle \mu_{ab}(\tau)\mu_{ba}(0)\rangle / \langle \mu_{ab}(0)\mu_{ba}(0)\rangle \quad , \tag{27}$$

so that we have

$$R^{(2)}_{bb,aa}(t-\tau) = \bar{\Omega}_{ab}^2 \ \mathrm{Re}\ \tilde{I}_{ab}(t-\tau) \equiv \bar{\Omega}_{ab}^2 \ I(t-\tau) \tag{28}$$

and I(0)=1. Equations (21)-(24) express P_n in terms of the hierarchy of intramolecular correlation functions $\langle\mu\mu\rangle$, $\langle\mu\mu\mu\mu\rangle$ etc. We shall now make use of the complexity of our system to further simplify the REM and reduce the amount of relevant molecular information. This will be done in two stages.

(i) The random-phase approximation

When each level contains many states and the various μ's have arbitrary phase we expect that

$$\sum_{\alpha\beta\beta'\gamma} \mu_{ab}^{\alpha\beta}(\tau_1)\mu_{bc}^{\beta\gamma}(\tau_2)\mu_{cb}^{\gamma\beta'}(\tau_3)\mu_{ba}^{\beta'\alpha}(\tau_4) \tag{29}$$

$$\simeq \sum_{\alpha\beta\gamma} \mu_{ab}^{\alpha\beta}(\tau_1)\mu_{bc}^{\beta\gamma}(\tau_2)\mu_{cb}^{\gamma\beta}(\tau_3)\mu_{ba}^{\beta\alpha}(\tau_4) \ ,$$

i.e. only the terms with $\beta=\beta'$ will contribute whereas the sum over $\beta'\neq\beta$ will average to zero. This is a form of the statistical random phase approximation. We further assume that the ab and bc transitions are uncorrelated so that Eq. (29) may be further factorized resulting in

$$\langle \mu_{ab}(\tau_1)\mu_{bc}(\tau_2)\mu_{cb}(\tau_3)\mu_{ba}(\tau_4)\rangle \tag{30}$$

$$\simeq \frac{1}{d_b}\langle \mu_{ab}(\tau_1)\mu_{ba}(\tau_4)\rangle\langle \mu_{bc}(\tau_2)\mu_{cb}(\tau_3)\rangle \ .$$

This implies that in the evaluation of $K^{(4)}_{cba}$ we have

$$\mathrm{I} = \mathrm{II} = 0 \ , \tag{31}$$

so that

$$\langle R^{(4)}_{cc,aa}(t-\tau)\rangle = \bar{\Omega}^2_{ab}\,\bar{\Omega}^2_{bc}\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \tilde{I}_{cb}(t-\tau-\tau_2)\tilde{I}_{ba}(\tau_1) \quad . \tag{32}$$

(ii) Separation of time scales - the Markovian limit

Suppose we have the desirable situation whereby $P_n(\tau)$ is changing on a time scale much slower than that of $\langle R(t-\tau)\rangle$. (This means that $P_n(\tau)$ consists of a complete set of slow variables) [10,11]. In this case the Markovian limit holds whereby on a coarse grained time scale ($\tau > \tau_c$) we may safely assume that $\langle R(t-\tau)\rangle$ acts as a δ-function inside the integrations (Eq. (21)) so that it may be factored out and we get the simple rate equations

$$\frac{dP_n}{dt} = \sum_{m=n\pm1} W^{(2)}_{nm}(P_m\sqrt{d_n/d_m} - P_n\sqrt{d_m/d_n}) + \sum_{\substack{m=n\pm2 \\ n\pm1}} W^{(4)}_{nm}(P_m\sqrt{d_n/d_m} - P_n\sqrt{d_m/d_n}) \quad , \tag{33}$$

where

$$W^{(k)} = \int_0^\infty d\tau \langle R^{(k)}(\tau)\rangle \quad . \tag{34}$$

Using Eqs. (22) and (34) we have

$$W^{(2)}_{nm} = \int_0^\infty d\tau \langle R^{(2)}(\tau)\rangle_{nn,mm} \equiv \bar{\Omega}^2_{nm}\,\tau_c \quad , \tag{35}$$

where τ_c is the dipole correlation time (typical time scale of $I_{nm}(\tau)$), i.e.

$$\tau_c \equiv \int_0^\infty d\tau\, I_{nm}(\tau) \quad . \tag{36}$$

Regarding $W^{(4)}$ we have utilizing Eqs. (32) and (34)

$$W^{(4)}_{ca} = \bar{\Omega}^2_{ab}\,\bar{\Omega}^2_{bc}\int_0^\infty d\tau \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2\, \tilde{I}_{cb}(\tau-\tau_2)\tilde{I}_{ba}(\tau_1) + \text{c.c.} \tag{37}$$

It is clear that the only contributions to the integral (37) come from the region $0<\tau,\tau_1,\tau_2 \lesssim \tau_c$, since otherwise the integrand vanishes. We thus have

$$W^{(4)}_{ca} \gtrsim \bar{\Omega}^2_{ab}\,\bar{\Omega}^2_{bc}\,\tau_c^3 \quad . \tag{38}$$

Similar arguments will hold also for the higher order correlation functions (34) so that we can write

$$W^{(2k)} \tilde{=} W^{(2)}(\bar{\Omega}\tau_c)^{2k-2} \qquad k=2,3,\ldots \tag{39}$$

Making use of the estimates (35) and (39) we may now state the condition for the applicability of the Markovian limit as follows

$$\eta \equiv \bar{\Omega}\tau_c \ll 1 \quad . \tag{40a}$$

When Eq. (40) holds the following things happen (i) the time scale of variation of $P(\tau)$ is $(\bar{\Omega}\tau_c)^{-1}$ which will be $\gg\tau_c$. This justifies replacing $\langle R\rangle$ by

W (separation of time scales). (ji) All the higher order rate constants will become much smaller than $W^{(2)}$, i.e.

$$W^{(2k)}/W^{(2)} = \eta^{2k-2} << 1 \ , \tag{40b}$$

so that we may ignore them and retain $W^{(2)}$ only in Eq. (33). Finally we note that if we assume

$$\tilde{I}_{nm}(\tau) = \exp(-i\bar{\omega}_{nm}\tau - \Gamma_{nm}\tau) \ , \tag{41}$$

then

$$\tau_c = \mathrm{Re}\int_0^\infty d\tau\, \tilde{I}_{nm}(\tau) = \frac{\Gamma_{nm}}{\bar{\omega}_{nm}^2+\Gamma_{nm}^2} \tag{42}$$

and

$$W_{nm}^{(2)} = \frac{\bar{\Omega}_{nm}^2\,\Gamma_{nm}}{\bar{\omega}_{nm}^2+\Gamma_{nm}^2} \ . \tag{43}$$

In concluding this section we note that we have demonstrated here how, when rate equations apply, the relevant molecular information necessary for the description of MMP reduces essentially to four numbers per transition: an integrated Rabi frequency $\bar{\Omega}$, a dephasing rate Γ, a detuning $\bar{\omega}$ and the ratio of statistical weights d_n/d_m.

V. REM for populations and coherences - derivation of generalized Bloch equations

In Sections III and IV 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.

We shall now construct and analyze a different set of REM for MMP by the addition of more variables corresponding to coherences(i.e. time derivatives of the population variables). This is done due to the following reasons:

(1) It is clear that at the early stages of the molecular driving (Region I) the random phase and separation of time scales assumptions made in the derivation of the rate equations do not hold and we should in fact solve the exact Schrödinger equation with few states and coherent driving. Although we can inprinciple retain the populations as our only variables and expand the evolution operator <R> in higher powers in the field, it is much easier 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. Thus the explicit inclusion of coherences as variables in Region I results in a considerable simplification of the description in this region.

(2) In spectroscopic studies other than multiphoton excitations (e.g. ordinary line shapes [14], coherent transients [15] and resonance fluorescence [16,4]), 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) [14]. In the present REM for the populations, the dephasing rates are "buried" inside the kernel <R>. 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.

(3) 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 (33) which will demonstrate how the explicit inclusion of coherence variables becomes redundant in this case.

The construction of the coherence variables is done by considering the cummutators of the population variables A_{nn} (Eq. (11)) with H' [9]. The k quantum coherence A_{nm} where $|n-m|=k$ is defined as

$$A_{nm} = \frac{1}{\gamma_{nm}} \sum_{\alpha\beta} |n\alpha\rangle \, \nu_{nm}^{\alpha\beta} \, \langle m\beta| \qquad (44)$$

$$|n-m|=k$$

where (taking m>n)

$$\nu_{nm}^{\alpha\beta} = \sum_{\substack{\gamma\delta\cdots \\ \beta'}} \mu_{n,n+1}^{\alpha\gamma} \, \mu_{n+1,n+2}^{\gamma\delta} \cdots \qquad \mu_{m-1,m}^{\beta'\beta} \, , \qquad (45)$$

and

$$\gamma_{nm}^2 = \sum_{\alpha,\beta} |\nu_{nm}^{\alpha\beta}|^2 \, . \qquad (46)$$

(for k=1 we take $\nu=\mu$). The number of coherence operators to be included in our REM will be determined for our convenience and we may stop at any k_{max} ($k=1,2,\ldots,k_{max}$). Using the set of relevant operators (11) and (44) we may now evaluate the REM making use of the formulation of Section II. This was done in detail in Ref. 9 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 [9]

$$\frac{dP_n}{dt} = \frac{-i\bar{\Omega}_{n,n+1}}{\sqrt{2}} (\sigma'_{n+1,n} - \sigma'_{n,n+1}) - \frac{i\bar{\Omega}_{n,n-1}}{\sqrt{2}} (\sigma'_{n-1,n} - \sigma'_{n,n-1}), \qquad (47a)$$

$$\frac{d\sigma'_{n,n+1}}{dt} = [-i\bar{\omega}_{n,n+1} - \Gamma_{n,n+1}]\sigma'_{n,n+1} - i\bar{\Omega}_{n,n+1}(P_{n+1}\sqrt{d_n/2d_{n+1}} - P_n\sqrt{d_{n+1}/2d_n})$$
$$+ \frac{i\bar{\Omega}_{n+1,n+2}}{\sqrt{2}} \sigma'_{n,n+2} - \frac{i\bar{\Omega}_{n,n-1}}{\sqrt{2}} \sigma'_{n-1,n+1} \, , \qquad (47b)$$

$$\frac{d\sigma'_{nm}}{dt} = [-i\bar{\omega}_{nm} - \Gamma_{nm}]\sigma'_{nm} + \frac{i\bar{\Omega}_{m,m+1}}{\sqrt{2}} \sigma'_{n,m+1} \qquad (47c)$$
$$+ i\bar{\Omega}_{m,m-1}\sqrt{d_m/2d_{m-1}} \, \sigma'_{n,m-1}$$
$$- i\bar{\Omega}_{n,n+1}\sqrt{d_n/2d_{n+1}} \, \sigma'_{n+1,m} - i\bar{\Omega}_{n,n-1} \, \sigma'_{n-1,m}/\sqrt{2} \quad (m>n+1) \, .$$

(In (47c) we have taken m>n+1. The REM for σ'_{nm}(m<n-1) and for $\sigma'_{n+1,n}$ are simply the complex conjugates of (47c) and (47b)). Here

$$\sigma'_{nm}=(d_n\, d_{n+1}^2\, d_{n+2}^2 \cdots d_{m-1}^2\, d_m)^{1/4}(A_{nm},\rho(t)) \tag{48}$$

(The first factor in Eq. (48) is the statistical weight of the nm coherence (the number of possible pathways to go from n to m). The following main assumptions were made [9] in the derivation of Eqs. (47).

(1) The random phase approximation

Four time dipole correlation functions which appear in $\langle\tilde{R}\rangle$ (Eq. (9)) were factorized as was done in Eq. (30).

(2) Separation of time scales - the Markovian assumption

The correlation functions $\tilde{I}_{nm}(\tau)$ are expected to exhibit a complicated behaviour at short times τ_c ($\tau_c \sim$ inverse of typical molecular frequencies) but to reduce to the simple exponential form (Eq. (41)) asymptotically for long times. This behaviour is typical for dipole correlation functions as calculated for other solvable model systems (impurities in solids [17], pressure broadening [18] and stochastic models of line shapes [14]). If our variables in the REM change on a time scale much slower than τ_c we may (on a coarse-grained time scale $t>\tau_c$) replace $\tilde{I}_{nm}$ by its asymptotic form (Eq. (41)). $\bar{\omega}_{nm}$ and Γ_{nm} are defined in terms of the asymptotic behaviour of the logarithmic derivative of $\tilde{I}_{nm}(t)$, i.e.

$$-i\bar{\omega}_{nm} - \Gamma_{nm} \equiv \lim_{t\to\infty} \frac{1}{\tilde{I}_{nm}} \frac{d\tilde{I}_{nm}}{dt} \,. \tag{49}$$

When the dephasing rates Γ_{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 (47)), 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 (Eqs. (33)). If we consider only single quantum coherences (i.e. set $\sigma'_{nm}=0$ for $|n-m|>1$) we have

$$\sigma'_{n,n+1} = \frac{-i\bar{\Omega}_{n,n+1}}{\sqrt{2}(i\bar{\omega}_{n,n+1}+\Gamma_{n,n+1})} \cdot \tag{50}$$

$$\cdot\, (P_{n+1}\sqrt{d_n/d}_{n+1} - P_n\sqrt{d_{n+1}/d}_n) \,,$$

which when substituted back into (47a) results in Eq. (33) where $W^{(2)}$ is given by Eq. (43) and $W^{(4)}=0$. Thus we have here an alternative derivation of the simple rate equations (33).

The present derivation of (33) provides us with a new insight regarding the significance of the simple rate equations. As is clearly seen from (47), 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 Γ_{nm} which tend to destroy them. When

$$\eta \equiv \bar{\Omega}_{nm}\tau_c = \frac{\bar{\Omega}_{nm}\,\Gamma_{nm}}{\bar{\omega}_{nm}^2+\Gamma_{nm}^2} \ll 1 \,, \tag{51}$$

(weak driving) we may solve for the steady state of the k quantum coherences perturbatively resulting in $\sigma'_{n,n+k}=O(n^k)$ and the contribution of the k quantum coherences to the rate equation will be $O(n^{2k})$. We recall that in the previous derivation of the simple rate equations (Sec. IV) we had $W^{(2k)}=O(n^{2k})$. It is thus obvious that the k quantum coherences play here the same role of $W^{(2k)}$ in the previous derivation. The fact that $W^{(2k)}$ k>1 become irrelevant in the Markovian limit (Eq. (40)) is thus a manifestation of the fact that the steady state values of the higher order coherences $\sigma'_{n,n+k}(k>1)$ are negligibly small in this case so that the MMP are insensitive to the detailed dynamics of the multiquantum coherences.

VI. Discussion

We shall now summarize our main results and discuss their physical significance.

(i) The systematic reduction scheme

We have constructed an appropriate set of molecular operators (Eqs. (11) and (44)) relevant for the description of MMP and making use of the Zwanzig-Mori projection operator formalism we were able to derive REM for their time evolution (Eqs. (33) or (47)). The relevant molecular information necessary as an input to our REM is expressed in terms of an infinite hierarchy of n-time dipole correlation functions $M^{(n)}$ (Eqs. (18),(19)).

(ii) The Bloch versus rate equations

We have examined two alternative choices of relevant molecular operators. The first (Secs. III and IV) includes population variables only and leads in the Markovian limit to simple rate equations. The second choice (Sec. V) includes also coherence variables and leads in the Markovian limit to Bloch equations. We should bear in mind that the Markovian limit actually means separation of time scales between the relevant (P) and the other (Q) variables, and it has a different meaning when we change the definition of P. Thus invoking the Markov assumption in both equations is not equivalent and therefore the resulting REM (Eqs. (33) and (47)) are not the same. Only when we further assume $n<<1$ (fast dephasing), then the Bloch equations (47) reduce to the simple rate equation (33). We have thus established two routes for the derivation of simple rate equations. The first is direct using the COP equations and the second is via the Bloch equations, making use of the POP formalism. The second method gives us a deeper insight on the dynamical meaning of the rate equations. The first derivation is however less restrictive. As we are not considering explicitly the multiquantum coherences we do not have to invoke unnecessary assumptions regarding their time evolution. This is demonstrated in the fact that in order to get the Bloch equations we had to assume that $\Gamma_{nm}(t)$ exhibits an exponential behaviour (Eq. (49)) whereas in the first derivation all we had to assume was that $\Gamma_{nm}(t)$ decays fast (short τ_c) regardless of its exact functional form.

(iii) The reduction of molecular information

When the simple rate equations (33) hold, there is an enormous reduction in the amount of molecular information necessary for an adequate description of MMP. Not only that all higher order correlation functions become insignificant (40b), but even the details of the two time correlation functions $\Gamma_{nm}(t)$ become irrelevant and all we need is their time integral (Eq. (36)). The molecular quantities that enter the rate equations are the following four numbers per consecutive transition: (i) $\bar{\Omega}_{nm}$, the integrated dipole for the

nm transition times the field amplitude; (ii) Γ_{nm}, inverse correlation time (i.e. a dephasing rate); (iii) a detuning frequency ω_{nm}, and (iv) ratios of statistical weights of the levels d_n/d_m.

The significance of $\bar{\Omega}_{nm}$ as defined in (26) lies in the reasonable assumption [9] 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 arises from an approximate oscillator strength sum rule [9]. Regarding the dephasing rates Γ_{nm} it is clear from their definition (49) that they are associated with the energetic spread of the states within the n and m molecular levels. (This may be verified using simple models) [9]. The ratio d_n/d_m enters as a detailed balance relation: (the rate of m→n)/(the rate of n→m) equals d_n/d_m. The Bloch equations contain the same types of parameters but there are more of them (one dephasing rate for each multiquantum coherence).

It is clear that during the lower stages of the molecular excitation process (region I) we have actually to solve the entire Liouville equation (coherent driving). The Bloch equations then provide the adequate description. In the absence of reduction (each level $|n\alpha\rangle$ contains only one state) then $I_{nm}(t)=\exp(-i\bar{\omega}_{nm}t)$ and there is no dephasing $\Gamma_{nm}=0$ (Eq. (49)). The Bloch equations are then equivalent to the complete Liouville equation. As the excitation builds up, the dephasing rates increase and in the quasicontinuum we expect simple rate equations to hold. The condition $\eta=\bar{\Omega}\tau_c<<1$ is expected to be met typically after the absorption of a few infrared quanta. Since even for the strongest laser fields used in MMP [6,7] we have $\bar{\Omega}<10cm^{-1}$ whereas the spread of molecular states τ_c^{-1} is expected to be around $100cm^{-1}$ quite early [1].

(iv) The REM as a starting point for simple models

In the construction of the REM we have assumed for the sake of formal convenience that we know the exact molecular eigenstates $|n\alpha\rangle$. We may enjoy this assumption only while remaining in the formal stage since the true molecular eigenstates are not known even for a single triatomic molecule. This, however, should not prevent us from using the REM, on the contrary. The REM are a convenient starting point for molecular calculations which should be focused on evaluating the necessary dipole correlation functions in some approximate manner. These correlation functions are a property of the isolated molecule (without the laser field) and when plugged into the REM will result in the entire multiphoton dynamics. A reasonable way to proceed is to use some of the classical or semiclassical methods which are well established in molecular dynamics calculations [19], for the evaluation of the necessary correlation functions. This could be much easier and more appropriate than the evaluation of the exact molecular eigenstates.

(v) Intramolecular vibrational redistribution and laser-chemistry

The way we chose our variables (Eqs. (11) and (44)) is convenient for studying the total energy absorbed by the molecule via MMP. The intramolecular vibrational redistribution (IVR) processes are hidden inside the dephasing rates Γ_{nm}. As a demonstration we may think of a situation where we have a zero order molecular basis set (say the harmonic basis) in which in each level there is only one state (a "doorway state") which carries oscillator strength and is coupled radiatively to the adjacent levels. This state is further coupled by intramolecular coupling to the rest of the molecular states within the same level so that it undergoes irreversible decay with rate Γ_n corresponding to intramolecular vibrational redistribution (IVR). In this idealized case, $I_{nm}(t)$ will exhibit an exponential behaviour(Eq. (41)), where

$$\Gamma_{nm} = \frac{1}{2}(\Gamma_n + \Gamma_m)$$

is the mean IVR rate of the $|n\rangle$ and $|m\rangle$ doorway states. Thus the dephasing rate in this case is connected directly to the T_1 relaxation rates corresponding to IVR of the zero order molecular states. If we wish to consider more realistic models (it is clear that there is more than one doorway state in each level) and to follow explicitly the intramolecular vibrational redistribution processes, we have to use a more fine grained set of variables. This may be done by partitioning each level variable (Eq. (11)) into several variables corresponding to different distribution of the available energy among the various molecular degrees of freedom. This requires, of course, a more detailed knowledge of the intramolecular interactions. The possibilities of achieving laser-induced and laser-controlled chemical reactions are crucially dependent on the competition between the energy pumping and IVR and the present formalism is suitable for studying these processes in detail.

(vi) Direct measurements of intramolecular line broadening in polyatomic molecules

An important result of the present formalism is the incorporation of the relevant molecular information in the form of the intramolecular dephasing rates Γ_{nm} (Eq. (49)). It is clear that studies of MMP are not ideal for careful examination of Γ_{nm} since in each experiment we have many levels involved and the experimental observables are extremely averaged and far from being microscopic. In recent years novel spectroscopic techniques were developed, which enable us to measure Γ_{nm} directly [3,4]. This information may be used in our REM to predict the outcome of multiphoton experiments. Ordinary molecular

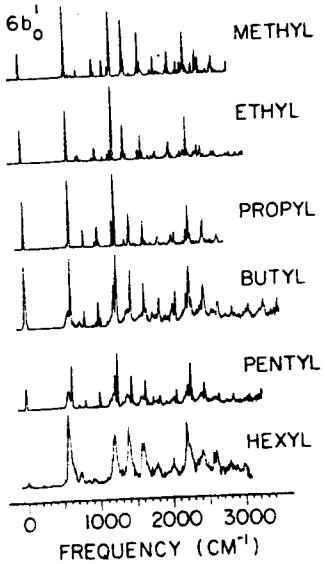

Fig.4

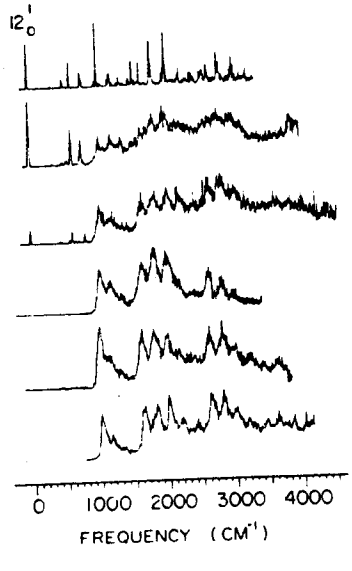

Fig.5

Figure 4. Fluorescence spectra from $6b_0^1$ excitation of n alkyl benzenes ($R\text{-}C_6H_5$ where $R=CH_3,\ldots C_6H_{13}$) in a supersonic beam (Ref. 4b). The available vibrational energy is $530cm^{-1}$.

Figure 5. Fluorescence spectra from 12_0^1 excitation of the same molecules of Fig. 4 (Ref. 4b). The available vibrational energy is $930cm^{-1}$.

line shapes as measured in cells and at room temperature are usually inhomogeneously broadened due to rotational envelopes, sequence congestion (overlapping transitions), Doppler broadening etc. and do not yield any dynamical information regarding intramolecular processes. It is possible to overcome these difficulties by performing high resolution spectroscopy of cold molecules (1-2°K) in supersonic beams. This technique eliminates the inhomogeneous broadening and results in homogeneously broadened line shapes. A beautiful example of this type of spectroscopy is shown in Figs. 4 and 5 where we show the fluorescence spectra of a series of molecules consisting of a benzene ring with a hydrocarbon side chain (R-$C_6H_5$where R=CH_3 (methyl), C_2H_5 (ethyl) etc. up to C_6H_{13} (hexyl)), obtained in a supersonic beam [4]. The vibrations which show up in these spectra belong essentially to the benzene ring (since the electronic transition is of the π electrons of the ring) and are changing very little within this series of molecules. The side chain provides the low frequency vibrations necessary for IVR. This series is a very successful choice since we have a clear separation of the molecular modes into a "system" and "bath" where the former show in the spectra and the later induce relaxation. By moving along the series we are able to change the bath without affecting the system. The two figures differ by the excitation wavelength. In Fig. 4 the excitation is to the 6b mode and in Fig. 5 to the 12 mode and the amount of available vibrational energy is $\sim 530 cm^{-1}$ and $\sim 930 cm^{-1}$ respectively. We note how the spectra become more complicated with the increase in the size of the side chains (R) and with the available energy. A careful analysis of such spectra [4] gives us a direct measure of IVR and the resulting dephasing rates may be used as an input to our REM for MMP.

Acknowledgements

The support of The Robert A. Welch Foundation, the National Science Foundation and the Westinghouse Educational Foundation Grant of the Research Corporation is gratefully acknowledged.

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