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Restoration of coherence effects in high-power excitation of an intramolecular quasicontinuum

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Three theoretical models were advanced for the dynamics of molecular multiphoton excitation: (i) The zero-order optically active mode connected by intramolecular random anharmonic couplings to a background manifold. (ii) Molecular eigenstates coupled by random radiative transition dipole moments. (iii) The kinetic master equation approach. It is demonstrated that in the Markoffian limit, as long as the intramolecular vibrational relaxation width is small relative to the Rabi frequency, these three approaches are equivalent. In the case of high-field excitation, coherent quantum effects are exhibited even in a randomly coupled system. Resurrection of the quantum oscillations and coherent pumping can be exhibited in intense field excitation on the time scale of intramolecular vibrational relaxation.

Key words: Multiphoton excitation — Intramolecular dynamics — Coherence effects

1. Introduction

High-order multiphoton excitation (MPE) of intermediate and large molecules has been intensively investigated both experimentally and theoretically [1-3]. A central concept pertinent to the MPE of large molecules is the molecular quasicontinuum (QC) [4, 5]. Above a certain energetic threshold the density of the molecular (vibrational) states becomes exceedingly large [6]. The zero-order states are no longer adequate for the description of intramolecular dynamics and interlevel coupling has to be explicitly considered. An appropriate description of the extremely congested dense level structure can be provided in terms of the

nuclear molecular eigenstates (NMEs) [7–9]. Experimental information [5, 10] regarding the dependence of the photofragmentation yield on the laser pulse energy (fluence) provides overwhelming evidence that incoherent dynamics prevails for the MPE of the molecular QC, whereupon all phase memory effects are eroded.

Two distinct approaches were advanced for the description of incoherent MPE of large molecules. One approach [11–14] rests on the notion of intramolecular vibrational energy redistribution (IVR), where successive absorption and stimulated emission of single photons were assumed to take place. An alternative description rests on the idea that the radiative coupling between the molecular vibrational-rotational eigenstates in the QC are essentially random functions of the quantum numbers of the molecular eigenstates [15–17]. This random coupling model leads to erosion of coherence effects and results in a master equation for the evolution of the probability distribution for the number of photons absorbed, evading the issue of the IVR. The results of numerical simulations [17] demonstrate that random radiative coupling results in the total erosion of phase coherence effects. In this treatment, the Markoffian condition entered implicitly is

$$\tau_{\mathrm{IVR}}^{-1} \gg |\mu|\varepsilon/\hbar, \tag{1}$$

where τ_{IVR} is the time associated with the intramolecular vibrational energy redistribution and ε is the electric field amplitude associated with the infrared (IR) absorption within the optically active mode. At very intense radiation fields the Markoffian condition, Eq. (1), breaks down and novel physical features of MPE of the QC are expected to be exhibited.

In this paper we explore some of the features of the MPE of a molecular QC, which is driven by medium-intensity and high-intensity laser fields. Random coupling models are extremely useful for the description of intramolecular dynamics in general and in particular for the elucidation of molecular MPE mechanisms, which are induced by medium-intensity laser fields. In this context, two models will be considered: (i) The random radiative coupling model (RRCM) where random radiative coupling prevails between NMEs. (ii) The intramolecular random coupling model (RCM) with constant radiative coupling between zero-order states. The relation between the predictions of these two models will be established within the validity range of the Markoffian condition, Eq. (1). These results are isomorphous to the predictions based on the kinetic master equation. Next, we shall proceed to discuss the intramolecular dynamics within the QC at extremely intense radiation fields, which render the Markoffian condition, Eq. (1), inapplicable. Within this limit, coherent pumping of the QC will be exhibited and quantum oscillations will be resurrected.

2. The Markoffian limit

Figure 1 portrays complementary models for the description of the MPE in the QC. These are simplified model systems for the MPE process, which incorporate all the physically relevant ingredients for the problem at hand. We shall

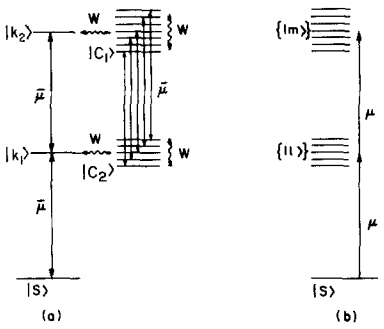

Fig. 1. A comparison between two molecular models. (a) Zero-order molecular levels with a single optically active mode and with unharmonic interactions. (b) Exact molecular eigenstates with diluted random radiative couplings

simplify the conventional molecular model for MPE by placing the low-lying sparse level energetic regime by a single discrete level $|s\rangle$ and the QC by the two sets of levels, $\{|l\rangle\}$ and $\{|m\rangle\}$ (Fig. 1). The radiative coupling elements are μ_{sl} and μ_{lm}. The Markoffian assumption, Eq. (1), allows us to disregard the systematic variations of μ_{sl} and μ_{lm} with the molecular indices l and m. Fig. 1a portrays the intramolecular and the radiative coupling scheme in the zero-order molecular basis set for the simple case where a single mode is optically active. Consider first the radiative coupling. At each level of excitation, vibrational states are selectively radiatively coupled to states located at the higher level. Thus, each zero-order state is radiatively coupled to a single higher zero-order state, which corresponds to a change of one quantum in the optically active mode with no change in the other modes. The radiative coupling matrix elements $\bar{\mu}\varepsilon$, appearing in Fig. 1a, correspond to the dipole matrix elements $\bar{\mu}$, which connect (zero-order) states corresponding to the optically active modes. The $\bar{\mu}$ terms are therefore weakly dependent of the level indices and can be taken as constant for each two consecutive manifolds. Next, the intramolecular coupling is considered. At each level of excitation, the zero-order molecular states are coupled by an intramolecular perturbation which corresponds to the anharmonicity and to off-diagonal kinetic energy contributions. This coupling W_{kc}, Fig. 1a, induces the intramolecular vibrational relaxation (that is intramolecular dephasing) between the state $|k\rangle$ of the zero-order active mode and $\{|c\rangle\}$ of the inactive mode. The characteristic time for the dephasing process is [15, 18]

$$\tau_{\mathrm{IVR}} = \hbar/\Gamma_k \tag{2}$$

where

$$\Gamma_k = 2\pi\langle W_{kc}^2\rangle\rho_k. \tag{3}$$

ρ_k is the density of states of the vibrational background at the energy level of k absorbed photons. $\langle W_{kc}^2\rangle$ is the averaged expression of W_{kc}^2. Γ_k and corresponds to the energetic width of the IR absorption line shape of a molecule pre-excited into the QC. The intramolecular coupling terms connecting zero-order states of the QC are taken as random functions of the zero-order level indices. An RCM for IVR was previously considered by several groups [19–21]. We can thus assert that this model, which rests on the zero-order molecular basis, Fig. 1a, involves random intramolecular coupling and approximately constant radiative coupling.

An alternative approach previously advanced by us [15–17] considers random radiative coupling between molecular eigenstates, resulting from diagonalization of the total molecular Hamiltonian, which includes the interaction $\{W_{kc}\}$. The manifolds $\{|l\rangle\}$ and $\{|m\rangle\}$, Fig. 1b, constitute linear combinations of the zero-order states appearing in Fig. 1a. The consequences of the transformation between the zero-order basis and the molecular eigenstates basis regarding the latter are: (a) The intramanifold intramolecular coupling W_{kc} no longer appears and only radiative coupling prevails. (b) The radiative coupling between adjacent manifolds of molecular eigenstates is non-selective. (c) The radiative dipole coupling terms can be taken as a random function of the level indices. (d) Conservation of integrated absorption intensities implies that level scrambling results in the "dilution" of the (constant) radiative coupling terms $\bar{\mu}$, which couple zero-order molecular eigenstates. It is expected that in general $\mu \ll \bar{\mu}$. To derive the relation between the radiative coupling terms in both representations one looks for the radiative coupling μ_{lm} in the NME representation. Since it is assumed that the only radiatively active zero-order set is $\{|k\rangle\}$, then

$$\mu_{lm} \equiv \langle l|\mu|m\rangle = (\alpha_l^k)^* \alpha_m^{k'} \bar{\mu}_{kk'} \tag{4}$$

where α_l^k is the amplitude of the contribution of the zero-order state $|k\rangle$ in the expansion of the NME $|l\rangle$. In order to evaluate the radiative width of the $|l\rangle \rightleftarrows |m\rangle$ transition, one should average the square of μ_{lm} over the statistical distribution. Since the values of $\{W_{kc}\}$ are considered to be random numbers, then the values of the coefficients $\{\alpha_l^k\}$ are also taken to be random functions of the level indices. Accordingly, the radiative coupling terms $\{\mu_{lm}\}$ of the NME basis are also random functions of the level indices. One then introduces the dilution factor for intramolecular coupling [16, 17]

$$D_k = \pi^2 \langle W_{kc}^2 \rangle \rho_k^2 = \pi \Gamma_k \rho_k / 2. \tag{5}$$

From Eqs. (4) and (5), we obtain the relation between the (properly averaged) second moment $\langle \mu^2 \rangle$ for the random radiative coupling in the molecular eigenstates basis and the value of $|\bar{\mu}|^2$ associated with an optically active mode in the zero-order molecular basis, which is given by

$$\langle \mu^2 \rangle \approx |\bar{\mu}|^2 / (\pi \Gamma \rho / 2). \tag{6}$$

Equation (6) establishes the relation between the variance of the diluted transition moments $\langle \mu^2 \rangle$ and the transition moments connecting the (zero-order) active modes.

To establish the relation between the RRCM (Fig. 1b) and the intramolecular RCM with the constant radiative coupling between zero-molecular states (Fig. 1a), some numerical computer simulations were performed. Each zero-order molecule manifold consisted of two equally spaced levels. The density of states was taken as $\rho = 1$. The zero-order transition moments, μ, were all taken to be constant, while $\{W_{kc}\}$ was chosen to be random (with $\langle W_{kc} \rangle = 0$), and Γ was determined from Eq. (3). $\langle \mu^2 \rangle$ was then calculated from Eq. (6). The diluted radiative coupling terms μ_{sl} and μ_{lm} were subsequently determined for the

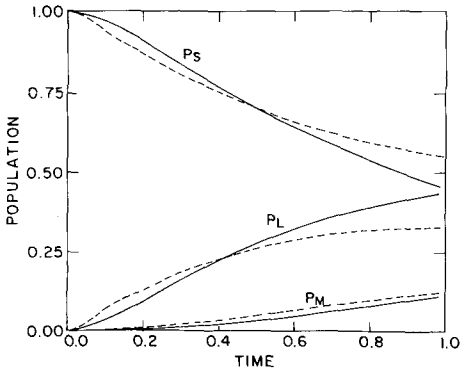

Fig. 2(a). Time evolution for the models described in Fig. 1. $\rho_s(t=0)=1$ in all cases. Each manifold consists of 70 levels with $\rho=1$. *Full line*: time evolution based on the coupling scheme from Fig. 1(a), $\mu=0.6\pi$ between all levels and W is taken to be Gaussian with $\langle W\rangle=0$ and $\langle W^2\rangle=3$. *Dashed line*: time evolution based on the coupling scheme from Fig. 1(b). μ is Gaussian with $\langle\mu\rangle=0$ and $\langle\mu^2\varepsilon^2\rangle=0.12$. $\Gamma=10\bar{\mu}\varepsilon$

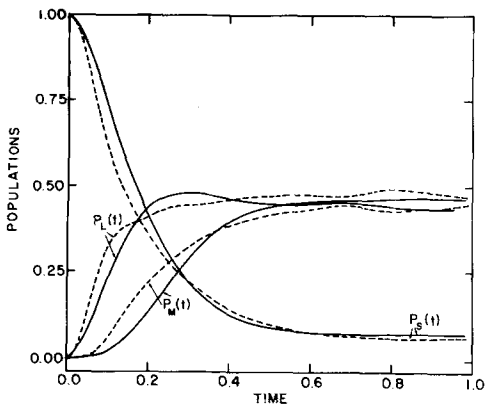

Fig. 2(b). Same as for Fig. 2(a). $\bar{\mu}\varepsilon=\sqrt{30}$, $\langle\mu^2\varepsilon^2\rangle=1.0$, $\Gamma=3.5\bar{\mu}\varepsilon$

radiative RCM taking $\langle\mu\rangle=O$ [17]. The relevant parameters were chosen so that $\Gamma>|\bar{\mu}|\varepsilon$, which is in accord with the Markoffian condition, Eq. (1).

Figure 2 confronts the time evolution for the two models calculated for different ratios of $\bar{\mu}\varepsilon/\Gamma$ ($\Gamma=10\,\bar{\mu}\varepsilon$ and $3.5\,\bar{\mu}\varepsilon$). From these results we infer that in the Markoffian limit, i.e. $\Gamma/\bar{\mu}\varepsilon\gg1$, the results for the RCM and RRCM models are practically identical. In Fig. 3, the model based on the intramolecular RCM is confronted with a kinetic solution resting on the assumption of the validity of the master equation for the populations of the energy "boxes" [15]. The numerical parameters are the same as for Fig. 2. We noticed that, since the energetic spread of the quasicontinuum manifold is final, there is a delay in the ground level population in both models, (i) and (ii). This final manifold incubation effect is exhibited in the non-exponential decay for the short times, when $t\ll\hbar\rho$, and the corresponding delay of the feeding of excited states. From agreement between the time evolution for the three models (Figs. 2 and 3), we conclude that:

(1) The dynamics of a system described by an intramolecular RCM with constant radiative coupling (Fig. 1a) results in a time evolution which is quite similar to the result obtained for the radiative RCM (Fig. 1b). The small difference between

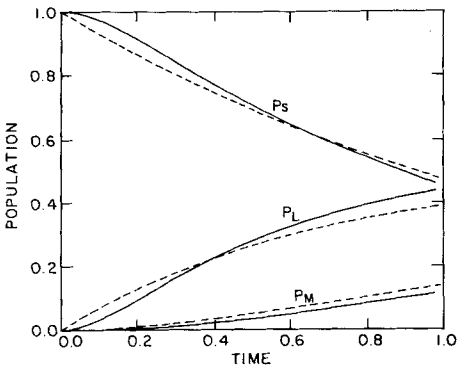

Fig. 3(a). Time evolution for the intramolecular RCM (*full line*) and for the kinetic model (*dashed line*). The numerical parameters are the same as for Fig. 2(a). $\Gamma = 10\bar{\mu}\varepsilon$

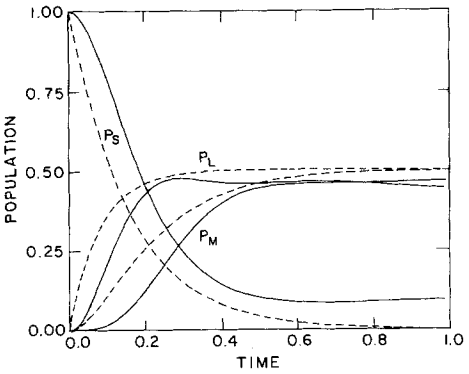

Fig. 3(b). Time evolution for the intramolecular RCM (*full line*) and for the kinetic model (*dashed line*). The numerical parameters are the same as for Fig. 2(b). $\Gamma = 3.5\bar{\mu}\varepsilon$

the two evolution pathways displayed in Fig. 2 results from the approximation involved in Eq. (5).

(2) The time evolution of a system, where random coupling prevails, is essentially determined by the lower moments of the distribution function of the relevant (radiative or intramolecular) coupling elements.

(3) The "coarse graining" argument utilized in the derivation of the dilution effect, Eq. (6), is justified.

(4) As long as the Markoffian condition $\Gamma > |\bar{\mu}|\varepsilon$ holds, it is expected that the three models (i), (ii) and (iii), are equivalent, yielding practically identical results for the time evolution of the system.

(5) The Markoffian condition, Eq. (1), essentially provides a necessary condition for the applicability of the RCM model (ii). In the numerical simulation a diluted Rabi frequency, $\langle\mu^2\rangle^{1/2}\varepsilon$, Eq. (6), was assigned to each intercontinuum transition in Fig. 1b. This procedure is valid as long as the intramolecular line widths exceeds the average radiative line width $2\pi\langle\mu^2\rangle\varepsilon^2\rho$ originating from the radiative coupling between the NMEs. The condition for the validity of model (ii), i.e.

$$2\pi\langle\mu^2\rangle\varepsilon^2\rho < \Gamma \tag{7}$$

results in

$$|\tilde{\mu}|\varepsilon < \Gamma/(2\pi)^{1/2}, \tag{8}$$

which is in accord with condition (1). Accordingly, for the intense fields, when condition (8) fails, model (ii) should not be utilized and model (i) has to be preferred.

(6) Numerical simulations for model (i) will be reliable provided that the radiative splitting $2|\tilde{\mu}|\varepsilon$ of the "dressed" molecular+radiation field states, together with the intramolecular full width 2Γ, do not exceed the energetic spread of the QC,

$$2|\tilde{\mu}|\varepsilon + 2\Gamma \leqslant N\rho^{-1} \tag{9}$$

where ρ is the density of the QC manifold. It is noted that condition (9) is supplementary to the condition $\Gamma \leq N\rho^{-1}$ previously discussed by us [17], which requires that the energetic spreads of the model QC manifolds should considerably exceed the uncertainty width of the levels.

(7) For very intense fields, when the Markoffian condition Eq. (1) and the technical condition Eq. (9) fails, both the intramolecular RCM and the RRCM models, as well as the kinetic model, fail to describe correctly the dynamics of the system.

It has been demonstrated [17] that both random radiative coupling between molecular eigenstates or, alternatively, random intramolecular coupling between zero-order states in the molecular QC is essential in eroding the effects of phase coherence in the MPE of a large molecule. The equivalence between the RCM (Fig. 1a) and the intramolecular RCM (Fig. 1b) inspires confidence in the validity of the random coupling approach [16, 17] for the description of collisionless MPE of large molecules. The present results demonstrate that the simple kinetic Pauli master equation is valid for the description of MPE of a molecular QC provided that three conditions are simultaneously satisfied:

(A) Rapid intramolecular dephasing, Eq. (1), is exhibited.
(B) Random coupling prevails.
(C) The Rabi frequency is sufficiently low to ensure the applicability of the Markoffian limit.

Several comments are now in order. First, our approach [15, 16] for MPE of a QC, which rests on the Markoffian and random coupling assumptions, differs from alternative theoretical approaches [12–14] which invoked just the Markoffian assumption, Eq. (1). The physical condition for rapid intramolecular dephasing, Eq. (1), provides a necessary, but not a sufficient, condition for the validity of the kinetic Pauli master equation for the MPE of a congested molecular level structure. Second, evidence has been provided for the applicability of a master equation which corresponds to a random strong intramolecular coupling situation. Third, it has been demonstrated that random coupling in collisionless MPE can be taken to involve either intramolecular or radiative interactions, depending on the choice of the molecular basis. As long as off-resonance intramolecular interactions between zero-order molecular modes are small, the choice of the molecular basis set (in terms of molecular eigenstates or at zero-order states) is merely a matter of convenience [21].

3. The breakdown of the Markoffian approximation

We have considered the Markoffian limit, where random coupling erodes all coherence effects. We shall now explore the other extreme situation of multiphoton excitation is extremely intense fields when the Markoffian limit is inapplicable. It is expected that for intense fields, when $|\bar{\mu}|\varepsilon > \Gamma$, coherent quantum effects will be exhibited even in the presence of random intramolecular coupling. In order to obtain a quantitative estimate for the laser flux required for the breakdown of the Markoffian condition, Eq. (1), let us take the typical transition moment in the low sparse energetic regime to be $|\bar{\mu}| \approx 0.1$ Debye. The Rabi frequency, $\Omega = |\bar{\mu}|\varepsilon$, induced by the laser flux Φ is given by

$$\Omega = |\bar{\mu}| \left(\frac{4\pi\Phi}{c}\right)^{1/2}, \tag{10}$$

where c is the light velocity. If the intramolecular width Γ is expressed in cm^{-1} units then the flux ϕ_c, resulting in $\Omega = \Gamma$, is given by

$$\Phi_c = 4.10^{11}[\Gamma(cm^{-1})]^2(W\,cm^{-2}). \tag{11}$$

A characteristic width inferred from the line broadening at high levels of vibrational excitation [22-24] is $\Gamma \simeq 3\text{-}10\,cm^{-1}$. We thus estimate $\phi_c \approx 4\times10^{12} - 4\times10^{13}\,W\,cm^{-1}$ for the onset of the breakdown of the Markoffian limit. When the QC is excited by very intense fields the effective up-pumping process within a specific mode can overcome the IVR process. Provided that $|\bar{\mu}|\varepsilon > \Gamma$, both models (i) and (ii) are inapplicable and a new approach is required. In order to provide some physical insight into the problem, the model system illustrated in Fig. 4 is considered. The two upper discrete levels are characterized by the decay widths Γ_2 and Γ_3, respectively, due to their coupling to the isoenergetic quasicontinua. These two quansicontinua are radiatively coupled between themselves. It is assumed that the level structures of these two QC manifolds are prediagonalized and that, in view of the random coupling effects which prevail in these energetic regions, all coherent effects are totally eroded. Therefore, the changes in these QC manifolds are determined by a kinetic master equation with rate constants Γ_{45} and Γ_{54} (Fig. 4). On the other hand, coherence effects do prevail in the excitation of the active mode, which should be described in terms of the complete density matrix for levels $|1\rangle$, $|2\rangle$ and $|3\rangle$. The equation of motion

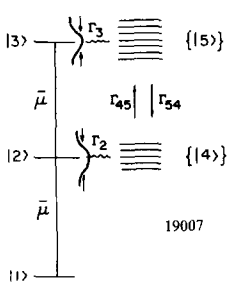

Fig. 4. A model for the intense-field excitation of the QC, which consists of: (1) a set of zero-order molecular levels as in Fig. 1(a) and characterized by the decay width $\{\Gamma_k\}$. (2) A set of quasicontinua which are radiatively coupled between themselves with the rate constants $\{\Gamma_{kl}\}$

for the nine elements of the three levels of the active mode and for the two diagonal elements of the QC are:

$$\dot{\rho}_{11} = -i\bar{\mu}\varepsilon\rho_{21} + i\bar{\mu}\varepsilon\rho_{12}$$

$$\dot{\rho}_{12} = -i\bar{\mu}\varepsilon\rho_{22} + i\bar{\mu}\varepsilon\rho_{11} + i\bar{\mu}\varepsilon\rho_{13} - \frac{\Gamma_2}{2}\rho_{12}$$

$$\dot{\rho}_{13} = -i\bar{\mu}\varepsilon\rho_{23} + i\bar{\mu}\varepsilon\rho_{12} - \frac{\Gamma_3}{2}\rho_{13}$$

$$\dot{\rho}_{21} = i\bar{\mu}\varepsilon\rho_{22} - i\bar{\mu}\varepsilon\rho_{11} - i\bar{\mu}\varepsilon\rho_{31} - \frac{\Gamma_2}{2}\rho_{21}$$

$$\dot{\rho}_{31} = i\bar{\mu}\varepsilon\rho_{32} - i\bar{\mu}\varepsilon\rho_{21} - \frac{\Gamma_3}{2}\rho_{31}$$

$$\dot{\rho}_{22} = -i\bar{\mu}\varepsilon\rho_{12} - i\bar{\mu}\varepsilon\rho_{32} + i\bar{\mu}\varepsilon\rho_{21} + i\bar{\mu}\varepsilon\rho_{23} - \Gamma_2\rho_{22}$$

$$\dot{\rho}_{33} = -i\bar{\mu}\varepsilon\rho_{23} + i\bar{\mu}\varepsilon\rho_{32} - \Gamma_3\rho_{33}$$

$$\dot{\rho}_{23} = -i\bar{\mu}\varepsilon\rho_{12} - i\bar{\mu}\varepsilon\rho_{33} + i\bar{\mu}\varepsilon\rho_{22} - \frac{\Gamma_2+\Gamma_3}{2}\rho_{23}$$

$$\dot{\rho}_{32} = i\bar{\mu}\varepsilon\rho_{31} + i\bar{\mu}\varepsilon\rho_{33} - i\bar{\mu}\varepsilon\rho_{22} - \frac{\Gamma_2+\Gamma_3}{2}\rho_{32}$$

$$\dot{\rho}_{44} = \Gamma_2\rho_{22} + \Gamma_{54}\rho_{55} - \Gamma_{45}\rho_{44}$$

$$\dot{\rho}_{55} = \Gamma_3\rho_{33} + \Gamma_{45}\rho_{44} - \Gamma_{54}\rho_{55}. \tag{12}$$

The intercontinua widths are Γ_{45} and Γ_{54}, corresponding to the kinetic rate constants which are obtained by kinetic assumptions [15, 25].

For weak fields ($|\bar{\mu}|\varepsilon < \Gamma$), the results of the numerical solution of Eq. (12) are identical with those obtained from models (i) and (ii), as well as from the kinetic model of Sect. 2. For the very strong field limit ($|\bar{\mu}|\varepsilon \gg \Gamma$), Eq. (12) has to be utilized to account for the evolution of the level populations. Figs. 5 and 6 show the time evolution of the population of the ground state for the cases $\bar{\mu}\varepsilon = 5\Gamma$ and $\bar{\mu}\varepsilon = 9.2$, respectively. An oscillatory pattern is exhibited, being characterized by the frequency $\sim 1.4\bar{\mu}\varepsilon$. These oscillations decay non-exponentially. This picture resembles the pattern of the optical free induction decay (OFID) of a molecular level which is coherently prepared by a C.W. laser beam [26]. It should be noted, however, that in the OFID an ensemble of molecules is considered, whereas in the present case an isolated molecule is driven by the intense field.

Since the levels of the active mode decay irreversibly into the corresponding QC, their dynamics can be analyzed independently. It is possible to represent the time evolution of the active mode by the effective Hamiltonian formalism [27]. The

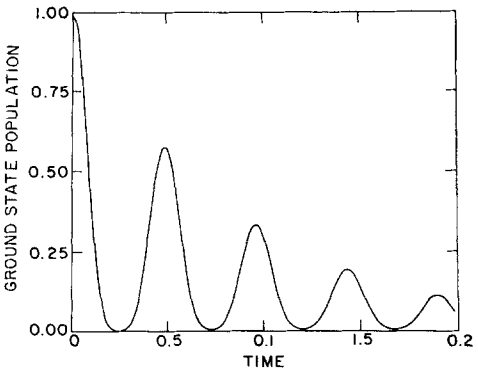

Fig. 5. Time evolution of the ground level population based on the coupling scheme of Fig. 4: $\bar{\mu}\varepsilon = 5\Gamma$

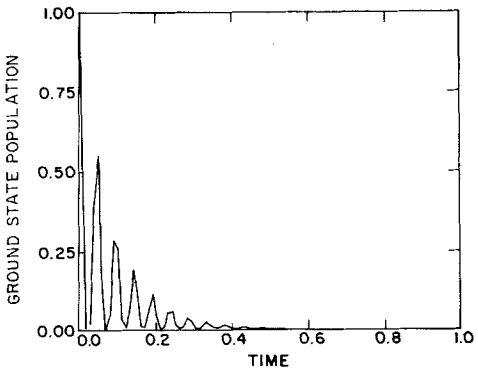

Fig. 6. The evolution of the ground level population based on the coupling scheme of Fig. 4: $\bar{\mu}\varepsilon = 9.2\Gamma$

time evolution is then determined by the roots of the effective Hamiltonian secular equation,

$$\begin{vmatrix} E - i\Gamma/2 & \bar{\mu}\varepsilon & 0 \\ \bar{\mu}\varepsilon & E - i\Gamma/2 & \bar{\mu}\varepsilon \\ 0 & \bar{\mu}\varepsilon & E \end{vmatrix} = 0 \tag{13}$$

The solutions of this cubic equation are discussed in Appendix A and are compared with the results of the numerical simulations. One limitation of the solution of Eq. (13) is that the populations of the QC are not explicitly considered. However, the population of the acive modes, including the ground state, obtained from the effective Hamiltonian, Eq. (13), and from the equations of motion, Eq. (12), should be identical.

Appendix A provides the solution of Eq. (13) for the population of the ground state in the strong field limit ($|\bar{\mu}|\varepsilon \gg \Gamma$). According to Eq. (A11) the fundamental oscillation frequency is $\sqrt{2}\,\bar{\mu}\varepsilon$, which cannot be resolved from the overtone of the $\sqrt{2}\bar{\mu}\varepsilon$ frequency. This analysis shows that the ground level population decays non-exponentially as a combination of three distinct exponentials with the time constants $2\Gamma^{-1}$, $(4/3)\Gamma^{-1}$ and $(8/5)^{-1}$. This analysis bears a close analogy to the case of the irreversible leakage from the uppermost level of the sparse energetic region into the QC under the extreme condition [28] $\Gamma \gg \mu\varepsilon$. On the basis of both

the analytical and the numerical results, we conclude that the quantum oscillations are expected to be exhibited on the time scale Γ^{-1}. At longer times, these oscillations are eroded by the IVR process.

4. Concluding remarks

From the present analysis several interesting conclusions emerge. First, the numerical simulations demonstrate that in the high fields, when the non-Markoffian limit applies, the kinetic master equation is inapplicable. Second, coherent quantum effects are exhibited in a randomly coupled system at high fields. Third, the resurrection of the quantum oscillation in high fields signals the limit where the Rabi frequency overcomes the IVR rate. Fourth, coherent pumping can be exhibited in an intense-field excitation on the time scale of intramolecular vibrational relaxation $\sim\Gamma^{-1}$. Fifth, this opens up the distinct possibility of photo-selective excitation of a single mode in the QC in intense fields. Sixth, the observation of such quantum oscillations in the excitation of the QC will provide new spectroscopic information on transition moments combining photoselective states. In order to realize photoselective excitation in high fields, the following condition is suggested,

$$\Gamma < \bar{\mu}\varepsilon < \gamma_c, \tag{14}$$

where γ_c denotes the reactive rate within a high-energy genuine intra-molecular continuum. The left-side inequality concerns the existence of quantum oscillations. The right-side inequality assures that the dominant decay rate will involve the reactive channel, which will dominate over the IVR process.

Appendix A: Solution of the three level secular equation

The determinant of Eq. (13) is expanded, giving

$$\lambda^3 + 2\lambda^2\gamma + \lambda(\gamma^2 + 2\bar{\mu}^2\varepsilon^2) + \gamma\bar{\mu}^2\varepsilon^2 = 0 \tag{A1}$$

where

$$E = -i\lambda; \qquad \gamma = \Gamma/2. \tag{A2}$$

The following notations for the cubic equation [29] will be used,

$$q = (2/3 - \alpha^2/9)\bar{\mu}^2\varepsilon^2 \tag{A3a}$$

$$r = (\alpha/6 + \alpha^3/27)\bar{\mu}^3\varepsilon^3 \tag{A3b}$$

where the ratio α is defined by

$$\alpha = \gamma/\bar{\mu}\varepsilon \tag{A4}$$

and the discriminant d is defined by

$$d = q^3 + r^2 = \bar{\mu}^6\varepsilon^6(8 - 13\alpha^2/4 + \alpha^4)/27. \tag{A5}$$

The following auxiliary terms are defined,

$$S_1 = (r + d^{1/2})^{1/3}$$
$$S_2 = (r - d^{1/2})^{1/3} \tag{A6}$$

$$\lambda_1 = (S_1 + S_2) - 2\alpha\bar{\mu}\varepsilon/3$$
$$\lambda_{2,3} = -1/2(S_1 + S_2) - 2\alpha\bar{\mu}\varepsilon/3 \pm i\sqrt{3}/2(S_1 - S_2). \tag{A7}$$

In the present case d is always positive (otherwise α will be complex). Consequently, there are always one real (decaying) term and two conjugate (oscillatory decaying) terms [29]. In the extremely strong field, $\alpha \ll 1$, the roots are given by

$$\lambda_1 \approx -\Gamma/4 \tag{A8}$$

$$\lambda_2 \approx -3\Gamma/8 \pm i\sqrt{2}\bar{\mu}\varepsilon. \tag{A9}$$

Then the ground level amplitude C_1 is

$$C_1 = A \exp(-\Gamma t/4) + \exp(-3\Gamma t/8)[B \exp(i\sqrt{2}\bar{\mu}\varepsilon t) + C \exp(-i\sqrt{2}\bar{\mu}\varepsilon t)] \tag{A10}$$

and the ground level population is

$$\begin{aligned}\rho_{11}(t) \equiv |C_1(t)|^2 = |A|^2 \exp(-\Gamma t/2) \\ + \exp(-3\Gamma t/4)\{|B|^2 + |C|^2 + 2\,\mathrm{Re}\,[BC^* \exp(i2\sqrt{2}\bar{\mu}\varepsilon t)]\} \\ + \exp(-5\Gamma t/8) 2\,\mathrm{Re}\,\{A^*[B \exp(i\sqrt{2}\bar{\mu}\varepsilon t) + C \exp(-i\sqrt{2}\bar{\mu}\varepsilon t)]\}.\end{aligned} \tag{A11}$$

Hence, ρ_{11} is a combination of decaying exponentials modulated by oscillatory terms. The oscillatory frequencies are $(2)^{1/2}\bar{\mu}\varepsilon$ and $2(2)^{1/2}\bar{\mu}\varepsilon$ and the exponential rates are $\Gamma/2$, $3\Gamma/4$ and $5\Gamma/8$.

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