

Random coupling models for intramolecular dynamics. II. Kinetic equations for collisionless multiphoton excitation of large molecules^{a)}

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(Received 28 February 1979; accepted 31 May 1979)

Multiphoton excitation and dissociation of large molecules under collisionless conditions is discussed in terms of an intercontinuum random coupling model. The mathematical approach described in a previous paper is used to obtain the general solution for a system of consecutively coupled discrete states, quasicontinuous manifolds, and continuous (dissociative) manifolds of molecular levels (eigenstates of the total molecular Hamiltonian), where the radiative coupling matrix elements are assumed to be given as a linear combination of smoothly varying and randomly varying (over level indices in the molecular manifolds) components. In the range of discrete molecular levels the time evolution is coherent and described in terms of the optical Bloch equation. In the quasicontinuous and continuous ranges the time evolution may be described in terms of Markoffian kinetic equations for the number of photons absorbed by the molecule, provided that the intramolecular vibrational relaxation widths associated with the optically active molecular modes is much larger than the Rabi frequency associated with the excitation of these modes. The kinetic evolution itself consists of direct multiphoton excitation processes (simultaneous transitions from the upper discrete levels to all higher energy molecular manifolds) resulting from the smooth component in the radiative coupling, and a consecutive excitation process described by the Pauli master equation with rates given by the golden rule expression. The interaction which enters into the golden rule expression is the *variance* in the radiative coupling. The direct excitation component contributes a negligible part of the overall excitation even if the random and smooth radiative coupling components are comparable. The resulting incoherent time evolution of the multiphoton excitation process is consistent with available experimental results. Coherent effects in the time evolution are expected for higher radiation field intensities, where the Rabi frequency becomes comparable to the intramolecular vibrational relaxation rate.

I. INTRODUCTION

The nature of collisionless multiphoton excitation and dissociation of polyatomic molecules in intense infrared (IR) radiation fields is a subject of much experimental and theoretical research.¹ The gross features of the process are best described in terms of three different energy regions (Fig. 1): At low vibrational energies (range I) the molecular levels are sparse and the excitation involves near resonance radiative interactions between individual levels (or groups of several levels), leading to a coherent multiphoton excitation. Range I processes are responsible for isotopic selectivity, coherent effects (multiphoton resonances, photon echoes, coherent wave propagation, etc.) and for the power dependence of the excitation process. At higher vibrational energies (range II) the excitation process consists of transitions between quasicontinuous manifolds of bound molecular vibrational-rotational states. Finally, above the first dissociation threshold, excitation occurs between manifolds of molecular levels which are coupled to dissociative continua. This is range III—the reactive regime. Experimental evidence²⁻⁵ has led workers to conclude that the excitation process in ranges II and III consists of incoherent consecutive absorption (and the reversible emission) steps with all phase memory lost and with rates proportional to the field intensity. This conclusion is based on the observation that when the

laser intensity is sufficiently high to overcome range I the multiphoton dissociation yield^{2,3} and also the delay time for observation of products^{4,5} are determined by the energy, rather than the power, of the pulse. Indeed, photodissociation of some molecular ions trapped in cyclotron trajectories under collisionless conditions was observed⁵ during a prolonged (~ 1 sec) irradiation with low intensity (~ 1 W/cm²) IR light under collisionless conditions, provided that the molecule enters the irradiation zone being (by virtue of its thermal energy) in range II. In addition experimental results for IR multiphoton dissociation of SF₆ was shown^{1(c),6} to be consistent with a Pauli master equation with rates constructed using simple statistical molecular models. One should

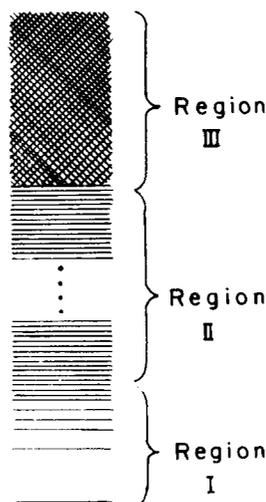


FIG. 1. A schematic representation of the discrete, quasicontinuous and dissociation regions of the energy level diagrams of a large molecule.

^{a)}Supported in part by the United States-Israel Binational Science Foundation, Jerusalem, Israel and by the Commission for Basic Research of the Israel Academy of Sciences.

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keep in mind however, that the number of observed parameters (i. e., dissociation probability and mean number of photon absorbed) is too small to permit a reliable distinction between differently constructed kinetic schemes.

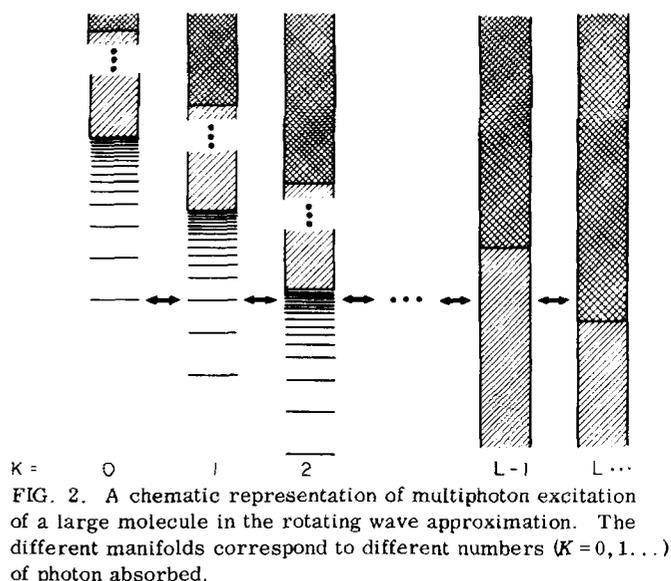
The coherent excitation process in range I is by now, at least in principle, well understood in terms of, e. g., the n level optical Bloch equation. No simplification schemes beyond the rotating wave approximation (RWA) are generally valid (or necessary) in this region. A rapid "decay" of the upper level of range I into the quasicontinuous range II may lead in principle to an incoherent consecutive evolution in range I.⁷ However conditions for this behavior are generally not satisfied (see Sec. IV).

Several theories have been advanced for the range II and range III processes; concerning in particular the erasure of coherence effects and the structure of the resulting kinetic equations. These theories may be divided into two groups:

(a) Yablonovitch,⁸ Hodgkinson and Briggs,⁹ Cantrell *et al.*,^{10(a)} and Goodman and Stone^{10(b)} have based their descriptions on the zero order (harmonic or bond) molecular modes dividing them into a "relevant" group consisting of the optically active modes and a "bath" consisting of all the other modes. These two subsystems are coupled by the molecular anharmonic interaction. In this picture the intramolecular bath provides the dephasing source, causing the erosion of phase coherence in the relevant system, thus leading to a Markoffian master equation for the evolution within the relevant subspace. The variables entering this master equation are the *populations of the relevant modes*.

While this approach may be quite useful for describing the time evolution of any particularly interesting molecular mode, it suffers from a few drawbacks in the present context: First, the role of the intramolecular bath in causing dephasing of the interesting mode is somewhat obscure. In particular when the bath is not or is only weakly excited, it can induce dephasing only via population relaxation. In this case phase coherence persists on the relevant time scale and the Bloch equation cannot be reduced to the Pauli master equation on this time scale. Secondly, the separation of zero order molecular modes into the optically active relevant modes and the other nonactive modes is based on a picture, true for low vibrational energy, of strict optical selection rules. While recent experimental data^{11,12} indicate that such selection rules hold to a large extent even in the higher levels of range II, giving rise to a (broadened) absorption resonance at the expected ν_3 mode absorption in highly excited SF_6 , it is reasonable to expect a growing background absorption resulting from the breakdown of the low energy optical selection rules. Such background absorption has been observed in the overtone vibrational spectrum of benzene¹³ and it is expected to be stronger in nonhydrogenic molecules like SF_6 .

Finally within the context of molecular multiphoton dissociation, the interesting variable is not the popula-



tion of a particular mode (or modes) but rather, the total energy content of the molecule. Thus, the total bath energy has to be taken as an additional relevant variable which complicates the theoretical treatment. Furthermore, it is not clear whether the time evolution of the intramolecular bath can be described in terms of a single parameter (e. g., temperature).

(b) Mukamel,¹⁴ Jortner and Schek,¹⁵ and Carmeli and Nitzan¹⁶ have advanced theories in which the total energy contents of the molecule, expressed in terms of the *number of photons absorbed*, is the relevant parameter. The model advanced recently by Quack¹⁷ may also be phrased in this way. More explicitly let the total Hamiltonian for the molecule in the radiation field be

$$H = H_0 + \mu \quad (I.1)$$

$$H_0 = H_M + H_R, \quad (I.2)$$

where H_M is the molecular Hamiltonian, H_R is the Hamiltonian for the radiation field, and where μ is the interaction between these two systems. In the dipole approximation μ is given as the scalar product between the molecular dipole moment operator and between the electric field operator associated with the radiation field. The following assumptions are made: (1) The excitation is monochromatic. (2) Throughout the excitation process the population of radiation field modes other than the exciting (initially populated) one may be disregarded (such modes are populated in principle by spontaneous IR emission). (3) The Rabi frequency μ is much smaller than the exciting photon frequency ω , implying the validity of the rotating wave approximation (RWA).

Given some initial population of the exciting radiation field mode (the final result has to be averaged over the initial distribution of states of these modes), the zero order dressed states (eigenstates of H_0) are written as direct products $\{|K\alpha\rangle\}$ of states of the radiation field and of the molecule. The former may be expressed by the number $0, 1, \dots, K, \dots$ of photons absorbed. The molecular basis set is taken to be the set of eigenstates $\{|\alpha\rangle\}$ of the total (anharmonicity included) molecular

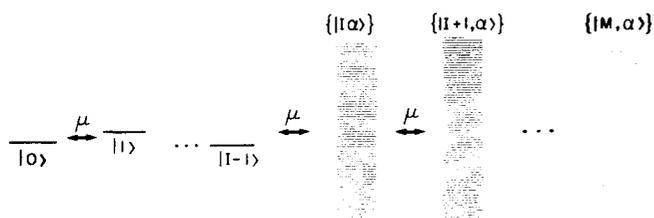


FIG. 3. A simplified model for multiphoton excitation of a large molecule, obtained from the model displayed in Fig. 2 by taking into account energetically relevant levels only.

Hamiltonian H_M . The set of eigenstates of H_0 is displayed in Fig. 2 which shows also the radiative coupling prevailing between nearest neighbor manifolds. In the RWA we may consider only (dressed) states within a limited energy range having width of the order of the Rabi frequency μ . As $\mu \ll \omega$ we may consider the multiphoton excitation process in terms of transitions between distinct manifolds of molecular levels (Fig. 3). Each manifold is characterized by a number K denoting the number of photons absorbed, and is composed of a set of molecular levels $\{|\alpha\rangle\}$. The variables of interest are now the populations P_K of the different manifolds $\{|K\alpha\rangle\}$.

$$P_K(t) = \sum_{\alpha} \rho_{K\alpha, K\alpha}(t), \quad (I. 3)$$

where $\rho_{K\alpha, K\alpha}$ is the diagonal $K\alpha$ element of the density matrix describing the molecule-radiation field system in the zero order $\{|K\alpha\rangle\}$ basis. Obviously $P_K(t)$ ($K=0, 1, \dots$) is the probability that K photons were absorbed by the molecules at time t .

This model is the basis for the theoretical treatments of Refs. 14–17. The details of these approaches are different. Mukamel has again invoked the notion of intramolecular dephasing to discuss the erosion of coherence in this model. As the reduction scheme leading to equations for the $\{P_K\}$ is different from that leading to equations for the populations of the optically active modes, the description of the dephasing process is naturally different. However the physical origin of this dephasing is identical in both approaches and lies in the intramolecular vibrational relaxation (IVR) process. Mukamel has thus concluded that provided IVR is fast relative to the optical process, a Markoffian Pauli-type master equation is obtained for the number of photons absorbed. On the other hand Schek, Jortner, Carmeli, and Nitzan^{15,16,18} have argued that rapid IVR is a necessary but not sufficient condition for a time evolution governed by a Pauli master equation. They have shown that one has to assume in addition that the radiative coupling between states in ranges II and III varies essentially randomly with the state indices. The approach by Schek and Jortner¹⁵ is based on some phenomenological arguments. Our approach is rigorous, leading to an explicit solution which becomes exact in the (practical) limit where the IVR rate greatly exceeds the Rabi frequency, provided that the latter is much larger than the inverse density of states in the radiatively coupled molecular manifolds.

The present paper gives the details of our approach which was briefly described in an earlier communication.¹⁶ In Sec. II we discuss in more detail the molecu-

lar model, focussing attention on the role of IVR and on the choice of the molecular basis set. In Sec. III we discuss the conventional approaches to the derivation of Pauli master equations and argue that they are not applicable in the present context. Section IV presents our approach based on the random coupling model (RCM) described in a previous paper¹⁹ (referred to as Paper I). We discuss the role of slow varying components in the coupling and argue that such contributions are negligible. Finally we discuss the implications of the results obtained and speculate about possible extensions of the model used.

II. THE MOLECULAR MODEL

It is clear from the discussion of the previous section that IVR plays an essential role in the dynamics of multiphoton excitation of polyatomic molecules. It will be useful for our future discussion to elucidate this point in greater detail. As all relaxation processes within isolated systems,²⁰ the existence of IVR as a relevant observable process, stems from the ability to prepare, at least in principle, a nonstationary molecular state whose subsequent evolution in time is observed as vibrational relaxation. Within the molecular vibrational manifold this may be achieved because of the optical selection rules characterizing the zero order molecular (normal mode or bond mode) basis. Transitions into optically active states appear as sharp resonances in range I. In range II these zero order states are imbedded in a quasicontinuum of similar states which do not carry oscillator strength for transitions from lower states.²¹ They then play the role of doorway states and appear in the spectrum as broadened resonances. Such broad resonances (width $\sim 100 \text{ cm}^{-1}$) have been recently observed in the overtone absorption spectrum of benzene¹³ and naphthalene.²³ The width of these absorption features provide a direct measure of the IVR or the intramolecular dephasing rate.

In applying this picture to multiphoton excitation of large molecules it is important to realize that the vibrational quasicontinuum which is responsible for the broadening of absorption resonances is not optically inert in the usual sense. Each zero order vibrational state is characterized by a given population of the optically active mode(s) and is radiatively coupled to states with one more or one less quantum in such mode. This situation is portrayed in Figs. 4 and 5(a) for the simple case with only one optically active mode. The strict optical selection rules are manifested in the fact that any given zero order level is radiatively coupled only to two levels—one above and one below it.

Figure 5(b) displays the same situation in terms of the exact eigenfunctions of the total molecular Hamiltonian H_M . This is the basis set which we use in the present approach. In this picture the doorway state concept does not apply. Each level is radiatively coupled to a group of other levels; the distribution of squared oscillator strengths traces the corresponding absorption line shape. The width $\Gamma^{(w)}$ of this line shape is again a measure for the IVR rate. It has been recently shown^{11,12} that marked structure, like that shown

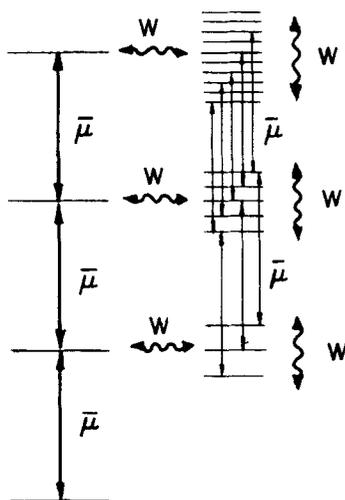


FIG. 4. Radiative coupling between zero order molecular levels, assuming a single optically active mode. $\bar{\mu}$ is the radiative coupling between levels of this mode. N denotes the intramolecular coupling.

in Fig. 5(b), persists in SF_6 even when it is excited to high vibrational levels (e.g., following absorption of ~ 20 CO_2 laser photons on the average,¹¹ or in hot molecules with temperature ~ 1000 – 2000 $^\circ\text{K}$ ¹²).

The distribution of oscillator strengths between eigenstates of the total molecular Hamiltonian resulting from the intramolecular interactions, leads to a dilution effect²⁴: Consider the matrix elements $\mu_{K\alpha, (K+1)\beta}$ of the radiative interaction between the zero order molecular states $|a\rangle$ and $|b\rangle$ (with K and $K+1$ photons absorbed) and the corresponding matrix elements $\mu_{K\alpha, (K+1)\beta}$ between the eigenstates $|\alpha\rangle$ and $|\beta\rangle$ of the total molecular Hamiltonian. We use the notations $\langle |\bar{\mu}| \rangle_{K, K+1}$ and $\langle |\mu| \rangle_{K, K+1}$ to denote the average magnitudes of these elements $\langle |\mu_{K\alpha, (K+1)\beta}| \rangle$ and $\langle |\mu_{K\alpha, (K+1)\beta}| \rangle$, respectively.²⁵ These quantities roughly satisfy (see Appendix A)

$$\langle |\mu|^2 \rangle_{K, K+1} = \langle |\bar{\mu}|^2 \rangle_{K, K+1} / \Gamma_{K, K+1}^{(\omega)} \rho_{K+1}, \quad (\text{II. 1})$$

where ρ_{K+1} is the density of vibrational states in the energy region $(K+1)\hbar\omega$ (ω is the frequency of the absorbed photons) and where $\Gamma_{K, K+1}^{(\omega)}$ is the sum of widths associated with IVR in the energy regions $K\hbar\omega$ and $(K+1)\hbar\omega$. More detailed expressions are provided in Appendix A.

With these concepts cleared, the molecular model is described in terms of the characteristic molecular parameters as follows:

(a) Range I is characterized by the positions of those levels which are radiatively coupled to the initial (ground) state by multiphoton absorption, and by the radiative couplings $\bar{\mu}$ (Rabi frequencies) for the corresponding transitions. In this region $|\bar{\mu}| \rho \ll 1$.

(b) Range II is characterized by the density of states ρ_K in the different manifolds K (corresponding to molecular energies $K\hbar\omega$) and by the diluted radiative coupling elements μ between states in these manifolds. The onset of range II is defined by the conditions²⁶

$$\Gamma^{(\omega)} \rho \gg 1 \quad (\text{II. 2a})$$

$$\langle |\mu| \rangle \rho \gg 1. \quad (\text{II. 2b})$$

Using Eq. (II. 1), condition (II. 2b) is seen to be equivalent to

$$\langle |\bar{\mu}|^2 \rangle \rho / \Gamma^{(\omega)} \gg 1, \quad (\text{II. 3})$$

where $|\bar{\mu}|$ now is the order of the Rabi frequency for range I transitions. Taking $|\bar{\mu}| \sim 1$ – 10 cm^{-1} and $\Gamma^{(\omega)} \sim 10$ – 100 cm^{-1} we see that this condition is satisfied already for regions of relatively small density of states ($\rho \gtrsim 10^3$ cm^{-1}). Another implication of inequality (II. 2b) is that the transitions between the quasicontinuous manifolds in range II (Figs. 2, 3) correspond to the strong intercontinuum coupling situation where

$$\pi^2 \langle |\mu|^2 \rangle_{K, K+1} \rho_K \rho_{K+1} \gg 1. \quad (\text{II. 4})$$

In what follows we shall impose another condition on the relative magnitudes of the radiative coupling and the IVR widths in range II. We require (in terms of the undiluted Rabi frequency)

$$|\bar{\mu}| / \Gamma^{(\omega)} \ll 1. \quad (\text{II. 5})$$

Physically it means that in the zero order basis (excitation in a ladder) the dephasing rate $\Gamma^{(\omega)}$ is much larger than the radiative coupling $\bar{\mu}$. In the molecular eigenstates basis inequality (II. 5) expresses the requirement that the spread $\Gamma^{(\omega)}$ of the absorption probability in range II is much larger than the Rabi frequency. In most theories which derive a Pauli type master equation from the Schrödinger equation (II. 5) constitutes a necessary and sufficient condition. We shall see however that one has to distinguish between the case where the dephasing results from random modulations of the system, created by an external source [where indeed (II. 5) provides a necessary and sufficient condition] and between the intramolecular dephasing where the required random nature of the modulation leads to another restriction on the nature of the radiative coupling μ , namely the random coupling requirement to be discussed below.

(c) Range III behaves, as far as the multiphoton dynamics is concerned, like range II. Photon absorption above the first dissociation threshold again amounts to

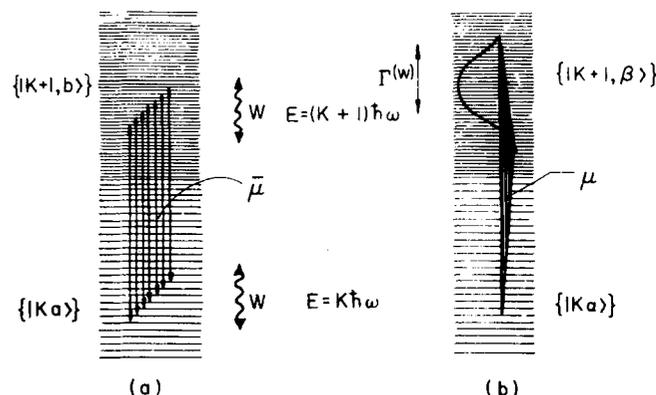


FIG. 5. Radiative coupling schemes in the zero order molecular basis (5a) and in the exact molecular basis (5b). The mixing of zero order states due to the intramolecular coupling W leads to a redistribution and dilution of the oscillator strength as shown in (5b). This redistribution determines the line shape for IR absorption by a molecule preexcited to the energy range $E = K\hbar\omega$.

transitions between manifolds of molecular levels. We introduce the dissociation process phenomenologically by assigning to each level in the K th manifold a width γ_K . γ_K vanishes (or rather becomes equal to the IR decay width) below the dissociation threshold, and may be small relative to the optical interaction slightly above it. Well above the dissociation threshold (7–8 quanta for SF_6)⁶ the dissociation probability becomes larger than the radiative transition rate and this region marks the effective termination of the photon absorption process.

(d) Between range I where $|\bar{\mu}| \rho \ll 1$ and range II which is characterized by $\langle |\mu| \rangle \rho \gg 1$ lies an intermediate energy range where $\langle |\mu| \rangle \rho \approx 1$. Here the direct solution of the Schrödinger equation is cumbersome while the statistical methods which simplify the treatment of range II are not applicable. Fortunately, the energy spread of the intermediate region is small. For SF_6 in this energy range the density of levels grows by about an order of magnitude per 1000 cm^{-1} and it is therefore likely that no more than one step in the multiphoton absorption process falls within the intermediate case. For larger molecules ρ rises more sharply, therefore the intermediate region may be “jumped over” altogether. In the present paper we disregard this region and assume that range I feeds directly into range II.

Anticipating the need for an essentially random behavior of the coupling we introduce now the random coupling model (see Paper I). We take range I to consist of the discrete levels $|0\rangle, |1\rangle, \dots, |I-1\rangle$, and ranges II and III as consecutively coupled manifolds $\{|I\alpha\rangle, \{(I+1)\alpha\rangle, \dots, \{M\alpha\rangle\}$, where α denotes the level index within the particular manifold. Physically $K=0, 1, \dots, I, I+1, \dots, M$ denotes the number of photons absorbed at each stage. It is assumed that levels in manifold M dissociate rapidly enough so that further photon absorption may be disregarded.

In the RCM the radiative coupling elements $\mu_{J, J', \alpha', \alpha}$ ($J, J' \geq I$) or $\mu_{I-1, I, \alpha}$ are assumed to be random functions of their level indices so that

$$\mu_{J, J', \alpha', \alpha} = \langle \mu \rangle_{J, J'} + \delta \mu_{J, J', \alpha', \alpha}, \quad (\text{II. 6})$$

where

$$\langle \delta \mu \rangle = 0 \quad (\text{II. 7})$$

and

$$\langle \delta \mu_{J, J', \alpha', \alpha} \delta \mu_{K, K', \alpha', \alpha'} \rangle = \langle \delta \mu^2 \rangle_{J, J'} (\delta_{J, K} \delta_{J', K'} \delta_{\alpha, \alpha'} \delta_{\alpha', \alpha'} + \delta_{J, K'} \delta_{J', K} \delta_{\alpha, \alpha'} \delta_{\alpha', \alpha}) \quad (\text{II. 8})$$

The averages here are simple arithmetic averages taken over all states of the corresponding manifolds (see Sec. II of Paper I for rigorous definitions). Similarly

$$\mu_{I-1, I, \alpha} = \langle \mu \rangle_{I-1, I} + \delta \mu_{I-1, I, \alpha}, \quad (\text{II. 9})$$

where again $\langle \delta \mu \rangle = 0$ and where

$$\langle \delta \mu_{I-1, I, \alpha} \delta \mu_{I-1, I, \beta} \rangle = \langle \delta \mu^2 \rangle_{I-1, I} \delta_{\alpha, \beta} \quad (\text{II. 10})$$

The rationale behind these assumptions lies in the observation that in ranges II and III the radiative coupling elements are essentially overlap integrals between highly exciting (therefore highly oscillatory) vibrational states of the molecule. These elements are therefore

rapidly varying functions of the level indices. These rapid, essentially random variations are superimposed on a much slower variation, taking place on the energy scale determined by the IVR rate $\Gamma^{(w)}$ (see Appendix A). The averages $\langle \mu \rangle$ and $\langle \delta \mu^2 \rangle$ vary indeed on this slow scale. In this paper we neglect this variation in the spirit of inequality (II. 5) and assume that $\langle \mu \rangle$ and $\langle \delta \mu^2 \rangle$ depend only on the manifolds involved and not on the individual levels (or the energies) within these manifolds.

In summary, the excitation process within manifolds II and III is characterized by the following parameters: density of states ρ [which determines also the energy scale for the rapid (random) variations of the radiative coupling; this scale is of the order of the level spacing ρ^{-1}]. The IVR width $\Gamma^{(w)}$ (which determines the range of the slow, systematic variation of the coupling), the radiative coupling μ , and the dissociation rate γ . We anticipate (and show later) that the multiphoton absorption process will involve rates given by $2\pi \langle |\mu|^2 \rangle \rho$ which determine the interesting experimental time scale τ . The inequality

$$\hbar \rho \gg \tau \gg \hbar / \Gamma^{(w)}, \quad (\text{II. 11})$$

which is equivalent to inequality (II. 10) of Paper I, is obviously satisfied. This is the necessary requirement for the validity of the procedure described in Paper I and used below in Sec. IV.

III. THE WEAK COUPLING LIMIT

Before describing the RCM solution to the multiphoton excitation problem we dwell briefly on the conventional derivation of the Pauli master equation which rests on a weak coupling assumption. In fact the weak coupling solution of Zwanzig²⁷ is given in a form which is applicable to the multiphoton absorption problem in ranges II and III. We review Zwanzig's solution in Appendix B. For simplicity we consider the case where range I contains a single discrete level $|0\rangle$, followed by manifolds $\{|1\alpha\rangle, \dots, \{M\alpha\rangle\}$. Provided that inequality (II. 11) holds, the weak coupling procedure results in the Pauli master equation

$$\frac{dP_J}{dt}(t) = \sum_{J'} [k_{J', J} P_{J'}(t) - k_{J, J'} P_J(t)] \quad (J, J' = 1, 2, \dots, M), \quad (\text{III. 1})$$

where the rates are given by the golden rule expression

$$k_{KL} = 2\pi \langle |\mu|^2 \rangle_{KL} \rho_L \quad (\text{III. 2})$$

It should be noted that this solution does not require any random coupling assumption. Indeed, for radiative coupling satisfying Eqs. (II. 6–8), Eq. (III. 2) may be written in the form

$$k_{KL} = 2\pi (\langle |\mu \rangle_{KL}|^2 + \langle |\delta \mu|^2 \rangle_{KL}) \rho_L, \quad (\text{III. 3})$$

so that the purely random part and the slowly varying background contribute additively to the rate. A similar result was recently obtained by Mukamel¹⁴ in the Markoffian limit of his approach to the multiphoton excitation problem when he keeps only the lowest order in the radiative interaction (i. e., the weak coupling limit). We shall see that this result does not hold in the strong

intercontinuum coupling limit [defined by (II.4)], which is the relevant limit for multiphoton excitation of large molecules.

IV. TIME EVOLUTION FOR MULTIPHOTON EXCITATION IN THE RANDOM COUPLING MODEL

In Paper I we have presented the solution for the time evolution in a random intercontinuum coupling model. The model discussed in Paper I can be adopted with slight changes to the model described in Sec. II for the problem of multiphoton excitation of large molecules. The following changes are needed:

(a) The single initial discrete level which precedes the quasicontinuous manifolds in the model of Paper I has to be replaced by several consecutively coupled discrete levels which correspond to the molecular range I.

(b) Each level in manifolds $\{|K\alpha\rangle\}$ with $K\hbar\omega$ larger than the dissociation limit should be assigned a width γ_K corresponding to the (irreversible) dissociation rate from this level.²⁸ This expresses the fact that above the dissociation threshold the molecular states used are no longer exact eigenstates of the molecular Hamiltonian: They are states obtained in an approximation which neglects the coupling leading to dissociation.²⁹

It may easily be seen, as noted by many workers, that the mathematical description of the time evolution in range I is not affected by the consecutive evolution in ranges II and III apart from the damping imposed on the upper $|I-1\rangle$ level. This results from the irreversible nature of the transition from this level into the upper energy manifolds, which enables us to obtain an effective Hamiltonian for the time evolution in range I. Let

$$\mathbf{a}(t) = \begin{pmatrix} a_0(t) \\ a_1(t) \\ \vdots \\ a_{I-1}(t) \end{pmatrix} \tag{IV.1}$$

be the vector of amplitudes for the levels in range I. Then the time evolution in this region is given by^(d)

$$i\dot{\mathbf{a}}(t) = \mathbf{H}_{\text{eff}} \mathbf{a}(t) \tag{IV.2a}$$

$$(\mathbf{H}_{\text{eff}})_{ij} = (E_i - \frac{1}{2}i\tilde{\Gamma}_{I-1}\delta_{i,I-1})\delta_{ij} + \mu_{ij}\delta_{i,j\pm 1}, \tag{IV.2b}$$

where $\tilde{\Gamma}_{I-1}$ is the inverse lifetime (discussed below) of the level $|I-1\rangle$ resulting from its "decay" into the upper manifolds.

Similarly, the time evolution in ranges II and III is affected by the range I dynamics only through the time dependence of the population of the state $|I-1\rangle$, $P_{I-1}(t) = |a_{I-1}(t)|^2$, which feeds these regions. This again results from the fact that the transition from level $|I-1\rangle$ to the quasicontinuous manifolds is an irreversible damping of the level $|I-1\rangle$, which depends only on its instantaneous population. This may be shown rigorously using the diagrammatic approach of Paper I.

Introducing the dissociation lifetime into the formal-

ism of Paper I is again a trivial matter. One needs only to realize that this amounts to replacing the Hamiltonian H_0 by an effective one, in which a diagonal imaginary part is added to account for the finite dissociation lifetime. The formalism of Paper I may thus be used where each free propagator of the form $(U - E_{K\alpha} + i\eta)^{-1}$ is replaced by $(U - E_{K\alpha} + \frac{1}{2}i\gamma_K)^{-1}$, and similarly $(U - E - E_{K\alpha} - i\eta)^{-1} \rightarrow (U - E - E_{K\alpha} - \frac{1}{2}i\gamma_K)^{-1}$.

With these additions, the formalism described in Sec. IV of Paper I is carried through with no other changes; the time evolution of the populations P_I, P_{I+1}, \dots, P_M is determined by the kinetic equations

$$\dot{\mathbf{P}}(t) = 1/\hbar[\mathbf{R}\mathbf{P}(t) + \mathbf{S}P_{I-1}(t)], \tag{IV.3}$$

where

$$\mathbf{P} \equiv \begin{pmatrix} P_I \\ P_{I+1} \\ \vdots \\ P_M \end{pmatrix} \tag{IV.4}$$

is the vector of populations of the different manifolds [$P_K(t)$, $K=I, I+1, \dots, M$, is the probability that K photons are absorbed at time t]. \mathbf{R} is the rate matrix (with row and column indices taking integer values from I to M).

$$R_{K,K} = -(\Gamma_{K,K-1}^{(r)} + \Gamma_{K,K+1}^{(r)} + \gamma_K) \tag{IV.5a}$$

$$R_{K,K\pm 1} = \Gamma_{K\pm 1,K}^{(r)}, \tag{IV.5b}$$

where

$$\Gamma_{K,K'}^{(r)} = 2\pi\langle\delta\mu^2\rangle_{KK'}\rho_{K'} \tag{IV.6}$$

is determined only by the random component of the coupling. Finally the vector \mathbf{S} may be written as a sum

$$\mathbf{S} = \mathbf{S}^{(r)} + \mathbf{S}^{(c)} \tag{IV.7}$$

$\mathbf{S}^{(r)}$ originates from the random coupling component and is given by

$$\mathbf{S}^{(r)} = \begin{pmatrix} \Gamma_{I-1,I}^{(r)} \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \tag{IV.8}$$

while $\mathbf{S}^{(c)}$ results from the underlying smoothly varying coupling. Its components

$$\mathbf{S}^{(c)} \equiv \begin{pmatrix} S_I^{(c)} \\ S_{I+1}^{(c)} \\ \vdots \\ S_M^{(c)} \end{pmatrix} \tag{IV.9}$$

are defined from

$$S_I^{(c)} = C_1^2 \Gamma_{I-1,I}^{(c)} \tag{IV.10a}$$

$$S_{I+J-1}^{(c)} = C_J \left[\prod_{j=1}^{J-1} (1 - C_j) \right] C_1 \Gamma_{I-1, I}^{(c)}, \quad (J=2, 3, \dots, M), \quad (\text{IV. 10b})$$

where

$$\Gamma_{I-1, I}^{(c)} = 2\pi \langle \mu \rangle_{I-1, I}^2 \rho_I, \quad (\text{IV. 11})$$

$$C_J = (1 + N_{I+J-1, I+J} C_{J+1})^{-1}, \quad (\text{IV. 12})$$

and where N is the intercontinuum coupling parameter associated with the smooth coupling component.

$$N_{KL} = \pi^2 \langle \mu \rangle_{KL}^2 \rho_K \rho_L. \quad (\text{IV. 13})$$

Equations (IV. 2), (IV. 3) (with $P_{I-1} = |\alpha_{I-1}|^2$), and (IV. 5–13) constitute our final results for the dynamics of multiphoton excitation in large molecules. The following points are in order:

(a) Range I processes are effectively decoupled from the consecutive absorption steps. Range I dynamics is determined by Eq. (IV. 2) which describes a relatively small (I level) system with an additional decay of the upper $|I-1\rangle$ level. If the corresponding decay width was larger than the Rabi frequency, it could cause damping of the coherence effects characterizing the small molecule behavior in range I.⁷ However we note that the radiative coupling elements between levels in range I are of the order $|\bar{\mu}|$ of the coupling between levels of the optically active mode(s), while the radiative elements between the level $|I-1\rangle$ and the levels $\{|I\alpha\rangle\}$ are of the order of the diluted coupling $\langle |\mu| \rangle \approx |\mu| / \sqrt{\Gamma^{(w)} \rho}$ [cf. Eq. (II. 1)]. Thus

$$\tilde{\Gamma}_{I-1} \approx 2\pi \langle |\mu|^2 \rangle \rho_I \approx |\bar{\mu}| (2\pi |\bar{\mu}| / \Gamma^{(w)}) \ll |\bar{\mu}|, \quad (\text{IV. 14})$$

where the expression for $\tilde{\Gamma}_{I-1}$ is discussed below and where we have used inequality (II. 5). We conclude that provided (II. 5) holds, i. e., intramolecular dephasing rate in range II is larger than the Rabi frequency of range I, coherent effects are observable in range I. Indeed photon echoes^{30(a)} and coherent pulse propagation^{30(b)} were observed in SF₆.

(b) The "escape" from range I to range II originates in principle from two processes which, in the approximations described in Paper I, contribute additively to the rate. If the radiative coupling elements are purely random so that $\langle \mu \rangle_{I-1, I} = 0$, the escape rate $\tilde{\Gamma}_{I-1}$ is

$$\tilde{\Gamma}_{I-1} = \Gamma_{I-1, I}^{(r)} = 2\pi \langle \delta \mu^2 \rangle_{I-1, I} \rho_I. \quad (\text{IV. 15})$$

In the presence of a constant (or smooth component $\langle \mu \rangle \neq 0$, Eq. (IV. 3) indicates that direct transitions from level $|I-1\rangle$ to all the higher manifolds are possible. Accordingly,

$$\tilde{\Gamma}_{I-1} = \Gamma_{I-1, I}^{(r)} + \sum_{J \geq I} S_J^{(c)}. \quad (\text{IV. 16})$$

It may be shown that

$$\sum_{J \geq I} S_J^{(c)} = C_1 \Gamma_{I-1, I}^{(c)}, \quad (\text{IV. 17})$$

where $C_1 < 1$ is defined as a continued fraction by Eq. (IV. 12).

In actual situations there is no reason to expect that

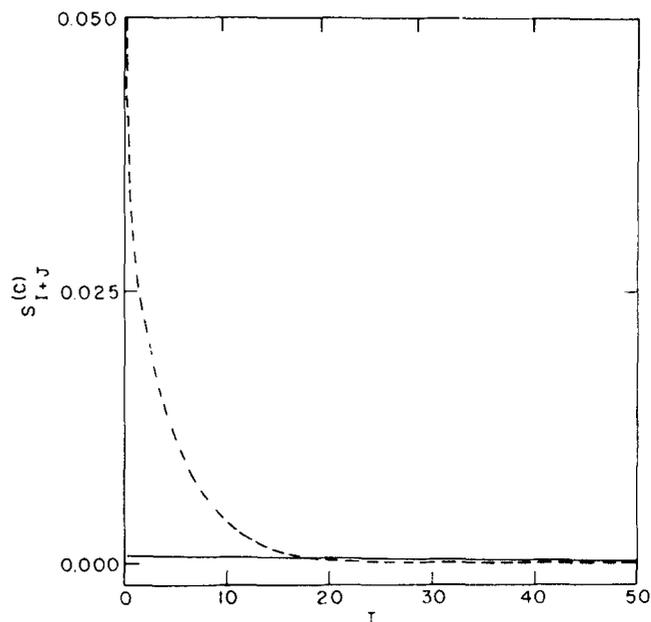


FIG. 6. Model calculation of the contribution of the smooth coupling component to the coherent (direct) multiphoton excitation. Dashed line—40 manifold model. Full line—80 manifold model. Parameters are given in the text.

radiative coupling elements involving molecular eigenstates from ranges II and III will have an unusually large smoothly varying component. Therefore in general either $\Gamma^{(c)} \ll \Gamma^{(r)}$ or $\Gamma^{(c)} \approx \Gamma^{(r)}$ and then Eq. (II. 4) implies that $N \gg 1$. [N denotes elements defined in (IV. 13).] In the presence of many possible absorption steps Eq. (IV. 12) then yields $C_1 \ll 1$. In either case we conclude that

$$\tilde{\Gamma}_{I-1} \approx \Gamma_{I-1, I}^{(r)}, \quad (\text{IV. 18})$$

and the contribution of a smoothly varying radiative coupling component to the rate of escape from range I may be disregarded.

(c) The molecular manifolds belonging to ranges II and III may be in principle directly populated by a coherent multiphoton absorption from the level $|I-1\rangle$. These coherent transitions arise from the smoothly varying radiative coupling component. The discussion above leads us to conclude that contributions of these direct steps to the overall transition probabilities may be disregarded. To see this point in greater detail we present in Fig. 6 two computations of the smooth coupling contribution to the multiphoton absorption rate. In one example ranges II and III are taken to contain 40 manifolds (corresponding to 40 photon absorption steps). The parameters in this computation are chosen to be $\langle \mu \rangle_{I-1, I} = 1.0$, $\langle \mu \rangle_{K, K+1} = 0.9$ ($K \geq I$), $\rho_I = 1.0$, and $\rho_K = 1.5$ ($K \geq I$). Shown are the transition rates for the coherent transitions from the level $|I-1\rangle$ to the K th manifold. Their sum $C_1 \Gamma_{I-1, I}^{(c)}$ [cf. Eq. (IV. 17)] which represents the rate of coherent transitions from level $|I-1\rangle$ to upper manifolds is obtained to be 1.79, while $\Gamma_{I-1, I}^{(c)} = 6.28$ which shows the damping of the coherent process. It should be noted that the cutoff $J=40$ imposed in this calculation is not based on any physical consideration: As we consider here essentially instantaneous transi-

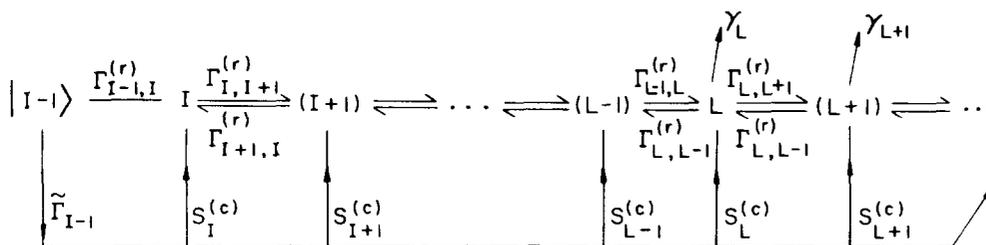


FIG. 7. The kinetic scheme for multiphoton excitation in ranges II and III of a large molecule.

tions, a cutoff based on the efficiency of the dissociation process is not relevant here. In principle the number of contributing manifolds is limited only by the value of the intermanifold radiative coupling (which go to zero at very high molecule energies) and may be much larger than 40. This implies an even stronger damping of the coherent transitions. In the second example displayed in Fig. 6 ranges II and III are represented by 80 manifolds, $\rho_K = 100$ for all $K \geq I$, $|V_{I-1,I}|^2 = 0.016$ and $|V_{K,K+1}|^2 = |V_{K-1,K}|^2 \exp(-0.037)$. Here we obtain $C_1 \Gamma_{I-1,I}^{(c)} = 0.25$ while $\Gamma_{I-1,I}^{(c)} = 10$.

It is interesting to mention that intercontinuum coupling models based on a constant (or smoothly varying) coupling have been solved before³¹ (yielding the coherent part of the evolution obtained here) and applied to molecular photodissociation and related problems.³² These cases involve coupling to translational continua rather than to dense manifolds of bound vibrational states, and a constant coupling assumption seems to be relevant here.

(d) The time evolution in ranges II and III, as described by Eqs. (IV.3–13) corresponds to the kinetic scheme shown in Fig. 7. Here L marks the onset of range III [i. e., the dissociation threshold lies between $(L-1)\hbar\omega$ and $L\hbar\omega$] and $\gamma_J \approx 0$ for $J < L$. As we saw above, the coherent processes in the continuous and quasicontinuous regimes may usually be disregarded leaving an incoherent time evolution described by the master equation

$$\dot{\mathbf{P}}(t) = \mathbf{R}\mathbf{P}(t) + \mathbf{S}^{(r)}\mathbf{P}_{I-1}(t), \quad (\text{IV.19})$$

which was proposed phenomenologically before, and applied for the purpose of fitting experimental multiphoton dissociation by several workers.^{1(c),6}

(e) We have recently¹⁸ tested the results obtained here by numerical simulation, solving the Schrödinger equation for a few coupled manifolds of levels with suitably chosen coupling elements. The simulation results are in excellent agreement with the kinetic scheme described above.

(f) The master equation (IV.19) is similar to that obtained under the weak coupling assumption, Eq. (III.1). The difference, as noted in Sec. III, lies in the fact that in the weak coupling equations the random and constant coupling components contribute additively to the rates, while our results indicate that in the strong coupling limit the constant coupling contribution may be disregarded.

(g) It is interesting to note that according to our re-

sults, if by some accident of nature a particular radiative transition in range II involves smoothly varying coupling elements (e. g., $\mu_{K\alpha, (K+1)\alpha'}$ for some K is independent of α and α' in the relevant energy range) the multiphoton absorption process is effectively blocked at the $(K+1)$ step. It may be shown³³ that for this to occur it is sufficient that $\mu_{K\alpha, (K+1)\alpha}$ is independent of α or α' so that this coupling is practically separable.

It is interesting to note that recent calculations by Quack^{34(a)} seem to imply that the noncoherent dynamics in multiphoton excitation of large molecules may result from the random initial phases characterizing the initial molecular distribution. In fact, Quack's calculations^{34(a)} have been performed using a random distribution of coupling matrix elements.^{34(b)} In Appendix C we show that initial random phases are not sufficient for a subsequent incoherent evolution in a model with smoothly varying coupling.

(h) The calculation leading to the results (IV.3–13) is based on the assumption that the systematic (as opposed to random) variation of the radiative coupling in ranges II and III is slow, so that $\langle |\mu_{K\alpha, (K+1)\alpha'}|^2 \rangle$ is taken to be independent of α and α' in the relevant energy region. The magnitude $\langle |\mu|^2 \rangle_{K,K+1}$ of this constant is determined in terms of the Rabi frequency of the optically active zero order mode and by the structure of the IR absorption line shape in ranges II and III as discussed in Appendix A. We have roughly [cf. Eq. (A7)]

$$\langle |\mu|^2 \rangle_{K,K+1} \approx \langle |\bar{\mu}|^2 \rangle_{K,K+1} / \rho_{K+1} \\ \times \frac{1}{2} \Gamma_{K,K+1}^{(w)} / [(\bar{E}_{K,K+1} - \hbar\omega)^2 + (\frac{1}{2} \Gamma_{K,K+1}^{(w)})^2]. \quad (\text{IV.20})$$

If $\langle \mu \rangle = 0$ this quantity should enter for $\langle |\delta\mu|^2 \rangle_{K,K+1}$ in calculating the rates (IV.6) for the master equation (IV.19). When transitions occur approximately on resonance, (IV.20) is equivalent to (II.1).

(i) It is of interest to examine the order of the error introduced into our results by disregarding the systematic variation in the radiative coupling elements in ranges II and III. In the mathematical procedure this approximation enters in the assumption that quantities like

$$\Gamma_{K,K+1}(E) = -2 \sum_{\alpha} \frac{\langle |\mu_{K\alpha, (K+1)\alpha'}|^2 \rangle}{E - E_{\alpha} + \frac{1}{2} i \gamma_K} \\ = -2 \int dE_{\alpha} \rho(E_{\alpha}) \frac{\langle |\mu_{K,K+1}(E_{\alpha}, E_{\alpha'})|^2 \rangle}{E - E_{\alpha} + \frac{1}{2} i \gamma_K} \quad (\text{IV.21})$$

are energy independent. Corrections to the results obtained in this way are of the order $d\Gamma(E)/dE$. Inserting Eq. (A7) and performing the integral it is easily seen that (for $\gamma_K \ll \Gamma^{(w)}$)

$$\left| \frac{d\Gamma_{K,K+1}(E)}{dE} \right| \sim \frac{|\bar{\mu}|^2}{E^2 + (\Gamma^{(w)})^2}. \quad (\text{IV. 22})$$

Thus the error in our results is of order $|\bar{\mu}/\Gamma^{(w)}|^2$. For high intensity fields $\bar{\mu}$ increases. As it approaches the IVR rate we expect increasing deviations from the incoherent evolution described by Eq. (IV. 19).

More insight into this point may be obtained by reconsidering inequalities (II. 3) (definition of ranges II and III) and (II. 5) (condition for a Markoffian behavior). Combined, they take the form

$$(\bar{\mu}\rho)^{-1} \ll \frac{|\bar{\mu}|}{\Gamma^{(w)}} \ll 1. \quad (\text{IV. 23})$$

(II. 3) (II. 5)

When (II. 3) is not satisfied, excitation takes place between individual levels—range I. Increasing the field intensity up to a level where (II. 3) is satisfied brings us to range II and the time evolution is governed by Eq. (IV. 19) provided (II. 5) is satisfied. Increasing the field intensity further until $\bar{\mu} \gg \Gamma^{(w)}$ (the radiative coupling within the zero order optically active mode is much stronger than the intramolecular dephasing rate) results in a situation where excitation proceeds mainly within a few zero order levels—those appearing on left in Fig. 4. Hence, we are back into a range I behavior. In practice $\Gamma^{(w)}$ increases and $\bar{\mu}$ decreases with increasing molecular energy, so that *increasing the field intensity may have the effect of increasing the size of range I*.

The limit $\bar{\mu} \gg \Gamma^{(w)}$ will be hard to reach if current estimates of $\Gamma^{(w)} \sim 10\text{--}100 \text{ cm}^{-1}$ (in range II) are correct. The intermediate case $\bar{\mu} \approx \Gamma^{(w)}$ is of more practical importance, and is currently under study.

V. CONCLUSION

In this paper we have described the basis for the Pauli master equation for multiphoton excitation of large molecules. We have seen that the time evolution is governed by such an equation provided that the inequalities summarized by (IV. 23) hold, and provided that the radiative coupling elements between molecular vibrational eigenstates vary *essentially randomly* on an energy scale of the order of the level spacing. The rates which enter into the master equation may be calculated from the Golden Rule expression with the *variance* in the radiative coupling entering for the interaction, and with the density of levels associated with the *effectively coupled modes*. As $\langle |\delta\mu|^2 \rangle$ is proportional to the field intensity, this master equation leads to dissociation probability which is a function of the pulse energy rather than its intensity, and to delay times associated with the appearance of dissociation products which are proportional to field intensity, in agreement with experimental results.

Inequality (II. 3) or other criteria²⁶ for the onset of range II always hold for large molecules after a few excitation steps. When the field intensity increases so that inequality (II. 5) ceases to hold, we expect that the time evolutions associated with the multiphoton excita-

tion process will become increasingly coherent. Further theoretical and experimental studies of this point are desirable.

ACKNOWLEDGMENTS

We are grateful to Professor J. Jortner and Mr. I. Schek for many helpful discussions and to Dr. M. Quack for useful comments.

APPENDIX A. DISTRIBUTION OF IR OSCILLATOR STRENGTHS

Consider the transition between the molecular manifolds K and $K+1$ corresponding, respectively, to K and $K+1$ photon absorbed by the molecule (Figs. 2, 3, 5). Let the density of states in these manifolds be ρ_K, ρ_{K+1} and denote the anharmonic widths (dephasing or IVR rates) within them by $\Gamma_K^{(w)}$ and $\Gamma_{K+1}^{(w)}$. (If W_K is the anharmonic interaction between the zero order molecular states in the energy region corresponding to K absorbed photons then $\Gamma_K^{(w)} = 2\pi |W_K|^2 \rho_K$). We denote (Fig. 5) the zero order vibrational states in the manifolds K and $K+1$ by $\{|a\rangle\}$ and $\{|b\rangle\}$, with the zero order energies E_a and E_b , respectively. The corresponding zero order dressed states are $\{|K\alpha\rangle\}$ and $\{|(K+1)\beta\rangle\}$ with energies $E_{K\alpha} = E_a + \hbar\omega K$, $E_{(K+1)\beta} = E_b + \hbar\omega(K+1)$, ω being the photon frequency. In the simple case where there is only one optically active mode, for any state $|a\rangle$ there is a single state $|b\rangle$ which is radiatively coupled to it. We denote the average distance between such pairs by $E_{K,K+1}$. The corresponding molecular eigenstates (diagonalized in the anharmonicity) are denoted $\{|\alpha\rangle\}$ and $\{|\beta\rangle\}$ and their dressed counterparts are $\{|K\alpha\rangle\}$ and $\{|(K+1)\beta\rangle\}$. Then³⁶

$$|\langle \alpha | a \rangle|^2 \approx |W_K|^2 / [(E_a - E_\alpha)^2 + (\frac{1}{2}\Gamma_K^{(w)})^2], \quad (\text{A1})$$

where we assumed that anharmonic broadening leads to Lorentzian line shapes. Similarly

$$|\langle \beta | b \rangle|^2 \approx |W_{K+1}|^2 / [(E_b - E_\beta)^2 + (\frac{1}{2}\Gamma_{K+1}^{(w)})^2]. \quad (\text{A2})$$

Consider how the radiative interaction $\mu_{K\alpha, (K+1)\beta} = \langle K\alpha | \mu | (K+1)\beta \rangle$. Expanding the state $|\alpha\rangle$ in the set $\{|a\rangle\}$ we obtain

$$\mu_{K\alpha, (K+1)\beta} = \sum_a \mu_{K\alpha, (K+1)\beta} \langle \alpha | a \rangle \quad (\text{A3})$$

or, taking the absolute squares and performing coarse grained averaging over the molecular manifold $\{\alpha\}$ (see Paper I, Sec. II), we obtain (assuming that cross terms may be disregarded because of the random nature of the overlap integrals $\langle K\alpha | Ka \rangle$)

$$\langle |\mu_{K\alpha, (K+1)\beta}|^2 \rangle = \sum_a |\mu_{K\alpha, (K+1)\beta}|^2 |\langle \alpha | a \rangle|^2. \quad (\text{A4})$$

It should be noted that the residual α and β dependence on the lhs of Eq. (A4) results from the systematic variation of the coarse grained average. Next we note that μ couples a single state $|(K+1)\beta\rangle$ to a given state $|K\alpha\rangle$, so that

$$\langle |\mu_{K\alpha, (K+1)\beta}|^2 \rangle = \sum_a |\mu_{K\alpha, (K+1)\beta}|^2 |\langle b | \beta \rangle|^2 |\langle a | \alpha \rangle|^2. \quad (\text{A5})$$

Inserting Eqs. (A1) and (A2) leads to

$$\langle |\mu_{K\alpha, (K+1)\beta}|^2 \rangle = \frac{\langle |\bar{\mu}|^2 \rangle_{K, K+1}}{\rho_{K+1}} \int dx \frac{(\Gamma_K^{(w)}/2\pi)(\Gamma_{K+1}^{(w)}/2\pi)}{[(x - E_\alpha)^2 + (\Gamma_K^{(w)}/2)^2][(x + \bar{E}_{K, K+1} - E_\beta)^2 + (\Gamma_{K+1}^{(w)}/2)^2]}, \quad (\text{A6})$$

where we have replaced \sum_a by $\rho_K \int dx$, E_a by x and E_b by $x + \bar{E}_{K, K+1}$. We also note that $|\mu_{K\alpha, (K+1)\beta}|^2$ is relatively weakly dependent on the particular zero order a and b levels, and we have pulled its average out of the integral. The integral in (A6) may be evaluated to a reasonable approximation by extending the limits to $\pm\infty$, yielding

$$\langle |\mu_{K\alpha, (K+1)\beta}|^2 \rangle = \frac{\langle |\bar{\mu}|^2 \rangle_{K, K+1}}{\rho_{K+1}} \times \frac{\frac{1}{2}\Gamma_{K, K+1}^{(w)}}{(E_\alpha + \bar{E}_{K, K+1} - E_\beta)^2 + (\frac{1}{2}\Gamma_{K, K+1}^{(w)})^2}, \quad (\text{A7})$$

where

$$\Gamma_{K, K+1}^{(w)} = \Gamma_K^{(w)} + \Gamma_{K+1}^{(w)}. \quad (\text{A8})$$

Equation (A7) relates the anharmonic width associated with the IVR at molecular energies $K\hbar\omega$ and $(K+1)\hbar\omega$ to the predicted IR absorption (or emission) line shape between the same energy regions. For a given E_α the dependence of (A7) on $E_\beta (= E_\alpha + \hbar\omega)$ determines this line shape. Note that some additional broadening may result from the distribution of energy differences $E_b - E_a$ around their average $\bar{E}_{K, K+1}$.

When the exciting photon frequency is approximately in resonance with the molecular IR transition, we have $\bar{E}_{K, K+1} \approx E_\beta - E_\alpha \approx \hbar\omega$. Then Eq. (A7) leads to

$$\langle |\mu|^2 \rangle_{K, K+1} \approx \frac{2|\bar{\mu}_{K, K+1}|^2}{\pi\rho_{K+1}\Gamma_{K, K+1}^{(w)}}. \quad (\text{A9})$$

In a more compact notation we write $\langle |\mu| \rangle$ for the diluted radiative interaction and $\langle |\bar{\mu}| \rangle$ for the "bare" one; the latter being the quantity known from optical data obtained in range I. Then

$$\langle |\mu| \rangle \approx \frac{\langle |\bar{\mu}| \rangle}{(\rho\Gamma^{(w)})^{1/2}}. \quad (\text{A10})$$

APPENDIX B. DERIVATION OF THE PAULI EQUATION IN THE WEAK COUPLING LIMIT

Here we review Zwanzig's derivation²⁷ of the Pauli master equation and adopt it for the multiphoton excitation process in ranges II and III. Starting from the Liouville equation for the density operator w ,

$$\frac{\partial w}{\partial t} = -i\mathcal{L}w (\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_1; \mathcal{L}_0 = [H_0, \] \mathcal{L}_1 = [\mu]). \quad (\text{B1})$$

Zwanzig introduces the projection operator D which projects w on to its diagonal part in the representation defined by the eigenfunctions of H_0 ,

$$(Dw)_{mn} = w_{mn}\delta_{mn}. \quad (\text{B2})$$

In the present problem m and n denote individual states belonging to the different manifolds

$$m \equiv (J\alpha); \quad n \equiv (J'\alpha'). \quad (\text{B3})$$

Using what is by now a conventional reduction procedure, Zwanzig obtains the following equation for the diagonal elements of the density matrix

$$\frac{dw_{mm}(t)}{dt} = - \int_0^t dt_1 \sum_{n \neq m} \mathcal{K}_{mm, nn}(t_1) [w_{nn}(t - t_1) - w_{mm}(t - t_1)], \quad (\text{B4})$$

where \mathcal{K} is the tetradic operator

$$\mathcal{K}(t) = \mathcal{D}\mathcal{L} \exp[-it(\mathcal{L} - \mathcal{D})\mathcal{L}](\mathcal{L} - \mathcal{D})\mathcal{L}, \quad (\text{B5})$$

and where \mathcal{L} is the tetradic unity. In the weak coupling limit \mathcal{K} is taken in the lowest (second) order in \mathcal{L}_1

$$\mathcal{K}(t) = \mathcal{D}\mathcal{L}_1 \exp(-it\mathcal{L}_0)\mathcal{L}_1\mathcal{D}, \quad (\text{B6})$$

where the identity $\mathcal{D}\mathcal{L}_0 = \mathcal{L}_0\mathcal{D} = 0$ was used. Equation (B6) leads, after some tetradic operator algebra to

$$\mathcal{K}_{mm, nn}(t) = -2|\mu_{mn}|^2 \cos(E_{mn}t) \quad (\text{B7})$$

$$E_{mn} = E_m - E_n \quad (\text{eigenvalues of } H_0).$$

Inserting Eqs. (B3) and (B7) into (B4) we obtain

$$\frac{dw_{J\alpha, J\alpha}(t)}{dt} = 2 \int_0^t \sum_{J', \alpha'} |\mu_{J\alpha, J'\alpha'}|^2 \cos(E_{J\alpha, J'\alpha'}t) \times [w_{J', \alpha', J'\alpha'}(t - t_1) - w_{J\alpha, J\alpha}(t - t_1)]. \quad (\text{B8})$$

Next we go through the following steps: First sum over the states α belonging to the manifold J , putting

$$P_J(t) = \sum_{\alpha} w_{J\alpha, J\alpha}(t). \quad (\text{B9})$$

Secondly, we assume that $|\mu_{J\alpha, J'\alpha'}|^2$ is weakly dependent (on the average) on α and α' and we pull its average, $\langle |\mu|^2 \rangle_{J, J'}$, out of the α, α' summations. This is equivalent to the assumption (II. 5) of large intramolecular dephasing rates made in this paper. This leads to a Markoffian behavior: The sum over the rapidly oscillating cosine functions vanishes unless t_1 is close to zero. We obtain on this coarse grained time scale

$$\frac{dP_J(t)}{dt} = 2 \sum_{J'} \langle |\mu|^2 \rangle_{J, J'} \left[\sum_{\alpha'} w_{J', \alpha', J'\alpha'}(t) \left(\sum_{\alpha} \frac{\sin(E_{J'\alpha', J\alpha}t)}{E_{J'\alpha', J\alpha}} \right) - \sum_{\alpha} w_{J\alpha, J\alpha}(t) \left(\sum_{\alpha'} \frac{\sin(E_{J'\alpha', J\alpha}t)}{E_{J'\alpha', J\alpha}} \right) \right]. \quad (\text{B10})$$

On this time scale the oscillating terms behave essentially as δ functions and

$$\sum_{\alpha} \frac{\sin(E_{J'\alpha', J\alpha}t)}{E_{J'\alpha', J\alpha}} \approx 2\pi\rho_J(E_{J\alpha} = E_{J'\alpha'}), \quad (\text{B11})$$

where $\rho_J(E)$ is the density of states in the manifold J at energy E . Here the summation over α was replaced by integration, which sets an upper time limit, $t < \hbar\rho$, on the validity of the result. Using (B11), Eq. (B10) leads directly to the result (III. 1) and (III. 2).

This treatment may be extended to the strong coupling situation only by invoking the repeated random phase assumption.^{35,15,17} However the justification for this assumption for an isolated molecule is not clear (repeated randomization is physically associated with random external perturbations as discussed in Sec. II).

APPENDIX C. RANDOM INITIAL PHASES ON THE CONSTANT COUPLING MODEL

Here we show that random initial phases are not a sufficient condition for a subsequent evolution governed

by a Pauli master question. We consider two coupled continuous or quasicontinuous manifolds $\{|l\rangle\}$ and $\{|m\rangle\}$ coupled to each other, so that $V_{lm} = V$, independent of l and m . We assume that at time $t=0$ only $|l\rangle$ states are populated so that $w_{ll}(0) = 0$ for $l \neq l'$ and $\sum_l w_{ll}(0) = 1$. $w(0)$ is the density operator at $t=0$. The Green's function elements for this model are found to be

$$G_{ml}^\dagger(E) = [V/(1+N)]1/(E - E_l + i\eta)(E - E_m + i\eta), \quad (C1)$$

so that for $\psi(t=0) = |l\rangle$ the amplitude for state $|m\rangle$ is

$$\begin{aligned} a_m(t) &= -\frac{1}{2\pi i} \int_{-\infty}^{\infty} \exp(-iEt) G_{ml}^\dagger(E) dE \\ &= \frac{V}{1+N} \frac{\exp(-iE_m t) - \exp(-iE_l t)}{E_m - E_l} \end{aligned}$$

In these equations $N = \pi^2 |V|^2 \rho_l \rho_m$ is the intercontinuum coupling parameter. With the given initial distribution the population of the $\{m\}$ manifold is

$$\begin{aligned} \left\langle \sum_m |a_m(t)|^2 \right\rangle &= \left| \frac{V}{1+N} \right|^2 \\ &\times \sum_l w_{ll}(0) \sum_m \left| \frac{\exp(-iE_m t) - \exp(-iE_l t)}{E_m - E_l} \right|^2, \quad (C3) \end{aligned}$$

where the average is taken over the initial distribution. Assuming that the summation over $\{m\}$ may be calculated as an unbound integral, $\sum_m \rightarrow \int_{-\infty}^{\infty} \rho_m dE_m$, Eq. (C3) leads to $\langle \sum_m |a_m(t)|^2 \rangle = [2/(1+N)^2] 2\pi V^2 \rho t$. In the strong coupling limit $N \gg 1$ the rate for populating the $\{m\}$ manifold is vanishingly small. Thus the $\{l\} \rightarrow \{m\}$ transition is blocked. A similar situation was mentioned in Sec. IV: When $\{l\}$ is populated by an essentially random process, the subsequent transition to $\{m\}$ is blocked if V_{lm} is weakly dependent on the level indices.

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