

## PREPARATION OF METASTABLE MOLECULAR STATES BY OPTICAL EXCITATION

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We explore the implications of Rhodes' "filtering" process for the reduced density operator of excited molecular states demonstrating that the relaxation characteristics of an isolated resonance in the statistical limit are independent of the excitation mode.

The nature of the "initially prepared" optically excited molecular state is crucial for a complete understanding of electronic relaxation processes in polyatomic molecules. Early discussions of this problem [1, 2] treated the radiative excitation process to lowest order and accounted properly for the non-radiative decay occurring during the excitation process. A formulation of the excitation-decay process subjected to this limitation has been provided by considering the time evolution of the molecular states [1] and alternatively by utilizing the time evolution of the density matrix [2, 3]. Rhodes [3] concluded that the decay characteristics in the large molecule limit will be determined by the excitation mode. It was argued by Rhodes [3] that the case of long time broad band excitation of a large statistical molecule "is intermediate between the case of pulse excitation of a pure (non-stationary) state and the small molecular limit". This conclusion contradicts the result of Bixon and Jortner [1] where the decay of an isolated molecular resonance is independent of the excitation mode, and where long time broad band excitation will result in a single exponential decay, which is characterized by the lifetime of the same metastable state prepared by a short pulse excitation. In view of current interest in the nature of molecular excited states produced by optical excitation we shall demonstrate that Rhodes' density matrix approach [3] leads to the original conclusions of Bixon and Jortner [1]. In particular, we shall prove that the "filtering" of the quasicontinuous density matrix which assumes a partially diagonal form for long excitation times [3] is still compatible with a decay pattern that is identical to the one obtained by a pulse excitation with a minimum possible excitation time.

The density operator at the beginning of the experiment may be described by a product

$$\rho = \rho^M \rho^R \quad (1)$$

of the molecular density operator

$$\rho^M = |g\rangle \langle g|, \quad (2)$$

and of the field density operator

$$\rho^R = \sum_n R(n) |n\rangle \langle n|, \quad (3)$$

where  $|g\rangle$  is the molecular ground state,  $n = \{n_k\}$  is the vector of the population numbers in the different modes

and where  $R(n)$  denotes the probability for the field to be in the state  $n$ . Eq. (3) describes  $\rho^R$  in the population number representation. It may be asserted that in this representation the density operator which corresponds to a chaotic radiation source (e.g., thermal source or discharge tube) is diagonal. An equivalent form for  $\rho^R$  is

$$\rho^R = \prod_k \sum_{n_k} R(n_k) |n_k\rangle \langle n_k|, \quad (3a)$$

where  $k$  is the mode index, so that

$$R(n) = R(\{n_k\}) = \prod_k R(n_k). \quad (4)$$

The time evolution of the molecule-field system during the excitation time  $\tau$  is given by

$$\rho(\tau) = U(\tau) \rho U^\dagger(\tau), \quad (5)$$

where the evolution operator  $U(\tau)$  in the lowest order of perturbation theory is

$$U(\tau) = \exp(-i\hbar^{-1}H_0\tau) \left[ 1 - i\hbar^{-1} \int_0^\tau V_1(\tau') d\tau' \right], \quad (6)$$

where

$$H_0 = H^M + H^R \quad (7)$$

is the sum of the molecular and the field hamiltonians and where

$$V_1(t) = \mu_1(t) \cdot \epsilon_1(t) \quad (8)$$

(with the molecular dipole moment  $\mu$  and the electric field  $\epsilon$ ) is the molecule-field coupling in the interaction representation, so that

$$A_1(t) = \exp(i\hbar^{-1}H_0t) A \exp(-i\hbar^{-1}H_0t); \quad A = \mu, \epsilon. \quad (9)$$

Inserting eq. (6) into eq. (5) and making use of eqs. (1)–(4) we obtain\*

$$\begin{aligned} \rho(\tau) &= \hbar^{-2} \exp(-i\hbar^{-1}H_0\tau) \left( \int_0^\tau V_1(\tau') d\tau' \right) \rho \left( \int_0^\tau V_1(\tau') d\tau' \right) \exp(i\hbar^{-1}H_0\tau) \\ &= \hbar^{-2} \int_0^\tau V_1(\tau'-\tau) \left( |g\rangle \langle g| \sum_n R(n) |n\rangle \langle n| \right) \int_0^\tau V_1^\dagger(\tau'-\tau) d\tau' \\ &= \hbar^{-2} \int_0^\tau \int_0^\tau d\tau' d\tau'' [\mu_1(\tau'-\tau) |g\rangle \langle g| \mu_1^\dagger(\tau''-\tau)] [\epsilon_1(\tau'-\tau) \sum_n R(n) |n\rangle \langle n| \epsilon_1^\dagger(\tau''-\tau)]. \end{aligned} \quad (10)$$

\* As we shall be interested only in the matrix elements of  $\rho$  between excited molecular states, we shall consider only this part of  $\rho$  which contributes to such matrix elements. In other words we discard these terms in  $\rho$  which contain  $|g\rangle$  at the left or  $\langle g|$  at the right side of the operator. Note also that from now on we treat one component of the scalar product (8).

As we are not interested in the final states of the radiation field one may consider the reduced density matrix for the molecule which is obtained by taking the trace of  $\rho(\tau)$  relative to the field states, i.e.,

$$\rho^M(\tau) = \hbar^{-2} \int_0^\tau \int_0^\tau d\tau' d\tau'' \mu_1(\tau' - \tau) |g\rangle \langle g| \mu_1^\dagger(\tau'' - \tau) \sum_n R(n) |n\rangle \langle n| \epsilon_1^\dagger(\tau'' - \tau) \epsilon_1(\tau' - \tau) |n\rangle, \quad (11)$$

where we have made use of the closure relation in summing over the final field states. Defining now the (first order) correlation function for the field

$$G(\tau' - \tau'') = \sum_n R(n) \langle n| \epsilon_1^\dagger(\tau'') \epsilon_1(\tau') |n\rangle \quad (12)$$

(which for stationary radiation fields depends only on the difference  $\tau' - \tau''$  of its time arguments), eq. (11) takes the form

$$\rho^M(\tau) = \hbar^{-2} \int_0^\tau \int_0^\tau d\tau' d\tau'' G(\tau' - \tau'') \mu_1(\tau' - \tau) |g\rangle \langle g| \mu_1(\tau'' - \tau). \quad (13)$$

The reduced density matrix  $\rho^M(\tau)$  describes the state of the molecular system after interacting with the radiation field during the time  $\tau$ . If the field is now terminated at this time  $\tau$ , the state of the system at any time  $\tau + t$  after the end of the illumination may be described by\*

$$\begin{aligned} \rho^M(\tau + t) &= \exp(-i\hbar^{-1}H^M t) \rho^M \exp(i\hbar^{-1}H^M t) = \hbar^{-2} \int_0^\tau \int_0^\tau d\tau' d\tau'' G(\tau' - \tau'') \exp[i\hbar^{-1}H^M(\tau' - \tau - t)] \\ &\times \mu |g\rangle \langle g| \mu \exp[-i\hbar^{-1}H^M(\tau'' - \tau - t)] \exp[-i\hbar^{-1}E_g(\tau' - \tau'')] , \end{aligned} \quad (14)$$

where we have utilized eq. (9) for  $\mu_1(t)$ , making use of the fact that  $H^R$  and  $\mu$  commute.

Eq. (14) for  $t = 0$  is mathematically equivalent to eq. (2) of ref. [3], although the present derivation is more pedantic. Following Rhodes [3] we may now recast the matrix elements of  $\rho^M$  in the molecular eigenstates ( $\{\Psi_j\}$ ) representation.

$$\begin{aligned} \rho_{j'j''}^M(t + \tau) &= \hbar^{-2} \langle j' | \mu | g \rangle \langle g | \mu | j'' \rangle \int_0^\tau \int_0^\tau d\tau' d\tau'' G(\tau' - \tau'') \exp[i\hbar^{-1}E_{j'}(\tau' - \tau - t)] \exp[-i\hbar^{-1}E_{j''}(\tau'' - \tau - t)] \\ &\times \exp[-i\hbar^{-1}E_g(\tau' - \tau'')] . \end{aligned} \quad (15)$$

This expression may be further simplified by noting that the field correlation function  $G(\tau' - \tau'')$  is centred around  $\tau' - \tau''$  and characterized by a width which is inversely proportional to the energy width of the exciting band. If this band is wide enough (i.e.,  $\Delta\omega \gg 1/\theta$  where  $\theta$  is a characteristic time for any transition in the excited molecule\*\*), we may replace  $G(\tau' - \tau'')$  by a delta function,

\* We assume that the termination act has no considerable effect on the system. This is expected to be true if the excitation band is wide enough so that it includes all the Fourier components which correspond to this termination act.

\*\* Note that this is a necessary condition also for our ability to terminate the radiation in time short enough to enable us to perform meaningful measurement of the relaxation process.

$$G(\tau' - \tau'') \approx A \delta(\tau' - \tau''),$$

(16)

where  $A$  is a suitable constant. Eq. (15) now results in

$$\rho_{jj'}(t+\tau) = A \hbar^{-2} \int_0^\tau d\tau' F_{jj'}(\tau' - \tau - t),$$

(17)

with

$$F_{jj'}(\tau' - \tau - t) = \langle j|\mu|g\rangle \langle g|\mu|j'\rangle \exp [i\hbar^{-1}(E_j - E_{j'}) (\tau' - \tau - t)].$$

(18)

Performing the  $\tau'$  integration we obtain

$$\rho_{jj'}(t+\tau) = A \hbar^{-2} \mu_{jg} \mu_{gj'} \exp [-i\hbar^{-1}(E_j - E_{j'}) (\frac{1}{2}\tau + t)] \frac{2 \sin [\hbar^{-1}(E_j - E_{j'})\tau]}{\hbar^{-1}(E_j - E_{j'})},$$

(19)

which as  $\tau$  increases, tends to zero for  $\hbar^{-1}(E_j - E_{j'}) > 1/\tau$  whereupon the density matrix assumes a partly diagonal form for long excitation times [3]:

A cursory examination of this feature of the molecular density matrix may lead to the conclusion (which was reached by Rhodes [3]) that the decay features of a large molecule subjected to a long excitation time (relative to its decay rate) will differ in nature from the relaxation characteristics following a short excitation pulse. We shall demonstrate that a proper treatment of the density operator [eqs. (17), (18)] leads to the Bixon-Jortner result [1], so that the decay characteristics of a molecule which corresponds to the statistical limit are not affected by the excitation time.

To extract information concerning the decay pattern from the molecular density matrix it will be helpful to consider the state  $|s\rangle$  which carries all the oscillator strength for transitions to and from the ground state. In the statistical limit  $|s\rangle$  has a simple physical interpretation. In more complicated cases  $|s\rangle$  may still be defined in terms of a suitable linear combination of molecular states [4]. In any case the decay pattern is given by the time dependence of the population of the state  $|s\rangle$  namely

$$I(t+\tau) = B \text{tr} \{ \rho(t+\tau) |s\rangle \langle s| \},$$

(20)

where  $B$  is an appropriate time independent constant. In the case where a definition of a radiative decay rate for the state  $|s\rangle$  is meaningful,  $B$  is just this decay rate. Utilizing eq. (17) we now obtain

$$I(t+\tau) = AB \hbar^{-2} \int_0^\tau d\tau' J(\tau' - \tau - t),$$

(21)

where we have defined

$$J(x) = \sum_j \sum_{j'} \langle j'|s\rangle \langle s|j\rangle F_{jj'}(x) = \sum_j \sum_{j'} \langle j'|s\rangle \langle s|j\rangle \langle j|\mu|g\rangle \langle g|\mu|j'\rangle \exp [i\hbar^{-1}(E_j - E_{j'})x].$$

(22)

Now, if  $|s\rangle$  is the only state (of some complete basis set) which is radiatively coupled to the ground state, we may write

$$\langle j|\mu|g\rangle = \langle j|s\rangle \langle s|\mu|g\rangle,$$

(23)

so that the function  $J(x)$  is determined by the Fourier transform of the line shape function

$$J(x) = |\langle g|\mu|s\rangle|^2 \left| \sum_j |\langle j|s\rangle|^2 \exp(i\hbar^{-1}E_j x) \right|^2 \quad (24)$$

$$= |\langle g|\mu|s\rangle|^2 \left| \int dE_j L(E_j) \exp(i\hbar^{-1}E_j x) \right|^2, \quad (25)$$

where the absorption line shape function (excluding high order radiation corrections) is

$$L(E_j) = \rho(E_j) |\langle j|s\rangle|^2. \quad (26)$$

In the case of a simple lorentzian resonance,

$$L(E_j) = (1/2\pi) \frac{\Gamma_s}{(E_j - \tilde{E}_s)^2 + (\frac{1}{2}\Gamma_s)^2}, \quad (27)$$

where  $\tilde{E}_s$  is the centre of the line profile\* and  $\Gamma_s$  is its width, eq. (26) yields

$$J(x) = |\langle g|\mu|s\rangle|^2 \exp(-\Gamma_s|x|). \quad (28)$$

Inserting this result into eq. (21) we readily obtain

$$\begin{aligned} I(t+\tau) &= \hbar^{-2} AB |\langle g|\mu|s\rangle|^2 \exp[-\Gamma_s(t+\tau)] \int_0^\tau d\tau' \exp(\Gamma_s\tau') \\ &= \hbar^{-2} AB |\langle g|\mu|s\rangle|^2 \{ [1 - \exp(-\Gamma_s\tau)] / \Gamma_s \} \exp(-\Gamma_s t), \end{aligned} \quad (29)$$

which is identical to the result obtained by Jortner and Bixon [1]. The following points are now in order:

(a) Eq. (29) describes the emission intensity from a single molecular resonance which corresponds to the statistical limit at time  $t$  after the termination of an excitation source of duration  $\tau$ , in the approximation which neglects high order radiative terms.

(b) Considering eqs. (19) and (29) we may conclude that a diagonal character of a quasicontinuous density matrix does not contradict the possibility of obtaining a decay pattern identical to what is obtained in the case of a coherent excitation.

(c) It is important to understand that the present formulation does not depend on our ability to "prepare" initially the system in the particular state  $|s\rangle$ . We may note that a formal definition of a state  $|s\rangle$  which carries the entire oscillator strength from the state  $|g\rangle$ , is  $|s\rangle = \mu|g\rangle [\langle g|\mu^2|g\rangle]^{-1/2}$ . Utilizing this formal definition we may replace eq. (20) by an equivalent form

$$I(t+\tau) = (B/\langle g|\mu^2|g\rangle) \text{tr} \{ \rho(t+\tau) \mu|g\rangle\langle g|\mu \}, \quad (30)$$

which subsequently yields eq. (21) where now eq. (22) is replaced by

$$J(x) = [1/\langle g|\mu^2|g\rangle] \left| \sum_j |\langle j|\mu|g\rangle|^2 \exp(i\hbar^{-1}E_j x) \right|^2 = [1/\langle g|\mu^2|g\rangle] \left| \int dE_j \tilde{L}(E_j) \exp(i\hbar^{-1}E_j x) \right|^2, \quad (31)$$

\* In case where a zero order molecular hamiltonian may be defined such that  $H_0^M|s\rangle = E_s|s\rangle$ , we find the line center at some shifted energy  $E_s$ .

where  $\tilde{L}(E_j)$  differs from  $L(E_j)$ , [eq. (26)], only by a constant factor. We see that without referring to a "zero order" state  $|s\rangle$  we obtain  $J(x)$  as essentially the Fourier transform of the line shape function.

(d) We may somewhat generalize the theory to include the main effects of the high order radiative corrections. This has been done in the evolution operator method [2] as well as in the Green's function formulation [4] of the problem. To accomplish this goal we have to invoke the following assumptions:

(1) the initial state of the radiation field is a single photon state (or, rather, a wave packet of single photon states),

(2) during the time in which the radiation field is active, only absorption of photons (and not, for example, emission of virtual photons) is taken into account.

These two assumptions enable us to consider the excited states of the system at the end of the excitation process as accompanied by vacuum states of the field.

Together with these two assumptions we must introduce (as before) the termination of the field phenomenologically (and not inherently via the field spectrum) by assuming that the initial absorption may occur only up to the time  $\tau$

The evolution operator

$$U(\tau+t; 0) = \exp[-i\hbar^{-1}H_0(\tau+t)] \left[ 1 - i\hbar^{-1} \int_0^{\tau+t} d\tau' U(\tau+t; \tau') V_1(\tau') \right] \quad (32)$$

will under these assumptions take the form

$$U(\tau+t; 0) = \exp[-i\hbar^{-1}H_0(\tau+t)] \left[ 1 - i\hbar^{-1} \int_0^{\tau} d\tau' U(\tau+t; \tau') V_1(\tau') \right] \quad (33)$$

As now the state of the radiation field at time  $\tau$  is well defined as the vacuum state, we need not take the trace relative to field states; the correlation function for the field takes the simple form:

$$G(\tau' - \tau'') = \langle i|\epsilon_1^\dagger(\tau'')|0\rangle \langle 0|\epsilon_1(\tau')|i\rangle, \quad (34)$$

where  $|i\rangle$  describes the initial photon wave packet. If this packet is sufficiently wide in energy, we may again approximate  $G(\tau' - \tau'')$  by  $A\delta(\tau' - \tau'')$  as in eq. (16). The states  $\{\Psi_j\}$  introduced in eq. (15) will now be defined as the exact molecule-field wavefunctions [6]. This in turn implies that the lineshape function  $L(E_j)$ , [eq. (26)], will now take the exact form. The isolated resonance case will yield for example an expression of the form (27) in which  $\Gamma_s$  is the sum of radiative and non-radiative contributions. The final result, eq. (29), will be similarly generalized.

(e) A density matrix approach to the present problem is by no means essential. We have chosen to utilize this procedure just for the sake of comparison with previous works [2, 3].

(f) It is interesting to note that long excitation times do not necessarily lead to damping of oscillatory phenomena in the fluorescence decay, which may be encountered in the small molecule case. To demonstrate this fact we start again from eqs. (21) and (24).

$$I(t+\tau) = \hbar^{-2} AB |\langle g|\mu|s\rangle|^2 \int_0^{\tau} d\tau' \left| \int dE L(E) \exp[-i\hbar^{-1}E(\tau+t-\tau')] \right|^2 \quad (35)$$

If  $L(E)$  is not a simple lorentzian but, say, a proper superposition of two resonances, its Fourier transform will contain an oscillating interference term. For example, when the molecular states may be described by two zero order discrete states which interact with each other and with a continuum (for details concerning the model, see ref. [5]) one obtains [5]

$$|\int dEL(E) \exp(-i\hbar^{-1}Ex)|^2 = A \exp(-\gamma_1 x) + B \exp(-\gamma_2 x) + C \operatorname{Re} \exp(-i\hbar^{-1} \Delta E x - \gamma x), \quad (36)$$

where  $\Delta E$  is the energy spacing between the two discrete levels,  $\gamma_1$  and  $\gamma_2$  are decay constants obtained from the diagonalization of the decay matrix [5],  $\gamma = \frac{1}{2}(\gamma_1 + \gamma_2)$ , and  $A$ ,  $B$  and  $C$  are suitable constants. If the excitation has a finite duration we now obtain

$$\begin{aligned} \operatorname{Re} \int_0^\tau d\tau' \exp[-i\hbar^{-1} \Delta E(\tau + t - \tau') - \gamma(\tau + t - \tau')] \\ = \operatorname{Re} \{ \exp[-i\hbar^{-1} \Delta E t - \gamma t] [1 - \exp(-i\hbar^{-1} \Delta E \tau - \gamma \tau)] / [i\hbar^{-1} \Delta E + \gamma] \}. \end{aligned} \quad (37)$$

It is obvious that the oscillatory behaviour is partially retained. Particularly for  $\tau \gg \gamma$  we obtain for the oscillating part of the fluorescence:

$$I(\tau + t) \approx \frac{\exp(-\gamma t)}{(\hbar^{-1} \Delta E)^2 + \gamma^2} [\gamma \cos(\hbar^{-1} \Delta E t) - \hbar^{-1} \Delta E \sin(\hbar^{-1} \Delta E t)], \quad (38)$$

where in the interesting case  $\gamma \approx \hbar^{-1} \Delta E$  both terms will contribute to the decay pattern.

## References

- [1] M. Bixon and J. Jortner, *J. Chem. Phys.* 48 (1968) 715.
- [2] W. Rhodes, *J. Chem. Phys.* 50 (1969) 2885; *J. Chim. Phys.* 67 (1970) 40.
- [3] W. Rhodes, *Chem. Phys. Letters* 11 (1971) 179.
- [4] K.F. Freed and J. Jortner, *J. Chem. Phys.* 50 (1969) 2916;  
A. Nitzan and J. Jortner, *J. Chem. Phys.*, submitted for publication.
- [5] A. Nitzan, J. Jortner and P.M. Rentzepis, *Proc. Roy. Soc.*, to be published;  
A. Nitzan, J. Jortner, J. Kommandeur and E. Drent, *Chem. Phys. Letters* 9 (1971) 273.
- [6] M. Bixon and J. Jortner, *J. Chem. Phys.* 50 (1969) 4061.