

## SEMICLASSICAL SIMULATION OF VIBRONIC PROCESSES

*Arieh Warshel*

Department of Chemistry  
University of Southern California  
Los Angeles, California

*P. Stern and S. Mukamel*

Department of Chemical Physics  
The Weizmann Institute of Science  
Rehovot, Israel

### I. INTRODUCTION

Many theories of vibronic processes are based on using experimental information in analyzing experimental results. Such theories are very powerful in extracting the maximum information content from a given experiment, but this information may not be sufficient to analyze uniquely the given experiment. For example, in most cases one cannot determine what mechanism leads to a given vibronic line broadening, using pure experimental information. In this respect there may be a great benefit in computer simulation approaches which evaluate molecular spectra using realistic molecular models.

Methods for calculating vibronic matrix elements were proposed before<sup>1,2</sup> and gave encouraging results. For example, quantum mechanical calculations of vibronic transition intensity gave reasonable agreement with the corresponding experiments.<sup>2,3</sup> However, approaches which are based on evaluating discrete vibronic transitions do not account properly for the observed line width, either because harmonicity effects are neglected or because time dependent effects are not taken into account.<sup>4</sup> In view of the possible complexity of vibronic relaxation processes it may be preferable to exploit semiclassical approaches in studying large molecules.

In this work we report a preliminary use of a semiclassical trajectory approach for studying different types of vibronic processes. This includes studies of the absorption and emission of substituted benzene and the radiationless transition of individual vibronic levels of porphines.

## II. THEORETICAL APPROACH

Our theoretical approach can be described in different alternative formalisms. The formalism used here is similar to that used in simulating semiclassically cis-trans isomerization reactions<sup>5</sup> and electron transfer processes.<sup>6</sup>

We will use for simplicity a diabatic representation and mention, when needed, the modifications associated with using the adiabatic representation.

Let us consider two diabatic electronic states  $\phi_1$  and  $\phi_2$ , which satisfy the time dependent Schrödinger equation

$$\begin{aligned} H(\underline{x})\phi_1(\underline{x}) &= \varepsilon_1(\underline{x})\phi_1(\underline{x}) + H_{12}(\underline{x})\phi_2(\underline{x}) \\ H(\underline{x})\phi_2(\underline{x}) &= \varepsilon_2(\underline{x})\phi_2(\underline{x}) + H_{12}(\underline{x})\phi_1(\underline{x}) \end{aligned} \quad (1)$$

where  $\varepsilon_1(\underline{x})$  and  $\varepsilon_2(\underline{x})$  are the diabatic energy surfaces of  $\phi_1$  and  $\phi_2$ . The time dependent wave function of the system can be expressed as:

$$\begin{aligned} \psi(\underline{x}, t) &= a_1(t)\phi_1(\underline{x}) \exp\left\{-\frac{i}{\hbar} \int^t \varepsilon_1(t') dt'\right\} \\ &+ a_2(t)\phi_2(\underline{x}) \exp\left\{-\frac{i}{\hbar} \int^t \varepsilon_2(t') dt'\right\} \end{aligned} \quad (2)$$

Substitution of this equation into the time dependent Schrödinger equation

$$H(\underline{x})\psi(\underline{x}, t) = i \hbar \partial \psi(\underline{x}, t) / \partial t, \quad (3)$$

and neglecting  $\partial \phi(\underline{x}) / \partial t$  gives the coupled equations

$$\begin{aligned} \dot{a}_1 &= \frac{i}{\hbar} H_{12} a_2(t) \exp\left\{\frac{i}{\hbar} \int^t \Delta \varepsilon_{21}(t') dt'\right\} \\ \dot{a}_2 &= \frac{i}{\hbar} H_{12} a_1(t) \exp\left\{-\frac{i}{\hbar} \int^t \Delta \varepsilon_{12}(t') dt'\right\} \end{aligned} \quad (4)$$

where  $\Delta \varepsilon_{21} = \varepsilon_2 - \varepsilon_1$ . In the adiabatic representation  $H_{12}$  is zero and  $\partial \phi(\underline{x}) / \partial t$  is not neglected. In this representation eq. (4) is changed in such a way that  $\langle \phi_1 | \partial \phi_2 / \partial t \rangle$  is substituted for  $(H_{12} / \hbar)$ .<sup>6</sup> The semiclassical approximation for eq. (4)

involves substitution of  $\Delta\varepsilon_{21}(t)$  by  $\Delta\varepsilon_{21}(r(t))$  where  $r(t)$  is the coordinate vector of the system along the classical trajectory pathway. The overall probability amplitudes  $a_1^2(t)$  and  $a_2^2(t)$  are obtained by

$$a_1^2(t) = \left| \left\langle \int_1^2 \dot{a}_i(t) dt \right\rangle \right|^2 \quad (5)$$

where the average  $\langle \rangle$  is over the initial conditions for the coordinates and momentum of the trajectory. The integration from 1 to 2 indicates that at points of large values of  $a_2^2$  the trajectory should "hop" from surface 1 to surface 2.<sup>7</sup> However, in this preliminary study we propagate trajectories only on one surface.

Eqs. (4) and (5) can be extended to cases that involve absorption of light by expressing the off diagonal element of the system as the matrix element of the radiation field Hamiltonian.

$$H_{12} = k\mu_{12}e^{-i\omega t} \quad (6)$$

where  $k$  is a constant,  $\mu_{12}$  is the transition dipole and  $\omega$  is the frequency of the radiation field. Eqs. (6), (5), and (4) give, for the initial conditions,  $a_1(0) = 1$ ,  $a_2(0) = 0$ , the transition probability per unit time

$$I(\omega) = \frac{a_2^2(\tau, \omega)}{\tau} = \frac{1}{\tau} \left| \left\langle \int_0^\tau k\mu_{12} \exp\left[-\frac{i}{\hbar} \int_0^t \Delta\varepsilon_{21}(t') dt'\right] \times \exp(-i\omega t) dt \right\rangle \right|^2 \quad (7)$$

This expression involves the Fourier transform of  $a_2(\tau)$  of eq. (5). In fact, one can consider  $I(\omega)$  as the crossing probability for the surfaces  $\varepsilon_1 + \hbar\omega$  and  $\varepsilon_2$ .

It is sometimes useful to express eq. (7) by expanding in a Fourier series at discrete frequencies. This gives

$$a_2^2(\tau, \omega) \approx (k\mu)^2 \left| \left\langle \int \exp\left\{ \sum_s (A_s / \hbar\omega_s) e^{i\omega_s t} \right\} \exp(-i\omega t) \right\rangle \right|^2 \quad (8)$$

where  $A_s$  are the Fourier component of  $\Delta\varepsilon(t)$  and  $\mu$  is approximated by its average value. For small  $A_s$  we obtain (by expanding eq. (8) and retaining only terms of first order in  $A_s$ ) the approximated expression

$$a_2^2(\tau, \omega) \propto \left| \left\langle \int \left[ 1 + \sum_s (A_s / \hbar\omega_s) \exp(i\omega_s t) \right] \exp(-i\omega t) dt \right\rangle \right|^2 \quad (9)$$

Replacing the square integral by a double integral we obtain

$$a_2^2(\tau, \omega) \propto \iint \langle [1 + \sum_s (A_s / \hbar \omega_s) \exp(i\omega_s t)] [1 + \sum_{s'} (A_{s'} / \hbar \omega_{s'}) \exp(i\omega_{s'} t')] \exp(-i\omega(t-t')) \rangle \quad (10)$$

which gives (retaining only  $A_2^2$  terms) the following expression

$$a_2^2(\tau, \omega) \approx \sum_s (A_s / \hbar \omega_s)^2 (\delta(\omega_s - \omega)) + \delta(\omega) \quad (11)$$

Eq. (9) gives peaks of equal intensities for positive and negative  $\omega$ . This corresponds to the high temperature limit (classical limit).<sup>8</sup>  $\omega_s$  corresponds to surface hopping from  $\epsilon_1 + \hbar\omega_0 - k\omega_s$  to  $\epsilon_2$  where  $\omega_0$  is the energy gap between the minima of  $\epsilon_2$  and  $\epsilon_1$ . This surface hopping does not conserve energy and should give small crossing probability in procedures that integrate the actual hopping step in complex time. Indeed in the quantum mechanical case we may use the fluctuation-dissipation theorem and at  $T=0$  we get:

$$a_2^2(\tau, \omega) \propto \sum_{s'} (A_{s'} / \hbar \omega_{s'})^2 (2\delta(\omega_{s'} - \omega)) + \delta(\omega) \quad (12)$$

where  $s'$  runs over the positive  $\omega_{s'}$ .

### III. RESULTS AND DISCUSSION

In order to implement eq. (7) in practical calculations of large molecules one needs the proper potential surfaces. The QCFF/PI potential surfaces<sup>2</sup> can be used for this purpose since they are given in an analytical form that allows for efficient trajectory calculations. The calculations should also involve an average over initial conditions. For a molecule with more than 5 degrees of freedom such an average is not practical at the present time. Instead it is possible to propagate trajectories on the harmonic part of the  $\epsilon_1$  potential surface with initial conditions that satisfy the corresponding quantum mechanical harmonic oscillator. That is, for the ground vibrational state the calculation starts with initial kinetic energy of  $\hbar\omega/2$  and zero potential energy in all normal modes of the system. Such calculations take into account the anharmonicity in  $\Delta\epsilon_{21}$  but the molecular motion is not affected by the anharmonicity in  $\epsilon_1$  (for jet cooled molecules that absorb at the ground vibrational state the anharmonicities in  $\epsilon_1$  can probably be neglected). Alternatively one can run trajectories on the real anaharmonic potential  $\epsilon_1$  with harmonic initial conditions. This, however,

might require extensive averaging over initial conditions for cases with significant energy randomization.

We chose to examine our approach by calculating the vibronic transitions for alkylbenzenes, which were subjected to extensive studies under jet cooled conditions.<sup>9,10</sup> Figure 1 and 2

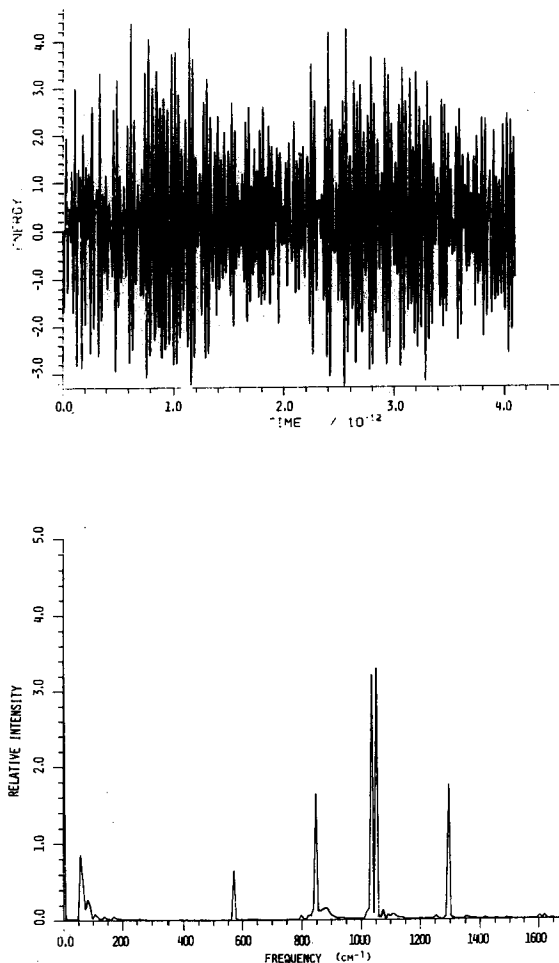


Figure 1. (a) The energy gap,  $\Delta\epsilon_{21}$ , for methylbenzene and, (b) the corresponding  $(A_{\omega}/\omega)^2$  of eq. (11) obtained by a Fourier transform of  $\Delta\epsilon_{21}(t)$ . The Fourier components at  $\omega < 100 \text{ cm}^{-1}$  are set to zero (see text). The calculations were done by propagating a trajectory on the anharmonic ground state of the molecule starting with initial momentum that correspond to  $\hbar\omega_g/2$  in each of the harmonic normal modes of the system.

describe the result of the calculations for methylbenzene and propylbenzene using the approximated expression of eq. (11), which is valid in the harmonic approximation for vibronic transitions with small origin shifts. The calculations were performed by running trajectories with harmonic initial conditions on the anharmonic  $\epsilon_1$ , evaluating the Fourier components of  $\Delta\epsilon_{21}(t)$  by fast Fourier transform and dividing each  $A_S$  by the corresponding

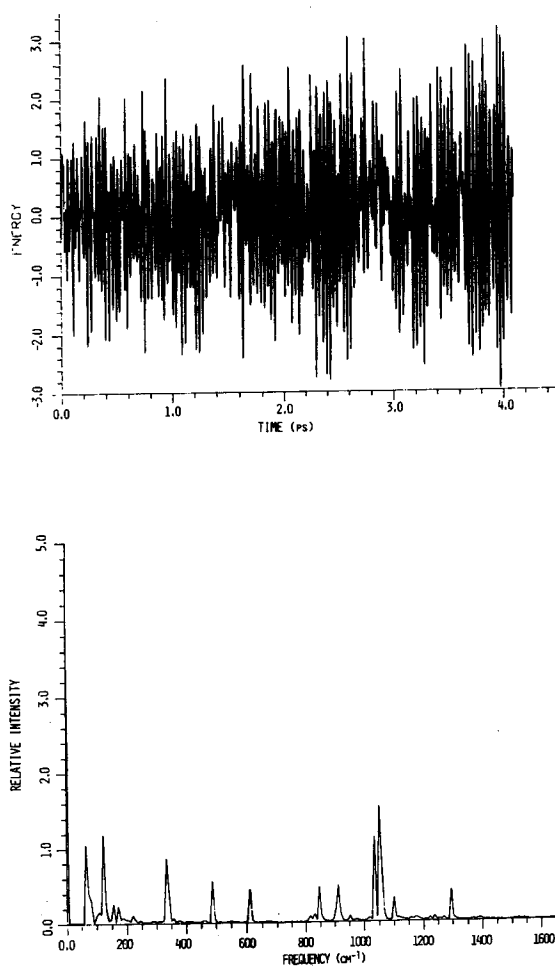


Figure 2. The calculated  $(A_S/\omega_S)$  for propylbenzene obtained in the same way as in Figure 1.

$\omega_s$ . The calculations involved truncation of the Fourier components for  $\omega_s < 100 \text{ cm}^{-1}$ ; in this region Eq. (11) gives a large peak (two orders of magnitude larger than the peaks in the figure). This peak is due to the numerical instability of the  $(A_s/\omega_s)$  function for short time trajectories and to the classical energy transfer between the zero point vibrational levels which will be discussed below.

Figure 3 describes the calculations for methylbenzene obtained by the direct use of eq. (7). Now the calculations do not require any truncation of the peak at  $\omega < 100$ . However, the lines are much broader than the experimentally observed lines. This non-physical broadening is due to both the numerical instability of the integral of  $\Delta\varepsilon(t)$  and to the fundamental problem of semiclassical evaluation of discrete vibronic transitions; the trajectory pathways do not follow a regular orbit (even on the ground vibrational state) but show nonperiodic energy transfer between different normal modes. This point is demonstrated in Figure 4 that describes the time dependent energy redistribution in the ground vibrational state of methylbenzene. The problem of classical preparation of vibrational states might be a major bottleneck in semiclassical calculations of vibronic processes. This problem might be overcome eventually by extensive averaging. At present, however, we recommend performing

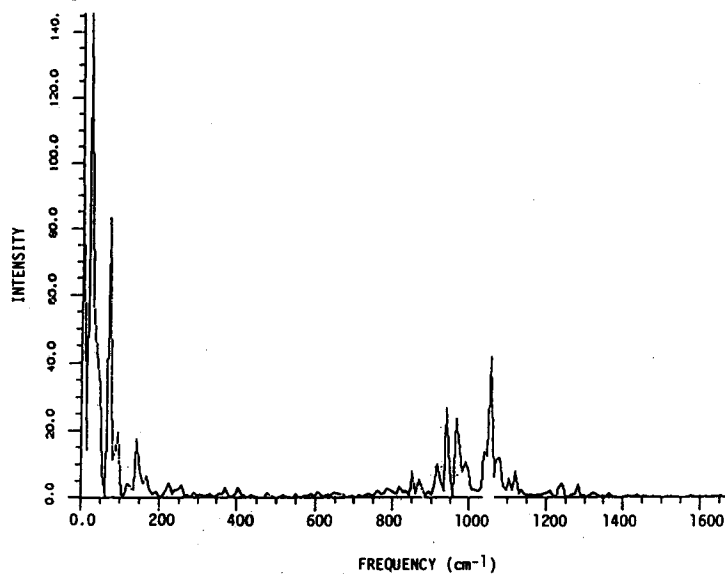


Figure 3. The calculated contribution to the vibronic spectrum of propylbenzene from a single trajectory with the initial conditions given in the caption of Figure 1. The calculations are performed using eq. (7).

absorption calculations propagating trajectories only on the harmonic part of the molecular potential surface or filtering the Fourier components at  $\omega_s < 100 \text{ cm}^{-1}$ .

As was shown above, it is not clear how to prepare a classical vibrational state on an anharmonic potential surface, yet,

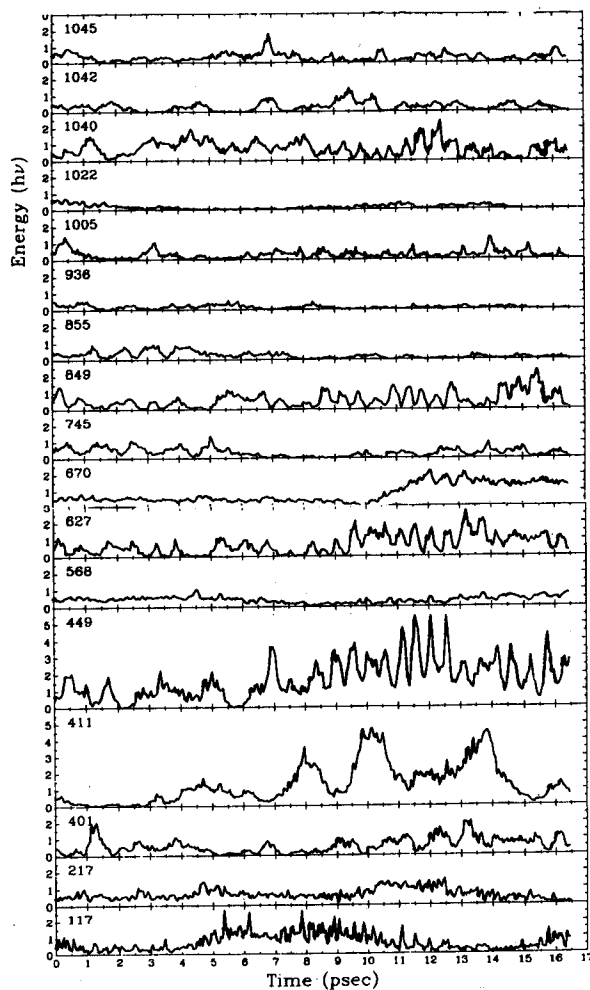


Figure 4. Energy redistribution within the vibrational ground state of methylbenzene. The figure gives the energy content of each of the harmonic normal modes of the molecule along a trajectory that moves on the anharmonic potential surface with the initial conditions of Fig. 1. The figure demonstrates the non periodic nature of the molecular trajectories.



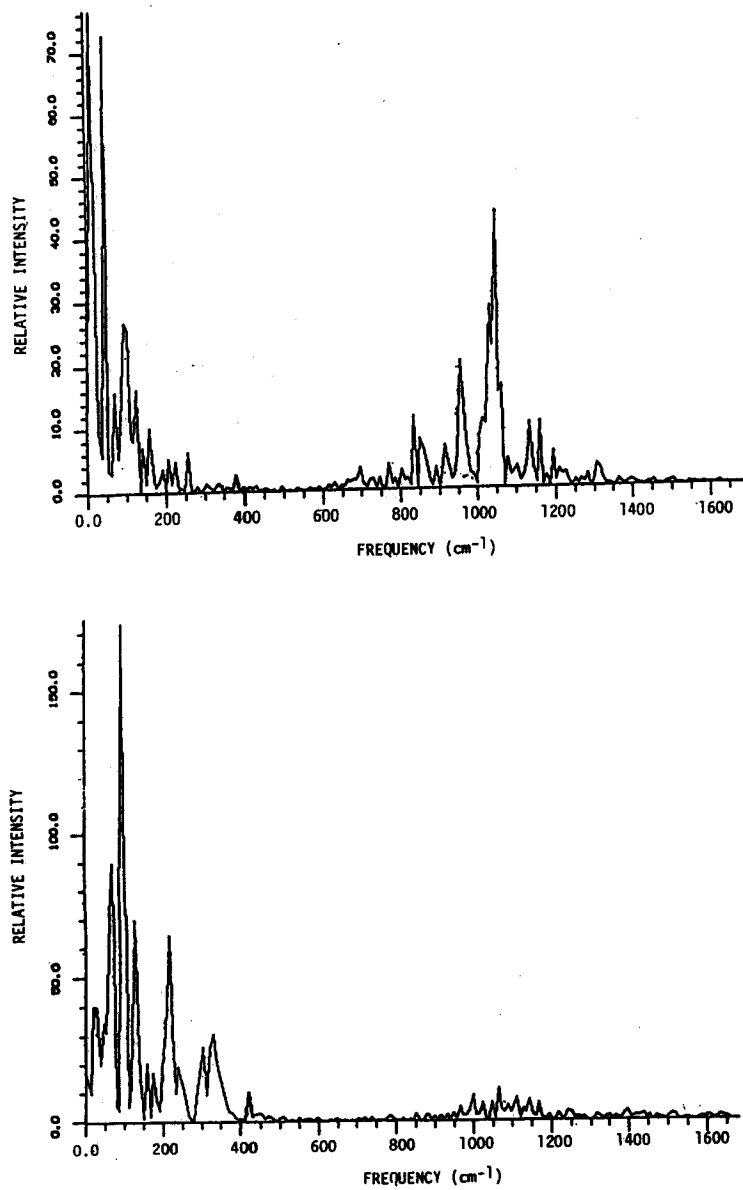


Figure 5. Calculated contribution to the fluorescence of propylbenzene (using eq. (7)) from a single trajectory which starts with  $\hbar\omega_s/2$  for all harmonic modes except  $\omega_{12}$  which was prepared with  $3\hbar\omega_s/2$ . (a) Calculated for the first 4 picoseconds. (b) Calculated for the time between 12 and 16 picoseconds.

one can use trajectory calculations to explore intramolecular vibrational relaxation in excited electronic states. That is, one can simulate experiments where single vibronic levels are excited by running trajectories with the corresponding harmonic initial conditions on the anharmonic electronic potential surface. Such simulations are expected to provide meaningful results only if the energy transfer between zero point vibrations is much slower than the relaxation process under study. In this work we made a preliminary attempt to study the broadening of the fluorescence spectrum of propylbenzene which is prepared by exciting a single vibronic line.<sup>10</sup> The calculations are summarized in Fig. 5 and indicate that the observed broadening may be due to time dependent intramolecular energy transfer from the excited mode to many other modes. Unfortunately, this result cannot in any way be considered conclusive since the transfer between zero point vibrational states (evaluated for trajectory with initial conditions of  $\hbar\omega_s/2$  for all modes) is as fast as the overall relaxation, making it impossible to judge if we have a real relaxation process. Obviously, this fundamental question requires much further studies.

The semiclassical trajectory approach provides a very powerful tool for studying radiationless transitions. That is, eq. (5) gives the probability for non radiative surface crossing between  $\epsilon_1$  and  $\epsilon_2$ . Previous studies with this approach<sup>5,6</sup> did not consider selective preparation in a specific vibronic state. In view of recent advances in preparing isolated excited vibronic states of large molecules and estimating their lifetime we have started preliminary studies of radiationless transitions from excited vibronic states of porphines. This study will be reported elsewhere.<sup>11</sup>

## REFERENCES

1. Albrecht, A.C. *J. Phys. Chem.* 33, 169 (1960).
2. Warshel, A. in *Modern Theoretical Chemistry*, Ed. G. Segal, Vol. 7, Plenum Press, New York, 1971.
3. Warshel, A. and Dauber, P. *J. Chem. Phys.* 66, 5477 (1977).
4. Warshel, A. and Karplus, M. *Chem. Phys. Letters*, 17, 7 (1972).
5. Warshel, A. and Karplus, M. *Chem. Phys. Letters*, 32, 11 (1975).
6. Warshel, A. *J. Phys. Chem.* 86, 2218 (1982).
7. Miller, W.H. and George, T.F. *J. Chem. Phys.* 56, 5637 (1972).
8. Mukamel, S. *J. Chem. Phys.* 77, 173 (1982).
9. Hopkins, J.B., Powers, D.E., Mukamel, S. and Smalley, R.E. *J. Chem. Phys.* 72, 5049 (1980).

10. (a) Mukamel, S. and Smalley, R.S. *J. Chem. Phys.* 73, 4156 (1980).  
(b) Mukamel, S. in *Relaxation of Elementary Excitation*, Ed. R. Kubo and E. Hunamuro, Springer Verlag Ber. (1980), p. 220.
11. Warshel, A. and Sharon, R., to be published.