STOCHASTIC APPROACH TO MULTIPHOTON MOLECULAR PROCESSES

Shaul Mukamel

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

One of the major problems in the description of the interaction of strong laser beams with large molecules is the lack of detailed information about the level structure and dynamical behavior of highly excited molecules. The interactions between the dense excited molecular levels may have a strong influence on the nature of the absorption (i.e. may turn it from a coherent to an incoherent driving) and thus change completely the multiphoton lineshape. A possible way for incorporating these interactions is by introducing a relaxation matrix (related to level-attenuation T_1 and dephazing T_2 processes) into a generalized N-level Bloch equation. Using this approach it is possible to describe a smooth transition between a coherent driving and a completely incoherent driving ($T_2 \to 0$) in which the N^2 Bloch equations may be reduced to N rate equations for the populations. A basic assumption underlying this approach is that the relaxation (T_1 and T_2) arise due to interactions with a bath having a very short correlation time (Markov on impact approximation). This assumption regarding time-scale separation may be valid for very highly excited molecules where the density of states is extremely large but need not hold for moderate excitation energies where intramolecular relaxation and correlation times can have a time scale comparable to the radiative processes.

We propose a method for incorporating the many-body (multi-mode) effects on the multiphoton absorption process without invoking the impact approximation. Our assumptions are:

(1) We consider a large molecule interacting with a strong electromagnetic field with frequency ω_L.

(2) We choose a "primary" set of levels which are radiatively near resonantly coupled with the driving field (e.g. A single molecular mode).

(3) The rest of the states ("secondary") (which do not interact with the field) are perturbing the primary levels. These perturbations are expected to increase the more energy is absorbed by the molecule.

(4) Kubo stochastic line-shape approach[1] is used to derive equations of motion for operators associated with the primary levels (or the density matrix of the primary levels). This approach has been recently successfully applied for 2-photon processes (resonance fluorescence and Raman) by Kubo and coworkers and is expected to hold as well for multiphoton processes provided we invoke a non-perturbative treatment for the radiation field.

As a simple illustrative example, consider a "primary" harmonic oscillator with frequency ω_0, being driven by an external field exerting a force $V = V_0 \exp(-i\omega_L t)$. The many-body effects are introduced by assuming the oscillator frequency to be a Gaussian random process with variance Δ and correlation time $\tau_c = \Gamma^{-1}$, i.e. we assume:

$$\langle(\omega_0(0) - \omega_L)(\omega_0(t) - \omega_L)\rangle = \overline{\omega}^2 + \Delta^2 \exp(-\Gamma t)$$

The equations of motion for $\langle a \rangle$ and $\langle a^+ a \rangle$ (where a and a^+ are the anthilation and creation operators for the oscillator and $\langle \ldots \rangle$ denotes a trace) can be integrated using Kubo formalism resulting in the

following expression for the rate of energy absorption from the field:

$$\frac{d<E(t)>}{dt} = 2V_o^2 \int_o^t d\tau \cos(\omega_L-\omega_o)\tau \exp[-\frac{\Delta^2}{\Gamma^2}(\exp(-\Gamma\tau) - 1 + \Gamma\tau)] \qquad (1)$$

From Eq. (1) we see the following: (1) In the fast modualation (motional narrowing) limit ($\Gamma >> \Delta$) we have

$$\frac{d<E>}{dt} \xrightarrow{t \to \infty} 2V_o^2 \frac{\Delta^2/\Gamma}{\bar{\omega}^2 + (\Delta^2/\Gamma)^2} \qquad (2)$$

This limit corresponds to a short correlation time of the bath and Eq. (2) could have been obtained by phenomenologically adding transverse relation term $T_2^{-1} = \Delta^2/\Gamma$ into the equation of motion of <a>.
(2) In the slow modulation limit ($\Delta >> \Gamma$) we have:

$$\frac{d<E>}{dt} \xrightarrow{t \to \infty} 2V_o^2 \sqrt{\frac{2\pi}{\Delta^2}} \exp[-\bar{\omega}^2/2\Delta^2] \qquad (3)$$

Eq. (1) thus allows the calculation of the multiphoton spectrum without invoking the impact limit.

For a general N level primary system we write equation of motion of the form:

$$\frac{d\rho}{dt} = -i <L(t)>\rho \qquad (4)$$

where ρ is the primary density matrix and $<L(t)>$ is an effective primary Liouvillian averaged over the stochastic part. Assuming the energy of the j'th level to be a Gaussian process with variance Δ_j and correlation time Γ_j^{-1} then we have

$$<L(t)> = <L(o)> -i \int_o^t d\tau <L(t)\, L(\tau)> \qquad (5)$$

Eq. (4) is reduced to a generalized Bloch equation in the narrowing limit (same as for the driven Browian oscillator) but may be useful for real molecular systems with arbitrary intramolecular time scale. The simplest way for solving Eq. (4) is by assuming that Δ_j and Γ_j correspond to a stationary Gaussian process. However, the formalism can be elaborated further by introducing a mechanism for energy transfer between the primary and secondary levels and take Δ_j and Γ_j to be a function of the energy in the secondary states. The resulting nonlinear equations may be useful for the interpretation of multiphoton processes and models for Δ_j and Γ_j are being examined.

(1) R. Kubo in Fluctuation relaxation and resonance in magnetic systems D. Ter Haar ed. Oliver and Boyd Edinburgh (1962).

I am grateful to Professor J. Ross and Professor I. Oppenheim for stimulating discussions.