

# Simplified models for vibrational energy transfer in proteins

Steven J. Lade<sup>\*</sup>, Yuri S. Kivshar

*Nonlinear Physics Center, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia*

Received 24 April 2007; received in revised form 8 August 2007; accepted 15 August 2007

Available online 14 September 2007

Communicated by C.R. Doering

## Abstract

We consider the transfer of vibrational energy in proteins and derive a simplified model for the resonant energy exchange between different vibrational modes. We use the parameters of an earlier study [K. Moritsugu, et al., *Phys. Rev. Lett.* 85 (2000) 3970] to compare our predictions with the results of the molecular dynamics simulations, and reveal an excellent agreement.

© 2007 Elsevier B.V. All rights reserved.

PACS: 87.14.Ee; 87.15.Aa; 05.45.Xt

Keywords: Proteins; myoglobin; Parametric resonance; Vibrational energy transfer; Nonlinear dynamics

## 1. Introduction

The study of energy transfer in excited polymer molecules is central for a deeper understanding of chemical and molecular dynamics, and has a long history [1,2]. It is well established that a protein molecule is likewise a complex system characterised by highly anharmonic dynamics [3]. Most current studies of the nonlinear dynamics of proteins and other macromolecular structures are computational, but serious limitations remain for the study of large-scale dynamics on timescales beyond nanoseconds, especially for large macromolecules. Therefore, novel approaches for analysing the dynamics of such complex nonlinear structures, sometimes based on the methods developed in other fields, may allow a deeper understanding of the complex dynamics occurring in such multi-particle structures.

Recently, Moritsugu et al. [4] studied the intramolecular transfer of vibrational energy in myoglobin. Specifically, they investigated the transfer of energy from one excited mode, one with a frequency in the same range as that excited by the photodissociation of a CO ligand from the heme group, to several

other modes. They found that the vibrational energy is transferred from a given normal mode to very few other modes, the modes selected by the relations between their frequencies. Repeating the molecular dynamics simulation with just these few modes, the results stayed the same, confirming that only these modes were important for the initial dynamics.

Tanaka et al. [5] performed a similar numerical study of the vibrational energy transfer in a third-generation aryl ether azodendrimer and an azobenzene. As well as identifying the corresponding mode selections, they observed that the vibrational energy relaxation does not occur homogeneously with time, but rapidly once a threshold has passed, and that the relaxation time for the resonant energy transfer is sensitively dependent on the magnitude of the excitation given initially.

The phenomenon of resonant energy transfer through coupled modes occurs in many fields of physics. One such well-known field is nonlinear optics [6], where the quadratic nonlinear response of a nonlinear medium governs many types of parametric wave interactions. In this Letter, we show how to employ this analogy and derive a system of coupled-mode equations for slowly varying envelopes of the vibrational modes which describes, with good accuracy, the dynamics of the resonant energy exchange between the macromolecular excitations. As we demonstrate below, this provides a natural link from many vibrational energy transfer processes to the problems of

<sup>\*</sup> Corresponding author.

E-mail address: [steven.lade@anu.edu.au](mailto:steven.lade@anu.edu.au) (S.J. Lade).

resonant parametric interaction between different harmonics in nonlinear optics.

Similar selection rules to those we will derive occur frequently in quantum mechanics, through conservation of energy  $E = \hbar\omega$ . In molecular dynamics, frequency selection rules—whether classical or quantum in origin—are often called ‘Fermi resonances’, after Fermi’s 2 : 1 rule for vibrations in carbon dioxide [7], a name sometimes conflated with Fermi’s Golden Rule [8] for first-order transition rates in quantum mechanics. We wish to emphasise that the energy transfer and frequency selection processes described in this Letter are purely classical. Quantum-mechanical approaches, for example that by Fujisaki [9], where computationally feasible, may yield more accurate results.

## 2. Model

We follow Moritsugu et al. [4] and consider the multi-particle system described by the effective Lagrangian

$$L = \sum_{j=1}^N \frac{1}{2} \dot{q}_j^2 - \sum_{j=1}^N \frac{1}{2} \omega_j^2 q_j^2 - \alpha q_1 q_2 q_3 - \beta q_1^2 q_4, \quad (1)$$

where  $q_i$  is the amplitude of the  $i$ th normal mode with frequency  $\omega_i$  and the overdot denotes the time derivative. The modes interact through third-order coupling. We model four normal modes,  $i = 1, \dots, 4$ , and include both types of third-order coupling between them: modes 1, 2 and 3 interact with what we shall call type 1 coupling, with coupling strength  $\alpha(\omega_1, \omega_2, \omega_3)$ , while modes 1 and 4 interact through type 2 with strength  $\beta(\omega_1, \omega_4)$ .

The Lagrangian (1) yields the effective equations of motion

$$\begin{aligned} \ddot{q}_1 &= -\omega_1^2 q_1 - \alpha q_2 q_3 - 2\beta q_1 q_4, \\ \ddot{q}_2 &= -\omega_2^2 q_2 - \alpha q_1 q_3, \\ \ddot{q}_3 &= -\omega_3^2 q_3 - \alpha q_1 q_2, \\ \ddot{q}_4 &= -\omega_4^2 q_4 - \beta q_1^2. \end{aligned}$$

Each of these equations has the form

$$\ddot{q}_j + \omega_j^2 q_j = f_j(q_1, q_2, q_3, q_4),$$

where  $f_j$  describes a weak coupling between the modes. Introducing the complex amplitudes  $\psi_j(t)$  such that  $q_j(t) = \psi_j(t)e^{i\omega_j t} + \text{c.c.}$ , we obtain

$$2i\dot{\psi}_j \omega_j e^{i\omega_j t} - 2\psi_j^* i\omega_j e^{-i\omega_j t} = f_j,$$

where it is assumed that  $\psi_j(t)$  varies slowly. Multiplying by  $e^{-i\omega_j t}$  and integrating over one period  $T_j = 2\pi/\omega_j$  gives

$$\dot{\psi}_j(t) = \frac{-i}{2\omega_j T_j} \int_t^{t+T_j} f_j e^{-i\omega_j t} dt.$$

The integrand in this equation is where mode selection is enforced. Only those combinations of coupling terms  $f_j$  which give an integrand near to constant will contribute significantly to  $\dot{\psi}(t)$ . This will occur for  $\omega_1 - \omega_2 - \omega_3 \equiv \Delta_\alpha \sim 0$  or

$2\omega_1 - \omega_4 \equiv \Delta_\beta \sim 0$ . There exist other possible frequency orderings for the type 1 coupling; we choose this one to match Moritsugu et al. [4]. There are also many possible pairs of  $\omega_2$  and  $\omega_3$ , but the coupling coefficients determine the dominant pair.

Assuming that  $\Delta_\alpha$  and  $\Delta_\beta \ll \omega_{1,2,3,4}$ , we obtain

$$\begin{aligned} \dot{\psi}_1 &= (i\alpha/2\omega_1)\psi_2\psi_3 \exp(-i\Delta_\alpha t) \\ &\quad + (2i\beta/2\omega_1)\psi_1^*\psi_4 \exp(-i\Delta_\beta t), \\ \dot{\psi}_2 &= (i\alpha/2\omega_2)\psi_1\psi_3^* \exp(i\Delta_\alpha t), \\ \dot{\psi}_3 &= (i\alpha/2\omega_3)\psi_1\psi_2^* \exp(i\Delta_\alpha t), \\ \dot{\psi}_4 &= (i\beta/2\omega_4)\psi_1^2 \exp(i\Delta_\beta t). \end{aligned} \quad (2)$$

Writing each complex amplitude as  $\psi_j \equiv A_j \exp(i\Phi_j)$ , it is then straightforward to obtain an integrable set of equations for the four mode amplitudes  $A_j$  and the two relative phases  $\Phi_A \equiv \Phi_1 - \Phi_2 - \Phi_3 + \Delta_\alpha t$  and  $\Phi_B \equiv \Phi_4 - 2\Phi_1 - \Delta_\beta t$ . The energy in each mode is given by  $E_j = \frac{1}{2}(\omega_j^2 q_j^2 + \dot{q}_j^2) = 2\omega_j^2 |\psi_j|^2$ .

The assumption of weak coupling is most accurate at low temperatures. At higher temperatures, there is an increased probability of transitions to different conformations; this is outside the scope of the present investigation.

## 3. Results and discussions

In their analysis, Moritsugu et al. [4] introduced a system of model oscillators based on a Lagrangian similar to Eq. (1). They modeled the resonant modes with frequencies  $\omega_1 = 5.385$ ,  $\omega_2 = 2.362$ ,  $\omega_3 = 3.024$  and  $\omega_4 = 10.779$ , and with coupling  $\alpha = -0.13$  and  $\beta = 0.12$ . Using these parameters, we solve numerically the system of amplitude equations (2). Mode 1 is assigned an initial energy of 0.5, to match Moritsugu et al.’s own model simulations. The three other modes are assigned initial energies of  $4.5 \times 10^{-5}$  each. Negative amplitudes are permitted, being interpreted as a  $\pi$  phase shift. The initial phases are  $\Phi_A(0) = \Phi_B(0) = 0$ . Fig. 1 shows our numerical results overlaid on the same figure as the molecular dynamics simulation of Moritsugu et al. The match is excellent.

The formalism employed for deriving Eqs. (2) is almost identical to that for the study of parametric processes in optics [6]. In particular, our type 1 interaction produces a resonant interaction like sum-frequency generation, except in reverse: the summed frequency here transfers energy to its two summands. Our type 2 interaction is analogous to optical second-harmonic generation.

The excellent match in Fig. 1 illustrates that accurate simulation of the initial dynamics is possible without resorting to the full molecular dynamics simulations, provided the normal modes and their coupling coefficients have been identified, and that the protein remains in the same conformational substate, such as at low temperature.

The simple form of the model permits some conclusions of a general nature. For example, from the present model, the re-

Download English Version:

<https://daneshyari.com/en/article/1861670>

Download Persian Version:

<https://daneshyari.com/article/1861670>

[Daneshyari.com](https://daneshyari.com)