THE WEAKLY COUPLED ROTOR-MORSE OSCILLATOR SYSTEM:A TOY MODEL FOR SELECTIVE CHEMICAL DISSOCIATION.

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In his famous pioneering work published in 1940, Hendrik Kramers understood chemical reactions, as the climbing of an energy barrier between two energy wells in a large configuration space where the first well represents the state of the reactant molecules and the second well those of the product molecules. In standard theories, chemical reactions are still essentially governed by the thermal (Brownian) motion in a potential of a point defined by the reaction coordinates which represents the configuration of the whole system. Many detailed investigations have been performed during the last decades for specific chemical reactions where energy landscape, basin and saddle point in energy (transition states) were accurately calculated.

However, these models assume that the diffusion process in the phase space is incoherent and ignore possible coherent phenomena which could bias the reaction process. Actually, numerous studies show that the polyatomic molecules seen as a set of non-linear coupled oscillators is not an ergodic system, but instead, they form a mixed phase space with regular and chaotic regions [1,2]. Particularly, it is now well-known that spontaneous energy localization may occur in complex molecular systems. Transitions from normal modes (extended motions) to local modes were first observed spectroscopically in molecules. These local modes in finite size systems are known to exist as well in infinite discrete and nonlinear lattices [3,4]. They appear as localized oscillations with large amplitudes well above the thermal noise and may persist out of thermal equilibrium over unexpected long life time. Their existence requires both the discreteness and the nonlinearity of the system but does not require its spatial periodicity. Many open problems concern DNA transcription through bubble opening, protein folding and biological machines which involve bond breaking/formation with a high degree of selectivity and specificity in conformational changes. Energy localisation phenomena could play an essential role in these processes.

There are several major problems to understand before practical application to those complex systems. How such localized energy packet could be spontaneously created and how it could be transported selectively from one place to another without being spread out thus favouring specific

reactions? Assuming that a local mode has been already produced by another mechanism (for example energy has been released at a specific location by ATP), our aim is to show on a simple toy model that then a coherent energy transfer may occur spontaneously at a selected site and induce a chemical reaction.

Local modes in complex system may be viewed as (almost) isolated nonlinear oscillators, the frequency of which depends on their amplitude. Their stability require in principle that they are nonresonant with the normal modes of the system but nevertheless coherent energy transport requires (special) resonances. Indeed, when two resonant harmonic oscillators are weakly coupled, it is well-known that any amount of energy injected on the first one is completely transferred to the second one after it is completely transferred (and subsequently oscillates back and forth). In contrast, such resonant energy transfer generally cannot occur for two weakly coupled anharmonic oscillators because the frequencies of these oscillators do not remain equal during the whole transfer. However, there are special situations where the anharmonic oscillators are well tuned one with each other (and are said to be conjugated). Beside the condition of linear resonance at the initial time, a precise condition is required on the nonlinearity [5]. Then, when a selected amount of energy is injected on the first one, this energy is completely transferred to the second one after some time while the frequencies of the two nonlinear oscillators both vary but persistently remain equal. We called this phenomena Targeted Energy Transfer (TET**).**

Applying our theory, we have shown that such a situation is met when a rotor chosen with an appropriate inertia momentum and an appropriate angular momentum is weakly coupled with a Morse oscillator [6]. TET trajectories of this nonintegrable model can be analytically calculated with a very good accuracy. Numerical simulations shown fig1 confirms that when the TET conditions are fulfilled, there is initially almost complete energy transfer according to the theory, but in addition due to the nonintegrability of the model, this energy transfer is followed by transient chaotic oscillations which rapidly ends by the ejection of the particle in the Morse potential at infinity. Considering this potential is those of a chemical bond, we thus obtain a selective chemical dissociation. Selectivity in energy appears fig.2 which shows the maximum energy transfered as a function of the initial velocity of the rotor. Only when the appropriate initial energy is selected, energy transfer is substantial and sufficient to induce chemical dissociation. Moreover, no chemical dissociation occurs when the rotor is not conjugate with the Morse oscillator.

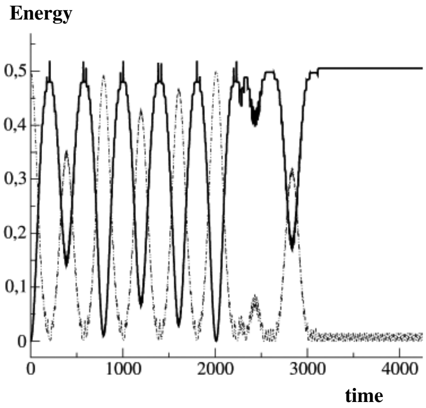

Figure 1. Energy of the Rotor (dot-dashed line) and of the Morse oscillator (full line) versus time when the oscillator is appropriately tuned for TET. After a chaotic transient, the particle is ejected with a nonzero velocity (and proved to never return)

Surely, this model suffers of many flaws and would need improvements for application to real systems. The main criticism is that it discards the dense set of resonances with the normal modes which could be expected from the surrounding environment. However, as noted above, if the nonlinearities of all the normal modes are not well-tuned (i.e. are nonconjugate with the rotor), they could be simply considered as a phonon bath generating a damping term in the dynamical equations of the system. We plan in the future to generalize the tuning conditions for TET in presence of damping and then to show that selective energy transfer and chemical dissociation may then persist in that case.

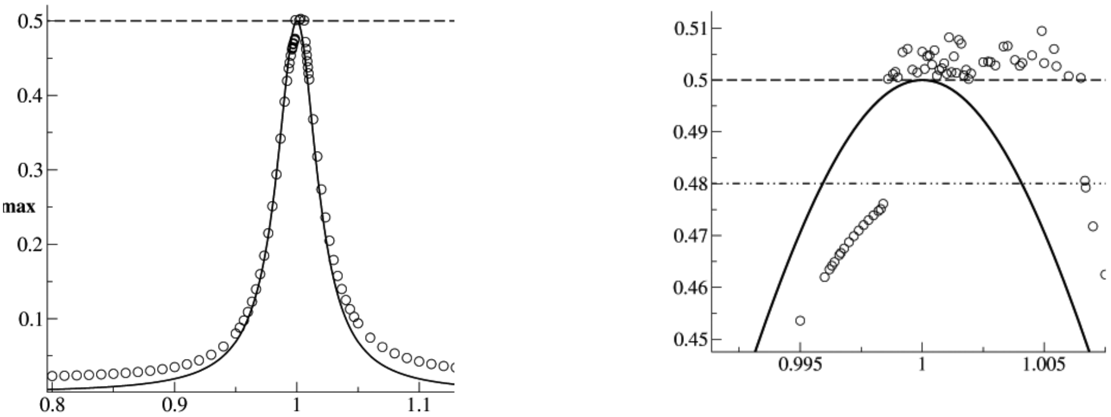

Figure 2. Comparison of the theoretical curve (full line) and the numerical results (open dots) of the maximum energy transferred to the Morse oscillator as a function of the initial velocity of the rotor(left) and magnification of the tip of the peak (right).Chemical dissociation occurs in the narrow interval where the transferred energy becomes larger than ½
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In summary, this toy model demonstrates the possibility to produce highly selective chemical reactions which do not obey to the standard theory of (incoherent) thermally activated process. We believe more generally that essential and highly specific reactions in biosystems could be triggered by a fine molecular machinery based on similar coherent energy transfers between specific local modes.

References

[1] http://tccc.iesl.forth.gr/cecam2004/cecam2004.html ; H. Ishikawa, R. W. Field, S. C. Farantos, M. Joyeux, J. Koput, C. Beck and R. Schinke, Ann. Rev. Phys. Chit.**50**, 443 (1999)
[2] M. Joyeux, S.C. Farantos and R. Schinke, J. Phys. Chem. A**106** 5407 (2002).
[3] S. Aubry, Physica **103D**, 201 (1997)
[4] S. Flach and C. R. Willis, Phys. Rep.**295**, 181 (1998)
[5] AKMT01 S. Aubry, G. Kopidakis, A-M. Morgante and G. Tsironis, Physica **B296** (2001), 222-236
[6] A. Memboeuf and S. Aubry, preprint submitted to Physica D (2004)