# DYNAMICS OF FORCED COUPLED OSCILLATORS: CLASSICAL PHENOMENOLOGY OF INFRARED MULTIPHOTON ABSORPTION

Ramakrishna Ramaswamy and R. A. Marcus

Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

## ABSTRACT

The classical mechanics of a system of two nonlinearly coupled oscillators of incommensurate frequencies driven by an oscillating electric field are studied. The presence of quasi-periodic and chaotic motion in the unforced system is shown to influence the nature of energy absorption. Two essentially different types of behavior are observed. In the first, energy is exchanged in a periodic manner between the system and the forcing field. The exact results are compared with perturbative analysis (based on Lie-transform techniques) employed in this regime. In the second regime, the energy exchange is erratic and a statistical analysis of a family of trajectories shows the role of the chaotic motion in the unforced system in the dissociation process. The results of the theory are compared with those obtained from an ensemble of exact classical trajectories and found to be in reasonable agreement.

## INTRODUCTION

The phenomenon of multiphoton absorption in molecules has been intensively studied in the past few years.[1,2] Several theoretical models[3,4,5] have been proposed for the treatment of this problem. One prevalent qualitative scheme is based on the separation of molecular eigenstates into sets of discrete, quasi-continuous and continuous levels with coherent absorption of energy in the discrete set, and incoherent absorption by the quasi-continuum and continuum, followed by dissociation.

Of interest to such studies is the classical phenomenology of (forced) driven molecular systems and the nature of mode-mode

energy transfer in facilitating dissociation. As an initial approach, we have studied[5] a system of nonlinearly coupled oscillators under the influence of an external field coupled to only one of the degrees of freedom. In essence, this resembles a simplified molecule interacting with a laser field.

In the first section we describe the classical Hamiltonian and some features of the autonomous and of the forced system dynamics, for a system without a zeroth order internal resonance. (For such nonlinear systems, exact analytic results are usually not possible; there is, however, the well-known KAM theorem[6] regarding the stability of motion under perturbations for both the autonomous and non-autonomous cases.) An approximate analytic and statistical theory is presented in the next section, followed by numerical results from trajectories and comparison with theory. A concluding discussion is given in the final section. The present symposium paper is an abbreviated version of a more detailed presentation given elsewhere.[5]

## THE CLASSICAL HAMILTONIAN

### Autonomous System

The Hamiltonian of the unforced coupled oscillator system investigated is

$$H' = \tfrac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) + \lambda x(y^2 + \eta x^2) \qquad (1.1)$$

where $(x,p_x,\omega_x)$ and $(y,p_y,\omega_y)$ denote the coordinate, momentum and zeroth-order frequency, respectively. The values of parameters chosen here are $\omega_x = 1.3$, $\omega_y = 0.7$, $\lambda = 0.1$, $\eta = -1$; this type of Hamiltonian has often been used in the nonlinear dynamics literature, and the parameters for the potential energy surface are similar to those used in Ref. 7, although the larger value of $\eta$ here corresponds to a higher anharmonicity than that used previously.[7b] The three saddle points for the dissociation channels are located at $(x,y) = (5.63,0)$ and $(-2.45, \pm 7.71)$ with a minimum dissociation energy of $E = 6.54$ units (at the last two points).

It is well known that the dynamics of the Hamiltonian H' has a rich structure associated with it.[7a] The trajectories are either quasi-periodic in time or "chaotic". The basic difference between these two types of motion is that the former trajectories are confined to a torus in phase space while the latter are not. This difference is easily characterized by the Poincaré surfaces-of-section,[7] which for the former type are smooth curves, while for the latter they are a seemingly random set of points.

It has become convenient in the discussion of such systems to describe a critical energy[8] $E_c$ above which most initial conditions lead to chaotic type trajectories. From the surfaces-of-section for the motion,[5] one can extract the relative fraction of phase space that leads to chaotic motion, by measuring the relative area not covered by smooth curves. This is shown in Fig. 1.

The Nonautonomous (Forced) System

The interaction with the driving term is chosen to occur through the y-degree of freedom, giving the total Hamiltonian,

$$H = H' - F\, y \cos \omega t \tag{1.2}$$

Here the driving frequency $\omega$ is equal to $\omega_y$.
Hamilton's equations obtained from (1.1) are

$$\begin{aligned} \dot{x} &= p_x, \quad \dot{y} = p_y \\ \dot{p}_x &= (\omega_x^2\, x + \lambda y^2 + 3\lambda\eta x^2) \\ \dot{p}_y &= -(\omega_y^2 y + 2\lambda x y) + F \cos \omega t \end{aligned} \tag{1.3}$$

and can be integrated numerically.

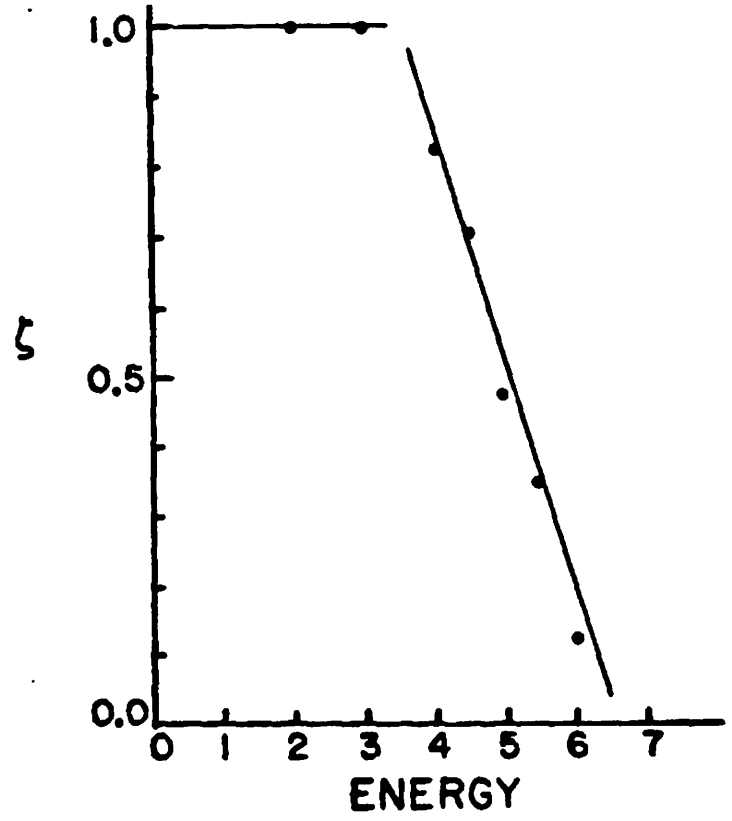


Fig. 1: Fraction of phase space covered by tori as a function of energy.[5]

We first consider some principal qualitative features associated with a typical trajectory. Shown in Fig. 2 is the total energy content of the oscillators, E (i.e., H'(t)) as a function of time. Two regions of behavior may be identified, separated by a vertical line in Fig. 2: Regular energy exchange between the system and the field, with a definite set of associated frequencies. Erratic energy exchange between the system and the field with several associated frequencies--in marked contrast to the previous region. Arrival at this region was, for all trajectories studied here, ultimately accompanied by dissociation, as in Fig. 2.

A related type of behavior was observed in an earlier classical trajectory study[9a] of multiphoton absorption in $CD_3Cl$ (Fig. 4 of Ref. 9a).[5] (See also Ref. 9b for an examination of individual trajectories.) The actual behavior of individual trajectories can differ considerably in the extent to which they sample the two regimes. Before presenting the numerical results obtained by integrating Eq. (1.3), we first present an approximate analytic and statistical theory of the process.

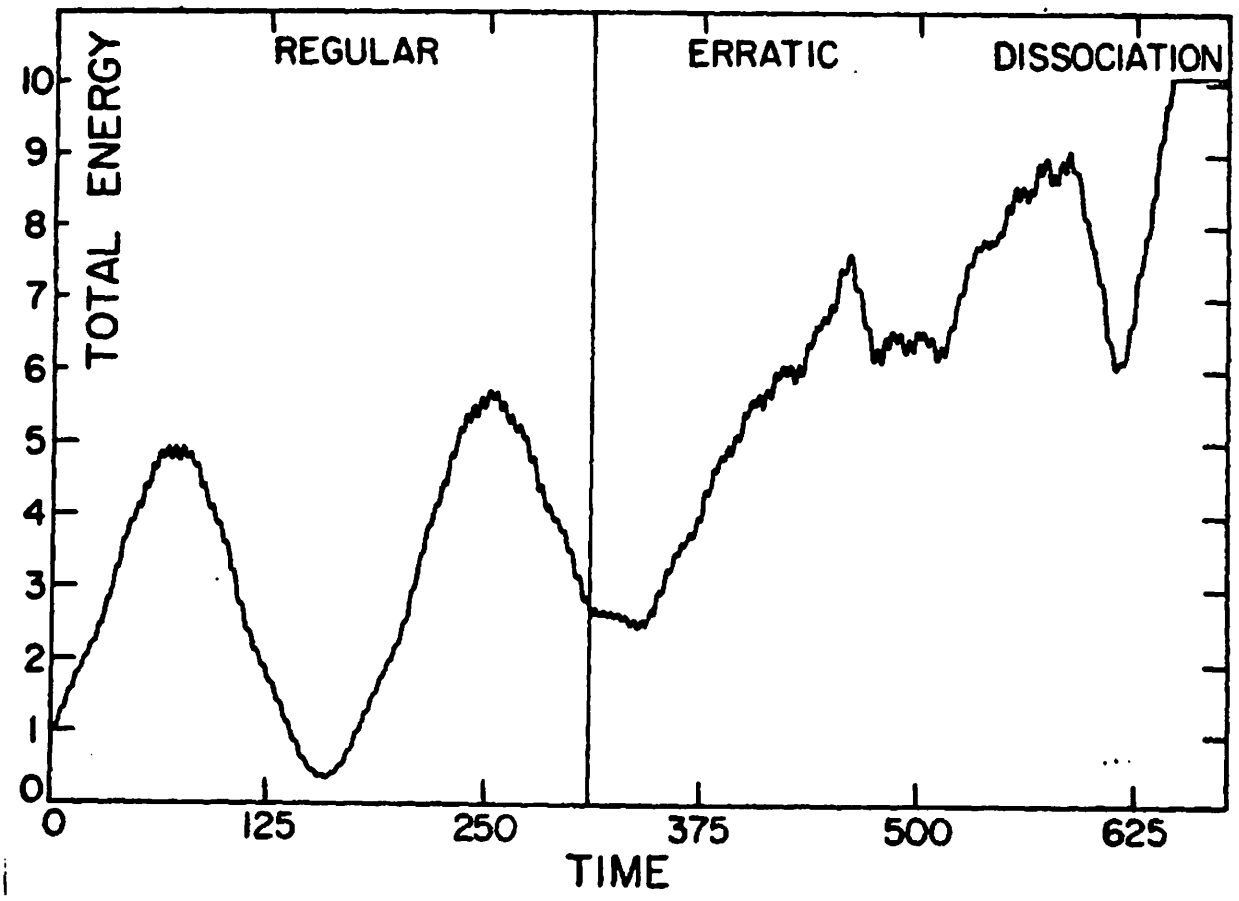


Fig. 2: Time dependence of the total energy for a given initial condition.[5]

## THEORIES FOR THE TWO REGIMES

### The Regular Regime

In this regime, we find[5] that the overall behavior of the total energy is well duplicated simply by treating the total system (with $F \neq 0$) as a single, y-type oscillator of altered frequency $\tilde{\omega}_y$, driven by the external field. Thus, we now get the equation of motion

$$\ddot{y} + \tilde{\omega}_y^2 \, y = F \cos \omega t \qquad (2.1)$$

where $\tilde{\omega}_y$ is not equal to $\omega_y$ and may be determined[5] by standard classical perturbation methods.[10]

Solution of Eq. (2.1) yields

$$y(t) = K \sin (\tilde{\omega} t + \theta) + \frac{F}{\tilde{\omega}_y^2 - \omega^2} \cos \omega t \qquad (2.2)$$

where K and $\theta$ are determined by the initial conditions. The total energy behavior, i.e., H'(t) determined mainly from (2.2), is shown in Fig. 3, and it can be seen by comparison with Fig. 2, that the overall features have the same behavior as the numerical results in the regular regime. In the event that mixing is widespread in the autonomous system (as in a 1:1 or 1:2 resonance case), replacement of the coupled system by a single oscillator may not be possible. The frequency

$$\beta = \tfrac{1}{2}(\tilde{\omega}_y - \omega) \qquad (2.3)$$

determines the long periodicity in the energy behavior, while the shorter oscillations have period equal to $\pi/\omega_y$.

### The Erratic Regime

In this regime, the total energy of the oscillators fluctuates in time in an irregular manner. The difference between this and the previous regime is similar to that between quasi-periodic and chaotic motion in the autonomous system. The current absence of rigorous analytic methods that are applicable for treatment of chaotic behavior makes a statistical approach a useful first alternative.

We made[5] the following assumptions for our present system. 1) In the periodic regime for an individual trajectory, the total energy is approximately the same for all maxima. 2) The erratic regime sets in for an individual trajectory when the forcing term leads the system into a portion of phase space where the underlying motion is chaotic. 3) All systems in the erratic regime ultimately dissociate. 4) The probability of entering the erratic regime

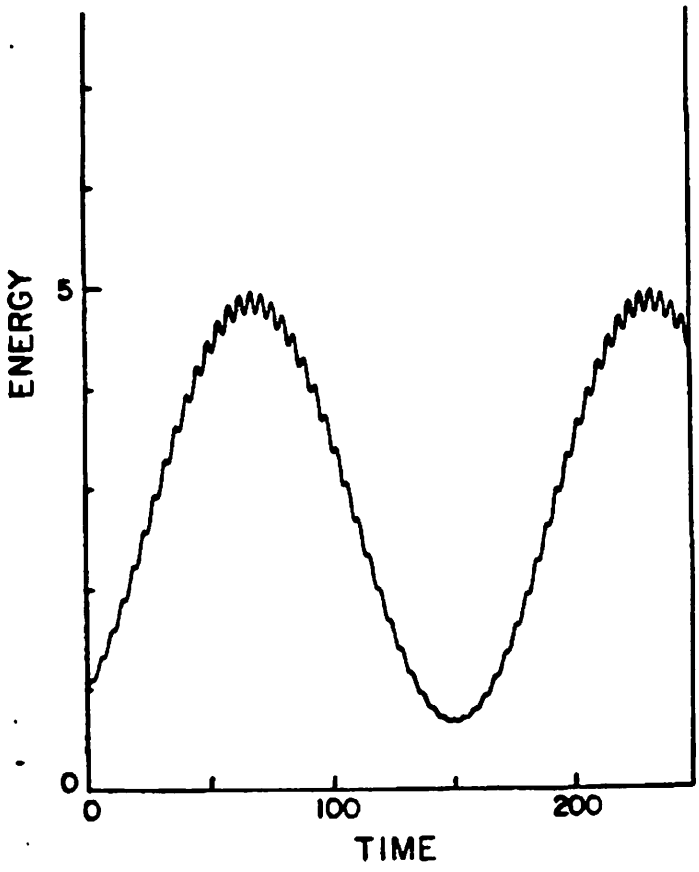


Fig. 3: Time dependence of total energy in the regular regime predicted by the Lie transform analysis.[5]

at a given peak is simply that fraction, $(1-\zeta)$, of phase space not covered by tori.

With the above assumptions, we deduced[5] that the fraction $f_s(t)$ of trajectories that are surviving at time t is given approximately by

$$f_s(t) = \zeta^{\beta t/\pi} \tag{2.4}$$

Here $\beta$ depends on the properties of the regular regime, and $\zeta$ is dependent on those of the autonomous dynamical system in the regular-chaotic regime. $\beta$ is given by (2.3).

## NUMERICAL RESULTS

### Regular Regime

In the quasi-periodic regime, a quantum state has its analogue in an eigen torus.[7b] We analyze the forced system in terms of a family of trajectories with initial conditions uniformly chosen

over the torus corresponding to the ground state of the system (1.1). Using the perturbation method of the Lie transform,[10] which is described in Ref. 5, the dependence of various dynamical quantities on system parameters is somewhat complicated. However, the long periodicity, which is determined by $\beta$, was 150 time units compared to the observed value of 160 time units. The amplitude of the first peak in Fig. 2, was 5.1, which agrees well with the value of 5.0 predicted by the Lie transform analysis[5] (cf Fig. 3).

## Erratic Regime

The connection between the onset of erratic behavior in the forced system and chaotic behavior in the forced system may be examined by turning off the field along the trajectory and then allowing the system to evolve from this "initial condition". When the field was turned off in the regular regime, a quasi-periodic trajectory was obtained, while turning off the excitation in the erratic regime produced a typically chaotic trajectory.

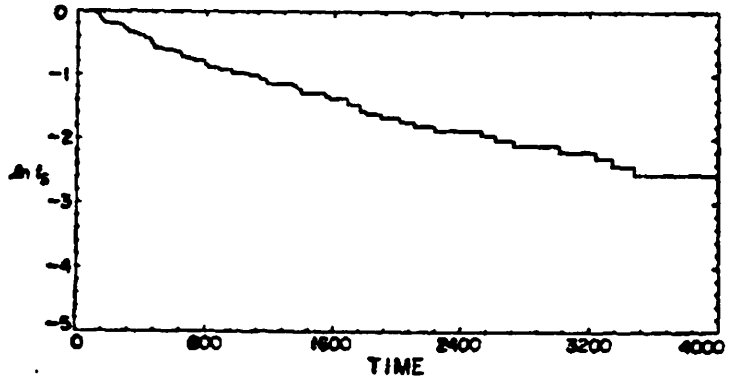


Fig. 4: Ln of fraction $f_s(t)$ of surviving trajectories as a function of time for $F = 0.1$, $\omega = 0.7$.[5]

On a logarithmic scale, $f_s(t)$ is very roughly linear, (during the first few half lives) in accord with Eq. (3.4) and has a slope at half life of -0.002. In applying Eq. (3.4), we estimate $\zeta = 0.5$ at $E_{max} = 5.0$ (from Fig. 1). Thus $(\beta/\pi) \ln \zeta = -0.004$. This value agrees to a factor of two with the empirical value obtained from Fig. 4. It must be emphasized that the model is only a first approximation. The decrease in slope of the $\ln f_s(t)$ vs t curve with time in Fig. 4, may be due to the residual unreacted systems being "locked" into a regular part of phase space instead of sampling the latter more randomly.

## CONCLUSION AND SUMMARY

In our study of this problem we have formulated a classical phenomenology of a driven coupled oscillator system. Two essentially different kinds of behavior can be distinguished: the exchange of energy between system and field occurs with a well-defined time scale

deriving from several aspects of the motion in the forced and unforced system. Secondly, the energy behavior can become highly erratic, and the latter motion inevitably led to dissociation under the conditions studied. The contrasting regular and erratic regimes in the forced system have their immediate analogue in quasi-periodic and chaotic motion in the autonomous system.

A time lag is observed in the appearance of dissociation when an ensemble of trajectories is analyzed. The distribution of life-times shows a power-law decay, which is tied into the extent of stability in the motion of the autonomous system. This distribution can be understood semi-quantitatively, and it is demonstrated how the parameters governing the decay rate can be approximately related to the parameters of the system.

In larger systems that are more typically "molecular", the analysis will necessarily become more complicated although the essential physics of multidimensional forced systems is likely to be similar for systems without internal resonances. The presence of several coupled modes will probably reduce the overall periodicity,[9] and indications are that chaotic motion can occur at fairly low energies (compared to dissociation). In higher-dimensional systems, methods based on spectral characteristics[11] or on the mean rate of separation of nearby trajectories[12] are more suited for measuring the extent of chaos since surfaces of section become considerably more difficult to compute. At this time considerable effort is being devoted in the literature to the prediction of widespread chaos in such systems,[8] and it may ultimately be possible to obtain $\zeta$ without recorse to numerical experiments.

ACKNOWLEDGMENT

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