INTRAMOLECULAR DYNAMICS: REGULAR AND STOCHASTIC VIBRATIONAL STATES OF MOLECULES

R. A. Marcus
Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125 U.S.A.

ABSTRACT

The nature of molecular vibrational states at low and high energies has been studied both classically and quantum mechanically. At low energies the classical vibrational motion is highly "regular" (quasi-periodic) in the usual harmonic normal mode regime. Interestingly enough, it can still remain so when the motion is anharmonic. However, at high enough vibrational energies numerical calculations indicate that the classical mechanical motion usually becomes chaotic (frequently termed "stochastic") although still deterministic, of course. The corresponding quantum mechanical behavior is discussed using semi-classical ideas, and a method of calculating eigenvalues in the quasi-periodic regime is described.

A definition of quantum stochasticity is proposed in terms of overlapping avoided crossings in quantum mechanical eigenvalue versus perturbation parameter plots. Some implications for phenomena such as intramolecular relaxation, spectra, unimolecular reactions, and infrared multiphoton dissociation of molecules are described.

INTRODUCTION

In the last twenty or so years, a "new phenomenon" has appeared in classical mechanics[1]. In this paper we describe this phenomenon and what we believe to be the analogous behavior in quantum mechanics. In the process we shall use some semiclassical results obtained by our research group[2] and indicate some of the implications for chemical behavior, as in intramolecular vibrational relaxation, unimolecular reactions, and infrared multiphoton dissociation of molecules.

Around the turn of the century, it was thought, we recall, that all was understood in physics; but then came quantum phenomena. However, not all was understood even in classical physics. In particular, in the classical mechanics of three-body systems in celestial mechanics,

K. Fukui and B. Pullman (eds.), Horizons of Quantum Chemistry, 107–121.

perturbation series were available for treating the motion, but these series were not shown to converge ("small divisors" problem) and were valid only for a limited time interval rather than for infinite time. Thus, the question of global time stability of the motion of an isolated solar system was unsolved. (Would some planet ultimately go to infinity?)

In the 1950's and early 1960's the existence of long time stability of classical mechanical systems was suggested[3] and proven[4], under restricted conditions, in the form of the now famous Kolmogorov-Arnol'd-Moser (KAM) theorem[3,4]. This theorem is concerned with the effect of small perturbations on integrable Hamiltonian systems. For integrable systems there exist as many single-valued constants of the motion, variously termed "first" or "isolating" integrals of the motion, as the number of degrees of freedom (N). This results in all the trajectories being forever confined to manifolds with the topology of N-dimensional tori (doughnuts) embedded in the 2N-1 dimensional phase space energy shell of the (conservative) system[5]. In this case the so-called action-angle variables are defined for all initial conditions (i.e., the Hamilton-Jacobi equation has a global solution). The KAM theorem states that for a sufficiently small nonintegrable perturbation, almost all tori are preserved, albeit in slightly distorted form. This means that with the exception of a set of small measure, the classical trajectories still display (infinite) long time stability. By contrast, the trajectories that do not lie on tori tend to wander in a pseudo-random manner (the motion is still deterministic) over large portions of the energetically available phase space. The integrals of the motion are, for the most part at least, not single-valued (? infinitely many sheets) and do not confine the trajectory the way tori do[6].

At low enough energies for weakly perturbed integrable systems such as coupled nonlinear oscillators, almost all of the trajectories lie on tori, while increasingly, in some transition region at higher energies, numerical calculations show that they tend to become of the wandering kind[1]. The two different classes of motion are often referred to as quasi-periodic and "stochastic" (or chaotic), respectively. Small changes in initial conditions can cause the trajectories to change from quasi-periodic to stochastic behavior[6].

CLASSICAL BEHAVIOR

A typical Hamiltonian for a pair of anharmonically coupled oscillators coordinates x and y and momenta, p_x and p_y, in a molecule is given by

$$H = \frac{1}{2}\left(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2\right) + \lambda x\left(y^2 + \eta x^2\right) \qquad (1)$$

(This Hamiltonian is also related[7] to that for a star in the vicinity of the galactic plane in an axially symmetric galaxy[7,8]. The non-

statistical velocity distribution of stars in a galaxy pointed to long time stability and restricted nature of the motion[7,8]. Thus, the dynamics based on (1) have been extensively investigated in the astronomy and related literature.)

When Hamilton's equations of motion for these coordinates and momenta are integrated numerically using a computer, one obtains a trajectory such as that in Fig. 1[9].

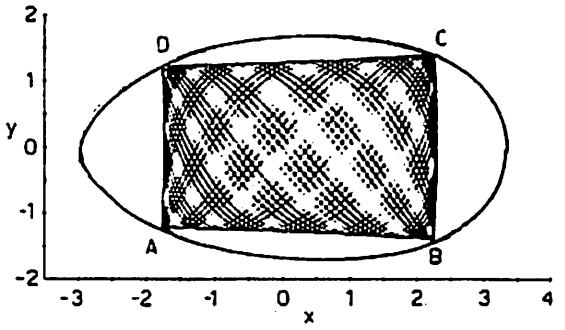

Figure 1. A trajectory for Hamiltonian (1), coordinate space xy, for the case ω_x and ω_y incommensurable.

The ellipse is the curve on which the potential energy equals the total energy and so the trajectory must lie in a region bounded by that curve. One sees, however, that the trajectory occupies a much more restricted region than the energetically accessible one. One sees, too, that the amplitude of the x-motion is approximately independent of y, and vice versa, and so there is relatively little energy interchange between the oscillators. The plot in Fig. 1 is a projection of the invariant torus in phase space onto the xy plane.

Another example is given in Fig. 2, now for the case that the unperturbed frequencies ω_x and ω_y are equal.

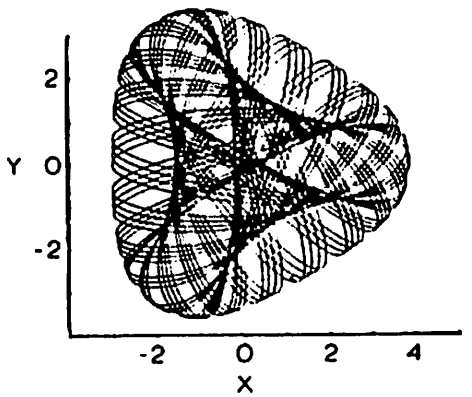

Figure 2. Same as Fig. 1 but for $\omega_x = \omega_y$.

The motion is again quasi-periodic at the low energy involved. Now,

however[10], because of the "resonance" between the two oscillators, there is seen to be extensive interchange of energy: sometimes the motion is largely along the x direction, sometimes largely along the y one, and sometimes in between, during the course of the motion. Similarly, in the case of a 1:2 ratio of frequencies (Fermi resonance)[11] there is a fairly extensive interchange of energy, as in Fig. 3.

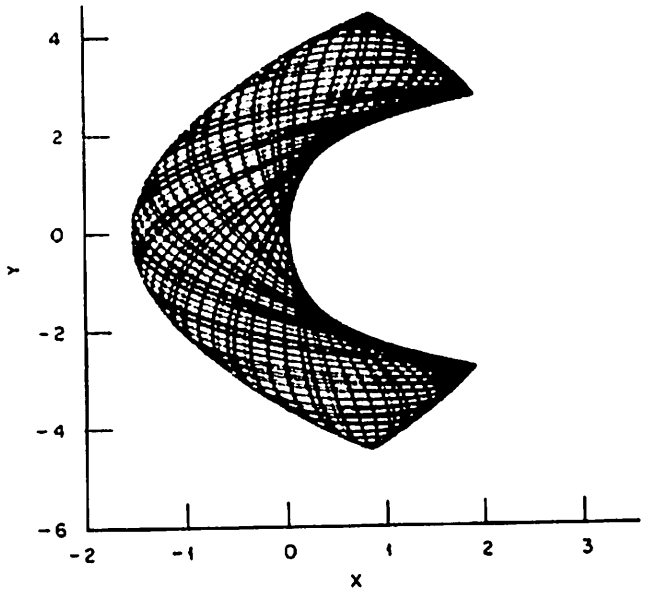

Figure 3. Same as Fig. 1 but for $\omega_x = 2\omega_y$.

A different plot is that of a Poincaré surface of section[12], e.g., a plot of p_x vs. x recorded each time the trajectory crosses the y = 0 axis with a (say) positive value of p_y, as in Fig. 4[9].

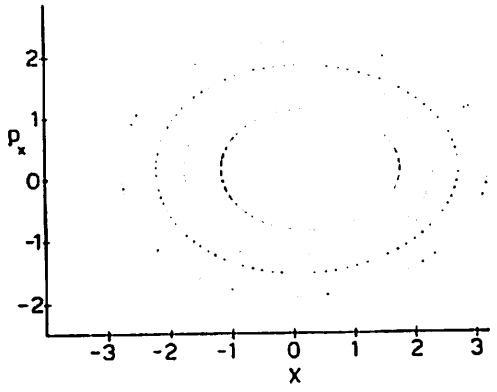

Figure 4. Poincaré surfaces of section for several trajectories, each a box-like one analogous to Fig. 1.

Here, the plot is given for a number of different trajectories at the same energy, each one giving rise to an ellipse-like figure. Related patterns arise in the 1:1 and 2:1 resonant systems, and here it has been convenient to introduce surfaces of section using curvilinear

coordinates, patterned from the shapes of the regions in xy space covered by the trajectories (e.g., polar coordinates for the 1:1 resonant case and parabolic coordinates when ω_x/ω_y equals 1:2)[10,11].

The connection of these diagrams for the quasi-periodic regime with quantum mechanics is the following. Many years ago Einstein[13] pointed out that to quantize a dynamically nonseparable system, it was necessary to find the canonical invariants $\oint \underset{\sim}{p} \cdot d\underset{\sim}{r}$ for the system, when they exist, and set them equal to nh [or now, really $(n_i + \frac{1}{2})h$, in the case of oscillators], each cyclic integral in the phase space being over a topologically independent path C_i in the phase space. Those for the Fig. 1 have been described elsewhere[9] and are, for example, the same as or equivalent to the y = 0 and x = 0 Poincaré surfaces of section. Those for Figs. 2 and 3 were obtained from curvilinear[10,11] surfaces of section. The number of independent integrals equals the number of coordinates (N, say). The allowed energies of the system are those for which the numbers $(n_1, \ldots, n_N)$ are integers. Using such semiclassical concepts, derived now from multidimensional WKB type arguments[14,2a], one obtains in this way good agreement between eigenvalues for the Hamiltonian (1) calculated quantum mechanically from a large variational basis set and those calculated semiclassically[9-11]. Semiclassical eigenvalues were calculated for the first time for two or more dimensional nonseparable systems with smoothly varying potentials in Refs. 15 and 9. More recently, a variety of methods have been developed[16].

The wave function is large and oscillatory in the shaded region in Figs. 1 to 3, and decreases exponentially outside that region in accordance with multidimensional semiclassical theory. The boundaries serve as caustics for the wave function. There is also a regular nodal pattern (where we have examined it) in this quasi-periodic regime[11].

From a classical trajectory a correlation function, e.g., for x(t) and y(t), has been calculated, and from it by a Fourier transform a power spectrum was obtained[17]. The spectrum consisted of several lines. The positions of the spectral lines agreed well with the corresponding quantum mechanically calculated lines (i.e., with the differences of quantum mechanical eigenvalues)[17].

At high energies, a quite different behavior occurs. The trajectory now tends to occupy much of the energetically accessible space. Correspondingly, the Poincaré surface of section produced by a trajectory tends to be a shotgun pattern, as in Fig. 4 of Ref. 1a, and one can no longer evaluate $\oint \underset{\sim}{p} \cdot d\underset{\sim}{r}$ integrals ("action" variables) from these surfaces of section. Indeed, in a truly stochastic regime, the only isolating integral of the motion is the total energy (and, where applicable, the angular and total momentum). The N $\oint \underset{\sim}{p} \cdot d\underset{\sim}{r}$ integrals appear to no longer exist. Thus, it has not been possible, as yet, to obtain semiclassical eigenvalues from classical trajectories. A method which gives the value to within one quantum state, for the system studied, from evaluations of volume of classical phase space has been devised[2f].

The classical spectrum, obtained from the correlation function, now consists of numerous lines, giving rise to a "band" near the fundamental frequency as in Fig. 6 of Ref. 2c. The quantum mechanical wave function in this region appears to have an irregular nodal pattern where studied[2e,11,18].

QUANTUM STOCHASTICITY

In a quasi-periodic energy regime, we have noted, the wave function is fairly localized, whereas in the stochastic energy regime it is expected to be more delocalized, largely over the microcanonically classically accessible region. On that basis we suggested[2e] that for a quantum state corresponding to a truly stochastic regime the quantum mechanical average of each dynamical quantity A(p,r) would approximately equal the microcanonical average at that energy (provided A does not weigh heavily the classically forbidden regions). A possible mechanism for the onset of this statistical nature of the wave function in the stochastic regime is the following.

For some unperturbed Hamitonian H_o which is integrable, there tend to be regular sequences of the energy levels. With increase of some perturbation parameter, some isolated energy levels may tend to come near each other and undergo an avoided crossing as in Fig. 5.

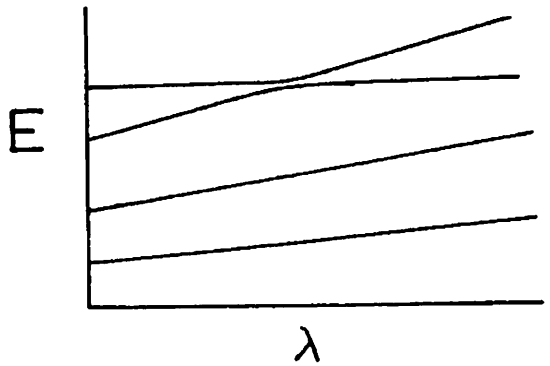

Figure 5. Example of an isolated avoided crossing in a plot of energy eigenvalues E versus a perturbation parameter λ.

An example of this behavior for the Hamiltonian (1) is given in Ref. 2f. In the vicinity of the avoided crossing each of the two perturbed wave functions takes on the character of both 'zeroth order wave functions' at that λ. Thus, the nodal pattern is more complex than before (in contrast to an actual crossing, which is not expected to change the nodal pattern). This isolated avoided crossing does not in itself yet constitute "quantum stochasticity." Rather, it represents the quantum analog of an isolated classical resonance. A classical Hamiltonian with an isolated resonance is integrable[1].

Classically, an isolated resonance occurs where, for some set of

initial conditions, the characteristic frequencies $\bar{\omega}_i$ of the motion (which depend on the perturbation parameter and on the action variables and hence on the initial conditions) become commensurable, i.e., when there are positive and negative integers m_i such that

$$m_1\bar{\omega}_1 + \ldots + m_r\bar{\omega}_r = 0. \tag{2}$$

One can then define new action variables, and thereby, new frequencies $\bar{\omega}_i'$, such that at this resonance one of the new frequencies is zero. Since frequencies correspond semiclassically to differences of quantum mechanical energy eigenvalues, the corresponding 'zeroth order eigenvalues' versus perturbation parameter plots should intersect.

We anticipate that quantum stochasticity will begin in some energy region when many eigenvalue curves undergo avoided crossings there[2f], as depicted schematically for the crossing of three such curves in Fig. 6.

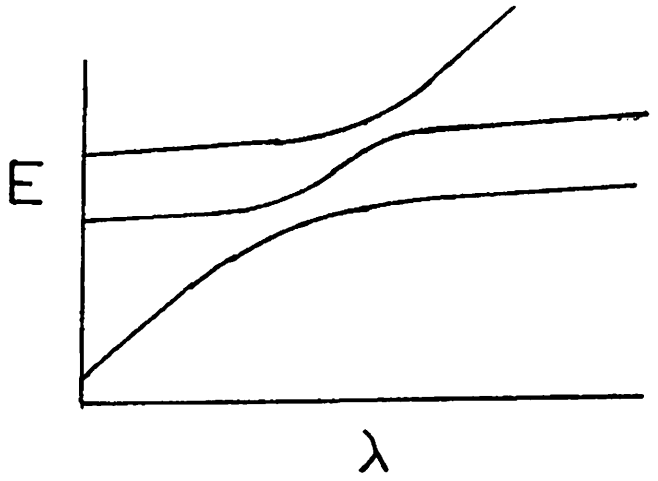

Figure 6. Example of overlapping avoided crossings in the plot for Fig. 5.

Now each of the wave functions contains the character of each of the three 'zeroth order wave functions', for λ in the vicinity of the crossings, and so has begun to take on a statistical character. When many such overlapping avoided crossings occur in the same region of parameter space and energy, something more likely to happen at high energies because in part of the higher density of states, each of the relevant wave functions has become "stochastic," and the average of any dynamical quantity in that state should become more nearly equal to the classical microcanonical average at that energy. At present, we are investigating the dynamics of this behavior[19]. The present definition is less basis-set dependent that one based on the projection of the exact wave function onto those for H_o.

We believe that 'overlapping avoided crossing' is a quantum analog of Chirikov's "overlapping" of classical mechanical resonances[20]. Chirikov has used this overlapping as a tool for predicting onset of

stochasticity[21] in classical mechanical systems. However, the presence of "quantum stochasticity" as we have defined it, i.e., the presence of overlapping avoided crossings, is not necessarily implied by the presence of a corresponding classical stochasticity. This is due to the finite size of $\hbar$, which can lead to a sufficiently large energy level spacing such that avoided crossings are relatively rare occurrences (see, for example, Ref. 2f). However, in the semiclassical limit $\hbar \to 0$ there could well be a close connection between the classical stochasticity and our definition of quantum stochasticity. In this case our "quantum stochastic states" would be closely related to the "irregular states" postulated by Percival[19a].

CONSEQUENCES OF QUANTUM STOCHASTICITY

One main difference in the two regimes lies in the spectrum. In the quasi-periodic regime it should be decipherable, in principle, into regular sequences (interlacing ones when there are several degrees of freedom). For example, for a set of N coupled oscillators these allowed frequencies are differences of eigenvalues

$$E_{n_1 \ldots n_N} = \sum n_i \omega_i(\underset{\sim}{n}) \hbar + \text{constant} \qquad (3)$$

where the frequencies ω_i, due to anharmonicity and to anharmonic coupling, are slowly varying functions of $n_1 \ldots n_N$. In the stochastic region, due to overlapping avoided crossings at the given value of the perturbation parameter, the spacings of eigenvalues become more complicated and "erratic," creating an irregular spectrum. Isolated avoided crossings would cause isolated irregularities in the spectrum. Because of the large number of vibrational states available at higher energies, it may be difficult to sort out any regular sequences (3) even if they occurred there.

A second effect of quantum stochasticity on a vibrational spectrum is to distribute the infrared oscillator strength in a particular frequency range over many true eigenstates and so "broaden" the spectrum. For example, if most of this oscillator strength came from a particular coordinate (say), it would, if the final vibrational quantum states were in the stochastic regime, be distributed over many final true vibrational eigenstates and so give rise to a broadened spectrum (cf. 19a). Some distribution of oscillator strength could also occur even if the final eigenstates were in the quasi-periodic regime, and so cause some (but less) broadening. It remains for detailed calculations for individual cases to compare the relative amount of broadening.

Examples of broadened spectra for low and high overtones are found in CH bonds in aromatics[22] (usually complicated by presence of several CH bonds) and C=O bonds in ketones[23]. The detailed interpretation of the width of a high overtone spectrum is of particular interest. It

may be due to "energy relaxation" or to a "pure vibrational dephasing" mechanism, or to both[24]. "Pump and probe" experiments should distinguish the two. In the latter one excites ("pumps") one absorption band and monitors the intensities of other bands. Such experiments are, for intramolecular vibrational relaxation, at or almost at hand.

When the width is predominantly due to an "energy relaxation mechanism," there is a close relationship between the width and the relaxation time for an upper state population formed from a pulse excitation of the entire band. When the spectral width is much larger than can be explained in this way and when it is not due to the presence of overlapping absorption bands ("inhomogeneous broadening"), one has, instead, a "pure vibrational dephasing mechanism."

To illustrate the relation of the two mechanisms to exact final eigenstates, it is convenient to consider first a very simple model. Here, one coordinate x_1 is assumed to carry the oscillator strength for the band, via a dipole matrix element over two zeroth order wave functions $\phi(x_1)$ and $\phi^*(x_1)$ for the lower and upper states, respectively. We let $\phi_m(x_1)$ denote the remaining zeroth order wave functions for x_1 and let $x_2 \ldots x_N$ be the remaining coordinates, with wave functions $\psi_n(x_2 \ldots x_N)$. We consider for simplicity the excitation from a single vibrational state, e.g., the ground state of the system.

The (normalized) "exact" wave function for the entire molecule in one of its upper vibrational states ψ_f in the band is then, for this model,

$$\psi_f(x_1 \ldots x_N) = \phi \sum_n a_n \psi_n + \phi^* \sum_n b_n \psi_n + \sum_{mn} c_{mn} \phi_m \psi_m \,. \tag{4}$$

There can be many ψ_f's, each differing in values of the a's, b's and c's. If, as one limit, the underlying perturbed classical motion for the final states were integrable and were as in Fig. 1, with x denoting x_1 and y denoting collectively $x_2 \ldots x_N$, each ψ_f would have only one dominant term and would be quasi-periodic: only a single $|b_n|$ in it is near unity, all remaining coefficients would be small, or, in the case of an isolated avoided crossing at most two of $|b_n|$'s in it would be appreciably large. If a ψ_f quantum state in this model were, instead, stochastic, none of the $|a_n|$'s $|b_n|$'s and $|c_{mn}|$'s would be typically large.

A pure vibrational dephasing mechanism would prevail if all of the "exact" states ψ_f containing ϕ^* did not contain a significant contribution from ϕ and from the ϕ_m's, i.e., if the exact wave functions ψ_f were of the form $\phi^* \sum_n b_n \psi_n$. In this case the ψ_f's are, at most, statistical only in their description of the $(x_2 \ldots x_n)$ motion. Other things being equal one expects the band width to be less when the ψ_f's are quasi-periodic than when they are statistical.

An energy relaxation mechanism prevails when all of the $|a_n|$'s, $|b_n|$'s and $|c_{mn}|$'s are small for the upper states. Then, the final quantum states are stochastic. (In more complicated situations there can also be intrinsic internal resonances which can contribute to the nature of the relaxation.) One model frequently used for other types of systems is the "discrete state in a continuum"[25,26] and is a particular case of Eq. (4). Here, the (unperturbed) "discrete state" is a single $\phi^* \psi_{n_0}$ and the continuum of states is $\phi \Sigma a_n \psi_n$, each such state with a different set of values of the a_n's. The "exact" eigenstates are then linear combinations of the discrete state and the continuum state, and so correspond to (4) with all b_n's but one equal to zero, and all c_{mn}'s equal to zero.

In contrast, when x_1 does not nearly parallel the x (or y) axis in Fig. 1, an "energy relaxation" in the x_1 coordinate, a relaxation defined operationally, would be observed even when the ψ_f's are quasi-periodic. (Cf. an analogous relaxation in an integrable system, the Toda lattice[27].)

In the above we have omitted for brevity the case where intrinsic internal resonances occur in H_0, as in Figs. 2 and 3. They permit periodic energy exchange instead of or superimposed on an "irreversible" one.

One also expects differences in behavior of a molecule undergoing optical excitation, according as it is excited to a quasi-periodic or a stochastic vibrational quantum state of an upper electronic state. In the former case, the subsequent behavior would depend very much on which vibrational state it is excited to, varying markedly from state to state. For example, if the excitation were to some given metastable electronic state and to various vibrational states, the subsequent fluorescence or predissociation behavior of this electronically and vibrationally excited molecule could depend significantly on that vibrational state. If the upper vibrational state were, instead, of a stochastic nature, then because of its statistical character, less dependence on the individual upper vibrational state would be anticipated.

Again, if a particular collision largely excited some terminal bond in a molecule and transferred enough energy to place the molecule in the stochastic regime, one could again form a "discrete state in a continuum" system. If the range of energies of excited states exceeded the width of states coupled to the discrete state, one would have a phenonemon of intramolecular energy relaxation. In the usual theory of unimolecular reactions (RRKM theory)[28] rapid intramolecular "randomization" is assumed so that the subsequent behavior of the molecule depends on its energy (and angular momentum) but not (or not noticeably) on any other integrals of the motion. A significant dependence on the latter could give deviations from RRKM theory[29]. A correlation function approach to time scales for energy relaxation is discussed in Ref. 30.

In the phenomenon of infrared multiphoton dissociation of a molecule current theoretical work assumes that these are two energy regimes of the molecule, with quite different properties--a discrete state regime and a quasi-continuum[31]. In the former a coherent absorption of the infrared radiation is assumed from state to state, while in the second regime rapid intramolecular randomization is frequently supposed. These two regimes may correspond largely to the present quasi-periodic and stochastic regimes, although the laser width is also involved in the definition. An example of a classical mechanical trajectory for a CD_3Cl molecule undergoing infrared multiphoton dissocation is given in Fig. 3 of Ref. 32, in which the energy absorbed by the molecule is plotted versus time. The "induction period" may correspond to a response of the molecule in its initial quasi-periodic regime with absorption and emission occurring. It is followed by a more cumulative increase of energy, perhaps when the molecule reaches the stochastic regime and can more readily undergo an intramolecular relaxation. A more detailed investigation of this phenomenon is underway[33].

SUMMARY

We have summarized briefly the "new" phenomenon in classical mechanics. Recent symposia and reviews attest to its widespread interest. It also arises in many other systems, as in a transition from laminar to turbulent flow. We have also indicated what we believe its counterpart in quantum mechanics to be and some implications for various experimental systems. Because of the detailed information becoming available through the use of lasers and other techniques, the subject is one of considerable current interest.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the contributions of my coworkers, Drs. M. Tabor, D. M. Noid, M. L. Koszykowski, W.-K. Liu, and R. Ramaswamy and the support of this research by the National Science Foundation. I am particularly indebted to Dr. Tabor for his critical reading of the manuscript and for his very helpful advice. Contribution No. 6145 from the California Institute of Technology.

REFERENCES

1. E.g. (a) Ford, J.: 1973, Adv. Chem. Phys. 24, p. 155; Ford, J.: 1975, in "Fundamental Problems in Statistical Mechanics," Cohen, E.D.G. ed. (North Holland, Amsterdam), vol. 3; Tabor, M.: 1980, Adv. Chem. Phys. (in press); P. Brumer, ibid., and the many references cited in these review articles; (b) Articles in "Stochastic Behavior in Classical and Quantum Systems, Volta

Memorial Conference, Como, 1977," Casati, G. and Ford, J. eds. (Springer Verlag, New York); (c) Berry, M. V.: 1978, Am. Inst. Phys. Conf. Proc. 46, "Topics in Nonlinear Dynamics," Jorna, S. ed., p. 16; for definitions of integrability, etc. see Helleman, R. G., ibid., p. 400.

2. E. g. (a) Marcus, R. A., Noid, D. W., and Koszykowski, M. L.: 1978, in "Advances in Laser Chemistry," Zewail, A. H., ed. (Springer Verlag, New York), p. 298; (c) Marcus, R. A., Noid, D. W., and Koszykowski, M. L.: 1979, in ref. 1b, p. 298; (d) Noid, D. W., Koszykowski, M. L., and Marcus, R. A.: 1979, J. Chem. Phys. 80, p. 2864 and refs. cited therein; (e) Marcus, R. A.: 1979, in "Extended Abstracts, 27th Annual Conference on Mass Spectrometry and Allied Topics, Seattle, Washington, June 3-8"; (f) Noid, D. W., Koszykowski, M. L., Tabor, M., and Marcus, R. A. (to be submitted), "Properties of Vibrational Levels in the Quasi-Periodic and Stochastic Regimes."

3. Kolmogorov, A. N.: 1954, Dokl. Akad. Nauk. SSSR, 98, p. 527; English translation: Ref. 1b, p. 51.

4. Arnol'd, V. I.: 1963, Russian Math. Surveys, 18, p. 85; Moser, J.: 1962, Nachr. Akad. Wiss. Göttingen, II Math. Physik Kl., No. 1, p. 1; Arnol'd, V. I. and Avez, A.: 1968, "Ergodic Problems of Classical Mechanics" (Benjamin, New York); Arnol'd, V. I.: 1978, "Mathematical Methods of Classical Mechanics, Graduate Texts in Mathematics (Springer Verlag, New York). The theorem is for non-degenerate oscillators, but applies also when there are two oscillators which, in zeroth order, are degenerate (cf. Arnol'd, V. I., loc cit. and Ref. 1a; Moser, J.: 1973, "Stable and Random Motions in Dynamical Systems" (Princeton Univ. Press, Princeton).

5. When total angular momentum and total momentum are also conserved quantities, the 2N-1 becomes 2N-5.

6. Thus, in this case, the only isolating integrals of the motion are the energy and, where applicable, the angular and linear momentum.

7. Contopoulos, G.: 1960. Z. Astrophys. 49, p. 273; Hori, G.: 1967, Publ. Astron. Soc. Japan 19, p. 229.

8. E. g., Ollongren, A.: 1962, Bull. Astron. Inst. Neth. 16, p. 241; Hénon, M. and Heiles, C.: 1964, Astron. J. 69, p. 73.

9. E. g., Noid, D. W. and Marcus, R. A.: 1975, J. Chem. Phys. 62, p. 2119.

10. E. g., Noid, D. W. and Marcus, R. A.: 1977, J. Chem. Phys. 67, p. 559.

11. E. g., Noid, D. W., Koszykowski, M. L., and Marcus, R. A.: 1979, J. Chem. Phys. 80, 2864.

12. Poincaré, H.: 1892, "Les Méthodes Nouvelles de la Méchanique Céleste," 1957 (Dover, New York), vol. 1; ibid.: 1976, English transl. NASA, Washington, D.C., vol. 3, chap. 27.

13. Einstein, A.: 1917, Verh. Dtsch. Phys. Ges. 19, p. 82.

14. Keller, J.: 1958. Ann. Phys. (N. Y.) 4, p. 180.

15. Eastes, W. and Marcus, R. A.: 1974, J. Chem. Phys. 61, p. 4301.

16. E. g., Percival, I. C. and Pomphrey, N.: 1976, Mol. Phys. 31, p. 917; Chapman, S., Garrett, B., and Miller, W. H.: 1976: J. Chem. Phys. 64, p. 502 ; Sorbie, K. S. and Handy, N. C.: 1976, Mol. Phys. 32, p. 1327; Sorbie, K. S.: 1976, ibid. 32, p. 1577; Handy, N. C., Colwell, S. M., and Miller, W. H.: 1977, Faraday Discuss, Chem. Soc. 62, p. 29; Sorbie,K. and Handy.N.: 1977, Mol. Phys. 33, p. 1319; Delos, J. B. and Swimm, R. T.: 1977, Chem. Phys. Lett. 47, p. 76; Jaffé, C. and Reinhardt, W. P.: 1979, J. Chem. Phys. 71, p. 1862; Percival, I. C.: 1979, ref. 2b, p. 259; Colwell, S. M., Handy, N. C. and Miller, W. H.: 1979, ref. 2b, p. 299.

17. Noid, D. W., Koszykowski, M. L., and Marcus, R. A.: 1977, J. Chem. Phys. 67, 404; Hansel, K. D.: 1978, Chem. Phys. 53, p. 35.

18. J. D. McDonald, unpublished results.

19. Other viewpoints for quantum stochasticity are found in (a) Percival, I. C.: 1973, J. Phys. B6, p. 1229; Pomphrey, N.: 1974, ibid. 7, p. 1909; (b) Pechukas, P.: 1972, J. Chem. Phys. 57, 5577; review by Tabor, M., ref. 1a; Nordholm, K. S. J. and Rice, S. A.: 1974, J. Chem. Phys. 61, p. 203, 768; Berry, M. V. and Tabor, M.: 1976, Proc. Roy. Soc. Lond. A349, p. 101; Percival, I. C.: 1977, Adv. Chem. Phys. 36, p. 1; Berry, M. V.: 1977, Phil. Trans. Roy. Soc. 287, p. 237; Heller, E.: 1979, Chem. Phys. Letters 60, p. 338; Heller, E., "Quantum Intermolecular Dynamics; Crtieria for Stochastic and Non-Stochastic Flows" (preprint); Stratt, R. M., Handy, N. C., and Miller, W. H.: 1979, J. Chem. Phys. 71, p. 3311; Shuryak, E. V.: 1976, Sov. Phys. JETP 44, 1070.

20. Zaslavskii, B. M. and Chirikov, B. V.: 1972, Sov. Phys. Usp. 14, p. 549; Chirikov, B. V.: 1979, Phys. Reps. 52, p. 265; cf. Ford, J. and Lundsford, G. H.: 1970, Phys. Rev. A1, p. 59.

21. For other criteria proposed for the onset of classical stochasticity, e.g., of the Toda-Brumer and Mo methods, see ref. 1a.

22. For review see articles by Reddy, K. V., Bray, R. G., and Berry, M. J., and by Albrecht, A. C.: 1978, in "Advances in Laser Chemistry," Zewail, A. H., ed. (Springer Verlag, New York), pp. 48, 235, respectively; Perry, J. W. and Zewail, A. H.,: 1979, J. Chem. Phys. 65, p. 31.

23. Smith, D. D. and Zewail, A. H.: 1979, J. Chem. Phys. 71, p. 540.

24. Cf. Jones, K. E. and Zewail, A. H., ref. 22, p. 196; Diestler, D. J.: 1976, Chem. Phys. Lett. 39, p. 39; Diestler, D. J.: 1976, Mol. Phys. 32, p. 1091; Oxtoby, E. W. and Rice, S. A.: 1976, Chem. Phys. Lett. 42, p. 1; Madden, P. A. and Lynden-Bell, R. M.: 1976, ibid. 38, p. 163. A molecular description of collisionally-induced T_1 and T_2 relaxation times is given in Liu, W. -K. and Marcus, R. A.: 1975, J. Chem. Phys. 63, pp. 272,290.

25. Fano, U.: 1961, Phys. Rev. 124, p. 1866; cf. Harris, R. A.: 1963, J. Chem. Phys. 39, p. 978.

26. For discussions of spectra and relaxation cf. Rhodes, W.: 1969, J. Chem. Phys. 50, p. 2885; Chock, D. P., Jortner, J., and Rice, S. A.: 1967, ibid. 49, p. 610; Langhoff, C. A. and Robinson, G. W.: 1973, Mol. Phys. 26,p.249; Tric. C.: 1973, Chem. Phys. Lett. 21, p. 83; Tric. C.: 1974, Chem. Phys. 14, p. 189, and references cited therein; Freed, K. F.: 1974, Topics Appl. Phys. 15, p. 23.

27. Ford, J., Stoddard, S. D., and Turner, J. S.: 1973, Progr. Theoret. Phys. 50, 1947; cf. Hénon, M.: 1974, Phys. Rev. B 9, p. 1921; Flashka, ibid., p. 1924.

28. Marcus, R. A.: 1952, J. Chem. Phys. 20, 359; 1965, ibid. 43, p. 2658; 1970, ibid. 52, 1018; Robinson, P. J. and Holbrook, K. A.: 1972, "Unimolecular Reactions" (Wiley, New York); Forst, W.: 1973, "Theory of Unimolecular Reactions" (Academic Press, New York); Spicer, L. D. and Rabinovitch, B. S.: 1970, Ann. Rev. Phys. Chem. 21, p. 349.

29. Marcus, R. A.: 1977, Ber. Bunsenges. Phys. Chem. 81, p. 190.

30. Tabor, M., Marcus, R. A., Koszykowski, M. L. and Noid, D. W. "On Correlation Functions and the Onset of Chaotic Motion" (to be submitted).

31. E. g., review of Bloembergen, N. and Yablonovitch, E.: 1978, Physics Today, 31, p. 23; Goodman, M. D., Stone, J., and Thiele, E.: 1979, in "Multiple-Photon Excitation and Dissociation of Polyatomic Molecules," Topics Curr. Phys., Cantrell, C. D., ed. (Springer Verlag, New York) (in press); Mukamel, S. and Jortner, J.: 1976, J. Chem. Phys. 65, p. 50-52; Grant, F. R., Coggiola, M. J., Lee, Y. T., Schultz, P. A., Sudbo, A. S., and Shen, Y. -R.:

1977, Chem. Phys. Lett. 52, p. 595; Quack, M.: 1979, Chem. Phys. Lett. 65, p. 140.

32. Noid, D. W., Kosykowski, M. L., Marcus, R. A., and McDonald, J. D.: 1977, Chem. Phys. Lett. 51, p. 540.

33. Ramaswamy, R. and Marcus, R. A. (unpublished).