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Unimolecular Processes and Vibrational Energy Randomization

R.A. Marcus

A.A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125, USA

Intramolecular vibrational energy transfer is the subject of much current experimental and theoretical research. Some aspects of this problem are reviewed in this talk, together with a few new additions. Inasmuch as extensive references have been given in a recent review,[1] they are omitted in this extended abstract in the interests of brevity. Topics discussed include (1) experimental work, (2) some theoretical concepts on "regular" and "chaotic" motion in the classical and quantum mechanics of anharmonic systems, and (3) the question of whether experiments can distinguish regular from chaotic behavior. By way of introduction we begin first with a review of the unimolecular rate constant of reactions occurring in the gas phase.

Unimolecular Reaction Rate Constant

The study of intramolecular energy transfer began with investigations of unimolecular reactions in the 1920's and 1930's, and was resumed especially in the post 1950's. The current interpretation of these data via a Lindemann mechanism for a reaction A → B involves activation by collision with a molecule M to form a vibrationally-hot molecule A*, which can either be deactivated by subsequent collisions or form a reaction product B:

$$A + M \rightleftharpoons A^* + M, \quad A^* \xrightarrow{k(E)} B \tag{1}$$

Current interpretation of experimental data in these reactions is typically via a statistical theory - RRKM theory - in which a microcanonical distribution of states is assumed for each A* of energy E and for the transition state of the second step in (1). Transition state theory is then used to calculate the rate constant k(E). One finds, in RRKM theory,

$$k(E) = N^{\dagger}(E)/h\rho(E), \tag{2}$$

where $N^{\dagger}(E)$ is the number of quantum states of the transition state of energy less than or equal to E, h is Planck's constant and $\rho(E)$ is the number of states per unit energy for molecule A*.

This expression for k(E) is then multiplied by the steady state distribution function $\rho_s(E)\,dE$ for the probability of finding an A* in the energy range (E, E + dE), and integrated over all E. k(E) may also depend on other quantum numbers, such as the angular momentum of A*, J, e.g., via the centrifugal potential, and then one integrates the corresponding $k(E,J)\,\rho_s(E,J)\,dE dJ$ over all E and all J.

Much of the current experimental research is designed, in effect, to avoid the need for this convoluting of k(E) by preparing molecules A* with a narrower energy distribution, namely by some way other than the collisional path in eq.(1). Before considering some of these methods, we first give another form of eq.(2) for k(E), derived in the Appendix. It is somewhat more revealing of its content and appears to be new:

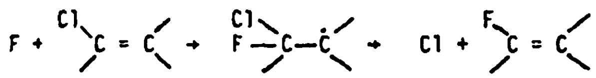
$$k(E) = \nu_c N^\dagger(E)/N_1(E), \qquad (3)$$

where ν_c is any classical vibration of A^* and $N_1(E)$ is the number of states of A^* with energy equal to or less than E and with this one degree of freedom removed. Thus, k(E) equals this frequency ν_c multiplied by the quantum equivalent of a ratio of phase space available to the transition state to that available to a molecule with the same number of degrees of freedom. The geometry and vibration frequencies may differ for $N^\dagger$ and N_1, and $N^\dagger(E)$ is zero until E exceeds some critical E_0, which in turn is related to the thermal activation energy. As a function of E, k(E) has a threshold at $E = E_0$, then rises and tends to "saturate" at high E.

<u>Some Experimental Studies</u>

Among the studies that have been made are those of (1) unimolecular reactions, (2) chemical activation (in bulk and in molecular beams), (3) photochemical excitation followed by internal conversion, (4) infrared multiphoton dissociation (in bulk and in beams), (5) high overtone induced reactions, (6) dissociation of van der Waals' complexes, (7) unimolecular reactions in beams at low energies, (8) infrared excitation followed by the study of subsequent fluorescence or absorption, (9) vibronic excitation followed by dispersed and other fluorescence, and (10) high resolution spectroscopy. Several of these are considered below:

One of the first methods used to secure a narrower range of E's for A^* involves its formation via a chemical activation step, e.g., the addition of an atom or free radical to an olefinic double bond, or the insertion of a CH_2 group into a CH bond,



(4)

The intervening free radical or molecule is vibrationally hot. Its energy distribution is mainly due to the thermal distribution of the initial substate. Chemical activation has been studied in bulk and in molecular beams. In the bulk case k(E) has been inferred via measurements of products in competition with the frequency of deactivating collisions, and E has been varied by varying the initial reaction leading to the formation of a hot molecule. A classic example of the use of the former to study the rate of vibrational energy randomization has been the measurement of ratios of products in carefully selected reactions by Rabinovitch <u>et al</u>. Typically, the intramolecular energy redistribution time thus inferred was about 1 ps at the high vibrational energies involved.

The products' energy distribution for chemical activation in beams has been used to infer that of the transition state and, thereby, whether or not the microcanonical assumption used for A^* in RRKM theory is valid. Such measurements are unambiguous when there are no exit channel effects (no subsequent translational-vibrational energy exchange in the exit channel), namely when the exit transition state is "loose". Reaction (4) displayed statistical behavior. An interesting example of nonstatistical behavior occurred, instead, in the reaction of Cl addition to a bromoolefin, with Br subsequently leaving the hot free radical. The estimated lifetime (< 1 ps) was presumably too short for statistical intramolecular randomization to occur.

Another method for preparing vibrationally hot molecules is a photochemical one in which the molecule is excited with light to form an electronically-excited state. In some systems the resultant excited molecule undergoes internal conversion to form a vibrationally hot ground state and its subsequent unimolecular reaction can be studied.

Vibrationally hot A^*'s have also been prepared by selectively pumping a vibrational mode of a molecule using infrared multiphoton absorption. Such studies provide interesting insight into different properties of the states of the molecule in the lower energy range and in the higher one (the so-called quasi-continuum). To be sure, the system yields a distribution of E's of the reactive A^*'s, rather than a nearly monochromatic one. A number of the studies have tested the RRKM form of k(E) indirectly, via measurement of the energy distribution of the reaction products, usually measuring the translational distribution but on some occasions a vibrational one. Another test has been via measurement of branching ratios, e.g., in the measurement of the HF/HBr ratio in a reaction in which CF mode was pumped:

$$CH_2FCH_2Br \xrightarrow{nh\nu} CH_2 = CHBr + HF \quad \text{or} \quad CHCF = CH_2 + HBr \tag{5}$$

The observed ratio was found to be the statistical one computed from RRKM theory.

By and large, the behavior of the dissociating or isomerizing A^* prepared by the above methods has been interpreted using RRKM theory. More recently, vibrationally-hot molecules have been prepared by excitation of a high CH overtone in a molecule. The lifetime has been measured indirectly as a function of the vibrational energy, via competition with deactivating collisions, and, subsequently, directly using studies in real time. In the case of $CH_3NC \rightarrow CH_3CN$, the results are in ballpark consistency with those inferred from RRKM theory and unimolecular studies, while data on the unimolecular studies is needed for comparison in the other cases. Some argument regarding nonrandom behavior has been made from apparent ±50% fluctuations from a monotonic k(E) vs E plot in one reaction. Such effects if real would probably go unnoticed in unimolecular plots, but the main question is rather whether or not the k(E) measured in such selectively-prepared molecules is or is not in rough agreement with that inferred from statistical (e.g., RRKM) theory.

Another interesting source of information has been initially cold van der Waals' complexes (such as I_2He) in which the I_2 is vibrationally-excited via lasers. The subsequent lifetime has been inferred indirectly from line width studies. Typically, one has $I_2(v)X \rightarrow I_2(v-1) + X$ and RRKM theory does not apply to such systems. In the language used below, their motion is much too regular, rather than chaotic.

Other more recent interesting and relevant studies include the infrared emission from a molecule (methyl formate) in which a CH band is excited (one photon) with an infrared laser and emission from other bands is observed, (McDonald), the observation of vibrational quantum beats (Zewail), the pump-probe work and vibrational quantum beats reported here by Bloembergen, the study of k(E) versus E for molecules in which the energy barrier for reaction is very low - ∿ 1500 cm^{-1} (reported here by Zewail) instead of the more usual 15,000 cm^{-1} barrier, the study of modal intramolecular relaxation via dispersed fluorescence in substituted benzenes, (Parmenter at this conference, Smalley) and the measurement of highly resolved spectral sequences in small molecules.

Some Theoretical Concepts

We turn next to current theoretical work on regular and chaotic motions within a molecule. An anharmonic molecule, viewed classically, is an example of a nonlinear mechanical system. Such a system has been extensively studied in recent years, particularly in astronomical journals. There is a relatively recent theorem (Kolmogorov-Arnold-Moser) which shows that at low energies the motion of such a system is for most initial conditions highly "regular" (i.e., quasi-periodic): In an N-coordinate system such a motion has N constant "action variables" and so moves on an N-dimensional surface in a 2N dimensional phase space, a torus, rather than on a 2N-1 constant energy surface. It is thus quite highly restricted in its motion. An example of this regularity is given for N=2 by the classical trajectory in coordinate space (e.g., Figs.1-4 below). Such motion is highly nonstatistical.

At higher energies the motion tends, for an increasing fraction of the initial conditions, to be chaotic rather than regular, as for example in Fig.5. The spectrum of the classical trajectory, determined from the Fourier transform of an autocorrelation function of the trajectory, changes correspondingly. It is "regular" for a quasi-periodic trajectory (N fundamental frequencies, plus overtones and combinations). In the chaotic case it is more diffuse, centered around principal frequencies usually red-shifted from those at lower E.

The above dynamical behavior is consistent with one current view in which statistical theory is appropriate for interpreting rate processes at higher energies; at lower energies, a quasi-periodic type of theory should be used, e.g., by treating a molecule as possessing independent vibrational modes, using some version of the usual radiationless transition theory and its Franck-Condon type matrix elements to treat rate processes. Such a treatment would, in a sense, be a quantum modification of N.B. Slater's treatment of unimolecular reactions. In that treatment, which was classical, a special case of quasi-periodic motion was assumed, namely, independent harmonic oscillations. The drastic effect of even small anharmonic coupling on the motion in the presence of internal resonances was neglected but can be included in any modified theory. The "transition state" (using transition state terminology) was assumed to be a hyperplane in the coordinate space.

The question arises as to whether this classical mechanical transition from quasi-periodic to chaotic motion has quantum implications. According to our recent findings in a numerical study, the former may be a necessary but not a sufficient condition for quantum "chaotic" behavior (as judged by the spectrum). Sufficient conditions have been postulated, both by Kay and by the writer, based on Chirikov's theory for the onset of chaotic motion ("overlap" of internal resonances). Our sufficient conditions for quantum chaos include one where the overlap region in phase space should (when divided by h^N) exceed unity, i.e., contain at least one quantum state.

One limitation of the Chirikov theory for classical chaos is that it is basis-set dependent, i.e., dependent on the choice of the unperturbed Hamiltonian, H_0. Another approach, which I am suggesting and which we are currently testing, is a basis-set independent extension of the Chirikov resonance, namely we examine the trajectories and find the various domain or domains in phase space where a trajectory of given shape dominates. One

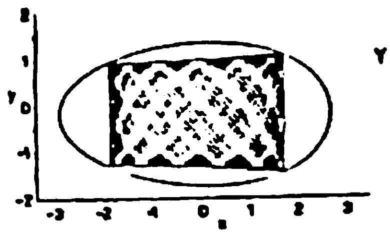


Fig.1

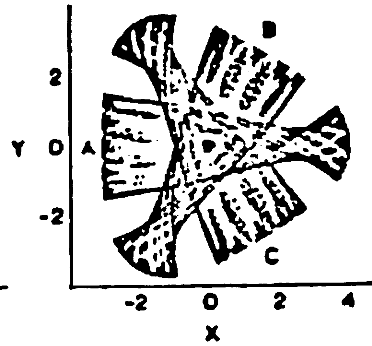


Fig.2

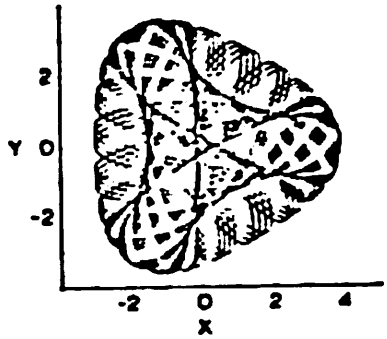


Fig.3

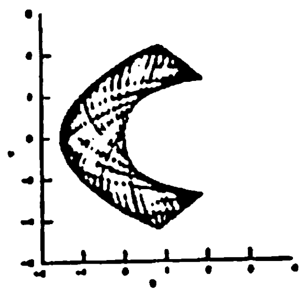


Fig.4

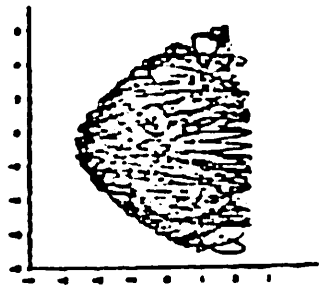


Fig.5

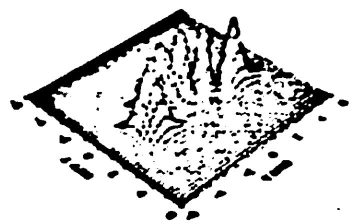


Fig.6

Legend to Figures 1-6

Classical trajectories y(t) vs x(t) for the Hamiltonian $H = \frac{1}{2}\left(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 x^2\right) + \lambda x(y^2 + \eta x^2)$, for several cases: Fig.1 ω_x and ω_y not commensurable; Fig.2, $\omega_x = \omega_y$ (3 librating ellipse-like trajectories); Fig.3, $\omega_x = \omega_y$ (1 precessing ellipse-like trajectory); Fig.4, $\omega_x = 2\omega_y$ (1 librating figure-eight like trajectory); and Fig.5, $\omega_x = 2\omega_y$ (chaotic trajectory). In Fig.6 is the wave function for the system of Fig.4

would then try to determine if a chaotic region corresponds to an overlap of such domains. Further, the size of that overlap domain relative to h^N would indicate, according to this model, whether or not a local "quantum chaos" exists. A trajectory of a given shape corresponds, incidentally, to a given resonance (cf Figs.2-4).

Another approach to "quantum chaos" that we have suggested, again basis-set independent, involves examination of plots of vibrational energy eigenvalue vs a perturbation parameter, and seeing whether avoided crossings and, more particularly, whether overlapping avoided crossings occur. Overlapping of avoided crossings will result in destruction of regular shapes of wave functions, so that fairly regular nodal patterns no longer occur. (A regular-shaped wave function is given in Fig.6.) The relation between the "overlap of different trajectory shapes" method and the overlapping avoided crossings method will be discussed elsewhere.

Can Experiment Distinguish Chaotic from Regular Behavior?

Not considered above is the relation, if any, between experiment and the classification of states as regular or chaotic. The more well-defined the "preparation of the initial state" in an experiment the more one expects a difference between regular and chaotic behavior. For example, if one examines the vibrational spectrum of a molecule at ultra high resolution and finds regular sequences of eigenvalues, the corresponding quantum states of the molecule are apt to be "regular": An isolated avoided crossing at the given value of a perturbation parameter will cause some mixing of two nodal patterns of the wave function, and some perturbation of the regular eigenvalues' sequence. [E.g., the eigenvalue sequence in a pendulum problem (libration-rotation), which is a model for an isolated resonance, is not as simple as that of, say, a Morse oscillator.] Overlapping avoided crossings will produce even more irregularity in the spectrum.

In reactions, the difference in rate constant of A* in the two models - quasi-periodic or chaotic - can be large, depending on the preparation of the initial state. (Strictly speaking, a dissociating molecule is never quasi-periodic, at most only approximately so, but we'll neglect this detail.) If A* is prepared via a collision in eq.(1) to form a nearly microcanonical distribution of states, or a distribution of states centered about the microcanonical, the energy dependence of the rate constant might be similar in the regular and chaotic cases. If, on the other hand, the state of preparation is less coarse-grained the experiment may distinguish between the two cases. Relaxation by itself is no indication: For example, it has been shown that even an integrable system (no classical chaos at any energy) shows relaxation of a classical state if the initial excitation involves the excitation of many KAM tori at once, by exciting some zeroth order mode, rather than by exciting motion on a single KAM torus.

This field is in its infancy, both experimentally and theoretically, and it will be interesting to see the growing relation between these new experiments and the new theories.

Appendix. Derivation of Eq.(3)

The $\rho(E)$ is $dN(E)/dE$, where $N(E)$ is the number of states of A* with energy equal to or less than E. $N(E)$ can be written, at least approximately, as $N_1(E-E')$, the number of states of an A* with one degree of freedom removed and with energy equal or less than E-E', times the number of states $\rho'(E')dE'$ of the missing degree of freedom having the energy in E', E' + dE', integrated over E' from 0 to E. If for this extra degree of freedom we select a vibration of A* whose frequency ν_c is low enough to be regarded as classical and which can also be treated as a harmonic oscillator, then $\rho'(E')$ equals $1/h\nu_c$. One then finds that $\rho(E)$ in eq.(2) equals $N_1(E)$ [using $dN_1(E-E')/dE = -dN(E-E')/dE'$]. From these results and eq.(2) eq.(3) follows.

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[1] D. W. Noid, M. L. Koszykowski, and R. A. Marcus, Ann. Rev. Phys. Chem. 32 267 (1981).