[Reprinted from Journal of Chemical Education, Vol. 57, Page 624, September 1980.]

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Molecular Vibration and the Normal Mode Approximation

The conventional ideas about normal modes and molecular vibration are currently undergoing closer examination for highly vibrationally-excited systems. The standard method involves calculating normal modes with the GF matrix technique (*1*). Normal modes assume a harmonic potential and, in fact, in high energy systems local anharmonic modes have given a better description of the spectrum than (harmonic) normal modes of the molecules as a whole (*2*).

In the currently used theory of unimolecular reaction (*3*), it is typically assumed that if one "normal mode" of a molecule is highly excited, it will share its energy with the other degrees of freedom and not keep it as the simple normal mode theory predicts. In an effort to understand the molecular vibrational motion of model systems, numerous classical trajectory studies have been made (*4*). In the future, these models will be aided by the fact that vibrational potential energy surfaces have been calculated for a number of triatomic molecules (*5*). It is the purpose of this article to discuss the new results which have been obtained in the theoretical understanding of vibrational motion.

Method

Once the potential energy surface $V(q)$ is known, the Hamiltonian can be written as

$$H = \frac{1}{2}\sum_i \frac{p_i^2}{2m_i} + V(q)$$

where $V(q)$ can be expanded about the equilibrium position, to yield

$$V(q) = \frac{1}{2}\sum k_i q_i^2 + \sum k_{ij} q_i q_j + \sum k_{ijk} q_i q_j q_k \cdots$$

The q_i's are generalized coordinates and the p_i's are their conjugate momenta. For simplicity, we shall omit the rotational part of the Hamiltonian. H is equal to the total energy of the system E. The correct solution of the vibrational motion would involve the use of quantum mechanics; howwever, because of the difficulty in obtaining a quantum mechanical solution in anharmonic systems, classical mechanics is often used. In the GF matrix or normal mode approach, one would consider only the quadratic part of $V(q)$ and neglect the rest of the terms of higher order. More generally, one can integrate the molecular vibrational Hamiltonian using Hamilton's equations (and using a computer):

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}$$
$$\frac{dp_i}{dt} = \frac{-\partial H}{\partial q_i}$$

and the exact nature of the vibrational motion is thereby determined. Integration of these equations yields q_i and p_i as a function of time, i.e., yields a "trajectory" for these coordinates.

Research sponsored by the U.S. Department of Energy under contract W-7405-eng-26-1 with the Union Carbide Corporation. The research was also supported in part by a grant from the National Science Foundation, and by the U.S. Department of Energy.

[1] Strictly speaking, the constants are the "action variables" $\oint p dq$, which for harmonic oscillators, are proportional to the squares of the amplitudes.

For the purpose of this paper, the vibrational behavior of a molecule will be illustrated using the behavior of two-dimensional systems (e.g., anharmonically coupled symmetric and antisymmetric stretching vibrational motion in a linear triatomic molecule). The Hamiltonian for the two modes x and y of an isolated molecule is then of the form:

$$H = \frac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) + H'$$

and

$$H' = \lambda x(y^2 - \eta x^2)$$

where H' is an example of a term neglected by the normal mode approach. (In general, H' would also contain other terms in addition to the two above.) For many problems the exclusion of H' makes some but not much difference to the shape of the trajectory. A trajectory for which this is the case is shown in Figure 1 (*6a*). The trajectory here is of the "box" type, and the ellipse is the contour for which V = E. When H' is neglected in the Hamiltonian, the trajectory is still of the box type. The motion for the anharmonic case of the trajectories of this type is reasonably well approximated by the normal mode motion, as is seen in Figure 2, which shows that the energy in a normal mode is nearly constant, even in this anharmonic system.

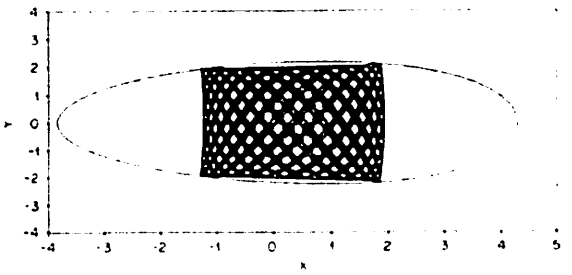

Figure 1. A box-like trajectory.

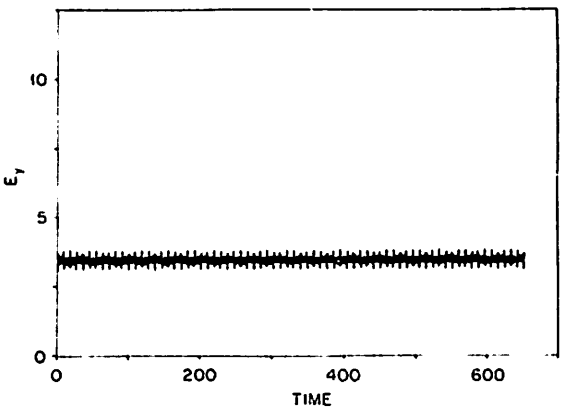

Figure 2. Energy in a "mode" versus time for the trajectory from Figure 1. All quantities are dimensionless.

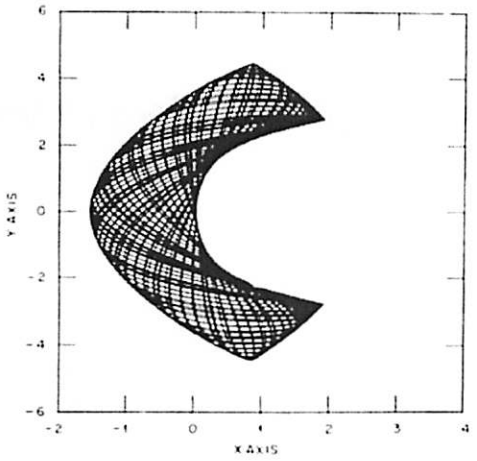

Figure 3. A Fermi-resonance trajectory.

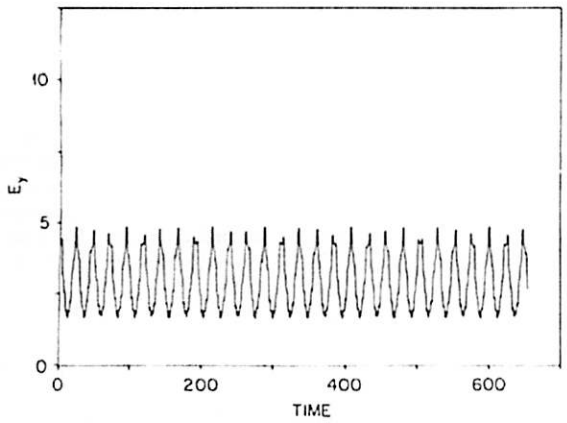

Figure 4. As Figure 2, except the trajectory is from Figure 3.

One way in which it is possible to obtain quantum mechanical results from classical mechanics is to use the semiclassical method (*6*), which has its beginnings in old quantum theory. Using this method, one can find the trajectory which corresponds to a quantum state. To do this, one finds the true constants of the motion of anharmonic modes of the system. For this case these true constants nearly equal the analogous normal mode constants ("amplitudes").[1]

A trajectory which has a Fermi resonance ($\omega_x = 2\omega_y$) is shown in Figure 3 (*6c*). These trajectories again do not fill the contour V = E, but have a very different shape from the box type. In this type of motion where $\omega_x = 2\omega_y$, the motion of the "normal modes" x and y is resonantly coupled by H'. However, it is still possible using semiclassical theory to find the constants of the motion and the eigenvalues for this type of trajectory (*6c*). The shift in energy of the quantum states from the normal mode approach can be substantially larger for these systems than in the "box" trajectory case, as shown in Figure 4, even though they also have types of normal modes.

The approximate vibrational spectrum can also be calculated directly from the trajectory (*7*). Figure 5 shows a typical spectrum, which shows several sharp peaks. These correspond to the frequency of infrared light which the system would absorb for those vibrations which are infrared active.

If one now looks at what happens when more energy is added to a molecule which had a trajectory like that in Figure 3, a new type of motion is observed. This motion is described as stochastic. The motion shown in Figure 6 (*6c*) covers the entire potential energy surface unlike the previous trajectories. There are no normal modes for these types of trajectories as seen in Figure 7, which shows large fluctuations in the normal mode energy. An excellent review on the transition of the

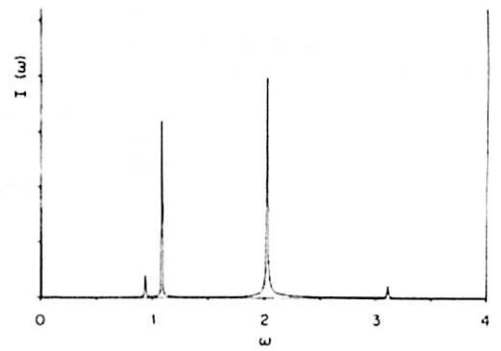

Figure 5. Spectrum of trajectory in Figure 1, a plot of intensity at frequency ω versus ω. The width of each line is due to a "round-off" error, which could be reduced in size using longer-time trajectories.

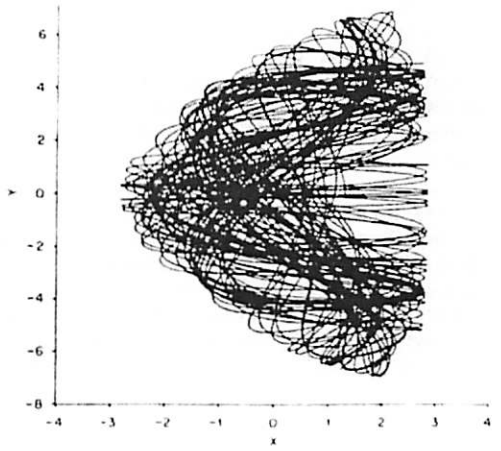

Figure 6. Ergodic trajectory.

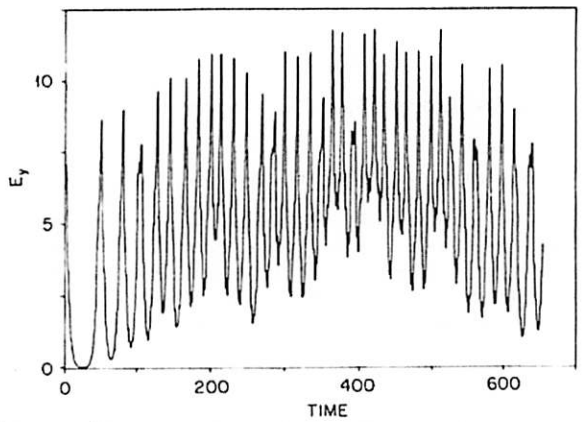

Figure 7. As Figure 2, except the trajectory is from Figure 6.

motion from that in Figures 1, 2, and 3 to that in Figure 6 can be found in an article by Ford (*8*).

The vibrational spectrum in the stochastic regime is shown in Figure 8. It is quite broad when compared to a spectrum at low energy. This broadening is characteristic of any spectrum calculated from a stochastic trajectory. The quantum analog of this transition is not completely understood, but it appears the wavefunction also exhibits a transition (*6c*) from one which is rather localized in space to one which is rather extended over the energetically accessible region.

Conclusion

Our current view of vibrational motion in molecules is summarized in Figure 9. A plot of generalized potential energy surface is shown in which the many-dimensional potential function has been simplified by only considering the potential energy function as a function of two coordinates. Along the vertical axis $V(x, y)$ is plotted versus x and y. The horizontal

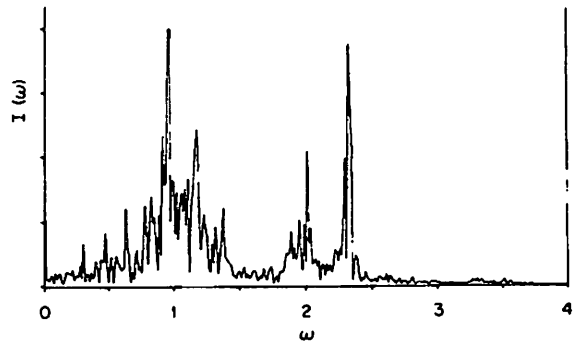

Figure 8. Spectrum of trajectory in Figure 6.

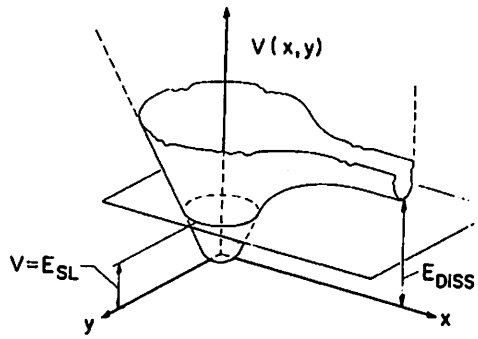

Figure 9. A plane of a potential energy surface showing the two regions of motion (regular motion for $E < E_{SL}$).

plane parallel to the xy plane indicates the stochastic limit (E_{SL}) where the motion changes from being "regular" to stochastic. Several possible ways exist for calculating this limit analytically. However, the most reliable seems to be integrating the molecular trajectory. Experiments for measuring the effects of this transition are presently indirect (study of unimolecular reactions, study of multiphoton infrared dissociation, shapes of spectral lines). However, with the advent of the pico-second lasers and new techniques for high resolution optical technology ("pump and probe" experiments), more direct studies may become possible. It is clear that a better understanding of this behavior is necessary to interpret these results in spectroscopy and in chemical kinetics.

Acknowledgment

One of us (R. A. M.) worked on this paper while a guest at Oak Ridge National Laboratory. He is greatly indebted to the staff of ORNL for their gracious hospitality. Contribution No. 6092 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology.

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