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We report the results of a theoretical/computational research program to develop methods and to investigate the fundamental chemical dynamics of elementary processes important in systems that can potentially yield large amounts of energy when they react. We describe a research program designed to further develop methods and to perform dynamics calculations for fundamental reactions in polyatomic molecules in which tunneling, electronic nonadiabatic processes, and vibrationally mode-selected reactions occur using theoretical methods based on classical trajectories and transition-state theory. Semiclassical corrections were employed to treat nonclassical processes such as tunneling and electronic transitions.

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FINAL REPORT

CHEMICAL DYNAMICS STUDIES OF HIGH ENERGY SPECIES
(AFOSR-90-0048)

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November 1992

Abstract

We report the results of a theoretical/computational research program to develop methods and to investigate the fundamental chemical dynamics of elementary processes important in systems that can potentially yield large amounts of energy when they react. We describe a research program designed to further develop methods and to perform dynamics calculations for fundamental reactions in polyatomic molecules in which tunneling, electronic nonadiabatic processes, and vibrationally mode-selected reactions occur using theoretical methods based on classical trajectories and transition-state theory. Semiclassical corrections were employed to treat nonclassical processes such as tunneling and electronic transitions.

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I. Overview of the Program

The propose of this theoretical/computational research program was to develop methods and to investigate the fundamental chemical dynamics of elementary processes important in systems that can potentially yield large amounts of energy when they react. The focus was on fundamental reactions in polyatomic molecules in which tunneling, electronic nonadiabatic processes, and vibrationally mode-selected reactions occur in an effort better understand some of the basic processes and some of the specific systems of interest in developing practical high energy density materials. The emphasis of the research was on studies of molecules with four or more atoms, particularly the effects of many modes and the energy distribution among them on adiabatic unimolecular reactions, predissociation, reaction via barrier tunneling, and intramolecular vibrational redistribution (IVR).

The theoretical methods included classical trajectories and transition-state theory. Semiclassical corrections were employed to treat nonclassical processes such as tunneling and electronic transitions. We have extended Monte Carlo transition-state theory,[1-5] which we originally used in treating adiabatic processes, to the treatment of electronically nonadiabatic (curve crossing) processes.[6]

II. Publications, Theses, and Oral Presentations.

The following is a list of the publications and manuscripts (in preparation for publication) that have resulted from the research during the grant period.

Alison J. Marks and Donald L. Thompson, "A Trajectory Surface-Hopping Study of Mode-Specificity in the Predissociation of N_2O," J. Chem. Phys. 95, 8056-8064 (1991).

Karen L. Bintz and Donald L. Thompson, "Theoretical Investigation of the Vibrational Predissociation of N_2O_3," Chem. Phys. Letters, 187, 166-172 (1991).

Alison J. Marks and Donald L. Thompson, "A Phase-Space Theory and Monte Carlo Sampling Method for Studying Nonadiabatic Unimolecular Reactions," J. Chem. Phys. 96, 1911-1918 (1992).

Thomas D. Sewell, Donald L. Thompson, and R. D. Levine, "Mode Selectivity in the Classical Power Spectra of Highly Vibrationally Excited Molecules" J. Phys. Chem. **96**, 8006-8022 (1992).

Thomas D. Sewell and Donald L. Thompson, "Semiclassical Demonstration of Mode Specificity in the Tunneling Splitting in a Model of the Malonaldehyde Molecule" Chem. Phys. Letters **193**, 347-354 (1992).

Thomas D. Sewell, Donald L. Thompson, J. Daniel Gezelter, and William H. Miller, "On Some Problems of Correcting the Zero-Point Energy Problem in Classical Trajectories of Polyatomic Molecules," Chem. Phys. Letters **193**, 512-517 (1992).

Karen L. Bintz, Donald L. Thompson, T. R. Gosnell, and P. Jeffery Hay, "Mode Localization and Dissociation Dynamics in the CF_2Br Radical," J. Chem. Phys., in press.

David Sahm and Donald L. Thompson, "Semiclassical Calculation of State Specific Unimolecular Electronic-Predissociation Rate Constants," Chem. Phys. Letters, in press.

Alison J. Marks and Donald L. Thompson, "Classical Trajectory Study of Mode Selectivity in Deuterium-Substituted Methyl Isocyanide," in preparation.

Ward H. Thompson and Donald L. Thompson, "A Slater Theory Treatment of Electronically Nonadiabatic Processes: Transition Rates and Mode Mixing Effects," in preparation.

David Sahm and Donald L. Thompson, " Unimolecular Rate Constants for the Predissociation of N_2O: Trajectory Surface-Hopping and Phase-Space Integral Evaluations," in preparation.

Yue Qin and Donald L. Thompson, "Tunneling Effects in the *Cis-Trans* Isomerization of Hydroxysilyene," in preparation.

The following theses are based in part on work supported by this grant:

Thomas D. Sewell (Ph.D., 1991) Thesis Title: Unimolecular Reaction Dynamics of Large Polyatomic Molecules.

Yue Qin (Ph.D., 1992) Thesis Title: Semiclassical Tunneling Corrections for Classical Dynamics of Unimolecular Reactions in Polyatomic Molecules.

Karen L. Bintz (Ph.D.) Thesis Title: Theoretical Investigations of Factors Which Affect the Mode-Specific Behavior of Unimolecular Reaction Dynamics.

The following is a list of oral presentations of the research results:

"Mode Specificity in Unimolecular Reactions," Department of Chemistry, Kansas State University, Manhattan, Kansas, May 24, 1990.

"Theoretical Dynamics Studies of Unimolecular Reactions." Symposium on *Computational Chemistry*, at the 36th Annual Pentasectional Meeting of the Oklahoma Sections, American Chemical Society, Lawton, Oklahoma, April 6, 1991.

Lecture Series on Chemical Dynamics at the Institute of Theoretical Chemistry, Jilin University, Changchun, P. R. China, August 16-23, 1991.

III. Review of Completed Research

The research focused upon the further development of methods, applications of some existing methods to new problems, and studies of fundamental dynamical behavior in systems of interest to the HEDM program.

The research has been concerned with the intramolecular dynamics, tunneling effects, electronically nonadiabatic reactions and other aspects of the fundamental processes that affect the lifetimes and reactions of long-lived, high energy systems. The central focus of this program are the dynamics of polyatomic systems, with the emphasis on realistic calculations.

A. Electronically Nonadiabatic Unimolecular Reactions

Nonadiabatic processes in diatomic molecules are well understood or can be straightforwardly treated. However, curve crossing problems in many-mode systems are much less easily treated and as a result we have a less thorough knowledge of the dynamics of them. We have carried out several calculations to study the dynamics of predissociation[6-10] and have suggested new theoretical approaches[6,10] to the problem.

We have used the classical trajectory surface-hopping method[13] to study the nonadiabatic spin-forbidden dissociation

$$N_2O(^1\Sigma^+) \rightarrow N_2(^1\Sigma_g^+) + O(^3P). \qquad (R1)$$
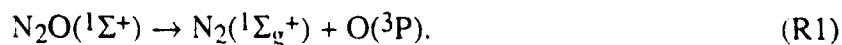
We chose this system because there have been several studies of other aspects of it. We used the model potentials of Zahr *et al.*[14] The crossing seam is higher for bent configurations than for linear ones in this potential. We investigated, treating all degrees of freedom, the effects of initial mode excitations on the predissociation rate.[7] More specifically, we calculated the rates for excitations of the bending and stretching normal

modes. We also studied the effect of the choice of "hopping coordinate" and the influence of the weak-coupling correction on the rate constant.

The rate was calculated using the Landau-Zener transition probability[15,16] plus the weak-coupling correction[16,17] (when the Landau-Zener probability became "large," i.e., greater than 0.1). About 10% of all reactive trajectories involved a transition requiring the weak-coupling approximation. The weak-coupling correction makes a significant difference in the rates (as much as a factor of 2).

Although it is understood that the hopping-direction coordinate is appropriately defined as the direction normal to the seam, we also calculated rates using definitions based on internal coordinates (the N_2 center-of-mass to O coordinate and the shortest N-O bond) since they are easily calculated and thus are sometimes used.[18]

One of the main interests in the study was mode selectivity in the predissociation. The rates are strongly dependent on the initial excitation because of incomplete energy redistribution along with a significant variation in crossing point energies with molecular geometry. That is, there is significant changes in the accessibility of the "dissociation channel" for different mode excitations.

The calculations just described were done using "mode-specific" initial conditions. That is, normal modes were initially excited. We have followed up these calculations with some in which "state-specific" initial conditions were used.[9] These were done for a two-mode collinear model of N_2O. Assuming that most trajectories on the initial potential are quasiperiodic, rate constants can be calculated for a particular torus. The tori were chosen to be those corresponding to semiclassical states according to EBK theory. As would be expected on the basis of the mode-specific results, there are wide variations in the state-selected rate constants. These calculations confirm our initial speculations (made when we proposed this work 3 years ago) that mode specificity in curve crossings might be rather significant due to the required "strong directionality" required to hop from one surface to another.

In addition to these dynamics studies, we have also developed Monte Carlo phase-space theory[7] method for treating nonadiabatic unimolecular reactions. In this approach, the rate constant is considered as a weighted flux through a "transition state," which is represented by the locus of intersection of two diabatic potential-energy surfaces. Phase space points in this region contribute to the rate with weights given by the transition probabilities (we used the Landau-Zener equation in our illustration of the method). The resulting expressions are evaluated by using Monte Carlo approximants. This leads to a general method that is easily applied to large systems and for general potentials. We have demonstrated the method for N_2O and shown that it gives results in good agreement with classical trajectory surface-hopping results. Thermal rate constants are easily computed using this method.

An important part of treating nonadiabatic reactions is the accurate representation of the potentials in the region of the seam. Yarkony[19] has development methods for obtaining this information from *ab initio* quantum mechanics. Our challenge is to incorporate this information into dynamics calculations. Usually one has the best data about the equilibrium geometries and (with the results such as Yarkony provides) the crossing seam. The potentials for unimolecular reactions are usually fit to functions based on valence force fields. Thus it is most convenient to write the potentials in the crossing regions using the same kinds of representations. We have explored this idea by using Slater's theory.[12]

One of the strengths of Slater's theory of unimolecular reactions[20] is that it provides a way of visualizing and illustrating some fundamental behavior of dissociating molecules. Its great weakness, of course, is that it is based on purely harmonic mode motions. Nevertheless, Slater's theory is often instructive because of its simplicity and because it relies on well-understood notions (i.e., normal mode motion) to treat the dynamics. We have adapted Slater's theory to treat problems involving electronically nonadiabatic transitions.

Slater's approach to unimolecular reactions involves monitoring the value of a time-dependent critical coordinate q_c, which is expressed in terms of a linear combination of the

normal mode coordinates Thus, its time dependence is trivially known. Dissociation is considered to have occurred when q_c exceeds some maximum value, q_0; that is, when there is an "up-zero" in $q_c(t) - q_0$. The rate is then related to the frequency of up-zeroes.

This approach has been generalized by Doll[21] and applied to more general cases of dissociation as well as surface diffusion[22] and desorption.[23] Doll used a result by Kac[24] to obtain an expression in integral form for the frequency of up zeroes. Thus, the statistical properties of $q_c(t)$ can be utilized rather than charting the coordinate as a function of time by calculating classical trajectories. Doll expressed the frequency of up zeroes in terms of a time average and showed that it can be extended to an average over phase space.[21]

We show how Slater's theory of unimolecular reactions can be adapted to electronically nonadiabatic transitions and provide insight into some fundamental aspects of them. The standard semi-classical approach to nonadiabatic transitions is two-fold: (1) Classical Trajectory Surface Hopping (CTSH);[13,14] and (2) statistical methods.[7,13] In the first approach a classical trajectory is evolved on the initial adiabatic potential surface. Each time the trajectory passes the crossing seam, defined to be the points at which the two adiabatic surfaces are of equal potential, it is given a certain probability of "hopping" to the other surface, which implies completion of a reaction or a quenching event. The hopping probability is most commonly determined by the Landau-Zener formula.[18,19] The rate is calculated from an ensemble of trajectories. This is costly in terms of computer time since the trajectories in the ensemble must be followed for long times. Thus, statistical methods are attractive since they circumvent this problem.

The statistical methods generally involve averages of the transition probabilities over phase space. Examples of such approaches are given by Zahr, Preston, and Miller,[13] Lorquet et al.,[25] and Marks and Thompson.[7] Zahr et al. assume that the trajectories are sufficiently long-lived that they behave ergodically. This assumption allows them to express the transition probability as an average over phase space. These methods are less expensive in computer

time than the CTSH approach. However, they provide much less insight into the fundamental behavior of the process.

The success of the application of Slater's theory to the problem of dissociation encourages a similar treatment of nonadiabatic transitions. Anharmonicity is an inherent aspect of dissociation that is contradictory to the assumption in Slater's theory of purely harmonic behavior. In the case of nonadiabatic transitions, one is interested in the dynamics which take place at the crossing seam, which can lie relatively low in the potential well. As pointed out by Lorquet and Leyh-Nihant,[25a] at these lower energies, anharmonicity is not as prevalent and the harmonic approximation more closely resembles the actual potential. Thus, one would expect that Slater theory might be well suited to the problem of nonadiabatic transitions. One of the primary advantages of a Slater approach to nonadiabatic transitions is that it provides a way to obtain information about the mode specificity of the process. Since the Slater trajectory is written in terms of the normal mode coordinates it is perfectly suited for calculating the effect of exciting a particular mode or combination of modes on the rate.

In summary, we have showed how Slater theory can be adapted to treat nonadiabatic transitions, and make some simple applications to illustrate it usefulness. Analytical expressions for the crossing seam and other relevant quantities are developed. We have described how Slater theory can be used to calculate nonadiabatic rates for real systems using *ab initio* information. An application to the N_2O system, using a model potential,[14] that illustrates the method (since there are insufficient *ab initio* results to fully define a crossing seam) is made. We have also shown how the model can be extended to include anharmonicity. We also apply Slater theory to the problem of mode mixing and illustrate how it can model intramolecular/intermode energy transfer.

B. Tunneling Corrections for Unimolecular Reactions

We have devoted considerable effort to developing methods and carrying out calculations of tunneling in unimolecular reactions.[26-29] Tunneling may be an important

factor in the behavior of energetic materials if they involve "storage" in a hydrogen environment. Thus, it is important that we be able to treat this effect if we wish to accurately model the behavior of these materials.

The tunneling splitting of the eigenvalues in symmetric, double-well molecules has long been a topic of considerable study. The symmetric hydrogen-transfer process in the malonaldehyde molecule (MA)
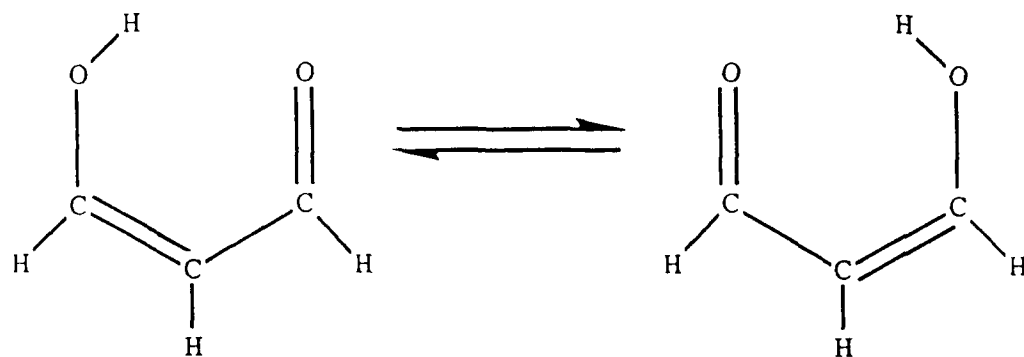
has been extensively studied. Leopold and co-workers[30] reported a ground-state tunneling splitting value of 21.58476 cm^{-1}. Hutchinson[31] has published the only study of the classical dynamics of hydrogen transfer in MA. He employed a two degrees-of-freedom potential-energy surface consisting of constrained three-body LEPS and harmonic angle-bending terms. Only the motion of the migrating hydrogen atom was treated explicitly; the skeletal C and O atoms were fixed and other hydrogen atoms were neglected completely. The study revealed the dynamics to be surprisingly regular even at energies considerably in excess of the barrier to hydrogen transfer. Moreover, the classical dynamics are relatively insensitive to modest variations in the potential-energy surface parameters. Tunneling was not considered in the calculation.

We have used classical trajectories[32] in conjunction with a semiclassical treatment of tunneling[33,34] to calculate the splitting in the Hutchinson model. We used the classical-plus-tunneling model of Waite and Miller[33] in conjunction with a more recent version due to Makri and Miller.[34] Common to both treatments is the assumption that the trajectory evolves classically until

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it experiences a turning point in the "tunneling direction", at which time a WKB tunneling probability is computed. Makri and Miller[34] assume a more general tunneling coordinate, specifically, the shortest straight-line distance connecting the caustics of the (assumed quasiperiodic and "quantized") trajectories in the reactant and product wells. Thus, in general, the Makri-Miller tunneling direction will correspond to motion of all the atoms in the system. In this system, a tunneling coordinate defined in terms of a single internal coordinate (a la Waite and Miller[33]) is not adequate; passage from the equilibrium geometry to the transition state requires significant displacement of both the bond and angle coordinates. Thus, the more general tunneling direction described by Makri and Miller is indicated.

Rigorously, Makri and Miller[34] require that the classical trajectories be quasiperiodic and correspond to a semiclassical state of the system. The latter can be accomplished by using adiabatic switching.[35] We did not attempt a semiclassical quantization of the system but, rather, chose to investigate the influence of various *ad hoc* distributions of energy on the semiclassical tunneling splitting. Initial conditions for the trajectories were obtained by partitioning the ground-state energy using four different schemes. Specifically, the energy was partitioned i) entirely into the zeroth-order stretch or ii) the bending mode; iii) in accordance with standard quasiclassical prescriptions; or iv) by totally random assignment of energy (with respect to the Cartesian coordinates and momenta).

The calculated tunneling splittings are given in Table 1. There is a clear dependence

Table 1. Calculated tunneling splittings

Excitation Scheme	Calculated Splitting (cm^{-1})
Pure angle	16.2
Pure stretch	41.5
Random	38.8
Quasiclassical	50.9

on the nature of the initial conditions, with the computed splittings ranging over roughly a factor of three. Interestingly, the results compare quite favorably to the measured value[30] of 21 cm^{-1}. The largest splitting, 50.9 cm^{-1}, corresponds to quasiclassical selection. The smallest splitting, 16.2

cm^{-1}, is obtained for pure angle-bending excitation. Pure bond-stretching and totally random excitation yield splittings of 41.5 and 38.3 cm^{-1}, respectively.

The results shown in Table 1 are qualitatively reasonable. The zero-point energy (6.6 kcal/mol) classical dynamics are essentially quasiperiodic.[31] Projection of all of the energy onto the bending coordinate results in a stable, highly excited bending motion and very little energy tends to leak into the stretching mode. The tunneling points are "far" from the transition state. By contrast, localized excitation of the stretching mode leads to a set of turning points that are closer to equilibrium, which means that the "distance" from the reactant well to the product well is decreased; and the height of the barrier through which tunneling must occur is decreased as well. These two factors lead to a much increased splitting for the case of pure stretching excitation. Quasiclassical excitation partitions energy into both the bending and stretching modes, suggesting that the tunneling splitting will be larger than for either of the two more selective excitations. Totally random distribution of the energy spans a considerably larger volume of phase space than the other three methods. Thus, it is likely that some trajectories have very large probabilities of tunneling (leading to a large splitting) while others will have correspondingly small tunneling probabilities.

The intuitive arguments of the preceding paragraph are illustrated by analysis of plots of the the tunneling points of the tunneling paths for ensembles of trajectories. The reason for the reduced splitting for pure angle-bending excitation is that the turning points for tunneling trajectories are tightly clustered such that the distance to the product "state" in the product well is on the order of 0.8 bohr, and the height of the barrier which must be penetrated is significant. Thus, tunneling must occur through a tall, wide potential -- and the probability of tunneling falls off exponentially with the area of the barrier which must be penetrated. The situation for pure stretching excitation is more conducive to tunneling. First, the average potential energy at the tunneling points is higher. Consequently, the average height of the effective barrier is decreased. Also, the width of the barrier is smaller. A final factor is the frequency of the motion in the tunneling direction. On average, four tunneling points were encountered for pure bending

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trajectories. By contrast, there were 10-11 per pure bond-stretching trajectory. Thus, not only is the probability of penetrating the barrier at each turning point greater for the case of bond-stretching excitation, but the frequency of turning points is more than twice as large. Quasiclassical excitation results in a broad swath of turning points. The individual tunneling probabilities fall off rapidly with increasing values of the ordinate. Individual quasiclassical trajectories typically exhibit a wide range of individual tunneling probabilities due to the relatively equitable partitioning of energy between the two modes. Totally random sampling allows for exploration of a much larger volume of the potential. The result is that the typical trajectory is less likely to explore regions corresponding to high tunneling probabilities.

The results suggest that it may be possible to observe mode-specific effects in the tunneling splitting of real molecules. Since tunneling is a sensitive function of the dynamics and the energy, selective, low-energy excitations could perhaps be designed to excite selected modes (i.e., C-O-H bends or skeletal modes) in the hopes of observing mode-specific splitting. Since the principal interest would be on low energies, the description could probably be couched in terms of normal modes and, moreover, the lifetime of the initially prepared states might be long enough to be chemically significant.

In summary, this study of the tunneling splitting for a model of the malonaldehyde molecule indicates significant mode-specific effects. The mode specificity is understandable in terms of the quasiperiodic dynamics that occur on the potential-energy surface. It is important that practical methods be developed for treating tunneling effects in large systems, and the semiclassical approach we have used offers the possibility of a general method.

The simplest case of tunneling is where the "tunneling coordinate" can be defined (at least, approximately) as a normal mode. We have carried out a semiclassical calculation[28] of the effects of vibrational energy on tunneling in the *cis-trans* isomerization in HSiOH using a potential-energy surface based on the available experimental and theoretical data. The isomerization channels, HOSi bend and torsion, both have barriers on the order of 11 kcal/mol. The effect of internal rotation

increases the barrier along the bending mode. The calculations show strong mode-specific behavior in the tunneling rate.

The calculated tunneling rates as a function of the excitation energy show that when the total energy of the system is low (15 kcal/mol or lower), the computed tunneling rate coefficient is three orders of magnitude larger for the *cis→trans* than that for the *trans →cis*. The ratio of the tunneling-corrected rate to the purely classical rate increases with decreasing total energy.

C. Mode Selective Dynamics in Highly Vibrationally Excited Polyatomic Molecules

Numerous studies have shown that the dynamics of few-mode models and molecules are chaotic at "high energies." [33a,36-54] However, it is not as clear to what extent chaos is a factor in unimolecular reactions involving large molecules.[54,55] Chaos obviously leads to statistical behavior in chemical reactions. The validity of statistical theories (such as RRKM) and the possibility of observing mode-selective chemistry depend on the nature of the dynamics at energies at and just above reaction thresholds. While a large body of literature deals with the phase-space structure of small (mostly three atoms), highly excited molecules,[56] relatively little has been reported for the dynamics of large molecules. This is primarily due to difficulties in extending the theoretical techniques used to study small molecules to large-molecule dynamics.

Among the more common ways of "detecting" chaos are techniques such as monitoring the separation in phase space of "initially adjacent" trajectories[40,43,44] or examination of Poincaire surfaces of section.[44,46,57] Brumer and Duff[40] have shown that the rate of divergence of initially adjacent trajectories can be used as a tool for diagnosing chaotic dynamics. Carter and Brumer[42] and Davis and Wagner[43,44] published a number of papers using this method to study chaotic vibrational motion in OCS. The surface-of-section method is usually restricted to two degrees-of-freedom systems although generalizations to 3-D systems have been developed.[57a] Another simple, though not totally satisfactoi. way of studying the dynamics of large systems is by

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calculating power spectra from classical trajectories.[37,42,45,46,54b,58-65] Power spectra can provide information about the structure of the phase space. For instance, purely periodic motion gives a "stick" spectrum. By contrast, chaotic motion gives a broadband spectrum having a characteristic pattern that, strictly speaking, only emerges in the long-time limit.[58,65] From a more pragmatic point of view, a "grassy" spectrum is usually associated with chaos in the (relatively) short-time dynamics of small systems. For most conditions of interest the spectra will likely be intermediate between these two extremes, and will be such that precise conclusions cannot be drawn. Nevertheless, power spectra are useful for obtaining information about the *qualitative* behavior of the dynamics.

Among the earliest publications in the chemical dynamics literature concerning power spectral analysis of the vibrational dynamics of "chemical" systems is a paper by Noid, Kozykowski, and Marcus.[65] Since then, there have been numerous studies that used power spectra as a qualitative means of classifying the classical dynamics as being either regular or chaotic.[42,45,46,58-64]

Smith and Shirts[37] concluded on the basis of power spectra that the dynamics of HNC isomerization become chaotic at a fairly well-defined energy. They reported "grassy" structure and broadening in the power spectra. Averaging the spectra over a small ensemble of trajectories tended to smooth out the grassiness but the broad features remained prominent in the spectra. Sumpter and Thompson[66,67] used power spectra to qualitatively examine the effects of rotational motion on the vibrational dynamics of H_2O_2. The presence of angular momentum results in a substantial broadening in the peaks relative to the nonrotating case and introduces new peaks into the spectrum.

We have employed power spectra in an attempt to ascertain whether the dynamics of several polyatomic molecules are primarily chaotic or nonchaotic.[68] The molecules we chose to study are: SiF_4, C_2H_4, CH_3ONO, and $\cdot CH_2CH_2Cl$. The results indicate the existence of well resolved (and assignable) bands in the vibrational spectrum of SiF_4, CH_3ONO, and (to a lesser extent) $\cdot CH_2CH_2Cl$ for energies up to and above the threshold for unimolecular dissociation.

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These bands are found to be present at low energies (i.e., the zero-point energy) and remain relatively unchanged over a wide range of internal energies. By contrast, the vibrational spectrum of C_2H_4 indicates a transition to chaotic motion at energies below the reaction threshold. The implication is that, contrary to conclusions often drawn for "small" molecular systems, the dissociation of large polyatomic molecules is likely *not* to be governed by chaotic dynamics.

We have used classical trajectories on an *ab initio*-based potential-energy surface to study the intramolecular dynamics and unimolecular dissociation of the CF_2Br radical.[69] Our interest here was to study mode localization and its influence on reaction. The CF_2Br radical has been observed as a primary product of the 248 nm photolysis of CF_2Br_2.[70,71] Krajnovich, Zhang, Butler, and Lee[70] examined the photochemistry of CF_2Br_2 in crossed laser-molecular beams. They concluded that the only primary reaction channel is the elimination of a Br atom. They also detected CF_2 radicals which they attributed to efficient secondary photodissociation of the CF_2Br radical. Gosnell, Taylor, and Lyman[71] used ultrafast time-resolved absorption spectroscopy to study the photodissociation of CF_2Br_2. They also detected the CF_2Br radical as a primary product. However, they concluded that the CF_2 radical is formed in the ground or first-excited vibrational state of its ν_2 bending mode during the "unimolecular reaction of a vibrationally hot CF_2Br intermediate species". In addition, they concluded that the evolution of the CF_2Br absorption spectrum over 6 ps is indicative of slow intramolecular vibrational redistribution. These results are sufficiently intriguing to warrent a study of the dynamics of this system.

Power spectra of CF_2Br show strong evidence of mode localization . Noid, Koszykowski, and Marcus[65] examined power spectra for two model Hamiltonians and attributed sharp line spectra, for which peaks are assignable as fundamentals, overtones, and combinations, to quasiperiodic dynamics. In contrast, they demonstrated that when the dynamics are known to be ergodic that the spectra become grassy and broadened. However, as noted by Noid, Koszykowski, and Marcus, centralization of certain frequencies is still apparent in the "chaotic spectra" indicative of some form of mode localization in the frequency domain.

The sharp peaks in a regular power spectrum will persist with increasing time with intensities which increase with time and widths which are inversely proportional to time (due to the increase in spectral resolution with increasing time), whereas chaotic power spectra become more grassy and do not display peaks which persist with increasing time.[58] This is well demonstrated in a study by Smith and Shirts[37] of HCN. They showed that the ensemble averaged spectra do not exhibit the expected grassiness with increasing energy but that individual power spectra do. However, the peaks in the ensemble averaged spectra decreased in intensity and broadened, as expected, as the number of bending mode quanta was increased. Dumont and Brumer[58] carried out a detailed analysis of the relationship between sharp/grassy power spectra and regular/chaotic dynamics. They concluded that "individual power spectra, computed over a finite time, are unable in principle to provide a distinction between formally regular and formally chaotic dynamics" but that "if one adopts the view that formal definitions of chaotic vs regular dynamics are less relevant than behavior over a finite time scale of observational interest, then simple vs complex power spectra do provide, *by definition*, useful distinguishing characteristics". It is the second view which we have adopted in our analysis of the power spectra which, when examined in conjunction with autocorrelation functions of the internal coordinates, provide evidence for mode localization in CF_2Br.

Five excitation energies, measured relative to the zero-point energy of the harmonic normal modes (approximately 6 kcal/mol), were considered. The lowest excitation energy is 35 kcal/mol which is slightly higher than the C-Br bond well-depth of 33.3 kcal/mol. Krajnovich *et al.*[70] estimated the *maximum* product internal energy of CF_2Br to be 39 kcal/mol. Other excitation energies (45, 50, and 60 kcal/mol) were considered to determine what effect (if any) higher excitation energies might have on the rate. Seven calculations were carried out at each of the five energies. Six of these calculations involved mode-specific excitation of the individual normal modes. The mode-specific initial conditions were determined by populating all but one of the normal modes with its calculated ground-state vibrational energy. The remaining normal mode

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was assigned a total energy which is the sum of the zero-point energy for that mode plus an arbitrary excitation energy .

Ab initio calculations were performed on CF_2Br at the Hartree-Fock level using the MESA electronic structure codes[72] with 6-31G basis sets[73] for C and F and a DZ basis on Br where an effective core potential[74] was employed to replace the $[Ar]3d^{10}$ core. The geometry was optimized using analytical gradient techniques and the vibrational frequencies were determined at the optimum geometry using numerical second derivatives. The optimized geometrical parameters were as follows: $R(C-Br)=1.953$ Å, $R(C-F)=1.346$ Å, $\theta(Br-C-F)=114.3°$, and $\theta(F-C-F)=110.4°$. For comparison, the calculated C-F bond length in CF_2 is 1.335 Å in the 6-31F basis used here, 1.283 Å in the 6-31G* basis, and 1.304 Å experimentally.[75] This information, along with experimental data, was used to formulate a global potential-energy surface.

The computed power spectra for CF_2Br clearly demonstrate mode localization. There is a sharp peak at about the ν_6 (Br-C-F bend) frequency in all the power spectra for the various initial conditions. Furthermore, in a series of power spectra for 5 ps time windows of a 45 ps time history, the peak remains well-defined over the entire time history. The power spectra show that at excitation energies well above the C-Br bond dissociation energy the dynamics are not globally chaotic and that, in fact, the frequency bands due to particular normal coordinates are still identifiable. However, the calculated rate constants show that sufficient interaction must be occurring between ν_6 and other modes to prevent a decrease in the rate of reaction when ν_6 initially contains all of the excitation energy. The rate constants demonstrate mode selectivity only with respect to direct excitation of the reaction coordinate mode (ν_4); there is no selectivity in the rates for excitations of the other normal modes. Furthermore, except for ν_4, the rate constants are comparable to those for equipartition of the excitation energy among the normal modes.

These results demonstrate that for the CF_2Br Hamiltonian used in this study, mode localization is not a sufficient condition for mode-specific reaction rates. Additional studies employing state-specific initial conditions would be useful for examining the effect of mode localization on the rates of chemical reactions.

As illustrated by the above study and many others, mode selectivity is not generally observed at the energies required to break a chemical bond. In contrast, the vibrational predissociation of van der Waals systems exhibits non-statistical behavior. Although van der Waals molecules are distinctly different from chemically bound systems, they serve as useful examples of mode selective systems and help to illustrate some fundamental aspects of nonstatistical behavior. In an effort to understand mode selectivity in general, it is useful to study systems that are intermediate between van der Waals and chemically-bound molecules. In this regard we have reported a series of intramolecular conversions that have energy barriers on the order of 10-15 kcal/mol.[76] More recently, we studied a "van der Waals/chemically bound" molecule, N_2O_3.

We used classical trajectories to study mode selective vibrational predissociation in N_2O_3.[77] The results are in accord with the conclusion of Chewter, Smith, and Yarwood[78] that N_2O_3 vibrational predissociation exhibits non-RRKM behavior. In fact, we find strong mode selective behavior as evidenced by the variation in the rate as a function of the initial partitioning of energy among the normal modes. This variation in the rates can be explained by the extent to which the excited modes project onto the reaction coordinate. The nitro group bending (v_4) and symmetric stretching (v_3) modes involve motion with significant components directed along the N-N bond (approximately the reaction coordinate), while the nitroso group stretch (v_1) and the nitro group asymmetric stretch (v_2) do not. The trajectory results show that v_4 mode excitation is the most efficient in promoting dissociation and v_3 is the second most effective mode. The lifetimes for v_1 and v_2 excitations are significantly longer than those for v_3 and v_4 excitations.

D. The "Zero-Point Energy Problem" in Classical Trajectories

Classical trajectories have been, and continue to be, a crucial component of the "toolkit" in chemical dynamics. Classical simulations are feasible for many problems where quantum treatments are not. Fortunately, many chemical processes are essentially classical. However, some systems are quantum mechanical and there are situations where classical mechanics fail. One

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such problem is the failure of classical mechanics to preserve zero-point energy constraints. We have raised the question,[79] of whether it is possible to "fix" the zero-point energy problem without altering the dynamics such that equally or more serious aphysical behavior is introduced. Various approaches have been tried to correct this problem.[80-85]

Some studies have been done to determine the contribution of the zero-point energy to reaction rates in classical studies by including only a fraction of the zero-point energy of the molecule. Guan et al.[80] used this approach in studies of the near-threshold overtone-excitation induced photodissociation of H_2O_2. They found that there is a significant dependence of the classically calculated dissociation rates on the amount of zero-point energy. However, they found that mode-specific effects are qualitatively the same for various amount of zero-point energy: Lu and Hase[81,82] studied the effect of zero-point energy in calculations of the linewidth of C-H overtones following excitation of a C-H local mode in benzene. They added only a fraction of the zero-point energy ($0 \leq f_{zpe} \leq 1$) to the modes of the system and they excluded zero-point energy from selected normal modes. They found that excluding zero-point energy from 7 normal modes having strong CCH bend character had a significant effect on the linewidth. By contrast, excluding zero-point energy from the other 14 normal modes but adding it to the 7 CCH modes gave results in near agreement with the full-ZPE case, except for higher overtone excitations. Lu and Hase also considered the effects of decreasing the number of degrees of freedom in the system in an effort to reduce the effects of aphysical classical energy flow. In particular, they extracted portions of the force field for the planar benzene molecule (C_6H_6) to yield force fields for two fragments (C_3H and C_3H_3) and compared linewidths for the two fragments with experimental measurements. The effect of doing so was to decrease the total energy content of the system and change the intramolecular couplings. They found that the overtone linewidths in the fragments were in considerably better agreement with the experimental measurements for benzene excited to the corresponding state.

Another possible route to understanding the effects of zero-point energy flow in classical trajectory calculations is illustrated by the work of Nyman and Davidsson[83] on the exchange

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reaction $O(^3P) + OH(^2\Pi) \rightarrow O_2(^3\Sigma_g^-) + H(^2S)$. They started with "all-or-none" of the zero-point energy in the $OH(^2\Pi)$ vibration, and then selectively "threw out" trajectories which did not satisfy predefined criteria regarding zero-point energy in the reaction products [$O_2(^3\Sigma_g^-)$ or, in the case of unreactive scattering, $OH(^2\Pi)$]. The critera range from retaining all trajectories regardless of the final vibrational energy to retaining only those trajectories that had at least the zero-point energy. The results showed a strong dependence on which scheme of categorizing the trajectories is employed: The treatment that yields the best agreement between the calculated and experimental results depends upon what properties are being compared.

These examples serve to exemplify "passive" methods for dealing with the zero-point energy problem and also illustrate the effects of zero-point energy flow. They are based on the idea of allowing the trajectories to evolve according to the classical equations of motion. By contrast, an "active" method for controlling the flow of zero-point energy during the course of individual trajectories has been proposed simultaneously by Bowman, Gazdy, and Sun[84] and Miller, Hase, and Darling.[85] The approach by Bowman et al. is encompassed in that of Miller et al. The gist of both methods is that, so long as none of the (assumed separable) mode energies in a system fall below the zero-point level, it should be allowed to evolve according to the classical equations of motion. However, when one or more of the mode energies falls below the zero-point, an instantaneous, external force is applied so as to exactly reverse the velocity in the mode(s) in which the energy has dropped below the zero-point level. If the kinetic energy is diagonal, then the total energy will be conserved. (However, the angular momentum will not be conserved except in special cases such as linear systems.)

We have addressed the question of whether or not it is feasible to employ "active" constraints to deal with the zero-point energy problem.[79] To this end we apply the methods suggested by Bowman et al.[84] and Miller et al.[85] to the simplest situation one can imagine, the dynamics of the ground state of a system of coupled oscillators (specifically, the Hénon-Heiles Hamiltonian). The results given by the usual, i.e., unconstrained classical mechanics and by the

zero-point energy constrained classical mechanics are compared to the correct quantum mechanical calculation of several quantities of interest.

We find that for this system of coupled oscillators (Henon-Heiles) initially in its (approximate) ground state, there is no zero-point energy problem as illustrated by a comparison of quantum and classical results. We find that the proposed model[84,85] for correcting problems with zero-point energy gives mode energies somewhat is better agreement with the quantum results, but the unconstrained classical trajectories are not in serious error either. This difficulty arises when one examines power spectra and plots of the configuration space projections. The unconstrained classical mechanics gives a single peak in the power spectra, indicating quasiperiodic motion, while the constrained classical mechanics spectra show broad, essentially continuous distributions of frequencies, characteristic of chaotic motion. The configuration space plots confirm the chaotic behavior in the constrained trajectories. The quantum results (spectra) are clearly closer to those of the unconstrained classical mechanics. We examined a variety of initial conditions, but all the qualitative results are as described above. The constrained dynamics very effectively prevent the energy in each mode from falling below its local zero point value, but does severe "damage" to the dynamics. In other words, the constraints severly modify the classical dynamics in a physically incorrect fashion. Thus, our work (nor that of others as far as we know) has not provided general solution for this vexing problem. We remain interested and plan to pursue it. Perhaps the problem with the above approach is that the "hard wall" character of the constraint is too harsh, inducing chaotic behavior in the dynamics and a "kinder, gentler" version of the model can be devised (e.g., a soft repulsive interaction in the action variable), but it remains to be seen whether any strictly classical "fix" can be successful and useful.

One may, of course, decide to give up on a strictly classical approach and try to utilize various semiclassical approximations. Alimi et al.[86] have recently suggested an approximate version of Heller's[87] semiclassical wavepacket methods for this purpose. This is a promising approach and certainly worth pursuing, though one notes that it involves more effort to apply than

does a purely classical treatment (e.g., matix elements of the potential energy surface must be computed), and Gaussian wavepackets can give unphysical results in very anharmonic systems.

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