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We have carried out a research program to investigate the chemical dynamics of unimolecular reactions in "large" polyatomic molecules. The purpose of the studies is an improved understanding of the fundamental behavior of highly excited, reactive molecules, with an emphasis on energetic materials. We have made some significant progress in extending theoretical chemical dynamics calculations to reactions in large molecules, as illustrated by our explicit, full-dimensional classical dynamics study of the unimolecular decomposition of RDX.[1] Leading up to this study of RDX, we performed a long series of dynamics calculations[2-30] for a variety of molecules to determine the important factors for accurately simulating processes in polyatomic molecules.

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Chemical Dynamics Studies of Reactions in Energetic Materials

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DEPARTMENT OF CHEMISTRY
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FOREWORD

We have carried out a research program to investigate the chemical dynamics of unimolecular reactions in "large" polyatomic molecules. The purpose of the studies is an improved understanding of the fundamental behavior of highly excited, reactive molecules, with an emphasis on energetic materials. We have made some significant progress in extending theoretical chemical dynamics calculations to reactions in large molecules, as illustrated by our explicit, full-dimensional classical dynamics study of the unimolecular decomposition of RDX.[1] Leading up to this study of RDX, we performed a long series of dynamics calculations[2-30] for a variety of molecules to determine the important factors for accurately simulating processes in polyatomic molecules.

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I. TECHNICAL REPORT

A. STATEMENT OF THE PROBLEM

The practical goal of this research program is to develop a better understanding of the initial steps of the reactions that occur in energetic materials. We have approached this problem assuming that energetic materials react in the various phases by a series of fundamental, elementary reactions which can be studied theoretically by formulating potential-energy surfaces (using both experimental and theoretical information) and then by following the time behavior of the reacting system by using classical mechanics (inserting semiclassical approximations where necessary, e.g., to treat barrier tunneling). Ultimately, one would like to be able to confidently formulate global potential-energy surfaces for energetic materials in the gas or a condensed phase and then, by using explicit chemical dynamics simulation methods, follow the overall decomposition reactions (occurring sequentially and in parallel) that are induced by various kinds of perturbations (e.g., shock waves, thermal, or laser pulses).

B. SUMMARY OF RESULTS

We have carried out a wide range of studies for a variety of systems as we have pursued the long-term practical goals of this research program. Reactions and IVR have been studied in molecules ranging from HONO to RDX (21 atoms). We have done extensive studies of IVR and unimolecular reactions (with an emphasis on mode selective behavior) in benzene,[2-5] toluene,[6] dimethyl-nitramine,[7,8] HONO,[9-13] H_2O_2,[14-18] methyl isocyanide,[19,20] methyl hydroperoxide,[21] RDX,[1,22] methyl nitrite,[23-25] nitromethane,[26] and several other systems.[27-37] These studies have provided insight into the role of molecular structure, rotation, initial vibrational energy partitioning, tunneling effects, and the potential-energy surface features (such as couplings, anharmonicity, etc.) on intramolecular dynamics.

Here we give a review of these studies, and point out some of the results and accomplishments we consider to be salient; in order to provide an overall picture of the results during the grant period covered by this report, we also briefly review the results of the previous grant period to provide background for the more recent results. There are two interwoven aspects of this research: practical simulations of energetic molecules and studies of the fundamental behavior of highly excited molecules. Following a discussion of our studies of energetic molecules, we review related studies on a variety of systems that contribute to our understanding of the fundamental behavior of highly excited polyatomic molecules.

i. Studies of Energetic molecules

We have carried out a number of classical dynamics calculations to gain a better understanding of the reactions in molecules of interest as energetic materials. These studies focused upon IVR and unimolecular reactions in nitro and nitramine compounds (nitromethane,[26] methyl nitrite,[23-25] HONO,[9-13] dimethylnitramine,[7,8] and RDX.[1,22]).

We began our studies of nitramines with dimethylnitramine (DMNA).[7,8] We used classical trajectories, treating all the degrees-of-freedom, to investigate the IVR and unimolecular reactions in DMNA.

Our first study focused on IVR.[7] We studied the energy transfer out of local CH_3 stretching modes for three potential energy surfaces, which were based on the available experimental data and some limited SCF-MO calculations we performed using the GUASSIAN-82 program. We used various potentials in order to investigate the validity of various approximations that might be used to reduce computation time. Furthermore, we studied various initial conditions to determine whether or not the molecule displays mode selectivity.

We considered two anharmonic potentials and one purely harmonic potential. The two anharmonic potentials differed mainly in how the torsional forces are represented; in one they are described by a truncated cosine series and in the other by nonbonding (Lennard-Jones) potentials. All the terms in the third potential (used to study IVR) were harmonic. All three potentials give approximately the experimental normal mode frequencies.

We found that the basic behavior of the IVR is the same for all three potentials. We studied the energy transfer out of excited methyl stretching modes. The energy flow is fast (requiring ~0.25 ps) and irreversible. The energy flow from the stretching modes is initially into the bending modes of the same methyl group. It then transfers to the other methyl group, flowing first into the bending modes and then into the stretching modes. While these results showing that the stretch-bend interactions play an important role in the IVR are not new, this study showed how the energy transfer occurs selectively along specific pathways (involving several modes) as it is redistributed over the molecule.

In our next study we considered the unimolecular decomposition of DMNA.[8] Since it has often been used (rightly or wrongly) as a prototype of the larger nitramines, it has been studied extensively experimentally.[38-46] It should be noted that there been some controversy about the decomposition mechanism for DMNA, although there is fairly clear evidence that NO_2 elimination is the main reaction.[47] There has been a question of whether or not nitro→nitrite isomerization occurs, however, recent experiments indicate that it is not competitive. We did not consider this channel in our calculations.

We chose to develop model potentials based on two dissociation channels: simple N-N bond rupture to give NO_2 as a product and concerted molecular elimination to give HONO. Although the HONO elimination channel has at times been proposed in nitramines, it is probably not competitive with N-N bond rupture.[38-46] Indeed, our calculations suggest that, even for our model potential (see below) for which we assumed that the HONO channel requires less energy, the N-N bond fission reaction dominates the decomposition. HONO elimination occurs in nitroalkanes[48] and similar H-atom transfer/bond fission molecular eliminations occur in other molecules such as ethers.[49]

The barrier to HONO elimination in our model is about 38 kcal/mol while that for N-N bond rupture is about 46 kcal/mol. The predominant path for the decomposition for "microcanonical" initial conditions is the N-N bond rupture even though it requires about 8 kcal/mol more energy. However, we found that placing the excitation energy selectively in a C-H stretch enhances the molecular elimination reaction. The first step for HONO elimination is the migration of an H-atom to an O-atom on the NO_2 group. By selectively exciting a C-H stretch, energy is initially located in a mode strongly involved in the reaction coordinate mode. Furthermore, the initial relaxation of a C-H mode occurs by transfer of energy to HCH bending motion, which may also facilitate the H-atom transfer. Although these results are for a model system, they suggest that mode selective reaction might be observed in other compounds (ethers,[49] nitroalkanes,[48] etc.) in which molecular elimination involves, as the first step, H-atom transfer.

We also examined the details of the IVR in the reactive trajectories. There is an increase in the transfer of energy into the nitro group prior to reaction. The energy in the nitro group appears to stabilize just before the N-N bond breaks. Following the bond breaking, the energy in the nitro group rapidly mixes among the bending and stretching modes in NO_2.

We have also used classical trajectories to study the dynamics of the nitromethane/methyl nitrite systems.[23,26] We first studied the IVR and *cis-trans* isomerization in methyl nitrite.[23] Following this, we developed a potential and carried out trajectory calculations to study the nitro→nitrite isomerization and unimolecular decomposition.[26]

In the initial study of methyl nitrite,[23] we investigated the influence of initial energy distribution, potential anharmonicity, and the initial geometry on the rate of *cis-trans* isomerization and IVR. As in our study of DMNA, one of our purposes was to examine simplifying approximations in the potential. We used three different potential-energy surfaces: two harmonic potentials, one of which included interaction terms, and one anharmonic (i.e., stretches). The anharmonic potential gave rates of isomerization and CH local bond mode relaxation rates that are significantly faster than those for the harmonic potentials. Based on the rates of IVR for CH excitations, these results suggest that the harmonic potentials are not adequate. This is the same conclusion we reached in an earlier, much more detailed, study of the influence of anharmonicity in benzene.[3]

The effects of mode selective excitation was studied by initially exciting overtone states of normal modes and CH local stretching modes. The results show no selectivity in the isomerization for initial CH excitations. The only selectivity found is for excitations of the ONO normal mode, which gave about a factor of 2 enhancement in the rate of isomerization.

The rates of *cis→trans* are significantly faster (as much as 5 times) than those for *trans→cis*. This result is similar to that obtained for HONO isomerization.[10,11] It is clear that the mode mixing in the *cis* is much stronger than in the *trans* in both these molecules.

Because of its size, nitromethane has been studied more extensive than have other nitroalkanes. We have also performed classical trajectory calculations of the unimolecular reactions of nitromethane.[26] Our modeling of the system was based on the reaction scheme suggested by Wodtke, Hintsa, and Lee.[48] They studied the decomposition of nitromethane by IRMPD in a molecular beam. They measured the branching ratio for the two competing reactions:

$$CH_3NO_2 \rightarrow CH_3NO_2^* \rightarrow CH_3 + NO_2, \qquad \text{(R1)}$$

$$CH_3NO_2^* \rightarrow CH_3ONO^* \rightarrow CH_3O + NO. \qquad \text{(R2)}$$

They determined the ratio of R2 to R1 to be 0.6. They predicted the barrier to the nitro → nitrite isomerization to be 55.5 kcal/mol, somewhat lower than the barrier for R1 (59.5 kcal/mol).

There is uncertainty about the transition state for the first step in R2 (the nitro→ nitrite isomerization). Some *ab initio* calculations[50,51] indicate a "tight" transition state (C-O and C-N bonds ~ 2 Å) while other calculations[52,53] indicate one with much longer bonds (~4 Å). There are no experimental data that help resolve the question, although measurements being done at USC by Prof. Curt Wittig's group may provide some information about it in the near future. We constructed three potential energy surfaces which differ mainly in the heights of the barrier to isomerization (216.4, 55.1, and 47.6 kcal/mol) although there are some differences in the locations of the transition state for the three surfaces (R_{CN}=1.57, 2.28, 2.2 Å; R_{CO}=1.71, 2.02, 1.95 Å corresponding, respectively, to the barrier heights given above), and carried our extensive classical trajectory calculations. In addition to R1 and R2, we observed

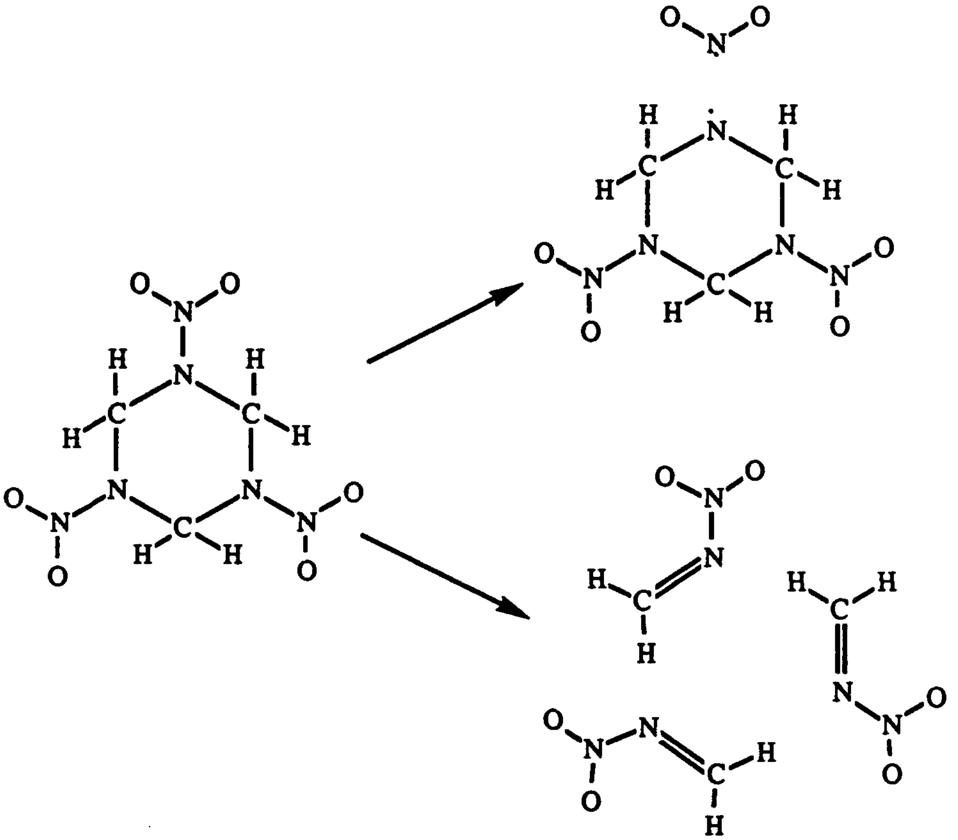
$$CH_3NO_2^* \rightarrow CH_3ONO^* \rightarrow CH_3 + NO_2 \qquad \text{(R3)}$$

in the trajectory calculations. The trajectory results for these potentials predict two mechanisms for the isomerization: i) a two-step process in which the C-N bond breaks and then a C-O bond forms and ii) a concerted process in which the C-O bond forms as the C-N bond breaks. The branching ratio for the potential with the lowest barrier (47.6 kcal/mol) is in closest agreement with experiment.[48] The potential with the 55.1 kcal/mol barrier gives branching ratios that are an order of magnitude larger than experiment.

It is clear that there is a need for additional experimental and theoretical studies of this system. It is important that more information be obtained about the nature of the transition state. While nitromethane is not an important energetic material, understanding it is important in the process of coming to understand larger, more practical systems.

We have carried out a series of studies to simulate both conformational changes[22,54] and reactions[1] in RDX. The long-term goal is to develop potentials suitable for simulating RDX chemistry in the condensed phase. At this point, much of the focus has been on understanding reactions in the isolated molecule and conformational changes in both the isolated molecule and in a dense gas of xenon.

We have used classical trajectories, calculated on an empirical potential-energy surface, to study the unimolecular reaction dynamics of RDX.[1] Although there have been a number of experimental studies, the elementary reaction mechanism for the initial decomposition steps of RDX is not totally understood.[47] Many of these studies have been for the condensed phase (which we discuss in Sect. III), where the N-N bond rupture seems to be the dominant reaction, however, Zhao, Hintsa, and Lee[55] have reported the results of a molecular beam/IRMPD experiment that indicate that the molecule decomposes by two competing channels. They find that the initial decomposition is due to simple N-N bond rupture and a concerted ring fission (simultaneous C-N bond cleavages) giving three $CH_2N_2O_2$ molecules:


(R4)

(R5)

The experimental data indicate a branching ratio of about 2:1 for the ring fission to N-N bond rupture reactions. The data are interpreted to indicate a concerted molecular elimination for the ring fission rather than a two-step process in which a $CH_2N_2O_2$

molecule is first eliminated followed by secondary decomposition of $C_2H_4N_4O_4$. Furthermore, they found no evidence to support a mechanism giving HONO as a primary product, a mechanism that has sometimes been invoked for nitramine decompositions.

We calculated rates for the N-N bond rupture and triple C-N fission reactions in RDX using classical trajectories computed on model potential-energy surfaces. We based our potential-energy surface on the results of Zhao *et al.*[55] The endothermicity of the ring fission was taken to be 24.4 kcal/mol and that of the simple N-N bond fission to be 47.8 kcal/mol. Most of the calculations are for a potential-energy surface with a barrier of 38.3 kcal/mol to the ring-fission reaction, but some were done for barriers of 35.7 and 41.0 kcal/mol.

The branching ratio (ring fission to N-N bond fission) reported by Zhao *et al.*[55] probably corresponds to total energies in the range 150 to 170 kcal/mol. The branching ratios computed from the trajectories over the energy range 250 to 350 kcal/mol are between 1.0 and 2.4. These results suggest that the potential-energy surface is qualitatively correct.

The calculated product translational energy distributions for ring fission gradually shift towards higher translational energies as the excitation energy of the reactant is increased; the average value increases linearly as a function of the total energy. Extrapolating to experimental conditions leads to a value that is within a few kcal/mol of the measured value.[55] Furthermore, the overall shapes of the calculated distributions are in good agreement with the experimental results. The ring-dissociation products are created vibrationally hot and rotationally cold. A significant number of the $CH_2N_2O_2$ products contain sufficient internal energy to undergo subsequent unimolecular reaction as observed experimentally.[55]

Typically, the product translational-energy distributions for simple bond-fission reactions in the absence of a back barrier are peaked at or near zero.[56] Our computed translational-energy distributions for NO_2 products are peaked at small but nonzero values. Vibrational-energy distributions for NO_2 indicate low levels of vibrational excitation.

The mechanism by which decomposition of the triazine ring occurs to yield three $CH_2N_2O_2$ molecules was studied by examining the details of the trajectories. Most of the ring fissions are complete within a few vibrational periods of the ground-state C-N bond, measured relative to the time of the last inner turning point of the first C-N bond that breaks. Decomposition of the ring appears to occur through a mixture of concerted dissociations and sequential depolymerizations.

The flexibility of the potential-energy surface formalism permits easy adjustment of the ring-dissociation barrier, thus a reasonably accurate value for the barrier can probably be obtained with the investment of sufficient computer time. We propose to continue studies of RDX and will refine the potential-energy surface as we do. Furthermore, it would be of interest to employ the final energy distributions of the fragments or the fragments themselves from the RDX calculations to study of the reaction dynamics of $CH_2N_2O_2$.

This study of RDX is encouraging for the prospects of meaningful simulations of reactions in large systems. It, along with several of our other studies, indicates that it is possible to formulate potentials, with limited information, which properly describe important aspects of the reaction dynamics in agreement with experiments.

We have also carried out calculations to study the conformational changes in RDX. The boat and twist structures are 4.5 and 4.0 kcal mol^{-1} higher in energy, respectively, than the chair structure, which is the lowest energy conformation. We used Monte Carlo methods to calculate thermodynamics quantities: $\Delta H = 4.5$ kcal mol^{-1}; $\Delta A(300\ K) = 4.0$ kcal mol^{-1}; $\Delta H^{\dagger} = 4.5$ kcal mol^{-1}; and $\Delta A^{\dagger}(300\ K) = 4.7$ kcal mol^{-1}.

We used classical dynamics simulations to study the flexibility and conformational changes in RDX in the gas phase and in a dense Xe-gas bath. We investigated the solvent effects on the equilibrium configurational distribution and the chair→boat/twist ring inversion rates at 500 K for eight Xe solvent concentrations. The configurational distributions for RDX in the gas and condensed-phases are markedly different. The equilibrium constant for the chair-boat/twist ring inversion of RDX in the gas-phase and in the condensed phase ([Xe] = 19.1 mol dm^{-3}) is 5.3 and 1.5, respectively. Our calculations show that the volume of the boat/twist structure is smaller than that of the chair structure. The decrease in volume makes the boat/twist conformations more favorable at higher concentrations. The solvent plays a large role in the equilibrium dynamics of RDX.

We also calculated the pressure dependence of the ring inversion rate constant. The calculations show that the rate constant for ring inversion obeys Lindemann theory at low solvent concentrations. That is, k_{uni} increases as the solvent concentration increases. A maximum in the rate constant is observed at [Xe] = 6.2 mol dm^{-3} after which it becomes a decreasing function of the solvent concentration (Kramer's turnover[57]). We attribute this behavior to the bulky exocyclic NO_2 groups which are directly coupled to the reaction coordinate and must sweep out a large volume during the ring inversion process. At high solvent concentrations, the rate constant increases with increasing solvent density. We attribute this behavior to a negative activation volume. Our results show that the transition-state structure is more compact than that of the chair conformation.

Unfortunately, there are no experimental data for RDX with which to compare these results, but comparison with a similar system,[58] hexahydro-1,3,5-trimethyl-1,3,5-triazine, indicates that the results are qualitatively correct. The rate constant for ring inversion in hexahydro-1,3,5-trimethyl-1,3,5-triazine in the gas phase is faster than that in the solution phase. This is attributed to the bulky exocyclic methyl groups which must sweep out a large volume for ring inversion to occur.[58]

ii. Studies of Fundamental Chemical Dynamics

We now describe some of the more important general findings and conclusions of our research concerning the fundamental chemical dynamics of highly excited, large molecules. The basic behavior of realistic systems has been a major focus of this research program, and mode selectivity has been of particular interest. The cumulative results of these studies indicate some systems and conditions where mode selective behavior might be observed, lead to some general conclusions about statistical and nonstatistical behavior in highly excited, large molecules, and provide the basis for further extension of these computational methods to new problems.

Before discussing our specific studies, it is useful to make some general observations concerning mode selectivity. It is clear from both calculations and experiments that when a mode or a group of modes are initially excited the energy transfers out of the initial location along specific pathways. Then, why is mode-selective chemistry not more commonly observed in experiments? Part of the answer to this question lies in the nature of the vibrational overtone excitation experiments. In most cases, a high frequency mode (e.g., an XH bond stretch) is excited, however, most chemical reactions (e.g., bond-rupture reactions) involve relatively low-frequency vibrational modes. Furthermore, often the amount of the excitation energy is on the order of that required for the reaction. Thus, it is likely that any mode-specific effects would be slight since it is necessary for almost all of the excitation energy to transfer from the high frequency XH mode to a low-frequency reaction-coordinate mode. In most molecules the excitation energy is redistributed among many "bath" modes before sufficient energy is transferred to the modes that promote reaction. At high energy the couplings between the various modes of a molecule are strong due to anharmonicity (leading to nonlinear resonances) facilitating intermode transfer and thus favoring energy randomization throughout the molecule over selective transfer of the energy into reaction coordinate modes. Nevertheless, since we know that the initial energy transfer takes place along well-defined pathways, it should be possible to observe mode specificity in chemical reactions if the excitation conditions are matched with the appropriate reactions. Our calculations have provided some insight into some conditions for which mode-selective chemistry is likely, as well as information about IVR rates and mechanisms. We currently doing some additional studies that should provide more direct evidence of mode selectivity.

We will discuss our results in the following order: First, studies of the fundamental behavior of molecules excited to levels above the dissociation limits, IVR, and, finally, unimolecular reactions.

It is well-established that most few-mode systems (models and small molecules) are chaotic at "high energies." But, are large molecules chaotic at energies at which chemical reactions occur? If one considers the amount of energy available per mode in a large molecule at energies required for dissociation, it is obvious that chaotic dynamics are unlikely. Consider, for example, a molecule with, say, 15 vibrational modes, and a lower limit for dissociation of about 100 kcal/mol -- the energy required for reaction is less than 7 kcal/mol per mode! This is a relatively small amount of energy compared to that required for chaotic behavior in simple molecules and models (such as the Henon-Heiles).

We have addressed this question in a simple, straightforward way by obtaining qualitative information about the nature of the dynamics of large molecules by calculating power spectra of classical trajectories for three very different types of molecules (C_2H_4, CH_3ONO, and SiF_4) at energies below and above the dissociation thresholds.[25] A variety of initial conditions were employed and the trajectories were integrated for 10 ps. On that time scale, which is longer in many cases than the reaction time, spectral mode identity is essentially retained in all cases even well above the threshold for dissociation and mode mixing (IVR) is quite limited even at energies where reaction is quite rapid. The trajectories do not sample all the available phase space.

In order to understand the behavior of unimolecular chemical reactions, it is necessary to first understand the rates and mechanisms of IVR. There are several fundamental aspects of IVR that one would like to understand. For example, there is the question of the validity of the assumption of rapid (relative to reaction) energy randomization underlying RRKM theory. With regard to mode selective chemistry, one would like to know the rates and mechanisms of the energy transfer from an excited mode to the reaction coordinate modes. Much of our interest has focused on the latter. More specifically, we have done a number of studies of energy redistribution following overtone excitations of local or normal modes in "large" molecules. We have studied H_2O_2,[14-18] HONO,[10-13] HNNH,[14,15] HCCH,[14,15] benzene,[2-5] toluene,[6] methyl nitrite,[23] methyl isocyanide,[19,20] dimethylnitramine,[7,8] RDX,[59] and other systems.

The rates of IVR from initially excited high-frequency overtones are rapid in most cases, often on a subpicosecond time scale[2-8] (a noteworthy exception being relaxation of O-H overtones[14-18]). Coarse-grain IVR (in which most of the energy has transferred from the activation coordinate to yield a quasistationary distribution) is also relatively fast. However, we know that longer periods of time (*ca.* 10 ps or more?) are required for complete equilibration of the energy throughout the molecule. In spite of the speed of the initial relaxation, the IVR occurs along specific intramolecular "pathways".

As an example, initially excited C-H overtones in benzene relax within about 0.5 ps.[2-4] The initial stages of this energy transfer occur *via* a well-defined stretch-bend interaction resulting from a near 2:1 nonlinear resonance between the C-H local mode and the adjacent CCH in-plane bends. The relaxation is irreversible, and thus the energy is quickly transported "away" from the initial excitation site. Substantially longer periods of time are required for global equilibration of the energy, which occurs by a specific mechanism. For instance, several of the normal modes of benzene do not participate in the energy transfer on a picosecond time scale (and probably for considerably longer times).[5] The initially fast relaxation of the C-H local modes in benzene is representative of aryl or sp^2 C-H modes.

The initial relaxation of an excited methyl C-H bond also occurs on a short time scale, however, the details of the pathway are somewhat different. We have illustrated this for toluene,[6] dimethylnitramine,[7,8] methyl nitrite,[23] and methyl hydroperoxide.[21] In each case, the initially excited bond rapidly loses its energy (although only about one-half as fast as in the previous examples). But, rather than rapidly diffusing through the molecule, the energy transfers preferentially into the CH_3 bending, stretching, and rocking modes where it remains "trapped" for conceivably chemically significant periods of time. Toluene provides a particularly interesting case since we can also study the reverse process, i.e., transfer of energy from an initially excited aryl C-H mode to the methyl-group modes. It is slow, and the methyl group acts as an isolated group mode. This trapping of energy may lead directly to mode specificity in scenarios such as concerted molecular elimination involving transfer of a methyl-group hydrogen atom (e.g., elimination of HONO in nitramine and nitro compounds); alternatively, "indirect "mode specificity may be achieved due to the retention of energy in the methyl group as compared with some other type of initial excitation that more readily allows for energy transfer among the molecular degrees of freedom.

Rapid relaxation appears to be the rule for CH local modes, but it is not the case for all high-frequency oscillators. Experiments and calculations have shown that relaxation of OH overtones in alkyl-peroxide molecules occur on much longer time scales than is the case for CH modes, and our theoretical studies reveal that the relaxation tends to occur by a rather different series of events.[14-18,21] Hydrogen peroxide provides a clear illustration of this point.[14-18] Energy initially localized in an OH stretch remains in that mode for relatively (as measured by a chemical clock) long periods of time, with roughly 6 to 25 ps required for vibrational predissociation. The relaxation of OH overtones in hydrogen peroxide occurs through a slowly evolving stretch-to-bend energy transfer with substantial beating between the two HOO bends, while the initially unexcited OH mode remains essentially isolated. Transfer of energy into the other OH bond is slow. Analogous behavior is observed for the relaxation of OH overtones in methyl hydroperoxide.[21]

We have also studied the effects of angular momentum on IVR and unimolecular reactions.[11,12,17] The effect of angular momentum in most cases is to enhance the rate of relaxation. Angular momentum tends to increase or decrease the reaction rate depending on how much of the total energy is "tied up" in molecular rotation.

Given the nature of the IVR of different kinds of high-frequency modes, it should be possible to capitalize on the distinctly different behaviors to effect mode-specific chemistry in the laboratory by careful selection of the molecule. Some of our studies should help guide this selection. For example, it might be fruitful to study reactions which involve H-atom migration between heavy atoms where one may be able to "fix the game" in favor of selective behavior since a CH stretch overtone excitation places the energy in a mode involved in the reaction and the initial relaxation moves the excitation energy to another mode (bending) that is also involved. The following is a brief review of our previous studies related to mode selectivity in reactions.

The central focus of our work is on unimolecular reactions and thus we have carried out a large number of studies probing mode selectivity in reaction dynamics. Mode selectivity requires that the coupling between the excited mode and the reaction-coordinate mode must be sufficient for the direct energy transfer promoting reaction to compete with the energy randomization among the various modes of the molecule. Thus, it is important that the excitation energy should be large compared to that required for reaction. For many reactions of interest such levels of excitation are not experimentally attainable. A way around this is to select systems with barriers low relative to the excitation levels. This is generally recognized and many processes with low barriers have been studied. An extreme example is the rupture of a van der Waals bond. While these systems provide some insight into mode selectivity, they are not particularly indicative of behavior chemical reactions. Another class of systems is intramolecular conversions such as *cis-trans* isomerizations, which usually involve barriers on the order of 15 kcal/mol or less. Thus, the barriers are quite small relative to the levels of excitation common in infrared single-photon experiments. We have investigated the influence of mode selective excitation on intramolecular conversion in HONO,[10-13] methyl nitrite,[23,60] and aziridine.[29] We recently reviewed this work.[34]

We have carried out extensive classical trajectory calculations for *cis-trans* isomerization in HONO to study the influence of initial vibrational mode excitations, IVR, potential coupling, molecular rotation, and barrier tunneling. This molecule provides an interesting set of conditions for investigating mode selective behavior. The energy required for the *cis*→*trans* and *trans*→*cis* conversions is about the same; the *cis*→*trans* barrier is 9.7 ± 0.7 kcal/mol. Thus, there is the possibility of influencing the isomerization by excitation of low overtones since even the $v = 1$ state of the OH stretching mode provides sufficient energy to cross the barrier. Calculations were carried out at a total energy of 1.7 eV for various initial conditions, with and without molecular rotation, and for two different potential-energy surfaces.[10-13]

The rate of *cis*→*trans* is significantly faster than *trans*→*cis* for the various initial conditions even though the energy barriers for the two processes differ by only about 0.6 kcal/mol. Large differences in the rates exist for potentials with and without coupling terms; the kinetic coupling in the *cis* is obviously much greater than in the *trans* conformer.

The results show that there is significant mode selective behavior. The largest rate is obtained when the HON bend is excited and the smallest for excitation of the OH stretch.

The influence of the torsional and bending modes on the dynamics can be illustrated by constraining them. We did this by incorporating Lagrangian multipliers into Hamilton's equations of motion.[12] We have calculated the isomerization rates for excitations of various modes with the HON and ONO bends fixed at their equilibrium values and the rate of relaxation of excited OH stretching by freezing the torsional motion.

The role of the torsional mode is illustrated by the results for constrained and unconstrained torsional motion in HONO on the relaxation of the $v=3$ state of the OH stretching mode. We find that during an initial period, ~0.5 ps, the rate of energy transfer is about the same for the two calculations; ~1/3 of the excitation energy transfers out of the OH. However, following this initial period, the rate of energy transfer is faster in the case of unconstrained torsional motion. A striking result is obtained when the HON bending motion is constrained. Essentially no energy flows out of the excited OH stretch over the entire period of integration (4.5 ps). These results suggest that the IVR is initially controlled by OH-to-HON energy transfer. The torsion plays a role after other modes have become excited due to IVR. Freezing the ONO mode has little effect on the rate of transfer out of the OH stretch.

The role of the bending angles in the transfer of energy can be studied indirectly by calculating the isomerization rate for constrained ONO and HON motion. Constraining the HON bend causes the greatest effect on the isomerization rate and it is most pronounced for *cis*→*trans*.

The influence of molecular rotation was also studied.[11] The calculations are for the same total energy, 1.7 eV, and for equipartitioning of the vibrational energy among all the modes except torsion. A significant increase in the isomerization rate results when only a small amount of energy (0.04 eV) is place in rotation, equally distributed among the three directions. The rate is also strongly dependent on the orientation of the angular momentum. When the molecule is allowed to rotate about the torsional axis the rate is more than a factor of 6 greater than in the nonrotating case. When it is allowed to rotate perpendicular to the torsional axis the rate is essentially the same as for no rotation. This behavior is contrary to what is predicted by statistical theory (RRKM), which predicts a lowering of the rate when energy is placed in rotation rather than vibration. However, the trajectory results are in agreement with RRKM when the rotational energy is somewhat higher (~0.1 eV). The observed increase in the rate for low rotational energy is due to active vibrational-rotational interactions. The energy transfer to the reaction coordinate (the torsion) is significantly increased by the rotational-vibrational coupling. We find that rotation has essentially no effect on the energy transfer from the OH stretch when the torsional motion is constrained to its equilibrium value.

We have used the Waite and Miller[61] classical-plus-tunneling model to study the *cis-trans* isomerization in HONO. There are significant mode selective effects in the tunneling rates. The rates range from 10^{-6} to about 3×10^{-1} ps^{-1}, depending on the initial energy partitioning in the molecule. The results suggest that, although there may be an effect due to IVR, the tunneling rates are strongly influenced by increasing the amplitudes of certain vibrations by exciting them. For example, consider the results for excited HON and N-O. The rate is much greater in the case of N-O excitation. This is the opposite of the specificity in the purely classical results. In fact, there is, in general, no correlation between the tunneling and classical rates.

Experimental studies have shown non-RRKM behavior in the *cis-trans* conversion of methyl nitrite.[62] The barrier to internal rotation is about the same as in HONO (~10 kcal/mol); the *cis* conformer is about 1 kcal/mol more stable than the *trans*. The *cis*→*trans* and *trans*→*cis* conversion rates in methyl nitrite have been calculated as functions of initial excitations of C-H local stretching modes and the ONO bending normal mode.[23] The results show no mode selectivity for excitations of the C-H stretches, however, excitation of the ONO bending mode gives rates that are about twice that for initial conditions in which the energy is equally distributed among all the modes or localized in the C-H stretching modes. The energy transfer from a C-H local stretch is essentially complete in less than 0.5 ps. The fact that excitation of the ONO bending mode gives faster rates than other energy distributions suggests that there is not energy randomization between the high and low frequency modes on the timescale of the inversion. As in the case of HONO, the rate of *cis*→*trans* conversion is much faster than the *trans*→*cis*.

Borchardt and Bauer[63] reported the measured rates for nitrogen inversion in aziridine in the gas phase for a range of temperatures and pressures, which differ significantly from RRKM predictions. They concluded that the energy transfer in the molecule is slow relative to the rate of inversion. We have investigated this molecule because its dynamical behavior may be relevant to energetic molecules such as TNAZ. We used classical trajectories to study the influence of initial energy partitioning on the rate of inversion.[29] We constructed a simple anharmonic (stretches) potential energy surface based on an experimentally determined force field. The barrier to inversion is 15.8 kcal/mol for this potential. Rates were calculated for various levels of excitations of the C-H and N-H local stretching modes. At a given total energy, the rate for N-H excitation is about 2.5 times that for C-H excitation or for equipartitioning of the energy. As the N-H relaxes energy flows into the bending mode, which is involved in the inversion, causing rate enhancement. The rate of energy transfer is fast relative to the rate of inversion, nevertheless, mode selective behavior is observed. This study shows how mode-selective reaction is favored if energy is deposited in a vibrational mode that is a component of the reaction coordinate mode. For example, rate enhancement of certain concerted molecular elimination reactions by mode-selective excitation should be possible (e.g., for HONO elimination in certain energetic molecules).

We have studied the decomposition of HOOH[14-18] and CH_3OOH.[21] The studies of H_2O_2 were among the first we carried out in this program. Much of the emphasis was on understanding the IVR, although we have calculated rates of decomposition. We have investigated the effects of OH overtones and excited stretch-bend combinations, rotational energy, potential energies, and other factors on both IVR and reaction.

The larger molecule, CH_3OOH, is more relevant to this program because of its size. And, although it has not been studied experimentally, the related molecule t-butylhydroperoxide has.[64] Furthermore, it is interesting since it contains an O-H stretching mode that is "isolated" from the bulk of the bath modes (CH_3 group) by the relatively weak O-O bond. It is a good candidate for mode selective chemistry because it contains both CH and OH local modes that can be excited to overtone states, and these modes are separated by the weak O-O bond. Our calculations show that the rate of decomposition is about twice as fast for OH excitation as it is for CH excitation.[21]

C. PUBLICATIONS, THESES, AND REPORTS

The following publications in refereed journals have resulted from the ARO-supported research:

Huadong Gai, Donald L. Thompson, and George A. Fisk, "A Classical Trajectory Study of IVR and Unimolcular Decomposition in Methyl Hydroperoxide," J. Chem. Phys. **90**, 7055-7063 (1989).

A. Preiskorn and Donald L. Thompson, "*Cis-Trans* Isomerization of Methyl Nitrite," J. Chem. Phys. **91**, 2299-2307 (1989).

Yuhua Guan and Donald L. Thompson, "Mode Specificity and the Influence of Rotation in *Cis-Trans* Isomerization and Dissociation in HONO," Chem. Phys. **139**, 147-161 (1989). (Invited - Special Issue on Mode Selectivity in Unimolecular Reactions)

Yuhua Guan and Donald L. Thompson, "Relaxation of Excited CH Stretching Modes in Toluene," J. Chem. Phys. **92**, 313-319 (1990).

Huadong Gai and Donald L. Thompson, "NH and CH Stretch Overtone-Induced Nitrogen Inversion in Aziridine" Chem. Phys. Letters, **168**, 119-125 (1990).

Thomas D. Sewell and Donald L. Thompson, "Mode Specificity in the Unimolecular Dissociation of the 2-Chloroethyl Radical," J. Chem. Phys. **93**, 4077-4093 (1990).

Betsy M. Rice and Donald L. Thompson, "Classical Dynamics Studies of Unimolecular Decomposition of Nitromethane," J. Chem. Phys. **93**, 7986-8000 (1990).

Thomas D. Sewell and Donald L. Thompson, "Classical Dynamics Studies of the Decomposition of RDX," J. Phys. Chem. **95**, 6228-6242 (1991).

Thomas D. Sewell, Harold W. Schranz, Donald L. Thompson, and Lionel M. Raff, "Comparisons of Statistical and Non-Statistical Behavior for Bond Fission Reactions in 1,2-Difluoroethane, Disilane, and 2-Chloroethyl Radical," J. Chem. Phys. **95**, 8089-8107 (1991).

Yue Qin and Donald L. Thompson,
"Classical Dynamics Study of HONO Using Constrained Trajectories,"
J. Chem. Phys. **96**, 1992-1999 (1992).

Eric P. Wallis and Donald L. Thompson,
"Molecular Dynamics Simulation of Conformational Changes in Gas-Phase RDX,"
Chem. Phys. Letters **189**, 363-370 (1992).

Huadong Gai and Donald L. Thompson,
"Collision-Induced Energy Transfer in p-Difluorobenzene by Light Atoms: A Wave Packet Scattering Calculation," Chem. Phys. Letters **191**, 441-447 (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, 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, Candee C. Chambers, Donald L. Thompson, and R. D. Levine,
"Power Spectral Study of the Classical Vibrational Dynamics of RDX"
Chem. Phys. Letters **208**, 125-134 (1993).

Eric P. Wallis and Donald L. Thompson,
"Molecular Dynamics Simulations of Ring Inversion in RDX,"
J. Chem. Phys. **99**, 2661-2673 (1993).

Yue Qin and Donald L. Thompson,
"Tunneling Effects in HONO *Cis-Trans* Isomerization,"
J. Chem. Phys., submitted.

Candee C. Chambers and Donald L. Thompson,
"Enhancement of Vibrational Mode Mixing Due to Isomerization Barrier Crossings,"
Chem. Phys. Letters, in press.

Other publications based on ARO supported research:

Donald L. Thompson, "Mode Specificity in Intramolecular Conversions," in the **Proceedings of the Twenty-Fourth Jerusalem Symposium on Quantum Chemistry and Biochemistry,** *Mode Selective Chemistry*, edited by J. Jortner, B. Pullman, and R. D. Levine (Kluwer Academic Publishers, The Netherlands, 1991), pp. 261-272.

Yuhua Guan, Turgay Uzer, Brian D. MacDonald, and Donald L. Thompson,
"Dissociation of Overtone-Excited Hydrogen Peroxide Near Threshold: A Quasiclassical Trajectory Study," in **Advances in Molecular Vibrations and Collision Dynamics**, Vol. 1B, Edited by J. M. Bowman and M. Ratner, (JAI Press, Greeenwich, Connecticut, 1991), pp. 81-104.

Betsy M. Rice and Donald L. Thompson,
"Classical Dynamics Studies of Unimolecular Decomposition of Nitromethane,"
Technical Report BRL-TR-3197, February 1991.

The following is a list of theses that have resulted from this research program during this report period:

Huadong Gai (Ph.D., 1990), Postdoctoral Research Associate, University of Pennsylvania (Prof. G. A. Voth). Thesis title: Theoretical Studies of Mode Specificity in Polyatomic Molecules.

Thomas Sewell (Ph.D., 1991), Postdoctoral Research Associate, University of Goteborg, Sweden (Prof. S. Nordholm). Thesis title: Unimolecular Reaction Dynamics of Large Polyatomic Molecules.

Eric P. Wallis (Ph.D., 1992), Research Scientist, Phillips Petroleum Company, Bartlesville, Oklahoma. Thesis title: Classical Dynamics Studies of Conformational Changes in Polyatomic Molecules in the Gas and Condensed Phases.

Yue Qin (Ph.D., 1992), Postdoctoral Research Associate, University of Oklahoma (Prof. Ralph Wheeler). Thesis title: Semiclassical Tunneling Corrections for Classical Dynamics of Unimolecular Reactions in Polyatomic Molecules.

D. SCIENTIFIC PERSONNEL

Graduate Students:

Huadong Gai (Ph.D., 1990)
Thomas Sewell (Ph.D., 1991)
Eric P. Wallis (Ph.D., 1992)
Yue Qin (Ph.D., 1992)
Candee Chambers (Ph.D. student)

Undergraduate Research Students:

William Davis (Summer 1993)
Project still in progress.

Postdoctoral Research Associates:

Dr. John Beauregard (1992-present)

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