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13. ABSTRACT *(Maximum 200 words)*

The research carried out under this program explored fundamental issues and mechanisms of chemical processes that are germane to the combustion and detonation of energetic materials; gas phase unimolecular and bi-molecular reactions; chemistry of surface-bound species; energy transfer (gas phase and at surfaces); molecular dynamics simulations; and the construction of potential energy surfaces. This work resulted in several significant scientific advances, over 50 publications, 18 Ph.D. theses, 3 M.S. theses, and the support of 18 postdoctoral fellows.

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STATEMENT OF THE PROBLEM STUDIED

This research was concerned with elementary chemical processes that are germane to the chemistry of energetic materials. It involved both experimental and theoretical studies of gas phase (unimolecular and bimolecular), gas-surface, and surface-bound systems. Models were developed that enable predictions to be made, in most cases with good numerical accuracy, for systems that are hard to examine experimentally in controlled environments. For example, the results of our work on unimolecular reactions will remain state-of-the-art for many years as a consequence of the thoroughness with which it was carried out. This is an example of a case in which fundamental and applied science complemented one another. Finally, many students and postdocs were trained to a high technical level — this is the *major* output of our program.

SUMMARY OF THE MOST IMPORTANT RESULTS

HANNA REISLER

1. The unimolecular reaction of NO_2: Overlapping resonances; fluctuations; transition states; tests of statistical theories

A main thrust of our work was the first experimental-theoretical study of overlapping resonances in unimolecular reactions. The fluctuations are the main form of deviations from smooth statistical behavior and also provide probes of the potential energy surface (PES) and the transition state (TS). In NO_2, fluctuations appear *from the onset of dissociation*, in the NO state distributions (PSDs), absorption linewidths, state-specific photofragment yield spectra, the oxygen spin-orbit ratios *correlated* with single NO levels, and in the state-to-state rates. The main manifestation of *overlapping* resonances appears in the state-specific photofragment yield spectra, which exhibit peak positions, widths and intensities that vary with the monitored final level.

Other important findings relate to the statistical nature of the decay and the properties of the TS: NO_2 dissociates in a largely statistical manner, but the pattern of fluctuations in the PSDs (which changes with increasing $E^{\dagger}$ from random fluctuations to distinct broad oscillatory structures) suggests that the TS tightens considerably with $E^{\dagger}$, and that different degrees of freedom become adiabatic at different locations along the reaction coordinate; NO vibrations becoming adiabatic first, the rotations next and the spin-orbit distributions last – at the largest O—NO internuclear separation. The question of how to describe best the PSDs in simple bond fission reactions has been addressed, but remains open.

The experimental/theoretical effort considers the evolution of overlapped resonances into final states via the TS, and is successful in interpreting qualitatively all the results. The model assumes that above dissociation threshold, D_0, overlapping resonances (i.e., resonances whose decay widths are larger than their separation) are excited. When these resonances interact coherently, interference results, giving rise to final state-selected absorption features whose widths and positions depend on the phases and amplitudes of the interacting resonances. Each product j state correlates with a different "mix" of overlapped resonances, and therefore gives rise to a different photofragment yield spectrum. The resonances, which already exhibit vibronic chaos, evolve to products via the TS, and their random projections onto levels of the TS are responsible for the (average) statistical behavior. The "mapping" of bending-like TS wavefunctions into rotational distributions, including the associated interferences, leads to the oscillatory structures seen at the higher excess energies (i.e., when the TS is tighter).

2. Collision-induced dissociation (CID) of vibrationally excited molecules in the gas phase and at surfaces.

This has been a main thrust of the project which was carried out both in the gas phase, and (in collaboration with Curt Wittig) at gas-surface interfaces. The work started with collision induced dissociation of hyperthermal molecules at surfaces. We found that the "stiff-

ness" of the collider was important in determining the efficiency of CID. For example, high energy collisions ($\leq$ 7 eV) CID of C_3F_7NO on a hard surface [MgO(100)] was more efficient than on "softer" surfaces, such as GaAs and Ag, which have lower Debye temperatures.

We then initiated the first experiments in which the CID of highly excited NO_2 (denoted hereafter NO_2*) is examined *with product state resolution* both in the gas phase and on surfaces. NO_2 is photoexcited to long-lived states (> 50 μs) just below D_0, producing admixtures of excited and ground electronic zeroth-order states that are weighted heavily by ground-state levels. NO detection is achieved by TOF/MS using REMPI.

Gas-phase CID of highly excited NO_2^* has been studied with different gas-phase colliders and on a MgO(100) surface at well-defined hyperthermal collision energies. Our experiments were aimed at determining the relative efficacies of translational and internal energy in promoting single-collision dissociation. CID yield spectra obtained by monitoring selected NO(j) levels while scanning the excitation laser down to 1000 cm^{-1} below D_0 reveal that near D_0 CID is quite efficient. This is expected, since the probabilities are comparable for adding energy to, or removing it from, the incident NO_2. Consistent with the energy gap law, the probability of CID decreases exponentially with the amount of energy needed to reach dissociation threshold. Rotational distributions of the NO CID product appear Boltzmann, with substantial rotational excitation; the NO spin-orbit distributions depend on the collider.

The average energy transferred per activating collision decreases with the level of complexity of the collider. It is possible that for molecular colliders the greater efficacy of T $\rightarrow$ V, R energy transfer involving internal degrees of freedom of the molecular colliders competes with conversion of translational energy to NO_2 internal energy.

The results are rationalized by assuming that dissociation is effected mainly via impulsive collisions; "stiff" atomic colliders are more effective than "soft" polyatomic colliders. Near D_0 the dominant process is inelastic scattering, even when reactive channels are open. This may be a consequence of (i) steric restrictions on approach geometries for reaction, and/or (ii) the fact that only specific vibrational motions correlate with the reaction coordinate.

CID can be described as a two-step process. First, impulsive collisions activate NO_2^*, generating a distribution of energies above D_0. This is followed by unimolecular decomposition to yield NO + O, in which the collider plays largely a spectator role. This two-step model reproduces the observations well. Exit-channel interactions of the activated NO_2^* with the collider may also influence the outcome of CID. The partitioning of excess energy among the NO + O products and the collider can be affected.

In the CID of internally excited NO_2 molecules colliding with a crystalline MgO(100) surface, exit-channel interactions are more complex than in the case of gas phase collisions, since molecule-surface binding energies of the parent as well as its fragments are significant and the surface-molecule forces are longer-range than are the weak attractive forces encountered in the gas phase experiments. Thus, one cannot assume *a priori* that unimolecular decomposition proceeds in a way that parallels the gas phase CID. At a distance of few Å from the surface, there will be an attractive interaction between the fragments and the surface that can alter their internal energy distributions. For example, one or both of the fragments may be temporarily captured by the surface, or undergo energy transfer in the exit channel.

In a reasonable scenario, at least some of the NO products will be attracted to the surface. In separate studies, it was found that when expansion-cooled NO is scattered from MgO(100), the $[^2\Pi_{1/2}]/[^2\Pi_{3/2}]$ ratio is near unity (i.e., the statistical value), which stands in sharp contrast to the NO product which derives from decomposition of isolated NO_2, and is more similar to the corresponding value obtained in NO_2 CID on MgO(100). Thus, secondary interactions with the surface are probably common. On the other hand, *the NO molecules which are detected* retain some memory of the momentum of the incident NO_2, *i.e.*, they are not the consequence of trapping followed by desorption. Thus, all of the evidence collected to date is consistent with a dissociation mechanism in which NO_2 gains energy in the collision and some percentage of it decomposes before it can free itself from the environs of the surface.

3. Ion imaging studies of the photodecomposition of HNCO

During the last phase of the funding period, an ion imaging detection system was incorporated into the CID machine, and was used in the study of NO_2 and HNCO. Our most detailed studies involve the photodissociation of jet-cooled HNCO following $S_1(^1A'') \leftarrow S_0(^1A')$ excitation at 280-215 nm. At the onset of our work, only two dissociation channels were identified, the thermochemistry was uncertain, and it was believed that only the S_1 PES participated in < 230 nm photolysis. Our studies have revealed a much richer dynamics: dissociation transpires on at least three potential energy surfaces (PES) to three chemically distinct channels: (1) $NH(X^3\Sigma^-)$ + CO, (2) H + NCO, and (3) $NH(a^1\Delta)$ + CO.

Our experiments result in a "road map" for the decomposition into channels (1)–(3) that is applicable over a broad wavelength range. Unravelling the mechanism was a challenge, providing its share of surprises, and taxing our ability to understand the subtle interplay between vibronic couplings, location of crossing seams, and couplings to dissociative continua. Imaging enabled us to characterize decomposition timescales and correlated product distributions. When combined with other techniques, the array of scalar and vector properties pinpointed major pathways, as well as photolysis energy regions where competition is important and/or mechanisms change. The surface couplings via internal conversion and intersystem crossing were found to be of comparable strength to the couplings to the dissociative continua, resulting in the coexistence of all three channels over a broad wavelength range.

CURT WITTIG

Barrierless Unimolecular Decomposition of Small Polyatomic Molecules

This component of our ARO-URI-sponsored research is the most scientifically significant body of work that has been carried out by my group since its inception in 1973. It has resulted in an improved understanding of unimolecular decomposition, particularly barrierless reactions, at a fundamental level. This class of reactions plays a central role in the combustion and detonation of energetic materials. The model that resulted from this research requires

little, if any, phenomenological input, and it contains all of the known physics of barrierless unimolecular decomposition on a single potential energy surface (PES), albeit qualitatively. Extensions to multiple PES's are straightforward. In this final report, I will describe the evolution that led to our present level of understanding, and summarize the important points.

I was first introduced to the statistical theory of unimolecular decomposition in 1981 by reading the book written by Wendell Forst. For several years thereafter, much of the data from my group were fitted by using standard models such as phase space theory (PST), RRKM theory, and the statistical adiabatic channel model (SACM). Our level of understanding was state-of-the-art, but no better. I was unable to see clearly the fundamental physical underpinnings of the models. This was due to a flawed approach: jumping right in without a sufficiently careful study of the fundamentals.

Around 1990, I became interested in models of unimolecular decomposition that make use of random matrix theory, *e.g.*, to describe the width matrix Γ in the non-Hermitian effective Hamiltonian $H^{eff} = H_0 - i\Gamma/2$, where H_0 describes the bound space. Since the mid-eighties this had been touted as the only theory of unimolecular decomposition, short of brute-force solution of the Schrödinger equation, that accounted for (qualitatively) all of the relevant quantum mechanical phenomena, most notably fluctuations. The books by Mehta (*Random Matrices*) and Cohen-Tannoudji, Dupont-Roc, and Grynberg (*Atom-Photon Interactions*) were helpful, and I read numerous journal articles on topics ranging from nuclear physics to unimolecular decomposition. Though the mathematics *per se* of random matrix theory is correct, it was clear that applications to unimolecular decay had serious problems, as discussed below.

When the reactive resonances are not severely overlapped, which is only the case just above threshold, the results are in accord with the available experimental data and our knowledge of the physics. However, such agreement is meaningless, because an acceptable answer is inputted as the diagonal matrix elements, and the off-diagonal matrix elements, which are the source of the problems, are too small to have an appreciable effect when only a few reactive channels are open.

Problems arise when the resonances are made to overlap severely. For example, when increasing the number of open channels and/or the magnitudes of the matrix elements, coupling amongst the zeroth-order levels becomes strong and the eigenstates behave strangely. Bifurcations appear in which there is a marked difference between reaction rates. Namely, two classes of rates appear — fast and slow. With sufficiently strong coupling, the number of fast rates approaches the number of open channels. This is unphysical; molecules do not do this. Yet, the random matrix model yields this result. Common sense tells us that the model is wrong.

There are other drawbacks as well. In most of the formulations, there is no energy dependence, because matrix elements are inputted over the full range of the matrix. This can be fixed by inputting open channels at their thresholds. Also, diagonalization causes reactive flux to appear at unreasonable energies, *e.g.*, below known thresholds. However, these problems are relatively minor compared to the appearance of bifurcations in systems where they make no sense.

Though I realized that the random matrix approach to modeling unimolecular decomposition was flawed, as exemplified by the bifurcation problem, I could not figure out why. Dur-

ing this period, all of my ideas led to dead-ends: (i) Should the off-diagonal matrix elements be complex rather than purely imaginary, *e.g.*, as required by the 2π relationship?† Maybe, but it makes no difference in the results. (ii) Would introducing open channels at their correct energy thresholds help? Somewhat, but not enough; the problem remains. (iii) Is bifurcation an "edge effect," *i.e.*, due to the strong coupling in which the decay width exceeds the energy range (*i.e.*, based on just the real parts) of the matrix? This is an indication that something is wrong, but it is not the reason. And so forth.

By the mid-nineties, it had become clear to many scientists doing research in this area that the problems associated with the random matrix models were lethal, *e.g.*, poor conceptualization of the physics and bizarre results. Some research groups continued to play computer games with the model and they filled the literature with mathematically sophisticated stuff that has no physical significance. Others, realizing something was not right, moved on to greener pastures. From my perspective, there was no progress.

It took me a long time to figure out what is going on with the random matrix model and why it is incapable of yielding physically reasonable results in the regime of overlaping resonances. At least for me, this was a psychologically important step on the way to a correct model that includes the threshold quantum statistics. The first hint came from solving a problem in which classical oscillators are coupled by friction plates. Increasing the magnitudes of the friction coefficients results in a bifurcation. With one friction plate, one vibrational mode becomes very lossy, whereas the other vibrational modes become nearly loss-free. In the limit of infinite friction, there are $N-1$ loss-free modes and one infinitely lossy mode. If there are M friction plates ($M < N$), then as the loss increases, $N-M$ modes are low-loss and M modes are high-loss. This example demonstates a bifurcation which has a clear physical significance. The mathematical correspondence between this problem and the eigenvalues of the effective Hamiltonian, $H^{eff} = H_0 - i\Gamma/2$, enabled us to understand the H^{eff} problem. Namely, when the magnitudes of the matrix elements of Γ are increased and a bifurcation occurs, it is the continuum that appears as the very lossy level. This has nothing to do with unimolecular decomposition.

It was then realized that the random matrix model, at least as implemented to date, is incompatible with transition state theory. The reason is that the zeroth-order levels are coupled directly to continua. Open channels, with their independent continua are treated by adding random matrices on top of one another. This has certain appealing features, such as some averaging over fluctuations. However, upon diagonalization the continua become coupled to one another, and therefore they are not independent. Choosing the random matrices independently does not make the continua independent. Upon diagonalization, the continua are coupled. This fatal flaw causes the model to yield bifurcations.

Next, we wrote the simplest model that contained the correct physics. A single independent reaction channel could be modeled by using the 2π relationship, inputting the statistical fluctuations with the average rate per open channel given by $1/h\rho$. Successive open channels are added at their thresholds. This ensures that the channels are independent. This model yields the following features:

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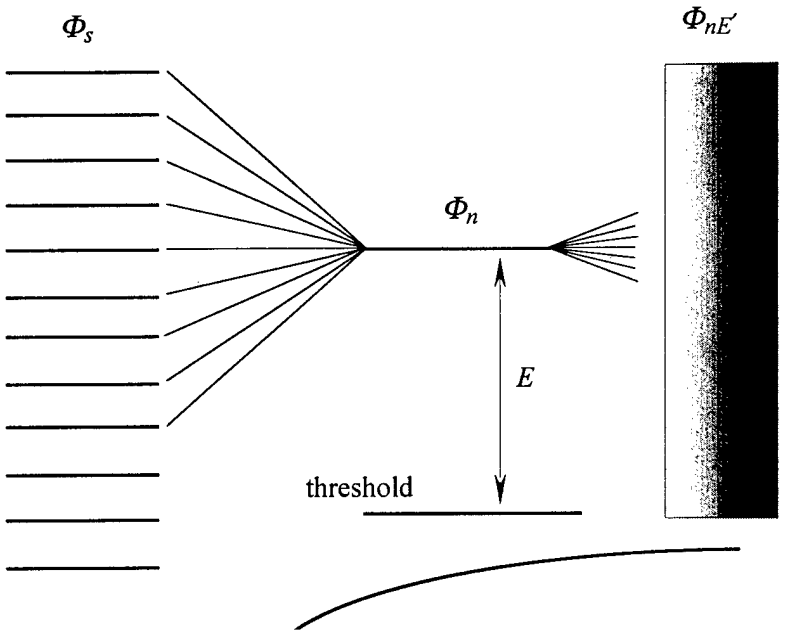
† The transition state for an open channel is coupled to the molecular region 2π times more strongly than to its continuum. Borrowing a term from optics, 2π is the "finesse" of the open channel, namely, it is the average separation between adjacent resonances divided by the average decay width ($1/h\rho$). The finesse is 2π for *each* of the open channels.

- Fluctuations in $k(E)$ are most prominent at threshold, decreasing with energy because of averaging; the average energy-independent rate is $1/h\rho$ per open channel.
- Transition states lie at large r for energies just above the channel thresholds, moving to smaller r with increasing energy in excess of the channel threshold. This is true for each channel. It is a unique feature.
- Lineshapes are overlapped Lorentzians for absorption spectra in the regime of overlapped resonances, and interference lineshapes for state-selected product yield spectra.

There are no bifurcations because the model treats the reaction channels as independent, consistent with transition state theory. There is no complicated calculation of any kind. Transition states are essential in order to have independent channels, which causes this model to differ radically from the random matrix models. Though this model is the result of years of effort, in the end, its implementation is deceptive in its simplicity. The figure below gives the main features for the case of a single open channel.



Bound levels Φ_s are coupled via a single intermediate level Φ_n to a continuum of levels $\Phi_{nE'}$. The subscript n in $\Phi_{nE'}$ is used in anticipation of there being one continuum per transition state level. All matrix elements $V_{n,nE'} = \langle \Phi_n | V | \Phi_{nE'} \rangle$ are assumed to be the same, and $V_{s,nE'} = \langle \Phi_s | V | \Phi_{nE'} \rangle = 0$ for all s and E'. The energy E_n of the Φ_n level is taken to be identical to the energy of concern, E, for all values of E. In other words, $E_n = E$ is maintained throughout the domain $E > 0$, where $E = 0$ is the threshold.

CHI MAK

1. Transferable Potentials for Reactive Systems and Reaction Dynamics

Under the ARO-URI program, we worked on developing potential energy surfaces for reactive systems based on the tight-binding Hamiltonian. Our objective was to construct a parametrization of the tight-binding potential so that a simple method can be used to generate reliable potential surfaces for describing reactions relevant to energetic materials research.

The tight-binding potential we chose to use was different from most conventional methods where empirical functional forms are used to parametrize both reactive degrees of freedom and internal motions. Our potential has several possible advantages over conventional schemes:

1. This potential describes bond breaking and bond forming naturally — these essential features for modeling chemical reactions in energetic materials are described in a unified and natural way;
2. The potential is intrinsically quantal — the total energy results from a diagonalization of a tight-binding Hamiltonian, making parametrization of potential energy surface to arbitrary functional forms unnecessary;
3. The potential is transferable — a small set of parameters describes the bonding characteristics of a large number of compounds. The potential is easily transferable to many different systems;
4. Parametrization is straightforward — because the potential is transferable, the potential is easily parametrized by fitting to small molecules and radicals for which reliable experimental measurements and high quality ab initio data exist.

The potential we constructed contains interactions between four different types of atoms: H, C, N and O, which are the most common atoms in many reactions involving energetic materials. The entire suite of the tight-binding (TB) Hamiltonians has been parametrized within the original formulation, as indicated in Table I. All interactions, except N-O, were successfully parametrized with excellent or good accuracy in comparison with known experimental and/or theoretical data.

	H	C	N	O
O	E	E	M	G
N	E	G	E	
C	E	E		
H	G			

Table I. Parametrization of bonding interactions in the tight-binding potential: E, excellent accuracy: G, good accuracy; M, moderate accuracy.

The most difficult part of the parametrization involved the N-O interactions. The simple formulation of the TB potential was found to be able to describe dative bonds, which are important to the chemistry of the NO_2 group. But the dissociation of the N-O bond turned out to require very high level of configuration interaction (CI) on top of the tight-binding potential. To be able to describe the bond breaking process in $CH_3NO_2 \rightarrow CH_3NO + O$, for example, even including triples in the CI calculations was unable to produce accurate energies along the reaction coordinate. Including higher levels of CI would be too costly to be practical for a dynamics simulation. Therefore, we had to resort to less rigorous methods.

One alternative method we explored was the Empirical Valence Bond method (EVB) of Warshel *et al.* The advantage of the EVB method is its natural ability to describe bond breaking in a qualitatively correct way without having to rely on high-level MO calculations. The main drawback of EVB, however, is its empirical nature, which does not guarantee the accuracy of the potential or that the potential constructed would be transferable from one molecule to another. To test the EVB alternative, we started with the parametrization of the EVB potential for N-O interactions in the NO_2 molecule. We found several sets of parameters that seemed to describe the energetics reasonably well. But when we attempted to transfer these parameters to the CH_3NO_2 molecule, the results were only marginal. Therefore, we did not pursue the EVB method further because it appeared that the EVB potential does not have the transferability we desired.

2. Molecular Dynamics Code for Energetic Reactions

Since large amounts of energy are typically transferred in many energetic materials reactions, simulating the dynamics of energetic materials reactions requires a special molecular dynamics (MD) engine. Conventional MD codes using the simple Verlet or leap-frog method would become unstable unless extremely small time steps are used. Therefore, one of our goals in the ARO program was to develop a MD code that could work with large time steps (to save CPU time) but would still be numerically stable in the presence of highly energetic bond breaking processes. To do this, we developed a MD code based on a high-order Romberg integrator. Using this MD engine, we were able to simulate the dynamics of highly energetic reactions with a time step of 3 to 5 fs in most cases.

3. Structures of Covalently-Bonded Molecular Systems

Using our molecular dynamics code developed under the ARO grant, we have studied several condensed phase systems using the TB potentials. First, to test the quality of our tight-binding potential in extended bulk systems, the structure and bonding characteristics of solid amorphous carbon (*a*-C:H, with arbitrary density of dangling bonds and hydrogen atoms) has been examined. Analogous to amorphous silicon in its structure, which has important technological applications for its usage in solar cells, amorphous carbon is important in coating technologies. To model amorphous (non-hydrogenated) carbon, simulations were carried out by first melting solid diamond at 5000 K and then slowly quenching the liquefied carbon sample down to room temperature in a number of 20 ps long simulations. The final equilibrated structures were analyzed for dangling bond densities. At the experimental density of 2.69 g cm^{-3}, we found 6.2, 71.6, and 22.2% sp, sp^2, and sp^3-hybridized carbon atoms,

respectively. These results are in good agreement with previous *ab initio* molecular dynamics calculations.

We have also studied the change in the dangling bond density when the sample is hydrogenated. The carbon-carbon radial distribution functions for two samples with different hydrogen concentrations now show an enhancement in sp^2 carbons. When the hydrogen concentration is increased from an atom fraction of 0.20 to 0.30, the concentration of sp^2 carbon decreases and the concentration of sp^3 carbon increases. This suggests that adding hydrogen promotes the rehybridization of the carbons from sp^2 into sp^3. This is because hydrogen atoms can terminate dangling bonds and they tend to force the carbon atoms to seek higher coordination geometries.

4. A New Formulation of the TB Potential

The original formulation of our TB potential treats electron-electron repulsion very crudely. In some dissociation reactions, this causes the system to end up in the wrong electronic states. In others, different electronic configurations lying close to each other in energy sometimes do not mix correctly. To try to cure these problems, we have explored a new formulation of the TB potential. This is based on Pople's early CNDO (complete neglect of differential overlap) formulation of molecular orbital theory. First, we parametrize the one- and two-electron integrals by using the TB formalism. Then, within the assumption of CNDO, we can implement a number of improvements over the original TB formulation. For example, we can now do configuration interaction (CI) to compute the energy of excited states with better accuracy and obtain dissociation curves that are more realistic. As an alternative, we can also use Moller-Plesset perturbation theory (MPPT) to improve the solution near the equilibrium position. In the course of the development of this alternative CNDO formulation of the TB potential, we discovered that the original formulation is actually related to the more sophisticated CNDO treatment if a set of simple approximations were made. This discovery allowed us to retain a large part of our earlier TB parameters. Because doing CI or MPPT is more costly, we have used the simple TB Hamiltonian in systems where we have sufficient accuracy from the original formulation. In systems where the simple TB potential fails (*e.g.*, $H + O_2 \rightarrow O + OH$), the new parametrization has been found to be useful. Unfortunately, this formulation was unable to circumvent the problems encountered with the N-O interactions in the original TB formulation.

BRUCE KOEL

Surface Chemistry of NO_2 and RNO_2 Groups

In combustion or explosion, reactive species are produced that have subsequent chemistry that must be accounted for in accurate modeling or simulations of these processes. The focus of our work under this grant was to improve the understanding of chemical reactions that can occur at solid surfaces containing NO_2 and RNO_2 functional groups and the role (if any) of

the high flux of H atoms generated in flames that impinge onto the surfaces of energetic materials. For several prototypical systems, we elucidated the reactivity (reaction cross section) and branching ratios for the possible reaction channels (*i.e.,* scattering, abstraction, or addition) in these interactions. The spectroscopic work that was done was a necessary foundation for these studies, and provides a firm basis for future work. In particular, we focussed on the condensed phase chemistry in both monolayer and multilayer solid films of nitrogen dioxide (NO_2 and N_2O_4), nitromethane (CH_3NO_2), methylnitrite (CH_3ONO), and nitrobenzene ($C_6H_5NO_2$) as prototypical molecules that contain chemical bonds and functional groups relevant to energetic materials. MgO(100), Au(111), and Pt(111) single crystal substrates were used to support these films for investigation with temperature programmed desorption (TPD) mass spectrometry and vibrational spectroscopy by HREELS or FTIR. The FTIR apparatus was constructed for this grant.

Spectroscopy of NO_2 and N_2O_4 films

We have studied the structure, bonding, and condensed phase chemistry of nitrogen dioxide, adsorbed as NO_2 or condensed as N_2O_4 in solid films, on MgO(100) and Au single crystal substrates using TPD and FTIR. The IR was performed in Transmission-Absorption mode (FT-ITAS) for MgO and Reflection-Absorption mode (FT-IRAS) for Au. We use the powerful polarization dependence and selection rules of IR absorption to deduce molecular geometries and orientations in surface layers. The studies on Au and Pt substrates were also carried out by using HREELS. This work provides a benchmark for studies of the reactivity of H and CH_3 radicals at the surface of condensed, solid films of these molecules in order to simulate the surface reactivity of solid energetic materials. These molecular solids can be grown with relatively smooth interfaces in a very controlled fashion via vapor deposition on these substrates. While perhaps not an important issue to combustion, the influence of the crystallinity of these deposited films on surface reactivity is major issue in understanding these types of controlled, model studies. Aspects of this were investigated in ice (H_2O) thin films, where we studied the structural phase transition from amorphous to crystalline ice for various film thicknesses in the temperature range from 137-145 K by using FTIR. Low surface temperatures and high deposition rates favor condensation into less ordered, crystalline, structures, and we see large differences in the reactivity of the ice surface depending on whether it is amorphous or crystalline. The amorphous ice surface has "free OH" species, and bonds strongly to polar molecules. The crystalline ice surface (and also the adsorbed water monolayer) is completely hydrogen-bonded leaving no "free OH" species and it is relatively inert to reactions. Analogous studies using nitrobenzene ($C_6H_5NO_2$) and phenyl iodide (C_6H_5I) were done to move closer to incorporating the complexity of actual energetic materials.

Reactions of H_2O with Molecular Solid Surfaces

These studies of H_2O adsorption and reaction provide benchmarks for our investigations of H + RNO_x chemistry and new information on H_2O + RNO_x chemistry. One important finding (for surface science in general) was that H_2O does not thermally dissociate on MgO(100), in contrast to reports in the literature that utilized model, thin epitaxial MgO films

grown on metal substrates. Water in the monolayer is tilted on the surface and extensively hydrogen-bonded such that no "free OH" groups are present.

Reactions of H Atoms with Molecular Solid Surfaces

Surface science studies of H atoms incident on solid surfaces were carried out with the sample at 100 K in order to stabilize the condensed phase of the molecular solids and to accumulate metastable reaction products due to H atom bombardment. This required characterization and calibration of several new H atom sources that are suitable for these low-temperature investigations. A suitable source incorporates a Pt capillary tube that is resistively heated. This is a very clean source due to the lower operating temperatures and the absence of volatile Pt oxides. The performance of this source was tested by novel H adsorption experiments utilizing Pt-Sn alloy surfaces. These Pt-Sn alloys are made in our lab and do not chemisorb H_2 so that an absolute H atom flux determination is possible using these surfaces and TPD. We also built and calibrated (flux) a new CH_3 (methyl) radical doser in novel studies of CH_3 radical adsorption and reaction Pt-Sn alloy surfaces.

We show that H atoms with a thermal energy of ~ 1300 K have reaction probabilities with NO_2 groups at surfaces and solid films of N_2O_4 and azomethane ($(CH_3N{=}NCH_3)$ that are very high (~ 1), with similar cross sections to those encountered in gas phase studies. This is in stark contrast to suggestions from simulations (done at Penn State Univ. under Prof. Kuo) that H atom reaction probabilities are of order 10^{-8}. Setting these reaction probabilites to unity in these codes should allow other parameters to be changed to more accurately model combustion of energetic materials.

PUBLICATIONS, REPORTS, AND BOOK CHAPTERS

Hanna Reisler

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REPORT OF INVENTIONS

No patents were applied for as a result of this research.