Our research into the chemical properties of highly vibrationally excited molecules has revealed a strong connection between large amplitude vibrational motion and the ability of a molecule to accept or donate electrons. In this proposal, we explain the work leading up to this insight and suggest ways to further test our understanding of this phenomenon. We suggest two experiments to extrapolate these results to completely new kinds of chemical encounters: the vibrational enhancement of electron capture and the direct observation of vibrational promotion of an electron transfer reaction. This work may have significant implications for electron scavenging around re-entry vehicles and accompanying communications blackouts.
**Final Technical Report**

*Reactive" vibrational relaxation in the Gas-Phase and on Surfaces", F49620-98-1-0173, March 1, 1998-Feb. 328, 2001*

**Approach**

Understanding the gas-phase and gas-surface collision dynamics of highly vibrationally excited NO is necessary to model the chemical reactivity, ro-vibrational population distribution and infrared emission spectrum of this important molecule in the upper atmosphere. There is increasing evidence that collisional relaxation of highly vibrationally excited molecules may be controlled by very unusual state-to-state cross-section associated with new dynamics that are not found for the low vibrational states.

The objective of this research is to understand and characterize new mechanisms as well as to predict and control the chemical reactivity and the flow of energy in such highly vibrationally excited molecules. Topics of interest include: the effect of vibrational excitation on reaction probability, chemical branching and survival probability of vibrationally excited NO upon collision with other molecules and surfaces. Experimental results can then be used in atmospheric chemistry and space vehicle emission modeling.

Quantum state selective laser-based optical pumping schemes such as stimulated emission pumping (SEP) and overtone pumping are used to prepare NO molecules in low and high vibrational states for comparison. Crossed molecular beams methods are used to study the rotational and vibrational energy transfer as well as chemical reactivity of these species under single collision conditions. Velocity mapping techniques are used to obtain product angular and velocity distributions. Ultra-high vacuum surface-science methods are combined with SEP and molecular beam techniques to study gas-surface interaction for the first time.
Results

We have developed and presented a new experimental method for measurement of collision-free infrared radiative lifetimes for single quantum states of a vibrationally excited sample. This method provides a more direct route to the infrared Einstein $A$-coefficients than has been previously possible. Results for NO($X^2\Pi$, $v=21$ and $v=7$) were presented. Comparison to results of \textit{ab initio} calculations shows excellent agreement. A controversy regarding the relative intensities of $1^{st}$-overtone and fundamental emission intensities in NO is laid to rest. The most complete least squares analysis of existing data was carried out to derive the electric dipole moment function (EDMF) to an accuracy of $\pm0.02\text{D}$ between 0.9 and 1.7\AA.

In another study we have investigated near resonant vibration-vibration energy transfer. Lack of understanding of the factors that compensate energy defects in near resonant V-V energy transfer constrains our ability to accurately predict resonance widths and, thus, the overall importance of such processes. We have carried out one of the first truly state-to-state measurements of near resonant V-V energy transfer under single collision conditions, employing the crossed molecular beams, stimulated emission pumping technique. We have varied the energy defect $\Delta E$ for the process: NO $X^2\Pi(v=1) + N_2O(0,0,1)$, by changing the prepared vibrational state from $v=22$ ($\Delta E= +14 \text{ cm}^{-1}$) to $v=21$ ($\Delta E= -18 \text{ cm}^{-1}$) to $v=20$ ($\Delta E= -49 \text{ cm}^{-1}$). Changes in the energy transfer efficiencies and rotational distributions of vibrationally inelastically scattered NO with energy defect both strongly suggest that molecular rotation (both of NO and N$_2$O) is responsible for compensating the energy defect. Furthermore it appears that relative translation is ineffective in compensating the energy defect.

Much of our work over the funding period has been geared toward trying to understand molecular interactions with metal and oxide surfaces. We developed and presented a new experimental approach to the study of vibrational relaxation of highly vibrationally excited molecules at solid surfaces. We observed NO in $v = 13$ and 15 losing up to five vibrational quanta in collisions with an O-covered copper surface. The data indicated this vibrational relaxation occurs via a direct scattering mechanism.
These studies were then expanded to study vibrationally promoted surface chemistry. The chemical dynamics of highly vibrationally excited molecules were studied by measuring the quantum state-resolved scattering probabilities of nitric oxide (NO) molecules on clean and oxygen-covered copper (111) surfaces, where the incident NO was prepared in single quantum states with vibrational energies of as much as 300 kilojoules per mole. The dependence of vibrationally elastic and inelastic scattering on oxygen coverage strongly suggests that highly excited NO (v = 13 and 15) reacts on clean copper (111) with a probability of 0.87 +/- 0.05, more than three orders of magnitude greater than the reaction probability of ground-state NO. Vibrational promotion of surface chemistry on metals (up to near-unit reaction probability) is possible despite the expected efficient relaxation of vibrational energy at metal surfaces.

In light of all of the new results on very highly vibrationally excited molecules, we decided to perform some experiments on lower vibrational states as well. Measurements of vibrational excitation and de-excitation of NO (v= 2) scattering from a Au(111) surface show that the probability of both processes increases strongly with the kinetic energy of the incident NO. These results were qualitatively consistent with a vibrational energy transfer mechanism involving electron-hole pairs but not with competing adiabatic models. The form of the energy dependence, and other features of the measurements, are not in accord with existing calculations.

One of our most exciting results used laser methods to prepare specific quantum states of gas-phase nitric oxide molecules, where we examined the role of vibrational motion in electron transfer to a molecule from a metal surface free from the complicating influence of solvation effects. The signature of the electron transfer process was a highly efficient multi-quantum vibrational relaxation event, where the nitrogen oxide loses hundreds of kilojoules per mole of energy on a sub-picosecond time scale. These results cannot be explained simply on the basis of Franck-Condon factors. The large-amplitude vibrational motion associated with molecules in high vibrational states strongly modulates the energetic driving force of the electron transfer reaction. These results show the importance of molecular vibration in promoting electron transfer reactions, a class of
chemistry important to molecular electronics devices, solar energy conversion, and many biological processes.

**Publications resulting from AFOSR support**


**Public scientific presentations of AFOSR supported work**

1. AFOSR contractors Meeting, Monterrey California, May 17-20, 1998, “Crossed-beam and surface scattering of highly vibrationally excited NO”


5. Invited Lecture, “Collisions and Chemistry of Super Excited molecules” Conference of Molecular Energy Transfer, COMET XVI, Assisi, Italy, June 20-25 1999


19. Invited Lecture, “Chemistry with stretched molecules”, Institute of Atomic and Molecular Science (IAMS), Taipei Taiwan, June 12, 2000


