ENERGY TRANSFER PROPERTIES AND MECHANISMS

TECHNICAL PROGRESS REPORT

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Introduction

Collisional energy transfer is the controlling factor in many nonequilibrium chemical systems. In combustion, both pyrolysis reactions and recombination reactions are largely controlled by energy transfer. In infrared laser-induced chemistry, collisional energy transfer is often a limiting factor, because of degradation of the excited species population distributions. In shock-heated gases and other hostile environments, energy transfer plays a significant role. In atmospheric science, radical recombination reactions are controlled largely by energy transfer.

The overall objective of the research carried out under this program is to determine the principles of collisional energy transfer and use them in predictive models and theories. In order to accomplish this goal, energy transfer properties must be determined and then analyzed to discern the underlying principles involved.

In this laboratory, the experimental determination of energy transfer parameters is based on techniques that use physical properties to monitor the amount of energy in excited molecules. These techniques differ from chemical methods, based on unimolecular reaction studies, which are susceptible to interferences from complex chemical mechanisms and other complications. The physical methods have their own weaknesses and limitations, however, and much of our effort has been directed toward gaining a better understanding of these deficiencies.

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Accomplishments and Plans

Large Molecule Energy Transfer Experiments

In previous work, we have used the infrared fluorescence technique to investigate energy transfer in azulene, benzene, benzene- d_6 , toluene, and toluene- d_8 . This work, which has used a single emission band (the C-H stretch modes near 3050 cm^{-1} or the C-D stretch near 2250 cm^{-1}), is capable of estimating the ensemble average excitation energy (the "bulk average energy", $\langle\langle E(t) \rangle\rangle$) as the excited species are being deactivated by collisions. The average energy in this "collisional energy cascade" is used to determine $\langle\langle \Delta E(t) \rangle\rangle$, the bulk average energy step size, which is a function of time and, hence, of the bulk average energy.

We have published the first experiments measuring the variance of the energy distribution (second central moment) for the benzene and benzene- d_6 systems, where a small fraction of the species are excited and are deactivated by the bulk of unexcited gas. This is the first time such detailed information has been obtained over essentially the entire collisional cascade. This was accomplished by a) the use of the time- and wavelength-resolved infrared emission spectrum of highly excited benzene and b) two-color IRF measurements of the fundamental and overtone emissions from the C-H (and C-D) stretch modes. The data analysis approach we have developed can be easily extended to other experimental techniques, including time and wavelength resolved ultraviolet absorption, as long as suitable calibrations exist. This approach results in refined estimates of both the mean energy and the variance of the energy distribution, and it is superior to the one-color IRF technique we have used previously, because more data are used in the analysis.

We are extending these experiments by measuring the deactivation of toluene isotopomers, which have favorable IRF emissions at three wavelengths. Our aim is to measure three moments of the evolving population distribution function. We have completed work on 1,1,1-trideuterotoluene and have good data on the C-H and C-D fundamentals in addition to the C-D overtone. The results are still being analyzed, but it now appears that we have good data on the first two moments, but the third moment is not well determined. We are also carrying out experiments on pyrazine, since this species has been the subject of investigations in several other laboratories.

In other experiments, we have begun using pump-probe techniques to measure the final state distributions of species involved in energy transfer collisions. The experiments utilize a REMPI probe of nitric oxide, following excitation of pyrazine at 248 nm. The first results are promising and we expect to have completed the first study by this time next year.

Triatomic V-T/R Energy Transfer: Memory Effects

For some time now, we have been puzzling over our data on the deactivation of NO_2 , CS_2 , and SO_2 by the rare gases. We used the time-dependent thermal lensing technique with very high dilution ratios (e.g. $\text{Kr}/\text{CS}_2 = 5000/1$) to isolate the V-T/R energy transfer process. With all three gases, our results have been a puzzle, because the energy deactivation does not seem to depend properly on the number of collisions. One might expect the energy deactivation to depend only on the number of collisions, but our data indicate that the deactivation is most efficient when the collision frequency is low. We have spent a considerable amount of time attempting to identify and eliminate possible experimental artifacts in these experiments, and the experimental results have remained essentially unchanged.

These results may be indicative of a "Memory Effect". This conclusion is supported indirectly by trajectory calculations carried out by Schatz and coworkers. The idea is as follows: when an energy transfer collision occurs, energy is removed preferentially and non-randomly from a subset of states (the symmetric stretch mode, for example), leaving a coherent superposition of states. After the collision, the coherent superposition of states scrambles with a time constant which depends on the density of states and other factors. Since the density of states in triatomics is rather low, the time constant is long and a subsequent collision may occur before the randomization is complete. If randomization is incomplete, the subsequent energy transfer collision is relatively ineffective. Thus, low collision frequencies (long times between collisions) favor efficient energy transfer. Our data for CS_2 are consistent with time constants for randomization on the order of a nanosecond.

We are testing this hypothesis by theoretical calculations in which we are evaluating the relaxation time of various superpositions of eigenstates. We expect to conclude this work in the next few months.

Energy Transfer in Extreme Environments

In collaboration with Keith D. King, we are analyzing shock tube data (Kiefer and coworkers) on the vibrational relaxation, decomposition, and incubation time in norbornene. We are using a combination of Gilbert's unimolecular reaction rate code and Barker's stochastic Master Equation code to obtain a unified model of the system, simultaneously fitting k_{uni} , the vibrational relaxation time, and the incubation time over the full range of temperatures. We have found that all of the measurements are consistent with an exponential model characterized by a $\langle \Delta E \rangle_{\text{down}}$ proportional to vibrational energy and to temperature (other models are also possible and have been investigated). The work on this project is essentially complete and a manuscript is in preparation.

Scientific Personnel

Dr. John R. Barker, Principal Investigator
Mr. Jerrell D. Brenner, Graduate Student
Mr. Alexander Chimbayo, Graduate Student
Ms. Laurie Miller, Graduate Student
Mr. Joseph P. Erinjeri, Undergraduate (recently graduated)
Ms. Venus Buller, Undergraduate

Recent Publications Supported by DOE

- "Infrared Emission Studies of the Vibrational Deactivation of Benzene Derivatives," John R. Barker and Beatriz M. Toselli, *Int. Rev. Phys. Chem.*, **12**, 305-338 (1993).
- "Population Distributions in the Vibrational Deactivation of Benzene and Benzene- d_6 : First and Second Moments Derived from Two-Color Infrared Fluorescence Measurements", Jerrell D. Brenner, Joseph P. Erinjeri, and John R. Barker, *Chem. Phys.* (Special issue on "Vibrational Energy Dynamics"), **175**, 99 (1993).
- "The Deactivation of Large Molecules," John R. Barker, Jerrell D. Brenner, and Beatriz M. Toselli, *Vibrational Energy Transfer Involving Large and Small Molecules*, *Adv. Chem. Kinetics and Dyn.*, Vol. 2, to be published.