ENERGY TRANSFER PROPERTIES AND MECHANISMS**TECHNICAL PROGRESS REPORT**

(20 October 1992)

DOE/ER/13442--7

DE93 008540

John R. Barker

Department of Atmospheric, Oceanic, and Space Sciences

The University of Michigan

Ann Arbor, Michigan 48109-2143

Introduction

Collisional energy transfer is the controlling factor in many non-equilibrium chemical systems. In combustion, 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. Two physical techniques have been proved to be particularly useful: time-resolved infrared fluorescence (IRF) and time-dependent thermal lensing (TDTL). As described later, we will shortly begin work using resonance enhanced multiphoton ionization (REMPI) techniques to investigate energy transfer in bulbs and "half collisions" in free jets.

We also have completed some experiments and model calculations which explore the approximations we previously have used in calculating infrared emission from highly excited

molecules. The results show that the calculations are quite adequate for most purposes and can be improved further, if the approximations are applied in a consistent manner.

Accomplishments and Plans

The IRF technique continues to be a real workhorse. The work on benzene, on toluene, on vibration-to-vibration (V-V) energy transfer to CO₂ from benzene derivatives, and on deactivation of benzene and toluene isotopomers have been published. All of this work tends to support an emerging general view of large molecule vibrational deactivation:

1. V-T and V-R energy transfer occurs with all colliders, probably due to short range repulsions on the potential energy surface.
2. V-V energy transfer takes place by long-range dipole-dipole interactions.
3. If the collision partner has a permanent dipole moment, V-R energy transfer is probably enhanced, due to coupling between the permanent dipole and the time-dependent transition dipole in the excited molecule.
4. Deuteration has little effect on vibrational deactivation, probably because most of the deactivation occurs by V-T/R transfer from the lowest frequency vibration mode (deuteration has little effect on the lowest frequencies).
5. Classical trajectory methods are inherently flawed. Even their *approximate* validity for simulations of large molecules has not been demonstrated and must be investigated.

In other IRF studies, we have obtained the time-resolved spectra of highly excited benzene as it is being deactivated. These spectra show three components, corresponding to $\Delta v = -1$ transitions originating from $v' = 1, 2$, and 3 . The anharmonic shifts agree with literature values and the whole spectrum is shifted for highly excited benzene, compared to the unexcited molecule. The relative intensities of the components at $t=0$ agree very well with theory. At later times, the relative intensities reflect, to some extent, the evolution of the population distribution of excited species. We are exploiting this property in order to determine more detailed information about the distribution as it evolves with time. Specifically, we are investigating simultaneously the IRF decays of the C-H stretch fundamental ($\sim 3.3 \mu\text{m}$) and of the overtone ($\sim 6.4 \mu\text{m}$). Although both emissions are controlled in the same collisional deactivation process, they respond differently, because of their intrinsically different energy dependencies. The details depend on the energy

transfer properties and we are using our Monte Carlo master equation computer code to simulate the experiments and find the energy transfer properties that reproduce the experiments. This work is still underway.

We have been using the measured relative intensities of the fundamental and overtone to test the theoretical methods we have routinely applied to calculate IRF intensities. Specifically, we have systematically investigated any changes in accuracy when harmonic oscillators (HO) are replaced by anharmonic oscillators a) in the state density calculations and b) in the expression for the Einstein coefficients for spontaneous emission. The results indicate that if the HO approximation is used in both, or in neither, the results are accurate to within a few percent, but the results are less good when a mixed approximation is used.

In another experiment, we have been using the TDTL technique to investigate highly excited CS₂ and SO₂ deactivated by Ar, Kr, and Xe. These results are in some ways similar to those we obtained previously for NO₂, and they disagree by orders of magnitude with time-resolved ultraviolet measurements by Troe and coworkers. They also disagree with the classical trajectory calculations carried out by Schatz and coworkers. In light of these major disagreements, we have been analyzing the experiments to determine whether they can be believed and, at this time, we have not identified anything wrong. We are planning to undertake infrared emission measurements on these systems to determine the energy transfer parameters by an independent method. IRF may not be easy to analyze in detail, but it is capable of resolving order-of-magnitude questions.

We are preparing to carry out REMPI experiments in bulbs and in molecular free jets (but have been delayed by the problems with the TDTL experiments). The first experiments will use a pump-probe arrangement to investigate the rovibrational populations of collision partners in the deactivation of highly excited benzene, or pyrazine, for example. The first laser pulse (248 nm) will excite the aromatic. After a selected time delay (time resolution of ~20 ns) the tunable dye laser pulse will be used to ionize the collision partner from selected states (REMPI). We expect that V-R energy transfer is very important and this technique will enable us to determine its magnitude, relative to V-V energy transfer, for example. This work will begin sometime this spring.

We have installed a linear time of flight mass spectrometer in our pulsed molecular jet apparatus and have obtained mass selected REMPI signals from monomers of benzene, nitric oxide, and oxygen gas. We plan to investigate the translational, rotational, and vibrational distributions of species produced in the predissociation of van der Waals molecules containing

benzene. Initially, we will excite the vdW molecule at 248 nm and probe the product state distribution. Later, we will require a tunable dye laser (which we do not have, at present) in order to select the excitation energy. This work should begin sometime this spring and summer and it promises to be an exciting extension of our work on energy transfer.

Scientific Personnel

Dr. John R. Barker, Principal Investigator
Mr. Jerrell D. Brenner, Graduate Student
Mr. Alexander Chimbayo, Graduate Student
Mr. Joseph Erinjeri, Undergraduate Student

Publications

- "Infrared Emission Spectra of Benzene and Naphthalene: Implications for the Interstellar PAH Hypothesis," Jerrell D. Brenner and John R. Barker, *Astrophys. J. (Letters)*, **388**, L39-L43 (1992).
- "Isotope Effects in the Vibrational Deactivation of Large Molecules", Beatriz M. Toselli and John R. Barker, *J. Chem. Phys.*, **97**, 1809-1817 (1992).
- "Polycyclic Aromatic Hydrocarbons and Molecular Equilibria in Carbon Rich Stars," Isabelle Cherchneff, John R. Barker, and Alexander G. G. M. Tielens, *Astrophys. J.*, **394**, 703-716 (1992).
- "Radiative Recombination in the Electronic Ground State," John R. Barker, *J. Phys. Chem.*, **96**, 7361-7367 (1992).
- "Polycyclic Aromatic Hydrocarbon Formation in Carbon Rich Stellar Envelopes," Isabelle Cherchneff, John R. Barker, and Alexander G. G. M. Tielens, *Astrophys. J.*, accepted for publication.
- "Infrared Emission Studies of the Vibrational Deactivation of Benzene Derivatives," John R. Barker and Beatriz M. Toselli, *Int. Rev. Phys. Chem.*, accepted for publication.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

END

DATE
FILMED

4 / 1 / 93