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**Technical Progress Report for
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Abstract

Experimental studies of dynamic molecular processes are described with particular emphasis on the use of a powerful infrared diode laser probe technique developed in our laboratory. This technique allows us to determine the final states of small (2-5 atom) molecules produced by collisions, photofragmentation, or chemical reactions with a spectral resolution of 0.0003 cm^{-1} and a time resolution of 10^{-7} sec. Such high spectral resolution provides a detailed picture, not only of the vibrational and rotational quantum states of molecules produced by these dynamic events, but also of the translational motion of the recoiling fragments as measured through the infrared Doppler line width profile. We have used this experimental method to probe collisions between cool bath molecules and vibrationally hot molecules with chemically significant amounts of energy in an effort to probe the quenching mechanism for unimolecular chemical reactions. This work has led to the surprising discovery that long range collisions appear to dominate the production of bath molecules which become vibrationally excited during this quenching process. In addition experiments of this type are providing first glimpses of the separate behavior of the translational and rotational degrees of freedom of the recoiling bath molecules during the relaxation of highly vibrationally excited donors. We have also completed an extensive study of collisions between hot hydrogen atoms and CO_2 molecules, one of the most important chemical systems in the combustion field, by measuring the probability for excitation of the antisymmetric vibrational overtone level $\text{CO}_2(00^02)$. Comparison of this work with earlier studies of the excitation of the 00^01 fundamental level suggests that translational and rotational energy distributions in this high energy collision system can be well described by classical mechanics, but that calculations of vibrational excitation probabilities require a fully quantum treatment with a high quality potential energy surface. Finally, we have begun experiments to study dynamic molecular processes using multiphoton ionization techniques. Although this experimental method has lower velocity resolution than available with our infrared diode laser probe technique, it is exceedingly sensitive and can be very useful in chemical reaction studies where rotational and vibrational distributions are of dominant interest or where significant recoil velocity is expected. All of this work is aimed at providing experimental data to test: potential energy surfaces, descriptions of chemical transition states in complex systems, and theories of reaction dynamics in molecules with more than 3 atoms. We hope through these experiments to provide dynamical and mechanistic information of fundamental interest for combustion and atmospheric reaction processes.

DOE Publications

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1. Lei Zhu, Scott A. Hewitt, and George W. Flynn, "Quantum Interference Effects in the Collisional Excitation of the Fermi Doublet States of CO₂ by Hot Electrons and Hot H(D) Atoms", J. Chem. Phys. 94, 4088(1991)
2. James Z. Chou, Scott A. Hewitt, John F. Hershberger, and George W. Flynn, "Diode Laser Probing of the Low Frequency Vibrational Modes of Baths of CO₂ and N₂O Excited by Relaxation of Highly Excited NO₂", J. Chem. Phys. 93, 8474(1990)
3. A. J. Sedlacek, R. E. Weston, Jr., and G. W. Flynn, "Interrogating the Vibrational Relaxation of Highly Excited Polyatomics with Time-Resolved Diode Laser Spectroscopy: C₆H₆, C₆D₆, and C₆F₆+CO₂", J. Chem. Phys. 94, 6483 (1991)
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13. Farooq A. Khan, Thomas G. Kreutz, George W. Flynn, and Ralph E. Weston, Jr., "Translationally and Rotationally Resolved Excitation of CO₂(00⁰₂) by Collisions with Hot Hydrogen Atoms", *J. Chem. Phys.*, **98**, 6183(1993).
14. Chi-Kung Ni and George W. Flynn, "State and Velocity Distributions of Cl Atoms Produced in the Photodissociation of ICl at 237 nm", *Chem. Phys. Letts.* **210**, 333(1993)
15. Amy S. Mullin, Jeunghye Park, James Z. Chou, George W. Flynn, and Ralph E. Weston, Jr., "Some Rotations Like It Hot: Selective Energy Partitioning in the State Resolved Dynamics of Collisions between CO₂ and Highly Vibrationally Excited Pyrazine", *Chem. Phys.* **175**, 53 (1993)
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17. Ralph E. Weston, Jr. and George W. Flynn, "Collisional Energy Transfer from Hot Atoms to Small Molecules", accepted for publication
18. George W. Flynn and Ralph E. Weston, Jr., "Glimpses of a Mechanism for Quenching Unimolecular Reactions: A Quantum State Resolved Picture", accepted for publication
19. C.-K. Ni, T. G. Kreutz and G. W. Flynn, "Experimental and Theoretical Velocity Profiles for Pure Rotational Scattering in CO₂-Hot Hydrogen Atom Collisions", submitted for publication
20. Chi-Kung Ni, George W. Flynn, and Sheldon Green, "Experimental and Theoretical Velocity Profiles for Pure Rotational Scattering: CO-Hot Hydrogen Atom Collisions", submitted for publication

Scientific Progress

Introduction

Our work over the past 36 months has concentrated on the following interrelated projects in the area of laser photochemistry and photophysics which impinge on a variety of questions in combustion and atmospheric chemistry and general chemical kinetics.

1. Infrared diode laser probes of energy loss in molecules with "chemically significant" amounts of vibrational energy (probing the mechanism for quenching unimolecular chemical reactions).
2. Infrared diode laser probes of "hot" atom collision processes involving CO₂ and hydrogen atoms.
3. Multiphoton ionization detection and infrared diode laser probing of photofragmentation processes.

The diode laser probe method, which we have developed for monitoring these collision and photofragmentation events, is an exquisite technique which has already provided a wealth of interesting dynamical information, and we expect that it will continue to enrich our understanding of dynamic molecular processes.

A detailed description of progress and results in these areas is given below. All of these projects involve laser excitation and/or fragmentation of molecules followed by probes of chemical reaction or collision processes and the electronic, vibrational, rotational or translational energy redistribution in the excited molecular systems. We hope through these experiments to improve our basic understanding of photochemical and photophysical phenomena and to provide dynamical and mechanistic data of fundamental interest for combustion and atmospheric reaction processes.

The Diode Laser Probe Technique

The application of infrared diode lasers to study time-dependent dynamic events was developed in our laboratory under DOE sponsorship¹⁻⁴³. While our efforts have focused on the use of diode lasers to study quantum state resolved dynamics, other investigators have been employing diode lasers in a variety of applications⁴⁴⁻⁵⁶, which include studies of chemical transients and molecular dynamics, as well as spectroscopy and analytical chemistry. The technique as applied to studies of dynamic molecular processes in our laboratory is by now well established. An overall description of the experimental method and of technical improvements that we have made in it during the past grant period is given in the Appendix to this report.

Collision Dynamics Studies

1) Introduction and Overview

One of our main research efforts, which is in the area of vibrational energy transfer, is aimed at developing an understanding of the mechanism by which unimolecular reactions are quenched. By mechanism, we mean the quantum state resolved picture of the quenching process, a picture which has been sorely missing from our understanding of this ubiquitous and incredibly important set of chemical reactions. The reason for this paucity of information is simply that molecules which are about to undergo unimolecular decomposition must have "chemically significant" amounts of internal vibrational energy. This almost guarantees that the vibrational state density of the reactant must be very high, so high that spectroscopic probe techniques must necessarily fail to resolve the vibrational quantum states. In spite of this difficulty (or perhaps driven by the challenge presented by this problem!), we have developed a remarkably simple, yet exceedingly powerful experimental method for elucidating the quantum "state-to-state" quenching mechanism for very internally energetic molecules, molecules with chemically significant amounts of energy. To appreciate our experimental method and how it works, we review briefly the accepted kinetic model for unimolecular reactions and then describe our technique along with some of our recent findings.

The simplest model for chemical reactions that proceed by unimolecular decomposition in the gas phase is the Lindemann mechanism, in which a substrate S is excited by collisions to a level S^* with energy sufficient to cause bond breaking or molecular rearrangement⁵⁷⁻⁵⁹. For large molecules the time scale for decomposition of S^* is sufficiently long that further collisions with the bath molecules can cause deactivation of the excited substrate, thus quenching the reaction process. The overall mechanism can be summarized by the equations

where B is a generalized representation for a bath molecule and P is the product, chemically distinct from S. Each of the three steps in this simple mechanism has been the subject of intense scrutiny in the past few years due to the emergence of a number of sophisticated and powerful quantum state resolved techniques for investigating the mechanisms that control the behavior of each step. We have made quite dramatic progress in developing new techniques for investigating processes such as step 3, in which a molecule with chemically significant amounts of energy is relaxed or quenched by "cold" bath molecules^{24,31,32,40}. While many studies of the quenching of such highly excited substrate molecules have been performed, until recently there were no techniques which could be used to follow these processes with quantum state resolved

detail on a single collision time scale, largely due to the high density of quantum states of the substrate S^* . Nevertheless, the last few years have produced some remarkable improvements in our ability to probe in great detail such events.

In the new basic experimental approach which we are using to study these energy transfer processes, substrates (S) of essentially arbitrary complexity are produced with high energy by laser pumping methods, but the collision processes that relax these highly excited S^* molecules are investigated by probing the quantum states of the bath molecules B produced by the interaction between S^* and B. By using relatively simple bath molecules and sophisticated laser probe methods to follow the quantum states of B, the nature of the mechanism for energy loss by S^* can be "seen" through the behavior of the (small) energy acceptor molecule B! To fully analyze the deactivation process for such highly vibrationally excited molecules as S^* , however, the level of excitation, rotational profiles and translational recoils of *different* vibrational modes of the bath acceptor B are required. Furthermore, the amount of energy transferred to the rotational and translational degrees of freedom of the *ground* (vibrationless) state of the bath molecules is also of interest. Our technique is capable of supplying all of this extremely valuable information! By focusing on the bath states instead of the excited substrate S^* , we are able to completely resolve not only the vibrational excitation of the molecule but also, due to the extraordinary resolution of the diode probe method, the rotational excitation and translational recoil of these same vibrationally excited bath molecules. Although this may be considered the dawn of a new era for these studies, which are capable of revealing the mechanism for the relaxation of molecules with chemically significant amounts of energy, the data forthcoming even at this early stage are already comparable in quality and information content to the kind that has been obtained for vibrational relaxation processes in small and medium sized molecules having only one or two quanta of vibrational excitation.

2) Quenching of Molecules with "Chemically Significant" Amounts of Energy

A) Super High Resolution Infrared Absorption Probes of Quenching Collisions

The application of the infrared diode laser probe technique to the study of quenching processes in highly vibrationally excited molecules can be illustrated with the relaxation of highly excited pyrazine, $C_4N_2H_4$, in collisions with CO_2 , a process which we have been investigating during the past year.⁴⁰ Excited $C_4N_2H_4$ molecules ($C_4N_2H_4(E)$) are produced at energy $E=40,640\text{ cm}^{-1}$ by an excimer laser ($\sim 20\text{ nsec}$ pulse width, 248 nm)

Photoexcitation followed by internal conversion leads to the production of highly vibrationally excited $\text{C}_4\text{N}_2\text{H}_4^{(\text{E})}=\text{S}^*$ ground electronic state molecules in less than 50 nsec. Collisions of $\text{S}^*=\text{C}_4\text{N}_2\text{H}_4^{(\text{E})}$ with CO_2 cause translational, rotational and vibrational excitation of the first antisymmetric stretching vibrational state (ν_3 , 00^01 , 2349 cm^{-1}) as well as rotational and translational excitation in the vibrationless (00^00) level

J and J' represent rotational angular momentum quantum numbers and V and V' the recoil velocities for the corresponding ro-vibrational states. A tunable diode laser operating cw (continuously) at $4.3\text{ }\mu\text{m}$ is used to probe the P and/or R branch bands of the following transitions,

Velocity recoils are measured by probing (at short times following excimer laser pumping of pyrazine) the *nascent* Doppler profiles for different spectral lines. The apparatus used in these studies is essentially identical to that which we have employed to study collisions between hot hydrogen atoms and CO_2 molecules^{1-3,6-10,12,15,17,18,20,21,26,27,35,38}.

Data obtained from the diode laser probe experiments as described here can be roughly divided into two categories. The first concerns collision processes in which donor energy loss shows up as a gain in vibrational, rotational, and translational energy of the acceptor.

Such quenching events, in which the bath gains at least one vibrational quantum of energy, are generally known to be relatively improbable (typically 0.1 - 0.001 per gas kinetic collision for *small* quenching partners) and account for rather small energy loss from the donor.^{11,31,58,59} One test of the accuracy of the diode probe method is that it confirms the well known inefficiency of this channel in the energy transfer process. A key question which has not been answered by earlier studies, however, is the degree to which vibrational excitation of the bath, as inefficient as it is, is accompanied by rotational and or translational excitation. [As we shall see below, the diode probe technique provides a direct and rather startling answer to this question!] In the second category of energy

transfer events are those collisions in which the bath molecules gain only translational and rotational excitation while remaining in the ground 00^00 (vibrationless) state:

Since, for small acceptors and large donors, these events account for most of the energy loss from the hot donor ("true" vibration-translation/rotation or V-T/R processes), understanding their behavior is crucial in establishing the *mechanism* for energy loss by highly vibrationally excited molecules. A key feature of the diode laser probe technique described here is its ability to separate the contributions of the translational degrees of freedom to the relaxation process from the contributions of the rotational degrees of freedom for bath molecules which do not become vibrationally excited. This is possible because both the population and the recoil velocity profile for molecules in each excited rotational level J are measured in the experiments. Thus, both vibration-translation (V-T) and vibration-rotation (V-R) energy transfer processes can be separately investigated in these experiments.

B) Evidence for Long Range Energy Transfer in Vibration-Vibration Energy Exchange Between Internally Hot Donors and Cool Bath Acceptors

Although general features of these high energy quenching processes, such as the mean energy transferred per collision and the relative inefficiency of V-V energy exchange, were already known both from studies of fall-off curves in unimolecular reactions and from the recent, elegant work of Troe⁶⁰⁻⁶⁹ and Barker⁷⁰⁻⁷⁵ and their co-workers, remarkable insights into the *dynamical mechanism* are now being obtained from the diode probe experiments, which provide separate information about translational, rotational, and vibrational degrees of freedom. Perhaps the most stunning new revelation is the fact that the vibrationally excited bath molecules, $\text{CO}_2(00^01, J, V)$, are produced with a rotational distribution that approximates the initial room temperature distribution of the unexcited $\text{CO}_2(00^00, J, V)$ ground state molecules⁴⁰, present before laser excitation of $\text{C}_4\text{N}_2\text{H}_4$. Thus, energy transfer events that produce $\text{CO}_2(00^01, J, V)$ are accompanied by almost no increase in rotational energy of the acceptor molecule, despite the fact that the vibrational energy of the acceptor for these events increases by 2349 cm^{-1} , more than 10 kT! An examination of the velocity recoil profiles for these same events tells a similar story. The vibrationally excited molecules are produced with a translational energy distribution that is near that of the original Boltzmann distribution of the sample⁴⁰. Thus, energy transfer events that lead to vibrational excitation of the bath seem to occur with little or no accompanying rotational and translational excitation^{24,31,32,40}.

The inefficiency of energy uptake from highly excited molecules by the vibrational modes of small bath acceptors is in agreement with trends observed in a number of earlier experimental studies performed with lower energy resolution. The observation of bath vibrational excitation *without* rotational or translational excitation in the quenching of highly vibrationally excited donors is, however, quite startling and totally unexpected! The data obtained so far, while on a limited subset of donors and acceptors^{24,31,32,40}, are consistent with a long-range, vibrationally resonant energy transfer mechanism in which vibrational energy loss in the donor is matched almost exactly by vibrational energy gain in the acceptor. The small rotational and translational energy transfer that accompanies vibrational excitation of bath states is indicative of long range, resonant energy transfer processes which are known to be of great importance in vibration-vibration energy transfer mechanisms involving small, weakly excited molecules.⁷⁶⁻⁸⁴

C) First Glimpses of the Separate Behavior of the Translational and Rotational Degrees of Freedom in the Vibration-Translation/Rotation Quenching of Internally Hot Molecules

For all donors and acceptors studied so far the behavior of the ground (00^0_0) state of the acceptor is dramatically different from that of the vibrationally excited states as described above. Acceptor molecules that remain in the ground state can, of course, take up energy from the highly excited donor only through their rotational and translational degrees of freedom. In the case of $C_4N_2H_4$ as a donor with CO_2 as an acceptor, excitation to high J levels is readily observed and the recoil line widths for these high rotational levels are substantially broader than room temperature Doppler widths.⁴⁰ Typical translational recoil energies are roughly 5-10 times kT at room temperature for pyrazine as a donor, with some dependence on the donor identity^{24,31,32,40} and its internal energy as well as some dependence on the final J level of the bath acceptor molecule.

These data show a number of interesting trends and offer one of the first opportunities to compare the translational energy changes that accompany rotational excitation into different specific CO_2 (00^0_0 , J) levels, brought about by collisions with a molecule having chemically significant amounts of vibrational energy. First, the change in translational energy increases monotonically with increasing J, so that changes in both translational and rotational energy scale roughly together for the pyrazine/ CO_2 donor acceptor pair. Similar trends are not observed when C_6F_6 is the donor. At present the reason for these differences is not known. In addition the amount of energy transferred to the bath acceptor CO_2 does depend on the internal energy of the donor in the pyrazine/ CO_2 system. Excitation of pyrazine at 308 nm produces much cooler recoiling CO_2 molecules in the 00^0_0 level.

D) General Overview of the Energy Transfer Mechanism for Relaxation of Hot Pyrazine by CO₂

The data presented above give clear evidence for the existence of two quite distinct mechanisms for energy loss by highly vibrationally excited molecules⁴⁰. To a first approximation, both mechanisms can be understood in the context of simple time dependent perturbation theory⁸⁵⁻⁹¹ in which the probability of vibrational energy loss to the translational degrees of freedom (V-T energy transfer) is optimized when the Fourier transform of the force acting during the collision has significant amplitude at the frequency $2\pi\Delta\nu = [2\pi/\hbar]\Delta E_{\text{vib}}$ corresponding to the vibrational energy loss ΔE_{vib} . For the case of V-T energy transfer, where a relatively large amount of vibrational energy is channeled into the translational degrees of freedom (large $\Delta\nu$), this can be achieved when the collision interaction potential changes significantly on a time scale $t < 1/\Delta\nu$. The most rapidly changing part of the intermolecular potential, the short range repulsive region, gives rise to the highest frequency Fourier components since the force changes most quickly near this repulsive wall. Collisions which sample this steep repulsive wall are, of course, also expected to have significant recoil velocity. The experimentally observed line widths for the ground vibrationless level (00⁰0) of CO₂ recoiling from hot pyrazine are, thus, in agreement with the above short-range repulsive force mediated energy transfer model.

Changes in the rotational energy for the ground vibrationless state of CO₂(00⁰0) correspond to observed changes in angular momentum $\Delta J \gg 1$. This observation is again completely consistent with a short range force mechanism for the translational-rotational (V-T/R) excitation of the ground level. The short range repulsive part of the potential can only be described reasonably well by a multipole expansion which includes rather high order terms. These higher order multipole terms, of course, can give rise to changes in ΔJ which are significantly larger than 1.

In contrast to the ground vibrationless state, energy transfer from excited pyrazine which produces *vibrational* excitation in the CO₂ bath occurs by a mechanism in which very little energy is transferred to the translational degrees of freedom as reflected by the narrow line widths observed for recoiling CO₂. Using the same Fourier transform argument as given above, these results suggest a resonant vibrational energy transfer mechanism in which vibrational energy in the pyrazine is exchanged for vibrational energy in CO₂ with $\Delta\nu = [1/\hbar]\Delta E_{\text{vib}} \sim 0$. Such a transfer can be brought about by the long range attractive part of the intermolecular potential,⁷⁶⁻⁸⁴ which changes only slowly with distance, yielding Fourier components of the interaction force which are near zero frequency. Indeed the weak recoil for the vibrationally excited species intuitively suggests

energy transfer at a distance indicating a long range force mechanism for the excitation of the bath vibrational modes.

The rotational profiles observed for the excited states of the CO₂ bath, which show only small changes in J upon vibrational excitation, are also consistent with an energy transfer process dominated by long range forces.⁷⁶⁻⁸⁴ Such a long range potential of interaction, which can be represented to first order by a dipole-dipole term, would have "collisional selection rules" with $\Delta J = \pm 1$, and produce a rotational profile in the excited vibrational state which has a 300 K Boltzmann distribution.

It is worth emphasizing that this (far too) simple picture is indeed only a first approximation to the detailed mechanism which must be occurring during the quenching of molecules with chemically significant amounts of energy. For example, the observation of a rotational distribution for the excited vibrational level of CO₂ which is slightly above 300 K indicates that short range forces, which can include changes in ΔJ that are greater than 1, play at least a small role in producing rotational levels in the excited 00⁰1 vibrational state with large ($J > 30$) angular momentum. The role of long and short range forces in the overall quenching mechanism goes to the heart of the relaxation process for highly vibrationally excited molecules and is a subject worthy of further investigation as described in our accompanying proposal.

3) Hot Atom Excitation of Vibrational and Rotational States of Molecules

In work completed during the present grant period, we have also used the infrared diode laser probe technique to follow high translational energy collisions. These studies have produced a remarkable variety of experimental data, revealing for the first time unexpected details about collisions between "hot" hydrogen atoms and carbon dioxide molecules^{1-3,6-10,12,15,17,18,20,21,26,27,35,38}. We have finished our experimental study of this hot H atom collision process with the publication of a paper describing the excitation of the overtone level CO₂(00⁰2)³⁸ and the submission of a paper describing pure rotational scattering in this system⁴².

The basic experiment for studying the production of vibrationally excited CO₂(00⁰2) can be described by the equations

The hydrogen atoms, H^{*}, produced in the first step have approximately 2.3 eV of translational energy, corresponding to a "temperature" of nearly 24,000 K. The 00⁰2 rotational population distribution and rotationally resolved line widths are remarkably similar to those previously obtained for 00⁰1 for the same collision process. As far as we

know, this is the first and only study of a collision process in which the vibrational excitation of a fundamental (00^01) and its overtone (00^02) have both been investigated in the same molecule with quantum state resolved detail. The similar rotational distributions and translational recoils for 00^01 and 00^02 suggest that these two states are excited by similar collision trajectories, even though the magnitude of population scattered into 00^02 is ~ 21 times smaller than that scattered into 00^01 .

This data can be used to test potential energy surfaces for the $\text{H}+\text{CO}_2$ collision system as well as to compare fully quantum, trajectory, and classical calculations of the collisional excitation probabilities and energy distributions for the final states of CO_2 . The system of interest here, $\text{H}^* + \text{CO}_2$, has strong inelastic and reactive channels as well as a number of stable HOCO intermediates and has been the subject of numerous theoretical and experimental investigations⁹²⁻⁹⁸. Two theoretical approaches have also been recently developed in our laboratory to model rotationally resolved inelastic scattering for the system H^*/CO_2 in which the final CO_2 vibrational state is the first antisymmetric stretch level 00^01 . The first employs an inversion procedure based on the infinite order sudden (IOS) approximation to extract *state-to-state* cross-sections from the experimental data for this system.²⁶ It was found that the rovibrationally inelastic cross-sections for $00^00, J' \rightarrow 00^01, J$ exhibit a large degree of rotational inelasticity, with a peak at $\Delta J = 41$. The second study treated the H atom as a point particle, CO_2 as a 3-dimensional "breathing ellipsoid", and modeled their interaction employing classical impulsive scattering.²⁷ This approach was remarkably successful in predicting the rotational population distributions for the vibrationally excited state 00^01 .

The relative or absolute probability of exciting the CO_2 (00^01) and (00^02) levels cannot be predicted using this classical "breathing ellipse" model, but rather requires a quantum mechanical treatment of the scattering process^{29,99-102}. In a very recent collaboration with Sheldon Green²⁹, we have used a simple repulsive, atom-atom potential approximation to the ellipsoid model in a more exact IOS/quantum mechanical calculation of the $\text{CO}_2(00^01)$ and $\text{CO}_2(00^02)$ excitation probabilities for hot H/CO_2 encounters. Like the classical "breathing ellipsoid" model²², this study also finds that the transition probability for excitation of $\text{CO}_2(00^01)$ has its optimum value near the end of the CO_2 molecule, but a small, secondary maximum between the C and O atoms is also observed. Physically, this is quite reasonable since H atom trajectories that strike between the C and O atoms, which naturally force the C and O atoms apart in a repulsive potential approximation, can be expected to have a significant excitation probability for the $\text{CO}_2(00^01)$ antisymmetric stretch level. Since the H atoms strike nearer the CO_2 center of mass for such collisions, these trajectories produce less CO_2 angular momentum than end

on collisions. As a result, the atom-atom quantum approach, not surprisingly, predicts slightly cooler 00^01 rotational profiles than the classical trajectory, ellipsoid model. The atom-atom repulsive potential approach, unlike the breathing ellipsoid model, can also be used to predict differences in the excitation probability for the 00^01 and 00^02 levels. This model predicts relative probabilities for excitation of $\text{CO}_2(00^02)$ to excitation of $\text{CO}_2(00^01)$ that are much smaller than obtained from the experimental data. On the other hand Schatz's ambitious theoretical treatment of high energy H (1.9-2.6 eV)- CO_2 collisions, employing quasiclassical trajectory calculations, gives about the right ratio for the probability of exciting $\text{CO}_2(00^02)$ versus $\text{CO}_2(00^01)$ but so far has been unable to reproduce the rotational distributions for these scattering events^{97,98}. It thus appears that the rotational and translational degrees of freedom of CO_2 can be treated classically for H^+ - CO_2 collisions which produce either the one quantum 00^01 state or the two quantum 00^02 state. The overall probability for excitation of one or two quanta of antisymmetric stretching vibration, however, requires a quantum mechanical approach with a proper potential energy surface.

The data now available describing the reactive channel⁹²⁻⁹⁶ along with our studies of the vibrationally, rotationally, and translationally inelastic channels present an astonishingly detailed picture of the collision dynamics for $\text{H}+\text{CO}_2$ encounters. It is perhaps not too much to expect that the H^++CO_2 system may, in the near future, become the first fully characterized four atom kinetic system in which precise comparisons between theory and experiment will be the norm rather than the exception. The results seem certain to deepen our understanding of chemical reaction mechanisms and ultimately to improve our control of the rates and products of chemical reaction processes.

4) Multiphoton Ionization Detection of Dynamic Molecular Events

We have begun a new project using multiphoton ionization/time of flight mass spectroscopy to study collision dynamics, chemical reactions, and photodissociation processes. In part this effort was kindled by the results of our infrared diode laser studies of the reaction between Cl atoms and cyclohexane molecules³⁴, which produced some very remarkable rotational distributions, and by infrared diode laser studies of the Cl atoms produced by photodissociation of a number of Cl atom precursors³³. MPI detection cannot provide sufficient resolution to resolve the small velocity recoil profiles that can be detected by IR probing, nevertheless, it is an extremely sensitive technique which complements well our diode laser probe method. We have used this apparatus to investigate the photodissociation dynamics of ICl with 237 nm laser light by 2+1 resonance enhanced multiphoton ionization and time of flight techniques³⁹. The Doppler profiles of the chlorine atom fragments in the two spin orbit states,

$^2P_{3/2}$, and $^2P_{1/2}$ indicate the presence of both parallel and perpendicular dissociative transitions. The translational energy of the atoms is 2.3 eV for Cl($^2P_{3/2}$) and 2.2 eV for Cl($^2P_{1/2}$).

We expect this apparatus to be quite useful in future studies of dynamic molecular processes. Photofragmentation events can be investigated much as for ICl as described above, and it should be possible to study bimolecular collisions with this same technique.

Appendix

Probing Quantum States and Recoil Velocities with Infrared Diode Lasers

1) General Description

The application of infrared diode lasers to study time-dependent dynamic events was developed in our laboratory under DOE sponsorship¹⁻⁴³. This technique provides exceptionally useful information about a wide variety of dynamic molecular processes. The essence of the diode absorption method is the realization that any vibration-rotation level in a variety of small molecules can be monitored through an absorption transition, as illustrated below for CO₂, of the following type

where m is the ν_1 (1388 cm⁻¹) mode quantum number, n the ν_2 (667 cm⁻¹) mode quantum number, p the ν_3 (2349 cm⁻¹) mode quantum number, J the rotational angular momentum quantum number, l the vibrational angular momentum quantum number, and V the translational velocity. The source of infrared light is a continuously tunable, spectrally pure, cw, low power diode laser. By selectively tuning to, and monitoring "hot band" transitions such as:

the entire time behavior of the populations in these states can be followed during and after a collision or photofragmentation process which produces CO₂ ($mn^l p, J$) as the result of an optical pulse. Moreover, since such transitions "ride" the very strong ν_3 absorption coefficient and have essentially the same oscillator strength as the $00^0 0 \rightarrow 00^0 1$ transition, even the ν_1 symmetric stretch level ($10^0 0$), whose $00^0 0 \rightarrow 10^0 0$ fundamental transition is infrared inactive, and the ν_2 bending state ($01^1 0$), whose emission at $\sim 15 \mu\text{m}$ is relatively difficult to detect (ν^3 factor plus detector limitations), can be easily observed and probed. The combination of small anharmonicities, which separate the $mn^l p \rightarrow mn^l p+1$ transitions for different values of m, n, l, p by 0.1-10 cm⁻¹, and the high spectral purity of the diode radiation (0.0003 cm⁻¹) allow us to separate with ease these different absorption features. All three CO₂ normal modes, as well as their overtone and combination levels, have been studied in detail. Because of the extremely high spectral resolution of the infrared diode

probe, the recoil velocity, V , of CO_2 molecules colliding with almost any high energy species [a high energy hydrogen or oxygen atom or a highly vibrationally excited polyatomic] can also be monitored by using a very stable interferometer to time resolve the infrared absorption profile through the Doppler effect¹⁰. The technique thus provides complete chemical reaction and energy transfer dynamical information regarding the vibrational and rotational states of molecules as well as their velocity recoil. The method is, of course, not limited to studies of the highly important combustion product CO_2 , and we have in fact used it to monitor OCS , N_2O , CS_2 , DCl , CH_4 , CD_3F , CF_3D , and CO .

The diode probe method is most exciting because it provides about a 100,000 fold improvement in resolution over the main previous infrared probe technique used in many kinetic studies (infrared fluorescence). In addition it has about a factor of 10 improvement in speed compared to the fluorescence method and shows remarkable sensitivity provided the experimental apparatus is properly configured. (For example, in a typical time resolved experiment we can comfortably detect approximately 3×10^9 molecules/ cm^3 in a single CO_2 quantum state for a molecule with a room temperature Doppler profile.) The increased resolution of the diode laser probe method has several advantages. First, specific details of kinetic processes such as photodissociation, collisions, or chemical reactions can be probed at a previously unheard-of level of precision. This will improve our understanding of these very fundamental processes. Second, the high resolution absorption method provides an almost unambiguous probe for a given molecule, or a specific state of a molecule, in the presence of many molecules or molecules distributed in hundreds of different quantum states. Thus in a complex mixture of reacting gases, the diode laser absorption probe allows us to follow a single "interesting" species or a single "interesting" state of a molecule without interference from a very large number of "uninteresting" processes. It is a very specific probe for the proverbial "needle in a haystack." Finally, because infrared spectra are generally well known and assignable for molecules with 2-5 atoms (compared to electronic spectra), the technique can be applied to probing the quantum states of polyatomic molecules. Indeed, most of our work has involved studies of the collision dynamics of three atom molecules, and we have recently used the technique to probe 4 and 5 atom molecules. There has been great progress over the past few years in efforts to describe the dynamics of systems which produce three atom molecules as a product, so that the experimental work in our laboratory has had a strong interplay with theoretical developments during this period.

2) Technical Improvements

A number of technical advances have been made over the past few years in our application of the diode laser probe technique. First, we have begun to use liquid nitrogen cooled dewars and laser diodes instead of the closed cycle helium refrigerators normal in this

field. The results so far are very promising. At liquid nitrogen temperatures, in the absence of refrigerator piston noise, the diodes are noticeably more stable in frequency and amplitude. This translates into an improved signal to noise ratio in our experiments. Even more important is the fact that we can now work with "garden variety" (moderate to low power) diodes instead of the highly selected versions we have needed over the past decade. Second, with the lower noise liquid nitrogen cooled diodes we have found that further improvements in operation can be achieved by using new, lower noise diode laser power supplies. The combination of these new power supplies and liquid nitrogen cooling has left mirror jitter from optics in the laser beam path as the main noise source. Third, we have developed a simple, two channel ratiocing technique which gives us much more accurate nascent Doppler line shapes, especially in the presence of background absorption.

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