

Technical Report

The publications in the attached list describe in detail the research progress made on several projects since our last report, submitted on January 1, 1994. Reprints of already published material are being forwarded to D.O.E. Headquarters. The present report spans the activities for grant DE-FG02-88ER13937, for the period January 1, 1994-February 28, 1995.

Introduction

The collision dynamics of gas-phase molecules with high levels of internal energy are a key feature in many important chemical processes such as unimolecular reactions and atmospheric photochemistry.¹ Molecular encounters in which substantial amounts of energy ($\Delta E \sim 1$ eV) are transferred in a single collision can have a significant influence on the overall collisional relaxation of highly vibrationally excited molecules.² Hence much experimental^{3,4,5,6} and theoretical^{7,8,9,10} attention has been focused on the nature of these "supercollision" energy transfer events, which were first observed experimentally by Oref, Steel and coworkers^{3,4} in collisions between cold bath molecules and highly vibrationally excited molecules that undergo reaction if they gain a large amount of energy in a single collision. In particular, excited azulene³ with ~ 110 kcal/mol vibrational energy has been reported to transfer ~ 33 kcal/mol in a single collision with quadricyclane, although with low probability (0.001). Using Kinetically Controlled Selective Ionization, Luther and coworkers^{5,6} have monitored the collisional relaxation of highly vibrationally excited toluene (~ 140 kcal/mol) and found that the internal energy distribution of the toluene broadens substantially with time, indicating that the average energy transferred per collision has a large dispersion. Additionally, they report that some excited toluene molecules have cooled completely to 300 K after only a few collisions, presumably with each collision relaxing the toluene considerably.

Classical trajectory calculations^{7,8,9,10} also support the existence of collisions which transfer unusually large amounts of energy. Brown and Miller⁷ studied the relaxation of excited HO_2 (40 kcal/mol) by collisions with He and found ΔE values up to 12 kcal/mol, although, as above, these events occurred relatively infrequently. For this system, a double exponential function was required to adequately describe the long tail of the energy transfer probability distribution. Bollati and Ferrero⁸ report quasiclassical trajectory studies on the collisional deactivation of excited HgBr ($B^2\Sigma$, $v = 52$) by a number of rare gases. They report that an accurate description of the high energy part of the transition probability function requires the use of double exponentials and sums of Gaussian and exponential functions and they stress the importance of including the HgBr anharmonicity. In addition, the probability for collisional transfer of relatively large amounts of energy ($\sim 6000 \text{ cm}^{-1}$) does not depend on the complexity of the encounter, with direct and multiple collision complexes having similar probabilities ($\sim 10^{-4}$). The collisional relaxation of excited CS_2 has been investigated in theoretical studies by Schatz and coworkers⁹. For CS_2 with 57.2 kcal/mol internal energy, as much as 36 kcal/mol is transferred to CO in a single collision. However, this type of event occurs only about 1 in 10^4 collisions. In trajectory studies of excited azulene colliding with Xe atoms, Gilbert and coworkers¹⁰ report that supercollision events are not associated with any particular range of impact parameters or initial velocities, but that they invariably involve the approach of the Xe atom toward a hydrogen atom which is compressed against the carbon backbone of azulene. This close approach forces the hydrogen/xenon interaction far up on the repulsive part of their potential wall which then results in an impulsive kick from the azulene to the Xe atom. These impulsive supercollision events can be compared with a mechanism of energy transfer in which excited azulene and Xe undergo multiple atom/atom interactions during a single encounter, a so-called "chattering" collision.¹⁰ Large amounts of energy may be transferred in these events, but because the energy transfer occurs in many small steps rather than in a single interaction, they are

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not considered supercollisions. Nevertheless, "chattering" collisions and supercollisions would be difficult to distinguish experimentally. As with the other theoretical studies, Gilbert and coworkers find that supercollision events are rare, but pervasive; that is, they are seen in a wide range of simulations.¹⁰

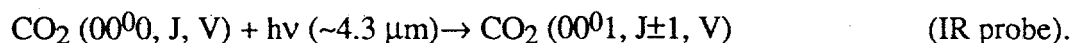
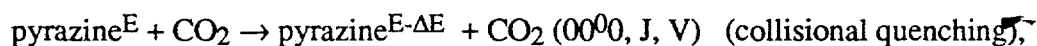
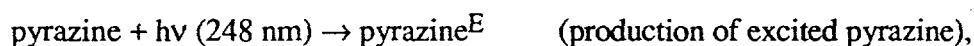
Typically, supercollisions are assumed to involve large polyatomic molecules. There are, however, reports of collisions between an atom and a diatomic molecule which are accompanied by surprisingly large energy transfer. Crim, Fisk and coworkers¹¹ found that in the molecular beam scattering of internally excited KBr ($E_{\text{int}}=41$ kcal/mole) with argon, as much as 28 kcal/mole were transferred to the argon in a single collision for some scattering angles. These results were successfully modeled by Sharma and Sindoni¹² who used a quantum mechanical spectator model for inelastic scattering off the repulsive part of the intermolecular potential. Ballistic collisions, observed by Herschbach and coworkers¹³, in which a substantial fraction of the relative translational energy (~ 1 eV) in a CsF/Ar collision is converted into internal energy of the CsF have also been reported. Using the impulse approximation, Sharma and Sindoni¹⁴ calculate that the $T \rightarrow V$ energy conversion for this case may be as large as 96%. These examples of small molecule energy transfer clearly have a number of features in common with supercollisions observed in large polyatomic molecule systems.

The UV absorption technique used by Troe¹⁵ and coworkers and IR emission studies by Barker and coworkers¹⁶ have resulted in an extensive body of data on $\langle \Delta E \rangle$, the average energy transferred per collision by highly vibrationally excited polyatomics. These experiments focus on energy loss from the hot donor molecule but do not provide a quantum state resolved picture of the quenching process, primarily because of very high densities of states in the donor. In an alternate approach,^{17,18} high resolution IR diode laser absorption has been used to monitor the individual states of bath molecules following collisions with an excited donor, thus permitting a quantum state-resolved look at the collision dynamics. Recently, we have used high resolution transient IR absorption to study the collisional relaxation of vibrationally excited pyrazine^E, ($\text{C}_4\text{H}_4\text{N}_2$, $\langle E_{\text{vib}} \rangle = 40,640$ cm^{-1}) by cool CO_2 ($T = 300$ K). After collisions with these high energy pyrazine molecules, the CO_2 bath molecules are either vibrationally hot and rotationally/translationally cold or vibrationally cold and rotationally/translationally hot ($T_{\text{rot}} \approx 1200$ K, $T_{\text{trans}} \geq 1500$ K!). The collisional relaxation of excited pyrazine apparently occurs through two distinct mechanisms. Long-range near resonant energy transfer results in vibrational excitation of the CO_2 bath molecules, while short-range repulsive interactions lead to CO_2 in its vibrationless ground state with very high levels of rotational and translational excitation. It is possible that this high energy tail in the ground vibrationless state of CO_2 is formed via supercollisions. The purpose of the present study is to investigate the origin of the pyrazine^E/ CO_2 scattering events which result in population of high energy rotational and translational states of vibrationless CO_2 and to determine the amount of energy transferred in a single collision as well as the partitioning of that energy between the rotational and translational degrees of freedom. This experimental investigation uses variations in the ambient temperature to modify the initial distribution of CO_2 states. The temperature dependence of the final, nascent, state-resolved rotational populations, translational energies and excitation rates are then used to glean information about the origin of the resulting high energy CO_2 states.

The collisional behavior of pyrazine in excited electronic states has been investigated by several other groups. Weisman and coworkers¹⁹ have studied the collisional relaxation of triplet state pyrazine containing varying amounts of excess vibrational energy. They find that the average amount of energy transferred per collision, $\langle \Delta E \rangle$, is very sensitive to the amount of excess vibrational energy, with average energy loss values increasing tenfold as the pyrazine vibrational energy increases from 2000 cm^{-1} to 5400 cm^{-1} . In particular, $\langle \Delta E \rangle$ from triplet pyrazine to CO_2 increases from 20 cm^{-1} to 330 cm^{-1} per collision as the excess pyrazine

- vibrational energy increases from 1500 cm^{-1} to 5600 cm^{-1} .²⁰ Rice and coworkers²¹ have found that intermode vibrational energy transfer in electronically excited singlet pyrazine is dominated by energy exchange among the low frequency breathing mode vibrations and that the probability for transfer is strongly dependent on the energy defect between modes.

The present study is the first state-resolved temperature dependent investigation of single collision energy transfer from vibrationally hot ground state pyrazine molecules to CO_2 . We have used the IR diode laser probe technique to measure the nascent rotational and translational excitation of CO_2 following collisions with vibrationally hot pyrazine for a range of ambient cell temperatures ($T_{\text{cell}} = 243 - 364\text{ K}$). The nascent rotational distribution for the high J tail of the ground state level (00^0_0) as well as the CO_2 translational energy recoil have been determined as a function of cell temperature. A key feature of this experimental approach is that we are able to study the energy transfer process by focusing on the quantum state behavior of the relatively simple CO_2 bath acceptor molecules. This provides state-resolved information about the collision dynamics without having to probe the large, complex donor molecule. The essential features of the experimental approach can be represented by the following equations:



Vibrationally excited electronic ground state pyrazine with $40,640\text{ cm}^{-1}$ internal energy, pyrazine^E , is prepared by excimer laser pumping at 248 nm, followed by rapid radiationless decay²² to the ground electronic state. This process occurs in approximately 35 ns.²³⁻²⁶ The pyrazine molecules are collisionally quenched by CO_2 to produce $\text{pyrazine}^{E-\Delta E}$ and rotationally/translationally excited $\text{CO}_2(00^0_0, J, V)$. J denotes the rotational angular momentum quantum number and V denotes the translational velocity along the direction of the diode probe beam. A high resolution cw diode laser ($\lambda \sim 4.3\text{ }\mu\text{m}$) is used to probe specific ro-vibrational states of CO_2 via absorption in the strongly allowed ν_3 band ($00^0_0 \rightarrow 00^0_1$). Due to vibrational anharmonicities in CO_2 and the high resolution ($\sim 0.0003\text{ cm}^{-1}$) of the diode laser, the IR absorption lines are easily resolved, and the rotational distributions of all low lying vibrational states can be probed. In addition, the transient absorption line profile, which allows us to determine the translational recoil velocity through the Doppler effect, can be measured with high accuracy. Absolute rate constants and energy transfer probabilities were determined for excitation within the 00^0_0 state. The temperature dependent behavior of the energy transfer probabilities provides an estimation of the energy of the initial CO_2 state, from which ΔE , the amount of energy transferred in a single collision, can be deduced.

The rotational distributions, velocity recoils, and quenching rates exhibit a very weak temperature dependence for production of CO_2 high J states, indicating that the CO_2 molecules involved in these energy transfer events originate from rotational levels only slightly greater than the thermal mean J value. Based on these results, values for ΔE , the energy transfer from hot pyrazine to CO_2 resulting in final CO_2 00^0_0 states $J=58$ through $J=82$, are estimated to range from 2550 cm^{-1} to 7090 cm^{-1} in a single collision. $\sim 20\text{ kcal/mol}$

The weak temperature dependence of the rate constants describing the collisional excitation of CO_2 molecules into high rotational states of the ground vibrationless level by highly excited pyrazine offers compelling evidence that the collisions which populate these states possess all of the defining features of "supercollisions"; the amount of energy transferred is unusually large ($\sim 20\text{ kcal/mol}$), and although such collisions are relatively infrequent (collisions which populate $J=82$ occur approximately 35 times for every 10,000 Lennard-Jones collisions), they clearly contribute significantly to the deactivation of

- vibrationally excited pyrazine. The interpretation of the experimental temperature dependence, which we have used here to provide a quantitative estimate of the energy transfer magnitudes, requires the use of angular momentum and translational energy exponential gap models. However, the model itself is based on concepts central to our current understanding of molecular energy transfer (i.e. the first Born approximation) and is remarkably similar to $P(E,E')$ energy transfer probability functional forms well established in numerous master equation analyses of the collisional deactivation of vibrationally excited, large molecules. Additionally, the qualitative conclusions about these V-R/T energy transfer events, based on the experimentally observed weak temperature dependence, are inescapable. This weak temperature dependence indicates that the molecules involved in these (V→R/T) energy transfer events must originate from near the center of the pre-collision energy distribution rather than from the high energy tail of this distribution, thus pointing to the fact that the energy transfer magnitudes accompanying these collisions are unusually large.

It should be noted that these collisions seem to be slightly more probable than other "supercollision" events observed previously, both in experimental³ and theoretical^{8,9,10} studies. Experiments currently underway in our laboratory are aimed at testing current speculation on the mechanistic origin of these relatively efficient "supercollision" events. These studies are intended to isolate properties of the donor molecule that promote "supercollisions", such as the nitrogen lone pairs of pyrazine or perhaps a large amplitude vibrational motion exhibited by the donor molecule upon photoexcitation, in transition from its Franck-Condon geometry to a high energy isomeric structure. For example, a prefulvenic form of pyrazine (prefulvene is an isomer of pyrazine in which one of the nitrogens is bent far out of the aromatic ring) has been proposed that adiabatically correlates with the $S_2(\pi\pi^*)$ electronic state accessed by excitation at 248 nm.²⁷ A large amplitude vibrational motion, such as the one involved in the transition between the ground state pyrazine geometry and the prefulvene structure, can be expected to impart a large impulse to a CO₂ bath molecule during a collision, thus resulting in large energy transfer. Although such a mechanism is rather speculative at this point, it does point to some experiments which should allow further clarification of the microscopic mechanism of these "supercollision" events.

Recently, Oref²⁸ has noted the similarity of the current debate over the role of supercollisions in the deactivation of vibrationally hot molecules to an earlier dialogue regarding the relative importance of frequent, nearly elastic collisions and infrequent, highly inelastic collisions in the promotion of unimolecular reactions.²⁹ The experiments described here indicate that, at least in the collisional deactivation of hot pyrazine, infrequent, highly inelastic ("super") collisions are more important than is suggested by their relative infrequency. However, it is also clear that the question of the relative, quantitative importance of these two types of collisions is still an open one, and that the prevalence of supercollisions may well depend on the detailed physical and chemical properties of the colliding pair.

Conclusions

The relaxation of vibrationally excited pyrazine ($E=40,640\text{ cm}^{-1}$) by collisions which populate the high J tail ($J=58-82$) of the vibrationless ground state (00^0_0) of CO₂ has been studied using tunable infrared diode lasers to probe the scattered CO₂ molecules. The nascent rotational populations and translational recoil velocities for a series of rotational states in the high J tail of the 00^0_0 level of CO₂ were measured at five collision cell temperatures: 243, 263, 298, 339, and 364 K. Both the rate constants describing these V-R/T processes and the translational temperatures describing the recoiling CO₂ molecules

exhibit a very weak positive temperature dependence indicating that the high energy CO₂ molecules must originate from near the center of the pre-collision energy distribution.

Quantitative estimates of the actual amount of energy transferred in collisions between CO₂ and vibrationally excited pyrazine, based on an angular momentum and translational energy exponential gap model of the cross section, indicate that ΔE_{total} can be as large as 7090 cm⁻¹ (≈ 20 kcal/mol). These experiments offer compelling evidence that these energy transfer events can indeed be classified as supercollisions since they involve unusually large, single collision energy transfer magnitudes; and despite their relative infrequency, they play a most important role in the collisional deactivation of vibrationally excited pyrazine by a CO₂ bath.

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DOE Publications

Papers published, accepted for publication or submitted for publication under DOE sponsorship, January 1, 1994-February 28, 1995. Only reprints are included with report.

- /1. Gregory E. Hall, James T. Muckerman, Jack M. Preses, Ralph E. Weston, Jr., George W. Flynn, and Avigdor Persky, "Time-resolved Fourier Transform Infrared Study of the Photodissociation of 1,1-difluoroethene at 193 nm", *J. Chem. Phys.* **101**, 3679 (1994)
2. Ralph E. Weston, Jr. and George W. Flynn, "Collisional Energy Transfer from Hot Atoms to Small Molecules", accepted for publication
3. George W. Flynn and Ralph E. Weston, Jr., "Glimpses of a Mechanism for Quenching Unimolecular Reactions: A Quantum State Resolved Picture", accepted for publication
4. 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", accepted for publication, *J. Phys. Chem.* (1995)
- /5. Chi-Kung Ni, George W. Flynn, and Sheldon Green, "Experimental and Theoretical Velocity Profiles for Pure Rotational Scattering: CO-Hot Hydrogen Atom Collisions", *J. Chem. Phys.*, **101**, 9499 (1994)
6. A. S. Mullin, C. A. Michaels, and G. W. Flynn, "Molecular Supercollisions: Evidence for Large Energy Transfer in the Collisional Relaxation of Highly Vibrationally Excited Pyrazine by CO₂", accepted for publication, *J. Chem. Phys.*, (1995)
- /7. Daniel R. Willey, Kenneth A. Ross, Amy S. Mullin, Susanna Schowen, Liedong Zheng, and George Flynn, "Gas-phase Infrared Spectroscopy of N₂O in an Equilibrium Cell at 10 and 5 K, *J. Mole. Spec.* **169**, 66(1995)
- /8. Chris A. Michaels, Amy S. Mullin, and George W. Flynn, "Long and Short Range Interactions in the Temperature Dependent Collisional Excitation of the Anti-symmetric Stretching CO₂(00⁰1) Level by Highly Vibrationally Excited Pyrazine", accepted for publication, *J. Chem. Phys.* (1995)
9. Chemical Displacement of Molecules Adsorbed on Surfaces: Low Temperature Studies with Applications to Surface Reactions, P. W. Kash, M. X. Yang, A. V. Teplyakov, G. W. Flynn and B. E. Bent, in preparation.
10. Surface Structure Sensitivity in the Ullmann Coupling Reaction on Copper, P. W. Kash, M. Xi, D.-H. Sun, G. W. Flynn, and B. E. Bent, in preparation.

11. Cross Coupling of Phenyl Groups with Alkyl Iodides on a Cu(100) surface: A Radical Mechanism?, P. W. Kash, D.-H. Sun, M. Xi, G. W. Flynn, and B. E. Bent, in preparation.
 12. Formation and Reactions of Vinyl Groups on Cu(100), M. X. Yang, P. W. Kash, J. Eng Jr., G. W. Flynn, and B. E. Bent, in preparation
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