

Vibrational Energy Transfer

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Many aspects of the collision dynamics of vibrational energy transfer are presented. Special emphasis is placed on three broad areas within this field: (1) vibrational energy transfer in large molecules (> 10 modes) at low excitation, (2) vibrational energy transfer in large molecules at high vibrational excitation, and (3) vibrational energy transfer of highly excited small molecules. Advances in laser methods have revolutionized experimental investigations of all of these areas. Recent results are presented, and directions for the future are discussed.

Introduction

Vibrational excitation plays a central role in many chemical phenomena. While its importance in high-temperature processes such as combustion has long been obvious, other examples range from laser operation to light-induced reactions to energetic species used for surface etching. Vibrationally hot molecules are prominent players in schemes to achieve mode-selective chemistry. Experiments involving precisely prepared vibrational states continue to hold center stage in fundamental studies of chemical reactivity. There has even recently emerged an appreciation of vibrationally hot molecules operating in the low-temperature environment of stratospheric chemistry.¹

Collisional vibrational energy transfer (VET) is fundamental to all of these processes, and as we celebrate the centennial of *The Journal of Physical Chemistry*, we also approach the centennial of VET study. It has been an active field for almost the entire lifetime of this journal. Indeed, the earliest reference in this discourse dates from 1911. As we shall relate, the activity has at no time been more vigorous than the present, and areas of VET studies still emerge from time to time as hot topics. While this continuum of attention attests to the central importance of VET, it also attests to the severe experimental challenges associated with characterizing the transfer.

Even though progress has been steady, major advances have emerged only sporadically as technological developments opened new approaches. For example, the combination of lasers with high-sensitivity IR detectors and the tools of surface analysis permit direct time-domain vibrational relaxation studies of adsorbates on metallic,^{2,3} semiconductor,⁴ and insulator⁵ single-crystal surfaces. The appearance of infrared lasers led to extensive studies of V–V and V–T,R processes that established many of the principles governing VET pathways in multicollisional systems.^{6,7} Picosecond lasers opened the way to defining the time scales of vibrational quantum loss in liquids.⁸ The development of tunable UV sources led to studies of molecules in S₁ electronic states that uncovered the existence of unexpectedly strong propensity rules for single-collision state-

to-state VET.⁹ In a complementary sense, the availability of large scale computing has moved the theory of large molecule VET from relatively simple models to successful three-dimensional, fully quantal inelastic scattering algorithms.^{10–14}

In describing the present state of VET, the authors have forgone action as a committee that might have sampled every area with a light dusting of citations. Even an avalanche of citations would inevitably fall short of completeness in this immense field. With apologies to many, we have opted to focus discussion on a few areas with which we are familiar by recent involvement. The treatments have been given some depth for accurate depiction of the vigor of the areas and of the progress on forefront issues.

The discussions concern gas phase collisional systems, and they are organized loosely by the vibrational complexity of the molecules. First, we consider large molecules (i.e., > 10 modes) in ground electronic states that contain the high vibrational energy content of reactive systems. The problem of vibrational activation and deactivation of such highly excited molecules has been active for over 70 years. Novel approaches with new laser technologies allow remarkably detailed descriptions of the collisional interactions in these hot systems where both the vibrational energy change and vibrational states must be described statistically. The second discussion also concerns large molecules, but at relatively low vibrational energies where the states are well-separated and zero-order harmonic descriptions remain useful. Here the present ambitions are to learn the fate of molecules in a specific vibrational state that have undergone a single collisional encounter. With the introduction of cold expansions and crossed molecular beams, the large molecule state-to-state VET now has rovibrational resolution with good progress toward complete characterization of a rovibrationally inelastic encounter. The discussion is given under the rubric of VET within excited electronic states since much, but certainly not all, the work has concerned S₁ states of the polyatomic molecules. We finally consider small molecules, including diatomics, that in principle constitute the least complex systems and, therefore, the area most accessible for both experimental and theoretical study. For this reason, diatomic

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molecules historically have received much of the energy transfer attention. Advances in laser technology have transformed the opportunities for instruction from study of small molecules, especially those with high vibrational excitation. This field is now one of the hot areas of gas phase dynamics.

Energy Transfer on the Ground Potential Energy Surface: Large and Medium Size Molecule Dynamics

Historical Perspective. Ultimately, interest in the mechanisms by which molecules lose or transfer energy during collisions is driven by the effect such events have on the potential chemical reactivity of the individual molecular species. The availability of a minimum amount of energy during a collision is the *sine qua non* for a chemical reaction. Thus, nonreactive loss of energy almost always leads to a decrease in the probability that a reaction will occur during an encounter between two molecules. Since virtually all thermally driven chemical reactions take place on the ground electronic state potential energy surface, energy transfer processes occurring on this surface are of overwhelming importance to anyone interested in reactive chemical dynamics. Thus, it is no surprise that the study of molecular energy transfer has occupied physical chemists for almost the entire 100 year history of *The Journal of Physical Chemistry*. During this period the loss of energy from the vibrational degrees of freedom of molecules in their ground electronic state has been a topic of special focus. The almost unique role of vibrational energy on the ground potential energy surface arises from the fact that all reactions ultimately involve the breaking and making of chemical bonds, a process that is accelerated by putting energy into the vibrational degrees of freedom of a molecule. Unimolecular chemical reactions are a particularly cogent example of the importance of vibrational energy, representing as they do a competition between vibrational energy transfer and chemical reactivity. In these processes molecules with “chemically significant” amounts of energy (sufficient energy for bond breaking to occur) can be quenched by energy-dissipating collisions. Indeed, the rates for such reactions are critically determined by the competition between vibrational energy flow within the molecule (the time scale on which sufficient energy for bond rupture finds its way into a single chemical bond) and the flow of energy in and out of the molecule via binary collisions.

A great deal of progress was made before the mid-1960s in developing an understanding of the rates for vibration to translation/rotation (V–T/R) energy transfer, the process by which vibrationally hot molecules lose their internal vibrational energy to the surrounding “heat bath” of cooler molecules. Much of the experimental progress in this field was due to the use of ultrasonic (sound propagation and loss) and shock tube techniques.^{15–19}

It would be difficult to overemphasize the remarkable effect that the invention of powerful pulsed lasers, and their subsequent introduction into the field in 1966, had on the study of vibrational energy transfer.^{20–25} The laser-based experiments were able for the first time to delineate the mechanism and characteristics of vibration–vibration (V–V) energy exchange in which one molecule loses vibrational energy to an acceptor species, which itself becomes vibrationally excited during a collisional relaxation process. Although such events do not result in complete equilibration of vibrationally hot molecules, they almost always dominate the initial vibrational relaxation of polyatomic molecules. Here we refer to collisions which change the energy of the initially prepared state, and not intramolecular vibrational relaxation (IVR) in which vibrational energy is redistributed among the different modes without a

change in total energy. The rates and mechanisms for V–V energy transfer processes were subsequently determined for many small molecules,^{26–51} and the role of both long- and short-range intermolecular forces in mediating such energy exchange events was delineated.^{52–66} Progress included both an understanding of the fundamental processes which controlled the exchange of energy between chemically distinct molecules and the rates and mechanisms by which different vibrational modes in the same molecule were equilibrated by collisions. In addition, excellent coupling between theory and experiment was made for the first time through the study of the temperature-dependent vibration to translation/rotation energy transfer probability in H₂, a molecular system sufficiently small to be theoretically tractable.^{67–69} For small molecules a general result of these laser-based energy transfer studies was the “unfortunate” realization that collision-induced mode-to-mode vibrational relaxation almost always proceeds faster than bimolecular chemical reaction.^{6,70–72} Thus, in any environment where multiple collisions occur on the time scale of a chemical reaction, the vibrational modes of a polyatomic molecule will equilibrate, and reaction occurs without the advantage of energy localization in a single mode.

The Past: Prologue to the Present. One of the continuing great frontiers in the study of vibrational energy transfer for molecules in their ground electronic state is the quenching of medium to large molecules having “chemically significant” amounts of internal energy. The loss of energy from such highly excited species is of particular interest in the field of unimolecular chemical reactions which have been studied for roughly 70 years.^{73–75} This long-standing preoccupation with the relaxation of highly vibrationally excited molecules has been carried forward to the present day where modern experimental and theoretical methods are being brought to bear on this exceedingly important chemical problem. Unlike the infrared laser-based studies of vibrational energy transfer characteristic of the 1960s through the 1980s, in which the overwhelming emphasis was placed on studying energy relaxation of molecules in their first few vibrationally excited states, many present-day energy transfer studies are being focused on molecules with an internal vibrational energy comparable in magnitude to that of a typical chemical bond.⁷³

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 S*, a level with energy sufficient to cause bond breaking or molecular rearrangement.^{73–75} S* is thus said to have a “chemically significant” amount of energy. 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. The close connection between unimolecular reaction kinetics and vibrational energy transfer is exemplified by this scheme and by earlier methods of studying energy transfer for the high-energy species S*. Falloff curves displaying the decrease in unimolecular rate constant (the rate of production of product P) with decreasing pressure can be used to determine collision efficiencies and amounts of energy transferred per collision in the quenching step (3). In addition to thermal reactions, reactions

due to chemical activation (in which a vibrationally excited molecule is produced in an exoergic reaction such as radical addition) have been studied in detail. These earlier methods have been extensively reviewed.^{73,74,76–78}

The obvious problem with such experiments is that the excited molecules have a wide and not easily defined distribution of vibrational energies. An important step forward was made by taking advantage of the photophysics of a large class of aromatic molecules, which can be excited to an S_1 or S_2 state that undergoes very rapid internal conversion (IC) to the ground electronic state. The excitation energy (well-defined by choice of excitation wavelength) is converted to internal energy of the ground state molecules. Using a pulsed laser as the excitation source and an appropriate spectroscopic technique to follow the time evolution of the excited state population provides a direct method for studying energy transfer either to the parent aromatic molecules or to added molecular species. In the initial applications of this type of photoactivation,^{79,80} the collision-free unimolecular isomerization of cycloheptatriene was studied with UV absorption (UVA) as the probe for vibrationally excited molecules. Soon thereafter, these studies were extended to determinations of collisional energy loss from vibrationally excited toluene molecules ($E_{\text{int}} \sim 52\,000\text{ cm}^{-1}$) produced in the isomerization reaction.^{81,82} More or less simultaneously with this work, an analogous photoexcitation method was employed to investigate azulene, but the population of the vibrationally excited molecules was followed by observing infrared fluorescence (IRF) in the C–H stretching region at $\sim 3\ \mu\text{m}$.⁸³

Since these initial pioneering experiments, both the UVA and the IRF methods have been applied to several molecules as the excited donor and a very large number of added gases as acceptor molecules.^{84–88} The results of these experiments show that the amount of energy lost per collision ($\langle\Delta E\rangle$) depends roughly linearly on the energy content of the excited molecule ($\langle E\rangle$). Initial results using the IRF and UVA methods gave different energy dependencies for $\langle\Delta E\rangle$, but neither technique is highly sensitive to the exact functional relationship between $\langle\Delta E\rangle$ and $\langle E\rangle$. At a given energy the value of $\langle\Delta E\rangle$ is strongly dependent on the size and complexity of the collision partner (bath gas), ranging from tens of wavenumbers per collision for the rare gases to a few thousand wavenumbers per collision for large molecules such as C_8F_{18} .

Present State of the Art

Total Energy Loss Probability Distributions. The methods described above for the study of energy transfer in molecules with chemically significant amounts of vibrational energy, which have characterized past efforts in the field, provide measurements of $\langle\Delta E\rangle$, the mean energy lost by a molecule per collision. This is the same as the first moment of the collisional energy transfer probability distribution function, $P(t,E)$, which gives the distribution of molecules at a given energy E at time t after initial excitation to some high energy E_0 . A number of elegant methods have been developed very recently^{89,90} for determining both the first and second ($\langle\Delta E^2\rangle$) moments of the distribution. The master equation for sequential collisional deactivation from a narrow initial energy distribution indicates that the population passing through a selected energy window far from the initial energy depends on the first and second moments. In addition, the presence of “supercollisions” in which ΔE is abnormally large can be detected by the arrival at the window of a rapid precursor to the main population. One method used to establish such an energy window is “kinetically controlled selective ionization” (KCSI).^{89–91} Molecules are prepared in a narrow energy range using the photoexcitation–IC scheme described

above, and their energy distribution subsequently broadens as the energy decreases. Two-photon ionization (one- or two-color) through the S_1 or S_2 state is used for detection. If the energy of the first photon ($h\nu'$) plus the S_0 energy is too large, the excited state will undergo IC or some other intramolecular process, before ionization by the second photon ($h\nu''$). If the energy $h\nu'$ is too small, the second photon energy $h\nu''$ will not be large enough to ionize the molecule. Thus, the choice of $h\nu'$ establishes the energy window, and the time-dependent ion current depends on the population of S_0 molecules within the window. Experiments of this kind are capable of providing information about the probability distribution $P(t,E)$. One of the most striking results of this kind of study has been the observation of a measurable number of molecules appearing at a low energy E at very short times t , following excitation to some initial high energy E_0 . Since time and collision number are essentially interchangeable variables in these experiments, this observation implies the existence of a small number of collisions with a very large ΔE or the presence of “supercollisions”.

The moment analysis method can be employed anywhere multiple independent measurements can be made that sense the distribution of molecules as a function of energy. An extension of the moment method has been employed that takes advantage of the emission at multiple infrared wavelengths from the vibrational degrees of freedom of a highly excited molecule.⁹² Since a number of different vibrational modes are infrared-active in large polyatomic molecules, it is almost always possible to measure IR emission at a number of different wavelengths and to reconstruct the moment distribution based on the emission intensity from the different bands. In principle, the number of moments that can be extracted from the infrared data is equal to the number of emission wavelengths probed, though as always, signal quality considerations limit the practical results more severely. So far, two-color IR fluorescence has been used to study benzene and fully deuterated benzene excited optically to an energy of $40\,700\text{ cm}^{-1}$. The results are again consistent with the presence of a small fraction of “supercollisions” in the overall deactivation of these highly excited molecules.

High-Resolution Quantum State and Velocity Probes of Energy Loss. These increasingly elegant studies of the quenching of the highly excited substrate molecules S^* are providing detailed information about the *distribution* as well as the average total energy transferred during a quenching collision. Until recently, however, there were no techniques which could be used to follow these processes with quantum-state-resolved detail on a single-collision time scale. The high density of quantum states of the substrate S^* makes such studies difficult to perform experimentally. Nevertheless, the past few years have produced some dramatic improvements in our ability to probe such events in great detail.^{93–97} A key difference between these quantum-state-resolved techniques and earlier methods of studying energy transfer for highly energetic molecules is the ability to separate the total energy transferred in a single collision into its vibrational, rotational, and translational “subdivisions”, thereby providing remarkable insight into the energy transfer mechanism. The recent experimental approaches being used to study these energy transfer processes tend to fall into two general categories. In the first, substrates 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 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, as well as the amount of energy transferred to the rotational and translational degrees of freedom of the *ground* (vibrationless) state of the bath molecules, are required. Techniques capable of supplying all of this extremely valuable information are now at hand. In the second approach, relatively small, light molecules, whose quantum states can be resolved with considerable accuracy even at high energy, are produced in highly excited states by a variety of clever laser pumping techniques. Loss of energy from these relatively simple, high-energy substrates can then be followed with a number of powerful laser probe methods that provide quantum state resolution of the relaxation processes by observing the S* donor itself. Though limited to relatively small donor species with moderate vibrational state densities in the energy region of interest, these techniques are frequently capable of revealing the underlying fundamental relaxation mechanisms, especially the way in which these processes differ for high and low levels of vibrational excitation. A variant on this approach is to produce medium to large molecules with just one or two quanta of vibrational excitation as donors and then to use high-resolution laser methods to probe the energy loss of these species.^{98–100} Although the energies involved (typically 1000–3000 cm⁻¹) are not “chemically interesting”, these large molecules have rather high vibrational state densities even at low levels of excitation. Since many features of vibrational energy transfer are sensitive to vibrational state densities, these experiments provide some insight into the features of interest for the relaxation of highly excited molecules and, in particular, the influence of vibrational state density on the energy transfer process.

Philosophically, these two general approaches are quite complementary. In the first, all quantum state information about the donor, except for its energy, is surrendered in favor of really complete quantum state information about the acceptor and the advantage of being able to study donor molecules of arbitrary complexity in a “chemically significant” energy range. In both variants of the second technique, donor species are kept in an energy range and/or size that still allows the quantum states of the donor to be reasonably well identified. Taken together, the two methods provide energy transfer information over a very wide range of vibrational state density. Both approaches are extremely powerful, giving substantial information about the relaxation processes of complex systems.

A particularly appealing aspect of quantum state resolved experimental studies of energy transfer is their ability to provide data that can be compared to theoretical calculations with a relatively minimal amount of averaging. Historically, most theoretical calculations of energy transfer processes in large or highly excited molecules have tended to present data averaged over many quantum states and often over many collisions. Such data can be compared conveniently to the huge body of experimental information obtained before the advent of quantum state resolved methods. These same theoretical approaches should be useful in analyzing state resolved results, since the averaging process is usually the last step in any theoretical calculation. Of course, theoretical methods employing classical or quasi-classical approaches must develop some algorithm for quantizing inherently classical results, but techniques for doing this have been well established.^{78,101–115}

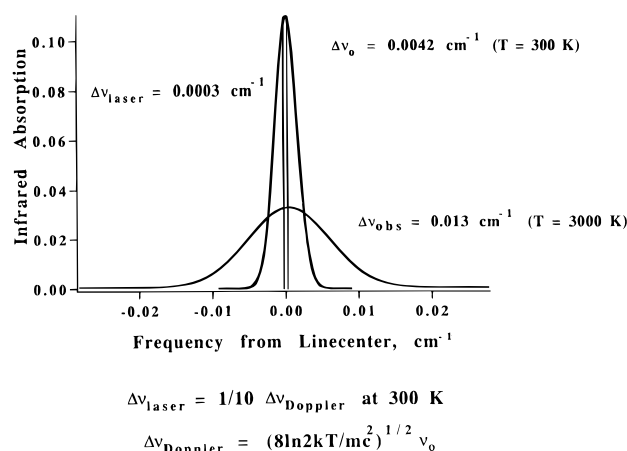
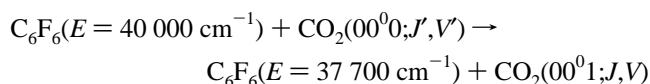


Figure 1. Shown are the laser line width for a typical infrared diode laser operating at 4.3 μm (0.0003 cm^{-1}), a Doppler broadened spectroscopic line for a transition at 4.3 μm for a molecule of mass 44 au at 300 K (width 0.0042 cm^{-1}), and a Doppler broadened line for a transition at 4.3 μm for a molecule of mass 44 at 3000 K (width 0.013 cm^{-1}).

Probing the Vibrational Modes of a Bath Molecule Excited by Collisions with a High-Energy Donor: A Prototype Experiment. An appreciation for the usefulness of modern high-resolution spectroscopic methods in the study of energy transfer processes can be gained by considering collision events in which a donor with a chemically significant amount of energy collides with a bath molecule, producing a vibrationally excited state of the bath. A typical process of this type is the collision between a C₆F₆ molecule with 5 eV (40 000 cm^{-1} or 115 kcal/mol) of internal vibrational energy and a CO₂ molecule in its ground vibrationless state 00⁰, which produces CO₂ in the first asymmetric stretch vibrational level 00⁰1.¹¹⁶ This collision process results in the loss of approximately 2300 cm^{-1} of internal energy from the C₆F₆:



J and V represent the rotational angular momentum quantum number and the velocity of the CO₂, respectively. The hot excited C₆F₆ donor can be readily produced via absorption of a 248 nm excimer laser pulse followed by rapid internal conversion of electronic energy to vibrational energy.^{79–83} The idea of the experiments is to “view” the collision through the eyes of the vibrationally excited bath molecule, CO₂(00⁰1; J, V), emerging from the collision.^{93,94,117} The excited bath molecule can be probed using a high-resolution infrared laser that uniquely identifies the vibrational and rotational quantum numbers 00⁰1; J of the scattered CO₂. Even the velocity of the bath molecule can be sensed by using this same infrared laser to measure the Doppler profile of the recoiling CO₂(00⁰1; J, V) at short times after the collision.^{93,94,118–123} Figure 1 compares the laser line width to the Doppler profile of a thermal (300 K) CO₂ absorption and the Doppler profile of a typical recoiling molecule. The laser line width is 10 times narrower than even the room temperature spectroscopic absorption profile.

A great deal of information can be obtained by this trick of viewing the collision process through the eyes of the “acceptor” molecule. Indeed, momentum and energy conservation often allow the behavior of the donor to be deduced quite accurately from the behavior of the acceptor so that this kind of experiment provides deep insight into the mechanism of quenching for molecules with chemically significant amounts of vibrational

energy. The average initial conditions for the collision are defined with an energy spread of about kT since the rotational angular momentum and velocity profiles of the collision partners are both essentially thermal (300 K), and the internal vibrational energy of the donor is determined by the photon used to excite the C_6F_6 . Infrared laser probing allows the final quantum and velocity state of the recoiling acceptor to be defined with almost arbitrary accuracy, and the total energy and velocity of the recoiling donor are known from energy and linear momentum conservation. Only the rotational angular momentum of the donor exiting from the collision retains significant ambiguity. The results of an energy transfer study of this kind are extremely revealing and were, at least initially, quite surprising.^{93,94,116,117} The vibrationally excited acceptor emerging from a collision of this kind has been found to have rotational and translational energies very near thermal, indicating that little of the internal vibrational energy of the hot donor is transferred to the rotational or translational degrees of freedom of the bath acceptor. Thus, despite the dramatic increase in the vibrational energy of the CO_2 (the energy of the 00^01 level is 2300 cm^{-1} , more than 10 times the mean thermal energy of CO_2 before collision), there is no significant translational or rotational recoil. Momentum conservation arguments rule out the possibility of significant recoil for the C_6F_6 donor emerging from the collision and lead almost inescapably to the conclusion that the collisions which produce vibrationally excited bath molecules must be soft, vibrationally resonant processes that occur at long range. Thus, when the bath vibrational modes are excited in such an event, there is an almost exact exchange of donor vibrational energy for acceptor vibrational energy! Indeed, temperature-dependent studies of similar processes in the hot pyrazine/ CO_2 collision system show both the characteristic "inverse temperature dependence" of a long-range, resonant energy transfer process as well as some measure of the weak degree of rotational and translational inelasticity. It is worth noting that the probability for such events in which the bath becomes vibrationally excited is small, ranging from roughly 1/70 to 1/1000 per gas kinetic collision.^{93,94,116,117} So far, the characteristic signature of long-range energy transfer in the quenching of molecules with chemically significant amounts of vibrational energy has only been observed with bath acceptors having stiff modes ($h\nu \gg kT$). It is likely that low-frequency bath modes ($h\nu < kT$) will exhibit effects arising from short-range force, hard collisions.

These kinds of experiments are typical of quantum state and velocity resolved studies that provide sufficient information for an unambiguous interpretation of collision mechanisms. The combination of low angular momentum transfer and low velocity recoil point almost uniquely to a long-range collision process. The existence of low angular momentum recoil by itself would not have proven such a mechanism since hard collisions occurring near the center of mass of the CO_2 would also produce low angular momentum in the bath but large translational energy recoil.

Collisions that excite vibrational levels of the bath provide exceedingly interesting insights into the energy transfer mechanisms for quenching highly excited molecules. Nevertheless, they occur with sufficiently small probability that they amount typically (with small bath acceptors such as CO_2 and N_2O) to less than 10% of the total energy loss from the donor. To "complete" the picture of the quenching mechanism, the changes in rotational energy and the translational recoils for bath molecules that do not become vibrationally excited must be measured. For example, in the quenching of C_6F_6 by CO_2 the distribution of population in the rotational states with angular momentum J and velocity V in the ground vibrationless state

00^00 must be determined. This has been done for final J states of CO_2 with $J = 58-82$, much larger than the mean ($\langle J \rangle = 23$ at $T = 300\text{ K}$).¹²⁴⁻¹²⁶ These states are significantly populated by collisions and exhibit Doppler line widths much larger than thermal, indicating that the loss of vibrational energy from the donor produces large rotational and translational inelasticity in the bath acceptor. A particularly appealing aspect of these kinds of experiments is that they provide for the first time a picture of the separate behavior of the translational and rotational degrees of freedom or a measure of the amount of energy going from the vibrationally excited states of the hot, high-energy donor into the translational degrees of freedom (true $V-T$ energy transfer) as well as to the rotational degrees of freedom (true $V-R$ energy transfer) of the bath acceptor. Even here the coupling of translational velocity recoil and angular momentum, predicted by conservation of orbital angular momentum in the collision process, $(h/2\pi)(\Delta J) = \mu \langle V_{\text{rel}} \rangle b$, where h is Planck's constant, μ is the collision reduced mass, V_{rel} is the collision recoil velocity in the center-of-mass frame, and b is the mean impact parameter, has been found to hold at least for the pyrazine/ CO_2 collision system.^{125,126} This suggests that the detailed partitioning of energy between rotational and translational degrees of freedom may be controlled by relatively simple kinematic factors. Nevertheless, the fact that the relationship between the recoil velocity and the change in angular momentum is related through the impact parameter should not be missed, since this is a flag that molecular orientation, point of impact, and distance of closest approach will control the fractional amount of energy transferred, respectively, to the rotational and translational degrees of freedom.¹¹⁸⁻¹²³ Ultimately, the hope lives that the intimate coupling among ΔJ , V_{rel} , and b can be unraveled, thus providing probes of the potential energy surface for the collision process.

Although the particular prototype experiment described here employed infrared absorption probing with sub-Doppler resolution, a number of energy transfer experiments are now being developed or are already in use which employ other very high-resolution probes.⁹⁵⁻¹⁰⁰ Laser-induced fluorescence has been used as a probe of both donor and acceptor molecules, providing rotational and vibrational resolution of the collisional energy transfer process. As lasers improve in quality, these techniques should be capable of resolving Doppler profiles for recoiling molecules as well, thereby providing an almost complete kinematic picture of these ubiquitous vibrational energy transfer processes. Indeed, the advent of diode lasers, with their remarkably narrow line width, that are now pushing near the visible wavelength range, hold out the promise of sub-Doppler resolution experiments using electronic transitions in molecules to probe vibrational, rotational, and translational degrees of freedom arising from energy transfer collisions.

"Supercollisions": A Fascinating Anomaly? Molecular encounters in which substantial amounts of energy ($\Delta E \sim 1\text{ eV}$) are transferred in a single collision can have a significant influence on the overall collisional relaxation of highly vibrationally excited molecules.¹²⁷ Hence, much experimental^{89,91,128,129} and theoretical^{101-114,130-132} attention has been focused on the nature of these "supercollision" energy transfer events, which have been observed experimentally^{89,129} 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 $\sim 110\text{ kcal/mol}$ vibrational energy has been reported to transfer $\sim 33\text{ kcal/mol}$ in a single collision with quadricyclane, although with low probability (0.001). Using kinetically controlled selective ionization⁸⁹⁻⁹¹ (see above), the

collisional relaxation of highly vibrationally excited toluene (~ 140 kcal/mol) has been monitored, and the energy transferred per collision was found to have a large dispersion. Additionally, some excited toluene molecules were observed to cool completely to 300 K after only a few collisions, presumably with each collision relaxing the toluene considerably.

Classical trajectory calculations^{101–114,130–132} also support the existence of collisions which transfer unusually large amounts of energy. Relaxation of excited HO₂ (40 kcal/mol) by collisions with He was found to produce ΔE values up to 12 kcal/mol,¹³⁰ although, as noted 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. Quasi-classical trajectory studies^{131,132} on the collisional deactivation of excited HgBr(B²S, $\nu=52$) by a number of rare gases suggest 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 as well as the inclusion of the HgBr anharmonicity. In addition, the probability for collisional transfer of relatively large amounts of energy (~ 6000 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 CS₂ has been investigated in a number of theoretical studies.^{101–107} For CS₂ 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 10⁴ collisions. In trajectory studies of excited azulene colliding with Xe atoms,^{108–114} supercollision events are observed, which are not associated with any particular range of impact parameters or initial velocities but 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.^{108–114} 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 not generally considered to be true supercollisions. Nevertheless, “chattering” collisions and supercollisions would be difficult to distinguish experimentally. As with the other theoretical studies, this investigation indicates that supercollision events are rare, but pervasive; that is, they are seen in a wide range of simulations.^{108–114}

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. In the molecular beam scattering of internally excited KBr ($E_{\text{int}} = 41$ kcal/mol) with argon,^{133–135} as much as 28 kcal/mol was transferred to the argon in a single collision for some scattering angles. These results were successfully modeled¹³⁶ using a quantum mechanical spectator model for inelastic scattering off the repulsive part of the intermolecular potential. Ballistic collisions 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.¹³⁷ Using the impulse approximation,^{138,139} model calculations find that the $T \rightarrow V$ energy conversion for this case may be as large as 96%. The deactivation of diatomic molecules with high-frequency vibra-

tions must necessarily proceed via a supercollision mechanism since these processes require *a priori* the conversion of a large quantum of vibrational energy ($h\nu \gg kT$) into translational and rotational energy. These examples of small molecule energy transfer clearly have a number of features in common with impulsive supercollisions observed in large polyatomic molecule systems. Furthermore, if we use the rather arbitrary definition that a supercollision is an event that transfers an energy greater than say $10 kT$ (roughly 2000 cm⁻¹ at room temperature), the excitation of the stiff ν_3 mode of CO₂ by energy transfer from hot donors with chemically significant amounts of energy (discussed above) is a supercollision. Note that this is a very special kind of supercollision, brought about by a nonimpulsive collision process, with little angular momentum or translational energy imparted to the bath molecule.^{93,94,116,117} All of the energy is instead placed neatly into the acceptor molecule's vibrational motion through long-range electrical forces.

Recent data collected for collisions involving hot pyrazine and cold (300 K) CO₂ suggest that the postcollision CO₂ molecules produced in high rotational states with large translational energy arise from collisions with a pyrazine molecule that is in the process of “exploding”, a true unimolecular quenching event.¹⁴⁰ Theoretical modeling studies of the quenching of high-energy SO₂ by argon atoms¹⁴¹ find that the magnitude of the energy transferred increases dramatically as the SO₂ donor internal energy increases from $E_0 - 20$ kcal/mol (20 kcal/mol below the threshold for fragmentation) up to the dissociation limit E_0 . In a study using both vibrational close-coupling, infinite-order sudden quantum scattering and classical trajectory methods, energy transfer for highly excited benzene/rare gas collisions has been investigated.¹⁴² The results suggest that the mechanism for “supercollisions” involves a head-on collision between a bath gas molecule and a rapidly moving substrate atom involved in large-amplitude motion associated with a highly excited, low-frequency, out-of-plane vibration. Though these results are very new, they suggest that supercollision events may be a general phenomenon that becomes particularly important for molecules near or above the threshold for fragmentation. The large-amplitude vibrations expected for a molecule undergoing dissociation in the energy region at or above the transition state might explain the large collisional energy transfer observed in this system. In small (triatomic) molecules the opportunity for studying quantum state resolved collisional energy transfer for a dissociating donor species at or above its threshold for fragmentation is limited because of the short lifetime of the decomposing species. The rather long lifetimes associated with the breakup of large molecules at or relatively near their unimolecular dissociation threshold energy provide an opportunity to study these processes using a variety of high-resolution laser/spectroscopic probing methods.

There is a remarkable similarity between the present preoccupation with and “controversy” surrounding supercollisions¹⁴³ and an earlier debate on the subject (in a slightly different guise) extant several decades ago between the Seattle and Cambridge unimolecular reaction groups.¹⁴⁴ At that time the argument involved the relative importance of average versus high-energy (read “super”) collisions in promoting “unimolecular” chemical reactions. Today we are fortunate that the experimental tools at our disposal (provided largely by the advent of high-resolution, high-intensity lasers, supersonic cooling techniques, and molecular beam machines) are capable of elucidating for the first time a detailed quantitative picture of the collision processes important in these ubiquitous chemical reactions. Thus, the questions, having been around for 20 years (or perhaps 70 counting from Lindemann's original conjecture¹⁴⁵ about the

mechanism of unimolecular reactions!), are well posed. To appreciate how important such quenching collisions are, we need only realize that such a large energy exchange is almost always capable of taking a molecule from above the energy threshold for unimolecular reaction to below threshold. Thus, quenching by such supercollisions can have a dramatic effect on the probability of unimolecular reaction.¹⁴⁶ Although such encounters are relatively improbable, they can carry away a substantial amount of the donor energy.

The Present: Prologue to the Future. The present era of energy transfer studies on the ground potential energy surface has been characterized by a continued reliance on the improved versatility and quality of pulsed lasers as pump sources. Perhaps far more important, however, has been the introduction of high- and superhigh-resolution spectroscopic probe methods that employ lasers to achieve both the necessary resolution and the requisite sensitivity needed for the most sophisticated experiments. Increasingly, these experimental techniques are moving toward the complete definition of collisional energy transfer processes in which the vibrational, rotational, and translational motions of molecules can be defined before and after a collision has occurred.^{93–96,147–151} (Indeed on the distant horizon can be seen the possibility of studying collisions in which the spatial orientation dependence and the impact parameter distribution can be controlled or revealed.^{152–156}) Equally impressive have been theoretical developments that now provide predictive values for quantum state resolved energy transfer processes as well as a description of collisional vibrational energy transfer for small molecules with chemically significant amounts of energy. For example, the “azimuthal and vibrational close-coupling, infinite-order sudden approximation” theoretical approach has been used to make quantitative predictions of the quantum state resolved rovibrational energy transfer in electronic ground state (S_0) glyoxal.¹⁵⁷ These calculations agree remarkably well with the rovibrational energy transfer cross sections for collisions of glyoxal with He, H_2 , and D_2 measured in the first electronically excited state (S_1) of this species.^{158–160} (See below.)

Future experiments seem certain to continue the move toward a better definition of both the initial and final states of the colliding partners in a molecular encounter that involves exchange of vibrational energy of a donor species with the vibrational, rotational, and translational degrees of freedom of a bath acceptor molecule. Indeed, for donor species at low vibrational energies (one or two vibrational quanta of excitation), where individual vibration–rotation quantum states can still be separated, assigned, and pumped by presently available “monochromatic” laser sources, experiments that fully define the initial and final vibrational and rotational quantum numbers are now being performed with excellent results.^{97–100,147,148,161–168} In fact, such studies have already shown that energy transfer processes can depend sensitively on the coupling between vibration and rotation in the donor and acceptor species.^{147,148,169–172} So far, velocity recoils have not been measured in such experiments but seem certain to be determined in future studies with small, weakly excited molecules.¹⁷³ The requisite, sub-Doppler resolution probe lasers are available already, and it only remains to find a molecular system with sufficient signal quality to perform these experiments. A particularly interesting area for study, which can be investigated with high-resolution sub-Doppler absorption techniques, is the probing of translational energy exchange in long-range energy transfer processes. Well-defined predictions^{62,63} for translational inelasticity in vibration-to-vibration energy transfer processes have existed for more than 25 years, predictions that have never been directly verified by

experiment due to the lack of requisite tools! (A particularly elegant set of experiments that sense both rotational and translational inelasticity without vibrational state change have been performed using microwave absorption techniques.^{174,175} If similar studies can be performed in which vibrational states change as well, the practice and art of vibrational relaxation studies will advance considerably. The challenge in these experiments is the relatively low probability for vibrational quantum number changes in such collisions.)

An important question that might be asked about the future of energy transfer studies is the degree to which the initial state of a highly vibrationally excited molecule can be defined. For large molecules at low energy (one or two vibrational quanta) and for small to medium sized molecules with moderate vibrational excitation, preparation of single initial vibrational and rotational states of a donor are possible using a variety of methods such as stimulated emission pumping, overtone excitation, and Raman scattering. For large molecules with “chemically significant” amounts of energy, where vibrational state densities generally exceed $10^{10}/\text{cm}^{-1}$, preparation of individual vibrational levels appears to be beyond the ability of any present technology. Nevertheless, it should be possible to prepare molecules with chemically significant amounts of *vibrational* energy where the initial *rotational* state and the initial *velocity* are relatively well defined. Linear and angular momentum considerations limit the values of J and V that can be excited by a laser photon no matter what the total vibrational energy of the hot donor molecule. Indeed, for the prototype experiment described above involving energy transfer between C_6F_6 with $40\,000\text{ cm}^{-1}$ of energy and thermal CO_2 , the amount of translational and rotational energy in the hot C_6F_6 ($40\,000\text{ cm}^{-1}$) donor can safely be described as negligible, since the rotational excitation induced by laser pumping only adds $h/2\pi$ units of angular momentum to the donor’s thermal rotational profile and essentially nothing to its velocity profile. Nevertheless, while the energy represented by these two degrees of freedom is very small, the spread in angular momentum and velocity is both considerable and undesirable and limits the amount of information that can be gleaned from the experiments. Of more importance perhaps is the final angular momentum state of the hot donor which is exceedingly difficult to determine after the collision. (The velocity recoil of the hot donor can be deduced reasonably well from the measurable velocity recoil of the bath acceptor and linear momentum conservation.) The combination of supersonic cooling techniques with clever laser excitation schemes provides an opportunity to produce a hot donor with chemically significant amounts of vibrational energy and very well-defined rotational and translational energy. Provided the bath acceptor molecule used to carry away the energy is kept small, as in the prototype experiment described above, the final state of the acceptor can be probed with almost arbitrary accuracy while the initial state rotational and translational energy can again be well-defined using laser pumping and/or supersonic expansion methods. The great challenge that remains is to measure the rotational recoil of the hot donor as it emerges from the collision still with so much vibrational energy that its spectroscopy remains intractable.

Even without going to experiments of exceptional spectroscopic resolution, a number of exceedingly interesting challenges remain in studying energy transfer for molecules with chemically significant amounts of energy. For example, it would be highly desirable to study systems that are in the process of breaking up due to unimolecular dissociation^{140–142} and to determine the energy transfer properties of these species at different times before the expected breakup. These experiments should be

possible with long-lived species where several microseconds pass between excitation by a laser photon and the onset of dissociation. To study shorter-lived species will require femtosecond/picosecond laser pump and probe methods.

Ultimately, all energy transfer experiments provide information that can be used to test the quality of the potential energy surfaces that define the collisional interaction between molecules. The outstanding progress that has been made in the theoretical description of these processes and the ever-increasing power of modern computers leave the theoretical determination of these potential energy surfaces a prime area of future effort. In addition, methods to test the quality of these surfaces, particularly individual regions of the surface, against the best experimental data are sorely needed. The combination of elegant, incisive experimental techniques and powerful theoretical methods coupled with the ever-increasing speed and sophistication of modern computers suggest that "everything we ever wanted to know about energy transfer on the ground potential energy surface" just might be apparent to us before we sit down to celebrate the 200th birthday of *The Journal of Physical Chemistry!*

State-to-State Vibrational Energy Transfer within Excited Electronic States of Polyatomic Molecules

Consider the ideal experiment for exploring VET in the low-energy region of a vibrational manifold where the levels are well separated and usefully labeled with a zero-order normal mode description. Here we wish to measure absolute state-to-state VET cross sections for single collisions with, say, a rare gas atom. We would like to see this V-T transfer from a selection of initial vibrational states, where for each case *all* important channels may be observed. It would be desirable to extend the measurements to rotational resolution, both in initial state selection and in destination state observations, so that the competition between rotational channels (R-T exchange) and rovibrational channels (V-T,R exchange) is mapped out. One would like to repeat the experiment over a range of narrow center-of-mass collision energy distributions. Ambitions may also extend to obtaining a measure of control over the collision orientation and perhaps monitor the influence of impact parameter. Differential cross sections may be added to the aspirations, and of course these measurements should involve a wide enough variety of polyatomic molecules and collision partners so that trends and generalities maybe perceived.

There is also a corresponding challenge for theoretical treatments of VET since no simple model could handle such detailed results. Ideally, theoretical predictions would lead the way.

While this wish list represents a road to a seemingly unobtainable destination, the distance so far traveled is surprisingly great. Some of the intermediate goals have been reached, but, sadly, only for one or a few polyatomic molecules. Much of this progress has come from studies of energy transfer within excited electronic states. Ironically, excited state observations are among the oldest in the discipline, yet they still offer much promise toward reaching further milestones in the quest for satisfactory characterization of state-to-state energy transfer.

Most excited electronic state explorations of polyatomic VET are conceptually simple. Focus first on the most elementary experiment, namely a mixture of the polyatomic molecule with its collision partner in a 300 K bulb. Absorption of a tuned laser pump creates an initial S_1 vibrational or rovibrational state in the polyatomic molecule. Fluorescence detection of this electronic state achieves two objectives. First, it takes advantage of the fluorescence lifetime (microseconds to nanoseconds), a

built-in molecular clock, to permit easy adjustment of added gas pressures for single-collision conditions. Second, the vibrational or rovibrational structure in dispersed fluorescence can often be used to follow quantitatively the important energy transfer channels occurring on the S_1 polyatomic surface. Since all S_1 vibrational states reached by the energy transfer participate in S_1-S_0 fluorescence, the probe of dispersed fluorescence in principle (and often in practice) allows one to see *all* significant channels. The result is a complete single-collision energy transfer map from the selected initial S_1 level. If the experiments are repeated with the polyatomic entrained in a cold supersonic beam, opportunity exists for introducing more definitive rotational state resolution in both initial state pumping and destination state observations. The use of crossed molecular beams adds collision energy control as well as the possibility of influencing collision geometry and of obtaining differential cross sections.

Studies in 300 K Bulbs. The 300 K bulb studies are well practiced while crossed beam studies are still relatively sparse. The prototypical bulb experiments are those involving the $B\ O_u^+$ state of I_2 . Their origins have been traced¹⁷⁶ back to 1911 when sunlight was the pump source and visual observations of the fluorescence color changes in response to added gases constituted the detector.^{177,178} A "chrestomathy" of the iodine experiments¹⁷⁶ as well as a later review¹⁷⁹ summarizes the evolution of the I_2 experiment as pump sources changed from carbon arcs through atomic emission lines, laser lines, and, finally, tuned lasers. Photographic plates were used as the fluorescence detector until 1964 when a switch to photomultipliers provided more quantitative measurements.

In comparison with the I_2 history, application of the tuned S_1 pump-fluorescence probe approach to polyatomic molecules is a newcomer. The 300 K bulb experiments began just prior to the introduction of commercial dye lasers by using excitation derived from Xe arcs coupled to a monochromator.¹⁸⁰ They have, of course, been greatly refined with laser pump sources and improved fluorescence detection schemes.

Most data concern single ring aromatic molecules with 30 or more modes. With sometimes scores of vibrational levels occurring within $2kT$ of an initially pumped level, including some nearly resonant, one would anticipate that the multiplicity of VET channels would completely obscure the outcome of single-collision encounters. A remarkable phenomenon was discovered, however, in the first experiments. The state-to-state VET was extraordinarily selective among the possible channels. Strong propensity rules were clearly at work. This high selectivity has since been seen in every polyatomic molecule study. High selectivity is the hallmark of state-to-state VET.

An example is shown in Figure 2. The S_1 energy level diagram depicts the state-to-state channel competition from an initial level with $\epsilon_{\text{vib}} \approx 410\text{ cm}^{-1}$ in *p*-difluorobenzene in single collisions with Ar.¹⁸¹ It shows that transfer to a level nearly resonant with the initially pumped level is ignored while 56% of the transfer involves a single channel reaching a level buried in the midst of many near neighbors about 120 cm^{-1} above the initial level. Another 10% reaches a higher level, and still another 8% selects a third level, even higher in energy. In all, five specific channels account for over 75% of the single-collision transfer probability.

The propensity rules that drive the aromatic selectivity were initially extracted¹⁸⁰ by a simple application of a quantum model of atom-diatom collisions^{182,183} that was adapted for polyatomic molecules.¹⁸⁴ This so-called SSH-T model factors into a product of squared matrix elements V^2 for each vibration

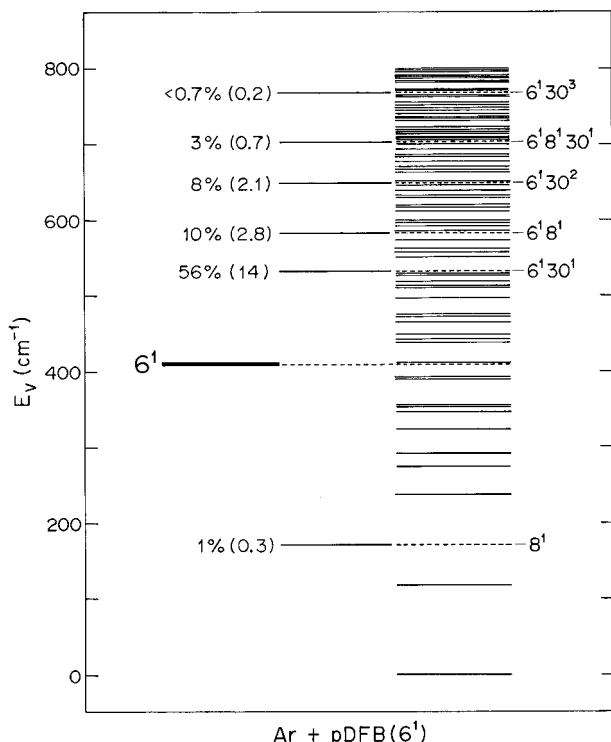


Figure 2. S_1 vibrational levels in *p*-difluorobenzene showing levels populated by single collisions with Ar after pumping the in-plane ring distortion fundamental, 6^1 . The dominant destination levels are identified along with the percent of VET out of 6^1 using each channel and of the transfer efficiency given in parentheses as the number of effective collisions per 100 gas kinetic encounters. Adapted from ref 9.

undergoing quantum change and an integral $I(\Delta E)$ dependent primarily on the amount of energy exchanged V–T, the temperature, and the collision-pair reduced mass. In their most primitive form, the V^2 terms become $10^{-|\Delta v|}$ so that each vibrational quantum change beyond $|\Delta v| = 1$ imposes an additional order of magnitude restriction on the transition probability. The $I(\Delta E)$ integral¹⁸⁵ for a “heavy” collision partner such as Ar as opposed to He or H_2 peaks for V–T process with ΔE about 100 cm^{-1} and then falls to a small value by the time ΔE reaches $\approx 300\text{ cm}^{-1}$. The net result is that *transitions with small quantum changes (small Δv) in low-frequency modes (small ΔE)* dominate the channel competition.

A more recent version, only slightly less primitive than the first, emphasizes the favored channel bias to low-frequency modes by including an SSH-T derived frequency-dependent term¹⁸¹ in V^2 . The fidelity of these rules in their various versions to the observed competition among channels is often semiquantitative. Considering that the data include transfer from a variety of initial modes in four aromatic molecules, the agreement is far better expected from the simple modeling.

The SSH-T modeling successes have been obtained without making specific account of level symmetries or of mode geometries. A systematic but *ad hoc* treatment of mode geometries has been introduced as an addendum with modest improvement of the data for certain molecules.¹⁸⁶ The lesson one draws is that these characteristics are of secondary importance for aromatic state-to-state V–T transfers. Small quantum changes in low-frequency modes are the defining aspects of the favored channels.

The importance of low-frequency modes is underscored by a theoretical treatment of the pDFB transfer that investigated specifically the relative roles of mode geometry and mode frequency. Since the low-frequency modes that dominate the VET in aromatic molecules are almost always out-of-plane

motions, the question arises whether it is the geometric character as opposed to the low frequency that makes the modes so active. With three-dimensional, fully quantal scattering calculations that reproduced aspects of the pDFB data,¹⁸⁷ it was possible to artificially reduce the frequency of some in-plane modes to that of the lowest out-of-plane mode. With their newly acquired low frequencies, the in-plane modes also display the large cross sections of the favored channels.

In addition to high selectivity among possible V–T channels, a second universal trait has emerged from the polyatomic bulb studies. The most favored V–T channels have remarkably large cross sections, at least when gauged by the general experience of diatomic V–T energy transfer that preceded the polyatomic studies. Cross sections of the dominant polyatomic channels are in the range 1–15% of hard-sphere values. Low frequencies are undoubtedly responsible for the generic V–T efficiently in polyatomic models. The SSH-T model is unable to account for the large size of cross sections. Quantal scattering calculations, on the other hand, reproduce the absolute magnitudes reasonably well.¹⁸⁷

In addition to a critical review,⁹ a compendium of the 300 K VET experiments has recently appeared.¹⁸⁸ Only a few non-aromatic polyatomic molecules have been visited seriously by the 300 K bulb technique of tuned laser pumping of a variety of levels with dispersed fluorescence detection. They include difluorodiazirine (CN_2F_2),^{189,190} glyoxal ($CHOCHO$),¹⁹¹ and CF_2 .¹⁹² While none has been modeled well by SSH-T rules, the dominant characteristic of the propensity rules may still be seen to operate, at least in the two larger molecules. High selectivity occurs, and again small quantum changes in the lower frequency modes account for the majority of observed channels. These cases also show some intriguing departures from the rather uniform behaviors of the aromatic molecules. Those differences underscore the need to explore single-collision state-to-state V–T transfer in a much wider selection of molecules. There are far too few examples from bulb studies to build even a reasonably encompassing picture of trends and generalities.

Vibrational relaxation studies of diatomic molecules in excited electronic states have shown that coupling among upper electronic states introduces relaxation paths that are inaccessible to ground state molecules. With this experience, a recurring question is whether VET in S_1 states of polyatomic molecules is generically different from that in their ground electronic states. In a general sense, the answer appears to be “no”. For example, while S–T mixing in pyrazine appears to reduce the S_1 VET cross sections moderately,¹⁹³ the effect is well understood as a special case.¹⁹⁴ The mixing seems to have little effect on the channel competition. The best comment on the S_0 vs S_1 question comes from an ensemble of four-de-force VET studies of selected S_0 levels of *p*-difluorobenzene. Using stimulated emission pumping (SEP) to populate various S_0 levels in both 300 K and cold jet experiments (see below), abundant energy transfer data emerged that may be compared with S_1 experiments.^{195–199} The behavior in S_0 and S_1 states is similar in all respects.

The theoretical modeling is consistent with this result. Quantal theoretical accounts of S_1 VET in *p*-DFB fit both S_1 and S_0 data without special account of an excited electronic state.¹⁸⁷ In a more stringent test, the detailed and highly successful theoretical fits to S_1 rotationally and rovibrationally inelastic scattering in glyoxal ($CHOCHO$) (see below) are also made without special attention to an excited electronic surface. Thus, certainly in these cases, and probably rather generally, the S_1 vibrational relaxation in polyatomic molecules is electronically adiabatic. S_1 VET appears to differ from what

would be found in the S_0 state only on account of incidental factors such as mode frequency differences, accidental Fermi resonances, and so forth.

The similarity of VET in ground and excited electronic states may not occur so generally in diatomic or small polyatomic molecules. For example, if the frequency of an active mode differs substantially among the electronic states, as is often the case for diatomic molecules, then qualitative changes in VET cross sections may be expected for excited electronic states. Diatomic and small polyatomic molecules may also be subject to collisional interactions between specific vibrational levels of two electronic states. The excited electronic state VET is not then electronically adiabatic, leading to substantial changes from ground electronic state characteristics.

Studies Using Cold Supersonic Expansions. The introduction of supersonic cold jet expansions has had an impact on spectroscopy that ranks second only to that of lasers. Energy transfer is one of many fields to benefit from this new chemical environment where rotational and, in many cases, vibrational degrees of freedom may be cooled to a few kelvin. The bulb optical pump-fluorescence detection method has been transferred to these cold jets in two types of experiments. The simplest is the study of energy transfer in the collisional part of the jet expansion that occurs within a few ($< \sim 5$) nozzle diameters downstream of the nozzle orifice. Here the translational temperatures and hence collision energies have typically fallen to a few kelvin but with the collision frequency still high enough to generate detectable VET from a S_1 pumped level. The polyatomic molecule is usually seeded at a few mole percent in, say, an inert gas carrier that serves as the VET collision partner. The more ambitious cold jet studies use cross molecular beams where high (and tunable) collision energies are created by the interaction of the beam carrying the polyatomic with a separate target beam.

Single-Beam Experiments. True to form, I_2 in its B state led the way in the single-beam experiments²⁰⁰ with the initial studies focusing on the very low collision energy vibrational transfer out of $v' = 25$ in one exploration,²⁰¹ $v' = 14, 16,$ and 28 in another,²⁰² and, subsequently, $v' = 43$ ²⁰³ in a third. The unique issue that arose from the iodine studies concerned the large size of cross sections. While the extraction of absolute cross sections involves the uncertainties associated with a collisional environment that is hard to quantify, all workers agreed that the cross sections for relaxation of I_2^* with He, primarily by $\Delta v' = -1$ transitions, are on the order of 100 \AA^2 as opposed to a geometric cross section of about 20 \AA^2 . Argument ensued concerning the extent to which a special mechanisms such as orbiting resonances that lengthens the I_2^* -He collision duration contributed to the large cross sections.^{202,204-212} Others have proposed that the data may be rationalized by ordinary impulsive collisions.²¹³ A specific revisit of the I_2 -He system over a temperature range of 2–12 K rather convincingly supported this interpretation.²¹⁴ Indeed, there seems still no clear-cut experimental evidence for the influence of resonances.

The first extension of single-beam studies to the S_1 state of polyatomic molecules was almost contemporary with the I_2 experiments. Unusually large cross sections were again reported for various molecules including glyoxal (CHOCHO),^{215,216} aniline,²¹⁷ and naphthalene.²¹⁸ Later naphthalene studies^{219,220} brought a new understanding to the issue by obtaining a set of VET cross sections for temperatures ranging from 1.6 to 15 K. When scaled against the strongly temperature-dependent Lennard-Jones elastic cross sections rather than the usual practice of comparison with hard-sphere cross sections, the data revealed

no need to invoke contributions from special mechanisms. Low collision energy VET cross sections tracked well with the L-J cross sections.

A most unique contribution to the discussion of polyatomic VET cross sections for very low energy collisions is found in a study of the *p*-difluorobenzene-Ar system over the range 1–12 K.¹⁹⁹ In this case, cross sections were obtained for the S_0 state, where stimulated emission pumping (SEP) was used for level population. These SEP generated cross sections exhibited ordinary behavior when scaled against Lennard-Jones elastic cross sections. Most remarkably, the correlation is sustained when extended to 300 K for the same SEP populated S_0 levels.¹⁹⁹ As the authors point out, "Clearly the attractive region of the intermolecular potential is an essential ingredient in understanding the collision dynamics of molecular systems" at these very low collision energies.

One of the great advantages of the cold jet experiments is the improvement in resolution that may be brought to the state-to-state experiments. With the narrow rotational band contours of polyatomics in the low-temperature expansions, overlapping of absorption bands is minimized and laser pumping becomes more selective. Molecules whose study at 300 K was precluded by thermal congestion in S_1 - S_0 absorption become accessible in cold jets. Naphthalene with 48 modes is a prime example of a complicated vibrational system opened for VET study by the cold jet approach.²¹⁸⁻²²⁰ Another is C_6D_6 ,²²¹ a difficult case at 300 K.

These cold jet studies have improved greatly the detail with which the individual state-to-state channel competition may be resolved. In 300 K bulbs, the dominant channels are often those that *add* single quanta of low-frequency modes to the pumped level. In contrast, only the exoergic channels ($V \rightarrow T$) are accessible in the very low energy collisions of cold jets. As a result, competition between less favorable channels constitutes the energy transfer. Now the channels with $|\Delta v| > 1$ as well as the $|\Delta v| = 1$ channels of higher frequency modes display their interplay.

The state-to-state VET competition in the very low energy collision domain of cold jets has been monitored for one initial S_1 level and several collision partners in benzene,^{222,223} benzene-*d*₆,^{221,223} and naphthalene.¹⁹⁹ It has also been observed from several levels in S_1 *p*-difluorobenzene,^{185,224,225} again with several collision partners. A compendium of conditions has been given.¹⁸⁸ In all cases the great rule of polyatomic VET is sustained; namely, high selectivity occurs among competing channels. Beyond this, no universal characteristics of the collisional energy flow emerge.

In all these cases, the channel competition is in qualitative accord with SSH-T predictions for at least some initial levels and some collision partners. As finer details are examined, however, the limitations of SSH-T modeling are revealed. These sticky points concern such observations as the temperature dependence of branching ratios for competing channels, or the unique behaviors from different initial states in the same molecule, or the response of the channel competition to different collision partners.

A particularly illustrative example concerns initial S_1 levels and collision partners in *p*-difluorobenzene VET. The channel competition from an initial S_1 level with $\epsilon_{\text{vib}} = 350 \text{ cm}^{-1}$ has been monitored with independent experiments for He and Ar collision.^{185,225} SSH-T modeling fits the data as well as the same VET observed at 300 K.¹⁸⁵ On the other hand, a similar cold jet experiment²²⁴ for another level with $\epsilon_{\text{vib}} = 238 \text{ cm}^{-1}$ reveals behavior for these collision partners that cannot be reconciled with a unified SSH-T model. Additional examples

of cold jet VET from other S_1 *p*-difluorobenzene levels show flow patterns that fit SSH-T modeling from some levels but not others,²²⁵ whereas the VET data at 300 K from many initial levels were all modeled well with SSH-T theory.¹⁸¹

For the purposes of modeling, it is clear that the very low collision energy regime is a far more subtle environment than the broad collision energy distributions of 300 K VET. Although few polyatomic molecules have been studied, these experiments are particularly instructive on account of the demands they impose for the development of new theoretical approaches. They need to be pursued for a far wider range of polyatomic molecules.

Crossed Molecular Beam Experiments. Crossed molecular beams provide the greatest opportunities for instructive cold jet VET explorations. The vast majority of crossed beam experiments do not deal with energy transfer but focus on reactive scattering because of the availability of a quasi-universal detector. A mass spectrometer can easily distinguish the small reactive scattering signal, here a new chemical species, from the massive background of elastic scattering. To follow inelastic scattering where only rotational and vibrational state changes occur, the detector faces more severe challenges. They have been met by following changes of translational energy that always accompanies the internal state changes (i.e., a time-of-flight detector or Doppler spectroscopy) or by probing directly the internal states themselves (i.e., various spectroscopies). A review of these “energy change” and “state change” methods has been given with citations of many examples, most of which involve diatomic or very small polyatomic molecules.⁹

Application of crossed molecular beams to state-to-state VET in large polyatomics was pioneered²²⁶ by “state-change” studies of aniline²²⁷ and *p*-difluorobenzene²²⁸ with He atoms. Vibrational excitation from the $T \rightarrow V$ inelastic scattering from the S_0 zero-point level was followed with $S_1 \leftarrow S_0$ laser-induced fluorescence, a highly sensitive state detector. These experiments exploit the unique capability of crossed beams to tune the collision energy, and in this case, an ingenious experimental design with variable beam intersection geometries permitted the relatively narrow collision energy distribution to range from about 150 to over 2000 cm^{-1} . Many S_0 fundamentals occur within these energies, and a diligent search with highly sensitivity for their activity revealed the expected result. Only two modes in aniline and one in *p*-difluorobenzene were active. They were always the lowest frequency modes, and all were seen in only $\Delta v = 1$ or $\Delta v = 2$ channels.

The great strength of these experiments is their ability to follow the cross section for a specific channel as the collision energy is tuned. They have provided the first (and still only) view of the collision energy dependence of state-resolved vibrationally inelastic scattering in molecules of such vibrational complexity. With one intriguing exception, the cross sections of the $T \rightarrow V$ channels increase smoothly as collision energy is increased over a range of about $15\times$. The trend is rationalized with a simple model as well as by a fully quantal 3-dimensional inelastic scattering calculation.¹⁸⁷

One of the limitations of the S_0 crossed beam approach concerns selection of the initial rovibrational state from which inelastic scattering occurs. Unless tough pumping strategies are imposed, the states are those produced by the cold expansion, namely a relatively narrow rotational distribution in the S_0 zero-point level. One of those pumping strategies involving three laser frequencies has been employed. By using stimulated emission pumping for initial state selection, several state-to-state rovibrationally inelastic scattering channels have been monitored from *single rovibrational* levels of S_0 glyoxal, a

molecule with 12 modes, as a function of collision energy.²²⁹ True to form, the technique was once again worked out with I_2 .²³⁰

As an alternative crossed beam approach, the optical pump-dispersed fluorescence detection scheme so effectively used in 300 K bulbs has been moved into beams for study of inelastic scattering in S_1 polyatomic molecules. This change brings two great advantages to the beam experiments. (i) A variety of initial levels is easily selected. (ii) *All* of the major single-collision channels may be observed. In bulbs, one obtains absolute cross sections. In beams, one obtains quantitative *relative* cross sections for the many channels defining the competition.

Since crossed beams are in many aspects a hostile environment for the 300 K bulb method, what is the motivation for its use? The great appeal is vastly improved resolution. With cold beams, it is practical to pump a vibrational level with a severely restricted rotational distribution so that information about rovibrational and even rotational energy transfer emerges. When combined with the relatively narrow collisional energy distribution of crossed beams, the experiment gives an encompassing view of the *competition* among single-collision state-to-state energy transfer channels that is far more detailed than any previously seen. The improvement in resolution is quite analogous to that obtained when spectroscopic studies are switched from 300 K bulbs to supersonic expansions. Thus, as with the S_0 crossed beam experiments, it has created an entirely new game for large molecule energy transfer.

Again, true to form, the first excited state studies^{179,231–233} using this crossed beam approach involved the B state of I_2 , the constant benchmark of energy transfer. (Indeed, I_2 served also as the precursor of the S_0 crossed beam experiments^{234–236} and their theoretical interpretations.²³⁷) The S_1 polyatomic studies so far have involved only glyoxal, CHOCHO.^{238–242} With 12 modes, it serves as a working example of a large, vibrationally complex molecule. On account of its symmetry and spectroscopic properties, glyoxal has exceptional experimental accessibility. It is similarly accessible for theoretical treatment.^{11–14}

Figure 3 displays all of the S_1 glyoxal vibrational levels up to 1200 cm^{-1} . Each of the four bold levels has been pumped by tuning a laser to rotational features in the appropriate S_1-S_0 vibronic absorption band. Glyoxal is almost a symmetric top ($\kappa = -0.99$), and prominent R sub-band heads in the cold (35 K) absorption spectrum allow selection of the angular momentum $K\hbar$ about the top axis (the “*a*” axis in Figure 3). In work so far completed, $K' = 0$ has been selected. For example, one may pump the S_1 level 7^2 with $K' = 0$ and $J' \leq 10$, for which the shorthand designation is 7^2K^0 .

Exceptionally strong vibrational propensity rules control the S_1 vibrationally inelastic scattering. Cross sections for $\Delta v = \pm 1$ changes in the lowest frequency mode, the CHO-CHO torsion $\nu_7' = 233 \text{ cm}^{-1}$, exceed those for other vibrational changes by at least an order of magnitude (see Figure 3).

The real power of crossed beams is the rotational resolution. That resolution transforms an energy transfer schematic from the vibrational level diagram of Figure 3 to that of Figure 4 involving many rovibrational levels. That schematic is for energy transfer after pumping 7^2K^0 . It is comprised of rovibrational levels within each of three types of inelastic channels. One may observe pure rotationally inelastic scattering with $\Delta K = 1$ or 2 or 3... up to the collisional angular momentum limit. One may observe rovibrationally inelastic scattering, again with $\Delta K = 1$ or 2 or 3... for $\Delta v_7 = +1$ collisional transitions. Finally, one may observe rovibrationally inelastic scattering for the analogous $\Delta v_7 = -1$ channel.

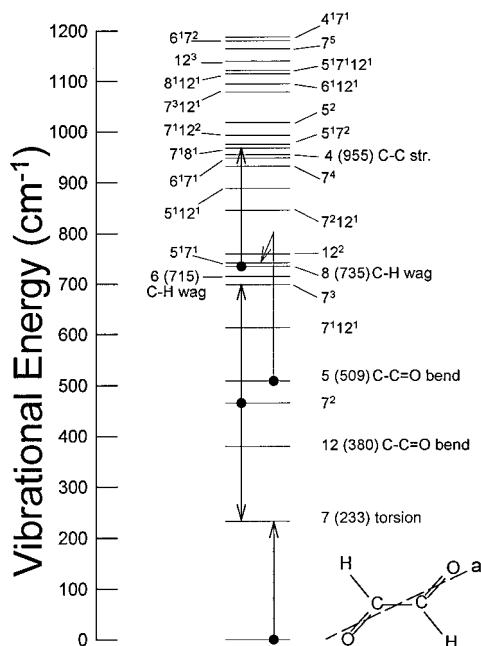


Figure 3. A display of all S_1 glyoxal vibrational levels below 1200 cm^{-1} . Arrows show the dominant vibrationally inelastic scattering channels ($|\Delta v_7| = 1$) from each of four initially pumped levels. Reproduced with permission from ref 239. Copyright 1994 American Institute of Physics.

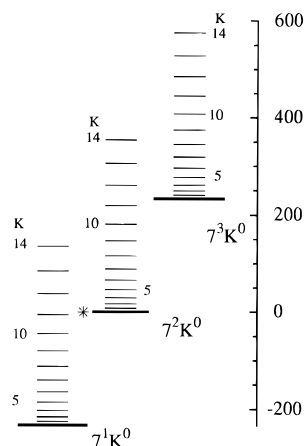


Figure 4. A display of rovibrational levels in S_1 glyoxal to which energy transfer with He may be observed after pumping the level $v_7' = 2$, $K' = 0$ (marked 7^2K^0). ΔE is the energy of the destination levels relative to that of the pumped level. Reproduced with permission from ref 239. Copyright 1994 American Institute of Physics.

This rich competition involving all important single-collision channels emerges naturally from analysis of the resolved inelastic scattering fluorescence. Many such spectra have been presented²³⁹ together with computer-simulated spectra that are fit to the data with essentially only one adjustable parameter. That parameter is the set of relative state-to-state cross sections that are sought.

The end result of a 7^2K^0 inelastic scattering experiment is the set of quantitative relative cross sections such as those displayed in Figure 5. With over 40 competing channels under observation, this is a picture of single-collision rotational and rovibrational energy transfer at a level of detail far beyond any previously available for large molecules. The results are full of surprises. While many are discussed in a published comparison of data for various collision partners and initial levels,²⁴⁰ only a few are considered here. For example, when the transferred energy ΔE is in the range $200\text{--}300\text{ cm}^{-1}$,

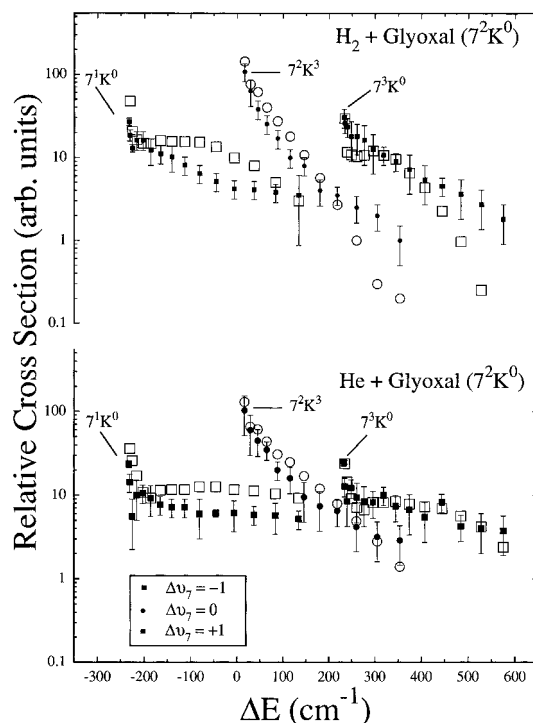


Figure 5. A comparison of theoretical (open symbols, refs 13 and 14) with experimental cross sections for inelastic scattering of H_2 and He with 7^2K^0 glyoxal. Cross sections are plotted against the amount of transferred energy and labeled with the identity of the destination states. The center set is for rotationally inelastic scattering. The right and left sets are for rovibronic inelastic scattering with $\Delta v_7 = +1$ and -1 , respectively. Reproduced with permission from ref 240. Copyright 1994 American Institute of Physics.

destination states with equal ΔE may involve either pure rotational energy transfer or rovibrational energy transfer. In defiance of energy transfer traditions, one sees that cross sections for the rovibrational channels equal or even exceed those for rotational channels. In defiance of another tradition, cross sections for adding a vibrational quantum ($\Delta v_7 = +1$) are about the same as those for losing a quantum. Another counterintuitive trend concerns rovibrational cross sections that *increase* as the energy gap ΔE grows. This series appears in Figure 5 as cross sections for the $\Delta v_7 = -1$ rovibrational channel where constraints on angular momentum transfer rather than ΔE appear to be in control.

If these experimental advances have been evolutionary, the recent theoretical advances might be considered revolutionary. The venerable SSH-T model, long the main approach to large molecules, is far too simple to deal with the subtle competition seen in crossed beam studies. In the past 10 years, a three-dimensional fully quantal scattering treatment has emerged with close allegiance to the quantum system. AVCC-IOS (azimuthal and vibrationally close-coupled, infinite-order sudden) inelastic scattering calculations¹⁰ have been applied to the energy transfer data of several complicated polyatomic molecules with encouraging success.^{11–14,187,243,244}

The abundance of S_1 glyoxal data with well-defined error bars and a narrow collision energy distribution provides fairly demanding benchmarks for theoretical predictions. The accuracy of the present theory may be seen by the overlay in Figure 5 of the predicted cross sections. Confidence in theory is established by repeatedly successful comparisons with high-quality experimental results. While the present comparisons are rigorous, they are also limited. Many more experimental examples (molecules and states) need to be generated.

Quantum State Resolved Energy Transfer in Highly Vibrationally Excited Molecules

Methods and Motivation. Quantum state resolved experiments on highly vibrationally excited molecules have followed two important trails, blazed by the two laser-based methods: overtone²⁴⁵ and stimulated emission pumping^{246,247} (SEP). The thriving field of overtone spectroscopy and dynamics,^{245,248–287} which is built entirely upon harmonically forbidden transitions, is testament to the amazing times in which we live. High spectral brightness lasers in the infrared and visible force one to consider carefully the meaning of the phrase “forbidden transition”. Bolometric studies have recently compared the pumping efficiency of hydride stretch fundamental transitions with the first overtone. Single-mode continuous lasers irradiated a continuous molecular beam, dictating an illumination time of only a few microseconds. The ratio of the bolometric (optothermal) signals for overtone to fundamental was found to be about 2 to 1, confirming saturation of both the fundamental and the nominally forbidden overtone transitions.²⁸⁸ Pulse-amplified single-mode CW lasers provide even greater spectral brightness. For example, excitation of the forbidden $\text{NO}(a^4\Pi \leftarrow X^2\Pi)$ bands, which exhibit a radiative lifetime ($A^{-1}_{a \rightarrow x}$) of ~ 1 s, was easily observed with such a laser system.²⁸⁹ Overtone experiments are particularly effective for pumping large amounts of vibrational energy into an anharmonic H atom stretching motion in a molecule. The method allows single quantum state preparation over a wide range of initial energies. Overtone spectra can be detected by photoacoustic methods,²⁴⁸ overtone fluorescence,²⁹⁰ infrared double-resonant absorption,^{291,292} optothermal methods,²⁶⁹ and the recently developed technique of CO_2 laser-assisted dissociation followed by laser-induced fluorescence (LIF) product detection.²⁵¹

SEP has also found very wide application in the study of highly vibrationally excited molecules.^{1,230,295–365} This method uses two laser pulses to excite molecules out of thermally populated levels into highly vibrationally excited states through an intermediate electronically excited state. See Figure 6. The large structure change upon electronic excitation in many molecules allows good Franck–Condon overlap to high vibrational states in the two-photon transition. For example, ground electronic state NO can easily be produced in vibrationally excited states up to $v = 25$ ²⁹⁸ (80% of its bond energy in vibration), and HCN can be prepared at internal energies above the $\text{HCN} \rightleftharpoons \text{HNC}$ isomerization barrier.^{300,315,320,346} In a spectacular new development, SEP has been used to prepare HCO ^{319,324,326,363,366} as well as HFCO ^{339,364,367} well above their dissociation limits. This has led to some very important work on quantum state specific unimolecular decomposition. Since the two-photon SEP transition is a sequential combination of two, allowed one-photon electronic transitions, the transfer efficiency can be quite high. The biggest advantage of this approach is the ability to excite vibrations other than H atom stretching.

Another exciting new method being developed is stimulated raman scattering with rapid adiabatic passage (STIRAP),^{349,368–376} which has been applied to some specific examples of molecular energy transfer.^{370,372,375,376} The energy level diagram for a STIRAP experiment looks like SEP, but it is there that the similarities end. In STIRAP, the coherent properties of single-mode lasers are used in the strong saturation limit to induced dressed optical/molecule states which under adiabatic passage conditions evolve cleanly from the initial to the final vibrationally excited state with 100% efficiency. This method not only improves the efficiency of preparation in comparison to

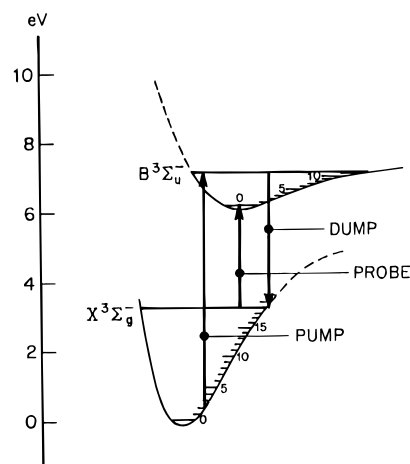


Figure 6. Potential energy curves for O_2 showing the way in which a stimulated emission pumping experiment can be carried out to obtain vibrational state specific relaxation data. The scheme looks superficially like that of a STIRAP experiment.

SEP but also eliminates any possible influence that the intermediate excited electronic state may have on the experiment.

In addition, significant contributions have been made using chemical or photochemical activation.^{377–385} In experiments such as these an exothermic chemical or photochemical reaction is used to produce an ensemble of highly vibrationally excited molecules. By following the time evolution of the individual vibrational states, for example by infrared emission, information regarding the collisional relaxation of the highly vibrationally excited molecules can be gleaned.

In one way or another, the logic of experimental design behind quantum state resolved studies of collisional energy transfer of highly vibrationally excited molecules is profoundly affected by the following fact: models of separable vibrational motion break down with increasing vibrational energy. Enormous state densities are found even for relatively small molecules at moderate excitation. For example, a harmonic approximation reveals that hexatomic propynal, $\text{HC}\equiv\text{CCHO}$, has more than $200/\text{cm}^{-1}$ rovibrational states with the same symmetry at a mere 23 kcal/mol of internal excitation.³³¹ Spectral resolution substantially better than 150 MHz is needed simply to resolve individual quantum states. When the symmetry-selected state densities become so high, even small coupling matrix elements induce strong mixing between nearby lying states,^{269,270,279–281,291,386–398} meaning that the quantum number assignment becomes problematic at best, even if the spectrum can be resolved.

Molecules that are in an intermediate regime between separable and nonseparable vibrational motion are usually tetratomic or smaller.^{339,364,365,367,399–401} The benchmark example, acetylene, exhibits assignable vibrational “feature states”, meaning that separable vibrational motion exists only on the subpicosecond time scale in the highly vibrationally excited molecule.^{343,402–404} Even the spectroscopy of highly vibrationally excited *triatomic*s can be a challenging undertaking, although there are now a few well-understood examples. The vibrational structure of HCN has been investigated and rigorously understood up to $\sim 19\,000\text{ cm}^{-1}$ of excitation energy.^{282,300,315,320,346} However, even for this simple case, theoretical calculations at energies high enough for isomerization to occur (forming HNC) reveal very complex nonseparable motion.^{405,406} HCO is another recent example where fully resolved spectra have been understood and assigned,^{319,324,326,363,407}

even at vibrational energies well above the dissociation limit. However, when the C atom is exchanged for O, theoretical prediction suggest that fully state resolved spectroscopy on highly excited HO₂ will not be assignable.^{366,408} This points out the subtle physics of vibration, even in a “small” molecule.

For molecules much larger than diatomics, it is clear that the effect of intramolecular vibrational anharmonicity in the isolated highly excited molecule is pervasive. At high vibrational excitation, the large vibrational state density and intramolecular vibrational coupling gives rise to a unique and complex arena of collisional behavior that is yet to be fully understood.^{359,409–417} For *diatomics* excited with a large amount of vibrational energy, fully quantum state resolved experiments are possible, and the quantum mechanical identities of all excited states are unambiguous. Connection to rigorous theoretical calculations can also be accomplished. For these reasons, the collisional dynamics of highly vibrationally excited diatomics is an interesting research area as it offers a clear bridge between experiments at low and high vibrational excitation. The investigation of small molecules has had an impact in our understanding of the mechanisms of energy transfer present in highly vibrationally excited molecules, and this is now reviewed.

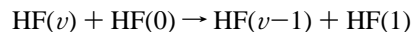
Important Mechanisms for Vibrational Energy Transfer in Collisions of Highly Vibrationally Excited Molecules.

Perhaps the most fundamental motivation for studying the quantum state resolved energy transfer of highly vibrationally excited molecules is the prospect of using such information to obtain a clear physical picture regarding their energy transfer mechanism. There has been remarkable progress in this regard. The earliest theories of vibrational energy transfer were developed to treat experiments that had been carried out on molecules in low vibrational states.^{183,418,419} From the enormously important pioneering work of that generation, many trends emerged and were explained. For example, it was often found that light collision partners have a vastly more rapid vibrational quenching effect than heavier ones. Although it could hardly be tested in the earliest experiments which were performed only on molecules in $\nu = 1$, theory predicted that single quantum relaxation (i.e., $\Delta\nu = -1$) would be the dominant relaxation mechanism. Another prediction of early theory was that vibration-to-rotation-and-translation (V–R,T) relaxation should be a linear function of the vibrational quantum number. The temperature dependence of V–R,T energy transfer was also found to be very strong and positive, while near-resonant vibration-to-vibration (V–V) energy transfer exhibited inverted temperature dependencies.

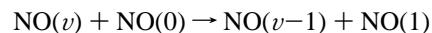
Many similarities have been found between vibrational energy transfer at high and low excitation. For example, SEP preparation of I₂(X, $\nu=42$) allowed experiments which showed a preference for single quantum relaxation.^{420–422} The single quantum rate constants were found to depend strongly on the mass of the collision partner, lighter collision partners relaxing more rapidly than heavier ones. Such behavior was also observed for similar SEP experiments carried out on NO(X, $\nu=23$).^{293–296,298,315,346} Of the collision partners investigated (Ar, He, and H₂), only relaxation by H₂ could be observed. In addition, it was found that single quantum relaxation dominated even for NO(X, $\nu=18$) + NO, a vibrational state with more than 84 kcal/mol of internal energy.

The first experiments that had the chance to test the prediction of the linear quantum number dependence of V–RT energy transfer were performed with overtone pumping of HF.^{290,292,423–428} This resulted in a complex vibrational quantum number dependence that did not fit the predictions of theory. This work pointed out one of the characteristic self-relaxation

mechanisms for molecules in $\nu > 1$: V–V energy transfer. For example, the collisional process



has been observed to dominate for $\nu = 2$. As ν increases, this process slows down due to the anharmonicity-induced growth of the energy defect.⁴²⁴ For self-relaxation there is always a range of ν 's where V–R,T energy transfer is masked by V–V energy transfer. This problem was overcome in SEP studies of the vibrational relaxation of NO(X, ν) + NO.^{293–296,298,315,346} In this work the vibrational quantum number dependence of vibrational self-relaxation was measured over a wide range of vibrational excitation ($8 < \nu < 25$). The analogous V–V process for NO self-relaxation,



is only important below $\nu = 8$. For vibrational states up to $\nu = 15$, the relaxation rate constant was found to scale beautifully as $k(\nu) = \nu k(1)$. This remarkable result shows that even up to extremely high vibrational excitation (72 kcal/mol), many if not all of the aspects of low-energy V–R,T energy transfer are retained.

Studies on the temperature dependence of vibrational energy transfer of highly vibrationally excited molecules are few. However, recent results have shown that V–R,T energy transfer in O₂(X, $\nu=26$) with O₂ does exhibit a strong positive temperature dependence,^{317,356} while near-resonant V–V energy transfer between O₂(X, $\nu=17$) and CO₂ and N₂O³⁵⁶ exhibits the expected inverted temperature dependence.

One of the fundamental questions that permeates this field of research concerns the differences that may exist between energy transfer collisions of highly excited molecules in comparison to those in low vibrational states. One way in which highly vibrationally excited molecules may differ qualitatively from molecules at low excitation is in their ability to participate in near-resonant V–V energy transfer. For molecules at low levels of vibrational excitation, vibrational resonances occur by accident. For example, CO₂(0,0, $\nu_3=0 \rightarrow 1$) has an accidental resonance with N₂($\nu=1 \rightarrow 0$), which is important to the pumping mechanism of the CO₂ laser.^{429,430} By varying the vibrational excitation of the energy donor molecule, energy resonance conditions are much more easily met. For example, if one considers the energy gap for $\Delta\nu = 1$ and $\Delta\nu = 2$ relaxation of O₂ as a function of vibrational excitation, the anharmonicity of the O₂ bond gives rise to a smoothly changing energy function from $\sim 1000 \text{ cm}^{-1}$ ($E(\nu''=27) - E(\nu''=26)$) to $\sim 3200 \text{ cm}^{-1}$ ($E(\nu''=2) - E(\nu''=0)$). This means that there will be a possible 1–1 or 2–1 resonance with a wide variety of molecules whose vibrational fundamentals fall within this range. Of course, the existence of an energy resonance is no guarantee that energy will indeed be transferred.

Because of its atmospheric importance (see below), the collisional processes in highly vibrationally excited O₂ have become one of the most completely studied set of examples of collision dynamics in highly vibrationally excited molecules. SEP as well as chemical activation studies have now been carried out yielding a complete picture for vibrational states below $\nu = 28$ for the following collision partners: O₂,^{303,304,317,377–379} N₂,^{303,377} CO₂,^{356,377} and N₂O.³⁵⁶ Chemical activation data on O₂(ν) with NO₂,^{378,379} CH₄,^{378,379} He,^{378,379} and O₃³⁵⁷ are also recently available. In all of these collision systems, 2–1 and/or 1–1 V–V resonant energy transfer is found. For example, Figure 7 shows the vibrational dependence of the total removal relaxation rate constant for O₂(X, ν) as a function of ν when quenched by N₂, CO₂, N₂O, and O₃.³⁵⁶ For CO₂, the data peak

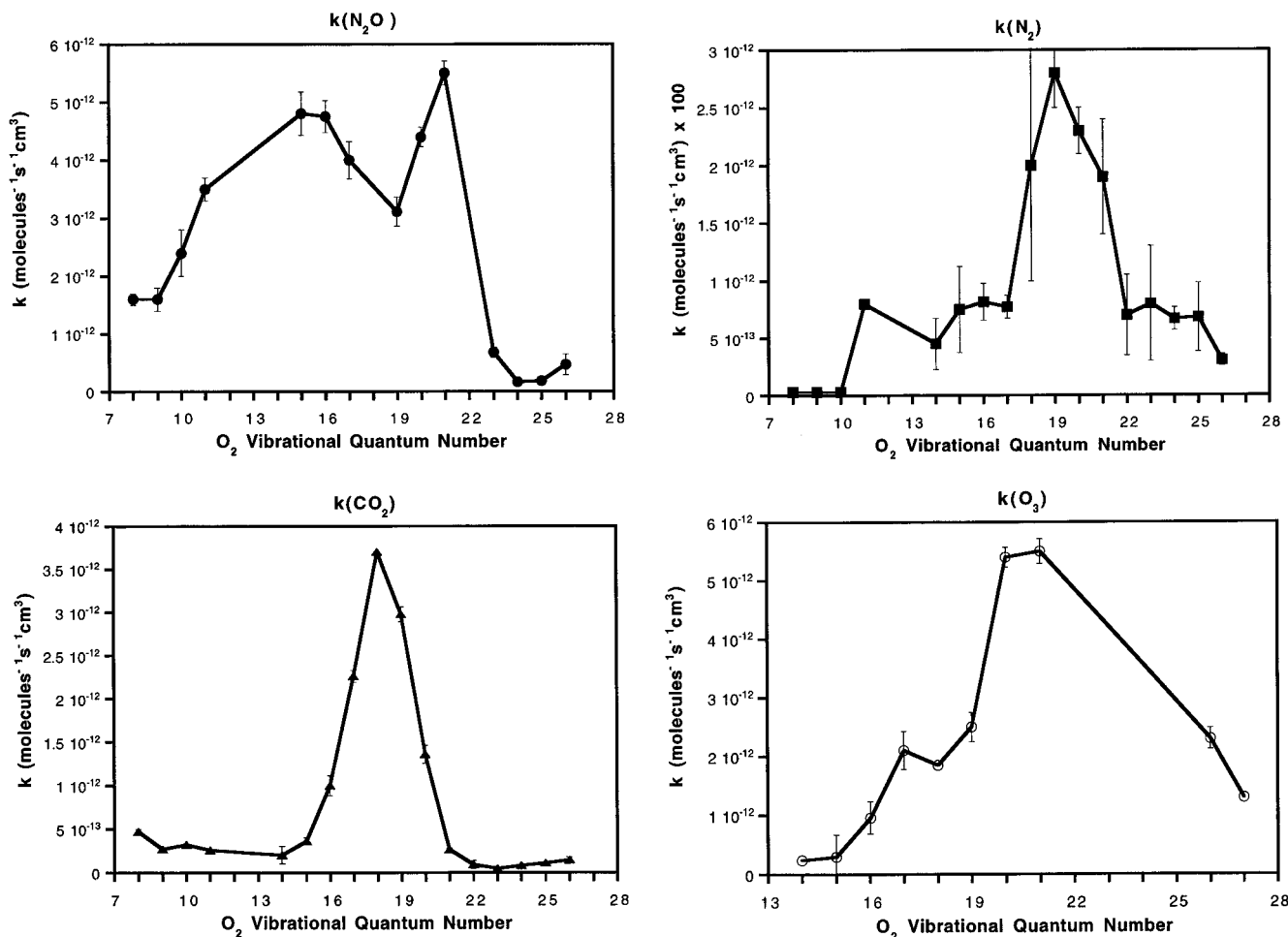


Figure 7. Vibrational state specific total removal rate constants for vibrational relaxation of $\text{O}_2(X^3\Sigma_g^-, \nu)$ with $M = \text{N}_2, \text{CO}_2, \text{N}_2\text{O},$ and O_3 . The appearance of resonances in the vibrational quantum number dependence of the rate constants is indicative of 1–1 and 2–1 V–V energy transfer in all of these molecules. Data for $\text{O}_2(X^3\Sigma_g^-, \nu=8-11)$ for $M = \text{N}_2, \text{CO}_2,$ and N_2O was used with the permission of the authors.^{377,378}

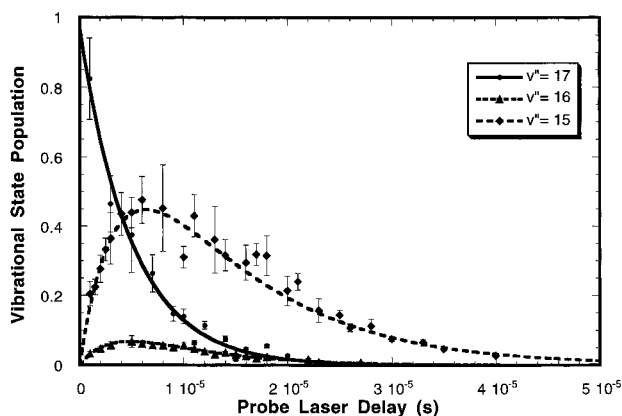
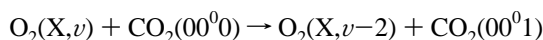


Figure 8. Vibrational state-to-state relaxation of $\text{O}_2(X^3\Sigma_g^-, \nu=17)$ with CO_2 . The time dependence was recorded with 2 mol % CO_2 in O_2 . One can clearly see the population of the initially prepared state ($\nu = 17$) shown as solid circle skip over the next lowest state ($\nu = 16$) shown as solid triangles and arrive in $\nu = 15$ (shown as solid diamonds). The lines are a kinetic model fit to the data which requires the O_2 self-relaxation to occur by a single-quantum mechanism and the relaxation by CO_2 to occur by a two-quantum relaxation mechanism. There is only one adjustable parameter to fit all three curves.

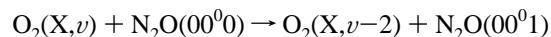
at $\nu = 18$ where the energy defect for the process



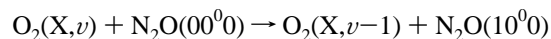
is a minimum. State-to-state measurements were also carried out.³⁵⁶ In those experiments, the $\text{O}_2(X, \nu)$ vibrational population

was observed to skip cleanly from the initially prepared $\nu = 17$ over $\nu = 16$ and into $\nu = 15$ when only 2% CO_2 is present, verifying the 2–1 resonant energy transfer mechanism. This can be seen in Figure 8. In this figure, the time dependence of the population of the prepared state ($\nu = 17$) is shown as solid circles, that for $\nu = 16$ as solid triangles, and that for $\nu = 15$ as solid diamonds. The fit to the data (shown as lines) is a kinetic model which requires O_2 relaxation to take place in single-quantum steps,³¹⁷ while CO_2 relaxation occurs in two-quantum steps only. With this kinetic model there is only a single free parameter used for generating the three fitted lines to the data in Figure 8, since the total removal rate constants were already known from total removal rate constant measurements (Figure 7).

Near-resonant V–V energy transfer is also observed in $\text{O}_2(\nu) + \text{N}_2\text{O}$. Here one sees the analogous 2–1 resonance



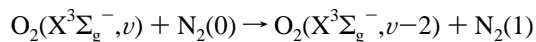
peaking at $\text{O}_2(\nu=21)$. In addition, the 1–1 resonance



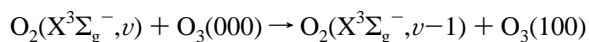
is observed peaking at $\sim \text{O}_2(\nu=15)$. Notice that the width of the vibrational quantum number scanned energy transfer resonance is much larger for the 1–1 resonance than for the 2–1 resonance. This is a result of the simple fact that the anharmonicity of O_2 is scanned twice as fast for the 2–1 resonance, and there is a narrower range of ν 's where the energy

defect is comparable to kT . The striking thing about this CO_2 and N_2O data is that it shows the relative efficiencies of the 2–1 vs 1–1 resonant energy transfer mechanisms. It is clear that 2–1 resonant energy transfer can be even stronger than its 1–1 analog.

Also shown in Figure 7 is a similar 2–1 resonance for N_2 relaxation³⁷⁷

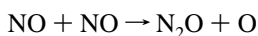


which has a minimum-energy defect for $\text{O}_2(\text{X}^3\Sigma_g^-, 19)$ as well as V–V energy transfer in O_3 relaxation



For O_3 , a minimum-energy defect calculation predicts a rate constant maximum in $\nu = 23$. This was difficult to observe, due to spectral congestion in this region of the O_2 spectrum. However, a decrease in the relaxation rate constant on both sides of $\nu = 23$ is apparent.

Another way that highly vibrationally excited molecules may differ from their low-energy counterparts is in their ability to sample low-lying chemical reaction transition states. This was apparently observed in the SEP studies of highly vibrationally excited NO .^{293–296,298,315,346} As mentioned above, in that work the V–R,T relaxation rate constants were found to scale linearly with vibrational quantum number up to about $\nu = 15$. Above this level of vibrational excitation, a threshold for enhanced vibrational relaxation was observed. Since it is at this energy that the lowest transition state for a chemical reaction occurs,



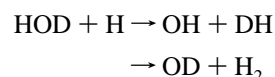
the enhanced vibrational relaxation was attributed to collisional events which are essentially failed reactions⁴³¹ or transient chemical bond formation. Above the threshold for this new mechanism the presence of two quantum ($\Delta\nu = -2$) relaxation could also be detected.

Another way in which highly vibrationally excited molecules differ from the low-energy counterparts is the possibility for vibrational-to-electronic or V–E energy transfer. There is very little information about this in the literature; however, recent experiments on NO_2 have shown some intriguing things.^{432–434} In these experiments, the visible and near-infrared emission of NO_2 , which had been excited by a UV laser, is resolved in time. A buffer gas is added to carry energy out of the excited NO_2 . Although not truly state resolved, the average amount of vibrational energy lost per collision, $\langle\Delta E\rangle$, can be extracted from the data and is found to change with time, and therefore $\langle\Delta E\rangle$ is a function of the NO_2 average energy content $\langle E\rangle$. The results of this kind of experiment is a plot of $\langle\Delta E\rangle$ as a function of $\langle E\rangle$. For a number of different buffer gases, a marked threshold in the plot of $\langle\Delta E\rangle$ vs $\langle E\rangle$ is found, and the position of the threshold is coincident with the lowest excited electronic state of NO_2 . It appears that, in a molecule where the intramolecular vibronic coupling between the ground and excited electronic states is strong, collisional energy transfer is significantly more efficient. Despite this unique dynamic, infrared Doppler profiles of recoiling N_2O from NO_2^* have given direct evidence of energy transfer mechanisms that resemble their low-energy counterparts: namely near resonant V–V and V–R,T energy transfer.⁴³⁵ This is yet another example which shows nicely the differences and similarities encountered at high internal excitation in comparison to low-energy results.

Another relaxation mechanism that distinguishes highly vibrationally excited molecules is chemical reaction. Recent

experiments have used a crossed molecular beam geometry, with laser excitation of NO_2 near to its dissociation limit.^{436,437} Collisions with Ar, CO, and O_2 all result in collision-induced dissociation. The NO product could be observed with a probe LIF laser. No evidence for O_3 formation was found in the O_2 experiments. The dissociation yield as a function of the initial NO_2 excitation energy was determined. The structure of the CID signal was similar to that observed in the fluorescence excitation spectrum of NO_2 , and the scaling of energy transfer could be described by an exponential decay law. NO was detected state selectively using laser ionization, and state distributions were determined.

One of the most beautiful quantum state resolved experiments carried out recently employed overtone pumping of both OH and OD stretching motion of HOD in contact with H or Cl atoms, inducing the reaction

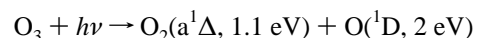


LIF was used to detect the OH or OD reaction product. The branching ratio between the two was found to depend dramatically on which vibrational mode had been excited.^{273–278,438}

The investigation of the collisional properties of highly vibrationally excited molecules is clearly of fundamental interest. It has recently become clear that it is not only scientists working in laboratories that are capable of producing these interesting species. The atmosphere can do it as well!

The Atmosphere and Vibrationally Excited Molecules.

The atmosphere is an extremely interesting chemical environment: essentially a low-pressure, low-temperature system, energetically driven by photochemistry; the occurrence of excited states is ubiquitous.^{439,440} Even the most mundane of atmospheric photochemistry produces highly energetic products. For example,

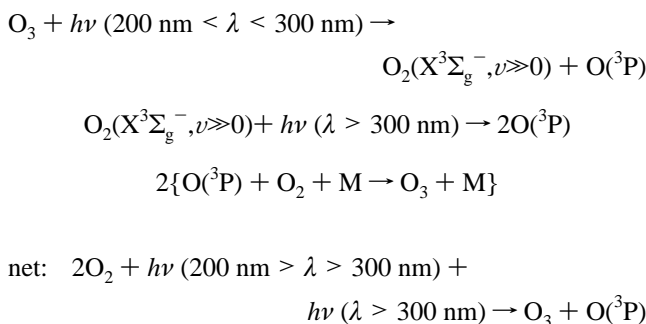


is one of the most common reactions. The energies of the indicated excited states are given in electronvolts. Satellite observations of the Earth's "night glow" are dominated by atomic and molecular emissions of excited metastable electronic states.⁴⁴¹ It has been known for years that the infrared emission from ozone results from vibrationally excited states as high as half its dissociation energy.^{442,443} This apparently results from the internal energy deposited in O_3 by the reaction $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$. Satellite studies of the earth's infrared emission have advanced dramatically in recent years. The CIRRIS-1A mission flown on the space shuttle used a cryogenically cooled interferometer to obtain high-resolution and high-sensitivity data of unprecedented quality.^{444–450} In those missions another infrared-active molecule, NO, was observed in vibrational states up to $\nu = 8$, and rotational bandheads in the *infrared* spectrum prove that states as high as $j = 100.5$ occur with significant population in certain parts of the earth's atmosphere. Similar results from OH show vibrational states as high as $\nu = 9$ and rotational states as high as $N = 35$. Even translation may not always be at equilibrium. Recent calculations of the translational energy distribution of thermospheric N atom suggest that kinetic energies as high as 3 eV may be important.⁴⁵¹

One of the most exciting developments in the quantum state resolved investigation of highly vibrationally excited molecules is the growing recognition that such molecules play an important role in atmospheric chemistry. There have been a number of experiments that have shown to what an unexpected extent the

atmosphere has the ability to produce highly vibrationally excited molecules.^{1,377,452} The method of ion imaging^{355,453–459} (discussed elsewhere in this issue) was used to study the quantum state specific kinetic energy distributions of O atoms emerging from ozone photolysis. These kinetic energy distributions suggested a bimodal vibrational distribution for O₂(X) when formed together with O(³P). The occurrence of highly vibrationally excited O₂ up to $v = 27$ was subsequently substantiated by direct spectroscopic observation using LIF.¹

Given the strong laboratory evidence for the atmosphere's tendency to produce highly vibrationally excited O₂, great interest has developed in the possible chemical consequences of this trace atmospheric constituent. Laboratory observations of ozone production from 248 nm photolysis of O₂, 6 nm to the red of the oxygen photodissociation threshold, led to wavelength-dependent studies that identified O₂(X³Σ_g⁻, $v=7$) as a reaction intermediate in the following autocatalytic cycle.⁴⁶⁰

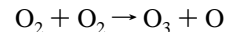


It was recognized that if highly vibrationally excited O₂ were formed in the stratosphere, it could be photodissociated by near-UV and visible radiation. In comparison to vacuum-UV radiation, which is normally required to photolyze O₂, light at these longer wavelengths is much more abundant in the stratosphere. This mechanism and the laboratory experiments that suggested it were the first evidence that highly vibrationally excited O₂ might play a role in ozone formation.

Because of the relatively low solar photon fluxes, it was not immediately clear that this mechanism would be important in the atmosphere. Unfortunately, at that time there was no information available concerning the competing collisional relaxation processes. SEP^{303,304,317,356} and chemical activation^{377–379} studies have now been carried out for vibrational states of O₂ up to $v = 28$ with a variety of atmospheric collision partners. The SEP studies use a tunable argon fluoride laser to gain access to the B³Σ_u⁻ excited electronic state. Stimulated emission down from this state provides good Franck–Condon overlap with vibrational states between $v = 13$ and 29. In these experiments it was possible to prepare individual vibrational states, applying pseudo-first-order kinetic theory to interpret the time dependence of the data. Initial experiments revealed room temperature collisional relaxation rate constants with respect to O₂ and N₂. These results as well as analysis of the complex vibrational cascade process occurring in chemical activation experiments⁴⁶¹ both led to the conclusion that the fate of highly vibrationally excited O₂ would be a collisional one and not photochemical. It appeared that the hot-band solar photolysis mechanism was dead.

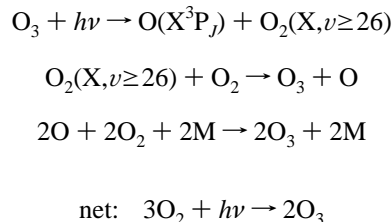
Initial investigation of the collisional relaxation of highly vibrationally excited O₂ focused on vibrational states below $v = 23$. It turned out that the most intriguing results appeared for $v > 25$. Here, a dramatically sharp threshold for a new collisional process was observed using the SEP method.³⁰³ It

was immediately suspected that this threshold belonged to the reaction



The unambiguous proof of this relaxation channel is still lacking, however, strong evidence supports this conclusion. Vibrational state-to-state experiments were carried out which showed clearly the existence of a dark channel.³¹⁷ In that work, for example, a controlled number of molecules could be prepared in $v = 27$, and the fraction of those molecules appearing in $v = 26$ and 25 could be determined. This allowed the determination of the rate constant for the dark process, presumed to be chemical reaction. The temperature dependence of that dark channel rate constant was also investigated. This allowed determination of vibrational state specific activation energies for the dark process. These activation energies were found to agree closely with the energy gap of the vibrational state below the known reaction threshold.³¹⁷ Very recently, the reverse reaction has been studied using LIF as a probe of the nascent vibrational state distribution of O₂.³⁵⁷ Here, the second harmonic of a YAG laser is used to photolyze pure O₃ in the Chappuis bands, producing ground electronic state O₂(X) and O(X³P_J). The undissociated O₃ reacts with the O atoms, and highly vibrationally excited O₂ is detected with LIF. This work has confirmed that O₂(v) is produced up to $v = 27$, the energetic limit. This gives further, albeit qualitative, evidence that highly vibrationally excited O₂ can react with O₂ to form O₃.

The positive outcome of the self-relaxation studies led to further investigation of the relaxation of highly vibrationally excited O₂ by other atmospheric constituents, in particular N₂, CO₂, and N₂O.³⁵⁶ It was immediately realized that N₂ was a much less efficient vibrational quench partner than O₂ for those vibrational states of O₂ that could react. Later studies on CO₂ and N₂O revealed that any O₂ produced in $v = 26$ and 27 would not be quenched by either of these trace gases. The constantly growing evidence for a new route to ozone lead to the first atmospheric models which included the following chemical mechanism:



This work showed that the effect of highly vibrationally excited O₂ would be most important in the tropics at an altitude of ~43 km,¹ filling in a well-known systematic ozone deficit in previous modeling attempts.^{462,463}

Directions for the Future. The time is truly prime for exciting investigations of the quantum state specific nature of collisional energy transfer in highly vibrationally excited molecules. One extremely logical direction is to carry out such experiments in the controlled environment of crossed molecular beams. Up to now there are few examples. Recent work showed the collisional energy dependence of specific $v'' \rightarrow v'$ transitions in SEP prepared I₂.²³⁰ Such experiments also promise to reveal the truly state-to-state nature of the collisional energy transfer of highly vibrationally excited molecules. What, for example, is the role of rotation in the V–R,T energy transfer? Except for some simple hydrides, which can convert the largest amount of energy to rotation, with the smallest change of the rotational quantum number, there is little experimental data.

What is the role of spin in an open-shelled system like NO? The Nikitin mechanism,⁴⁶⁴ originally proposed for NO/NO relaxation in 1960, has yet to be confirmed or disproved. The application of molecular beams would facilitate the investigation of free radical and atomic collision partners. What will be the Δv propensity rule for a relaxation process like the following:



In this reaction the formation of a stable intermediate, with strong intramolecular coupling and presumed statistical decomposition, is thought to lead primarily to NO($v=0,1$). What becomes of all of the excess energy in such a collision?

Another fascinating area of research that offers itself to this field is that of surface scattering. Molecular beams of vibrationally excited molecules can be prepared using lasers and directed to well-characterized metal, semiconductor, and insulating surfaces. This represents an area of research where nothing is known for molecules above the first vibrationally excited state.⁴⁶⁵

Of course, the existing methodologies can be applied to different molecules, and one is always tempted to push methods to larger molecules. As discussed above, this may be an inherently difficult approach to the investigation of collisions in highly vibrationally excited molecules. There are, however, a number of molecules that are clearly tractable. One of these is HCN, and there has been some work done using overtone pumping.²⁸³⁻²⁸⁷ Eventually one must come to grips with the fact that larger molecules have complex spectra that cannot be easily assigned. It remains a fascinating challenge for the future to see what can be learned about the collisional properties of such molecules.

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