"Energy Transfer Properties and Mechanisms"

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Introduction

The ultimate goal of this research is to understand highly vibrationally excited molecules in sufficient detail so that models and theories can be developed for quantitative predictions of collisional energy transfer involving moderately large polyatomic molecules. Energy transfer can control the rates of unimolecular and recombination reactions. In chemical activation systems, energy transfer can have major effects on the branching ratios, if multiple reaction paths are available. It also can affect the efficiency of laser-induced chemical processes and the heating rates of fuels in practical combustion environments. Knowledge of collisional energy transfer and properties of high excited polyatomic species is crucial to understanding and predicting chemical reaction rates in non-equilibrium systems and hostile environments.

Studies of energy transfer have shown that no single molecular property is dominant and no single experimental technique can be identified as the best method for energy transfer experiments. Thus, we have used both time-dependent infrared fluorescence (IRF) and time-dependent thermal lensing (TDL) to study energy transfer in various systems. We are currently investigating pump-probe techniques employing resonance enhanced multiphoton ionization (REMPI) to determine whether they will be useful in future studies.

The specific goals of this research project during the current funding period can be summarized as follows:

- Obtain a high quality data base using physical techniques. The specific objectives are to determine how energy transfer depends on internal energy and on the molecular properties of excited molecules and colliders.
- From experiments, deduce mechanisms of energy transfer and determine the important molecular parameters involved. The specific objectives are to determine the relative importance of V-V, V-R, and V-T transfer.
- Obtain information about the evolution of the energy distribution of excited molecules during the energy transfer cascade. The specific objectives are to determine the higher moments of the energy step-size distribution and establish whether "super collisions" are important.

In addition to the experimental work, we have continued to develop numerical codes for Master Equation calculations which include unimolecular reactions, collisional energy transfer, and

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infrared emission in non-equilibrium systems where highly vibrationally excited species are important. Such systems may include shock tube experiments and excited molecules in the interstellar medium, but they also include our experiments and the codes are needed for a full interpretation of the experiments.

The IRF Technique

To understand energy transfer, where so many different molecular parameters may participate, it is very important to have a data-base obtained using a single experimental technique. The use of a single technique helps in comparisons of different systems, because systematic errors are presumably similar in the various investigations. It is also important to make comparisons with other techniques whenever possible in order to recognize and minimize any systematic errors.

The IRF technique is straightforward: The excited species is prepared by absorption of light from a pulsed excimer laser (usually 308 nm or 248 nm) and IRF is monitored through a side window using a fast infrared detector (usually 77°K InSb or HgCdTe). The emission is isolated with a suitable interference filter or circular variable filter (CVF) and the observed time decays are nearly, but not exactly, exponential. To measure energy transfer in the electronic ground state, the technique relies on fast radiationless transitions from the initially excited electronic state to high vibrational levels of the electronic ground state. For benzene, the radiationless transitions are complete within a fraction of a microsecond.

Because state densities are so great, the individual vibrational states cannot be resolved and the whole emission band usually is passed by the band-pass filter. Because the C-H stretch band emission frequency is much higher than other molecular frequencies, it is most convenient to monitor the 3.3 μm band ($\sim 3060\text{ cm}^{-1}$). We measured the time- and wavelength-resolved IRF spectrum of highly excited benzene (and naphthalene) as it underwent collisions with unexcited molecules and from that deduced the emission spectrum shown in Figure 1 of the nascent molecules excited to $\sim 40800\text{ cm}^{-1}$. Each experimental point was obtained after extrapolating the time-resolved emission to $t=0$ and the emission decays required extensive signal averaging (it is much more convenient to measure the integrated band intensity without attempting to resolve the band).

Figure 1. Low-resolution ($\sim 30\text{ cm}^{-1}$) benzene emission spectrum at $\langle E_{\text{vib}} \rangle \sim 40700\text{ cm}^{-1}$. Experimental points (dark circles, $\pm 1\sigma$ error bars) and three-component Gaussian fit to the spectrum are shown. Dotted lines show contributions of individual $\Delta v = -1$ transitions.

Figure 1 shows that the C-H stretch band is well-isolated and mainly consists of contributions from $\Delta v = -1$ transitions, with added minor contributions from quasi continuum emission. For a $\Delta v_i = -n$ spontaneous transition originating in level v_i of the i^{th} vibrational mode, the energy-dependent emission rate coefficient is given by^{16,17}

$$A_{3i}(E, v_i) = \frac{1}{\rho_s(E)} A_i^{v, v-n} \rho_{s-1}(E - E_{v_i}) \quad (1)$$

where $A_i^{v, v-n}$ is the Einstein coefficient for the $(v-n) \leftarrow v$ vibrational transition of the i^{th} oscillator, $\rho_{s-1}(E)$ is the density of states for the $s-1$ degrees of freedom that remain after omitting the emitting mode, and E_{v_i} is the energy contained in the emitting mode ($= v_i h\nu_i$ for a harmonic oscillator). Under most experimental conditions, several specific transitions occur simultaneously and Equation (1) must be summed over the appropriate vibrational modes and initial energy states. For example, all of the benzene C-H stretching modes occur near 3060 cm^{-1} (although only one is infrared active) and if emission from the whole C-H stretching band is captured with a broad bandpass infrared filter, i is summed over the six modes and v_i ranges from $v_i = 1$ up to the highest energy consistent with conservation of energy. It is noteworthy that the observed infrared emission near $3.3 \text{ }\mu\text{m}$ from benzene excited to $\sim 40000 \text{ cm}^{-1}$ (Figure (1)) shows anharmonically shifted $\Delta v = -1$ transition features with intensities in excellent agreement with those predicted by Equation (1). At 40000 cm^{-1} , the density of vibrational states is $\sim 10^{15} \text{ states/cm}^{-1}$ and thus the underlying continuum seen in the spectrum is probably due to the many combination and difference bands which may have borrowed intensity from the allowed transition.

The IRF technique has several advantages, compared with other methods, for monitoring the excitation energy in large molecules. It is quite general and can be used with most molecules which contain C-H or C-D bonds, as long as the species can be prepared in a vibrationally excited level. The theory describing IRF is straightforward and has been thoroughly tested. Thus, the theoretical "calibration curves" relating IRF intensity to vibrational energy can be used with confidence. An example of such a calibration curve is shown in Figure 2.

Figure 2. IRF calibration curve for azulene (C_{10}H_8) (Shi et al. 1988). Experimental points and uncertainties ($\pm 1\sigma$); solid line from Equation (1), scaled to unity at 337 nm (29674 cm^{-1}).

Data-Base for Large Molecule Energy Transfer

The simplest way to use $I[\langle\langle E(t) \rangle\rangle]$ is to invert the experimental decay curves point-by-point. This is done by inverting the expression to get $\langle\langle E[I(t_0)] \rangle\rangle$, the average vibrational energy corresponding to the measured intensity. Calculations have shown that the observed intensity depends mostly on just the ensemble average energy $\langle\langle E(t) \rangle\rangle$, which varies with time: $I[\langle\langle E(t) \rangle\rangle]$. Thus, the IRF decay at a single wavelength gives information about the average energy during the decay. As will be shown below, information about the width and higher moments of the distribution can be obtained by combining results from two or more IRF wavelengths.

To obtain the energy transfer parameters, the IRF time-dependent data are least-squares fitted and the derivative of $\langle\langle E \rangle\rangle$ with respect to the number of collisions gives $\langle\langle \Delta E \rangle\rangle$, the average energy transfer step size:

$$\frac{d}{dt} \langle\langle E \rangle\rangle = \omega \langle\langle \Delta E \rangle\rangle, \quad (2a)$$

$$\frac{d}{dZ} \langle\langle E \rangle\rangle = \langle\langle \Delta E \rangle\rangle. \quad (2b)$$

Here, the double brackets denote bulk averages of vibrational energy and energy transfer step sizes, k_{LJ} is the Lennard-Jones collision rate constant, $[M]$ is the number density of collider, and $Z (= \omega t)$ is the number of collisions. It is important to note that the product $\omega \langle\langle \Delta E \rangle\rangle$ appears in Equation (2a), and not the individual terms; the separation of this product into separate terms is arbitrary and is done for historical reasons and for convenience. In comparisons with other work, it may be necessary to adjust the values for $\langle\langle \Delta E \rangle\rangle$ to compensate for different choices of k_{LJ} .

Note that the population distributions evolve with time and thus both $\langle\langle E \rangle\rangle$ and $\langle\langle \Delta E \rangle\rangle$ are time-dependent. Since both $\langle\langle E(t) \rangle\rangle$ and $\langle\langle \Delta E(t) \rangle\rangle$ are determined for the same instant of time, $\langle\langle \Delta E \rangle\rangle$ can be expressed as a function of $\langle\langle E \rangle\rangle$. To emphasize that the bulk average energies and step sizes were obtained from experimental data according to the inversion methods described in this section, the subscript "inv" is often added: $\langle\langle E \rangle\rangle_{inv}$ and $\langle\langle \Delta E \rangle\rangle_{inv}$.

This basic approach has now been used in measurements involving azulene and benzene (obtained during the previous funding period), and benzene- d_6 , toluene- d_0 , and toluene- d_8 (obtained during the present funding period). Each of these excited species has been investigated in collisions with 15-20 collider gases, providing a substantial data base. Typical results are shown in Figure 3, where it is apparent that deuteration affects both the magnitudes and shapes of the curves. The results for all gases investigated so far show a near-linear dependence of $\langle\langle \Delta E \rangle\rangle_{inv}$ on $\langle\langle E \rangle\rangle_{inv}$ at low energy and tendency to level off at higher energies. The studies using benzene derivatives have been summarized in a recent review article and the results are shown in Figure 4.

The results in Figures 3 and 4 show that isotopic substitution has little effect on energy transfer for the lighter collider gases, but a substantial effect on the heavier collider gases. This result is still not understood, but it may be related to the relative amounts of energy transfer which occur by vibration-to-vibration (V-V) transfer, relative to vibration-to-translation (V-T/R) transfer [the notation reflects the fact that rotations and translations are tightly coupled]. We have carried out some limited investigations of the mechanisms of energy transfer, as described in the next section. A brief summary of our current working hypothesis on large molecule energy transfer will be presented at the end of this Progress Report.

Figure 3. Average energy transferred per collision as a function of the average vibrational energy for isotopically substituted benzene derivatives deactivated in collisions with the unexcited species.

Figure 4. A comparison of the average energy transferred per collision (at $\langle E \rangle_{\text{inv}} = 24000 \text{ cm}^{-1}$) in deactivating benzene and toluene isotopomers.

Mechanisms of Energy Transfer

Spontaneous infrared emission from the product of an energy transfer collision can be used to investigate V-V energy transfer. In collisions with excited benzene derivatives, the rate of production of excited CO_2 was monitored by observing the spontaneous emission of the asymmetric stretch mode (ν_3) isolated with a band-pass filter near $4.3 \mu\text{m}$. The actual states of the excited CO_2 cannot be identified from these measurements, except that the $4.3 \mu\text{m}$ band is associated with $\Delta\nu_3 = -1$. There is some evidence in the azulene + CO_2 system that two or more vibrational modes

of CO_2 can be excited simultaneously, but there is no direct evidence that more than one quantum resides in ν_3 , which has a relatively high vibrational frequency. Thus, the CO_2^* probably can be identified with $\text{CO}_2(\nu_1 \nu_2 1)$, where $\nu_1, \nu_2 \geq 0$.

The CO_2^* emission was isolated with an interference filter that also transmitted some of the emission from the C-D stretching vibrations. In the case of the benzene- d_0 or toluene- d_0 , the total emission measured through the interference filter was mostly due to CO_2^* , although there was a small IRF intensity due to the emission of the excited parent. Typical signals observed near $4.3 \mu\text{m}$ for benzene- CO_2 are shown in Figure 5. In the case of the deuterated species, the analysis of the IRF signal is complicated due to the presence of strong emission from the C-D stretching modes near $\sim 2300 \text{ cm}^{-1}$ and little quantitative information on production of CO_2^* could be obtained.

Figure 5. Infrared fluorescence observed near $4.3 \mu\text{m}$ for 248 nm excitation of benzene- d_0 mixed with CO_2 . The solid line represents the actual measured intensity and the dashed lines show the contribution to the total intensity from CO_2^* and excited parent emissions.

Each of the IRF intensity decay curves in Figure 5 is characterized by a detector-limited rapid rise, often followed by a more gradual rise to a maximum, followed by a slower decay. The general features of this behavior can be explained as the sum of contributions at $4.3 \mu\text{m}$ from excited parent and from CO_2^* . The CO_2^* is deactivated only very slowly by unexcited CO_2 , and so the long decay is due to diffusion and to collisional deactivation by the parent molecule.

The total yield of CO_2^* produced was determined relative to the initial concentration of excited parent. We can write the rate of production as a bimolecular reaction between the excited aromatic and CO_2 , with the rate constant set equal to the collision rate constant (k_L^c) and multiplied by the probability $Q(t)$ that V-V energy transfer will take place. Thus, at any instant of time, $Q(t)$ is associated with the excitation energy $\langle\langle E \rangle\rangle$, thus the probability can be expressed as $Q(E)$, a function of excitation energy. Note that the energy-dependence of $Q(E)$ does not depend in any strong way on the particular gas mixture composition or total pressure, which mainly affect the time-dependences of $Q(t)$ and $\langle\langle E \rangle\rangle$.

The probabilities obtained from the experimental data are shown in Figure 6 as closely spaced vertical bars of $\pm 1\sigma$ statistical uncertainty. In all cases investigated, the probabilities are small, in agreement with other studies, indicating that V-V energy transfer from highly excited molecules is not very efficient when the receptor is a high frequency vibration, such as the

asymmetric stretch in CO₂. The energy-dependent $Q(E)$ can be used to calculate the ratio $[CO_2^*]_{\infty}/[P^{**}]_0$ for any mixture of CO₂ and parent, and when $F_c = 1$, $\langle\langle\Delta E\rangle\rangle_m$ corresponds to pure CO₂ and the calculated $[CO_2^*]_{\infty}/[P^{**}]_0$ ratio corresponds to infinite dilution. For benzene-d₀ and toluene-d₀, the ratios at infinite dilution were found to be 0.078 ± 0.026 and 0.052 ± 0.017 , respectively, where the uncertainties are estimated to be $\pm 33\%$. These results cannot be compared directly with those obtained by Sedlacek et al. (1991), because those authors obtained their results for a mixture consisting of 20 mtorr of benzene diluted in 80 mtorr of CO₂, where they found $[CO_2^*]_{\infty}/[P^{**}]_0 = 0.032 \pm 0.011$. From the present energy transfer data and for the specific conditions of their experiments, it is calculated that $[CO_2^*]_{\infty}/[P^{**}]_0 = 0.032 \pm 0.011$ for 20 mtorr of benzene diluted in 80 mtorr of CO₂, in remarkable agreement (the exact numerical agreement is coincidental).

To explain the observed magnitude of the probabilities and to predict the amount of energy transferred to the other vibrational modes of CO₂, we derived a simple model based on long range dipole-dipole interactions. The derivation is similar to that for Förster energy transfer (Yardley 1980), but it also incorporates three other concepts: 1) natural broadening of the upper state due to its short lifetime with respect to intramolecular vibrational redistribution (IVR), 2) statistical distribution of vibrational energy among the normal modes, and 3) straight line trajectories, because the dipole-dipole forces are effective over long distances. The only adjustable parameter in the model is the IVR time constant, τ_D , since all other parameters are obtained from infrared spectra of the aromatics.

Figure 6. Experimental ("hatched" area) and calculated (solid line) per collision probabilities of CO₂* formation. Also indicated are the IR transitions in the excited polyatomic that make the major contributions to the calculated probabilities.

The experimental probabilities and those calculated according to this model are presented in Figure 6. It was found that $Q_c(E)$ goes through a maximum as τ_D is varied, and the best fit for the non-deuterated molecules is obtained for the value of τ_D which maximizes $Q_c(E)$. As shown in Figure 6, the agreement between $Q(E)$ and $Q_c(E)$ is good, although $Q_c(E)$ is near the maximum value that this simple model can predict for non-deuterated species. There are many assumptions incorporated in the model that may affect the magnitude of $Q_c(E)$, but despite the limitations, the

major conclusion is that dipole-dipole interactions appear to explain the V-V energy transfer process.

Time-Dependent Population Distributions

During the energy transfer cascade, the population distribution $P(t,E)$ is expected to start as a near-delta function, broaden and migrate to lower energies, and ultimately collapse again to a narrow thermal Boltzmann distribution. It is the time-evolving population distribution which is directly important in determining unimolecular reaction rates and branching ratios. The detailed behavior of this distribution function is in turn controlled by the collision step-size distribution, which has never been measured directly.

When measurements are available only at a single wavelength, the IRF technique is sensitive to the average energy as the population distribution evolves, as discussed above. Although the IRF intensities depend mostly on the average energy, there are small but significant differences in the decays measured at different wavelengths. We recently discovered how to use these differences in a systematic way to extract the moments of the population distribution. This advance will enable us to learn much more detailed information about the energy transfer process. We feel that this is a very significant development.

The population distribution is difficult to measure directly and few of its properties have been inferred from experiments to date. The property most often inferred is the bulk average energy, which is determined in energy transfer experiments using the time-resolved IRF and UVA techniques. In terms of the unknown population distribution $P(t,E)$, the average energy is given by

$$\langle\langle E(t) \rangle\rangle = \int_0^{\infty} E P(t,E) dE . \quad (3)$$

In general, the n^{th} moment of the distribution is given by

$$M_n(t) = \int_0^{\infty} E^n P(t,E) dE . \quad (4)$$

The moments of a distribution can be used to describe its properties. For example, the variance, σ^2 , is determined by the first two moments:

$$\sigma^2 = M_2 - M_1^2 . \quad (5)$$

Other properties, such as "skewness" (the asymmetry) and "kurtosis" (related to sharpness of the peak), are expressed in terms of the higher moments. If all the moments are known, they uniquely define the distribution. Furthermore, if all of the moments of one distribution are equal to the moments of another distribution, the two distributions are exactly equal to each other. When only a few moments are known, they can be combined to produce approximate (non-unique) functional forms for the distribution function.

The moments provide convenient and well-defined measures of distributions. In the analysis of our results, we use what we term "upper partial moments", m_n , which are closely related to the full moments M_n :

$$m_n(t) = \int_{E_0}^{\infty} E^n P(t,E) dE \quad (6)$$

where E_0 is some threshold energy. The upper partial moments are well-defined and are equal to the corresponding full moments when $P(t,E) = 0$ for $E \leq E_0$. The partial moments are particularly closely related to IRF experimental measurements and can be used to describe the partial mean (m_1) and partial variance ($m_2 - m_1^2$) of the unknown distribution $P(t,E)$. Comparisons between experiments and Master Equation simulations are very convenient when framed in terms of the (full) moments and partial moments of $P(t,E)$.

We have developed a *moments analysis method* to extract the moments from the experimental data. This method for determining $P(t,E)$ is applicable to all experimental techniques in which multiple energy-dependent observables can be measured. This includes both multiple band IRF and uv absorption, in which the observed signal for each band has a unique dependence on the energy of the vibrationally excited emitting or absorbing molecule. In principle, measurement of n uniquely energy-dependent bands can yield information about n moments of $P(t,E)$, subject to some experimental limitations. In the case of IRF studies, the IRF intensity for each band depends on vibrational energy according to Equation (1), and the time-dependent total observed fluorescence can be expressed as:

$$\langle\langle I(t) \rangle\rangle_i = \int_0^{\infty} P(t,E) I_i(E) dE \quad (7)$$

If $I_i(E)$ in Equation (7) is expressed as a polynomial of order n , such that

$$I_i(E) = \sum_n C_{in} E^n, \quad (E \geq E_0) \quad (8)$$

then Equation (7) becomes

$$\langle\langle I(t) \rangle\rangle_i = \sum_n C_{in} m_n(t) \quad (9)$$

$$= \sum_n C_{in} M_n(t) \quad \text{when } P(t,E) = 0 \text{ for } E \leq E_0. \quad (10)$$

where $m_n(t)$ and $M_n(t)$ are the full and "upper partial" moments of $P(t,E)$ as defined in Section II.B. For two-color experiments, $n=2$ and quadratic fits of $I_i(E)$ produce the coefficients C_{in} , which are then used to determine the first and second upper partial moments $m_1(t)$ and $m_2(t)$. Multiple color measurements ($n > 2$) can produce information about higher moments and increase the precision with which lower moments are determined. The energy range of the moments determined in this way is limited at low energies by the threshold energy for emission E_0 (the energy of the highest frequency emission band used in the analysis). Below E_0 , no emission can be measured, and consequently no information can be determined about $P(t,E)$. The energy range is also restricted at the very highest energies by finite IR detector response times. Moreover, it is likely that only the first few moments can be extracted from the data, due to signal/noise limitations.

The moments analysis approach has been applied in two-color IRF experiments on benzene and benzene- d_6 . In these experiments, IRF (Figure 7) from the C-H stretching mode fundamental

band at $\sim 3060\text{ cm}^{-1}$ and first overtone band at $\sim 6010\text{ cm}^{-1}$ was measured simultaneously following excitation to $E_{\text{init}} \approx 40700\text{ cm}^{-1}$. A similar analysis was carried out using the time- and wavelength-resolved IRF spectrum of excited benzene, and the partial variance results from both experiments are shown in Figure 8.

The partial variance ($=m_2 - m_1^2$) serves as a width parameter for $P(t, E)$, and is seen to reach a maximum at intermediate energies before decreasing at low energies in Figure 8. A decrease at high energies is also indicated, although finite IR detector response times limit measurement at the highest energies (short times following laser excitation). Symbols at 40700 and 6010 cm^{-1} indicate the narrow initial (assumed to be the thermal distribution shifted by the laser photon energy) and final (thermal distribution with all population below E_0) distribution partial variances.

Recent experiments and trajectory calculations have provided evidence that $P_c(E', E)$ for certain excited molecule/collision partner combinations may be best characterized by a function which includes a higher probability for collisions transferring relatively large amounts of energy ($\geq \sim 10\langle\Delta E\rangle$), than do the exponential or Poisson-type models. Inclusion of even a small fraction ($\sim 0.1\%$) of such "supercollisions" into models for $P_c(E', E)$ results in significant distortion of the shape of the population distribution at intermediate energies during collisional deactivation, altering the moments of $P(t, E)$ and allowing the presence of supercollisions to be detected.

Figure 7. Experimental IRF signals for benzene- h_6 (pressure = 37 mtorr), normalized to unity. Upper curve : fundamental band. Lower curve: overtone band.

For benzene, a bi-exponential model with $\sim 3\%$ of energy transferred via supercollisions best fits the experimental data, while for benzene- d_6 a model with $< 1\%$ of energy transferred by supercollisions produces the best agreement. In addition, the widths of the population distributions (as reflected by the partial variances) are greater for benzene deactivated by relatively more efficient self-collisions than for benzene- d_6 ($\langle\Delta E(E)\rangle$ is approximately 50% larger for benzene self-collisions). This is consistent with trends predicted by theoretical analysis of the exponential energy transfer model for strong and weak collisions.

Thus, this method for obtaining the partial moments of the evolving population distribution opens the door to a very sensitive method for learning about the collision step-size distribution: the second and higher moments are much more sensitive than the first moment to the details of the process. There have been only been two or three previous determinations of the higher order

properties of the evolving population distribution and each of the methods used previously is more limited in its potential applications than is the multi-color IRF method. We feel this new approach holds much promise.

Figure 8. Variance vs. $m_1(t)$ for benzene- h_6 , calculated by partial moments analysis. Small circles: experimental two-color broadband results; large circles: experimental wavelength-resolved results; solid line: exponential model for $P_c(E',E)$; dashed lines: bi-exponential model for $P_c(E',E)$; $f_c\beta = 40 \text{ cm}^{-1}$ (short dashes) and $f_c\beta = 100 \text{ cm}^{-1}$ (longer dashes), where $f_c\beta$ is the contribution of the stronger collision component.

In our current experiments, we are attempting to measure emission from a third band. We are investigating the feasibility of two possibilities: 1) monitoring a higher overtone by using a monochromator and photomultiplier combination, and 2) monitoring a lower frequency fundamental by using a HgCdTe infrared detector. Both of these experiments are difficult, but the second option has produced some very preliminary data which appear promising. Measurement of a third band will improve our results for the first two moments, in addition to providing a third moment of the distribution function. It will be very interesting to measure the time-evolution of the population distribution for excited molecules and colliders with various selected properties.

Time-Dependent Thermal Lensing (TDTL) Studies of CS_2 and SO_2

During a previous funding period, we used the TDTL technique to measure $\langle\langle\Delta E\rangle\rangle$ vs. $\langle\langle E\rangle\rangle$ for NO_2 excited to 21631 cm^{-1} in collisions with noble gases. Those results showed a very strong energy dependence, including a sharp change in slope at energies corresponding to the origins of the excited electronic states. This result was recently confirmed by H.-L. Dai and G. Hartmann (private communication, 1993). Our conclusion was that the excited electronic states strongly affected the energy transfer process. Since CS_2 and SO_2 are similar to NO_2 with respect to coupling between the excited states and the ground electronic state, we extended the measurements to these two gases and have completed the experiments.

Analysis of TDTL experiments is not straightforward, but requires detailed simulations using a hydrodynamic description which includes thermal conductivity, diffusion, acoustic effects, and optical paraxial ray analysis, in addition to the energy transfer parameters. By maintaining high dilution ratios of CS_2 or SO_2 in the rare gases (typically, 5000:1), the transport properties of

the mixture are well known, however, enabling an accurate simulation. The results of the simulations are in the form of plots of average excitation energy $\langle\langle E \rangle\rangle$ as a function of time; differentiation with respect to the number of collisions gives $\langle\langle \Delta E \rangle\rangle$.

The results we have obtained are puzzling. For simple bimolecular energy transfer, we expect $\langle\langle E \rangle\rangle$ to depend only on the number of collisions and to be independent of collision frequency. The results we have obtained show, however, that $\langle\langle E \rangle\rangle$ near the beginning of the cascade tends to depend on *time* and not on the *number of collisions*, as shown in Figures 9 and 10. We have been unable to identify any experimental problems which can explain this effect and conclude that it may be real.

Figure 9. Energy vs. time in CS₂ + Xe deactivation for various pressures.

Figure 10. Energy vs. collisions in CS₂ + Xe deactivation for various pressures.

If this unusual effect is real and our analysis is correct, the results may indicate that some sort of "radiationless transition" from the initially excited electronic state is very slow (several microseconds) and controls the rate that energy is made available for transfer to the collider gas, as in the following mechanism:

According to this mechanism, the over-all rate of energy transfer Reaction (13) can be controlled by the rate of Reaction (12), if the time constant for the latter is long enough.

If this mechanism is correct, it is somewhat disturbing, because it contradicts conventional wisdom regarding the strongly mixed states in these particular triatomics. One would expect the excited states to be mixed with the ground state so that the levels excited by absorption of the laser pulse already have ground state electronic character and no "radiationless transition" is required.

We are still studying these results and have not reached a final conclusion. If we are unable to find a problem with the TDTL technique or our analysis, we will publish the result and invite discussion in the scientific community.

Master Equation Simulations

In addition to routine Master Equation simulations IRF experiments, we carried out simulations to investigate the effect of spontaneous infrared emission on recombination reactions at low pressures. The effects of spontaneous IRF on ion-molecule association reactions have been recognized for years, because the experiments are carried out at low pressures where infrared emission rate competes effectively with collision frequency. The analogous effects in the reactions of neutrals have not been investigated thoroughly.

The simulations considered a suite of typical radical-radical recombination reactions. In all cases, vibrational assignments were used to calculate exact state densities and IRF emission rates, according to Equation (1). Einstein coefficients for spontaneous IRF were obtained from the literature. The proper chemical activation distribution of nascent species was employed and the full RRKM treatment was applied.

The remarkable result of the simulations is that IRF is sufficient to deactivate the excited species when the temperature is low enough, and collisions are unnecessary. At low temperatures, the specific unimolecular reaction rate constant [i.e., $k(E)$] is slow, because the nascent excited species is formed just above the reaction threshold and IRF deactivation competes effectively, stabilizing the molecule and completing the recombination process. At higher temperatures, the excited species is formed with more excitation energy and decomposes faster: IRF deactivation can no longer compete. In Figure 9, the efficiency of the recombination is shown as a function of temperature for several reactions.

The effect of IRF stabilization is that pressure fall-off of the recombination rate constant is greatly reduced. For lower temperatures, where the efficiency of IRF stabilization is near 100%, there is no pressure fall-off. At higher temperatures, there may be some fall-off, but there is also a finite rate constant in the limit of zero pressure, as illustrated in Figure 10.

At room temperature and below, this process can be neglected only in the recombination of methyl radicals, among the reactions considered here. Because the radiative stabilization is so efficient, stabilization by collisions is not necessary and pressure fall-off becomes negligible. Thus, unimolecular reaction rate calculations that neglect radiative stabilization may be seriously in error at low and moderate temperatures.

These conclusions will have relatively little effect on laboratory investigations that use conventional and VLPP experiments, because pressures are sufficiently high so that collisional stabilization always dominates. In low pressure environments, however, radiative stabilization is dominant and rapid enough so that there is very little pressure fall-off. This means that recombination reactions of the type considered here will occur efficiently in molecular beams, creating possibilities for new laboratory techniques of preparing highly excited molecules. These reactions also will occur efficiently in the interstellar medium, where recombination reactions of neutral species may make greater contributions than are currently recognized.

Figure 9. Efficiency of infrared radiative recombination as a function of temperature.

Figure 10. Pressure fall-off (argon collider, 700 K). The effect of infrared emission deactivation is shown (the random fluctuations and 2σ error bars reflect statistical uncertainties in the stochastic results).

Polycyclic Aromatic Hydrocarbons in Extreme Environments

Some effort was also spent in using combustion chemical mechanisms of soot formation to estimate polycyclic aromatic hydrocarbon production in stellar outflows. The work on interstellar systems has been a secondary effort that is interesting, but not central to this project. It is a natural extension, however, because most of our work has been concerned with aromatic species and infrared emission. Most of the work was supported by NSF (Galactic Astronomy Division), but it is impossible to cleanly separate the efforts and thus DOE is acknowledged for its support.

Large Molecule Energy Transfer Mechanisms

Our work is aimed at understanding the mechanisms of large molecule energy transfer and providing a data base for comparisons with theory. One would expect that the same physical properties that are important for small molecules would also be present in large molecule energy transfer. Thus it is not surprising that dipole-dipole interactions can explain the extent of V-V energy transfer, as described above, and they must be considered in future theoretical calculations.

In our present view, the collisional deactivation of large molecules can be described with the following components:

- 1) V-T and V-R energy transfers take place with all colliders, probably due to the short-range repulsive interactions invoked in the Biased Random Walk model (although a classical mechanics description is not quantitatively valid);
- 2) V-V energy transfer can take place by long-range dipole-dipole interactions, and thus resonance may play a role;
- 3) if the collider gas has a permanent dipole moment, it is likely that the permanent dipole can interact with the vibrating dipoles of the excited molecule and therefore V-R energy transfer will be enhanced;
- 4) if low-lying excited electronic states are present, they may enhance energy transfer rates very substantially.

These components must be combined with properties of the large molecules involved: very large densities of states and rapid distribution of energy among the vibrational modes.

The challenge of energy transfer investigations is due to the fact that so many different factors can be important and no single one of them appears to be dominant in all systems.

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Publications Describing DOE-Supported Research

1. "Vibrational Relaxation of Highly Excited Toluene," Beatriz M. Toselli, Jerrell D. Brenner, Murthy L. Yerram, William E. Chin, Keith D. King, and John R. Barker, *J. Chem. Phys.*, **95**, 176 (1991).
2. "Polycyclic Aromatic Hydrocarbon Optical Properties and Contribution to the Acceleration of Stellar Outflows," Isabelle Cherchneff, John R. Barker, and Alexander G. G. M. Tielens, *Astrophys. J.*, **377**, 541-552 (1991).
3. "Excitation of CO₂ by energy transfer from highly vibrationally excited benzene derivatives," Beatriz M. Toselli and John R. Barker, *J. Chem. Phys.*, **95**, 8108 (1991).
4. "Infrared Emission Spectra of Benzene and Naphthalene: Implications for the Interstellar PAH Hypothesis," Jerrell D. Brenner and John R. Barker, *Astrophys. J. (Letters)*, **388**, L39-L43 (1992).
5. "Isotope Effects in the Vibrational Deactivation of Large Molecules", Beatriz M. Toselli and John R. Barker, *J. Chem. Phys.*, **97**, 1809-1817 (1992).
6. "Polycyclic Aromatic Hydrocarbons and Molecular Equilibria in Carbon Rich Stars," Isabelle Cherchneff, John R. Barker, and Alexander G. G. M. Tielens, *Astrophys. J.*, **394**, 703-716 (1992).
7. "Radiative Recombination in the Electronic Ground State," John R. Barker, *J. Phys. Chem.*, **96**, 7361-7367 (1992).
8. "Polycyclic Aromatic Hydrocarbon Formation in Carbon Rich Stellar Envelopes," Isabelle Cherchneff, John R. Barker, and Alexander G. G. M. Tielens, *Astrophys. J.*, **410**, 269-287 (1992).
9. "Infrared Emission Studies of the Vibrational Deactivation of Benzene Derivatives," John R. Barker and Beatriz M. Toselli, *Int. Rev. Phys. Chem.*, **12**, 305-338 (1993).
10. "Population Distributions in the Vibrational Deactivation of Benzene and Benzene-d₆: First and Second Moments Derived from Two-Color Infrared Fluorescence Measurements", Jerrell D. Brenner, Joseph P. Erinjeri, and John R. Barker, *Chem. Phys.* (Special issue on "Vibrational Energy Dynamics"), in press.
11. "The Vibrational Deactivation of Large Molecules by Collisions and by Spontaneous Infrared Emission," John R. Barker, Jerrell D. Brenner, and Beatriz M. Toselli, *Vibrational Energy Transfer Involving Large and Small Molecules*, Adv. Chem. Kinetics and Dyn., Vol. 2, in press.
12. "Time-Dependent Thermal Lensing Studies of CS₂ and SO₂ Vibrational Deactivation," Alexander Chimbayo and John R. Barker, manuscript in preparation.

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