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LETTERS

Independent Determination of Supercollision Energy Loss Magnitudes and Rates in Highly Vibrationally Excited Pyrazine with $E_{\mathrm{vib}} = 36000-41000\ \mathrm{cm}^{-1}$

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We report results of the first state-resolved study of large ΔE energy transfer resulting from collisions of highly excited pyrazine with initial vibrational energies of $36000-41000\ \mathrm{cm}^{-1}$. We have used transient infrared absorption spectroscopy to monitor the rotational and translational energy gain in a CO_2 bath at short times following collisions with highly excited pyrazine. We have measured nascent distributions of high-energy rotational states, $J = 56-84$, for CO_2 in its ground vibrationless (00^00) state, the translational energy gain associated with these excited rotational states, and state-resolved rate constants for excitation of the high-energy bath states. Our results show that for the CO_2 rotational states investigated, the nascent rotational distributions and translational energies change very little for a 13% change in pyrazine energy. In contrast, the rate constants for these events are strongly influenced by the donor internal energy content and increase by an order of magnitude for a $5000\ \mathrm{cm}^{-1}$ increase in pyrazine vibrational energy. Our state- and energy-resolved results are compared with experimental measurements of $\langle \Delta E \rangle$, and implications for the energy dependence of the probability distribution function are discussed.

Introduction

Collisional relaxation of highly excited molecules is the primary mechanism by which hot molecular systems return to thermal equilibrium. As such, uncovering the dynamics of these relaxation processes will greatly enhance our understanding of combustion, atmospheric photochemistry, and unimolecular decomposition of activated species.[1−6] Of particular importance is the role of internal energy in the collisional relaxation process, especially for energies near the dissociation threshold. The energy dependence holds important information about the behavior of molecules at high energies and can provide clues as to the microscopic details of intermolecular energy transfer.

A number of techniques have been used previously to investigate the energy dependence of collisional relaxation.[7−23] Many of the experimental techniques, such as UV absorption and IR emission, focus on the excited donor molecule and monitor the average donor energy content in an ensemble of highly excited molecules as a function of time. Treating data from these experiments with a master equation analysis provides information on the average energy transferred per collision $\langle \Delta E \rangle$ as a function of the average energy content $\langle E \rangle$ of the hot molecule. Generally it is found that $\langle \Delta E \rangle$ increases monotonically with $\langle E \rangle$, being linear at some energies and quadratic (or higher) at others. In some molecules, $\langle \Delta E \rangle$ becomes independent of $\langle E \rangle$ near dissociation, such that the energy dependence is observed to level off. This behavior is seen both experimentally[7−23] and in classical trajectory calculations.[24−28] It has been suggested that the general shape of the energy dependence is sigmoidal[29] but that intervening dissociation and electronic state coupling can influence the observed energy dependence.[23,30] The exact shape of the energy dependence is a function of the donor molecule, the collisional bath, the internal

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content of the donor, and, in some cases, the technique used to study the energy transfer. It is important to recognize that experimental measurements of $\langle \Delta E \rangle$ represent an average change in energy and that $\langle \Delta E \rangle$ values contain weighted contributions from all types of energy transfer processes that occur in the collisional relaxation. Therefore, the observed energy dependence of $\langle \Delta E \rangle$ represents an overall average of the energy dependence for a number of possible relaxation pathways. Recent calculations for vibration-to-translation ($V \rightarrow T$) energy transfer based on a statistical-dynamical theory[31,32] predict that the energy dependence of $\langle \Delta E \rangle$ for deactivating collisions results from changes in the fraction of inelastic collisions, while the shape of the ΔE distribution remains essentially the same for donor vibrational energies between 20 000 and 40 000 cm^{-1}. In the work presented here, we explore this issue experimentally by investigating the energy dependence of collisional relaxation involving large changes in donor internal energy that result from single collisions with the bath.

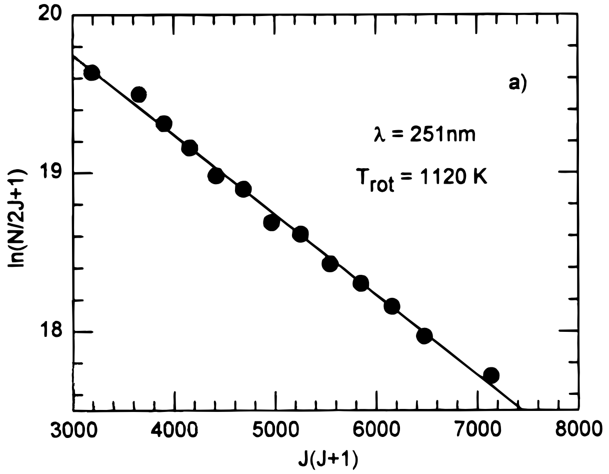
Developing a microscopic understanding of collisional relaxation in highly excited molecules using spectroscopic techniques that focus on the hot molecule is complicated by extremely large densities of states at energies near dissociation. For example, pyrazine with 38 000 cm^{-1} of vibrational energy has a state density of $\sim 10^{14}$ states/cm^{-1}. Another approach to this problem is to investigate the dynamics by monitoring the state-resolved energy gain in bath molecules.[33-35] This approach can yield independent information about the amount of energy transferred, the partitioning of that energy, and the rates for individual energy flow pathways. High-resolution transient IR absorption has been used both by Flynn and co-workers and ourselves to investigate the energy flow from a number of hot molecules, such as pyrazine,[34-38] pyridine,[39] and hexafluorobenzene,[40] into specific modes of a CO_2 bath. These experiments have shown that single impulsive collisions of highly vibrationally excited donor molecules with CO_2 initially at 300 K can result in rather large exchanges of energy that go exclusively into CO_2 rotational and translational energy. For example, rotationally and translationally excited CO_2 (00^00) molecules that result from collisions with highly excited pyrazine ($E_{\mathrm{vib}} = 38\,000\ \mathrm{cm}^{-1}$) have been observed with energies corresponding to ΔE values as high as 2000−10000 cm^{-1}. This type of energy transfer makes up the high-energy tail of the energy-transfer probability distribution and accounts for only $\sim$4% of all collisional relaxation. While these large ΔE energy transfer events do not occur very often, they are very important because they provide the means by which chemically relevant amounts of energy are exchanged between molecules in a single collision. Such large ΔE events have been associated with what are referred to as "supercollisions", whereby large amounts of energy are transferred in a single collision.[17,18,24-26,34-36,38,41-46] Early experimental evidence for supercollision energy transfer stems from the observation that large activation energies for isomerization could be overcome through a single collision with a highly vibrationally excited donor.[41,42] At the same time, an independent report of high-energy tails in energy-transfer distribution functions came from kinetically controlled selective ionization experiments (KCSI).[17,18,43] Supercollision energy transfer also has been observed in a number of theoretical studies.[24-26,44-46] Since then, transient IR absorption experiments have demonstrated that large changes in internal energy in highly excited donors resulting from single collisions with bath molecules correspond to the high-energy tail of a distribution of ΔE and are associated with rotational and translational bath excitation.[34-36] As such, transient IR absorption measurements are a sensitive probe of collisions involving large changes in donor energy. Until now, however, this type of experiment has been performed using only one or two excitation energies so that the *functional form* of the supercollision energy dependence has not yet been directly established. In this paper, we report the results of the first state-resolved energy-dependent study of supercollision energy transfer over a range of well-defined initial energies, corresponding to a 13% change in donor energy.

Experimental Methods

All experiments were performed using a transient infrared laser absorption spectrometer[35,39] coupled to a pulsed tunable UV laser source. The essential experimental features are described here. A 1:1 mixture of pyrazine and CO_2 was introduced to a flowing 3 m collision cell with a total pressure of $\sim$20 mTorr at $T = 298$ K. Vibrationally excited pyrazine molecules in their ground electronic state were prepared by absorption of pulsed UV light, followed by rapid radiationless decay. Tunable UV light with wavelengths ranging from $\lambda =$ 246 to 281 nm was generated by tripling the pulsed output of a Nd:YAG-pumped Ti:sapphire laser having a 5 ns pulse width and 0.1 cm^{-1} frequency bandwidth. The nascent rotational states of CO_2 (00^00) molecules that gain energy through collisions with vibrationally excited pyrazine were detected by measuring the change in transmitted intensity of the single-mode output of a liquid-nitrogen cooled lead-salt diode laser operating at $\lambda = 4.3\ \mu$m. Following UV excitation, populations in individual quantum states were measured at short times (1.5 μs) relative to the gas-kinetic collision time (4.5 μs) at the experimental pressure. Doppler-broadened transient line shapes were collected by locking the diode laser to the output of a scanning Fabry−Perot etalon and measuring changes in transmitted IR laser intensity as a function of infrared wavelength.

Results and Discussion

Nascent populations for a number of individual rotational states, $J = 56-84$, of CO_2 (00^00) were obtained using transient infrared absorption following excitation of pyrazine at a number of different UV wavelengths ranging from $\lambda = 246$ to 281 nm. At these wavelengths, pyrazine is prepared in an excited electronic state, which undergoes radiationless decay to a highly vibrationally excited state on the ground electronic surface in less than 100 ns with a near unity quantum yield, thus converting the photon energy into pyrazine internal energy.[47-49] The populations for individual CO_2 (00^00) rotational states obtained at 1.5 μs following pyrazine excitation were determined using Beer's Law and well-established IR transition strengths for CO_2 and include contributions from the experimentally measured transient line profiles (see below). Distributions of nascent rotational populations of CO_2 (00^00) $J = 56-84$ resulting from collisions with pyrazine excited at $\lambda = 251$, 256, 261, 266, and 271 nm were obtained from the 1.5 μs population data. (Low UV powers for $\lambda < 251$ nm and $\lambda > 271$ nm precluded measuring complete rotational distributions at all pyrazine excitation wavelengths.) The distributions for $\lambda = 251$ and 271 nm are shown in Figure 1. The distributions for all wavelengths investigated are well described by Boltzmann statistics and have rotational temperatures of $T_{\mathrm{rot}} = 1120 \pm 70$ K (251 nm), 1130 ± 70 K (256 nm), 1090 ± 70 K (261 nm), 1140 ± 80 K (266 nm), and 1110 ± 70 K (271 nm), with uncertainties corresponding to 1 standard deviation resulting from at least three measurements of T_{rot}. These results are consistent with previously reported values of $T_{\mathrm{rot}} = 1200 \pm 150$ K ($\lambda = 266$ nm)[35]



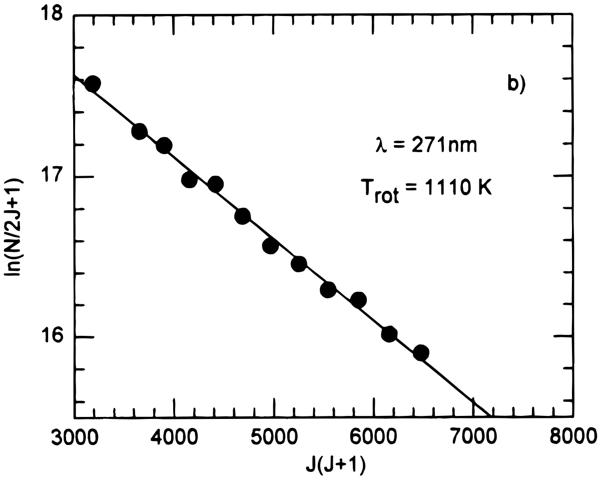


Figure 1. Rotational populations of CO_2 (00^00) for (a) $J = 56-84$ resulting from collisions with highly excited pyrazine having $E_{vib} = 40\,140$ cm^{-1} and (b) $J = 56-80$ when pyrazine has $E_{vib} = 37\,000$ cm^{-1}. All populations were measured at 1.5 μs following UV excitation of pyrazine and include contributions from experimentally measured transient line widths.

and 1200 ± 180 K ($\lambda = 248$ nm).[34,36] The energy dependence of the CO_2 (00^00) $J = 56-84$ distribution is illustrated in Figure 2 for collisional relaxation of pyrazine excited at $\lambda = 248-271$ nm. It is noteworthy that for a change in donor vibrational energy of nearly 4000 cm^{-1} the distribution of CO_2 (00^00) high-J states shows very little variation.

Distributions of recoil velocities have also been measured for CO_2 (00^00) rotational states having $J = 56$, 62, 68, 74, and 78 for pyrazine excitation at $\lambda = 251$, 256, 261, 266, 271, and 276 nm. Populations for individual rotational states were measured at 1.5 μs following pyrazine excitation as a function of IR wavelength, and translational temperatures were obtained by fitting the data to Gaussian line profiles. In Figure 3, the nascent Doppler-broadened transient line profiles for CO_2 (00^00) $J = 74$ are shown for pyrazine excited at $\lambda = 251$ and 271 nm, along with the best Gaussian fits (solid lines). The resulting translational temperatures for CO_2 (00^00) $J = 74$ in the laboratory frame are $T_{trans} = 2650 \pm 420$ K (251 nm) and $T_{trans} = 2550 \pm 410$ K (271 nm). The measured transient line shapes are substantially broadened relative to 298 K line widths (shown in Figure 3 as dashed lines), and this broadening illustrates that large recoil velocities accompany rotational excitation of the CO_2 bath. A complete listing of our energy-dependent line widths will be presented in the near future, but the key result is that the Doppler broadening for each J state investigated changes very little over the range of UV excitation wavelengths. This result, taken together with the energy dependence of T_{rot} for CO_2 (00^00) $J = 56-84$, indicates that the *shape* of the high-energy part of the energy-transfer distribution function is surprisingly insensitive to the exact energy content of the highly excited pyrazine. To develop a complete picture of the energy-transfer dynamics, we must also consider the energy-dependent rate constants, and hence probabilities, for rotational and translational energy gain in the bath.

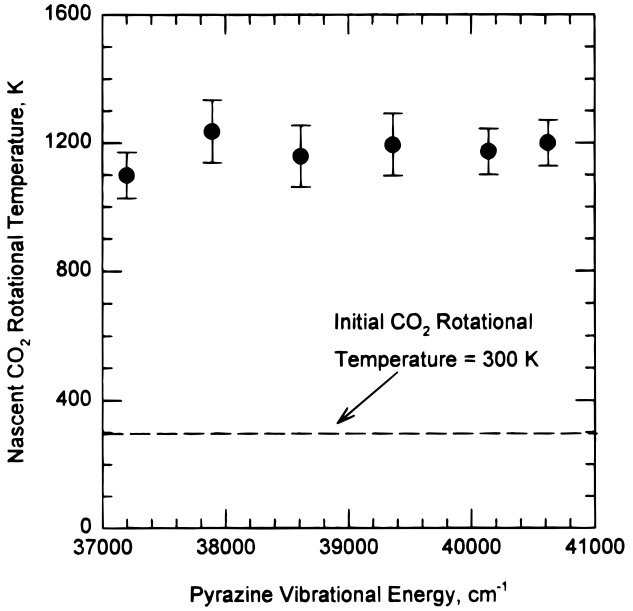


Figure 2. Nascent CO_2 (00^00) $J = 56-84$ rotational temperatures as a function of pyrazine internal energy. The rotational temperatures describe the high-J states for CO_2 (00^00) and show very little deviation over the range of donor energies investigated. T_{rot} at 40 680 cm^{-1} is taken from ref 36.

Absolute bimolecular rate constants for energy gain into CO_2 (00^00) have been measured for a large number of rotational states $J = 56-84$ at eight different UV wavelengths $\lambda = 246-281$ nm. All rate constants were determined from the early time linear part of the transient absorption and include population contributions from Doppler-broadened transient line shapes, as described in detail in ref 35. Briefly, rate constants are determined by measuring the time-dependent population for each CO_2 (00^00) J state and normalizing it to the number density of vibrationally excited pyrazine and the initial CO_2 concentration at 300 K. The transient absorption signal for CO_2 (00^00) $J = 62$ is shown in Figure 4a, illustrating the linear behavior at early times. In Figure 4b, energy-dependent rate constants for appearance of individual CO_2 (00^00) rotational states resulting from collisions with highly vibrationally excited pyrazine are presented. Unlike the rotational and translational energy distributions for CO_2 (00^00) $J = 56-84$, the observed rate constants for appearance of the individual rotational states depend strongly on the pyrazine energy and demonstrate a monotonic increase as the pyrazine energy increases. Over a donor energy range of 5000 cm^{-1}, we observe an *order of magnitude increase* in the energy-transfer rate constants associated with appearance of each final CO_2 J state investigated. For example, the bimolecular rate constants for appearance of $J = 62$ are $k_2{}^J = (4.2 \pm 1.1) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for 246 nm pyrazine excitation and $k_2{}^J = (3.9 \pm 3.1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for 281 nm excitation.

The rate constants for energy gain in the bath are directly proportional to the probability for such events occurring, and

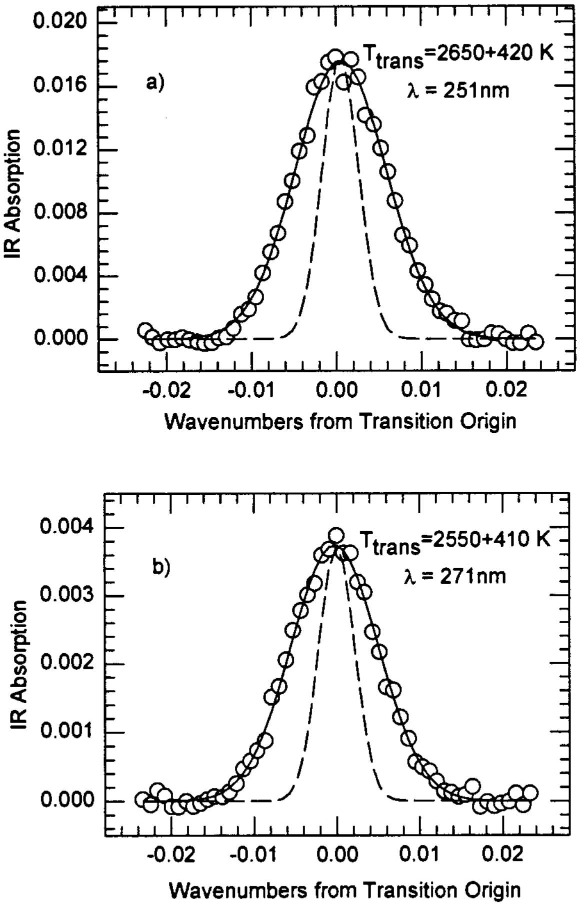


Figure 3. Transient absorption line widths for CO_2 (00^00) $J = 74$ resulting from collisions with highly vibrationally excited pyrazine with (a) $E_{vib} = 40\,140$ cm^{-1} ($\lambda = 251$ nm) and (b) $E_{vib} = 37\,200$ cm^{-1} ($\lambda = 271$ nm). CO_2 populations were measured at 1.5 μs following UV excitation of pyrazine with a total cell pressure of 20 mTorr (1:1 pyrazine:CO_2). The translational energy gain remains constant for a 4000 cm^{-1} change in pyrazine energy. The open circles are experimental data, the solid lines are Gaussian line profiles best fit to the data, and the dashed lines are line shapes for a 298 K velocity distribution.

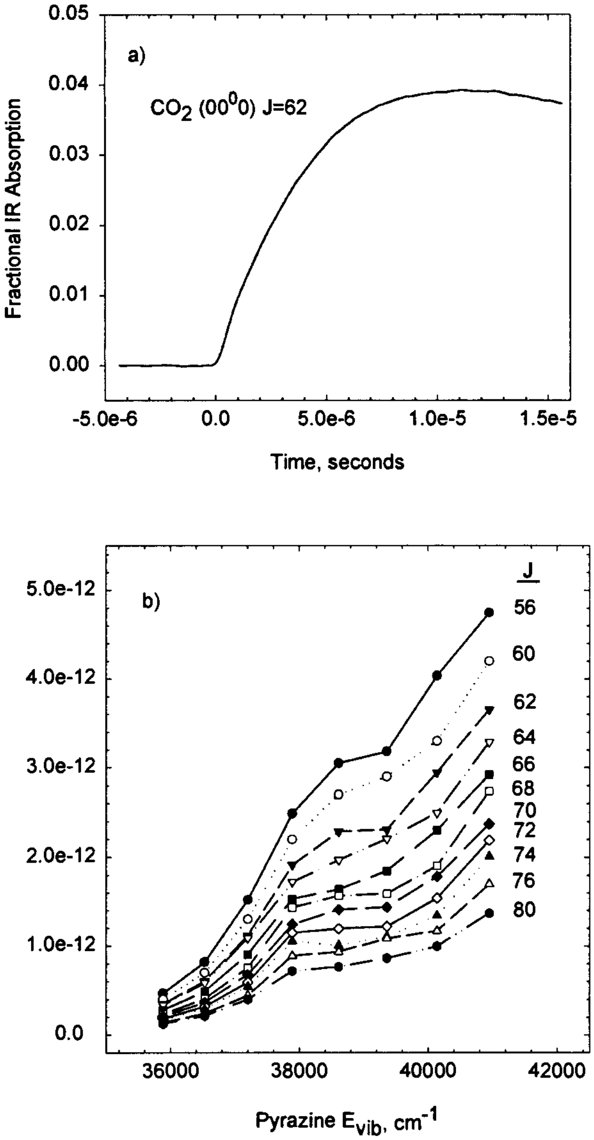


Figure 4. (a) Transient IR absorption of CO_2 (00^00) $J = 62$ following pyrazine excitation at $\lambda = 261$ nm. (b) Rate constants for appearance of high-J rotational states of CO_2 (00^00) as a function of pyrazine vibrational energy. Unlike the distributions of rotational and translational energy gain, the rate constants are strongly dependent on pyrazine energy. Rate constants have units of cm^3 molecule^{-1} s^{-1}. Data for pyrazine energies of 37 900 and 40 900 cm^{-1} were reported previously in ref 35.

thus the data in Figure 4b indicate that the probability for collisional excitation of the high-J states of CO_2 (00^00) depends keenly on the pyrazine internal energy. One of the key findings of this study is that, for pyrazine with 36000−41000 cm^{-1} vibrational energy, the *probability* of energy transfer into high-energy bath rotations and translation demonstrates a remarkably strong energy dependence while the *shape* of the high-energy part of the energy-transfer distribution function is fairly insensitive to donor energy content. IR emission measurements[12] of $\langle \Delta E \rangle$ for collisional relaxation of hot pyrazine by CO_2 show that the total $\langle \Delta E \rangle$ is a linear function of the average internal energy $\langle E \rangle$ when pyrazine is initially excited near 30 000 cm^{-1}. Our results show that the contribution to the total $\langle \Delta E \rangle$ energy dependence from collisions involving large ΔE values arises almost entirely from the energy-dependent changes in the probability, since the shape of the high-energy ΔE distribution shows little variation over the range of donor energies investigated here. It is important to recognize that the transient IR absorption studies presented here provide information only about the high-energy tail of energy-transfer distribution function, while the observed $\langle \Delta E \rangle$ energy dependence includes all energy-transfer pathways. Previous work[36,37] has shown that rotational and translational bath excitation, as opposed to excitation of bath vibrations, dominates the collisional relaxation of hot pyrazine and that the majority of these collisions involve small ΔE values. Hence, the energy dependence of $\langle \Delta E \rangle$ will be most influenced by collisions involving small ΔE values. Since we expect integrated probabilities to be close to unity for the large donor energies used in this study (i.e., some energy transfer occurs on every collision), the low-energy part of the distribution function must adjust accordingly as $\langle E \rangle$ decreases in order to compensate for the decreasing probability in the high-energy ΔE tail. To be consistent with experiments indicating that, for pyrazine and CO_2, $\langle \Delta E \rangle$ decreases linearly with $\langle E \rangle$, both the shape and the magnitude of the probability distribution function at low ΔE values must undergo energy-dependent changes, notably a shift in the distribution toward lower ΔE values. From the viewpoint of chemical reactions, it is remarkable that the shape of the high-energy part of the distribution function, consisting of measured ΔE values as high as 10 000 cm^{-1}, persists for pyrazine energies of 36000−41000 cm^{-1}. However, Figure 4b highlights the fact that such events become increasingly less probable as the donor energy decreases, so much so, in fact, that extrapolating the rate constants to zero suggests that a threshold for the large ΔE collisions exists near 35 000 cm^{-1}. It is interesting that the red edge of the pyrazine $S_0 \rightarrow S_2$ absorption band used in this study is found near 36 000 cm^{-1}. It is possible that this nearby electronic state influences the vibrational behavior on the S_0 surface. Pyrazine is considered an "intermediate" case molecule with respect to radiationless transitions. Thus, upon UV excitation, pyrazine is truly prepared in a mixed state. However, in light of the enormous density of states in vibrationally excited S_0, it is quite unlikely that the influence of the S_2 state is very pronounced once the excited wave packet has evolved to the S_0 surface. We are currently investigating this further by extending our energy-dependent measurements to donor energies as low as 31 000 cm^{-1}, energies at which vibrationally hot pyrazine is prepared via the lower energy S_1 electronic state.

In summary, we have performed transient IR absorption experiments to investigate the energy dependence of rotational and translational energy gain in a CO_2 (00^00) bath following collisions with pyrazine excited to a number of initial energies ranging from 36 000 cm^{-1} to 41 000 cm^{-1}. These single-collision measurements provide us with important insights into the energy dependence of collisional relaxation involving large changes in energy, ΔE. We find that for more than a 10% increase in donor energy, the magnitude of the transferred energy ΔE and its partitioning into high-energy rotation and translation of a CO_2 bath show very little change while the probability for such events increases by an order of magnitude. These results are consistent with theoretical predications that the shape of the energy-transfer distribution function does not change with donor energy but that the magnitude of the energy-transfer probability increases with increasing donor energy. Studies are currently underway in our laboratories to investigate the nature of large ΔE collisions for a broader range of pyrazine energies and to explore whether an energy threshold exists for large ΔE collisions.

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