

Picosecond infrared double resonance studies on pentafluorobenzene

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Utilizing synchronized 50 ps pulses from two independently tunable CO₂ lasers, a pump-probe experiment is performed on pentafluorobenzene. The molecule, which has two infrared active modes accessible to the CO₂ laser wavelengths, allows an extensive investigation into the statistical nature of the intramolecular vibrational energy relaxation process. We find discrete state effects, indicated by oscillatory behavior in the time-resolved absorption spectrum, disappear when the molecule is heated into the quasicontinuum. Using the anharmonic redshifting and broadening of the normal mode absorption features in the infrared spectrum as a measure of local temperature, our results indicate rapid equilibration (< 50 ps) of absorbed energy among modes, with the final distribution of energy consistent with thermal heating.

INTRODUCTION

Intramolecular vibrational relaxation (IVR) of polyatomic molecules remains a topic of extremely high interest, especially since the experiments in this field have strong implications with regard to the feasibility of mode selective laser chemistry. Experiments to determine IVR rates, however, encounter significant difficulties, since internal relaxation seems to occur rapidly. Rapid timing techniques have included using van der Waals predissociation¹ and high pressures (10 kTorr and higher) of quenching gas² to serve as timing elements in the fluorescence spectra of vibrationally excited molecules. We are continuing investigations on the statistical nature of infrared multiple photon energy deposition in the ground electronic state of polyatomic molecules by performing standard pump-probe experiments using picosecond pulses from independently tunable CO₂ lasers. The picosecond pulse domain allows us to conduct gas cell experiments at reasonable pressures and yet observe the excitation and relaxation dynamics in a collisionless environment. This feature is essential to observing truly intramolecular relaxation, an aspect that has recently become apparent as experimentalists continue to observe collisional energy redistribution effects with large cross sections.^{3,4}

In earlier experiments³ on SF₆, we studied the behavior of the triply degenerate ν_3 normal mode when subjected to a strong 30 ps infrared pump pulse. By using our capability to pump and probe at independent wavelengths, we were able to time resolve the entire ν_3 mode absorption spectrum. Our results indicated for this molecule that energy randomization was completed within 30 ps. Furthermore, the redshift produced in the absorption spectrum by the picosecond pump pulse was entirely consistent with the thermal shift expected for the same energy deposition, indicating the infrared multiple photon absorption (IRMPA) process produced by picosecond pulse heating was essentially thermal in nature. In order to further eluci-

date the statistical nature of the IRMPA process, we have chosen to fully exploit the capability of our apparatus to pump and probe at independent wavelengths by studying the molecule pentafluorobenzene (C₆F₅H, or PFB), which has *two* normal modes accessible to the CO₂ laser wavelengths. By time resolving the anharmonic redshifting and broadening of each of the normal mode features (in a collisionless environment), and by using redshifts as a measure of the local temperature of each mode, we can determine if the normal modes rapidly equilibrate the energy deposited in one or the other by our picosecond laser pulses.

EXPERIMENT

The details of the apparatus used to obtain the picosecond time resolved spectrum changes have been presented elsewhere.³ Briefly, the experiment requires the use of two synchronized, independently tunable, CO₂ oscillators. The output beams of the two oscillators are combined to pass through a single plasma shutter followed by a free induction decay cell, generating synchronized 50 ps FWHM pulses with independent wavelengths. After separating the picosecond pulses by both wavelength and polarization, a translation stage is used to provide a variable delay between the pump and probe picosecond pulses in the standard manner for time resolved pump-probe experiments. Data acquisition and control of the experiment are facilitated by a homebuilt computer interface to a LSI-11 micro-computer.

The pentafluorobenzene samples were commercially obtained (< 98% purity, liquid) and purified by repetitive freeze-pump-thaw cycles when installed on the vacuum system for the experiments. The experiments were conducted with a 0.13 cm long gas cell at the room temperature vapor pressure of PFB (~ 49 Torr). A 2.5 in. focal length lens was used to focus and cross the pump and probe picosecond pulses through the sample. Just as for our earlier work on SF₆, the confocal parameter of the beams at the focus was kept longer than the cell length, insuring that the pulses are essentially collimated through the cell. Due to a factor of 25 smaller absorption cross section for C₆F₅H rela-

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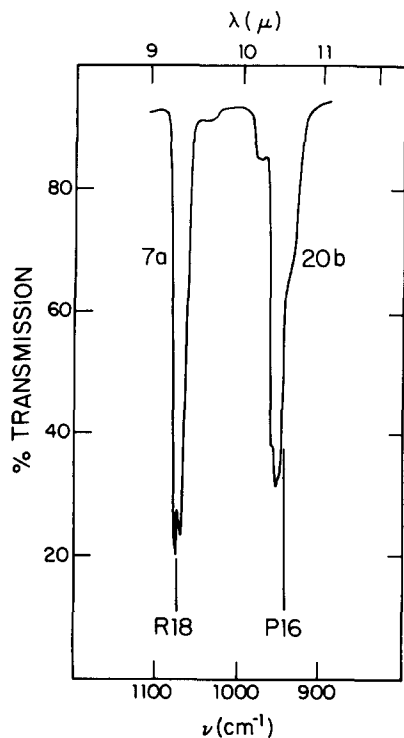


FIG. 1. The infrared absorption spectrum of pentafluorobenzene, with CO₂ laser lines indicated.

tive to SF₆, the transmission of the pump pulse through the sample always remained above 75%.

Figure 1 illustrates the infrared absorption spectrum of PFB in the 9 to 11 μ region. Although very little work has been done on this molecule, the infrared features have been assigned by Long and Steele.⁵ For most of our experiments, the pump laser was fixed at the R18 CO₂ line at 1077.3 cm⁻¹, coinciding with the strongest absorption in mode 7a of PFB. Probing in this experiment was conducted in one of two ways. For probing the low frequency mode 20b slightly to the red of its peak absorption, the second CO₂ oscillator was turned to the P16 line at 947.7 cm⁻¹ or the P14 line at 949.5 cm⁻¹. For experiments conducted with the pump and probe at identical wavelengths, only the pump oscillator was used. In this case a small fraction of the pump pulse was split off and used as a weak probe. This greatly improves the signal-to-noise ratio in the time resolved scans, since fluctuations due to synchronization of independent laser pulses at the plasma shutter are eliminated. Regardless of which experimental arrangement is used, the probe pulse in this work is attenuated to a level several hundred times weaker than the pump pulse, insuring that the probe pulse is in the linear absorption regime.

RESULTS

Using a 1077.3 cm⁻¹ pump pulse, Fig. 2 illustrates typical time resolved scans obtained for the probe tuned to the pumped mode 7a at 1077.3 cm⁻¹ (lower trace) and for the probe tuned to the unpumped mode 20b at 947.7 cm⁻¹ (upper trace). The 50 ps pump pulse fluence was in the 70 to 85 mJ/cm² range for these

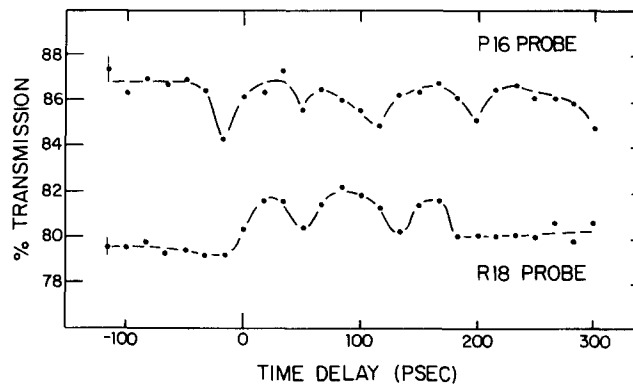


FIG. 2. Time resolved scans, showing the variation in transmission of the weak probe pulse induced by a 1077.3 cm⁻¹ (R18) 50 ps pump pulse depositing 2.5 photons per molecule. Lower trace: probe at 1077.3 cm⁻¹. Upper trace: probe at 947.7 cm⁻¹. Points are raw data. Lines are drawn only as a visual aid.

scans, for which the average number of photons absorbed per molecule $\langle n \rangle$ was approximately 2.5 (deconvolved for the Gaussian spatial profile of the laser pulse). Time zero in the scans has been defined as the overlap of the peaks of the pump and probe laser pulses. The unique feature which appears in the scans is the oscillatory behavior obtained in the absorption spectrum after excitation by the pump pulse. At the pump wavelength these oscillations are superimposed on a small bleaching effect, while in the unpumped low frequency mode 20b the oscillatory behavior is superimposed on an overall increase in absorption produced by the pump pulse heating. Within our signal-to-noise ratio, the oscillatory behavior cannot be described as a single sinusoidal wave.

In order to investigate this effect further, several experiments were performed. Figure 3 illustrates the

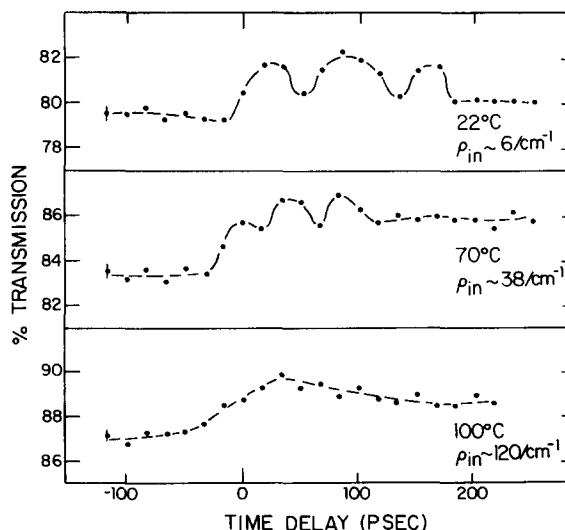


FIG. 3. Time resolved scans indicating the effect of increasing gas cell temperature (with initial vibrational density of states ρ_{in}) on the oscillations observed with 50 ps pulses. Pump and probe are both at 1077.3 cm⁻¹. Connecting lines are for visual aid only.

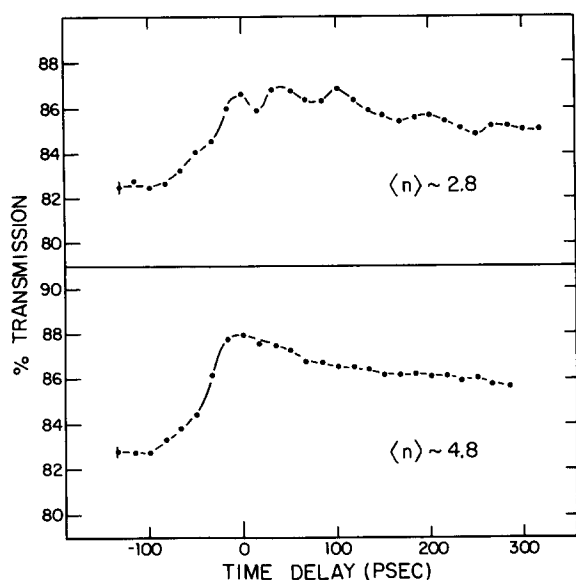


FIG. 4. Time resolved scans illustrating the disappearance of all oscillatory behavior as the average energy deposition in pentafluorobenzene is increased. Pump and probe are both at 1077.3 cm^{-1} and 70 ps pulses are used. Connecting lines are for visual aid only.

effect of heating the gas and performing the pump-probe experiment at 1077.3 cm^{-1} for $\langle n \rangle \sim 2.5$. The experiments were conducted at constant pressure, giving rise to slight changes in the ordinate for each scan. At the highest cell temperature ($\sim 100^\circ \text{C}$), where the superimposed oscillations have disappeared, the redshift in the absorption profile of mode $7a$ is extremely small ($< 0.5 \text{ cm}^{-1}$). As a further check that this variation in profile plays no significant role, the pump-probe experiment was also performed at the $R16 \text{ CO}_2$ laser line at 1076.0 cm^{-1} with the cell at the elevated temperature. Just as for the $R18$ data, there was no evidence of oscillatory behavior under the high temperature conditions. Along with each scan is listed

the initial vibrational density of states of the PFB molecule at that temperature, as obtained from calculating the vibrational heat capacity of PFB using the harmonic approximation and then using the Whitten-Rabinovitch method to obtain the density of vibrational states ρ . It is readily apparent from these scans that as the vibrational density of states is increased, the discrete state nature exhibited by the oscillatory effect rapidly disappears.

In order to study the effect of increasing the pump fluence, limitations of the apparatus require the use of longer pulses in order to deposit more energy into the PFB molecule. By going to 70 ps FWHM pulses the results of Fig. 4 were obtained for the pump and probe tuned to 1077.3 cm^{-1} . In the upper trace for which $\langle n \rangle \sim 2.8$, the oscillatory behavior is apparent, but not as obvious as when the 50 ps pulses were used. In the lower scan, a fluence of approximately 140 mJ/cm^2 produces an energy deposition of 4.8 photons per molecule, and clearly there is a complete absence of discrete state effects as indicated by the lack of oscillatory behavior. From our energy deposition experiments we note there is no measurable intensity effect between 70 and 50 ps pulses for PFB. At the same fluence the 70 and 50 ps pulses deposit essentially the same energy in the molecule.

Finally, the addition of helium as a buffer gas shows the PFB oscillations are rapidly quenched by long range collisions with helium atoms. Figure 5 shows scan results using a 50 ps pump pulse at $\langle n \rangle \sim 2.5$ for the addition of 9, 20, and 46 Torr of helium buffer gas. From these experiments we have obtained a 2 ns Torr relaxation rate of the coherent state prepared by the pump laser pulse, implying a hard sphere collision diameter of 20 \AA between the PFB molecule and the helium atom. These long-range collisional interactions once again emphasize the importance of working in a collisionless environment when studying intramolecular relaxation processes.

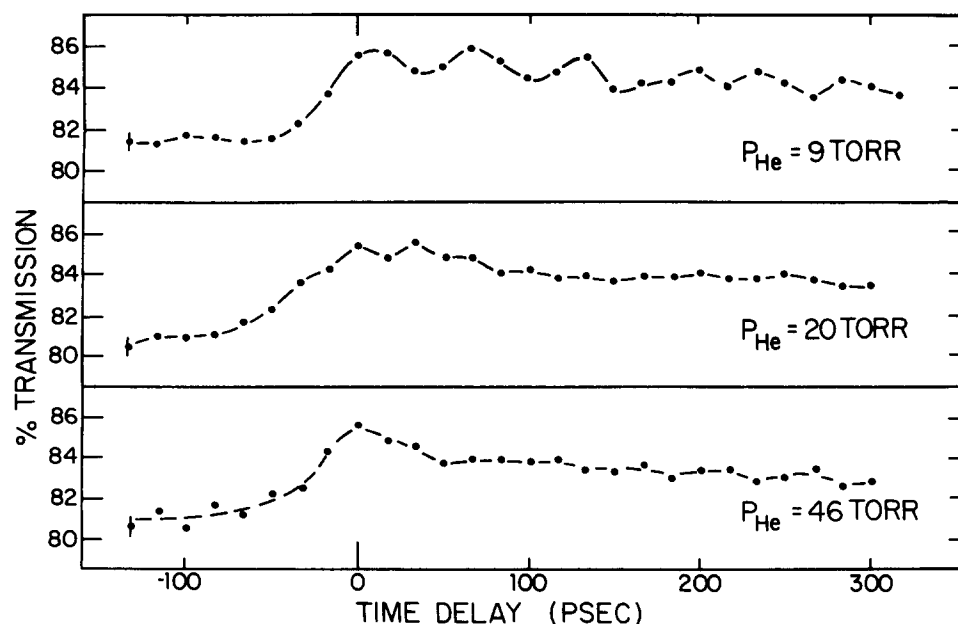


FIG. 5. 50 picosecond pulse pump-probe experiments at 1077.3 cm^{-1} showing the effects of the addition of helium gas. The pressure dependent relaxation rate obtained from long range interaction between helium and PFB is 2 ns Torr.

TABLE I. A comparison of the relative cross section change obtained at various CO₂ laser wavelengths in modes 7a and 20b by picosecond pulse heating (collisionless domain) to the relative cross section change obtained at the same wavelength by thermally heating the molecule to the same vibrational energy deposition. Error limits are for the random fluctuations apparent in the signal-to-noise ratio of the time resolved scans. Systematic corrections to the shifts $\Delta\sigma/\sigma$, accounting for the deconvolution of the overlap of the weak Gaussian probe pulse with the intense pump pulse, are not included in these errors.

Laser line (cm ⁻¹)		Pulse duration (ps)	Initial cell T (°C)	Energy deposition (CO ₂ quanta)	$\Delta\sigma/\sigma(\%)$	
Pump	Probe				Pump-probe	Thermal (spectrometer)
(1) 1077.3(R18)	1077.3	50	95	2.5	-30 ± 4	-33 ± 2
(2) 1076.0(R16)	1076.0	50	95	2.5	-29 ± 2	-29 ± 2
(3) 1077.3	1077.3	70	22	4.8	-32 ± 2	-33 ± 2
(4) 1077.3	947.7(P16)	50	22	2.5	+16 ± 6	+18 ± 4
(5) 1077.3	949.5(P14)	50	22	2.5	+9 ± 12	+2 ± 2
(6) 1077.3	1077.3	50	22	2.5	-10 ± 3	-14 ± 4

As an additional and very important point, we investigate the statistical nature of the energy randomization process by using the anharmonic shifts of the absorption spectrum. As is well known, thermally heating a large polyatomic molecule produces red-shifting and broadening of the absorption features in the IR spectrum of the molecule. Figure 6 shows on an expanded scale the mode 7a and 20b IR features of PFB, obtained from measurements on a Perkin Elmer model 567 infrared spectrophotometer. Each of the red-shifted and broadened absorption curves corresponds to a temperature for the molecule, as is indicated in the figure.

As we have seen from the time resolved scans, the picosecond pump pulse also produces absorption spectrum changes. These changes have been monitored at various wavelengths with the weak probe. Although it is not experimentally possible to obtain the entire absorption spectrum of each mode with our picosecond pulse heating apparatus, we can make the following semiquantitative observations. By using the relative

cross section changes as a temperature gauge, we can establish the strong similarity between our picosecond pulse heating and the thermal heating results of Fig. 6. In Table I a comparison is made between the relative cross section change obtained from the 50 and 70 ps pump-probe experiment and the thermal heating experiment, under identical initial conditions and for equal energy deposition in the molecule. The errors in the pump-probe column for $\Delta\sigma/\sigma$ are experimental and arise from the signal-to-noise fluctuations in the time resolved scans. We note there is also a systematic error in the experimental shifts $\Delta\sigma/\sigma$, due to the fact that the weak probe pulse spatially averages $\Delta\sigma$ over the entire Gaussian intensity profile of the pump, rather than sampling the peak intensity region only. Deconvolution for this effect is involved, but possible, and can give rise to corrections as large as 25% of the reported experimental shifts $\Delta\sigma/\sigma$ in Table I. The errors for the thermal shifts $\Delta\sigma/\sigma$ occur from instrumental error in measuring the transmission of the heated pentafluorobenzene samples on the spectrophotometer. At this point, we simply point out the strong

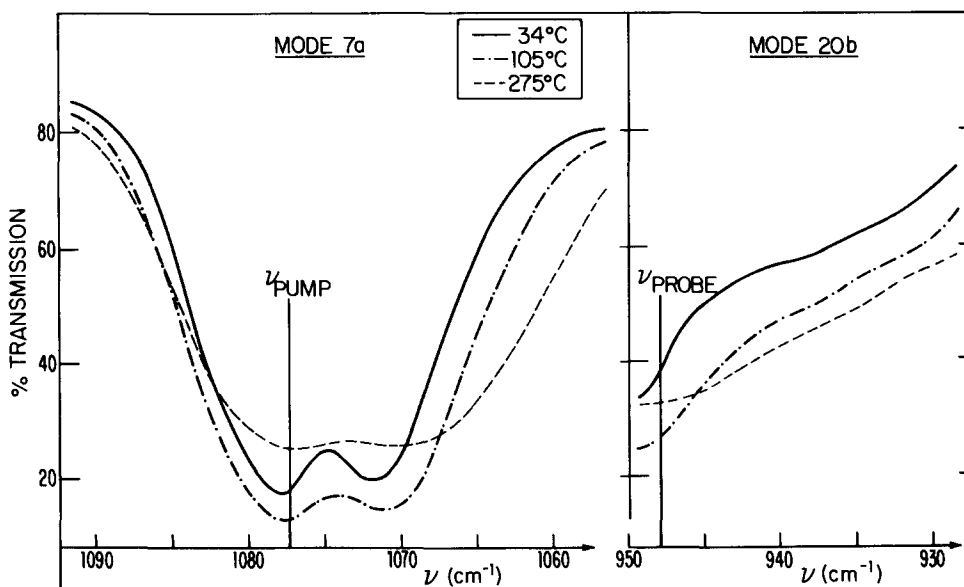


FIG. 6. On an expanded scale, the mode 7a and 20b infrared spectra as a function of temperature, obtained from an infrared spectrophotometer. Instrumental error in the transmission is approximately +1%.

agreement between the thermal shifts and the picosecond pulse produced shifts. The implications of this agreement will be discussed further in a later section.

DISCUSSION

From the effects of heating the PFB gas cell and then conducting the picosecond pulse pump-probe experiments, we offer the following conclusions, based on the quasicontinuum (QC) model⁶ for IRMPA. It is apparent at room temperature PFB is not yet completely in the QC as defined by

$$\frac{1}{\hbar\rho} \ll \text{transition rate} \ll \frac{1}{T_2}, \quad (1)$$

where ρ is the vibrational density of states and T_2 is the intramolecular vibrational dephasing time. The oscillator strength of the zero order vibrational state (the normal mode) is spread out over an envelope of width proportional to $1/T_2$. The transition rate may be estimated from either the Rabi frequency $\omega_R = \mu E/\hbar$ or from $I\sigma/\hbar\omega$, where σ is the absorption cross section and $\hbar\omega$ is the photon energy.

From the Whitten-Rabinovitch calculation, ρ is approximately $6/\text{cm}^{-1}$ at room temperature. The transition rate for the conditions of the experiment is approximately 1.6 cm^{-1} (2.5 photons absorbed in 50 ps). Hence, the left-hand side of the expression for the QC in Eq. (1) is not strongly satisfied. For an average energy deposition of 2.5 photons per molecule, there should be a significant fraction of molecules for which the energy deposited is a photon or less. These molecules, for which the density of states is low, may coherently interact with the laser field. Experimentally, we observe these discrete state effects at room temperature, as indicated by oscillatory behavior in the time resolved absorption spectrum.

For PFB, merely preheating the gas from room temperature to 100°C is sufficient to produce a large increase in the density of vibrational states. Under these conditions, the initial density of states ρ is approximately $120/\text{cm}^{-1}$. The 50 ps pump pulse energy deposition of $\langle n \rangle \sim 2.5$ is now sufficient to produce interaction among a large number of states for essentially every molecule in the ensemble. In the preheated cell experiment, we emphasize there is also a lack of any discrete state behavior in the time resolved spectra. Once the 50 ps pump pulse disappears, the absorption spectrum exhibits temporally a quasistatic value as shown in Fig. 3. With the entire molecular distribution elevated into the QC [the left-hand side of Eq. (1) is satisfied now for essentially all molecules], we observe no collisionless transients such as oscillations or exponential decays. Essentially, the same result is indicated by our 70 ps pulse data at an energy deposition of 4.8 photons per molecule. At this higher level of excitation, the resulting distribution of molecules is pushed into the QC, resulting in a complete disappearance of the discrete state oscillations, which are observable at the lower deposition of 2.8 photons per molecule.

The importance of studying the molecules in the QC

rests in the ability to describe the infrared multiple photon absorption process using rate equations rather than a full Schrödinger equation approach. If the expression for the QC is satisfied, then $\omega_R \ll 1/T_2$, and the off diagonal elements of the density matrix are small due to rapid dephasing. We can then describe the driven mode population W_s by

$$\frac{dW_s}{dt} = [s\sigma(W_{s-1} - W_s) + (s+1)\sigma(W_{s+1} - W_s)] \frac{I}{\hbar\omega} + \text{damping}, \quad (2)$$

where s represents the quantum occupation number of the driven mode. If the pump laser pulse is applied and removed in a time short compared to the population damping, then we are left after the disappearance of the excitation pulse with

$$\frac{dW_s}{dt} = \text{damping} = -\frac{W_s}{T_1}. \quad (3)$$

Integrating this equation, we find exponential decays are indicative of energy relaxing from the driven mode. If, however, the T_1 damping is fast relative to the pulse duration, we should observe only a quasistationary value in the absorption spectrum. All transient effects after the disappearance of the pump pulse should be collisional in nature. This appears to be the situation in our results on PFB heated into the QC, for which the rate equation approach is applicable, and indicates T_1 is less than 50 ps for molecules in the QC. We note that so long as the molecule is in the region of sparse level density (the so-called intermediate coupling limit of electronic relaxation), we can, in principle, expect to observe a double exponential decay. An initial decay, which may include quantum beat type effects, occurs from the rapid dephasing of the coherently excited superposition of states.⁷ A subsequent decay would indicate energy relaxation of the excited state.

Implicit in our preceding statement $T_1 < 50$ ps, is the assumption that the right-hand side of the expression in Eq. (1) is satisfied. We feel this is justified for several reasons. To clarify our arguments, a further discussion of T_1 and T_2 is merited, since these have proven to be rather troublesome concepts in the literature.

One should note the interpretation of our results depends upon the basis set used to describe the dynamical effects. The description may be based in the language of the true molecular vibrational eigenstates or in terms of the zero order (normal mode) states of the molecule. In either case we must account for the state prepared by the pump laser pulse. Two cases may exist, as illustrated in Fig. 7. In each the laser pulse bandwidth is sufficiently broad to overlap with several or more true vibrational eigenstates. However, in case (1) the zero order normal mode oscillator strength is spread out over a region narrower than this bandwidth, while in case (2) the oscillator strength of the normal mode is spread out over a width broader than the pulse bandwidth. In either case (1) or (2) the laser pulse excites a superposition of exact states which may dephase very rapidly, on the order of the pulse duration, but only in

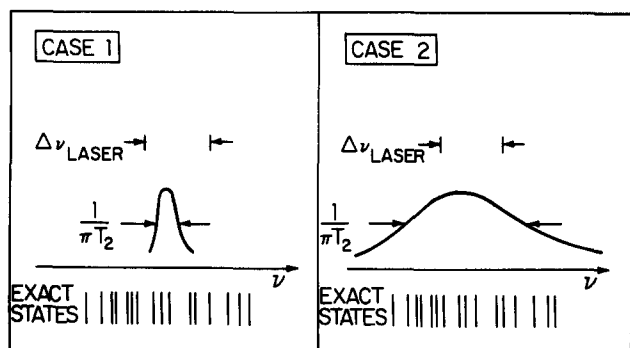


FIG. 7. An illustration of the relationship between the laser bandwidth and the zero order state spread of oscillator strength over the true eigenstates. Case 1: Zero order state oscillator strength spread ($1/\pi T_2$) less than bandwidth of pulse $\Delta\nu_L$. Case 2: Oscillator strength spread ($1/\pi T_2$) greater than $\Delta\nu_L$.

case (2) is it appropriate to say that T_1 can be faster than the pulse duration. In the language appropriate for the QC model and the zero order states, T_1 is the time for energy relaxation from the driven mode into the heat bath of states, comprised of the rest of the molecule. For the true vibrational eigenstates the concepts of intramolecular T_1 and T_2 are inapplicable. However, they may be used in a different context to describe the fluorescence lifetime of the exact state or collisional effects on them.

The expression in Eq. (1) is derived from Fermi's golden rule and, if satisfied, should give rise to strictly fluence dependent energy absorption. From our 50 and 70 ps energy deposition results, this appears to be reasonably satisfied. Furthermore, if the right-hand side of Eq. (1) is not satisfied, then we expect the transition rate to be larger than $1/T_2$. From our experimental results, the transition rate of 1.6 cm^{-1} is not significantly different in magnitude from the laser pulse bandwidth of $1.3 \text{ cm}^{-1} (=2\pi\Delta\nu_L)$. Since the pulse bandwidth is proportional to the inverse of the pulse duration t_{pulse} , the implication is that $t_{\text{pulse}} < T_2$ if the transition rate is larger than T_2^{-1} . If this is the case (case 1 of Fig. 7), temporal structure in the absorption spectrum beyond the pump pulse duration should be pro-

duced, even when the left-hand side of expression (1) is satisfied at 100°C . Clearly this is not observed in our results, indicating case (2) is correct, and $T_1 < 50 \text{ ps}$. In a later argument we will show that the anharmonic shifts of modes $7a$ and $20b$ indicate an equilibration with each other during the laser pulse. This also supports case (2) as the correct situation, indicating rapid randomization.

It is worth noting that the oscillatory behavior we observe may arise from one of several effects which are related to the different types of dephasing that are experimentally observable. The first effect may involve the coherent excitation of a linear superposition of vibrational states of the molecule. This gives rise to quantum beats and is a homogeneous effect. A second cause is related to the inhomogeneous broadening of the absorption band. The laser pulse excites simultaneously states in different molecules that fall within the bandwidth of the laser pulse. The different precession frequencies of the excited dipoles then give rise to beats in a manner similar to free induction decay. Rather than establishing the exact nature of the oscillations, we choose to emphasize the ability to make all oscillatory behavior disappear by increasing the temperature of the molecule. It is this behavior which delineates the discrete state region from the QC region in the quasicontinuum model.

A unique feature of this experiment is the ability to time resolve the shifting and broadening of independent normal modes. These shifts can be used as a measure of the temperature of each mode, and therefore serve as an indicator of the equilibration of energy between the different normal modes. From Table I we can readily observe that the shifts $\Delta\sigma/\sigma$ produced by picosecond pulse heating are in good agreement with the thermal shifts obtained on the Perkin Elmer spectrophotometer. To further underscore this agreement, in Table II we have converted the spectrum shifts of Table I into a final temperature. From the first three lines of Table I it is established that heating the entire molecular distribution into the QC, either by preheating the gas cell or by using a very energetic pump pulse, produces a similarity in the thermal shift of the pumped mode and the shift obtained by picosecond pulse heating.

TABLE II. A comparison of the local temperature of modes $7a$ and $20b$ (obtained from relative cross section changes) as produced by picosecond pulse heating to the thermal temperature expected for the mode. The rows of Table II correspond to the same row in Table I. Error limits on temperatures correspond to 95% confidence limits. Not included in the error limits for the laser obtained temperatures are systematic corrections which may arise from deconvolution of overlapping Gaussian pump and probe pulses.

Laser line (cm^{-1})		Initial cell T ($^\circ\text{C}$)	Energy deposition (CO_2 quanta)	Final T ($^\circ\text{C}$)			
Pump	Probe			Pump/probe	Thermal	Difference	
(1)	1077.3	1077.3	95	2.5	275 ± 40	310 ± 20	35
(2)	1076.0	1076.0	95	2.5	310 ± 40	310 ± 20	0
(3)	1077.3	1077.3	22	4.8	410 ± 40	430 ± 40	20
(4)	1077.3	947.7	22	2.5	280 ± 40	270 ± 20	-10
(5)	1077.3	949.5	22	2.5	255 ± 40	270 ± 20	15
(6)	1077.3	1077.3	22	2.5	245 ± 45	270 ± 20	25

From Table II we see the difference in temperature of the pumped mode produced by the two heating methods (picosecond laser pulse or thermal) for the same molecular energy deposition is no larger than the uncertainty in those temperatures. Furthermore, by using the anharmonic shifts of the unpumped mode $20b$ as the temperature gauge, it not only appears that modes $7a$ and $20b$ reach roughly identical temperatures, thereby indicating complete equilibration (lines 4, 5, and 6), but also picosecond pulse heating is very similar to thermal heating. This last result agrees with our previous work on SF_6 , for which the pump laser pulse produced anharmonic shifts entirely consistent with the thermal shifts expected for the molecule.

It should be mentioned that the thermal shifts $\Delta\sigma/\sigma$ and the picosecond pulse produced shifts should not necessarily be expected to produce absolute agreement even in the case of extremely rapid IVR. Thermally heating the PFB and determining IR spectral shifts on a spectrophotometer also measures the rotational population shifts superimposed on the vibrational band. The pump-probe experiment, however, measures spectral changes which may not include a rotational population which is thermally equilibrated with the vibrations, since collisions would be required for the vibrationally hot PFB to thermalize with all degrees of freedom (rotation and translation). A further assumption regarding the correlation we have drawn between the thermal shifts and the picosecond pulse shifts regards the inhomogeneous broadening of the molecular distribution. Because it is not experimentally feasible, we are unable to obtain the entire double resonance absorption spectrum of each mode $7a$ and $20b$ as was done for the ν_3 mode of SF_6 .³ Instead, we can obtain cross section shifts at only selected wavelengths. In comparing the thermal shifts of the spectrum to the picosecond pulse produced shifts, we have implicitly assumed that every molecule can interact with the picosecond pulses so that inhomogeneous effects such as hole burning do not occur (see, e.g., our SF_6 work). Using $\Delta\sigma/\sigma$ at selected wavelengths rather than obtaining the entire absorption spectrum of the mode could conceivably lead to large discrepancies between the temperature assigned to the molecular distribution after laser heating and the actual temperature of the fraction of molecules that were pumped. For a large molecule such as C_6F_5H , with 30 normal modes, the density of states is large and the assumption that every molecule has an allowed transition within the broad 50 ps pulse bandwidth may be good. Otherwise, the agreement noted in Tables I and II between the laser pulse heating and thermal heating would be extremely fortuitous.

From the mode $7a$ absorption linewidth of the 270 °C PFB IR spectrum, we estimate $(\pi T_2)^{-1}$ is at most no larger than 24 cm^{-1} . For $2T_1 > T_2$, this indicates a lower limit on T_1 at $\langle n \rangle \sim 2.5$ of about 0.2 ps. Therefore, at approximately 3850 cm^{-1} above the ground state zero point (the room temperature vibrational heat capacity of PFB plus 2.5 photons of 1077 cm^{-1} energy), we conclude 0.2 ps $< T_1 < 50$ ps. While the upper limit for T_1 is established from experiment, the lower limit should be understood as approximate only, since the

relationship between T_1 and T_2 for a multilevel system such as C_6F_5H is not established.

CONCLUSIONS

By using picosecond time resolved spectroscopy, we have monitored the shifting and broadening of the pentafluorobenzene IR absorption spectrum when the molecule is subjected to picosecond pulse heating. Basing our description on the QC model, we have observed discrete state effects, as exhibited by oscillatory behavior in the time resolved absorption spectrum, to disappear when the molecule is heated into the QC. This was accomplished by preheating the molecules followed by a 50 ps pump pulse, or by using a very energetic 70 ps pump pulse. Using either method to put the molecular ensemble into the QC, the lack of transient temporal structure in the absorption spectrum after the disappearance of the pump pulse indicates rapid equilibration of energy in the molecule, on a time scale faster than our 50 ps pulse duration.

The ability to pump and probe at independent wavelengths gives this experiment the added feature of being able to study independent normal modes. This allows us to more firmly establish the statistical nature of the intramolecular relaxation process. By using the relative cross section changes obtained from picosecond pulse heating as a measure of the temperature of each mode, our results indicate rapid equilibration of the energy between modes. Furthermore, the picosecond pulses appear to produce shifts in reasonable agreement with the thermal shifts of the molecule for the same energy deposition. The implication of these results is consistent with the absence of any transient temporal structure in the absorption spectrum for molecules heated into the QC. Together, these imply the 50 ps pump pulse distributes its energy throughout the molecule within the pulse duration, and produces an equilibrium state very nearly thermal.

Extremely fast collisional effects have been observed in PFB by using helium as a buffer gas. The approximately 2 ns Torr collisional phase relaxation rate of the coherent state prepared in PFB compares with an equally rapid rate obtained in earlier work on SF_6 . These long range interactions emphasize the essential need of ultrashort pulses and low densities for studying intramolecular vibrational relaxation in order to eliminate collisional effects.

ACKNOWLEDGMENTS

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