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 predissociation and high pressures (10 kTorr and higher) of quenching gas to serve as timing elements in the fluorescence spectra of vibronically 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.

In earlier experiments on SF6, we studied the behavior of the triply degenerate ν2 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 ν2 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 elucidate 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. 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 microcomputer.

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-
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 μm region. Although very little work has been done on this molecule, the infrared features have been assigned by Long and Steele. 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 7α 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 7α 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 scans, for which the average number of photons absorbed per molecule (μ) 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
effect of heating the gas and performing the pump–
probe experiment at 1077.3 cm\(^{-1}\) for \(<\nu>\sim 2.5\). The
experiments were conducted at constant pressure,
giving rise to slight changes in the ordinate for each
scan. At the highest cell temperature (~ 100 °C), where
the superimposed oscillations have disappeared, the
redshift in the absorption profile of mode \(7a\) is ex-
trremely small (< 0.5 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 CO\(_2\) laser line at 1076.0 cm\(^{-1}\) with the cell at the
elevated temperature. Just as for the R16 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 cal-
culating the vibrational heat capacity of PFB using
the harmonic approximation and then using the Whitten–
Rabinovitch method to obtain the density of vibrational
states \(\rho\). 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 \(<\nu>\sim 2.8\), 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 mole-
cule, and clearly there is a complete absence of dis-
crete state effects as indicated by the lack of oscil-
latory behavior. From our energy deposition experi-
ments 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 \(<\nu>\sim 2.5\) 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 Å between the PFB molecule and the
helium atom. These long-range collisional interac-
tions once again emphasize the importance of working
in a collisionless environment when studying intra-
molecular relaxation processes.

![Figure 5](image-url)
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 Δσ/σ, accounting for the deconvolution of the overlap of the weak Gaussian probe pulse with the intense pump pulse, are not included in these errors.

<table>
<thead>
<tr>
<th>Laser line (cm⁻¹)</th>
<th>Pulse</th>
<th>Initial</th>
<th>Energy</th>
<th>Δσ/σ(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump</td>
<td>Probe</td>
<td>duration (ps)</td>
<td>cell T (°C)</td>
<td>deposition (CO₂ quanta)</td>
</tr>
<tr>
<td>(1) 1077.3(R18)</td>
<td>1077.3</td>
<td>50</td>
<td>95</td>
<td>2.5</td>
</tr>
<tr>
<td>(2) 1076.0(R16)</td>
<td>1076.0</td>
<td>50</td>
<td>95</td>
<td>2.5</td>
</tr>
<tr>
<td>(3) 1077.3</td>
<td>1077.3</td>
<td>70</td>
<td>22</td>
<td>4.8</td>
</tr>
<tr>
<td>(4) 1077.3</td>
<td>947.7(P16)</td>
<td>50</td>
<td>22</td>
<td>2.5</td>
</tr>
<tr>
<td>(5) 1077.3</td>
<td>949.3(P14)</td>
<td>50</td>
<td>22</td>
<td>2.5</td>
</tr>
<tr>
<td>(6) 1077.3</td>
<td>1077.3</td>
<td>50</td>
<td>22</td>
<td>2.5</td>
</tr>
</tbody>
</table>

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 Δσ/σ 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 Δσ/σ, due to the fact that the weak probe pulse spatially averages Δσ 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 Δσ/σ in Table I. The errors for the thermal shifts Δσ/σ 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) model for IRMPA. It is apparent at room temperature PFB is not yet completely in the QC as defined by

\[ \frac{1}{\hbar \rho} \ll \text{transition rate} \ll \frac{1}{T_2}, \]

(1)

where \( \rho \) 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 \( 1/\tau \), where \( \sigma \) is the absorption cross section and \( \hbar \omega \) is the photon energy.

From the Whitten–Rabinovitch calculation, \( \rho \) is approximately \( 6/cm^4 \) at room temperature. The transition rate for the conditions of the experiment is approximately \( 1.6 \text{ cm}^{-1} \) (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 spectra.

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 \( \rho \) is approximately \( 120/cm^4 \). The 50 ps pump pulse energy deposition of \( \rho \) 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 temporarily 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 \( \omega _R \approx 1/T_2 \), 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

\[ \frac{dW_s}{dt} = \left[ s \sigma (W_{s+1} - W_s) + (s + 1) \sigma (W_{s+1} - W_s) \right] \frac{1}{\hbar \omega _R} + \text{damping}, \]

(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

\[ \frac{dW_s}{dt} = -\frac{W_s}{T_1} . \]

(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. A subsequent decay would indicate energy relaxation of the excited state.

Implicit in our preceding statement \( T_1 < 50 \text{ ps} \), 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

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 fluorescence 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 from the laser pulse bandwidth of 1.3 cm$^{-1}$ ($\Delta v_L$). Since the pulse bandwidth is proportional to the inverse of the pulse duration ($1/\tau$), the implication is that $\tau_{\text{pulse}} < T_2$ 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 produced, 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 $T_1 < 50$ ps.

In a later argument we will show that the anharmonic shifts of modes 7a and 20b indicate an equilibrium 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 quasi-continuum 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 equilibrium 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.

<table>
<thead>
<tr>
<th>Laser line (cm$^{-1}$)</th>
<th>Initial cell $T$ (°C)</th>
<th>Energy deposition (CO$_2$ quanta)</th>
<th>Final $T$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pump</td>
<td>Probe</td>
<td></td>
</tr>
<tr>
<td>(1) 1077.3</td>
<td>1077.3</td>
<td>95</td>
<td>2.5</td>
</tr>
<tr>
<td>(2) 1076.0</td>
<td>1076.0</td>
<td>95</td>
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</tr>
<tr>
<td>(3) 1077.3</td>
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<td>22</td>
<td>4.8</td>
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<tr>
<td>(4) 1077.3</td>
<td>947.7</td>
<td>22</td>
<td>2.5</td>
</tr>
<tr>
<td>(5) 1077.3</td>
<td>949.5</td>
<td>22</td>
<td>2.5</td>
</tr>
<tr>
<td>(6) 1077.3</td>
<td>1077.3</td>
<td>22</td>
<td>2.5</td>
</tr>
</tbody>
</table>
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 mo-
lecular energy deposition is no larger than the uncer-
tainty in those temperatures. Furthermore, by using
the anharmonic shifts of the unpumped mode 206 as the
temperature gauge, it not only appears that modes 7a
and 206 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 SF₆, for which the pump laser pulse produced anhar-
memonic shifts entirely consistent with the thermal shifts
expected for the molecule.

It should be mentioned that the thermal shifts Δω/σ
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 popu-
lation 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 (ro-
tation and translation). A further assumption regard-
ing the correlation we have drawn between the thermal
shifts and the picosecond pulse shifts regards the in-
homogeneous broadening of the molecular distribution.
Because it is not experimentally feasible, we are un-
able to obtain the entire double resonance absorption
spectrum of each mode 7a and 206 as was done for the
ν₃ mode of SF₆. 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 SF₆ work). Using Δω/σ at
selected wavelengths rather than obtaining the entire
absorption spectrum of the mode could conceivably lead
to large discrepancies between the temperature as-
signed 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
C₆F₅H, 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 band-
width 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 (τ7a) is at most no
larger than 24 cm⁻¹. For 27a > Tg, this indicates a lower
limit on Tg at (ω) ~ 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 < Tg < 50 ps. While the upper limit for
Tg is established from experiment, the lower limit
should be understood as approximate only, since the
relationship between Tg and T₂ for a multilevel system
such as C₆F₅H is not established.

CONCLUSIONS

By using picosecond time resolved spectroscopy, we
have monitored the shifting and broadening of the penta-
fluorobenzene IR absorption spectrum when the mole-
cule is subjected to picosecond pulse heating. Basing
our description on the QC model, we have observed
discrete state effects, as exhibited by oscillatory be-
havior 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 independently 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 agree-
ment with the thermal shifts of the molecule for the
same energy deposition. The implication of these re-
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 approxi-
mately 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 SF₆.
These long range interactions emphasize the essential
need of ultrashort pulses and low densities for studying
intramolecular vibrational relaxation in order to elim-
nate collisional effects.

ACKNOWLEDGMENTS

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