

Picosecond infrared double resonance studies on SF₆

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A classic pump-probe experiment is performed on SF₆. Using 30 psec pulses from two independently tunable CO₂ lasers, we have studied the intramolecular energy transfer processes occurring in a collisionless environment. Distinct from nanosecond pulse experiments, we find an extremely narrow and deep hole burning feature at the pump wavelength. Experimental results exhibit both discrete state bottlenecking effects and quasicontinuum absorption. New evidence of an extremely rapid collisional relaxation is found, which may be related to rotational hole filling.

INTRODUCTION

Following the discovery of infrared multiple photon absorption¹ there has been a great deal of interest in laser induced chemistry. Experiments purporting to show molecules for which mode selective chemistry may be feasible, as a result of some nonstatistical nature in the excitation process, have recently been reported.² Very fundamental questions concerning molecular behavior are raised by such work. First, it would be extremely useful to establish if the energy of excitation remains localized to a small subset of the total number of degrees of freedom, or whether it is randomized throughout the entire molecule. Perhaps even more important would be a determination of the rate at which energy relaxation occurs in the isolated molecule. Clearly, if the rate at which an equilibrium condition is restored is relatively slow, the potential of utilizing the excited state in a chemical manner would be greatly enhanced. Theoretical models for calculating the rates exist,³ but as yet there have been few direct experimental attempts to measure the intramolecular relaxation rates in a collisionless environment.⁴ With this in mind, we report the results of a standard pump-probe experiment conducted on SF₆, utilizing 30 psec pulses from two independently tunable CO₂ lasers. These experiments show the dynamic response of the ν_3 mode fundamental absorption spectrum to a multiple photon excitation, and indicate large qualitative differences with respect to nanosecond pulse experiments.

The quasicontinuum model⁵ is generally accepted for describing the multiple photon absorption process in SF₆. At low excitation, the discrete states of the fundamental ν_3 mode are expected to be important and intensity effects may be apparent. Saturation, or bottleneck effects, may be observed; when the internal energy is relatively small, the density of states is low and, therefore, the laser pump rate may exceed the intramolecular damping rate. At higher levels of excitation, the discrete nature of the driven mode is no longer significant. The heat bath, comprised of the rest of the molecule, forms a nearly continuous background to which the driven mode relaxes by a T_1 -type damping process. We may regard each state in the quasicontinuum of states as a superposition of all the normal modes. In this re-

gime laser fluence rather than laser intensity plays the dominant role. The size of the molecule and the strength of coupling between the driven mode and heat bath determine the relative importance of the discrete states versus the quasicontinuum (QC), as has been well determined in experiments by Black.⁶

Earlier work by Kwok⁷ on SF₆, limited experimentally to pump and probe pulses of identical wavelength, investigated the behavior on a picosecond time scale at the 10.59 μ CO₂ P20 laser line. By extending the techniques of that experiment, we are now able to obtain a complete double resonance spectrum on a 30 psec time scale. The short pulse domain allows us to observe the excitation and relaxation dynamics in a collisionless environment. This feature is established here with more certainty than in the many double resonance experiments performed on SF₆ using nanosecond CO₂ laser pulses.⁸ Their collisionless conditions are often assumed or implied without adequate proof.

The general technique we employed involved pumping the ν_3 mode of SF₆ with a CO₂ laser tuned to the P20 line at 944.2 cm⁻¹. The 1 cm⁻¹ bandwidth of the 30 psec pulses washes out all fine structure effects in the absorption spectrum. The vibrational Hamiltonian of the molecule may be approximated as

$$H_0(v) = \sum_i \omega_i v_i + \sum_i X_{i_i} v_i (v_i + g_i) + \frac{1}{2} \sum_i \sum_{k \neq i} X_{i_k} v_i (v_k + g_k) + \sum_i \sum_{k \neq i} G_{i_k} l_i l_k + \dots,$$

where the X_{i_k} 's and G_{i_k} 's are anharmonicity coupling constants between the i and k normal modes, and ω_i , g_i , l_i , and v_i are the normal mode frequency, degeneracy, vibrational angular momentum, and quantum occupation number, respectively. Recent analysis of the high resolution spectrum of the $3\nu_3$ manifold of SF₆ has determined many of the anharmonicity constants for this mode, and thereby enabled the determination of many of the ν_3 mode vibrational eigenstates and energies.⁹ In addition to the states identified in Ref. 9(d) (which already includes anharmonic splitting within the ν_3 mode), one should consider the effects of the non-negligible hot band background and Coriolis coupling (which causes a breakdown in the standard selection rules for $J > 30$ ^{9d}) when dealing with room temperature SF₆. The proliferation of states available for pumping by a CO₂ laser when all important effects are included (rotational states must also be ac-

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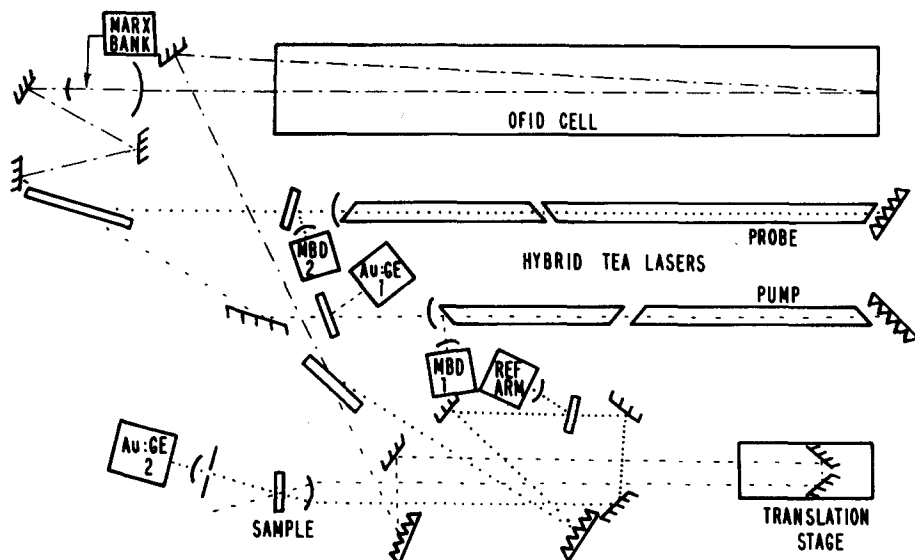


FIG. 1. A schematic diagram of the apparatus. Electronic feedback from MBD (mode beating detector) 1 and 2 stabilize each of the lasers to a single longitudinal mode. Au:Ge 1 is a gold-doped germanium detector used to trigger the Marx bank at the plasma shutter synchronous with the peak of the pump pulse. Au:Ge 2 monitors the probe transmission through the sample.

counted for³⁰) implies the multiple photon absorption pathways for SF₆ at 300°K are extremely numerous and complex.

The previously accepted method for analyzing the dynamic behavior of the ν_3 mode is based on the crude approximation that the vibrational Hamiltonian is dominated by the term X_{33} . This simplification implies the pumping process produces an initial redshift given by $2X_{33}$ per CO₂ photon absorbed. As the energy leaks from the driven ν_3 mode, the redshift would approach a value given by the temperature shift of the absorption spectrum. Only if the time scale for this T_1 -type relaxation is longer than the picosecond pulse duration would a transient behavior of the absorption spectrum as depicted in Fig. 1 of Ref. 7 be seen.

There are several reasons this line of reasoning is no longer as compelling as it once was. From the $3\nu_3$ overtone spectroscopy and its analysis, the constant X_{33} has been revised to -1.74 cm^{-1} , down from values in the range of -2.5 cm^{-1} from earlier studies. Therefore, the decrease in redshift from $2X_{33} = -3.5 \text{ cm}^{-1}$ to -2.6 cm^{-1} per CO₂ photon absorbed (which is the thermal redshift obtained from the shock tube experiments of Nowak and Lyman¹⁰) would be small, although probably not impossible to observe with our apparatus. Furthermore, the recent overtone spectroscopy analysis indicates the anharmonic splittings within the ν_3 mode are large relative to the difference between the self-anharmonic shift $2X_{33}$ and the thermal redshift of -2.6 cm^{-1} per photon. This implies the vibrational Hamiltonian is no longer dominated by the term X_{33} and so the crude approximation of neglecting all other anharmonic terms is no longer justified. It is, therefore, exceedingly difficult to determine the exact effect one would expect the collisionless energy randomization to have on the absorption spectrum under the conditions of our experiment (SF₆ at 300°K and a 1 cm^{-1} bandwidth pulse). However, we emphasize strongly that if the energy damping process occurs on a time scale faster than the 30 psec pulse duration, or if the initial excitation involves a superposition of states in the QC which

dephase just as rapidly, then one *should not expect any* transient behavior of the absorption spectrum after the excitation pulse has disappeared. Under these conditions, only a steady state value of the excited state absorption spectrum would be observed in our experiment. Collisional effects would be responsible for producing all subsequent changes after the disappearance of the pump pulse.

EXPERIMENT

A schematic diagram of the apparatus used in this experiment is presented in Fig. 1. Essentially, the apparatus consists of four parts: (1) two independently tunable CO₂ lasers, (2) a plasma shutter and optical free induction decay (OFID) cell for generating picosecond pulses, (3) a translation stage to provide the variable delay between the pump and probe pulses, and (4) a computer and interface to control data acquisition and monitor the experimental variables shot to shot.

Both CO₂ lasers are grating tuned hybrid TEA lasers. The pump laser is a Tachisto model 215 CO₂ oscillator which, for the purposes of this work, was tuned to the P20 CO₂ line. The probe laser was of the pin resistor variety, operated at approximately 1/2 atmospheric pressure. Using a novel feedback circuit designed in our laboratory¹¹ in conjunction with the low pressure intracavity gain section, both lasers were stabilized to oscillate single axial mode and TEM₀₀. The smooth temporal profile of the pulses greatly reduced fluctuations in the experiment. The lasers were operated at 1 pps and synchronized to a point such that the rms jitter between their onset of lasing was only 60 nsec. Before the plasma shutter short pulse producing process, we have an 80 nsec FWHM pump pulse of approximately 0.6 J and a 220 nsec FWHM probe pulse of approximately 60 mJ.

The orthogonally polarized pump and probe beams were combined into a single path and passed through a plasma shutter, triggered to fall at the peak of the pump laser pulse. The details of the plasma shuttering and

OFID cell used to produce short pulses has been reported elsewhere.¹² The smooth temporal profile of the pump pulse, along with Marx bank triggering of the plasma shutter, leads to only a 6% fluctuation in the amplitude of the truncation point of the pump pulse. This in turn reduced the amplitude fluctuation of the picosecond pump pulse produced by the free induction decay process. The 60 nsec rms jitter between the lasing of the pump and probe lasers means the point at which the probe pulse was clipped at the falling of the plasma shutter varied from shot to shot. However, in addition to its smooth temporal profile, the probe pulse was nearly three times longer in duration than the pump. Hence, the fluctuation in the amplitude of the truncation point of the probe was minimized. By varying the pressure of hot CO₂ in the OFID cell following the shutter from 140 to 250 Torr, we could control the pulse duration from 50 psec to approximately 30 psec FWHM. Since only one shutter is used, there is no time jitter between the pump and probe picosecond pulses; the time jitter in lasing between the two pulsed CO₂ lasers has been converted predominately to an amplitude jitter in the picosecond pulse of the probe laser. However, even this was not a severe problem. A reference arm was constructed and inserted in the probe arm to measure the energy of the picosecond probe pulse shot to shot. Fluctuations in probe pulse amplitude were eliminated by normalizing to its energy. Since the probe pulse was attenuated to a point where it operated in a linear absorption regime (i.e., a very weak probe), it could be normalized in a straightforward manner.

Once the picosecond pulses emerged from the OFID cell, they were separated by polarization (using a Brewster angle beam splitter) and wavelength (using gratings). As previously stated, a reference arm consisting of a Moletron P1-51 pyroelectric detector and FET preamp along with a homebuilt gain 100 amplifier, was inserted in the probe beam path. A Velmex Uni-slide translation stage and Superior Electric stepping motor provided a variable delay to the picosecond pump pulse in the standard arrangement for this type of experiment. For the work on SF₆, attenuators (CaF₂) were inserted in the probe arm to greatly reduce the picosecond probe pulse energy.

Zero time delay in this experiment is determined by monitoring the probe transmission through a crystal of p-type germanium, a known intensity saturable absorber for the 10.6 μ radiation ($J_s \sim 3.2 \text{ MW/cm}^2$). When a strong saturating pump pulse overlaps spatially and temporally with the probe pulse in the crystal, the probe pulse absorption is strongly bleached. In addition, since the p-Ge is known to relax from this saturating process in about one picosecond, we were able to obtain information on the picosecond pulse autocorrelation function. The OFID process produces a ringing in the tail of the picosecond pulse which we are now experimentally able to observe using this newly constructed apparatus. From the pseudoautocorrelation traces obtained from the p-Ge experiment and from theoretical calculations we can estimate that the ringing in the tail has a peak intensity seven times smaller than the peak intensity of the pulse, but that the tail contains approximately 25%

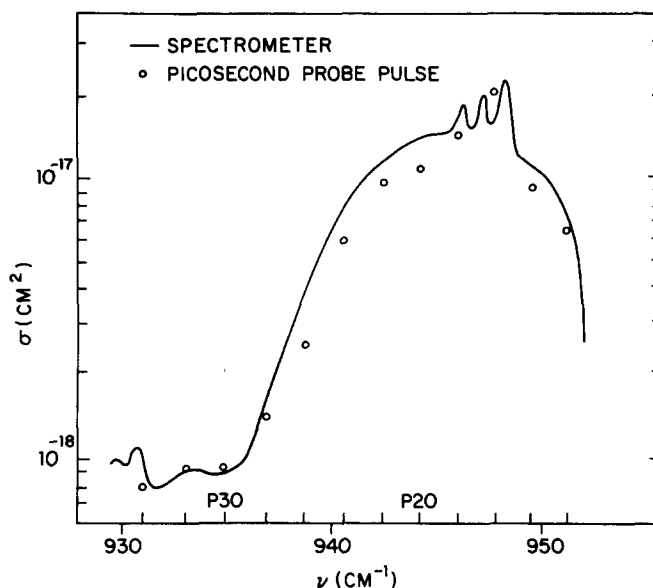


FIG. 2. A low-level cw version of the ν_3 band of SF₆ at room temperature [from Ref. 8(d)] versus the one we obtain from the probe pulse (no pump).

of the total pulse energy.

The focussing arrangement for the crystal or the gas cell experiment is also shown in Fig. 1. In the gas cell experiment, the cell length was kept at least twice as short as the confocal parameter for the beams at that point in order to minimize fluence variations through the cell. Cell lengths were 3.4 mm or less. The probe laser short pulse was attenuated such that its integrated energy was typically several hundred times less than the pump pulse. The best check that our probe laser pulse was indeed in the linear absorption regime is indicated by Fig. 2, where a comparison is made between a spectrometer version of the SF₆ absorption spectrum, and our measured absorption spectrum using the probe laser pulse. The absence of preheating by the probe pulse seen here is not apparent in most nanosecond pulse double resonance experiments, which complicates their interpretation. The transmission through the sample (crystal or gas) was monitored by a liquid nitrogen cooled Au:Ge detector followed by a second homebuilt gain 100 amplifier. Both detector and amplifier signals were kept well within their linear regime of operation.

A home assembled Digital Equipment Corporation LSI-11 microcomputer and interface monitored analog signals (the reference arm and probe transmission signal), the quality of the laser pulses (a check for mode beating), and controlled the movement of the translation stage. Data were displayed on a Type 611 Tektronix storage display screen as it was accumulated, and repetitive scans of the translation stage were made until a reasonable signal to noise ratio was obtained. Data from the run were then stored on a floppy disk.

An advantage to using 30 psec pulses is that pressure requirements can be relaxed relative to those used in 100 nsec CO₂ laser pulse experiments, and yet still remain in a collisionless environment for several hundred picoseconds. The SF₆ gas pressure for our experiments

was in the range of 4 to 16 Torr; variations of the absorption cross section through the ν_3 spectrum necessitated these pressure adjustments. For a given pump pulse fluence, the induced change in the absorption cross section, obtained from the transmission data, was independent of the pressure in this range. In support of the collisionless domain in which we work, a significant deviation from Beer's law of the P20 pump (at constant input fluence) occurred at pressures above 20 Torr. The deviation was towards a larger effective cross section (decreased transmission of the pump pulse) at these higher pressures, indicating collisions may be aiding the absorption process. The gas itself was commercially obtained electronic grade and used without further purification.

At no time was the optical thickness of the sample allowed to exceed a value that produced more than 50% absorption of the pump pulse. Fluence corrections for the absorption along the path were made as previously reported.¹³ The number of photons absorbed by SF₆ for a 30 psec, or a 50 psec, CO₂ P20 laser pulse of a given fluence, corrected for the Gaussian profile of the beam, has also been previously determined.¹⁴ Beer's law was used to obtain the gross absorption cross section of the probe laser pulse.

Recently, it was reported that self-focusing effects were observed in SF₆ and represented an overlooked problem in previous high intensity multiphoton data of this molecule.¹⁵ The reported experiments utilized 1.5 nsec CO₂ laser pulses on SF₆ in a 10 cm long cell. Despite the higher intensities achieved with 30 psec pulses, the considerably shortened cell in this work (≤ 3.4 mm) more than compensates for the problem. Textbook treatment of the matter¹⁶ indicates that Z_f , the beam focusing distance, varies in a manner proportional to $I^{-1/2}$. Hence if we are in a cell 30 times shorter and have an intensity 30 times higher than the corresponding 1 nsec pulse experiments, then self-focusing effects present less of a problem for the picosecond pulse experiments. For the purposes of this work, we have fixed the pump laser to the CO₂ P20 line. We estimate the absolute error in the laser fluence to be 50%, although the relative error is much smaller (10%). Slight self-focusing or defocusing effects will change the relative error in the pump fluence only slightly in the narrow fluence range studied with the 30 psec pulses (0–30 mJ/cm²) and will not change the temporal behavior or absorption characteristics of the probe pulse at the different laser lines at all.

RESULTS

Figure 3 illustrates typical scan results obtained for various probe laser lines, as indicated. The fluence of the 30 psec pump laser pulse for these scans was in the 20–30 mJ/cm² range, for which the average number of photons absorbed per molecule $\langle n \rangle$ was 4–6. The zero of the time scale was taken as the overlap of the peaks of the pump and probe laser pulses. There are several general features to be pointed out. In addition to the bleaching of the probe absorption at the P20 pump line, there is a saturation effect from which there is a rapid

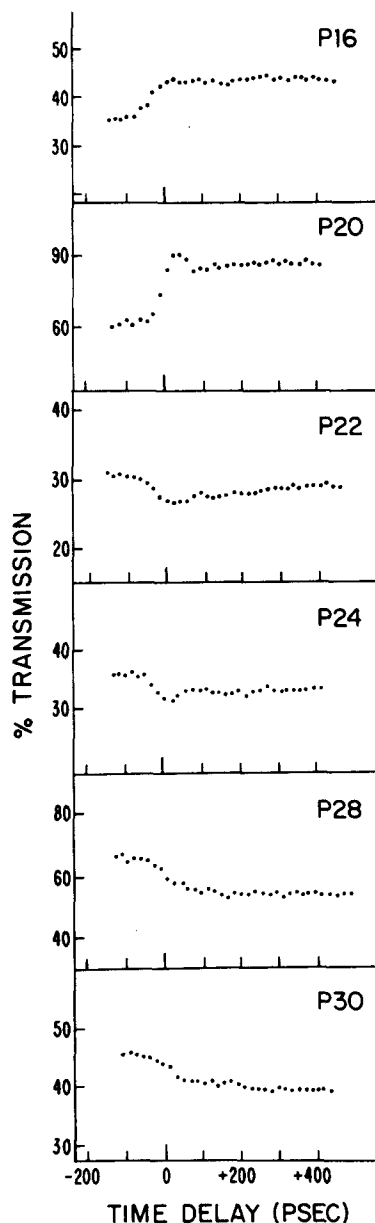


FIG. 3. Typical transmission data obtained at the probe lines indicated in the figure, for an average excitation of 4–6 photons/molecule by the P20 pump. Note the difference in the vertical scale for the scans.

recovery at the same wavelength. To a much lesser degree, the P24 and P22 probe lines also show rapid partial recovery from a similar saturation effect. At no other probe wavelengths were such rapid saturation transients observed. This saturation "spike" at the pump wavelength has previously been observed,⁷ but is seen here for the first time at off pump lines.

In the region 7–11 cm⁻¹ to the long wavelength side of the pump, in the neighborhood of the P28, P30 and P32 probe lines, we observe the increase in absorption induced by the pump excitation, i. e., redshifting. In this region the temporal behavior of the induced absorption very nearly follows the instantaneous integrated energy of the pumping pulse. No rapid recovery from saturation is observed at these wavelengths. To the short

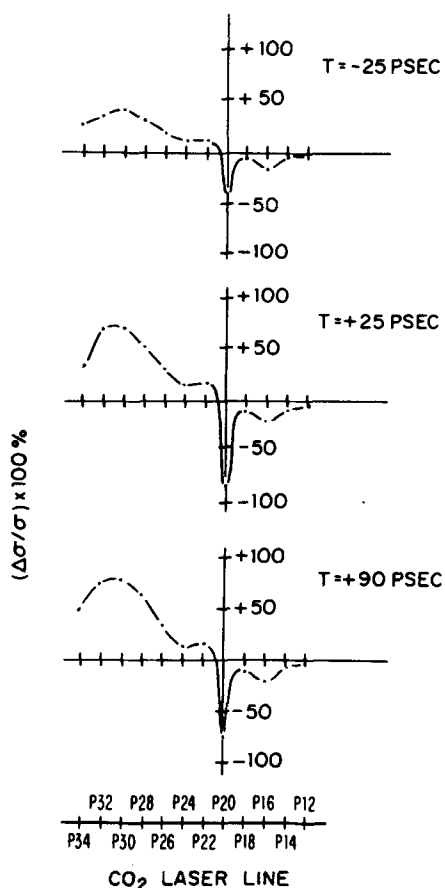


FIG. 4. Collisionless behavior of the absorption spectrum of SF₆ for P20 pump pulse excitation of 4–5 photons/molecule ($J=22.5 \text{ mJ/cm}^2$). The connecting line is drawn only as a visual aid.

wavelength (blue) side of the pump line, induced transmission occurs. In comparison, the amount of bleaching at these lines is far less than occurs at the pump wavelength.

Curves such as those in Fig. 3 were obtained over the fundamental ν_3 absorption spectrum for a range of fluences up to approximately 25 mJ/cm^2 for the 30 psec pump pulse. A simple Beer's law analysis was then used to express the result in terms of an absorption cross section as a func-

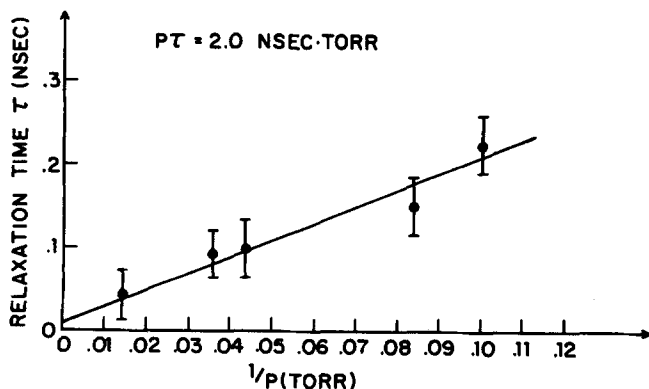


FIG. 5. Pressure-time relaxation constant obtained from the collisional effects observed at P18 and P22. The line is a least squares fit of the data with slope 2.0 nsec-Torr .

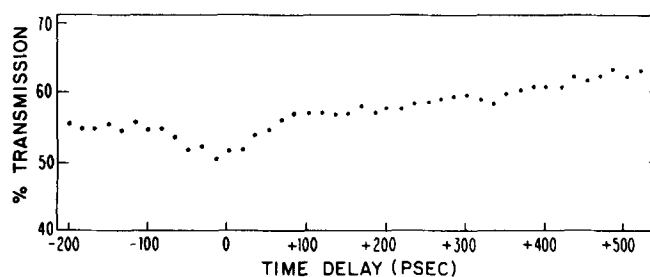


FIG. 6. Transmission of a P22 probe for very high levels of excitation ($\langle n \rangle > 10$ photons/molecule) showing the initial induced absorption occurring at the leading edge of the pump pulse followed rapidly by induced transmission as the pump pulse reaches peak intensity. At later times ($t > +200 \text{ psec}$) the induced transmission due to the rapid 2 nsec-Torr collisional effect is seen.

tion of time and pump laser fluence. Figure 4 shows such a time sequence for which the average number of photons absorbed per molecule is approximately four to five. The noteworthy features are the extremely sharp hole burned at the pump laser line, the buildup of absorption at around P30–P32, and the lack of significant bleaching to the blue side of the pump wavelength. The sharp hole is in distinct contrast to the results of previous nanosecond double resonance experiments, for which broad bleaching occurs to both sides of the pump line. Temporally, the transient behavior is such that only a monotonic increase in the absorption in the P30 to P32 region is observed; this increased absorption does not shift from these wavelengths with time (in the absence of collisions). Essentially no change in the absorption spectrum occurs after the pump pulse disappears, until collisional effects begin to occur.

In addition to the previously observed pressure dependent recovery at the P20 pump line (with a pressure time relaxation rate of 13 nsec-Torr), even faster collisional effects occur to both sides of the hole burning feature. At both the P18 and P22 probe lines we were able to detect a small increase in the probe transmission which rapidly leveled off to a quasistationary value. Within the signal to noise ratio the pressure-dependent relaxation rate was the same at both probe lines. The results are plotted in Fig. 5 and give a pressure-time relaxation constant of 2 nsec-Torr , at an average excitation of four–six photons per molecule.

Using 50 psec pulses, the region of P20 to P24 was studied at higher fluences. The following effects were observed. At the P20 pump line, the saturation spike gradually decreased in size until it was almost nonexistent when an average of approximately 15 photons were deposited in the molecule. At P22, 1.8 cm^{-1} to the red, bleaching occurred at the high excitation ($\langle n \rangle \sim 15$ photons/molecule, where previously only induced absorption was observed ($\langle n \rangle \sim 5$). This is consistent with burning a wider hole at the larger Rabi frequencies achieved by the higher fluence levels. In fact, at the P22 line, for $\langle n \rangle \sim 10$ –12 photons/molecule we were able to observe induced absorption occurring simultaneously with the rising edge of the pump pulse, which then rapidly turned to bleaching as the pump reached its peak intensity. Figure 6 shows this feature and also

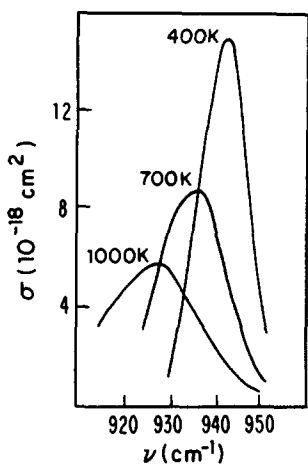


FIG. 7. Absorption cross section/molecule in a thermal ensemble of SF₆. Not shown is the background absorption of about 10^{-20} cm².

the collision induced increase in transmission observed at both sides of the pump line.

The $\nu_2 + \nu_6$ combination band was checked for transient behavior with the P32 CO₂ line at 983.2 cm⁻¹. The factor of 100 smaller cross section at this probe wavelength made observation difficult, and within the signal to noise no detectable changes in the absorption were found to be induced by the P20 pump.

DISCUSSION

Earlier we noted the temporal response of the absorption spectrum in the P28–P32 region reflected the instantaneous integrated energy of the pump pulse. The buildup in absorption at these wavelength did not shift position with time, indicating the SF₆ has already completed all intramolecular relaxation of the four or five CO₂ photons it has absorbed. In comparison, the thermal heating data of Nowak and Lyman,¹⁰ shown in Fig. 7, indicates that at 700–800 °K the peak absorption should occur near the P30 and P32 CO₂ lines. From their calculations, the difference in the average internal vibrational energy of molecules absorbing at P20 at 300 °K and absorbing in the P30 to P32 region when thermally heated to 800 °K is determined to be ~ 4000 cm⁻¹. This is in excellent agreement with our value of $\langle n \rangle \sim 4$ to 5944 cm⁻¹ CO₂ P20 photons deposited as shown in Fig. 4. These results are all consistent with molecular behavior in the QC. Whether the initial excitation involved a superposition of states already in the QC, or whether this indicates energy randomization on a time scale faster than 30 psec, is not determined.

In addition to the narrow hole burning feature in the absorption spectrum, the different nature of the temporal response at the P20, P24, and P30 lines deserves special consideration. The saturation spikes that appear at the P20 and P24 probe lines (illustrated in Fig. 3) are similar in behavior as a function of time and pump fluence and should be considered as related effects. Both transient effects decay away as the pump pulse disappears. By comparing the energy difference be-

tween the P20 and P24 CO₂ lines (-3.6 cm⁻¹), and the self-anharmonic red shift (approximated by $2X_{33} = -3.5$ cm⁻¹) for a single CO₂ photon absorbed by the ν_3 mode, it seems possible that the fast transient is associated with the saturation of some vibrationally excited state of the ν_3 manifold.

It is known from the work of Alimpiev¹⁷ and the assignments of Patterson⁹ that the CO₂ P20 line has a strong two-photon resonance to the $2\nu_3$, A_{1g} level at 1889 cm⁻¹ [the (200) state in the Cartesian basis of Refs. 9(b)–(d)]. This path is believed to play a very important role in the multiple photon dissociation of SF₆ by the CO₂ P20 line. But we also note the states $(n00)$ $n=2, 3, 4 \dots$ are predicted to be the most anharmonically depressed in their respective manifolds and have the greatest likelihood of producing a population bottleneck when pumped by a CO₂ laser. With both the pump and probe laser tuned to P20, strong saturation of a transition by the pump would enhance the transmission of the probe. As the system recovered from the saturation the P20 probe would suffer a corresponding decrease in transmission. If the recovery from saturation is very rapid, the P20 probe transmission will remain enhanced as long as the system is maintained in a state of saturation by a high pump pulse intensity. Hence, the probe transmission will follow the pump pulse shape. The P24 probe could be expected to monitor the saturated excited state population at a redshifted transition frequency of $\sim 2X_{33} = -3.5$ cm⁻¹. This is in accord with the drop in transmission that occurs for the P24 probe while the strong saturation is maintained by the pump pulse. If the state (200) was indeed the saturated state, the (300) level would be expected 938.5 cm⁻¹ above it, coincident with the P26 CO₂ line. We do not observe the saturation spike in the absorption spectrum at this CO₂ line. However, we have ignored the possibility that the saturation effect may be of a hot band transition and have not included such factors as the energy shifts from the ΔJ transitions (~ 0.2 cm⁻¹ per transition). In addition, the bulk red shifting will tend to mask the smaller saturation transients in the absorption spectrum, so it is not unreasonable to expect the saturated excited state might best be detected at the P24 (and P20) probe line. We offer this as only a possibility of the states involved in the saturation process.

The exact nature of the saturation is not clear either, since the distinction between coherent bleaching (self-induced transparency) and incoherent bleaching (where the stimulated absorption rate $I\sigma$ is comparable with or greater than the incoherent decay rate $\hbar\omega/T_1$), is not well characterized in a multilevel, inhomogeneous absorber such as room temperature SF₆. Nevertheless, this saturation spike should be regarded as a manifestation of the discrete states and their role in the excitation process, and as such can be regarded as a bottleneck effect.

Further experimental evidence supports this interpretation. The saturation spike has been shown to decrease as the level of excitation is increased, either by raising the pump fluence, or by using truncated CO₂ pulses to preheat the SF₆.⁷ This is consistent with excitation with-

in the quasicontinuum. Saturation effects become insignificant once a molecule is excited into the QC, since damping rates are expected to be very fast.

In terms of the frequency domain, the hole burned is extremely narrow, less than 2 cm⁻¹ wide, for an average excitation of 4–5 photons per molecule. The maximum Rabi frequency for this field strength is of the order of 10 cm⁻¹. However, in addition to the variation of the effective transition moment for each state $|Jm\rangle$ in the ground state manifold, we also have to consider states in the non-negligible hot band background. These and other effects imply there is a distribution of Rabi frequencies, so a narrow hole is not inconsistent.

For an inhomogeneously broadened line shape function, the important inequalities to satisfy for saturating on resonance, but not off resonance, are

$$1 < \omega_R^2 T_1 T_2 \ll 1 + 4\pi^2 (\nu - \nu_L)^2 T_2^2,$$

where ν_L is the laser frequency, ω_R is the Rabi frequency, and T_2 is the dephasing time obtained from the total rate of phase loss due to all intramolecular energy exchanges. From the experimental data in Fig. 4 we can obtain an estimate of the damping times.¹⁸ From the amount the absorption coefficient g is depressed at the pump wavelength ($\sim 75\%$), we have

$$g_{\text{unsat}}/g_{\text{sat}} \sim 4 = 1 + \omega_R^2 T_1 T_2.$$

The gain is depressed over an interval $\Delta\nu_{\text{hole}}$ given by

$$\Delta\nu_{\text{hole}} \sim (1 + \omega_R^2 T_1 T_2)^{1/2} / T_2.$$

For an average Rabi frequency of 5 cm⁻¹ and a 2 cm⁻¹ wide hole, we find $T_2 \sim 11$ psec and $T_1 \sim 13$ psec. Although these numbers are not surprising, they should only be considered as indicative of the damping times. The model does not include many important effects such as the dynamic redshift (anharmonicity), the distribution of Rabi frequencies because of the multilevel nature of the problem, and the variation of T_1 and T_2 with the internal energy of the molecule. We have not allowed for the fact that our initial excitation may already involve a superposition of states in the QC. We can say that these results are consistent with previous results obtained by Kwok,⁷ for which a lower limit of 1 psec and an upper limit of 30 psec was obtained for the damping time in SF₆ under similar conditions. The upper limit is arrived at easily since intramolecular damping times longer than the pulse duration of 30 psec should produce transients in the absorption spectrum beyond the decay of the pump pulse. Such transients are not observed in our work.

The 11 and 13 psec relaxation times are also consistent with the ability to saturate in the discrete states. Regardless of whether the saturation is coherent or incoherent, the fact that we are able to observe a recovery from the effect implies our pulse duration is approaching the intramolecular damping rates. For example, from $I\sigma \sim \hbar\omega/T_1$ and the intensities involved in the experiment, we would estimate T_1 of the order of 15 psec, again a result consistent with the previous values.

The fast collisional effects observed adjacent to the pump line, at P18 and P22 for the 30 psec pulse low

fluence data, and out to P24 for the higher excitations achieved with 50 psec pulses, have a 2 nsec-Torr relaxation rate. This implies a hard sphere collision diameter of approximately 44 Å. One process which might have such a large gas kinetic cross section would be the relaxation of a coherent state prepared by the pump laser pulse. Another possibility would be a rotational hole filling, occurring either in the ground state or in the non-negligible hot band background. Transitions between the anharmonically split vibrational multiplet components, separated in energy by only a few cm⁻¹, should also be included in this collisional process.

There are several reasons the rotational hole filling interpretation may be correct. First, such a collisional process would be expected to initially deplete states to either side of the burned hole. This depletion of states would continue in the wings until the hole filled and an equilibrium was approached. Furthermore, by increasing the pump pulse fluence, we should expect a wider and wider hole to be burned. The collisional hole filling should then be observed to occur farther and farther into the wings. Both of these effects are observed in our experimental results.

A second reason for the rotational hole filling interpretation is obtained from the comparison of our SF₆ excited state spectrum of $\langle n \rangle \sim 4\text{--}5$ to the work of Fuss^{8d} for the same average excitation. We see that their 70 nsec FWHM pulse achieves significantly large bleaching effects to the red and, especially, the blue side of the pump wavelength (the pressure range stated for their experiment is 0.02–2.5 mbar). Unless they used significantly less than 0.03 Torr (0.04 mbar) in this region of their work, they would suffer from the 2 nsec-Torr collisional process. Obviously, rotational hole filling of some sort would then produce a far greater amount of bleaching to the blue side for the nanosecond pulses as a result of the continual pumping, redshifting, and hole filling process. To a certain extent we were able to check this by probing at the P18 line with 30 psec pulse and increasing the pressure of SF₆ to 70 Torr, which is comparable to the 70 nsec pulse working at 0.03 Torr. The experimental difficulty is that this required us to use an extremely short cell, only 0.05 cm long, in order that the sample did not become optically opaque to the probe. At $t = +200$ psec delay, we observed an 18% decrease in the gross absorption cross section, compared to only a 10% decrease when a pressure of 6 Torr was used (collisionless domain) and at the same pump fluence. This result points out the dramatic difference in heating effects that can be achieved with picosecond pulses when compared with nanosecond pulses, not to be attributed to any nonstatistical behavior, but rather because collisions are avoided.

In experiments utilizing a cw CO₂ probe laser and pulsed pump, Moulton *et al.*¹⁹ observed a 36 nsec-Torr rate of relaxation for a double resonance signal in SF₆. They also attributed this to a rotational relaxation process. The relaxation rate was observed to be faster in the first excited state, 32 nsec-Torr. Perhaps an extrapolation may be made to a 13 nsec-Torr relaxation rate of recovery at the P20 pump wavelength for the ex-

citation to $\nu = 4$ or 5, which we achieve.

By way of comparison, the molecule glyoxal (C₂H₂O₂) is perhaps one of the few large nonpolar polyatomic molecules for which an investigation of level-to-level rotational relaxation has been made. A rotational relaxation rate of $4 \times 10^7 \text{ sec}^{-1} \text{ Torr}^{-1}$ was observed for ΔK transitions.²⁰ Furthermore, a propensity for very small ΔK changes induced by collisions was not found. Individual ΔJ transitions were not experimentally detectable, but conceivably could have an even faster relaxation rate. When the glyoxal decay rate is compared to the 13 nsec-Torr ($7.4 \times 10^7 \text{ sec}^{-1} \text{ Torr}^{-1}$) relaxation found at the pump wavelength and the 2 nsec-Torr ($5 \times 10^8 \text{ sec}^{-1} \text{ Torr}^{-1}$) relaxation rate in the side bands, it is plausible that these effects are related to rotational hole filling. The rotational constant of SF₆ being a factor of twenty smaller than that of glyoxal in its S₁ (¹A_g) state would also contribute to a faster decay rate for SF₆, since a smaller energy exchange would be involved in the inelastic collision.

CONCLUSIONS

Under essentially collisionless conditions and at moderate levels of excitation of SF₆, we have observed two types of behavior in the time evolution of the absorption spectrum. First, a pronounced red shift of approximately 10 cm⁻¹ at an average level of excitation of $\langle n \rangle \sim 4-5$ photons per molecule is found. The temporal response at this longer wavelength generally reflects the integral of the pump pulse energy, and the increase in absorption in this region matches that of thermal heating to 700–800°K. This first effect is consistent with the molecular behavior expected for the quasicontinuum and is essentially a thermal response. A second, more rapidly varying transient, which follows the pump pulse shape, is apparently a saturation effect involving a vibrationally excited state. This second effect is distinctly different in nature from the first and consistent with the behavior expected for a bottlenecked fraction of the molecules.

We have observed an extremely narrow hole burned into the absorption spectrum at the pump wavelength. This observation has not been reported elsewhere because the truly collisionless domain in which the picosecond pulse experiment is conducted is essential. Collisional effects, causing rotational hole filling and state scrambling of vibrational multiplets, have been observed with the extremely fast time constant of 2 nsec-Torr. This would explain the different heating effect achieved with the nanosecond pulse.

Our time-resolved spectroscopy shows no temporal structure, except for collisional effects, beyond the pulse duration. This is consistent with the upper limit previously placed on the relaxation time by Kwok.⁷ Two-level system models can be used to estimate the damping times from our frequency domain results. These models estimate the damping times to be in the range of 10 to 15 psec for $\langle n \rangle \sim 4-5$ photons/molecule. However, we emphasize the need for a more sophisticated treatment which would include the anharmonic and multi-level nature of the problem. Indeed, the initial excita-

tion process for a molecule the size of SF₆ could involve states already in the quasicontinuum.

For SF₆, we are limited in the double resonance experiment to pumping and probing the same mode. In order to observe whether the energy randomization process is actually ergodic would require an astronomically large number of measurements to probe the entire vibrational phase space of the molecule. Operating on a much smaller scale, we are now undertaking experiments in our laboratory to pump and probe molecules with at least two infrared active modes accessible to the CO₂ laser picosecond pulses. These experiments should provide further answers concerning the statistical nature of the collisionless intramolecular relaxation process.

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