

SLOW RELAXATION PROCESSES IN SF₆ GAS AFTER PUMPING BY A CO₂ LASER PULSE

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The vibrational energy relaxation and distribution in SF₆ at the collisional condition of 2 Torr was measured with the pump-probe method by use of two tunable CO₂ 300 ns-pulse lasers at the delay time up to 400 μ s. The 10.6 μ s P(30) pump intensity was 0.4 J/cm². The probed spectra, divided into two parts, the induced transmission at the P(10)–P(22) and the absorption at the P(24)–P(32), were red-shifted by 50 μ s and then slowly back to the initial. The time variation of induced signals was divided into the four regions due to the following processes; (I) the formation of nonthermal distribution in the ν_3 mode and quasi-continuum with 1 μ s, (II) the broad redistribution by the rise-up of vibrational temperature in 50 μ s-duration, (III) the molecular diffusion or expansion out of the pumped region locally heated up by the V–T relaxation in another 60 μ s, (IV) the gas cooling corresponding to the energy relaxation or population depletion over 400 μ s. So, this pump-probe method at the collisional conditions will easily give us some informations, with a short gas cell and a suitable time scale, on those slow processes.

KEY WORDS: Sulfur hexafluoride gas, slow relaxation, carbon dioxide laser, vibrational energy.

INTRODUCTION

The nonlinear absorption properties of SF₆ at CO₂ laser wavelengths have been an interesting subject of research since it was used as the saturable absorber for passive Q-switching in 1967.¹ In addition, after the experiment of the multiphoton dissociation in 1971,² a number of studies of nonlinear absorption or multiphoton excitation in SF₆ were reported on several CO₂ 10.6 μ m P-branch lines.^{3–5} The SF₆ molecule, a typical heavy polyatomic one, has 15 vibrational modes divided into 6 parts (ν_1 – ν_6), which result in formation of the quasi-continuum from a comparatively low energy level (3000 or 5000 cm⁻¹) to the dissociation limit (40,000 cm⁻¹) due to stochasticization of vibrational energy by anharmonic shift, splitting and interaction between the modes.

Up to date there have been a number of pump-probe measurements on vibrationally excited SF₆.^{6–14} However, the dynamic properties of the quasi-continuum are not yet completely understood. Today it is supposed that the vibrational distribution in the state is nonequilibrium and that the energy relaxation depends nonlinearly on the rate of excitation.^{5,15} The molecular collision effects on excitation and relaxation must be also considered because, in fact, collisions are inevitable in most experiments such as a saturable absorber cell usually filled with more than a few Torr of SF₆ gas for the laser pulse duration of a few hundred nanosecond.

We have studied on the properties of nonlinear absorption in SF₆ for a TEA CO₂ laser and found that the absorption spectra was red-shifted with increasing the laser intensity and that the significant difference between the additive effects of He and N₂ suggested the stochastization limit effectively lower down near 2000 cm⁻¹ in the collisional condition.¹⁶ Here, we performed the pump-probe measurement on the vibrational energy relaxation by use of two tunable CO₂ pulse lasers^{9,10} with good time-resolution, without saturation effect by the probe laser itself, and avoiding some coherent interactions between the two beams,¹⁷ instead of the more conventionally used CW probe laser.^{6-8,11-14} We observed the time evolution of absorption spectrum or the induced absorption and transmission by the probe pulse after pumped the SF₆ molecules. Some discussions on slow energy relaxation and dissipation processes will be mentioned.

PRINCIPLE OF MEASUREMENT

As simplified in Figure 1, the energy structure in SF₆ consists of the ν_3 ladder, the quasi-continuum, and the other discrete levels including the lowest state (ν_6 mode) of the bottle-neck for the V-T relaxation. When the first excited state ($\nu_3 = 1$) is

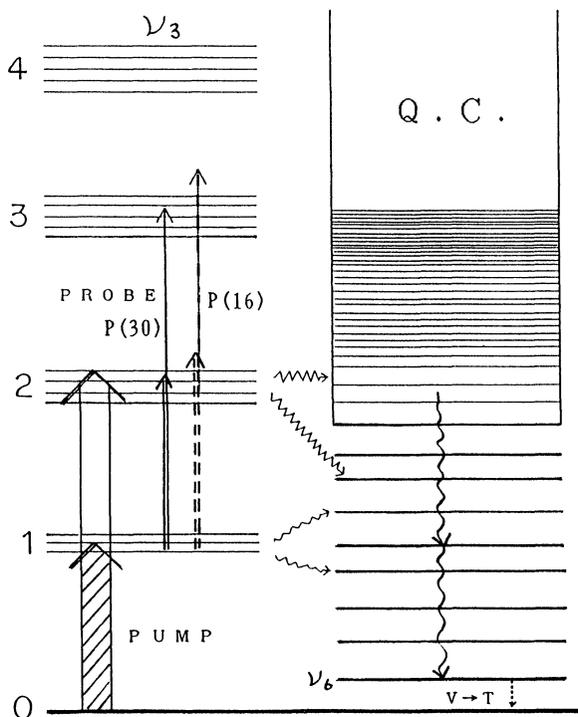


Figure 1 Principle of pump-probe measurements on vibrational energy distribution in SF₆ molecules. The simplified energy structure consists of ν_3 mode, other discrete levels, and quasi-continuum.

pumped by the IR laser and fully populated, the probe beam at the blue side of CO₂ 10.6 μm P-branch shall easily transmit the gas cell without any absorption. The optical transition from the ground state ($\nu_3 = 0$) to the $\nu_3 = 1$ state is suppressed, until the excess population in this state is depleted. In addition, the transition from the $\nu_3 = 1$ to the $\nu_3 = 2$ is also impossible in this situation since the energy difference $\Delta E_{21}(=E_2-E_1)$ is 5 cm^{-1} smaller due to the anharmonicity than the $\Delta E_{10}(=E_1-E_0)$.¹⁸ Namely, the probe transmission after pumped will be larger than that before, that is called the “induced transmission.”

On the other hand, the probe at the red side is weakly absorbed before the gas is pumped by the IR laser but more absorbed after it. The probe photon energy at the red side is, comparable to the difference ΔE_{21} , profitable for the transition from the $\nu_3 = 1$ to the $\nu_3 = 2$. Namely, the probe transmission after pumped will be smaller than that before, that means the “induced absorption.”

When the $\nu_3 = 2$ state is pumped, the boundary between the induced transmission and absorption will be more 5 cm^{-1} red-shifted with the energy shrinkage of $\Delta E_{21} < \Delta E_{10}$. In this way, the probed spectra may reflect the vibrational energy distribution. In addition, the time resolved induced signals will make up clearer the spectral evolutions. Therefore, one can clearly probe, with the delayed weak laser pulse, the time variation of the distribution after pumping by the intense laser pulse.

EXPERIMENTAL SETUP

As shown in Figure 2, a tunable TE CO₂ laser pulse (300 ns duration) as the pump beam was focused in 0.6 mm radius into a gas cell (25 mm radius, 14 mm thick) filled

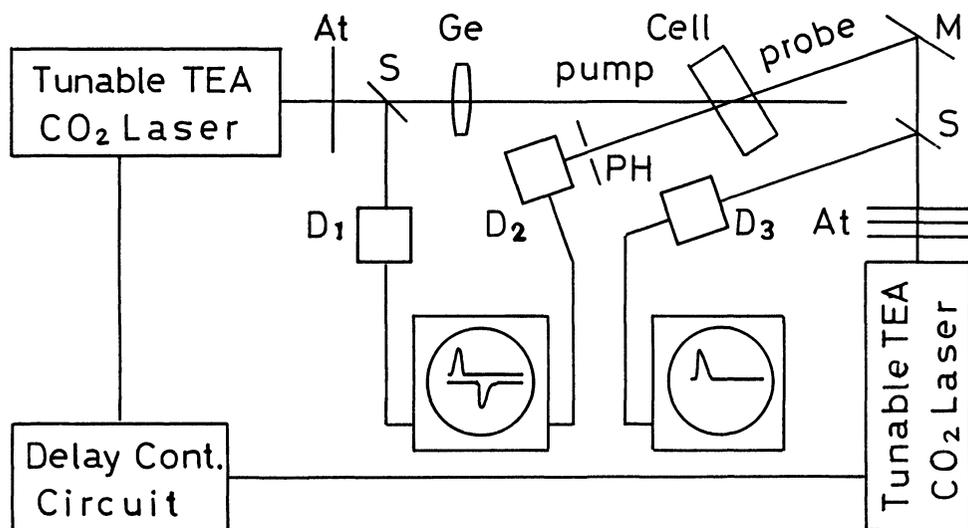


Figure 2 Apparatus diagram for pump-probe measurements. At; attenuator, D₁, D₂, D₃; pyro-detectors, Ge; lens, M; gold mirror, PH; pin hole, and S; ZnSe splitter.

with 2 Torr of pure SF₆. Another pulse laser of the same quality was used with an intensity attenuator of 1/1000 as the probe beam to be passed through the excitation region in the gas cell toward a pyro-detector with 0.5 mm radius area. As the beam cross angle is rather large (15°), the probe volume is essentially small. The pump line was selected to the P(14) of 949.4 cm⁻¹ or P(39) of 934.9 cm⁻¹ since the former in the high energy side is typical for the 2-level absorption model and the latter in the low side is for the 4-level model.¹⁶ The pump intensity was 0.4 J/cm² enough for multi-photon (a few photons) excitation into the quasi-continuum,⁵ but not for dissociation.^{10,15} The SF₆ gas pressure was varied up to 10 Torr for the studies on collisional effects. The time delay between the pump and probe pulses was varied from 0 to 400 μs with the accuracy of 1 μs, much longer than the R-R and V-V relaxation times in this experiment. The Doppler shift is negligibly small (0.001 cm⁻¹) compared with the difference between CO₂ rotational lines (2 cm⁻¹). A normalized measure of induced signals is the relative intensity difference between the probe beam through the cell after pumped and that before (as unity). For the first time, the pump line was fixed at the P(30) while the probe was varied from the P(10) to the P(32).

EXPERIMENTAL RESULTS

Figure 3 shows the fundamental or ground state absorption of the transition [$\nu_3 = 0 \rightarrow \nu_3 = 1$]. The solid curve, illustrated in Figure 6 of Ref. 6, indicates the

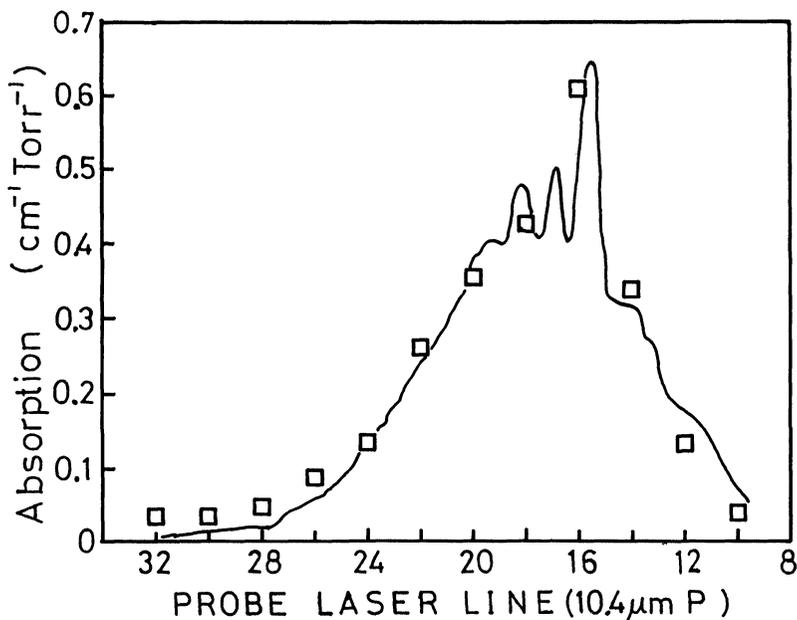


Figure 3 Fundamental or ground state absorption coefficient [$\text{cm}^{-1} \cdot \text{Torr}^{-1}$] of SF₆. Open square points were observed with pulsed weak CO₂ laser (300 ns, 0.41 mJ/cm²), and solid curve is usual absorption profile (after J. I. Steinfeld⁶).

profile observed with a Perkin-Elmer spectrometer and an IR source of globar. The open square points show the absorption coefficients observed by the probe beam before the IR excitation of the molecules. Those seem in good agreement with the solid curve, although somewhat splitted at the red and blue tails.

Figure 4 shows the time variation of the probed absorption spectrum with a parameter of the delay time (0, 50, 100, 300 μ s) after pumped. illustrated by the solid curves. The dashed curve or open square shows the fundamental absorption before pumped. The probed spectrum changed even at the 0 μ s, immediately when the pump beam irradiated into the gas cell. The blue-side absorption at the P(10)–P(22) decreased significantly whereas the red-side at the P(24)–P(32) increased. After the 50 μ s, the spectrum was most broadened and red-shifted. After that, however, the spectrum recovered slowly toward the fundamental profile.

As shown in Figure 5, the induced transmission and absorption or the temporal change of the probe absorption relative to the fundamental were deduced from the time variation of the absorption spectra in Figure 4. Some significant features are noticed again as following. First of all, the spectra may be divided into two parts, namely the induced transmission in the high energy region [P(10)–P(22)] and the induced absorption in the low region [P(24)–P(32)]. Secondly, the boundary is almost fixed; the P(22) at the initial time and shifted to the P(24) at the intermediate time (50 μ s), but becomes again the P(22) of the initial at 400 μ s. So, the induced spectrum is gradually red-shifted until the delay time of 50 μ s and then goes back

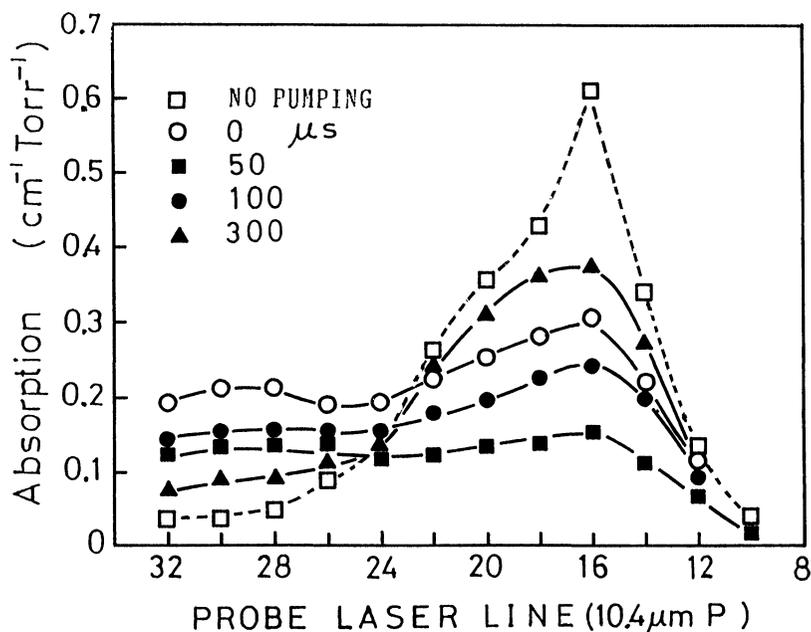


Figure 4 Probed spectra of SF₆ 2 Torr at delay time (0, 50, 100, 30 μ s) after pumped by CO₂ laser pulse of 0.4 J/cm² at P(30) line.

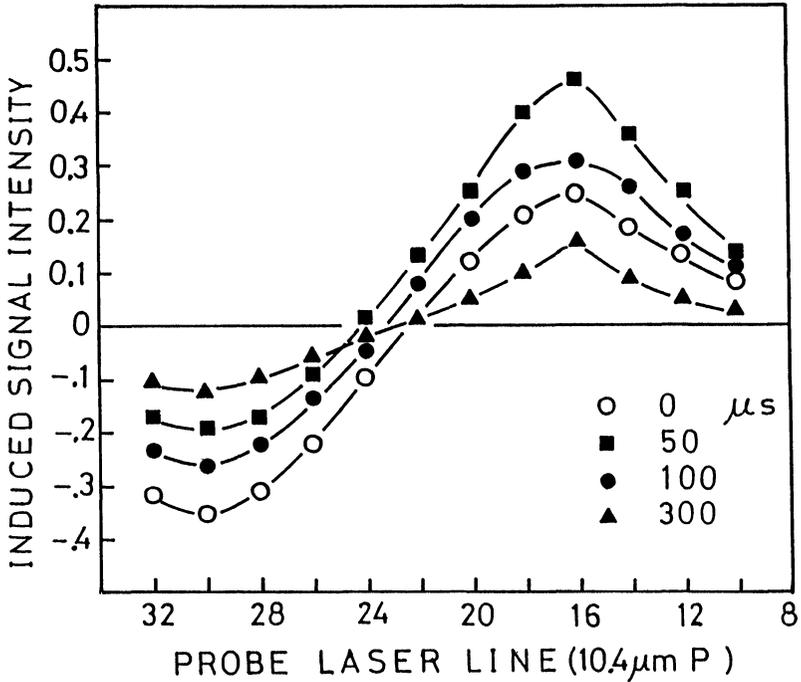


Figure 5 Spectral evolution of the induced signals with parameter of time delay. Positive side corresponding to induced transmission and negative to absorption.

slowly to the initial with some decay of the amplitude. In addition, the boundary was hardly changed even when the P(14) line was used as the pump beam.

As shown in Figure 6, the temporal behavior of the induced signals at typical probe lines of the P(16), P(24) and P(30), was observed in the same condition of Figure 5. These variations can be clearly divided into four regions or periods as following. The induced transmission at the P(16) probe line appears as soon as the P(30) pump pulse irradiates the cell (this is called the Ist region within $1 \mu\text{s}$), and then increases with a rather short time constant until the delay time of $50 \mu\text{s}$ (IInd period). After this time the induced signal decreases down fast until the delay of about $110 \mu\text{s}$ (IIIrd), followed by a slower decay of more than $400 \mu\text{s}$ delay (IVth). On the other hand, the strong signal of induced absorption at the P(30) probe line also appears as soon as the gas is pumped in the Ist region. Then the signal decreases down exponentially until the $50 \mu\text{s}$ -delay in contrast with the induced transmission in this region II. It is noticed, however, the induced absorption increases again until $110 \mu\text{s}$ on the contrary to the transmission in the IIIrd region. The absorption is also followed by a slow decay over the IVth region as the same as the transmission. The induced transmission or absorption at the other lines changes as well as the time behavior of the P(16) or P(30) line, respectively. At the boundary of the P(24) line, the Ist response is the instantaneously induced absorption, followed by an exponential decay until the $50 \mu\text{s}$ -delay, when the signal appears as the induced transmission

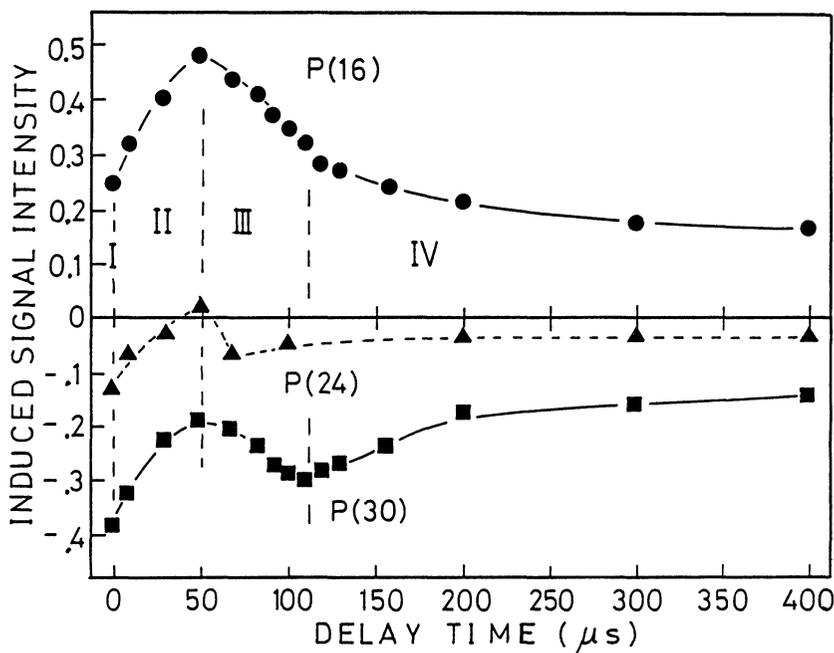


Figure 6 Time variation of the induced signals at the probe lines P(16), P(24) and P(30) at the same condition of Figure 5.

transiently, but then the induced signal goes back to the absorption as similar as the behavior at the P(30) line. Anyway, these features must surely reflect the time variation of the probed absorption spectra.

DISCUSSIONS

- 1) As seen in Figure 4, the probed spectra were red-shifted and broadened after pumped by the laser. This means that the vibrational energy is broadly distributed over the ν_3 ladder, resonantly coupled with the quasi-continuum, after the IR excitation. In addition it is noticed the spectrum at the delay of 50 μs is most broadened and red-shifted. This long time behavior must come from the rise-up of the vibrational temperature induced by the localized gas heating-up due to the $V \rightarrow T$ relaxation. The detailed discussions will be mentioned below.
- 2) As seen in Figure 5, the induced spectra are reasonably divided into two parts; the high energy region [P(10)–P(22)] for the induced transmission and the low region [P(24)–P(32)] for the absorption. The boundary is almost independent of the pump wavelength, although not expected by the previous report.⁶ These facts will surely correspond to the explanation of the 2-level and 4-level models for the nonlinear absorption, as based on the anharmonic shift.¹⁶ The small spectral red- and blue-shift with delay time is related to the time variation of vibrational temperature T_v , (if the Boltzmann distribution is assumed).

- 3) The time variation of induced signals in either the transmission or the absorption may be divided into four regions as indicated in Figure 6. However, the Ist response within 1 μs is related to the multiphoton excitation, vibrational energy evolution or redistribution by intra- and inter-molecular R-R, V-V relaxation^{4,8} there are too fast to observe in this time-resolved experiment. the IInd period is about 50 μs , related to collisional relaxations with the gas heating-up, just corresponding to the V-T relaxation time of 100~120 $\mu\text{s} \cdot \text{Torr}$ observed by Steinfeld *et al.*⁶ The IIIrd is another 60 μs , perhaps required for the molecular diffusion, as partially suggested by Deutsch *et al.*¹¹ The IVth is much longer, about 500 μs , affected by the gas cooling rate, almost the same as 1.2 ms for 1.15 Torr.⁶ Over all the regions, the time variation of induced transmission at the P(16) line is essentially contrasted and compared with that of induced absorption at the P(30).
- 4) As the state density of vibrational levels increases rapidly with the energy, the distribution of population after multiphoton excitation will not be exactly the Boltzmann in the quasi-continuum. The transient distribution in the quasi-continuum, as hardly affected by the gas temperature T_g , is different from that in the low discrete levels.¹³ Therefore, the time variation of the probed spectrum or both the induced transmission and the absorption may be further explained by the excitation and relaxation model as following.
- 5) The Ist period is within about 1 μs , comparable to the accuracy of delay time. As soon as the SF₆ is strongly pumped by a TE CO₂ laser, the absorbed energy is localized in a nonthermal distribution within the ν_3 mode. Soon after that the energy will be rapidly spread into a broad redistribution in the quasi-continuum by V-V, R-R relaxations,¹⁹ as hardly relaxed to the ground state by slow V \rightarrow T process.
- 6) In the next period II, some part of the vibrational energy is relaxed by the collisional process from the bottom of discrete levels or the $\nu_3 = 1$ state to the ground state, resulting in the rise-up of the gas temperature in the pumped zone. This enhances the collisional V-V up-pumping, as SF₆(1) + SF₆(n) \rightarrow SF₆(0) + SF₆($n + 1$), to rise up the vibrational temperature.²⁰ The V \rightarrow T relaxation is, however, rather slow as restricted by the gas temperature, although not slower than the 10 μm and 16 μm fluorescences in this situation.²¹ On the other hand, the other part of the vibrational energy is stored in the higher levels of ν_3 mode and quasi-continuum so as to form the hot molecules providing the long induced signals. Therefore, the induced transmission increases gradually, while the absorption decreases down, with the spectral red-shift in this duration of 50 μs .
- 7) In the next region III, the localized molecules heated up during the IInd period increase the collision frequency. In turn, the collisions between hot and cold molecules enhance the V \rightarrow T relaxation rate so that T_v will drop down. However, the gas temperature and pressure in the pumped region increase up with the development of the V \rightarrow T process. So, the molecular diffusion or expansion will be promoted by the heating-up and temperature gradient in the

pumped zone. So, the hot or highly excited molecules themselves, and/or their vibrational energy by collisional transfer, will go out of the pumped zone microscopically and, in turn, unexcited (cold) ones outside the zone come into there so as to compensate the molecular density, so, as the localized gas is cooled by collision between them, the vibrational temperature will also decrease down. Thus, the probed absorption spectrum will go back to the blue side, as seen in Figure 5. That is to say, the induced transmission is suppressed down while the absorption grows up again, as distinctly seen in Figure 6.

- 8) In the IVth region, the induced transmission decreases down slowly with a long time decay over several 100 μs as well as the absorption. This long decay may be explained by the slow rate of gas cooling or thermal equilibration in the sample cell.^{6,22} The localized high gas temperature T_g will be lowered by the molecular diffusion, thermal expansion and conductivity to the walls, and then the gas is cooling down macroscopically all over the cell. As the $V \rightarrow T$ relaxation rate is almost limited by the temperature T_g , either the vibrational temperature T_v or the population excited in the quasi-continuum will decrease very slowly. Thus, the intensity decay of either the transmission or the absorption is essentially restricted by the slow rate of gas cooling.

CONCLUSIONS

The probed spectra are divided into two parts, the induced transmission at the P(10)–P(22) and the absorption at the P(24)–P(32), slightly red-shifted by 50 μs , and then slowly back to the initial. The boundary is hardly depending on the pump line in our experiment, although was not expected before,⁶ that is straightly corresponding to the 2-level and 4-level model for the nonlinear absorption.¹⁶ The time variation of induced signals was divided into the four regions: (I) The initial signals come from the formation of nonthermal distribution in the ν_3 mode and quasi-continuum with 1 μs . (II) The transmission increases and the absorption decreases with the spectral red-shift during 50 μs . This fact is related to the broad redistribution of vibrational energy or the rise-up vibrational temperature. That is to say, some part of the vibrational energy is relaxed from the discrete levels, while the other is still stored in the higher levels or quasi-continuum, resulting in the gas heating-up with a time constant of about 100 $\mu\text{s} \cdot \text{Torr}$ expected by the previous values.^{11,15} (III) The *avec* variation of the transmission decay and absorption recovery with the spectral blue-back in another 60 μs is according to the molecular diffusion or expansion out of the pumped region locally heated up by the $V \rightarrow T$ relaxation and to the subsequent gas cooling by collisions with cold molecules that come into there to compensate the density. (IV) The twin-like slow decay over 400 μs of the mirror-imaged signals is according to the population depletion or $V \rightarrow T$ relaxation of the quasi-continuum, that is strongly limited by the gas temperature either microscopically or macroscopically.

Finally speaking, let us consider about the collision conditions. Some of the investigators^{8,11–14} have used long gas cells filled with the sample gas of low pressure

(≤ 0.5 Torr) so as the molecular collisions should hardly happen within the pump duration (100–300 ns). This collisionless condition is favourable for studying on intramolecular fast processes of the R–R' and V–V' relaxations, since the instruments such as detectors, oscilloscopes and electronic circuits are easily used in a suitable time scale of 1–100 μ s. This condition is, however, not convenient for studies on slower collisional processes as the V \rightarrow T relaxation, molecular diffusion and so on, because it sometimes requires a long troublesome measurement over several milli-seconds. The collisional relaxation times can be shortened by increasing the gas pressure. By use of two pulse lasers with a few 100 ns duration, the pump-probe method at the collisional conditions will easily give us some informations, with a short gas cell and a suitable time scale, on moderately slow processes, such as the V \rightarrow T relaxation, population depletion, molecular expansion, diffusion and dissipation in SF₆ gas after pumped.

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