Study of collisionless multiphoton absorption in SF_6 using picosecond CO_2 laser pulses

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The dynamics of collisionless infrared multiphoton absorption in SF_6 was studied using picosecond CO_2 laser pulses. It was found that at this new regime of light-matter interaction at very high laser intensities, the absorption in the quasicontinuum has a considerable intensity dependence. The deviation from an energy fluence scaling law was found to begin at about 200 MW/cm². Above this intensity, the multiphoton interaction between the laser and the molecule should be described by the full coherent Schrödinger equation rather than by the usual master rate equations. A novel method of preheating the SF_6 molecules is also described and the saturation behavior of these preheated molecules is measured with the picosecond pulses.

I. INTRODUCTION

Much understanding of the process of infrared laser-induced multiphoton absorption (MPA) and dissociation (MPD) has been gained in the past several years.[1(a),1(b),1(c)] It is generally believed that the initial excitation of the polyatomic molecule over the low-lying discrete levels contributes to the frequency selectivity and intensity dependence of the overall multiphoton processes. The fact that sharp resonances can occur in MPD has been demonstrated recently by Dai *et al.*[2] It is also commonly accepted that once the molecule has been excited to the quasicontinuum (QC) of vibrational states where the multitude of energy levels interact strongly with each other, the absorption of energy by the polyatomic molecule will become a linear absorption process. The laser fluence rather than the laser intensity will determine the total energy absorbed by the molecule.[1(a),3(a),3(b)] When sufficient energy has been absorbed, unimolecular decomposition of the polyatomic molecule will occur in complete agreement with the RRKM (Rice-Ramsperger-Kassel-Marcus) theory predictions.

While the general picture is quite clear, there are many questions remaining for a complete understanding of the process of MPD. For example, more quantitative information about the transition from the discrete levels to the QC is needed. More important, there is still the question of the frequency and intensity dependence of the QC adsorption, such as how the energy redistributes among all the vibrational modes and whether there exists any sharp resonance in the QC. The dynamics of the dissociations, especially if there are several possible decomposition channels are also in need for further study.[4]

Evidently, the best apparatus to study MPD experimentally is a molecular-beam machine where in addition to being collision free, the dynamics of the dissociation process can be explored by obtaining both the angular distribution and the time-of-flight spectra of the various dissociation products.[5(a),5(b)] However, there are many situations where we are only interested in having multiphoton excitation in the molecule without dissociating it. Moreover, it is necessary that MPA be understood more thoroughly before any study of MPD can be complete. As a matter of fact, to acquire a thorough understanding of MPA, one should try to avoid dissociation which contributes complications that render the interpretation of the experimental data very difficult. In this paper we shall describe a study of collisionless MPA in SF_6 in a gas cell using picosecond CO_2 laser pulses up to very high levels of excitation without dissociating the molecules.

There are many advantages of using picosecond laser pulses. First of all, with a pulse duration of 30 psec, there can hardly be any collision during the laser-pulse interaction, even at cell pressures as high as 20 torr. Thus the stringent requirement on cell pressure for nanosecond pulse experiments can be relaxed by almost a thousandfold.

Secondly, the peak intensity of a picosecond pulse is at least three orders of magnitude larger than a nanosecond transversely excited atmosphere (TEA) laser pulse with the same fluence. Therefore, one can expect the relative importance of the initial excitation to diminish and hope to study the QC more directly. However, because of exactly the same reason, care should be taken in generalizing the result of this experiment to the ordinary situations using nanosecond TEA CO_2 pulses.

Thirdly, with picosecond pulses, and their accompanying high intensities, there may be a chance of having the up-pumping rate competing with intramolecular energy transfer within the molecule. Hence there exists a possibility of seeing some previously unobserved effects, such as

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coherent pumping in the quasicontinuum.

The most important advantage is that one can study the SF_6 molecules *near or above* its dissociation limit without the complications of dissociation and problematic effects such as absorption by dissociation products, because even at very high levels of excitation there can hardly be any dissociation *during* the laser pulse. For example,[5(c)] the RRKM lifetime for SF_6 with ten excess CO_2 photons of energy above its dissociation limit is 7 nsec, which is much longer than the picosecond pulse duration. Therefore one can measure the true MPA characteristics of the SF_6 molecules at very high levels of excitation. This cannot be accomplished with longer duration pulses where dissociation will inadvertently occur during the laser interaction. Therefore, by using picosecond pulses as an excitation source, we should be able to study a new aspect of MPA and hopefully provide new information on the nature of the QC.

We have performed two experiments on measuring the absorption of multiple CO_2 photons by the SF_6 molecule. In the first experiment, we measured the energy deposition with pulses of 30, 50, 90, and 145 psec duration. This provided us with an idea of the importance of pulse intensity in multiphoton interaction in the quasicontinuum. In another experiment, using a method of collisional laser excitation we preheated the SF_6 molecules to the QC and then measured the saturation characteristics of the absorption cross section of SF_6 as it is further excited. This heating method enables us to study molecules which are already in the QC and therefore the question of interference from the discrete levels can be avoided. Since the saturation of any system is closely related to the relaxation mechanism, such a measurement should provide some clues to the nature of intramolecular damping and relaxation in the molecule.

In Sec. II, we shall describe briefly the picosecond CO_2 laser system used in this experiment. In Sec. III, the experimental techniques and procedures are described. The data handling methods to obtain the true average number of CO_2 photon absorbed $\langle n \rangle$ and the absorption cross section σ is also discussed. A novel way of thermally heating a polyatomic molecule by a collisional MPA process will then be presented in Sec. IV. The results of the picosecond measurements are presented in Sec. V where their significance will also be discussed. A brief conclusion will then be drawn in the final section.

II. THE LASER SYSTEM

The generation of picosecond CO_2 laser pulses using the process of optical free-induction decay

has been described previously.[6(a),6(b)] Essentially, a group of CO_2 molecules are prepared in their upper $(00°1)$ lasing level by passing a normal 100-nsec TEA laser pulse through a long CO_2 gas tube at high temperature. The traditional way of obtaining optical free-induction decay is by Stark switching the absorbing system out of resonance with the incident laser.[7] The free-induction decay will then occur at a slightly different frequency. In our system, we simply turn off the incident laser pulse suddenly using a plasma shutter.[8] The optical free-induction decay pulse that follows will be at the same frequency as the incident TEA laser pulse.

The laser system is shown in Fig. 1. A hybrid grating tuned TEA and a low-pressure CO_2 laser[9] was employed to provide a single longitudinal mode laser pulse of 100 nsec duration and 5 MW peak power in the TEM_{00} mode. The hydrid configuration was necessary in order to narrow the bandwidth of the CO_2 laser. Moreover, the smooth pulse profile provides much better stability with the plasma shutter, and produces picosecond pulses with very little amplitude fluctuations.

The plasma shutter was a 1:1 telescope with a pair of $f/1$ germanium lenses. Premature untriggered gas breakdown was prevented by passing clean nitrogen gas through the focal volume. At the peak of the laser pulse, a dc spark was fired which in turn triggered the main gas breakdown stopping completely the transmission of the TEA laser pulse. Since the dc spark was trigger-
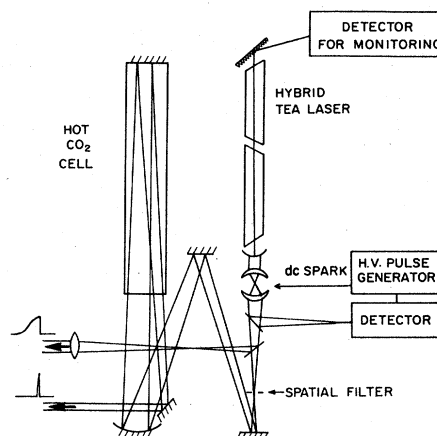

FIG. 1. The picosecond CO_2 laser system. A fast oscilloscope is used to monitor the zeroth-order output of the grating. The output mirror of the CO_2 laser is translatable by a double differential micrometer for the adjustment of the cavity length. This procedure guarantees a single longitudinal mode output at all times. The dc spark gap is formed by two sharp points on a carbonized surface and is placed 2 mm from the focal point of the plasma shutter.

ed by the laser pulse itself,[8] this plasma shutter could be timed extremely precisely and had practically no fluctuation.[10]

Part of the truncated laser pulse was split off using a coated germanium substrate beam splitter, and sent to the SF_6 gas cell after some mild focusing. The remaining portion was sent through a 3 m-long tube containing typically between 50 and 250 torr of CO_2 gas in double pass. The tube was heated to 400 °C in order to populate the lower $(10°0, 02°0)_I$ lasing level thermally. Also, to prevent saturation of absorption by the CO_2 molecules, the TEA laser pulse was spatially filtered before entering the hot gas tube. The optics were arranged such that upon leaving the CO_2 absorption tube, the laser pulse was collimated and had a Gaussian spot size of 3.3 mm in diameter.

As discussed by Yablonovitch et al.,[11] the optical free-induction decay pulse at the output of the hot CO_2 gas tube has the same pulse peak power as the input TEA laser pulse. The pulse duration can be approximated by $T_2/\alpha l$, where T_2 is the dephasing time of the excitation in the CO_2 gas, α is the linear absorption coefficient, and l is the path length. In our system, α has been measured and the result is shown in Fig. 2. This measurement is in agreement with the results of Gerry et al.[12] when scaled to the same temperatures. From Fig. 2 we can obviously distinguish a low-pressure regime of Doppler broadening and a high-pressure regime of pressure broadening. Since we always operate above 500 torr in the CO_2 gas tube, αl can be regarded as a constant with a value of 12.5 nepers.

The pulse durations of the optical free-induction decay pulses have been measured with both an autocorrelation method[6] and a double resonance method.[13] The measurements agreed quite well with the prediction of $T_2/\alpha l$ for the pulse durations. In our experiments on SF_6, we used CO_2 gas pressures of 40, 70, 140, and 250 torr, cor-

responding to pulse widths of 145, 90, 50, and 30 psec, respectively.

III. EXPERIMENTAL

In the experiments reported here, we measured the mean energy absorbed by the SF_6 molecule, represented in terms of the average number of CO_2 photons $\langle n \rangle$, and the absorption cross section σ of the excited vibrational state of SF_6. We deduced the values of $\langle n \rangle$ and σ as a function of the laser fluence J by observing the attenuation of the laser pulse through an SF_6 gas cell.[14] Provided the experimental data are analyzed properly as discussed below, this method is quite suitable to the study of MPA, especially at low levels of excitation where the optoacoustic method becomes insensitive.[1(b)]

Before dwelling on the details of the experimental procedure, let us discuss some of the design criteria for the experiment. Most important of all is the energy-fluence requirement. The picosecond CO_2 laser pulses we used typically had a peak power of 2 MW. Therefore to generate a fluence of 1 J/cm^2, the laser has to be focused quite tightly. In our experiments, we used a 50.8-in focal length AR-coated germanium lens for the picosecond laser pulses. For such tight focusing, the corresponding Fresnel length is rather small. The measured beam waist before focusing was 1.65 mm. Using Gaussian optics, for a 50.8-in focal length, the area of the focused beam increases by a factor of 2 at a distance of 3 mm from the focal point. Therefore, in order to ensure a uniform parallel beam in the SF_6 gas cell, the thickness of the gas cell must be smaller than 4 mm.

Another consideration for a more or less uniform laser beam inside the gas cell was that the transmission must be close to 100%. However, one required the gas cell to be reasonably optically thick in order that the measurement be accurate and sensitive. As a compromise, we limited the transmission of the laser pulse to fall within 50 and 80%. This then imposed a lower limit on the SF_6 gas-cell pressure. On the other hand, the gas pressure should be low enough to ensure collisionless interaction. The smallest collisional deactivation time ever measured[15] for SF_6 was 13 nsec torr. Therefore, in order to avoid any collisional effect in our experiments, we have to limit the SF_6 pressure to be less than 60 torr for a 200-psec pulse. Thus the gas-cell length and pressure have to be chosen such that the transmission falls within the range stated above. In our measurements, we typically used a cell pressure of 20 to 30 torr and cell lengths of 1 and
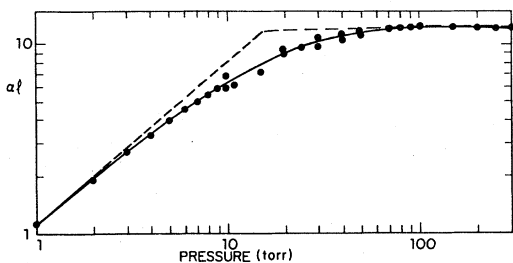

FIG. 2. Experimentally measured absorption coefficient of the TEA laser pulse by the hot CO_2 molecules as a function of gas-tube pressure. The CO_2 gas was heated to 700 K. Two separate regions of Doppler and pressure broadening can clearly be distinguished.

3.7 mm.

The experimental setup is shown in Fig. 3. There are two laser beams going into the gas cell. The picosecond pulse was delayed with respect to the truncated pulse by 32 nsec. The truncated preheating pulse was not in use for the energy deposition measurement with room temperature SF_6 molecules. As shall be explained in the next section, the truncated pulse in Fig. 3 was used to thermally heat up the SF_6 molecules. A 635-mm focal length BaF_2 lens was used to focus the truncated pulse onto the gas cell to ensure that all the gas molecules the picosecond pulse sees are uniformly preheated.

The 99.9% SF_6 gas was purchased from Matheson Gas Company without further purification. A Pennalt-Wallace absolute pressure gauge was used to monitor the gas-cell pressure. The change in fluence passing through the gas cell was accomplished by moving the calibrated CaF_2 attenuators in front of or behind the gas cell while keeping the total attenuation constant. This allowed us to perform the entire measurement on the same scale of the amplifier and reduced the requirement on the dynamic range of the detection system. The CaF_2 attenuators were sufficiently flat so that no beam deflection occurred while they were moved. To further minimize sensitivity to misalignment onto the detector, the output beam from the gas cell was refocused onto the detector with a 1:1 magnification.

A liquid-nitrogen-cooled Ge:Au detector was used throughout the experiments. It was always checked that the detector was well below saturation to ensure a linear response. The detector output was integrated by capacitive loading and displayed on a Tektronix 7904 oscilloscope. Typically
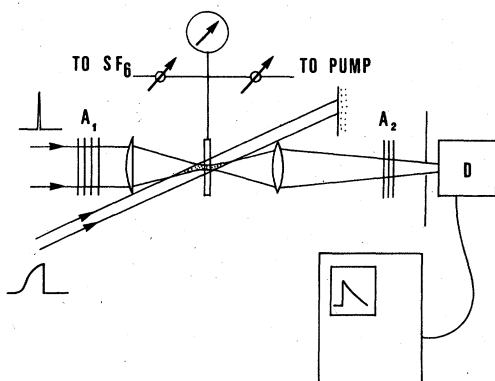

FIG. 3. Experimental setup for the measurement of the transmission of the picosecond CO_2 laser pulse as a function of pulse intensity. A second preheating truncated pulse channel is also shown. The Ge:Au detector was placed inside a copper box for shielding from electromagnetic noise.

many laser shots were taken and the data were averaged. The blackbody radiation produced by the plasma shutter mentioned in the last section was detectable even after a more than 10-m optical path and spatial filtering. They were eliminated by an OCLI 8-μm-long wavelength pass filter. All other stray lights were blocked by a diaphragm in front of the detector.

NaCl windows were used in the SF_6 gas cells. To make certain that the gas cell was located at the exact focus of the Germanium lens, which was important in determining the laser energy fluence, it was mounted on a translation stage. To locate the focus, we simply filled the gas cell with SF_6 and moved it back and forth to find the maximum transmission. This procedure ensures that the cell was located at a place of maximum light intensity.

Since we could not measure the picosecond pulse energy directly using an energy meter, the laser fluence was determined indirectly as follows. First of all, using a normal TEA pulse we calibrated the Ge:Au detector-integrated voltage output in terms of the true absolute energy using a well-calibrated Scientech power meter. This was done by emptying the hot CO_2 absorption tube and turning off the plasma shutter so that the detector would gel the entire TEA laser pulse. We then filled the CO_2 gas and turned on the plasma shutter to produce the optical free-induction decay pulses. Since the detector integration time is much longer than both the TEA laser pulse and the picosecond pulse durations, the output voltage of the detector should simply be proportional to the pulse energy and independent of the pulse shapes. Therefore, from the detector output, we could infer the picosecond pulse energy. Incidentally, the ratio of the picosecond pulse energy and the TEA pulse energy always came out to be simply the ratio of the pulse durations which was expected if the two pulses had the same peak intensities. Since the spatial profile of the picosecond pulse was very close to a Gaussian, we could infer accurately the focal area by measuring the beam size at the entrance of the 2-in Ge lens, thus completing our estimation of the pulse fluence.

In all measurements, we always checked for the absence of saturation in the CO_2 gas tube which was required in order that the picosecond pulse should have maximum contrast ratio.[6] This is important because the prepulse duration is three orders of magnitude longer than the picosecond pulse. Every precaution must be taken in order not to have the integrated signal from the prepulse interfere with the real signal. After the preliminary checks and calibrations, the experiment can be performed. The transmission T of

the SF_6 gas cell was defined as the ratio of the integrated detector signal with the cell filled and at vacuum. The absorption was calculated by

$$\langle n \rangle = \frac{(1-T)}{NL} \frac{J}{\hbar \omega} , \qquad (1)$$

where N and L are the number density of molecules and the gas-cell path length, respectively, and $\hbar \omega$ is the CO_2 photon energy. J is the energy fluence of the laser pulse in J/cm^2. Since it changes its value along the pathway inside the gas cell, some sort of averaging is necessary to get a correct value of J in (1). One can either use the geometrical mean[3] $\sqrt{T} J$ or the arithmetic average of the fluence at the entrance and the exit of the SF_6 cell. The two means are identical provided the transmission is close to unity. In the experiment, we never let the transmission T fall below 50%.

Corresponding to every value of $\langle n \rangle$, we can define a gross absorption cross section σ_G for the molecule

$$\sigma_G = \langle n \rangle \hbar \omega / J . \qquad (2)$$

We can also obtain the excited-state absorption cross section σ given by

$$\sigma = \frac{d\langle n \rangle}{dJ} \hbar \omega . \qquad (3)$$

This quantity can be thought of as the *small-signal* absorption cross section of a molecule already prepared in its excited state. It is obvious that σ is more physically meaningful than σ_G in investigating the properties of the QC.

Let us discuss now the data-reduction procedure that is necessary in this kind of measurement. The main observation about the experimental data is that they are already averaged spatially in the sense that the laser fluence varies across the laser beam. Fortunately, for lasers with a Gaussian profile, there exists an exact deconvolution procedure[16] whereby the truly fluence-dependent transmission T can be obtained from the measured transmission $T_M(J)$ by

$$T(J) = T_M(J) \left(1 + \frac{d \ln T_M(J)}{d \ln J} \right) . \qquad (4)$$

Physically, we can think of $T_M(J)$ as the transmission measured with a pulse with spatial profile $J(r) = J_0 e^{-2r^2/w_0^2}$ and $T(J)$ as the transmission measured with a pulse of constant spatial profile, e.g.,

$$J(r) = \begin{cases} J_0, & r \leqslant w_0 \\ 0, & r > w_0 \end{cases} . \qquad (5)$$

Obviously, formula (4) need not be used if such a

laser pulse exists.

Notice that in (4), the correction term $d \ln T_M / d \ln J$ is always negative for a saturating system. Without saturation, i.e., for linear absorption, this term will be zero. It is generally correct that whenever the data are manipulated in any way, new uncertainties will be introduced which will increase the error bars. Fortunately as we shall see later, the saturation of absorption for the picosecond pulses is very small. Hence the correction needed to our raw data was quite small and did not introduce undesirable additional errors.

Once the truly fluence-dependent transmission is obtained, $\langle n \rangle$ and σ_G can be calculated using (1) and (2). In principle, σ can be obtained by (3), applying the differentiation on the data for $\langle n \rangle$. In practice it is easier to obtain σ for σ_G, employing the relationship,

$$\sigma = \sigma_G \left(1 + \frac{d \ln \sigma_G}{d \ln J} \right) . \qquad (6)$$

This relationship can be obtained from (2) and (3) as follows. Observe that $\langle n \rangle \hbar \omega = \sigma_G J$. Differentiating both sides with respect to J, we obtain

$$\hbar \omega \frac{d\langle n \rangle}{dJ} = \sigma_G + J \frac{d\sigma_G}{dJ} , \qquad (7)$$

(6) then follows from (7) and (3) after a little algebraic manipulation. For a system that does not saturate too rapidly in absorption, such as the SF_6 molecules under the irradiance of picosecond pulses, the correction factor in (6) is small and σ is numerically close to σ_G. Therefore it is much better to obtain the absorption cross section from σ_G rather than from $\langle n \rangle$.

IV. THERMAL EXCITATION OF SF_6 USING TRUNCATED CO_2 LASER PULSES

In this section, we shall describe a novel way of obtaining thermally excited SF_6 molecules using collisional laser excitation. In many experiments on MPA and MPD, it is desirable to use SF_6 molecules which are already in the quasicontinuum whereby the discrete levels can be ignored. A brute force method of getting these excited molecules is by heating the entire gas cell to a few hundred degrees. Here we present an alternative method of heating the SF_6 molecules. It has the merits of simplicity, and can be generalized to other molecules in a straightforward manner.

The vibrational excitation in a given polyatomic molecule generally redistributes first among the rotational levels via collisional V-R energy transfer (rotational hole filling), and then among the various vibrational levels via collisional V-V

transfer. It will then be followed by V-T relaxation where the internal energy will equilibrate with the thermal translational energy of the molecule. In ordinary thermal heating, the translational, vibrational, and rotational temperatures are the same. However, in MPA interaction, the translational temperature of the molecule does not play any significant role since it only contributes negligible Doppler broadening anyway. Therefore, the molecule can be considered "thermally" excited if the vibrational-rotational temperature has been established, i.e., after the competion of V-R and V-V energy relaxation, but not V-T relaxation. For SF_6, the V-R and V-V relaxation times are 150 nsec-torr and 1.2 μsec torr, respectively.[17] Our scheme of "thermally" heating the SF_6 molecules consists of exciting the molecules using a truncated CO_2 laser pulse and then allowing the excitation to relax among the vibrational-rotational states by collisions.

To determine whether the molecules are sufficiently thermalized, we need a reference standard of thermal heating. Nowak and Lyman (NL) measured the absorption cross section of SF_6 molecules using a weak cw CO_2 laser after thermal-shock-tube heating.[18] Their results provide an excellent calibration standard to test for thermal heating in our experiment. To see that this is the case, we plot in Fig. 4 the absorption cross section σ at $P(20)$ as measured with a truncated TEA CO_2 pulse, at various cell pressures. Since the truncated pulse is ~30 nsec duration, we ex-
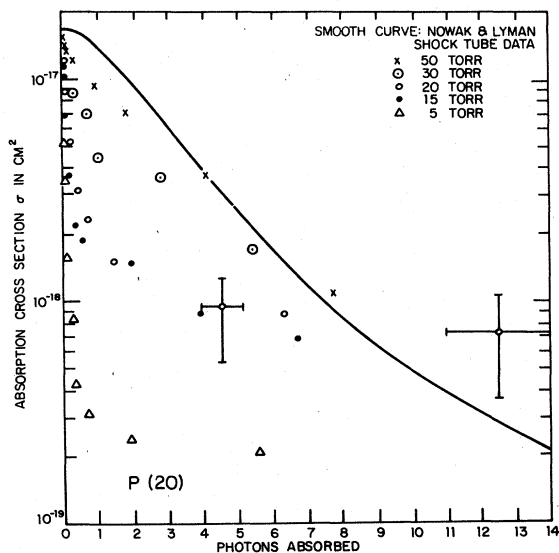
pect increasingly better thermalization as we increased the cell pressure. Indeed, as seen from Fig. 4, the measured result approached that of the measurement of NL as the pressure increased from 5 to 50 torr. The discrepancies at low values of $\langle n \rangle$ is probably due to the initial bottlenecking effect which is not negligible even at 50 torr for weak excitation pulses.

To further allow the SF_6 molecules to thermalize before we study them with picosecond pulses, we allowed a 32-nsec time delay between the truncated pulse and the picosecond pulse. Moreover for experiments done with thermally heated SF_6, we always turned the CO_2 laser to the $P(28)$ line. This is because the absorption spectrum of SF_6 exhibits a redshift as it is heated. Therefore, to obtain a larger σ, the laser should be correspondingly tuned to the red. Moreover, the maximum σ as a function of the truncated heating-pulse fluence is experimentally very convenient for adjusting the fluence of the heating pulse.

Figure 5 shows the absorption cross section measured by a weak picosecond probe laser pulse when the truncated pulse fluence was varied. The horizontal axis was obtained from an independent measurement of $\langle n \rangle$ versus J using the $P(28)$ truncated pulse. Two different SF_6 pressures were used. It can be seen that with 50 torr of SF_6 in the gas cell, the measured σ agrees with the thermal-shock-tube measurement exactly, indicating that the internal energy deposited by the truncated pulse is fully vibrationally thermalized by collisions. The 20 torr curve in Fig. 5
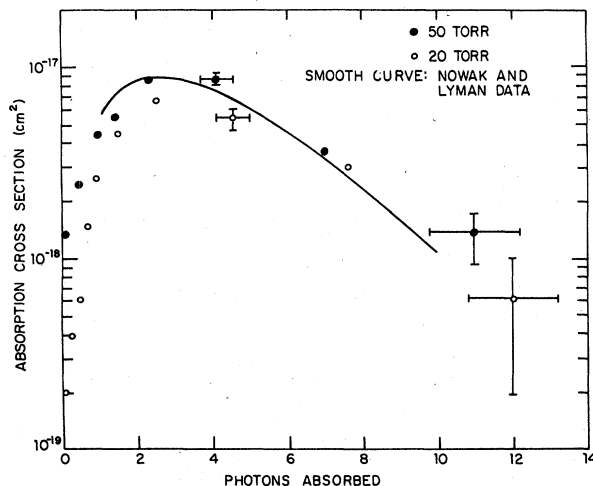

FIG. 4. SF_6 absorption cross section at $P(20)$ under collisional laser excitation. A 30-nsec-long truncated CO_2 laser pulse was used.

FIG. 5. A measurement of the absorption cross section at $P(28)$ showing the achievement of thermal heating of the SF_6 molecules by collisional multiphoton absorption. Experiment was done with a truncated pulse, followed by a picosecond probe pulse with 32-nsec time delay.

follows the same pattern but shows considerably saturation of absorption at low fluences. This is presumably due to insufficient collisional-population redistribution. The peak σ in Fig. 5 corresponds to a heating-pulse fluence of only 0.054 J/cm^2.

We note here that this technique of *collisional* thermal excitation in a *collisionless* experiment is possible only because we are using both nanosecond and picosecond laser pulses. Twenty torr of SF_6 in a gas cell is high pressure enough for vibrational and rotational relaxation for the truncated pulse, but at the same time low pressure enough for collisionless interaction with the picosecond pulses. Presumably this technique can be generalized to nanosecond TEA pulse experiments provided a μsec pulse is available for thermal heating. From NL, the peak of the absorption at $P(28)$ corresponds to a temperature of 650 K. Thus we have an accurate definition of the temperature of the SF_6 molecules before the picosecond pulses arrive.

V. RESULTS AND DISCUSSION

A. SF_6 at 300 K

Figure 6 presents the data on the average photon number absorbed $\langle n \rangle$ by an SF_6 molecule as a function of the laser-pulse fluence. We made the measurements at four different optical free-induction decay pulse durations of 30, 50, 90, and 145 psec, respectively. The data-reduction pro-
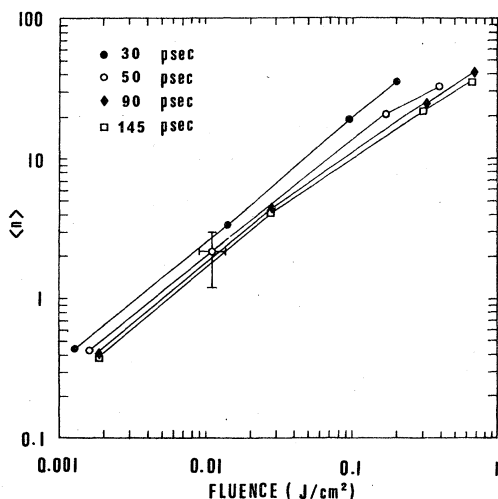

FIG. 6. Energy deposition $\langle n \rangle$ as a function of the laser fluence for four different picosecond pulse durations. As explained in the text, no dissociation can occur during the pulse interaction even at $\langle n \rangle > 40$. The maximum absolute error of 50% is also indicated. The relative error between different curves is 10%.

cedure described in Sec. III has been carefully applied. The data were very reproducible upon repeating the experiment. The only sources of error came from the uncertainty in knowing the laser fluence exactly, together with an ~5% error in reading the signal voltages. So the relative error between the different curves in Fig. 6 should be quite small (10%) while the absolute error was estimated to be 50%. Since the experimental curves are almost straight lines with unity slope, making an error in J will produce the same error in $\langle n \rangle$. This means that the data point will simply slide along the experimental curve. Hence, the uncertainty in exactly knowing the laser fluence should not alter the absolute position of the experimental curves in Fig. 6.

The experimental results show that at very high intensity levels the energy deposition curves do not have any tendency to saturate and converge near the dissociation threshold. As mentioned in the Introduction, for the range of fluences used, there should not be any dissociation occurring during the laser pulse because of the finite dissociation lifetime[5(a)] (although dissociation may occur after the laser pulse is gone, it does not affect our measurement). So we were indeed measuring the true laser absorption by the SF_6 molecules at very high level of excitation. This is different from experiments done with longer duration pulses where at large $\langle n \rangle$ there may be competition due to dissociations and complications from absorption by the dissociation products.

One interesting observation is that even at an excitation level as high as $\langle n \rangle = 20$, where all the molecules should be excited to the quasicontinuum, the differences between the various curves persist. This implies that the absorption in the QC is not straightly fluence dependent. To elucidate on the interpretation of the experimental data, we plotted the 30-psec data together with the 500-, 30-, and 100-nsec data of Black *et al.*[3(b),19] in Fig. 7. Plotted on the same figure is also the derived data of Nowak and Lyman[18] (see Appendix A). The last curve is a hypothetical case of MPA in SF_6 where the absorption cross section of the SF_6 molecules follows exactly the thermally measured value. This is a very useful curve for comparing with the data obtained using laser pulses, especially in testing the thermal bath model.

There is considerable discussion in the literature on whether the population distribution in the QC is thermal,[3(b)] narrower than thermal,[20(d)] or wider than thermal.[20(a)] No claim is made here that curve (e) represents the true situation of fluence-dependent absorption. It is useful mainly because it represents an absorption behavior of the SF_6 molecule where the bottlenecking effects

are absent. Of course, the absolute magnitude of this curve, and to a smaller extent the shape, will depend on the exact population distribution under a multiphoton pumping situation.

Since we are trying to compare the results of two different measurements, it is perhaps imperative to note the differences in experimental conditions and the error limits. The laser pulses used in the experiments of Black et al. were as well characterized as the present paper: Their 100-nsec pulse was smoothed by the same technique as described in this paper, the truncated 30-nsec pulses were obtained by a triggered plasma shutter, and the 500-psec pulses were produced also by the process of optical free-induction decay. Their MPA results were obtained by the optoacoustic method. Reference 3(b) presented a very thorough discussion on the data reduction and the correct handling of various corrections. The procedure used was by fitting the experimental curve with an analytic function, and then performing the Gaussian beam correction. The biggest correction came from the high fluence portion of their data where the accuracy might be complicated by dissociation. However, we are only interested in fluences below 1 J/cm^2 where there is no dissociation and the measured result had very little spatial correction. Therefore, there should not be any serious problem in comparing their results with ours.

The biggest source of error in optoacoustic measurements is the absolute calibration of the optoacoustic signal to the real average energy absorbed by the molecules. To do so, an energy transmission measurement has to be performed
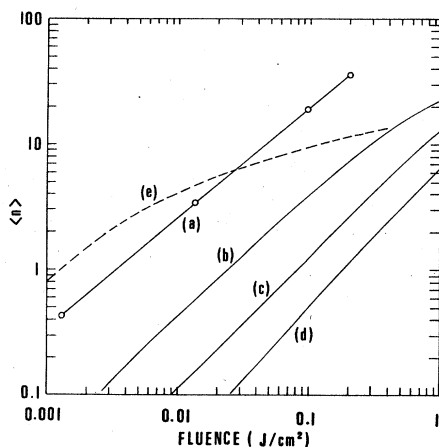
the same way as described in this paper. Other than this extra step of calibration, all the data handling procedures are the same between the present experiment and that of Black et al.

With these limitations in mind, let us examine the various curves in Fig. 7. At low fluences and small number of CO_2 photons absorbed, the shorter duration pulses have much larger absorption. There is almost a two order of magnitude difference in $\langle n \rangle$ between the 30-psec and the 100-nsec data. This is certainly due to the bottlenecking effect[1(a)] of the discrete levels. However, if absorption in QC is strictly fluence dependent, all the experimental curves should merge at high intensities. As seen from Fig. 7, this is definitely not the case. Instead, the differences in $\langle n \rangle$ between the different duration pulses persisit up to very high excitation levels of $\langle n \rangle \sim 40$, and show no resemblence to curve (e) at all.

The dependence of the energy absorption on the laser intensity in the QC is more transparent if we plot $\langle n \rangle$ as a function of the peak intensity at a fixed energy fluence. Figure 8 presents such a plot at a fixed fluence of 0.2 J/cm^2. The range of intensities almost varies by four orders of magnitude. For $\langle n \rangle < 4$, the increase in energy deposition is attributable simply to the bottlenecking effect of the discrete levels. As the laser intensity is increased, more and more molecules are coupled to the QC where the stepwise energy absorption takes place.
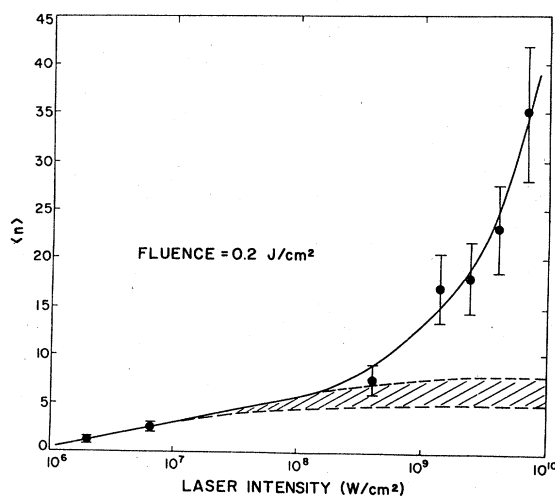

FIG. 7. Energy deposition curves $\langle n \rangle$ at P (20) for various pulse conditions (a) 30-psec data from this experiment, (b) 500-psec data from Ref. 19, (c) 30-nsec data from Ref. 19, (d) 100-nsec data from Ref. 19, (e) derived thermal absorption data from Ref. 18.

FIG. 8. Energy absorbed by the SF_6 molecule as a function of pulse intensities at fixed energy fluence of 0.2 J/cm^2. The shaded area represents the asymptotic behavior of the absorption curve if energy-fluence scaling law or the rate-equation model of the QC applies. Considerable deviation from this asymptotic behavior is observed with the ultrashort laser pulses due to the onset of coherent excitation.

If energy absorption in the QC depends only on the laser-pulse fluence, a plot of $\langle n \rangle$ versus laser intensity at a fixed fluence should approach a horizontal asymptote at high intensity where all the molecules are pumped into the QC. Schulz et al.[23] estimated that this should occur at 500 MW/cm^2, while Galbraith et al.[20(a)] estimated a value of 40 MW/cm^2 for this total transition into the QC. They imply a horizontal asymptote of $\langle n \rangle = 8$ or 5, respectively, for a fluence of 0.2 J/cm^2. However, without an exact knowledge of where the QC begins, it is impossible to determine the exact value for this horizontal asymptote. In Fig. 8, we represent the possible asymptotic behavior of $\langle n \rangle$ versus intensity by the shaded area. Regardless of the exact asymptotic value of $\langle n \rangle$, it can be seen that the measured experimental data using the picosecond CO$_2$ laser pulses deviate from the fluence scaling picture considerably. The breakdown of the energy-fluence scaling law, which states that energy absorption in the QC depends only on the laser fluence but not the intensity, seems to begin at 200 MW/cm^2.

Recently, there was a claim of observing self-focusing effects in MPA experiments.[21] Let us discuss here the implications on our experimental results if self-focusing does exist. If there is self-focusing in the absorption cell, our knowledge of the fluence J will be destroyed. The actual fluences will be larger than the numbers we used in Fig. 6. However, from Eq. (1), $\langle n \rangle$ will also be larger by exactly the same factor. Thus the experimental data points will be translated up on a straight line with the unity slope. Therefore as far as the $\langle n \rangle$ versus J curves are concerned, they will be translated upwards if self-focusing does occur. Since Fig. 8 is obtained from Fig. 6 at a fixed fluence of 0.2 J/cm^2, this implies that the picosecond data points in Fig. 8 will have to be moved upwards also. Hence, the net effect of including self-focusing in Fig. 8 is to enhance the deviation from energy-fluence scaling law, and shows greater intensity dependence of $\langle n \rangle$ within the QC. Of course it is very difficult to estimate how much self-focusing exists or if it exists at all in our 4-mm-length cell. But the conclusion of the intensity-dependent MPA in the QC is not affected by the consideration of self-focusing effects.

The result of Fig. 8 is not very surprising if we recall the conditions for the validity of the energy-fluence scaling law. It is derived from a rate-equation description of MPA in the QC.[22] For the rate-equation approximation to the Schrödinger equation to be valid, the transition rates given by Rabi frequency ω_R must obey the inequality

$$1/\hbar\rho(E) \ll \omega_R \ll 1/T_2 , \qquad (8)$$

where $\rho(E)$ is the density of states, T_2 is the intramolecular dephasing time, and

$$\omega_R = \mu E/\hbar , \qquad (9)$$

where μ is the transition moment and E is the electric-field strength of the laser pulse. In the QC, the left-hand inequality of (8) is easily satisfied. For nanosecond TEA CO$_2$ laser pulses, the right-hand inequality must also be satisfied as evidenced by the success of applying rate equations to model the MPA processes.[20,21,24] However, for picosecond pulses with more than ten-thousandfold increase in intensity, it is not surprising at all that the inequality in (8) is not obeyed, and hence the rate-equation approximation becomes invalid and the full coherent interaction picture has to be used.

Stone and Goodman[25] recently reexamined the rate equations to include the effects of intramolecular energy transfer and dephasing in the QC. It would be interesting therefore to go to the limit of rapid up pumping in their formulation and check if the behavior of energy absorption in Fig. 8 can be predicted. It is obvious that the picosecond pulse experiments can provide critical additional data in the formulation of a more general model of MPA.

It should be emphasized here that the description of the QC is very complicated as various normal modes of the molecule interact strongly. The quantities T_2 and μ in (8) and (9) should depend on the energy content and the quantum states of the molecule. The implication of Fig. 8 is that the up-pumping rate of the molecule by the picosecond laser pulses is comparable or even faster than the intramolecular relaxation rate. This must be the reason why intensity-dependent effects are observed in the QC.

There is no contradiction between this last conclusion and the fact that the absorbed energy is completely randomized during the laser pulse.[15] The up-pumping rate may be faster than the dephasing rate $1/T_2$. But after the laser-pulse duration, the absorbed energy will still be randomized. The only difference between the usual MPA with nanosecond pulses and the present study is that the final population distributions are different, which is manifested by a vastly different average number of photons absorbed $\langle n \rangle$. It is evidently true that using picosecond laser pulses, there is much more efficient coupling of energy into the molecule.

This superexcitation of a polyatomic by picosecond laser pulses offers an interesting possibility. If we increase the laser fluence still further, say beyond 1 J/cm^2 with the 30-psec

pulses, we may have a situation where the up-pumping rate is counterbalanced only by the dissociation rate. With such high levels of excitation, it is possible for the corresponding dissociation rate to be comparable or even faster than the energy randomization rate. This would imply a breakdown of the RRKM theory of unimolecular reactions. This new regime of interaction of a strong laser with a polyatomic molecule merits further systematic study.

In summary, we have demonstrated that using picosecond CO_2 laser pulses it is possible to achieve superexcitation of the SF_6 molecules. This interaction is not amenable to the usual rate-equation approach to MPA and requires the full coherent interaction descriptions. The deviation seems to begin at 200 MW/cm^2.[26]

B. SF_6 at 650 K

In this experiment we used the $P(28)$ line of the laser. A fixed fluence (0.054 J/cm^2) truncated pulse of 30-nsec duration was used to preheat the SF_6 molecules as described in Sec. IV. A 50-psec pulse was then used to obtain the $\langle n \rangle$ versus fluence curve for the hot molecules using the procedure as described in Sec. III. In this experiment we were not so much interested in the pulse duration dependence of $\langle n \rangle$ as the saturation properties of the QC. Therefore, only one laser-pulse duration was used. Since all saturation phenomena are closely related to the relaxation mechanisms, a study of the saturation properties of the QC should provide some information on the intramolecular energy-relaxation rate.
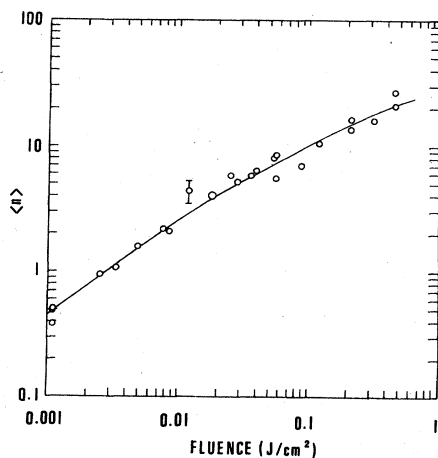
Figure 9 presents the measured energy-deposi-

tion curve using 50-psec pulses with a 38.1-mm focal length germanium lens. A gas cell of 1 mm thichness containing 30 torr of SF_6 was used in this experiment. The experiment has been repeated several times, and also different focal length lenses were used to make sure the results were reproducible. The spacial correction, as described in Sec. III, has already been applied in Fig. 9.

From the experimental data, one can also obtain the absorption cross section σ of the preheated molecule as a function of the laser fluence. Combining this curve with Fig. 9, one can then get the absorption cross section as a function of internal energy in the molecule. This is shown in Fig. 10. On the same figure, we also plotted the thermal absorption data of Nowak and Lyman using a procedure as described in Appendix A.

From Fig. 10 we notice an intial saturation of absorption at low picosecond pulse fluences which seems to be universal for all polyatomic molecule MPA experiments. However, the absorption cross section rapidly approaches that of a thermally excited molecule at a moderate level of excitation of $\langle n \rangle \sim 8$. Unfortunately, the thermally measured data does not extend beyond 8.5 CO_2 photons of internal energy. However, comparing with a thermal-band contour calculation,[28] represented as a dashed line in Fig. 10, we can see that at higher values of $\langle n \rangle$, the observed absorp-
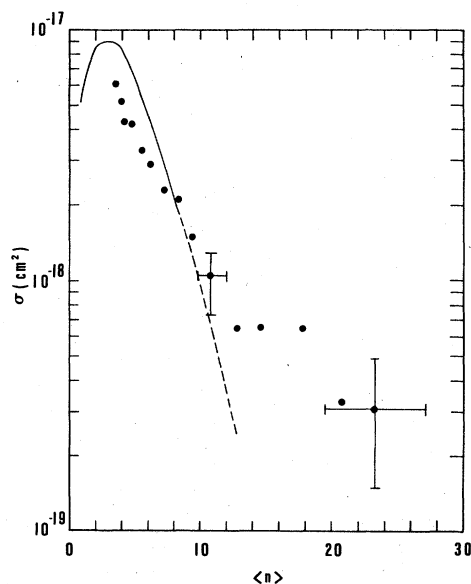

FIG. 9. Energy deposition $\langle n \rangle$ as a function of pulse fluence. Fifty-psec $P(28)$ CO_2 laser pulses were used. SF_6 cell pressure was 30 torr and preheated to 650 K before the picosecond pulse arrived.

FIG. 10. Absorption cross section σ as a function of internal energy of the SF_6 molecules at the $P(28)$ line of the CO_2 laser. Data became more inaccurate at high energies. Solid curve shows the thermal data from Ref. 18, dotted line is the theoretical calculation from Ref. 27.

tion cross sections of the molecule is definitely larger than the value predicted with a thermal distribution of excitations. This is in agreement with the results obtained with 300 K SF_6 molecules in the previous section. It is further evidence that the nonthermal behavior of the SF_6 molecules does not come from the initial discrete levels, but rather is a property of the QC at such high laser intensities. The experimental values at high $\langle n \rangle$ have quite large error bars on them because they have the most experimental uncertainty and also the largest correction factors.

Let us estimate here whether 650 K is hot enough for the molecules to be considered in the QC. A heuristic definition of the QC is that the power broadening introduced by the laser is sufficient to bring about an overlap of all the resonant lines of the system, or

$$\omega_R \gg 1/\hbar\rho(E) , \qquad (10)$$

where $\rho(E)$ is the density of states of the molecule. This operational definition of the QC depends on the experimental situation and is therefore not universally applicable. In particular, it is easily satisfied by the picosecond pulses because of their large Rabi precession frequencies and power broadening. For SF_6 at 650 K, $\rho(E) \sim 10/cm^{-1}$.[6(c)] The power broadening for the lowest data point in Fig. 9 is estimated to be ~ 1 cm^{-1}. Hence the QC condition is satisfied. However, it is expected that for a thermal distribution of population at 650 K, there must be still some molecules trapped in the initial discrete levels. This presumably is the cause of the initial saturation of absorption in Fig. 10. To alleviate this problem and perform a cleaner experiment on the QC, one can either preheat the molecule with a stronger prepulse, or use a picosecond pulse for preheating, or use overtone pumping by a strong dye laser.

The thermal curves used in Figs. 7 and 10 should only be regarded as a reference. Since no simple statistical definition of temperature exists for a molecule under MPA pumping conditions, it is unfair to claim that SF_6 should behave as if an equilibrium Boltzmann population distribution has been achieved.

Figure 10 represents the saturation of absorption in the QC. All previous measurement of this phenomenon had blended to a great extent the effects of the discrete level bottleneck. As mentioned above, the observed absorption can be called "superthermal" because it is always larger than the thermal absorption at the same internal energy. Stone and Goodman[25] recently pointed out a new formulation of the absorption

in the QC using a fully coherent interaction picture. They showed that energy deposition and hence the absorption cross section can be intensity dependent if the radiative pumping time scale is comparable to the intramolecular relaxation time. This also was pointed out by Quack[20(c)] in deriving the master rate equations from the Schrödinger equation describing the laser-molecule interaction. Multiphoton interaction in polyatomic molecules using very strong laser fields and short pulse durations is characteristically different from ordinary TEA laser interactions and merits much more careful investigation, both experimentally and theoretically. While the observation can be explained qualitatively, a thorough understanding of the role of intensity is still lacking. The population distribution and possible multilevel coherence especially still need to be studied and clarified.

Notice that there are two types of dephasing of the coherent state prepared by the CO_2 laser. The T_2-type intramolecular relaxation couples the energy into the heat bath. This dephasing converses the energy in the molecule. The other kind of dephasing arises from the inhomogeneous broadening of the ν_3 band. The laser pulse will excite simultaneously states that are within the linewidth $\Delta\nu_L$ of the laser. They will beat together incoherently and dephase the coherence[21] in a time $1/\Delta\nu_L$ which is simply the laser-pulse duration. This type of dephasing is responsible for the adiabatic decay observed by Kwok et al. Recently Steel et al.[29] observed a collisionless dephasing time of 1.8 nsec for the $2\nu_3$ level using degenerate four-wave mixing. Since 1-nsec pulses were employed, their results were probably due to the second type of dephasing, which has nothing to do with intramolecular energy relaxation, contrary to the interpretation by Galbraith et al.[20(a)]

VI. CONCLUSION

In this paper we have described two measurements of MPA in SF_6 using picosecond CO_2 laser pulses. We found that for such pulses, the energy-fluence scaling law no longer holds. Instead, a remarkable intensity dependence was observed. This effect is inherent with the picosecond pulses because (i) the corresponding intensities and Rabi frequencies are high, comparable or larger than the intramolecular relaxation rate of the molecule, and (ii) the transform limited lifetime broadening of these pulses enables the coupling of more states in the QC. Thus, the reduced oscillator strength as discussed by Goodman et al.[30] is no longer very small, as in the case of ordinary TEA CO_2 pulses.

Although energy-fluence scaling has played an important role as a zeroth-order approximation in the description of multiphoton dissociation, the limitations of its validity must be recognized. For picosecond pulses the Rabi frequency can readily be increased to levels where the one-photon rate equations for QC absorption have to be modified by coherent effects. It is also well known that at small Rabi frequencies bottlenecking effects are important. This occurs for pulses of $0.1 \, J/cm^2$ or lasers with durations of more than 1 nsec. In both cases intensity-dependent effects are observed which depend on the pulse duration at constant energy fluence. Although it is difficult to vary the pulse duration at constant fluence over many orders of magnitude, more experiments on absorption of picosecond pulses by other molecules are desirable. The dissociation probability by a pulse of fixed picosecond duration should also be measured as a function of intensity. It is believed that picosecond data can test more precisely various theoretical models of excitation in the QC regime.

Although it is possible to achieve a nonthermal population distribution by picosecond pumping, no claim for mode selective chemistry is made. Energy equipartition will occur rapidly, albeit in a time longer than the Rabi period. It is believed that molecules can be excited to energies considerably higher than with longer pulses.[31] This should be observable as an increase in the internal and kinetic energies of dissociation products in molecular-beam experiments.

APPENDIX: THERMAL MPA IN SF_6

In this appendix, we explain how the thermal curves in Figs. 7 and 10 were obtained from the thermal-shock-tube measurements of Nowak and Lyman.[18] In that experiment the small-signal absorption cross section σ of an excited SF_6 molecule was measured as a function of the temperature T K. Using quantum statistics, it is possible to relate the total internal energy in the molecule E and the temperature T. The average number of photons $\langle n \rangle$ deposited is related to E by

$$E = E_0(\text{at } 300 \text{ K}) + \langle n \rangle \, \hbar \omega . \tag{A1}$$

Therefore, from the NL data of σ versus T, we can obtain a curve of σ versus $\langle n \rangle$ for both the $P(20)$ and $P(28)$ lines of the CO_2 laser. This was the smooth curve in Fig. 10.

The next step involves the reduction of the data to get the $\langle n \rangle$ versus fluence J. This is the hypothetical energy deposition curve if the absorption of the molecule follows the thermal cross section. Note that

$$\sigma = \frac{d\langle n \rangle}{dJ} \, \hbar \omega \tag{A2}$$

can be written as

$$\hbar \omega \, \frac{1}{\sigma} \, d\langle n \rangle = dJ .$$

Integrating both sides from the initial condition $\langle n \rangle = 0$ at $J = 0$, gives

$$\hbar \omega \int_0^{\langle n \rangle} \frac{1}{\sigma} \, d\langle n \rangle = J .$$

Since σ has already been reduced to be a function of $\langle n \rangle$, the integral on the left-hand side can be evaluated numerically with the upper limit as a parameter. Thus one can obtain a curve of $\langle n \rangle$ versus J as in Fig. 7.

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