Multiphoton Absorption of Broad-Band CO_2 Laser Radiation by SF_6

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Abstract. Increase of the emission bandwidth of a high-pressure CO_2 laser up to $1.5\,\mathrm{cm}^{-1}$ increases the multiphoton absorption cross-section of SF_6. Comparison with the previously found [9] increased absorption for shorter pulses suggests that this is also a bandwidth effect. Spectral structures as narrow as $1\,\mathrm{cm}^{-1}$ above the 10th absorption step are invoked to explain the observations. The temperature effect, which disappears in the broad-band case, confirms this view.

From the many mechanisms (for a compilation see [1]) which have been suggested to explain infrared multiphoton excitation two extremely opposite concepts can be distilled. The first of them, which may be called statistical, extrapolates behavior of states near the dissociation energy down to lower states. Typical assumption are that the energy is equi-distributed between the modes, either by direct optical absorption or by relaxation; that spectra above about the third absorption step (in the case of $\sim 1000\,\mathrm{cm}^{-1}$ quanta) are broad and nearly continuous; and that spectral details like anharmonic shifts can be ignored above this step.

In the other concept spectroscopic features of low states are extrapolated to high energies, sometimes up to two thirds of the dissociation energy. The energy stays concentrated in the few modes carrying oscillator strength. Anharmonic shifts in high states are larger than spectral widths. A wide-spread feature, however, is a multiplet structure generated by overtone and combination states of (infrared-active) nearly degenerate or anharmonically split degenerate modes. Each multiplet component can (at least, at high energies) consist of a few lines generated by spectral intensity lending to background states. If this intensity borrowing does not fill up the gaps between the multiplet components, spectroscopic assignments make sense.

Detailed mechanisms are considered in [1], where evidence in favor of the spectroscopic concept is emphasized. More recently, in CARS work on multiphoton-excited SF_6 [2] states up to $v_3 = 4$ have been detected. Also more and more success is brought about by quantum-mechanical calculations [3–6] assuming sparse densities of spectral lines and few modes only, but not assuming broadening or relaxation.

A direct decision between a nearly continuous and a structured spectrum would be a comparison of excitation efficiency for different laser bandwidths. The larger bandwidth should cover several multiplet components (distance in SF_6 typically 1–$3\,\mathrm{cm}^{-1}$), the smaller one should not. If and only if there are gaps in the spectrum, the larger bandwidth should be more effective in excitation. An experiment of this kind has been made [7–9]: the pulse length of a CO_2 laser at $944\,\mathrm{cm}^{-1}$ was varied by orders of magnitude; the associated intensities generated interaction widths ("power broadenings") varying between fractions of one cm^{-1} and $15\,\mathrm{cm}^{-1}$ (calculated for the first step); although these widths are too small to compensate anharmonic shifts in high steps, the shorter pulses were much more efficient in excitation of SF_6. In [1, 10] this difference was attributed to the bandwidth effect

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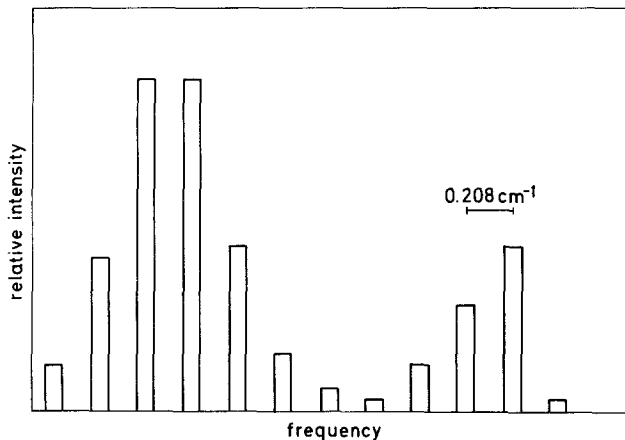 ** Institute of Electronics, Academia Sinica, Beijing, China

Fig. 1. Emission spectrum of the laser. The CO_2 laser 10 $P20$ line (944.2 cm^{-1}) would be between the two strongest peaks. The absolute positions were not determined. The individual lines are narrower than the spectral resolution. For determination of the spectrum we made burn patterns at the exit of a spectrograph (described in [11]), attenuating the laser by reflective beam splitters of various transmissions T; then we plotted T^{-1} vertically versus the positions of equal brightness of the different burn patterns

discussed, the larger bandwidth (of the shorter pulses) covering several multiplet components, and it was concluded that there are gaps between these multiplet components.

A drawback of this experiment is that the interaction widths are not well defined: they vary during the pulse and as a function of the pulse energy (for given pulse length) and they depend on the transition (multiplet component) considered. Furthermore, other intensity-sensitive effects like direct two-photon transitions cannot be excluded. Relaxation could also explain the results if it would adversely affect the excitation efficiency [10]. (The wide-spread assumption of a relaxation which assists excitation is disproved [1, 10] by this experiment [9].)

We report about results nearly free of this drawbacks: Our CO_2 laser emits with broad bandwidth at 20 bar, but with narrow bandwidth at 4 bar. Pulse lengths are equal. The differences found in the absorption of SF_6 at 944 cm^{-1} are qualitatively the same as in the experiment with the varied pulselengths [9]. So the conclusions of [1, 10] and also [9] about the spectral structure of highly excited SF_6 are confirmed.

Experimental

The experiments were performed by measuring the transmission of the 10 $P20$ line of a CO_2 laser through a 1 m long cell containing SF_6 at a density of 6.5×10^{15} molecules/cm^3. The laser used was the high pressure,

electron beam preionized, continuously tunable laser described in [11]. In the experiments with a narrow line it was operated at a pressure of 4 bar and tuned by a grating (135 grooves/mm, 75 mm wide) and an intracavity telescopic beam expander to the maximum of the 10 $P20$ line. In the broad-band case the laser was operated at 20 bar and tuned by a NaCl prism to a region of around 1.5 cm^{-1} full bandwidth, centered at the same frequency. In this case the laser output consisted of a structure of frequencies separated by about 0.2 cm^{-1}, the free spectral range of the output coupler which acted as a Fabry-Perot etalon due to imperfect antireflection coating. The emission spectrum is displayed in Fig. 1. In all cases the laser pulsewidth at half height was about 60 ns without any tail and without any modulation at a time resolution of 10 ns. It exhibited a nearly pure Gaussian profile with a full width ($2w_0$) of around 6 mm.

The transmission of the cell was obtained by placing identical, calibrated joulemeters in front and behind the cell. Before and soon after each series of measurements the meters were calibrated with the cell empty, and the various values of energy density were obtained by using different calibrated CaF_2 attenuators before and after the cell, in such a way that we could always use the same scale of the detectors. To avoid uncertainties of transmissions owing to optical interferences which are temperature sensitive, the beam splitter placed before the cell was a 15 mm thick NaCl disk, and for each situation the measurements were performed many times and the mean values were taken as results.

Dissociation was measured in a 6 mm wide and 100 mm long copper cell equipped with NaCl windows. The cell was placed at a distance of 2 m from an $f = 3$ m mirror, with a flat mirror immediately after the cell reflecting the beam back within itself. The depletion of SF_6 was measured several times after 10 to 100 pulses by an infrared spectrometer.

Evaluation

The directly measured quantity was in all cases the transmission of the cell, T_M, defined as the ratio between the transmitted and the incident energies, as read in the joulemeters.

The values of the energy densities used in the calculations and plots are averages over the length of the cell:

$$\bar{\phi} = L^{-1} \int_0^L \phi(l)dl \cong -\phi_{in}L^{-1} \int_0^L \exp[-\sigma(l)Nl]dl$$

$$\cong -\phi_{in}(1 - T_M)/\ln T_M, \qquad (1)$$

where N is the number of molecules per cm^3, L is the length of the cell, and $\sigma(l)$ is the local absorption cross-

section. For the incident energy density we took the maximum of the Gaussian beam:

$$\phi_{in} = 2E_{in}/\pi w_0^2, \qquad (2)$$

where the e^{-2} radius $w_0 = 3$ mm in our case.

The measured values of T_M, on the other hand, are, of course, averages over the whole beam. The values that really correspond to the fluences defined in (1) are obtained following the procedure given in [12] for the deconvolution of a Gaussian beam. The deconvoluted transmission is given by

$$T = T_M \left(1 + \frac{d \ln T_M}{d \ln \bar{\phi}} \right) \qquad (3)$$

and the total cross section is obtained in the usual way

$$\bar{\sigma} = - \ln T/NL. \qquad (4)$$

The mean number q of quanta absorbed per molecule is related to $\bar{\sigma}$ and to the absorbed energy ΔE by

$$q = \bar{\sigma}\phi/hf \qquad (5)$$

$(hf:$ quantum energy$)$ and

$$q \cong \Delta E/SLNhf = (1 - T)\phi/NLhf \qquad (6)$$

$(S = \pi w_0^2/2$ is the effective area of the Gaussian beam$)$. Equation (6) involves an averaging along the cell length, whereas (5) is defined locally. For small absorptions (5) and (6) are identical. The differential cross-section, defined as

$$\sigma = hf \frac{dq}{d\phi} \qquad (7)$$

can be expressed as

$$\sigma = hf \frac{q}{\phi} \frac{d \ln q}{d \ln \phi}. \qquad (8)$$

Equation (8) is more convenient to evaluate than (7), because the logarithmic slope varies only slowly.

The cross-section σ can be evaluated from Fig. 2 which shows q as a function of ϕ. Instead of plotting it versus ϕ, it is shown in Fig. 3 as a function of the average excitation q, which was also taken from the data of Fig. 2.

Under our conditions of measurement, self-focusing in SF_6 [13–16] was observable. According to [16] the transition from defocusing to focusing occurs between 0.1 and 1 J/cm^2 at 944 cm^{-1}. Our set-up made sure that all transmitted energy – deflected or not – reached the detector. So self-focusing can only affect the average energy density ϕ, over which q is plotted. We neglected this effect in the evaluation, because it probably affects narrow and broad band data in a similar way.
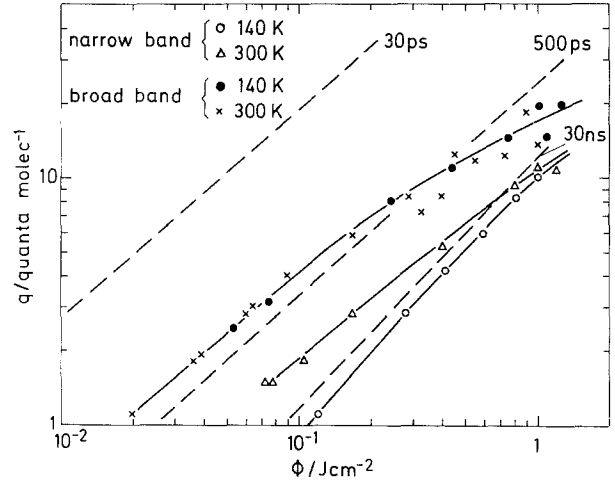

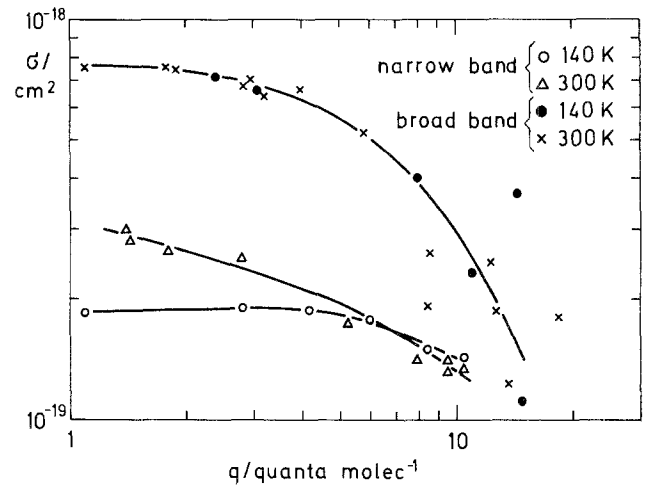Fig. 2. Absorbed energies as functions of incident energies. Broken lines from [9]

Fig. 3. Differential absorption cross-section versus average absorbed energies

Results

In Fig. 2 is shown the mean number of photons absorbed per molecule for narrow and broad band excitation at room temperature and at 140 K. One can see that the broadening of the line has increased the absorption relatively to the narrow line cases by factors between 3 and 5 for fluences of 0.1 J/cm^2 and by a factor 2 for a fluence of 1 J/cm^2.

In the same figure are also displayed the results obtained by Kwok et al. [9] (broken lines), with 30 ps pulses, and those of Black [7, 8] with 500 ps and 30 ns pulses, used as reference in the same work [9].

Our 60 ns narrow-band data lie very close to the 30 ns data of [7–9]. Our 60 ns broad-band absorptions are very close to those measured by 500 ps pulses [9]. It is also worth noting, that the temperature has no effect

on absorption of broad-band radiation, in contrast to the narrow-band case.

Similar observations can be made in Fig. 3, where we show the differential absorption cross-section as a function of average excitation level.

Interpretation

The absorption data of Fig. 1 show that the difference between narrow and broad bandwidth is very similar to the difference between the 30 ns and 500 ps data presented in [9]. For the 500 ps pulses one calculates interaction widths $2\hat{\mu}\hat{E}/hc$ of 6.5 cm^{-1} at 1 J/cm^2 and 2 cm^{-1} at 0.1 J/cm^2, taking the transition moment of the first step, 1.4×10^{-30} C m [17], for $\hat{\mu}$. This assumption may be too high or slightly too low, depending on the multiplet component considered. Allowing for this uncertainty and also for the double peaked envelope of our laser spectrum (Fig. 1), the agreement is good. (The fine structure of the laser spectrum will be blurred by the interaction width.) So we conclude that the pulse length effect of [9] is due to the associated bandwidths. One must not invoke relaxation (as done in [9]) or direct multiphoton transitions which would also be sensitive to intensity.

At substantially higher energies, the difference between narrow and broad-band laser should disappear, because power broadening (interaction width) alone will cause sufficient bandwidth. Our setup did not allow to measure at much above 1 J/cm^2. Instead we measured the dissociation probability P_d at 8 J/cm^2 (in the peak of the Gaussian beam). Within our accuracy we found the same value of $P_d = 0.10$ for both the narrow and the broad band laser. The interaction width is calculated to be 1.7 cm^{-1}.

The band-width effect can be due to two different reasons: The first one can be called hole-burning mechanism. It has to do with the distribution of molecules over initial rotational and vibrational states and the fact that only a fraction of these molecules can respond to the laser frequency. This fraction depends on bandwidth including interaction width ("power broadening"). As argued below, this effect cannot explain all observations, but certainly contributes to them.

The second mechanism was already mentioned in the introduction. It invokes spectral structures in higher steps. A laser with a bandwidth narrower than the typical gaps in this structure will sooner or later encounter a bottleneck. The bandwidth, at which such bottlenecks disappear, indicates the width of the spectral gaps.

The increase of excitation efficiency for shorter pulses has been interpreted [1, 9, 10] to be due to the second mechanism. The main argument was, that at average excitations of up to 35 quanta/molecule the first absorption step cannot anymore have a dominant

influence. Although our data do not go much above 15 quanta/molecule, the same statement can be made in our case. The argument becomes clearer, if the differential cross section σ is plotted versus average excitation q (Fig. 3): At $q = 15$ the probability σ of absorption of one more photon should not depend very much on the first step, because few molecules only are left in the initial states. A more quantitative reasoning invokes the fractions f of molecules which can respond to the laser frequency: According to [18, 19], $f \gtrsim 0.6$ at 2 J/cm^2 of a narrow-band laser around 944 cm^{-1} and with pulse length of about 50 ns. In our broad-band case f will have increased certainly not to 1, but maybe to 0.8. So the hole burning mechanism can account only for part of the bandwidth effect.

A nice confirmation of this interpretation is the temperature effect. As it has repeatedly been found [20–22], the absorption of narrow-band radiation (on the long-wavelength side of the band center) increases with temperature. This increase can be correlated with hot bands starting from thermally populated vibrational states. As suggested in [1], these additional vibrational quanta cause additional splittings. They are small compared to the usual anharmonic splittings, as can be concluded from low resolution spectra, in which hot bands generally look very similar to the corresponding fundamentals. But because of the small spectral widths discussed here, small splittings may already be good to remove bottlenecks. If these bottlenecks are overcome in another way, e.g. by laser bandwidth, the temperature effect must disappear. That is exactly what Fig. 2 shows. This lack of temperature effect on absorption of broad-band radiation will be difficult to explain in another way.

Recently, it has been found [23] that the exchange of v_3 quanta with ground state SF$_6$ occurs at a rate proportional to the v_3 quantum number ($k_{VV} \cong v_3 \cdot 1 \times 10^{-9}$ cm^3/s · molec), whereas the $V \times V'$ transfer was more than 20 times slower. So for our densities, a molecule with e.g. $v_3 = 10$ would have exchanged one v_3 quantum in 15 ns. Such an exchange tends to equalize the populations of v_3 sublevels. The resulting spectra will certainly have more resonances. If they were continuous (and homogeneous), there would be no difference of absorption between narrow and broad band case. Obviously, there is still structure, in spite of beginning relaxation. However, this becomes plausible if one remembers that such a fast VV transfer can change the rotational quantum numbers only by 0 or 1 [24]. Therefore, in the narrow-band case only few rotational states are populated, and the spectrum can still have a sparse structure.

It may be worth noting that in several studies of SF$_6$ [8, 25–28] and other molecules (see the review [29]) the laser bandwidth was altered into the other direction: They employed a laser with a single longitudinal mode

(bandwidth $\leq 10^{-3}$ cm^{-1} compared to ~ 0.03 cm^{-1} for an atmospheric pressure laser). They found smaller absorption probabilities which have been explained as an effect of the very first (one-photon or two-photon) step: Single-mode radiation contains no power fluctuations (no spiking). Intensity-dependent effects like direct two-photon excitation and power broadening (affecting the number of rotational states which can respond to the radiation) are reduced. Our large bandwidth data have implications concerning higher steps.

Conclusion

Our experiment confirms the previous interpretation [1, 10] of the short-pulse measurements which postulated spectral structure as narrow as 1 cm^{-1} also in higher steps. Concluding from the high average excitations involved (up to 15 and 35 quanta/molecule in this work and in [9], respectively), these structures seem to survive above the 10$^{\text{th}}$ absorption step, at least. Although, at present the contrast ratios of the structures are not known, a *spectrum* with such narrow features should not be called quasicontinuous. (Of course, one can talk about spectral structure in the quasicontinuum of *states*.)

Of course, there may also be structure very much narrower than 1 cm^{-1}. This is what the prefix of "quasicontinuum" hints to. However, as long as the line distances are smaller than the interaction width, this structure will not be noticed.

At first sight it is surprising to see an effect of bandwidth which is much smaller than anharmonic shifts, e.g. at $v = 10$. However, [1] gives a compilation of mechanisms which tend to restore resonance in spite of anharmonicity. A central role play alternate absorptions in the (e.g.) R branch and emissions in P branch to different sublevels of multiplets (cooperation of rotational compensation with anharmonic splitting). The spread of the multiplets is governed by the largest anharmonic constants, probably g_{33} and t_{33}. The widths of the components which are caused by smaller anharmonic constants, are smaller than their distance (~ 1 to 3 cm^{-1}). Since the spectra have gap, at some step the resonance will not be perfect and excitation will encounter a bottleneck.

However, if the laser covers the gaps in the spectrum by its bandwidth, such a mechanism *must* work. Such an excitation could be accurately calculated with present-day knowledge. Exact positions of multiplet components and small spectral broadenings (by spectral intensity lending to background states) could be ignored in such a calculation.

A referee pointed to the excitation by blackbody radiation calculated in [30]. The fundamental difference to our case should thus be stressed: The extreme bandwidth of blackbody radiation covers any

anharmonic shifts and spectral structure, so that the molecules can be treated like harmonic oscillators. Conclusions about spectra are not possible, in contrast to our case, where the bandwidth is even smaller than the mean anharmonic shift in a single step.

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