

Spectral Characteristics of IR-Multiphoton Excitation in Supersonic Molecular Beams

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Abstract. The multiphoton absorption of SF_6 was investigated in supersonic molecular beams in dependence on the fluence and the wavelength of the CO_2 laser. The temperatures of the SF_6 molecules have been reduced using seeded beams of different concentrations. The experimental results are discussed on the basis of the known spectroscopic data of SF_6 and provide some novel information about the spectral characteristics of the ir-multiphoton excitation of strongly cooled molecules in the collision-free case.

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Many laboratories reported studies on the multiphoton absorption of molecules in a strong ir-laser field [1,2]. In most experiments carried out, the spectral characteristics of this absorption process is masked by collisions in the absorbing gas and is complicated by a high number of thermally populated levels in the vibrational ground and excited states. Therefore, one can expect novel information by the application of the supersonic-molecular-beam technique, where there are no collisions during the interaction and a strongly reduced energy distribution due to the extreme cooling of the gas [3]. If additionally the molecules are seeded in atomic gases like He or Ar, the rotational temperature can be reduced to a few K and also the vibrational temperature should be decreased significantly. That means a narrow rotational distribution at small J -numbers and nearly complete absence of hot-band transitions.

We have used this method to investigate the spectral features of the multiple photon absorption in SF_6 , the molecule for which most spectroscopic information has been obtained in the past [4].

1. Experimental Equipment

In the experiments we used an arrangement schematically shown in Fig. 1 and discussed in more detail in

[5]. It bases on a home-made pulse nozzle with an opening time of $30\ \mu\text{s}$ (FWHM). Within this time the molecules travel through an orifice of $0.65\ \text{mm}$ and expand from a back pressure of $1\ \text{Atm}$ to vacuum with a residual pressure of about $10^{-4}\ \text{Torr}$. The number N_0 of molecules per pulse of the nozzle depends on the gas mixture (Table 1). The energy of the molecules in the free is detected using a pyroelectric detector, a $2 \times 10\ \text{mm}^2$ PVDF-foil of $6\ \mu\text{m}$ thickness. The time constant of the detection system is about $5\ \mu\text{s}$.

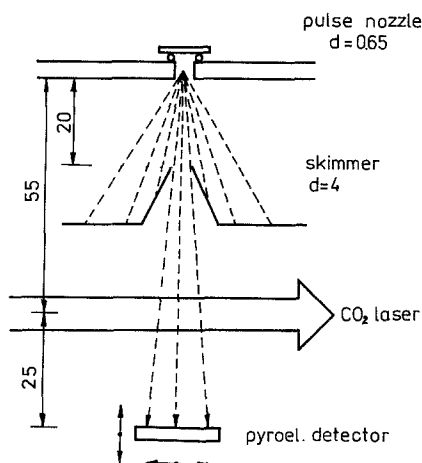


Fig. 1. Scheme of experimental equipment (all measures in mm)

Table 1. Characteristic molecular-beam parameters

c	N_0	$n(\text{SF}_6)$ [cm^{-2}]	\bar{v} [m/s]	T_{rot} [K]	T_{vib} [K]
100% SF_6	10^{16}	1.75×10^{14}	450	≈ 40	≈ 160
10% SF_6 in He	2.3×10^{16}	1.0×10^{14}	880	≈ 5	T_v^{He}
20% SF_6 in H_2	1.8×10^{16}	1.1×10^{14}	770	≈ 10	$T_v^{\text{H}_2} < T_v^{\text{He}}$

Changing the lateral position of the detector we have probed the angular distribution which yields the density n of molecules at the detector (Table 1). Moving the detector to different positions parallel to the beam we have measured the mean velocity \bar{v} of the molecules (Table 1). For pure SF_6 one can estimate – from the broadening of the molecular beam pulses – the translational temperature T_{trans} and assuming $T_{\text{rot}} \approx T_{\text{trans}}$ can estimate the vibrational temperature T_{vib} by means of the energy balance of the molecular system. This method, however, fails for small SF_6 concentrations in seeded beams. Here, an estimation of $T_{\text{rot}} \approx T_{\text{trans}} = T$ was possible by means of the relation

$$\frac{T_0}{T} = \frac{\gamma-1}{2} M^2 + 1$$

with

$$M = 2.05 \left(\frac{\lambda}{0.25D} \right)^{(1-\gamma)/\gamma}, \quad (1)$$

where M denotes the Mach number which depends on the mean free path length λ , the nozzle diameter D and the ratio γ of the effective specific heats of the gas mixtures [6]. The obtained rotational temperatures agree approximately with values, determined spectroscopically with tunable lasers [7].

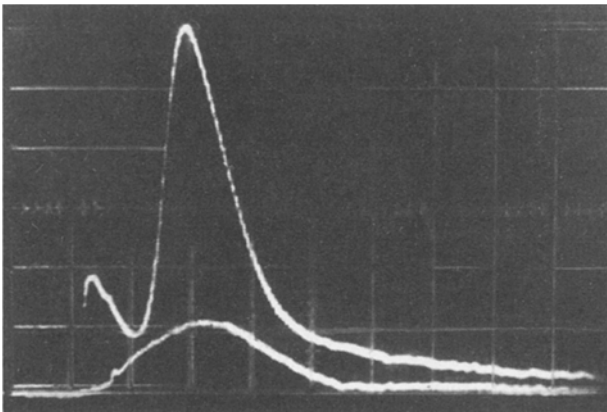


Fig. 2. SF_6 molecular beam pulse signals (above: with laser, below: without laser). Time base: 20 $\mu\text{s}/\text{cm}$

The molecular beam was intersected perpendicularly by the pulsed CO_2 laser field at a distance of 55 mm from the nozzle. We used a line-tunable TEA CO_2 laser in the TEM_{00} mode but longitudinal multimode regime. The pulse shape is characterized by standard values: a linewidth of 80 ns for the peak and about 1 μs for the tail at nearly equal energy contents. The laser beam was focused more or less, and attenuated with CaF_2 plates. For the multiphoton absorption measurements we used additionally a skimmer with a diameter of 4 mm and placed at a distance of 20 mm apart from the nozzle.

Synchronizing the laser to the molecular-beam pulse we have obtained characteristic signals, as shown in Fig. 2 above. The small background signal without laser radiation is due to the kinetic and internal energy of the molecules. The difference of both signals represents the energy absorbed by the molecules; this quantity is proportional to the mean photon number η absorbed per molecule. This signal was measured in dependence on the fluence and the wavelength of the laser field for different gas mixtures and, hence, different temperatures of the investigated SF_6 molecules.

2. Experimental Results and Interpretation

Firstly, we have studied the fluence dependence of the absorption signal for the 10P(16) line of the CO_2 laser, the wavelength which nearly coincides with the Q -branch of the ν_3 vibrational mode of SF_6 . The experimental results are depicted in Fig. 3. The non-linear absorption curves for the molecular beams show a nearly constant slope up to about 2 J/cm^2 where the dissociation of SF_6 molecules begins. The plateau is reached at fluences where the maximum of the distribution of vibrationally excited molecules corresponds to the dissociation limit, i.e., the mean photon number absorbed per molecule should be about 30 here. We have supposed that at these fluences all molecules interact with the laser field [3]. On this way we have normalized both curves to the same estimated value of the absolute η scale.

For comparison it is drawn the result of corresponding cell measurements carried out with an optothermal detector calibrated absolutely by means of transmission measurements [8]. The slope has the characteristic value 0.65 slowly increasing above 0.2 J/cm^2 where the quasi-continuum of the molecular levels of SF_6 is arrived. In this case the absorption process is dominated by single-photon transitions with step-by-step excitation within the vibrational ladder. Only at relatively high fluences where the slope is larger than 1, also multiphoton transitions can be included.

In supersonic beams, however, without collisions and with strong cooling “pure” multiphoton processes

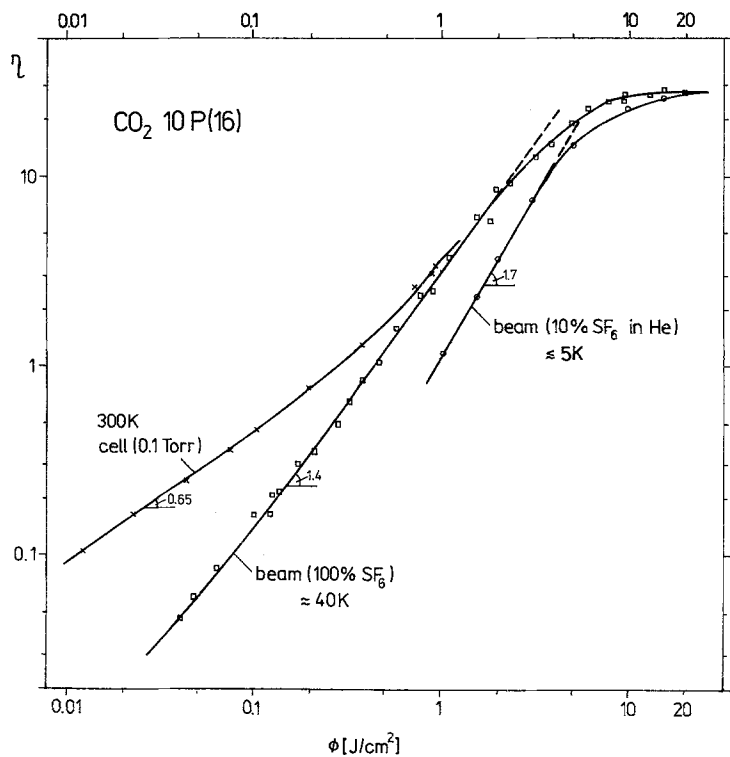


Fig. 3. Mean photon number η absorbed per molecule vs. fluence ϕ for SF_6 molecules in a beam and a cell, respectively

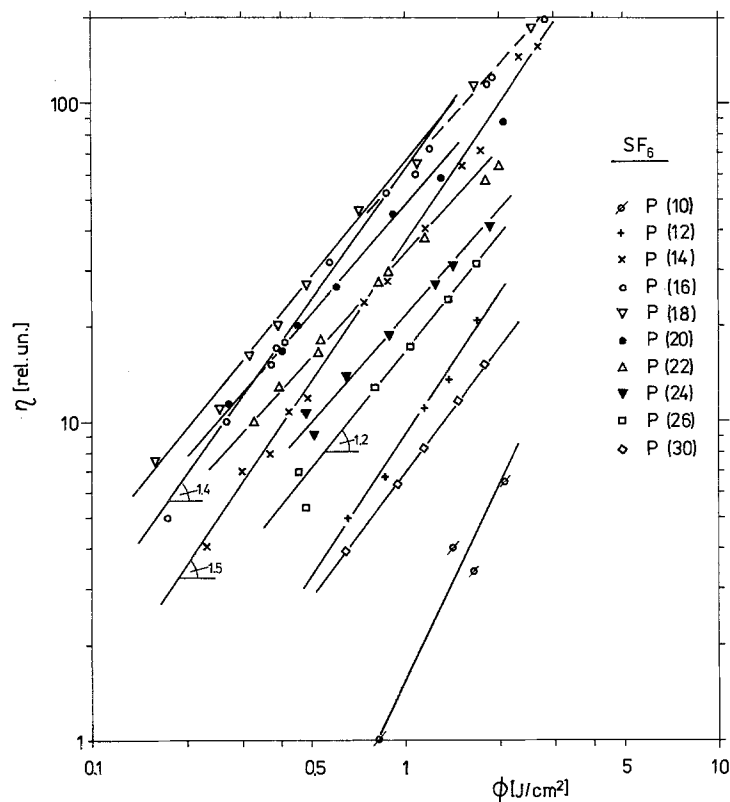


Fig. 4. Absorbed energy η vs. fluence ϕ at different laser wavelengths for 100% SF_6

contribute in an extending way, because the probability decreases to fulfil the resonance condition for single-photon transitions. Hence the slope is larger than 1. This tendency is more pronounced for stronger cooling, that means further reduced density of popu-

lated energetic states as realized for SF_6 molecules seeded in He (Fig. 3).

To investigate the spectral features of the SF_6 absorption at different temperatures, we have measured the fluence dependence of the signals for different wave-

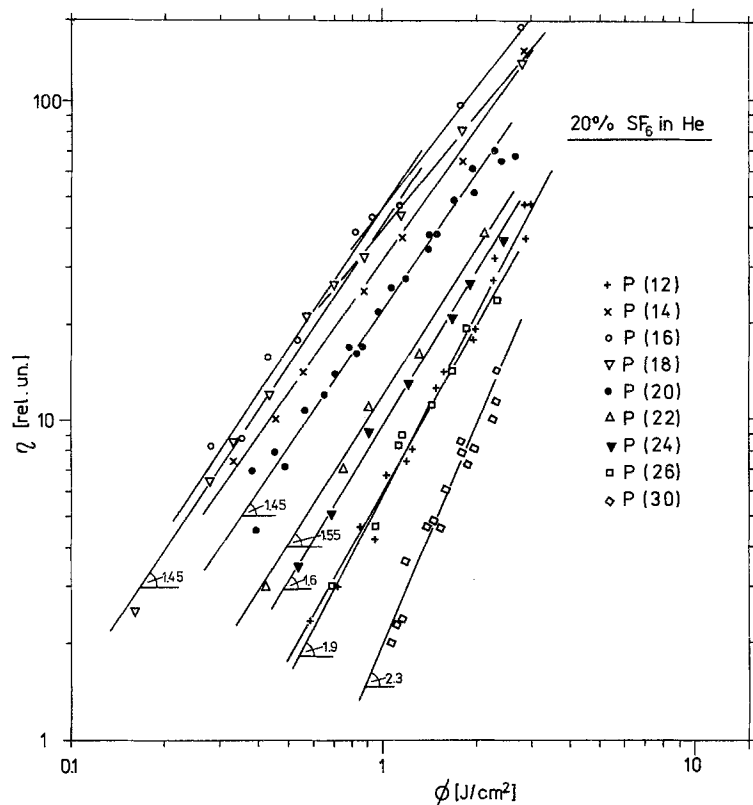


Fig. 5. Absorbed energy η vs. fluence ϕ at different laser wavelength for 20% SF₆ in He

lengths of the CO₂ laser in the *P*-branch at 10.6 μm using different gas mixtures. In Figs. 4–7 are represented the results for pure SF₆, 20% SF₆ in He, 10% SF₆ in He, and 20% SF₆ in H₂, respectively. We observed significant differences for the strength of the signals and the slope of the curves for different wavelengths and temperatures. Of particular interest is the enlargement of the slopes comparing pure SF₆ with SF₆ in seeded beams which is especially strong at the low and high frequency wings of the SF₆ absorption spectrum. Looking, for example, to the wavelength of the *P*(22)-line of the CO₂ laser, we found the following result:

Mixture	SF ₆	20% SF ₆ in He	10% SF ₆ in He	20% SF ₆ in H ₂
Slope	1.1	1.55	1.7	2.2

The spectral peculiarities of the multiphoton absorption will be discussed by means of Fig. 8, where the wavelength dependence of the absorption signal is shown at a constant fluence of 1.5 J/cm² for distinct SF₆ concentrations and, hence, different temperatures. The absorption curves are normalized with respect to the maximum. Their spectral width decreases from 7.2 cm⁻¹ for pure SF₆ to 5.1 cm⁻¹ for 20% SF₆ in H₂, mainly due to the fact that the signals at the low-

frequency wing are strongly diminished. In our opinion this reduction is caused preferentially by the lowering of the vibrational temperature of the SF₆ molecules leading to a stronger suppression of the hot-

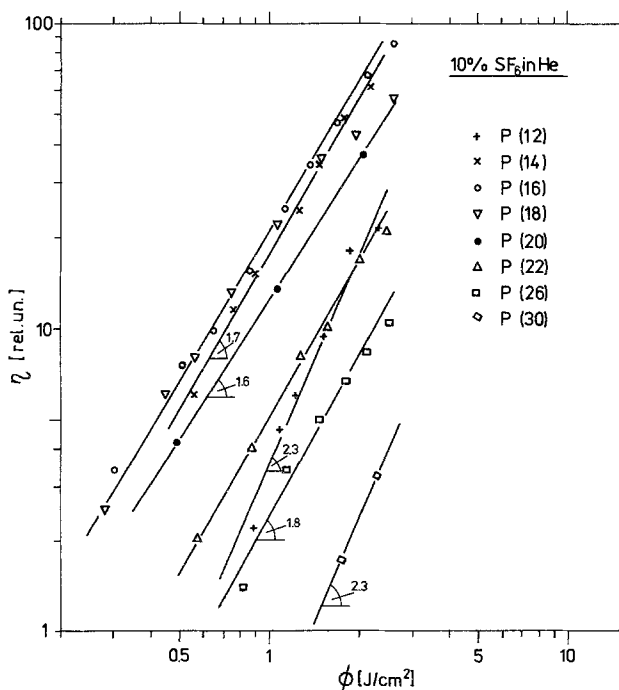


Fig. 6. Absorbed energy η vs. fluence ϕ at different laser wavelengths for 10% SF₆ in He

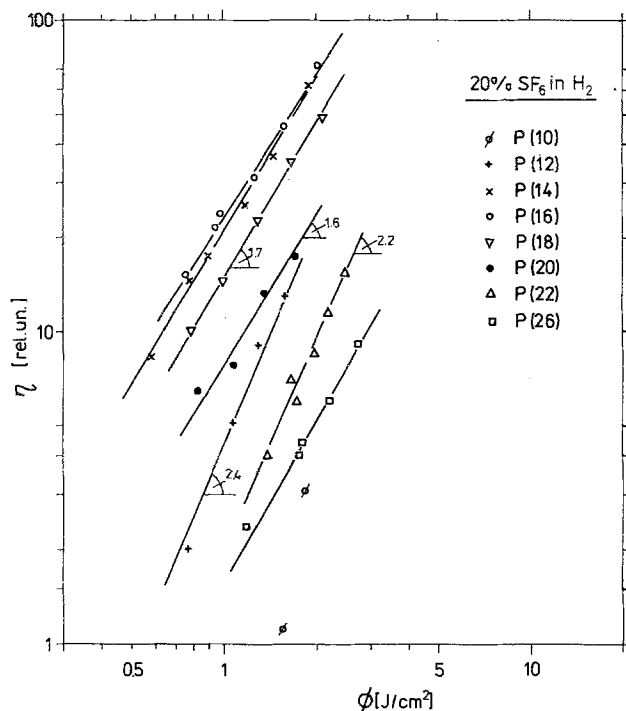


Fig. 7. Absorbed energy η vs. fluence ϕ at different laser wavelength for 20% SF₆ in H₂

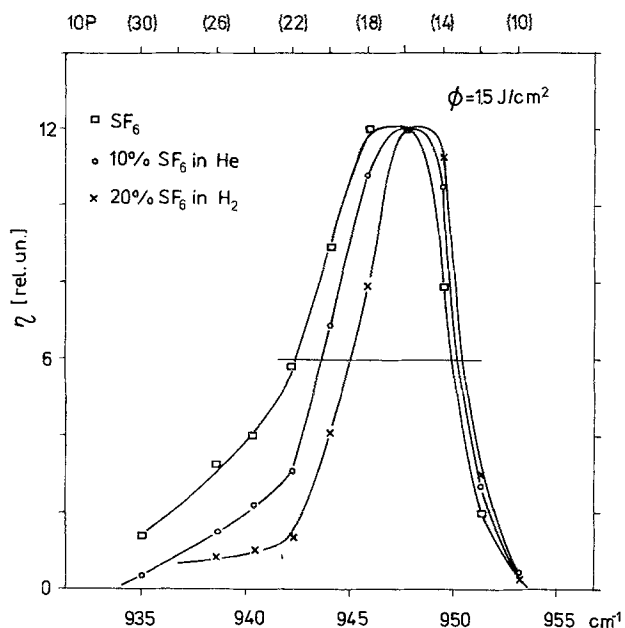


Fig. 8. Absorbed energy η vs. laser wavelength for different gas mixtures at constant fluence 1.5 J/cm²

band absorption. For pure SF₆ we have a vibrational temperature of about 160 K, which means, that about 15% of the molecules are in excited vibrational states. Despite the low population of a single state the corresponding hot-band multiphoton absorption can provide a relatively large contribution due to an

enlarged variety of resonant and near-resonant pathways caused by the anharmonic shift and splitting of the threefold degenerate vibrational modes (e.g., ν_4, ν_6) [9]. At the temperatures realized for pure SF₆ we have a superposition of single and multiphoton transitions starting from the vibrational ground state as well as from low-lying excited vibrational states (e.g., $\nu_4=1, \nu_6=1$). Especially the absorption at larger wavelengths [P(24)–P(30)] can be interpreted only as hot-band multiphoton transitions.

The contribution of hot-band absorption is further reduced for stronger cooling of SF₆ seeded in He and is strongly suppressed for SF₆ mixed with H₂. In the latter case we have a higher rotational temperature as in the former but a lower vibrational temperature because the V-T relaxation rate for SF₆–H₂ is about 5 times larger than for SF₆–He. For the mixture of 20% SF₆ in H₂ the absorption signal nearly vanishes for laser wavelengths above P(22). (The small residual signal is probably due to a small cluster concentration in the beam). The contribution of hot-band absorption should be very small at these temperatures, the multiphoton transitions start preferentially from the vibrational ground state.

This conclusion is also confirmed by comparison of the different slopes for the fluence dependence of the absorption signal. Whereas we found relatively small slopes for the temperature of pure SF₆ because there exists a large variety of single and multiphoton pathways we have observed significantly larger slopes for stronger cooling of the molecules in seeded beams. For the wavelength of the P(22) laser line, e.g., this tendency is clearly demonstrated above. At the lowest vibrational temperature the absorption process should start with a three-photon transition from the vibrational ground state because according to the resonance condition the probability for single- or two-photon transitions from the ground state are very small at this wavelength [10]. The measured slope larger than 2 confirms this interpretation.

The relative enhancement of the absorption signals for lower temperatures at the high frequency wing of the SF₆ spectrum [P(22) and P(14) in Fig. 8] can be understood as due to the increasing population of the vibrational ground state, at which the excitation starts in this wavelength region.

3. Conclusion

We have obtained characteristic dependences of the strength and the slope of the multiphoton-absorption signals on the laser wavelength and the temperature of the SF₆ molecules in seeded molecular beams. It is found that further reduction of the rotational tempera-

ture provides no significant effect whereas decreased vibrational temperatures lead to a characteristic narrowing of the absorption spectrum due to the stronger suppression of hot-band contributions.

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