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IR multiphoton absorption of SF_6 in flow with Ar at moderate energy fluences

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Abstract. IR multiple photon absorption (MPA) of SF_6 in flow with Ar (SF_6: Ar $= 1:100$) in conditions of a large vibrational/rotational temperature difference ($T_V \simeq 230$ K, $T_R \simeq 60$ K) was studied at moderate energy fluences from $\simeq 0.1$ to $\simeq 100$ mJ/cm^2, which are of interest for isotope selective two-step dissociation of molecules. A 50 cm Laval-type slit nozzle for the flow cooling, and a TEA CO_2-laser for excitation of molecules were used in the experiments. The laser energy fluence dependences of the SF_6 MPA were studied for several CO_2-laser lines which are in a good resonance with the linear absorption spectrum of the ν_3 vibration of SF_6 at low temperature. The effect of the laser pulse duration (intensity) on MPA of flow cooled SF_6 with Ar was also studied. The results are compared with those obtained in earlier studies.

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The use of IR multiple photon dissociation (MPD) of molecules for laser isotope separation is well known [1–3]. In the molecular laser isotope separation (MLIS) of heavy elements (like U, W, Mo, ...), when the isotope shift in the infrared absorption spectra of molecules (UF_6, WF_6, MoF_6, ...) is rather small, (≤ 1 cm^{-1}) only flow cooling of the gas of interest with or without a carrier gas can provide a noticeable selectivity of the IR multiphoton excitation (MPE) process. In the case of heavy elements, even at low temperatures, the infrared absorption spectra of molecules of different isotopic compositions are overlapped. An isotopic selectivity in these cases can be achieved only due to the appearance of narrow structures in the linear and/or multiphoton absorption spectra of molecules when flow cooled. Therefore, moderate energy fluences have to be applied at least for the first step of the excitation process in order to avoid large power broadening. Furthermore, it is also interesting to know the absolute values of the absorbed energy by the molecules in flow.

In our present study we have chosen SF_6 which is a classical object for the IR MPE and, regarding structure and spectroscopy, a model for UF_6. The IR MPA of SF_6 is rather well studied at room temperature [4–16], at low (140–150 K) temperatures in static conditions in the cell [16–20], as well as in molecular beams [15, 21–27]. The depletion of individual rotational sublevels of the vibrational ground state of SF_6 under IR MPE was also studied [28–30]. In this paper we present the results on MPA of SF_6 in flow with Ar at moderate energy fluences from $\simeq 0.1$ to $\simeq 100$ mJ/cm^2, which has not been studied before in flow cooled gas.

1 Experiment and method

A two-dimensional 50 cm length Laval-type nozzle was used for cooling of SF_6 in flow. The experiments were performed with a mixture of 1% SF_6 in Ar. The upstream pressure of the gas in the flow could be changed and in the present studies was equal to 10 or 15 kPa. The excitation of molecules in the flow was carried out at a distance of about 3.5 cm downstream from the nozzle throat. The pressure of the gas in the excitation region was calculated to be $p \simeq 150$ and 290 Pa at upstream pressure 10 and 15 kPa, respectively. The corresponding density of SF_6 in the excitation zone was estimated to be $N \approx 1.85 \times 10^{15}$ cm^{-3} and $N \approx 2.8 \times 10^{15}$ cm^{-3}. The estimation was done using the gas kinetic relation $N = p/kT$, where p is the pressure of the gas in the flow, k is the Boltzmann constant and T is the translational temperature of the gas in the flow. The vibrational T_V and rotational T_R temperatures of SF_6 in the flow were calculated [31] on the basis of the linear absorption spectrum of the ν_3 band of SF_6 taken by a Fourier-transform IR spectrometer. These were $T_V \approx 230$ K and $T_R \approx 60$ K for the 10 kPa upstream pressure of the gas, and $T_V \approx 220$ K and $T_R \approx 55$ K for the 15 kPa upstream pressure. In the case of large polyatomic molecules the rotational temperature is very close to the translational one, therefore, one can assume that in our case the translational temperature of SF_6 in the flow was $T_{Tr} \approx 55$–60 K. The mean flow velocity of the gas was calculated to be ≈ 450 m/s.

A line tunable TEA CO_2-laser was employed with a gas composition of CO_2:N_2:He in the ratio of 1.9 : 1 : 2.3 at a total pressure of 56 kPa. An aperture inserted in the resonator served as a TEM_{00} mode selector. The laser pulse energy in

TEM_{00} mode operation was up to 30 mJ. The energy was measured by a Scientec HPF-25 joulemeter. The time evolution of the laser pulse was measured by a photon-drag detector. It consisted of a spike with duration of about 100 ns (FWHM) and a tail of about 1.5 µs duration. The energy content in the tail was about 60%. A "short" laser pulse (80 ns FWHM spike) without a tail was obtained by using the gas mixture with a small content of nitrogen (CO_2:N_2:He = 1.8 : 0.4 : 7.2) at a total pressure of 92 kPa. The laser pulse energy in this case was up to 10 mJ. The beam profiles were Gaussian. For identifying the laser frequency a compact CO_2 spectrum analyzer was used. The laser radiation was directed into the SF_6/Ar flow by a flat and a 5 m radius-of-curvature gold coated copper mirrors. ZnSe windows (AR/AR coated) were utilized to contain the flow. The laser beam crossed the gas flow perpendicular to the flow axis and was reflected back at a small angle ($\approx 3\,°$) relative to the first pass. The incident and transmitted energy of the laser pulses was measured in the experiment. The detectors and the registration system had linear response from about 10 µJ to 30 mJ. The laser radiation was attenuated by 1 mm and 2 mm thick CaF_2 plates. The signals from the detectors were averaged over 30 shots. The laser ran at a repetition rate of about 3 Hz. We determined the absorbed energy from the transmitted energy without and with gas. In most cases the absorbed energy was in the range of 1–12% of the incident energy. Consequently, the variation of the energy fluence along the laser beam axis due to absorption was negligible for the evaluation.

2 Results and discussion

2.1 *Fluence dependence of the absorbed energy*

Figure 1 shows the dependence of the absorption by SF_6 molecules in photons per molecule ($\langle n \rangle$) on the excitation energy fluence for several CO_2-laser lines, which in good resonance with the linear absorption spectrum of the ν_3 vibration of SF_6. The $\langle n \rangle$ is determined as

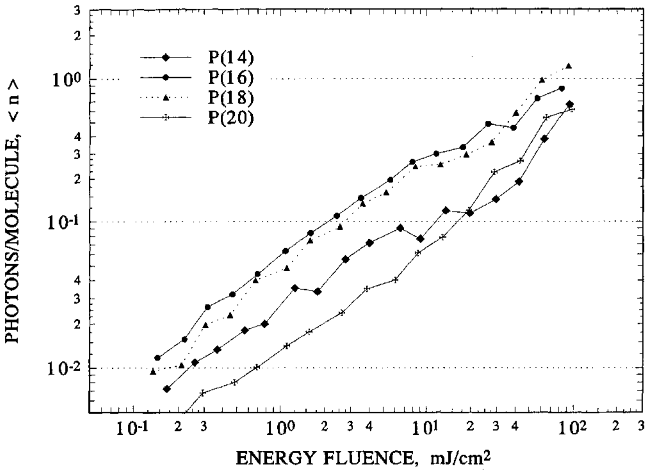

Fig. 1. The dependence of the absorbed energy by SF_6 molecules (in photons per molecule) on the excitation energy fluence for the 10P(14), 10P(16), 10P(18) and 10P(20) CO_2-laser lines. The upstream pressure of SF_6/Ar in the flow is 15 kPA

$$\langle n \rangle = E_{ab}/\hbar\omega NV\,, \tag{1}$$

where E_{ab} is the energy absorbed by the gas, $\hbar\omega$ is the laser photon energy, N is the concentration of SF_6 molecules in the flow in the excitation region and V is the irradiated volume ($V = Sl$, $S = 0.23\,cm^2$ is the laser beam spot size, and $l = 100$ cm is the double path length of the laser beam across the flow).

One can see from Fig. 1 that the dependences look rather similar to each other. They have a logarithmic slope of about 0.75, i.e. $\langle n \rangle \sim \phi^{0.75}$. At energy fluences $\phi \geq 50\,mJ/cm^2$ the slope becomes steeper. These slopes are in good agreement with the earlier results on MPA of SF_6 in a cell both at ambient temperature [14] and at $T \approx 150$ K [16] at pressures $p \geq$ 13 Pa, when the MPA is partly influenced by collisions [14]. For SF_6 at room temperature $p\tau_R \approx 36$ and 32 ns Torr for the ground and first excited vibrational state, respectively [32, 33]. In our case the rotational relaxational time is probably two to three times longer because the temperature of SF_6 in the flow is rather low ($T \approx 60$ K). Nevertheless, at pressures in the excitation region of about 2.2 Pa of SF_6 and 288 Pa of Ar during an exciting CO_2-laser pulse (≈ 1.5 µs), rotational relaxation of SF_6 at least partly took place [14]. Nearly the same slope at $\phi \leq 0.1\,J/cm^2$ was also obtained for SF_6 in a molecular beam [22].

At energy fluences $\phi \leq 50\,mJ/cm^2$ the increase of $\langle n \rangle$ with ϕ is probably mainly connected to the increase of the fraction of interacting molecules due to power broadening, whereas at $\phi \geq 50\,mJ/cm^2$ the multiphoton processes become dominant, and molecules are excited to higher vibrational states leading to $\langle n \rangle$ increasing faster [14, 22, 34].

The absolute values of absorbed energy in our experiment (for example, for 10P(16)) are somewhat lower than those obtained in [16] for room-temperature SF_6 and very close to those obtained at $T \approx 140$ K [16]. In principle, the absorbed energy in our case should be somewhat lower than in [16] because lower SF_6 pressures were employed in our experiment. However, the values of $\langle n \rangle$ measured in this study should be a little higher compared to those measured at static conditions. This is due to the fact that in a flow system the effective irradiated volume is always larger than that of static conditions due to the movement of molecules across the laser beam. For example, during an excitation laser pulse of ≈ 1.5 µs the SF_6 molecules move a distance of about 0.6 mm. This is not negligible compared to the small spot size of the laser beam. The number of irradiated molecules thus increased by a factor of about 1.1 (not taken into account in the evaluation).

2.2 *The dependence of the absorption cross-section on the energy fluence*

From the results presented in Fig. 1, one can obtain the dependences of the effective absorption cross-section $\overline{\sigma}$ on excitation energy fluence. The accepted definition is used:

$$\overline{\sigma} = -\ln(T)/Nl\,, \tag{2}$$

where $T = E_{gas}/E_0$ is the ratio of transmitted energies with and without gas. As always, if the absorption is small, one can

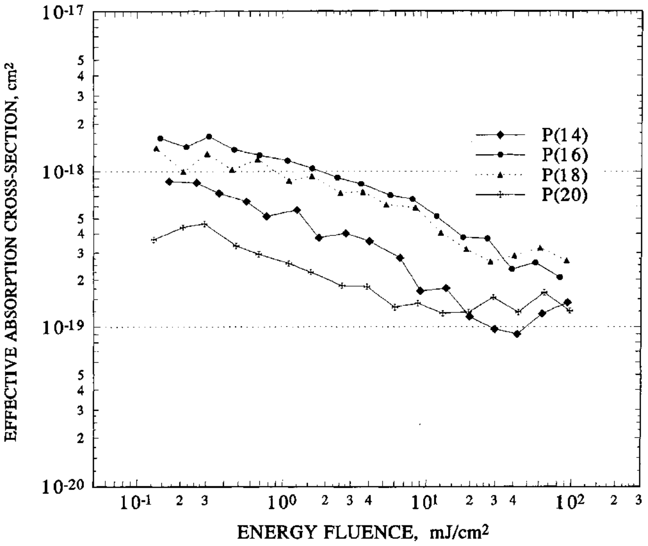

Fig. 2. The dependence of the absorption cross-section on the exciting energy fluence for the 10P(14), 10P(16), 10P(18) and 10P(20) CO_2-laser lines. Experimental conditions are the same as in Fig. 1

obtain [22]

$$\langle n \rangle = \overline{\sigma} \Phi \, . \qquad (3)$$

The values of $\overline{\sigma}$ obtained from (3) are shown in Fig. 2 for several laser lines. Obviously, $\overline{\sigma}$ decreases with increasing ϕ. The values of $\overline{\sigma}$ and the main features of its dependene on energy fluence are in good agreement with the earlier analogous results on MPA studies of SF_6 at low temperature in a cell [18, 20], as well as in a molecular beam [22]. The increase of $\overline{\sigma}$ with ϕ for some CO_2-laser lines was observed in [21, 22] only at $\phi \geq 0.2\,\mathrm{J/cm^2}$. It is very likely connected with the multiphoton character of the absorption at high energy fluences.

2.3 *The frequency dependence of absorbed energy*

In the present studies due to a large vibrational/rotational temperature difference ($T_V \approx 230\,\mathrm{K}$, $T_R \approx 60\,\mathrm{K}$) rather interesting experimental conditions were realized, which differ from those with SF_6 cooled at static conditions in the cell ($T_V \approx T_R \approx 140$–$150\,\mathrm{K}$) [17–20], as well as in a pulsed jet [21, 22].

At $T_V \approx T_R \approx 150\,\mathrm{K}$ about 85% of the molecules are in the ground vibrational state [35] and, as a consequence, hot bands are fairly weak, but the rotational distribution of molecules is rather broad, since many J-levels are still populated. In experiments with pulsed molecular beams (jets) of SF_6, $T_V \leq 150\,\mathrm{K}$ and $T_R \leq 50\,\mathrm{K}$ were obtained [21, 22]. At these temperatures the ground vibrational state is highly populated as well, but the rotational distribution of molecules is rather narrow, since only the low J-levels are populated. In the present experiments we also have a low rotational temperature for SF_6 ($T_R \leq 60\,\mathrm{K}$), but a fairly high vibrational one ($T_V \approx 230\,\mathrm{K}$), with about 50% of the molecules in higher vibrational levels (ν_6, ν_5, $2\nu_6$, ν_4, ...) [35]. This leads to the appearance of rather intensive hot bands in the linear absorption spectrum, and the MPA spectra should be affected as well. Similar temperatures to those in the present study were realized earlier [36] in experiments on the MPA of SF_6 in a molecular beam ($T_V \sim 230\,\mathrm{K}$ and $T_R \leq 50\,\mathrm{K}$). However, the excitation of molecules in [36] was carried out under collisionless conditions and at fairly high energy fluences ($\phi \geq 0.5\,\mathrm{J/cm^2}$). This work presents data at lower fluences.

Figure 3 shows the frequency dependence of the absorbed energy by SF_6 molecules (the MPA spectra of SF_6) at three different energy fluences: $80\,\mathrm{mJ/cm^2}$, $10\,\mathrm{mJ/cm^2}$ and $1\,\mathrm{mJ/cm^2}$. For comparison a small-signal absorption spectrum of SF_6 recorded at $T_V \approx 230\,\mathrm{K}$ and $T_R \approx 60\,\mathrm{K}$ in a flow system similar to ours (with narrower slit nozzle) with a Fourier-transform IR spectrometer is also shown in the lower part of the figure. Two features of the obtained MPA spectra can be pointed out: (1) the shift of the main maximum from the P(16) to P(18) laser line with increasing energy fluence, and (2) the existence of a second maximum at P(22). In [36] only the maximum at P(18) was observed, whereas in other MPA studies of cooled SF_6 [17, 19, 22] the maximum was observed at P(16). As discussed in [36] this peculiarity is connected with a rather large contribution to the absorption from excited vibrational states (ν_6, ν_5, $2\nu_6$, ν_4, ...) strongly populated, at $T_V \approx 230\,\mathrm{K}$. The maximum at the P(22) laser line is very likely connected with the three-photon resonance from the ground vibrational state to the (300) F_{1u} sublevel at $942.5\,\mathrm{cm^{-1}}$ [37] and/or some multiphoton resonance from low-lying excited vibrational states. A maximum at the P(22) line in the MPA spectrum of cooled SF_6 (at $T \approx 198\,\mathrm{K}$) was also observed in [17], when SF_6 was pumped by a 6 μs-long CO_2-laser pulse, and this was explained by laser-induced hot bands. As one can see from Fig. 1 and 3, at energy fluences $\phi \geq 10\,\mathrm{mJ/cm^2}$ the absorption on the P(20) laser line increases very rapidly, probably due to two-photon transitions from the ground vibrational state to the $2A_{1g}$ level [38]. Therefore, at higher energy fluences the MPA spectra of SF_6 will

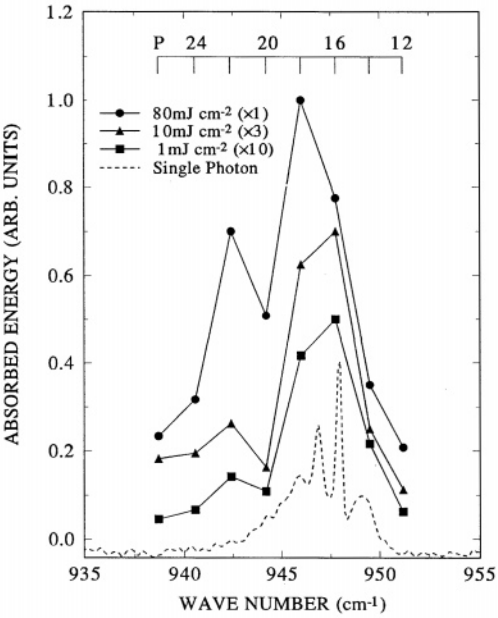

Fig. 3. The MPA spectra of flow cooled SF_6 with Ar at different energy fluences. The upstream pressure of SF_6/Ar in the flow is 15 kPA. In the lower part of the figure the linear absorption spectrum of SF_6 at $T_V \approx 230\,\mathrm{K}$ and $T_R \approx 60\,\mathrm{K}$ is shown for comparison. The CO_2-laser line positions are shown in the upper part of the figure

very likely look similar to those obtained in [36] with only a maximum on the 10P(18) laser line.

2.4 The dependence of the MPA of SF_6 *in flow with* Ar *on excitation pulse duration (intensity)*

Figure 4 shows the dependence of $\langle n\rangle(\phi)$ obtained in the case of excitation of SF_6 in flow with Ar by "long" and "short" laser pulses on the 10P(16) line. It was found that the absorption is considerably larger in the case of excitation of SF_6 by the "long" laser pulse. Let us discuss this result. The role of intensity (pulse duration) in MPA of SF_6 was studied in many works both at static conditions in a cell and in molecular beam and the detailed analysis of these studies can be found in [14, 39, 40]. For the excitation of SF_6 in a molecular beam under collisionless conditions it was shown that the absorption is greater from the "short" or higher-intensity laser pulse, whereas under collisional excitation conditions the reverse is seen and greater absorption from the "long" laser pulse can be observed [14].

As mentioned above, in the present experiments the excitation process was influenced by collisions. The obtained results are in good agreement with those of [14], and they can be explained as follows. Both the pulse intensity and pulse duration are important in the involvement of larger fractions of molecules in the excitation process due to dynamic power broadening in the first case and to rotational relaxation in the second. Since the rotational relaxation took place during the excitation pulse, the absorption can be greater for the "long" laser pulse. It is the latter situation which was seen in our experiments.

3 Conclusions

The IR-MPA of SF_6 molecules cooled in flow with Ar ($SF_6/Ar = 1/100$) down to $T_V \approx 230\,K$ and $T_R \approx 60\,K$ was investigated at moderate energy fluences ($0.1 \leq \phi \leq 100\,mJ/cm^2$), which are of interest for isotope-selective two-step dissociation of molecules. The dependences $\langle n\rangle(\phi)$ and $\sigma(\phi)$ obtained in the present study are in good agreement with those obtained in earlier studies on MPA of SF_6 at low temperature in a cell [18, 20] and in a molecular beam [22]. The MPA spectra of SF_6 are shown to differ from those obtained in earlier works with cooled SF_6 [17, 19, 25, 26, 36]. They reveal some structure, which is very likely a consequence of a rather high vibrational temperature of SF_6 in the flow and the multiphoton character of the excitation. The absorption from a "long" laser pulse was shown to be considerably larger (1.5–2 times) than that from a "short" pulse. The method described and the results obtained provide a good basis for the study of IR-MPA of other polyatomic molecules in similar flow systems.

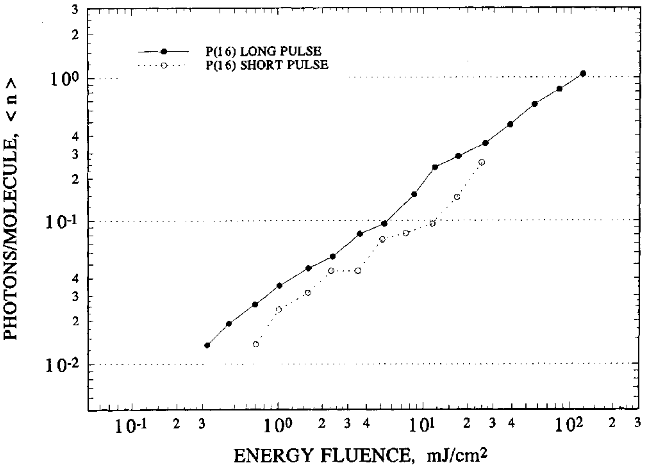

Fig. 4. The dependence of the absorbed energy on the excitation energy fluence for "long" and "short" laser pulses. Excitation of molecules was carried out at the 10P(16) CO_2-laser line. The upstream pressure of SF_6/Ar in the flow was 15 kPA

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