About nondegenerate four photon mixing gain spectroscopy of the $SF_6$ molecules.

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Abstract

Infrared-infrared double resonance measurements of the $\nu_3$ absorption band of $SF_6$ using a $CO_2$ TEA laser radiation have been carried out. The results obtained in the present and in some earlier works are discussed taking into account existence of a wide component of lines, nondegenerate four photon mixing (NFPM) and time invariance violation in the photon-molecule interactions. It is proposed to use the NFPM effect in investigations of the shape of the optical transition in polyatomic molecules and especially for evaluation of the homogeneous width of the wide component of lines. The need and problems of experimental study of existing effects of the T-invariance violation in optics are discussed.

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Introduction

Studies of the IR-IR double resonance in $SF_6$ were widely carried out in 70’s with a purpose to clarify the mechanism of the IR multiple photon excitation (IR MPE) of the polyatomic molecules. Large experimental material was obtained in this area in the subsequent years [1,2]. Also, a substantial progress was achieved in understanding the underlying physical processes. All this demands to reexamine the old experiments, as they contain interesting and important information.

A very strong bleaching in $SF_6$ was observed in the work [3]. This bleaching was destroyed by molecular collisions at characteristic rate of $pr = 48$ns mbar. An effect of the direct multiphoton absorption of the pump laser radiation by molecules was proposed as a candidate for explanation of this bleaching. On the contrary, in works [4,5] a hypothesis was proposed of existence of some wide component in the absorption line of the polyatomic molecules. If the natural width of this wide component greater, than anharmonicity of vibrations, the IR MPE can occur in a natural way. Later, this idea was proved experimentally, when the far wings in the absorption band of polyatomic molecules were found [6], which were independent on the gas pressure. The intensities of these lorentzian-like band wings well coordinate with the saturation data of molecular absorption at low pressure, with the data of depletion of rotational levels in the $SF_6$ molecules [7,8] and with the data on the $SF_6$ absorption of laser radiation in the molecular beam conditions [9]. Integrated intensity of this wide component can be rather easily estimated from the saturated spectrum data. But the natural width can be measured correctly only in the molecular beam conditions, where rotational temperature is extremely low. Therefore, development
of methods for measuring this width in the room temperature cell conditions is of great interest.

Experiments on the IR-IR double resonance provide such an opportunity. The bleaching, observed in work [3], is very similar to the coherent effect of NFPM. In the latter case, redistribution of energy between a powerful pump beam and a weak probe beam takes place. It is well known, that such a process proceeds in SF$_6$ very effectively (up to depletion of the pump beam) as a superradiation in the case of degenerative four photon mixing (DFPM) in a somewhat specific conditions (a short cell and high SF$_6$ pressure) [10]. As in the case of the coherent Raman gain spectroscopy [11,12], spectral dependence of the NFPM efficiency contains information about the shape of the optical transition. The peculiarity of this case is that the NFPM effect occurs within a very wide optical transition. Thus, the spectral width of the bleaching effect characterizes the homogeneous width of the optical transition.

The purpose of the current work was to repeat the experiments of work [3], to perform some more detailed study of the spectral characteristics of the bleaching effect, to discuss the role of the NFPM and to propose to use it for determination of the widths of line wings of polyatomic molecules in the condition of cell experiments at room temperature. However, in the present experiments any nondegenerative bleaching was absent.

**Experiment**

The experimental set-up is shown in Fig.1. The main difference from work [3] was that a separate mirror (3) with R=-2m was used for focusing the laser radiation in the copper waveguide absorption cell (ø10mm and length 110cm). The probe laser radiation passed through the hole ø8mm in the mirror (4) without focusing and was registered by an integrated calorimeter 2. Such an experimental set-up allows to work without a monochromator and to measure absorption of the probe laser radiation in the case of coinciding frequencies of the pump and the probe lasers. The difference in divergences of the scattered pump radiation and that of the probe laser is so great, that total energy of pump radiation, registered by the calorimeter 2 at the distance $\sim 1m$ from the mirror (4) is $< 10\mu J$ and does not prevent to measure the energy of the probe pulse.

The resonator of the probe laser was formed by a rather flat mirror (R=-50m) and a diffraction grating. Its radiation was characterized by small divergence and good uniformity of the beam. Nitrogen free gas mixture was used. Multimode laser pulse had a full width about 100ns at half maximum without any "tail" and consisted of chaotic spikes.

The pump laser had an unstable resonator and two very old BaF$_2$ coated NaCl windows. In the far field region, where it was focused, radiation was very non-uniform and had a typical speckle-structure. With small contents of nitrogen in the gas mixture, the multimode pulse consisted of a spike about 100ns FWHM and a "tail" about 3$\mu$s full length, that contained about 20% of the total pulse energy. Directions of polarization of both laser beams coincided. Temporal characteristics were measured by means of a photon-drag detector and an oscilloscope (not shown in the figure).
The measurements were carried out at pressures 1.5 Torr \( SF_6 \) for the P10—P14 and R10—R20 lines, 1.0 Torr for line P16 and 0.4 Torr \( SF_6 \) for lines P18—P30.

**Experimental results**

The results of the IR-IR double resonance experiments are presented in Fig.2. The pump laser was tuned in the P16 line. Similar results were obtained when the pump laser was tuned in the P20 line. Incident pump laser fluence in the waveguide was 250\( \text{mJ/cm}^2 \). Energy fluence of the probe laser radiation was 7\( \text{mJ/cm}^2 \). The latter was decreased down to 1\( \text{mJ/cm}^2 \) in some experiments without any changes in the results. In the whole range of testing (including the R10—R20 area) only increase in absorption of the probe laser radiation was observed.

Some bleaching effect was observed only when both lasers were working on the same line. Apparent mutual influence of the lasers was observed in this case. Were the pulses of both lasers synchronized, energy of the probe laser pulse decreased by \( \sim 10\% \), and its beam pattern became non-uniform. The distance between two lasers was about 10m in this case, so that only scattered pump laser radiation could get into the resonator of the probe laser.

Also, a set of experiments was carried out in which the same laser radiation was used both for pumping and for probing. Again, the bleaching effect was found in this case. An open square in Fig.2 corresponds to the case, when the probe laser was used, and the full square illustrates the case of using only the pump laser radiation.

**Discussion**

IR-IR double resonance was studied in numerous works [3,13-17]. These experiments frequently gave contradictory results, and it was difficult to give satisfactory explanations to these contradictions. At present, however, the situation has substantially cleared up.

A wide component with Lorentzian FWHM \( \sim 150\text{GHz} \) exists in the spectrum of narrow absorption lines of \( SF_6 \) molecule [6]. Its integral intensity for the 1 ← 0 transition of the \( \nu_3 \) band contains only \( \sim 0.2\% \) of the integral intensity of this optical transition. However, absorption of the powerful pump laser radiation takes place just through this component. The weaker probe radiation can be absorbed mainly through the narrow or through the wide component of the line. Thus, the results of probing can be different. All experiments on the IR-IR double resonance in \( SF_6 \) can be conditionally broken into three classes: (1) when the probing occurs through the narrow component of lines, (2) when the probing occurs through the wide component of lines and (3) an intermediate case.

In the work [13] very weak probe radiation of the CW \( CO_2 \) laser with intensity \( \sim 1\text{mW/cm}^2 \) was used. Both induced transmissions in the P8—P22 region of the probe laser frequencies and induced absorption in the red side were observed. Saturation of the narrow component of lines was absent in this case. The main cause of the observed effects was an anharmonic shift of the optical transitions of the excited molecules.

It is surprising, but experiments with megawatt intensity and picosecond
timescale probe pulse laser radiation belong to the same class [14]. In this case laser radiation has large spectral width (\( \sim 1 cm^{-1} \)). Therefore, any saturation of the narrow component of lines is again absent, and the results of these experiments coincide practically with those of work [13].

CW CO\(_2\) probe laser radiation with intensity about 0.1 – 0.5 W/cm\(^2\) was used in works [15-17]. These experiments belong to the intermediate class. Here we can see appearance of appreciable saturation of the narrow component of lines. Also, absorption through the wide component of lines begins to play some role. This role depends on exact tuning of the probe laser radiation frequency: is it set-up on a strong rotational line or between lines. Thus, in the area P8-P22 both induced transmission and induced absorption can be observed.

A specific effect of short-time induced absorption in the course of the pump pulse was observed in work [16]. One should keep in mind, that planes of polarization of the probe and the pump laser radiation were orthogonal in this experiment. A coherent polarization effect could take place in this case, that is due to the population transfer between degenerated levels. Phenomena of this kind are studied in the atomic polarization spectroscopy [18], and they are out of scope of the present paper.

Experiments of the present paper belong to the next class, when probing occurs mainly through the wide component of lines. Average probe laser intensity was 10 – 70 kW/cm\(^2\). Saturation of the narrow component of lines was much stronger in this case. The role of the wide component in absorption of the probing radiation became essential.

In this case, besides the anharmonic shift, an effect of sharp growth of integral intensity of the wide component in the region of low lying vibrational levels should be taken into account. This effect manifests itself through a strong temperature dependence of the IR MPE process [9,19]. In some range of the experimental conditions this effect becomes decisive, and then induced absorption of the probe laser radiation can be observed in all spectral intervals.

To the same class of experiments the works [9,20] belong. In the work [9] the experiments were carried out in the molecular beam conditions. Along with rather high intensity of the probe laser radiation (\( \sim 10kW/cm^2 \)), these experimental conditions were characterized by ultralow (\( \sim 5^0K \)) rotational temperature [21]. A number of rotational lines were very low, and the probe laser radiation interacted practically with the wide component of lines only. The obtained results were similar to those of the present work. One should keep in mind, however, that experiments of work [9] were carried out with rather hot gas (\( T = 500^0K \)).

A special case is work [3], where, as we believe, a coherent NFPM effect was observed. The first argument for such a conclusion is unusually strong effect of collisions. Even elastic collisions can destroy coherency. The second argument is amplification in the region R12-R20, that clearly indicates the combination \( \nu_2 + \nu_0 \) band can contribute to this process. In this case the phase-matched radiation must exist in the region near 915 cm\(^{-1}\), and it is better to search for it in the direct beams without waveguide. And the third argument is that in our experiments, which were carried out in rather similar conditions, the character-
istic bleaching was absent. This fact can be due to rather poor coherency of the pump beam in our case. It is known, that efficiency of the DFPM effect is extremely sensitive to the divergence and uniformity of the laser beam [10,22,23]. In the works [15-17] the NFPM effect might be absent as a result of low intensity of probe radiation, and in the experiments with molecular beam [9] its absence could be a consequence of low density and small size of the interaction zone.

Is the bleaching effect, observed in our work, when both lasers radiate on the same line, a result of four photon mixing? Absence of such an effect in the molecular beam conditions (9, Fig.3, without exact adjusting) is an indirect argument for the positive answer. In this case, the NFPM effect can be a consequence of a very small difference in the frequencies of the pump and probe radiation.

Thus, detailed experimental studies of occurrence of the NFPM effect in SF$_6$ are of undoubted interest. They can give information about the shape of optical transitions, and not only about the forward transitions, but maybe about the backward ones.

Why one needs the NFPM effect to present within the wide and homogeneous optical transition? Here we are concerning a very important and interesting question about the time invariance violation in the photon-atom and photon-molecule interactions. Basing on the considerations of symmetry, the theorists assume the existence of the T-invariance violation effects in optics for a long time. It is not known, however, in which part of optics and in which form could these effects exist. For many years the scientists try to find them in the form of the so-called electrical dipole moment (EDM) [24]. The EDM is not found till now.

General situation, however, is that the whole nonlinear optics based on or connected with T-invariance violation. **The principle of T-invariance violation is obviously a quantum analog of the nonlinear susceptibility principle.** Most of the nonlinear effects in optics can be explained from the quantum point of view on the basis of the T-invariance violation principle. The effect of T-invariance violation usually manifests itself only in an indirect way, for example, as a population transfer effect at sweeping the resonance conditions [25]. Usually, experimenters cannot control the natural width and the cross-section of optical transitions in such a way to be able to compare these parameters for the forward and backward processes.

Maybe a unique exception for this day is the wide component of lines. It is a unique physical object that is characterized by an unusual combination of properties: a huge homogeneous width of transition is combined with long lifetime of the excited state. This allows to divorce in time and in space the process of laser excitation and that of monitoring the exited states of molecules [9]. These experiments yield fantastic results: the width of the backward optical transition proves to be more than five orders of magnitude less than that of the forward one, the cross-section of the backward transition being more, than four orders of magnitudes greater, than that of the forward one [26]. These experiments provide a direct and full experimental proof of existence of the strong T-invariance violation in the photon-molecule interactions. For more detailed
experimental study of the T-invariance violation effect we need to reanimate
and straightforwardly continue experiments of work [9] (fig.5, 6).

In principle, experiments of this type can be carried out in the cell conditions
also. It is possible to study the dependence of absorption of the probe radiation
on the angle between the probe and the pump beams. We expect to see a
transition from direct stimulated deexcitation of molecules to the four photon
mixing effect, which can reach a superradiation regime in optimum conditions
[10,22]. We hope to prolong such experiments in future using the straight crossed
beams without waveguide. It would be useful, if the same studies were conducted
somewhere else.

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Fig. 1. Experimental set-up. 1, 2- flat mirror. 3- focusing mirror. 4- flat mirror with the hole.
Fig. 2. Measured absorption cross-section versus probe laser line. Different points were determined at different times before and after the onset of the pump laser spike. 1) -1µs, 2) 0µs, 3) +1µs, 4) +2µs.