

Singularities of the SF₆ absorption spectrum at high IR intensities

N. G. Basov, V. T. Galochkin, A. N. Oraevskii, and
N. F. Starodubtsev

P. N. Lebedev Physics Institute, USSR Academy of Sciences

(Submitted April 10, 1976)

Pis'ma Zh. Eksp. Teor. Fiz. 23, No. 10, 569-574 (20 May 1976)

It is demonstrated experimentally that the frequency of the maximum of SF₆ molecule absorption shifts to the long-wave region at high incident-radiation energies and at IR pulse durations exceeding the time of the vibrational-translation relaxation. An explanation is offered for the observed absorption-spectrum singularities.

PACS numbers: 32.20.Dr

We have investigated the singularities of resonant absorption of laser IR radiation by the SF₆ molecule. Interest in research of this type is due to the use of lasers to stimulate chemical reactions^[1,2] (including reactions in chemical lasers^[3,5]) and other processes.^[6,7]

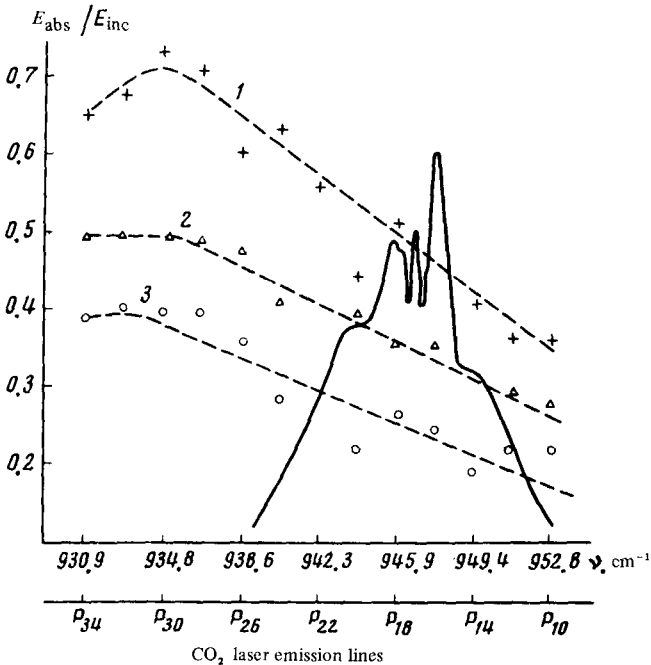


FIG. 1. Ratio of absorbed to incident energy as a function of the frequency of the incident radiation (concentration SF₆: H₂ = 2.5 : 1, pressure 4 Torr, cell length 40 cm: 1) radiation intensity $I = (1.7-3) \times 10^6$ W/cm²; 2) $I = (3.4-5.3) \times 10^6$ W/cm²; 3) $I = (7-9) \times 10^6$ W/cm².

We measured the CO₂-laser radiation energy absorbed by SF₆ molecules as function of the wavelength. We used in the experiment a pulsed CO₂ laser with emission frequency tunable by a diffraction grating to different lines of the rotational-vibrational spectrum of the 00⁰0 → 10⁰0 transition of the CO₂ molecule. The lasing pulse duration at half height was 3 μsec; the maximum lasing energy for individual vibrational-transitions reached 6 J. The SF₆ used in the experiments had a natural isotopic composition ³²SF₆ - 94%, ³³SF₆ - (1 ± 0.2)%; ³⁴SF₆ - (4.4 ± 0.2)%; ³⁶SF₆ - (0.6 ± 0.2)%. The extraneous impurities did not exceed 0.1%. The laser-radiation energy absorbed by the SF₆ molecules was determined by measuring the difference between the energies entering and leaving the cell containing the sulfur hexafluoride.

Figure 1 shows the dependence of the energy absorbed in the cell on the frequency of the incident radiation. The energy at each frequency was maintained constant within 20%. For comparison, we show the frequency dependence of the energy absorbed by the sulfur hexafluoride ³²SF₆ at low energy^[10] when Bouguer's law holds. A shift of the resonance frequency to the long-wave region is observed at large values of the radiation-pulse energy.

Figure 2 shows the dependence of the energy absorbed in the cell on the energy of the radiation pulse entering the cell. The experiments were performed at two frequencies corresponding to the rotational-vibrational lines P₁₆ and P₃₀ of the 00⁰1 → 10⁰0 transition of the CO₂ molecule. The P₁₆ line is close to the resonant frequency of the linear absorption by the ³²SF₆ molecule; the P₃₀ line corresponds to the maximum absorption at a high pulse power (energy).

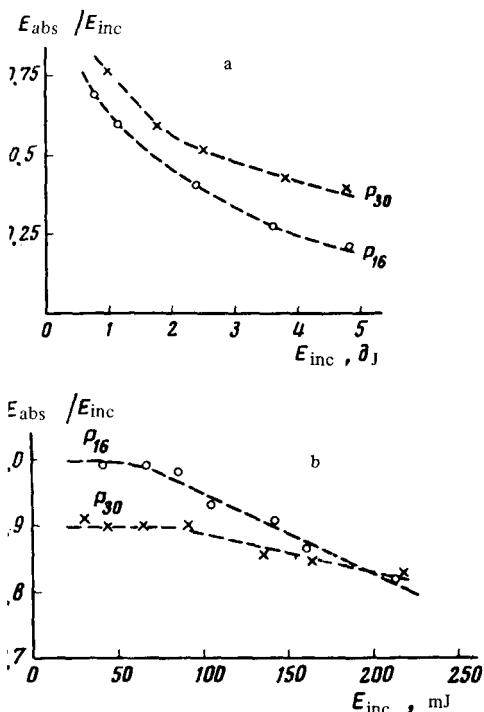


FIG. 2. Dependence of the absorption of IR radiation on the irradiation energy for two CO₂-laser frequencies (concentration SF₆:H₂=2.5:1, pressure 4 Torr): a — high irradiation energies, b — low irradiation energies (near the saturation region).

Dilution of the SF_6 with hydrogen up to a ratio $(\text{SF}_6):(\text{H}_2)=2.5:1$ did not influence noticeably the results shown in Figs. 1 and 2.

Why is the lower-frequency transition preferable for the absorption of high-power radiation?

At high radiation intensities and in the saturation regime, a noticeable contribution to the absorption can be made by successive transition between excited vibrational levels. The anharmonicity of the molecule vibrations hinder this process. However, the decrease, due to the anharmonicity, in the transition frequency with increasing number of vibration level can be offset by the rotation of the molecule. This circumstance was pointed out already in^[1,8]. In order for the maximum number of successive rotational-vibrational transitions to be at resonance, it is necessary to choose the radiation frequency as small as possible. Transitions with $J > J_m$ are not suitable because of the rapid decrease of the population of the rotational levels with increasing J . This means that the first should be the transition of the P branch with large rotational quantum number J . To compensate for the anharmonicity, the next rotational-vibration transitions must begin with a level having a smaller value of J (if this is a P transition) or must be replaced in succession by Q and R transitions. There is no need here for the next transition to start with the level at which the preceding transition terminates, since the rotational equilibrium is established in the SF_6 molecule within a time $\tau = 40 \cdot p^{-1}$ nsec^[9] (p is the pressure in Torr), which is much shorter than the duration of the pulse used in our experiments. Figure 3 illustrates the described mechanism. It might seem that the larger J for the

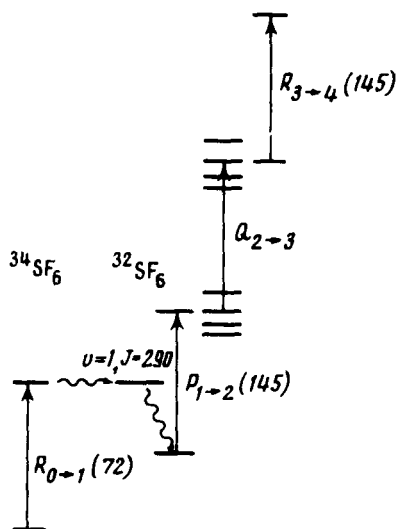


FIG. 3. Compensation of the anharmonicity frequency shift by the rotational energy of the molecule.

initial transition the smaller the initial resonant frequency of the laser, meaning that it is possible to compensate for the anharmonicity of higher and higher rotational transitions. However, the use of transitions with very large J is difficult, since the intensity of the rotational-vibrational transitions (the effective cross section of the transition) decreases abruptly with increasing J in accordance with the law

$$\frac{B}{J^2 e^{-\frac{B}{kT}}} J(J+1) = J^2 e^{-J^2/J_m^2}.$$

$n_2 = 50$ for SF_6 . We present numerical estimates for our experiments. The frequency of the P transition $\nu = 0$, $J \rightarrow \nu = 1$, $J - 1$ in standard notation is given by the relation $\nu_{10} = \nu_3 - 2B(1 - \xi)J$. According to^[10-12], $\nu_3 = 948.2 \text{ cm}^{-1}$, $B \approx 0.09 \text{ cm}^{-1}$, and $\xi = 0.73$. The anharmonicity factor for the SF_6 molecule is $\Delta\nu_a \approx 6-7 \text{ cm}^{-1}$.^[13] A shift in the frequency of the laser radiation by 14 cm^{-1} relative to ν_3 towards lower frequencies (see Fig. 1) makes it possible to effect a cascade of resonant transitions $P_{0-1}(-14 \text{ cm}^{-1})$, $P_{1-2}(-7 \text{ cm}^{-1})$, Q_{2-3} ; $R_{3-4}(+7 \text{ cm}^{-1})$; $Q_{4-5}(+14 \text{ cm}^{-1})$, etc. However, if the absorption at the frequency $\nu_0 - 14 \text{ cm}^{-1}$ were ascribed to P_{0-1} in $^{32}\text{SF}_6$, then this transition would correspond to $J \approx 290$. The intensity of $P_{0-1}(290)$ is less by a factor 10^{-13} than the most intense transition $[P_{0-1}(J_m)]$, showing that it is impossible to make the first step in this cascade as a result of the transition $P_{0-1}(290)$. However, our mixture contains 4% of the isotopic modification of the molecule, $^{34}\text{SF}_6$. The frequency 934 cm^{-1} corresponds to the transition $P_{0-1}(72)$ of this molecule, that is, it falls practically in the region of the maximum absorption of $^{34}\text{SF}_6$. We can therefore propose as the first step in the absorption the transition $R_{0-1}(72)$ in $^{34}\text{SF}_6$, with rapid transfer of the excitation to the $^{32}\text{SF}_6$ molecules: $P_{1-2}(145)$, Q_{2-3} , $R_{3-4}(145)$. The intensity of the P or R transition with $J = 145$ is smaller by only a factor 100 than the maximal (with $J_m = 50$), indicating that this cascade of successive transitions is possible.

In the saturation regime, the absorbed energy ϵ can be estimated in the following manner: In a cascade of n transitions we have $\epsilon_n = h\nu(n/2)N$. In our case, $n = 4$, so that $\epsilon_2 = 2h\nu N$. At the frequency of the $P(16)$ transition of the CO_2 laser, a cascade of 2 transitions is possible: $0 \rightarrow 1$, to which contributions can be made by the transitions Q , $R(J_m)$, and $P(J_m)$, and the transition $R_{1-2}(145)$. Therefore the energy absorbed at 948 cm^{-1} should not exceed $\epsilon_2 = h\nu N$, which is half the value of the expected absorption at the frequency 934 cm^{-1} . Experiment shows that $\epsilon_{934 \text{ cm}^{-1}}/\epsilon_{948 \text{ cm}^{-1}} = 1.6$, which is in satisfactory agreement with the approximate theoretical prediction.

It was observed in^[14] that the most effective frequency for separation of the sulfur isotope ^{32}S is shifted towards the "red" side of ν_3 by 7 cm^{-1} (and not by 4 as in our experiments). In contrast to our experiments, in the experiments of^[14] the final level of the preceding transition must serve as the start of the succeeding one, so that three transitions are at resonance with the radiation.

A number of interesting effects occurring under the influence of resonant radiation have been published in the literature: visible luminescence,^[15,16] production of charged particles,^[17,17] and others. It is of interest to find a resonance frequency that ensures a maximum yield for these effects in both the collision and collisionless variants of the excitation. This will permit a deeper understanding of their nature.

The authors consider it their pleasant duty to thank A. G. Lyapin and M. M. Lazurin for supplying the purifying sulfur hexafluoride, to N. A. Vishnyakov and V. G. Kartyshev for help with the experiments, and to Yu. S. Leonov for his isotopic analysis of the sulfur hexafluoride.

¹N. G. Basov, E. P. Markin, A. N. Oraevskiy, and A. V. Pankratov, Dokl.

- Akad. Nauk SSSR 198, 1043 (1971) [Sov. Phys. Dokl. 16, 445 (1972)].
- ²N.G. Basov, A.N. Oraevsky, and A.V. Pankratov, Chemical and Biochemical Application of Laser, ed. C.B. Moore, Acad. Press, New York, 1974, chapter 7.
- ³N.N. Akinfiev, N.G. Basov, V.T. Galochkin, S.I. Zavorotnyĭ, E.P. Markin A.N. Oraevskiĭ, and A.V. Pankratov, Paper at 7th Conference on Nonlinear Optics, Tashkent, March 10-19, 1974.
- ⁴V.T. Galochkin, S.I. Zavorotnyĭ, V.N. Kosinov, A.A. Ovchinnikov, A.N. Oraevskiĭ, and N.F. Starodubtsev Kvantovaya Elektron. 3, 125 (1976) [Sov. J. Quantum Electron. 6, 66 (1976)].
- ⁵A.V. Belotserkovets, G.A. Kirillov, S.B. Kormer, G.G. Kochemasov, Yu.V. Kuratov, V.I. Mashendzhinov, Yu.V. Savin, E.A. Stankeev, and V.D. Urlin, Kvantovaya Elektron. 2, 2412 (1975) [Sov. J. Quantum Electron. 5, 1313 (1975)].
- ⁶R.V. Ambartsumyan, Yu.A. Gorokhov, V.S. Letokhov, and G.N. Makarov, Zh. Eksp. Teor. Fiz. 69, 1956 (1975) [Sov. Phys.-JETP 42, 993 (1975)].
- ⁷V.T. Galochkin, S.I. Zavorotnyĭ, V.N. Kosinov, A.A. Ovchinnikov, and A.N. Oraevskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. 22, 153 (1975) [JETP Lett. 22, 70 (1975)].
- ⁸N.G. Basov, A.N. Oraevskiĭ, and A.V. Pankratov, Paper at Vavilov Conf. on Nonlinear Optics, Novosibirsk, June 1975; Kvantovaya Elektron. 3, 814 (1976) [Sov. J. Quantum Electron. 6, No. 4 (1976)].
- ⁹J.F. Bott and T.A. Jacobs, J. Chem. Phys. 50, 9, 3850 (1969).
- ¹⁰H. Brunet and M. Perez, J. Mol. Spectrosc. 29, 472 (1969).
- ¹¹F. Shimizu, Appl. Phys. Lett. 14, 12, 378 (1969).
- ¹²P.L. Houston J.I. Steinfeld, J. Mol. Spectrosc. 54, 335 (1975).
- ¹³J.I. Steinfeld, I. Burak, and D.J. Sutton, J. Chem. Phys. 52, 5421 (1970).
- ¹⁴R.V. Ambartsumyan, Yu.A. Gorokhov, V.N. Kosinov, A.A. Ovchinnikov, and A.A. Puretskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. 23, 26 (1976) [JETP Lett. 23, 22 (1976)].
- ¹⁵N.G. Basov, V.T. Galochkin, S.I. Zavorotnyĭ, V.N. Kosinov, A.A. Ovchinnikov, A.N. Oraevskiĭ, A.V. Pankratov, A.N. Skachkov, and G.V. Shmerling, Pis'ma Zh. Eksp. Teor. Fiz. 21, 70 (1975) [JETP Lett. 21, 32 (1975)].
- ¹⁶V.S. Letokhov, E.A. Ryabov, and O.A. Tumanov, Zh. Eksp. Teor. Fiz. 63, 2025 (1972) [Sov. Phys.-JETP 36, 1069 (1973)].
- ¹⁷N.V. Karlov, N.A. Karpov, Yu.N. Petrov, A.M. Prokhorov, and L.A. Shelepin, Dokl. Akad. Nauk SSSR 226, 305 (1976) [Sov. Phys. Dokl. 21, 32 (1976)].