

EFFECTIVE EXCITATION OF HIGH VIBRATIONAL STATES OF
 SF_6 MOLECULES IN A BEAM BY A MULTIPLE-FREQUENCY IR
RADIATION

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Abstract Presented here are the first results of experiments on multiple-photon excitation (MPE) of molecules upon their being concurrently irradiated by several IR pulses differing in frequency. Effective population of the high vibrational states (HVS) of SF_6 was found to occur even when the frequencies of exciting pulses were fairly far ($10-20\text{ cm}^{-1}$) from the linear absorption spectrum (LAS) of the molecules. The method enables one to obtain narrow vibrational distributions of excited molecules (VDEM) and make a wider use of the capabilities of IR lasers for selective photochemistry purposes.

INTRODUCTION

A search for ways to effectively excite HVS of molecules, enhance the excitation selectivity, and make a fuller use of the capabilities of discretely tunable IR lasers for molecular excitation is an important aspect of the problem of selective interaction of IR laser radiation with molecules [1, 2]. The two-frequency molecular dissociation [3,4] is a significant step in this direction. With this method, however, as in the case with one-frequency excitation, the population of HVS is determined only by the radiation parameters of the first-step excitation laser whose fluence must be kept low in order to attain high selectivities, and the possibility of

resonant excitation of HVS by a single-frequency radiation, can, in the case of discretely tunable lasers, be realized but extremely seldom. That is why the efficiency of populating HVS is low and the excited molecules are, as a rule, distributed among many vibrational states. In this connection experiments on the excitation of the HVS of molecules by photons of different frequencies whose sum satisfies the multiple-photon resonance condition are of considerable interest. In this case, it becomes possible to tune the exciting radiation to resonance with the HVS more accurately, to populate them effectively, and to obtain narrow VDEM. The present paper reports on the first results of experiments on multiple-frequency IR MPE of high vibrational states of SF₆ molecules flow-cooled in a pulsed expanding supersonic jet stream. The molecules were excited by temporally synchronized output pulses from two or three CO₂ lasers, the sum of the laser output frequencies satisfying the multiple-photon resonance condition. Effective polulation of the HVS of SF₆ was found to occur even when the frequencies of exciting pulses were fairly far (10-20 cm⁻¹) from the LAS of the molecules. The efficiency of this excitation method materially surpasses that of not only one-frequency excitation, but also of consecutive two-frequency excitation [2].

EXPERIMENTAL

A detailed description of the experimental setup can be found in [5,6]. A beam of jet-cooled ($T_R \approx 20$ K, $T_V \approx 160$ K) SF₆ molecules was subjected to excitation by the output pulses of several CO₂ lasers temporally synchronized to an accuracy of ± 50 ns. The laser beams were spatially matched and made

to intersect the molecular beam axis at right angles 6 cm downstream of the supersonic nozzle. The cross section of the laser beam in the excitation region was about $1 \times 0.7 \text{ cm}^2$. The laser pulses were of the same polarization and consisted of a 100-ns (FWHM) peak and a $0.5\text{-}\mu\text{s}$ tail containing around 30% of the total pulse energy. Measured in the experiments was the energy absorbed by the molecules from the laser pulses in conditions of concurrent multiple-frequency excitation (with all the exciting pulses being temporally superimposed) and also in those of one-frequency and consecutive two- or three-frequency excitation. The absorbed energy was measured by means of a pyroelectric detector.

RESULTS AND DISCUSSION

Figure 1 shows spectral dependences (for the light field of frequency ω_2) of the energy absorbed by the SF₆ molecules in the case of temporal superimposition of two exciting pulses and also in conditions of one- and consecutive two-frequency excitation. In the latter case, the output pulse of the second (tunable) laser was delayed by 1 μs with respect to the first laser pulse. The output frequency of the first laser was fixed at 947.74 cm^{-1} (10P(16)line). It is obvious that the absorbed energy in the case of concurrent irradiation with two pulses, where the possibility of MPE of high vibrational states by the two-frequency radiation is realized, substantially exceeds that in the case of one-frequency excitation (where average absorbed energies in excess of a quantum per molecule were already attained [5]) and in the case of two-frequency excitation with a delay between the pulses. The efficiency of concurrent multiple-frequency ex-

citation is still higher in comparison with that of consecutive multiple-frequency excitation in the case where the exciting pulse frequencies do not coincide with the LAS of the

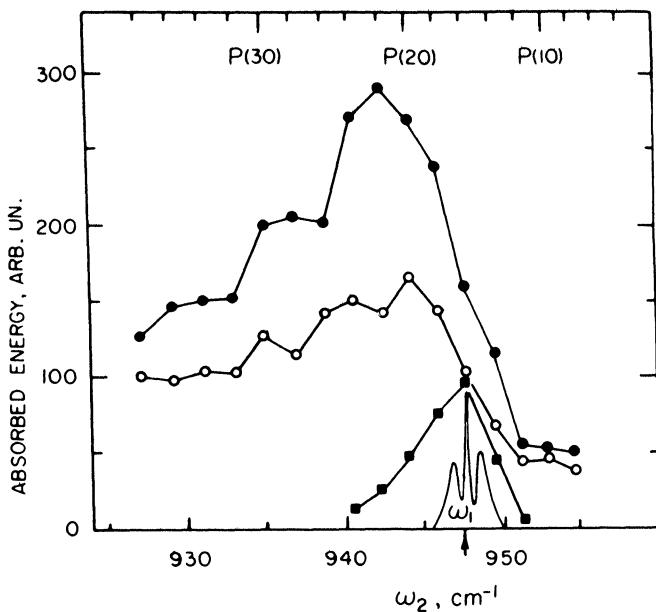


Figure 1. Spectral dependences (for the light field of frequency ω_2) of the energy absorbed by SF_6 molecules upon concurrent two-frequency excitation (\bullet), one-frequency excitation (\blacksquare), and consecutive two-frequency excitation with a delay time between the exciting pulses of $1 \pm 0.05 \mu s$ (\circ). The frequency ω_1 is fixed on the P(16) line of the $10.6-\mu$ band. Laser fluences: $\Phi_1 = 0.07 J/cm^2$, $\Phi_2 = 0.6 J/cm^2$. Shown in the bottom part of the figure is the LAS of SF_6 in a beam.

molecules. Figure 2a shows a schematic diagram of a three-photon excitation of the F_1 state of the $3\nu_3$ level in SF_6 by pulses of three different frequencies which are such that neither of them separately nor any pair of them is in reso-

nance with the low-lying transitions of the molecule, but their sum satisfies the multiple-photon resonance condition $\omega_1 + \omega_2 + \omega_3 = 3\nu_3$ (F_1). Presented in Fig. 2b is the dependence of the absorbed energy on the delay time between a

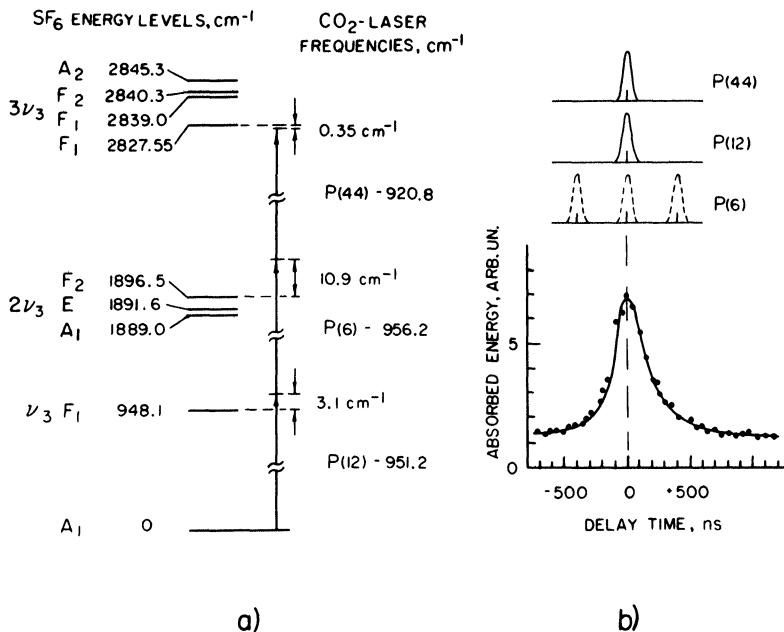


Figure 2. (a) Schematic diagram of a three-photon excitation of the F_1 state of the $3\nu_3$ level in SF_6 and (b) the dependence of the energy absorbed by SF_6 molecules on the delay time between a pair of preliminarily synchronized pulses ($P(12) + P(44)$) and a third pulse ($P(6)$). Laser fluences: $P(6) \sim 0.6 J/cm^2$, $P(12) \sim 0.2 J/cm^2$, $P(44) \sim 0.5 J/cm^2$.

pair of preliminarily synchronized pulses ($P(44) + P(12)$) and a third pulse ($P(6)$). A considerable increase in the absorbed energy is observed when all the three pulses are temporally superimposed, which is associated with the three-photon population of the $3\nu_3$ level and, possibly, further exci-

tation of the molecules into higher states. Our estimates show that no less than 10-12 % of the molecules were excited in this case. A similar picture was observed when any of the other two pulses was delayed. Likewise, using two pulses ($P(4) + P(34)$ or $P(6) + P(32)$), the frequencies of which were detuned from the LAS of SF_6 by $8-17\text{ cm}^{-1}$, we excited the two-photon resonance $A_{1g}^2 \nu_3$ (1888.8 cm^{-1} [6]), approximately 35 % of the molecules being brought into this state at laser fluences of around 0.5 J/cm^2 .

CONCLUSION

The method described in the present paper enables one to populate the HVS of molecules more effectively than it can be done with a one-frequency or a consecutive two-frequency excitation, obtain narrow VDEM, provided that the frequencies ω_i of the exciting pulses are selected so as to exclude one-photon transitions (and the excitation selectivity is thus enhanced), and make a wider use of the capabilities of discretely tunable IR lasers for selective photochemistry purposes. The results obtained, as well as the data presented in [5,6 and 7], show that multiple-photon transitions, higher order transitions included, play an important part in the excitation of supercooled SF_6 molecules with CO_2 laser pulses. The described method of effective excitation of HVS can be used to produce inverse populations in vibrational-state systems of molecules.

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