ELEMENTARY PHYSICOCHEMICAL PROCESSES

Two- and Four-Photon Satellites in the Saturated Absorption Spectrum

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Abstract—Two-photon satellites in the saturated absorption spectrum of the SiF_4 molecule were obtained experimentally and interpreted. The splitting of the sublevels was determined based on the interpretation. The transitions were attributed to the *P* branch of the vibrational transition of the molecule.

Keywords: saturated absorption resonances, multiplet satellites, hyperfine structure of the spectrum, Cohen–Tannoudji resonances

INTRODUCTION

Saturated absorption spectroscopy is one of the key methods of nonlinear laser spectroscopy [1]. The laser wave passes through the cell with the gas under study, is reflected by a mirror, and then travels through the cell in the opposite direction. A light receiver records the dependence of the wave capacity on the laser radiation frequency. If the light frequency coincides with the center of the absorption line, the counter-waves are absorbed by the same set of molecules with zero velocity projection and clear the medium for one another. This is just the absorption saturation resonance.

Each line forms its own resonance. A cross resonance corresponds to each pair of transitions with a common energy level [2]. One transition from a pair of transitions related by the common energy level may be forbidden [3]. In this case, the amplitude of the cross resonance is close to the mean geometrical value of the resonance amplitudes of the related transitions. In addition, the saturated absorption spectrum contains Cohen–Tannoudji resonances characteristic of the Λ scheme of the energy levels [4] and formed with participation of stimulated Raman scattering.

In this study, we investigated the saturated absorption spectrum of SiF_4 [5] in the frequency range of low-pressure generation of the CO_2 laser. Previously, we have already observed the two- [6] and four-photon [7] satellites similar to Cohen–Tannoudji resonances, which appear near the multiplets of the superfine [8] structure of the saturated absorption spectrum. Here we give new experimental data and their analysis, which will allow us to obtain more spectroscopic information.

RESULTS AND DISCUSSION

The SiF_4 molecule is a regular tetrahedron. In a state with a definite energy, the molecule simultaneously rotates around equivalent symmetry axes. In the state with a definite energy, the wave function of the molecule is the sum of the wave functions of rotation around different equivalent axes with different amplitudes and phases. The resulting structure of the energy levels is called the superfine structure [8].

The selection rules allow only the transitions between the levels of the superfine structure with the same symmetry. As a result, the superfine structure of the spectral line repeats the superfine structure of the levels. The molecules of XY_4 or XY_6 type have multiplets of four types: *AFFA*, *FEF*, *AFE*, and *FF*. Here *A*, *F*, and *E* are the symbols of the irreducible representations that determine the symmetry of the corresponding energy levels.

The figure shows the experimental curve with a doublet *FF* and its satellites which we found in the absorption saturation spectrum of the hot vibration bands ν_3 of the SiF_4 molecule within the range of the CO_2 laser frequency tuning on the *P*(32) line of the band at 9.6 μm (the 00^01–02^00 vibrational transition). Here satellite *2* inside the multiplet is the cross resonance between the allowed and forbidden transitions with a possible addition of collision cross resonance. Satellites *1* and *3* outside the doublet are the Cohen–Tannoudji two-photon satellites.

The frequencies of the counter-light waves in the reference system of the molecule differ from the frequency ω in a laboratory reference system by the value of the Doppler shift kV_z. The first (stronger) wave in the figure is shown by a double arrow; the counter-wave is shown by a single arrow. The right double arrow
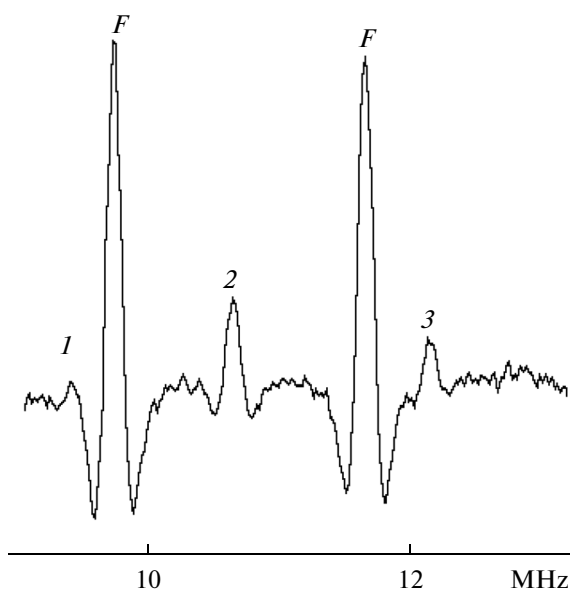
Doublet *FF* of the superfine structure, its satellites, and formation mechanism of satellite *1*.
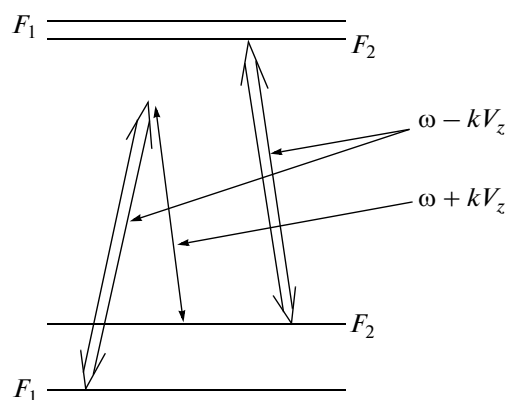
reflects the resonance light absorption of the first wave with transition of the molecule from the F_2 sublevel of the lower level to the F_2 sublevel of the upper level. This process depletes the F_2 sublevel of the lower energy level. As a result, the two-photon transitions between the F_1 and F_2 sublevels of the lower level are mainly directed from F_1 to F_2. This two-photon process is accompanied by photon absorption from the strong wave and photon emission to the weak counter-wave. Light is reflected from the cell without passing through it. This reflection leads to light amplification on the receiver and forms low-frequency satellite *1*. Satellite *3* forms in a similar way.

The frequency distance between satellites *1* and *3* is slightly smaller than the doubled distance between the parent resonances. This corresponds to the situation shown in the figure when the splitting of the upper sublevels has the opposite order relative to that of the lower sublevels. The reverse order of sublevels means that the difference between the rotational quantum numbers of the upper and lower energy levels equals an odd number plus or minus unity if the selection rules are taken into account. That is, the observed multiplets correspond to the *R* or *P* branch of the hot vibrational transition corresponding to the ν_3 vibration. The fact that the splitting of the upper sublevels is weaker than that of the lower ones means that the angular momentum projection to the molecular axis for the upper level is a better quantum number than for the lower level. Therefore, this projection (which has the same value for the upper and lower levels according to the selection rules) is closer to the rotational quantum number of the upper level than to that of the lower level. This means that the rotational quantum number of the upper level is smaller than that of the lower level;

i.e., the doublet in question refers to the *P* branch of the hot vibration band.

The laser frequency ω in the laboratory reference system equals the half-sum of the counter-wave frequencies. Then the half-sum of the double and single arrows in the figure equals the frequency of satellite *1*:

$$\omega_1 = \frac{\omega_{F_2} + \left(\omega_{F_2} - \delta\omega\right)}{2} = \omega_{F_2} - \frac{\delta\omega}{2},$$

where ω_{F_2} is the frequency of the transition between the F_2 levels or the F_2 component of the *FF* doublet, and $\delta\omega$ is the frequency of the splitting of the lower energy level. In the figure, $\omega_{F_1} > \omega_{F_2}$ for certainty. It follows from this equation that satellites *1* and *3* are separated from the parent resonances by $\delta\omega/2$ (half of the splitting of the lower energy levels). Accordingly, satellites *1* and *3* are separated from the F_2 and F_1 parent resonances by slightly less than half of the difference between the frequencies of the parent resonances, this "slightly" being half of the frequency splitting of the upper level. A similar analysis for the four-photon satellite shows that the expected frequency distance from the satellite to the nearest parent resonance is $\delta\omega/4$.

CONCLUSIONS

The multiplet satellites in the absorption saturation spectrum of the SiF_4 molecules were obtained experimentally. The satellites were interpreted as resonances formed with participation of the two-photon transitions similar to the Cohen–Tannoudji resonances. The energy splitting of the upper and lower sublevels of the superfine structure of the spectral transition was

determined based on this interpretation. The transition in question was attributed to the *P* branch of the vibrational transition spectrum of the molecule.

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