

Observation of a hot vibrational transition in the spectrum of SF₆ in a cryosystem at 140 K

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Absorption from the excited vibrational level $v_3 = 1$ of SF₆ in liquid Kr is first reported. Population of this level is determined in the case of optical pumping, and it is shown that nonequilibrium absorption is dependent on transitions to anharmonic structure sub-levels of the $v_3 = 2$ state.

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Information concerning the structure and anharmonic displacement of excited vibrational terms of molecules are essential to qualitative interpretation of phenomena occurring in strong ir fields. The nonlinear absorption in the v_3 band of sulfur hexafluoride in the liquid krypton observed earlier⁽¹⁾ indicates the possibility of a marked depopulation of the ground states of molecules in weak solutions at low temperatures. This constitutes a reason for setting up experiments for the observation of absorption spectra of cryosystems under nonequilibrium conditions, while the well known advantages of cryosystem spectroscopy⁽²⁾ create favorable conditions for the acquisition of data on the anharmonic structure of excited states.

The experiments were carried out by means of the double ir resonance method. The solution of SF₆ in Kr (concentration 3×10^{16} cm⁻³) was excited by pulses with a

duration of ~ 150 nsec at half maximum. The frequency of pumping radiation (line P (28), $\nu_0 = 936.8$ cm^{-1}) at the solution temperature of 140 K coincides with the absorption band maximum of SF_6 . The source of diagnostic radiation—whose frequency was discretely tunable near ν_0 —was also pulsed ($\tau_p = 100$ μsec) at an intensity not greater than 50 W/cm^2 . Because of high saturation of the transition $\nu_3 = 0 \rightarrow 1$, variations in the time constant of a recording system in the range 150 – 350 nsec failed to affect the results of measurements.

The pumping and the probing pulses are concurrently absorbed, as is indicated by the dashed line in the Fig. 1 below. The maximum of this “hot” absorption is shifted with respect to ν_0 by -4.5 cm^{-1} , and the intensity remains practically constant with the increasing flux density of the pump I from 0.5 to 1.5 MW/cm^2 . The latter may be explained in terms of absorption data for SF_6 in a cryosystem which, under the foregoing conditions of pumping, may be described with high accuracy within the framework of a three-level model.⁽¹³⁾ If we allow for degeneracy of the participating states, relaxation of the $\nu_3 = 1$ level is ~ 3 nsec and its population at $I = 0.5$ MW/cm^2 attains 0.7 , i.e., it differs from the limiting value of 0.75 .

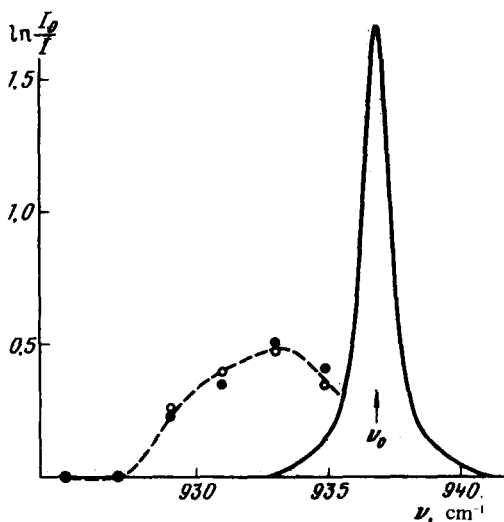


FIG. 1. Nonequilibrium absorption in the solution of SF_6 in liquid Kr at pumping intensities $I = 0.5$ MW/cm^2 (\bullet) and 1.5 MW/cm^2 (\circ). The solid line indicates the absorption profile in a weak field.

The first observation of absorption from an excited vibrational level in a cryosystem is more applicable—in comparison to a diffused pattern characteristic of the gaseous phase—to the study of the anharmonic structure of the $\nu_3 \geq 2$ states of the SF_6 molecule. We calculated the structure for a potential which represents the sum of expanded Morse functions⁽⁶⁾ for individual SF bonds:

$$V = \sum_{i=1}^6 \frac{1}{2} f q_i^2 - \frac{1}{2} \beta f q_i^3 + \frac{7}{24} \beta^2 f q_i^4,$$

where q_i is change in the length of the i -th bond, $f = 5.5$ $\text{mdyn}/\text{\AA}$ ⁽⁷⁾ is harmonic force constant, and cross-force constants and the anharmonicity of valence angles are ne-

glected. Inasmuch as the extent of detuning $\Delta = \nu_3\nu(0 \rightarrow 1) - \nu(0 \rightarrow \nu_3)$ is of primary interest, calculation was limited by the valence portion of the vibrational problem. In terms of the foregoing model an expression may be formed for the potential function in normal coordinates—which we chose not to present here because of its cumbersome—and earlier results⁽⁸⁾ may be used for calculating the frequency difference. In Ref. 8, the problem was solved for the point group T_d that is homomorphic with the octahedron group O_h . We shall limit our study to data for the state $\nu_3 = 2$. The detuning Δ for the three components of this state may be expressed as follows:

$$\Delta(A_{1g}) = 2X_{33} - 4G_{33}, \quad \Delta(E_g) = 2X_{33} + 2G_{33} + 12T_{33},$$

$$\Delta(F_{2g}) = 2X_{33} + 2G_{33} - 8T_{33},$$

where the anharmonic constants X_{33} , G_{33} , T_{33} depend on the only parameter of the model β . In contrast to Ref. 9, we consider it more appropriate to calculate β from the experimental value of frequency of the $3\nu_3$ SF band⁽¹⁰⁾ that corresponds to transition to one of the sub-levels F_{1u} of the $\nu_3 = 3$ state than from the SF bond dissociation energy)*. Depending on the relation used this yields two possible values of the parameter β : 1.2 or 2.7 \AA^{-1} . At $\beta = 1.2 \text{ \AA}^{-1}$, the anharmonic constants (in cm^{-1}) are: $X_{33} = -1.2$; $G_{33} = 0.53$ and $T_{33} = 0.27$ which yield Δ (in cm^{-1}): $-4.5(A_{1g})$, $-4.6(E_g)$ and $+0.8(F_{2g})$. Thus, if we assume that the observed "hot" band is dependent on the transitions $\nu_3 = 1(F_{1u}) \rightarrow \nu_3 = 2(A_{1g}; E_g)$, its position is in a good agreement with the calculated one. The ratio of integral cross sections of the foregoing $(A_{1g}; E_g)$ transitions and cross section of the primary transition equals two. Knowing the value of the population of level $\nu_3 = 1$ we find that the ratio of integral band intensities of "hot" and primary transitions should be about 1.4, while the experiment yields 1.1 ± 0.4 .

In conclusion, we note that the results of this work point to the real possibility of obtaining population inversion as a result of optical pumping of cryosystems.

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