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#### FERMI RESONANCE IN THE SRS SPECTRUM OF CRYSTALLINE n-NITROANILINE

Ya. S. Bobovich and A. V. Bortkevich  
S. I. Vavilov Optics Institute  
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According to the quantum-mechanical theory of stimulated Raman scattering (SRS) developed by Javan in [1], a Stark shift of the line towards the violet side of the spectrum should be observed in a powerful light-wave field. In the typical case, sufficiently far from resonance, the magnitude of this shift is estimated in [1] to be on the order of  $1 \text{ cm}^{-1}$ . This effect is therefore difficult to observe in the condensed phase of matter, but it has been reliably established and is persistently investigated in gases [2]. Indirect information on the Stark level shift can be obtained in any phase of matter by investigating the Fermi resonance that accompanies this shift in certain spectra.

Fermi resonance is observed in the form of splitting of spectral lines whenever the frequency difference between oscillations of equal symmetry is of the same order of magnitude as their mechanical anharmonicity. The sharpness of the Fermi resonance is subject to the influence of intermolecular fields, or in general other external fields [3]; the character of this influence can be assessed from the position and relative intensity of the splitting components. We used this very property in the present investigation.

The object of the investigation was powdered n-nitroaniline, for which Fermi resonance is possible between the fundamental oscillations in the C-NO<sub>2</sub> and C-NH<sub>2</sub> groups [4,5]. Under certain conditions, the spontaneous Raman spectra of this substance actually revealed line splitting in the  $\sim 1330 \text{ cm}^{-1}$  region, but its unique interpretation was made complicated by formation of a hydrogen bond [6]. The SRS generation in powders, which made it possible to perform the present investigation, was discovered by Sushchinskii and his co-workers [7]. The SRS spectra of n-nitroaniline were excited by us with a Q-switched ruby laser and were observed in reflected light. The maximum power in the ruby line was  $20 \text{ MW/cm}^2$ . The beam was focused on the material with a long-focus lens. A spectrograph with diffraction grating and  $6 \text{ \AA/mm}$  dispersion was used.

At room temperature, the n-nitroaniline spectrum reveals, even at the maximum excita-

tion power available to us, one line of frequency  $1276 \text{ cm}^{-1}$  (Fig. 1a). When the substance was cooled to the temperature of liquid nitrogen, a second line  $1313 \text{ cm}^{-1}$ , albeit of lower intensity than the first, appeared even at a power  $2 \text{ MW/cm}^2$  (Fig. 1b). A systematic increase of the excitation power up to  $20 \text{ MW/cm}^2$  leads to a splitting of the  $1276 \text{ cm}^{-1}$  line into two close components (Fig. 1c). The distance between them ( $3 - 5 \text{ cm}^{-1}$ ) depends little on the excitation power, but the intensity distribution is strongly dependent on it. In some cases we even observed intensity reversal. This is seen in Fig. 1d.

The formulas for the intensities of the splitting components at Fermi resonance between the fundamental oscillations can be written in simplified form as follows:

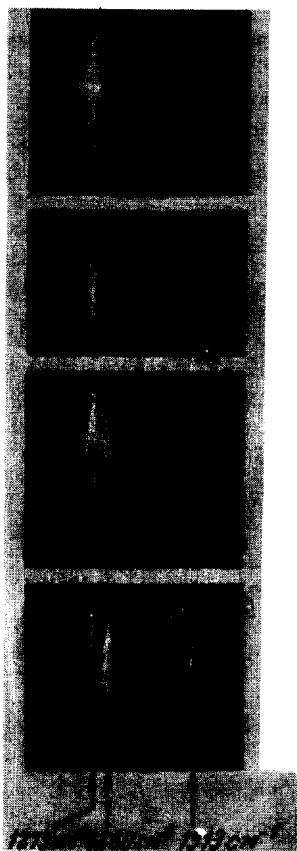
$$I \sim \left\{ \sqrt{\kappa + |\Delta|} \alpha_1^{01} \pm \sqrt{\kappa - |\Delta|} \alpha_2^{01} \right\}^2,$$

$$I' \sim \left\{ \mp \sqrt{\kappa - |\Delta|} \alpha_1^{01} + \sqrt{\kappa + |\Delta|} \alpha_2^{01} \right\}^2,$$

where  $\kappa$  is the distance between the splitting components and equals  $\sqrt{\Delta^2 + 4p^2}$ ,  $\Delta$  is a measure of the sharpness of the resonance,  $p$  is a measure of the mechanical anharmonicity, and  $\alpha_1^{01}$  and  $\alpha_2^{01}$  are the matrix elements of the polarizability for each of the resonating oscillations. The upper signs in the formula are used when the signs of  $p$  and  $\Delta$  are the same, and the lower when they are different [8].

It is seen directly from the formula that if the resonance is sufficiently sharp, the anharmonicity is large, and the intensities of the initial oscillations are commensurate, the entire energy may be concentrated wholly in one component. Consequently if the value of  $\Delta$  changes under the influence of the field and passes through zero, we should observe in the limit complete reversal of the intensity of the components. We are postulating only a partial redistribution of the intensities. This is apparently evidence that  $\kappa$  does not exceed  $\Delta$  by more than 2 - 3 times. Taking into consideration, on the other hand, the experimental value of  $\kappa$  ( $5 \text{ cm}^{-1}$ ) we can conclude that the anharmonicity is small in our case, and  $\Delta$  is of the order of  $1 \text{ cm}^{-1}$ , which agrees well with theory in accord with Javan's estimate [1].

The authors of [9], who investigated SRS in cyclohexane, observed, near the intense  $2852 \text{ cm}^{-1}$  anti-Stokes line, a weak satellite on the violet side of the spectrum, starting with a certain pulse power. Its distance from the fundamental line increased systematically with increasing power, up to a value  $55 \text{ cm}^{-1}$ . In spite of so large a value of the splitting, the authors of [9] attributed it to the optic Stark effect. They were forced to propose that the shifted and unshifted SRS lines are excited by different cavity modes. We propose that Fermi resonance, due to



SRS spectra of n-nitroaniline: a - room temperature; b,c,d - liquid-nitrogen temperature and excitation at 2, 10, and  $20 \text{ MW/cm}^2$  respectively.

small shifts of the line frequencies in the field of the powerful pulse, cannot be excluded in this case. Judging from the published data, Fermi resonance between the valence fundamental oscillations and an overtone of the deformation oscillations in C-H groups is a widespread phenomenon [10].

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#### ELECTRIC CONDUCTIVITY OF THIN BI FILMS IN STRONG ELECTRIC FIELDS

V. I. Vatamanyuk, Yu. A. Kulyupin, and O. G. Sarbei  
Physics Institute, Ukrainian Academy of Sciences  
Submitted 9 November 1967  
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Quantization of the electron energy spectrum in crystals of limited dimensions leads to an oscillatory character of the dependence of the kinetic coefficients in thin metallic films on the thickness [1-3]. It is possible to obtain from these relations a number of data on the structure of the energy spectrum of the electrons in these films. Another possibility for the study of this question is to investigate the electric conductivity of thin films as a function of the electric field [4]. It must be borne in mind, however, that the structure of such films depends strongly on the thickness, on the preparation conditions, the state of the substrate, etc. It is known, for example, that in many cases very thin films cease to be continuous and constitute a two-dimensional assembly of islands of limited dimensions. Nonetheless, even in this case the discreteness of the energy spectrum should apparently lead to singularities on the current-voltage characteristics of the films in strong electric fields, provided the electron gas does not become "heated" in them [5].

The experiments were made with bismuth films sputtered in a vacuum not worse than  $5 \times 10^{-9}$  mm Hg on a mica substrate of temperature 70 - 80°C; the sputtering rate was 50 Å/min. The film thickness was determined by an optical method [1]. The fields needed to reveal the singularities of the current-voltage characteristics can be estimated for films of this type from the condition that the average electron energy in the field should change by an amount on the order of the distance between the discrete levels. At film thicknesses on the order of 100 Å this estimate yields  $U \approx 10^3$  V/cm. Such fields can be easily obtained as a result of the configuration of the samples, which is shown in Fig. 1. The investigated film 1 was