

# Resonant Raman scattering of light in anthracene crystals

V. I. Broude, A. A. Maksimov, and I. I. Tartakovskii

*Institute of Solid State Physics, USSR Academy of Sciences*

(Submitted 2 March 1978)

*Pis'ma Zh. Eksp. Teor. Fiz.* 27, No. 7, 424–426 (5 April 1978)

Excitation of anthracene crystals ( $T = 4.2\text{--}30$  K) by a tunable dye laser near the bottom of the lowest exciton band ( $\nu_0 = 25097$   $\text{cm}^{-1}$ ) has revealed a sharp increase in intensity of the Raman scattering (RS) of light, and no less sharp a decrease of its intensity in the immediate vicinity of the resonance. The RS intensity was found to be extremely sensitive to the intensity of the exciting light and to the crystal temperature. The results are discussed within the framework of the concept of stimulated resonant Raman scattering of light.

PACS numbers: 78.30.Jw, 42.65.Cq

Investigations of resonant Raman scattering of light (RRS) in anthracene crystals were carried out on sublimated single crystal samples  $5\text{--}30$   $\mu\text{m}$  thick with developed ab plane. The freely standing samples were placed in an optical thermostat with adjustable temperature ( $4.2\text{--}100$  K). The RRS was excited by a tunable laser with BPO dye in the range  $\nu_{\text{exc}} = 25\,000\text{--}25\,100$   $\text{cm}^{-1}$ ; the half-width of the excitation line was  $\lesssim 1.5$   $\text{cm}^{-1}$ . The exciting light was directed normal to the ab plane of the crystal (along the  $c^*$  axis) and was linearly polarized ( $E_{\text{exc}} \parallel \mathbf{b}$ ). The observation of the RRS was carried out in the same direction and at the same polarization (see the diagram in Fig. 1).

Figure 1 shows the dependence of the intensity  $I_R$  of the RRS with participation of the intermolecular vibration  $1402$   $\text{cm}^{-1}$  of the anthracene crystal ( $\sim 15$   $\mu\text{m}$ ) on the frequency  $\nu_{\text{exc}}$  of the exciting light at an optical pump density  $\sim 1$   $\text{MW}/\text{cm}^2$  (curve 1). The width of the RRS line was close to the width of the excitation line ( $\sim 1.5$   $\text{cm}^{-1}$ ). As the frequency  $\nu_{\text{exc}}$  was scanned, a simultaneous change was observed in the frequency of the scattering light  $\nu_R$ , such that  $\nu_{\text{exc}} - \nu_R = 1402 \pm 2$   $\text{cm}^{-1}$ . At  $\nu_0 - \nu_{\text{exc}} = 100\text{--}40$   $\text{cm}^{-1}$ , an increase of the intensity  $I_R$  was observed, followed by an abrupt decrease of this intensity at  $\nu_0 - \nu_{\text{exc}} = 35\text{--}15$   $\text{cm}^{-1}$ . At  $\nu_{\text{exc}} \geq 25\,060$   $\text{cm}^{-1}$ , an intrinsic luminescence band of the crystal was produced in the spectrum, with a frequency  $23\,692$   $\text{cm}^{-1}$ , and a width  $\sim 5$   $\text{cm}^{-1}$ , consisting of the bottom of the exciton band at  $1404$   $\text{cm}^{-1}$ , regardless of the value of  $\nu_{\text{exc}}$  (curve 2 on Fig. 1). Thus, at  $\nu_{\text{exc}} \geq 25\,060$   $\text{cm}^{-1}$  the spectrum revealed a doublet of bands with variable spacings between them and with varying relative intensities. A similar picture could be observed also in the region of the  $395\text{-cm}^{-1}$  molecular vibration, the only difference being that the intensity of the RRS line was noticeably lower in this case.

The RRS intensity depended strongly on the intensity of the exciting light and decreased to one-third when the intensity was decreased  $\sim 20\%$ . This nonlinear dependence, as well as the anomalously high relative intensity of the line  $\nu_R = \nu_{\text{exc}} - 1402$   $\text{cm}^{-1}$  in the RRS spectrum in comparison with the usual RRS spectrum offer evidence

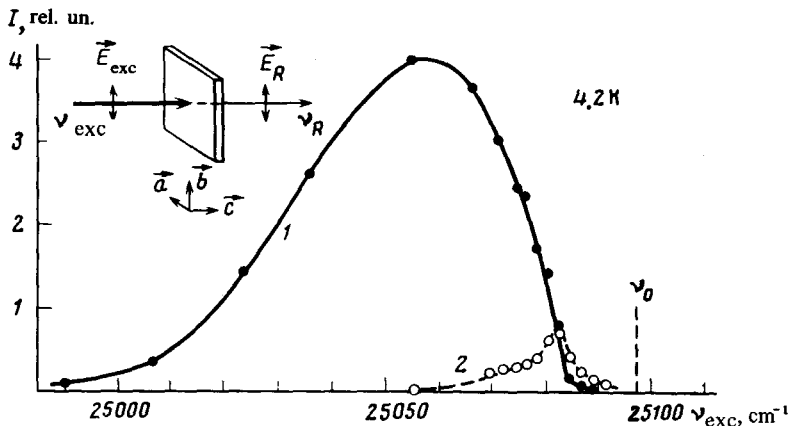


FIG. 1.

that in this case stimulated resonant Raman scattering of light (SRRS) takes place. Direct proof of the stimulated character of the scattering was the obtained superlinear increase of the scattering intensity with increasing sample thickness. For a crystal of thickness  $\sim 30 \mu\text{m}$ , at pumps  $\sim 10 \text{ MW/cm}^2$ , we obtained a 20% conversion of the exciting light into SRRS. Under these conditions we observed, when  $\nu_{\text{exc}}$  was varied, a deep modulation of the intensity of the SRRS, with a periodicity  $\sim 25 \text{ cm}^{-1}$ . It can be assumed that this modulation is due to a realignment of the generated modes of the specific resonator, whose length coincides with the sample thickness, and that the feedback is due to reflection of the light from the developed parallel surfaces of the crystal.

The increase of the RS intensity as resonance is approached is well known and is presently under intensive study. It is known also that stimulated Raman scattering (SRS) takes place in sufficiently extended scattering media. Naturally, the growth of

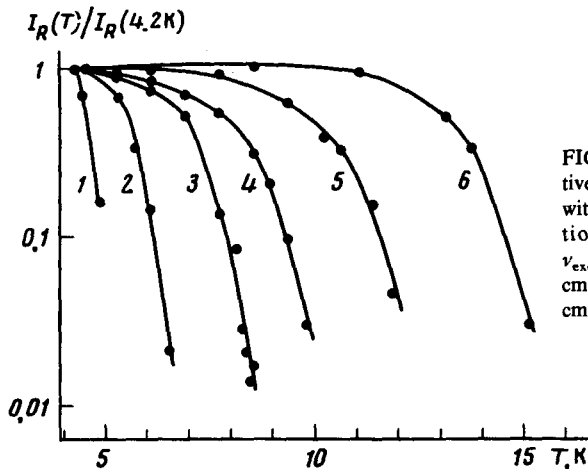


FIG. 2. Temperature dependence of the relative intensity  $I_R(T)/I_R(4.2\text{K})$  of the SRRS line with participation of the intramolecular vibration  $1402 \text{ cm}^{-1}$  for different values of  $\nu_{\text{exc}}$ : 1-25085  $\text{cm}^{-1}$ ; 2-25078  $\text{cm}^{-1}$ ; 3-25072  $\text{cm}^{-1}$ ; 4-25066  $\text{cm}^{-1}$ ; 5-25053  $\text{cm}^{-1}$ ; 6-25041  $\text{cm}^{-1}$ .

the RS cross section as resonance is approached should favor a transition into the stimulated scattering regime even at such small sample thicknesses as in our case. We do not know, however, of any other published data on the growth of the intensity of stimulated RS under resonance conditions. Nor was the decrease of the intensity of the scattering in the immediate vicinity of the resonance noticed previously. We assume that the decrease of  $I_R$  observed by us  $\nu_0 - \nu_{\text{exc}} < 35 \text{ cm}^{-1}$  is due to the small effective attenuation of the intensity of the exciting light on account of the long-wave absorption tail near the bottom of the exciton band, and also on account of the increase of the reflection coefficient in this frequency interval. Owing to the high sensitivity of the SRRS to the pump intensity, a weak decrease of the latter exerts such a noticeable effect on the scattering. The presence of absorption at  $\nu_0 - \nu_{\text{exc}} < 35 \text{ cm}^{-1}$  is confirmed also by the onset of luminescence under such excitation (Fig. 1).

A similar interpretation of the decrease of the SRRS near the resonance was confirmed in a study of the temperature dependence of the SRRS. Figure 2 shows the influence of the temperature in the thermostat bath on the intensity of the SRRS at different  $\nu_{\text{exc}}$ . It is seen from these data that an unusually abrupt temperature dependence is observed in the SRRS intensity, and this dependence is stronger the closer  $\nu_{\text{exc}}$  is to resonance. This means apparently that small changes in the absorption with increasing temperature are sufficient to cause, owing to the nonlinear relation, a noticeable decrease in the scattering intensity.

It should be noted in conclusion that the quantitative results of the measurement of the SRRS depend substantially on the geometry of its observation and excitation.