Resonant Raman scattering and hot luminescence of anthracene in the region of exciton absorption

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The spectrum of resonant secondary luminescence at the bottom of the S_1 absorption band was measured for the first time. The hot lines attest to the presence of a quasibound phonon of internal frequency $v = 395/cm^{-1}$. With the exciting light polarized along the a-axis of crystal the Raman scattering lines assume shapes that fail to conform to elementary treatment.

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1. Investigation of the resonant secondary luminescence (RSL) and the special features of hot luminescence (HL) of different impurity systems (see review[1]) have made it possible to determine the picosecond lifetimes and decay channels of vibrational states of molecules in host matrices. In the case of molecular crystals heretofore only one of three RSL components has been considered—ordinary luminescence (OL)—and, most recently, anthracene was used to study the pre-resonant Raman scattering (RS).[2,3] We measured the polarization RSL spectra of anthracene single crystals in the case of excitation of the electron-vibrational absorption band in order to detect the weak components of RSL—HL and RS—and to determine excitation lifetimes of the crystal.

2. Crystals measuring $2 \times 5 \times 5$ mm^3 were placed in an immersion helium cryostat. Spectra were recorded in the "reflection" geometry. RSL was excited by linearly-polarized uv radiation ($\lambda_{exc} = 3638$ Å, power incident on the crystal ~ 100 mw), from an argon-ion laser (spectra Physics 171–19). Radiation was recorded with a 10 cm^{-1} resolution on an automated spectrometric device[4] consisting of the DFS-12 monochromator, photon counter with a cooled FEU-16 photomultiplier, multi-channel NTA-512B counter and the Nairi-2 electronic computer. The spectra—averaged over a large number of data points—were fed to a two-coordinate curve plotter.

3. Figures 1 and 2 show polarization spectra containing all the RSL components (The excitation light E_{exc} is polarized along the b-axis of crystal and parallel to the **a**-axis, respectively). In the case of $\mathbf{E}_{exc} || \mathbf{b}$, the spectra contain in addition to known OL lines[5] several extra-weak narrow bands in the antistokes spectral region from the 0–0 transition, which we attribute to RS and HL[1] on the basis of criteria given in Ref. 1. The line numbering in Fig. 1 is as follows: 1–7—RS lines with respect to transitions[2] $v_{12} = 395$ cm^{-1}, $v_{11} = 622$ cm^{-1}, $2v_{12}$, $v_8 = 1163$ cm^{-1}, $v_7 = 1260$ cm^{-1}, $v_6 = 1403$ cm^{-1} and $v_4 = 1557$ cm^{-1}, respectively; 8—HL line corresponding to the simultaneous annihilation of the exciton and v_{12} transition; 9—surface exciton luminescence; 10—OL of anthracene molecules perturbed by a lattice defect; and 11–18—OL lines. The significant features of these spectra are:[3] a) low intensity of the RS and HL lines (5–6-fold weaker than the OL lines); b) occurrence of two-photon RS lines
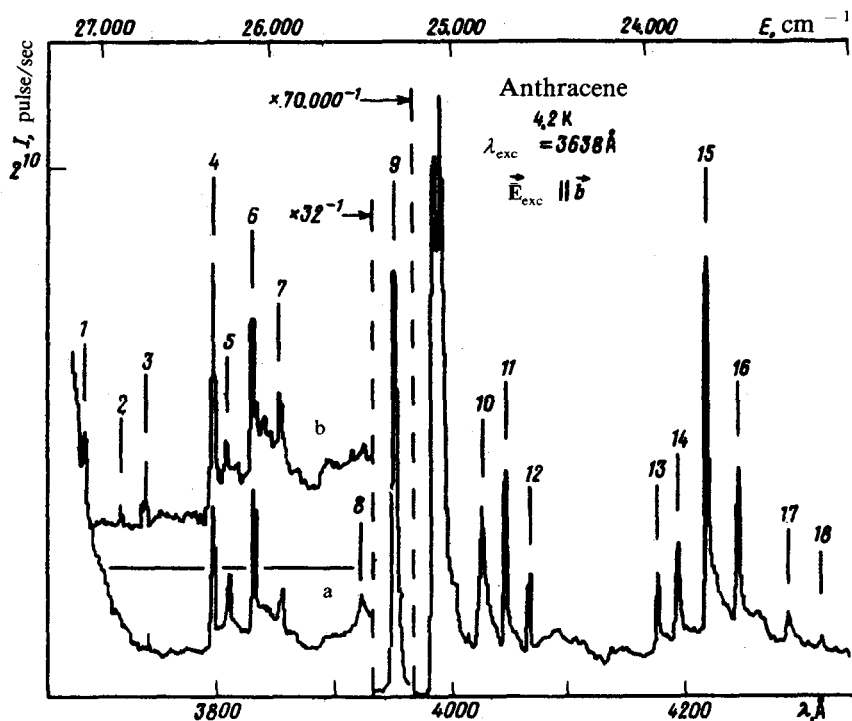
FIG. 1. SL spectrum of anthracene excited 2385 cm^{-1} above 0–0 transition; a—$E_{reg}\|b$; b—$E_{reg}\perp b$.

$(2\nu_{12})$; c) HL—polarized along the **b**-axis—is observed only from the lowest region of the ν_{12} vibron.

4. We shall first determine the nature of excitation occurring in a crystal. The weakness of the RS and HL lines may be caused by reabsorption and the rate of relaxation processes. It is estimated that reabsorption may weaken the signal 10-fold at which point the other cause takes over. The presence in the spectra of multiphoton RS lines and their high relative intensity, and also the intensity of the RS lines due to the ν_8 and ν_6 states which correspond to the $2\nu_8$ and $\nu_9\nu_6$ levels in the energy spectrum located near the laser transition, provides us with a basis to consider scattering as a natural resonance. This notion is non-trivial—non-resonant components of the scattering tensor may, under certain conditions of resonant excitation, provide a comparable or even greater contribution to the RS cross section. In the case of excitation of rapidly relaxing vibronic states in the bands we should not expect dominance of the resonant RS over the nonresonant since the process cross section energy denominator is small for the entire RSL cross section, the dominant part of which, however, reduces to OL.[8] The reason for appearance in the RSL spectrum of a single HL line is, above all, attributed to the large width of the electron-vibrational bands and the negligible lifetime of the quasi-bound states above the lower (A_u) band of the ν_{12} vibron and, correspondingly, the super-fast relaxation that leads to the occurrence of a continuous
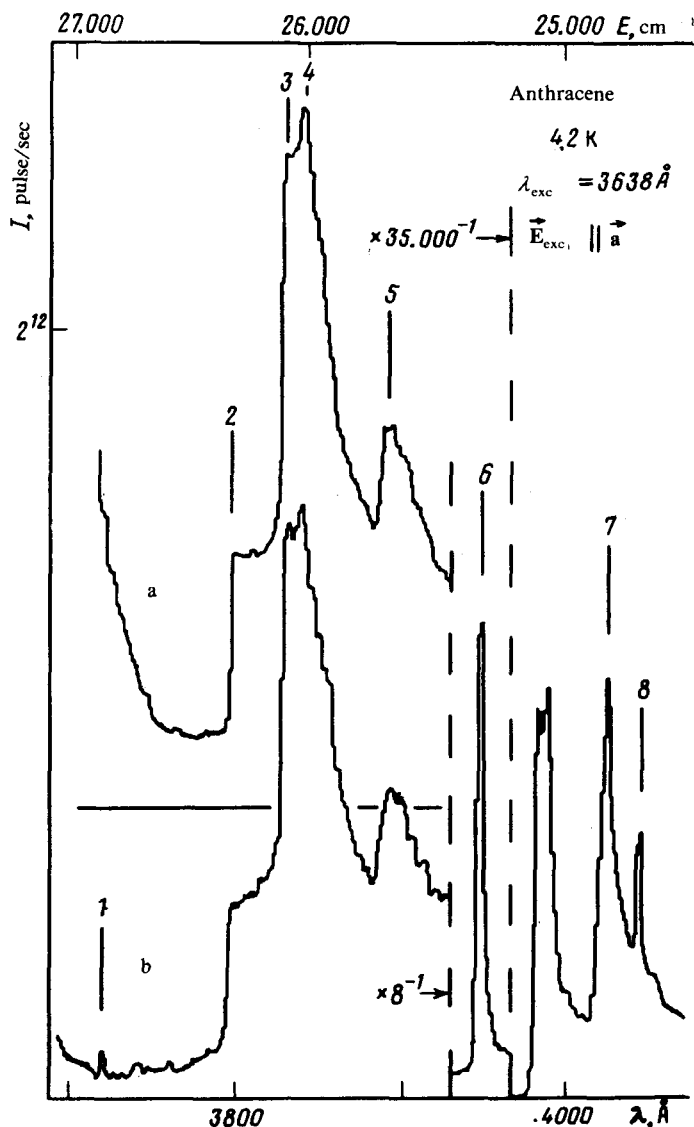
FIG. 2. SL spectrum of anthracene excited 2385 cm^{-1} above 0–0 transition; $(\mathbf{E}_{exc}\|\mathbf{a})$; a—$\mathbf{E}_{reg}\|\mathbf{a}$; b—$\mathbf{E}_{reg}\perp\mathbf{a}$).

background under the RS lines in place of discrete HL lines. Polarization of the HL lines $\nu_{12}\to0$ along the b-axis corresponds to the A_u-A_g transition. Rates of relaxation processes may be judged from the relative intensity of the HL line $[I(\nu_{12}\to0)/I(0\to\nu_{12})\approx0.33\times10^{-5}]$. Assuming an average lifetime of an exciton with respect to luminescence ($\tau_0=2$ nsec[9]) we get the ν_{12} vibron lifetime of the order of 100 femtoseconds (the HL linewidth does not contradict this value). We touch on the

question of separation of "bound" and "free" exciton and internal phonon states.[4] Due to frequency invarience of intramolecular oscillations for an electronic transition and the smallness of the Stokes losses, anthracene does not give rise to a region of single-frequency excitation which is detached from a two-frequency region of the exciton and internal phonon. Nevertheless, a maximum with a width of the order of 20 cm^{-1} should occur in the two-frequency excitation spectrum[10] for a dimensionless Stokes shift of 0.4 (as is the case for the ν_{12} transition) and width of exciton band $L \approx 100$ cm^{-1}. This corresponds to the occurrence of a quasi-bound state with a characteristic lifetime of the order of 0.25×10^{-12} sec, a value which is also in a good agreement with our estimate. Finally, we should note that in the case $\mathbf{E}_{exc} \parallel \mathbf{a}$ (Fig. 2) individual RS spectral lines are replaced by broad bands with steep violet edges (excluding line 1 which corresponds to RS from a partly-symmetric vibration ν_{11}). The coincidence of these band fronts with the positions of the 4 and 6 RS lines in the spectra with $\mathbf{E}_{exc} \parallel \mathbf{b}$ is noteworthy. The reasons for the special features of spectra with $\mathbf{E}_{exc} \parallel \mathbf{a}$ currently remain unclear, although they may be associated with an interaction between $\mathbf{a}$-polaritons and acoustic phonons.

[1] A line at 3951 Å which corresponds to luminescence of a surface exciton[6] is excluded.
[2] Designation of vibrations was borrowed from Ref. 7.
[3] We also investigated RSL spectra at $\lambda_{exc} = 3511$ Å which are characterized by the same features, with the RS present to the third order.
[4] The authors thank E.F. Sheka for directing their attention to this question.

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