

Fine structure of fluorescence spectra of anthracene adsorbates

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(Submitted 9 November 1986)

Pis'ma Zh. Eksp. Teor. Fiz. **45**, No. 1, 40–41 (10 January 1987)

The appearance of a fine structure has been detected in the luminescence spectra of anthracene adsorbates in the temperature interval 423–623 K.

It has been the understanding that fine structure can be achieved in a fluorescence spectrum in two cases: in the fluorescence of anthracene vapor in the case of excitation in the band of the 0–0 transition^{1,2} and in observation of Shpol'skiĭ spectra,^{3,4} which occur for solutions of anthracene in normal paraffins at 77 K.

We have observed the appearance of a fine structure in the fluorescence spectra of anthracene adsorbates on $\text{Al}_2\text{O}_3\text{-SiO}_2$ and SiO_2 during heating to 423 K. The fluorescence spectra were measured on a pulsed spectrofluorimeter. The excitation source is a pulsed nitrogen laser ($\lambda = 337.1$ nm); the length of the excitation pulse is 8×10^{-9} s. The samples are prepared by the technique described in Ref. 5.

Figure 1 shows fluorescence spectra of an anthracene adsorbate on $\text{Al}_2\text{O}_3\text{-SiO}_2$, measured at $T = 293$ K and 423 K at various delays after the excitation pulse. At 293 K we observe the emission of physically adsorbed anthracene with a lifetime of 10^{-8} s (curve 1) and the emission of a charge-transfer complex of anthracene in an excited state (exiplex) with a lifetime of 20×10^{-9} s (curve 2).⁵ Heating the samples to 423 K gives rise to a fine structure in the emission of anthracene (curves 3 and 4). As the delay is lengthened, the fine structure becomes more obvious. The lifetime of the excited anthracene molecules here is 25×10^{-9} s. The spectrum of the anthracene adsorbate consists of five distinct groups of lines, separated by an interval of 1405 cm^{-1} . Each group corresponds separately to a band of the ordinary diffuse spectrum of anthracene (curve 5). Analysis of the fine structure in the spectrum, which consists of 25 lines, shows that all of the lines can be interpreted as fundamental vibrational frequencies of anthracene: 390, 930, 1030, 1170, 1265, 1405, 1565, and 1665 cm^{-1} .

The fluorescence spectra which we are seeing here cannot be the spectra of the gaseous state of anthracene, since (first) the spectrum is not excited in the band of the 0–0 transition and (second) the fine structure in the spectrum is observed at temperatures up to 623 K. An analogy between the observed spectra and Shpol'skiĭ spectra would be more accurate, since anthracene adsorbates may be regarded as being embedded in a porous matrix, i.e., as forming a system to which the "oriented-gas" model is applicable. Adsorbates of anthracene molecules in a state of physical adsorption may retain, without substantial perturbation, the electronic and vibrational levels corresponding to the free state of these molecules. An aluminosilicate matrix, like a silicate matrix, satisfies all the requirements which would be imposed on the matrix in order to produce Shpol'skiĭ spectra: The aluminosilicate matrix is transparent on the absorp-

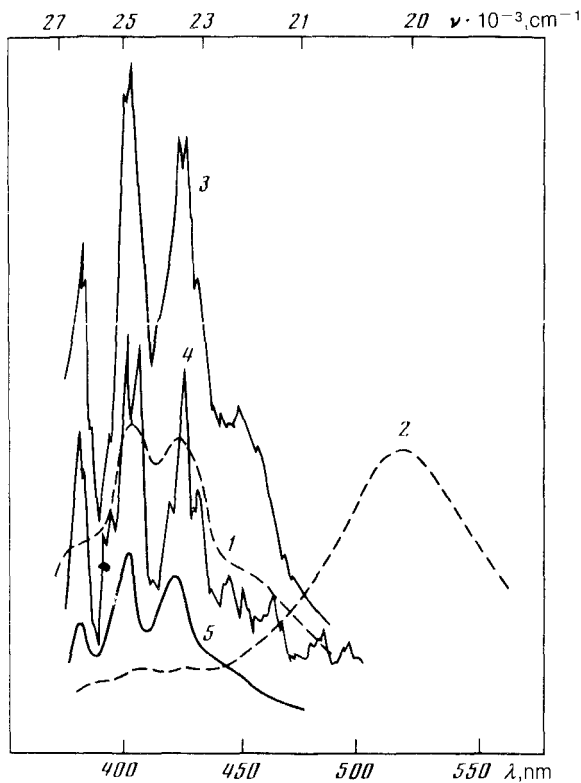


FIG. 1. Fluorescence spectra of anthracene adsorbates on $\text{Al}_2\text{O}_3\text{-SiO}_2$, measured at various delays with respect to the excitation pulse. 1—Fluorescence spectrum of adsorbate, $T = 293 \text{ K}$, $\tau_3 = 5 \times 10^{-9} \text{ s}$; 2—fluorescence spectrum of adsorbate, $T = 293 \text{ K}$, $\tau_3 = 20 \times 10^{-9} \text{ s}$; 3—fluorescence spectrum of adsorbate, $T = 423 \text{ K}$, $\tau_3 = 5 \times 10^{-9} \text{ s}$; 4—fluorescence spectrum of adsorbate, $T = 423 \text{ K}$, $\tau_3 = 20 \times 10^{-9} \text{ s}$; 5—fluorescence spectrum of a cyclohexane of anthracene.

tion and emission region of the anthracene, and it contains pores with dimensions comparable to those of the anthracene molecules. The condition of a weak interaction of the matrix with the radiating molecules is apparently satisfied when the system is heated to 423 K. Furthermore, the fine structure in the spectrum is observed during excitation of the anthracene adsorbates by light at 337.1 nm, far from the band at the 0-0 transition.

The fluorescence of an anthracene adsorbate on silica gel also reveals the appearance of a fine structure in the spectrum upon heating at 423 K.

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Translated by Dave Parsons