Spectral Effects in Cetyltrimethylammonium Bromide for the Temperature PhaseTransitions

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It is known that in molecular crystals in the temperature range below the melting point the molecules can perform the orientation disorder motions of the different nature. It is clear that any distortions in periodic location of the atoms in the plane perpendicular to the long axis of the molecules must result in some peculiarities in the intermolecular interactions. In particular, one could expect the change in resonance dynamic intermolecular interaction (Davydov splitting of vibrational excitons) in orientational disordered phase. In this work we report on temperature dependence of Davydov splitting value IR spectra study for the in-phase CH_2 rocking vibrations of methylene chains in crystalline bulk and film specimens of cetyltrimethylammonium bromide (CTAB) for the temperature region from 300 K to the melting point. The analysis of obtained temperature dependencies allows observing the next peculiarities. In the region of room temperatures the slow decreasing of the splitting value takes place. In the nearest region to the crystal melting point (about 370 K) we observe the sharp decreasing to zero of this value. A statistic and dynamic model is proposed which provides adequate description of the observed effect. In the framework of this model the damping of vibrational excitons on two kinds of orientational defects takes place. Such defects arise due to the excitation of librational and conformational, and then rotational molecular degrees of freedom at the different temperatures. Theoretical analysis of resonance dynamical intermolecular interaction in the spectra of intramolecular vibrations in such crystals has been carried out in terms of stochastic equations in range of these phase transitions. We obtained the explicit expression for theoretical dependence of Davydov splitting value on temperature. This spectral effect is related to the damping of vibrational excitons at their interaction with orientational defects in the crystal lattice. Computer fitting of such dependence were performed and theoretical estimations of corresponding energetic parameters of phase transitions were obtained. Good agreement between the experimental and computer results was obtained (see Fig.).

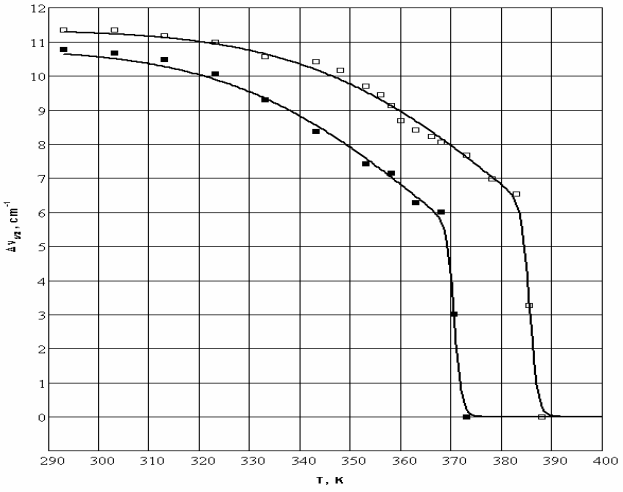

Fig. Calculated (lines) and experimental data for DS for 720-731 cm^{-1} range for CTAB bulk (□) and film (■).