Strong redistribution of the intensities between two fluorescence bands of *N*,*N*'-Dimethylaminobenzonitrile (DMABN) in acetonitrile under selective excitation by UV light with different photon energies was discovered and studied. Fluorescence of solution in all cases exhibits two broad bands, short wavelength near 350 nm belonging to the local excited (LE) states and longer at 470 nm ascribed to the charge transfer (CT) states of DMABN. The 350 nm band localization depends weakly on excitation, shifting to the blue side with a growth of quanta of excitation energy, on contrary the 470 nm band is practically the same for all excitation wavelengths in the range 220-290 nm. Remarkably, that at the same time permanent drop of relative intensities LE/CT band is registered with excitation shift to the red side of spectrum and that is strong, especially at reduced temperature 274K, from 0.82 to 0.23, at a change of excitation in the range 220 ÷ 280 nm. The obtained data allow to suggest that competition between spontaneous emission in the LE band and the CT reaction depends on the excited singlet state and an excess of vibrational energy.

 Independent support of our explanation were obtained applying to experimental spectra the Kennard –Stepanov (K-S) relation. This relation gives us instrument for revealing breaks of vibrational equilibrium over sublevels in the excited singlet states of organic molecules. Temperatures calculated with the K-S relation are 328, 586, 878, and 898 K for excitation by wavelengths 310, 290, 260 and 220 nm, respectively. In neutral hexane where CT reaction is absent, we have emission from fully relaxed vibrational manifold with effective temperature ~300K. These results indicate that only in acetonitrile, fast CT reaction depletes the first singlet state and in emission of the LE band we have essential cotribution from nonrelaxed vibrational sublevels. This finding is not consistent with the Kasha-Vavilov’s rule.