The Local Temperature Dependence of Fluorescent Centres in PVA Films on the Excitation Wavenumber

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The temperature difference $\Delta T = T^* - T$ (where T^* is the local temperature and T the ambient temperature) is studied as a function of the excitation wavenumber $\tilde{\nu}_{exc}$ in the longwave region of the absorption band of 4-amino-4′-nitrostilbene (ANS) and 4-dimethylamino-4′-nitrostilbene (DNS) as well as rhodamine S, rhodamine 6G and Na-fluorescein in poly(vinyl alcohol) (PVA) films heated up to 403 K. Local temperatures T^* are determined by a universal Kennard-Stepanov relation. A linear dependence of ΔT on $\tilde{\nu}_{exc}$ has been found for all investigated luminescent compounds. For dyes, due to the big spectral overlaps between the absorption and fluorescence bands, it was possible to excite also in the anti-Stokes region. In this case for $\Delta T = 0$, i.e. when $T^* = T$, one has $\tilde{\nu}_{exc} = \tilde{\nu}'_{0-0}$. In view of the slow geometrical relaxation of excitation energy excess in PVA polymers, the relaxation time τ_R for thermal equilibration between the luminescent molecule and the vicinal polymer exceeds distinctly the mean fluorescence lifetime τ_F.

Key words: Kennard-Stepanov Universal Relation; Local Temperature; PVA Fluorescent Films.