Evidences of the cascade violation of Kasha´s rule in Tetrapyridil Zinc Porphyrin molecules

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Molecular systems currently have a large range of applications, either in photoconvertion technologies or in therapies for the treatment of diseases. Detailed understanding of the properties of these systems often guarantees the success of an application and / or inspires the creation of new applications. Over the last century, after the consolidation of the new quantum mechanics, it was possible to explain and predict several properties of a molecule based on the concepts of wave function; adiabatic aproximation; perturbation theories, etc. All the spectroscopy experiments were then based on these concepts. Processes such as optical absorption; Fluorescence or phosphorescence can be very well explained by the association of quantum mechanics with classical electromagnetic theory. Theorems, postulates, and spectroscopic rules have been developed over the last years, among which the Kasha´s rule and the corollary of Vavilov stand out. The Kasha´s rule postulates that after absorption of light, if a molecule is capable of emitting light, such emission should be caused by a transition from the excited state of least energy to the ground state. From this rule, the physicist Sergey Vavilov proposed a corollary where it was established that such light emission processes should not depend on the energy of the excitation photons adopted. In this study, we observed the violation of such rules through analysis of the photoluminescence spectra of Zinc Tetrapyridyl porphyrin molecules dissolved in a mixture of the solvents chloroform and methanol (in the ratio 9: 1 respectivaly). When we light the sample at different wavelengths we detected distinct photoluminescence spectra. With this result we see the violation of Vavilov's hypothesis. Further analysis of the data has shown that not all the emission bands of such a molecule arise from less energetic excited states. We observed that these bands that violate the Kasha´s rule occur together in three distinct wavelengths according to the excitation adopted. This behavior suggests a kind of cascade violation of such a rule, that is, a kind of correlation between those bands that exihibit the anti

Kasha´s behavior and that happen just for certain excitations. Our analysis shows that this phenomenon is due to the coupling of vibronic levels caused by the presence of the Zinc atom in the tetrapyridyl porphyrin ring.