

PROTON TUNNELING DYNAMICS OF PORPHYCENE AND 2,7,12,17-TETRA-t-BUTHYLPORPHYCENE UPON $S_1 \leftarrow S_0$ EXCITATION

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Two systems: porphycene (PC) and 2,7,12,17-tetra-t-butyl-porphycene (PCTP) have been studied by means of laser induced fluorescence (LIF) and double-resonance fluorescence depletion technics in supersonic free jets. In the case of the porphycene splitting of vibrational bands ($\Delta \approx 4.4 \text{ cm}^{-1}$) have been discovered ^a. This effect has been described in terms of penetration through the barrier by proton tunneling. By adopting the model of proton coherent oscillations, Δ could be converted into the time domain: the proton transfer in the electronic ground state takes place within about 4 ps.

The LIF spectra of the PCTP have been carried out by the new type of narrow-band ($\text{FWHM} \leq 0.1 \text{ cm}^{-1}$) dye-laser designed by *Jan Jasny* ^b. Substitution of PC by four t-butyl-groups produces the red shift of the $S_1 \leftarrow S_0$ origin by 138 cm^{-1} . The origin of PCTP consists of two bands, separated by $\approx 2.4 \text{ cm}^{-1}$. The difference in shapes, widths, influence on NH/ND exchange suggest the different nature of the doublet. In the case of PCTP, no tunneling splitting has been observed and the statement about ground state proton tunneling can not be concluded. The role of the different ground state conformers of PCTP as well as the their dynamics in respect to proton transfer will be discussed.

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^a J. Sepioł, Y. Stepanenko, A. Vdovin, A. Mordziński, E. Vogel, J. Waluk, *Chem. Phys. Lett.* **296** (1998) 549.

^b E. Nosenko, J. Jasny, A. Mordziński, in preparation