

Spectroscopy of porphycene and its derivatives in supersonic-jet conditions by conventional heating and/or laser desorption techniques

Ephriem Tadesse Mengesha

Supervisor: Prof. dr hab. Jerzy Sepioł

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warsaw

Abstract

Supersonic jet-isolated porphycene (Pc) and its isotopomers have been studied using the techniques of laser induced fluorescence (LIF) excitation, single vibronic level fluorescence (SVLF) and hole burning spectroscopy, combined with quantum mechanical calculation of geometry and vibrational structures of the ground (S_0) and lowest electronically excited (S_1) states. Porphycene is a model for coherent double hydrogen tunneling in a symmetrical double well potential, as evidenced by tunneling splitting observed in electronic absorption and emission. The results led to reliable assignment of low frequency modes in the S_0 and S_1 electronic states. The values of tunneling splitting were determined for ground state vibrational levels. In the case of tautomerization promoting $2A_g$ mode, values of tunneling splitting were found to increase with vibrational quantum number in the ground state of Pc. Replacement of one or two hydrogens in the NH cavity by deuterons lead to drastic decrease of tunneling splitting. Different values of tunneling splitting were observed for co-excitation of two or more vibrations.

The effect of weak perturbations brought about by hydrogen/deuterium substitution on the outer rim of porphycene has been studied in detail and reported for jet-cooled heterogenous, perdeuterated Pc samples (Pc-d_{mix}) with the prevailing contribution of rim deuterated Pc-d₁₂ isotopologue. In this case, laser desorption method was successfully applied to introduce the samples in the jet. The samples introduced into the gas phase were then studied by means of LIF excitation and SVLF measurements, in combination with quantum chemical calculations. The influence of molecular symmetry is studied by comparing Pc, Pc-d₁₂ and Pc-d₁₁. The 0-0 transition in the LIF spectrum of Pc-d₁₂ shows a blue-shift of about 32 cm^{-1} relative to that of the parent undeuterated Pc, although similar spectral patterns were observed in the two isotopologues. Comparable tunneling splitting was observed in the two isotopomers, both for the 0-0 transition and the most efficient promoting $2A_g$ mode. In contrast, an unexpected isotopic



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effect is observed for the totally symmetric $4A_g$ mode. While this vibration behaves as a neutral mode in Pc, neither enhancing nor decreasing the tunneling efficiency, it strongly promotes hydrogen transfer in Pc-d₁₂. This observation is explained in terms of modification of the displacement vectors of the $4A_g$ mode upon deuteration.

Symmetric mode coupling (SMC) model was applied to map effect of mode coupling in two dimensional potential surfaces (one along the tunneling coordinate and the other along the coordinate of the promoting $2A_g$ mode) of porphycene. The experimental values of tunneling splitting were well reproduced using this model.

More stringent electronic and structural perturbation on proton tunneling is reported for jet cooled 2,7,12,17-tetra-tert-butylporphycene (TTPc). LIF and SVLF measurements by conventional heating method, in combination with quantum chemical calculations show the presence of two Trans- (one C_{2h} and the other C_s symmetries) and one Cis- (C_{2v}) isomers of TTPc in the supersonic jet. The trans- C_{2h} TTPc was found to be the most stable in the gas phase. A tunneling splitting of about 10 cm^{-1} is found for the Cis-form while no tunneling splitting is found for either of the trans isomers. This observation is in accordance with the shortest NH...N distance calculated for the Cis isomer. Interestingly, the presence of only the Cis-form of TTPc was manifested in the LIF spectrum measured in supersonic jet using laser desorption method.



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