Ultrafast Electronic State Coupling in Aromatic Cromophores

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The understanding of photophysic properties of aromatic cromophores (in particular benzene and naphthalene derivatives) plays a key roll in revealing the mechanisms of many photoinduced phenomena in chemistry and biology. Some relevant light triggered processes are: electronic energy and charge transfer in photosynthesis¹, photochemistry of DNA and RNA basis², *cis-trans* photoisomerization³, etc. In the case of monosubstituted naphthalene derivatives, and despite of the enormous theoretical and experimental effort intended to relate their electronic structure with the observed photophysical behavior, many questions still remain open⁴.

We have investigated the relaxation of several X-1-naphthalene derivatives, where X: H, NH₂, OH and CN. Mass resolved transient ionization signals were recorded following excitation from the ground state S_0 to a number of vibrational levels (within the pulse spectral bandwidth) of the first electronic excited state S_1 . Further ionization was achieved by multiphoton absorption of the 800 nm. probe pulse. The time dependent ion signals of the naphthalene derivatives show relaxation channels involving non adiabatic couplings among two close lying excited states L_a and L_b , and the ground state. The nature of these states and the mechanisms of energy transfer that govern the relaxation processes will be discussed in the light of the experimental results.



Fig. 1- Transient ion signal for the 1-aminonaphthalene molecule (circles), fragment of mass 115 a.u. (triangles) and autocorrelation function (dashed line), together with the best calculated fit (red and blue lines) collected at wavelengths of 266 and 800 nm. for pump and probe pulses respectively in a 1+2 photon process.

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