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Time-resolved photoelectron spectroscopy studies of excited states dynamics of molecules

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Abstract

This thesis is mainly focused on using time-resolved photoelectron spectroscopy to study the dynamics of electronically excited states in molecules. These dynamics are induced ("pumped") by absorption of a UV/visible-energy photon, exciting the molecule from its ground state into an excited state. This evolution is followed ("probed") by a time-delayed subsequent laser pulse which creates a photoion and a photoelectron. The kinetic energy of the photoelectron is determined, and a photelectron energy spectrum as a function of delay time between the pump and probe pulses.

With respect to the molecules studied here, the dynamics of the simple molecule, ethylene, serve as a reference. Here, C=C bond torsion happens on the $\pi\pi^*$ state, and when the molecules transfer from the excited state back to the ground state, this is accompanied with pyramidalization of CH_2 group or hydrogen migration from one carbon atom to the other. With stepwise methyl-substitution of the ethylene molecules, the dynamics changes with increased methylation.

With this template of the dynamics of ethylene, the dynamics will also be influenced by (1) adding hetero atoms. Alkyl vinyl ether, which adds an alkoxy group to ethylene, opens up a new reaction channel on the $\pi\sigma^*$ state, which is cleavage of the $-OCH_3$ group, while also retaining the C=C bond torsion on the $\pi\pi^*$ state, as in the dynamics of ethylene. (2) making cyclic systems. 1,3-cyclohexadiene, in which a second C=C double bond ("ethylene") is added to form a six-carbon ring system. Compare with ethylene, the molecules only have one potential energy surface involved in the dynamics. And molecule switches from the excited $\pi\pi^*$ state to the ground state without any pyramidalization. The dynamics proceed to the ground state either via a ring-opening or back to the cyclohexa-1,3-diene ground state.

Combining time-resolved photoelectron spectroscopy, i.e. measuring the kinetic energy of photoelectron, in combination with detailed computational studies, the dynamics in increasingly complex molecules, for examples, acrylonitrile, furan, pyrrole, etc, can be studied.

Akademisk avhandling för avläggande av licentiatexamen vid Stockholms universitet, Fysikum

Licentiatseminariet äger rum den 07 December 2015 kl 13:15 i sal FP41, Fysikum, Albanova universitetscentrum, Roslagstullsbacken 33, Stockholm.