MODELING LASER-INDUCED DYNAMICS IN BENZYLURACIL

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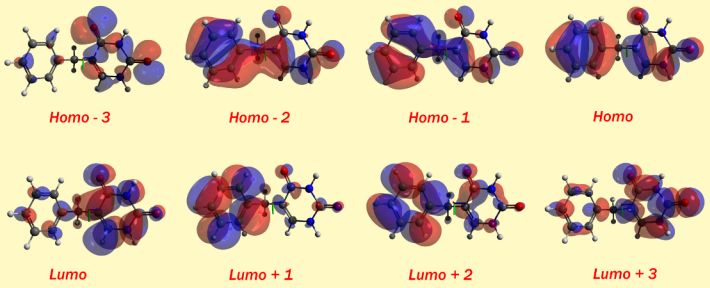
Abstract

The molecular orbital dynamics in formaldehyde and two different position isomers of benzyluracil (5-benzyluracil and 6-benzyluracil) is studied. The time-dependent Hartree-Fock and Kohn-Sham theories [*H. Eshuis, G. G. Balint-Kurti and F. R. Manby, J. Chem. Phys.* ***128****, 114113 (****2008****)*] implemented in the Molpro program package *[MOLPRO, version 2010.1, H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz, and others, see http://www.molpro.net.*] is used. The electron population of the occupied and virtual orbitals is given and their behavior under different laser field direction is presented. Conclusions about the efficiency of the laser field excitation of benzyluracil are drawn up.

5BU orbitals:



Methods

Solving the time-dependent Schrödinger equation (TDSE):

$$i\frac{\partial\Psi(t)}{\partial t}=\hat{H}(t)\Psi(t)$$

For arbitrary variations δΨ(t) of the time-dependent wavefunction Ψ(t):

$$\langle\delta\Psi(t)|\left(\hat{H}-i\partial/\partial t\right)|\Psi(t)\rangle=0$$

The solution for the TDSE in terms of single Slater determinant is:

$$\left(\hat{F}(t)-i\partial/\partial t\right)|\phi_i(t)\rangle=\sum_j|\phi_i(t)\rangle\epsilon_{ij}(t)$$

$$\left(\mathbf{F}(t)-i\partial/\partial t\right)\mathbf{c}(t)=\epsilon(t)\,\mathbf{c}(t)$$

If we apply a laser field:

$$e_z(t)=\mathcal{E}(t)\sin(\omega t)$$

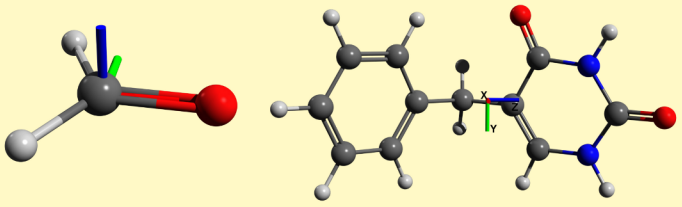
The total Fock matrix is:

$$\mathbf{F}(t)=\mathbf{F_0}(t)+D_z e_z(t)$$

The orbital occupation number is:

$$n_k(t)=\mathbf{C}_k^*\boldsymbol{\rho}(t)\,\mathbf{C}_k(t)$$

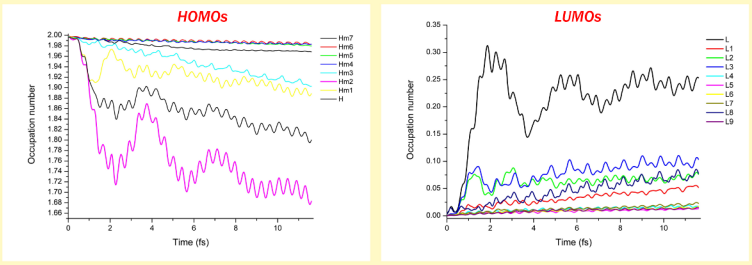
Molecular structures:



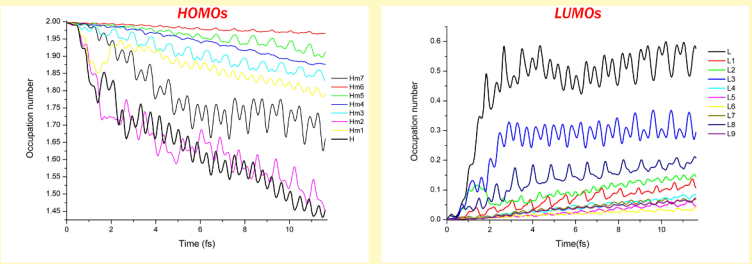
Formaldehyde

5-benzyluracil

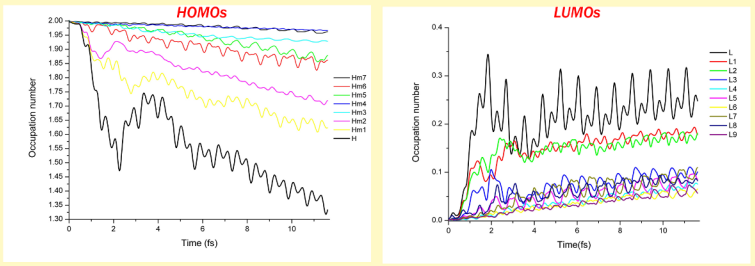
Excitation along the Y axis with λ=251 nm laser frequency for 5BU:



Excitation along the Z axis with λ=251 nm laser frequency for 5BU:



Excitation along the Z axis with λ=251 nm laser frequency for 6BU:



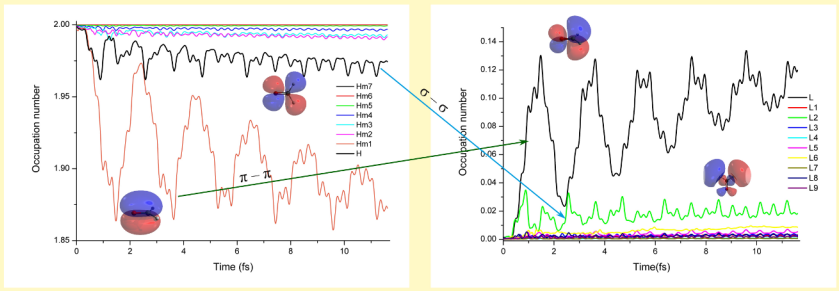


Figure 1. *The Homo - Lumo orbital populations and the characteristic transitions in the Formaldehyde molecule using λ=162 nm laser frequency ($S_0 \rightarrow S_2$ excitation along the C=O bond direction).*

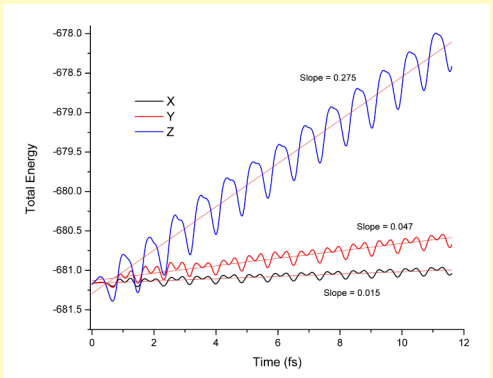


Figure 2. *Total Energy Evolution during Molecule - Laser Field interaction.*

Conclusions

- TDSE was solved for the case of monochromatic laser field interacting with position isomers of benzyluracil.
- A simple system (formaldehyde) was solved in order to reveal the features of laser - molecule interaction.
- We evidenced the Rabi oscillation of the populations of the orbitals involved in transition (π - π and σ - σ), modulated by the laser field oscillation.
- The response (Rabi period and population level) of 5BU was studied as a function of laser wavelength.
- The level of excitation stronly depends on the relative directions of dipol moment and laser field.
- The two position isomers of benzyluracil show different response to the laser field in terms of orbitals involved as well as the level of excited population.
- Further investigation aims at setting laser parameters in order to optimize the transfer of energy from laser to molecule.

Acknowledgement

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