

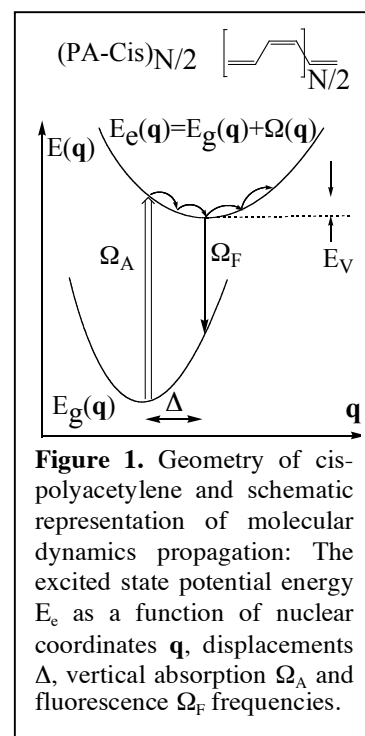
## Photoexcited breathers in conjugated polyenes: an excited state molecular dynamics study

$\pi$ -conjugated polymers have become an important class of materials for electronic devices. Design of these devices requires understanding such processes as photochemical reactions, spatial dynamics of photoexcitations, and energy and charge transport, which in turn involve complex coupled electron-vibrational dynamics<sup>1</sup>. The theoretical description of these molecular systems is challenging because of electronic correlation effects and strong electron-phonon interactions. Development of powerful computers and versatile program packages leads to the growing importance of quantum chemistry for the understanding underlying fundamental electronic phenomena and providing accurate predictions of relevant observables in the organic matter<sup>2</sup>.

We investigate the formation of photoexcited *breathers* i.e., multiquanta vibronic states in polyacetylene (Fig. 1). A breather is a dynamic state representing a spatially localized, time-persistent nonlinear excitation. Extensive studies based on simple Hamiltonian models predicted the formation of breather-like states in polyenes after either photoexcitation or electronic ground state perturbations of sufficient energy. However, it took almost two decades to develop ultrafast sub 5 fs experimental spectroscopic techniques to monitor real-time vibronic dynamics of conjugated polymers which support the existence of breathers<sup>3</sup>. Our results reproduce all the essential features of the early studies and provide quantitative information necessary for modeling a variety of spectroscopic techniques, which allows us to connect these simulations with recent experiments and to predict additional spectroscopic signatures of breathers.

We use the recently developed Excited State Molecular Dynamics approach, schematically illustrated on Fig. 1, which allows adiabatic photoexcitation dynamics to be followed on picosecond timescales in molecules with hundreds of atoms<sup>4</sup>. To analyze excited state dynamics of cis-polyacetylene we calculate oligomers (with free boundary conditions) long enough (inset in Fig.2) to mimic the infinite chain limit and up to a 1 ps timescale. To monitor the vibrational dynamics we focus on

the bond-length alternation parameter, which reflects an uneven distribution of the  $\pi$  electrons over the bonds (Peierls distortion) and is, therefore, strongly coupled to the electronic system<sup>4</sup>. To follow the electronic dynamics we further use a real-space two-dimensional

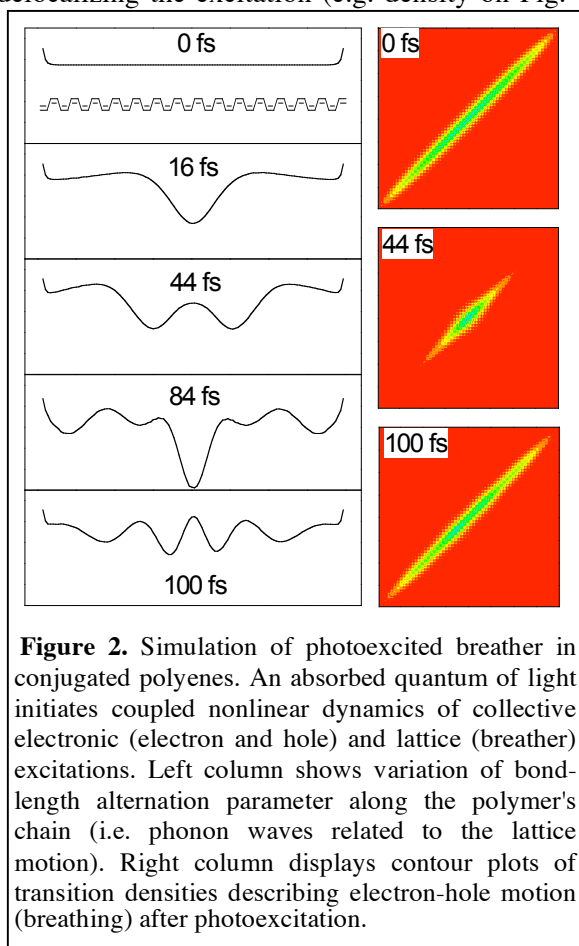


**Figure 1.** Geometry of cis-polyacetylene and schematic representation of molecular dynamics propagation: The excited state potential energy  $E_e$  as a function of nuclear coordinates  $\mathbf{q}$ , displacements  $\Delta$ , vertical absorption  $\Omega_A$  and fluorescence  $\Omega_F$  frequencies.

representation of the transition density matrices which characterize the properties of an exciton or bound electron-hole pair created upon photoexcitation<sup>2,4</sup>.

Left column of Fig.2 shows the variation of bond-length alternation parameter and right column of Fig. 2 displays the correspondent transition densities at specific times up to 100 fs. At the moment of photoexcitation ( $t=0$ ) the molecule in the ground state has a constant dimerization 0.095 Å). The effects from the molecular ends are small and local. Therefore, upon the photoexcitation, the exciton created is initially delocalized along the entire chain (Fig. 2,  $t=0$ ). Due to strong electron-phonon coupling an exciton rapidly distorts the lattice in the middle of the chain (Fig. 2,  $t=16$  fs) and localizes itself in this region on the timescale of  $\sim 20$  fs. When an exciton distorts the lattice, dynamical vibrational excitations (phonons) are created, appearing as waves in the bond-length alternation on the edges of the exciton potential well (Fig. 2,  $t=44$  fs). The subsequent dynamics can be qualitatively described as following: the phonon "waves" propagate in opposite directions, reflect from the chain ends, and meet in the middle of the chain (e.g. Fig. 2,

t=100 fs) pulling an exciton out of its well and delocalizing the excitation (e.g. density on Fig.



**Figure 2.** Simulation of photoexcited breather in conjugated polyenes. An absorbed quantum of light initiates coupled nonlinear dynamics of collective electronic (electron and hole) and lattice (breather) excitations. Left column shows variation of bond-length alternation parameter along the polymer's chain (i.e. phonon waves related to the lattice motion). Right column displays contour plots of transition densities describing electron-hole motion (breathing) after photoexcitation.

2, t=100 fs). The exciton, in turn, attempts to localize again, creating more phonons, i.e. the energy is exchanging between electronic and vibrational degrees of freedom. This variation of diagonal delocalization is a characteristic "breathing" pattern with period of 34 fs.

The characteristic timescales of this electron-vibrational motion appear on the power spectra of all spectroscopic observables (transition frequencies, transition dipoles, and polarizabilities) which contain frequency components with periods of  $\sim 18$ ,  $\sim 34$ , and  $\sim 70$  fs. Only the  $\sim 18$  fs harmonic is related to C=C stretching vibrational normal mode ( $\omega=1826$   $\text{cm}^{-1}$ ), whereas the other two harmonics are not associated with the vibrational spectrum with  $\sim 34$  fs being the breather excitation. We observe that the breather component has the strongest signature in transition dipoles and oscillator strengths, whereas energy variables (such as transition frequencies) are dominated by vibrational mode frequency components (in particular the C=C stretching). The magnitudes

of the transient absorption spectra are related to the respective transition dipole moments and, therefore, contain the breather vibrational component in their power spectra, which allow identification of breather excitations experimentally<sup>3</sup>.

In conclusion, strong nonlinear coupling among electronic and vibrational degrees of freedom leads to a complex spatially localized photoexcited vibronic dynamics which is a distinctive property of conjugated polymers. Modeled photoexcitation dynamics<sup>5,6</sup> shows several characteristic features i) an excitation moves to the largest conjugated segment of the polymer chain (where it has the lowest electronic energy); ii) an exciton creates phonon excitations and significant local distortions of the lattice. These phonons form a complex nonlinear localized vibrational excitation (breather) which cannot be associated with any specific single linear vibrational normal mode. The subsequent dynamics is spatially localized and appears as an exchange of the energy between an exciton and a breather; iii) the breather excitation has distinct spectroscopic signatures in the power spectra of all spectroscopic observables. We expect that these processes are typical for conjugated materials featuring strong electron-phonon coupling, including disordered nanomolecules. Development of ultrafast sub-femtosecond spectroscopic techniques and efficient quantum-chemical approaches allows monitoring of time-dependent vibronic processes. This opens the way to understand more deeply a number of photochemical, time-dependent spectroscopic and carrier transport processes in electronically-active soft and biological nanoscale matter.

## References

1. A. J. Heeger, *Rev. Mod. Phys.* **73**, 681 (2001).
2. S. Tretiak and S. Mukamel, *Chem. Rev.* **102**, 3171 (2002).
3. S. Adachi, V. Kobryanskii, and T. Kobayashi, *Phys. Rev. Lett.* **8902**, 7401 (2002).
4. S. Tretiak, A. Saxena, R. Martin, and A. Bishop, *Phys. Rev. Lett.* **8909**, 7402 (2002).
5. S. Tretiak, R. L. Martin, A. Saxena, and A. R. Bishop, *Proc. Nat. Acad. Sci. USA*, **100**, 2185 (2003).
6. S. Tretiak, A. Piryatinski, A. Saxena, R. L. Martin, and A. R. Bishop, *Phys. Rev. B*, **70**, 233203 (2004).

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