

# The Dynamophore – Localization of Excited State Dynamics Studied by Time-Resolved Photoelectron Spectroscopy

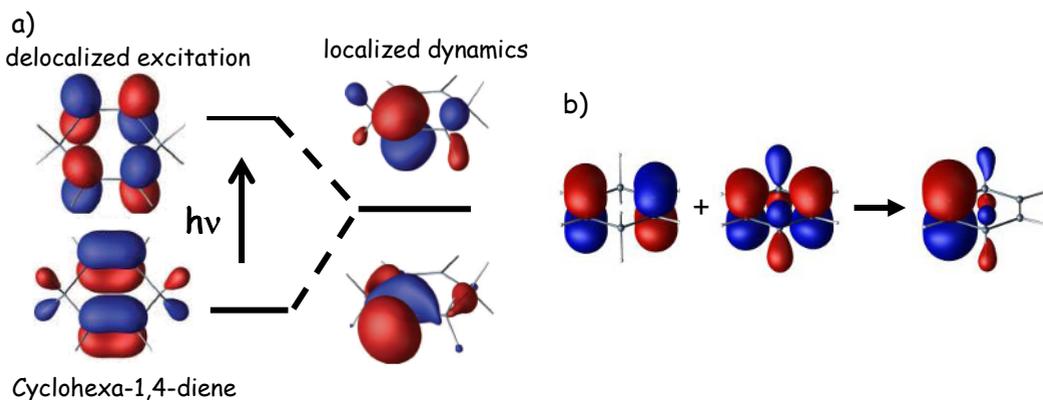
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**Abstract.** Photoinduced dynamics tend to localize at a confined region of a molecule, called dynamophore. Here, we show examples from time-resolved photoelectron spectroscopy.

## 1 The Dynamophore - A Definition

In organic molecules, UV- and vis-photons are absorbed by a chromophore which constitutes the part of a molecule where the electronic transition for a given spectral band is localized. However, dynamics induced by these photons may take place in another, localized region of the molecular framework which is defined as dynamophore [1]. An example is cyclohexa-1,4-diene which is excited along the delocalized  $\pi$ -manifold of two hyperconjugated double bonds but whose dynamics takes place only at one of the two sites of the molecule [1] (Fig. 1a).



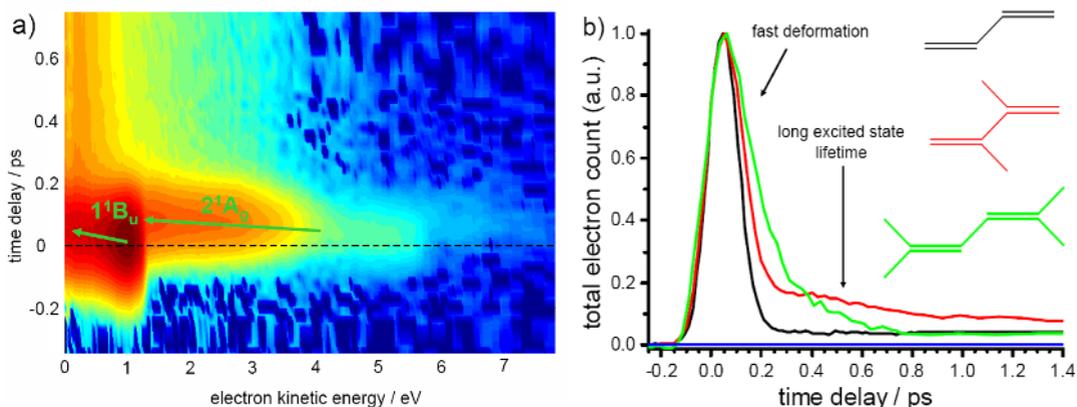
**Fig. 1.** a) Sketch of the localization of dynamics in cyclohexa-1,4-diene. b) Localization through linear combination.

## 2 Types of Dynamophores

Various types of dynamophores are recurring in our investigations, the most important being the ethylene moiety. Ethylene exhibits a characteristic set of motions to return from the excited  $\pi\pi^*$ -state to the electronic ground state: It twists about its double bond and either pyramidalizes at one of the two carbon atoms or forms a H-bridged structure which can lead to a [1,2]-hydrogen migration [2-4]. Other examples of dynamophores are the allyl-group ( $\text{CH}=\text{CH}-\text{CH}_2$ ) which performs an [1,3]-H shift or the cyclohexa-[1,3]-diene group exhibiting a ring opening reaction [5]. The concept of a dynamophore allows for the classification of a wide range of dynamical processes in terms of a small set of prototypical types. For example, ethylenic-type pyramidalization results in bond cleavage in the constrained six-membered ring of cyclohexa-1,4-diene [1] and a cis-trans isomerization in the case of stilbene [3]. One challenge is to find rules how changes in the local bonding framework of a dynamophore affect these prototypical types (formerly called multidimensional analogues of the Polyani rule [6]).

## 3 Localized vs. Delocalized Dynamics – The role of large amplitude motions

Localization of excited state dynamics is often correlated with large amplitude motions which are necessary to separate conjugated groups and reduce the coupling between them. In this case, small perturbations can lead to localization of the wavepacket through a favorable linear combination of orbitals as highlighted in Fig. 1b for cyclohexa-1,4-diene. In butadiene ( $\text{C}_4\text{H}_6$ ), the two conjugated double bonds are separated by a twist about the central single bond and the photodynamics get localized at one side of the molecule. In time-resolved photoelectron spectroscopy (TRPES), this behavior is recognized by a large time-energy shift of a photoelectron band which arises due to an increase of the ionization potential along the pathway of the molecular wavepacket (see Fig. 2a). For butadiene, this shift is seen for both the initially excited  $1^1\text{B}_u$ -state and the intermediate  $2^1\text{A}_g$ -state.



**Fig. 2.** a) TPRES-spectrum of butadiene excited at 200 nm and probed at 267 nm (logarithmic scale) b) Total electron yield of TRPES-experiments on butadiene (black), 2,3-dimethylbutadiene (red) and 1,1,4,4-tetramethylbutadiene (green) using the same wavelength as in a).

## 4 The Influence of Substitutions on Dynamics

While the general aspects of the dynamical response may be understood in terms of the relevant dynamophore, the molecule-specific dynamics may be perturbed or influenced by altering the local bonding environment. One example is the dynamics of substituted butadienes as shown in Fig. 2b. While the full TRPES-spectra of all molecules under investigation look similar to the one of butadiene in Fig. 2a, substitution at the terminal position (green curve) slows down the pyramidaization dynamics and, therefore, the initial deformation of the molecule (seen by a slower decay of the initial dynamics). On the other hand, substitution in the 2 and 3 position (red curve) does not prevent a fast deformation; however, it prevents quick access to the conical intersection with the ground state.

Another example highlighting the influence of the surrounding can be seen when exciting ethylene to its  $\pi 3s$ -Rydberg-state [2,4]. While increased substitution to up to three methyl groups only leads to a retardation of the dynamics due to a slower twisting motion, addition of the fourth methyl group pushes the Rydberg state energetically below the  $\pi\pi^*$ -state and causes the dynamics to slow down by two-three orders of magnitude.

## 5 Multiple Dynamophores

Another challenge in finding multidimensional analogues of Polyani rules are the possibility of molecules to localize at different dynamophores. A branching is found, e.g., in cyclohexa-1,4-diene where the ethylene ([1,2]-H shift, bond cleavages) as well as the allyl dynamophore ([1,3]-H-migration) are used. This poses the question which of the available dynamophores is and can be accessed. For example whether the presence of an allyl group enforces a [1,3] shift or when this channel might become dominant. In addition, one could ask how the yield of the pathways depends on the excitation wavelength and whether it is possible to control it.

## 6 Multiple Dynamophores

The concept of a dynamophore is a direct analogue to the concept of a chromophore, allowing a simplified view on otherwise complex dynamics. We believe that this concept allows categorizing types of photoinduced reactions and helps predicting dynamics of larger molecules.

## References

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