

# Quantum Dynamics of Molecular Reactions Directed by Explicit Solvent Environment

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**Abstract:** We present the first method that combines molecular quantum dynamics of the solute with classical molecular dynamics of the solvent. Its mechanical impact on the ultrafast internal motions is decisive for the reaction outcome.

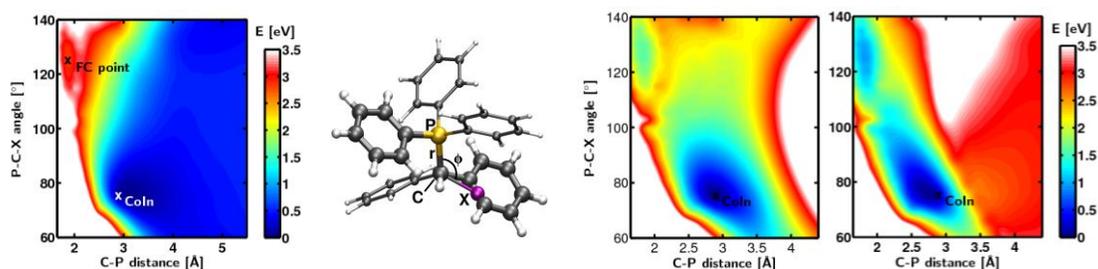
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## 1. Ultrafast chemical reactions in solution

It is well known that solvents can influence the outcome of chemical and biochemical reactions. Their electrostatic effects stabilize polar configurations along the reaction path. In addition dynamic solvent effects can emerge. They intervene on the ultrafast time scale and are in the focus of this study. A direct connection to the reaction process, involving either bond cleavage or formation or both, can be established. Besides the change in the molecular structure of the reactants also the volume and the shape of the solute's cavity within the solvent are affected. Therefore the dynamics of the solute is not governed by its internal degrees of freedom alone but in addition the position and orientation of the surrounding molecules can play an important role. In a given arrangement of solvent molecules specific internal motions of the solute can be hindered and areas of the molecular potential surface, dissimilar to the free molecule, are explored. The areas within reach change with the temporal arrangement of the solvent molecules. The average over all accessible arrangements defines the final yield. The dynamic solvent effects become especially important for ultrafast reactions with a substantial change of the shape of the reactants like in photochemical dissociations or isomerizations. Not only can internal motions be hindered, but additional channels can be opened.

## 2. Photochemical bond cleavage in acetonitrile

Our example is the photochemical bond cleavage of diphenylmethyltriphenylphosphonium ions ( $\text{Ph}_2\text{CH}-\text{PPh}_3^+$ ) in acetonitrile.  $\text{Ph}_2\text{CH}-\text{PPh}_3^+$  is a common precursor for the generation of  $\text{Ph}_2\text{CH}^+$  cations which was experimentally demonstrated by ultrafast broadband transient absorption measurements [1]. Electrostatic effects play no role for the product formation as each of the two possible product channels include one charged and one neutral fragment and their relative energy gap remains unchanged [2]. Therefore  $\text{Ph}_2\text{CH}-\text{PPh}_3^+$  is perfectly suited to test our new method for the dynamic solvent effect combining quantum dynamics on ab initio potential energy surfaces (PES) for the solute with classical molecular dynamics (MD) of solvent molecules.



**Fig. 1:** Molecular PES of a diphenylmethyltriphenylphosphonium ion ( $\text{Ph}_2\text{CH}-\text{PPh}_3^+$ ) calculated at the ONIOM level of theory (CASSCF / M06-2X / 6-31g(d)) for the two reactive coordinates  $r$  and  $\phi$  (1<sup>st</sup> panel). Visualization of the two reactive coordinates in  $\text{Ph}_2\text{CH}-\text{PPh}_3^+$  (2<sup>nd</sup> panel).  $r$  denotes the distance between the C and the P atom;  $\phi$  the angle between P, C and the dummy atom X. The thicker atoms are part of the high-level system of the ONIOM calculations; the thinner ones belong to the low-level system. Two exemplary total PES used for the quantum dynamics (3<sup>rd</sup> and 4<sup>th</sup> panel). The crucial influence of the solvent cage is in the area where  $r$  is larger than 3.5 Å. The solvent hinders the free dissociation along the  $r$  coordinate and guides the wave packet toward the conical intersection (CoIn). The Franck-Condon (FC) point lies around  $r = 1.87$  Å and  $\phi = 125^\circ$ , the CoIn where the experimentally observed  $\text{Ph}_2\text{CH}^+$  cations are formed is located at  $r = 2.9$  Å and  $\phi = 75^\circ$ .

After a  $\pi-\pi^*$  excitation of  $\text{Ph}_2\text{CH}-\text{PPh}_3^+$  induced by an ultrashort UV laser pulse (275 nm, 35 fs FWHM), the system crosses a small barrier in the excited state  $S_1$  [2]. Subsequently the leaving group  $\text{PPh}_3$  is separated by C-P bond cleavage. Previous quantum dynamical simulations that included the dynamic solvent effect in an implicit formalism demonstrated its importance [3]. The solvent controls the reaction outcome. It guides the system through

a conical intersection (CoIn), non accessible in the gas phase, to form the experimentally observed  $\text{Ph}_2\text{CH}^+$  cations. Our new approach goes beyond the implicit solvent model, it includes the environment explicitly.

### 3. Solvent potential extracted from classical molecular dynamics simulations

The number of accessible arrangements of the solvent molecules surrounding a solute is very large. To average statistically over all possible solvent orientations, we perform classical MD simulations of the solute in a box of solvent molecules. Snapshots are taken at every 10 fs and the interaction in each solute-solvent arrangement is taken individually into account in form of a potential energy term  $E_{\text{solv}}(r, \phi)$ , which depends on the chosen internal reactive coordinates  $r$ , the C-P distance and the P-C-X angle  $\phi$  (see Fig. 1, 2<sup>nd</sup> panel). This potential energy term consists of all contributions  $E_{sf}(d_{sf}(r, \phi))$  between every solvent molecule  $s$  and the solute splitted into the fragments  $f$  of the leaving group  $\text{PPh}_3$  and the  $\text{Ph}_2\text{CH}$  group.  $E_{sf}$  depends explicitly on the  $s$ - $f$  distance  $d_{sf}(r, \phi)$ , which in turn is evaluated along the two-dimensional surface spanned by the reaction coordinates  $r$  and  $\phi$ . Thus  $E_{\text{solv}}(r, \phi)$  is given as:

$$E_{\text{solv}}(r, \phi) = \sum_{s=1}^{N_{\text{solv}}} \sum_{f=1}^2 E_{sf}(d_{sf}(r, \phi)). \quad (1)$$

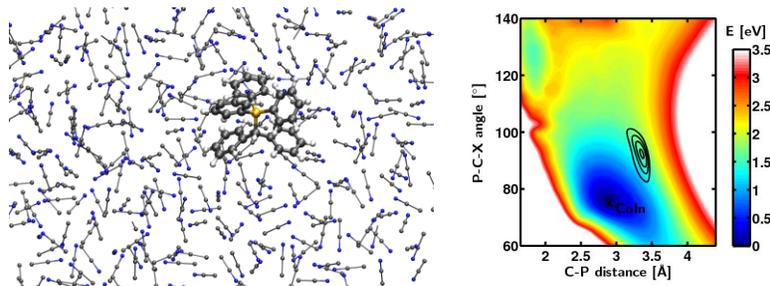
The total PES  $E_{\text{tot}}(r, \phi)$ , used for the quantum dynamics, is the sum of  $E_{\text{solv}}(r, \phi)$  and the molecular PES  $E_{\text{mol}}^{\text{ONIOM}}(r, \phi)$  (Fig. 1, 1<sup>st</sup> panel) calculated at the ONIOM level of theory (CASSCF(10,10) / M06-2X / 6-31g(d)).

$$E_{\text{tot}}(r, \phi) = E_{\text{mol}}^{\text{ONIOM}}(r, \phi) + E_{\text{solv}}(r, \phi) \quad (2)$$

Fig. 1 (3<sup>rd</sup> and 4<sup>th</sup> panel) shows the total PES for two exemplary snapshots of a MD trajectory. The individual solvent configurations show up in the different height and shape of the potential barrier beyond C-P distances of 3.5 Å. The CoIn connecting the competing reaction channels of the higher lying radicals  $\text{Ph}_2\text{CH}^\bullet$  and the lower lying experimentally observed  $\text{Ph}_2\text{CH}^+$  cations is located at  $r = 2.9$  Å and  $\phi = 75^\circ$ .

### 4. Quantum dynamics in the combined potential of the molecule and its surrounding

Fig. 2 shows a dissociating wave packet in a selected total PES (right) about 170 fs after crossing the barrier close to the FC region together with its explicit solvent arrangement (left). Obviously the dissociation of the wave packet along the  $r$  coordinate is hindered by the solvent cage and the wave packet is reflected toward the CoIn.



**Fig. 2:** Explicit solvent arrangement of an exemplary snapshot of the MD trajectory (left) and the dissociating wave packet (black isolines) in the corresponding total PES (right). The dissociation along the  $r$  coordinate is hindered by the potential barrier around  $r \approx 3.5 - 4.0$  Å and the wave packet is guided toward the CoIn next to the global minimum.

This new ansatz reproduces the experimental findings and the results obtained with the implicit solvent formalism. Furthermore it takes into account the explicit arrangements of a given solvent and its effect on the PES, allows for the description of solvent mixtures and opens a way to include the feedback of the decelerated wave packet on solvent cage.

### 5. References

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