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Electric field control of proton-transfer molecular switching: molecular dynamics study on salicylidene aniline

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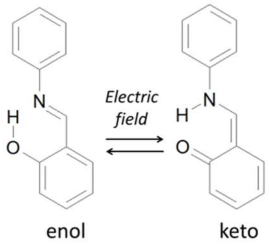
In this letter we propose a novel, ultrafast, efficient molecular switch whose switching mechanism involves electric field-driven intramolecular proton transfer. By means of *ab initio* quantum chemical calculations and on-the-fly dynamics simulations we examine the switching performance of an isolated salicylidene aniline molecule and analyze perspectives of its possible use as an electric filed-controlled molecular electronics unit.

Understanding and controlling conformational changes of single molecules is currently one of the fundamental goals leading towards electronic device miniaturization. In this context bistable molecular systems attract much attention due to their possible applications as molecular memories, switches, and data processing maerials.[1-4] The two forms of a switching molecule may differ by numerous attributes such as *cis-trans* conformation, chirality, open-closed ring structure or tautomeric hydrogen atom position. The reversible transformation between them is most often triggered by an external electromagnetic irradiation or electric current transmission, but may also be controlled by electric field, short-range forces or temperature.[5-9] Among molecular switches operated by light, systems whose transformation mechanism involves excited state intramolecular proton transfer (ESIPT)[10-12] are receiving increasing interest due to expected ultrafast performance (femtosecond domain of the proton transfer process)[13-16] and predicted favorable electronic properties (substantial difference in electric current conductance between the switching forms)[17-20]. On the other hand, among the controlling stimuli, the external electric field seems to be especially promising as easy-operable (e.g. through the STM setup) and harmless for the molecular switching units.[21]

In this letter, we investigate in detail the mechanism and dynamics of a novel molecular switch combining advantageous features of the ESIPT systems with the possibility of electric field switching control in the ground electronic state. First study suggesting such a way of triggering the proton position isomerization was performed in the late 1990s by J. Manz *et al*.[22] The authors applied quantum control theory to optimize IR laser pulse to induce proton transfer (PT) in malonaldehyde-like systems. As a result, they obtained a static electric filed pulse enhancing coupling and, thus, also proton tunneling between ground vibronic states of the investigated isomeric structures. However, the mechanism of field-induced PT may also base on a barrierless transfer of a proton on a field-modified PES. First system of this type has been recently proposed by one of us.[23] Here, by means of *ab initio* quantum chemical calculations and on-the-fly dynamics simulations, we examine electric field-driven intramolecular proton transfer in a model system of salicylidene aniline (SA). The SA molecule representing aromatic Schiff bases family is known for its ESIPT-induced photochromism and its photophysical and possible photoswitching properties have been thoroughly studied, both theoretically and experimentaly,[24-30] This, together with recent current transduction investigations,[18] constituted a good groundwork for more advanced molecular electronics studies.



Scheme 1. Chemical structure of the two SA switching forms under investigation.

In the lack of external fields, the SA global minimum structure is the enol form (see Scheme 1) with the hydrogen atom attached to oxygen. Under these conditions the keto form corresponds to a local minimum situated 0.21 eV over the enol on the ground electronic state potential energy surface with a tiny keto-to-enol transformation energy barrier of 0.04 eV. Inclusion of the zero-point energy correction removes the barrier and makes the keto form unstable (situated ca. 0.20 eV over the enol form). The minimum-energy profile for the PT between the enol and keto forms of SA in the absence of the electric field is presented in Fig. 1. (full black circles).

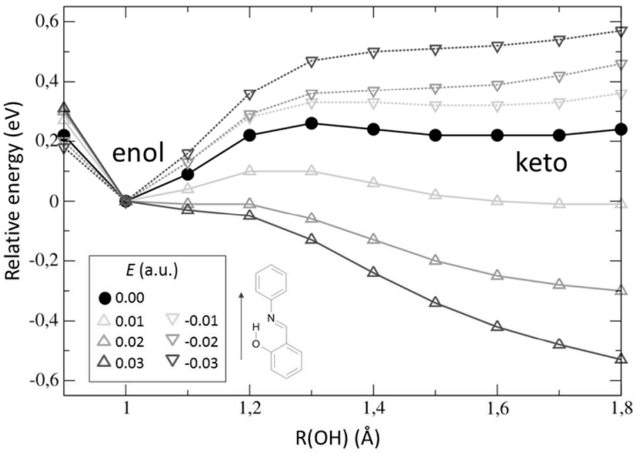


Figure 1. Proton transfer minimum-energy profiles calculated for PT reaction in SA at various electric field values.

To investigate the possibility of stabilizing the keto form, we applied a static electric field (*E*) along the main molecule axis in the direction favouring the PT from enol to keto (positive *E* values, up-triangles with solid line in Fig. 1.). Upon inspection of the figure, one observes a clear stabilization of the keto form, even for the weakest applied field (*E* = 0.01 a.u.) when the enol and keto become approximately isoenergetic. For higher field strengths, the keto form becomes more stable and the enol-to-keto transformation does not show any noticeable energy barrier anymore. Results for the inversely oriented electric field (negative *E* values, down-triangles with dotted line in Fig. 1.), favouring the keto-to-enol transformation, show gradual increase of the keto relative energy. The shape of the curves suggests also its barrierless transition to the enol form (starting from *E* = -0.02 a.u.).

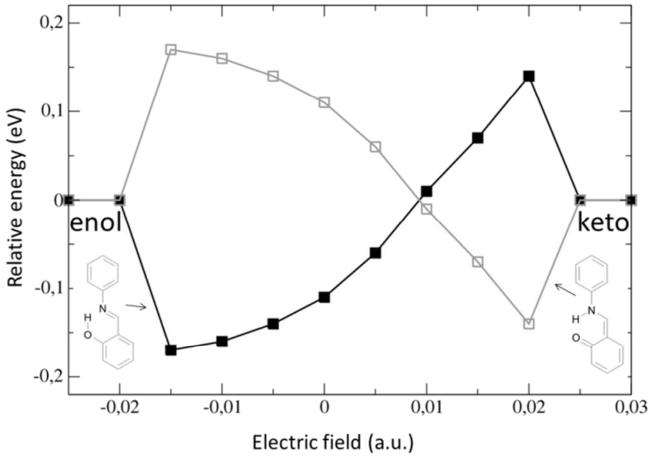


Figure 2. Static electric field hysteresis curve calculated for field-induced PT reaction in SA (full black squares – enol branch; empty grey squares – keto branch).

The already formulated findings may be further deepen by the analysis of calculated static electric field hysteresis presented in Fig. 2. Structural optimizations of the enol and keto forms for various electric field values show three regions of the SA stability. For field intensities lower than -0.015 a.u. the only stable form is the enol isomer (the keto-to-enol transformation is barrierless and exoergic). For fields between -0.015 and 0.02 a.u. the SA system shows bistability and, for field variation within this range, maintains its enol/keto character. For field intensities higher than 0.02 a.u., one finds the keto as the only stable structure (barrierless, exoergic enol-to-keto transformation is observed). This characteristics illustrates the system's potential performance as a molecular memory device. However, one should keep in mind that the static quantum chemical approach used for hysteresis curve calculation does not account for kinetic effects such as zero-point energy correction or higher temperature vibrations which may play an important role, especially in systems exhibiting only small energy barrier between the switching forms.

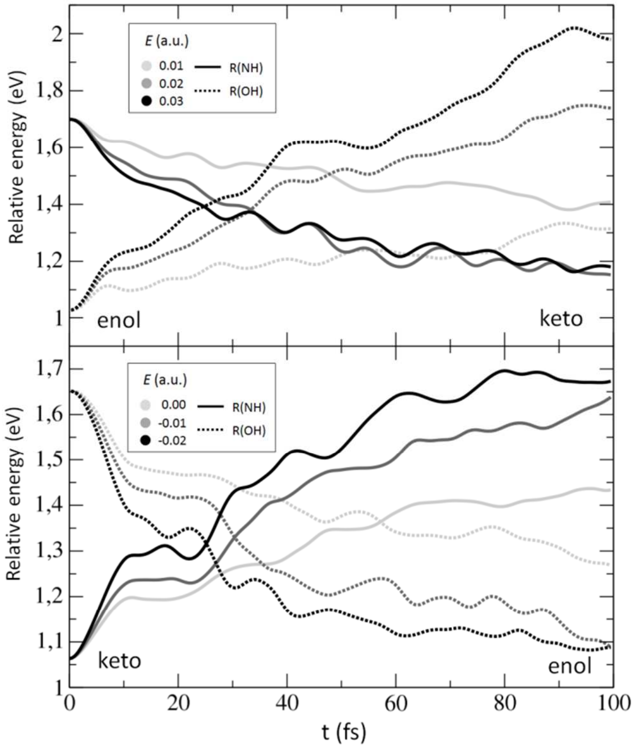


Figure 3. Mean R(NH) and R(OH) distances for enol (upper panel) and keto (lower panel) dynamics for chosen external electric field values.

To learn about the dynamic characteristics of the investigated phenomenon and to supplement the discussed above 'static' observations by the kinetic effects, we performed a set of the on-the-fly adiabatic dynamics simulations investigating the time evolution of isolated SA molecule exposed to external electric field. Each simulation consisted of 50 independent 100 fs long trajectories in the ground electronic state. Within the applied approach, the electron density and properties are calculated with use of quantum *ab initio* methods, however the nuclei are treated classically. Such way of addressing the molecular adiabatic dynamics does not allow for inclusion of the quantum effects such as nuclei tunnelling, still, in the performed study, due to barrierless or quasi-barrierless character of investigated transformations, these effects are not expected to play an important role on the timescale of the investigated phenomenon. Fig. 3. illustrates time evolution of the both switching forms: enol – upper panel and keto – lower panel, respectively. The two sets of lines show mean R(NH) and R(OH) distances plotted against simulation time for chosen electric field values. One may see that in the enol dynamics the R(NH) distance decreases and the R(OH) distance increases with time for all investigated cases, which is a sign of the occurring PT process. The rate of this process depends on the electric field intensity. Characteristic PT timescale (t_{PT}), defined as the time for which mean R(NH) and R(OH) distances become even, equals ca. 25 and 35 fs respectively for $E = 0.03$ and 0.02 a.u.. For $E = 0.01$ a.u. the PT time may be assumed as longer than 100 fs, however one may also expect that the enol and keto forms exist in an equilibrium in this case. Analogous simulations performed for the keto form also reveal ultrafast PT for all investigated electric field intensities. For the no-field case the keto-to-enol switching occurs within ca. 55 fs. For $E = -0.01$ and -0.02 the transformation happens within 30 and 25 fs, respectively.

If one relates these findings to the results of the static hysteresis curve analysis, it becomes clear that the possibility of SA application as a molecular memory unit is limited due to too low energy barrier separating the enol and keto forms. Namely, the system's bistability region vs. the *E*-field strength, although predicted to be as wide as 0.035 a.u. (from -0.015 to 0.02 a.u.) within the static picture, shows to be restraint by the dynamics results to 0.01 a.u. at most (from 0.00 to 0.01, when the keto-to-enol and enol-to-keto transformations are observed).

Finally, on the basis of the dynamics study, one may learn about the switching efficiency expected for the field-operated PT in the SA system. Having a direct look on the trajectories calculated in dynamic simulations, we found that for low electric field values ($E = 0.01$ a.u. for enol and $E = 0.00$ a.u. for keto, respectively) the inter-isomer transformation efficiency stays close to 40%, suggesting rather an even equilibrium than a true switching process. In contrast, for higher applied field values (starting from 0.02 a.u. for enol and -0.01 a.u. for keto), the switching efficiency in both directions rises significantly reaching ca. 90% which makes the electric field-controlled SA molecule unprecedentedly robust comparing to already known switching systems.[31-38]

Combining results of the static and dynamic studies on the switching properties of the SA molecule exposed to an external electric field, we formulate the following conclusions:

(i) In the no-field case the isolated SA molecule is stable in its enol form. Under such conditions the keto isomer, if formed, transforms spontaneously to enol form on the femtosecond timescale.
(ii) One may control the relative energy of the enol and keto isomers by applying the electric field along the main molecule axis.
(iii) For sufficiently strong electric fields, the enol-to-keto transformation through the electric field induced PT is observed. The back transformation may be triggered either by switching off the field or applying the field oriented in the opposite direction.
(iv) The rate of the switching process depends on the applied electric field intensity and the PT is expected to occur within the few tens femtoseconds for the field-induced transformations.
(v) The static electric field hysteresis study combined with the dynamics simulations results shows that the model SA system, despite being a promising candidate for the electric field-driven switch, is not expected at this stage to perform well as a stable molecular memory device due to low energy barrier between the switching forms. However, to predict exact SA memory characteristics, a separate, more detailed study should be performed.
(vi) The efficiency of the electric field-controlled switching of the SA system is predicted to be exceptionally high in both directions (close to 90%).

The proposed electric field-operated PT molecular switch, by its predicted properties, may be qualified as a new type of ultrafast molecular transistor. The experimental verification of its switching performance might be probably most easily carried out with use of the STM setup, in analogy to successful experiment with azobenzene-based compound reported in Ref. 21. Although, the standard frequency of the STM electric field operation stays nowadays at the range of GHz (corresponding to ps timescale), some promising materials and setups allowing for THz (fs timescale) electric field generation are currently an object of intense study (c.f. for instance Ref. 39 reporting on one of the successful realizations of such a setup). The calculated electric field values necessary to control the PT may seem high (0.01 a.u. corresponds to ~5.66 V for this system) but, as was also discussed in Ref. 21, these values, predicted for molecules in the gas phase, become significantly lower in experiment involving systems adsorbed on a metal surface (in the reported case, the required field intensities decreased at least by a factor of 3). With respect to predicted conducting properties, in the SA case the enol/keto current ratio is expected to reach even ~70,[18] depending on the electrode and electric contacts choice which, together with the expected high efficiency of the switching process, places this system among very promising units for molecular electronics applications.

Methods

All electronic structure calculations presented in this paper have been performed at the DFT level of theory with use of the B3LYP hybrid correlation-exchange functional together with a cc-pVDZ correlation consistent basis set as implemented in TURBOMOLE.[40]

The PT-profiles presented in Fig. 1. show relative energies of the SA structures optimized with fixed R(OH) distance for various electric field values. The reference energy for each profile is set to the corresponding energy of the R(OH) = 1.0 Å form in the same electric field.

For each point of the hysteresis curve presented in Fig. 2., the reference energy is set to the mean of the enol and keto energies at the particular electric field value. The enol (keto) branch corresponds to energy of a structure optimized starting from the enol (keto) form optimized in the no-electric field conditions.

The dynamics simulations have been carried using Newton X[41,42] program package. The time step for nuclear motion was set to 0.5 fs. The initial geometry and velocity conditions were generated by Wigner sampling.

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Notes and references

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