Supporting Information: Driving and Controlling Molecular Surface Rotors with a Terahertz Electric Field

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System Preparation

An energy minimization of the system is simulated using steepest descent with a maximum step size of $0.01nm$. A cut-off radius of $1.1nm$ is used for Coulomb interactions and $1.0nm$ for van-der-Waals interactions. This energy minimized structure is used as starting structure for field free simulations.

All simulations are done at 300K. For all further simulations electrostatics are calculated with Fast Particle-Mesh Ewald electrostatics (PME)[1] with an order of four and a cutoff for coulomb and van-der-Waals interactions of $1.0nm$. Temperature coupling is done by a velocity rescaling thermostat[2] coupled to the whole system.

Angle Definition

The rotation angle α is calculated using the vector v connecting the two inner C_α atoms by $\alpha = \arctan(\frac{v_x}{v_y}) - \text{sign}(v_y) * 90° + n_{cyc} \times 360°$ with n_{cyc} being the number of full rotations.

Relative Energies

The free energies are calculated from the population of the angles α by $\delta E(\alpha) = -k_B T \times ln(\frac{N(\alpha)}{N_{\min}}) - \min(E(\alpha))$, with the rotation angle α (from 0° to 120°), the number of timesteps N(α) in which the angle is populated and the minimum population count of all angles $N_{\min}$.

Initial Structures for free rotation

For further simulations including an electric field, a set of 10 structures have been chosen from the final structures of the free rotation simulations with 200ns simulation each, alltogether representing a sample of different rotation angles α to increase sampling especially at high fields. A new starting velocity distribution is generated for each new simulation.

Initial Structures for restrained simulations

For the restrained simulations, the structures of a 200ns long undisturbed rotation trajectory are clustered. The six prominent clusters (every 60°) of each trans conformation are chosen as initial structures. In addition two prominent clusters for each cis state are simulated.

Restrained simulations

The dihedral angle restraints allows a free development of the system in a range of ±20° around the energy minimum of the dihedral angle distributions. Thus, the rotor could freely explore its energy landscape in the restraint conformation preventing switching to unwanted conformations.

External Electric Field

An external electric field is applied perpendicular to the gold surface in z-direction. The electrical field is positive if it points from the rotor to the surface (Fig. 1B). The electric field strength ranges from -9 to +9 V/nm. The simulation time is 2ns per trajectory. In the highest field regimes the partial charge distribution of the molecular rotor might be subject to additional polarization effects, not taken into account by the DFT derived partial charge distribution.

External Oscillating Electric Field

We apply an oscillating field $E(t) = E_0 \times \cos(\omega t) \times \hat{e_z}$ perpendicular to the gold surface with $\hat{e_z}$ pointing from the rotor to the gold surface. The strength of the oscillating field E_0 ranges from 0.75 to 9 $\frac{V}{nm}$, while the oscillation frequency of the electric field ω ranges from 1.5 to 7.5 THz. Lower oscillation frequencies interpolated the behavior of the rotor between zero field and 1.5 THz driving, showing no additional features. Higher frequencies strongly arrest the rotor on the surface and no further rotation is observed.

References and Notes

[1] Ewald, P.P., Die Berechnung Optischer und Elektrostatischer Gitterpotentiale, *Annalen der Physik*, **1921**, *369*, 253-287 .

[2] Bussi, G., Donadio, D., Parrinello, M., Canonical sampling through velocity rescaling, *J. Chem. Phys.*, **2007** *126*, 1–44 .