Laser Field Alignment of Organic Molecules on Semiconductor Surfaces: Toward Ultrafast Molecular Switches

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An ultrafast, nanoscale molecular switch is proposed, based on extension of the concept of nonadiabatic alignment to surface-adsorbed molecules. The switch consists of a conjugated organic molecule adsorbed onto a semiconducting surface and placed near a scanning tunneling microscope tip. A low-frequency, polarized laser field is used to switch the system by orienting the molecule with the field polarization axis, enabling conductance through the junction. Enhancement and spatial localization of the incident field by the metallic tip allow operation at low intensities. The principles of nonadiabatic alignment lead to switch on and off time scales far below rotational time scales.

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Considerable progress has been achieved in the localization of light to the nanoscale with the recent revival of interest in plasmonics [1,2]. In particular, a variety of imaginative approaches to combine laser spectroscopies with the scanning tunneling microscope (STM) have been demonstrated [3]. To date, however, the exciting goal of applying the tools and concepts of coherent control to manipulate current in the nanoscale has not been realized. The synergism of the fields of coherent control and molecular electronics to coherently manipulate electric current in the nanoscale is interesting not only for the new fundamental questions introduced [4], but also for a growing class of potential applications in logic, computation and sensing. Although schemes to that end have been developed [5], competing phenomena have prevented their laboratory realization. One is substrate-mediated excitation. Light applied to a molecule in contact with a metal electrode (or adsorbed onto a metal surface) is rarely absorbed by a molecular bond or by the molecule-surface bond. Rather, it is absorbed by the substrate, generating hot carriers that attach to the molecule, creating an excited or ionic transient. Interesting chemistry often ensues, but coherence is lost [6]. A second phenomenon of concern is heating of the tip, as is often found in studies that combine light with a STM [7] to cause thermal processes.

Here we propose and numerically illustrate the application of nonadiabatic alignment to coherently control electric current in single-molecule junctions. Specifically, we suggest an ultrafast, nanoscale switch for electrons. Substrate-mediated excitation and thermal processes are circumvented, and the switching time scale is determined by the driving laser properties. The critical role of molecular-scale switches as the basic elements in integrated electronic circuits has been often discussed in the past [8–10]. Our message, however, is more general. We point to the importance of strong-field effects in the emerging field of molecular nanoplasmonics and to opportunities for coherent and strong-field control in molecular-scale electronics.

Nonadiabatic alignment [11,12] is a rapidly progressing approach for controlling the spatial properties of neutral molecules, based on the interaction of the (permanent, transition, or induced) electric dipole with a short [13], moderately intense laser pulse. The short pulse gives rise to a broad superposition of angular momentum states whose relative phase relations guarantee alignment of the molecular axis with the polarization vector of the laser electric field. Although most studies of nonadiabatic alignment to date have considered isolated, linear, and rigid molecules, extensions to solvated molecules, to asymmetric tops, and to molecules undergoing torsion have been recently reported. One of the main advantages of nonadiabatic laser alignment is the availability of field-free aligned molecules after turn-off of the laser pulse. In the isolated molecule limit, the coherent rotational wave packet aligns at a controllable time after the pulse peak and subsequently exhibits a coherent revival pattern; in the case of linear or symmetric tops, the initial alignment is precisely reconstructed at multiples of the rotational period. In dissipative media, as the one of relevance here, undamped revivals are generally not expected, but field-free alignment is exhibited and multiple pulses may be applied to regenerate it. In what follows, we extend the alignment concept to the case of a surface-adsorbed molecule, and combine it with the sharp enhancement of an external field by a metallic tip and with the junction problem to devise an ultrafast, nanoscale electric switch controlled by the coherence properties of a laser field.

The setup envisioned is depicted schematically in Fig. 1(a). At the simplest level, we consider a linear, conjugated organic molecule adsorbed onto a doped silicon surface, but variations that apply nonlinear molecules are noted in closing. At its field-free equilibrium configuration [dashed line in Fig. 1(a)], the molecule rests at a system-dependent nonzero angle θ_{eq} with respect to the surface normal. The considered laser pulses are linearly polarized parallel to the tip axis and tuned to a low frequency, below the substrate band gap (ca. 1 eV for silicon). Applied to the

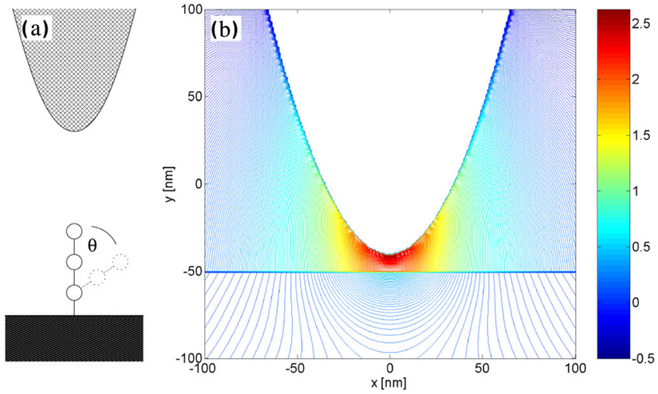

FIG. 1 (color online). (a) Schematic illustration of the envisioned, coherently controlled switch. The dashed and solid lines show the equilibrium and oriented configurations, respectively, and θ is the polar angle between the field and molecular axis. (b) Steady-state intensity enhancement distribution (normalized to the incident intensity, logarithmic scale) in a plane bisecting the tip. (The silicon surface is placed at $y = -50$ nm).

junction, the field is plasmon-enhanced and strongly localized below the tip axis, while its linear polarization is conserved under the tip apex.

At the nonresonant frequencies considered, the tip-enhanced field interacts predominantly with the molecular polarizability tensor (as modified by the surface); hence, the field-matter interaction Hamiltonian is of the form [12], $V_{\mathrm{ind}}(\theta, t) = -\vec{\varepsilon}(t) \cdot \boldsymbol{\alpha}(\theta)\vec{\varepsilon}(t)/4$, where $\boldsymbol{\alpha}$ is the space-fixed polarizability tensor, $\vec{\boldsymbol{\epsilon}}(t) = \vec{\varepsilon}(t)\exp(-i\omega t) + \mathrm{c.c.}$ is the plasmon-enhanced electric field vector, $\vec{\varepsilon}(t) = \hat{\varepsilon}\varepsilon(t)$, $\hat{\varepsilon}$ is a unit vector along the field polarization axis, and $\varepsilon(t)$ is the pulse envelope function. The complete molecular Hamiltonian is then $H(\theta, t) = T + V_{\mathrm{ads}}(\theta) + V_{\mathrm{ind}}(\theta, t)$, where T is the kinetic energy and $V_{\mathrm{ads}}(\theta)$ is the field-free adsorption potential. Provided that the laser-induced potential well depth, $V_{\mathrm{ind}}(\theta \sim 0)$, exceeds the field-free barrier, $V_{\mathrm{ads}}(\theta \sim 0)$, the molecule responds to the pulse by rapidly switching into the oriented configuration. Given that tunneling through a vacuum falls exponentially with distance, the junction switches upon laser illumination from an "off" (unoriented) state, in which the conductance essentially vanishes, to an "on" (oriented) state, in which current flows. The tunneling current through a vacuum barrier increases by roughly an order of magnitude for each Å decrease in the tunneling distance in typical STM configurations; hence, an on/off ratio of orders of magnitude is expected. Nonadiabatic laser alignment (orientation) takes place on time scales well below the system time scales (*vide infra*), largely determined by the field intensity [11,12]; hence, rapid operation is an inherent property. These qualitative considerations are substantiated numerically below.

As a concrete example of an effect we expect to be general, we consider a hydrogen-terminated, fourteen carbon oligoyne (with formally alternating single- and triple-bonds) molecule that is adsorbed to a silicon surface via an oxygen atom. Such a molecule has been proposed as a one-dimensional wire [14] and also exhibits sufficiently generic features to make the model basic and representative of a large class of molecules. In what follows, we focus on the dominating dependence of the adsorption potential on the polar angle θ [Fig. 1(a)], neglecting its weak dependence on the azimuthal angle (corresponding to rotation in the surface plane).

To compute the field-free (V_{ads}) and field-induced (V_{ind}) interaction potentials *ab initio*, we constructed a cluster of 14 silicon atoms to model a hydrogen-passivated Si(001)-(2×1) surface [15]. The molecule was attached to the cluster and a potential energy curve was computed vs θ using density functional theory (B3LYP/6-31G). The molecular polarizability tensor for each geometry was calculated in space-fixed coordinates using coupled-perturbed Hartree-Fock theory (6-31G**).

To account for the enhancement and spatial localization of the incident field by a gold STM tip, we employed a three-dimensional finite-difference time-domain (FDTD) approach for the numerical integration of Maxwell's equations on a grid [16]. Since the optical frequencies of interest are below the silicon band gap ($\lambda \gtrsim 1\ \mu$m), we implemented quasistatic simulations of the electromagnetic fields in the vicinity of a STM tip; i.e., a silicon slab with dimensions of 155 $\mathrm{nm}^2 \times 1.81\ \mu$m and a gold STM tip of a circular paraboloid shape (apex radius $\sim$25 nm) were placed in a time-independent external field polarized along the STM tip axis. The subsequent FDTD iterations converged to steady-state electromagnetic field distributions, which are equivalent to off-resonant cw laser pulse excitations. Figure 1(b) illustrates the steady-state intensity distribution, showing enhancements higher than 2 orders of magnitude near the tip apex.

At a surface-tip distance of 10 nm, the tip-induced field enhancement at the molecule is a factor of 12 and the field is spatially homogeneous on the molecular scale [much larger enhancements are expected at plasmon resonance frequencies, but for our present application nonresonant (sub-band gap) frequencies are advantageous and the tip enhancement has a reduced role]. Figure 2 shows the complete potential vs cosθ and the laser intensity. The insets of Fig. 3 illustrate the molecule-surface model in its equilibrium and oriented geometries. Lastly, the ratio of transmission probabilities through the vacuum barrier between the molecule and the tip in the oriented and equilibrium configurations is $\sim 4 \times 10^4$ (such a large ratio is expected, since the width of the vacuum barrier increases by 3 Å from the oriented configuration to the equilibrium configuration). This ensures a large on/off ratio (*vide infra*).

With the Hamiltonian defined, we proceed to examine the intensity dependence of the molecular orientation, and, to that end, first consider the case of a long pulse [13] that adiabatically switches the molecule into and out of orien-

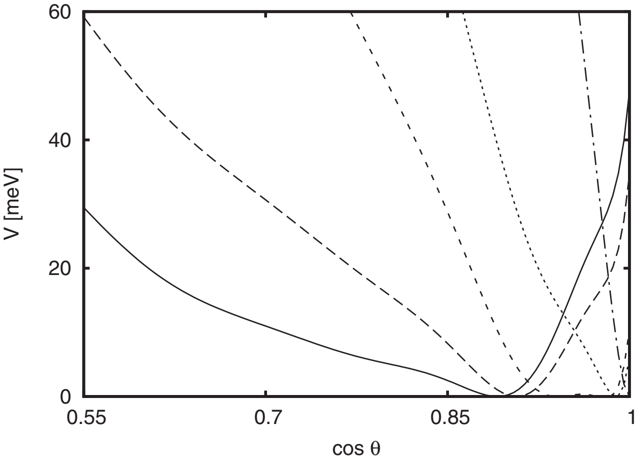

FIG. 2. The complete potential $V_{\mathrm{ads}} + V_{\mathrm{ind}}$ vs $\cos\theta$ and the laser intensity. Solid line: field-free; Long dashed line: $I \approx 2.3 \times 10^9\ \mathrm{W\,cm^{-2}}$; Short dashed line: $I \approx 7.7 \times 10^9\ \mathrm{W\,cm^{-2}}$; Dotted line: $I \approx 1.3 \times 10^{10}\ \mathrm{W\,cm^{-2}}$; Dash-dotted line: $I \approx 3.6 \times 10^{10}\ \mathrm{W\,cm^{-2}}$.

tation. The degree of orientation is quantified in Fig. 3 via the expectation value of $\cos\theta$, where $\langle\cos\theta\rangle = 1$ corresponds to perfect orientation of the molecular axis with the polarization and tip axes. With an orientation parameter $\langle\cos\theta\rangle = 0.95$ (corresponding to $\langle\theta\rangle \approx 18°$), the tunneling current falls to 1% of its value at the oriented configuration (that is, to an on/off ratio of 100). Below we take this orientation to define the switch turn-on.

As the intensity increases, the molecular equilibrium configuration migrates to smaller values of θ and the molecule gradually orients in parallel to the field polarization vector, reaching nearly perfect orientation at the maximum intensity. Temperature has only a minor effect throughout the range of relevance to low-temperature STM experiments (see, e.g., [17,18]), in contrast to the gas-phase counterpart. This result is expected, since gas-phase alignment is determined by the competition of the field-induced potential and the thermal energy, whereas on the surface it is determined by the competition of the field-free and field-induced potentials. The rapid increase of the orientation with the intensity about $I \sim 7.7 \times 10^9\ \mathrm{W\,cm^{-2}}$ corresponds to the intensity range where the laser-induced potential nears and exceeds the field-free barrier at $\theta \sim 0$; see Fig. 2.

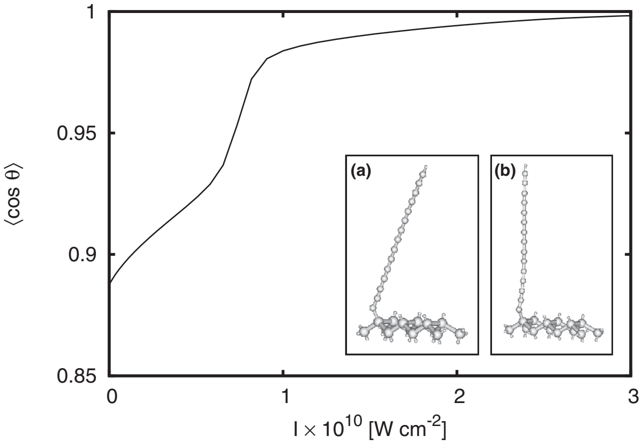

FIG. 3. Averaged orientation vs incident intensity for adiabatic excitation at 10 K. The insets show the molecular system in the (a) equilibrium, $\theta \sim 27°$ or $\cos\theta \sim 0.89$, and (b) oriented, $\theta \sim 0°$, configurations.

Having established the possibility of sharply orienting the surface-adsorbed molecule at moderate laser intensities, we proceed to investigate the quality and time-scale of nonadiabatic alignment. The latter problem is of interest from a fundamental perspective, as the extension of alignment by intense laser pulses from the domain of isolated diatomic molecules to complex systems is at an early stage. In the device context, the rate at which the molecule can switch between the oriented and unoriented configurations is important, as this determines the time scale of the current switch.

Figure 4 displays $\langle\cos\theta\rangle$ and ε as functions of time under nonadiabatic conditions. In Fig. 4(a) the peak intensity is $I \approx 3.6 \times 10^{10}\ \mathrm{W\,cm^{-2}}$ and the fluence varies with the pulse duration, whereas in Fig. 4(b) the intensity is increased in inverse proportion to the pulse duration, maintaining constant fluence. The orientation in Fig. 4 exhibits several of the general features of nonadiabatic alignment (orientation) by short [13] pulses. Notably, it rises from its field-free value near 0.89 after the pulse turns off, and reaches a maximum in the field-free domain, with the delay between the pulse and orientation peaks increasing with

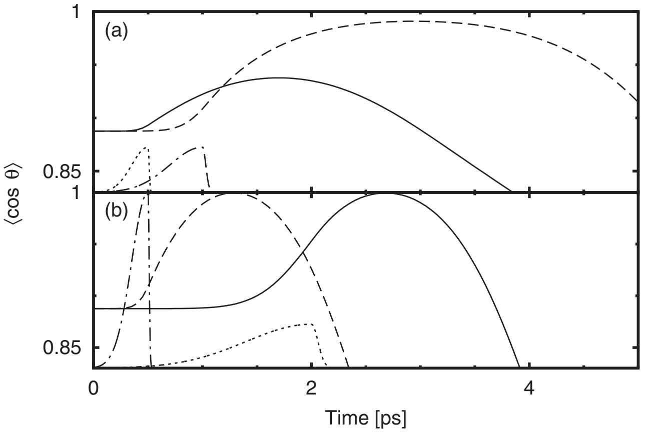

FIG. 4. Averaged orientation in the nonadiabatic domain: $\langle\cos\theta\rangle$ (solid and long-dashed curves) vs intensity and pulse duration at 10 K. The incident laser pulse, $\varepsilon(t)$, is shown as dotted and dot-dashed curves, normalized to $I_0 = 1.4 \times 10^{11}\ \mathrm{W\,cm^{-2}}$. (a) Constant intensity: solid and dotted lines $I = I_0/4$, $\tau = 0.5$ ps; long-dashed and dot-dashed lines $I = I_0/4$, $\tau = 1$ ps; (b) Constant fluence: solid and dotted lines $I = I_0/4$, $\tau = 2$ ps; long-dashed and dot-dashed lines $I = I_0$, $\tau = 0.5$ ps.

decreasing pulse duration. The degree of rotational excitation is determined by the fluence of the pulse and, in turn, largely determines the time scale of the orientation switch-off. Thus, both an increase of the intensity and an increase of the pulse duration (provided that the pulse remains short with respect to the system time scales [13]) have the effect of enhancing the rotational excitation and speeding up the switch. While the trends exhibited in Fig. 4 are general and well understood [11,12], in the junction context they translate into controllability of the switch and carry new implications. In particular, as seen in Fig. 4(b), the orientation turn-off time is ~0.6 ps and is independent of the temperature. It is exciting to note that methods of probing the effects predicted here in the laboratory have already been developed [19,20].

In summary, we proposed an ultrafast, molecular-scale switch that is coherently controlled by an optical pulse. To that end we extended the concept of nonadiabatic alignment to the case of a surface-adsorbed molecule, taking advantage of the enhancement and localization of external fields by metal tips to allow operation at low intensities. A variety of extensions to our approach can be envisioned. One is a biphenyl derivative that is switched into and out of the coplanar (conducting) from the twisted (nonconducting) configuration upon application of a circularly or an elliptically polarized pulse. Another is a molecular monolayer, where all molecules are uniformly switched into the oriented configuration upon illumination, establishing long-range orientational order. Depending on the function of the switch, a variant where the equilibrium corresponds to the oriented configuration and a laser field polarized in parallel to the surface serves to switch the current off can be envisioned.

Our study carries interesting implications to, and potential applications in, several fields. One is molecular nanoplasmonics—the combination of molecules with nanoparticles in hybrid constructs—where our results point to the importance of strong-field effects and hence to opportunities for the present and other strong-field control approaches. A second is the nonadiabatic alignment (orientation) problem, where we illustrate that several of the concepts established in gas-phase studies extend to surface-adsorbed molecules, thus opening a host of new applications. A third is the field of transport through molecular junctions, where we suggest a route to the application of coherence-based control and characterization approaches.

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