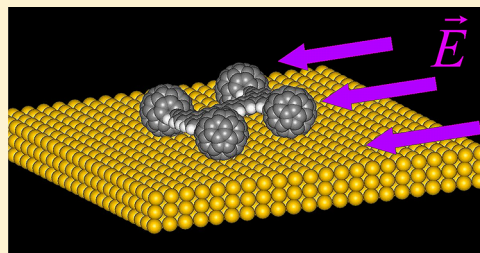


## Unidirectional Rolling Motion of Nanocars Induced by Electric Field

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## S Supporting Information

**ABSTRACT:** Understanding microscopic mechanisms of motion of artificial molecular machines is fundamentally important for scientific and technological progress. It is known that electric field might strongly influence structures and dynamic properties of molecules at the nanoscale level. Specifically, it is possible to induce conformational changes and the directional motion in many surface-bound molecules by electric field in scanning tunneling microscopy (STM) experiments. Utilizing a recently developed theoretical method to describe charge transfer phenomena for fullerenes near metal surfaces, in this work we theoretically investigated dynamics of fullerene-based nanocars in the presence of external electric field. Our approach is based on classical rigid-body molecular dynamics simulations that allow us to fully analyze dynamics of nanocars on gold surfaces. Theoretical calculations predict that it is possible to drive nonpolar nanocars unidirectionally with the help of external electric field. It is shown also that charge transfer effects play a critical role in driving nanocars and for understanding mechanisms of the directionality of the observed motion. Our theoretical predictions explain experimental observations on moving nanocars along metal surfaces.



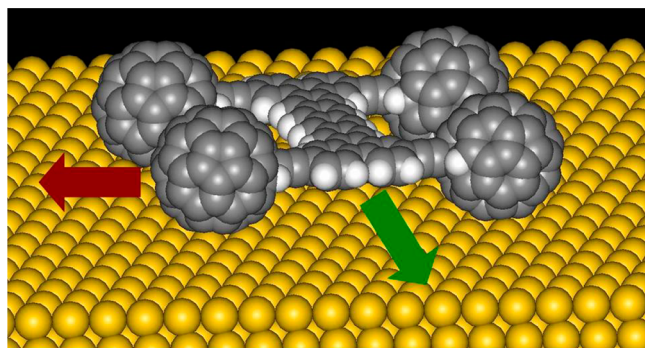
## 1. INTRODUCTION

Future technological progress strongly depends on development of nanosized devices and machines that can be effectively controlled by external means. Creation of artificial molecular machines, known as nanocars,<sup>1–8</sup> is a promising step in this direction. Such nanometer-scale objects morphologically resemble macroscopic automobiles. They are typically composed of the moderate size acene compounds, which act as the chassis of the nanocar and a few relatively spherical organic groups, such as fullerenes or carboranes, which mimic the wheels (Figure 1). One of the important properties of such systems is their ability to move in specific directions under certain conditions. For example, in the STM manipulation experiments<sup>5</sup> the nanocar showed significant translational

motion in one of orthogonal (in-plane) directions (forward direction, Figure 1), when the STM tip pushed the molecule in that direction. No significant motion of the nanocars was observed when the STM tip force was applied in the other orthogonal direction (side direction, Figure 1). It has been argued that such orientational preference of the nanocar mobility can be explained by the mechanism that involves rolling of the fullerene wheels.<sup>5,9,10</sup>

Although the rolling wheel mechanism seems to be reasonable in interpretation of experimental observations on nanocars, the microscopic details of these interactions between the nanomachines and the STM tip are not well understood yet. In particular, it is known that near the STM tip there is a significant local electric field, which can affect the probed molecules. For example, it has been shown earlier that electric field (including that of the STM tip) can induce conformational changes in adsorbed molecules,<sup>11–14</sup> modify their directional motion,<sup>5,15–25</sup> and lead to enhanced diffusion<sup>26</sup> and patterning.<sup>27</sup> In other studies, it has been shown that the electric field can also be used for effective pumping of water molecules at nanoscale.<sup>28–32</sup>

In order to be able to manipulate nanomachines at the microscopic level, the most promising route is to apply external forces. Various chemical energy sources have been proposed for driving the nanocars<sup>33</sup> and molecular motors.<sup>34–38</sup> In addition, it has been suggested that excitations by light or laser might also move artificial molecular motors<sup>3</sup> by promoting reversible conformational changes in molecules. However, the electric



**Figure 1.** Nanotruck molecule on the Au(111) surface. Orthogonal directions of motion are shown by arrows: forward direction, green arrow; side direction, red arrow.

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field probably still remains the most convenient and versatile method for controlling dynamics of nanomachines on surfaces. Thus, it is important to understand how the external electric field interacts with nanocars on metallic surfaces.

From classical electrostatics picture, a neutral molecule is only able to interact with the electric field if it possesses a nonzero dipole moment. For isolated single aromatic hydrocarbon molecules, such as lander<sup>13</sup> and nanotruck,<sup>5</sup> which have been manipulated with the STM tip, the dipole moment is vanishing. However, in the presence of the metal surface they acquire a significant dipole moment because of the charge transfer between the molecule and the substrate, and hence they might interact with the external electric field. For example, the authors of the work<sup>13</sup> explained the conformational changes observed for the lander molecule in the presence of the STM electric field by changes of the potential due to the presence of the electric field. Although such a description is qualitatively correct, the detailed quantitative picture is not yet available.

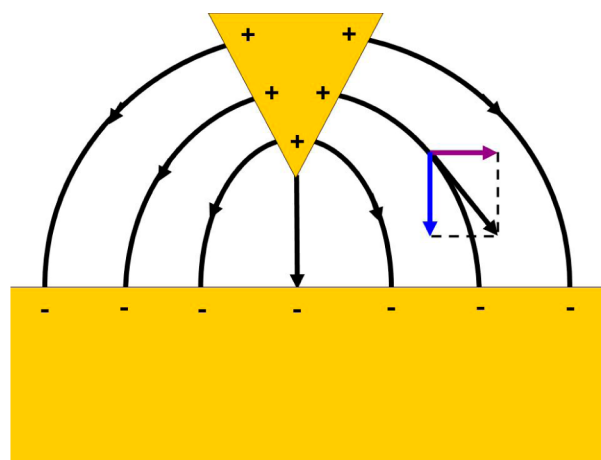
The high-level theoretical analysis of the change in the potential energy surface, induced by the external electric field, can be performed with the *ab initio* or density-functional theory (DFT) calculations. However, such approaches are very expensive for nanoscale systems and are prohibitive for direct dynamics simulations. Thus, the computationally cheaper molecular mechanics methods can be used successfully for studies of the dynamic processes in such systems, but only if they are able to describe properly the charge transfer and chemisorption effects that are important for interactions between molecules and external electric fields. Recently, we proposed a new theoretical method for taking into account the charge transfer processes on the interface between C<sub>60</sub>/nanocar molecules and gold metal.<sup>39</sup> The model predicts the dynamical charge redistribution on atoms in the C<sub>60</sub> wheels of the nanocar, which depends on their orientation with respect to the metal surface. As a consequence, the dipole moment of the system is not zero. Thus, the interactions between such adsorbed molecules and the external electric field can be described quantitatively from the classical molecular mechanics point of view.

In this work we show that it is possible to induce a unidirectional motion of the fullerene-based nanocars adsorbed on the metal surfaces by applying the electric field in direction consistent with the rotation of the nanocar wheels. Such a field might for example be created by the STM tip. Although the electric field surrounding the STM tip is not uniform and to a large degree is normal to the surface on its boundary, there is always a nonzero tangential component of the field for the finite surface-atom distances (Figure 2).

## 2. METHOD

In present work we focus on the effect of such tangential component of the electric field (Figure 2). The effect of the normal component may lead to the variation of the energy barriers for surface diffusion, and it is unlikely to contribute to the directionality of the induced motion. In other words, it might only affect the quantitative parameters, such as absolute values for diffusion constants and velocities, but not the qualitative results.

Another approximation we utilize in this work is that the electric field can be viewed as homogeneous, and no significant field gradients are present. This assumption could be justified by comparing the size of the nanocar molecule with the inversed curvature of the electric field that specifies the length



**Figure 2.** Electric field surrounding the STM tip. The blue arrow corresponds to the component of electric field normal to the surface. The magenta arrow shows the tangential component of the electric field which is parallel to the surface.

over which the electric field changes significantly its amplitude. For a single adatom the gradient of the field may be strong enough to drive it just under the tip.<sup>25</sup> For the molecules such as nanocars, on the contrary, such effects most probably are negligible.

It is important to note that, in general, the charge distribution in the nanocar molecule in the presence of the electric field is different from the one without the field. However, we verified by direct calculations (see Supporting Information, section S1) that for the fields used in our simulations the difference in the charges on carbon atoms with and without electric fields is negligibly small. The notable difference appears only for the fields stronger than  $\sim 10^{10}$  V/m. This defines the range of applicability of the approximations used in this work. For stronger fields the modification of the charge transfer model should be introduced or another treatment of charge transfer process must be utilized.

In order to quantitatively characterize the possibility of fullerenes to interact with the external electrical field, we perform a series of rigid-body molecular dynamics (MD) simulations of the single fullerene and the nanotruck molecules in the presence of external fields. The interactions of the molecular species with the metals substrate are described by the universal force field (UFF),<sup>40</sup> combined with our charge transfer model.<sup>39</sup> The charge transfer model predicts that charge from metal is transferred to the fullerene group, when the latter is brought close enough to the metal surface. The magnitude of the charge transferred from metal to the nanocar molecule is 0.7–0.8 electrons per C<sub>60</sub> group for flexible nanocar model and 0.45–0.5 electron per C<sub>60</sub> group for rigid nanocar model.<sup>39</sup> The charge transfer for four-wheel nanocar is smaller compared with pure fullerene molecules, most probably because of the coadsorption effects.<sup>39</sup>

Most importantly, the charge distribution is not uniform, resulting in the nonzero dipole moment on each fullerene wheel. The partial charges for some representative C<sub>60</sub>/Au configurations in the presence of the field and without it are given in the Supporting Information (section S1), showing a typical charge redistribution pattern. It should be noted that although the metal surface acquires net positive charge, the partial charges on gold atoms as computed, for example, from Mulliken population analysis after PM6 calculations, are not

physical. Instead, our charge transfer/chemisorption model uses the method of image charges as described in details in our earlier work.<sup>39</sup> The polarized  $C_{60}$  group is then able to interact with the field according to classical electrostatics laws.

We consider the external electric field of various strengths, namely, 1, 5, 10, and 20 units (where each unit is  $4.146 \times 10^8$  V/m) applied to the system kept at different temperatures in the range of 100–1000 K. Each trajectory is integrated for 100 ps with 1 fs time step using q-Terec integration scheme for rigid-body molecular dynamics with a 10-term expansion.<sup>41</sup> Each nanocar molecule is represented by five fragments (flexible model) or by one fragment (rigid model). The metal surface is viewed as a single rigid fragment with frozen translational and rotational degrees of freedom. Such coarse-graining technique is known to affect quantitative parameters, such as diffusion coefficients,<sup>42–44</sup> but it is unlikely to affect qualitative results.<sup>9,10</sup> The electric field does not influence the metal because it is known that in conductors the field is equal to zero. The temperature of the system is maintained by the Nose–Hoover thermostat.<sup>45–48</sup> The electric field is applied in the direction parallel to the surface.

The nanocar/metal system subject to the external electric field is a nonconservative system. Thus, its total energy  $H$  is not an integral of motion, but rather it is a quantity which increases with time. It is, however, possible to define the total energy of the system and the field together, by adding the potential energy of interaction of the molecule with the field:

$$U_{\text{system-field}} = -(\vec{E}, \vec{\mu}) \quad (1)$$

where  $\vec{\mu} = \sum_i q_i \vec{r}_i$  is a dipole moment of the molecule, such that a new quantity  $\tilde{H} = H + U_{\text{system-field}}$  is conserved. The drift of the system's Hamiltonian  $H$  during the time period  $[t_1, t_2]$  can then be calculated by the integral

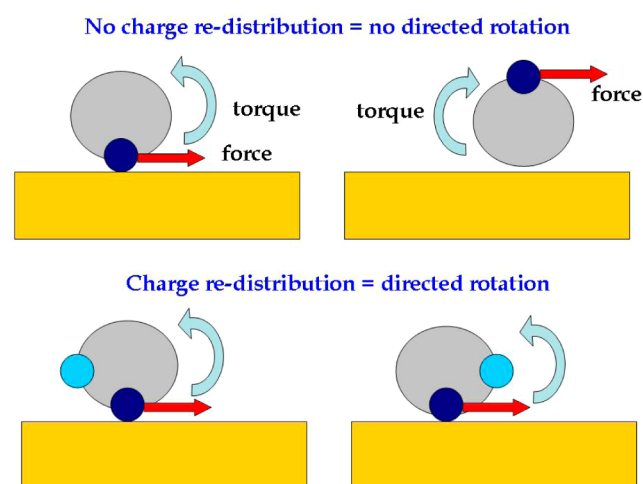
$$\Delta H = \int_{t_1}^{t_2} \frac{dH}{dt} dt = \int_{t_1}^{t_2} -\frac{dU}{dt} dt = U(1) - U(2) \quad (2)$$

This quantity is the work performed by the field on the nanocar.

### 3. RESULTS AND DISCUSSION

**3.1. Mechanism of Unidirectional Rolling Motion in the Presence of Electric Field.** It is important to emphasize that the charge transfer between the fullerene wheels and the metal substrate is a crucial factor determining the dynamics of nanocars under the effect of external electric field. It leads to the directed motion of the nanocar by inducing unidirectional rotation of its wheels. Because of the charge transfer, the initially nonpolar nanocar molecule acquires some finite dipole moment in the presence of the metal substrate.

The charge distribution on the carbon atoms of the fullerene wheels depends on their distance from the surface (Figure 3, darker dots correspond to charged atoms with bigger absolute value of charge, lighter dots correspond to charged atoms with smaller absolute value). Therefore, it dynamically changes in such a way that the bottom of the nanocar wheel is negatively charged at all times (Figure 3, darker dots), while the upper part of the wheel is only slightly charged or neutral (Figure 3, lighter dots). As a consequence, the component of the electric field, parallel to the surface, creates a unidirectionally oriented torque on the wheel (Figure 3, bottom). It is important to note that we assume here that charge redistributions takes place very fast.



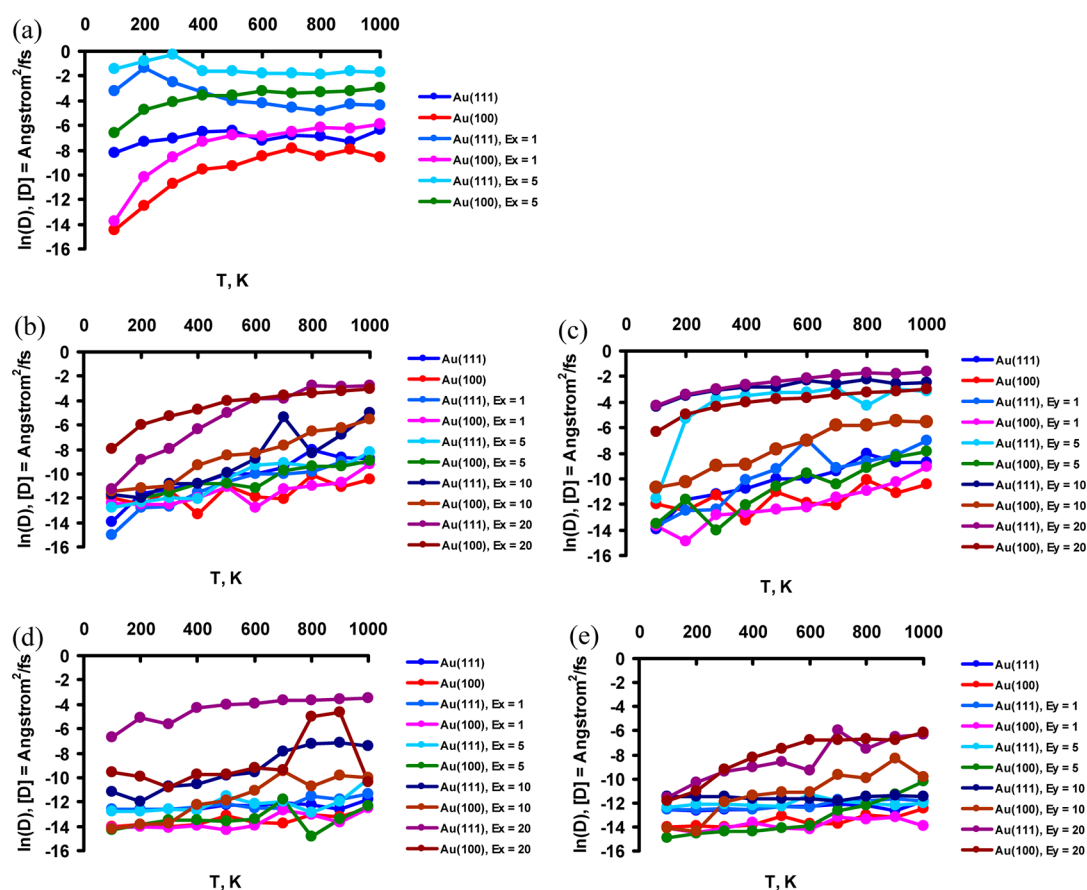
**Figure 3.** Mechanisms of the unidirectional rotation of the wheel with and without charge transfer.

Without taking into account the charge transfer, if the charges on wheel atoms remain constant, the torque will change its direction, depending on the orientation of the wheel (Figure 3, top). This will only lead to stochastic fluctuations in rotation without directionality. But in reality the partial charge of the given atom will decrease as its distance to the metal surface increases. In other words, it loses its initial charge by redistributing it quickly to those atoms which are closer to the fullerene/substrate interface. A similar mechanism of unidirectional rotary motion has been established recently for the carbon nanotubes (CNT) on the water surfaces.<sup>49</sup> Initial light excitation creates the asymmetry of the charge distribution on the wall of the CNT. The latter effect leads to nonzero torques, eventually rotating the CNT unidirectionally.

**3.2. Molecular Dynamics Calculations.** To test the mechanisms of the directed rotation of the fullerene wheels, described in the previous section, we performed a set of nonequilibrium rigid-body MD simulations as described below. In the presence of the external electric field, the diffusion coefficient of the fullerene molecule increases significantly, even for smallest fields applied (Figure 4a). One can expect a monotonous increase of the  $C_{60}$  mobility with the increase of the strength of external field applied, what is indeed observed in our simulations. The situation is different for the nanocar molecule, where there is a threshold value of the field strength (Figure 4b). For fields weaker than the threshold, the mobility of the nanocar is relatively independent of the field strength, and it is small. Once the field is stronger than the threshold, the mobility of the nanocar becomes sensitive to the field applied, similarly to the case of single fullerene molecule, and it increases by several orders of magnitude.

To illustrate the dynamics of nanocars in the presence of external fields, we calculate the diffusion coefficients with the fields, parallel to the surface, but oriented in two orthogonal directions—either along the main axis of the nanocar ( $y$ -axis, Figure 4c,e) or perpendicular to it ( $x$ -axis, Figure 4b,d). Although the diffusion coefficient by itself is not a measure of directionality, it becomes a convenient indicator of preferred direction when the spatial symmetry of the system is broken. From such simulations we found that the diffusion coefficients strongly depend on the direction of the field applied, indicating different mobility mechanisms (Figure 4b–e). For the flexible model of the nanocar, if the external field is applied in direction





**Figure 4.** Diffusion coefficients (logarithmic scale) of the fullerene molecule (a), of the flexible nanocar with the field orthogonal to the rolling direction (b), of the flexible nanocar with the field parallel to the rolling direction (c), of the rigid nanocar with the field orthogonal to the rolling direction (d), and of the rigid nanocar with the field parallel to rolling direction (e) on both Au(111) and Au(100) surfaces.

parallel to the expected direction of the nanocar motion (Figure 4c), the diffusion coefficients are several orders of magnitude larger than in the case when the driving field applied in the orthogonal direction (Figure 4b). On the contrary, for the rigid model of the nanocar, where wheel rotations are not allowed, the diffusion is very slow for the case of the external field applied in the direction of expected motion (Figure 4e), while if the field is applied in the orthogonal direction, the diffusion is faster (Figure 4d). In addition we found that, in agreement with the suggested mechanism,<sup>39</sup> the stronger fields are required to induce the motion of nanocars by sliding/hopping mechanism. The fields which induce the rolling motion of nanocars with flexible wheels are not able to bring the rigid nanocars to the motion (see the movies in the Supporting Information section S2). Note also that for rigid nanocars only the hopping motion is possible. Thus, the comparison of rigid and flexible nanocars is a convenient tool for analyzing the contribution of the rolling motion in the overall dynamics.

All these observations indicate that the motion of the nanocars depends on the direction of the external fields and that the rotation of the fullerene wheels indeed facilitates the directional diffusion of the nanocars by decreasing the activation energy for this process. For very strong fields or very high temperatures or both, however, the anisotropy in the diffusion coefficient decreases since the role of the activated motion for nanocars at these conditions becomes less important (driven motion versus the activated). Under these

conditions the nanocar molecule may undergo pivoting motion, and this will also strongly affect the directionality.

For quantitative characterization of the anisotropy of the nanocar motion in the presence of external fields and without fields, we introduce the anisotropy measure

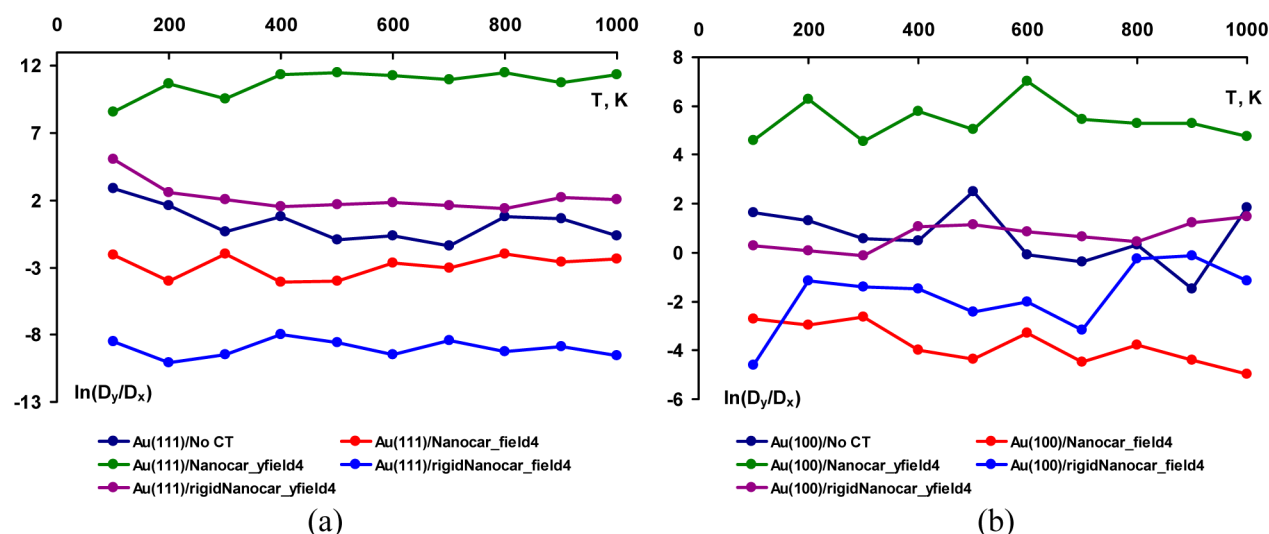
$$A = \ln \left( \frac{D_y}{D_x} \right) \quad (3)$$

where  $D_x$  and  $D_y$  are the 1-D diffusion coefficients in  $x$  and  $y$  directions, respectively. Such a quantity is an adequate measure for anisotropy of the nanocar motion, which provides much more information about dynamical properties of the nanocars mobility than simply the diffusion coefficient. However, this quantity still cannot be used to show the unidirectionality of such motion. For this purpose we additionally calculate the average velocities in each of the orthogonal directions ( $x$  and  $y$ ) on the surface plane:

$$V_x = \left\langle \frac{d(X(t) - X(0))}{dt} \right\rangle \quad (4a)$$

$$V_y = \left\langle \frac{d(Y(t) - Y(0))}{dt} \right\rangle \quad (4b)$$

where  $\langle \rangle$  denotes the averaging over all initial conditions (trajectories), and the differentiation is substituted by the slope of linear fit of the nominator vs denominator.



**Figure 5.** Measures of anisotropy for the nanocar motion (semilogarithmic scale) in the presence of electric field and without it: (a) on Au(111) surface; (b) on Au(100) surface. Abbreviations are as follows: field1, field2, field3, and field4 correspond to electric field directed along the  $x$ -axis with the magnitude of 1, 5, 10, and 20 units, respectively, where  $1 \text{ unit} = 4.146 \times 10^8 \text{ V/m}$ ; yfield1, yfield2, yfield3, and yfield4 are the same but for electric field directed along the  $y$ -axis (parallel to the main axis of the nanocar).

From the analysis of the anisotropy measure  $A$  (Figure 5) one can clearly see that in the absence of the external fields (dark blue lines) it fluctuates around the value of 0, which corresponds to totally isotropic diffusion, and it agrees with the second law of thermodynamics. The fluctuations are rather large because of the moderate number of trajectories. In the case when the electric field is applied in the  $y$ -direction (expected direction of the rolling motion) the diffusion coefficient in the  $y$ -direction becomes larger by 4–6 orders of magnitude (Figure 5:  $A$  quantity in the range of 10–12, green lines) than that in the  $x$ -direction. If the electric field is applied in the  $x$ -direction (direction orthogonal to the rolling motion), the quantity  $A$  fluctuates in the range of  $-3$  to  $-1$  (red lines), indicating that the diffusion in the  $x$ -direction is faster than in the  $y$ -direction, but not significantly. This is still much smaller compared with the case of the field in the parallel direction, so the most clear anisotropy of motion is observed only in the case when the field is applied in the rolling direction of nanocar.

It is also interesting to point out that freezing of nanocar wheels completely inverts the directionality order. Once such constraints are imposed, the field applied in the rolling direction of (now rigid) nanocar (purple lines) causes more isotropic motion (smaller absolute values of  $A$ ) than when it is applied in the orthogonal direction (light blue lines). In both cases the motion is faster in the direction of external field, but the ratios vary by many orders of magnitude.

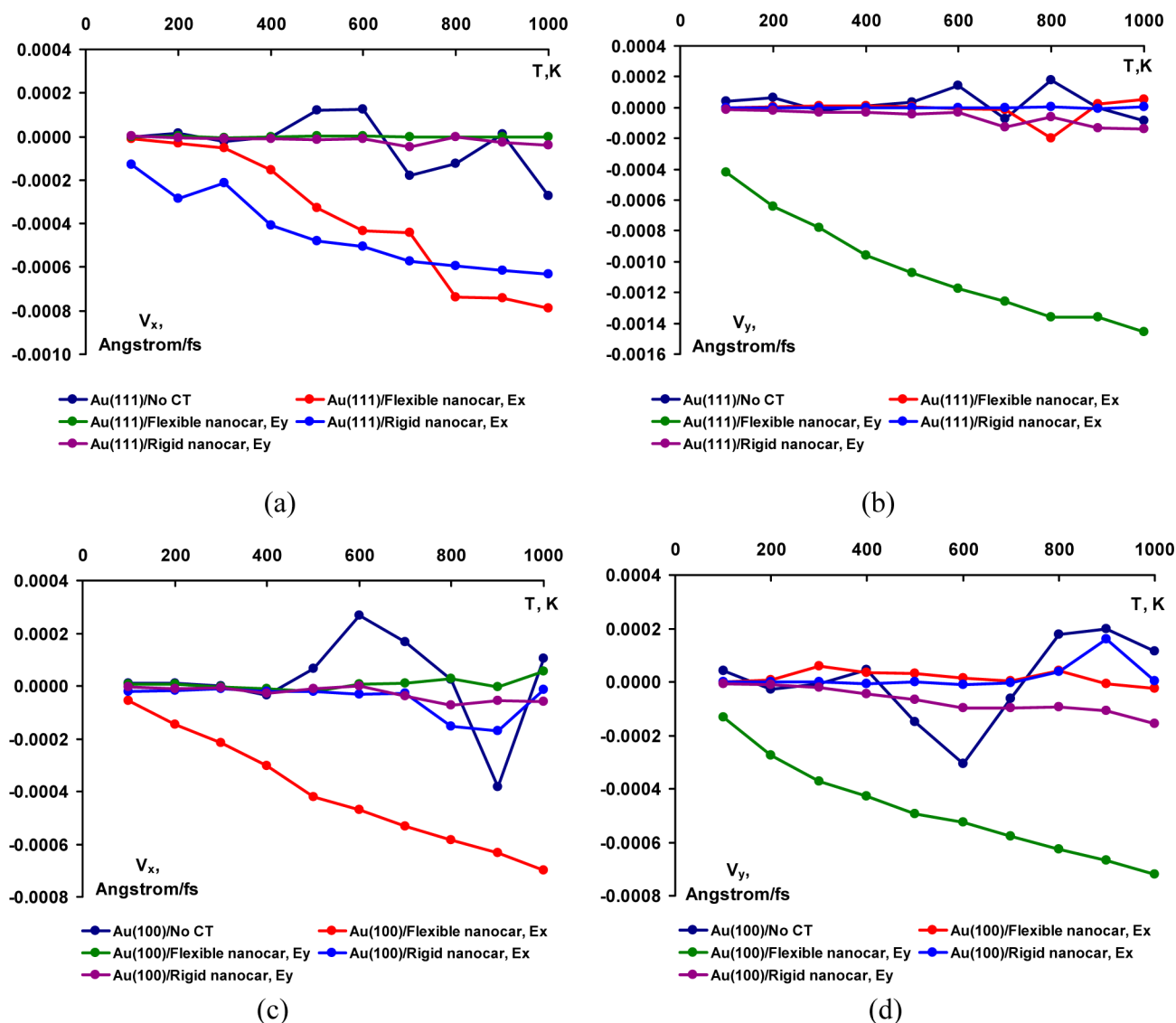
We verify that described effects take place on both Au(111) (Figure 5a) and Au(100) (Figure 5b) surfaces. The only difference is that the anisotropy measures are smaller in absolute values on the Au(100) surface, although the qualitative relations remain unchanged. The reason for this is the fact that the Au(111) surface is more symmetric (isotropic) than the Au(100) surface, and it makes effects of the field anisotropy more pronounced in the case of the Au(111) surface.

The calculated average velocities in  $x$ - and  $y$ -directions (Figure 6) clearly show the unidirectionality of the nanocar motion in the presence of field. For example, if the field is applied in the  $x$ -direction, the motion will be observed only in this direction (Figure 6a, red and light-blue lines), while the velocity along the  $y$ -direction is negligible (Figure 6b, red and

light-blue lines). It is interesting that on the Au(111) surface the velocities along the  $x$ -direction are similar for both types of nanocars—with flexible or frozen wheels. This may be explained by the fact that the rotation of the nanocar wheels (toward the  $y$ -direction) does not help it to move in the orthogonal direction (along the  $x$ -axis). Thus, effectively, the flexible and fully frozen representations are practically indistinguishable in this case. This, however, is not the case for Au(100) surface, where additional flexibility of the molecule increases the probability of finding the transition states with lower activation barriers. In such case the flexible molecule shows a significantly higher mobility (Figure 6c, red line).

If the electric field is applied in the  $y$ -direction, which is parallel to the main axis of the nanocar, it may induce the rolling motion of the nanocar wheels. This leads to a drastic increase in the velocity  $V_y$  for the flexible nanocar (Figure 6b,d, green lines). If the rotation of the wheels is impossible because of the artificial constraints (light-blue and purple lines), the velocities of such nanocars fluctuate around 0 or increase only slightly. This is consistent with the rolling mechanism of the motion of nanocars.

The results of our simulations are in good agreement with available experimental findings. Namely, the experiments similar to our simulations setup have been performed when the nanocar was pushed by STM tip along two orthogonal directions.<sup>5</sup> It was found that if it is pushed along the rolling direction, the directional motion can be induced. On the contrary, the molecule remained immobile if it was pushed in the orthogonal direction. During the experiment the voltage at STM tip was 0.1 V. If the tip is  $\sim 1 \text{ nm}$  apart from the atom, the local electric field at position of such an atom is close to  $1 \times 10^8 \text{ V/m}$ . This is comparable in order of magnitude to the field strengths used in our simulations. Thus, one may argue that during the experimental manipulations the charge transfer and electrostatic interactions play a significant role in the nanocar dynamics, and it ultimately leads to the anisotropy in the molecular mobility. Moreover, it is possible to create such conditions at which the nonpolar nanocar might be driven by external electric field in a controllable way.



**Figure 6.** Average velocities of the nanocar's center of mass: (a)  $x$  projection for nanocar/Au(111) systems; (b)  $y$  projection for nanocar/Au(111) system; (c)  $x$  projection for nanocar/Au(100) system; (d)  $y$  projection for nanocar/Au(100) system. Presented results are for various directions of the applied electric field and for different rigid-body representations as explained in the text.

#### 4. CONCLUSIONS

In this work we investigate the dynamics of nanocars on metal surfaces in the presence of the external electric field. We found that the charge transfer and related dynamic redistribution of charges on nanocar wheels is the main reason for unidirectional motion of surface-bound nanocars in the presence of the electric field. Such dynamic redistribution of charges supports the idea that rolling mechanism is the dominant factor in the nanocar surface diffusion, and it is shown that rolling is energetically more favorable than the simple hopping and sliding mechanism. Since the rotation of the wheels is possible in only one direction, there is a directional anisotropy in the nanocar motion.

The dynamically induced dipoles on the fullerene wheels make interaction between the nanocar and external electric field possible, despite the fact that the isolated molecule has vanishing dipole moment. The dynamic nature of the charge redistribution is especially important for the directionality of the nanocar motion in the presence of constant electric field. With the help of our rigid-body MD simulations in non-

equilibrium conditions we characterized the dynamical properties of the fullerene-based nanocars on gold surfaces. In particular, we found that the electric fields applied in both  $x$ - and  $y$ -directions parallel to the metal surface lead to the motion of the molecule unidirectionally in the direction parallel to the field direction. However, the motion is highly anisotropic only when the field is applied in the direction consistent with the rolling mechanism. If the field is applied in the orthogonal direction, the motion is still unidirectional, but with significantly smaller anisotropy.

In conclusion, our theoretical calculations closely mimic recent experimental observations where the STM tip was used to perform the manipulations of the nanocars. The field magnitude, required to induce the motion of the nanocar, is of the same order of magnitude in our simulations and in the experimental setup. The model used in this work thus provides a convenient theoretical framework for understanding the dynamic processes in nanomachines on metal surfaces. It will be useful for development of future molecular devices and for further progress in the growing field of nanotechnology.

## ■ ASSOCIATED CONTENT

## ■ Supporting Information

Animated movies of the nanocar motion subject to various external electric fields; verification of the charge transfer model in presence of electric fields. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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