Symmetry Rules for Brownian Photomotors

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Abstract

A number of symmetry rules have been derived which govern the occurrence of directed motion and its reversals in Brownian photomotors both for individual molecules and for molecular ensembles. The exclusion principles and sufficient conditions for the photoexcited transport of molecules are found in terms of electron density distribution symmetries in the substrate and moving molecules. Thus, the most general sufficient condition for a nonzero directed velocity of a single molecule at any symmetry type of the substrate is as follows: symmetric or antisymmetric components of the molecular electron density distribution change on excitation, the remaining symmetry components not vanishing in the ground and excited states simultaneously. The exclusion principle for motion reversals (stopping points) in single-molecule transport is such that symmetric and antisymmetric components of the molecular electron density distribution change proportionally on excitation. For collective molecular transport to occur, it is sufficient that the substrate not be symmetric and that symmetric components of the molecular electron density distribution not vanish in the ground and excited states simultaneously. The symmetry relationships established offer much promise for the effective quantum-chemistry based screening and rational molecular design of light-driven nanodevices.

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I. INTRODUCTION

Rectification of the Brownian chaotic motion to the directed transport of particles (molecules) which takes place at the nano-scale in living organisms has been in the focus of research attention for decades [1-3]. Since nineties, a huge diversity of rectifying nano-machines referred to as molecular (Brownian) motors have been thoroughly studied, classified, theoretically modelled, mimicked from natural prototypes, and independently invented [4-8]. They all are based on the following general principle: For a Brownian particle to move unidirectionally, it is necessary that it exist in, at least, two interchanging states and the particle potential energy in one or both of them is spatially asymmetric. In the simplest case, this condition is implemented when the particle (i) is placed into a spatially periodic asymmetric potential produced by an appropriate substrate and (ii) fluctuates between two states with the different values of charge, dipole moment, or another potential-sensitive characteristic. The two states can be interswitched by, e.g., a temperature change, a chemical reaction, or light excitation. Here we address the last-mentioned case, which is realized in so-called Brownian photomotors.

Among the abundance of light-driven molecular devices [9] generating, as a rule, unidirectional rotations [10-13] or reciprocations along a restricted path [13, 14], there are very few examples of special interest which afford unrestricted translational motion [13, 15]. Previously we suggested two types of translational photomotors, which involved switching on/off the resonant laser radiation so as to induce the difference in the potential energy between two states of the motor working cycle. Potential energy fluctuations in the mechanisms developed arise from excitation-induced changes in the molecular electronic structure, one model taking into account a dipole moment change [7] and the other overall electron density redistribution [16]. The latter approach is based on different molecule-substrate interaction of electron density distributions (EDDs) in the ground and excited electronic states of the molecule. This electron-density-redistribution photomotor (EDRP) is more general than its predecessor, a dipole photomotor [7], since it implicitly includes multipole contributions of higher-order than dipole interactions thus affording a more accurate assessment of changes in the potential energy. Accordingly, this mechanism enables larger average velocities of directed motion and, even more importantly, reveals a number of

physically meaningful trends and effects that could not be noticed within the formerly used dipole approximation.

In particular, the EDRP model gives much space to the investigation of symmetry role in motor operation. It is known that the asymmetry of the potential energy is vital for generation of directed motion [6]. In most of Brownian motor models, it is caused by the asymmetry of the substrate potential [4-15]. However, it was shown in our previous works on EDRP [16, 17] that the substrate-induced potential need not necessarily be asymmetric for a motor to function. Instead, EDD should be asymmetric in the ground and/or excited state [16]. Moreover, it has even been proved that either state, as well as the substrate, can have symmetric electronic structure but the potential energies of two states should then be of appropriate different periodicity [17]. In this case, so-called dynamic asymmetry emerges which suffices to provide directed molecular transport. Among nontrivial ways of spatial symmetry breaking is the embedding of asymmetry in the geometry of the transported particle, rather than in the channel design [18]. Instead of or in addition to spatial asymmetry, temporal asymmetry can arise, as a result of different state lifetimes [17]. Irrespective of its origin, the asymmetry of potential energy governs the direction motion and enables, under certain conditions, its reversal at some frequencies of resonant laser pulses or temperature.

In the present paper, we focus on the interplay between the symmetries of moving (molecule) and immovable (substrate) parts of the Brownian EDRP. This treatment may provide a number of practicable recommendations for a design of molecular photomotors with controllable properties. Among the most interesting consequences of symmetry relationships, there is a possibility for a collective motor effect to occur; it is exhibited by a molecular ensemble near a substrate, provided the molecules and the substrate are appropriately structured.

II. RESULTS AND DISCUSSION

II. 1. Theoretical background

As a simple model of a polar substrate involved in the photomotor concerned, we consider a 1D chain with the linear density $\rho(x)$ of periodically distributed charge. At the distance z from the chain, it generates the electrostatic potential

$$\varphi(x,z) = \int_{-\infty}^{\infty} \frac{\rho(x')dx'}{\sqrt{(x-x')^2 + z^2}} = 2\sum_{q\neq 0} \rho_q K_0\left(\left|k_q z\right|\right) e^{ik_q x} \tag{1}$$

where $K_0(z)$ is the Macdonald function and $k_q = 2\pi q/L$ (q is an integer, L is a spatial period of charge distribution), and ρ_q is the Fourier component of the charge density:

$$\rho_q = L^{-1} \int_0^L dx\rho(x)e^{-ik_q x} \tag{2}$$

Then the potential energy of a molecule, with atomic charges p_j and atomic coordinates x_j is written as:

$$V(x,z) = \sum_j p_j \varphi(x+x_j, z+z_j) = 2\sum_{q\neq 0} \rho_q e^{ik_q x} \sum_j p_j K_0\left(\left|k_q(z+z_j)\right|\right) e^{ik_q x_j} \tag{3}$$

Notably, the moving part of the EDRP considered here is an extended molecule rather than a point object (unlike most of studies on Brownian motors). Going from point-like to finite-size particles generally makes the behaviour of the motor much richer, as shown, e.g., for a unidirectionally moving single file of interacting particles [19, 20].

For a quasi-1D molecule, with its axis parallel to the chain axis and $|z_j| \ll z$, we introduce a single parameter

$$R_q = \sum_j p_j e^{ik_q x_j} \tag{4}$$

sensitive to the fluctuations of atomic charges and the molecular conformation; it represents a generating function of the multipole expansion. Then the expression for the potential energy is simplified:

$$V(x,z) = \sum_{q\neq 0} V_q(z)e^{ik_q x}, \quad V_q(z) = 2\rho_q R_q K_0\left(\left|k_q z\right|\right) \tag{5}$$

($V_q(z)$ is the Fourier component of the potential energy, with its fluctuations governed by the fluctuations of the quantity R_q).

The average velocity of the motor concerned along the longitudinal x axis of the system (coinciding with the molecular axis) appears as [16]:

$$\langle v \rangle = -\frac{D}{L} \frac{16\pi(1-\varepsilon^2)Z}{(k_B T)^3 (1+4Z)^2 (1+Z)} \, \mathrm{Im}\left[(1+4Z)u_1 w_1 w_2^* + 2(1+Z)w_1^2 u_2^* + 6\varepsilon Z w_1^2 w_2^*\right] \quad (6)$$

Here $D = k_B T / \zeta$ is the diffusion coefficient (with k_B denoting the Boltzmann constant, T the equilibrium absolute temperature and ζ the friction coefficient); $Z = \Gamma L^2 / \left[(4\pi)^2 D\right]$ is a dimensionless parameter depending on the laser operating regime (through $\Gamma = \tau_+^{-1} + \tau_-^{-1}$ determined by the light and dark phase durations, τ_+ and τ_-) and temperature (through the diffusion coefficient D); $\varepsilon = (\tau_+ - \tau_-)/\tau$; u_q and w_q are the half-sum and half-difference of the Fourier components $V_q(z)$:

$$u_q = \rho_q K_0\left(\left|k_q z\right|\right)\left(R_q^{(+)} + R_q^{(-)}\right), \quad w_q = \rho_q K_0\left(\left|k_q z\right|\right)\left(R_q^{(+)} - R_q^{(-)}\right) \quad (7)$$

(with $q = \pm 1, \pm 2$ and $R_q^\pm = \sum_j p_j^\pm e^{ik_q x_j^\pm}$ referring to the "+" and "–" phases).

In the general case, the motion can change its direction, i.e., involve so-called stopping points where the velocity becomes zero. If fluctuations involve both the amplitude and shape of the potential energy [16, 17], stopping points result at certain $Z = Z_0$ provided that $Z_0 = -(1+2W)/[2(2+W)]$ (with $W = \mathrm{Im}(w_1^2 u_2^*)/\mathrm{Im}(u_1 w_1 w_2^*)$). By virtue of the positivity condition for the parameter Z_0, it is obtained that $-2 < W < -1/2$.

II. 2. Symmetry theorems for a single-molecule motor

To derive the symmetry rules for EDRP operation, we use a system of a triatomic molecule and a periodic substrate containing three atoms per unit cell (see Fig. 1). Here p_0 characterizes the net charge of the molecule; Q_s, p_s and Q_a, p_a respectively denote the symmetric and antisymmetric contributions to the atomic charges of the substrate and the molecule, with the symmetry represented by the C_{2v} group; l and r are respective interatomic distances in the substrate and molecule, respectively; the superscripts ($\pm$) refer to the two

states involved. (The (−) state corresponds to the ground state of the molecule and the parameters in the (+) state are arithmetical means of those in the ground and excited states [16]). In this case, the complex quantities ρ_q and R_q appear as:

$$\rho_q = L^{-1}[2Q_s(\cos k_q l - 1) + 2iQ_a \sin k_q l], \quad R_q^{(\pm)} = p_0^{(\pm)} + 2p_s^{(\pm)}(\cos k_q r - 1) + 2ip_a^{(\pm)} \sin k_q r \quad (8)$$
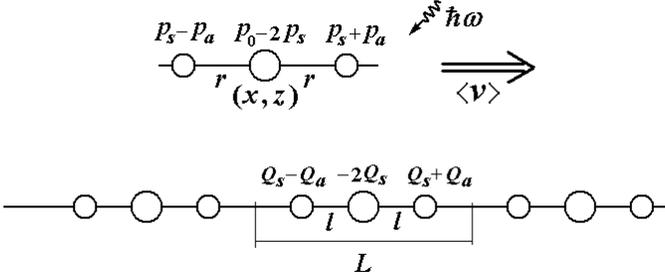
Figure 1. A model system of a triatomic molecule and a periodic substrate with three potential-generating atoms in the unit cell (p_0 is the net charge of the molecule; Q_s, p_s and Q_a, p_a respectively denote the symmetric and antisymmetric contributions to the atomic charges of the substrate and the molecule).

Using expression for motor velocity (6), along with model representation (8), one can conveniently analyze the relationships between basic motor characteristics and the EDD symmetry in the molecule and the substrate. First, if two states of the system differ by the charge centrally positioned on the motor molecule having no the dipole nor the quadrupole moment ($p_0^{(+)} - p_0^{(-)} \neq 0, p_s^{(\pm)} = p_a^{(\pm)} = 0$), the substrate should be asymmetric ($Q_a \neq 0$) for a motor to function. Indeed, this case implies $R_q^{(\pm)} = p_0^{(\pm)}$ (see Eq. (8)) and hence, given the zero value of Q_a, neither u_q nor w_q specified by Eq. (7) have an imaginary part so that average velocity (6) vanishes. Further, if an uncharged molecule free of the quadrupole moment both in the (+) and (−) states changes its dipole moment on excitation ($p_0^{(\pm)} = 0, p_s^{(\pm)} = 0, p_a^{(+)} - p_a^{(-)} \neq 0$), it is necessary for directed motion to occur that the substrate should not be antisymmetric (i.e., should have $Q_s \neq 0$), otherwise all u_q and w_q become real values and expression (6) becomes zero again. Correspondingly, if a pure molecular quadrupole (having neither the charge nor the dipole moment so

that $p_0^{(\pm)} = 0$, $p_a^{(\pm)} = 0$, $p_s^{(+)} - p_s^{(-)} \neq 0$) fluctuates on excitation, then the substrate should not be symmetric (i.e., should have $Q_a \neq 0$) for the average velocity to be nonzero. The necessary and sufficient conditions for the occurrence of directed motion (starting from the molecular EDD and from the substrate symmetry) are listed in Tables 1a, b. As seen, the most general sufficient condition for nonzero molecular velocity (6) at any symmetry type of the substrate is as follows: symmetric or antisymmetric molecular EDD components change on excitation, the remaining symmetry contributions to the EDD not vanishing in two states simultaneously. With this condition satisfied, the values w_q never go to zero and the values u_q are never purely real.

Some exclusion principles for the occurrence of stopping points can also be derived from relationships (6-8). We have calculated them with the varied values of $p_s^{(\pm)}, p_a^{(\pm)}$ for the molecular EDD and Q_s, Q_a for substrate charges to find that $W = 1$ (stopping points are ruled out) at certain combinations of molecular charge, dipole, and quadrupole moments with the symmetries of the substrate-generated potential. Table 2 presents the resulting symmetry rules for an uncharged molecule ($p_0^{(\pm)} = 0$). To illustrate them, consider an asymmetric substrate ($Q_s = 0.3$, $Q_a = 0.8$) with two molecules having the same antisymmetric but different symmetric EDD components (see Fig. 2). The latter are fitted such that $p_s^{(+)}/p_s^{(-)} = p_a^{(+)}/p_a^{(-)}$ for one of the molecules and chosen arbitrarily for the other. As a result, $W = 1$ in the first case and hence no motion reversals occur, whereas $W = -0.72$ in the second case thus falling within the interval $(-2, -1/2)$ and affording a stopping point (at $Z \approx 0.17$). Interestingly, after passing the stopping point, the molecule moves in the opposite direction with the increasing velocity, all conditions being the same.

Table 1a. Necessary and sufficient conditions for EDRP operation (starting from the EDD in the molecule involved).

Molecular EDD	Meaning	Substrate	Meaning
$p_s^{(\pm)} = p_a^{(\pm)} = 0$ and	The charge is located on the central moiety of the molecule; the molecule has no dipole and quadrupole moment.	$Q_a \neq 0$	An asymmetric substrate
$p_0^{(+)} - p_0^{(-)} \neq 0$	The molecular charge changes on excitation.		
At least one of $p_a^{(\pm)}$ is nonzero.	The molecule has a nonzero dipole moment at least in one of two states involved:		
$p_a^{(+)} - p_a^{(-)} \neq 0$	i) it changes on excitation.	$Q_s \neq 0$	i) A substrate is not antisymmetric.
$p_a^{(+)} - p_a^{(-)} = 0$ (so $p_s^{(+)} - p_s^{(-)} \neq 0$ and/or $p_0^{(+)} - p_0^{(-)} \neq 0$	ii) it does not change on excitation (so the quadrupole moment and/or the charge change on excitation).		ii) No limitations on the substrate.
$p_a^{(\pm)} = 0$ (so $p_s^{(+)} - p_s^{(-)} \neq 0$ and/or $p_0^{(+)} - p_0^{(-)} \neq 0$	The molecule has no dipole moment in the ground and excited states (so the quadrupole moment and/or the charge change on excitation).	$Q_a \neq 0$	A substrate is not symmetric.
At least one of $p_0^{(\pm)}, p_s^{(\pm)}$ is nonzero.	The molecule has a nonzero charge or quadrupole moment at least in one of two states involved:		
$p_s^{(+)} - p_s^{(-)} \neq 0$ and/or $p_0^{(+)} - p_0^{(-)} \neq 0$	i) the charge and/or quadrupole moment change on excitation.	$Q_a \neq 0$	i) A substrate is not symmetric.
$p_s^{(+)} - p_s^{(-)} = 0$ and $p_0^{(+)} - p_0^{(-)} = 0$ (so $p_a^{(+)} - p_a^{(-)} \neq 0$)	ii) the charge and quadrupole moment do not change on excitation (so the dipole moment changes on excitation).		ii) No limitations on the substrate.
$p_0^{(\pm)} = p_s^{(\pm)} = 0$ (so $p_a^{(+)} - p_a^{(-)} \neq 0$)	The molecule has no charge and quadrupole moment in the ground and excited states (so the dipole moment changes on excitation).	$Q_s \neq 0$	A substrate is not antisymmetric.

Table 1b. Necessary and sufficient conditions for EDRP operation (starting from the substrate symmetry).

IF	Meaning	THEN the directed motion is possible if	Meaning
$Q_a = 0$	A symmetric substrate	$p_a^{(-)}$ and/or $p_a^{(+)}$ are nonzero and if $p_a^{(+)} - p_a^{(-)} = 0$, then $\begin{cases} p_0^{(+)} - p_0^{(-)} \neq 0 \\ \text{and/or} \\ p_s^{(+)} - p_s^{(-)} \neq 0 \end{cases}$	The molecule has a nonzero dipole moment at least in one of the two states involved and, if the dipole moment does not change on excitation, the charge and/or the quadrupole moment change.
$Q_s = 0$	An antisymmetric substrate	At least one of $p_0^{(\pm)}$, $p_s^{(\pm)}$ is nonzero and if $\begin{cases} p_0^{(+)} - p_0^{(-)} = 0 \\ \text{and} \\ p_s^{(+)} - p_s^{(-)} = 0 \end{cases}$, then $p_a^{(+)} - p_a^{(-)} \neq 0$	The molecule has a nonzero charge and/or quadrupole moment at least in one of the two states involved and, if neither the charge nor the quadrupole moment changes on excitation, the dipole moment changes.
$Q_s \neq 0$ and $Q_a \neq 0$	An asymmetric substrate	$p_0^{(+)} - p_0^{(-)} \neq 0$ and/or $p_s^{(+)} - p_s^{(-)} \neq 0$ and/or $p_a^{(+)} - p_a^{(-)} \neq 0$	Any change in the molecular EDD occurs on excitation
Arbitrary Q_a, Q_s	Any type of the substrate	i) $p_0^{(+)} - p_0^{(-)} \neq 0$ and/or $p_s^{(+)} - p_s^{(-)} \neq 0$ and at least one of $p_a^{(\pm)}$ is nonzero. ii) $p_a^{(+)} - p_a^{(-)} \neq 0$ and at least one of $p_0^{(\pm)}$, $p_s^{(\pm)}$ is nonzero.	The charge (and/or quadrupole moment) or the dipole moment changes on excitation, the remaining (constant) parameter not vanishing in two states simultaneously.

Table 2. Exclusion principles for the occurrence of stopping points (starting from the substrate symmetry).

IF	Meaning	THEN no stopping points occur if	Meaning
$Q_a = 0$	A symmetric substrate	$p_a^{(+)} - p_a^{(-)} \neq 0$ and $\left\{ \begin{array}{l} p_s^{(+)} - p_s^{(-)} = 0 \\ \text{or} \\ p_s^{(+)} / p_s^{(-)} = p_a^{(+)} / p_a^{(-)} \end{array} \right.$	The molecular dipole moment changes on excitation, whereas the quadrupole moment does not change or changes proportionally to the dipole moment.
$Q_s = 0$	An antisymmetric substrate	$p_s^{(+)} - p_s^{(-)} \neq 0$ and $\left\{ \begin{array}{l} p_a^{(+)} - p_a^{(-)} = 0 \\ \text{or} \\ p_s^{(+)} / p_s^{(-)} = p_a^{(+)} / p_a^{(-)} \end{array} \right.$	The molecular quadrupole moment changes on excitation, whereas the dipole moment does not change or changes proportionally to the quadrupole moment.
$Q_s \neq 0$ and $Q_a \neq 0$	An asymmetric substrate	$p_s^{(\pm)} = 0$ or $p_a^{(\pm)} = 0$, or $p_s^{(+)} / p_s^{(-)} = p_a^{(+)} / p_a^{(-)}$	The molecular dipole or quadrupole moment changes on excitation or they both change proportionally.
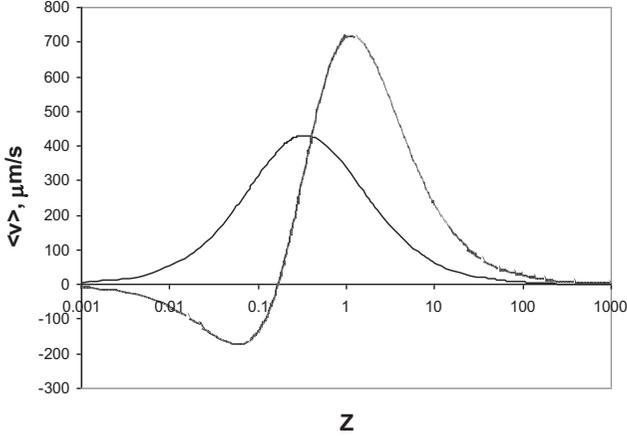
Figure 2. The average velocity of directed motion without (solid curve) and with (broken curve) stopping points for two individual model molecules (as in Fig. 1) on the asymmetric substrate ($Q_s = 0.3$, $Q_a = 0.8$, $L = 0.66\,\text{nm}$, $l/L = 0.3$) versus the parameter Z (proportional to the laser-induced frequency of potential fluctuations and to the reciprocal temperature). The antisymmetric contributions to the molecular EDD in units of the electron charge are $p_a^{(-)} = 0.3$, $p_a^{(+)} = 0.1$ (the same for both curves), whereas the symmetric contributions are $p_s^{(-)} = 0.15$, $p_s^{(+)} = 0.05$ (changing proportionally to $p_a^{(\pm)}$, solid curve) and $p_s^{(-)} = 0.1$, $p_s^{(+)} = 0.5$ (broken curve). It is assumed for the calculation that $D = 10^{-9}\,\text{m}^2/\text{s}$, $T = 300\,K$, $z = L$, and $\varepsilon = 0$.

II. 3. Symmetry theorems for a collective motor

If a substrate has no orienting effect on molecules, they are randomly positioned relative to the motion axis. Therefore, collective rectification of chaotic motion is only possible if the velocity vector projection on the motion axis has the components independent of the molecular orientation. This is not the case for molecules having only odd-order multipoles, as for instance, the dipole or octupole moment. As a result, though individual molecules of this kind can move directionally under appropriate conditions ($Q_s \neq 0$ – see Tables 1a, 1b), their collective transport can never occur as the molecular ensemble diffuses in all directions equiprobably rather than moves as a whole. For example, a dipole photomotor previously described by us [7] cannot be collectivized since its orientation-averaged velocity would be zero. Quite different behaviour is exhibited by the molecules that interact with an external potential through their even-order multipoles, as for instance, the charge, quadrupole moment,

etc. These molecular EDD components contribute to velocity (6) solely by the interaction with Q_a substrate charges and, accordingly, a symmetric substrate ($Q_a = 0$) rules out the directed motion of individual charged and/or quadrupole-possessing molecules as well as of their ensembles.

Table 3 presents the exclusion principles for the occurrence of collectivized directed motion starting from the substrate symmetry. As seen, a symmetric substrate enables no collective molecular transport at all (see also Fig. 3a). Indeed, at $Q_a = 0$, only orientation-sensitive asymmetric molecular EDD components can give rise to directed motion of individual molecules; as a result, the imaginary parts of u_q and w_q in Eq. (7) have different signs for oppositely oriented molecules and the nonzero contributions to Eq. (6) are thus cancelled on averaging over molecular orientations. An antisymmetric substrate requires at least a single nonzero symmetric EDD component of the molecule (such as the charge or quadrupole moment) in the ground or excited state, for the corresponding ensemble to move as a whole. If this condition is satisfied, then at least u_q values have an orientation-invariant imaginary part and hence provide a nonzero contributions to the orientation-averaged velocity (in contrast, at $p_0^{(\pm)} = p_s^{(\pm)} = 0$, u_q and w_q change sign on molecular reorientations and the collective velocity vanishes). It is obvious that the same requirement is valid for the general case of an asymmetric substrate ($Q_s \neq 0$, $Q_a \neq 0$) because the symmetric components to substrate charges are "inactive" and need not be taken into account as far as collective transport is concerned. An additional exclusion principle in this case (for uncharged molecules) is that the ensemble cannot move directionally if $p_s^{(-)} = p_a^{(-)}$ and $p_s^{(+)} = p_a^{(+)}$ simultaneously (with these equalities substituted into relations (6)-(8), we obtain that all three contributions to velocity (6) change sign on molecular reorientations).

The most general sufficient condition for the realization of collective molecular transport is fulfilled when the substrate is not symmetric ($Q_a \neq 0$) and symmetric molecular EDD components do not vanish in two states simultaneously (at least one of $p_0^{(\pm)}, p_s^{(\pm)}$ is nonzero); for an uncharged molecule ($p_0^{(\pm)} = 0$), it is also required that symmetric and antisymmetric EDD components be not equal in two states simultaneously ($p_s^{(-)} \neq p_a^{(-)}$ if $p_s^{(+)} = p_a^{(+)}$ and vice versa). This condition provides that the contributions to velocity (6) are nonzero for individual molecules and do not vanish on averaging over molecular orientations.

The role of the substrate symmetry in the degree of collective motion rectification is illustrated well by Fig. 3. A symmetric substrate allows no directed motion of a molecular ensemble at all – see Fig. 3a. A slightly asymmetric substrate (with $Q_s \gg Q_a$), as in Fig. 3b, already provides a noticeable nonzero orientation-averaged collective velocity. The degree of motion rectification increases together with the substrate asymmetry, and for a strongly asymmetric substrate (with $Q_s \ll Q_a$), as in Fig. 3c, it approaches the possible maximum at which individual and collective velocity curves should merge.

From general considerations, stopping points should occur much more rarely in the collective than in individual molecular motion. Indeed, a nonzero velocity of the molecular ensemble suggests that in the general case, oppositely oriented molecules do not have opposite velocities. Thus, the most typical situation is shown in Fig. 3b: the curves of individual molecular velocities contain stopping points whereas that of the collective velocity does not. However, particular singular points may well exist at which the collective velocity vanishes by chance, as exemplified by Fig. 4: motion reversal can occur (a) for the molecular ensemble as well as for individual molecules or (b) only for the ensemble as a mere result of orientation averaging of individual velocities (free of stopping points).

Table 3. Exclusion principles for a collective EDRP operation (starting from the substrate symmetry).

IF	Meaning	THEN the collective transport is impossible at	Meaning
$Q_a = 0$	A symmetric substrate	Any values of $p_0^{(\pm)}, p_s^{(\pm)}, p_a^{(\pm)}$	Directed motion is completely ruled out irrespective of molecular EDDs.
$Q_s = 0$	An antisymmetric substrate	$p_0^{(\pm)} = p_s^{(\pm)} = 0$	The molecule is uncharged and has no quadrupole moment in the ground and excited states.
$Q_s \neq 0$ and $Q_a \neq 0$	An asymmetric substrate	$p_0^{(\pm)} = p_s^{(\pm)} = 0$	The molecule is uncharged and has no quadrupole moment $Q_s \neq 0$ in the ground and excited states.
$Q_s \neq Q_a \neq 0$	An asymmetric substrate having no uncharged moieties	$p_s^{(-)} = p_a^{(-)}$ and $p_s^{(+)} = p_a^{(+)}$ (at $p_0^{(\pm)} = 0$)	Symmetric and asymmetric EDD components of an uncharged molecule are equal in the ground and excited states.
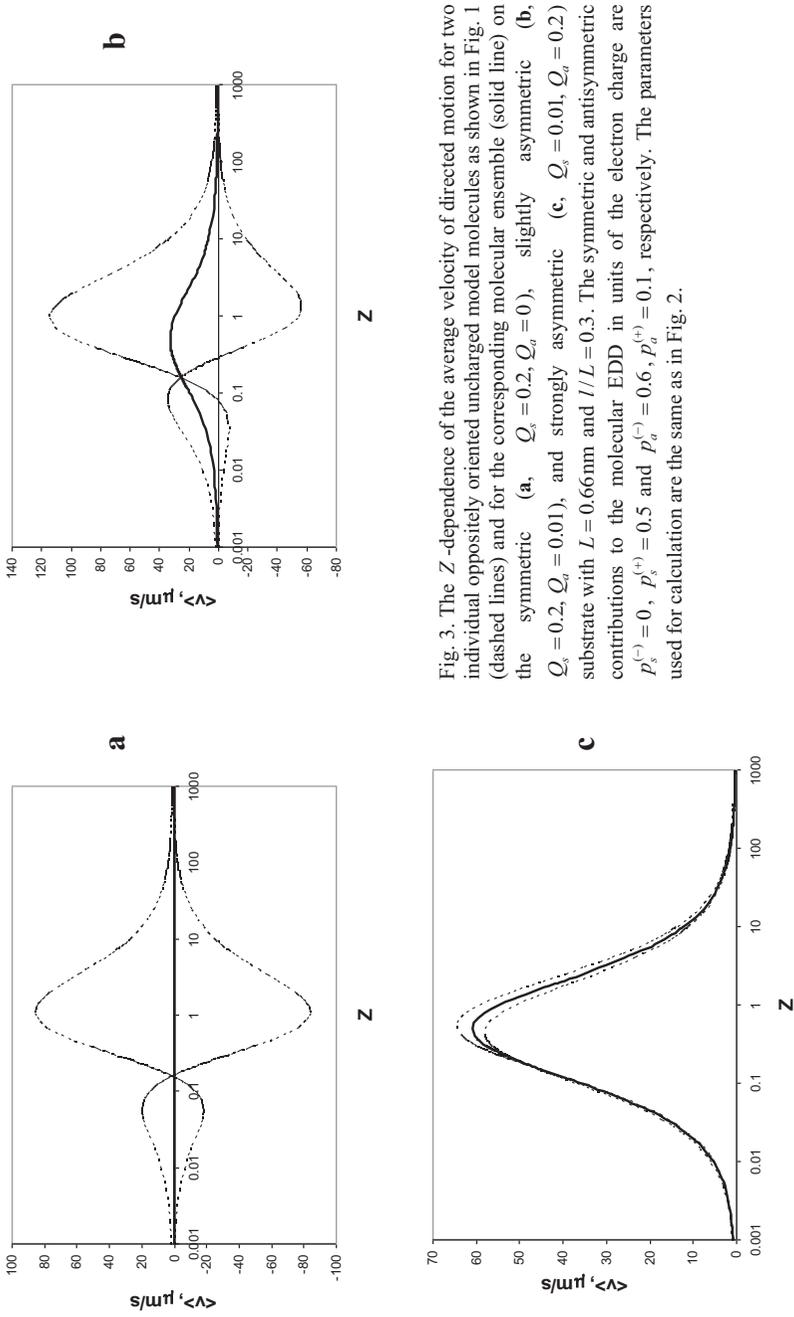
Fig. 3. The Z-dependence of the average velocity of directed motion for two individual oppositely oriented uncharged model molecules as shown in Fig. 1 (dashed lines) and for the corresponding molecular ensemble (solid line) on the symmetric (**a**, $Q_s = 0.2$, $Q_a = 0$), slightly asymmetric (**b**, $Q_s = 0.2$, $Q_a = 0.01$), and strongly asymmetric (**c**, $Q_s = 0.01$, $Q_a = 0.2$) substrate with $L = 0.66$nm and $l/L = 0.3$. The symmetric and antisymmetric contributions to the molecular EDD in units of the electron charge are $p_s^{(-)} = 0$, $p_s^{(+)} = 0.5$ and $p_a^{(-)} = 0.6$, $p_a^{(+)} = 0.1$, respectively. The parameters used for calculation are the same as in Fig. 2.
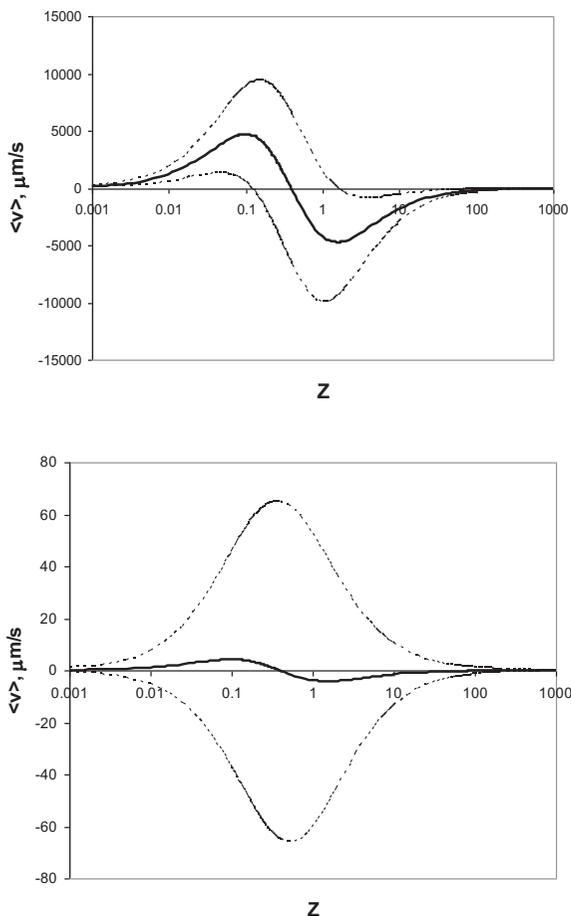
Figure 4. The Z-dependence of the average velocity of directed motion for two individual oppositely oriented model molecules as shown in Fig. 1 (dashed lines) and for the corresponding molecular ensemble (solid line) on two strongly asymmetric substrates (**a**, $Q_s = 0.01, Q_a = 1$ and **b**, $Q_s = 0.01, Q_a = 0.1$), with $L = 0.66\,\text{nm}$ and $l/L = 0.3$. The symmetric $(p_0^{(-)} = 0, p_0^{(+)} = 0.8, p_s^{(-)} = 0, p_s^{(+)} = 1.5)$ and antisymmetric contributions $(p_a^{(-)} = 1, p_a^{(+)} = 1.5)$ to the molecular EDD (in units of the electron charge) are so chosen that the stopping point is maintained s (**a**) or emerges (**b**) on the orientation averaging of individual velocities. The parameters used for calculation are the same as in Fig. 2.

III. CONCLUSIONS

We have derived a number of symmetry selection rules which govern the directed motion generation in Brownian photomotors based on individual molecules and molecular ensembles. In this context, the exclusion principles and sufficient conditions for motor functioning are established based on the symmetries of the substrate and molecular EDDs in the ground and excited states. The occurrence of motion reversal points is also found to obey certain symmetry relationships.

As far as collective molecular transport is concerned, it can be rationalized and modelled only beyond the previously employed dipole approximation, since antisymmetric components of molecular EDDs (such as the dipole moment) provide no contribution to the directed motion velocity. As a result, a collective dipole photomotor cannot function in principle. In contrast, the photomotor based on the excitation-induced overall electron density redistribution, as considered here, takes into account both symmetric and antisymmetric molecular EDD components thus affording a conceptual possibility for a molecular ensemble to move as a whole. This possibility can be realized or not, depending on the symmetry interplay between the substrate and molecular EDDs.

The model representation of the molecule and the substrate concerned offers a convenient tool to purposefully modify their structure. To exemplify, a molecule having only symmetric EDD components ($p_a^{(\pm)} = 0$) and placed on an arbitrary asymmetric substrate ($Q_a \neq 0$) should move directionally on periodic photoexcitation and its velocity is most efficiently controlled by varying antisymmetric rather than symmetric substrate charges.

As another example, a molecular ensemble with arbitrary EDD components, if periodically photoexcited on an arbitrary substrate, should move as a whole and diffuse simultaneously. The symmetric contributions to molecular EDDs (interacting with antisymmetric substrate charges) are responsible for the directed motion of the ensemble, whereas the antisymmetric contributions to EDDs (interacting with symmetric substrate charges) cause the molecular velocities to deviate from their orientation-averaged value so that oppositely oriented molecules drift apart. Thus, one can intentionally enhance molecular transport or diffusion by increasing $p_s^{(\pm)}$ along with Q_a or $p_a^{(\pm)}$ along with Q_s, respectively.

To conclude, the molecule-substrate symmetry relationships found for a Brownian EDRP can provide helpful molecular engineering guidelines to create single-molecule or

collective photomotors, with and without direction reversals, aimed at controllable migration of individual molecules, purposeful drug delivery in biological systems, segregation of molecules with different orientations, etc.

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