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Photoinduced Molecular Transport in Biological Environments Based on Dipole Moment Fluctuations

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Consideration is given to the possibility of a molecule moving unidirectionally in an electric field of a polar periodic substrate as a result of the fluctuations of molecular dipole moment occurring on the photoexcitation of the molecule. As estimated for such motion, molecules with sufficiently long fluorescence and strongly differing dipole moments in the ground and excited states can move with an average velocity of the same order as that typical of protein motors such as kinesin. This effect results from the mutual compensation of two opposite factors acting in dipole photomotors, namely, a lower energy of interaction with the substrate relative to that for protein motors and a shorter excited-state lifetime as compared with the duration of the hydrolytic splitting of adenosinetriphosphate in protein motors.

Protein motors have been known since the 1950s, and their ceaseless manifold activities have been fascinating both theoretical and experimental biochemists and biophysicists for decades: these nanosized devices are responsible for the intracellular transport of molecular materials and organelles, the excretion of vital activity products from the cell, generation and duplication of the genetic code, and so forth. Motors of this kind can be exemplified by the enzyme kinesin, belonging to the so-called Brownian motors, which transports chemical substances along microtubes of synaptic axons by the energy of adenosinetriphosphate (ATP) hydrolysis. The physical principles underlying the functioning of such biological nanomachines are currently under vigorous study (see, e.g., the reviews of refs 1−4 and references therein). Linear protein motors move along substrates, viz., one-dimensional polar periodic cellular structures, as a result of nonequilibrium fluctuations of the motor potential energy in the asymmetric periodic electric field of the substrate. A periodic asymmetrical potential is normally caused by the cellular fibers along which the particle (molecule) travels, and the fluctuations of the corresponding potential energy are governed by the changing state of the moving particle itself. They can be attributed to a varying charge on the particle involved in a chemical reaction or possibly originate from conformational changes within the particle, which influence the potential energy of its interaction with the substrate. As an example, a kinesin molecule periodically becomes a charged structure because its globular head forms a complex with an ATP molecule carrying four negative charges at physiological pH values; the charge is retained on the particle until the products of ATP hydrolysis are eliminated into the environment.[5]

The functioning of a Brownian motor is most clearly elucidated in the framework of the so-called flashing potential energy model.[1−3] When charged, a particle is localized in a potential minimum, which, in view of the potential asymmetry, is not equidistant from the two closest maxima. As soon as the charge vanishes, the diffusion stage of motion follows; it implies that the particle distribution function is symmetric relative to the position of the initial localization and diffuses with time. The subsequent charging makes the particle localize in the potential minima again, with different probabilities for it to fall into the left and right potential wells (as a result of the potential asymmetry), which gives rise to a preferred direction of motion or, statistically, to unidirectional motion. Some interesting peculiarities of the particle transport caused by collective effects are discussed elsewhere.[6]

The present communication is concerned with another model of a translational molecular motor in which potential energy fluctuations result from a change in molecular dipole moment on photoexcitation. This model has some essential distinctions from those known hitherto. First, a dipole and an electric field interact several orders weaker than a charge and a potential of the corresponding magnitudes. Second, a photoexcited state lifetime (as a rule, limited to a few nanoseconds) may not be long enough for the molecules to diffuse over the potential period, whereas such a diffusion transport is an integral stage of the Brownian motor functioning. Moreover, the diffusion stage is normally complicated by the partial localization of molecules in the potential minima, since ground-state molecular dipole moments are nonzero in the general case; as a consequence, the diffusion is not as efficient as that in the flashing potential energy model. Thus, to rationalize the very possibility of a "dipole photomotor" (a motor with a photoinduced change in the molecular dipole moment) functioning, it is necessary to estimate and compare the operating characteristics of real protein

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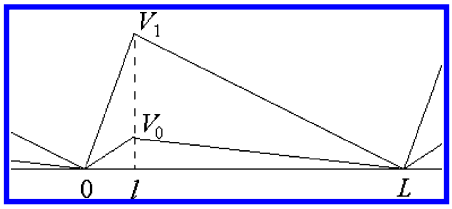

Figure 1. The potential energy profile for a particle in a sawtooth potential with fluctuating energy barrier heights.

motors and the suggested mechanism. In what follows, we show that a dipole photomotor is, beyond expectation, quite comparable with its protein counterpart in the average velocity, provided certain conditions are satisfied.

State Energies. The force acting on the dipole moment μ in the inhomogeneous electric field **E** is equal to $(\boldsymbol{\mu}\cdot\nabla)\mathbf{E}$. Since the electric field in biosystems is generated by a polar periodic structure of the cellular fiber with the period $L \sim 10$ nm, the corresponding amplitude of the changing potential energy of the dipole within the period L can be estimated as μE. The dipole moment fluctuations between the values μ_0 and μ_1 in the ground and excited states affect only the potential energy amplitudes, whereas the positions of its extrema remain unchanged. The simplest representation of the asymmetric periodic coordinate dependence of the potential energy $V(x)$ is a sawtooth function extensively used in the theory of Brownian motors. With regard to the constant positions of extremum points, it assumes the following form (see Figure 1):

$$V_i(x) = \begin{cases} \dfrac{V_i}{l}x, & 0 \le x \le l \\ \dfrac{V_i}{L-l}(L-x), & l \le x \le L \end{cases} \qquad (1)$$

This function enables one to conveniently calculate the motor velocity in relation to the potential profile fluctuations, and it is characterized by the minimum number of parameters, namely, the amplitude fluctuating between two values, $V_i = \mu_i E$ ($i = 0,1$), and the asymmetry coefficient, $\kappa = 1 - 2l/L$, which is sufficiently small in real biosystems. Such a dependence approximates well substrate-induced electric fields, which are represented by rapidly decreasing power-series expansions in the trigonometric functions $\sin(2\pi nx/L)$, $n = 1,2,...$ For instance, the sawtooth approximation of the function $\sin(2\pi x/L) + (1/4)\sin(4\pi x/L)$ implies the asymmetry coefficient $\kappa \approx 0.24$, which will be involved in further estimations. With the dipole moment μ written as a product of the charge q and the effective distance $r \sim 0.1$ nm (then μ is on the order of 1 D at q on the order of the electronic charge), and the potential specified as $\varphi \sim EL$, we obtain $\mu E \sim (r/L)q\varphi \sim 0.01q\varphi$, that is, the energy of interaction with the field proves to be 2 orders of magnitude smaller for a dipole than for a charge. A typical energy of a kinesin molecule in the field of the microtube substrate, $q\varphi$, is usually assumed to be of the same order as $10k_BT$, where k_BT denotes the thermal energy of molecules at room temperature T (k_B is the Boltzmann constant). Thus, $\mu E \sim 0.1k_BT$, suggesting that molecular dipoles are only slightly localized in the potential energy minima, in contrast to strongly localized charged kinesin molecules. With these estimates, the characteristic electric field intensities E caused by biological substrates are found to be about 10^5 V/cm.

State Lifetimes. The time it takes for a particle to diffuse to the distance L is estimated, in the order of magnitude, by the parameter $\tau_D = L^2/D$, where $D = k_BT/\zeta$ is the diffusion coefficient expressible in terms of the friction coefficient in a viscous medium, ζ. In its turn, the friction coefficient for a particle with a linear size R in a medium with a viscosity η is estimated as $\zeta \sim 10R\eta$. The quantity R for kinesin is known to be 10−100 nm (according to whether only a globular head or a whole protein macromolecule is taken into account). With the value $\eta \approx 10^{-9}$ pN·s/nm^2 substituted for water, we obtain $\zeta \sim 10^{-7}-10^{-6}$ pN·s/nm, so that the diffusion coefficient is estimated as $D \sim 10^{-11}-10^{-10}$ m^2/s, and the characteristic diffusion time is $\tau_D \sim 10^{-6}-10^{-5}$s (we put $k_BT \approx 4.1$ pN·nm at room temperature). If the so-called protein friction (the friction between the kinesin molecule and the substrate surface) is also included, the values of ζ can be even 2 orders larger, so that the value of τ_D can amount to 10^{-3} s.[7] On the other hand, the lifetime of the state with a certain nonzero potential energy of the protein particle is dictated by the duration of the ATP hydrolysis cycle, $\tau \sim 10^{-3}-10^{-2}$ s.[5,7] The above estimates suggest that $\tau_D \le \tau$, and hence the potential-free phase is long enough to provide an efficient diffusion of the particle.

Let us now estimate a diffusion time for a molecule with an alternating dipole moment in the field of the same substrate as that for kinesin assuming that the molecular linear size $R \sim 1$ nm is much less than that for the kinesin macromolecule. Then we have $\zeta \sim 10^{-8}$ pN·s/nm, $D \sim 10^{-9}$ m^2/s, and $\tau_D \sim 10^{-7}$ s. The excited-state lifetime of the molecule is determined both by the duration of electromagnetic pulses resonating with the first electronic transition and by the fluorescence lifetime. The former time parameter is easy to control by laser tuning, whereas the latter is an intrinsic molecular characteristic rarely exceeding $10^{-9}-10^{-8}$ s so that $\tau \ll \tau_D$.

Resulting Velocities. The nanoparticles under consideration move in the inertialess regime because the characteristic velocity relaxation time, $\tau_v = m/\zeta$ (m is the particle mass), is under 10^{-10} s, that is, much less than the characteristic diffusion time, τ_D. As a consequence, the motion of a particle fluctuating between two states with different energetic profiles obeys the Smoluchowski equation. If the potential energy fluctuations occur randomly in time with the frequency τ^{-1}, the equation should be supplemented with the terms accounting for the probabilities of transitions between the two states (see the Appendix). The application of this technique to nanomotors with fluctuating barriers has been described in the literature.[8,9] The differential equations defining the average velocity s of the unidirectional particle motion can be solved only numerically at an arbitrary value of the τ/τ_D ratio. Analytical solutions are possible in two particular cases, $\tau \gg \tau_D$ and $\tau \ll \tau_D$.

The case of $\tau \gg \tau_D$. The system has enough time to relax to the equilibrium state between the interstate switches.[10] One can concretely write eqs A3 and A4 derived in the Appendix so as to express an average velocity at long times τ with regard to the sawtooth potential energy profile (1):

$$s = \kappa\frac{L}{4\tau} f\left(\frac{V_0}{2k_BT}, \frac{V_1}{2k_BT}\right) \qquad (2)$$

where κ is the above-defined asymmetry coefficient, and the explicit form of the function $f(v_0, v_1)$ ($v_i = V_i/2k_BT$) appears as

$$f(v_0,v_1) = \frac{v_0}{\sinh^2 v_0} + \frac{v_1}{\sinh^2 v_1} - \frac{v_1 + v_0}{v_1 - v_0}\frac{\sinh(v_1 - v_0)}{\sinh v_0 \sinh v_1} \qquad (3)$$

At $V_0 = 0$, eqs 2 and 3 are reduced to the result obtained in the flashing potential energy model.[11] The low-temperature limiting behavior of the function $f(v_0, v_1)$ (at $v_i \to \infty$ and an arbitrary ratio $\alpha \equiv V_0/V_1$) is described by the expression

$$f(v_0, v_1) = \begin{cases} 0, & 0 < \alpha \le 1 \\ 1, & \alpha = 0 \\ 2\dfrac{1+\alpha}{1-\alpha}, & -1 \le \alpha < 0 \end{cases} \quad (4)$$

The jump of the function $f(v_0, v_1)$ from 0 to 2 in going from positive to negative α values in the vicinity of zero results from certain features of molecular motion at sufficiently low temperatures. In the case of $\alpha > 0$, the directed flow of the particles vanishes, since the diffusion stage becomes impossible, provided only barrier heights but not extremum positions fluctuate in the potential energy relief. The value $f(v_0, v_1) = 1$ at $\alpha = 0$ in the extremely asymmetric potential ($\kappa = 1$) implies that the diffusion motion stage leads a molecule to move to the right over the distance L in the time τ with the probability 1/2, so that the total velocity within the whole motion period, 2τ, appears as $s = L/(4\tau)$. At $\alpha < 0$, the diffusion motion stage is also absent (like in the case of $\alpha > 0$), but the potential energy minima and maxima interchange their places, as a fluctuation occurs. As a result, the molecule moves to the right with a probability equal to unity, and hence $s = L/(2\tau)$. This effect is consistent with the previously reported regularity:[12] omission of the diffusion stage, if caused by the shift between the extrema of the fluctuating potential, enhances the unidirectional particle flow. It is noteworthy that the model with the fluctuation-induced half-period shift in the potential energy profile underlies a variety of existing molecular motors distinguished by the high efficiency of energy conversion.[13−15]

The asymptotic behavior of the function $f(v_0, v_1)$ at $v_i \ll 1$ is described by the expression

$$f(v_0, v_1) = \frac{2}{45} v_1^3 (1+\alpha)(1-\alpha)^2 \quad (5)$$

It follows from eq 5 that the average velocity of unidirectional motion is proportional to the cubed small ratio V_1/k_BT, goes to zero at $\alpha = \pm 1$, and reaches the maximum at $\alpha = -1/3$.

The case of $\tau \ll \tau_D$. The system does not have enough time to come to equilibrium after the switch between two states occurs. Then we employ formula A5 (Appendix) with the sawtooth profile of the potential energy specified by eq 1 to derive

$$s = \frac{2\kappa}{(1-\kappa^2)^2 \sinh^2[v_1(1+\alpha)/2]} (1+\alpha)^3 (1-\alpha)^2 \frac{v_1^5}{\tau_D^2} \frac{\tau L}{\tau_D^2}. \quad (6)$$

Note that, at $|V_0| < V_1 \ll k_BT$, this expression characterizes a dipole photomotor and contains the same functional dependence on the potential energy parameters, v_1 and α, as in expression 5, with the ratio of potential energy amplitudes represented by the ground-to-excited-state ratio of the molecular dipole moments, $\alpha = \mu_0/\mu_1$. For photoexcited molecules, therefore, the average velocity of unidirectional motion changes nonmonotonically as the difference in polarity between the two states rises; it reaches the maximum in the case where the dipole moment changes its sign and increases 3-fold in absolute magnitude on excitation. The dependence of the average velocity on the dimensionless barrier height v_1 also shows an interesting behavior. At $\tau \gg \tau_D$, the velocity s increases monotonically with rising v_1, which implies that the localization of a molecule in the state with high barriers favors the unidirectional motion generation. At $\tau \ll \tau_D$, the v_1 dependence of s becomes nonmonotonic with a maximum at $v_1(1+\alpha) \approx 4.928$. A decrease in s at large v_1 is attributed to the fact that a short time τ of the diffusion stage does not permit a strongly localized molecule to reach the position of the closest potential maximum from which it can fall into the next minimum, and thus it preferably stays in the same well. Hence, for a dipole photomotor to generate unidirectional motion, a certain thermal-noise-induced delocalization of the molecule in the excited state is necessary.

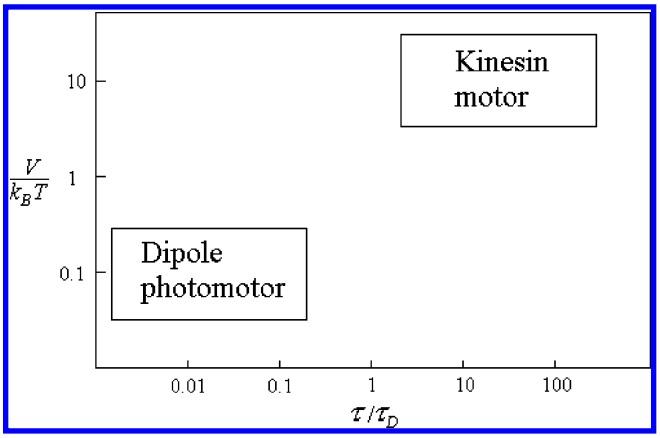

Figure 2. The operating regions for a typical protein (kinesin) motor and a dipole photomotor in the energy−time coordinates.

Equation 6 employed with the appropriate parameter values—$\mu_0 = 1$ D, $\mu_1 = 10$ D, $E = 10^5$ V/cm, $k_BT = 4.1$ pN·nm (so that $v_1 \approx 0.04$ and $\alpha = 0.1$), $L = 10$ nm, $\kappa = 0.24$, $\tau = 10^{-9}$ s, and $\tau_D = 10^{-7}$ s—yields the estimated average velocity $s \approx 125$ nm/s, which is of the same order of magnitude as the corresponding value for the kinesin motor.[8] The latter is characterized by the estimates $v_1 \gg 1$, $\alpha = 0$, $f \approx 1$, and $\tau = 10^{-3}$ s $\ge \tau_D$, which enables us to use relation 2, affording $s = \kappa L/(4\tau) \approx 600$ nm/s.

Operating Regions and Guidelines for Design of the Motors. The comparative analytical estimation demonstrates that, although the "classical" protein motor and the dipole photomotor function in essentially different ranges of energy and time parameters (see Figure 2), they provide much the same average velocity of the unidirectional particle flow. The close velocity values originate from the compensation of opposite effects: on one hand, the energy of interaction with the substrate is much less for a dipole photomotor than for a protein motor; on the other hand, the fluorescent-state lifetime in a dipole photomotor is very short compared to the duration of the ATP hydrolysis cycle in a protein motor. To design promising dipole photomotors, one should select molecules with the strongly differing dipole moments in the ground and excited states[16] and the long fluorescent-state lifetime (on the order of 1−10 ns), the former factor being more significant according to eq 6. These requirements are satisfied by many merocyanines representing a widely applied class of polymethine dyes;[17] some of them having sufficiently long-living fluorescent states[18,19] deserve special attention. It is also advantageous that compounds of this kind can be treated by a convenient method for selecting molecules with a large ground-to-excited-state change in dipole moment.[16] It should be noted that the maximum velocity of unidirectional motion would be expected for the molecules with $\mu_0/\mu_1 = -1/3$. The unidirectional motion velocity can be additionally increased by using a substrate that generates an electric field of a larger intensity and asymmetry.

Appendix

Consider the dynamics for a Brownian particle motion in the periodic potentials $V_0(x)$ and $V_1(x)$ alternating with the frequency

τ^{-1}. The particle distribution function satisfies the Smoluchowski equation[20] with an additional term accounting for random jumps of the particle between the potentials:

$$\frac{\partial \rho_i(x,t)}{\partial t} = -\frac{\partial j_i(x,t)}{\partial x} - \tau^{-1}[\rho_i(x,t) - \rho_{i'}(x,t)],\ i,i' = 0,1;1,0. \tag{A1}$$

Here the particle flows $j_i(x,t)$ are specified as

$$j_i(x,t) = -D\mathrm{e}^{-\beta V_i(x)}\frac{\partial}{\partial x}[\mathrm{e}^{\beta V_i(x)}\rho_i(x,t)] \tag{A2}$$

where D is the diffusion coefficient and $\beta = (k_B T)^{-1}$ is the reciprocal temperature, with the Boltzmann constant denoted by k_B, and the absolute temperature denoted by T. The total flow of particles $J \equiv j_0(x) + j_1(x)$ is constant in the stationary state; it dictates the average velocity of the particle unidirectional motion, $s = JL$ (where L is the potential period).

Assuming that thermodynamic equilibrium in either potential is established in time τ (i.e., $\tau \gg \tau_D$, where $\tau_D = L^2/D$), the distribution functions obey the Boltzmann distribution:

$$\rho_i(x) = \mathrm{e}^{-\beta V_i(x)}/2\int_0^L \mathrm{e}^{-\beta V_i(x)}\mathrm{d}x,\ i = 0,1 \tag{A3}$$

In this case, integration of eqs A1 and A2 in the approximation linear in τ^{-1} leads to a simple expression for the flows (see, e.g., refs 10 and 11 where an analogous relation was obtained for deterministic potential switching):

$$j_i(0) = \tau^{-1}\frac{\int_0^L \mathrm{d}x\mathrm{e}^{\beta V_i(x)}\int_0^x \mathrm{d}x'[\rho_i(x') - \rho_{i'}(x')]}{\int_0^L \mathrm{d}x\mathrm{e}^{\beta V_i(x)}},\ i,i' = 0,1;\ 1,0 \tag{A4}$$

Another situation that allows for analytical solutions of eqs A1 and A2 in the stationary state refers to the short times τ ($\tau \ll \tau_D$). Invoking the perturbation theory with the small parameter τ (as, for instance, in refs 3 and 21), we arrive at the expression for the average velocity of the motor:

$$s = \frac{\tau L D^2 \beta^3 \int_0^L \mathrm{d}x V'_+(x)[V'_-(x)]^2}{2\int_0^L \mathrm{d}x\mathrm{e}^{-\beta V_+(x)}\int_0^L \mathrm{d}x\mathrm{e}^{\beta V_+(x)}} \tag{A5}$$

where $V_\pm = (V_1 \pm V_0)/2$, and $V'_\pm(x)$ denotes the first derivative of $V_\pm(x)$ with respect to x.

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