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INTERACTION OF TERAHERTZ RADIATION WITH DNA

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A nonlinear model of DNA dynamics with coupling between conformational dynamics and proton tunneling is presented. It is demonstrated that terahertz radiation can influence both vibrational excitations and proton motion in DNA hydrogen bonds. The irradiation at the edge of far IR spectral range can promote proton tunneling. If the radiation frequency matches the vibrational mode, the generation of localized excitations in form of dissipative solitons is possible. These solitons decrease the probability of proton tunneling.

Keywords: DNA, terahertz radiation, proton tunneling, dissipative soliton.

1. Introduction

There has been renewed interest in understanding the dynamics and properties of DNA due to recent advances in both single-molecule experiment techniques [1], molecular dynamic simulations [2] and theoretical modeling for such nanosystems [3]. Such modeling played an important step towards nanobiotechnology [4, 5].

It is believed that many biological processes depend on the nonlinear properties of DNA. A number of theoretical studies of nonlinear physics of DNA were related to localized conformational excitations [3] and electronic conductivity [5]. The motion of protons in hydrogen bonds causes a great number of interesting physical effects. The importance of proton tunneling in chemical and biological systems is well known for the DNA base pairing and mutagenesis [6, 7]. The proton can tunnel into less energy favorable tautomer state of base pair, which may cause incorrect pairing during DNA replication. There are a lot of theoretical studies of proton tunneling in such systems [7–9]. An important conclusion from these studies is that the vibrational excitations in conformational subsystem can significantly influence the proton tunneling.

The frequencies of vibrationalrotational transitions of biological molecules and frequencies of intermolecular interactions as well as the frequencies of tunneling transitions fall into terahertz range (0.1-10 THz). It is demonstrated that terahertz radiation can induce conformational changes in proteins and nucleic acids [10], and also can influence the number of spontaneous and induced point mutations [11]. However, the underlying physical mechanisms of this interactions remain unclear. Some theoretical models suggest that collective nonlinear excitations can be responsible for such effects [12].

In the present paper a response of DNA to external terahertz electric field is studied on a basis of nonlinear model taking account of coupling between elastic vibrational dynamics and proton tunneling.

2. Theoretical model

Let us consider the self-consistent model of conformational and proton dynamics. A movement of the proton can be considered inside the asymmetric two-well potential per each hydrogen bond, as was initially proposed by Löwdin [6]. In conditions of terahertz excitation one can neglect the upper proton states considering only ground states in the right and left wells.

In this case it is useful to consider the tunneling dynamics within the framework of pseudospin formalism [13]. The corresponding proton Hamiltonian $\hat{H}_p$ can be represented as:

$$\hat{H}_p = -\Omega_0 \sum_{n,i} \hat{S}^x_{n,i} - \Delta \sum_{n,i} (-1)^{i+1} \hat{S}^z_{n,i} - \frac{1}{2} J_\perp \sum_{n,i \neq j} \hat{S}^z_{n,i} \hat{S}^z_{n,j} - \frac{1}{2} \sum_{n,i,j} J_{ij} (\hat{S}^z_{n+1,i} \hat{S}^z_{n,j} + \hat{S}^z_{n-1,i} \hat{S}^z_{n,j}), \quad (1)$$

where indexes 'n' correspond to n-th base pair and indexes i, j denote the number of hydrogen bonds in a base pair (from 2 in Adenine/Thymine to 3 in Guanine/Cytosine). Here pseudospin operators $\hat{S}^z$ and $\hat{S}^x$ have the sense of the electrical dipole moment operator and the tunneling operator, respectively, Ω_0 is the tunneling integral, $J_\perp$ and J_{ij} are the exchange integrals, and Δ is the asymmetry parameter of the potential well.

The conformational subsystem can be treated classically [3] since it corresponds to collective movements of large groups of atoms. The Hamiltonian is taken as in a well-known Peyrard-Bishop-Dauxois model (PBD) [14]

$$H_c = \sum_n \left[\frac{m}{2} \dot{r}_n^2 + \frac{K}{2} (r_{n+1} - r_n)^2 + D_n (\mathrm{e}^{-\beta r_n} - 1)^2 \right], \quad (2)$$

where r_n is the relative displacement (stretching) of base pairs inside the nucleotide, m is the reduced mass of the nucleotide, coefficient K characterizes the stacking interaction, and parameters D and β define the potential depth and width.

The interaction of proton subsystem with vibrations and terahertz electric field E is taken into account by interaction operator

$$\hat{H}_{int} = -\mu E \sum_{n,i} \hat{S}^z_{n,i} - g \sum_{n,i} r_n (\hat{S}^z_{n,i} - \bar{S}^z_{n,i}) - \sum_{n,i} \Omega_1 (\hat{S}^x_{n,i} - \bar{S}^x_{n,i}), \quad (3)$$

where μ is the dipole moment, and g is proportional to the linear piezoeffect coefficient, $\bar{S}^z$ and $\bar{S}^x$ are the equilibrium mean values of the pseudospin operators. The last sum corresponds to modulation of tunneling integral and can be approximated as $\Omega_1 = \Omega_0(\exp(-\sigma r_n^2/2) - 1)$, where σ is the material constant which is reversely proportional to the De Boer parameter of proton in DNA.

The Heisenberg equations of motion for the mean values of the pseudospin operators supplemented by phenomenological relaxation terms in the random-phase approximation have the form:

$$\hbar \frac{dS^x_{n,i}}{dt} = M^z_{n,i} S^y_{n,i} - (S^x_{n,i} - \bar{S}^x_{n,i}) \left(\frac{\cos\alpha}{T_1^*} + \frac{\sin\alpha}{T_2^*} \right), \quad (4)$$

$$\hbar \frac{dS^y_{n,i}}{dt} = -M^z_{n,i} S^x_{n,i} + M^x_{n,i} S^z_{n,i} - S^y_{n,i}/T_2^*, \quad (5)$$

$$\hbar \frac{dS^z_{n,i}}{dt} = -M^x_{n,i} S^y_{n,i} - (S^z_{n,i} - \bar{S}^z_{n,i}) \left(\frac{\cos\alpha}{T_2^*} + \frac{\sin\alpha}{T_1^*} \right), \quad (6)$$

where

$$M^{x,z}_{n,i} = -\frac{\partial (H_p + H_{int})}{\partial S^{x,z}_{n,i}}, \ \mathrm{tg}\alpha = \bar{S}^z_{n,i} / \bar{S}^x_{n,i},$$

T_1^*, T_2^* are the longitudinal and transverse relaxation times of pseudospins, and the equilibrium mean values of the pseudospin operators $\bar{S}^z$ and $\bar{S}^x$ are defined through the molecular field components:

$$\bar{S}^{x,z}_{n,i} = \frac{\bar{M}^{x,z}_{n,i}}{2M_{n,i}} \mathrm{th} \frac{M_{n,i}}{2k_bT}, \ \bar{M}^{x,z}_{n,i} = -\frac{\partial H_p}{\partial S^{x,z}_{n,i}}, \ M_{n,i} = \sqrt{(\bar{M}^x_{n,i})^2 + (\bar{M}^z_{n,i})^2}.$$

The equations for the conformational subsystem under conditions of low-amplitude vibrations have the following form:

$$\frac{d^2 r_n}{dt^2} - \frac{K}{m}(r_{n+1} + r_{n-1} - 2r_n) + \omega_a^2 r_n - \frac{3}{2}\beta\omega_a^2 r_n^2 + \frac{7}{6}\beta^2\omega_a^2 r_n^3 = \\ = \frac{g}{m}\sum_i (S_{n,i}^z - \bar{S}_{n,i}^z) + \frac{2\sigma}{m} r_n \sum_i (S_{n,i}^x - \bar{S}_{n,i}^x) - \gamma_R \frac{dr_n}{dt} + \frac{\chi E^2}{8\pi m} r_n, \quad (7)$$

Additionally the external damping term (with damping constant γ_R) and Maxwell-Helmholtz pressure term are taken into account. The last one arises from the uncompensated difference in dielectric permittivity between disturbance in DNA and surrounding medium (water). The equations (4)-(7) describe the self-consistent dynamics of proton and conformational systems under the action of external terahertz electric field.

3. Parametric excitation of conformational solitons and their influence on proton dynamics

The response of the system (4)-(7) posses high frequency modes, which correspond to tunneling transitions. Unlike the typical hydrogen-bonded crystals, in DNA the tunneling integral is much smaller than asymmetry parameter of potential. This gives relatively small probability for finding the proton in the tautomer positions $P_0^* \sim 10^{-4}$. The tunneling frequencies are determined mostly by the asymmetry parameter Δ, and their values are at the order of $10 - 20$THz [9]. The slow conformational subsystem cannot follow such excitations, therefore the increase of tunneling probability into tautomer state occurs under irradiation. This simple conclusion is supported by experiments, where the increase of point mutations have been observed after irradiation in the far IR spectral range [11]. The exact expression for response of the system can be calculated in a usual form [13].

The excitation of conformational subsystem with low frequency (optical phonon mode) requires special consideration. Its characteristic frequency (taken at the center of Brillouin zone) is $\omega_a = \sqrt{2D\beta^2/m} \sim 2 - 3$ THz [8, 12].

Since the conformational system is much slower, the response of proton subsystem can be calculated using the approximation of adiabatic following [15, 16]. In general case we obtain an expansion

$$S_{n,i}^z = \bar{S}_{n,i}^z + (s_{n,i}^{(1)} + s_{n,i}^{(11)} r_n + s_{n,i}^{(12)} r_n^2 + ...)E + (s_{n,i}^{(2)} + s_{n,i}^{(21)} r_n + s_{n,i}^{(22)} r_n^2 + ...)E^2 + ... \quad (8)$$

The calculation of probability for finding the proton in the tautomer state of base pair A-T or G-C in the leading order gives:

$$P^* = P_0^* - \chi_{i,n}^{(1)} r_n^2 + \chi_{i,n}^{(2)} E^2 + \chi_{i,n}^{(12)} r_n E + ... \quad (9)$$

The second term is produced by the modulation of the tunneling integral, while the others result from the tunneling far from the resonant frequency. Thus, there are competing effects, which depend on conformational disturbance.

Let us consider small amplitude oscillations in conformational subsystem. The solution in a semidiscrete approximation can be cast as

$$r = r_{(0)}(\zeta - vt)\exp[i(\omega_a(q)t - qn)] + c.c. + r_{(1)}(\zeta - vt) + r_{(2)}(\zeta - vt)\exp[2i(\omega_a(q)t - qn)] + c.c.. + ..., \quad (10)$$

where $\vec{q}$ is the reciprocal lattice vector, ζ is the coordinate along the DNA axis. Since the characteristic size of DNA is much lower than terahertz wavelength, the expression for the external electric field with frequency ω takes form $E = E_0 \exp[i\omega t] + c.c.$. Therefore the resonance is possible for the nearly standing excitation ($q \approx 0$).

The resulting equation for the slowly varying amplitudes in the dimensionless form can be written as

$$2i\frac{\partial\psi}{\partial\tau}-\frac{\partial^2\psi}{\partial\xi^2}-|\psi|^2\psi=-i\gamma\psi+\varepsilon\psi^*\mathrm{e}^{-2i\varepsilon\tau}, \tag{11}$$

where $\psi=(2\beta)^{-1}\beta_s r_{(0)}\exp(2i\varepsilon\tau)$, β_s -denotes the modulation of nonlinear coefficient by the proton response, $\tau=\omega_a t$, $\xi=\zeta/L_0$, $L_0=(\omega_a/a)\sqrt{2m/K}$ is the characteristic spatial scale, a is the base spacing in DNA, $\gamma=\gamma_R/\omega_a$. The main influence of external field is given by ponderomotive force, therefore $\varepsilon\approx a\chi E_0^2/(8\pi m\omega_a^2)$.

The approximate solution of (11) can be found in form of perturbed soliton of nonlinear Schrödinger equation locked to the external frequency [17]

$$\psi=2\sqrt{2}i\eta\,\mathrm{sech}(\eta\xi)\mathrm{e}^{-i\Phi}, \tag{12}$$

$$\Phi=2\varepsilon\tau+\arccos\left(\frac{2\gamma}{\varepsilon}\right)/2-\pi/2,\quad \eta^2=2\varepsilon+\sqrt{\varepsilon^2/4-\gamma^2},$$

This solution has the only free parameter ε, which correspond to external parametric pumping by terahertz electric field. Therefore the solution (12) has a sense of dissipative soliton. We should note that parametrically driven solitons of equation (11) can form complexes [18] or transfer to periodic or quasiperiodic structures.

The structure of (12) requires $\varepsilon>2\gamma$, that gives a threshold for excitation depending on the terahertz field intensity. Taking $\gamma\sim 10^9\mathrm{s}^{-1}$, we can make an estimation of threshold intensity $I_{thr}\sim 10-100$ mW/cm^2. This estimation agrees reasonably with experimentally observed effects of change in DNA conformation and function [10, 11, 19]. An experimental observation in the neuron system [20] gives even lower threshold values ~ 1 mW/cm^2.

After substitution of characteristic values of induced deformation from (12) to (9) we obtain $(\tilde{\chi}_{i,n}^{(1)}-\chi_{i,n}^{(2)}-\tilde{\chi}_{i,n}^{(12)})E_0^2>0$, thus the localized deformation decreases the probability of tautomer shift. This is confirmed by the experimental observations [11].

4. Conclusion

On the basis on simple nonlinear model of DNA dynamics it is demonstrated that terahertz radiation can influence both vibrational excitations and proton motion in DNA hydrogen bonds. It is highlighted that irradiation at the edge of far IR spectral range can promote proton tunneling and thus make the tautomer states of DNA base pairs to be more probable. If the irradiation frequency matches the vibrational mode, the parametric generation of localized excitations is possible. These dissipative solitons decrease the probability of tautomer shift due to modulation of the tunneling integral.

This preliminary theoretical results can qualitatively explain the results of experimental observations of terahertz influence on the number of spontaneous and induced point mutations [11]. The low-amplitude DNA collective breathing modes can serve as precursors to generation of the transcription bubbles and other large-scale conformational changes such as B-Z transition. This may relate to experimental observations of DNA conformation change [10] and gene transcription [19] in the presence of terahertz field. However, the precise mechanisms of these effects are too complex and require further experimental and theoretical studies of such nanosystems.

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