Electron-molecular-vibration coupling for small polarons in DNAs

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Within a tight-binding electron-phonon interacting model, we calculated the spectrally resolved polaron binding energy between electrons and phonons and between holes and phonons on poly(dA)·poly(dT) and poly(dG)·poly(dC). Poly(dA)·Poly(dT) is a DNA where one single strand consists only of adenine(A) and the other single strand consists only of thymine(T), while Poly(dG)·Poly(dC) is a DNA where one single strand consist only of guanine(G) and the other of cytosine(C). We found that the polaron binding energies of poly(dA)·poly(dT) were larger than those of poly(dG)·poly(dC), and that the polaron binding energy and the electrical conductance were strongly temperature dependent. These findings agree well with the current experimental data. We concluded that small polaron hopping occurs by a conduction mechanism on the DNA molecules examined.

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The conduction in DNA has been investigated from the viewpoint of the electron transfer by measuring the photoinduced electron transfer velocity in donor-DNA-acceptor molecules [1–4]. In recent years, the development of nanosize technology has enabled measurements of electric conduction in a few DNA molecules, and the conduction in DNA is now investigated from the viewpoint of the electron transport. DNA is a simple one-dimensional polymer composed of a layered structure consisting of base molecules. Precise details concerning the electric conduction mechanism in DNA remains unknown. Some reports have described the transport property of DNA as an insulator [5–7], while others claimed that it resembled a semiconductor [8,9] or superconductor [10]. From a theoretical calculation based on a band theory of the conduction in DNA assuming an extremely narrow bandwidth [11], we assumed the polaron conduction to be the conduction mechanism in DNA.

Yoo *et al.* measured the electric conduction of poly(dA)·poly(dT) and poly(dG)·poly(dG) with nanosize electrodes and found that the electric conductivity was strongly temperature dependent [9]. However, they reported that the dependency was quite different between these two DNA types. The ratio of the conductivity of poly(dA)·poly(dT) at room temperature and at 50 K, $\sigma(\mathrm{rt})/\sigma(50)$, was approximately 10^4, while that of poly(dG)·poly(dG) was approximately 10^2. They also analyzed the conductivity based on a small polaron model and found that the activation energy (E_a) of polaron hopping was temperature dependent. In their analysis, the activation energy of poly(dA)·poly(dT) and poly(dG)·poly(dC) was 0.18 and 0.12 eV, respectively, at a temperature higher than 160 K. Electrons or holes were coupled with phonons of 1.3×10^{14} Hz in the former case, and with phonons of 1.8×10^{14} and 5.2×10^{12} Hz in the latter, reflecting a clear difference between the two DNA types. In order to delineate the polaron formation mechanism, it is essential to determine which phonon interacts with the electrons and holes. Clarification of this point is critical in terms of accounting for the temperature dependence of E_a and the conductivity, in addition to explaining the difference in physical properties between the two DNA types.

In this paper we theoretically calculated the spectrally resolved polaron binding energy between electrons and phonons or between holes and phonons, based on a Hamiltonian in the tight-binding band approximation with no electron-electron interactions. We provide a detailed description of the polaron formation mechanism by showing that the polaron binding energy of poly(dA)·poly(dT) is larger than that of poly(dG)·poly(dC), and that electrons and holes interact strongly with high-energy phonons. We also detail the results of a calculation that is consistent with three experimental results: the E_a of poly(dA)·poly(dT) is larger than the E_a of poly(dG)·poly(dC), the E_a is temperature dependent, and the temperature dependence is quite different between the two DNA types. We then show theoretically that the conduction mechanism of the two DNA types can be explained in terms of small polarons.

We first constructed a *B*-type structure that contains sugar, a phosphate group, and sodium as a counter cation with a unit cell composed of 10 base molecule pairs. Molecular dynamics calculations were then employed to relax the structure [11]. The valence and conduction bands of poly(dA)·poly(dT) and poly(dG)·poly(dC) are formed by highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of base molecules, respectively. The electron density, therefore, is localized on the base molecules, indicating that the sugar, phosphate group, and sodium do not act as a conduction path. In an effort to obtain the energy of polaron coupling between the molecular vibration and the electrons or holes, we focused on the base pairs of adenine-thymine and guanine-cytosine from the relaxed structure. Using these base pairs as an initial structure, we performed structural optimization by the density functional method with the base functions 6-31G* [12] and calculated the molecular vibration frequency and the polaron

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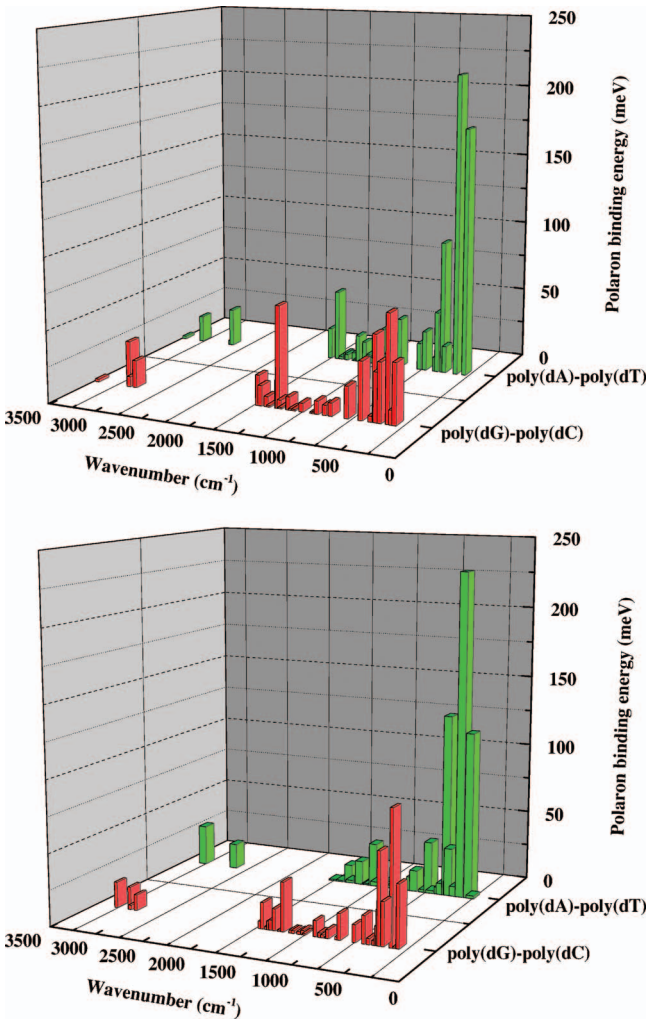

FIG. 1. (Color) Polaron binding energy spectra of (a) electron-molecular-vibration coupling and (b) hole-molecular-vibration coupling on poly(dA)·poly(dT) and poly(dG)·poly(dC) as a function of wave numbers.

binding energy. When we used the A-type structure composed of 11 base pairs as an initial structure, we obtained base pairs of the same optimized structure as those obtained from the B-type structure.

To calculate the polaron binding energy between electrons and phonons and between holes and phonons, we used the following Hamiltonian of one-dimensional isolated chains of N base pair molecules:

$$H = \sum_j \varepsilon_j c_j^\dagger c_j + \sum_n \left(b_n^\dagger b_n + \tfrac{1}{2}\right)\hbar\omega_n + \sum_{j,n} g_{jn} c_j^\dagger c_j (b_n^\dagger + b_n)\hbar\omega_n + \sum_{i,j} t(c_i^\dagger c_j + \text{H.c.}), \quad (1)$$

where $c_j^\dagger$ and c_j represent the creation and annihilation operators for an electron (or hole) on the jth base molecule pair, $b_n^\dagger$ and b_n represent the creation and annihilation operators, respectively, of a phonon of mode n with energy $\hbar\omega_n$, g_{jn} represents a dimensionless coupling constant defined in Eq. (2) [13,14], t denotes the transfer integral between the base pair molecules, and the bandwidth W is given by 4 t. The electron-phonon coupling constant is given by

$$g_{jn} = \frac{1}{\sqrt{2N}\hbar\omega_n}\left(\frac{\partial\varepsilon_j}{\partial Q_n(j)}\right)_0, \quad (2)$$

where ε_j is the energy of LUMO for the jth base pair molecule and Q_n represents the normal coordinates of the mode n. The hole-phonon coupling constant is given by interpreting ε_j in the above equation as the energy of HOMO for the jth base pair molecule. The polaron binding energy between the electron phonon or hole phonon is described by the following equation with the corresponding coupling constants [13,14]:

$$E_b = \sum_n g_{jn}^2 \hbar\omega_n. \quad (3)$$

The spectrally resolved polaron binding energy of adenine-thymine pairs and guanine-cytosine pairs is shown in Fig. 1, and large polaron binding energy is summarized in Tables I and II [15–18]. The assignment of the vibration mode to the molecular vibration frequency that we calculated was performed in the calculation of g_{jn}. The electron-phonon

TABLE I. Frequencies, binding energy of electron- and hole-molecular-vibration coupling, and assignment of poly(dA)-poly(dT). ω_i, ω_{exp}, ε_{ep}, and ε_{hp} represent the calculated and experimental frequencies, and the polaron binding energy of electron- and hole-molecular-vibration coupling, respectively. A, T, and H show adenine and thymine molecule, and hydrogen atoms involved in hydrogen bonding, respectively.

ω_i (cm^{-1})	ω_{exp} (cm^{-1}) [15,16]	ε_{ep} (meV)	ε_{hp} (meV)	Assignment [15,16]
313	327	176	118	A: NH_2 bending
408	391	213	230	T: C═O bending
553	545	94	129	T: bending
1753	1742–1759	50	1	T: C═O stretching
2920		27	18	H: stretching

TABLE II. Frequencies, binding energy of electron- and hole-molecular-vibration coupling, and assignment of poly(dG)-poly(dC). ω_i, ω_{exp}, ε_{ep}, and ε_{hp} represent the calculated and experimental frequencies, and the polaron binding energy of electron- and hole-molecular-vibration coupling, respectively. G, C, and H the show the guanine and cytosine molecule, and hydrogen atoms involved in the hydrogen bonding, respectively.

ω_i (cm^{-1})	ω_{exp} (cm^{-1}) [17,18]	E_{ep} (meV)	E_{hp} (meV)	Assignment [17,18]
413	400	74	92	C: bending
539	557	34	63	G: bending
548	533	59	24	C: bending
1539	1550	1	34	G: bending
1566	1538	70	0	C: bending
3122	3114, 3169	32	16	H: stretching

TABLE III. Calculated polaron binding energy of electron- and hole-molecular-vibration coupling of poly(dA)poly(dT) and poly(dG)poly(dC). Energy units in eV. W_v, W_c, E_b^{ep}, and E_b^{hp} represent the bandwidths of the valence and conduction bands, and the polaron binding energy of electron- and hole-molecular-vibration coupling, respectively.

	W_v [11]	W_c [11]	E_b^{ep}	E_b^{hp}
A-poly(dA)·poly(dT)	0.244	0.360	0.866	0.745
A-poly(dG)·poly(dC)	0.081	0.133	0.582	0.493
B-poly(dA)·poly(dT)	0.045	0.120	0.866	0.745
B-poly(dG)·poly(dG)	0.421	0.143	0.582	0.493

binding energy of adenine-thymine pairs is represented by large values such as 213, 176, 94, 50, and 27 meV at 408, 313, 553, 1753, and 2920 cm^{-1}, respectively. The vibrations at 408 and 1753 cm^{-1} correspond to the in-plane bending and stretching modes of the carbon-oxygen double bond of the thymine molecule. The vibration at 313 cm^{-1} corresponds to the in-plane bending mode of NH_2 of the adenine molecule. The vibration at 553 cm^{-1} corresponds to the in-plane bending mode of the carbon-nitrogen bond of the thymine molecule and that at 2920 cm^{-1} corresponds to the in-plane stretching mode of the hydrogen of the thymine molecule that is involved in hydrogen bonding. In guanine-cytosine pairs, the in-plane bending vibration mode of the carbon-nitrogen double bond ($C{=}NH_2$) of the cytosine molecule is located at 413 cm^{-1} and has the largest binding energy, being 74 meV. The large binding energy of 59 and 70 meV at 548 and 1566 cm^{-1}, respectively, corresponds to the in-plane bending vibration modes of the carbon-nitrogen bond of the cytosine molecule. Furthermore, the large binding energy of 32 meV at 3122 cm^{-1} corresponds to the in-plane stretching vibration mode of the hydrogen involved in hydrogen bonding, as in the case of adenine-thymine.

Large hole-phonon binding energies of the adenine-thymine pairs of 230, 129, and 118 meV at 408, 553, and 313 cm^{-1}, respectively, were found, not unlike the trend observed for the electron-phonon binding energy. The binding energy of 29 meV at 3285 cm^{-1} corresponds to the molecular vibration related to the hydrogen bond in the adenine molecule. The largest binding energy in the guanine-cytosine pairs of 92 meV at 413 cm^{-1} is not unlike that observed for the electron-phonon binding energy. The second-largest binding energy of 63 meV at 529 cm^{-1} corresponds to the in-plane stretching mode of the carbon-nitrogen bond of the guanine molecule. The binding energy of 34 meV at 1539 cm^{-1} corresponds to the in-plane bending vibration mode of the guanine. As in the other molecules, the in-plane stretching vibration mode at 3122 cm^{-1} of the hydrogen involved in the hydrogen bond of the guanine molecule yields a relatively high binding energy of 16 meV.

As shown above, the characteristic feature of the electron-phonon and hole-phonon interaction in poly(dA)·poly(dT) and poly(dG)·poly(dC) is that the electron or hole is coupled strongly with the vibration of the atoms involved in the hydrogen bonding. Alexandre *et al.* calculated the polaron coupling energy of poly(dG)·poly(dC) from the energy difference between the neutral state and monovalent state of four guanine-cytosine pairs [19]. Their results showed that the variation in the distance between the hydrogen and oxygen involved in hydrogen bonding, namely the vibration of atoms involved in hydrogen bonding, is strongly coupled with holes. This is consistent with our results. Furthermore, it was shown by application of an infrared absorption measurement that the molecular vibration related to the hydrogen bond was coupled with electrons or holes [20]. This is also consistent with our results.

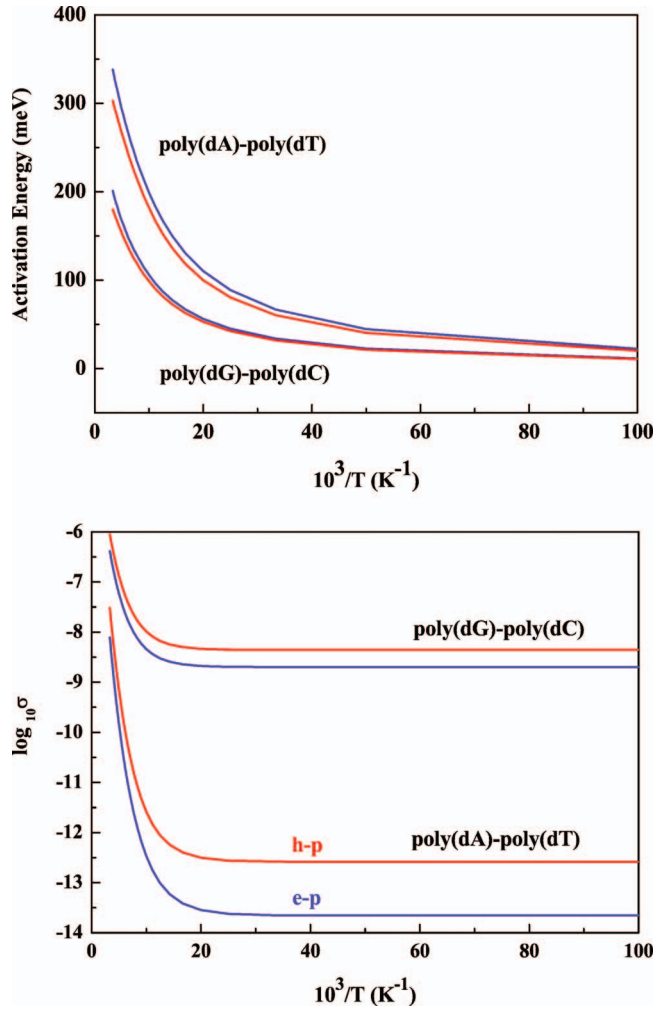

FIG. 2. (Color) Temperature dependence of (a) polaron activation energy and (b) electrical conductance of poly(dA)·poly(dT) and poly(dG)·poly(dC). E_{ep} and E_{hp} represent the activation energy of the electron-phonon and hole-phonon, respectively. The *e-p* and *h-p* indicate the conductance for electron-phonon and hole-phonon coupling, respectively.

The electron-phonon binding energy E_b^{ep} of poly(dA)·poly(dT) and poly(dG)·poly(dC) is 0.866 and 0.582 eV, respectively, and the hole-phonon coupling energy E_b^{hp} of poly(dA)·poly(dT) and poly(dG)·poly(dC) is 0.745 and 0.493 eV, respectively. The electronic state of poly(dA)·poly(dT) and poly(dG)·poly(dC) differs between the *A*- and *B*-type structures [11]. The bandwidth of the va-

lence (W_v) and conduction (W_c) bands is summarized in Table III. If we compare the polaron binding energy with the bandwidth of poly(dA)·poly(dT), we find that the polaron binding energy is greater than 2.4 times the bandwidth of the *A*-type structure, while E_b^{ep} and E_b^{hp} are 7 and 17 times larger, respectively, than the bandwidth of the *B*-type structure, indicating that small polarons were well formed in the *B*-type structure [21]. In poly(dG)·poly(dC), on the other hand, both electrons and holes form small polarons in the *A*-type structure since $E_b/W > 4$. Both carriers also form small polarons in the *B*-type structure of poly(dG)·poly(dC), although it should be noted that the localization of the polarons is extremely weak, compared to polarons in other DNA types, since $E_b^{hp} \cong W_v$. Therefore the electric conduction mechanism in both DNA types can be accounted for in terms of hopping of the small polarons and the E_b/W values show that the electrons are coupled more strongly than holes. Kato *et al.* employed a resonant photoemission spectral study and demonstrated that the conduction band electrons of these DNA types are strongly localized [22], which agrees qualitatively with our calculated results.

The Holstein model with dispersionless phonons gives the polaron activation energy as $E_a = E_b/2$ at a high temperature range $kT \gg \hbar\omega_n$ [21]. However, electrons and holes in DNA are coupled with high-energy phonons and therefore the activation energy [23] is given by

$$E_a = 2kT \sum_n g_{jn}^2 \tanh\left[\frac{\hbar\omega_n}{4kT}\right]. \tag{4}$$

The activation energy is temperature dependent as in Fig. 2(a) and the energy is always higher in poly(dA)·poly(dT) than in poly(dG)·poly(dC) at any temperature. This agrees qualitatively with the results given by Yoo *et al.* [9]. The dependence of E_a on temperature for both DNA types results from the coupling of electrons or holes with high-energy phonons possessing energy higher than kT.

The conductivity is given by $\sigma = \sigma_0 \exp(-E_a/kT)$ if the activation energy is described by Eq. (4). The dependence of conductivity on temperature was calculated by employing 100 and 1.3 MΩ as the room-temperature resistivity of poly(dA)·poly(dT) and poly(dG)·poly(dC), respectively [9]. The result is shown in Fig. 2(b) and $\sigma(\mathrm{rt})/\sigma(50)$ of poly(dA)·poly(dT) and poly(dG)·poly(dC) is approximately 10^5 and 2×10^2, respectively, which is consistent with the experimental results, being 10^4 and 10^2, respectively. The large difference observed in the dependence of conductivity on temperature can be attributed to the fact that the coupling between molecular-vibration modes with an energy less than 500 cm^{-1} and electrons or holes is much stronger in poly(dA)·poly(dT) than in poly(dG)·poly(dC), as shown in Fig. 1. The temperature dependence we calculated of the conduction in poly(dG)·poly(dC) does not agree with the experimental result under 50 K, although the cause is unclear.

In summary, we theoretically calculated the coupling energy of electron-phonon pairs or hole-phonon pairs of poly(dA)·poly(dT) and poly(dG)·poly(dC). The polarons in the DNA types examined were formed by the binding of electrons or holes with the vibration of the atoms involved in hydrogen bonding between the base pairs. It was determined that the polaron coupling energy of poly(dA)·poly(dT) was larger than that of poly(dG)·poly(dC). A characteristic feature of the polarons in DNA is that the activation energy is dependent on temperature and hence the conductivity is strongly temperature dependent since electrons and holes were coupled with phonons possessing energy higher than the thermal energy. We also found that differences in the dependence of conductivity on temperature between the two DNA types resulted from the fact that the carriers were coupled with phonons possessing energy lower than 500 cm^{-1} more strongly in poly(dA)·poly(dT) than in poly(dG)·poly(dC). The results of our calculations concerning the magnitude of the relation of E_a between poly(dA)·poly(dT) and poly(dG)·poly(dC), the dependence of E_a on temperature, and the strong dependence of the conductivity on temperature agrees well with the experimental results. We therefore conclude that small polarons represent the origin of the conduction mechanism in the DNA types examined.

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