Infrared spectroscopic studies on incorporating the effect of metallic ions into a *M*-DNA double helix

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(Received 9 March 2009; published 3 June 2009)

Infrared spectra at room temperature under relative humidity (RH) of 0% and 90% have been measured on dry salmon-sperm DNA incorporating various metallic ions (*M*-DNA, *M*=Li, Na, Mg, Ca, Mn, Fe, and Zn); the effects of which are examined from the molecular-vibrational points of view. Among many absorption bands, the antisymmetric and symmetric stretching modes of the phosphate group (PO_2^-) are found to show distinct spectral change depending on *M*. At RH=90%, the band shifts appear for both modes, reflecting that the magnitude of the electric dipole of PO_2^- is affected by *M*. At RH=0%, a band splitting induced by the spatial anisotropy around PO_2^- is detected in the antisymmetric stretching mode for Mg-DNA, Ca-DNA, Mn-DNA, Zn-DNA with divalent counterions, and Fe-DNA with trivalent counterions. The configurational change in *M* leads to these shifts and splittings; the divalent or trivalent ions do not connect to PO_2^- but are incorporated into the base-pair sequence as already pointed out by the previous measurements of NMR, ESR, and fluorescence. In *M*-DNA with *M*=Mg, Ca, Mn, Fe, and Zn, a kink appears around 3100 cm^{-1} corresponding to the NH stretching, and additionally a slight minimum disappears around 310 cm^{-1}. These phenomena are caused by a generation of N-*M* stretching vibrations due to the replacement of proton in the imino group to *M*.

DOI: 10.1103/PhysRevB.79.235201 PACS number(s): 78.30.Jw, 87.14.gk, 87.15.−v

I. INTRODUCTION

The electric conduction of dry DNA with double-helical structures has been widely studied for the potential application to nanoelectronic devices. According to the measurements on electronic conduction employing bundles or single DNA molecules, controversial results ranging from insulator to metal have been reported so far.[1–8] These results involve some problems concerning contact resistances between DNA sample and nanoelectrodes, sample preparation methods, and experimental environments such as relative humidity and temperature. Especially, the results suggesting metallic conduction[9] or polaron hopping[10] are poorly reproduced experimentally. The electric transition with π-π^* character is observed in the vicinity of 260 nm in ultraviolet spectra.[11,12] The spectral shape and position are influenced by the conformation associated with the stacking of base pairs and the environment of DNA sample. Nowadays the conventional dry DNA with Na^+ counterions is considered as a wide-gap semiconductor, essentially insulator.

Water plays a significant role for the structure and biological functions in DNA as well as in protein. Even in dry DNA, we are unable to neglect the role of primary hydration shell, the dynamics of which depends sensitively on relative humidity (RH) and temperature. Infrared (IR) measurements are powerful probes to identify the conformation of DNA and to examine the hydration state.[13,14] Our IR experiments on poly(dG)-poly(dC) and poly(dA)-poly(dT) with Na^+ counterions have already clarified that the hydration density is reduced with increasing temperature, and there exists about one water per nucleotide (=1 wpn) even under vacuum condition.[15] Together with previous IR studies by Falk *et al.*,[14] we conclude that such water locates at negatively charged phosphate group (PO_2^-), around which strong hydration occurs in comparison with the sugar group and base molecules. In the IR spectra obtained so far, however, there is no indication of metallic or polaron conductions.[15]

The microwave experiments based on a cavity perturbation method in poly(dA)-poly(dT) have made clear how the dynamics of hydrated water is affected by the relative humidity and temperature.[16] For RH=0%, the microwave response originates from a thermal rotation of the electric dipole in the single water molecule hydrated to PO_2^-. For RH =11%, the dynamics is associated with a collective motion of the water bridge formed in the A-form major groove. In case of the B form at RH=93%, the microwave dielectric constant is expressed by both contributions of the collective mode and freezing process around 250 K. Eventually these microwave responses are not dominated by the electronic conduction on the base-pair sequence but by the hydrated water.

A couple of attempts have been done to create an electric conduction of base-pair sequence in dry DNA. One of them is an iodine doping to poly(dG)-poly(dC).[17] By the doping, the radical cations may be formed in the guanine sites, and the chemical structure of dopant species is identified to be I_3^- by x-ray photoemission spectra and Raman spectra.[18] It is pointed out that the injected carriers possess a hole nature in the electronic states, while the electric conductivity in the base-pair sequence has not been confirmed yet.

In general, a counterion of dry DNA is Na^+, which is necessary to compensate negative charge of PO_2^-. The Na^+ counterion can be replaced by other metallic ions such as alkali metals, alkaline earth metals, and transition metals. It

is reported that divalent metallic ions such as Co^{2+}, Ni^{2+}, and Zn^{2+} are incorporated inside the helix at pH values above 8.5.[19,20] The DNA complexes that introduced the metallic ions are referred to as *M*-DNA. The experiments of NMR and ethidium bromide fluorescence imply that the hydrogen of imino groups is replaced by the metallic ions. The *I-V* characteristics using *M*-DNA fibers exhibit an Ohmic behavior suggesting a metallic conduction.[9] For Zn-DNA, it is pointed out from the absorption spectra in ultraviolet range that the π-π^* gap is reduced.[21]

The measurements of electron spin resonance (ESR) have been performed in *M*-DNA (*M*=Zn, Mn, Ca, and Mg), while the ESR signal originating from the π electrons is never observed.[22] The results indicate that charge injections are not achieved by the incorporation of metallic ions, and consequently the previous metallic conduction obtained by the *I-V* characteristics is not supported. On the other hand, the valence of Fe ions in Fe-DNA is determined to be trivalent through the ESR,[23] and hence charge transfers may occur from the Fe^{3+} ions to the base π band. Furthermore the ESR studies show that the Mn ions in Mn-DNA introduced in the center of base pairs construct a one-dimensional chain along the helical axis of B form in high RH, and three-dimensional network of the A form is formed in low RH. In terms of charge neutrality, the divalent and trivalent ions could compensate both end phosphate groups in the same nucleotides. In this situation, drastic changes may occur not only in the base molecules but also in the circumstance around phosphate groups and hydration states.

The infrared measurement has been carried out on film of dry DNA containing Ca, Mn, and Cu ions prepared in buffer solution at pH=7.[24,25] The IR spectra suggest that the metallic ions Ca and Mn dominantly bind to the phosphate groups, and Cu ions bind to the base molecules.

In this paper, we report systematic studies of the IR spectra in *M*-DNA (*M*=Li, Na, Mg, Ca, Mn, Fe, and Zn) for RH=0% and 90% at room temperature. From the investigation of the IR spectra, it will be deduced how the incorporation of the metallic ions affects the band shift and absorbance change for specific absorption bands. Then we will identify the configuration of the metallic ions in the double helix and environmental change around PO_2^- corresponding to the hydration states. Finally we will comment on the electric conduction of the base-pair sequence.

II. EXPERIMENTAL

The *M*-DNA samples have been prepared from the 1 mmol/L aqueous solution of salmon-sperm DNA (Wako Pure Chemical) mixed with the 5–10 mmol/L aqueous solution of MCl_2. After stirring for 10–30 min, excess cold ethanol at −20 °C is poured into the mixed solution of DNA and MCl_2. The residual MCl_2 is washed out thoroughly from the obtained precipitate in pure ethanol.

IR absorption spectra at 600–8000 cm^{-1} are obtained by a Fourier-transform-infrared (FT-IR) spectrometer (FT-IR 6100LT, JASCO) equipped with a Cassegrain microscope. We have carried out the present IR experiments with resolution of 2 cm^{-1} and the aperture size as 100×100 μm.

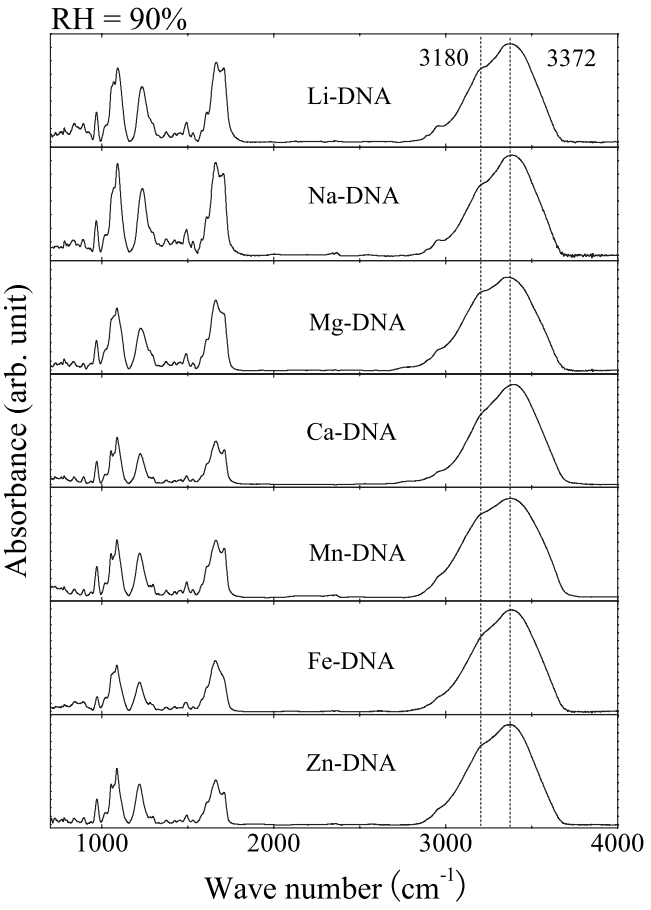

FIG. 1. Infrared absorbance at RH=90% at room temperature on *M*-DNA in the range of 700–4000 cm^{-1}. The broad band around 3400 cm^{-1} is dominated by OH stretching because of high hydration density. The peak around 3372 cm^{-1} and kink at 3180 cm^{-1} correspond to the NH stretching vibrations.

Every thick-filmy sample of *M*-DNA, which orients randomly and holds inhomogeneous thickness, has been made on a Si plate (1×1 cm^2) of 0.6 mm in thickness. The sample is placed in an optical cryostat (ST-300MS, JANIS), which controls the sample temperature from 8 to 400 K. The infrared spectra are measured under vacuum (RH=0%) and high humid condition (RH=90%). For Fe-DNA, we have measured the temperature change of IR spectra for RH =0% at 6–400 K.

The far-infrared (FIR) spectra in the range of 100–600 cm^{-1} are measured with the same spectrometer by changing the optical setup. The filmy samples on the Si plate are also used for the FIR experiments, while the aperture size is chosen to be 5 mm in diameter.

III. RESULTS

A. IR spectra for *M*-DNA at room temperature

Figure 1 depicts the IR spectra in the entire wave-number range measured for all the samples at RH=90%, where the primary hydration shell is completely filled by water molecules. Together with the IR experiments by Falk *et al.*,[13] the

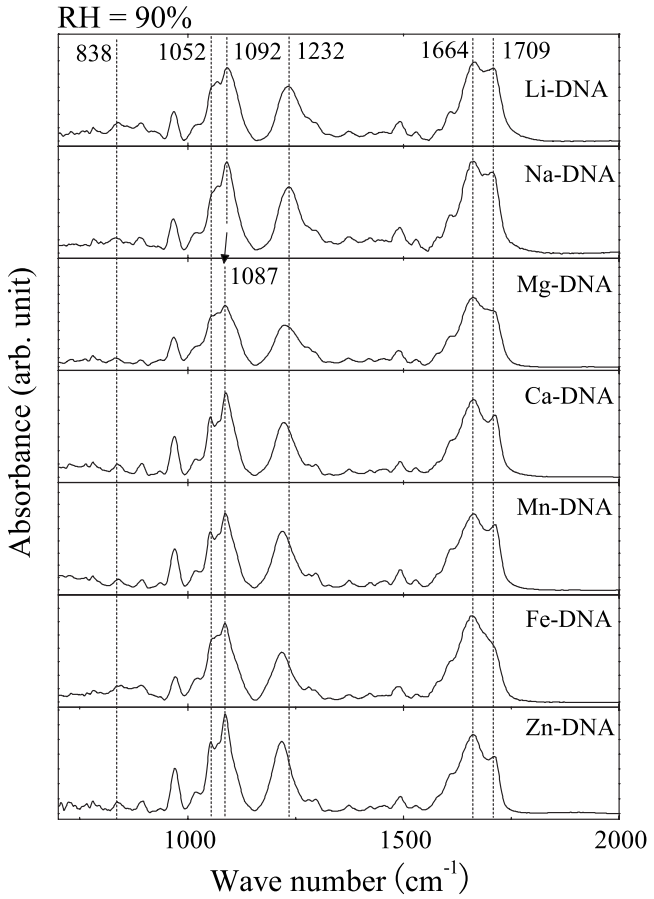

FIG. 2. Infrared absorbance at RH=90% on *M*-DNA in the range of 700–2000 cm^{-1}. The molecular vibrations due to bases are observed at 1600–1700 cm^{-1}, where the OH bending mode is overlapped. The symmetric and antisymmetric stretching modes of PO_2^- are detected around 1090 and 1230 cm^{-1}, respectively. These bands shift depending on the type of *M*. The sugar vibrations are measured below 1052 cm^{-1}, and the absorption of 838 cm^{-1} is confirmed as B-form marker band.

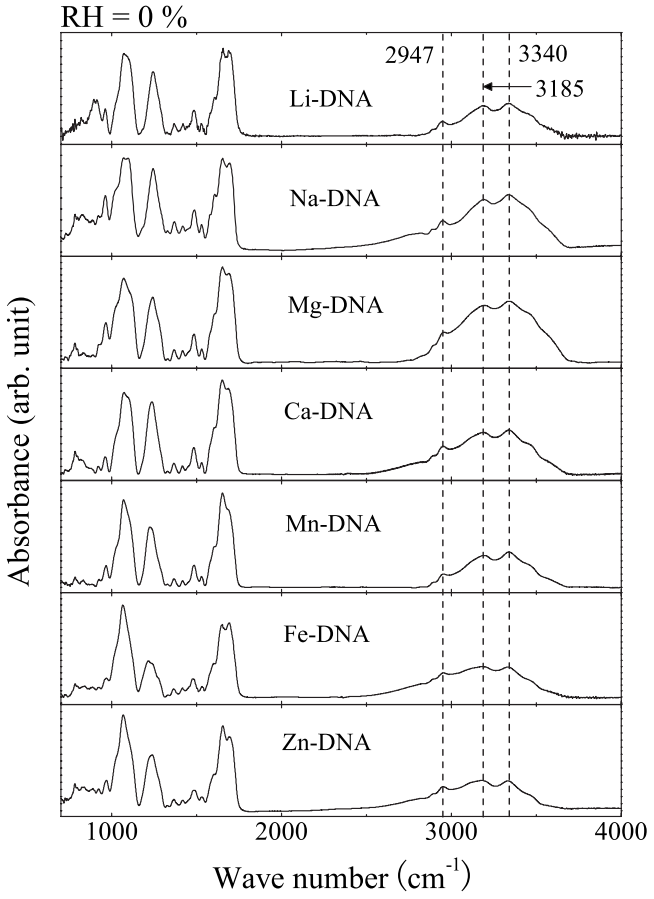

FIG. 3. Infrared absorbance at RH=0% at room temperature on *M*-DNA in the range of 700–4000 cm^{-1}. The absorbance of broad band around 3400 cm^{-1} is reduced due to the dehydration. The peaks around 3185 and 3340 cm^{-1} are assigned to the NH stretching modes, and additionally CH stretching is observed at 2947 cm^{-1}.

hydration density of primary hydration shell is determined to be about 26 wpn in Na-DNA. Taking the microwave dielectric response at RH=93% into account,[16] the secondary hydration shell is known to be occupied to some extent.

Broad absorption bands around 3300 cm^{-1} involve several components of molecular vibrations: OH symmetric and antisymmetric stretching modes (~3400 cm^{-1}), NH stretching modes (~3100 and ~3300 cm^{-1}), and overtone of a bending mode of water molecules (~3300 cm^{-1}).[26] As shown by the dotted straight lines, the broad peak and kink are observed at 3372 and 3180 cm^{-1}, respectively, the position of which little depends on the type of metallic ions introduced.

The data below 2000 cm^{-1} of Fig. 1 are enlarged in Fig. 2. The absorption at 838 cm^{-1} is assigned to an important maker band of B-form sugar corresponding to a puckering of C2′-endo.[11,27,28] The antisymmetric stretching mode of PO_2^- is observed around 1232 cm^{-1} also indicating B form. By increasing the atomic number of the metallic ions, the antisymmetric stretching band systematically shifts to lower-wave-number side. The symmetric stretching band of PO_2^- is detected at 1092 cm^{-1} in Li-DNA and Na-DNA, while the bands for other metallic ions abruptly shift to 1087 cm^{-1}. The amount of the shift is larger than the resolution of FT-IR spectrometer. The absorbance of the symmetric stretching mode is larger than that of sugar vibration at 1052 cm^{-1} for all the *M*-DNA.

Broad bands in the range of 1600–1750 cm^{-1} consist of various stretching modes (C=C, C=N, C=O) and NH_2 bending vibrations due to the base molecules. Moreover the bands contain the OH bending mode of hydrated water molecules. The absorption peaks at 1709 cm^{-1} are assigned as B-form marker band. Both the peaks at 1664 and 1709 cm^{-1} are almost independent of the metallic ions.

In Fig. 3 for RH=0%, the absorbance of broad bands around 3300 cm^{-1} is suppressed because of a dehydration in the primary hydration shell.[13,15] An absorption band appears at 2947 cm^{-1}, which is assigned to the CH stretching mode of the sugar. Another two peaks (3185 and 3340 cm^{-1}) little depend on the type of metallic ions as well.

Figure 4 demonstrates the IR spectra below 2000 cm^{-1} at RH=0%. The absorption at 885 cm^{-1} is identified to A-form marker. The sugar vibrational mode is measured at 1068 cm^{-1}, which exhibits no shift. The band around

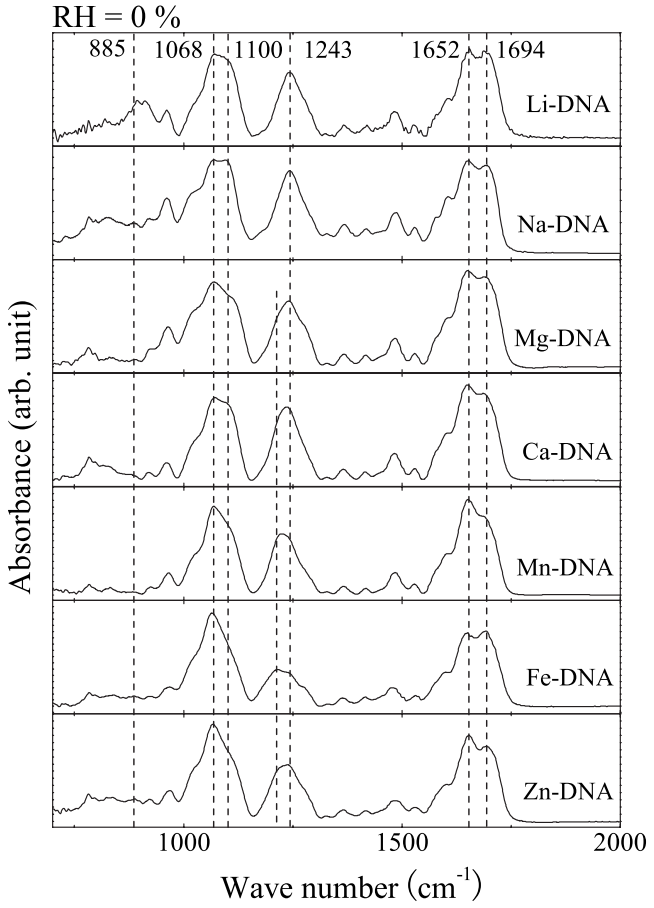

FIG. 4. Infrared absorbance at RH=0% on *M*-DNA in the range of 700–2000 cm^{-1}. The molecular vibrations due to bases are observed at 1600–1700 cm^{-1}. The symmetric and antisymmetric stretching modes of PO_2^- are detected around 1100 and 1240 cm^{-1}, respectively. The symmetric stretching band becomes broad with increasing atomic number of *M*. The spectral splitting is observed in Mg-DNA, Ca-DNA, Mn-DNA, Fe-DNA, and Zn-DNA. The sugar vibrations are measured below 1068 cm^{-1}, and the absorption of 885 cm^{-1} is confirmed as A-form marker band.

1100 cm^{-1} due to a symmetric stretching mode of PO_2^- gradually broadens as the atomic number of metallic ions increases. Such broadening is especially remarkable in Mn-DNA, Fe-DNA, and Zn-DNA. The peaks around 1652 and 1694 cm^{-1} shift to low wave-number side compared to the case of RH=90% in all the *M*-DNA. These shifts are associated with structural transitions from B form (RH=90%) to A form (RH=0%).

For Li-DNA and Na-DNA at RH=0%, the antisymmetric stretching mode of PO_2^- is detected at 1243 cm^{-1}, which is assigned to A-form marker.[27,28] These absorptions are reproduced by a single Lorentzian. Nevertheless the band shape in other *M*-DNA alters; the absorptions are fitted by assuming two different Lorentzians. Thus the antisymmetric stretching modes are found to split at low-hydration density.

Figure 5 plots the wave-number change for the antisymmetric stretching modes of PO_2^- shown in Figs. 2 and 4. In the horizontal axis, the metallic ions are arranged in the order of atomic number of *M*. At RH=90%, the absorption wave

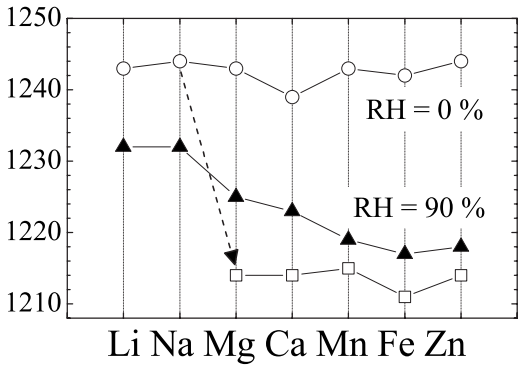

FIG. 5. Wave-number dependence of absorption peaks in the antisymmetric stretching mode of PO_2^- with respect to the metallic ion. Solid triangles and open symbols denote the data for RH =90% and 0%, respectively.

number is reduced as increasing atomic number so that a softening takes place in these bands.

As seen in Fig. 5, band splitting is found to appear except for Li-DNA and Na-DNA at RH=0%. The peak position is determined by assuming two Lorentzians to the spectra of PO_2^- in Fig. 4. The higher part observed around 1243 cm^{-1} takes nearly constant, which is almost identical to the values in Li-DNA and Na-DNA. The lower part is measured at 1214 cm^{-1} without depending on the metallic ion. The higher part is confirmed as A-form marker band, while the lower one is amazingly rather close to B-form maker band. These spectral changes are associated with the configuration of metallic ions, the details of which will be discussed later.

FIR spectra are obtained in all the *M*-DNA as illustrated in Fig. 6. A broad maximum is observed around 540 cm^{-1} together with fine structures in the vicinity of 420 and 500 cm^{-1}. Moreover Li-DNA and Na-DNA take a minimum around 310 cm^{-1}, which agrees with previous report.[29] Such a minimum, however, is hard to observe in other *M*-DNA (*M*=Mg, Ca, Mn, Fe, and Zn). In the next section, we will mention that the spectral change around 310 cm^{-1} originates from the incorporation of metallic ions into the base molecule.

B. Temperature dependence of IR spectra in Fe-DNA

Among *M*-DNA, in which the splitting of the antisymmetric stretching mode of PO_2^- is found, the temperature change of IR spectra is measured in Fe-DNA. The IR spectra are obtained under RH=0% and heating process from 8 to 400 K. After the sample has once experienced the highest temperature at 400 K, we cool the sample down to 293 K to measure the IR spectrum. The absorbance of the broad band around 3400 cm^{-1} is reduced with increasing temperatures in Fig. 7(a). The change in absorbance at 293 K before and after experiencing 400 K results from a dehydration in the primary hydration shell. Molecular vibrations due to the sugar and base molecules, however, are little affected by the heating process.

Figure 7(b) enlarges the small wave-number region in Fig. 6. The suppression of the spectra around 1700 cm^{-1}, containing the OH bending mode, originates from the dehydra-

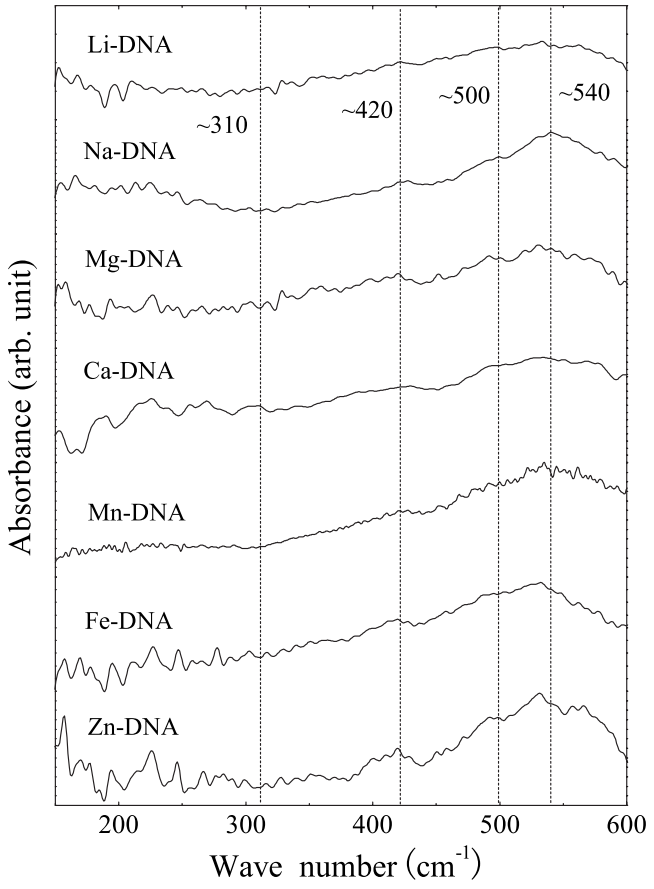

FIG. 6. Far infrared spectra on *M*-DNA at room temperature. Slight maxima are observed around 420, 500, and 540 cm^{-1}. Broad minimum is seen around 310 cm^{-1} in Li-DNA and Na-DNA, while such minimum disappears in other *M*-DNA.

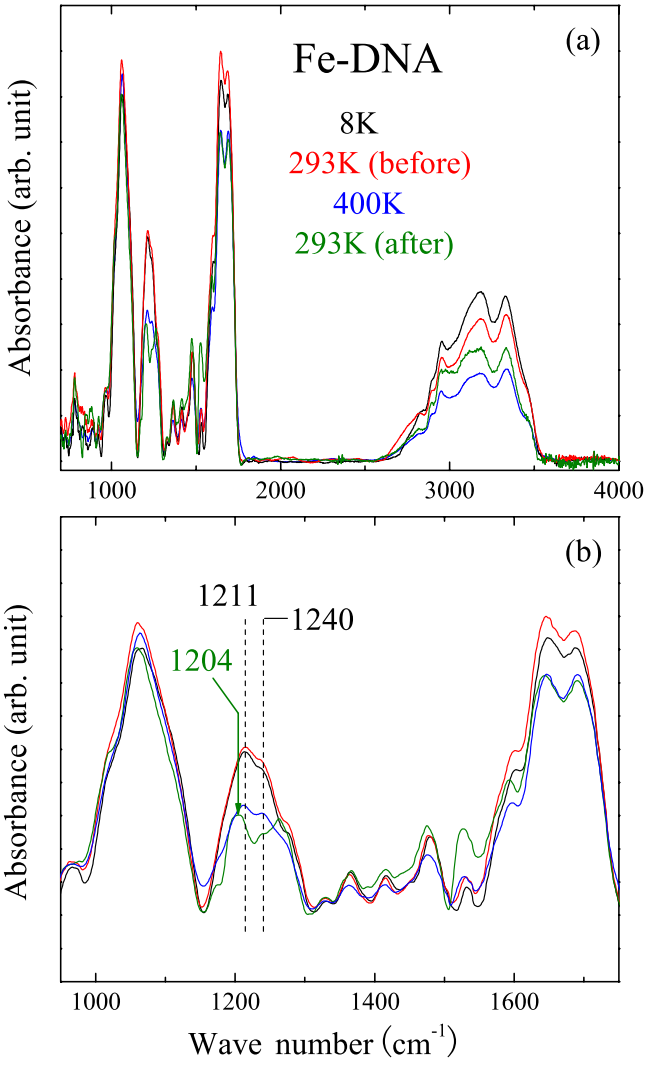

FIG. 7. (Color online) (a) IR spectral change in Fe-DNA as a function of temperature at 8–400 K. The suppression around 3400 cm^{-1} originates from dehydration from the primary hydration shell. (b) The spectrum in antisymmetric stretching of PO_2^- drastically varies after experiencing 400 K.

tion. A remarkable spectral change is observed around 1200 cm^{-1} corresponding to the antisymmetric stretching band of PO_2^-. When we compare the spectrum at 293 K after experiencing 400 K to the spectrum before, the peak shifts from 1211 cm^{-1} to 1204 m^{-1}, and the intensity is reduced nearly by half. Furthermore the absorption at 1240 cm^{-1} disappears. These spectral changes suggest that the negatively charged phosphate group may become unstable because of the dehydration.

Such spectral change is never obtained in poly(dA)-poly(dT) and poly(dG)-poly(dC) with the Na^+ counterions through a heating process.[15] The IR spectra for these DNA with homogenous base-pair sequence almost agree with ones for Na-DNA with random base-pair sequence, and then the hydration structures little depend on the type of base-pair sequence. Variations in the spectra due to the heating process in Fe-DNA are expected to be a characteristic phenomenon for *M*-DNA with divalent and trivalent counterions. In the next section, we will discuss that the spectral change corresponds to the configuration of *M* and environmental change around PO_2^-.

IV. DISCUSSION

Let us discuss the molecular-vibrational modes strongly affected by the introduction of metallic ions and the configuration of metallic ions in the double-helical structure. The C-O stretching vibration of sugar is observed at conventional absorption wave number of ~1052 cm^{-1} for B form in Fig. 2 and ~1068 cm^{-1} for A form in Fig. 4.[27,28] Furthermore various absorption bands around 1700 cm^{-1} in Figs. 2 and 4 due to stretching vibrations of C=C, C=N, and C=O, constructing a fundamental framework of purine and pyrimidine bases, never show a band shift with respect to the metallic ion. Then both the sugar molecule and the framework of bases are not influenced by the metallic ion at all and maintain the original structure.

As mentioned in the previous section, significant spectral changes are found in the absorption band due to the antisymmetric stretching mode of PO_2^-. These changes must provide information on the arrangement of metallic ions. In Fig. 5, the absorption band at RH=90% shifts toward lower wave number with increasing atomic numbers. On the other hand, the band splitting appears at RH=0% excluding Li-DNA and

Na-DNA. In dry DNA, the valence of Li and Na ions has +1, while it for Mg, Ca, Mn, and Zn ions is identified to be +2. It is important to note that the valence of Fe ions in Fe-DNA is determined to be +3 through ESR experiments.[23]

Here we consider the difference of IR response between symmetric stretching and antisymmetric stretching in PO_2^-. Generally speaking, an interaction of infrared waves with matter is expressed in terms of changes in molecular electric dipoles associated with vibrations and rotations.[30] The symmetric stretching of PO_2^- is generated by the variation in magnitude of electric dipole for applying electric fields of IR waves, while the antisymmetric stretching corresponds not only to the variation in the magnitude but also to the orientational change. If some spatial anisotropy of electric fields is induced around the electric dipole of PO_2^-, the antisymmetric stretching band may exhibit some shift. In the present system, the anisotropy is probably caused by hydrated water dipoles, charge distribution of metallic ions, and neighboring DNA double strands.

Particularly in Mn-DNA, Fe-DNA, and Zn-DNA at RH =0%, the antisymmetric stretching mode of PO_2^- is reduced nearly half the absorbance of the stretching mode in sugar ($\sim$1070 cm^{-1}). These reductions are related to the splitting. Similar reduction and broadening seem to appear in the symmetric stretching bands of PO_2^- ($\sim$1090 cm^{-1}) in which a splitting has not been identified due to overlapping the contribution of sugar. Anyway it is proved that the magnitude of electric dipole in PO_2^- is also affected by the metallic ions.

In case of RH=90%, a large amount of hydrated water screens the electric dipole of PO_2^-, and hence the field anisotropy around PO_2^- is reduced. When the hydration density is extremely small, the anisotropy around PO_2^- becomes remarkable and the spectral splitting occurs at RH=0% because the screening effect due to water is extremely suppressed.

To achieve charge neutrality, a monovalent ion connects to single phosphate group with a valence of −1. If a divalent (trivalent) ion contacted neighboring two (three) phosphate groups, electric fields around the phosphate groups could become considerably anisotropic even in large hydration density. Then the band splitting ought to be observed in antisymmetric stretching mode at RH=90%. The disappearance of a splitting indicates that the divalent or trivalent metallic ions never couple to PO_2^-; there appears free PO_2^-, around which a large amount of water is hydrated.

The symmetric stretching modes of PO_2^- at RH=90% in Fig. 2 exhibit sudden shift to 1087 cm^{-1} in *M*-DNA with divalent or trivalent counterions. The shift is led by changing the magnitude of electric dipole associated with the occurrence of free PO_2^-. The gradual shift in antisymmetric stretching modes at RH=90% may also relate to the free PO_2^- as well.

From the temperature dependence of the IR spectra for Fe-DNA in Fig. 7(b), the band shape due to antisymmetric stretching mode of PO_2^- changes after experiencing the highest temperature of 400 K. This result reveals that PO_2^- becomes unstable through the heating process. When a monovalent counterion contacts every PO_2^-, an electric stability is retained even under low-hydration condition at high temperatures. Against the free PO_2^- without counterions, Coulomb repulsions between PO_2^- are hard to suppress under extremely low-hydration density.

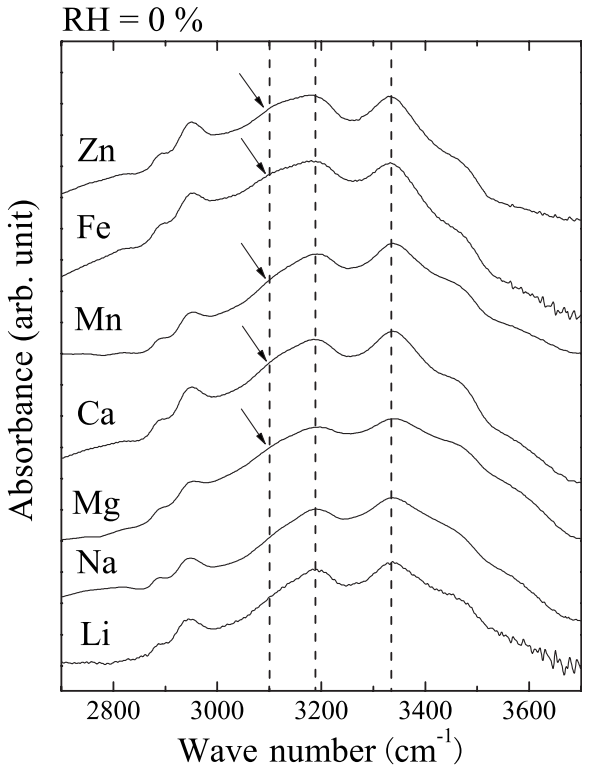

FIG. 8. Spectra around 3400 cm^{-1} at RH=0% enlarged from Fig. 3. Around 3100 cm^{-1}, the spectra change linearly in Li-DNA and Na-DNA, though a kink develops in other *M*-DNA as denoted by arrows.

Figure 8 enlarges the spectra at 2700–3700 cm^{-1} in Fig. 3. The OH stretching has broad feature over the wavenumber region shown in Fig. 8. The absorption bands at 3185 and 3340 cm^{-1} are assigned to the NH stretching.[27,28] We should notice that a kink emerges near 3100 cm^{-1}, which especially becomes remarkable in Fe-DNA and Zn-DNA. For Li-DNA and Na-DNA, however, the spectra linearly change around 3100 cm^{-1}. The appearance of the kink represents the divalent and trivalent metallic ions having some influence on the imino group. In addition, in FIR spectra of Fig. 6, a slight minimum around 310 cm^{-1} (Ref. 29) disappears except for Li-DNA and Na-DNA. If the imino proton replaces *M*, N-*M* stretching vibrations may be generated—the intensity of which is usually weak.[31] Although distinct peaks are not seen, the disappearance of the minimum around 310 cm^{-1} implies that some broad bands due to N-*M* stretching overlap in the spectra. Therefore these spectral changes around 310 and 3100 cm^{-1} support the formation of N-*M* bonds as predicted by the previous studies such as NMR, fluorescence, and ESR.[20,23]

Finally we would like to comment on the electric conduction in base-pair sequence. All the absorption bands for *M*-DNA measured in this study are attributable to molecular vibrations of DNA. Theoretical studies have predicted various models of electronic states: (1) appearance of conducting states in the gap in the presence of magnetic ions,[32] (2) narrowing the gap due to spreading the highest occupied mo-

lecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) bands,[33] and (3) hole carriers induced by the hydrated Mg cations.[34] Nevertheless we do not observe any electronic transition reflecting a Drude response or electronic transitions at all. Then it is concluded that *M*-DNA remains a wide-gap semiconductor in terms of the IR spectra. Although the metalliclike conduction has been reported in *I-V* characteristics of bundle Zn-DNA samples,[9] the buffer and other residues such as $ZnCl_2$ may affect to their experiments.

V. CONCLUSIONS

We have measured the infrared spectra in *M*-DNA at room temperature under relative humidity of 0% and 90%. In terms of the molecular vibrations, the incorporation effects of metallic ions are investigated in detail. Among various absorption bands, the antisymmetric and symmetric stretching modes of PO_2^- are found to show distinct spectral change depending on *M*. At RH=90%, the band shifts appear for both the modes, and then the magnitude of electric dipole of PO_2^- is affected by *M*. At RH=0%, band splitting, which is induced by the spatial anisotropy around PO_2^-, is detected in the antisymmetric stretching mode for Mg-DNA, Ca-DNA, Mn-DNA, Zn-DNA with divalent counterions, and Fe-DNA with trivalent counterions. These shifts and splittings are conducted by the change in configuration of *M*. The divalent or trivalent ions do not connect to PO_2^- but incorporate into the base-pair sequence as already pointed out by the studies of NMR, ESR, and fluorescence. Therefore free PO_2^- emerges, around which lots of water are hydrated to compensate the negative charge. In the vicinity of 3100 cm^{-1} assigned to the NH stretching, a kink appears in *M*-DNA with counterions of Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{3+}, and Zn^{2+}. Furthermore some broad band is induced additionally around 310 cm^{-1} except for Li-DNA and Na-DNA. The appearance of the kink and the broad band is caused by the replacement of proton in imino group to *M* (=Mg, Ca, Mn, Fe, and Zn) generating N-*M* stretching. In the IR spectra, there is no indication of electronic states, and consequently *M*-DNA samples still remain as a wide-gap semiconductor.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research from JSPS (Grant No. 19340088) and a Grant-in-Aid for Scientific Research on the Priority Areas of "New Materials Science Using Regulated Nano Spaces," "Super-Hierarchical Structures," and "Molecular Conductors" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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