

# Local Modes in a DNA Polymer with Hydrogen Bond Defect

V. K. Saxena and L. L. Van Zandt

Department of Physics, Purdue University, West Lafayette, Indiana 47907 USA

**ABSTRACT** Vibrations of a homopolymer DNA with localized hydrogen bond defects have been examined using the recently developed decaying mode theory for long-chain polymers with local structural defects. For a poly(dA)-poly(dT) homopolymer having perturbed hydrogen bonds in one base pair, a localized mode at  $63.2\text{ cm}^{-1}$  has been found. This mode has a very nearly pure H-bond stretch or "breathing" character, although the backbones do not separate. This agrees in frequency with a similar result found by other authors using a different approach. We search the full microwave frequency range for other local modes for several models of weakened H bonds. Besides the local mode with breathing characteristics, local modes with other characteristic motions were found, but only for asymmetrically perturbed bonds. We find in general that local modes are not very robust, requiring quite specific, narrow ranges in parameter space. They are also not abundant, there being only three in our most prolific model.

## INTRODUCTION

Atomic and collective motions are fundamental in understanding the physical and biological behavior of DNA polymers. In a perfect infinite-chain polymer, due to the inherent helical symmetry, these motions can be described and analyzed in terms of propagating normal vibrational phonon modes of the system. The symmetry-based simplifications of the dynamics are applicable only to homopolymers or copolymers with repeated subunit structures (Eyster and Prohofsky, 1974; Saxena and Van Zandt, 1992). In real biological systems and most of the experimental samples normally used for spectroscopic studies one in general has DNA polymers with a variety of structural variations and defects. The helical symmetry of a homo- or co-polymer is broken by the presence of such structural variations or defects. The system can then support, along with the ordinary propagating modes, localized vibrational modes with atomic or collective motions confined to the defect and the neighboring region of the polymer.

There has been interest in the localized motions of DNA polymer for some time (Putnam et al., 1981). The problem is of considerably greater computational difficulty than the case of propagating modes. We have recently developed the theory and computer codes for studying the dynamics of local structural defects on otherwise perfect polymer chains. This method exploits the existence of exponentially decaying modes along the polymer chain on either side of the central defect site (Saxena et al., 1991a). We shall refer to these as the "one-sided" solutions. Application of appropriate boundary conditions at interfaces between defect region and unperturbed chain leads to solutions for modes with localized motions. Unlike the Green's function methods (Kim and

Prohofsky, 1986), which use integrals covering the continuous bands over the complete Brillouin Zone (containing various singularities corresponding to in-band modes), this method utilizes summations over a finite number of degrees of freedom and may be computationally quite modest, depending on the number of interactions across the defect-chain interface. As a first simple application it was used to find local modes on a semi-infinite polymer with a free end (Saxena et al., 1991b). The mathematical and computational simplicity of the method makes it useful for local-mode studies for structural variations of any size or complexity.

The two strands of the double-helical DNA are held together in part by the hydrogen bonds across the base pair. These hydrogen bonds play an important role in denaturation of DNA, in turn related to its biological activity (Prabhu et al., 1989). It has been shown that thermal fluctuations in a DNA polymer can introduce localized variations in the hydrogen bond force constants (Awati and Prohofsky, 1989). This local alteration of hydrogen-bond strengths leads to a localized structural defect and breaking of the helical symmetry. This creates a self-sustaining local vibrational mode whose amplitude diminishes with distance from the defect.

In this report we take the local H-bond strength as a parameter. We present a calculation of the local mode due to a weakened hydrogen bond defect as described above. We have utilized our new method, analysis in terms of decaying waves (Saxena et al., 1991b), to find the local-mode frequencies and to examine the conditions for the existence of local modes in the presence of such a defect. It is found that the existence of a local mode is very sensitive to the values of the weak hydrogen bond strengths. In the present discussion we have restricted our calculations to a B-form poly(dA)-poly(dT), which has two hydrogen bonds in each monomer.

We consider a polymer with the central unit cell (or monomer) containing an adenine-thymine base pair and corresponding sugar-phosphate backbones. It is assumed that the two hydrogen bonds in this central monomer have strength different from those of the rest of the chain.

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Address reprint requests to Dr. V. K. Saxena, Department of Physics, Purdue University, 1396 Physics Building, West Lafayette, IN 47907-1396. Tel.: 317-496-9575; Fax: 317-494-0706; E-mail: Saxena@physics.purdue.edu.

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The model used for bonded and nonbonded interactions has been discussed at length elsewhere (Saxena et al. 1989; Saxena and Van Zandt, 1992). We use here the same model as in the previous work. We would elaborate the main features of the model and the interactions included in this calculation. For the sake of completeness of presentation, we will first discuss the theoretical model used for the normal mode calculations of an infinite polymer chain, in absence of any local defect. We will, then, describe the features needed to be included in the theory to account for the presence of local structural defects.

Since 1971 (Small and Peticolas, 1971), the helical symmetry of the DNA homopolymer has been exploited for the calculation of dynamical and other properties of the system. The DNA and the associated, surrounding hydration sheath can be viewed as a one-dimensional lattice with a unit cell containing a complete monomer. The dynamics of a dissolved DNA polymer, along with the hydration sheath and the counterions, can be described by a set of equations of motion for the dynamical coordinates of the component atoms in a unit cell. Assuming partial site-binding condition for the counterions (Saxena and Van Zandt, 1992) as a most general case, we assign mass-weighted dynamical coordinates  $\bar{\Pi}_l^\alpha = \sqrt{x_c M_c} \Pi_l^\alpha$  ( $\alpha = x, y, z$ ;  $l = 1, 2$ ; and  $M_c$  is the mass of a counterion;  $x_c M_c$  is the average coupled site bound mass loading to the polymer) for the motion of the two monovalent counterions within a unit cell.  $x_c$  is a parameter that defines the degree of site binding of the counterions. ( $x_c = 1$  means the counterions are completely site bound, whereas  $x_c = 0$  corresponds to a situation in which the counterions are area bound when their charge and mass are assumed to be uniformly distributed over the hydration sheath.)  $\Pi_l^\alpha$  is the  $\alpha$  component of the displacement vector  $\Pi_l$  of counterion  $l$ . Then equations of motion of the system are written as:

$$-\omega^2 q_i^\alpha = \sum_{j,\beta} D_{ij}^{\alpha\beta} q_j^\beta + e_i' E_\alpha - i\omega \Gamma_i (\bar{\Pi} - q_i^\alpha \eta_i) \delta_{ip} \delta_{\alpha z} + \sqrt{x_c} \sum_{l,\beta} F_{il}^{\alpha\beta} \bar{\Pi}_l^\beta \quad (1)$$

$$-\omega^2 \bar{\Pi}_l^\beta = \sqrt{x_c} \left[ e_c' E_\beta - i\omega \Gamma (\bar{s} - \bar{\Pi}_l^\beta \mu_c) \delta_{\beta z} + \sum_{j,\alpha} F_{lj}^{\beta\alpha} q_j^\alpha \right] + x_c \sum_{l'\alpha} C_{ll'}^{\beta\alpha} \bar{\Pi}_{l'}^\alpha \quad (2)$$

and

$$-\omega^2 \bar{s} = -q^2 v_w^2 \bar{s} - \lambda E_z - i\omega \sum_i \Gamma_i (q_i^z - \bar{s}/\eta_i) \delta_{ip} - i\gamma \omega \bar{s} - i\omega \Gamma \sqrt{x_c} \sum_l (\bar{\Pi}_l^z - \bar{s}/\mu_c), \quad (3)$$

where  $\omega$  is the frequency of a mode of the system.  $q_i^\alpha$  ( $\alpha = x, y, z$ ) are the components of the mass-weighted displacement amplitude vector  $\mathbf{q}_i$  of atom  $i$ , defined by  $\mathbf{q}_i = \sqrt{m_i} \delta \mathbf{r}_i$ , with mass  $m_i$  and the corresponding coordinate  $\mathbf{r}_i$ , within a monomer. Assuming only longitudinal motion of the

water sheath, we represent its motion by a dynamical variable  $\bar{s} = \sqrt{a\rho s}$  where  $s$  represents the displacement amplitude of the near-water sheath containing the counterions.  $\rho = \rho_0 + 2(1 - x_c)M_c/a$  is the linear mass density of the sheath where  $\rho_0$  is the linear mass density of water sheath and  $M$  is the counterion mass.  $a$  is the helix rise.

The first term on the right of Eq. 1 contains the contributions to the dynamical matrix, within the harmonic approximation, from the bonded interactions (bond stretch, angle bend, and torsion) between polymer atoms. This term also contains contributions from the direct Coulomb and the Van der Waals interactions between the pairs of DNA atoms within a unit cell, and contributions from the Van der Waals interactions between pairs of DNA atoms within the central monomer and the nearest-neighbor monomers on either side. A dielectric constant of 2.00 was used for direct Coulomb interactions within a monomer, and the partial atomic charges were taken from the calculations of Miller (1979). Collection of all these forces is contained in the force-constant matrix  $D_{ij}^{\alpha\beta}$ .

The third term on the right of Eq. 1 incorporates the damping forces at the polymer-solvent interface, with a similar term in Eq. 3, the equation of motion for the water sheath. Eq. 3 also contains the term  $-i\omega\gamma\bar{s}$  for damping at the sheath-bulk water interface. The first term on the right side of Eq. 3 represents the elastic contribution to the sheath motion.  $v_w$  is the sound wave speed in bulk water, and  $q$  the wave vector for propagation of the disturbance along the DNA-solvent system.  $\eta_i \equiv \sqrt{a\rho/m_i}$ . Kronecker deltas  $\delta_{ip}$  and  $\delta_{\alpha z}$  restrict the damping forces at the DNA-sheath interface to the coupling of the  $z$  component of the motion of phosphorus atoms on the two backbones with longitudinal motion of the sheath. The damping parameter  $\gamma$ , for the sheath-bulk water coupling, is derived from the viscosity of bulk water (Dorfman and Van Zandt, 1984).

The last terms on the right of Eqs. 1 and 2 describe the motion of the counterions. The last term in Eq. 1 contains the elements  $F_{ij}^{\beta\alpha}$  of the force constant matrix of direct interactions between counterions and DNA polymer. A similar, equal and opposite term appears in Eq. 2 for the motion of atoms in the DNA monomer. These are action/reaction pairs. We have introduced a damping term, second term in Eq. 3, between the  $z$ -motion of the counterions and the motion of the water sheath. The constant  $\Gamma$  in this term couples the  $z$ -motion of the counterions with the water. An elementary calculation based on the DC conductivity of ionic solutions shows that  $\Gamma$  is so large that they move together almost perfectly as if the counterions were glued to the water.  $\mu_c = \sqrt{a\rho/M_c}$ .

The last term in Eq. 2 is the force contribution arising from counterion-counterion interaction. As the two counterions, on opposite sides of the monomer, are far apart, this term involves relatively smaller contributions.

The nonbonded, long-range interactions between distant parts of the polymer and corresponding counterions on distant monomers are accounted for in terms of the effective electric field  $\mathbf{E}$  (Saxena et al., 1989; Saxena and Van Zandt,

1990) with components  $E_\alpha$  acting on the partial atomic charges on the polymer atoms and the counterion charges within the sheath. In Eqs. 1 and 2 the local field terms contain the scaled charges  $\acute{e}_i = e_i/\sqrt{m_i}$  where  $e_i$  is the partial charge on DNA atom  $i$  within a monomer.  $\acute{e}_c = e_c/\sqrt{M_c}$  is the scaled charge on a counterion.  $\acute{\lambda} = \lambda/\sqrt{a\rho}$  where  $-\lambda = \sum_i e_i - 2x_c e_c$  is the total average charge, of the area-bound part of the counterions, within the water sheath. As before, we have assumed complete charge neutrality within the molecule-sheath system. Poisson-Boltzmann theory indicates that this assumption is correct to about 95%.

The local field  $\mathbf{E}$  is determined from the geometry of the system as solutions of Maxwell's equations and satisfy appropriate boundary conditions at the DNA-sheath and sheath-bulk water interfaces. The radial and longitudinal electric fields  $E_r$  and  $E_z$  turn out to be given by Bessel functions. In the case of dissolved DNA polymer considered here the appropriate Bessel functions are Hankel functions of the first kind. The radial and longitudinal fields have the form:

$$E_r(q, r) = E_1(q)H_1^1(\kappa r) \quad (4)$$

and

$$E_z(q, r) = E_0(q)H_0^1(\kappa r) \quad (5)$$

where  $H$  are the Hankel functions.  $\kappa$  is given in terms of wave vector  $q$  and frequency  $\omega$  of an excitation along the polymer chain, the dielectric constant  $\epsilon_{\text{out}}$  and DC electrical conductivity  $\sigma$  of the hydration sheath as

$$\kappa = \{-q^2 + \epsilon_{\text{out}}\mu_0\omega^2 + i\sigma\mu_0\omega\}^{1/2}. \quad (6)$$

where  $\mu_0$  is the constant of magnetostatics. The amplitudes  $E_1$  and  $E_0$  are determined by the boundary condition at the interface between hydration sheath and the bulk water at  $r = r_1$  where  $r_1$  is the radius of the hydration sheath taken to be 13.1 Å. (This corresponds to bare DNA surrounded by a one-molecule-thick layer of water). These boundary conditions (for details see Saxena et al., 1989) give expressions for the  $E$  field amplitudes in terms of the local polarization density vector  $\mathbf{P}$ . Finally, the longitudinal and radial components of the fields are given by:

$$E_z(q, \omega) = \frac{1}{\epsilon_{\text{in}} \Psi(\kappa, \omega) - 1} P_z \quad (7)$$

and

$$E_r(q, \omega) = -\frac{iqr_1}{2} \frac{1}{\epsilon_{\text{in}} \Psi(\kappa, \omega) - 1} \left[ P_z + \frac{2}{iqr_1} P_r \right] \quad (8)$$

where

$$\Psi(\kappa, \omega) = \frac{2}{\kappa r_1} \frac{i\sigma + \omega\epsilon_{\text{out}}(\omega)}{\omega\epsilon_{\text{in}}} \frac{H_1^1(\kappa r_1)}{H_0^1(\kappa r_1)} \quad (9)$$

where  $\epsilon_{\text{in}}$  is the dielectric constant in the sheath region.  $P_z$  and  $P_r$  are the longitudinal and radial components of the local polarization density vector  $\mathbf{P}$ , which is given in terms of local

atomic displacements as

$$\mathbf{P} = \frac{1}{\pi\kappa r_1^2 a} \left[ \sum_i e_i \delta \mathbf{r}_i + x_c e_c \sum_i \Pi_i - \hat{\mathbf{z}} s \lambda \right]. \quad (10)$$

The effect of the surrounding polarizable aqueous medium is accounted for by means of a frequency-dependent dielectric constant and elastic properties known from the speed of sound in water (Saxena and Van Zandt, 1990). The frequency-dependent dielectric function of the medium  $\epsilon_{\text{out}}\omega$  is given by Pethig (1979):

$$\epsilon_{\text{out}}(\omega) = \frac{\epsilon_{\text{DC}} - \epsilon_\infty}{1 + i\omega\tau_s} + \epsilon_\infty \quad (11)$$

where  $\epsilon_{\text{DC}}$  and  $\epsilon_\infty$  are the zero-frequency static dielectric constant and infinite-frequency dielectric constant of the aqueous medium, respectively.  $\tau_s$  is the dielectric relaxation time of the solvent medium,  $7.9 \times 10^{-12}$  from the most recent value reported from microwave absorption measurements (Garner et al., 1989). This gives the range of most rapid variation of  $\epsilon_{\text{out}} \sim 50\text{--}100 \text{ cm}^{-1}$ . Again, these matters have been described earlier (Saxena et al., 1989; Van Zandt and Saxena, 1989; Saxena et al., 1991a).

The frequency dependence of the local field terms and the damping terms renders the set of Eqs. 1–3 nonlinear in  $\omega^2$  and makes them difficult to solve by direct diagonalization. We have calculated the spectrum of B-form homopolymer poly-(dA)-poly(dT) DNA within this model using an iterative procedure to get self-consistent eigenmode frequencies and corresponding eigenvectors for each of the modes separately. From the spectroscopic point of view (i.r. absorption) one needs to calculate the normal mode spectrum only at the zone center  $\theta = 0^\circ$  and at  $\theta = 36^\circ$  where  $\theta = qa$  is the phase angle. For the frequency-independent parts of the force constant matrix  $D_{ij}^{\alpha\beta}$ , the damping coefficients, the sound speed for bulk water, and the values of  $\sigma$  and  $r_1$  in the effective field terms we used the same set of values as in our earlier calculation (Saxena and Van Zandt, 1990). Brillouin scattering studies of DNA and its hydration shell (Tao et al., 1988) show that the dielectric relaxation time within the first hydration shell is  $4.0 \times 10^{-11}$  s. In accord with this in Eqs. 7–9 we have used a value of  $2.0\epsilon_0$  for  $\epsilon_{\text{in}}$ , the dielectric permittivity of the cylindrical region containing the DNA helix and the primary hydration sheath. In Eq. 11 for  $\epsilon_{\text{DC}}$  we have used a value of  $68.0\epsilon_0$  corresponding to water with a counterion concentration of about 15%.  $\epsilon_\infty$  was taken to be  $1.77\epsilon_0$  from the optical index of refraction.

Since we are mainly interested in the situation of a dissolved DNA polymer where the counterions mainly behave as area bound (for a detailed discussion refer to our earlier work on counterion effects, Saxena and Van Zandt, 1992), in the present calculation we would be considering the case  $x_c = 0$  corresponding to a uniform charge and mass loading of the hydration sheath (Manning, 1979).

With the above considerations, for a perfect chain homopolymer the dynamics can be described by equations of

motion written in matrix notation as follows (Saxena et al., 1991):

$$[\mathbf{A} + \exp(i\theta)\mathbf{B} + \exp(-i\theta)\mathbf{B}^T - \omega^2\mathbf{I}]\mathbf{q} = \mathbf{0}, \quad (12)$$

where  $\mathbf{A}$  is the  $N \times N$  matrix of Hooke's law force constants within a unit cell as described above. ( $N$  is the total number of degrees of freedom in a monomer.) Matrices  $\mathbf{B}$  and  $\mathbf{B}^T$  represent the force constant contributions from the connections of the unit cell to the neighboring cell on both sides. It is assumed that dynamical connections across the cell boundaries are of no longer range than one monomer spacing (which means that the contributions to  $\mathbf{B}$  are mainly from the bonded interactions between pairs of atoms across the boundary between neighboring monomers.)

Our ability to include this important part of the dynamics is a distinct advantage of our treatment as compared with earlier calculations. The dynamical problem can be solved by direct diagonalization to obtain the mode frequencies and the corresponding eigenvectors, which can be expressed as:

$$\mathbf{q}(m) = \mathbf{q}(0)\exp(i\theta m). \quad (13)$$

$\theta$  is a relative phase angle, and  $m$  is an integer cell index. These modes represent propagating harmonic waves on the infinite polymer.

The wave solutions given by Eq. 13 assume periodic boundary conditions appropriate to the translational symmetry. One can also construct other solutions satisfying different boundary conditions such as waves with finite amplitude at  $m = 0$  and vanishing amplitude as  $m \rightarrow \infty$ , written as

$$\mathbf{q}(m) = \mathbf{q}(0)\exp\{(i\theta - \Delta)m\}, \quad (14)$$

which decays to the right.

For a polymer with a symmetry-breaking defect such as weak hydrogen bonds in a monomer, there will be solutions with amplitudes exponentially decaying along the chain to either side of the defect. The most general solution for the unperturbed regions to the right of the defect can be expressed as a sum of solutions such as those of Eq. 14,

$$\mathbf{Q}(m) = \sum_{\lambda} b_{\lambda} \mathbf{q}_{\lambda}(0) \exp\{(i\theta_{\lambda} - \Delta_{\lambda})m\}, \quad (15)$$

where the  $\Delta_{\lambda}$  describe the amplitude decay of component waves. The allowed values for  $\theta_{\lambda}$  and  $\Delta_{\lambda}$  can be found by solving an algebraic problem as described in our earlier work (Saxena et al., 1991). The number of allowed solutions for these quantities strictly depends on the number of bonds across the cell boundaries connecting the defect cell to the semi-infinite chains on either side. This number turns out to be very small as compared with the number of degrees of freedom  $N$  in a monomer on a perfect polymer. For a homopolymer of adenine-thymine base pairs the total number of degrees of freedom (including that for the surrounding water sheath) is 124. It turns out that the number of permissible solutions for  $\Delta_{\lambda}$  is 14 for each half of the chain.

One can also set down the equations of motion for the central defect cell in a similar way including all the effects, which can be written as:

$$[\mathbf{A}_0 - \omega^2\mathbf{I}]\mathbf{Q}_0 + \mathbf{B}_1\mathbf{Q}(1) + \mathbf{B}_{-1}\mathbf{Q}(-1) = \mathbf{0}, \quad (16)$$

where  $\mathbf{A}_0$  is the force constant matrix for the defect cell, and  $\mathbf{Q}_0$  is the vector representing the amplitudes of atomic motions within the defect.  $\mathbf{B}_1$  and  $\mathbf{B}_{-1}$  are the matrices for the interaction of the defect atoms with the right and left halves of the chain, respectively. The effects of symmetry-breaking interactions at the defect-polymer interface are thus formulated in terms of boundary conditions such that the net forces on both sides are balanced, the simultaneous solutions of Eqs. 13 and 15. This leads to a set of conditions to be satisfied by the solutions given by Eq. 14 and the solutions of the equation of motion for the defect cell. One of the important features of this method is that the size of the final problem, i.e., the size of the boundary condition equation, is very small, equal to the number of allowed  $\Delta_{\lambda}$  irrespective of the size either of the defect or the unit cell in the original perfect polymer chain. Thus, once the one-sided solutions of the unperturbed polymer have been found, various defects of arbitrary size and configuration can be easily studied. The boundary conditions are checked by scanning a wide range of frequencies  $\omega$  of interest. When a frequency is found for which the set of boundary conditions is exactly satisfied, a solution exists having non-zero vibrations in the defect portion and decaying amplitudes in the perfect chain halves to either side. This, of course, corresponds to a local mode of the system.

The procedure described above was used to find the localized vibrational modes on a poly(dA)-poly(dT) polymer having a single monomer with weakened hydrogen bonds. Various combinations of weak hydrogen bond strengths were examined.

This polymer has two hydrogen bonds N(1)—H—N(3) and N(6)—H—O(4). The equilibrium length of the N—O bond in a perfect infinite chain polymer is longer than that of the N—N bond. As a consequence of this the N—O bond is weaker than the other one. The force constants, which are the second derivatives of the potential energy, for these bonds can be calculated from the famous Lippincott-Schroeder model (Schroeder and Lippincott, 1957; Schroll et al., 1991). As the bonds are stretched due to increased bond length, they become weaker and their force constants are reduced. In poly(dA)-poly(dT) as the lengths of the bonds increase, the stronger (in the perfect chain) N—N bond weakens faster than the weak N—O bond. At some point both N—O and N—N bonds may have almost equal lengths. In that case the strengths and the corresponding force constants for both bonds will be approximately equal, since they lie in the same part of the potential energy curves. This, therefore, leads to a variety of possibilities for the weakening of the hydrogen bonds.

We performed calculations to examine the possibility of local modes for different combinations of weak hydrogen

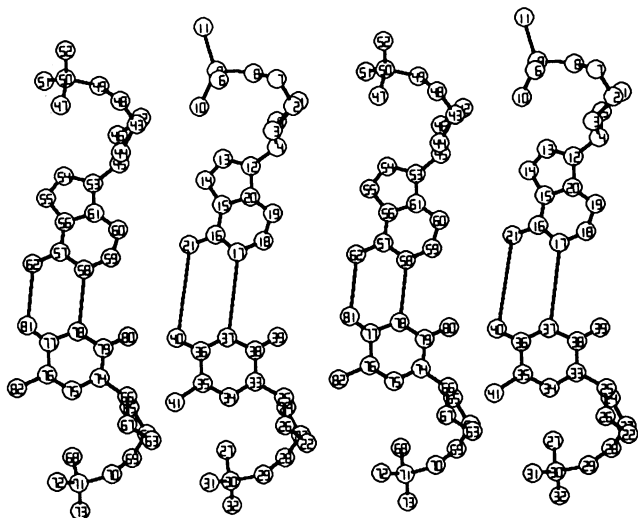


FIGURE 1 Stereo-paired views of a monomer of poly(dA)-poly(dT) DNA polymer with perturbed hydrogen bonds. Numbers 1–41 represent the positions of the atoms of the defect cell with displacements corresponding to the localized mode at  $63.2\text{ cm}^{-1}$ . Numbers 42–82 show the equilibrium positions of the same atoms. The helix axis (the  $z$  axis) is perpendicular to the plane of the figure and the two hydrogen bonds are almost parallel to the  $y$  axis. This view clearly shows the stretched hydrogen bonds. A different view, along the  $z$  axis, does not show substantial motion of the atoms.

bond force constants. For the case when both hydrogen bond force constants were reduced to half their normal perfect chain strength we found a local mode at  $63.2\text{ cm}^{-1}$ . This agrees with Awati and Prohofsky's (1989) calculation for the same mode. This combination of force constants for the weak bonds can be considered as an average stretching of the bonds such that they still have different lengths. A detailed analysis of the eigenvector for the defect cell for this mode shows that it has a strong hydrogen-bond breathing character. Interestingly, however, the phosphate groups maintain the same separation, so this motion is not merely a simple "breathing". In Fig. 1 we display side-by-side stereo-paired images of the equilibrium positions of base pair atoms and the positions of the same atoms under the displacements corresponding to the said eigenvector. Examinations and comparison of the two situations displayed clearly show the character of the motions of the atoms corresponding to this particular mode. The total hydrogen-bond stretch amplitudes were found to diminish as expected to either side of the central cell. This mode was found to be a purely local mode; its frequency lies in the forbidden band gap of the spectrum of the infinite-chain perfect polymer and is found to emerge from the band edge at  $63.5\text{ cm}^{-1}$ . Over the full microwave range ( $<200\text{ cm}^{-1}$ ) no other local mode was found to exist for this set of weak bond strengths.

Very useful and instructive information about the localized excitations is the distance over which they extend. As is clear from the theory, each local mode combines a small number (14) of different basis modes, each with characteristic decay lengths, each of which contributes to the localized motion with a certain amplitude determined from the bound-

ary conditions. Analyzing the numerical data for the local mode at  $63.2\text{ cm}^{-1}$ , we find that there are 12 contributions from the decaying waves whose amplitude drops very fast, to about  $\frac{1}{3}$  the maximum amplitude, within only two nearest neighbors on either side of the defect. In addition there are contributions from two longer-range waves but with relatively smaller amplitudes, which decay within 100 cells on both sides. Overall the net effect is given by the linear combination given by Eq. 15. For this particular mode it is found that the shorter-range contributions are relatively very strong, and the vibration amplitude essentially vanishes within a few cells to either side of the defect cell.

The presence of this mode strongly depends on the choice of the strengths of the weak bonds. When only one bond, particularly the weaker N—O bond, is weakened and the other bond is kept with normal infinite chain strength, the local mode at  $63.2\text{ cm}^{-1}$  is not found. An extreme case is when one bond, the weak N—O bond, is completely broken and the other bond is left unperturbed. In this case no local mode with hydrogen-bond breathing character was found. However, another local mode was found at  $72.4\text{ cm}^{-1}$  with strong propeller twist motion in the central defect cell, again diminishing on either side of the defect cell. Repeated calculations for a variety of weak bond strengths showed that the strong hydrogen-bond stretch local mode exists only when both hydrogen bonds are weakened simultaneously.

The hydrogen-bond stretch local mode found at  $63.2\text{ cm}^{-1}$  agrees with similar local modes found by Awati and Prohofsky (1989) in the frequency range of  $63.9$  to  $66.7\text{ cm}^{-1}$  for a B-form poly(dA)-poly(dT) DNA. However, there are certain differences in the hydrogen-bond strengths used by these authors and those used by us. Another item agreement between our calculations and those of Awati and Prohofsky (1989) is the nonexistence of any other local mode for the particular combination of the weak bond strengths. However, these authors have not explored other different possibilities for weak hydrogen bonds as we have described above. From our analysis one of the most important facts we find is that for the existence of large-amplitude hydrogen-bond stretch local mode there is some minimum size of perturbations required. The existence of any local mode is extremely sensitive to the way the hydrogen bonds are weakened.

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