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Theory of Complex Defects on DNA Polymer Chain

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(1) A theoretical/computational study of vibrational states of long chain polymeric DNA of nearly perfect translational symmetry but containing isolated damage, substitutions, or defects of other sorts. A new, closed form, computational algorithm is developed for such systems and applied to certain simple example cases.
(2) A computationally modest scheme for estimating relative intensities of Raman scattered lines is developed and applied to simple molecules, preparatory to application to DNA polymer.

14. SUBJECT TERMS

Molecular Vibration, DNA Polymer, Local Mode,
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OBJECTIVE: To develop and use the theory of molecular vibrations for localized defect structures on DNA polymer chains. To demonstrate how spectroscopy serves as an assay of defect types.

APPROACH: Equations of motion of all the atoms of a DNA polymer chain are set up using a model of linear, pairwise forces between nearest neighbors. The physics of charged, moving bodies in dielectric, conducting media are used to model the presumed forms of the interactions. The equations of motion are reduced to algebraic equations and solved by numerical methods on the computer. Eigenvalues and eigenvectors resulting are studied for what they reveal about DNA dynamics and structure.

ACCOMPLISHMENTS: (three years) We have completed the development of the closed form solutions of the localized normal mode problem for the polymer chain. This methodology offers a great saving in computational effort over previous attempts to construct a theory of local mode vibrations. More important, it also allows incorporation of long range effects which were impossible to include in earlier theories. We have published a complete description of the mathematics of our treatment, as well as several examples of application to the DNA system.

We have continued in our long effort to improve the connection between molecular physics and the parameters of the linearized theory of normal mode vibrations. We have studied the physics of hydrogen bonds, long range Coulomb interactions, and dissolved charged ions in the nearby solute.

We discovered that the freedom to take various shapes in three dimensions greatly influences the elastic parameters of the hydrogen bonding process. In the

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compressional phase of a stretching vibrational motion of an H-bonded pair, the ability of the intermediate H ion to move off the symmetry axis greatly increases the range over which it may be safely assumed that the forces are linear. It also reduces the effective force constant.

We have studied the sensitivity of spectral frequencies in the lowest frequency range to sample water content, finding that a number of important spectral features are completely transformed as water is removed. Of note in this regard, all "area bound" systems of counterions must eventually become "site bound" under progressive dessication. Furthermore, the strongly polar, long range sound waves - the linear plasmon states - lose their acoustic character in that they no longer drop to zero frequency in the infinite wavelength limit. This mechanism seems to provide an explanation of the very strong experimentally observed features at 25 cm^{-1} in a number of DNA film samples.

We have constructed a model system that permits parameterization of systems of intermediate water content that can not be said to be purely either of the site-bound or the area-bound type with respect to their counterion behavior. Counterions which remain for longer periods in favored locations, but eventually drift loose to move about the near region before becoming attached again can be treated in this formalism. We also discovered that the sites of localization for monovalent counterions assumed in other studies were unstable loci, and that counterions localize in quite different places.

We have pointed out that simple spectroscopic studies, either infra-red or Raman, are subject to a fundamental problem of overlapping in the lower frequency range. We have emphasized that this overlapping must either be attacked by a more complex and complete form of spectroscopic study, or treated as an insuperable bar to further investigation at these frequencies.

As a tool for overcoming the problem of spectral overlap, we have developed a method of calculating absolute Raman intensities by computationally modest, feasible means. We will be applying this new method in later work, but for now have treated only small molecules for which the predictions of the theory could be compared against very well understood spectral systems.

SIGNIFICANCE: The development of a spectroscopy of local defects on DNA polymer offers 1) a tool for study of the physics of atomic interactions and 2) a potential diagnostic tool for disease or insult to the chromosomes. Our results are encouraging in that local modes have proved to be much fewer - and thereby less confusing to the spectroscopist - than the more common phonons in this system.

PUBLICATIONS: (supported wholly or in part by this contract)

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