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Millimeter-microwave spectrum of DNA: Six predictions for spectroscopy

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A recently presented model of long-range interatomic interactions in a DNA polymer is compared to an earlier approach. Comparison of the results of both approaches is made to existing experiments. The newer method consistently produces good experimental agreement within the context of a single, physically reasonable parametrization. It is therefore sensible to consider some observable but not yet observed features of the calculation as valid predictions. We offer a dozen or so resonances in the frequency range from 10^{10} to 10^{12} Hz as potentially new observable absorption lines.

INTRODUCTION

We have recently reported[1,2] on a new calculation of the vibrational spectrum of a dissolved long-chain DNA polymer. The new feature of our methodology is that we find those elastic force constants arising out of relatively weak long-range interactions in a new way. Rather than individually summing over all pairs of mutually interacting atoms as in the past, we explicitly introduce an electric field acting locally on the atomic partial charges. Maxwell's equations then yield the global, long-range behavior of the fields and therewith effective atomic interactions.

Since the elucidation of the low-frequency sound speed on DNA polymer by Mei *et al.*[3] it has been known that the long-range interactions, while individually small, in virtue of their great numbers accumulate to a dominating role in the microwave regime. It was recognized even initially, however, that interactions between distant atoms are not simple Coulombic forces, but are modified in some way by the intervening material. This was taken into account by some heuristic assignment of effective "dielectric constants," the constants being modified for each interacting pair according to relative distance and/or location within the polymer. For example, if both atoms are in bases, a low value for $\epsilon_{i,j}$ was assigned, in contrast to the case for phosphate-phosphate interactions, where a higher value presumably takes account of wetter intervening material. One peculiar feature of the Mei model as it has been subsequently applied[4] is that the partial charges enter in the form of their absolute, rather than algebraic, values. In any case, the atomic partial charges are always an ingredient of the resulting force-constant expression, recognizing that the long-range interactions are basically electrical in nature.

In our new approach to these questions the electromagnetic field accompanying a mechanical disturbance of partially charged objects accounts for the intervening-medium effects in a natural way. We find that characteristically the fields extend out a considerable distance into the surrounding medium; the dielectric behavior of the medium is thus incorporated when the fields are forced to satisfy electromagnetic boundary conditions at the interface between molecule and solvent. This together with the propagation characteristics of the fields through the combined molecule-solvent system give a more nearly first-principles account of the distance dependence of the interactions.

The partial atomic charges enter the vibration spectrum calculation in two ways: first, the local electric field causes a force on a charge which we include in the corresponding atomic equation of motion. Second, the partial charges and their dynamic displacements define the dielectric polarization density **P**. Since **E** and **P** are connected by Gauss's law through their divergences, the local electric field can be expressed in terms of the local atomic displacements. Requiring consistency of the whole logical-chain couples displacements with displacements, thereby expressing long-range effects as effective elastic constants. These are finally simply added in with the true elasticities.

MEI'S MODEL OF LONG-RANGE DNA INTERACTIONS

The Mei formulation of the long-range problem was a response to the appearance of experimental data, Brillouin scattering work of Maret *et al.*[5] on the velocity of sound. The still older calculations of Eyster and Prohofsky[6], based entirely on short-range covalent forces, had given sound velocities nearly two orders of magnitude too small. The parameters of the Mei formulation, while lacking a fully satisfactory first-principles justification, could be adjusted to give a reasonable match to the sound speed, and thus represented a substantial improvement. Unfortunately, the results did not necessarily bear on other independent experiments even within this frequency range.

Since the appearance of the Maret measurements[5] of Brillouin scattering which determined the sound speed, their confirmation and extension by Lindsay[7] and Mei's long-range force model in response, other relevant data on the low-to mid-frequency DNA spectrum have been published. Recently, Grimm *et al.*[8] have done inelastic neutron scattering studies on ordered DNA chains. Prabhu *et al.*[9] and Schroll *et al.*[10] have shown that the re-

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sults of their measurements are well interpreted as the higher-frequency extension of the compressional sound wave spectrum. In this higher-frequency range, however, the sound speed turns out to be considerably higher than that measured below 20 GHz. The Mei model deals with this shift by changing parameter values, the $\epsilon_{i,j}$; it cannot simultaneously reproduce the two results.

Urabe, Tominaga, and Kubata[11] have measured a feature in the DNA Brillouin scattering spectrum at about 12 cm^{-1} which has been interpreted as a reststrahl frequency arising out of an optical-phonon branch. The lowest optical frequency appearing in the Mei model is found around this frequency.[4]

In 1987, Powell *et al.*[12] published infrared absorption spectra of oriented films in the frequency region from 50 to 110 cm^{-1}. In the best samples a series of four prominent resonances was observed. The Mei model managed to rationalize the two highest of these, but the other two, and especially the most prominent at 64 cm^{-1}, seemed particularly difficult to obtain. This intractability gave rise to some speculations that this mode might rather be associated with couplings between neighboring chains of the relatively more dense film material, rather than a spectral feature of isolated polymer. Similar spectra in this frequency region have been obtained by Urabe *et al.*[11] in Brillouin scattering.

RESULTS OF THE ELECTRIC FIELD MODEL

The electric field methodology we have developed reproduces well all of the known experimental effects listed in the preceding section. It does this in the framework of a single model with a single set of parameters. In Fig. 1 we show our most recently calculated spectrum for *B*-form poly (dA) · poly (dT). For short-range interactions taking place within the interior of a single-base-pair monomer we have used a value of $2\epsilon_0$ for the dielectric permittivity. (The results are not sensitive to this choice. For the surrounding medium, we have used $20\epsilon_0$. We take this value to be "typical" for the range of frequencies for which the solvent dielectric constant exerts an important influence. While we intend eventually to repeat these calculations using an explicitly frequency-dependent solvent permittivity, we anticipate only minor changes compared to the present less exact results.

The low-frequency sound speed, in the gigahertz range, is 1.8 km/sec. This compares very favorably with Lindsay's measurements[7] for well-hydrated material.

Note the series of crosses in the figure roughly following the dashed line rising from the origin. The crosses are extracted from Grimm's neutron scattering results. The dashed line is not a single-phonon branch, but rather an average of several branches weighted by their relative contributions to the density oscillations. This predicted neutron scattering spectral density is more completely explained by Schroll *et al.*[10] It is clear that this model provides an excellent representation of the neutron data.

Direct photon absorption by the polymer chain is possible only for phonon modes of wavelengths equal or comparable to the total chain length; this means for $\theta=0°$ or $\theta=36°$. To the extent that the dipole moment of the atomic motion lies along the longitudinal chain direction, absorption occurs by 0° modes. Dipole components transverse to the polymer axis cause absorption at 36°. Thus from Fig. 1, we would expect absorption features to appear at 63–67 cm^{-1}, another band or line pair at 80–84 cm^{-1}, a band at 96 cm^{-1}, and a band at 108 cm^{-1}. These are all within a few wave numbers of the strong absorption features reported by Powell *et al.*[12]

As noted above, this model also shows an absorption feature at 13 cm^{-1}. This value matches well the observed Brillouin scattering peak in well-hydrated material. We are not yet in a position to comment on how this feature might be shifted in drier material.

In summary, the explicit field model provides a good match for all presently available experimental features within the framework of a single set of physically reasonable parameters. Since the number of these parameters (2) is smaller than the number of experimental data (6) it is clear that the model has considerable predictive power.

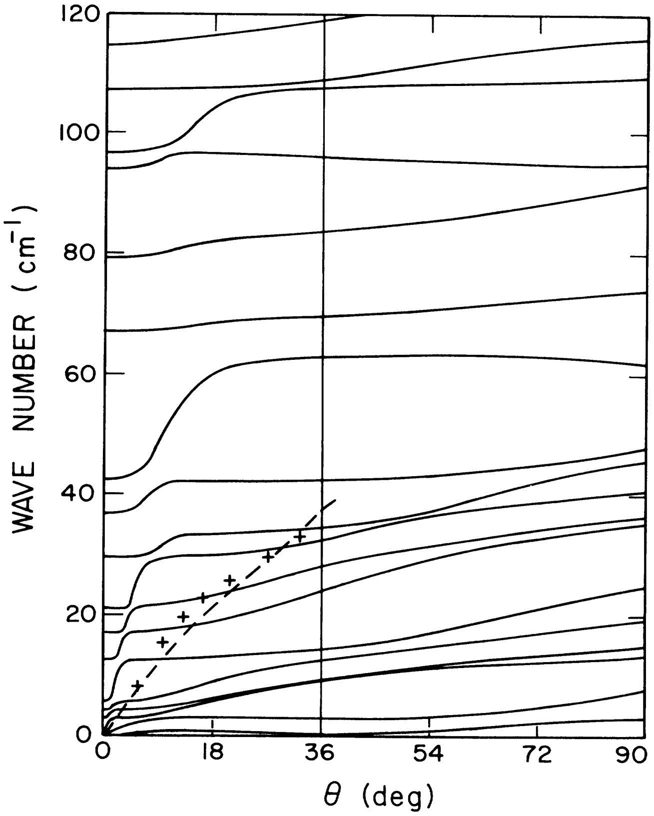

FIG. 1. Calculated spectrum of a long-chain DNA polymer, *B*-form poly(dA)·poly(dT), in the frequency range below 120 cm^{-1} (500 μm). Interesting spectral features in absorption occur at the intersections of the phonon branches with the $\theta=0°$ axis and the $\theta=36°$ axis. Resonances are also predicted in connection with the the disconnected but generally straight acoustic branch formed by various pieces of the optical branches, the plasmons. Crossed indicate experimental data from inelastic neutron scattering, and the dashed line shows the weighted average longitudinal density oscillation.

We thus reasonably extend our attention to the remaining features of the model.

SOME PREDICTIONS OF NOT YET OBSERVED FEATURES

The most striking new feature predicted by this model is the existence of plasmon resonances. We have elsewhere[1,2] called attention to the possibility of seeing these modes. Since those papers were published, we have made some improvements on the force-constant model; our present best value for the theoretical plasmon wave velocity is 19.6 km/sec. This means that in a sample composed of homogeneous length pieces like that prepared in lower-frequency studies[13]—2740 base pairs $=0.932\mu$m—a series of resonances should occur at 10.5, 21.0, 31.5, ... GHz (0.32, 0.63, 0.94, . . . cm^{-1}) corresponding to 1,2,3, . . . , half waves on the chain. Depending on assumed boundary conditions and directional homogeneity of the long molecule, the even-numbered members of this series may or may not cause absorptions. End effects and concomitant frequency shifts will be more pronounced for the lowest members of the series. The plasmon branch of the spectrum is seen in Fig. 1 as the series of disconnected pieces out of successive optical-phonon branches, rising in a more or less straight line from the origin at $\vartheta=0^\circ$.

By contrast with the Mei model, the explicit field model predicts observable optical resonances below the 13-cm^{-1} feature at 3.0, 4.3, and 5.8 cm^{-1} for longitudinal polarization and 3.0 and 9.3 for transverse interaction. We are also led to expect longitudinal absorptions above 13 cm^{-1} at 17, 30, 37, and 43 and transverse polarized resonances at 14, 28, 35, and 43.[14]

We are aware that much of what we are predicting lies in experimentally awkward frequency ranges. This is particularly true in light of our insistence upon considering only the high-hydration case, for in these frequency ranges the absorption of water adds a large obscuring background. We are encouraged, however, not only by calculations[2] showing that the predicted resonances should be sharp and well defined, but also by the previously demonstrated ingenuity of our various experimenter colleagues. Current development advances of tunable sources in the microwave to far-infrared region such as the free-electron laser hold great promise for the near future.

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[14] *In toto* we have predicted rather more than the six lines promised in the title. However, not all these predictions are distinct, the longitudinal and transverse lines being aspects of the same bands. and the plasmon series being part of a single phenomenon. The "six" is thus a literary rather than a literal count.