We have carried out transmission measurements as a function of power for DNA films irradiated near the absorption maximum at 43 cm\(^{-1}\) using the Santa Barbara Free Electron Laser. Initial results show no non-linear effects, such as bleaching, up to power densities of a few kW/cm\(^2\).

An experiment to search for unstacking of DNA bases when the molecule is exposed to intense radiation near the "melting mode" frequency (>80 cm\(^{-1}\)) is nearing completion: exposure to available FEL power does not cause significant heating of the solution.

Phonon damping mechanisms have been investigated in the range 0.1 to 200 cm\(^{-1}\) by both Raman and Brillouin spectroscopy experiments made as a function of temperature and frequency. Coupling to relaxational motion of the hydration shell appears to be the main damping mechanism. At low (GHz.) frequencies, Debye-like reorientation (over)
Properties of DNA in the far Infrared

S.M. Lindsay
Department of Physics
Arizona State University
Tempe, AZ 85287

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Properties of DNA in the far Infrared

S.M. Lindsay
Department of Physics
Arizona State University
Tempe, AZ 85287

Abstract

We have carried out transmission measurements as a function of power for DNA films irradiated near the absorption maximum at 43/cm\(^{-1}\) using the Santa Barbara Free Electron Laser. Initial results show no non-linear effects, such as bleaching, up to power densities of a few kW/cm\(^2\).

An experiment to search for unstacking of DNA bases when the molecule is exposed to intense radiation near the 'melting mode' frequency (-80 cm\(^{-1}\)) is nearing completion: exposure to available FEL power does not cause significant heating of the solution.

Phonon damping mechanisms are being investigated in the range 0.1 to 200/cm\(^{-1}\) by both Raman and Brillouin spectroscopy measurements made as a function of temperature and mode frequency. Coupling to relaxational motion of the hydration shell appears to be the main damping mechanism. At low (GHz.) frequencies, Debye-like reorientation of the bound water dominates the loss process, while at much higher frequencies (-10\(^{12}\) Hz), the hydrogen-bond breaking relaxations may contribute.

Transmission of DNA films in the far infrared

DNA films have most unusual optical properties, associated in some way with the DNA-counterion interaction\(^1\). Since counterions are involved in the low frequency motions of the polymer\(^2\), it is interesting to investigate the possibility that DNA is a non-linear material in the far infrared. We have made transmission measurements as a function of incident power at the 43 cm\(^{-1}\) absorption maximum\(^3\) (the far infrared absorption of a dry film is shown in Figure 1a - the FEL frequency used is marked by an arrow.

The experimental arrangement is shown in Figure 1b. A pyroelectric detector (PED1) monitors the incoming power via the mylar beamsplitter BS1. Mirrors M1 and M2 focus the beam onto the sample and back onto the second detector PED2. The output of each detector is stored in a boxcar triggered by the FEL. The FEL was operated in an unstable mode, giving rise to wide power variations from pulse to pulse (each pulse was approximately gaussian with a FWHM of about 1 \(\mu\)s and a maximum energy of 400 nJ). The sample was sandwiched between two fused silica slides.
(which accounted for about 30% transmission loss). The remaining loss of about 50% was consistent with the transmission measured by Wittlin et al.\textsuperscript{3}. The sample was moved to several different positions about the focus (displacement marked as $\delta$ on Figure 1b) to check for interference effects.

We have yet to analyze the data from this experiment, but the uncalibrated output from one run is shown in Figure 1c. The transmission appears to be linear.

**Heating measurements with the athermal melting apparatus**

A first step in our experiment to search for base unstacking as non-equilibrium phonons are pumped near the 'melting' mode frequency is to determine the thermal heating of the buffer solution by the FEL. For this purpose, we operated the absorption cell (fabricated from single crystal quartz) in one arm of an optical interferometer as shown in Figure 2. A probe beam is split off by BS\textsubscript{1}, and recombined with the reference beam by BS\textsubscript{2} to form an interference fringe system on the pinhole, PH. When fluid in the cell is heated, the fringes sweep past PH, causing oscillations on the output of a photodetector, PD. The system was tested by heating the cell directly, and the calculated sensitivity of about 3 fringes per degree confirmed. The probe beam was positioned within about 2 $\mu$m of the window exposed to the FEL, with a beam waist no larger than about 2 $\mu$m over the probe region. When exposed to the maximum available FEL power at 43 cm$^{-1}$ (400 $\mu$J in 1 $\mu$s), less than 0.05 fringe motion was detected, corresponding to no more than about 0.1$^\circ$ of heating. (The temperature is monitored dynamically by recording the output on a boxcar integrator with about 20 ns overall response time.)

This upper limit of heating would be no more than a factor 2 worse at 80 cm$^{-1}$ if the same power were available from the FEL\textsuperscript{4}.

At the time of writing, the FEL has been brought into operation at the desired higher frequency, although the available power is rather limited. Therefore we plan to duplicate the proposed phonon-pumping experiments using a molecular vapor laser set up at the FEL facility at UCSB. Using ammonia vapor, approximately 4000 $\mu$J is available at 80 cm$^{-1}$ as 200 ns pulses\textsuperscript{5}.

**Damping of phonons in DNA**

We have reported our Brillouin studies of phonon damping by the hydration shell elsewhere\textsuperscript{6,7}. Briefly, damping is controlled by relaxation of the bound water which results in the possibility of resonant motion in dissolved DNA at much lower frequencies than might otherwise be expected if the DNA were damped by the motion of 'classical' water\textsuperscript{8}. We have extended this work to a wide variety of hydration conditions. Figure 3 shows typical phonon loss data vs. frequency (see ref. 7 for details) for samples between 0% and 95% r.h. (the solid lines are calculated).
We find that the loss process builds up in intensity in proportion to the number of molecules in the primary hydration shell (a number we have obtained by extending the Raman measurements described elsewhere9). The timescale and activation energy of the loss process corresponds to the Debye relaxation time and the activation energy which might be expected for reorientation of the bound water, so the loss mechanism is presumably coupling to simple reorientation of the molecules in the primary shell (excluding the first 5 most tightly bound at the phosphates).

We have also gained some insight into loss mechanisms in the wavenumber region by examining the low frequency Raman spectra of single-crystal oligonucleotides (samples provided by W.L. Peticolas). The really striking feature of these spectra is their similarity to the fiber spectra taken with sample of natural DNA. Sample spectra are shown in Figure 4a (Na-DNA, Calf Thymus film, 86% r.h.) and 4b (d(CGCGAATTCCGG)). The solid lines are least squares fits. The data for a number of samples are summarized in Table I below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location of bands (v) (cm(^{-1}))</th>
<th>Width of bands ((\Delta)) (half width cm(^{-1}))</th>
<th>(\Delta/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-DNA (CT film, 88% r.h.)</td>
<td>18, 49, 85</td>
<td>7.5, 23, 29</td>
<td>0.42, 0.47, 0.34</td>
</tr>
<tr>
<td>Na-DNA (CT film, 86% r.h.)</td>
<td>21.2, 34, 58, 88.4</td>
<td>8.4, 7, 16, 34</td>
<td>0.4, 0.21, 0.28, 0.38</td>
</tr>
<tr>
<td>d(CGCGAA TTCGCG)</td>
<td>20.5, 47, 89</td>
<td>7.5, 22, 25</td>
<td>0.37, 0.47, 0.28</td>
</tr>
<tr>
<td>d(GGTATA CC)</td>
<td>12.5, 21, 57, 107</td>
<td>3.3, 18, 27, 28</td>
<td>0.26, 0.86, 0.47, 0.26</td>
</tr>
</tbody>
</table>

Table I
Location and widths of a number of low lying Raman bands

The similarity of bandwidths in both the oligonucleotides and natural samples eliminates the possibility of inhomogeneity broadening due to base sequence or the morphology of the fibers.
What little data we have on the temperature dependence of these widths suggests that they may not be solely a consequence of very anharmonic phonons. There is a possibility that they arise from relaxational coupling to a fast water mode (hydrogen-bond breaking) and we are investigating this with further temperature studies.

We note, in closing, that the Raman linewidths measure the phonon dephasing time (if they are not inhomogeneously broadened), while the non-equilibrium effects needed for athermal melting of the double helix presumably require a long population lifetime. The two lifetimes may be very different. We hope to establish some limits with CARS pump and time delayed-probe measurements currently in hand.
References


FIGURE 1(a) Transmission of DNA film in the far IR.

FIGURE 1(b) Apparatus for transmission measurements in the far IR.

FIGURE 1(c) Summary of transmission measurements at 43 cm$^{-1}$.

FIGURE 2 Optical heating detector for athermal melting experiment.
The data points are for phonon propagation perpendicular to the helix axis.
FIGURE 4a. Low frequency Raman spectrum of an Na-DNA film (calf thymus) at 86% r.h.

FIGURE 4b. Low frequency Raman spectrum of d(GGCCGATTGGCG)₂.
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