

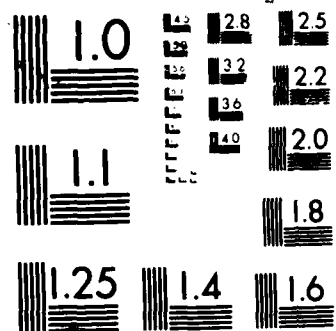
AD-A187 143 PROPERTIES OF DNA IN THE FAR INFRARED(U) ARIZONA STATE 1/1
UNIV TEMPE DEPT OF PHYSICS S M LINDSAY 12 OCT 87
N00014-84-C-0487

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1a REPORT SECURITY CLASSIFICATION (u)			1b RESTRICTIVE MARKINGS NA	
2a SECURITY CLASSIFICATION AUTHORITY NA			3 DISTRIBUTION/AVAILABILITY OF REPORT Distribution Unlimited	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE NA				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Arizona State University			5. MONITORING ORGANIZATION REPORT NUMBER(S) NA	
6a NAME OF PERFORMING ORGANIZATION Arizona State University	6b OFFICE SYMBOL (If applicable) NA	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) Department of Physics Tempe, AZ 85287		7b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000		
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b OFFICE SYMBOL (If applicable) ONR	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-C-0487		
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000		10 SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO 61153N	PROJECT NO RR04108	WORK UNIT ACCESSION NO
11 TITLE (Include Security Classification) Properties of DNA in the far Infrared				
12 PERSONAL AUTHOR(S) S.M. Lindsay				
13a TYPE OF REPORT Annual	13b TIME COVERED FROM July 86 to July 87	14. DATE OF REPORT (Year, Month, Day) October 12, 1987		15 PAGE COUNT 10
16 SUPPLEMENTARY NOTATION				
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	DNA, Free electron laser, DNA vibrations, phonons, non-equilibrium phonons, unwinding	
19 ABSTRACT (Continue on reverse if necessary and identify by block number)				
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 ($\sim 80 \text{ cm}^{-1}$) 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)				
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION (u)	
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. J.A. Majde			22b TELEPHONE (Include Area Code) 202-696-4055	22c OFFICE SYMBOL ONR

Properties of DNA in the far Infrared

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Contents

Abstract	Page 1
Transmission of DNA films in the far infrared	Page 1
Heating Measurements with the athermal melting apparatus	Page 2
Damping of phonons in DNA	Page 2
References	Page 5
Figures	Page 6

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Properties of DNA in the far Infrared

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Abstract

We have carried out transmission measurements as a function of power for DNA films irradiated near the absorption maximum at $43/\text{cm}^{-1}$ 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 ($\sim 80/\text{cm}^{-1}$) 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 $200/\text{cm}^{-1}$ 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 ($\sim 10^{12}$ 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 interaction¹. Since counterions are involved in the low frequency motions of the polymer², 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 $43/\text{cm}^{-1}$ absorption maximum³ (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 $1\ \mu\text{s}$ and a maximum energy of $400\ \mu\text{J}$). 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.³. The sample was moved to several different positions about the focus (displacement marked as δ 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 BS1, and recombined with the reference beam by BS2 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 μm of the window exposed to the FEL, with a beam waist no larger than about 2 μm over the probe region. When exposed to the maximum available FEL power at 43 cm^{-1} (400 μJ in 1 μs), less than 0.05 fringe motion was detected, corresponding to no more than about 0.1° 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 FEL⁴.

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 μJ is available at 80 cm^{-1} as 200 ns pulses⁵.

Damping of phonons in DNA

We have reported our Brillouin studies of phonon damping by the hydration shell elsewhere^{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' water⁸. 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(CGCGAATTCGCG)₂). The solid lines are least squares fits. The data for a number of samples are summarized in Table I below.

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

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 inhomogeneous 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.

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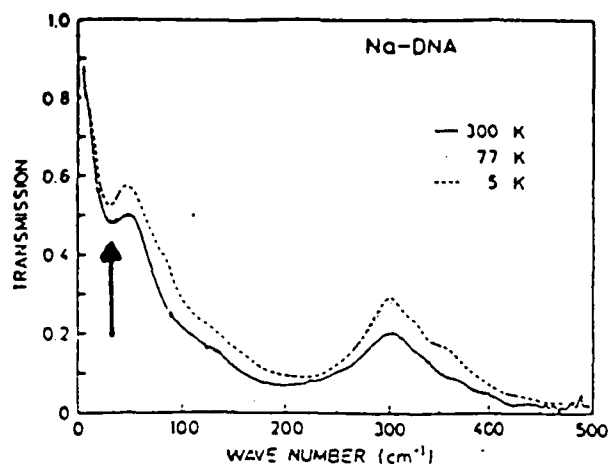


FIGURE 1(a) Transmission of DNA film in the far IR.

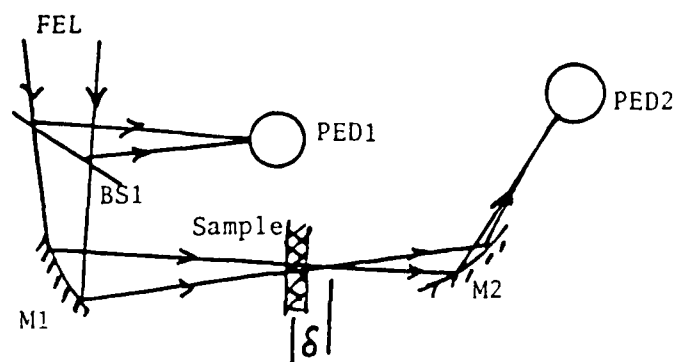


FIGURE 1(b) Apparatus for transmission measurements in the far IR.

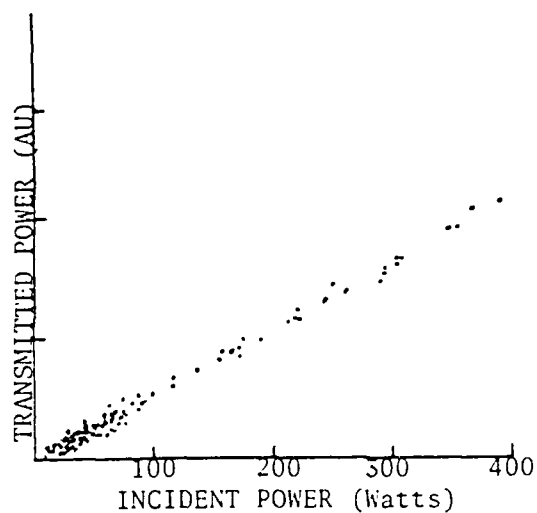


FIGURE 1(c) Summary of transmission measurements at 43 cm^{-1} .

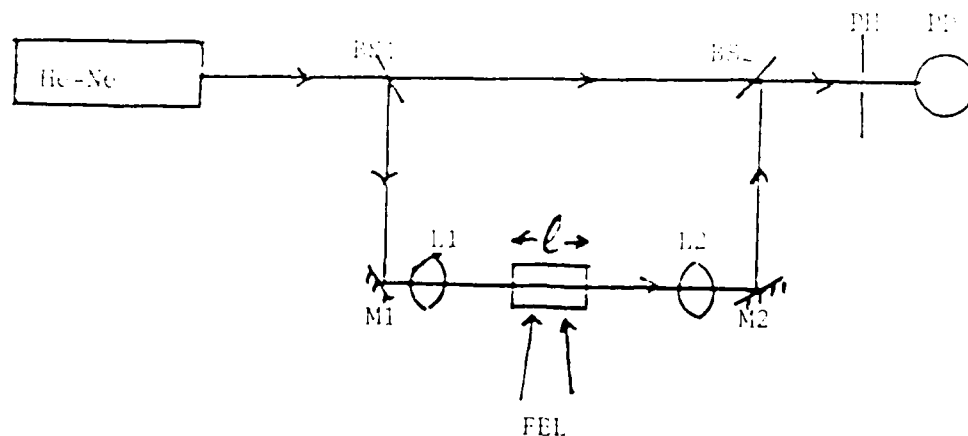


FIGURE 2 Optical heating detector for athermal melting experiment.

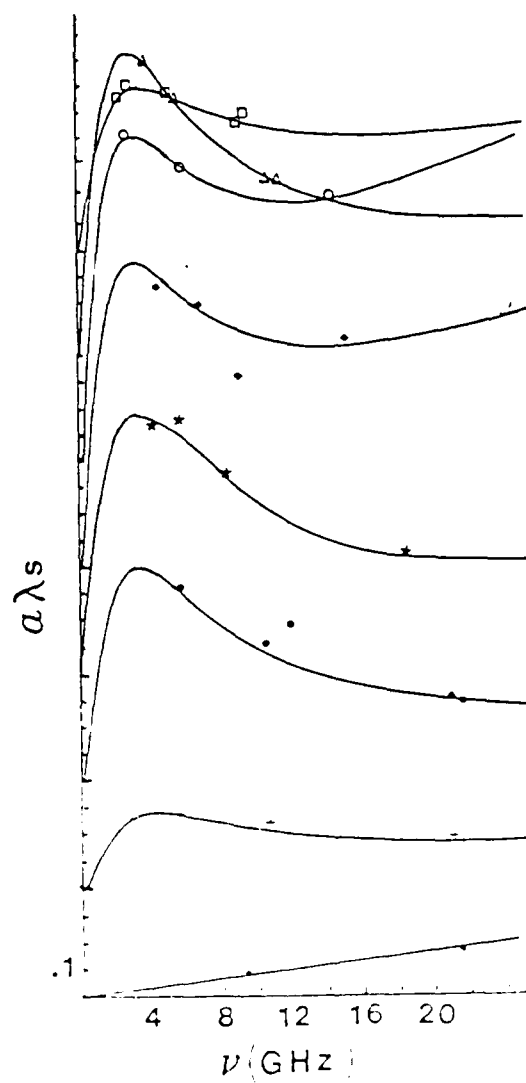


FIGURE 3. Normalized phonon linewidths vs. phonon frequency for samples at various relative humidities. The data (points) and theoretical curves are arbitrarily displaced vertically for clarity. The data points are: 0% r.h. (*), 23% r.h. (+), 45% r.h. (●), 59% r.h. (✱), 80% r.h. (◆), 86% r.h. (◐), 93% r.h. (▲) and 95% r.h. (◑). The data are for phonon propagation perpendicular to the helix axis.

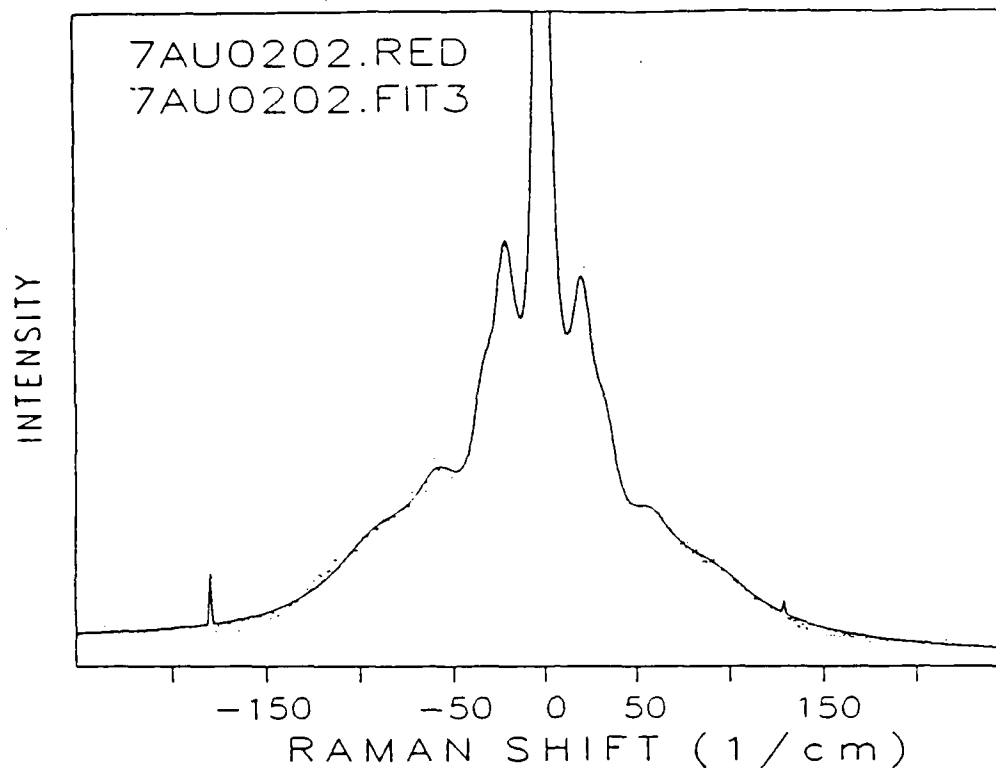


FIGURE 4a. Low frequency Raman spectrum of an Na-DNA film (calf thymus) at 86% r.h.

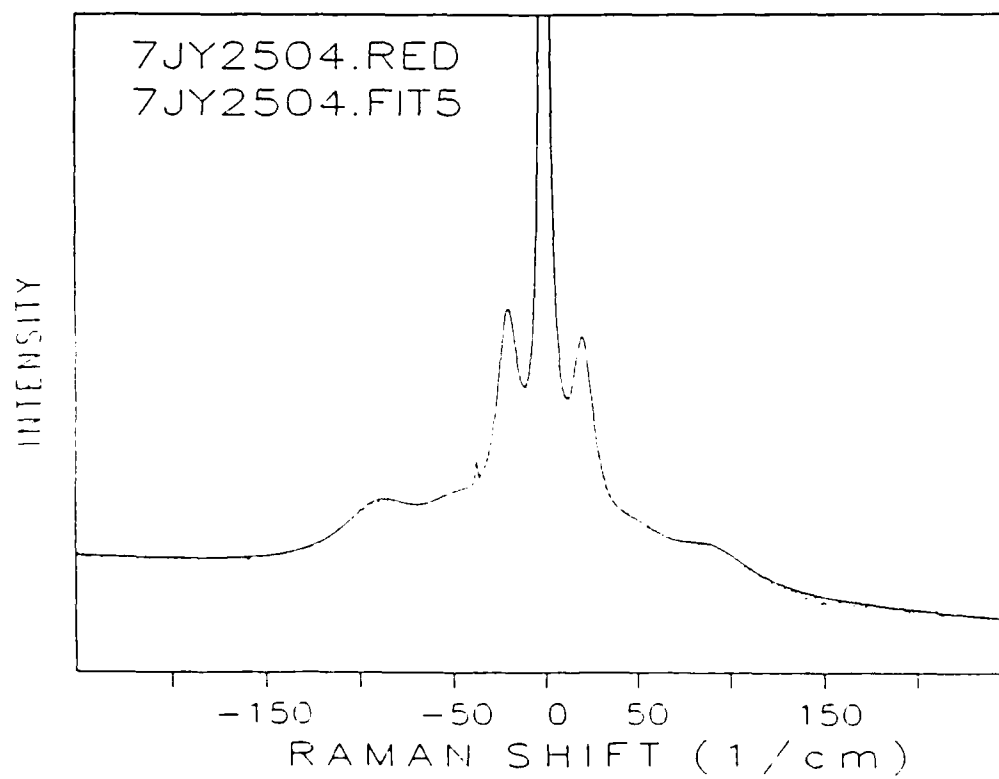


FIGURE 4b. Low frequency Raman spectrum of $d(\text{CGCGAATTCGCG})_2$.

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