Brillouin and Rayleigh studies of urea single crystals

A. Yoshihara and E. R. Bernstein

Citation: The Journal of Chemical Physics **77**, 5319 (1982); doi: 10.1063/1.443802
View online: http://dx.doi.org/10.1063/1.443802
View Table of Contents: http://aip.scitation.org/toc/jcp/77/11
Published by the American Institute of Physics

Brillouin and Rayleigh studies of urea single crystals[a)]

A. Yoshihara and E. R. Bernstein

Colorado State University, Department of Chemistry, Fort Collins, Colorado 80523

(Received 8 June 1982; accepted 9 August 1982)

Brillouin and Rayleigh scattering techniques have been employed to study the elastic behavior of single crystals of urea over the temperature range 15–300 K. An extensive investigation of the room temperature elastic constants is presented yielding a complete evaluation of their anistropy. The temperature dependence of these elastic modes along the [001] and near the [110] directions is followed to 15 K; no evidence of a structural phase transition has been found. Rayleigh scattering experiments reveal a correlation time in the ms range and an intensity behavior that are temperature dependent but show no anomalies as a function of temperature for a number of directions in the crystal. It is found that scattering intensity and correlation time are caused by the modulation and driving of defects by an external periodic applied stress pulse. Neither the correlation time nor the intensity behavior supports the conclusion that urea undergoes a structural second order phase transition in the temperature range 15–300 K.

I. INTRODUCTION

Urea $(NH_2)_2CO$ crystallizes in a tetragonal space group structure, D_{2d}^3 $(P\bar{4}2_1m)$ with two molecules per unit cell.[1] Because of its simple structure and well-established intermolecular interactions (short range and dipolar), extensive studies on the static and dynamic properties of urea have appeared over the last 30 years. Urea has been used as a model for hydrogen bonded molecular crystals and consequently most of the crystal's physical properties have been measured: elastic constants,[2] optical phonon frequencies by Raman scattering[3-5] and infrared spectroscopy,[4,5] neutron diffraction,[6-8] x-ray structural analysis,[9-12] Compton profile,[13] NMR,[14] and specific heat.[15] Several models have been developed to explain the dynamics of the urea crystal based on these data.[6,16-18] It appears to be agreed that, at least to 133 K, there is no structural phase transition in this system.[11]

Urea is known to possess highly nonlinear optical coefficients determined by measurements at 1.06 μm using powdered samples.[19] Recently, it has been demonstrated that urea is an excellent nonlinear optical crystal for second harmonic generation and sum frequency mixing in the ultraviolet (to 238 μm) with a higher efficiency than the well-known KDP isomorphs.[20-22]

One of the later x-ray structural studies on urea[10] has suggested that an isostructural phase transition exists in this system ~ 190 K. This transition as reported is quite unique in that no symmetry change (translation or rotational) takes place at this temperature. The reported transition is characterized only by a continuous anomaly in the thermal expansion coefficient along the *c* (fourfold) axis.

The planar urea molecule with C_{2v} symmetry possesses a large dipole moment of 4.6 D[23] and the crystal structure arrangement is such that these dipoles are antiferroelectrically ordered. A similar material, thiourea $(NH_2)_2CS$ is a well-known organic ferroelectric crystal which crystallizes in the orthorhombic space group D_{2h}^{15} (Pnam) and has five crystal phases below 300 K.[24] If urea does indeed possess a phase transition, it will be a very interesting case to investigate because of its structural and molecular simplicity, well established interactions, and its ready comparison with thiourea.

We have investigated phase transitions in a number of molecular crystals recently (e.g., triazine,[26] benzil,[25] chloranil[27]) by Brillouin and Rayleigh light scattering techniques. These are quite powerful methods for the study of both the dynamic and static properties of molecular solids at phase transitions. In this present report, we present results on the possibility of a phase transition in urea and determine a new set of room temperature elastic constants for this system.

II. EXPERIMENTAL

Single crystals of urea up to $5\times 5\times 20$ mm^3 in size were grown from methanol solutions by slow evaporation. Crystal growth from aqueous solutions with habit modifiers such as NH_4Cl, NaCl, and KCl has also been attempted. Aqueous solutions, however, tend to produce only needles ($1\times 1\times 20$ mm^3) using the slow evaporation technique. As the crystals are readily cleaved, samples were carefully cut with a razor blade and polished with lens paper wet with methanol. The [001] direction is always the easy growth direction and the well developed faces of the crystal are of the {100} type. Using the as grown surfaces, [110] and [1$\bar{1}$0] phonons are easily observed. For anisotropy measurements in the *ab* and *ac* planes, two kinds of cylindrical samples were prepared; 3 mm diam × 10 mm for the *ab* plane scattering and 3 mm diam × 2 mm for the *ac* plane scattering. Although these crystals are of high optical quality with no evidence of macroscopic defects, Rayleigh component in-internsities are about 3×10^4 counts/s. The crystals were examined under a polarizing microscope and found to be single in all instances.

The light scattering apparatus for simultaneous measurement of Brillouin and correlation scattering has already been presented in some detail.[25,26] The spectra were excited by 100 mW of 5145 Å light from an Ar^+ laser. Free spectral ranges of 20, 47, and 53 GHz

---

[a)] Supported in part by the AFOSR.

are used to analyze the Brillouin spectra with a typical finesse of 50 for a triple pass optical system. Data acquisition times of 10 to 100 min are used depending on the phonon, propagation direction, and temperature. The lowest temperature reached in the present experiment is 15 K and the temperature stability is better than ± 0.1 K during the data acquisition time. The estimated errors in the Brillouin shifts are ±1% for LA modes and ±2% for TA modes in regions for which overlapping features do not occur. Precise crystal orientation is determined from selection rules and actual spectra obtained. The estimated errors in direction dependence are ±2.5° for absolute directions and ±1° for rotation angles.

The correlation data were obtained and analyzed as previously described.[25–27]

Two crystals were annealed to 40 °C for roughly two days and the data set was recollected. Unfortunately, this temperature is much too far below the melting temperature of urea to be very effective for annealing. Moreover, urea readily decomposes upon heating over 60 °C. Most likely the annealing process for urea is not a positive contribution to overall crystal quality. Brillouin data obtained from these annealed samples were, however, indistinguishable from that of as grown crystals.

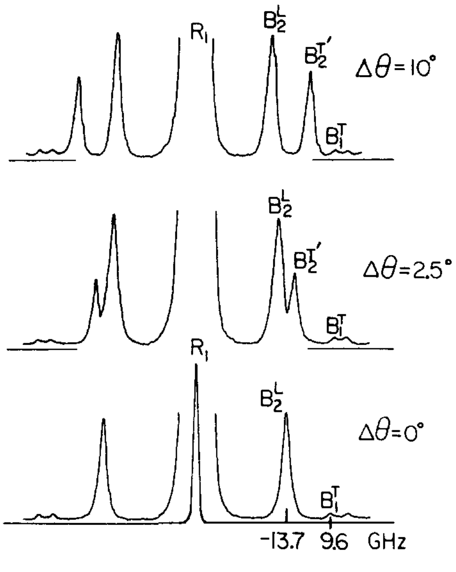

FIG. 1. Urea Brillouin spectrum in the region of the [110] axis [$\Delta\theta = 0$]. The free spectral range of these spectra is 20 GHz and three orders of the interferometer are overlapped. Labels 1 and 2 as subscripts stand for two of these orders; the Rayleigh peak of order 1 is shown (R_1). Brillouin features are labeled B, 1 or 2 for the order, T or L for transverse and longitudinal, and the prime (′) distinguishes between the two anticipated transverse modes. Along [110] ($\Delta\theta = 0$) $B^{T\prime}$ is not Brillouin active. $\Delta\theta$ is the rotation angle from the [110] direction in the ab plane. At $\Delta\theta = 0$ $B^{T\prime}$ and B^{L} are accidentally degenerate. This is due to the accidental degeneracy between $(c_{11}+c_{12}+2c_{66})/2$ for the B^L mode and $(c_{11}-c_{12})/2$ for the $B^{T\prime}$ mode, as discussed in the text. The other transverse mode B^T is governed by elastic constant c_{44} and does not change within experimental error.

III. RESULTS

Brillouin spectra obtained around the [110] direction are shown in Fig. 1. The study presented here is for a deviation angle of phonon propagation direction from the [110] direction in the ab plane. In the [110] direction, only two phonon modes, governed by elastic constants c_{44} and $(c_{11}+c_{12}+2c_{66})/2$, could be observed. Another TA mode, the frequency of which is related to the elastic constant $(c_{11}-c_{12})/2$, is forbidden by Brillouin scattering selection rules in this direction.[28]

As the sample is rotated in this orientation the high frequency phonon peak splits and the new peak increases

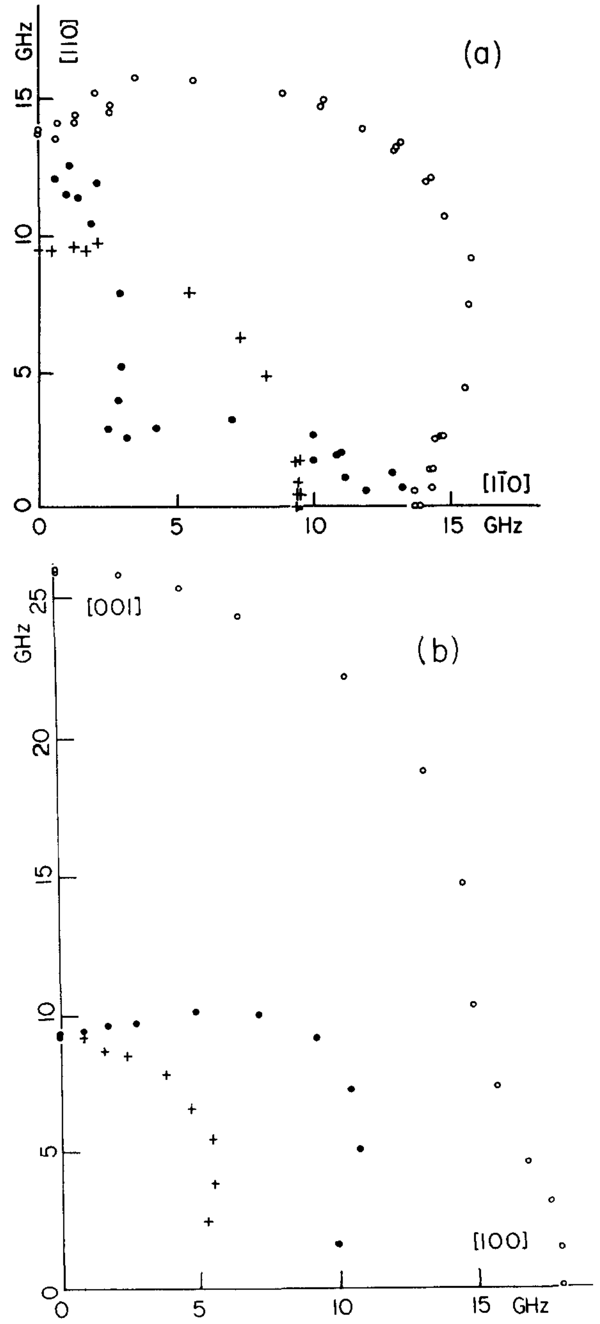

FIG. 2. (a) Brillouin shift anisotropy in ab plane; (b) Brillouin shift anisotropy in ac plane.

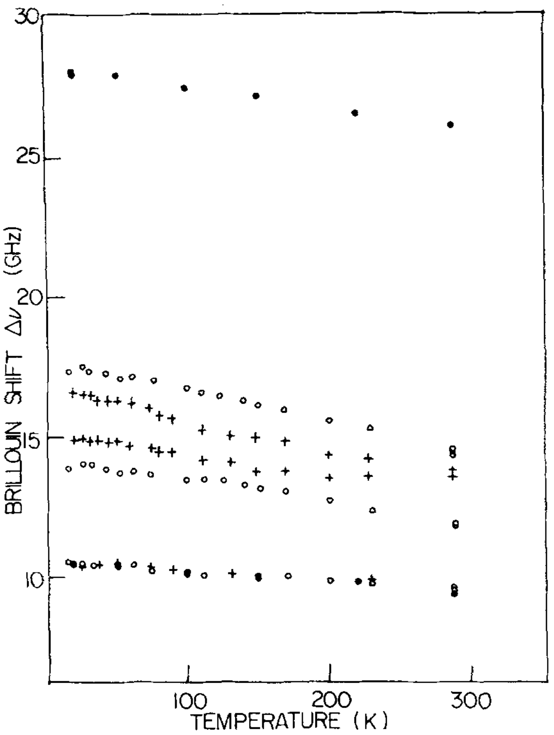

FIG. 3. Temperature dependences of phonon frequencies (●): phonons along [001] direction in which only two modes are observable; LA phonon $(\sim c_{33})^{1/2}$ and doubly degenerated TA phonons $(c_{44})^{1/2}$; (+): phonons near the [110] direction: LA phonon $\{\sim [(c_{11}+c_{12}+2c_{66})/2]^{1/2}\}$, TA′-phonon $[\sim (c_{11}-c_{12}/2)^{1/2}]$ and TA phonon $(\sim c_{44})^{1/2}$. See Fig. 4 also. LA and TA′ are degenerate at the [110] direction; (o): phonons along ~ [110] + 50 direction QLA phonon, QTA phonon, and TA phonon $(c_{44})^{1/2}$. These quasiacoustic mode frequencies are related to elastic constants given by Eq. (2) with $\theta \sim 5°$.

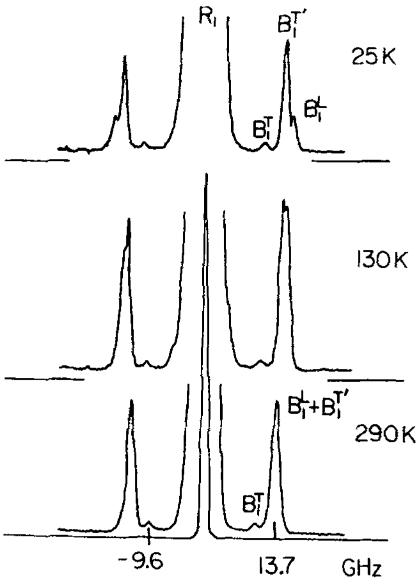

FIG. 4. Temperature behavior of the accidental degeneracy in the [110] direction. Note that if the phonons correctly propagate along this direction, the TA mode (B^{T}) should be always Brillouin inactive. To observe this mode also without destroying the degeneracy, the phonon propagating direction was slightly tilted (~ 1°). As a 47 GHz free spectral range was employed, every phonon peak belongs to the Rayleigh peak (R_1) shown in this figure. The notation for peak assignment is the same as in Fig. 1.

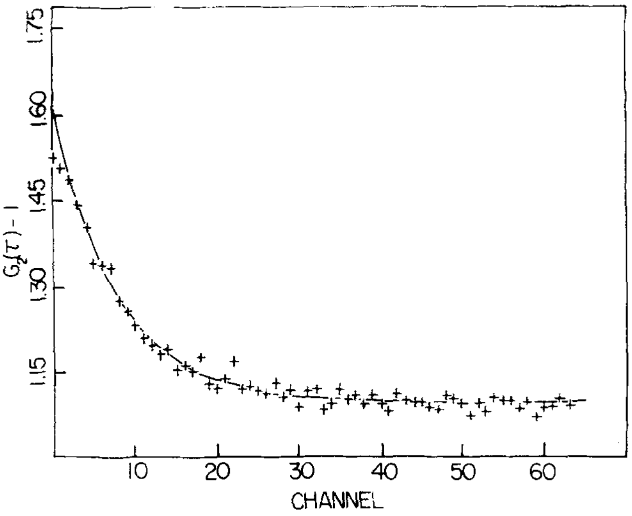

FIG. 5. An example of the correlation function obtained at 75 K. External stress was applied along the [010] direction. The sample was the same sample used to determine the anisotropy of the elastic constants in *ac* plane. The scattered beam direction is along the [100] direction. The full line is derived from a least-squares fit of the data to an exponential function with a finite base line. The exact equation is $G_2(\tau) = 1 + 0.095 + 0.514e^{-2t/1.59}$, with time in ms. The standard deviation of the fit is 1.3×10^{-2}. Experimental conditions: sampling time = 0.1 ms, experimental duration = 500 s and intensity = 340 photon/s with 100 mW power. The full correlation mode of the correlator was employed.

in intensity. The weaker lower energy phonon does not shift within the present experimental error. The high frequency phonon in the [110] direction is thus accidentally degenerate. Complete results of such anisotropy studies are presented in Fig. 2(a) and 2(b) for the *ab* and *ac* planes.

To investigate the possibility of a phase transition in urea, phonons propagating along the [001] and around the [110] directions have been examined for their temperature dependence from room temperature to 15 K. Each phonon frequency shows a monotonic temperature dependence as portrayed in Fig. 3. Apparently, to within the experimental uncertainty, no phase transition can be detected through Brillouin scattering techniques. It is concluded that the phase transition, if present, does not manifest itself in the acoustic modes. As the temperature decreases, the accidental degeneracy along the [110] direction is lost and two peaks are observed as shown in Fig. 4.

In Fig. 5 an example of the observed correlation function at 75 K is presented. The correlation can be observed only with the external applied refrigerator stress pulse and in polarized light.[25-27] The qualitative features of this effect are almost identical to those observed for benzil and chloranil. No correlation function, as previously reported, can be found for NH_4Cl and triazine under comparable experimental conditions for either polarized or depolarized scattering.[25-27]

Figure 6 gives the temperature dependences of the relaxation time and scattering intensity for urea. As can be seen, both results have a similar temperature

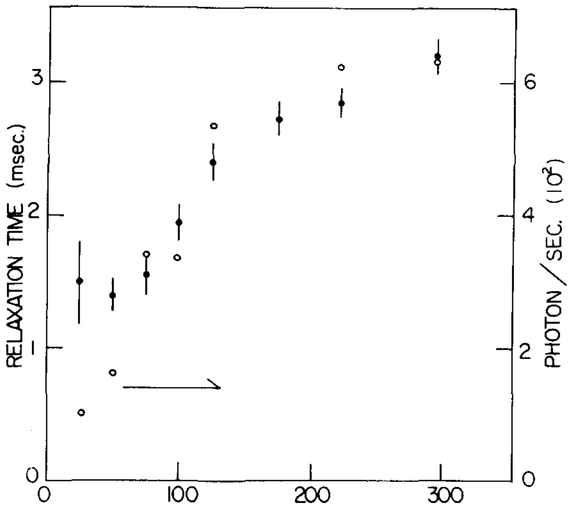

FIG. 6. Temperature dependences of the relaxation time τ and scattering intensity I. Data at 185 K were obtained in a heating run and the intensity result is omitted for this point. (o) refers to intensity, (ɸ) refers to relaxation time.

behavior. As pointed out previously, annealing urea is not useful in reducing the defect/impurity level as observed in light scattering experiments; both low annealing temperatures and further defect generation through decomposition are the main problems. "Annealed" crystals typically show a longer relaxation time indicating a larger defect distribution than found in as grown crystals, as would be expected for a crystal that undergoes decomposition upon heating.

Finally, a section of a urea crystal used for light scattering was studied by x-ray structural analysis at room temperature. The crystal has a tetragonal structure with lattice constants $a = 5.647 \pm 0.003$ Å, and $c = 4.704 \pm 0.003$ Å. The corresponding density ρ is $1.339\ \mathrm{g/cm^3}$ in agreement with published data.

IV. DISCUSSION

A. Elastic constants

The elastic constant matrix for D_{2d} symmetry has six independent components. The wave equation for this system can be written in a compact form given by,

$$\rho\omega^2\mathbf{U} = q^2 \begin{bmatrix} c_{11}\hat{q}_x^2 + c_{66}\hat{q}_y^2 + c_{44}\hat{q}_z^2 & (c_{12}+c_{66})\hat{q}_x\hat{q}_y & (c_{13}+c_{44})\hat{q}_x\hat{q}_z \\ (c_{12}+c_{66})\hat{q}_x\hat{q}_y & c_{11}\hat{q}_y^2 + c_{66}\hat{q}_x^2 + c_{44}\hat{q}_z^2 & (c_{13}+c_{44})\hat{q}_y\hat{q}_z \\ (c_{13}+c_{44})\hat{q}_x\hat{q}_z & (c_{13}+c_{44})\hat{q}_y\hat{q}_z & c_{33}\hat{q}_z^2 + c_{44}(\hat{q}_x^2+\hat{q}_y^2) \end{bmatrix} \mathbf{U} \tag{1}$$

in which $\mathbf{q} = q(\hat{q}_x, \hat{q}_y, \hat{q}_z)$. Solving this equation in the ab and ac planes, one obtains the following eigenvalues:

ab plane: $\hat{q}_x = \cos\theta$, $\hat{q}_y = \sin\theta$, and $\hat{q}_z = 0$,

$$\rho\omega^2/q^2 = \begin{cases} c_{44} \\ \frac{1}{2}\{c_{11} + c_{66} \pm [(c_{11}-c_{66})^2\cos^2 2\theta + (c_{12}+c_{66})^2\sin^2 2\theta]^{1/2}\} \end{cases} , \tag{2}$$

ac plane: $\hat{q}_x = \cos\theta$, $\hat{q}_y = 0$, $\hat{q}_z = \sin\theta$,

$$\rho\omega^2/q^2 = \begin{cases} c_{44}\sin^2\theta + c_{66}\cos^2\theta \\ \frac{1}{2}\{c_{11}\cos^2\theta + c_{33}\sin^2\theta + c_{44} \pm [(c_{11}\cos^2\theta - c_{33}\sin^2\theta - c_{44}\cos 2\theta)^2 + (c_{13}+c_{44})^2\sin^2 2\theta]^{1/2}\} . \end{cases} \tag{3}$$

Brillouin scattering selection rules for a given acoustic mode and scattering geometry are given by,[28]

$$\mathbf{E}_0 \cdot (\delta\epsilon_0 \cdot \mathbf{P} \cdot \mathbf{e} \cdot \delta\epsilon_0) \cdot \mathbf{E}_s = \sum_{\substack{ijlm \\ \alpha\beta}} (E_0)_i (\delta\epsilon_0)_{il} P_{lm,\alpha\beta}\, e_{\alpha\beta} (\delta\epsilon_0)_{mj} (E_0)_j \ , \tag{4}$$

in which $\hat{\mathbf{E}}_0$ and $\hat{\mathbf{E}}_s$ are the displacement vectors of the incident and scattered light, respectively, $\delta\epsilon_0$ is the dielectric constant matrix, $\mathbf{P}$ is the Pockel's coefficient tensor, and $\mathbf{e}$ is the strain matrix defined by

$$e_{ij} = \frac{\delta U_i}{\delta X_j} + \frac{\delta U_j}{\delta X_i} \quad \text{for } i \neq j$$

and

$$e_{ii} = \frac{\delta U_i}{\delta X_i} \quad \text{for } i = j \ .$$

As urea belongs to the class of piezoelectric crystals, Eq. (4) should actually include an additional effect due to piezooptical coupling. We omit this as it is most likely small and will not change our major conclusions. In Table I, elastic constants, phonon modes, and selection rules for several high symmetry directions are collected. For other directions, all modes are active and the corresponding elastic constants can be found from Eqs. (2) and (3).

Urea is also a uniaxial crystal and birefringence effects should be taken into account in the calculation of sound velocities and elastic constants based on Brillouin shift data in some directions. For 90° scattering, elastic constants and Brillouin shifts are related by a well known formula for anisotropic crystals,[29]

$$c = \rho v^2 = \rho \left[\frac{\Delta\nu_B \lambda_0}{\sqrt{n_i^2 + n_s^2}}\right]^2 , \tag{5}$$

in which n_i and n_s are the indices of refraction for the incident and scattered light respectively, ρ is the mass

TABLE I. Observable phonons and selection rules in several high symmetry directions.

Phonon direction	Displacement	Mode	Elastic constant	Selection rule
	[100]	L	c_{11}	V_v
[100]	[010]	T	c_{66}	$\cdots$[a]
	[001]	T	c_{44}	V_h[a]
	[110]	L	$(c_{11}+c_{12}+2c_{66})/2$	V_v
[110]	[1̄10]	T	$(c_{11}-c_{12})/2$	$\cdots$
	[001]	T	c_{44}	V_h
	[100]	T	c_{44}	$\cdots$
[001]	[010]	T	c_{44}	V_h
	[001]	L	c_{33}	V_v

[a] For *ab* scattering geometry. For the *ac* scattering geometry, the c_{44} mode becomes inactive and the c_{66} mode can be observed in V_h polarization.

density of the crystal (= 1.339 g/cm³ at room temperature), and λ_0 is the incident light wave length (5145×10^{-8} cm). Effective values of the refractive indices, n_i and n_s depend on the experimental geometry, crystal orientation and the direction of light propagation. To obtain the appropriate values it is necessary to solve an equation for the index of refraction given by[30]

$$\sum_{i=xyz}\frac{n_i^2}{n^2-n_i^2}(\hat{K}_i)^2=0\ , \tag{6}$$

in which $\hat{K}$ is a unit vector of the light propagation direction $n_x=n_y=n_0=1.492$ and $n_z=n_e=1.597$ for 5145 Å at room temperature.[22]

Combining these calculations, the elastic anisotropies in the *ab* and *ac* planes are obtained and are presented in Figs. 7(a) and 7(b). From these results, six independent elastic constants can be determined. In the high symmetry directions for which the elastic constants have simple forms, one of the *TA* modes is always forbidden. c_{11}, c_{33}, and c_{44} can be determined in the high symmetry directions (as given in Table I). The remaining three elements of the elastic matrix, c_{66}, c_{12}, and c_{13} are determined by the theoretical expressions for the anisotropies [Eqs. (2) and (3)] and visual curve fitting. These derived values are presented in Table II along with the ultrasonic results.[2]

The diagonal elastic constants c_{11}, c_{33}, c_{44}, and c_{66} are in reasonable agreement for the two methods of evaluation, Brillouin scattering and ultrasonic techniques. However, the off diagonal elements c_{12} and c_{13} are not at all in agreement for the two techniques. The difference should be particularly well defined in the [110] direction. In this direction our results shown in Fig. 1 reveal an accidential degeneracy with

$$(c_{11}+c_{12}+2c_{66})/2\sim(c_{11}-c_{12})/2\ ,$$

and, therefore, $c_{66}+c_{12}\approx0$. The ultrasonic results for c_{11}, c_{12}, and c_{44}, however, yield a different accidental degeneracy as follows:

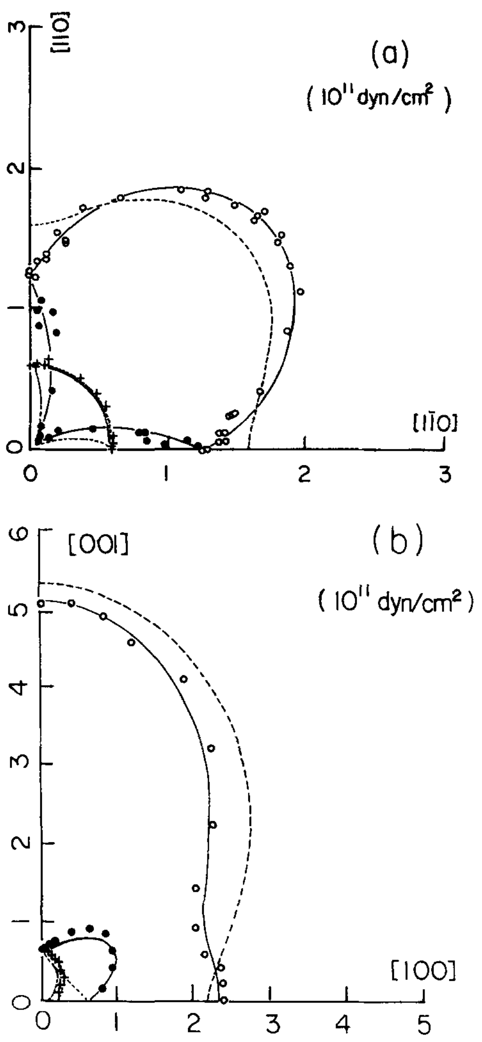

FIG. 7. (a) A polar plot to the elastic constant anisotropy in *ab* plane. The full lines are the best fitted results using the theoretical expression [Eq. (2)] and visual determination for the fit quality. The broken lines are obtained by Eq. (2) and the ultrasonic results given in Table II. Notation: (+) ≡ c_{44}, (o) ≡ + combination in Eq. (2), and (●) ≡ − combination in Eq. (2); (b) a polar plot of the elastic constant anisotropy in *ac* plane. The full lines are obtained by using Eq. (3) and visual fitting as indicated above. The broken lines are due to the ultrasonic results given in Table II. The obtained six-independent elastic constants at room temperature are listed in Table II with the ultrasonic values for comparison. Notation: (o) ≡ + combination in Eq. (3), (●) ≡ − combination in Eq. (3), and (+) ≡ pure *T*-mode in Eq. (3).

TABLE II. Elastic constants at room temperature.

	Brillouin scattering ($\times10^{11}$ dyn/cm²)	Ultrasonics ($\times10^{11}$ dyn/cm²)
c_{11}	2.35 ± 0.05	2.17 ± 0.05
c_{33}	5.10 ± 0.10	5.32 ± 0.05
c_{44}	0.62 ± 0.01	0.626 ± 0.006
c_{66}	0.050 ± 0.005	0.045 ± 0.002
c_{12}	−0.050 ± 0.005	0.89 ± 0.19
c_{13}	0.75 ± 0.08	2.4 ± 0.4

$$(c_{11}-c_{12})/2 \sim 0.64\times 10^{11}\ \mathrm{dyn/cm^2} \sim 0.63\times 10^{11}\ \mathrm{dyn/cm^2} = c_{44}\ ,$$

and, therefore, $(c_{11}-c_{12})/2 \sim c_{44}$. In this later data set then, the *TA* modes would be accidentally degenerate along the [110] direction, contrary to the observations shown in Figs. 1–3. Moreover, a calculation using the ultrasonic values of the elastic constants and Eq. (3) fails to reproduce the observed anisotropy results in the *ac* plane. Both predictions in addition to the observed anisotropies are plotted in Fig. 7; the anisotropy predictions based on the ultrasonic elastic constant are shown in broken lines in Fig. 7.

B. Phase transition

The possibility of a phase transition in urea at roughly 190 K has been suggested by an x-ray structural analysis.[10] The thermal expansion coefficient in the [001] direction (*c* axis) has been reported to evidence an anomaly in this temperature range. Since no other axis shows any similar effect, the crystal maintains its tetragonal (rotational) and translational structure below 190 K. This is, of course, consistent with another x-ray analysis at 133 K[11] and also the present Brillouin results which show that the degenerate TA modes in the [001] direction remain degenerate to 15 K. Furthermore, the low temperature x-ray structure indicates that the translation symmetry is also unaltered. The observed x-ray anomaly seems to be a continuous one suggesting a continuous or higher order phase transition.

If the transition does indeed take place, the order parameter should belong to the A_1 irreducible representation of D_{2d} at the Γ point and one can expect a bilinear coupling between the order parameter and lattice strain e_3. It is this strain that would evidence the anomaly at the transition temperature in the [001] direction. Such a longitudinal acoustic anomaly would be a unique finding, however.

Ignoring for the moment odd power terms in the free energy expansion that may arise for a totally symmetric order parameter, a simple Landau theory based on these ideas predicts a free energy expansion near the transition point as follows:

$$F = \tfrac{1}{2} c_{33} e_3^2 + \tfrac{1}{2}\alpha(T-T_0)Q^2 + A e_3 Q\ , \qquad (7)$$

in which Q represents the order parameter of A_1 symmetry. This generates in the usual manner

$$c_{33} = \frac{\partial^2 F}{\partial e_3^2} = c_{33}^0 - \frac{A^2}{\alpha(T-T_0)} = c_{33}^0\,\frac{T-T_1}{T-T_0}\ , \qquad (8)$$

with

$$T_1 = T_0 + \frac{A^2}{\alpha c_{33}^0}\ .$$

As shown in Fig. 3, neither the soft acoustic mode related to the LA mode along the [001] direction nor any other anomalous behavior could be observed within the experimental accuracy between room temperature and 15 K. Actually, this type of phase transition cannot be a second order transition as discussed by Landau and Lifshiftz[31] because the order parameter belongs to the A_1 irreducible representation. The phase transition, as indicated in the x-ray structure report, would appear to be of a higher order than that typically discussed and studied.

It is in principle possible that observation of the phase transition could be masked by a cancellation [in Eq. (5)] of the changes in n and ρ. However, it can be shown that this effect is quite small in urea. As the indices of refraction at 5145 Å and the lattice parameters are known at room temperature, the molecular polarizabilities α_e and α_0 can be calculated by the Lorentz–Lorenz relation,

$$\frac{n^2-1}{n^2+2} = \frac{4}{3}\pi\left(\frac{\rho}{M}\right)\alpha\ ,$$

in which n, ρ, M, and α are, respectively, the index of refraction, mass density, molecular weight of the urea molecule, and the polarizability. Temperature dependence of the index of refraction is then primarily due to the density term and the polarizability can be approximately regarded as a temperature independent constant. Thus, using the values for these parameters mentioned above,

$$\alpha_e = 6.11\times 10^{-24}\ \mathrm{cm^3} \quad \text{and} \quad \alpha_0 = 5.20\times 10^{-24}\ \mathrm{cm^3}.$$

As shown in Eq. (5), the Brillouin scattering elastic constant depends on both the density and the index of refraction. This dependence can be approximated by

$$\frac{c}{(\lambda_0 \Delta\nu_B)^2} \sim \tfrac{1}{2}\rho\,\frac{1-\frac{4}{3}\pi(\rho/M)\alpha}{1+\frac{8}{3}\pi(\rho/M)\alpha}\ ,$$

if for simplicity an isotropic system is assumed. The cancellation would be less likely for an anisotropic crystal. Using $\alpha = 6\times 10^{-24}\ \mathrm{cm^3}$, the right-hand side of the above expression can be calculated as a function of temperature because $\rho(T)$ is known through the temperature dependence of the lattice parameters. The calculations reveal that the thermal expansion anomaly introduces about a 0.3% additional contribution to the background value of the elastic constant. The thermal expansion anomaly thus gives almost negligible contribution to the temperature dependence of the elastic constant around 190 K.

We also observe an external stress induced autocorrelation function, which has been reported for benzil[25] and chloranil,[27] in the urea system. The observed temperature dependence of the correlation time for urea is presented in Fig. 6 along with the temperature dependent scattering intensity. While both observables exhibit a relatively rapid change around 110 K, no divergent behavior at this or any other temperature could be characterized.

Thus, from Brillouin scattering and correlation spectroscopy it is not possible to corroborate the existence of a phase transition in urea as suggested by one x-ray structural analysis.[10] Temperature dependences of the Raman active modes between 295 and 85 K have been measured again with negative results for a phase transition.[3] The acoustic and optical phonons do not show any instability at 190 K.

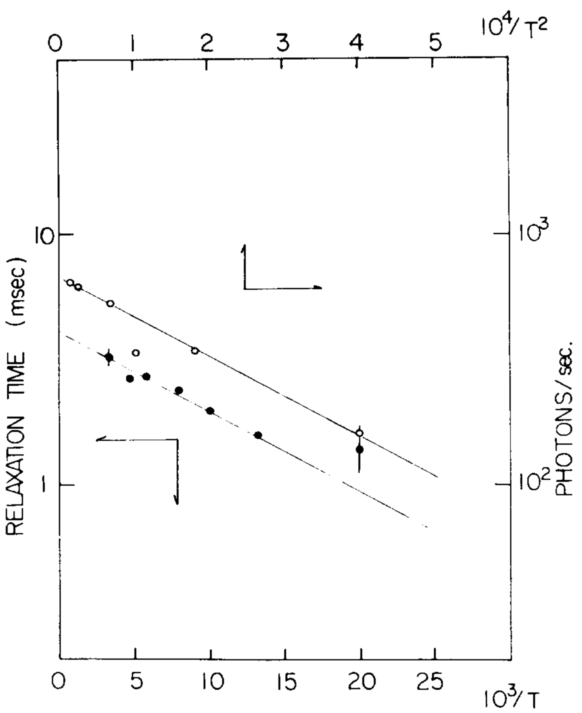

FIG. 8. $\log_e \tau$ vs $1/T$ and $\log_e I$ vs $(1/T)^2$ plot; (●): relaxation time data, (o): intensity data. Both data sets could be fit to straight lines, the equations for which are given in the text. [See Eqs. (9) and (10).]

C. Correlation scattering and relaxation times

The correlation function in urea is most pronounced in the polarized scattering spectra and appears only with the external stress pulse present. The details of these observations are at present qualitative as the pulse intensity and precise pulse shape[25,27] at the sample have not been quantified. Such experiments are now underway using both electrical and pressure techniques.

The major impact of and conclusions from these observations are clear, however: the Rayleigh scattering intensity and the relaxation time of the correlation function are related to one another and to the applied stress pulse; the effect is anisotropic and polarization dependent; the correlation function is associated with the concentration of defects in the sample; and, in comparison with benzil[25] and chloranil,[27] the data corroborate the absence of a phase transition in urea.

A phenomenological analysis of the intensity and relaxation data can, nonetheless, be presented. In Fig. 8 are shown plots of $\ln \tau$ vs $1/T$ and $\ln I$ vs $1/T^2$. Both sets of data are well fit to straight lines in these plots. For these lines, the following results can be obtained:

$$\tau = \tau_0 \exp(-\Delta E_a/k_B T) \ ,$$

$$\tau = 4.1 \exp(-74.7/T)$$

and

$$\Delta E_a = 0.15 \text{ kcal/mol} \qquad (9)$$

and

$$I = I_0 \exp[-\Delta E'_a/k_B T)^2] \ ,$$

$$I = 670 \exp[-(60.3/T)^2] \ ,$$

and

$$\Delta E'_a = 0.12 \text{ kcal/mol} \ . \qquad (10)$$

ΔE_a and $\Delta E'_a$ are certainly equal to within the experimental uncertainty although it has not as yet been demonstrated that this equality should hold theoretically. A detailed defect model would have to be generated, within the anelastic solid or cell defect models,[25,32] which could explain the rather unusual intensity/temperature behavior. To the best of our knowledge, no other data exist with which to compare these results.

V. CONCLUSIONS

Acoustic properties and defect/impurity motion excited by an external stress pulse have been examined for urea by Brillouin and correlation spectroscopy from room temperature to 15 K. The results of these studies are: (1) The anisotropies of the elastic wave frequencies in the *ab* and *ac* planes were determined at room temperature and are summarized in Table II and Fig. 7. (2) The temperature dependences of the acoustic phonons propagating along the [001] and near the [110] directions have been determined as a function of temperature. These modes evidence only monotonic changes within the experimental temperature range. No evidence of a phase transition could be found within the experimental uncertainty. (3) A correlation function is observed in urea only under an applied external stress pulse. The temperature dependences of both the scattering intensity and the relaxation time give no indication of a phase transition. (4) The temperature dependence of the scattering intensity and relaxation time (for a particular direction) can be expressed in the simple forms, given in Eqs. (9) and (10), with an activation energy for relaxation of $\Delta E = 0.15$ kcal/mol.

The theoretical explanation of these results, especially the intensity behavior, is presently under investigation based on the anelastic solid and cell defect models. Experimental efforts to quantify the pulse shape and intensity dependence are also in progress.

ACKNOWLEDGMENTS

The authors express their thanks to Professor O. P. Anderson and C. Schauer for help with the x-ray structural analysis of urea.

[1] P. Vaughan and J. Donohue, Acta Crystallogr. 5, 530 (1952).
[2] G. Fischer and J. Zarembowitch, C. R. Acad. Sci. (Paris) Ser. B 270, 852 (1970).
[3] J. Lefebvre and F. Wallart, C. R. Acad. Sci. (Paris) Ser. B 271, 227 (1970).
[4] A. L. Geddes and G. L. Bottger, J. Chem. Phys. 55, 1990 (1971).
[5] J. P. Arnau and P. A. Giguere, C. R. Acad. Sci. (Paris) Ser. B 268, 245 (1969).
[6] J. Lefebvre, M. More, R. Fouret, B. Hennion, and R. Currat, J. Phys. C 8, 2011 (1975).
[7] J. Lefebvre, Solid State Commun. 13, 1873 (1973).
[8] A. W. Pryor and P. L. Sanger, Acta Crystallogr. Sect. A

26, 543 (1970).

[9] A. Caron and J. Donohue, Acta Crystallogr. 17, 544 (1964).

[10] L. Lebioda, S. Hodorowicz, and K. Lewinski, Phys. Status Solidi A 49, K27 (1978).

[11] N. Sklar, M. E. Senko, and B. Post, Acta Crystallogr. 14, 716 (1961).

[12] D. Mullen and E. Hellner, Acta Crystallogr. Sect. B 34, 1624 (1978).

[13] W. A. Reed, L. C. Snyder, H. J. Guggenheim, T. A. Weber, and Z. R. Wasserman, J. Chem. Phys. 69, 288 (1978).

[14] A. Zussman, J. Chem. Phys. 58, 1514 (1973).

[15] R. A. Ruehrwein and H. M. Huffman, J. Am. Chem. Soc. 68, 1759 (1946).

[16] D. R. McKenzie and A. W. Pryor, J. Phys. C 4, 2304 (1971).

[17] J. Lefebvre, Phys. Status Solidi B 49, 673 (1972).

[18] C. Scheringer, D. Mullen, M. Hellner, H. L. Hase, K. W. Schulte, and A. Schweig, Acta Crystallogr. Sect. B 34, 2241 (1978).

[19] S. Kurtz and T. Perry, J. Appl. Phys. 39, 3798 (1968).

[20] D. Bauerle, K. Betzler, H. Hesse, S. Kapphan, and P. Loose, Phys. Status Solidi A 42, K119 (1977).

[21] K. Betzler, H. Hesse, and P. Loose, J. Mol. Struct. 47, 393 (1978).

[22] J. M. Halbout, S. Blit, W. Donaldson, and C. L. Tang, IEEE J. Quantum Electron. QE15, 1176 (1979).

[23] W. D. Kumler and G. M. Fohlen, J. Am. Chem. Soc. 64, 1944 (1942).

[24] For example: H. Futama, J. Phys. Soc. Jpn. 17, 434 (1962); V. Winterfeldt and G. Schaack, Z. Phys. B 36, 303, 311 (1980).

[25] A. Yoshihara, W. D. Wilber, E. R. Bernstein, and J. C. Raich, J. Chem. Phys. 76, 2064 (1982); A. Yoshihara, E. R. Bernstein, and J. C. Raich, J. Chem. Phys. 77, 2768 (1982).

[26] A. Yoshihara, C. L. Pan, E. R. Bernstein, and J. C. Raich, J. Chem. Phys. 76, 3218 (1982).

[27] A. Yoshihara, E. R. Bernstein, and J. C. Raich (unpublished results).

[28] R. Vacher and L. Boyer, Phys. Rev. B 6, 639 (1972); more detailed calculations for D_{2d} system are given by M. Sawafuji, M. Tokunaga, and I. Tatsuzaki, J. Phys. Soc. Jpn. 47, 1860 1870 (1979).

[29] V. Chandrasecharan, Proc. Indian Acad. Sci. A 33, 183 (1951).

[30] M. Born and E. Wolf, *Principles of Optics* (Pergamon, New York, 1970).

[31] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1968).

[32] B. I. Halperin and C. M. Varma, Phys. Rev. B 14, 4030 (1976).