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# Pressure dependence of the elastic properties of composite host/guest type crystals

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## Abstract

The elastic properties of host/guest type composite crystals, with urea as the host and an alkane as the guest, have been studied by Brillouin spectroscopy as a function of hydrostatic pressure. The effect of changing hydrostatic pressure in the range from 0 to 1400 bar on the propagation of acoustic phonons has been determined using three gases—helium, nitrogen and argon—as the pressure-exerting media.

(Some figures in this article are in colour only in the electronic version)

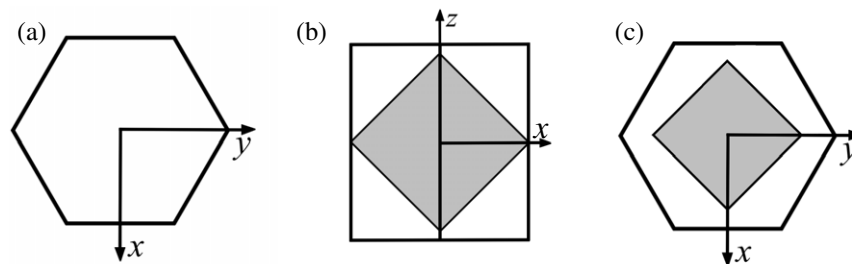
## 1. Introduction

Composite compounds based on a stable lattice of a host and well matching molecules of a guest have been the subject of investigation for a long time. The main reason for the great interest in compounds of this type is the possibility of using the well-developed structures of the host with a number of guest molecules of different functional groups for different purposes [1, 2]. A model system of this type, whose physical properties have been intensely studied, is that of urea and alkanes. Molecules of urea form a host lattice with a structure resembling a honeycomb. The symmetry of the host lattice (CO(NH<sub>2</sub>)<sub>2</sub>) at room temperature is described as hexagonal  $P6_122$ , with the lattice constants  $a = b = 8.227 \text{ \AA}$ ,  $c = 11.02 \text{ \AA}$  [3]. The urea molecules are connected by hydrogen bonds to form helical ribbons with six molecules per helical pitch. The molecules of urea form channels parallel to the  $z$  axis of the hexagonal system. The diameter of the channels is close to 0.55 nm, which permits classification of the material as nanoporous [4].

The tunnel structure of urea is stable only when the channels are filled with molecules of the guest [2]. The gamut of possible guest molecules in the structure of urea comprises mainly those of hydrocarbons of different chain lengths and different functional substituents. The crystals have been found to undergo a phase transition accompanied

by a symmetry change from hexagonal to low-temperature orthorhombic  $P2_12_12_1$  one [5]. The phase transition temperature strongly depends on the length of the guest alkane chain [6]. The change in symmetry indicates the appearance of the ferroelastic domain structure in the low-temperature phase. The ferroelastic phase transition should also lead to changes in the crystal elasticity constants. A comprehensive discussion of the procedures for characterizing the phase transition and the classical approach to the orientational states in the sense of Sapriel is given in [7, 8]. The subtle thermal effects observed in the clathrate system of urea/C<sub>19</sub>H<sub>40</sub> alkane, with the alkane in pure form or fully or partly deuterated, reported in [9] indicate that the phase transition, close to a first order transition, is not a single-stage process.

Determination of the elasticity constants of the organic supramolecular crystals, represented by the crystals studied, is performed with the help of the Brillouin scattering method because of its non-invasive character. The aim of this study was to determine the elastic properties of urea compounds containing alkanes of 20 or 22 carbon atoms, with the length of the C<sub>20</sub>H<sub>42</sub> and C<sub>22</sub>H<sub>46</sub> molecules being 27.58 Å and 30.20 Å, respectively [10]. The question is if the Brillouin scattering spectra could provide information on the interactions between the host and the guest molecules. This question was formulated in view of suggestions of the presence of such interactions following a cycle of theoretical works [11, 12].



**Figure 1.** Orientation of samples of the urea/alkane crystals studied (a), sample of the orientations  $xz45$  (b) and samples of the orientations  $xy45$  (c).

Moreover, our earlier results of the Brillouin scattering experiment in the  $180^\circ$  geometry performed for the crystals of urea/ $C_{20}H_{42}$  and urea/ $C_{22}H_{46}$  also indicated the possibility of such interactions [13].

The main aim of the study was to establish the effect of hydrostatic pressure exerted by different gases on the elastic properties of the clathrate compounds studied. The use of different gases as pressure exerting media was a consequence of suggestions that the fine gas molecules can act as a piston inside each channel [14]. The results presented were obtained for the first cycles of pressure measurements of the urea/alkane crystals studied, from the Brillouin spectra collected in the  $90^\circ$  geometry.

## 2. Experimental procedure

Single crystals of the urea compounds  $CO(NH_2)_2/C_{20}H_{42}$  and  $CO(NH_2)_2/C_{22}H_{46}$  were grown from a saturated solution of chemically pure urea and appropriate alkanes in a 50% propanol–methanol mixture using the isothermal dynamic method at 313 K of Breczewski [15].

The optical quality of the crystals grown was good enough to permit the cutting out of two rectangular samples of the cut  $xz45$  and  $yz45$  or  $xy45$  from one crystal (figure 1). The edge of the rectangular samples was a few millimetres, and the crystal orientation was assumed the same as in [8]. This type of cut and preparation of the samples was necessary to be able to subject the samples to Brillouin spectroscopy.

In the urea/alkane crystals the light refraction coefficients along the main crystallographic axes are  $n_x = n_y = 1.56$  and  $n_z = 1.67$  at room temperature for urea/ $C_{20}H_{42}$  and  $n_x = n_y = 1.56$  and  $n_z = 1.63$  for urea/ $C_{22}H_{46}$ . The density of the crystals studied is  $1.20 \text{ g cm}^{-3}$  and  $1.21 \text{ g cm}^{-3}$ , respectively [16, 17].

Brillouin scattering spectra were recorded on a Brillouin spectrometer working in a tandem system (JRS Scientific Instruments) [18]. The arrangement of the measuring setup permits simultaneous observation of phonons propagating in two directions, which is achieved because of the simultaneous work in two geometries of  $90^\circ$  and  $180^\circ$  [19]. The light source was a Nd:YAG single-mode diode-pumped laser of power 200 mW, emitting the second harmonic of the length  $\lambda_0 = 532 \text{ nm}$  (Coherent Laser Group, model 532).

The pressure dependences of the elastic properties of the crystals were established for the oriented samples placed in a pressure chamber with optical windows, constructed according

to the design given in [20, 21]. The pressure chamber permitted recording of the Brillouin scattering spectra for pressures from 0 to 1400 bar. The pressure-exerting medium was helium, argon or nitrogen, whose van der Waals radii are 0.140 nm (he), 0.188 nm (Ar), 0.155 nm (N) and 0.210 nm ( $N_2$ ) [22], and are smaller than the urea channel radii (the diameter of the urea channel is 0.55 nm). This choice of fine gas molecules is expected to permit verification of the hypothesis about the gas molecules being able to play the role of pistons inside channels [14].

In general, the Brillouin scattering spectra provide information on the velocity of bulk phonons propagating in the material studied:

$$v_B = \frac{\lambda_0 \Delta \nu_B}{\sqrt{n_i^2 + n_s^2 - 2n_i n_s \cos \theta}} \quad (1)$$

where  $\Delta \nu_B$  is the frequency shift determined from the Brillouin scattering spectra,  $n_i$  and  $n_s$  are the refractive indices along the directions of incident (i) and scattered (s) light and  $\theta$  is the scattering angle [23].

The elastic properties of a given crystal are described by the elasticity tensor  $c_{ijkl}$ . The number of independent components of the elasticity tensor  $c_{ijk}$  for particular point groups can be found from the Christoffel equation [24]. For hexagonal symmetry the nonzero components of the elasticity tensor are  $c_{11}$ ,  $c_{33}$ ,  $c_{44}$ ,  $c_{12}$  and  $c_{13}$ , while in the low-temperature phase they are  $c_{11}$ ,  $c_{22}$ ,  $c_{33}$ ,  $c_{44}$ ,  $c_{55}$ ,  $c_{66}$ ,  $c_{12}$ ,  $c_{13}$  and  $c_{23}$ .

In our earlier works on Brillouin scattering in urea-based composite crystals the  $180^\circ$  geometry was applied [13, 25]. However, successful growth of crystals with good optical quality permitted the use of  $90^\circ$  geometry in this work.

## 3. Results

The Brillouin spectra were recorded in the  $90^\circ$  geometry for the principal crystallographic directions [100], [010] and [001] for both clathrate compounds studied. Figure 2 presents typical Brillouin spectra for urea/ $C_{20}H_{42}$ .

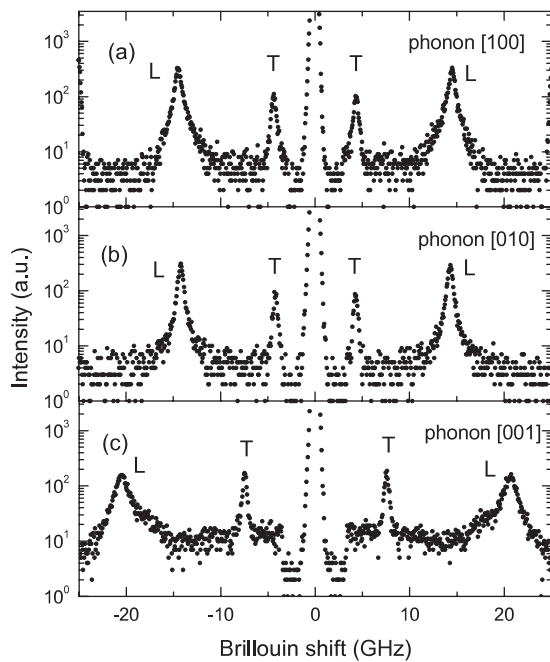
In the  $90^\circ$  geometry, two modes were observed in each direction for each crystal. For the [100] and [010] directions the positions of the modes are the same. For the [001] direction the Brillouin shift of the modes observed has a different value from that in the [100] = [010] direction. The values of the

**Table 1.** The Brillouin shift values obtained for the principal directions in the urea/alkane crystals studied.

Urea/alkane	Brillouin shift (GHz)					
	[100] direction		[010] direction		[001] direction	
Urea/C <sub>20</sub> H <sub>42</sub>	4.24 ± 0.07	14.27 ± 0.11	4.26 ± 0.07	14.31 ± 0.11	7.28 ± 0.07	20.38 ± 0.13
Urea/C <sub>22</sub> H <sub>46</sub>	4.21 ± 0.07	14.21 ± 0.11	4.25 ± 0.07	14.26 ± 0.11	6.96 ± 0.07	20.35 ± 0.13

**Table 2.** Elastic constants (10<sup>10</sup> N m<sup>-2</sup>) of the composite crystals studied at room temperature.

	$c_{11} = c_{22}$	$c_{33}$	$c_{44}$	$c_{66}$
CO(NH <sub>2</sub> ) <sub>2</sub> /C <sub>20</sub> H <sub>42</sub>	1.33 ± 0.05	2.70 ± 0.09	0.35 ± 0.02	0.12 ± 0.01
CO(NH <sub>2</sub> ) <sub>2</sub> /C <sub>22</sub> H <sub>46</sub>	1.36 ± 0.05	2.79 ± 0.08	0.33 ± 0.02	0.12 ± 0.01



**Figure 2.** Brillouin spectra for phonons propagating in the direction [100] (a), [010] (b) and [001] (c) for urea/C<sub>20</sub>H<sub>42</sub>, where *T* is the transverse phonon and *L* is the longitudinal phonon.

Brillouin shift in this geometry for both the urea/alkane crystals are given in table 1. For each direction, the first Brillouin shift refers to the transverse mode while the second refers to the longitudinal mode.

In our earlier work, searching for confirmation of the presence of a sliding mode [26], the phonons observed along the [001] direction were analysed [13]. Particular attention was paid to the behaviour of the longitudinal and transverse modes as a function of temperature and hydrostatic pressure applied, with helium as a working medium. At a frequency close to 6 GHz an extra mode was observed in the 180° geometry, used in our earlier study. This mode is definitely extra with respect to the lattice vibrations of the host. In the Brillouin scattering spectra recorded in the 90° no extra modes were noted, and all the modes observed were longitudinal or transverse.

Imposing the polarizations of the incident and scattered beams, the spectra obtained permitted determination of polarizations of particular phonons and the elasto-optical Pockel's coefficients [27].

On the basis of the positions of the longitudinal mode the elastic constants  $c_{11} = c_{22}$  and  $c_{33}$  were calculated, while the transverse mode observed in the [001] direction at about 7 GHz permitted the calculation of the elastic constant  $c_{44}$ . On the basis of the positions of the transverse modes in the [100] and [010] directions the elastic constant  $c_{66}$  was found. The values of the elastic constants calculated from the Brillouin spectra recorded in the 90° geometry are given in table 2. In the 90° geometry it was possible to find the elastic constant  $c_{66}$ , which was impossible in the 180° geometry.

The problem is, what is the response of the Brillouin shift to varying hydrostatic pressure? The use of different gases as pressure-exerting media was a consequence of the suggestions that the fine gas molecules (of a size much smaller than the host channel diameter) may enter the channels and stiffen the guest structure, facilitating the observations of modes related to the guest structure [14]. The measurements were performed for the principal directions of the composite crystals at room temperature. On collecting subsequent Brillouin spectra at different pressures, the polarization of the incident beam was *V*, while no polarization restrictions were imposed on the scattered beam, which permitted observation of both *L* and *T* modes.

An example of the changes in the Brillouin shift as a function of hydrostatic pressure (with argon as the pressure medium) is presented in figure 3.

For longitudinal vibrations along the main crystallographic axes the Brillouin shift increases with increasing pressure. The slopes of the dependence of the Brillouin shift on the pressure for different pressure-exerting gas media and measured in the directions specified are given in table 3. The measurement uncertainty was assumed as the threefold standard deviation.

Changes in the Brillouin shift values for the transverse vibrations in the composite crystals as a result of application of hydrostatic pressure are given in table 4.

The plot of the Brillouin shift of the transverse vibration propagating in the [001] direction related to the host structure as a function of pressure has a positive slope (figure 4). With increasing pressure the Brillouin shift value increased. Changes in the Brillouin shift of the transverse vibration are smaller than those of the longitudinal mode propagating in the same direction. On the basis of the position of the transverse mode the elastic constant  $c_{44}$ , in full notation  $c_{2323}$ , was determined.

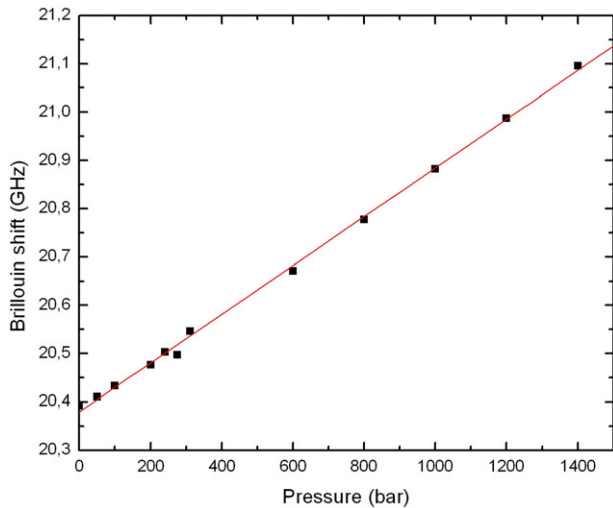


Figure 3. Brillouin shift as a function of pressure for the longitudinal mode in the [001] direction in the crystal urea/C<sub>20</sub>H<sub>42</sub>.

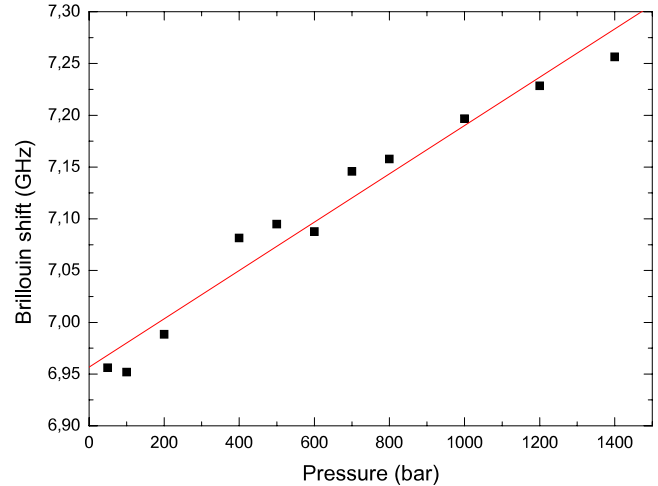


Figure 4. The Brillouin shift as a function of pressure for transverse vibrations propagating in the [001] direction in urea/C<sub>22</sub>H<sub>46</sub>.

Table 3. The slope of Brillouin shift versus pressure (GHz/10 kbar).

Medium	Direction	
	[010]	[001]
(a) For urea/C <sub>20</sub> H <sub>42</sub> —longitudinal mode		
Helium	5.73 ± 0.27	5.01 ± 0.26
Nitrogen	5.05 ± 0.25	5.41 ± 0.28
Argon	5.21 ± 0.23	5.42 ± 0.22
(b) For urea/C <sub>22</sub> H <sub>46</sub> —longitudinal mode		
Helium	3.51 ± 0.22	6.73 ± 0.38
Nitrogen	3.87 ± 0.17	6.71 ± 0.36
Argon	3.94 ± 0.26	6.95 ± 0.39

Table 4. The slope of Brillouin shift versus pressure (GHz/10 kbar).

Medium	Direction	
	[010] mode 4.26 GHz	[001] mode 7.28 GHz
(a) For urea/C <sub>20</sub> H <sub>42</sub> —transverse mode		
Helium	-0.65 ± 0.13	1.22 ± 0.11
Nitrogen	-1.39 ± 0.18	1.33 ± 0.12
Argon	-1.52 ± 0.21	1.27 ± 0.12
(b) For urea/C <sub>22</sub> H <sub>46</sub> —transverse mode		
Helium	-1.49 ± 0.15	2.03 ± 0.22
Nitrogen	-1.31 ± 0.12	1.89 ± 0.18
Argon	-1.22 ± 0.11	1.65 ± 0.25

Interesting results were collected for the transverse modes propagating in the [100] and [010] directions. The pressure dependence of the Brillouin shift of these modes has a negative slope (see figure 5).

The Brillouin shift of the mode propagating in the [100] = [010] directions permitted a determination of the elastic constant  $c_{66}$ , in full notation  $c_{1212}$ . The negative slope of the pressure dependence of the Brillouin shift for the mode corresponding to the elastic constant  $c_{66}$  means that with increasing hydrostatic pressure the motion of the atoms

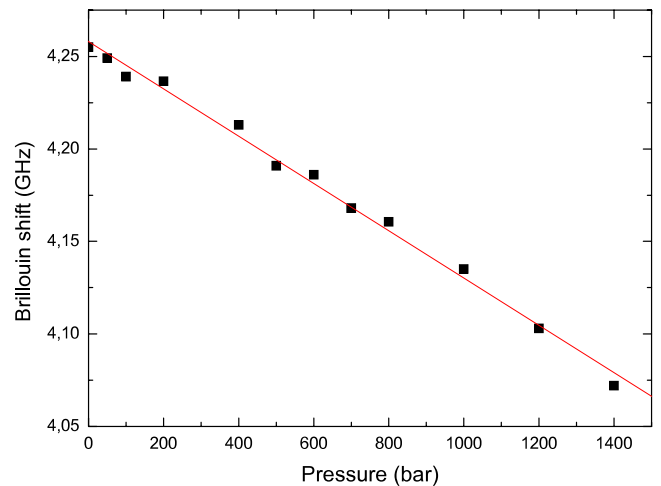


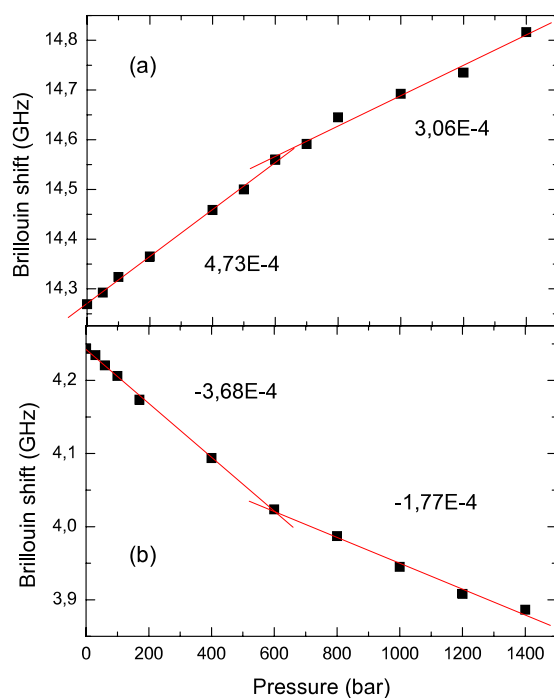
Figure 5. The Brillouin shift of the transverse mode propagating in the [100] direction in the crystal urea/C<sub>22</sub>H<sub>46</sub> as a function of pressure.

forming the channels becomes increasingly less restricted in the plane perpendicular to the direction  $z$ . Therefore, the negative slope of the pressure dependence of the Brillouin shift of the mode corresponding to the elastic constant  $c_{66}$  is an inherent feature of the composite crystals studied.

No anomalies were observed in the first recording of the pressure dependence of the Brillouin shift, but in subsequent recordings an anomaly at a pressure close to 600 bars was observed, for a few modes studied. The rate of change in the Brillouin shift for the pressure varying from 0 to 600 bars is greater than that for the pressure varying from 600 to 1400 bars, figure 6.

#### 4. Discussion

Urea/alkane composite crystals are not classified as hard materials. Their channel structure is determined by the presence of a guest. Detection of the extra modes on the



**Figure 6.** The Brillouin shift of the longitudinal mode in the crystal of urea/C<sub>22</sub>H<sub>46</sub> (a) and of the transverse mode in the crystal of urea/C<sub>20</sub>H<sub>42</sub> (b), propagating in the [010] direction as a function of pressure.

basis of analysis of the Brillouin spectra of composite crystals would first require identification and characterization of the vibrations of the host structure. This would be possible if crystals of pure urea with hexagonal symmetry could be obtained, but unfortunately pure urea crystallizes in the tetragonal system [28]. On the other hand, removal of the guest molecules from the host channels leads to destruction of the crystal [2]. In view of the above, a comparative analysis can be performed on the basis of the Brillouin spectra recorded for urea-based composite crystals with guests of a different number of  $-CH_2-$  groups and with different functional groups. In this way the values of the Brillouin shift given in table 1 permitted us to draw conclusions about the elastic constants for the hexagonal system of the host.

The effect of hydrostatic pressure on the dynamics of particular vibrations is different for the longitudinal and transverse modes of the compounds studied. The slope of the Brillouin shift versus pressure is higher for the longitudinal modes in all directions studied. Increasing hydrostatic pressure results in the stiffening of the crystal lattice and an increase in the Brillouin shift of the longitudinal modes in these materials (table 3). The character of the pressure dependence of the transverse modes changes with the direction of propagation. For transverse modes propagating in the [100] and [010] directions, in the samples of the orientations  $xz45$  and  $yz45$ , respectively, the Brillouin shift of these modes decreases with increasing pressure (the negative slope of the Brillouin shift versus pressure; table 4). The propagation of the transverse modes in the crystal and the atomic displacements are equivalent to a shear. An interesting open question is

that of the mutual interaction between the host and the guest under such shearing stress. Particularly interesting results were obtained for the [010] direction. A change in the slope of the pressure dependence of the Brillouin shift was observed at about 600 bar in both crystals studied. The mechanism leading to the appearance of the anomaly at about 600 bar has not yet been resolved.

The results have shown that the type of gas medium applied to exert the pressure had no effect on the magnitude of the Brillouin shift. Therefore, the hypothesis of the beneficial role of small molecules penetrating into the host channels has not been confirmed by the results for the elastic properties of clathrate crystals.

In clathrate crystals of the urea/alkane type it seems impossible to determine the effect of the guest on the elastic properties of the host. The longitudinal modes have very high FWHM values, indicating that the host lattice vibrations feel the presence of the guest molecules.

## 5. Concluding remarks

The host structure devoid of the guest could not be obtained, so the elastic constants of the pure host structure could not be found and a quantitative determination of the effect of the guest could not be made. The values of the elastic constant presented here should be treated as directly related to the type of host/guest structure studied.

The elastic properties of the urea/alkane crystals depend on the changes in the hydrostatic pressure applied, and the character of this dependence does not depend on the type of gas used as the pressure-exerting medium (helium, nitrogen, argon).

The crystals of urea/C<sub>22</sub>H<sub>46</sub> have been found to be more sensitive to the pressure changes. The Brillouin shift changes as a function of the pressure applied for the urea/C<sub>22</sub>H<sub>46</sub> crystal were greater than for the urea/C<sub>20</sub>H<sub>42</sub> crystal. In the former crystal (with C<sub>22</sub>H<sub>46</sub>) the dependences of the Brillouin shift on the pressure had different character for different directions.

An interesting finding was the negative slope of the pressure dependence of the Brillouin shift for the transverse mode. No significant differences in the elastic constants of the urea/alkane crystals were found to accompany the changes in the length of the guest molecule.

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