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Phase transitions in adamantane derivatives: 2-chloroadamantane

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This paper is dedicated to Professor Charles A. McDowell on the occasion of his seventieth birthday

RALPH M. PAROLI, NANCY T. KAWAI, IAN S. BUTLER, and DENIS F. R. GILSON. Can. J. Chem. **66**, 1973 (1988).

The phase transition behaviour of 2-chloroadamantane, 2-$C_{10}H_{15}Cl$, has been investigated by differential scanning calorimetry (DSC), and FT-IR and Raman spectroscopy. Two transitions were detected by both DSC and vibrational spectroscopy at 231 and 178 K, on cooling, and at 242 and 227 K, on heating. The measured enthalpies were 8.3 kJ mol^{-1} for the first transition (phase I → phase II), and 0.47 kJ mol^{-1} for the second (phase II → phase III). The entropies were 35 and 2.3 J K^{-1} mol^{-1}, respectively. These are similar to those observed for other 2-substituted adamantanes, but significantly different from those for 1-substituted derivatives. The large hystereses observed for the two transitions are independent of the DSC scanning rate and are characteristic of first-order phase transitions. The dramatic differences observed in the vibrational spectra of phases I and II provide clear evidence of an order–disorder transition at about 235 K.

RALPH M. PAROLI, NANCY T. KAWAI, IAN S. BUTLER, et DENIS F. R. GILSON. Can. J. Chem. **66**, 1973 (1988).

Utilisant la calorimétrie différentiel programmé (CDP) ainsi que la spectroscopie Raman et IR par TF, on a étudié le comportement du chloro-2 adamantane, 2-$C_{10}H_{15}Cl$, lors de sa transition de phase. Les trois méthodes ont permis de détecté deux transitions, soit à 231 et 178 K lors du refroidissement et 242 et 227 K lors du chauffage. On a évalué que l'enthalpie de la première transition (phase I → phase II) est de 8,3 kJ mol^{-1} et de 0,47 kJ mol^{-1} pour la deuxième (phase II → phase III). Les entropies sont respectivement de 35 et de 2,3 J K^{-1} mol^{-1}. Ces valeurs sont semblables à celles qui ont été observées pour d'autres adamantanes substitués en position 2; toutefois, elles diffèrent beaucoup des valeurs observées avec dérivés en position 1. Les hysterisis importantes que l'on observe pour chacune des deux transitions sont indépendantes du taux de balayage du CDP et sont caractéristiques de transitions de phase du premier ordre. Les différences dramatiques que l'on observe dans les spectres vibrationnels des phases I et II fournissent des preuves nonambigues que la transition à 235 K en est une d'ordre/désordre.

[Traduit par la revue]

Introduction

Molecular solids with high vapour pressures and melting points, and low entropies of fusion (<20 J K^{-1} mol^{-1}) are often referred to as "plastic crystals" (1–4). These materials are generally soft, colourless, transparent solids that are difficult to fracture or pulverize. Solid–solid phase transitions occur from an ordered to a disordered structure in which the molecules rotate about one or more of their axes in the crystal lattice. Furthermore, since the phase transitions are often strongly exothermic, these materials are currently receiving considerable attention as passive thermal storage systems (5–8).

The cage hydrocarbon, adamantane ($C_{10}H_{16}$), is one of the best known "plastic crystals" and its properties have been widely studied (9). The order–disorder transitions in 1-substituted adamantanes ($C_{10}H_{15}R$; R = 1-COOH (10), 1-$NH_3^+Cl^-$ (11), 1-CN (12), 1-Cl (16), 1-Br (16)) have been examined. Little work has been done on 2-substituted derivatives (13, 17, 18), and as part of a study of the phase-transition behaviour of adamantane derivatives, we report here the results of an investigation of the order–disorder transitions in 2-chloroadamantane, 2-$C_{10}H_{15}Cl$, by differential scanning calorimetry (DSC), and variable-temperature FT-IR and Raman spectroscopy.

Experimental

2-Chloroadamantane (Alfa Products) were purified immediately prior to use by slow vacuum sublimation (21°C, 10^{-3} Torr). Infrared spectra were recorded on an Analect AQS-18 FT-IR spectrometer equipped with a triglycine sulfate (TGS) detector. Raman spectra were obtained using an Instruments S.A. spectrometer with a Jobin-Yvon U-1000 1.0-m double monochromator that was interfaced to a Columbia Commandor microcomputer. The 514.532-nm line of a Spectra-Physics model 164, 5-W argon-ion laser was used to excite the Raman spectra; the laser power was 300 mW at the sample. The resolution for both the IR and Raman measurements was about 2 cm^{-1}. The Raman studies were done on samples sealed in glass capillary tubes which were mounted on to the cold finger of a cryostat using indium foil as the conducting junction. For the IR analysis, several sampling techniques were attempted: KBr pellets, diffuse reflectance, sublimation on to KBr windows, and pressing into a thin layer film. Since similar spectra were obtained in each case (including the large hystereses observed in phase transition temperatures), the KBr pellet technique was used as it proved to be the most convenient method. The effect of KBr pelleting on phase transitions has been studied previously and it was found that it only increases the degree of the hysteresis at a phase transition (14). Variable-temperature FT-IR and Raman spectra were recorded with the aid of a Cryodyne Cryocooler model 21 (Cryogenics Technology, Inc.) and a silicon-diode temperature sensor attached to a Cryophysics model 4025 controller (range 400–4 K). The sample temperatures remained essentially constant (±0.5 K).

Differential scanning calorimetric experiments were performed on a Perkin-Elmer DSC-7 calorimeter. The temperature and enthalpy calibrations were based on the phase and melting transitions of cyclohexane (Aldrich Chemical Co. "gold" grade). The sample weights were typically 5–10 mg, and the samples were hermetically sealed in aluminium pans. The phase transition temperatures and enthalpies did not show any dependence on scan rate (2.5 and 5 K min^{-1}).

Results and discussion

Two phase transitions (phase I → phase II → phase III) were detected by diffential scanning calorimetry. The transition temperatures were 231 and 178 K (on cooling) and 242 and 227 K (on heating) with enthalpies of 8.3 kJ mol^{-1} for the first transition and 0.47 kJ mol^{-1} for the second. Although large hystereses are observed (10 K for the first transition and 50 K for

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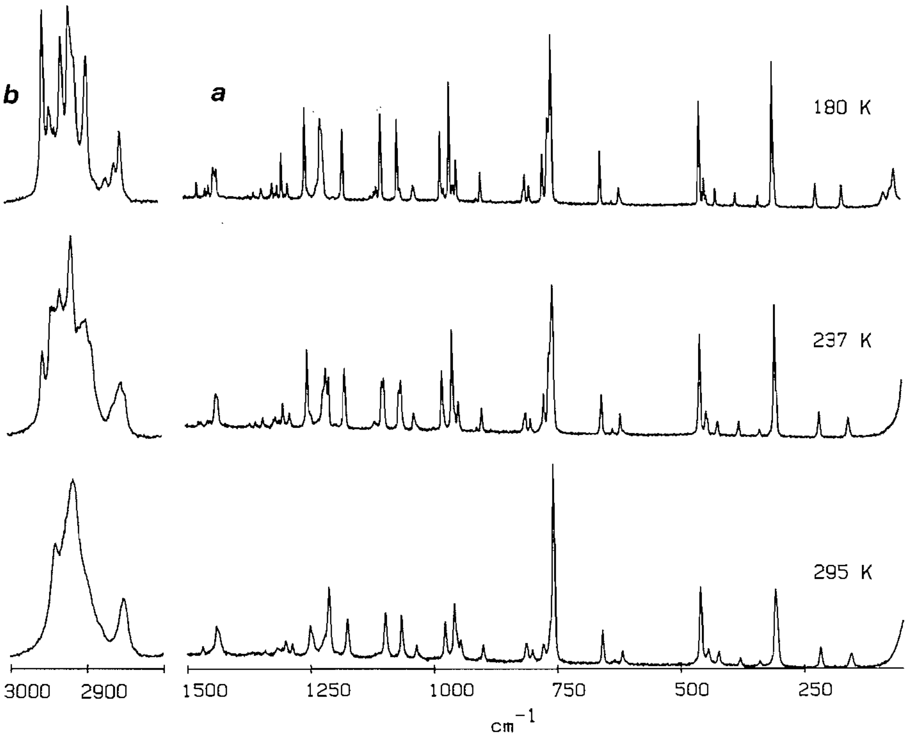

FIG. 1. Raman spectra on heating of phases I, II, and III of 2-$C_{10}H_{15}Cl$ in the (*b*) 3000–2800 and (*a*) 1500–50 cm^{-1} regions. Slits: 300 μm. Acquisition: 1 s pt^{-1}, 1 cm^{-1} step. Intensity: counts. Laser line: 514.532 nm, power 300 mW.

the second), 2-chloroadamantane did not exhibit any memory effects, i.e., the phase transition temperatures and enthalpies were not dependent on the previous thermal history of the sample. The hystereses are characteristic of first-order transitions. Rapid quenching, cycling at 20 K min^{-1}, did not reveal any exotherms on heating, hence no glassy state was formed. The entropies of transitions are 35 and 2.3 J K^{-1} mol^{-1} for the first and second phase transition, respectively. The entropy of the first phase transition is much larger than that of adamantane itself (15) and of various 1-substituted halo-derivatives which have entropies less than 25 J K^{-1} mol^{-1} (16), but is similar to the entropies of 2-bromoadamantane (17) and adamantanone (18) which are greater than 35 J K^{-1} mol^{-1}. Although the 2-derivatives (except 2-adamantanone) have lower symmetry (C_s), they still exhibit plastically crystalline behaviour (unpublished data).

The Guthrie and McCullough equation (19) for the interpretation of entropies of transition in plastic crystals is

$$[1] \quad \Delta S_{tr} = R \ln (N_1/N_2)$$

where N_1/N_2 is the ratio of the number of distinguishable positions on going from the ordered (N_2) to the disordered (N_1) phase. For the phase I → phase II transition the ratio is 70, while the second transition (phase II → phase III) only has a ratio of orientations slightly greater than one. This is an unreasonably large number of distinguishable orientations. Clark and coworkers (15, 16) have examined the entropies of transition for several cage hydrocarbons and proposed an empirical equation involving an excess entropy, which depends upon the temperature range of the disordered phase, eq. [2].

$$[2] \quad \Delta S_{tr} = R \ln(N_1/N_2) + 10.3 + 45 \exp \{- [0.0183(T_m - T_{tr})]\}$$

where $10.3 + 45 \exp \{- [0.0183(T_m - T_{tr})]\}$ is the excess entropy and $(T_m - T_{tr})$ is the temperature range of the plastically crystalline phase. There are two transitions in 2-chloroadamantane, and since phase II is probably partially disordered, the total entropy change between ordered and disordered structures is given by the sum of the two transition entropies, plus a small, negligible term for the heat capacity. Assuming that phase I is face-centered-cubic (fcc), which is typical for these materials, then there are 24 possible orientations for a molecule with C_s symmetry in the fcc lattice. Using eq. [2], with T_m = 458 K and T_{tr} = 202.5 K (the average of the heating and cooling transition temperatures), the calculated total entropy is 37.1 J K^{-1} mol^{-1}. This agrees very well with the experimental value of 37.3 J K^{-1} mol^{-1}. These results imply that there is a change in the unit cell dimensions that is accompanied by a decrease in volume only for the first phase transition.

Another method to probe phase transitions is by vibrational spectroscopy. The isolated 2-chloroadamantane molecule has C_s symmetry for which 72 normal modes of vibration are predicted (40*A′* and 32*A″*). Since the *A′* and *A″* modes are both Raman and IR active, 72 peaks should be observed in both the Raman and the IR spectra.

The Raman and IR spectra of phases I–III are shown in Figs. 1*a*, *b* and 2*a*, *b*; the measured peak positions and the proposed vibrational assignments are given in Table 1. These assignments are based on literature values for various adamantane derivatives (20–22) and on Raman spectra of 2-$C_{10}H_{15}Cl$ in CCl_4 and CS_2 solution. Only 58 bands out of a possible 72 have been clearly identified, probably as a result of the overlapping of peaks. Even amongst those observed it is possible that some may be combinations and/or overtones.

Many interesting changes were observed in the Raman spectra as the sample was cooled and then heated between 298 and

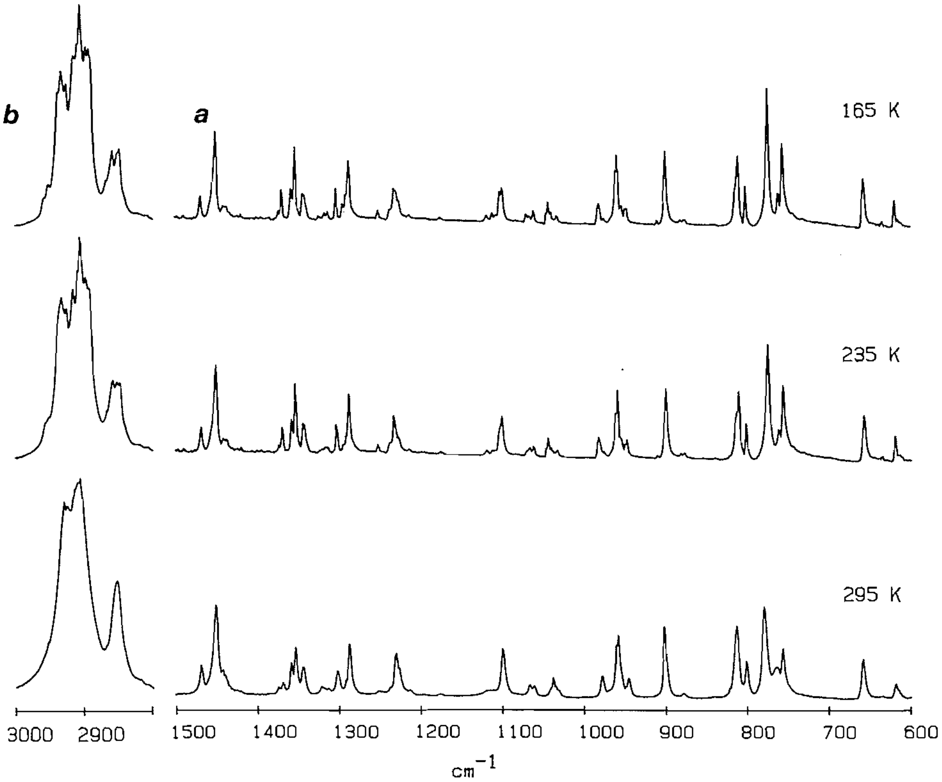

FIG. 2. IR spectra (in KBr) on heating of phases I, II, and III of 2-$C_{10}H_{15}Cl$ in the (*b*) 3000–2800 and (*a*) 1500–50 cm^{-1} regions. Intensity: absorbance units. Resolution: 2 cm^{-1}.

150 K. Consider the lattice region (100–20 cm^{-1}) shown in Fig. 3; the tail extending to 100 cm^{-1} in phase I is featureless. However, in phase II some weak features develop at ~60 and 80 cm^{-1}, and in phase III some very distinctive peaks appear. These results corroborate those of the DSC measurements, i.e., phase I is the completely disordered phase since it exhibits a total absence of lattice modes. The weak, broad peaks observed in this region for phase II indicate that it is orientationally disordered, while the sharp peaks in phase III show that it is a completely ordered phase.

In Fig. 3, the changes that occur in the Raman for the C—C—Cl bending mode are shown. In phase I, the peak appears at 156 cm^{-1}. As the sample is cooled down towards the first transition (phase I → phase II), the peak width narrows and the peak shifts to slightly higher wavenumber (159 cm^{-1}) once in phase II. However, on going from phase II to phase III, a new peak appears at 167 cm^{-1} and the 159 cm^{-1} peak decreases in intensity. The 167 cm^{-1} peak eventually shifts to 169 cm^{-1} and becomes a sharp singlet for phase III, while the peak at 159 cm^{-1} disappears completely.

The symmetric C—C stretching mode (Fig. 1*a*) also undergoes distinct changes as the sample proceeds from phase I to phase III. In the plastic phase, the peak occurs as a singlet at 760 cm^{-1} with a smaller peak at 780 cm^{-1}. In phase II, the 760 cm^{-1} peak is split into a doublet at 757 and 764 cm^{-1}. Moreover, the 780 cm^{-1} peak sharpens and increases in intensity moving finally to 775 cm^{-1}. Little change occurs as the sample progresses from phase II to phase III. Since this spectral region is solely due to C—C stretching, i.e., cage skeletal stretching, the observed changes must result from a change in crystal structure.

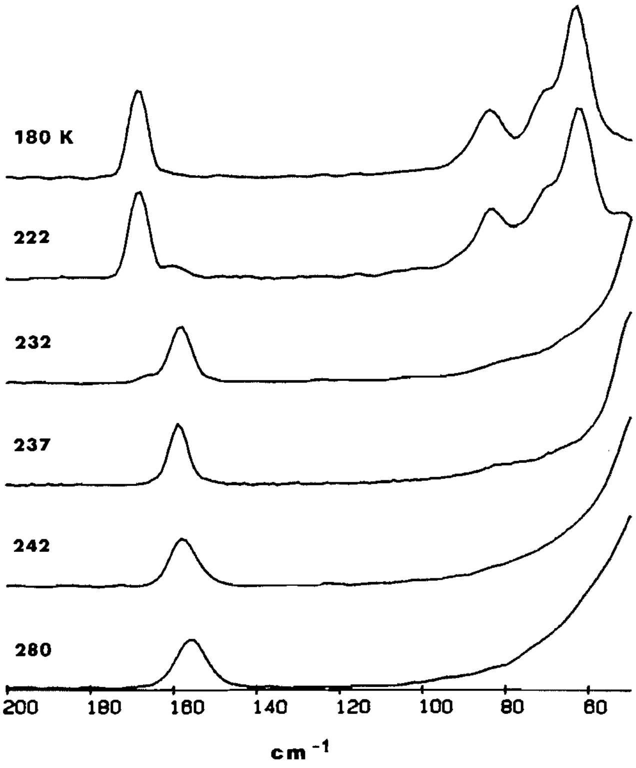

FIG. 3. Low frequency region of the Raman spectra of 2-$C_{10}H_{15}Cl$ on heating (180–280 K). Slits: 300 μm. Acquisition: 1 s pt^{-1}, 1 cm^{-1} step. Intensity: counts. Laser line: 514.532 nm, power 300 mW.

TABLE 1. Vibrational data (cm^{-1}) for 2-chloroadamantane

	Phase I (295 K)		Phase II (237 K)		Phase III (180 K)		
Solution[a]	Raman	IR	Raman	IR	Raman	IR	Assignments
			2956s	2959w		2960w	A' CH str.
				2952sh		2953s	
					2950vs	2951m	
2940s, pol	2941s		2943s		2942m		
			2939s	2938s		2939v	
			2934s	2933s	2935sh	2935vs	
		2930s				2930vs	A'' CH$_2$ anti-symmetric str.
		2926s	2926sh	2926s	2926s	2928vs	
2918s	2918vs	2916sh	2918vs	2917s	2915vs	2913vs	
		2910sh		2910s	2909sh		
		2906vs		2906vs		2905vs	
		2903sh	2903sh				
			2899s	2899s		2896s	
			2891s	2895sh	2894vs	2890s	
						2871sh	A'' CH$_2$ symmetric str.
			2865sh	2867sh	2868m	2867m	
			2858sh	2859s	2857m	2859s	
2852m	2853m	2853s	2854m	2853s	2850m	2851s	
			2848m	2849s		2847s	
		2660w		2667w		2665w	
			1474w		1474w		A' CH$_2$ Def.
1471w,pol	1470w	1468w	1469vw	1469w		1469w	
			1456vw		1457vw		
			1454vw		1450vw		
		1450m		1451m		1451m	
1443m,pol	1441m	1442w	1438m	1442br,w	1440m	1441br,w	
	1435sh		1435sh		1435w		
		1374w		1374vw		1373vw	A'' CH$_2$ wag and CCH def.
		1368w		1370w		1370w	
1356w		1358w	1359vw	1358w	1359w	1358w	
		1353m		1353m		1353m	
1345w	1344vw	1343w	1344vw	1343w	1344vw	1344w	
		1321w	1321vw	1321w	1322w	1323br,w	
						1320br,w	
1319w	1319w		1319vw	1316w	1319vw	1318w	
		1313w	1310vw		1312w		
1304w	1302w	1301m	1304w	1302m	1303m	1303m	A' CC str.
			1294sh	1295vw	1295vw	1295w	
1290w,pol	1289w	1290sh	1290w	1291sh	1290w	1290vw	
		1287m		1287m		1287m	
1252w	1252m	1251w	1255s	1251w	1256s	1251w	A'' C—C str. CH$_2$ def.
		1234sh		1236sh		1237sh	
		1230m		1231w		1232w	
	1228sh	1226sh	1220sh	1225sh	1223s	1225sh	
1215s	1214s		1218m		1221sh		A'' CH$_2$ twist and CCH def.
		1212vw	1211m	1213vw		1213vw	
1178m	1177m	1175vw	1179m	1175vw	1179m	1175vw	
1123w	1123w		1118w	118vw,br		1118br,vw	
		1114w,br			1115vw		CCH def.
			1112sh		1112w	1111sh	
				1108vw		1107vw	
			1103m	1104sh	1102s	1102sh	A'' CCH def.
1101m	1100m	1099m	1098m	1100w		1100w	
						1070vw	
1068m	1067m	1066w	1068w	1066w	1069s	1066vw	
		1061w	1063m	1061w	1063sh	1061w	
		1040sh		1045sh		1045sh	CCH def.
		1038w		1043w		1043w	
1039w,pol	1037w	1035sh	1039w	1037vw	1036w	1039br,w	A' CCH def.
		1032sh		1032vw		1032vw	

TABLE 1. Vibrational data (cm^{-1}) for 2-chloroadamantane

	Phase I (295 K)		Phase II (237 K)		Phase III (180 K)		
Solution[a]	Raman	IR	Raman	IR	Raman	IR	Assignments
			982m	982w	982m	982w	A'' CH$_2$ rock and CCC bend and CC str.
980m	979m	978w	976sh	979sh			
				975vw	975w	975vw	
		960sh		960sh		960sh	
961m	960m	958m	961s	958m	963s	958m	
	955sh		955sh		955w	953w	
948m	947m	949sh	949w	950sh	949m	950sh	
		945w		946w		947w	
	910sh		911vw	910vw	911vw	909vw	
903m	902w	901m	901w	900m	900w	899m	
		878vw		880vw		881vw	
				876vw		876vw	
		822sh					
815w	815w	813m	813w	814w	811w	814sh	
				810m		810m	A' C—C str. and C—C—C bending
803w,pol	803w	801w	802w	801w	802w	801w	
781vw,pol	780w	779m	775m	774m	775m	774m	
	764sh	764br,w	764s	761w	762s	761w	
760vs,pol	760vs	756m	757vs	756m	757vs	756m	
660m	660m	659m	658m	657m	658m	657m	
	637vw	635vw	636vw	634vw	634vw	634vw	
621w	620w	619w	620w	618w	620w	617w	
				614br,vw		614br,vw	
	462s	462m	459s	462m	458s	462m	C—Cl str.
	446w	445w	446w	445w	448w	445w	
			443sh		442vw		
	425w		424w		425w		
380w	381w		381w		385w		A'' skeletal modes
340w	341vw		338vw		339vw		
309m	309s		308s		309s		
			303sh		305sh		
220w	218w		218w		222w		C—C—Cl str.
157w	156w		159w				
					169w		
					84w		
					62sh		
					29w		

[a] In CCl$_4$ and CS$_2$ solutions

The C—C stretching and CH$_2$ twisting modes at 1067 cm^{-1} and the C—C—H deformation and CH$_2$ wag at 1100 cm^{-1} alternate between singlets and doublets as the sample goes from phase I to phase III. The doublets in phase I collapse to singlets in phase II which then split into doublets in phase III. Since the C—C and CH$_2$ modes contribute to the two bands, it is not surprising that the bands are sensitive to crystal structure (C—C) as well as to orientational (CH$_2$) changes. The same is true for the 3000–2800 cm^{-1} (symmetric and asymmetric CH stretching) region, which also undergoes dramatic changes as the sample transforms from phase I to phase III (Fig. 1*b*).

Figures 2*a* and *b* show variable temperature FT-IR spectra obtained for 2-chloroadamantane. As expected for a C_s symmetry molecule, all the changes parallel those observed in the Raman spectra. Again, phase III contains many sharp, well-resolved peaks indicating an ordered phase, whereas phase I has mostly broad, featureless bands implying a high degree of disorder. The 765 cm^{-1} peak is broad but well resolved in phase I. As the sample approaches phase II, the peak decreases in intensity until the transition to phase II in reached, at which point the peak becomes a shoulder. In phase III, the band reappears as a sharp, well-defined peak. The major differences between the IR and Raman data are that the effects observed in IR are gradual, as would be expected when using a KBr matrix (14), whereas in the Raman they are sudden. Moreover, some IR peaks are not observed in the Raman spectra, probably due to narrower peaks and better signal-to-noise ratio available for FT-IR.

Based on the vibrational splittings observed in phases II and III, the ordered phases have at least two molecules per unit cell.

Acknowledgements

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