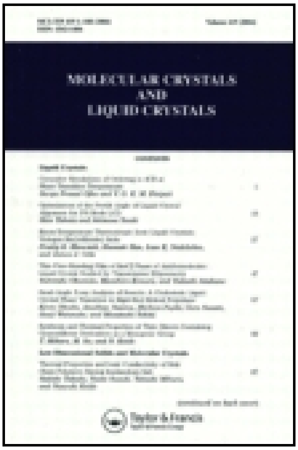

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Phase Transitions of Pyrazine

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Phase Transitions of Pyrazine

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Phase transitions of pyrazine crystal have been studied by calorimetry, X-ray diffraction and low frequency vibrational spectroscopy. Three phases have been shown to exist: phase I stable up to 28.5°C, phase II between 28.5 and 37°C and phase III between 37 and 51°C. Phase III is characterized by the space group Cmmm and its unit cell ($Z = 8$) is the quadruple of that of phase I. Phase II is similar to phase III and the most significant spectroscopic feature of the former is the presence of two Raman bands at 23 and 10 cm^{-1}. The lattice modes of phase I and the librational amplitude have been calculated. The amplitudes are very large and amount up to 10° for the motions about the x-axis. They may play a major role in the mechanism of phase transitions and are likely to be responsible for some disagreements between the calculated and observed lattice frequencies.

1 INTRODUCTION

There has been a considerable interest in the dynamics of the pyrazine crystal since Ito and Shigeoka reported the first low frequency Raman spectrum and the corresponding normal coordinate calculations.[1] Other authors have investigated this crystal[2–4] however they encountered the same difficulties in adjusting the calculated and observed lattice frequencies. On the other hand, there appears to be a controversy about the phase transition of pyrazine crystal. Schettino *et al.*[5] using differential scanning calorimetry and infrared spectroscopy reported a phase transition at 29°C while Péneau

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et al.[6] suggest two phase transitions at 27 and 35°C on the ground of the temperature dependence of the nuclear quadrupole resonance frequency of ^{14}N. Only one crystalline structure (at 25°C) has been determined by X-ray diffraction.[7] Other spectroscopic works were published by Sbrana *et al.*,[8] Gerbaux and Hadni,[9] Larkin and Stidham[10] on internal vibrations, far infrared spectrum and polarized low frequency Raman spectra, respectively.

We have thus reinvestigated the pyrazine crystal using microcalorimetry, X-ray diffraction and infrared and Raman spectroscopy in order to complete these studies and to enquire about the unknown structures and the nature of phase transitions.

2 EXPERIMENTAL

Pyrazine-d_0 was a commercial product, pyrazine-d_4 was prepared by decarboxylation of pyrazine tetracarboxylic acid. Both compounds were purified by vacuum sublimation.

Calorimetric measurements were realized using a Calvet type microcalorimeter working in the −190 to 200°C region.

X-ray diffraction study was made on both polycrystalline sample and single crystals using a Guinier-Lenné and a Weissenberg camera, respectively. The latter was adapted for variable temperature measurements. In both cases the sample was sealed in a Lindemann glass capillary in order to avoid sublimation.

The far infrared spectra of pyrazine pellet were recorded in the 150–20 cm^{-1} range using a Beckman IR 11 and a Cameca IRL 1000 spectrophotometers. The low-frequency (100–5 cm^{-1}) Raman spectra of polycrystalline samples sealed in glass tubes were obtained on a Coderg T800 triple monochromator equiped with a Spectra-Physics 164 argon ion laser (5145 Å) as exciting source. The spectra were investigated at different temperatures down to that of liquid helium. A Coderg cryostat was used in the 40 to 20°C range and the temperature was regulated to ±0.5°C; a Meric cold cell without temperature regulation was employed below −196°C. The spectral slit width was always lower than the half of the line width of the measured line.

3 RESULTS AND DISCUSSION

1 Calorimetry

The results of the calorimetric measurements, i.e. the variation of the specific heat capacity with temperature, calculated from the calorimetric curves, are shown in Figure 1. Two crystalline phase transitions are observed. The first

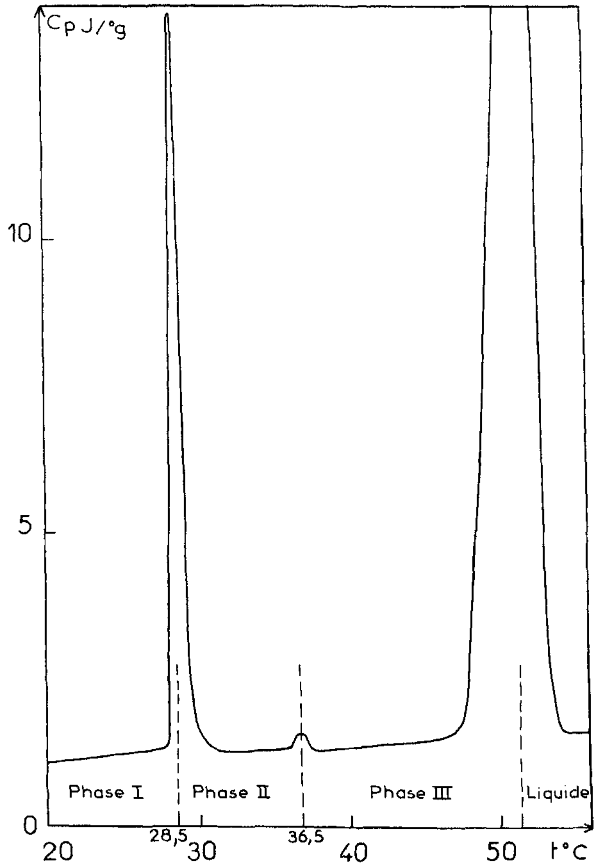

FIGURE 1 Specific heat capacity (C_p) of pyrazine as a function of temperature.

corresponds to a strong peak at 28.5°C and the second to a weak peak at 36.5°C. The very strong peak near 51°C is due to the melting of the pyrazine crystal. The enthalpies can be determined from these curves and they amount to 228, 15 and 3095 cal/mole for the first, second and third transition, respectively. There are thus three crystalline phases of pyrazine: phase I stable below 28.5°C, phase II between 28.5 and 36.5°C, and phase III between 37 and 51°C, in agreement with the results of Péneau *et al.*[6] The second peak is very weak indeed and it is not surprising that it was not observed by Schettino *et al.*[5]

2 X-ray diffraction

The calorimetric results of the Figure 1 can be compared with the X-ray diffraction powder diagram of the Figure 2. The phase transitions manifest

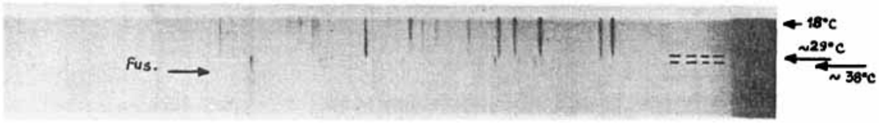

FIGURE 2 Guinier–Lenné diagram of different phases of pyrazine ($X = 1549$ Å)

themselves on the corresponding Guinier–Lenné diagram at approximately the same temperatures as those indicated by calorimetry, i.e. near 29 and 38°C, respectively. The first phase transition (29°C) appears much clearly than the second one (38°C). Nevertheless, the diffraction diagrams of phase II as well as those of phase III do not contain enough reflections for a thorough phase analysis. We thus continued our work on single crystals using the Bragg technique and the Weissenberg technique. The following study is limited to phase III at 38°C.

When a single crystal is heated from 25°C to 38°C, its lattice appears to be maintained through the two phase transitions as shown by the Bragg diagram and the Weissenberg diagram in Figure 3. The reflexions of the reciprocal lattice although broadened and deformed are not destroyed. There appears to be a superstructure in two directions as shown by diagrams of the ($hk0$) and ($hk1$) planes (Figure 3). This phenomenon can be interpreted in terms of a doubling of the phase I unit cell constants a and b, while the constant c remains practically the same. The unit cell constant values of the two phases I and III are given in Table 1.

The inspection of the reflections of the ($hk0$) and ($hk1$) planes of the phase III shows that systematic absence of reflections occurs for ($hk1$) with $h + k$ even, ($hk0$) with $h + k$ even, $h01$ with h even and $0k1$ with k even. This indicates that the space group is one of the following ones: $C_{mmm}(D_{2h}^{19})$, $C_{mm2}(C_{2v}^{11})$, $C_{222}(D_2^1)$, $C_{2221}(D_2^5)$. However, the P_{mnn} space group of phase I has a symmetry plane which is expected to remain in the high temperature phase. The most likely space groups are thus reduced to C_{mmm} and C_{mm2}. Finally, the unit cell of phase III, being four times larger than that of phase I, contains eight molecules.

TABLE I

Unit cell constants of phase I and III of pyrazine

Phase III at 38°C	Phase I at 25°C (Ref. 7)
Orthorhombic system	Orthorhombic system (Pmnn)
$a = 18.57$ Å	$a = 9.316$ Å
$b = 11.31$ Å	$b = 5.911$ Å
$c = 3.85$ Å	$c = 3.815$ Å
$z = 8$	$z = 2$

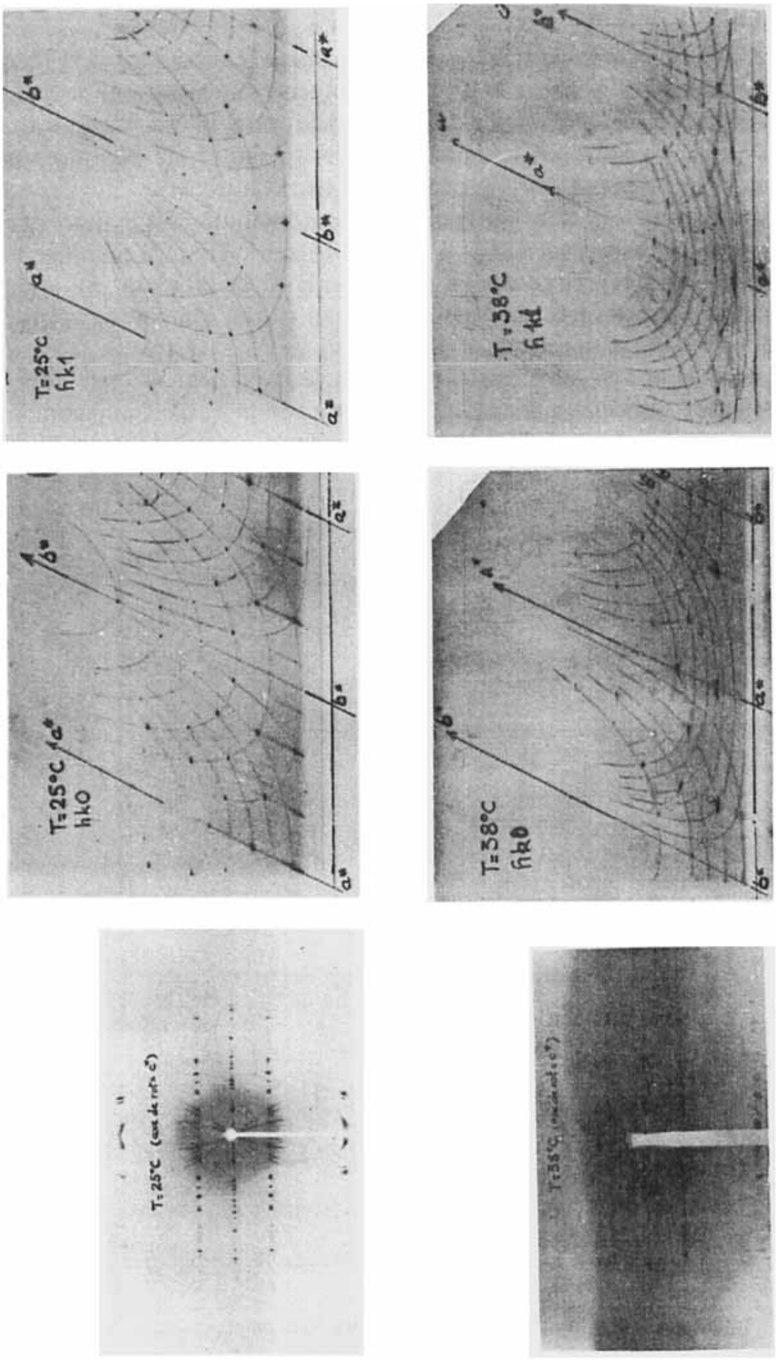

FIGURE 3 Bragg diagram and Weissenberg diagram of pyrazine crystal at 25 and 38°C.

3 Infrared and Raman spectra

Phase I The low frequency infrared (Figure 4) and Raman spectra (Figure 5) of phase I of pyrazine ($P_{mnn} - D_{2h}^{12}$, $Z = 2$) generally agree well with those reported by Gerbaux and Hadni[9] and by Larkin and Stidham,[10] respectively. In particular, we can confirm a conclusion of the latter, i.e. that the lowest frequency band near 44 cm^{-1} (at 25°C) has two components. However, this accidental degeneracy does not persist at liquid helium temperature for we observed two well distinct bands at 58 and 54 cm^{-1} (Figure 5) under these conditions. We propose to assign these bands to the B_{2g} and B_{1g} species, respectively, according to the frequency order of the calculation (Table 2). Finally, our Raman spectrum of pyrazine-d_4 at 25°C (Table 2) shows two bands near 94 and 87 cm^{-1} instead of a single band near 97 cm^{-1}.[10]

The phase I lattice frequencies at 25°C are given in Table 2 and compared with the calculated ones. The normal coordinate calculations reported in

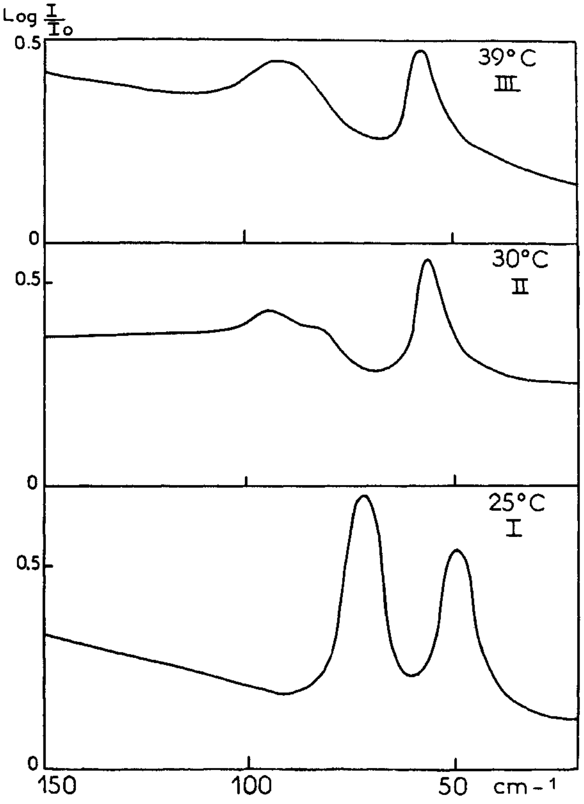

FIGURE 4 Far infrared spectra of pyrazine-h_4 at different temperatures.

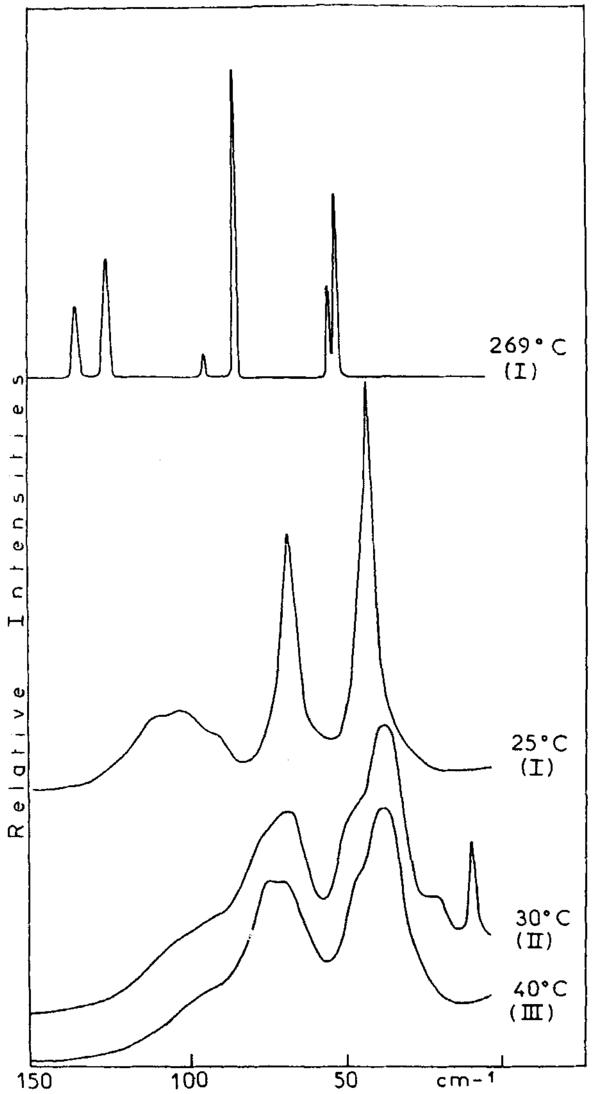

FIGURE 5 Low frequency Raman spectra of pyrazine-h_4 at different temperatures.

TABLE II

Lattice frequencies in the different phases of pyrazine crystal

Phase I (25°C)						
$C_4N_2H_4$			$C_4N_2D_4$			
IR	Raman	Calc	Raman	Calc	ν/ν'[a]	Assignment[b]
—	112	118	105	107	1.07	B_{3g} $R'z$
—	105	110	94	100	1.10	A_g $R'z$
—	92	93	87	89	1.05	B_{1g} $0.73R'x + 0.27R'y$
72	—	67	—	66	—	B_{1u} $T'c$
—	70	59	67	55	1.04	B_{2g} $0.90R'y + 0.10R'x$
51	—	64	—	63	—	B_{2u} $T'b$
—	44	44	42	42	1.05	B_{2g} $0.90R'x + 0.10R'y$
—	44	38	42	36	1.05	B_{1g} $0.73R'y + 0.27R'x$
—	—	113	—	111	—	A_u T'_a

Phase II (30°C)			Phase III (40°C)				
$C_4N_2H_4$		$C_4N_2D_4$	$C_4N_2H_4$		$C_4N_2D_4$		
IR	Raman	Raman	IR	Raman	Raman	ν/ν'[a]	Assignment[b]
—	97	—	—	97	—	—	$R'z$
95	—	—	—	—	—	—	T'
—	93	84	—	93	84	1.10	$R'z$
83	—	—	90	—	—	—	T'
—	77	73	—	77	73	1.06	$R'y$
—	69	66	—	69	66	1.04	$R'x$
57	—	—	57	—	—	—	T'
—	48	46	—	48	46	1.04	$R'x$
—	39	37	—	39	37	1.07	$R'y$
n.o.[c]	23	23					
n.o.[c]	10	10					

[a] ν/ν': isotopic frequency ratio of a vibration of pyrazine-d_0 and of the corresponding vibration of pyrazine-d_4. The calculated isotopic frequency ratios are 1.10, 1.07 and 1.03 for $R'z$, $R'y$ and $R'x$ librations respectively.

[b] z and x are the axes situated in the molecular plane, the former coincides with the line joining two nitrogen atoms and the latter is perpendicular to this direction; y axis is perpendicular to the molecular plane.

[c] The 30–0 cm^{-1} range was not investigated in the far infrared.

detail elsewhere[11,12] complete those published by other authors[2–4] since our work takes into account pyrazine-d_0 and -d_4 species simultaneously while each species has been treated separately in previous works.[2,3] Nevertheless, the agreement between the calculated and experimental frequencies is similar to that of Besnaïnou[3] and Reynolds:[2] the average absolute error amounts to 5.5 cm^{-1}. The disagreement concerns the same frequencies corresponding to a libration near 70 cm^{-1} and the two infrared active translational modes. The calculated frequency difference between the latter (3 cm^{-1}) is much smaller than the observed value of 21 cm^{-1}. Finally, the calculations show that coupling occurs between the R'_x and R'_y librations for the B_{1g} as well as for the B_{2g} species, a coupling consistent with the corresponding experimental isotopic frequency ratios which are intermediate between those expected for pure R'_x and pure R'_y librations (Table 2).

The difficulties encountered in the lattice frequency calculations are not likely to be due to unsuitable intermolecular potentials involving nitrogen atoms. In fact, our studies of some crystals of heterocyclic nitrogen bases[12–14] have shown that the nitrogen potentials are generally transferable and not very sensitive to different environments. We rather think that the disagreement between the calculated and the observed values must be associated with some particular dynamical properties of this crystal and its phase transitions. For example, very large librational amplitudes could be estimated for phase I using the Cruickshank method.[15] Assuming that the librations about the z, y and x axis are not coupled (which is exact for B_{3g} species, a good approximation for B_{2g} but less good for B_{1g} species—see Table 2) the experimental frequencies at 25°C yield the mean amplitudes of 5.2°, 7° and 9.3° for the z, y and x axis, respectively. These results agree well with the values published by Wheatley on the basis of X-ray diffraction data.[7] Since these amplitudes correspond to average values it can be expected that the low frequency librations, in particular that of the B_{2g} species at 44 cm^{-1}, have amplitudes larger than 10° and that the corresponding motions are highly anharmonic. This is consistent with the NQR results: the relationship between the longitudinal relaxation time T_1 and the temperature T does not follow a T^2 law as expected for harmonic motions.[16]

Phase III The infrared and Raman spectra of phase III differ from those of phase I (Figures 4 and 5). There are two infrared and six Raman bands and their frequencies as well as those of pyrazine-d_4 are given in Table 2. The non coincidence of Raman and infrared frequencies is observed not only for the external but also for the internal vibrations,[8] which implies that the molecules occupy at least $\bar{1}$ (C_i) sites in phase III. The infrared bands are thus likely to correspond to the translational vibrations and the Raman bands to the rotational vibrations. The observed isotopic frequency ratios of the latter are close to the calculated values (Table 2) and indicate that there is but little coupling between librations, at any rate much less than in phase I.

The infrared and Raman data are thus consistent only with the C_{mmm} space group since the other three groups proposed by X-ray diffraction do not contain $\bar{1}$ sites. The NQR spectra of phase III, on the other hand, show two signals[6] which imply the existence of two fourfold crystallographic sites. In the C_{mmm} space group there are two types of fourfold sites, $mm(C_{2v})$ and $2/m$ (C_{2h}), and one type of twofold site, mmm (D_{2h}). The molecules could be either on $2/m$ sites only or on one $2/m$ (or one mm) and two mmm sites. The first assumption implying only even hkl reflections is not consistent with the X-ray diffraction data because of the 111, 311, 331, 511, 711 reflections observed. The second assumption is more likely since the conditions required for the $2/m$ sites could be masked by the presence of mm or mmm sites. Finally, the primitive cell contains four molecules. Twelve Raman and nine infrared bands are thus expected. However, there are no new bands in the phase III spectrum with respect to that of phase I, but the bands appear much broader; this band broadening may be ascribed to the new components which are not resolved under our experimental conditions. The temperature increase could also cause some broadening, but the small temperature difference (10°C) does not appear to be a dominant factor.

Phase II Phase II is the most difficult to study because its domain is limited within 7 or 8°C depending on the method employed. However, the comparison with the data of the other two phases allows to derive some conclusions about its structure.

The infrared and Raman spectra corresponding to internal vibrations are identical in phases II and III. The low frequency spectra (Figures 4 and 5) on the other hand, are different. The infrared spectrum shows two components at 95 and 83 cm^{-1} instead of the single absorption band at 90 cm^{-1} of phase III. The Raman spectrum of the two phases are practically the same except for the occurrence of two new bands at 23 and 10 cm^{-1}. The small spectroscopic differences between the phases II and III can be compared with the weak calorimetric effect (Figure 1) and the small NQR frequency variation.[6] There are 11 lattice frequencies (Table 2), eight Raman and three infrared and the mutual exclusion rule appears to be obeyed. The unit cell of phase II is thus expected to contain at least four molecules on at least $\bar{1}$ sites and the similarity of the spectra with those of phase III indicates a similar molecular arrangement.

The most significant difference between the phases III and II concerns the new Raman bands of the latter. Their very low frequencies remind of soft modes, but no frequency variation could be detected within the limited temperature range of this phase. No assignment in terms of translational or librational modes can be given since their frequencies do not shift measurably on isotopic substitution, which is not surprising for bands at very low frequencies. The 23 and 10 cm^{-1} Raman bands are likely to correspond to some kind of collective motions but they are presently not well understood and no detailed assignment can be given.

CONCLUSIONS

There are three crystalline phases in solid pyrazine as shown by calorimetry, X-ray diffraction and infrared and Raman spectra in agreement with NQR spectroscopy.[6]

Phase III, stable between 37 and 51°C, belongs to the orthorhombic system, space group C_{mmm} with eight molecules in the crystallographic cell. The molecules are on sites of at least $\bar{1}$ symmetry. The crystallographic cell can be described as a cell quadruple of that in phase I.

Phase II, stable between 28.5 and 37°C appears to have a structure intermediate between those of phases I and III and more similar to that of phase III. Its Raman spectrum is characterized by the presence of two bands at 23 and 10 cm^{-1} which do not appear in the spectra of the other phases.

The mechanism of pyrazine phase transitions can probably be interpreted in terms of librational motions with very large amplitude such as the librations about the x axis of the molecule, the average amplitude of which is close to 10° in the 25 to 40°C temperature range.

The large librational amplitudes may explain the difficulties concerning the normal coordinate calculations in phase I.

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