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Temperature Dependence of the Entropy and the Heat Capacity Calculated from the Raman Frequency Shifts for Solid Benzene, Naphthalene and Anthracene

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Abstract

Temperature dependences of the free energy (F), entropy (S) and the heat capacity (C_v) are calculated (P=0) for the organic compounds (solid benzene, naphthalene and anthracene) by using the quasiharmonic approximation. Contributions to those thermodynamic functions due to the Raman frequencies of lattice modes (solid benzene), librational modes (naphthalene), phonons and vibrons (anthracene) are taken into account in our calculations. We obtain that similar linear increase of F and nonlinear increase of S and C_v, occur with the increasing temperature in benzene and naphthalene. This linear (F) and nonlinear (S, C_v) increase is rather different for anthracene as the molecular structure becomes complex (benzene-naphthalene-anthracene), as expected. Our calculations by the quasiharmonic approximation can be compared with the experiments for those organic compounds.

Keywords: *Quasiharmonic approach; free energy; entropy; heat capacity.*

1. Introduction

Hydrocarbons are the simple organic compounds with the H and C atoms [1] as good fuels occuring naturally. In particular, benzene (C_6H_6) is categorized as the first (elementary) example of the hydrocarbon compounds and in the same family naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) have similar molecular structure as benzene. A number of studies on those hydrocarbons have been published over the years. In particular, for benzene near the phase transitions its thermodynamic properties such as the volume [2-4], specific heat [5-7], thermal expansivity [8] and T-P phase diagrams [3,4,9-11] have been investigated experimentally. We have calculated various thermodynamic functions near the phase changes in benzene as reported previously [12-14]. Spectroscopically, a number of works on the mechanism of phase changes in benzene have been given in the literature. Among those studies, X-ray [3, 4, 15], infrared [4,16-19], fluorescence [20] and Raman [3, 11, 21] spectra of benzene have been obtained experimentally. Raman frequencies near the phase transition in benzene have been evaluated in our earlier studies [22, 23]. Some other theoretical studies and model systems for benzene have been reported [24-28]. More recently, structural properties of solid benzene have been studied experimentally in neutron and x-ray diffraction under high pressure-high temperature conditions and the phase diagram of benzene has been obtained [29]. Also, the solid state structural properties and phase transition (order-disorder) behaviour of benzene derivatives have been studied [30]. Phase diagrams of mixtures of benzene and acetonitrite have been obtained [31]. Very recently, the P-T phase diagram has been constructed to determine the solid, liquid and gaseous states for benzene [32]. Phase transitions in liquid benzene (solid-liquid transition) has been studied by using high-resolution time-resolved Raman spectroscopic technique [33].

Regarding some earlier studies for compounds (naphthalene and anthracene) near the phase changes, measurements of the heat capacity [6, 34, 35] and also Raman [36], neutron scattering [37], X-ray and neutron diffraction [38] studies for naphthalene, have been performed. Using quasi-harmonic approximation, lattice dynamics calculation for naphthalene [39] and the heat capacity prediction using vibration spectra for benzene, naphthalene and anthracene [7] have been made.

For anthracene, some of experimental studies are the following: measurements of thermal conductivity of specific heat [6], pressure dependence of the lattice frequencies [36], wave velocities [40] and determination of the crystalline structure by the high pressure X-ray diffraction [41].

Theoretically, structure and dynamics of anthracene have been studied [42] and using the DFT (density-functional theory) ab initio calculations have been reported [43]. Crystallographic phase transition in anthracene with a large hysteresis has been studied under high pressure [44]. A study on a solid mixture of naphthalene and anthracene at room temperature has also been reported [45]. By differential scanning calorimetry (DSE), a depression of the phase transition temperature was observed [46]. An entropy change in anthracene has been studied [47]. Regarding gas phase of naphthalene, it has been studied at low temperatures [48]. Another study on naphthalene was on its elastic properties, mainly by using the Vinet equation for the P-V phase diagram to obtaine its thermal coefficient [49]. A numerical simulation of naphthalene for the melting and solidification process has been performed [50]. Calculations for the Raman frequencies of naphthalene [51] and anthracene [52] have been reported in our earlier

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studies. Experimentally, the decomposition of naphthalene, anthracene, pyrene and coronene at high pressures and temperatures have been examined [53]. Ab initio study of the crystal structure, mechanical and acoustic properties of naphthalene and anthracene has been performed [54]. Very recently, anthracene's molecular structure, optical properties and phase transitions have been reviewed [55]. Thermal properties of anthracene-manganese complex have been studied [56]. Also phase transitions in the aromatic naphthalene have been investigated [57].

The three organic compounds (benzene, naphthalene and anthracene) have similar molecular structures and the unit cell parameters which show some differences, can be considered with the differences appearing in the sizes of the molecular units [9]. Structurally, benzene contains Raman active lattice modes and vibrons [3], naphthalene has six librational modes (A_g and B_g) with some other phonon modes [39], similarly anthracene exhibits six phonon modes (A_g and B_g) [36] and nine vibrons [58]. Benzene, naphthalene and anthracene are in the monoclinic phase which changes to another phase as the pressure varies [9]. In both naphthalene and anthracene, decomposition occurs below the triple point whereas in benzene it occurs above that point where the liquid phase meets with the two solid (II and III) phases [2]. Regarding our calculations of the Raman frequencies in our earlier works [51,52], we consiederd the librational modes of $3A_g+3B_g$ as functions of temperature (P=0) and pressure (T=300K) in naphthalene [51]. Also we considered six (A_g+B_g) phonon modes and nine vibrons at various temperatures (P=0) and pressures (T=300K) in anthracene [52]. By means of the mode Grüneisen parameter which relates the vibrational frequencies to the volume changes (with the temperature and pressure), the Raman frequencies of those Raman modes were calculated for both molecular solids (naphthalene and anthracene). By analyzing the observed Raman frequency and volume data from the literature according to the $\vartheta(T,P)$ in the quadratic form, values of the coefficients were first determined. This allowed us to determine the mode Grüneisen parameter for each mode and then the Raman frequencies of those modes were predicted for naphthalene [51] and anthracene [52]. For the solid I-II transition in benzene, similar analysis for the Raman frequencies of the six lattice modes (A,B,C and X,Y,Z) and the volume data from the literature, was conducted to calculate the specific heat C_P of this molecular solid [59]. This calculation of C_P as functions of temperature and pressure was performed by using the thermodynamic relations for benzene. Differently from our earlier studies for the calculation of the Raman frequencies in the naphthalene [51] and anthracene [52], and also the calculation of the specific heat C_P from the Raman frequencies in benzene [59], in the present work by the quasi-harmonic approximation, the vibrational free energy, entropy and the heat capacity are predicted as a function of temperature for those three hydrocarbons (benzene, naphthalene and anthracene). The analysis of the observed Raman frequencies $\vartheta(T)$ from the literature data is performed by using the same functional form (quadratic) with those coefficients determined as given in our earlier publications [51,52 and 59].

This work presents calculation of the thermodynamic quantities (entropy and heat capacity) from the vibrational frequencies of benzene, naphthalene and anthracene by means of the quasi-harmonic approximation. The observed Raman frequencies of those solid systems from the literature, are used to calculate the temperature dependence of the heat capacity as derived from the quasi-harmonic free energy.

Our motivation in this study is to investigate whether those three solid systems (benzene, naphthalene and anthracene) exhibit similar molecular structures thermodynamically. This is of interest for those molecular solids due to increasing complexity of their molecular structures (benzene-naphthalene-anthracene). Our calculations show that the temperature dependence of the free energy, entropy and the heat capacity for benzene and naphthalene behave almost the same, whereas this behaviour is comparatively different for anthracene.

This calculation of S and C_V from the free energy is carried out by using the Raman frequency of the (A,B,C and X,Y,Z) external modes (benzene), six translational A_g and B_g modes (naphthalene) and A_g, B_g modes with the vibrons (anthracene).

Derivation of the entropy and the heat capacity from the free energy is given. By analyzing the experimental Raman data from the literature, entropy and the heat capacity are evaluated at various temperatures for those three substances.

Below, in Section 2, we derive the thermodynamic functions from the free energy by using the Raman frequency shifts. Section 3 gives our calculations. We present discussion in Section 4. Section 5 gives our conclusions.

2. Theory

The method of study is to use the quasi-harmonic approximation for the three hydrocarbons (benzene, naphthalene and anthracene). By considering the vibrational energy which is mainly the frequency dependence of the thermal energy, the temperature dependence of the entropy and the heat capacity can be predicted in those hydrocarbons. Contributions to the free energy due to the vibrational frequencies (Raman frequencies) of various modes in benzene, naphthalene and anthracene are taken into account in the quasiharmonic approximation and those thermodynamic quantities (entropy and heat capacity) can be deduced. Predictions of the free energy, entropy and the heat capacity can be examined by the experimental measurements in those three hydrocarbons.

By using the quasi-harmonic free energy, entropy (S) and heat capacity (C_V) of solid can be obtained at various temperatures Raman frequency shifts of the external modes (benzene), ($3A_g+3B_g$) modes (naphthalene) and, (A_g, B_g) (anthracene) are considered for this calculation.

In general, quasi-harmonic (QH) description of crystals neglects the population driven anharmonic shifts [34]. In particular, we assumed that those three hydrocarbons are harmonic ossilators with the Helmholtz free energy,

$$F = U + \sum_i \frac{h\vartheta_i}{2} + k_B T \sum_i ln\left[1 - exp\left(-\frac{h\vartheta_i}{k_B T}\right)\right] \qquad (1)$$

In Eq. (1), i denotes their modes, k_B Boltzmann constant, h is the Planck constant. U is the total potential energy and the second term in Eq. (1) is zero point energy. We represent the frequency dependence of the thermal energy as the third term in Eq. (1), which is the vibrational energy of the crystal.

Thus, the vibrational free energy is defined a

$$F_{vib} = \frac{1}{2}\sum_i h\vartheta_i + k_B T \sum_i ln\left(1 - exp\left(-\frac{h\vartheta_i}{k_B T}\right)\right) \quad (2)$$

This energy gives rise to the entropy using the definition

$S = -\left(\frac{\partial F}{\partial T}\right)_V$, as

$$S_{vib} = -\left(h/2\right)\sum_i \left(\partial\vartheta_i/\partial T\right) + \sum_i \frac{h_{exp}\left(-h\vartheta_i/k_B T\right)\left[\vartheta_i/T - \left(\partial\vartheta_i/\partial T\right)\right]}{1-exp\left(-h\vartheta_i/k_B T\right)} - k_B \sum_i \ln[1 - exp(-h\vartheta_i/k_B T)] \quad (3)$$

Also, the C_V (heat capacity) calculated by means of the vibrational entropy S_{vib} (Eq. 3) using the definition

$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$, as

$$C_V = -hc + \sum_i \frac{hexp\left(-h\vartheta_i/k_B T\right)\left[-\left(2h\vartheta_i/T^2\right) + 2\left(\partial\vartheta_i/\partial T\right)/T - \left(\partial^2\vartheta_i/\partial T^2\right)\right]}{1-exp\left(-h\vartheta_i/k_B T\right)} + \sum_i \frac{2hexp\left(-h\vartheta_i/k_B T\right)\left[-\left(\partial\vartheta_i/\partial T\right)/T + \left(\vartheta_i/T^2\right)\right]}{1-exp\left(-h\vartheta_i/k_B T\right)} + \frac{exp\left(-2h\vartheta_i/k_B T\right)\left(h^2/k_B T\right)\left[\vartheta_i/T - \left(\partial\vartheta_i/\partial T\right)\right]}{\left[1-exp\left(-h\vartheta_i/k_B T\right)\right]^2} + \frac{exp\left(-h\vartheta_i/k_B T\right)\left(h^2/k_B T\right)\left[\vartheta_i/T - \left(\partial\vartheta_i/\partial T\right)\right]}{1-exp\left(-h\vartheta_i/k_B T\right)} \quad (4)$$

3. Calculations and Results

We calculated the temperature dependence of the vibrational free energy (F_{vib}), entropy (S) and the heat capacity (C_V) due to the contributions of the vibrational frequencies (ϑ_i) of benzene, naphthalene and anthracene. For this calculation, we assumed the temperature dependence of the vibrational frequency in the functional form of

$$\vartheta_p(T) = d_0(P) + d_1(P)T + d_2(P)T^2 \quad (5)$$

where the coefficients d_0, d_1 and d_2 are the pressure dependent in general. By taking those coefficients constant at P=0, they were determined by fitting Eq. (5) to the temperature dependence of the experimental Raman frequencies for benzene, naphthalene and anthracene. This was done for the six lattice modes (A,B,C and X,Y,Z) of benzene by using their observed Raman frequencies [3]. The values of the coefficients d_0, d_1 and d_2 were then determined which we give in Table 1, as also presented in our previous study [59]. By taking $\vartheta_i(T)$ dependence of the six phonon modes of benzene as a sum ($i = 6$) in Eq. (2), we calculated the free energy (F) as a function of temperature as plotted in Figure 1. Similarly, this calculation of the free energy was performed for the six librational modes ($3A_g$+$3B_g$) of naphthalene. By fitting Eq. (5) to the observed Raman frequencies [39] of those modes of naphthalene, we determined the coefficients d_0, d_1 and d_2 as given in Table 2, which we have reported in our earlier study [51]. The vibrational free energy (F_{vib}) was then calculated from the Raman frequencies of the six librational modes of naphthalene as a function of temperature (Eq. 2), which we plot in Figure 1. Also, by determining the coefficients d_0, d_1 and d_2 (Eq. 5) for the six intermolecular (A_g and B_g) and nine intramolecular vibrational modes of anthracene using the observed Raman frequency data [58], which we tabulate in Table 3, as we have given previously [52], we were able to calculate F_{vib} at various temperatures (Figure 1).

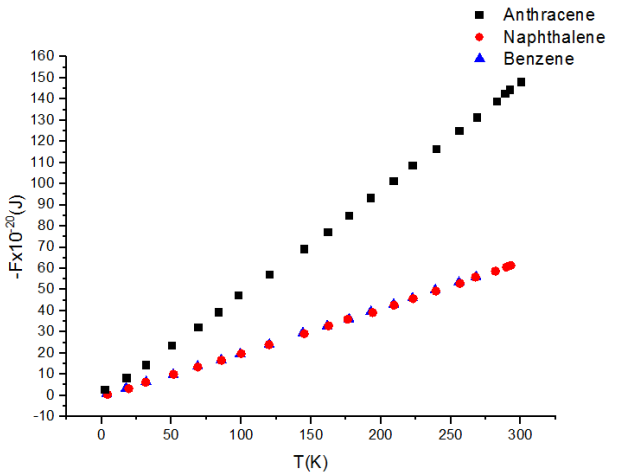

Figure 1. Vibrational free energies calculated as a function of temperature due to of six lattice modes (A,B,C and X,Y,Z) of solid benzene, six librational modes ($3A_g$+$3B_g$) of naphthalene and, six intermolecular (A_g and B_g) and nine intramolecular vibrational modes of anthracene according to Eq. (2).

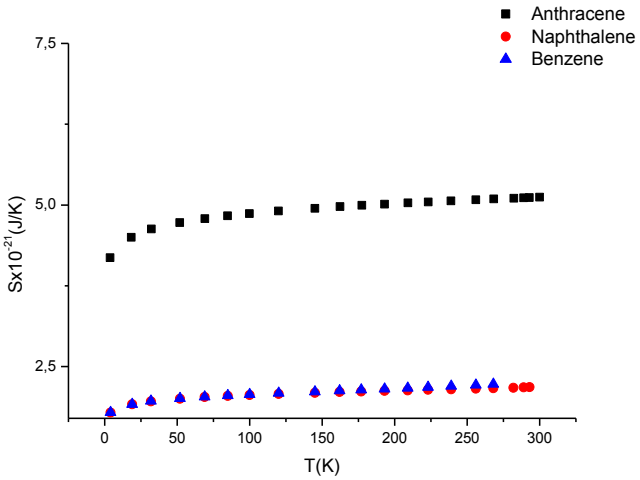

Figure 2. Vibrational entropies calculated as a function of temperature due to of six lattice modes (A,B,C and X,Y,Z) of solid benzene, six librational modes ($3A_g$+$3B_g$) of naphthalene and, six intermolecular (A_g and B_g) and nine intramolecular vibrational modes of anthracene according to Eq. (3).

4. Discussion

Temperature dependences of the vibrational free energy (F), entropy (S) and the heat capacity (C_V) were calculated, as plotted in Figures 1-3, respectively, for the three hydrocarbons studied. We find that the vibrational free energies (F_{vib}) of three hydrocarbons increase linearly and the values of F_{vib} for the anthracene are considerably larger

than those of benzene and naphthalene as the temperature increases (Figure 1).

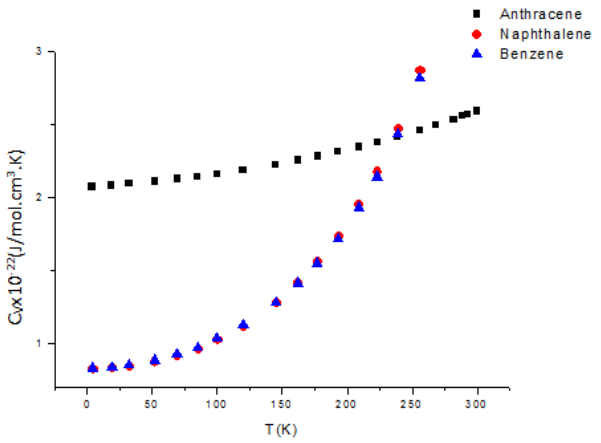

Figure 3. Vibrational heat capacities calculated as a function of temperature due to of six lattice modes (A,B,C and X,Y,Z) of solid benzene, six librational modes ($3A_g$+$3B_g$) of naphthalene and, six intermolecular (A_g and B_g) and nine intramolecular vibrational modes of anthracene according to Eq. (4).

Table 1. Values of the coefficients d_0, d_1 and d_2, which were determined by fitting Eq. (8) to the observed Raman frequencies [3] of the modes (A,B,C and X,Y,Z) indicated for the phases I-II of solid benzene (P=0).

Benzene	d_0 $(cm^{-1}/mole)$	$-d_1$ $(cm^{-1}/mole.K)$	$-d_2$ $(cm^{-1}/mole.K^2)$
Mode A	61.42	1.16	2.12
Mode B	70.44	6.46	0.87
Mode C	139.28	6.58	0.23
Mode X	68.79	3.15	0.28
Mode Y	100.30	3.45	2.66
Mode Z	110.91	3.40	2.89

Table 2. Values of the coefficients d_0, d_1 and d_2, which were determined by fitting Eq. (8) to the observed Raman frequencies [39] of the A_g and B_g modes indicated for solid naphthalene (P=0).

Naphthalene	d_0 (cm^{-1})	$-d_1$ $\times 10^{-2}$ (cm^{-1}/K)	$-d_2$ $\times 10^{-4}$ (cm^{-1}/K^2)
Mode A_{g1}	69.35	2.82	1.19
Mode A_{g2}	88.75	1.37	2.64
Mode A_{g3}	121.64	1.24	1.14
Mode B_{g1}	57.36	2.26	0.59
Mode B_{g2}	84.18	1.79	1.05
Mode B_{g3}	142.35	2.65	1.19

Although the F_{vib} increases monotonically, variations of F_{vib} namely, entropy (S) and the heat capacity (C_v) increase non-linearly for the three compounds (benzene, naphthalene and anthracene), with the increasing temperature (Figures 2 and 3). As a result of the larger values of F_{vib} for anthracene compared to those of benzene and naphthalene (Figure 1), the vibrational entropy (S) and the heat capacity (C_v) become significantly larger in magnitude with increasing temperature for anthracene (Figures 2 and 3). Notice that the curves we obtained for benzene and naphthalene in fact overlap for F_{vib}, S and C_v with the lower values in comparison to the anthracene as stated above (Figures 1-3). Thus, the higher values of F_{vib}, S and C_v in anthracene can be considered as in the sequence from benzene and naphthalene towards anthracene in terms of the impact of the increased complexity of molecular structure. This would imply an increase in the number of intramolecular modes of vibration, as also pointed out previously [6], which occurs in anthracene. Changes in the sequence from benzene and naphthalene to anthracene, are large in terms of mass and relatively simple in terms of molecular structure [6]. Depending on the number of atoms (N) per unit cell (N=24, 36 and 48 for benzene II, naphthalene and anthracene, respectively), we considered in our treatment the contributions to the F_{vib}, S and C_v due to the six lattice modes (A,B,C and X,Y,Z) of solid benzene, six librational modes ($3A_g$+$3B_g$) of naphthalene and, six intermolecular (A_g *and* B_g) and nine intramolecular vibrational modes of anthracene, as stated above. As shown in Figures (1-3), solid benzene II, naphthalene and anthracene exhibit similar behavior with their simple molecular structures involving one, two and three carbon rings, respectively [6].

Table 3. Values of the coefficients d_0, d_1 and d_2, which were determined by fitting Eq. (8) to the observed Raman frequencies [58] of the intermolecular (A_g and B_g) and intramolecular vibrational modes indicated for solid anthracene (P=0).

Anthracene	d_0 (cm^{-1})	$-d_1$ $\times 10^{-2}$ (cm^{-1}/K)	$-d_2$ $\times 10^{-5}$ (cm^{-1}/K^2)
Intermolecular Vibrational Modes			
A_g	46.26	1.76	2.35
B_g	53.63	1.83	2.57
B_g	81.15	2.93	4.01
A_g	86.76	3.35	4.43
A_g	138.52	4.39	6.37
B_g	149.10	5.04	7.11
Intramolecular Vibrational Modes			
$12A_g$	399.64	0.77	0.50
$10B_{3g}$	523.17	0.24	0.50
$10A_g$	756.61	0.54	1.16
$9A_g$	1011.26	0.48	0.98
$8A_g$	1166.13	0.22	0.56
$7B_{3g}$	1190.35	0.45	1.20
$7A_g$	1265.75	0.97	2.19
$6A_g$	1407.31	0.92	1.84
$4A_g$	1560.26	0.47	1.02

For the calculation of the vibrational F, S and C_v , the quasi-harmonic approximation was used due to the Raman frequency shifts of the vibrational modes of solid benzene, naphthalene and anthracene. The quasiharmonic shifts may be related to the deformation of the lattice known as the deformation shifts and the anharmonicity can also be caused by the phonon-phonon interactions [37]. The anharmonic shift can be determined from the temperature dependence of phonon frequencies at a fixed volume [60], as stated above. It has been obtained experimentally that at ambient pressure and for temperatures up to 300 K, the shifts for most low-frequency modes are dominated by quasi-harmonic effects [37].

In our earlier study [52], we have compared the variation of the Raman frequencies of intramolecular (internal) modes with the intermolecular (external modes) as functions of temperature and pressure in anthracene. This is accompanied with the mode Grüneisen parameter which measures the anharmonicity in a crystalline system, as indicated previously. We have found that the values of the mode Grüneisen parameter for the six intermolecular modes are much larger than those of nine intramolecular vibrational modes of the solid anthracene (between 3 and 4 for the intermolecular modes and between 0.03 and 0.2 for the intramolecular modes) [52]. Thus, the anharmonicity which occurs as the relation between the thermal expansion (isothermal compressibility) and the variation in frequency with temperature (pressure) in anthracene, is dominated by the lower-frequency modes (external modes) as in the benzene and naphthalene.

The heat capacity C_v which we calculated as a function of temperature overlaps for benzene and naphthalene whereas the calculated C_v of anthracene exhibits completely different behaviour although all C_v's increase nonlinearly with the temperature (Figure 3) as stated above. On the other hand, we found that the heat capacity C_p which we calculated [59] for the I-II transition in benzene and naphthalene (P=0) differed from the C_v for those two compounds (Figure 3). For both calculations of C_p and C_v, we used the observed Raman frequencies of six lattice modes (A,B,C and X,Y,Z) of solid benzene [3] and six librational modes ($3A_g$+$3B_g$) of naphthaline [39] at various temperatures. For the calculation of C_p, by means of the temperature-induced Raman frequency shifts of those modes and the volume $V_p(T)$, the isobaric mode Grüneisen parameter (γ_p) at P=0 was determined for the Raman modes studied in benzene and naphthalene [59]. Similarly, the pressure-induced Raman frequency shifts of the modes which were studied and the volume V_T(P), were employed by extracting the isothermal mode Grüneisen parameter (γ_T) to calculate the C_p at various pressures (T=300K) for the I-II transition in benzene and naphthalene [59]. Those pressure-induced frequency shifts are directly related to the large initial compressibility κ_T of benzene as a typical molecular crystal [4]. This also applies to the solid naphthalene and anthracene. It has also been pointed out that under the pressure applied to molecular solids such as benzene, the intermolecular interactions can be compared in magnitude to intramolecular ones [3]. Due to the fact that for the calculation of C_p the change in the slopes of the ϑ-P curves of the modes I,II and III as lattice modes, is significant compared to the internal modes in benzene, which we have reported [61] as also pointed out previously [4], we expect similar behaviour of the C_v for the solid benzene and naphthalene. This is because of the fact that we used in our C_v calculation also the Raman frequencies of six lattice modes (benzene) and six librational modes (naphthalene) as stated above. For the C_v calculation of anthracene since we used the Raman frequencies of six intermolecular (external) and nine intramolecular (internal) vibrational modes, we expect rather different behaviour of C_v as a function of the temperature (Figure 3). Consequently, decrease in the Raman frequencies with the increasing temperature can be attributed to the thermal expansion (α_p) increasing. Also, increase in the Raman frequencies decreases the isothermal compressibility (κ_T) with the increasing pressure by means of the isothermal mode Grüneisen parameter (γ_T). This results in the heat capacity C_p which becomes larger than C_V according to the thermodynamic relation

$$C_p = C_v + TV\left({\alpha_p}^2/_{\kappa_T}\right) \tag{6}$$

for the molecular solids, in particular, benzene and naphthalene.

As we calculated the temperature dependence of the free energy (F), entropy (S) and the heat capacity (C_V) for solid benzene, naphthalene and anthracene from the temperature-induced Raman frequency shifts, the pressure dependence of those thermodynamic functions can also be calculated using the pressure-induced Raman frequency shifts in the three hydrocarbon substances by means of the quasiharmonic approximation. As we calculated F, S and C_V due to the Raman frequency shifts of intermolecular and intramolecular vibrational modes as a function of temperature (P=0), those thermodynamic quantities can also be calculated at various pressures (T=300K). They can then be compared with the measurements for solid benzene, naphthalene and anthracene.

5. Conclusion

Vibrational energy (F_{vib}), entropy (S) and heat capacity (C_v) were evaluated at various temperatures using the Raman data for the external modes (benzene), ($3A_g$+$3B_g$) modes (naphthalene) and, (A_g and B_g) modes and vibrons (anthracene) by means of the quasiharmonic approximation. We find that the vibrational free energy increases linearly, whereas its variation (entropy and heat capacity) increases non-linearly with increasing temperature (P=0) in the sequence of benzene to naphthalene to anthracene.

Our calculated values for the free energy, entropy and the heat capacity by using the quasiharmonic approximation, can be compared with the experimental measurements for solid benzene, naphthalene and anthracene. The quasiharmonic approximation can also be applied to some other hydrocarbons such as the phenanthrene, a more stable isomer of the anthracene.

Using the experimental Raman frequencies, the pressure dependence of the F_{vib}, S and C_v can also be calculated using quasiharmonic approximation for those organic compounds. The quasiharmonic approximation can be applied to some other organic compounds.

Nomenclature

C_v Heat capacity at constant volume [J/mol.cm^3.K]
F Free energy [J]
F_{vib} Vibrational free energy [J]

h Planck constant [J.s]
k_B Boltzman constant [J/K]
P Pressure [Pascal]
S Entropy [J/K]
T Temperature [K]
U Potential energy [J]
ϑ Frequency $[s^{-1}]$
ϑ_p Frequency at constant pressure $[s^{-1}]$
γ_T Grüneisen parameter [-]
κ_T Isothermal compressibility [J/K]
α_p Thermal expansion $[K^{-1}]$

Subscript

A_g and B_g	Librational modes
A,B,C and X,Y,Z	Lattice modes
QH	Quasi-harmonic
C	Carbon
H	Hydrogen

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