

Temperature and pressure dependence of the Raman frequency shifts in anthracene

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In this study, the Raman frequency shifts of phonons and vibrons of crystalline anthracene as functions of temperature (at zero pressure) and pressure (at ambient temperature) have been calculated using the experimental volume data from the literature. This calculation is performed for six phonons and nine vibrons through the mode Grüneisen parameters which have been determined from the Raman frequency and volume data at various pressures. Our predicted Raman frequencies of the phonon modes decrease with increasing temperature (zero pressure) linearly, whereas they increase with increasing pressure (ambient temperature) nonlinearly, as observed experimentally for anthracene. For vibrons, we find that the Raman frequencies are almost independent of temperature and pressure in this crystalline system.

Keywords: Raman frequency shifts, Mode Grüneisen parameter, Anthracene

1 Introduction

Anthracene ($C_{14}H_{10}$) has been studied extensively as an example of the polycene family^{1,2}. Its isothermal compressibility³, the Hugoniot⁴ and other physical properties² including spectroscopic data^{5,6} have been obtained using various experimental techniques.

Anthracene is in the hydrocarbon group with the same structure as benzene and naphthalene. Its stable phase at ordinary temperature and pressure is monoclinic, space group $P2_1/a$, with the lattice parameters of $a = 8.562$, $b = 6.038$, $c = 11.184$ Å, $\beta = 124.7^\circ$ and $V = 475.35$ Å³ at room temperature (290 K) with two molecules to the unit cell⁷. The structure and dynamics of a new phase of anthracene have been studied⁸. Its thermal motion⁹ and the low-temperature elastic properties¹⁰ have also been studied previously.

Regarding the high pressure effect on the physical properties of anthracene, isothermal compressibility¹¹ up to 45 kbar and its crystal structure¹²⁻¹⁴ have been reported in the literature. The pressure effect on the internal molecular orientation has been calculated up to 10.2 GPa by the density functional theory¹⁵.

In this study, we calculate the Raman frequencies of the six lattice modes and nine vibrons as a function of pressure by means of the mode Grüneisen parameter in anthracene. In our previous studies, using this method we have predicted the Raman frequencies of some phonon modes in benzene¹⁶ and

in naphthalene¹⁷. For this calculation of the Raman frequencies in anthracene, we use the volume data¹¹ up to 45 kbar and the observed Raman frequencies of the six lattice modes and nine vibrons⁶ through the mode Grüneisen parameters^{5,6}. The temperature and pressure dependences of the Raman frequencies of those phonon modes and vibrons are predicted for anthracene.

2 Mathematical Analysis

The temperature and pressure dependences of the Raman frequency shifts for the six phonon and nine vibron modes of solid anthracene have been calculated using the observed volume data^{9,11}, $V_p(T)$ and $V_T(p)$. By determining the pressure dependence of the isothermal mode Grüneisen parameter, $\gamma_T(p)$, the Raman frequencies were predicted for the crystalline anthracene.

The crystal volume of anthracene can be expressed as functions of temperature and pressure, respectively:

$$V_p(T) = a_0(p) + a_1(p)T + a_2(p)T^2 \quad \dots (1)$$

and

$$V_T(p) = b_0(T) + b_1(T)p + b_2(T)p^2 \quad \dots (2)$$

The coefficients a_0 , a_1 , a_2 and b_0 , b_1 , b_2 were determined by fitting Eqs. (1) and (2) to the observed volume data^{9,11}, $V_p(T)$ and $V_T(p)$ as given in Table 1 for anthracene crystal.

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Table 1 – Coefficients a_0 , a_1 and a_2 as determined by Eq. (1) using the observed volume data¹¹, $V_T(p)$, and the coefficients b_0 , b_1 and b_2 as determined by Eq. (2) using the observed volume data⁹, $V_T(p)$, for anthracene

a_0 (Å ³ /mole)	a_1 (Å ³ /mole.K)	$a_2 \times 10^{-5}$ (Å ³ /mole.K ²)	b_0 (Å ³ /mole)	b_1 (Å ³ /mole.GPa)	b_2 (Å ³ /mole.GPa ²)
451.72	0.04	1.06	470.95	-48.95	7.05

Table 2 – Coefficients c_0 , c_1 and c_2 as determined (Eq. (6)) using the experimental data for the Raman frequencies⁶ $\vartheta_T(p)$ of and the coefficients d_0 , d_1 and d_2 (Eq. (7)) for the phonon modes and vibrons of solid anthracene.

Raman Modes	c_0 (cm ⁻¹)	c_1 (cm ⁻¹ /GPa)	$-c_2$ (cm ⁻¹ /GPa ²)	d_0 (cm ⁻¹)	$-d_1 \times 10^{-2}$ (cm ⁻¹ /K)	$-d_2 \times 10^{-5}$ (cm ⁻¹ /K ²)
Phonon Modes						
A _g	38.47	11.06	1.37	46.26	1.76	2.35
B _g	46.00	17.86	1.33	53.63	1.83	2.57
B _g	68.19	24.13	2.28	81.15	2.93	4.01
A _g	73.59	27.94	3.24	86.76	3.35	4.43
A _g	122.73	38.82	4.55	138.52	4.39	6.37
B _g	129.70	43.58	4.89	149.10	5.04	7.11
Vibrons			$\times 10^{-4}$			
12A _g	396.95	0.53	19.1	399.64	0.77	0.50
10B _{3g}	521.94	0.17	15.8	523.17	0.24	0.50
10A _g	754.19	0.38	8.2	756.61	0.54	1.16
9A _g	1008.78	0.33	14.3	1011.26	0.48	0.98
8A _g	1164.81	0.21	13.8	1166.13	0.22	0.56
7B _{3g}	1189.70	0.23	11.7	1190.35	0.45	1.20
7A _g	1261.01	0.70	37.9	1265.75	0.97	2.19
6A _g	1403.34	0.62	30.2	1407.31	0.92	1.84
4A _g	1558.78	0.33	18.2	1560.26	0.47	1.02

We can also define the mode Grüneisen parameter as:

$$\gamma = -\frac{d \ln \vartheta}{d \ln V} = -\frac{V}{\vartheta} \cdot \left(\frac{d \vartheta}{d V} \right) \quad \dots (3)$$

From this definition of the mode Grüneisen parameter (γ), we can then define the isobaric mode Grüneisen parameter as:

$$\gamma_p(T) = -\left(\frac{\partial \ln \vartheta}{\partial \ln V} \right)_p = -\frac{V_p(T)}{\vartheta_p(T)} \cdot \frac{(\partial \vartheta / \partial T)_p}{(\partial V / \partial T)_p} \quad \dots (4)$$

and the isothermal mode Grüneisen parameter γ_T as:

$$\gamma_T(p) = \left(\frac{\partial \ln \vartheta}{\partial \ln V} \right)_T = \frac{V_T(p)}{\vartheta_T(p)} \cdot \frac{(\partial \vartheta / \partial p)_T}{(\partial V / \partial p)_T} \quad \dots (5)$$

Also, the frequency ϑ for the phonon modes of anthracene can be obtained as a function of pressure:

$$\vartheta_T(p) = c_0(T) + c_1(T)p + c_2(T)p^2 \quad \dots (6)$$

By fitting Eq. (6) to the observed Raman frequency data⁶ $\vartheta_T(p)$, we obtained the coefficients c_0 , c_1 and c_2 , for the Raman modes studied, as given in Table 2.

In order to determine the isothermal mode Grüneisen parameter $\gamma_T(p)$, the derivatives $(\partial \vartheta / \partial p)_T$ (Eq. (6)) and $(\partial V / \partial p)_T$ (Eq. (2)) were used.

Similar to Eq. (6), the frequency ϑ can be obtained as a function of temperature in a quadratic form as:

$$\vartheta_p(T) = d_0(p) + d_1(p)T + d_2(p)T^2 \quad \dots (7)$$

By fitting Eq. (7) to the experimental data⁶, the coefficients were determined for the Raman modes studied, as also given in Table 2. For this procedure, the temperature dependence of the Raman frequencies $\vartheta_p(T)$ was calculated at $P = 0$ from the pressure dependence of the observed Raman frequencies⁶ $\vartheta_T(p)$ for the phonon modes and vibrons of anthracene in a given temperature and pressure interval. By obtaining the functional forms of the observed volume V - T data⁹ and V - P data¹¹ at $T = 300$ K within the temperature interval of $94 < T(\text{K}) < 295$ and the pressure interval $5 < P(\text{kbar}) < 45$, respectively, we extracted the Raman frequencies $\vartheta_p(T)$ using the observed⁶ $\vartheta_T(p)$. This was done one to one correspondence of the volume ratios $V_{p=0}(T) / V_0$ and $V_{T=300\text{K}}(P) / V_0$ in the same temperature and pressure intervals as stated above. Finally, using the observed $\vartheta_{T=300\text{K}}(p)$ data⁶ within the same T - P interval as we used for the volume ratios, $\vartheta_{p=0}(T)$ values were predicted for the phonon modes and vibrons of anthracene. Then, Eq. (7) was fitted to those $\vartheta_{p=0}(T)$ values, as extracted from the observed $\vartheta_{T=300\text{K}}(p)$ values⁶ to determine the

coefficients d_0 , d_1 and d_2 (Table 2). As stated above, by means of Eq. (5), the isothermal mode Grüneisen parameter $\gamma_T(p)$ was determined for all the modes studied using $\vartheta_T(p)$, $(\partial\vartheta/\partial p)_T$ (Eq. (6)), $V_T(p)$ and $(\partial V/\partial p)_T$ (Eq. (2)), as given in Table 3. We compare in this table our calculated $\gamma_T(p)$ values at $P = 0$ for various Raman modes with the observed γ_T (isothermal mode Grüneisen parameter) values⁶.

Once the mode Grüneisen parameters $\gamma_P(T)$ and $\gamma_T(P)$ are determined according to Eqs. (4) and (5), respectively, the Raman frequencies can then be calculated as functions of temperature and pressure from those equations. By solving Eq. (4) for the Raman frequency $\vartheta_p(T)$, we get:

$$\vartheta_p(T) = \vartheta_0 \exp \left[-\gamma_P(T) \ln \left(V_P(T)/V_0 \right) \right] \quad \dots (8)$$

Similarly, by solving Eq. (5), we obtain

$$\vartheta_T(p) = \vartheta_0 \exp \left[-\gamma_T(p) \ln \left(V_T(p)/V_0 \right) \right] \quad \dots (9)$$

In both equations, ϑ_0 and V_0 represent the values of the Raman frequency and the crystal volume at ambient conditions ($T = 300$ K, $p = 0$), respectively.

Using the observed volume $V_p(T)$ data⁹, we calculated (Eq. (8)) the Raman frequencies for the six phonon and nine vibron modes of anthracene at various temperatures at zero pressure ($p = 0$), as plotted in Figs. 1 and 2, respectively. For this

calculation of the Raman frequencies, we used the γ_T values (Eq. (8)), as given in Table 3. Since there were no experimental data for the Raman frequencies as a function of temperature, we were not able to determine the isobaric mode Grüneisen parameter $\gamma_P(T)$ for the Raman modes studied in anthracene. By using the calculated γ_T values (Table 3) of the Raman modes, we predicted the Raman frequencies at various temperatures ($p = 0$) (Figs. 1 and 2).

The pressure dependence of the six phonon and nine vibron modes has also been calculated, as plotted in Figs. 3 and 4, respectively, according to Eq. (9) using the observed volume $V_T(p)$ data¹¹ at $T = 300$ K,

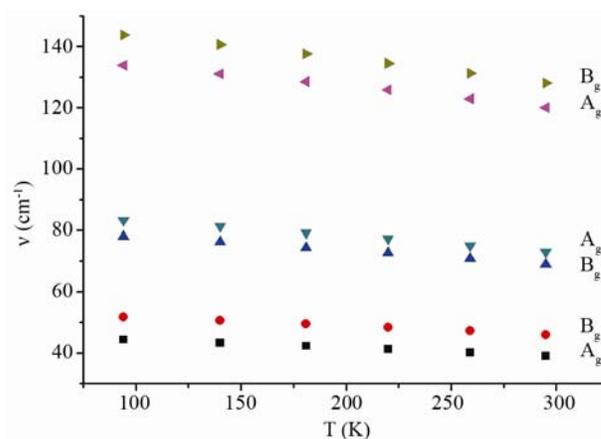


Fig. 1 – Calculated Raman frequencies as a function of pressure at ambient temperature of nine vibrons of crystalline anthracene

Table 3 – Calculated (Eq. (5)) values of the isothermal mode Grüneisen parameter γ_T at $P = 0$ and the observed γ_T values⁶ for the Raman modes for anthracene (Table 2). Observed $\vartheta_T(p)$ values⁶ and calculated $\vartheta_p(T)$ values for the Raman modes according to Eqs. (6) and (7), respectively, with the difference in the Raman frequency, $\Delta\vartheta$, between $\vartheta_T(p)$ and $\vartheta_p(T)$ at $P = 0$ and $T = 300$ K for anthracene, are also given here

	ϑ_0 (cm ⁻¹)	γ_T (p = 0) (Calculated)	γ_T (Observed ⁶)	$\vartheta_T(p)$ (cm ⁻¹)	$\vartheta_p(T)$ (cm ⁻¹)	$\Delta\vartheta$ (cm ⁻¹)
Phonon modes						
A _g	39	3.61	4.01	38.47	38.87	0.40
B _g	46	3.25	4.00	46.00	45.83	0.17
B _g	69	3.43	2.96	68.19	68.75	0.56
A _g	73	3.65	3.06	73.59	72.72	0.87
A _g	120	3.04	2.78	122.73	119.62	3.11
B _g	128	3.23	2.87	129.70	127.58	2.12
Vibrons						
12A _g	396	0.196	0.186	396.95	396.88	0.70
10B _{3g}	522	0.048	0.035	521.94	522.00	0.06
10A _g	754	0.074	0.073	754.19	753.95	0.24
9A _g	1009	0.048	0.054	1008.78	1008.94	0.16
8A _g	1165	0.026	0.021	1164.81	1164.97	0.16
7B _{3g}	1188	0.043	0.042	1189.70	1187.92	1.78
7A _g	1261	0.081	0.068	1261.01	1260.87	0.18
6A _g	1403	0.065	0.057	1558.78	1557.93	0.14
4A _g	1558	0.031	0.031			0.85

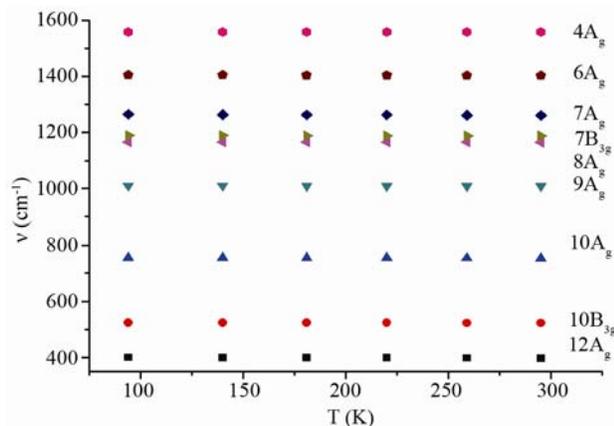


Fig. 2 – Calculated Raman frequencies as a function of temperature at zero pressure of nine vibrons of crystalline anthracene

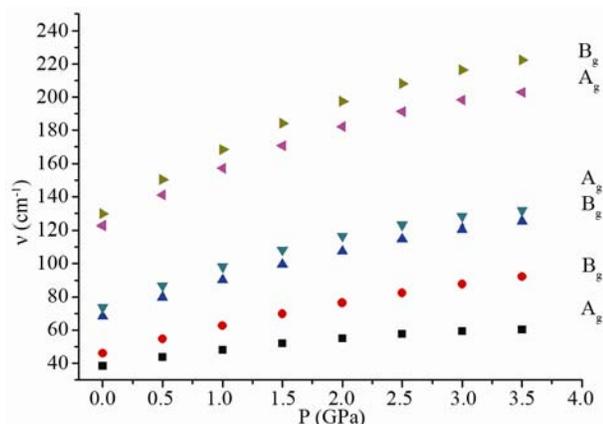


Fig. 3 – Calculated Raman frequencies as a function of pressure at ambient temperature of six Raman modes of crystalline anthracene

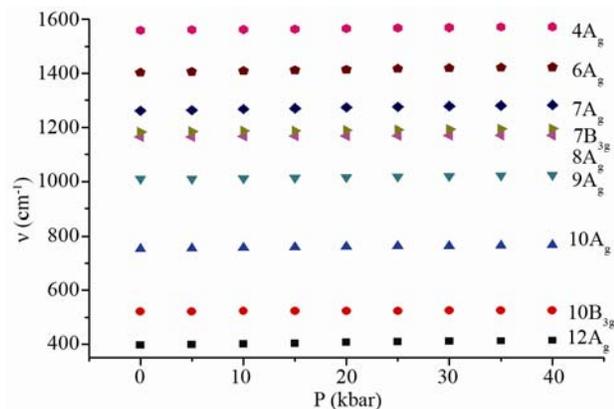


Fig. 4 – Calculated Raman frequencies as a function of pressure at zero pressure of six Raman modes of crystalline anthracene

Table 4 – Parameters derived from the experimental data and those calculated for anthracene

Equation	Parameters
1	a_0, a_1, a_2 : derived from the experimental volume data ¹¹ , $V_p(T)$.
2	b_0, b_1, b_2 : derived from the experimental volume data ⁹ , $V_T(p)$.
6	c_0, c_1, c_2 : derived from the experimental Raman frequency data ⁶ , $\vartheta_T(p)$.
7	d_0, d_1, d_2 : calculated from the experimental Raman frequency data ⁶ , $\vartheta_T(p)$ in the pressure interval of 0 to 40 kbar and the temperature interval of 94 to 295 K.
5	$\gamma_T(p)$: calculated from the experimental volume data ⁹ , $V_T(p)$, $(\partial V / \partial p)_T$ and from the experimental data for the Raman frequency ⁶ , $\vartheta_T(p)$, $(\partial \vartheta / \partial p)_T$.
8	$\vartheta_p(T)$: calculated from the experimental Raman frequency, $\vartheta_T(p)$ data ⁶ in the pressure interval of 0 to 40 kbar and the temperature interval of 94 to 295 K.
9	$\vartheta_T(p)$: calculated from the experimental volume data ⁹ , $V_T(p)$ and from the calculated $\gamma_T(p)$.

Table 4 summarizes the parameters derived from the experimental data and those calculated according to the equations given above for anthracene.

3 Results and Discussion

The Raman frequencies were calculated as functions of temperature and pressure with the observed volume data^{9,11} for the six phonon and nine vibron modes of solid anthracene through the values of the isothermal mode Grüneisen parameter $\gamma_T(p)$ at $P = 0$ for those modes studied (Table 3). As shown in Figs. 1 and 2, our calculated Raman frequencies for the six phonon and nine vibron modes, respectively, decrease with increasing temperature, due to the thermal expansion, whereas they increase with increasing pressure (Figs. 3 and 4) as also observed experimentally^{5,6}. It has been found experimentally⁶ that the vibron modes exhibit a nearly linear shift with pressure, whereas the pressure-induced shifts in the phonon frequencies are nonlinear. In fact, these decreases with temperature and increases with pressure in the Raman frequencies are more apparent for the phonon modes, as shown in Figs. 1 and 3, respectively. For vibrons, decreases in the Raman frequencies with temperature are very small so that the Raman frequencies are almost independent from the temperature within the frequency scale of vibrons (Fig. 2), whereas, increases in the Raman frequencies with the pressure are

significant for the phonon modes (Fig. 3) as stated above. Similar to the temperature dependence of the Raman frequencies of the vibrons, their pressure dependence looks almost insignificant so that they are also independent of pressure (Fig. 4).

It has been indicated that intra-molecular vibration (vibron) frequencies are uniformly much less pressure-sensitive, which involves the volume dependence only, whereas the temperature variation of the vibrational frequencies of crystal lattices involves both temperature and volume⁵. This indicates that variation in phonon frequencies with temperature is due to both the deformation of the unit cell with temperature and the phonon-phonon interaction¹⁸.

In order to predict the Raman frequencies, we determined the values of the isothermal mode Grüneisen parameter γ_T at $P = 0$ for the six phonon and nine vibron modes of solid anthracene (Table 3). As seen from this table, our values of the mode Grüneisen parameter of those modes studied, are in good agreement with the observed ones⁶. Notice that the values of the mode Grüneisen parameter for the six phonon modes (external modes) are much larger than those of the nine vibrons (internal modes) of the solid anthracene, as expected in general for the molecular solids. A small variation in crystal volume leads to a large change in frequency, which results in a large Grüneisen parameter, in particular, for the six lattice modes of anthracene. This small change in the unit cell parameters results in a weaker rearrangement of the molecules at higher pressure, as also pointed out previously¹³. It has been reported that the values of the Grüneisen parameters for the A_g and B_g modes of anthracene, which vary from 3 to 6 are higher than those obtained for ionic crystals⁵. This also applies to our calculated γ_T and the observed⁶ γ_T (at $P=0$) values of the mode Grüneisen parameter for the phonon modes (external modes) (Table 3). It has been explained that the relatively large γ values observed for intermolecular phonon modes (external modes) are due to the relatively large compression of the vibrational coordinate and also, relatively small γ values observed for some intramolecular vibrons (internal modes) are due to the compression along intermolecular coordinates orthogonal to the vibron coordinate⁶. Within those relatively large values of the isothermal mode Grüneisen parameter γ_T ($P = 0$) and relatively small γ_T ($P = 0$) values which we determined for the phonon modes (external modes) and the vibrons (internal modes), respectively, we

calculated not only the pressure dependence of the Raman frequencies (Eq. (9)) but also their temperature dependence (Eq. (8)) using the observed volume data^{9,11} (and also the observed $\vartheta_T(p)$ data⁶), in anthracene, as stated above. When the Raman frequencies of six phonons and nine vibrons are measured experimentally as a function of temperature ($P = 0$) in anthracene, then the isobaric mode Grüneisen parameter $\gamma_p(T)$ can be determined using the volume⁹ $V_p(T)$ according to Eq. (4) at $P=0$. From the $\gamma_p(T)$ values calculated at $P = 0$, the temperature dependence of the Raman frequencies $\vartheta_p(T)$ of the modes studied, can be calculated using the observed volume $V_p(T)$ data⁹ by means of Eq. (8). By comparing with the observed $\vartheta_p(T)$ data at $P = 0$ when available in the literature, this then examines our method of predicting the $\vartheta_p(T)$ values for the Raman modes studied in anthracene.

By determining the Raman frequencies at different temperatures and pressures, in anthracene, its P - T phase diagram can be obtained, as also suggested for a P - T phase diagram of benzene (C_6H_6) at high pressures¹⁹. By measuring the Raman frequencies of various modes at room temperature as a function of pressure up to 25 GPa, first order and second order phase transformations among the pressure-induced solid phases of benzene have been proposed and the phase boundaries have also been suggested in this molecular crystal¹⁹.

In the case of anthracene, we calculated the Raman frequencies as functions of temperature (at normal pressure) and of pressure (at room temperature), as stated above. Thus, by predicting the Raman frequencies at different pressures (Figs. 3 and 4) on the basis of the Raman measurements⁶ at ambient temperature up to 3.1 GPa, and also by predicting the Raman frequencies at different temperatures at normal pressure (Figs. 1 and 2), various phase transformations in anthracene can be obtained and its P - T phase diagram can be determined from the Raman frequencies of the phonon modes and vibrons in this molecular crystal.

The Raman frequencies determined at different temperatures and pressures can then provide some applications for pressure/temperature sensing. As the thermodynamical PVT system, by means of the correlations between the volume V and the Raman frequency ϑ through the mode Grüneisen parameter γ , spectroscopically $P\vartheta T$ system can be used for

various applications of the molecular crystals such as anthracene as exemplified here. Thus, various physical properties of molecular crystals, in particular, of anthracene can be investigated spectroscopically through the Raman frequency shifts which can be measured to high accuracy as compared to the thermodynamic *PVT* measurements in the phases or close to the phase transitions. Therefore, temperature and pressure dependences of the thermodynamic quantities such as the heat capacity, thermal expansivity and the isothermal compressibility can be predicted from the Raman frequency shifts in anthracene or in more general for the molecular crystals.

4 Conclusions

The Raman frequencies of the six phonons and nine vibrons of anthracene were calculated by determining their values of the mode Grüneisen parameter. It was found that values of the mode Grüneisen parameter are between 3 and 4 for the phonon modes (external modes), whereas they vary between 0.03 and 0.2 for the vibrons (internal modes), as also obtained in previous studies.

The Raman frequencies of the phonon modes (external modes), which we predicted, decrease as the temperature increases (zero pressure) whereas they increase as the pressure increases (room temperature) in anthracene as expected. However, variation of the Raman frequencies of vibrons (internal modes) with temperature and pressure is insignificant for this crystal. Our predicted Raman frequencies agree with the observed data for anthracene. This indicates that the method of calculating the Raman frequencies from

the volume data through the mode Grüneisen parameter, which we used for anthracene is adequate as we have also studied for benzene and naphthalene previously.

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