

Calculation of the Raman frequencies as a function of pressure in the solid phases II and III (III') of benzene

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Abstract We calculate here the Raman frequencies of the lattice modes $A(A_g)$, $B(B_{2g})$ and $C(B_{1g}B_{3g})$ as a function of pressure at room temperature for the solid phases (II, III and III') of benzene. This calculation is performed using volume data through the mode Grüneisen parameter. It is found that our calculated frequencies of those lattice modes increase with increasing pressure, as expected. Calculated frequencies are in good agreement with the measurements of the three lattice modes for the solid phases studied in benzene.

Keywords Benzene · Raman frequency · Solid phases (II, III, III') · Volume

Introduction

Benzene as an aromatic organic molecule has been studied extensively using various experimental techniques. Near the melting point, thermodynamic [1–3] and spectroscopic [4, 5] studies have been reported in the literature. The melting curves of liquid–solid phase I and liquid–solid phase II terminate at the triple points T_1 and T_2 , respectively, as shown in the T - P phase diagram (Fig. 1) [6]. Also, the melting curve of liquid–solid phase IV terminates at the chemical decomposition point A [6] in this molecule. The

melting lines in benzene occur at high temperatures and at low pressures. As the pressure increases, other solid phases of III and III' occur. The occurrence of another solid phase III' is about 20 GPa at room temperature, whereas solid phase IV occurs at relatively low pressure of a few GPa at high temperatures of above 400 °C [6, 7].

As the pressure is applied at high temperatures (around 4 GPa and 600 °C), hydrocarbons are decomposed which yields amorphous carbon [8, 9]. Theoretical models have been used to explain decomposition [10] and more recent ab initio studies on decomposition [11–15], dimerization and polymerization [16–18] in benzene which also exhibits “polymer” 1 and “polymer” 2 phases with increasing pressure, as shown in the T - P phase diagram (Fig. 1) [6].

In regard to the transitions among the various phases in benzene as obtained experimentally in the P - T phase diagrams of benzene [6, 8, 19–21], all the liquid-I, liquid-II and liquid-IV transitions are of a first order. Transitions between the solid phases, as reported first time by Bridgman [19], solid I–solid II transition is also of a first order in character. Later studies have revealed the first-order transition for benzene II–benzene III at about 4 GPa [4, 22], a second-order transition for benzene III–benzene III' at 11 GPa and a first-order transition for benzene III'–benzene IV [7]. It was pointed out that the III'–IV transition is an irreversible chemical transformation which occurs at 24 GPa [6], as observed at 30 GPa [9]. Melting lines (first order), first order (solid I–solid II, solid II–solid III, solid III'–solid IV) and second order (solid III–solid III') lines including the phase of decomposed compounds, and polymer phases have been calculated using mean field models in our recent studies [23, 24] on the basis of the experimental T - P phase diagram for benzene [6].

Temperature and pressure dependence of the volume as well as the Raman frequencies have also been studied

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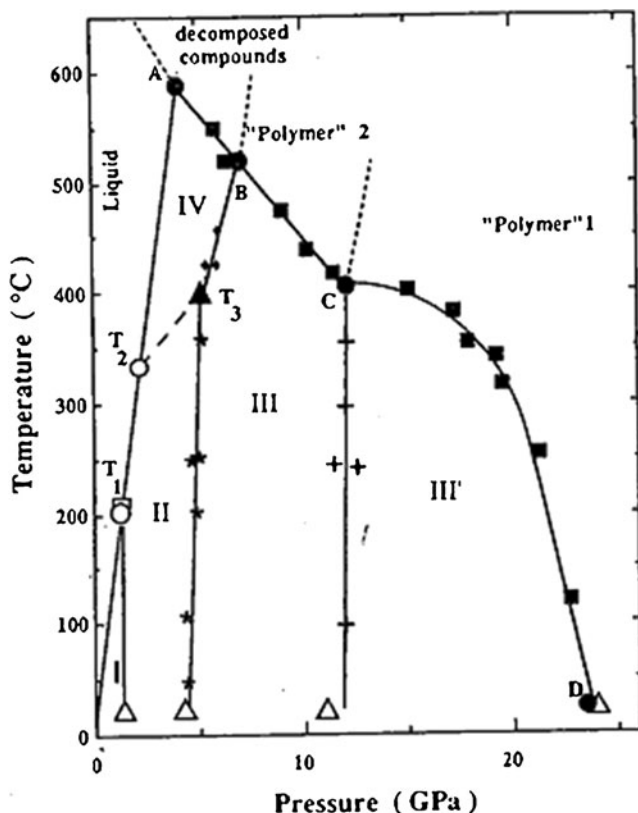


Fig. 1 T-P phase diagram of benzene taken from ref. [6]

extensively in various phases of benzene. Pressure and temperature dependence of volume for crystalline benzene have been reported in the literature [1–3, 7, 19]. We have calculated the molar volume as a function of temperature [25] and pressure [26] near the melting point in benzene.

Regarding the temperature and pressure dependence of the Raman frequencies in benzene, experimental and theoretical studies have been given in the literature. Some of those previous experimental studies have focused on the solid phases [2, 4–7, 27]. We have analyzed the pressure dependence of the vibrational Raman frequencies in phase II of solid benzene in our recent study [28]. The temperature or pressure dependence of the vibrational frequencies can be calculated from the crystal volume using the mode Grüneisen parameter. In our earlier studies, we have calculated the frequencies of various modes using the volume data by means of the mode Grüneisen parameter for ammonium halides, in particular NH_4Cl [29], NH_4Br [30], NH_4I [31], ammonia solid II [32], $NaNO_2$ [33], solid nitrogen [34] and SiO_2 -moganite [35].

In this study, we calculate the Raman frequencies of the lattice modes (A , B and C) at various pressures for the solid phases of II, III and III' of benzene at room temperature using the experimental volume data [7] through the mode Grüneisen parameter.

Table 1 Values of the coefficients a_0 , a_1 and a_2 according to Eq. (7) using the experimental data [7] at $T=294$ K for the phases indicated of benzene. The V_I values were determined for pressures of 2.7 GPa (solid II), 4.9 GPa (solid III) and 11 GPa (solid III') using Eq. (7)

$V_m(\text{cm}^3)$	$a_0(\text{cm}^3)$	$a_1(\text{cm}^3/\text{GPa})$	$a_2(\text{cm}^3/\text{GPa}^2)$	$V_I(\text{cm}^3)$
Phase II	70.34	-3.52	0.16	61.99
Phase III	65.97	-2.25	0.09	57.05
Phase III'	56.73	-0.44	-0.002	51.62

In “Calculations and results”, we present our analysis and results. Discussion of our results and conclusions are given in “Discussion” and “Conclusions”, respectively.

Calculations and results

The Grüneisen parameter γ_G (Grüneisen gamma) is directly related to the thermodynamic quantities according to the relation [36]:

$$\gamma_G = \frac{\alpha_P V}{C_V \kappa_T}, \quad (1)$$

where α_P is the thermal expansion, V is the volume, C_V is the heat capacity at constant volume and κ_T is the isothermal compressibility. Individual Grüneisen parameters $\gamma(J)$ can also be defined as the contributions to the heat capacity C_V given by [37]

$$\gamma_G = \frac{1}{C_V} \sum_J \gamma(J) C_{V_J}, \quad (2)$$

where C_{V_J} denotes the heat capacity at constant volume for the J th mode. Using the values of the mode Grüneisen parameters $\gamma(J)$, the Raman frequencies of those phonon modes can be calculated from the thermodynamic quantities such as C_V (or C_P heat capacity at constant pressure), V , α_P and κ_T .

In particular, the Raman frequencies can be calculated as a function of pressure at a constant temperature for various solid phases of benzene. This calculation can be performed using the volume data through the mode Grüneisen parameter.

Table 2 Observed (first column) [7] and calculated frequencies (second column) using Eq. (8) for the lattice modes A , B and C at constant pressures indicated for the solid phases II, III and III' of benzene

Lattice modes (cm^{-1})	Solid II (2.7 GPa)	Solid III (4.9 GPa)	Solid III' (11 GPa)
$A(A_g)$	98	96	117
$B(B_{2g})$	156	158	190
$C(B_{1g}B_{3g})$	181	185	220

Table 3 Values of the coefficients b_0 , b_1 and b_2 for the lattice modes indicated according to Eq. (8) using the observed data [7] in solid II of benzene. Values of the mode Grüneisen parameter γ_T [7] and the ν_I

values at T=294 K for the lattice modes are given. Values of the coefficients c_0 and c_1 according to Eq. (6) for each lattice mode at T=294 K are also given here

Raman bands (cm ⁻¹)	b_0 (cm ⁻¹)	b_1 (cm ⁻¹ /GPa)	b_2 (cm ⁻¹ /GPa ²)	γ_T	ν_I (cm ⁻¹)	c_0 (cm ⁻¹)	c_1 (cm ⁻¹ /K)
$A(A_g)$	67.81	9.20	0.39	2.9	96	-146.70	0.50
$B(B_{2g})$	77.45	37.28	-2.79	3.1	158	-147.64	0.49
$C(B_{1g}B_{3g})$	113.74	30.77	-1.58	2.6	185	-146.90	0.50

The volume dependence of the Raman frequency can be defined as the mode Grüneisen parameter, γ

$$\gamma = -\frac{V}{\nu} \frac{d\nu}{dV}, \tag{3}$$

here ν is the Raman frequency and V is the crystal volume. By considering the pressure dependence of the Raman frequency and the crystal volume, the isothermal mode Grüneisen parameter γ_T can be defined at various pressures (P) for a constant temperature (T) as:

$$\gamma_T = -\frac{V}{\nu} (\partial\nu/\partial P)_T / (\partial V/\partial P)_T. \tag{4}$$

Thus, the volume dependence of the Raman frequency (anharmonicity) can be obtained from Eq. (4) as:

$$\nu_T(P) = A(T) + \nu_I \exp[-\gamma_T \ln(V_T(P)/V_I)], \tag{5}$$

where the temperature-dependent term is assumed to be linear as:

$$A(T) = c_0 + c_1 T, \tag{6}$$

with the constants c_0 and c_1 . In Eq. (5) $\nu_T(P)$ and $V_T(P)$ represent the pressure dependence of the Raman frequency and the crystal volume at constant temperatures, respectively. ν_I and V_I denote the values of the Raman frequency and the crystal volume at a given constant temperature, respectively. The temperature-dependent $A(T)$ term is added to the solution for $\nu_T(P)$ from Eq. (4) in order to predict the Raman frequencies as a function of pressure at some other constant temperatures using the volume data.

To calculate the Raman frequencies $\nu_T(P)$ for various solid phases of benzene, we first analyzed the pressure

dependence of volume as measured experimentally [7] according to a quadratic function:

$$V = a_0 + a_1 P + a_2 P^2, \tag{7}$$

where a_0 , a_1 and a_2 are constants. By analyzing the volume data for the solid phases of II, III and III' at various pressures (T=294 K) [7], we determined the coefficients, as given in Table 1. The V_I values obtained at T=294 K for the solid phases of II, III and III' are also given in Table 1.

We predicted in this study the pressure dependence of the Raman frequencies for the lattice modes of $A(A_g$ mode), $B(A_g B_{2g}$ mode) and $C(B_{1g} B_{3g}$ mode) at T=294 K using the volume data [7], as stated above. As the initial data, we used the observed Raman frequencies [7] of those lattice modes (A , B and C), which we analyzed according to the relation:

$$\nu = b_0 + b_1 P + b_2 P^2, \tag{8}$$

where b_0 , b_1 and b_2 are constants. In Table 2, we give the observed Raman frequencies [7] of the lattice modes of A , B and C in the solid phases of II (at 2.7 GPa), III (at 4.9 GPa) and III' (11 GPa) for benzene (first column) and the corresponding values by fitting Eq. (8) to the observed data, as given in the second column. Values of the coefficients b_0 , b_1 and b_2 (Eq. 8) are tabulated for the lattice modes A , B and C for the solid phases II, III and III' in Tables 3, 4 and 5, respectively. In these Tables, we also give the values of the mode Grüneisen parameter γ_T of those lattice modes studied, as obtained from the experimental study [7] for the solid phases of II, III and III' of benzene. Additionally, in these Tables the ν_I values at T=294 K for the lattice modes of A , B and C for the solid phases considered, are given.

Table 4 Values of the coefficients b_0 , b_1 and b_2 for the lattice modes indicated according to Eq. (8) using the observed data [7] in solid III of benzene. Values of the mode Grüneisen parameter γ_T [7] and the ν_I

values at T=294 K for the lattice modes are given. Values of the coefficients c_0 and c_1 according to Eq. (6) for each lattice mode at T=294 K are also given here

Raman bands (cm ⁻¹)	b_0 (cm ⁻¹)	b_1 (cm ⁻¹ /GPa)	b_2 (cm ⁻¹ /GPa ²)	γ_T	ν_I (cm ⁻¹)	c_0 (cm ⁻¹)	c_1 (cm ⁻¹ /K)
$A(A_g)$	66.91	12.10	-0.37	2.7	117	-145.83	0.50
$B(B_{2g})$	109.60	19.87	-0.55	2.9	193	-145.39	0.50
$C(B_{1g}B_{3g})$	128.63	22.95	-0.71	2.8	224	-146.63	0.50

Table 5 Values of the coefficients b_0 , b_1 and b_2 for the lattice modes indicated according to Eq. (8) using the observed data [7] in solid III' of benzene. Values of the mode Grüneisen parameter γ_T [7] and the ν_I

values at T=294 K for the lattice modes are given. Values of the coefficients c_0 and c_1 according to Eq. (6) for each lattice mode at T=294 K are also given here

Raman bands (cm^{-1})	b_0 (cm^{-1})	b_1 ($\text{cm}^{-1}/\text{GPa}$)	b_2 ($\text{cm}^{-1}/\text{GPa}^2$)	γ_T	ν_I (cm^{-1})	c_0 (cm^{-1})	c_1 (cm^{-1}/K)
$A(A_g)$	76.46	9.42	-0.19	2.0	157	-144.95	0.50
$B(B_{2g})$	172.45	9.19	-0.09	2.0	262	-144.04	0.51
$C(B_{1g}B_{3g})$	217.57	8.27	-0.06	1.8	302	-144.43	0.51

Finally, using the volume data and the observed Raman frequencies as the initial data [7], the values of the temperature-dependent term $A(T)$ were determined with the coefficients c_0 and c_1 (Eq. 6) according to Eq. (5) for the lattice modes of A , B and C for the solid phases of II, III and III', as tabulated in Tables (3, 4 and 5), respectively. This then enabled us to calculate the pressure dependence of the Raman frequencies (A , B and C) at T=294 K using the volume data [7] according to Eq. (5) for the solid phases of II, III and III' of benzene. We plot our calculated Raman frequencies of the lattice modes of A , B and C for phase II in Fig. 2. The observed Raman frequencies [7] are also shown in this figure. Similarly, the pressure dependence of the Raman frequencies calculated for the lattice modes (A , B and C) are plotted for the solid phases of III and III' of benzene, in Figs. 3 and 4, respectively.

Discussion

The Raman frequencies calculated for the lattice modes of A , B and C (Figs. 2, 3 and 4) using Eq. (5), increase with increasing pressure in the solid phases of II, III and III' of benzene, as expected. This increase of the Raman

frequencies for those lattice modes was obtained at room temperature (T=294 K) using the volume data [7] by Eq. (5) through the isothermal mode Grüneisen parameter γ_T in the solid phases II, III and III' of benzene. In Eq. (5) it was assumed that the temperature dependence of the additional $A(T)$ term was linear (Eq. 6) for the three lattice modes (A , B and C) and it was obtained that the values of the coefficients c_0 and c_1 of $A(T)$ were almost the same for the lattice modes of A , B and C in the solid phases of II, III and III' (Tables 3, 4 and 5). Figures (2, 3 and 4) show that a linear temperature dependence of $A(T)$ with constants c_0 and c_1 is reasonable, and our calculated Raman frequencies of the lattice modes of A , B and C are in good agreement with the observed data for the solid phases of II, III and III' of benzene. For this calculation of the Raman frequencies, the isothermal mode Grüneisen parameter γ_T was taken as a constant in Eq. (5) with the values of $\gamma_T \cong 3$ for the solid phases of II and III (Tables 3 and 4) and $\gamma_T \cong 2$ for the solid phase III' (Table 5). This assumption based on a constant γ_T value for each lattice mode of the solid phases considered is also reasonable to calculate the Raman frequency in benzene.

Calculation of the vibrational frequencies from the crystal volume applies to the molecular crystals which exhibit anharmonic properties. Since the Grüneisen parameter

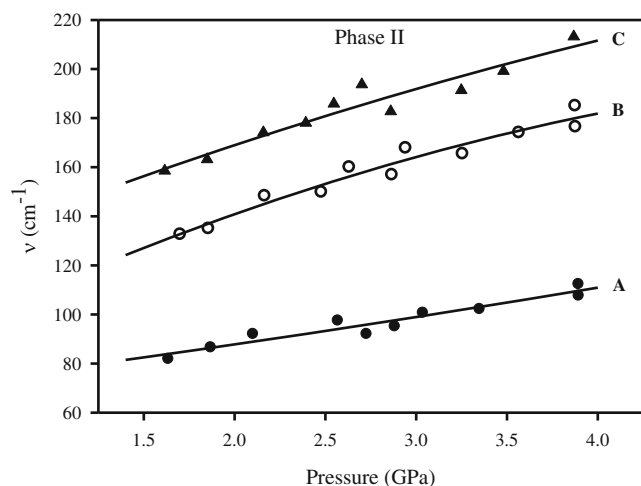


Fig. 2 Calculated Raman frequencies of the lattice modes A , B and C as a function of pressure for the solid phase II of benzene at T=294 K according to Eq. (5). The observed data [7] are also shown here

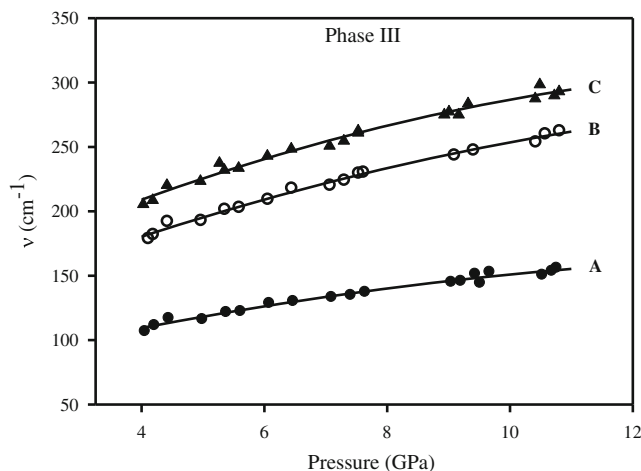


Fig. 3 Calculated Raman frequencies of the lattice modes A , B and C as a function of pressure for the solid phase III of benzene at T=294 K according to Eq. (5). The observed data [7] are also shown here

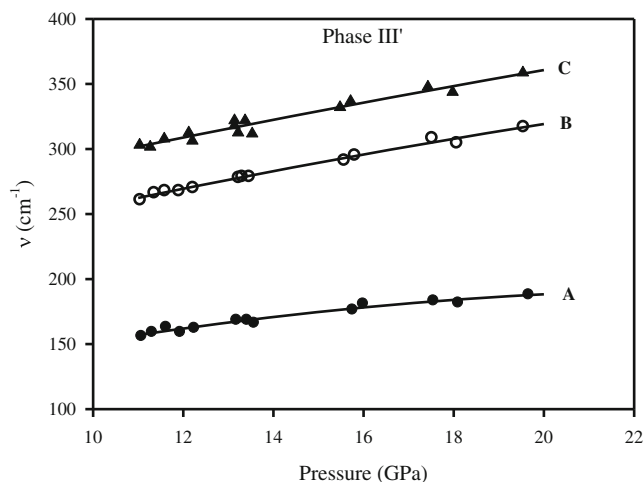


Fig. 4 Calculated Raman frequencies of the lattice modes *A*, *B* and *C* as a function of pressure for the solid phase III' of benzene at $T=294$ K according to Eq. (5). The observed data [7] are also shown here

measures the anharmonicity of a crystalline system, the temperature or pressure dependence of the frequency can be calculated through the mode Grüneisen parameter using the volume data, as stated above. In our approach given here, we assumed that the mode Grüneisen parameter of each mode should be constant for the solid phase considered in benzene (see Tables 3, 4 and 5), as stated above. This predicts the observed frequencies satisfactorily, as given in Figs. 2, 3 and 4. However, a constant mode Grüneisen parameter within a phase or between the two phases close to the phase transitions, as we studied for various molecular crystals previously [29–35] may not be validated due to the fact that the mode Grüneisen parameter can depend on temperature or pressure. In this case, by taking the temperature or pressure dependence of the mode Grüneisen parameter, the frequencies can be calculated according to Eq. (5). So, our approach of calculating the frequencies is not limited to the variation of the mode Grüneisen parameter at different pressures and temperatures in various phases of molecular crystals. Our approach is also not limited to the room temperature ($T=294$ K) to predict the pressure dependence of the Raman frequencies for the lattice modes (*A*, *B* and *C*) as studied here. When the observed volume data are available at various pressures at constant temperatures above the room temperature, the Raman frequencies of those lattice modes can be predicted using Eq. (5) with the temperature dependent $A(T)$ term in the solid phases of II, III and III' of benzene (Fig. 1).

By molecular modeling based on the quantum mechanical calculations, the pressure (or temperature) dependence of the frequency (or volume) can be obtained.

One such model is an Ising spin-phonon coupled system of Yamada et al. [38] which is a microscopic theory on the phase transitions in NH_4Br . This model considers interaction

between one pseudospin and phonon. In this model, hamiltonian (potential energy) of the crystalline system is expressed in terms of the coordinate and momentum of the phonon with its characteristic frequency. Using the canonical transform of the coordinates, the interaction hamiltonian can be obtained. By expressing the Gibbs free energy $G(T, P)$ in terms of the order parameter (frequency) and using the minimization condition, the pressure (or temperature) dependence of the phonon frequency can be derived. From the Gibbs potential, the temperature or pressure dependence of the lattice parameter can also be derived. Thus, the temperature or pressure dependence of the lattice parameter and of the frequency can be correlated.

By considering interactions between pseudospins (NH_4^+ tetrahedra) and phonons, Matsushita [39] has extended an Ising spin-phonon coupled model of Yamada et al. [38]. From the two different orientations of an NH_4^+ tetrahedron that can be regarded as eigenstates of a pseudo-Ising spin, Matsushita [39] assumed the pair potential of ions constituting the crystal which was dependent upon the pseudospins. Using this extended hamiltonian, he obtained the frequency and the damping constant of the phonons by means of perturbation theory. He then explained qualitatively anomalous temperature dependence of the frequency and damping constant of phonons near T_λ in ammonium halides (NH_4Br and NH_4Cl). Similarly, the pressure dependence of the order parameter (phonon frequency) can be obtained from Matsushita's model, which can also be correlated to the variation in the crystal volume.

In analogy with an Ising spin-phonon system of Yamada et al. [38], ammonium sulfate has also been treated using a pseudospin-phonon coupled system, and the temperature dependence of the order parameter and the lattice constant have been calculated [40].

Conclusions

The Raman frequencies of the lattice modes (*A*, *B* and *C*) were calculated from the volume data through the mode Grüneisen parameter γ_T at various pressures at room temperature for the solid phases of II, III and III' of benzene.

We obtained that the Raman frequencies of those lattice modes increase as the pressure increases for all the solid phases studied, as expected. Our calculated Raman frequencies are in good agreement with the experimental data. This shows that the method of calculating the Raman frequency from the volume data using the mode Grüneisen parameter is adequate, as applied to the solid phases of II, III and III' of benzene. This method can also be applied to the other phases of benzene and as we applied previously, also to some other molecular crystals such as ice, carbon tetrachloride, cyclohexane and hexadecane.

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