Journal of Molecular Structure 1080 (2015) 117–121

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Pressure dependence of the Raman frequencies for the modes I, II and III at constant temperatures in phase II of benzene

H. Özdemir, H. Yurtseven [*]

Department of Physics, Middle East Technical University, 06531 Ankara, Turkey

HIGHLIGHTS

- The Raman frequencies of the modes I, II and III are calculated in phase II of benzene.
- Frequencies are calculated at various pressures at $T = 300$ K (I, II) and 450 K (III).
- The observed volume data are used to calculate the Raman frequencies.
- The mode Grüneisen parameters decrease as the pressure increases.
- Calculated frequencies are in agreement with the observed data at low pressures.

ARTICLE INFO

Article history:
Received 23 July 2014
Received in revised form 17 September 2014
Accepted 19 September 2014
Available online 23 October 2014

Keywords:
Raman frequencies
Phase II
Benzene

ABSTRACT

We study here the pressure dependence of the Raman frequencies for different modes in phase II of benzene at constant temperatures. By using the experimental data for the volume, we calculate the Raman frequency as a function of pressure at constant temperatures through the isothermal mode Grüneisen parameter for the modes studied. Our calculations show that the Raman frequencies predicted, agree well with the observed frequencies for the modes in phase II of benzene. The isothermal mode Grüneisen parameter decreases with the pressure for the Raman modes studied at constant temperatures for benzene II.

© 2014 Elsevier B.V. All rights reserved.

Introduction

Benzene is an organic chemical compound with the molecular formula C_6H_6. Its molecule is composed of six carbon atoms joined in a ring with one hydrogen atom attached to each carbon atom. Because its molecule contains only carbon and hydrogen atoms, benzene is classified as a hydrocarbon.

In benzene as the prototype of the aromatic compounds, the stability of the aromatic ring requires pressures of some tenths of gigapascals and/or temperatures as high as hundreds of degrees Celcius for the reaction to occur [1]. So, benzene is one of the famous aromatic compounds for testing the stability of the crystalline forms.

Benzene has five different solid phases, namely, phases I, II, III [2,3], III′ and IV [1,4,5]. Phase I occurs at normal pressure below 278.5 K and it has an orthorhombic Pbca structure. In its solid state, it is transformed into the phase II at 1.2 GPa at 373 K [2]. Phase II has monoclinic $P2_1/c$ structure. The transition line between phases II and III is roughly parallel to the temperature axis up to the point T_3 (340 °C and 5.1 GPa) (Fig. 1) and does not cross the melting line at the triple point T_2. Then, this transformation line diverges towards the higher pressures up to the point B (470 °C and 8.0 GPa). Phase III with the $P2_1/c$ monoclinic structure exists at 373 K and at about 4 GPa. Up to 11 GPa at 25 °C, Phase III′ occurs which has the same structure as phase III. The transition line of benzene III–III′ is between 11 GPa at 25 °C, 12 GPa at 410 °C and it ends at point C (12 GPa, 410 °C), as reported in Ref. [1]. Phase IV appears at 24 GPa. Starting from the existence of the triple point T_2 (335 °C and 2.25 GPa) and from this slight divergence of the phases II to III equilibrium line, T_3 can be considered as a triple point. Beyond C, benzene goes into an irreversible transformation, for this reason point C is not a triple point. Apart from the points A, B and C, point D is located at 25 °C with the 24 GPa pressure. High pressure solid phases of benzene have been observed by Raman scattering [1,4], X-ray diffraction [4,5] and infrared [6–11]. A chemical transformation of benzene under static pressurization to 30 GPa has been obtained by the infrared spectroscopy [12]. Recently, using X-ray Raman spectroscopy the pressure-induced phases of benzene have been investigated [13]. Various

---

[*] Corresponding author.
E-mail address: hamit@metu.edu.tr (H. Yurtseven).

http://dx.doi.org/10.1016/j.molstruc.2014.09.057
0022-2860/© 2014 Elsevier B.V. All rights reserved.

experimental techniques have also been applied to investigate the phase transitions in benzene. High-pressure benzene amorphization has been studied [14–16].

Theoretical models have been used under the shock wave conditions to investigate the decomposition [17], dimerization and polymerization [18,19] in benzene. High-quality polymeric materials have been obtained under high pressures [16,20]. Above 20 GPa, static high-pressure experiments have been performed [1,5,11,14,21,22]. In regard to the high pressure studies in benzene, in our recent works [23,24], we have calculated T–P phase diagram of benzene on the basis of the mean field theory using the experimental T–P phase diagram [1].

Thermodynamic properties of benzene have been studied both experimentally and theoretically. The thermal conductivity and heat capacity of the solid phases I and II in benzene have been measured [25]. Volume was also measured as a function of pressure in the solid and liquid phases of benzene [26]. Near the melting point, thermal expansivity was measured in benzene [27]. Using the experimental data for the thermal expansivity [27], we calculated the molar volume as a function of temperature [28] and pressure [29] close to the melting point in benzene. On the basis of this experimental data [27], we have also established the Pippard relations [30] near the melting point in benzene in our recent study [31]. In particular, for the solid phase II of benzene, we have calculated the pressure dependence of the thermodynamic quantities such as the thermal expansivity, isothermal compressibility and the heat capacity recently [32] by using the experimental data [5].

Spectroscopic studies on the phase transition of the solid phases and also close to the melting point in benzene, have been reported in the literature, as stated above. Infrared [5,8,11] and Raman [1,4,33–35] studies have focused on the solid phases of benzene. In our recent study [36], we have calculated the pressure dependence of the isothermal compressibility for the solid phase II of benzene using the observed infrared frequencies [5]. Also, very recently, we have calculated the Raman frequencies of various lattice modes as a function of temperature [37] and pressure [38] in phase I, and in solid phases of II and III(III′) of benzene [39]. Near the melting point, we have calculated the Raman frequencies of various modes as a function of pressure at constant temperatures [40].

In this study, by means of the correlation between the vibrational frequencies and the crystal volume we determine the pressure dependence of the isothermal mode Grüneisen parameter γ_T for the three phonons at constant temperatures of 300 K (two phonons) and 450 K (one phonon) in the solid phase II of benzene. For this determination of the γ_T values, we use the observed infrared [5], Raman frequencies [11] and volume data [4]. Using the values of the isothermal mode Grüneisen parameter of those Raman modes and the volume data [4], we then predict the Raman frequencies of three phonons studied in the solid phase II of benzene.

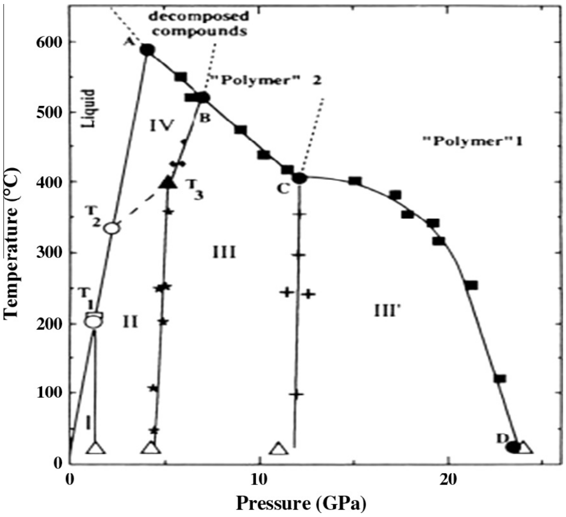

Fig. 1. Phase diagram of benzene [1].

Below, in Section 'Calculations and results' we give our calculations and results. A discussion of our results is given in Section 'Discussion'. Finally, we give our conclusions in Section 'Conclusions'.

Calculations and results

The Grüneisen parameter that measures the anharmonicity due to the volume dependence of the vibrational frequencies can be defined as

$$\gamma = -d\ln\vartheta / d\ln V \quad (1)$$

where ϑ is the frequency and V is the crystal volume. As a function of temperature at constant pressure, the isobaric mode Grüneisen parameter γ_P can be defined as

$$\gamma_P = \frac{V}{\vartheta}\frac{(\partial\vartheta/\partial T)_P}{(\partial V/\partial T)_P} \quad (2)$$

The isothermal mode Grüneisen parameter γ_T can also be defined as

$$\gamma_T = -\frac{V}{\vartheta}\frac{(\partial\vartheta/\partial P)_T}{(\partial V/\partial P)_T} \quad (3)$$

when both the frequency ϑ and volume V depend on the pressure P at a constant temperature T.

Analysis of $V_T(P)$

The crystal volume as functions of temperature and pressure can be expressed as

$$V(P,T) = a_0(T) + a_1(T)P + a_2(T)P^2 \quad (4)$$

where the coefficients a_0, a_1 and a_2 are all temperature dependent, in general. Here by using the experimental data for volume [4] at various pressures (T = 300 K) for phase II of benzene, the values of a_0, a_1 and a_2 were determined, as given in Table 1. Values of those coefficients were then used to obtain the isothermal mode Grüneisen parameter γ_T for the Raman modes at various pressures (T = 300 K).

Analysis of $\vartheta(P)$

The temperature and pressure dependences of the frequency can be analyzed according to the relation

$$\vartheta(P,T) = b_0(T) + b_1(T)P + b_2(T)P^2 \quad (5)$$

where b_0, b_1 and b_2 are the coefficients determined by using the experimental data. Those coefficients are the temperature dependent in general as in the volume (Eq. (4)). Values of the isothermal mode Grüneisen parameter γ_T for the Raman modes of I, II and III were then determined using the values of b_0, b_1 and b_2, as given in Table 2. So, the vibrational frequency can be calculated as a function of pressure at a constant temperature using the volume data. Thus, the pressure dependence of the frequencies for the Raman modes I, II (300 K) and III (450 K) were obtained for the solid phase II of benzene using Eq. (3) according to the relation,

$$\vartheta_T(P) = A(P) + \vartheta_0\exp[-\gamma_T\ln(V_T(P)/V_0)] \quad (6)$$

In Eq. (6), ϑ_0 and V_0 represent the Raman frequency and volume at ambient conditions, respectively. ϑ_0 was taken the extrapolated

Download English Version:

https://daneshyari.com/en/article/1402129

Download Persian Version:

https://daneshyari.com/article/1402129

Daneshyari.com