



Analysis of the Raman Frequency as an Order Parameter Close to the Melting Point in Biphenyl

Research Article

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Abstract

We analyze the observed Raman frequencies of the three lattice modes (modes A, B and 70cm⁻¹) near the melting point in biphenyl by calculating the temperature dependence of the order parameter from the mean field theory. This is based on the correlation between the frequency and the order parameter close to the melting temperature (T_m=343K) in biphenyl. The Raman frequencies of the modes A and B decrease rapidly as the melting temperature is approached, whereas the Raman frequency of the 70 cm⁻¹ is smoothly decreasing, as observed experimentally. It is indicated that the structural phase change toward the melting point in biphenyl is associated with the decrease in the Raman frequencies of the lattice modes A and B, in particular mode A, as observed experimentally in this molecular crystal.

This method of calculating the Raman frequency in relation to the order parameter as calculated from the mean field theory is significant in comparison with some previous methods such as using the quasi-harmonic approximation and also from the crystal volume by means of the mode Grüneisen parameter.

Keywords: Raman frequency; Order parameter; Melting point; Biphenyl

Introduction

Aromatic compounds are important for industrial applications in polymer chemistry, nanotechnology, molecular biology and molecular energetic and in the condensed phase their phase transition equilibria becomes of fundamental importance [1, 2].

Biphenyl C₆H₅C₆H₅ is a crystalline non polar aromatic molecular compound in the series of para-polyphenyl crystals with each molecule consisting of two phenyl groups C₆H₅ connected by a single C-C bond in Para position [3]. It exhibits at low temperature two structural phase transitions from the high temperature, phase I to two incommensurate phases (phase II and III), which are the second order at T_I=40K and the first

order at T_{II}=17K, respectively [4]. Transitions between those phases and the dynamic properties have been studied using various techniques such as absorption and fluorescence spectroscopy, Raman, neutron, NMR and EPR as also pointed out previously [3-9, 11-13].

Studies on the physical and chemical properties of biphenyl have also been reported in the literature. Some of those studies are the following: surface melting in biphenyl, chemical shift in the solid state of biphenyls, calorimetric study on two biphenyl liquid crystals, phase equilibria and heat capacity of diphenyl ether + biphenyl, electro-optic and dynamic studies of biphenyl benzoate ferroelectric liquid crystals and thermal

conductivity epoxies containing substituted biphenyl mesogenic [14-19].

At ambient pressures and temperatures between 40K and the melting point of biphenyl (~343K), biphenyl crystals in the high-temperature commensurate phase (CI) have a monoclinic structure with space group $P2_1/a$ (C_{2h}^5) with two molecules in the unit cell [3].

Biphenyl as one of the molecular solids melts from the solid state at $T_m=343K$. Its melting has been detected experimentally by obtaining the Raman spectra of low frequency modes at various temperatures. Differently from the other lattice modes, one low frequency mode at $70cm^{-1}$ at 104K decreases to $52cm^{-1}$ at the melting point (343K), which is unusual as observed experimentally [20].

$$S = 1 - 2 \exp\left(-\frac{2T_m}{T}\right), T \ll T_m \quad (1a)$$

$$S = \left[3\left(1 - \frac{T}{T_m}\right)\right]^{1/2}, 0 < (T_m - T) \ll T_m \quad (1b)$$

$$S = 0, T > T_m \quad (1c)$$

For this calculation of S , we used Equation (1a). We analyzed the observed frequency shifts of the Raman modes of A and B at various temperatures (below T_m). Since the order parameter S varies between 0 ($T > T_m$)

$$\frac{\nu}{\nu_0} = a_0 + a_1 S + a_2 S^2 + a_3 S^3 \quad (2)$$

Where a_0, a_1, a_2 and a_3 are constants. This fitting procedure was employed for the three lattice modes of A, B and $70cm^{-1}$ with the coefficients a_0, a_1, a_2 and a_3 as given in Table 1. Figures 1-3 give our calculated Raman frequencies of the lattice modes of A, B and $70cm^{-1}$,

In this study, we analyze the temperature dependence of the Raman frequency shifts for the lattice modes of A and B, which increase as the temperature decreases as expected for the molecular solids. We also analyze the Raman frequency shifts of the $70cm^{-1}$ mode. By calculating the temperature dependence of the order parameter S from the mean field theory, we correlate between the Raman frequency shifts and the order parameter S for biphenyl below the melting temperature T_m .

Calculations and Results

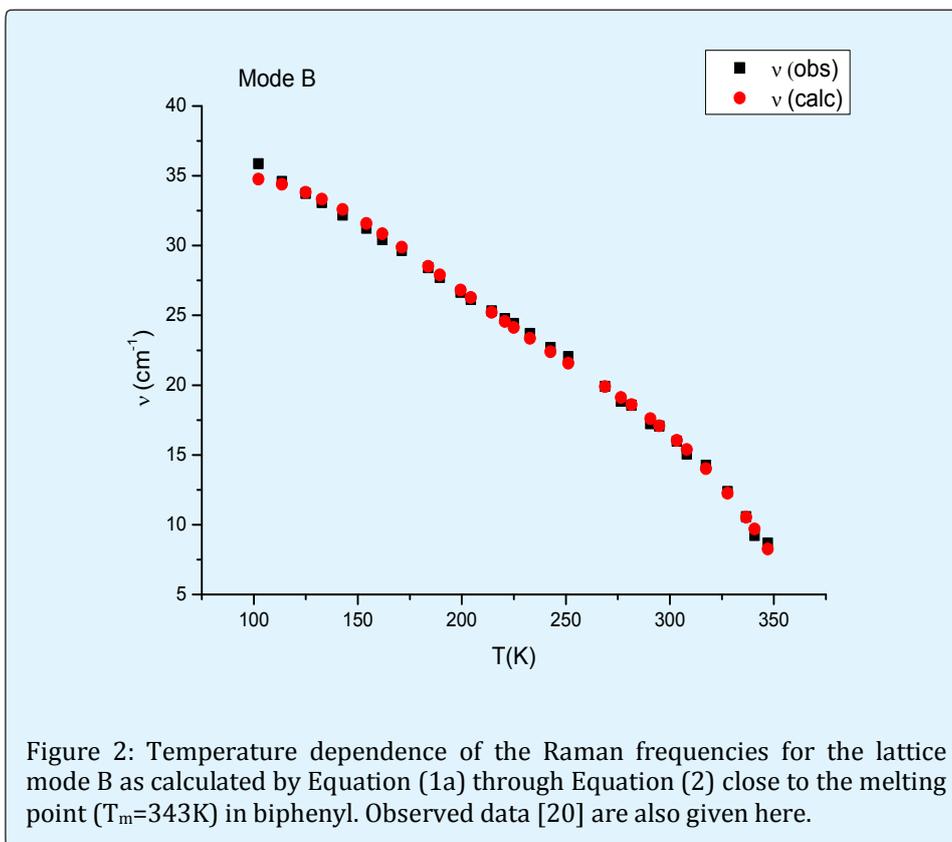
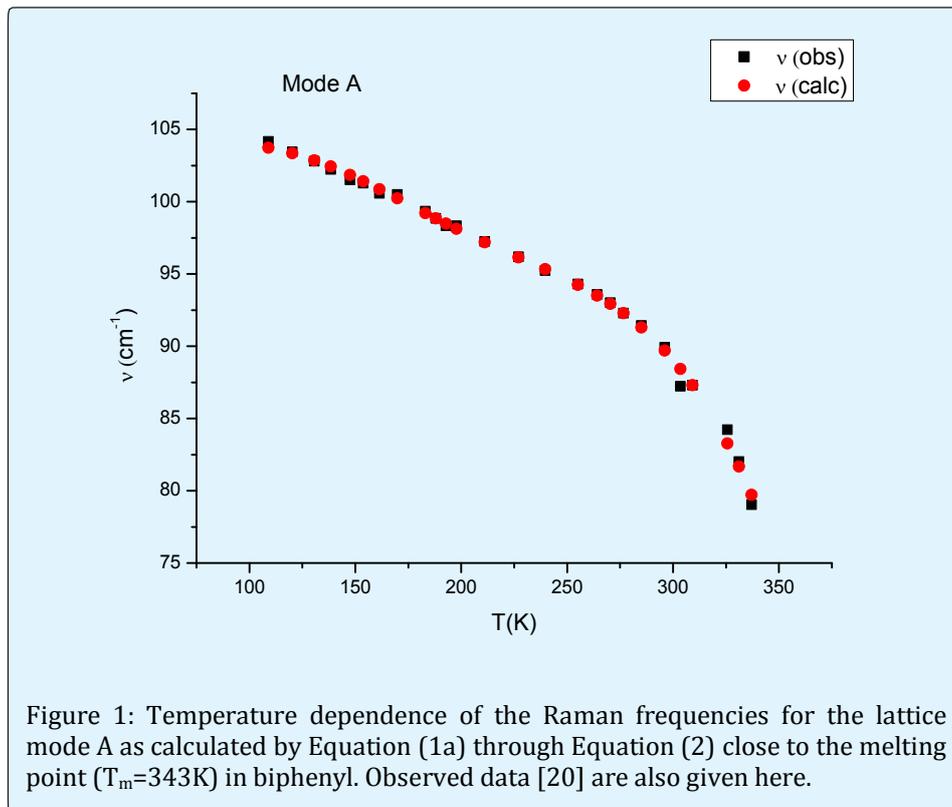
We calculated the order parameter S as a function of temperature ($T_m=343K$) for biphenyl according to the mean field theory.

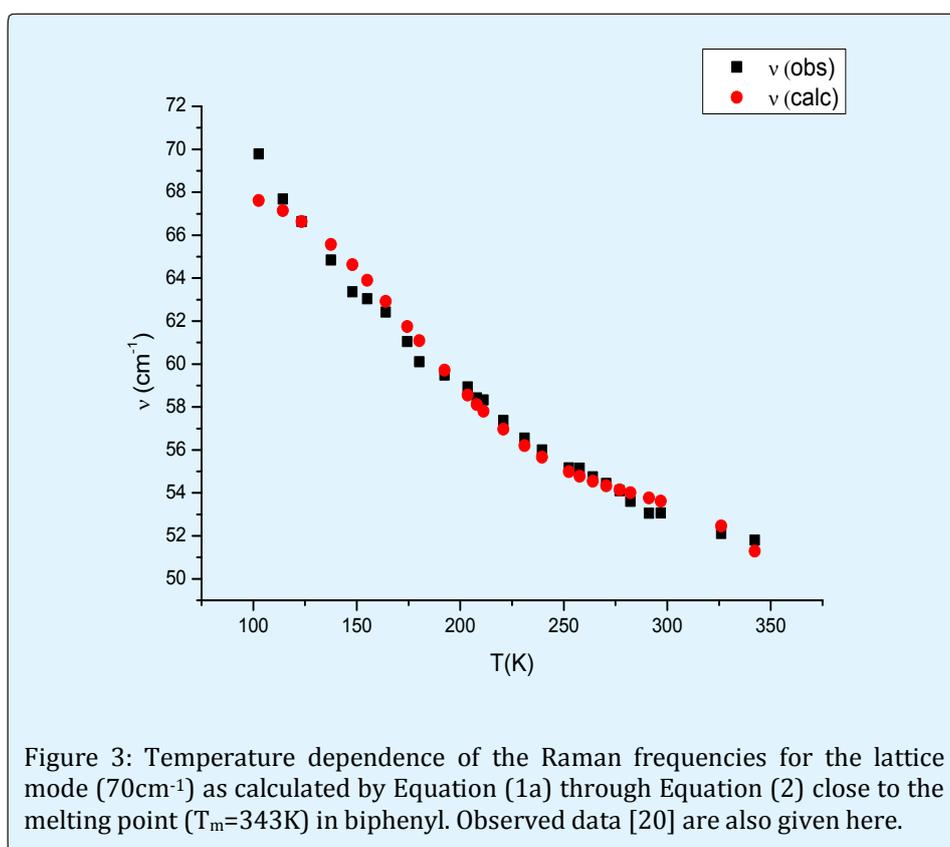
and 1, the frequency was normalized as ν/ν_0 where ν_0 represents the maximum value of the Raman frequency. The order parameter was then fitted to the ν/ν_0 according to

respectively close to the melting temperature ($T_m=343K$) in biphenyl. The observed Raman frequencies of those modes are also given in these figures [20].

Raman Modes	$-a_0$	a_1	0	a_3	Temperature Interval (K)
A	16.28	57.09	63.68	23.87	$109.1 < T < 337.1$
B	28.96	100.06	115.02	44.9	$102.3 < T < 347.2$
$70cm^{-1}$	13.35	51.41	62.69	25.6	$102.6 < T < 342.3$

Table 1: Values of the coefficients (Equation 2) for the lattice modes of A, B and $70cm^{-1}$ within the temperature intervals indicated below the melting point ($T_m=343K$) in biphenyl.





Discussion

In this study, we analyzed the experimental data for the Raman frequencies of the modes of A, B and 70cm^{-1} (at 104K) [20], as plotted in Figures (1-3), respectively at various temperatures below the melting point ($T_m=343\text{K}$) in biphenyl. By calculating the order parameter S as a function of temperature from the mean field theory (Equation 1), which was fitted to the observed frequency shifts ν/ν_0 (Equation 2), the Raman frequencies of the modes A, B and 70cm^{-1} were obtained as observed experimentally.

The Raman frequency of those modes decrease with increasing temperature toward the melting temperature ($T_m=343\text{K}$). This is a drastic decrease for the modes A and B (Figures 1 and 2) as the melting point is approached, whereas decrease in the Raman frequencies for the 70cm^{-1} mode (Figure 3) is somehow different from those of the modes A and B. This critical behaviour of the 70cm^{-1} lattice mode is unusual as observed experimentally, as also pointed out previously. For the modes A and B, a near linear decrease at low temperatures is followed by an increasing rapid decrease as the melting point is approached as stated above and the plots (Figures 1 and 2) Show that the frequency is going rapidly down, in a non linear way, near the melting point it reaches a very low value [20].

This is more apparent for the mode A (Figure 1) as compared to mode B (Figure 2). The fact that the frequency of a particular mode (mode A) of intermolecular vibration approaches zero, leads to the limit of stability of a crystalline phase in the pre-melting process [21]. Since the variation of the frequencies of phonon modes is directly related to the binding forces in a molecular crystal, the occurrence of certain phase changes should be accompanied by a decrease in frequency or decrease and vanishing of some force constants, as suggested by Cochran and Rosenstock, as also pointed out previously. In the case of biphenyl the occurrence of the phase change (melting) should be accompanied by a rapid decrease in the Raman frequencies of the mode A (Figure 1). Mode B can also be considered in the mechanism of the phase change toward the melting point (Figure 2). However, decrease in the Raman frequencies of the 70cm^{-1} mode is continuous (not a rapid decrease) and it reaches about 52cm^{-1} at the melting temperature ($T_m=343\text{K}$) from the 70cm^{-1} (at 104K), as stated above. This indicates that the 70cm^{-1} mode is not associated with the phase change in the pre-melting process, which can be regarded as an internal mode as compared to the external modes (A and B) due to the torsion of the phenyl-phenyl bond [20,22,23].

Conclusions

Raman frequencies of the lattice modes of A, B and 70cm^{-1} in biphenyl near the melting point, were calculated by relating to the order parameter as predicted from the mean field theory. The observed frequencies of those Raman modes were fitted to the temperature dependence of the order parameter near the melting temperature ($T_m=343\text{K}$) in this molecular crystal. The mode frequencies decrease as the melting temperature is approached, which is more pronounced (rapid decrease) for the modes A and B compared to the 70cm^{-1} mode, as observed experimentally. This indicates that the phase change in the pre-melting process is associated with a rapid decrease of the frequencies of those Raman modes (A and B), in particular, mode A near the melting point in biphenyl.

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