1. Introduction

Seeking novel properties in organic materials, such as the better electronic conductivity, thermoelectricity, and even superconductivity, is always an interesting and significant study for the scientific research and applications. Among the organics, poly(paraphenylene) (PPP) have received a lot of attentions as the excellent conductivity, thermoelectricity, and even superconductivity [16-18]. On the other hand, this typical structure makes the neighboring phenyl rings strongly librate around the long molecular axis which is resulted from the competition between two contrary types of forces of the steric repulsion between the neighboring four H atoms and the conjugation resulting from the delocalized π-electrons [19,20]. However, the phenyl rings in the individual molecules are confirmed parallel to each other on average even though the thermal librations are strong in the crystals [21-25]. Interestingly, the molecules become non-planar arising from the freeve of the molecular librations at low temperature, i.e., angles with stable values appear between the neighboring rings [21-25]. Moreover, the torsion angles of the adjacent molecules along the a and b crystal axes are further confirmed opposite with each other. Thus, the lattice parameters a and b will have double enlargements. Such a structural transition can have significant impacts on the natural properties of p-oligophenyls [25-32]. Since the 120-K superconducting phase was found in the potassium-doped p-quaterphenyl, studies of the properties of it become increasingly interesting and requisite.

p-Quaterphenyl exhibits semiconducting behavior at normal state. This material and its derivatives are always extensively applied...
in organic thin film transistors [33], organic light emitting diodes [34], and organic lasers [35,36] due to the excellent optical activation [37]. p-Quaterphenyl exhibits an monoclinic structure at ambient condition, and it is confirmed to occur an “order-disorder” type structural transition at 233 K [31]. This transition shares the same behaviors with p-terphenyl [38,39]. Raman spectroscopy is a powerful method to detect this transition. A plenty of works have been performed on biphenyl and p-terphenyl. However, to data, only a few works have been taken to study the vibrational properties of the low frequency phonon bands of p-quaterphenyl [40], study of the high energy band behaviors is rare. Thus, comprehensive analyses of the vibrational properties of p-quaterphenyl are essential for the further study.

In this work, we measure the 660-nm laser excited Raman spectra of p-quaterphenyl from 5 K to 350 K. The vibrational properties of the phonon bands from the lattice vibrations to the high frequency modes of C−H vibrations are comprehensively analyzed and compared to biphenyl and p-terphenyl to study the order−disorder phase transition occurred at around 233 K. Our work provides a basic footstone for the further study of p-quaterphenyl.

2. Experimental Details

In the experiment the high-purity p-quaterphenyl was purchased from Alfa Aesarare. The sample was sealed in quartz tubes with the diameter of 1 mm for Raman-scattering experiment in a glove box with the moisture and oxygen levels less than 0.1 ppm. The wave-length of the exciting laser beam was 660 nm. The power was less than 1 mW before a x20 objective to avoid possible damage of sample. An integration time of 20 s was used to obtain the spectra. The scattered light was focused on 1200 g/mm grating and then recorded with a 1024 pixel Charge Coupled Device designed by Princeton.

3. Results and Discussion

We measured the Raman spectra of p-quaterphenyl at the temperature range from 5 K to 350 K by a 660-nm excitation. All the spectra have obvious broad fluorescent background, and they seemingly exhibit a growing tendency with decreasing temperature. In order to analyze the vibration modes, a constant background was removed from the raw data. Then the scattering intensity was normalized by the statistical factor n for the Stokes side by

\[ I(\omega) = I_0(\omega) / \left[ n(\omega, T) + 1 \right] \]

where \( n(\omega, T) \) is the Bose-Einstein distribution function evaluated at mode energy \( \omega \) and temperature \( T \), and \( I_0(\omega) \) is the observed intensity. The scattering intensity is very sensitive to the temperature because that the intensity of the low frequency modes increases with decreasing temperature whereas it is decreases before normalizing. The normalized Raman spectra at 300 K, 200 K, 100 K, and 5 K are presented in Fig. 1. The Raman spectra of p-quaterphenyl show more complex behaviors than p-terphenyl. Such a situation should result from the additional phenyl ring and the different symmety compared with p-terphenyl. In the whole temperature range, no additional peaks can be observed. This indicates that this transition belongs to order-disorder transition which has not any structural modulation. In addition, nearly all the vibrational modes increase their intensities as temperature is decreased, and their full widths at half maximum (FWHMs) simultaneously decrease. That is also the reason why the phonon bands, especially the librational motion modes, exhibit obvious splits at low temperature. A broad peak appears at low temperatures, which can also be seen in biphenyl and p-terphenyl [42]. This peak should result from the fluorescence effects.

Detailed evolution of the low frequency modes is presented in Fig. 2 (a). Modes in this energy range are corresponding to the lattice vibrations. The upper figure in Fig. 2 (a) is the temperature evol-utionary Raman intensity maps of p-quaterphenyl, and the bottom depicts the Raman spectra at 5 K and 350 K and the details of the fitting results for clarify. Upon cooling, the scattering intensities of all the modes increase. And below around the transition temperature of 233 K [31], the librational peaks all exhibit dramatic splits. At 5 K, at least 18 peaks appear in the frequency range from 5 to 170 cm\(^{-1}\). In those peaks, the lowest energy peak always draws a lot of attention due to the anomalous tendency on the FWHM, which is confirmed resulting from the anharmonic effect. This characteris-tic behavior makes this peak a good indicator of the order-disorder transition [30,42,43]. We fitted the lowest energy peak with the Lorentzian function. Details of the fitting models are shown in Fig. 2 (a), and the fitted frequencies and FWHMs are shown in Fig. 2 (b). The energy of this peak rapidly increases with decreasing temperature. Below the transition temperature, the increase rate decreases. Meanwhile, its FWHM exhibits a sudden drop from an almost constant value at this temperature. It indicates that the anharmonic effect of the phonons drastic decreases after entering into the ordered state. Other modes also have the same modifications. This is the dominating reason to result in the peak splits after the transition temperature. It is worth mentioning that the anomalous temperature in our experiment is about 240 K. It is a little higher than 233 K confirmed by specific heat measurements, such a case should arise from the thermal fluctuations [31,42].

The two modes at around 1220 cm\(^{-1}\) and 1280 cm\(^{-1}\) are always used to as the molecular chain length and planarity indicators in PPP materials [44-49]. The detailed temperature evol-utional spectra of p-quaterphenyl in the frequency range from 1170 cm\(^{-1}\) to 1320 cm\(^{-1}\) are painted in Fig. 3 (a). In this figure, these two peaks all show anomalous changes not only on the frequencies but also on the FWHMs and intensities with decreasing temperature. Below the transition temperature, all these two modes have drastic splits. In addition, one can also see that the 1220 cm\(^{-1}\) mode shows more complicated behaviors than 1280 cm\(^{-1}\) mode. In order to ana-lyze the properties of these two peaks, we fit them by Lorentzian function, results are shown in Fig. 3 (b) and (c). The frequency and
The frequency of the 1280-cm$^{-1}$ mode firstly increases with decreasing the temperature, and then becomes constant after transition. The FWHM of this mode shares the same behavior with the 1220-cm$^{-1}$ mode. Such behaviors of these two modes are almost the same with $p$-terphenyl except the frequency tendency of the 1220-cm$^{-1}$ mode [42]. Previous works [47] proposed that the 1220-cm$^{-1}$ mode is closely related to the delocalized $\pi$-electrons stemmed from the C atoms on the long molecular axis, and the localized electrons of the off-axis C atoms make important contributions to 1280-cm$^{-1}$ mode. Thus, the former is susceptible to the conjugation effects, whereas the latter is far less. Our Raman data is well in accord with this scenario, the variations of the frequency, FWHM, and even the intensity of the former mode is visibly greater than the latter mode (see in Fig. 3 (a)). On the other hand, the anomalous frequency behavior of the 1220-cm$^{-1}$ mode should result from the gradually increased angles among the phenyl rings in one molecule. With decreasing the temperature, the torsion angle between the neighboring phenyl rings increases. It will strongly impact the delocalized electrons, and the localized orbitals will be enhanced.

**Fig. 3 (d) and (e)** present the temperature dependent intensity ratio and frequency difference of the 1220-cm$^{-1}$ and 1280-cm$^{-1}$ modes, respectively. The intensity ratio of these two modes is always used to distinguish the phenyl ring numbers in PPP materials [44,48], and the frequency difference of them is also a good indicator of the molecular planarity [45-47, 49]. Upon cooling, an extreme point can be observed in the intensity ratio figure at around the order-disorder transition temperature. Meanwhile, the frequency difference also exhibits an inflexion point at the same temperature. These situations imply that these two indicators are also suitable for the low temperature case.

The two modes at around 1600 cm$^{-1}$ also possess interesting properties and thus are always used to estimate the planarity [44,48,50]. The Raman intensity map at around 1600 cm$^{-1}$ from 5 K to 350 K is painted in Fig. 4 (a), and the Raman spectra at 5 K and 350 K are provided in the bottom for clarity, as well as the fitting models. There are at least 6 peaks existed here. We fitted the two strong peaks (lower energy peak A and higher energy peak B), and the results are shown in Fig. 4 (b), (c), and (d). The frequencies of these two modes all increase with decreasing temperature, and the FWHMs of them simultaneously decrease. No special anomalies can be found in the frequency and FWHM tendencies except an inflexion point in the frequency data of the high energy peak. It almost shares the same behaviors with $p$-terphenyl [42]. We also calculated the intensity ratio $I_B/I_A$ and the frequency difference $\omega_B-\omega_A$ of these two peaks. Their intensity ratio decreases as the temperature then gradually decreases upon further cooling. The frequency of the 1280-cm$^{-1}$ mode firstly increases with decreasing the temperature, and then becomes constant after transition. The FWHM of this mode shares the same behavior with the 1220-cm$^{-1}$ mode. Such behaviors of these two modes are almost the same with $p$-terphenyl except the frequency tendency of the 1220-cm$^{-1}$ mode [42]. Previous works [47] proposed that the 1220-cm$^{-1}$ mode is closely related to the delocalized $\pi$-electrons stemmed from the C atoms on the long molecular axis, and the localized electrons of the off-axis C atoms make important contributions to 1280-cm$^{-1}$ mode. Thus, the former is susceptible to the conjugation effects, whereas the latter is far less. Our Raman data is well in accord with this scenario, the variations of the frequency, FWHM, and even the intensity of the former mode is visibly greater than the latter mode (see in Fig. 3 (a)). On the other hand, the anomalous frequency behavior of the 1220-cm$^{-1}$ mode should result from the gradually increased angles among the phenyl rings in one molecule. With decreasing the temperature, the torsion angle between the neighboring phenyl rings increases. It will strongly impact the delocalized electrons, and the localized orbitals will be enhanced.

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is decreased, and no any clear anomalies can be observed here. This indicates that the intensity ratio of these two modes is no longer a good indicator of the molecular conjugations at low temperature. The frequency difference of them exhibits a reverse tendency at around 270 K. This phenomenon should also result from the order-disorder transition, and this also signals that p-quaterphenyl already enters into the thermal anomalous state at around 270 K. Fig. 4 (e) indicates the molecular conjugation at low temperature. Our work provides the basis to understand the internal vibrational properties of p-quaterphenyl due to the thermal fluctuations. Nearly all the modes were found to exist already show anomalous behaviors above this temperature due to the phonon behaviors, and the results have been compared with previous works discovered that the higher energy peak is as functions of temperature. (d) Temperature dependent intensity ratio of these two modes. (e) Temperature-dependent frequency difference and the difference between \( v_4 + v_1 \) and \( v_5 \). The vertical dashed lines indicate the structural transition temperature of around 233 K.

4. Conclusions

In conclusion, vibrational properties of the crystalline p-quaterphenyl have been investigated by Raman scattering with a 660-nm laser from 5 K to 350 K. Detailed analyses have been performed on the intra- and intermolecular terms to understand the phonon behaviors, and the results have been compared with biphenyl and p-terphenyl. The order-disorder transition temperature was confirmed at around 233 K, whereas most vibrational modes already show anomalous behaviors above this temperature due to the thermal fluctuations. Nearly all the modes were found to exist anomalous tendencies on the energies, widths, and intensities before and after the transition temperature, especially the phonon widths, it is the major reason to result in the peak splits at low temperatures. The intensity ratio of the 1280-cm\(^{-1}\) mode and the 1220-cm\(^{-1}\) mode is still a good indicator of the molecular planarity for p-quaterphenyl at low temperature, as well as the frequency separations between them and between the higher energy mode and the lower energy mode around 1600 cm\(^{-1}\). However, the intensity ratio of the two modes at around 1600 cm\(^{-1}\) has almost no obvious anomalies around the transition temperature, thus it can hardly indicate the molecular conjugation at low temperature. Our work provides the basis to understand the internal vibrational properties of p-quaterphenyl.

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References


