Anharmonic Lattice Vibrations in Small-Molecule Organic Semiconductors

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The intermolecular lattice vibrations in small-molecule organic semiconductors have a strong impact on their functional properties. Existing models treat the lattice vibrations within the harmonic approximation. In this work, polarization-orientation (PO) Raman measurements are used to monitor the temperature-evolution of the symmetry of lattice vibrations in anthracene and pentacene single crystals. Combined with first-principles calculations, it is shown that at 10 K, the lattice dynamics of the crystals are indeed harmonic. However, as the temperature is increased, specific lattice modes gradually lose their PO dependence and become more liquid-like. This finding is indicative of a dynamic symmetry breaking of the crystal structure and shows clear evidence of the strongly anharmonic nature of these vibrations. Pentacene also shows an apparent phase transition between 80 and 150 K, indicated by a change in the vibrational symmetry of one of the lattice modes. These findings lay the groundwork for accurate predictions of the electronic properties of high-mobility organic semiconductors at room temperature.

Small-molecule semiconducting crystals are studied extensively due to their potential for (opto)electronic applications such as light-emitting diodes, field-effect transistors, and solar cells.[1–8] Linear oligoacenes are an archetypical family of such organic crystals that serve as an excellent testbed to study intrinsic properties of π-conjugated solids. This is due to their well-defined crystal structure[9–11] and their wide range of tunable optical and electronic properties.[12–15]

Thermal fluctuations of the nuclei in organic crystals have a significant role in determining their optical,[16] electronic,[17] and thermal[18] properties. These fluctuations stem from both intermolecular and intramolecular vibrations, which contribute to the dynamic disorder.[17,19,20] Contemporary theoretical studies are in agreement that low-frequency (<150 cm⁻¹) lattice vibrations dominate charge carrier mobility in organic crystals via nonlocal electron–phonon interactions.[19,21–24]

To the best of our knowledge, current models for charge transport and optical properties of organic semiconductors use the harmonic approximation to describe lattice vibrations. The anharmonic components of the lattice vibrations, i.e., phonon–phonon interactions are therefore entirely neglected. However, organic crystals are known to be mechanically soft,[30] exhibit large molecular displacements,[31] and have large thermal expansion coefficients[32] all of which are indicative of strong lattice anharmonicity.[33,34]

Strongly anharmonic lattice dynamics are expected to have a disruptive effect on the electronic coupling between the molecules, and therefore they may profoundly impact charge transport in the organic crystal. Therefore, it is imperative to characterize the degree of lattice anharmonicity in small-molecule organic crystals. The main experimental methods for measuring the lattice dynamics to infer about anharmonicity are THz spectroscopy, inelastic neutron scattering, and Raman spectroscopy.[24]

In this study, we use polarization-orientation (PO) Raman spectroscopy to directly probe the evolution of phonon symmetry with temperature. We present unambiguous experimental evidence for strongly anharmonic behavior of specific lattice vibrations in oligoacene crystals. This anharmonic behavior is expressed by temperature-activated symmetry breaking of the average crystal structures well-below their melting temperature. By combining PO Raman with first-principles calculations based on density functional theory (DFT), we show how specific lattice modes gradually lose their vibrational symmetry and become liquid-like due to
enhancement of vibrational anharmonicity as the temperature is increased.

Single crystals of anthracene and pentacene were prepared via physical vapor transport (PVT). We measured their crystal structure and orientation by conducting single-crystal X-ray diffraction (XRD) measurements (Section S1, Supporting Information). The crystal orientation for both was found to be (001), in line with previous reports.

Figure 1 shows the raw PO Raman data for the single crystals of anthracene and pentacene at 10 K. In this measurement, the crystal oriented along the crystallographic ab plane is excited by a linearly polarized laser (785 nm). The scattered light is then filtered by an analyzer for polarization parallel and perpendicular to the incident light. This measurement is repeated after rotating the polarization of the incident light while the sample position is fixed. The false-color plots show the fluctuations in scattering intensity as a function of the angle between the polarization of the incident light and an arbitrary axis in the ab plane. In the top panel of Figure 1, we present the normalized unpolarized (i.e., integrated over all polarization angles) Raman spectra (black line) along with the DFT-calculated Raman intensities (red line). The agreement between theory and experiment is overall very good (i.e., frequencies differ by at most 10 cm\(^{-1}\)). We note that the apparent redshifts (e.g., in the higher-energy part of the pentacene spectrum) can be explained by a tendency of underbinding in organic crystals when the here-applied, many-body dispersion (MBD) correction is used. In Section S2 in the Supporting Information, we demonstrate the superior performance of the MBD approach compared to using the regular Tkatchenko–Scheffler (TS) method.

To analyze the PO results of Figure 1, we first fit each spectrum to the product of the Bose–Einstein distribution and a multi-Lorentzian line shape (Section S3, Supporting Information). Then, we extract the integrated intensity of the deconvolved Lorentzian of each peak and monitor its fluctuation with the polarization angle. Finally, we fit the intensity fluctuations for each mode using a model proposed by Kranert et al. in order to extract the Raman tensors (Section S4, Supporting Information). This model considers the anisotropic nature of the crystals (i.e., birefringence), the scattering cross-section dependence of each mode on the vibration frequency, and the coordinates of the crystal with respect to the optical table.

We perform a factor group analysis to extract the number of lattice modes and the form of the Raman tensors. Anthracene has a monoclinic crystal structure with a \(P_2_1/\)a space group for which factor group analysis predicts six Raman-active lattice modes, namely, three \(A_g\) modes and three \(B_g\) modes. The form of the Raman tensors is

\[
R_{A_g} = \begin{pmatrix} a & 0 & e \\ 0 & b & 0 \\ e & 0 & c \end{pmatrix}, \quad R_{B_g} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & f \\ 0 & f & 0 \end{pmatrix}
\]

All the six modes are observed in the data presented in Figure 1a.

Pentacene has a triclinic crystal structure with a \(P\bar{T}\) space group for which factor group analysis predicts six Raman-active lattice modes. All of them have \(A_g\) symmetry with a Raman tensor form

\[
R_{A_g} = \begin{pmatrix} a & d & e \\ d & b & f \\ e & f & c \end{pmatrix}
\]

The data presented in Figure 1b shows seven modes. The additional mode is due to the mixing of inter- and intramolecular vibrations, as discussed previously.

To extract the Raman tensor of each mode, we perform a global fit (i.e., simultaneous fit to all peaks) to the PO dependence of the integrated intensity (Section S5, Supporting Information). For each mode in Figure 1, we present the fit results in Figure 2 (solid lines) along with...
the deconvolved integrated intensity (squares) and results of the same model based on the DFT-calculated Raman tensors (dashed lines). We find an overall good agreement between the experimental data, the global fit, and the DFT results. This shows that at 10 K the lattice dynamics are well-captured by the harmonic approximation that is inherent to our DFT-based Raman calculations. Interestingly, the agreement is somewhat less favorable for pentacene than anthracene, especially in regard to the $A_g^{(6)}$ mode in pentacene, which will be discussed below.

Figure 3 shows the temperature-dependent (10–360 K) PO data in parallel configuration for anthracene (a) and pentacene (b). The experimental procedure and analysis are equivalent to those described for the data in Figure 2 and the raw Raman spectra for each temperature are presented in Section S6 in the Supporting Information. For a perfectly harmonic crystal and in the absence of structural phase transitions, the PO behavior is expected to be temperature independent. Remarkably, we find that $B_g^{(1)}$ and $B_g^{(3)}$ modes in anthracene and $A_g^{(6)}$ mode in pentacene gradually lose their PO dependence as temperature is increased. This temperature range is well below the crystals melting temperature which is 212 °C for anthracene and 600 °C for pentacene. As the PO dependence becomes weaker, these modes become more liquid-like, since for liquids the Raman intensity is PO independent (see Section S8 in the Supporting Information for an example of a PO measurement of a liquid). This is despite the fact that single-crystal XRD at 100 and 293 K show no change in the average crystal structure (Section S1, Supporting Information). We note that the same trend is observed also in the PO of the perpendicular configuration (Section S7, Supporting Information).

Since the PO of each mode reflects its symmetry, our findings reveal a continuous and mode-specific symmetry breaking in anthracene and pentacene crystals. This symmetry breaking must stem from the temperature-driven lattice fluctuations in the crystals since the trends in the PO intensities are fully reversible with temperature, which rules out the appearance of static disorder.

We interpret this dynamic symmetry breaking as a manifestation of vibrational anharmonicity that increases with temperature. Traditional expressions of anharmonicity include phonon...
“softening” (decrease in vibrational energy) and decreasing phonon lifetimes (increase in vibrational linewidth). The observed symmetry breaking is not accompanied by any anomalous effect in the temperature dependence of the modes’ energies or their linewidth (Section S9, Supporting Information). This is consistent with DFT-calculated phonon density of states of anthracene and pentacene (Section S10, Supporting Information) that show no distinct features that would imply a strong coupling of the anomalous vibrations (i.e., the vibrations that exhibit symmetry breaking) to the thermal bath (i.e., acoustic phonons). Importantly, strong anharmonicity does not necessarily lead to mode softening and decreasing phonon lifetimes. Anharmonic effects are usually modeled by three- and four-phonon decay processes where a dominance of four-phonon processes can lead to phonon hardening and increasing lifetimes. A possible explanation of this finding is that due to anharmonic effects, the phonon dispersion relation evolves with temperature. 

A second important finding presented in Figure 3b is that the A1g mode of pentacene changes its PO periodicity from 180° below 80 K to 90° above 150 K. This change is reversible with temperature and indicative of a profound change in the Raman tensor elements of this vibration. Unlike the gradual PO loss discussed in the previous paragraph, this change in PO periodicity is accompanied by changes in the temperature evolution of the unpolarized Raman spectra, since the temperature dependence of the A1g mode width shows a subtle change in its slope between 80 and 150 K (Section S9, Supporting Information). These observations may be indicative of a phase transition (which is an explicit anharmonic phenomenon) to a different polymorph or could be another manifestation of the complex effect of anharmonicity on the lattice vibrations of the crystal. Yet, we are unaware of a reported phase transition in pentacene in this temperature range. It is at first sight surprising that such a large change in PO behavior has a relatively small effect on the unpolarized Raman spectrum. However, phase transitions between polymorphs can be very subtle and have little or no effect on the spectrum because Raman scattering probes only Raman-active modes at the center of the Brillouin zone.

In conclusion, we discover a new manifestation of anharmonic vibrational behavior in anthracene and pentacene single crystals, by using temperature-dependent Raman PO measurements and first-principles calculations. We detect a liquid-like behavior in specific lattice modes, indicated by a gradual loss of the PO dependence at temperatures that are well below the melting point of the crystals. This PO-dependence loss is a signature of dynamic symmetry breaking of the crystal structure due to anharmonic thermal fluctuations. The mechanism that leads to mode-specific symmetry breaking is still unclear and requires further study. We also detect what seems to be a subtle phase transition in pentacene between 80 and 150 K, manifested in a change in vibrational symmetry of the A1g mode. Since the low-frequency modes are known to be important sources of electron–phonon interactions in organic crystals, our findings have many interesting implications, since they question the validity of the harmonic approximation when describing the transport properties of these materials.

**Experimental Section**

**Crystal Growth:** Single crystals of anthracene and pentacene were grown by PVT. For anthracene, a 99% powder (Sigma-Aldrich), a temperature of 135 °C in the tube furnace, and an argon flow of 60 mL min⁻¹ were used. For pentacene, a 95% powder (Toronto Research Chemicals) was used with a similar method except for the temperature of the tube furnace being 280 °C. The temperatures of the furnace were set to lower temperatures from those in the literature to ensure the growth of high-quality single crystals. Crystals were also grown by using a two-zone furnace with the same source temperature and deposition temperature of 100 and 200 °C for anthracene and pentacene, respectively. The PO Raman results of these crystals were very similar, suggesting similar crystal quality.

**Temperature-Dependent PO Raman:** A custom-built dispersive Raman spectrometer was used to conduct the Raman measurements. The system was based on a 1 m long Horiba FHR-1000. Notch filters were included in the system to allow access to the low-frequency region (≥10 cm⁻¹) and simultaneous acquisition of the Stokes and anti-Stokes signals. To avoid photoluminescence (PL), a 785 nm Topica diode laser was used. For pentacene, a small PL signal was detected at some temperatures so the laser intensity on the sample was kept below 2 mW to avoid sample heating. No such problem arose in the case of anthracene, so the laser intensity on the sample was kept at ~30 mW. The system also included a 50° objective and a 1800 mm⁻¹ grating. The spectral resolution was 0.15 cm⁻¹. To control the polarization of the incident and scattered light, half-wave plates and a polarizer–analyzer combination was used (Section S11, Supporting Information). The temperature was set and controlled by a Janis cryostat ST-500 and a temperature controller by Lakeshore model 335. The polarization dependence of anthracene and pentacene (steps of 10°) was measured in parallel and perpendicular configurations at 10, 80, 150, 220, 290, and 360 K. For anthracene, no measurement at 360 K was performed due to the sublimation of the sample.

**First-Principles Calculations:** DFT calculations were performed with the projector augmented-wave method[40] as implemented in VASP,[61] Exchange-correlation was described using the Perdew–Burke–Ernzerhof (PBE) functional.[62] Dispersive corrections were computed using the MBD method.[37,38,63,64] Unless noted otherwise, a plane-wave cutoff energy of 900 eV was used, and 3 × 4 × 3 and 4 × 1 × 2 centered k-point grids were applied for anthracene and pentacene, respectively. The unit cells of the crystals were optimized in internal coordinates with Gadget,[65] applying a force threshold of 10 meV Å⁻¹. Phonon frequencies were calculated with the phonopy package,[66] using the finite-displacement method and a plane-wave cutoff energy of 800 eV. Raman tensors associated with the respective vibrational modes were obtained using the phonopy-spectroscopy package.[67] In the experiment, the 2 component of the Raman tensor was not measured because of the limitation to a specific crystal orientation (see above). Therefore, the unpolarized Raman intensities were calculated from the Raman tensors using only the 2 × 2 submatrices of the tensors that are associated with their x and y components. In these calculations, the parallel and perpendicular intensities, integrated over the polarization angle, were added and the experimentally determined linewidth was used for each mode in a Lorentzian broadening.

**X-Ray Crystallography:** Single-crystal XRD measurement for pentacene was performed using Rikagu XtaLab Pro dual-source diffractometer equipped with PILATUS 200 detector and microfocus and Cu Kα radiation. For anthracene, the measurement was performed using Bruker APEX-II diffractometer equipped with KappaCCD detector and microfocus and Mo Kα radiation. The measurements were taken at 100 K after cooling at a rate of 1 K min⁻¹, and at 293 K.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Keywords

first-principles calculations, low-frequency Raman modes, oligoacenes, polarization-orientation Raman spectroscopy, small-molecule organic semiconductors
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