

Phonon dispersion curve of the organic semiconductor rubrene

Organic semiconductors are now commercially available for electronic devices. The carrier transport mechanism in them is, unlike that in inorganic semiconductors, believed to involve phonons. Local modes that cause molecular deformation alter molecular orbitals, and nonlocal modes alter intermolecular transfer integrals. Both of them break the periodicity, and thus, scatter the carriers. The flexibility of the organic materials makes the importance of lattice vibration prominent. However, experimental observations of the phonon dispersion of organic semiconductors are scarce. There is only one clear report on it: the neutron inelastic scattering measurement on deuterated naphthalene C₁₀D₈ single crystal [1]. Although deuteration is needed to perform the neutron inelastic scattering measurements, it alters the lattice vibration frequency as well as the electronic property of molecular crystals. To avoid deuteration, inelastic X-ray scattering (IXS) is employed [2] for the measurement of the phonon dispersion of rubrene C₄₂H₂₈, one of the most studied organic semiconductors.

Single crystals of rubrene were grown by the physical vapor transport method. The typical size of the crystals was 4 mm × 1 mm × 0.1 mm along the orthorhombic *a*, *b*, and *c* directions. The lattice parameters were a = 7.18 Å, b = 14.43 Å, and c = 26.9 Å. The large unit cell makes the Brillouin zone small, and the number of phonon branches is 420. These characteristics result in a heavy overlap of the phonon branches, which makes the experimental observation of phonon dispersion difficult. We overcome the difficulties by using density functional theory (DFT) calculations, thermal diffuse scattering (TDS) measurement, and the IXS techniques.

DFT calculation provides the eigenmodes characterized by the wavevector $\boldsymbol{q} = (0, 0, 0)$. The modes were indexed in the order of increasing energy. Modes 1–3 are acoustic modes. We constructed atomic displacement models for the modes characterized by various \boldsymbol{q} vectors using the calculated $\boldsymbol{q} = (0, 0, 0)$ modes to derive the TDS intensity distribution caused by them. The calculated total TDS intensity distribution is obtained as an incoherent sum of the distributions caused by the 25 lowest energy modes. It is presented in Fig. 1 together with the measured value. The TDS intensity distribution at room temperature was measured with an 18 kW Mo $K\alpha$ X-ray generator and a standard four-circle diffractometer. The results appear similar, which validates the mode-discriminated TDS calculation based on q = (0, 0, 0) modes. Since the IXS is a means of measuring the energy spectra of the TDS, we selected the Brillouin zone to measure the IXS to determine the dispersion of specific modes using this information.

The IXS measurements were performed at SPring-8 **BL35XU**, with 1.5 meV resolution optics. Typical inelastic spectra along the (6, 1+ η , 0)-, (0, 10– η , 0)- and (0, η , 12)-lines are presented in Fig. 2. There are strong Bragg reflections at $\eta = 0$ positions. Therefore, the signal from acoustic-mode phonons characterized by the wavevector (0, η , 0) is observed at the $\eta < 0.5$ regions. Phonon dispersion at $\boldsymbol{q} = (0, 0, 0)$ is directly related to the sound velocity and elastic constants. The elastic stiffness obtained by the present IXS measurement is similar to the values obtained from Brillouin scattering [3], except for the systematic difference of ~25%.

The IXS peak positions in the $\eta > 0.5$ regions show the optical mode phonons characterized by the wavevector (0, 1- η , 0). According to the modediscriminated TDS intensities presented in Figs. 2(ac), the spectra presented in Figs. 2(d-f) reflect the dispersions of modes 5, 13 and 4, respectively. The phonon dispersion relations of the acoustic modes and some optical modes are derived in the same manner, as shown in Fig. 3. The shape of the Brillouin zone is presented in panel (a), and the dispersions along a^* , b^* , and c^* directions in the *B*-centered orthorhombic cell are shown in panel (b). There is one interesting finding; the phonon energies measured on the (0, 10- η , 0) line, which should reflect the energy of the



Fig. 1. (a) TDS intensity distribution on the (hk0) plane measured with Mo $K\alpha$ X-ray. Reciprocal lattice points were not measured. (b) Calculated TDS intensity map on the same plane.



Fig. 2. (**a**–**c**) Calculated mode-discriminated TDS intensity along the (a) (6, k, 0), (b) (0, k, 0) and (c) (0, k, 12) lines. (**d**–**f**) IXS spectra measured along $(6, 1+\eta, 0)$, $(0, 10-\eta, 0)$, and $(0, \eta, 12)$ lines.

longitudinal acoustic (LA) mode, are the same as those of the transverse acoustic (TA) mode shown in the Γ -Y line in Fig. 3(b). The energy of the LA mode is usually twice as large as that of the TA mode; thus, this feature appears physically unreasonable. We have interpreted this as the mixing of the local mode with the nonlocal mode. The molecules are significantly deformed by the acoustic mode phonons, which reduces the scattering intensity corresponding to the LA mode on the (0, 10– η , 0) line and increases the signal from the TA mode on the

(6, 1+ η , 0) line. Such mode mixing is expected in short-wavelength modes, but in the present case, the mixing is observed even in the mode with the wavelength of 14 nm.

The phonon dispersion of the most studied organic semiconductor rubrene was clearly observed experimentally. The procedure for measuring the phonon energies of particular modes was demonstrated. This knowledge provides a robust basis for the study of organic semiconductors.



Fig. 3. (a) Brillouin zone and (b) phonon dispersion relation of rubrene. The closed symbols show the experimentally observed phonon energies. The symbol color represents the measured position in the reciprocal space, and the symbol shape represents the phonon mode. The open symbols on the Γ point show the calculated energies.

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References

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