

**Resonant Raman spectroscopy on  $\alpha$ -hexathiophene single crystals**

J. R. Weinberg-Wolf and L. E. McNeil

*Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3255, USA*

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Resonant Raman measurements of  $\alpha$ -hexathiophene at 33 K have identified over ten vibrational modes that couple to electronic excitations in the single crystal. These excitations at 2.066 eV and 2.068 eV with a width of 2 meV have been tentatively identified as bound singlet Frenkel excitons or a triplet Frenkel exciton.

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**I. INTRODUCTION**

Recently, interest has grown in organic semiconductors and their possible applications as organic light emitting diodes (OLED's) and other "plastic electronic" devices. Oligothiophenes, and  $\alpha$ -hexathiophene ( $\alpha$ -6T) in particular, are one main focus of this recent research because the thiophene oligomers are model  $\pi$ -conjugated systems.<sup>1</sup> Compared to some other organic molecules,  $\pi$ -conjugated molecules demonstrate especially high stability, making them good candidates for devices. In addition, the energy levels associated with such systems tend to have transitions within the visual range. For example, the value of the band gap of this material published in the literature is approximately 2.2 eV.<sup>2</sup> This means these materials are good candidates for a host of photonic devices. Most of the work with  $\alpha$ -6T has concentrated on thin-film devices; however, studies of the pure single crystal of the oligomer are necessary to understand the intrinsic optical and electronic properties. There is still not a complete picture in the literature of the electronic structure in the solid state despite all of the recent attention.

Oligothiophenes, such as  $\alpha$ -6T, form molecular crystals. In such crystals, molecules bound internally by strong covalent bonds are in turn weakly bound to neighbor molecules, thereby retaining many of the molecular characteristics in the solid state. The primary photoexcitations in these crystals are Frenkel excitons. Frenkel excitons are tightly bound electron-hole pairs that can be localized spatially on individual molecules in such a crystal. The theory of these excitons has been widely developed in the literature.<sup>3</sup>

Raman spectroscopy is a nondestructive characterization tool that probes the vibrational states of a material. If the excitation energy used in an experiment is at or near an electronic transition of the material, the coupling of the phonon and electron modes can create an enhancement of the Raman signal. Thus, resonant Raman spectroscopy<sup>4</sup> is an excellent probe of both the vibrational and electronic excitations of a crystal.

**II. EXPERIMENT**

Alpha-hexathiophene is an aromatic hydrocarbon consisting of six thiophene rings bound at the  $\alpha$  carbon of each ring, creating a rigid-rod molecule that has a deviation from planarity smaller than measurement accuracy ( $< 1^\circ$ ).<sup>1</sup> The molecule crystallizes in a herringbone structure with monoclinic unit cells containing four molecules with  $C_{2h}$  point group symmetry. The single crystals of  $\alpha$ -6T were provided by re-

searchers at Lucent Technologies; the growth process for these crystals has been described elsewhere.<sup>5</sup>

Raman spectra were recorded using a Dilor XY triple spectrometer in a backscattering configuration and collected using a charge-coupled device (CCD) cooled with  $LN_2$ . The resolution of the spectrometer is  $1\text{ cm}^{-1}$ . The crystal was cooled to 33 K with an Air Products closed-cycle He refrigerator and was mounted in the cryogenic chamber such that the  $bc$  plane of the crystal was perpendicular to the incoming laser beam. A Coherent 310 Ar<sup>+</sup> laser was used to pump a Spectra Physics 375B dye laser using Rhodamine 6G dye. The output energy of the dye laser is continuously tunable from 1.97 eV to 2.17 eV. Spectra were acquired in energy steps that ranged from 20 meV far from the resonant energy to 1 meV close to the resonant energy. Data were collected over the spectral range from approximately  $70\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$ , a range that includes both intermolecular and intramolecular vibrations. The integration time for each scan depended on the excitation wavelength in use, but was chosen to maximize the signal while protecting the CCD from saturation from the background luminescence. As the excitation energy approached the band gap, the background luminescence increased; therefore, multiple shorter scans were averaged together to improve the signal-to-noise ratio of the data. All peaks were fit using a least-squares routine with Voigt line shapes (where the Raman signal is assumed to be pure Lorentzian but equipment effects convolve the signal with a Gaussian distribution).

**III. RESULTS AND DISCUSSION**

Previous researchers have measured the vibrational spectra of  $\alpha$ -6T single crystals using infrared and Raman spectroscopies, as well as inelastic neutron scattering.<sup>6</sup> The off-resonance Raman spectra recorded in this experiment at room temperature agree with the previously published data.

Measurements were first performed at fixed excitation energies (2.043 eV and 2.073 eV) while the temperature of the sample was varied from 300 K to 33 K. Figure 1 shows this off-resonance room-temperature spectrum of  $\alpha$ -6T. The observed upshifts of Raman mode frequencies upon cooling from room temperature to 33 K are 0.2%–0.4% for intramolecular modes (higher-energy modes with frequencies above  $500\text{ cm}^{-1}$ ) and 1%–5% for intermolecular modes (lower-energy modes with frequencies below  $500\text{ cm}^{-1}$ ). The temperature dependences of the peak positions for some modes are plotted in Fig. 2. These upshifts agree with the expected shifts in frequency for cooled molecular crystals.

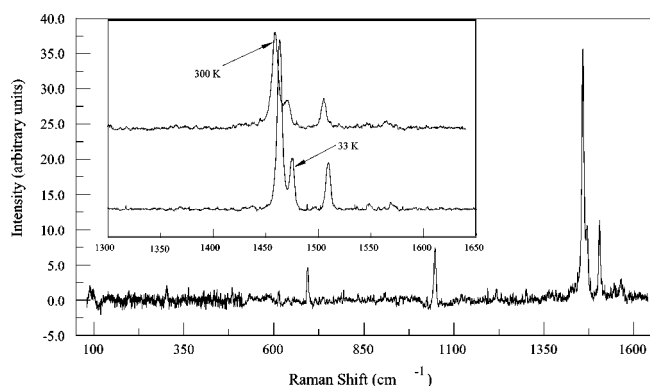


FIG. 1. Room-temperature Raman spectra of  $\alpha$ -6T with  $\lambda_{exc} = 607$  nm (2.043 eV). The background luminescence as well as all instrumental effects have been subtracted out of the original spectra. The inset shows one region of the Raman signal at both 300 K and 33 K, demonstrating the small upshift of the vibrational frequency caused by cooling of the crystal. The modes pictured are the strongest-intensity vibrations in the spectrum and have been assigned to carbon-carbon stretching within a single molecule (Ref. 5).

This vibrational shift with decreasing temperature is caused by a slight decrease in the lattice spacing, which stiffens the bonds and thus shifts the Raman modes to higher frequencies. Weak intermolecular van der Waals forces are affected more by temperature changes than are covalent intramolecular bonds, resulting in larger shifts for the lower-energy Raman peaks. Lowering the temperature of the crystal also reduces thermal broadening effects, thereby reducing the overlap of the peaks. Table I lists the intramolecular modes previously recorded in the literature, as well as those measured in the present work.

More unusual effects were measured in the resonant Raman experiment. At the resonant excitation energy, at least ten vibrational lines were observed in the 800–1600  $\text{cm}^{-1}$  spectral window that were not previously recorded in any

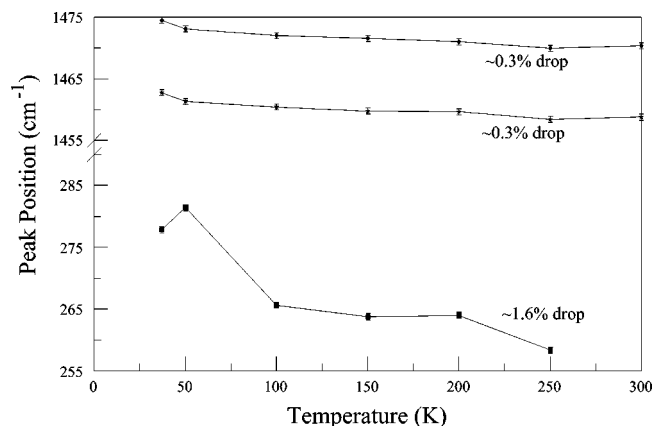


FIG. 2. Peak position vs temperature for both intermolecular and intramolecular modes. The peaks were fit with a least-squares routine using Voigt line shapes. Some of the highest-frequency intramolecular modes (with very little temperature dependence) are plotted, along with the strongest intermolecular modes that display up to a 2% shift with temperature.

TABLE I. Intramolecular Raman modes from the published literature (Ref. 5) as well as those measured in this work. The symmetry assignments for the different vibrational modes are from the literature. Some of the modes seen originally by Esposti *et al.* are not visible above the noise in the nonresonant spectrum, but are clearly visible with excitation energies near the electronic transitions and are listed in Table III. The spectra were collected with  $\lambda_{exc} = 1024$  nm (1.21 eV) by Esposti *et al.* and with  $\lambda_{exc} = 607$  nm (2.043 eV) in this work. There are additional lines predicted by Esposti *et al.* in this region that were not observed by either experiment.

Symmetry for $C_{2h}$	$E_{\text{literature}}$ ( $\text{cm}^{-1}$ )	$E_{\text{expt}}$ ( $\text{cm}^{-1}$ )
8 $A_g$	1562	
9 $A_g$	1541	
10 $A_g$	1504	1507
11 $A_g$	1469	1473
12 $A_g$	1458	1461
13 $A_g$	1426	1436
14 $A_g$	1366	
17 $A_g$	1265	
18 $A_g$	1237	
19 $A_g$	1218	1223
25 $A_g$	1050	1054
30 $A_g$	740	
33 $A_g$	696	698
39 $A_g$	304	309

published Raman spectrum of  $\alpha$ -6T. The on-resonance spectrum of  $\alpha$ -6T is displayed in Fig. 3. Tables II and III display the frequencies for all of the newly measured intramolecular and intermolecular resonant Raman modes.

Unlike the good correspondence between the predicted and observed frequencies that exists with the off-resonance spectra, these resonant modes do not correspond directly to other modes predicted by Esposti *et al.*<sup>6</sup> However, not all of

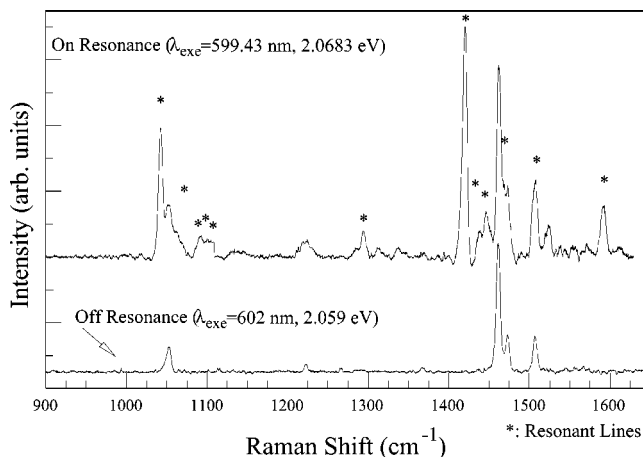


FIG. 3. Raman spectra of  $\alpha$ -6T on resonance,  $\lambda_{exc} = 599.43$  nm (2.0683 eV), and off resonance,  $\lambda_{exc} = 607$  nm (2.043 eV). The background luminescence as well as all instrumental effects have been subtracted out of the original spectra. All resonant vibrational modes are marked with asterisks.

TABLE II. Additional intramolecular Raman modes observed in this work. The spectra were collected with  $\lambda_{exc}=599.43$  nm (2.0683 eV). The vibrational modes listed below are in addition to those modes already listed in Table I. The energy values listed below correspond to the peaks marked with asterisks in Fig. 3.

Frequency (cm <sup>-1</sup> )	Freq. cont. (cm <sup>-1</sup> )
1592	1063
1587	390.5
1522	365
1468.5	343
1446	327
1420.5	318
1417	296
1293.5	277
1284	269
1116	250
1103	239
1091	209

the predicted modes have actually been observed. Therefore, it is conceivable that some of the modes observed in the present work correspond to vibrational modes that were predicted at incorrect frequencies. Additional improvements of the force fields used in their theory (including a coupling to electronic transitions at 2.066 eV and 2.068 eV) would presumably improve the predictions.

The ratio of resonant peak intensity to nonresonant peak intensity is plotted in Fig. 4. The excitation profile clearly has two maxima, suggesting the existence of two excitations. All of the excitation profiles associated with the resonant Raman lines have the same two maxima, at excitation energies of 2.066 eV and 2.068 eV, with a full width at half maximum (FWHM) of 2 meV for each peak. The splitting  $\Delta E=0.002$  eV between the two peaks is 16 cm<sup>-1</sup> when expressed in wave number units.

Both the small width of these resonances and their proximity in energy to the band edge support the identification of the resonance being due to a Frenkel exciton. Previous researchers have identified the lowest-energy singlet Frenkel exciton in a single crystal of  $\alpha$ -6T by photoabsorption spectroscopy at 2.3 eV,<sup>7</sup> but this  $S_1$  exciton is identified to have  $A_u$  symmetry. All Raman modes of a centrosymmetric molecule must be of  $A_g$  or  $B_g$  symmetry. If the resonances measured involve only a single electronic excitation, it must have the same symmetry as the vibrational modes it is coupled to, so both excitations must be of  $A_g$  or  $B_g$  symmetry. Both the difference in energy and the symmetry of the mode to which the electronic excitations couple indicate that the excitations observed in the present work are different from the one Frolov *et al.*<sup>7</sup> observed. Therefore, there must be other, lower-energy electronic transitions in the single crystal of  $\alpha$ -6T, with gerade symmetry, that have not been observed in other experiments.

The fact that the transitions are lower in energy than the previously identified exciton suggests that the resonances observed in this work are due to bound Frenkel excitons. The two different peaks in the intensity profile could correspond

TABLE III. Intermolecular Raman modes observed in this work. The spectra were collected with  $\lambda_{exc}=599.43$  nm (2.0683 eV).

Frequency (cm <sup>-1</sup> )
174.5
145
121
111
96
66
50

to the excitation of two different bound excitons, with different binding energies. Alternatively, the resonances may be due to a triplet state of the Frenkel exciton measured by Frolov *et al.* In the triplet symmetry state, the exciton would have lower energy than the previously measured singlet state. Typical singlet-triplet energy splittings  $\Delta E_{S-T}$  are on the order of 0.5 eV for organic molecules.<sup>8</sup> If the resonances observed in this work are due to the triplet state of the exciton observed by Frolov *et al.*,  $\Delta E_{S-T}=0.23$  eV. Also, typical Davydov splitting energies  $\Delta E_D$  for triplet excitons are of order 10 cm<sup>-1</sup>, whereas  $\Delta E_D$  for singlet excitons generally range from 100 to 1000 cm<sup>-1</sup> (Ref. 8). The  $\Delta E$  observed in this experiment is approximately 16 cm<sup>-1</sup>. Finally, if the singlet exciton is of  $A_u$  symmetry (as identified by Frolov *et al.*), the triplet state must have  $A_g$  symmetry, which is an allowed coupling to the observed Raman modes.

#### IV. CONCLUSION

The Raman spectrum of  $\alpha$ -6T has been measured at multiple temperatures and with multiple excitation wavelengths. The resonant Raman spectra have permitted the identification of electronic transitions not previously measured that couple strongly to vibrational modes. These electronic transitions have been tentatively identified as either trapped Frenkel excitons or a triplet Frenkel exciton state.

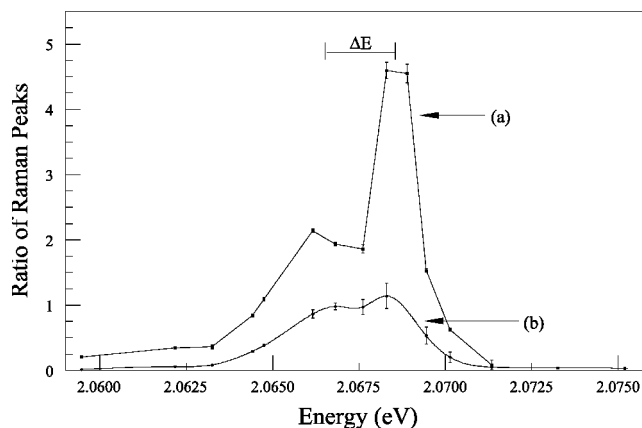


FIG. 4. (a) Ratio of the intensity of the 1045 cm<sup>-1</sup> resonant mode to the 1052 cm<sup>-1</sup> nonresonant mode vs excitation energy. (b) Ratio of the intensity of the 1422 cm<sup>-1</sup> resonant mode to the 1463 cm<sup>-1</sup> nonresonant mode vs excitation energy. The fits for the peaks were made with a least-squares routine assuming Voigt line shapes.

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<sup>1</sup>*Handbook of Oligo- and Polythiophenes*, edited by Denis Fichou (Wiley-VCH, New York, 1990).

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<sup>8</sup>Martin Pope and Charles E. Swenberg, *Electronic Processes in Organic Crystals* (Oxford University Press, New York, 1982).