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RAMAN CHARACTERIZATION OF THE BEDT-TTF(ClO₄)₂ SALT

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Abstract The major Raman scattering peaks of BEDT-TTF(ClO₄)₂ have been assigned by comparison to the isotopically labeled ¹³C(4)-BEDT-TTF(ClO₄)₂ and ¹³C(6)-BEDT-TTF(ClO₄)₂ salts. The ν_2 , ν_3 , and ν_6 A_g modes are associated with the C=C vibrations and the Raman shifts are found to decrease with increasing oxidation state of the ET molecules. The ν_9 and ν_{10} A_g modes are associated with the sulfur (C–S) related vibrations and the Raman shifts are observed to increase with increasing oxidation state of the ET molecules.

INTRODUCTION

Vibrational spectroscopy measurements provide direct information concerning intramolecular and intermolecular vibrations. It has played an essential role in the characterization of various isotopically labeled neutral BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene or ET] molecules during our studies of the isotope effects on the superconducting critical temperatures of (ET)₂X salts.^{1,2} Previous vibrational spectroscopy studies on the charge-transfer salts were largely focused on the infrared measurements due to the difficulty in obtaining good Raman spectra. Black colored charge transfer salts tend to absorb the incident laser beam which often causes severe sample decomposition. The problem is now largely overcome by the use of an optical microscope attachment, a low power laser source (0.06 to 6 mw), and a highly sensitive CCD area detector. With the use of such a Raman microscope spectrometer, we recently reported a study on the C=C double bond related vibrational modes (1400 to 1600 cm⁻¹) of the ET salts.³ Among the (ET)₂X (2:1) salts, we found no major differences in the Raman spectra of the α , β , and κ -phase salts in the 1400 to 1600 cm⁻¹ region, because one would expect the differences which would result from crystal packing should occur at a much lower intermolecular vibration (phonon) region of \sim 200 cm⁻¹ or below. Sharp Raman absorptions with large shifts toward lower wave numbers are observed in the (ET)X (1:1) salts, and an approximately linear correlation between the decrease of the C=C vibration frequencies and the increase of the oxidation states (0 to +1) of the ET molecules, has been found.³ Recently, (ET)X₂ (X⁻ = ClO₄⁻, PF₆⁻) salts have been synthesized and structurally characterized.^{4,5} The oxidation state of the ET

molecule is +2, which is double the value in previously studied ET salts. In order to test the validity of the aforementioned correlation, we have prepared and carried out Raman spectroscopic measurements on the (ET)X₂ salts. Major absorption peaks are assigned according to the isotope shifts in the [¹³C(4)-ET]X₂ and [¹³C(6)-ET]X₂ salts. The results are presented in this article.

EXPERIMENTAL

The preparation of ET, ¹³C(4)-ET, and ¹³C(6)-ET molecules has been reported elsewhere.^{1,2} The isotopic purities of the precursors for the synthesis of ¹³C(4)-ET and ¹³C(6)-ET molecules, ¹³C(2)-1,2-dibromoethane and ¹³CS₂, were better than 99%. The preparation of the corresponding ET(ClO₄)₂ salt was adopted from Talham *et al.*^{4,5} and the typical experimental conditions were as follows: neutral ET (10 mg), NBu₄ClO₄ (~250 mg), solvents: chloroacetylchloride (ClCH₂COCl, Aldrich) with 10% carbon disulfide (CS₂, Aldrich). Immediate color change to deep brownish green, due to chemical oxidation of the ET molecules, was always observed upon mixing. Electrocrystallization was carried out at 1 μA/cm² current density and the (ET)X₂ crystals were harvested after about three weeks. Crystals were observed both on the anode and at the bottom of the anode compartment.

All Raman measurements were carried out at room temperature with a Raman microscope spectrometer (Renishaw Ltd.) equipped with a He-Ne laser (6328 Å). The incident laser power applied was kept below 0.6 mW as higher laser intensity caused sample decomposition to a mixture of 2:1, 1:1, and 1:2 salts. Raman shifts were calibrated against a standard Si peak (520 cm⁻¹). Each spectrum was collected with a 200 sec time constant at a 1 cm⁻¹ resolution and was averaged over 20 scans. Typical time required for data collection of each sample was four to six hours.

RESULTS AND DISCUSSION

The Raman spectrum of ET(ClO₄)₂ between 200 and 1600 cm⁻¹ is shown in Figure 1. There are three groups of strong scattering peaks near 1300, 900, and 500 cm⁻¹. In contrast to the (ET)₂X salts, the strongest peak in ET(ClO₄)₂ occurs near 535 cm⁻¹. The C=C double bond related peaks shift to lower frequencies near 1300 cm⁻¹. Weak and broad peaks near 1460 and 1412 cm⁻¹ indicate the presence of small amounts of (ET)₂X and (ET)X salts, respectively. Two new strong peaks occur near 900 cm⁻¹.

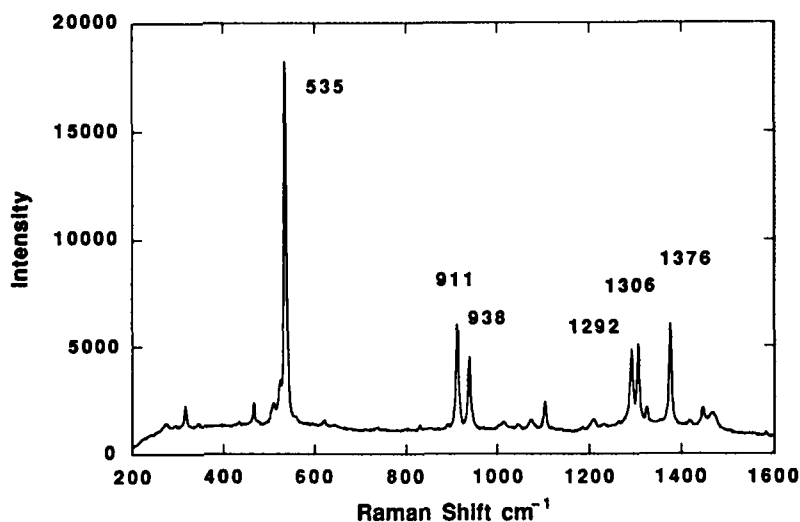


FIGURE 1 Raman spectrum of a ET(ClO₄)₂ crystal at room temperature.

The crystal structure of ET(ClO₄)₂ has been reported in the literature.^{4,5} All ET dications are equivalent and are located in a distorted octahedral environment with six surrounding ET molecules. The intermolecular interactions between ET molecules are weak. The shortest S...S contacts are reported to be 3.621 Å^{4,5} which is slightly longer than the van der Waals sum distance of 3.60 Å.

In order to assign these peaks, we have synthesized and carried out Raman measurements on ¹³C(4)-ET(ClO₄)₂ and ¹³C(6)-ET(ClO₄)₂ salts. The ¹³C(4)-ET and ¹³C(6)-ET denote ET molecules with the outer four ethylene carbon atoms substituted with four ¹³C atoms and the inner six C=C double bonded carbon atoms substituted with six ¹³C atoms, respectively. A schematic drawing of ET, ¹³C(4)-ET, and ¹³C(6)-ET, is shown in Figure 2.

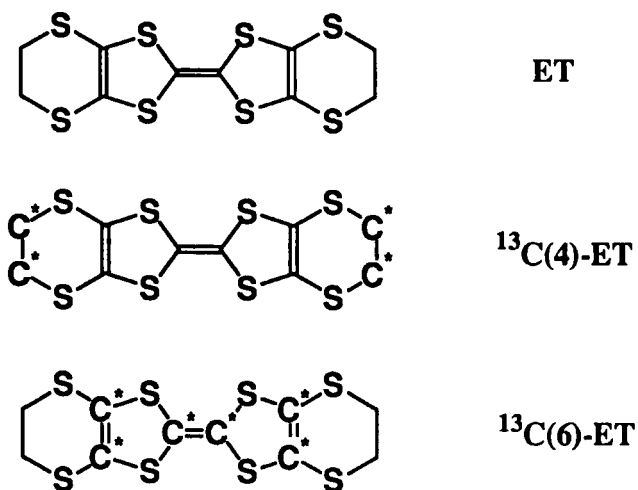


FIGURE 2 Schematic drawing for ET, $^{13}\text{C}(4)\text{-ET}$, and $^{13}\text{C}(6)\text{-ET}$.

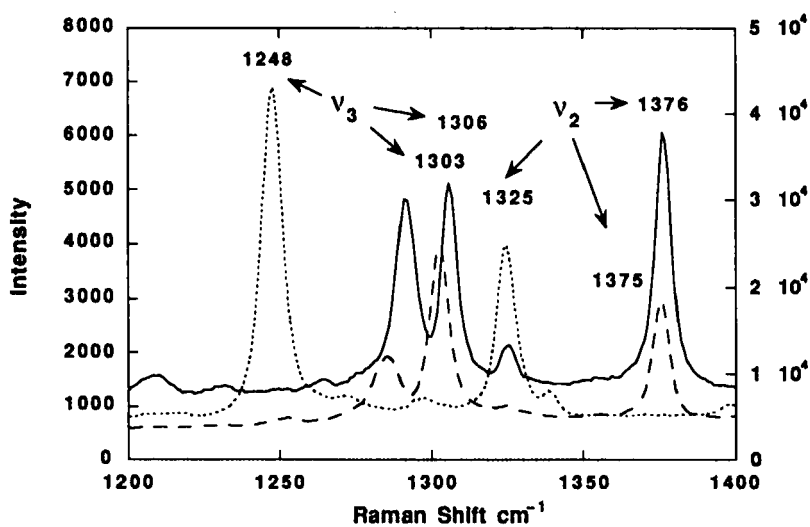


FIGURE 3 Raman spectra of ET(ClO₄)₂ (solid line), $^{13}\text{C}(4)\text{-ET}(\text{ClO}_4)_2$ (long dashed line), and $^{13}\text{C}(6)\text{-ET}(\text{ClO}_4)_2$ (short dashed line) in the C=C region.

We first focus on the C=C double bond region (1200 -1400 cm⁻¹). The Raman spectra of ET(ClO₄)₂ (solid line), ¹³C(4)-ET(ClO₄)₂ (long dashed line), and ¹³C(6)-ET(ClO₄)₂ (short dashed line) between 1200 and 1400 cm⁻¹ are shown in Figure 3. Based on the normal mode calculations by Eldridge, et al.,^{6,7} the ν_2 and ν_3 modes involve the central and two outer C=C double bond in-phase and out-of-phase vibrations. Substitution of the six C=C double bond carbon atoms with ¹³C atoms is expected to cause a large isotope shift between 50 and 60 cm⁻¹.⁸ However, substitution of the outer four ethylene carbon atoms with ¹³C atoms is expected to have little effect on the C=C related Raman shift. This trend is exactly observed in Figure 3. Therefore, the ν_2 and ν_3 bands are assigned as follows: ET(ClO₄)₂: 1376, 1306 cm⁻¹, ¹³C(4)-ET(ClO₄)₂: 1375, 1303 cm⁻¹, and ¹³C(6)-ET(ClO₄)₂: 1325, 1248 cm⁻¹. The remaining strong peaks at 1292 cm⁻¹ for ET(ClO₄)₂, and 1286 cm⁻¹ for ¹³C(4)-ET(ClO₄)₂, are assigned to ν_5 A_g mode (calcd: 1283 cm⁻¹ for neutral ET). The corresponding ν_5 peak for ¹³C(6)-ET(ClO₄)₂ may be associated with a weak hump at ~1295 cm⁻¹.

A new plot of $\nu_{C=C}$ for ET salts including the ET(X)₂ salts against the oxidation state of the ET molecule is shown in Figure 4. The linear correlation for both ν_2 and ν_3 A_g modes with the oxidation state of ET is consistent with the previous result, i.e., the C=C vibration frequency decreases with increasing positive charge on the ET molecule.^{3,9} The result of removing electrons from the ET molecule is taking electrons out of the HOMO which has bonding characteristics with respect to the central and two outer C=C double bonds. The net effect is weakening of the C=C bonds and reduction of the C=C vibration frequencies.

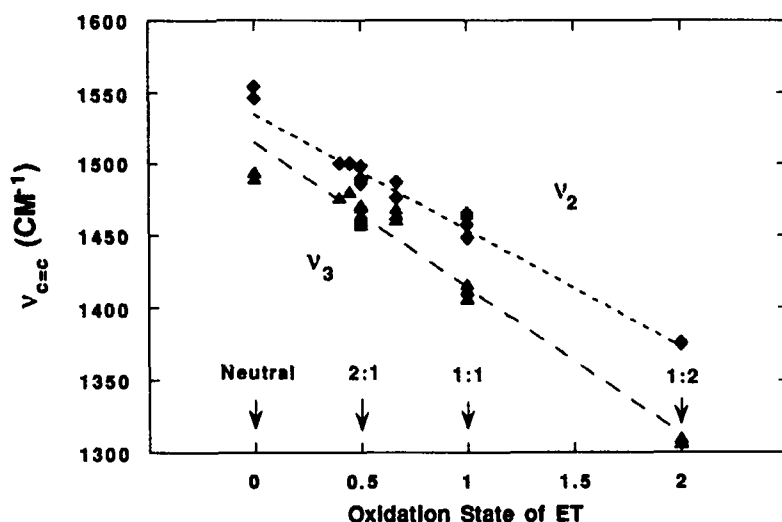


FIGURE 4 The C=C vibration frequencies vs. the oxidation states of the ET molecules in neutral, (ET)₂X, (ET)X, and (ET)X₂ salts.

We now focus on the two strong bands of ET(ClO₄)₂ at 938 and 911 cm⁻¹. The Raman spectra of ET(ClO₄)₂, ¹³C(4)-ET(ClO₄)₂, and ¹³C(6)-ET(ClO₄)₂ in the 800 to 1000 cm⁻¹ region are shown in Figure 5. The most likely assignments for the two absorption peaks are $\nu_6 A_g$ (calcd. 983 cm⁻¹ for neutral ET) and $\nu_7 A_g$ (calcd. 918 cm⁻¹) modes. The calculated shift for the ν_6 mode of neutral ¹³C(6)-ET is 32 cm⁻¹, while the labeling of the four outer ethylene carbons, ¹³C(4)-ET, is not expected to cause a significant shift. This pattern can be identified in Figure 5. Therefore, the $\nu_6 A_g$ mode is assigned as follows: ET(ClO₄)₂: 938 cm⁻¹; ¹³C(4)-ET(ClO₄)₂: 933 cm⁻¹; and ¹³C(6)-ET(ClO₄)₂: 891 cm⁻¹.

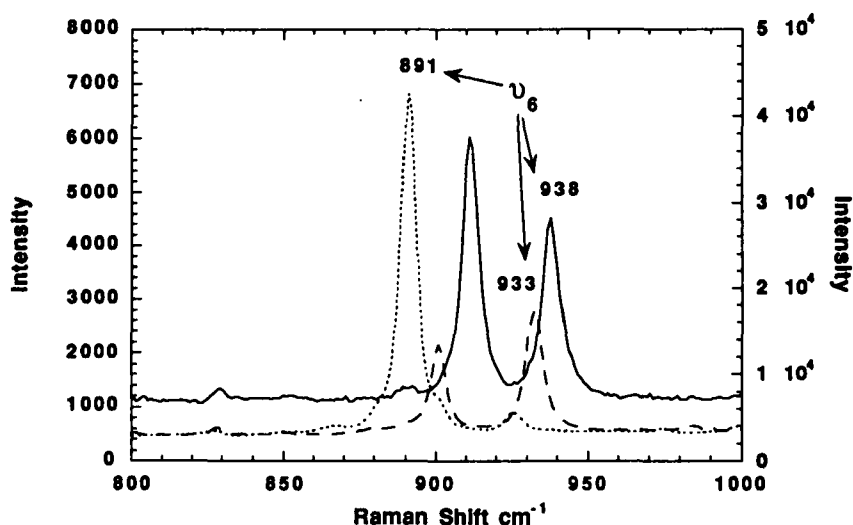


FIGURE 5 Raman spectra of $\text{ET}(\text{ClO}_4)_2$ (solid line), $^{13}\text{C}(4)\text{-ET}(\text{ClO}_4)_2$ (long dashed line), and $^{13}\text{C}(6)\text{-ET}(\text{ClO}_4)_2$ (short dashed line) in the 800 to 1000 cm^{-1} region.

The remaining strong peak of $\text{ET}(\text{ClO}_4)_2$ at 911 cm^{-1} is assigned to the $\nu_7 A_g$ mode which involves the outer ethylene carbon-carbon bonds and the carbon-hydrogen bonds. The corresponding $\nu_7 A_g$ mode of the $^{13}\text{C}(4)\text{-ET}(\text{ClO}_4)_2$ occurs at 901 cm^{-1} that is consistent with a notable isotope shift of 10 cm^{-1} . The $\nu_7 A_g$ mode of the $^{13}\text{C}(6)\text{-ET}(\text{ClO}_4)_2$ seems to be a shoulder centered around $\sim 902\text{ cm}^{-1}$ and overlapped with the strong 891 cm^{-1} ν_6 mode. In Figure 6, the ν_6 and ν_7 vibration frequencies of neutral ET,^{6,10} $\kappa\text{-(ET)}_2\text{Cu[N(CN)}_2\text{]Br}$,¹¹ $(\text{ET})\text{Br}$,¹² and $\text{ET}(\text{ClO}_4)_2$ are plotted against the oxidation state of ET. The ν_6 vibration frequency decreases with increasing oxidation state of ET. The trend is the same as that of the ν_2 and $\nu_3 A_g$ modes. The ν_7 mode shows a similar trend but with a much smaller decrease. Since the ethylene carbon and hydrogen atoms are not in the π system, removing electrons from the ET molecule is not expected to have a significant effect on the ν_7 vibration frequency.

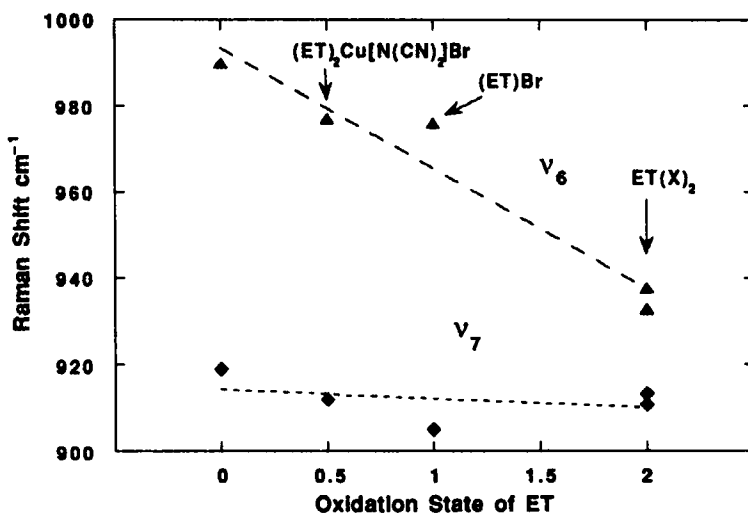


FIGURE 6 The ν_6 and ν_7 frequencies vs. the oxidation states of ET in neutral, $(\text{ET})_2\text{X}$, $(\text{ET})\text{X}$, and $(\text{ET})\text{X}_2$ salts.

We now focus on the strongest peak of the $(\text{ET})\text{X}_2$ salt, which occurs near 500 cm^{-1} . The spectra for $\text{ET}(\text{ClO}_4)_2$ (solid line), $^{13}\text{C}(4)\text{-ET}(\text{ClO}_4)_2$ (long dashed line), and $^{13}\text{C}(6)\text{-ET}(\text{ClO}_4)_2$ (short dashed line) in the 400–600 cm^{-1} region are shown in Figure 7. The frequencies of the three Raman scattering peaks at 535.6, 533.5, and 533.5 cm^{-1} for ET, $^{13}\text{C}(4)\text{-ET}$, and $^{13}\text{C}(6)\text{-ET}$ salts, respectively, are nearly identical. Apparently, ^{13}C labeling has little or no effects on this Raman peak. A reasonable assignment of this scattering peak is ν_9 which is associated with sulfur related vibrations (calculated for neutral ET: 490 cm^{-1}). The remaining peaks at 509.8, 508.8, and 505.7 cm^{-1} for ET, $^{13}\text{C}(4)\text{-ET}$, and $^{13}\text{C}(6)\text{-ET}$ salts, respectively, are similarly assigned to the $\nu_{10} A_g$ mode.

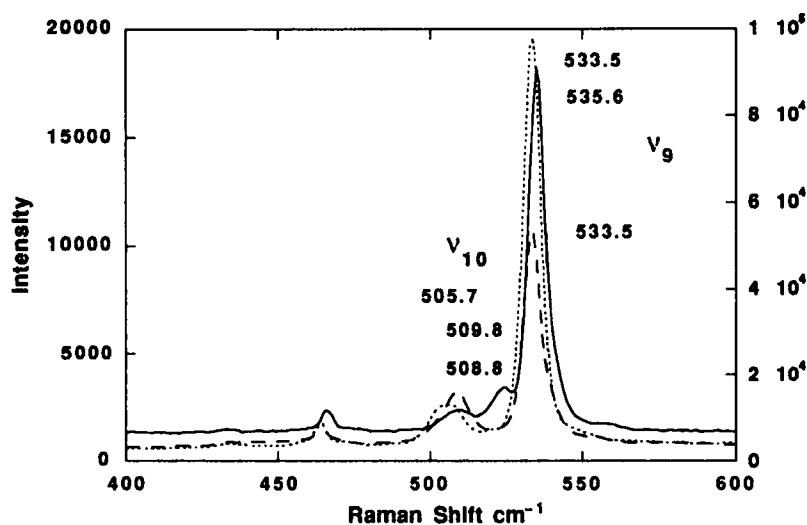


FIGURE 7 Raman spectra of $\text{ET}(\text{ClO}_4)_2$, $^{13}\text{C}(4)\text{-ET}(\text{ClO}_4)_2$, and $^{13}\text{C}(6)\text{-ET}(\text{ClO}_4)_2$ in the 400–600 cm^{-1} region.

Based on the ν_9 and ν_{10} assignments for the $(\text{ET})\text{X}_2$ salts, the newly obtained scattering frequencies along with data for ET ,^{6,7,10} $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$,¹¹ and $(\text{ET})\text{Br}$ ¹² are plotted against the oxidation states of ET in Figure 8. In contrast to the trend shown in Figures 4 and 6, the Raman shifts for the ν_9 and ν_{10} A_g modes increase with increasing positive charge on the ET molecules. The result can be understood in the following way. When electrons are taken from the HOMO which has antibonding characteristics with respect to the C–S bonds, the net result is strengthening of the C–S bonds and increasing of the double bond character between C and S atoms. The observed vibration intensities should be strong and the vibration frequencies shifted toward higher frequency.

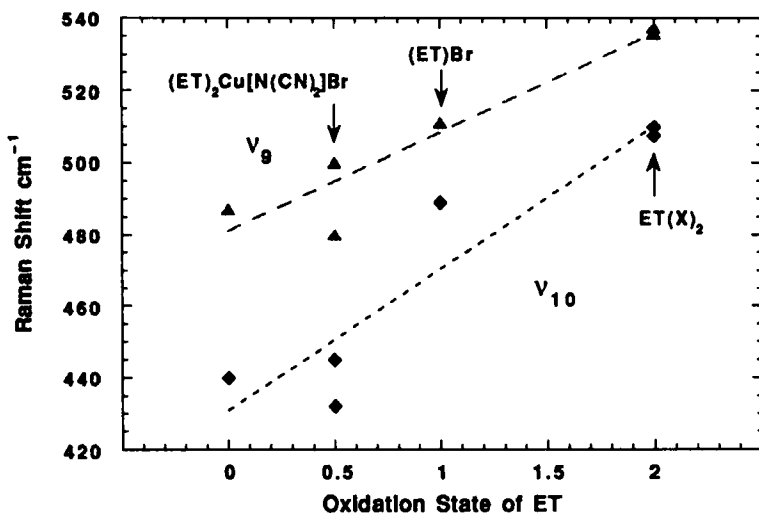


FIGURE 8 The ν_9 and ν_{10} vibrations of ET, κ -(ET) $_2$ Cu[N(CN) $_2$]Br, (ET)Br, and ET(ClO $_4$) $_2$, showing a shift toward higher frequency with increasing oxidation state of ET.

CONCLUSION

The major Raman scattering peaks of ET(ClO $_4$) $_2$ have been assigned with the use of isotopically labeled $^{13}\text{C}(4)\text{-ET}$ and $^{13}\text{C}(6)\text{-ET}$ salts. The ν_2 , ν_3 , and $\nu_6 A_g$ modes show a strong decrease in vibration frequencies with increasing oxidation state of the ET molecules, whereas the ν_9 and $\nu_{10} A_g$ modes show the opposite trend. The results can be rationalized in terms of the bonding characters between the C=C double bonds and the antibonding characters between the C-S bonds.

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