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Low-frequency dynamics of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ observed by ^{13}C NMR

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κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [BEDT-TTF: bis-(ethylenedithio)-tetrathiafulvalene] behaves as a semiconductor at high temperatures, whereas it behaves as a Fermi liquid just above the superconducting transition temperature. To reveal the cause of this behavior, we experimented on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, in which one side of the central C=C in the BEDT-TTF molecules is substituted with ^{13}C nuclei. We perfomed ^{13}C-nuclear magnetic resonance (NMR) spectroscopy on this salt and measured the temperature dependence of its spectral linewidths and its spin-spin relaxation time T_2. We found anomalies in its linewidths and T_2, which we connected to the ethylene motion within the salt. Compared with the ^{13}C-NMR measurements of κ-(BEDT-TTF-$d8$)$_2$Cu(NCS)$_2$, we obtained the experimental evidence of the connection between the ethylene motion and the conduction electrons. Considering this connection, we examined the semiconductive behavior of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at high temperatures. The contribution of ethylene motion to the electronic state is thought to be a common feature of BEDT-TTF salts.

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I. INTRODUCTION

(BEDT-TTF)$_2$X [BEDT-TTF: bis-(ethylenedithio)-tetrathiafulvalene] is characterized by its quasi-two-dimensional electronic properties. It consists of alternating layers of conducting sheets of BEDT-TTF molecules and insulating sheets of anions. In κ-type salts, two BEDT-TTF molecules form a dimer in the conduction sheet.[1]

As shown in Fig. 1(a), the physical properties of κ-(BEDT-TTF)$_2$X were described by a P-T phase diagram, whose horizontal axis corresponds to the chemical and physical pressures.[2–4] Our previous study revealed that κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ shows Fermi-liquid behavior just above the superconducting transition temperature T_c, with an antiferromagnetic correlation and a correlation between the Korringa factor and T_c.[5]

However, this salt does not behave as a simple Fermi liquid at high temperatures. The electrical resistance of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ shows semiconductive behavior with a peak at around 80 K; below 80 K, it steeply decreases showing T^2 dependence just above T_c.[6] This behavior is a feature of all κ-type salts.[2] Several theoretical mechanisms have been proposed to reveal the cause of this complicated behavior;[6,7] however, the actual cause is still unknown. Moreover, anomalies in the thermal-expansion measurements connected to the freezing of the intramolecular motion of the ethylene groups of the BETD-TTF molecules in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ suggest glass transitions at 53 and 70 K.[8] While the relationship between the glass transition and the resistance is interesting and appears to be the main cause of the complicated behavior of the resistance,[6,8,9] there is no experimental evidence of the relationship between the molecular motion and the conduction electrons.

Nuclear magnetic resonance (NMR) spectroscopy enables us to detect the slow dynamics corresponding to the glass transition through the measurement of the spin-spin relaxation time T_2. Therefore to investigate the slow dynamics of the molecular motion and the conduction electrons, we measured the ^{13}C-NMR spectral linewidths and T_2 of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Moreover, to clarify the mechanism of the T_2 process, we performed a measurement of T_2 in κ-(BEDT-TTF-$d8$)$_2$Cu(NCS)$_2$ which had the ^{1}H nuclei of the ethylene groups of the BEDT-TTF molecules substituted with ^{2}D nuclei.

II. EXPERIMENT

To prevent the Pake doublet effect, we enriched one side of the central C=C bond in BEDT-TTF molecules with ^{13}C nuclei [Fig. 1(b)] by using the cross-coupling method.[10,11] Next, we obtained the crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF-$d8$)$_2$Cu(NCS)$_2$ from the electrochemical oxidation of BEDT-TTF and BEDT-TTF-$d8$ in 1,1,2-tricholoroethane in the presence of CuSCN, KSCN, and 18-crown-6 ether.[1] Then, we performed the NMR measurements at an external magnetic field of 9.4 T, parallel to the a axis, which corresponds to a resonant frequency of about 100.7 MHz. The linewidths were taken as full width at half-maxmum (FWHM). We define T_2 as the time corresponding to the Lorentz decay.

III. RESULTS AND DISCUSSION

A. Linewidth and T_2 anomaly

As shown in Fig. 1(c), we observed four peaks in the ^{13}C-NMR spectrum (labeled A through D), because there are two dimers in a unit cell with two central C=C sites which have the different hyperfine coupling constant due to the overlap mode of the dimer.[1] Figure 2(a) shows the temperature dependence of the linewidths in the ^{13}C-NMR spectrum of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The linewidths increase with decreasing temperature from room temperature to a maximum at around 90 K; the linewidths then decrease with decreasing temperature to about 50 K, where they begin increasing again due to magnetic impurities.

In Fourier transform (FT)-NMR, the linewidth is described as

$$\Delta\omega = \frac{2\pi}{T_2} + \gamma \Delta H.$$

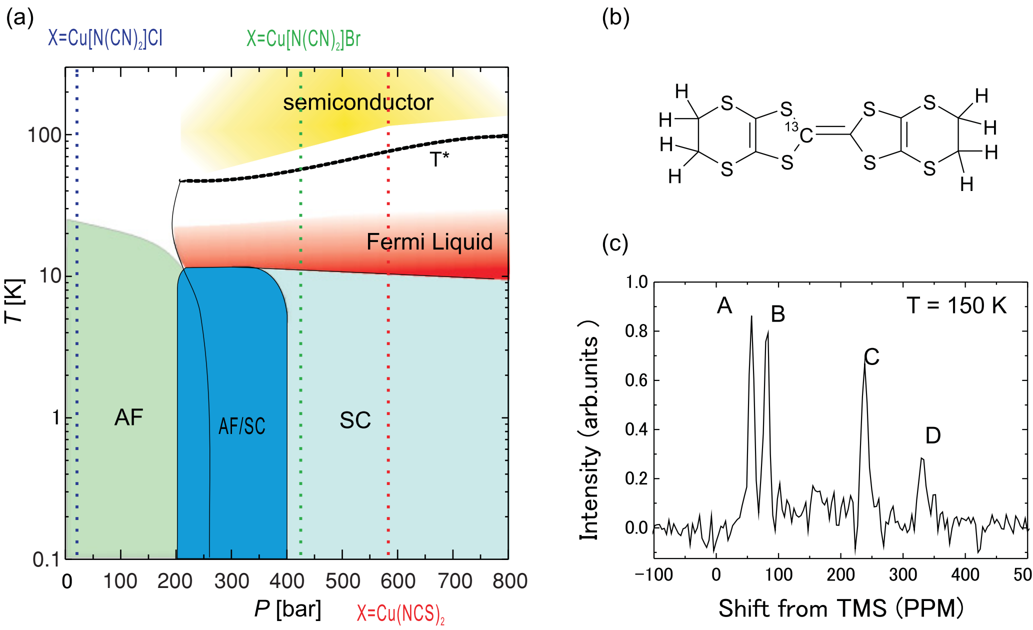

FIG. 1. (Color online) (a) Phase diagram of κ-(BEDT-TTF)$_2$X. (b) BEDT-TTF molecular structure with one side of the central C=C bond replaced with ^{13}C. (c) ^{13}C-NMR spectrum of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.

Here, γ is the nuclear gyromagnetic ratio and ΔH is the inhomogeneity of the local magnetic field at the nuclei. The homogeneous width due to T_2^{-1} and the inhomogeneous width due to ΔH both contribute to the linewidth. To verify whether the increase in the linewidth is due to the homogeneous or inhomogeneous contribution, we measured the temperature dependence of T_2^{-1}.

Figure 2(b) shows the temperature dependence of $T_2{}^{-1}$ at each site in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. We observed two-peak behavior at around $T = 100$ and 125 K in all sites, corresponding to the anomaly in the linewidth near 90 K. Note that T_2^{-1} is higher for sites with a higher hyperfine coupling constant.[5] Below 70 K, the values of T_2^{-1} for all sites are approximately the same and comparable to their values at room

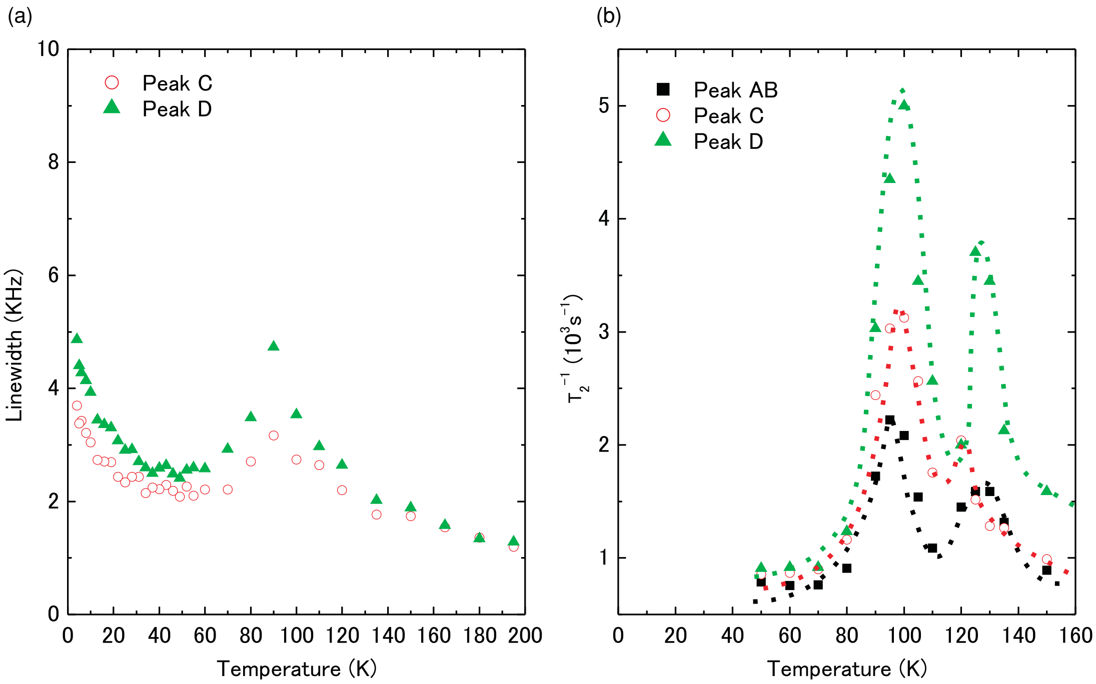

FIG. 2. (Color online) (a) Temperature dependence of the linewidths of the C and D sites in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. We could not evaluate the linewidths of the A and B sites because of their merged of peaks in the ^{13}C-NMR spectrum [Fig. 1(c)]. (b) Temperature dependence of T_2^{-1} in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The dashed lines are guides to the eyes.

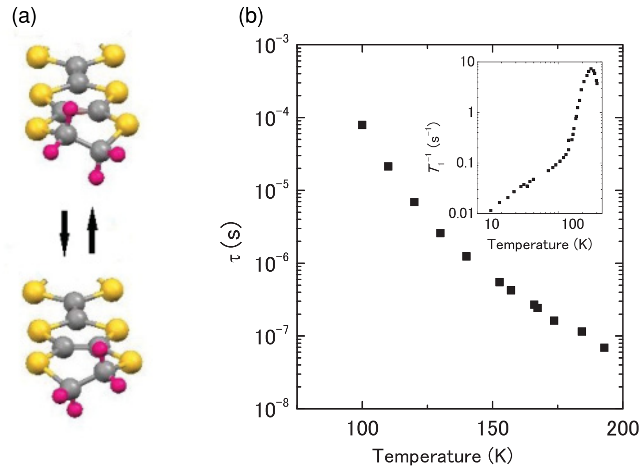

FIG. 3. (Color online) (a) Ethylene motion of the BEDT-TTF molecule. (b) Temperature dependence of τ_c. Inset: temperature dependence of T_1^{-1} for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (data taken from Ref. 14).

temperature. These results suggest that the linewidth anomaly is due to the homogeneous contribution of T_2^{-1} to the linewidths because of the T_2 process. Although the resolution seems not enough to resolve the two anomalies in the linewidths, the shoulder structures were observed at around 120 K.

B. Ethylene dynamics of BEDT-TTF molecule

Here, we discuss the origin of the T_2 anomaly. The slow dynamics below ~10 kHz contribute to the T_2 process.[12,13] At low temperatures, the ethylene motion shown in Fig. 3(a) is probably frozen. We estimated the time scale of the ethylene motion from the temperature dependence of T_1^{-1} for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ from ^{1}H-NMR by Kanoda *et al.*[14,15] [see the inset of Fig. 3(b)]. According to the Bloembergen-Purcell-Pound (BPP) theory,[16] T_1 in a coupled-spin system is described as

$$\frac{1}{T_1} = C\left(\frac{\omega\tau_c}{1+\omega^2\tau_c^2} + \frac{4\omega\tau_c}{1+4\omega^2\tau_c^2}\right),$$

where ω is the NMR frequency, τ_c is the correlation time, and C is a constant. Because the relaxation rate has a maximum at $\omega\tau_c = 0.616$, we determined $C = 5.1\ \mathrm{s}^{-1}$. Assuming the Arrhenius model with $\tau_c = \tau_0 \exp(\Delta E/k_B T)$, we determined $\Delta E = 1500$ K and $\tau_0 = 3.7 \times 10^{-11}$ s. We estimated that the time scale of the ethylene motion decreases to ~10 kHz at around 100 K, as shown in Fig. 3(b), suggesting that ethylene motion is the origin of the T_2 anomaly.

Moreover, the two-peak behavior of T_2^{-1} is consistent with the result of the thermal-expansion measurement. Note that the glass transition occurs at two temperatures in the salt.[8] The peaks of T_2^{-1} at 100 and 125 K correspond to the glass transitions at 53 and 70 K, respectively, because the thermal-expansion measurement detects the phenomenon with the slower time scale than that by the T_2 measurement. The correlation time of the ethylene motion slows down with decreasing temperature and can be detected by the T_2 measurement. At lower temperature, the correlation time increases and corresponds to the "time scale of our daily life" (~10^3 s), and the anomalies were observed as the glass transition by the thermal-expansion measurement. Since κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ belongs to the space group $P2_1$ and the BEDT-TTF dimer is crystallographically nonequivalent, the two ethylene end groups in the dimer are crystallographically nonequivalent. Therefore these are expected to freeze at two different temperatures.

C. Coupling mechanism of T_2 process

It is important to discuss the mechanism causing the T_2 process in the salt. We consider two possible coupling mechanisms. One is that the ethylene motion causes a direct fluctuation in the local field via the dipole interaction; the other is that conduction electron causes an indirect fluctuation in the local field. To determine whether the mechanism is direct or indirect, we substituted ^{13}C nuclei for one side of the central C=C bond in the BEDT-TTF molecule and ^{2}D nuclei for the ^{1}H nuclei of the ethylene groups. While Kawamoto *et al.*[17] observed remarkable isotope effects in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, no significant isotope effect was reported including the lattice constants and the electromagnetic properties in the paramagnetic phase of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. From the thermal-expansion measurement, one of the glass transition temperatures also appears to be the same after the deuteration.[8]

In the case of direct coupling caused by the ethylene motion and the dipole field, T_2^{-1} is proportional to $\gamma^2\tau_c$. Hence the T_2^{-1} anomaly is expected to decrease by ~0.024 after deuteration because the ratio of γ of ^{1}H to γ of ^{2}D is $\gamma_D/\gamma_H \sim 0.15$.

Figure 4(a) shows the temperature dependence of T_2^{-1} of each site in κ-(BEDT-TTF-$d8$)$_2$Cu(NCS)$_2$. The T_2^{-1} of each site has two maximums near 100 and 130 K, similar to the T_2^{-1} of nondeuterated salt (which had two maximums near 100 and 125 K). The isotope effect in which the mass number of the ethylene group increases by 14% was not found within experimental precision. This result indicates that the interaction between ^{13}C nuclei and the ethylene motion is indirect via the conduction electrons. In the case of indirect coupling caused by conduction electrons, the fluctuation parallel to the external field, which contributes to T_2, depends on the hyperfine coupling constant $A_{//}$ at each site. Therefore T_2^{-1} is proportional to $A_{//}^2\tau_c$. This indicates that the ratio of T_2^{-1} for the D site to T_2^{-1} for the C site is about 2:1 ~ 3:1, consistent with the ratio of the hyperfine coupling constants of these sites: $A_{//D}/A_{//C} = 1.8$.[5]

The slow dynamics on the conduction electrons was also reported in (TMTSF)$_2$ClO$_4$, in which the conduction electrons were coupled with the lattice dynamics.[18] The connection between the conduction electrons and not the lattice dynamics but the molecular motion was immediately proposed when scientists discovered molecular conductors; however, there has not been any direct experimental evidence of it. Our results provide direct experimental evidence of the connection between the conduction electrons and the ethylene motion.

D. Consideration from MO calculation

We consider this connection from the aspect of the molecular-orbital approach. BEDT-TTF's highest occupied molecular orbital (HOMO) is approximately distributed on

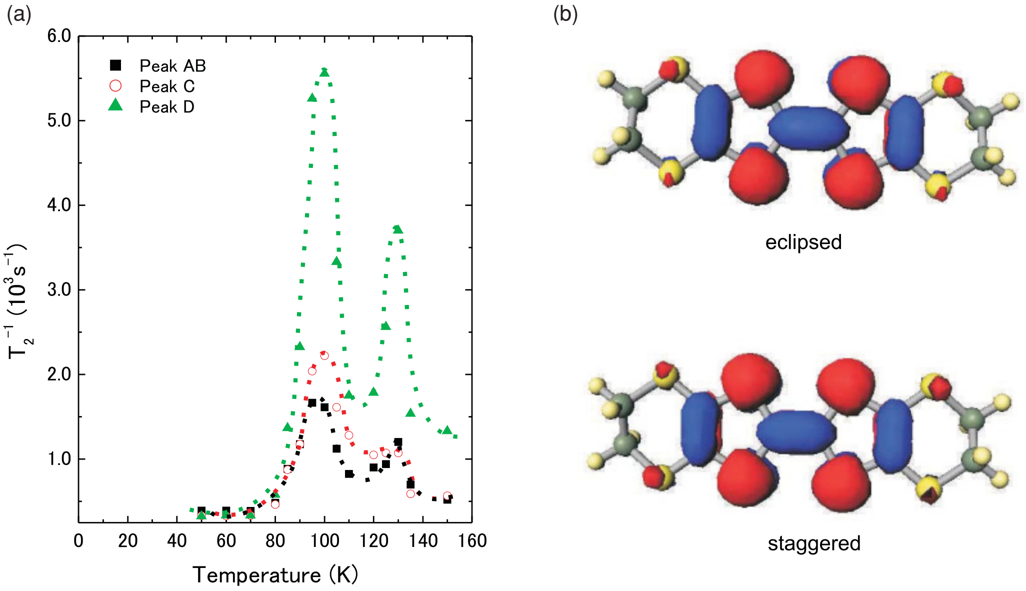

FIG. 4. (Color online) (a) Temperature dependence of T_2^{-1} in deuterated κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The dashed lines are guides to the eyes. (b) BEDT-TTF's HOMO for staggered (upper) and eclipsed (lower) conformations.

the central TTF frame and four outer sulfur atoms with D_{2h} symmetry. However, the symmetry of BEDT-TTF molecule is accurately D_2 for its staggered conformation or C_s for its eclipsed conformation. Figure 4(b) shows the probability amplitude of BEDT-TTF's HOMO calculated for both stable conformations by MOPAC including the structural optimization with the options of AM1, EF, PRECISE, and GNORM=0.05.[19,20] From the symmetry of the amplitude on outer sulfur atoms, they are distinctly different from each other and the difference of the orbital energy between two conformations is 20 meV. The fluctuation of the symmetry is likely to scatter the conduction electron dynamically. This phenomenon is characteristic of molecular conductors whereas the atomic orbital in inorganic conductors does not fluctuate.

E. Comparison with other BEDT-TTF salts

The connection between the conduction electrons and the ethylene motion may be common in BEDT-TTF salts. Indeed, the T_2 anomaly was also observed in β′-(BEDT-TTF)$_2$ICl$_2$[22] and β″-(BEDT-TTF)$_3$Cl$_2$·2H$_2$O.[21] Moreover, the linewidths and T_2 from a ^{13}C-NMR study of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br were also studied in detail. The T_2^{-1} in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br showed a maximum structure at about 135 K.[12] In contrast to that in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, the linewidth begins to increase rapidly at around 150 K and did not decrease.[23,24] This broadening of the linewidth indicates a distribution of the spin or charge density. De Soto *et al.*, claimed that the distribution was associated with the formation of a spin-density-wave (SDW) transition, and T_2 anomaly was regarded as the slowing down of the SDW fluctuation.[23] Mayaffre *et al.*, claimed that the weak Anderson localization model resulting from the static disorder of the ethylene groups[24] was the same as in β-(BEDT-TTF)$_2$I$_3$.[25] However, the static disorder of the two conformations was not observed by the x-ray-diffraction measurement.[26] Contradictorily, the development of the superlattice below 200 K in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br was reported by Nogami *et al.*,[27] This complex behavior is still open. From the view of the ethylene dynamics, we estimated the temperature at which the ethylene motion freezes as about 120–150 K from ^{1}H-NMR,[14,28] and the clear hysteresis of the resistance in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (Ref. 29) at around the glass transition of 80 K was reported, suggesting that the connection between the resistance and the glass transition is the same as in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. More detailed studies of the connection between the ethylene dynamics and structural disorder are required.

F. *T** anomaly

We should mention the T^* anomaly. The κ-type salts show this anomaly in T_1 in ^{13}C-NMR,[5,11,24,30] thermal-expansion measurements,[31] and their optical spectra[32] at the characteristic temperature, $T^* \approx 50$ K. Below T^*, the electronic properties of κ-type salts show Fermi-liquid behavior.[5] Although the mean free path of the conduction electrons begins to increase below T^*,[32] the resistance of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has a maximum above T^* (around 100 K).[6,33] This maximum corresponds to the temperature in which the ethylene motion is slowing down and freezing. We believe that the fluctuation of HOMO by the ethylene motion contributes to the resistance and the reduction of this contribution causes the decrease of the resistance at around 100 K. The anomalies at the T^* differ from the glass transition, suggesting that the decrease in the ethylene motion does not contribute to the mechanism of the T^*. The T^* seems to be the crossover temperature (or transition) to the Fermi-liquid state. The mechanism causing the T^* anomaly is still unknown.

IV. CONCLUDING REMARKS

We observed the anomalies in the linewidths and T_2 from a ^{13}C-NMR spectrum of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. We confirmed that these anomalies are due to the T_2 process connected to the decrease in the ethylene motion. Moreover, by studying T_2 in a deuterated sample, we found that ethylene motion is strongly linked to the conduction electrons. Considering this connection, we can examine the behavior of the electrical resistance of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at high temperatures. The contribution of the ethylene motion to the electronic state is believed to be a common feature of BEDT-TTF salts.

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