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Absence of charge order in the dimerized κ-phase BEDT-TTF salts

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Utilizing infrared vibrational spectroscopy we have investigated dimerized two-dimensional organic salts in order to search for possible charge redistribution that might constitute electronic dipoles and ferroelectricity: the quantum spin liquid κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ [BEDT-TTF: bis-(ethylenedithio)tetrathiafulvalene], the antiferromagnetic Mott insulator κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, and the superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. None of them exhibit any indication of charge disproportionation. Upon cooling to low temperatures all BEDT-TTF molecules remain homogeneously charged within $\pm 0.005e$. No modification in the charge distribution is observed around $T = 6$ K where a low-temperature anomaly has been reported for the spin-liquid material κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. In this compound the in-plane optical response and vibrational coupling are rather anisotropic, indicating that the tilt of the BEDT-TTF molecules in c direction and their coupling to the anion layers has to be considered in the explanation of the electromagnetic properties.

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I. INTRODUCTION

Electronic ferroelectricity and magnetodielectric phenomena are one of the central issues in solid state physics in recent years due to fundamental questions as well as possible applications. It is extensively explored in inorganic transition-metal oxides such as LuFe$_2$O$_4$ or YbFe$_2$O$_4$ (Refs. 1 and 2) but also in organic charge-transfer salts (TMTTF)$_2X$ (TMTTF: tetramethyltetrathiafulvalene).[3] An additional aspect is brought in by multiferroics, i.e., materials with coupled electric, magnetic, and structural order parameters that result in simultaneous ferroelectricity, ferromagnetism, and ferroelasticity.[4,5] While there are different scenarios realized by now,[6,7] here we focus on multiferroicity due to charge ordering, described in the seminal review by van den Brink and Khomskii.[8] In charge-driven ferroelectricity a large magneto-dielectric coupling and a fast polarization switching are expected, since the electric polarization is governed by electrons compared to ions in conventional ferroelectrics.[9]

These phenomena are well studied in one-dimensional organic TMTTF salts,[10–12] for which charge order was proven by NMR spectroscopy,[13,14] dielectric permittivity measurements,[15,16] and Raman and infrared investigations.[17] Calculations based on the extended Hubbard Hamiltonian could reproduce the charge-ordered state.[18,19] The charge per molecule alternates along the stacking direction a between charge-rich ($\rho_0 + \delta$) and charge-poor molecules ($\rho_0 - \delta$). Recent electron spin resonance experiments strongly suggest that two inequivalent magnetic TMTTF chains coexist in the charge-ordered regime,[20] most probably due to the loss of translational invariance in the bc plane. The increase of mosaicity around T_{CO} inferred by x-ray investigations supports the development of ferroelectric domains in the nanometer scale.[21]

As far as two-dimensional organic crystalline materials are concerned, BEDT-TTF [bis-(ethylenedithio) tetrathiafulvalene] salts with quarter-filled conduction band, such as α-(BEDT-TTF)$_2$I$_3$ and θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$, have been established as model compounds of charge order by theory[18] and experiment.[22] The possibility of charge disproportionation in BEDT-TTF systems with half-filled band has been intensely debated in recent years,[23–27] with particular emphasis on the κ-phase salts,[28] which form a triangular lattice of dimerized BEDT-TTF molecules that is subject to frustration.[29–32] Frequencies of certain intramolecular vibrational modes in BEDT-TTF crystals strongly depend on molecular charge, which makes optical spectroscopy one of the most sensitive local probes to investigate the charge distribution.[33–38]

We have performed comprehensive in- and out-of-plane infrared measurements on κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, and κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. For none of these systems do the molecular vibrational modes split upon cooling; thus there is no indication of charge redistribution as the temperature is reduced. This result is seemingly at odds with a dielectric relaxation found in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl,[39–42] which has recently been interpreted as an indication of electronic ferroelectricity.

II. MATERIALS

Single crystals of the quasi-two-dimensional organic charge-transfer salts κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (abbreviated κ-Br), κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (called κ-Cl), and κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (κ-CN hereafter) were grown by standard electrochemical methods.[43,44] In the crystallographic κ phase, conducting layers of cationic BEDT-TTF molecules are separated by essentially insulating anion sheets, as depicted in Fig. 1. The BEDT-TTF donors form face-to-face dimers which themselves are rotated by about 90° with respect to neighboring dimers, as sketched in Fig. 1(b).

κ-CN crystallizes in a monoclinic structure (space group $P2_1/c$) with the long axis of the BEDT-TTF molecules inclined by about 35° with respect to the layer normal,[45] as displayed in Fig. 1(d). For convention, in κ-CN the layer

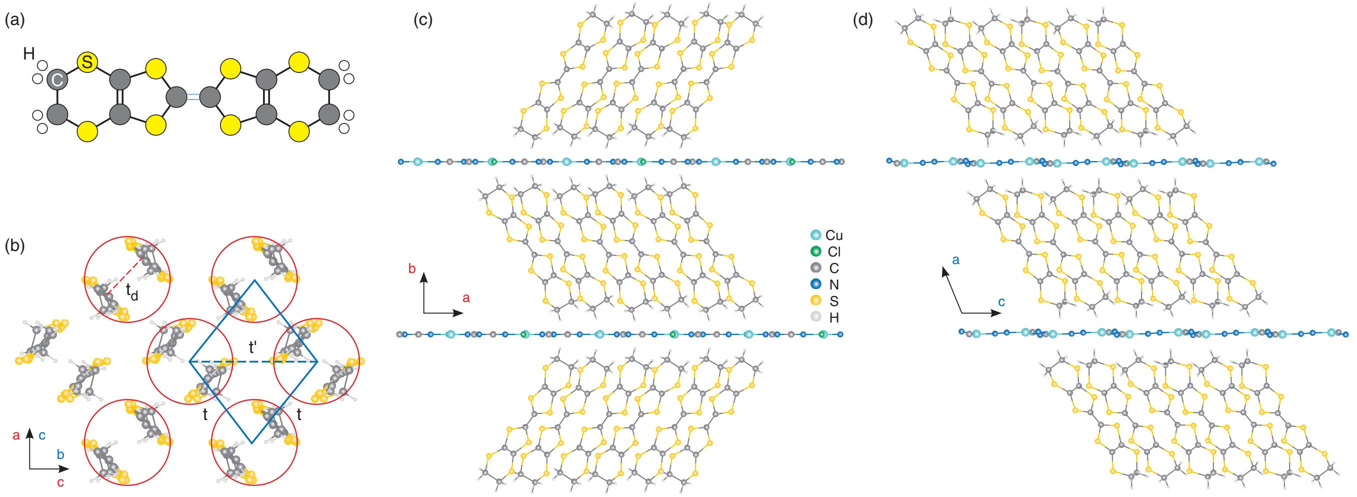

FIG. 1. (Color online) (a) Sketch of the BEDT-TTF molecule. (b) For κ-(BEDT-TTF)$_2X$ the molecules are arranged sideways in dimers (strongly coupled by t_d), which constitute an anisotropic triangular lattice. The interdimer transfer integrals are labeled by t and t'. In the case of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl the plane is labeled as *ac*, while it is the *bc* plane in the case of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, as denoted by the arrows, labeled red and blue, respectively. (c) The side view on κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl demonstrates the staggered layers of BEDT-TTF molecules separated by sheets of polymeric anions. (d) The structure of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ consists of one layer tilted by $\beta = 123^\circ$ at room temperature (125° at low temperatures).

spans in the *bc* plane and the *a* axis points between the layers, i.e., parallel to the BEDT-TTF molecules (a^* is normal to the *bc* plane). The Cu$_2$(CN)$_3$ anions form a flat infinite two-dimensional network of copper and cyano groups in the *bc* plane. In the case of isostructural compounds κ-Br and κ-Cl the polymeric anions consist of parallel infinite zigzag ···dicyanoamido-Cu(Cl/Br)-dicyanoamido··· chains running along the *a* direction. The compounds form orthorhombic (space group *Pnma*) two-layer systems (anion layers in the *ac* plane, with the *b* axis perpendicular to it) with four (BEDT-TTF)$_2$ dimers per unit cell due to the tilting along *a* in the opposite direction for adjacent layers, as displayed in Fig. 1(c).[46,47]

All three compounds are two-dimensional half-filled electron systems with considerably strong electronic correlations that places them close to a metal-insulator transition driven by effective electronic correlations U/t, where U is the on-site Coulomb repulsion and t is the transfer integral. Due to the large orbital overlap, κ-Br is the organic superconductor with the highest transition temperature of 11.8 K at ambient pressure;[46] upon cooling it crosses over from a bad metal to a Fermi liquid around $T_{\rm coh} \approx 30$ K.[48,49] The sister compound κ-Cl is a Mott insulator with antiferromagnetic order at low temperatures ($T_N \approx 25$ K).[50–52] Applying a small amount of pressure (300 bars) reduces U/t sufficiently to cross the insulator-metal phase boundary (where it becomes superconducting at $T_c = 12.8$).[47] Also chemical pressure by Br substitution is a tuning parameter to investigate the bandwidth-driven Mott insulator-metal transition.[48,53] For the Mott insulator κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ hydrostatic pressure of 1.5 kbar is required to reach the superconducting state at $T_c = 2.8$ K.[45,54] This compound has triggered particular interest because at ambient pressure no indication of magnetic order could be observed down to lowest temperatures, despite the considerable antiferromagnetic exchange of $J \approx 250$ K within the triangular lattice.[55,56]

The transfer integral t_d of the two molecules composing the dimer is commonly assumed to be approximately 0.2 eV (Refs. 54 and 57) and the on-site Coulomb repulsion, $U \approx 2t_d$.[58,59] The coupling between the dimers is smaller by a factor of 3–6 compared to the intradimer transfer integrals. The effective Coulomb interaction U/t increases considerably when going from the metal κ-Br to the Mott insulator κ-CN, as summarized in Table I. More important, however, is the degree of frustration expressed by the ratio of the interdimer transfer integrals, that is, $t'/t \approx 0.42$ and 0.44 in the case of the Fermi-liquid κ-Br and the Mott insulator κ-Cl, respectively. For the spin-liquid compound κ-CN, the effective Hubbard U is larger ($U/t = 7.3$), and most importantly, the transfer integrals $t'/t = 0.83$ are very close to equality.[30] Similar values for the frustration have been obtained from *ab initio* derivations by Nakamura *et al.*[60] It should be pointed out, however, that the origin of a spin liquid is not the strong frustration in the Heisenberg term (measured by t'/t), but the higher-order exchanges due to charge fluctuations, such as ring exchange.[27,56] For most models and theoretical descriptions, the interaction between BEDT-TTF layers and anions is neglected, however,

TABLE I. Hopping parameters t' and t of different κ-phase salts obtained from density functional theory calculations (Ref. 30). The ratio t'/t is a measure of frustration. In all cases the intradimer transfer integral is assumed to be $t_d = 0.2$ eV and the on-site Coulomb repulsion, $U \approx 2t_d$ (Refs. 54 and 57–59). The Hubbard U with respect to t is a measure of the effective electronic correlations.

κ-(BEDT-TTF)$_2X$ $X =$	t'/t	U/t	t_d (meV)	t (meV)	t' (meV)
Cu[N(CN)$_2$]Br	0.42	5.1	200	78	33
Cu[N(CN)$_2$]Cl	0.44	5.5	200	73	32
Cu$_2$(CN)$_3$	0.83	7.3	200	55	45

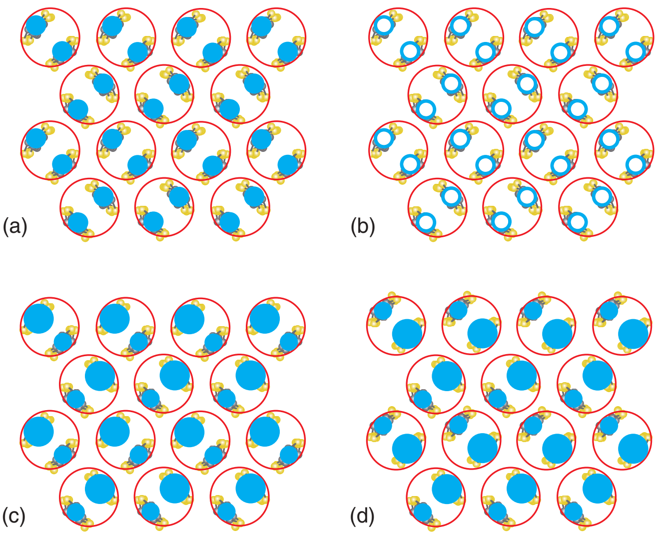

FIG. 2. (Color online) For κ-(BEDT-TTF)$_2X$ the molecules are arranged in dimers of two BEDT-TTF molecules. Commonly each molecule is assumed to carry equal charge (symbolized by the blue dots); this can be (a) static or (b) fluctuating. Alternatively, it is suggested that the molecules carry unequal charge. This charge disproportionation could form a dipolar solid with the net polarization along the (c) vertical or (d) horizontal direction.

recently performed first-principles density-functional theory calculations indicate the importance of donor-anion hydrogen bonding.[61]

Hotta suggested[23,27] that despite the strong intradimer coupling, t_d quantum electric dipoles are formed on the dimers which interact with each other and thus modify the exchange coupling J between the spins on the dimers, crucial for the formation of the spin-liquid state. Starting with a quarter-filled extended Hubbard model that includes the interaction V between molecules on the same but also different dimers, she derives an effective dipolar-spin model. The quantum electric dipoles fluctuate by t_d. For large t_d ($t_d \gg V$) a dimer Mott insulator is stable, forming a dipolar liquid, but if V is large compared to t_d, charge order emerges (dipolar solid), as sketched in Figs. 2(c) and 2(d).

Similar considerations have been put forward by other groups.[24,25] Clay, Mazumdar, and collaborators[26] focus on the magnetic properties of these dimerized systems. They could show that a frustration-induced transition occurs from Néel antiferromagnetism to a spin-singlet state in the interacting quarter-filled band on an anisotropic triangular lattice. In the spin-singlet state the charge on the molecules becomes uneven: a paired-electron crystal is formed with pairs of charge-rich sites separated by pairs of charge-poor sites, as depicted in Figs. 2(c) and 2(d). This spin-singlet formation is caused by quantum effects and does not depend on the nearest-neighbor interaction V; it is solely driven by frustration. A so-called paired-electron liquid might form that contains both charge and singlet-bond fluctuations.

Within the dimer model, Imada and collaborators[62] presented an *ab initio* study of κ-phase materials applying a single-band extended Hubbard model. They discovered that charge fluctuations are enhanced by the interdimer Coulomb interaction. It is not clear whether the magnetic phase is stable in the presence of charge fluctuations[63] or whether magnetic and ferroelectric order exclude each other.[24] Certainly further experiments are needed before these issues can be resolved.

III. VIBRATIONAL SPECTROSCOPY

Reflection measurements were performed on as-grown surfaces of single crystals with light polarized along the two principal optical axes, which are $E \parallel b$ and $E \parallel c$ in the case of κ-CN and $E \parallel c$ and $E \parallel a$ in the case of κ-Cl and κ-Br. Besides regular in-plane experiments, we put particular emphasis on the polarization perpendicular to the conducting BEDT-TTF planes, a direction which couples to the most charge-sensitive infrared-active intramolecular vibrational mode $\nu_{27}(b_{1u})$. To this end we utilize a Bruker Hyperion infrared microscope attached to the Fourier-transform spectrometer Bruker IFS 66v/s or Vertex 80v.[34,36] The data were collected on the narrow side of the crystals[64] with a spectral resolution of 1 cm^{-1}. The sample was cooled down to $T = 12$ K by a Cryovac Microstat cold-finger cryostat. For the in-plane reflection of κ-CN we also performed temperature-dependent far-infrared measurements using a Bruker IFS 113v equipped with a cold-finger cyostat and *in situ* gold evaporation as reference.[34] In addition, the high-frequency optical properties (up to 35 000 cm^{-1}) were determined by spectroscopic ellipsometry at room temperature. In order to perform the Kramer-Kronig analysis using a constant reflectivity extrapolation at low frequencies and temperatures for the Mott insulators κ-CN and κ-Cl, while a Hagen-Rubens behavior was assumed for elevated temperatures; for κ-Br it was, in general, utilized.[65]

In order to follow the vibrational modes down to lower temperatures, we additionally conducted optical transmission measurements on a powdered sample. For that purpose single crystals of κ-CN were mixed with KBr and ground to a fine powder that was pressed to a 0.35-mm-thick disk. The freestanding pellet was placed in a He-bath cryostat and cooled down to $T = 2.3$ K and measured by a Bruker IFS 113v in the midinfrared range.

IV. RESULTS AND ANALYSIS

In Fig. 3 the frequency-dependent conductivity of κ-Br, κ-Cl, and κ-CN is displayed for the midinfrared range between 500 and 2000 cm^{-1} measured at room and low temperatures ($T = 12$ K). The in-plane optical spectra (upper panels) are dominated by the electronic background that changes strongly with temperature. Since it has been investigated previously by several groups,[53,66–69] we present our latest results in the Appendix. For the out-of-plane conductivity (lower panels) the conductivity is an order of magnitude lower and exhibits no significant temperature dependence in the overall behavior.[70] The vibrational features are well resolved and become narrower upon cooling. The present communication deals only with the analysis and discussion of the molecular vibrations.

As pointed out by Girlando,[37] Yakushi, and collaborators[33,35] the totally symmetric molecular vibrations $\nu_2(a_g)$ and $\nu_3(a_g)$ (sketched in Fig. 4) exhibit a strong dependence on ionicity of approximately -125 cm$^{-1}/e$. As presented in the Appendix, neither for κ-Br, κ-Cl, nor for κ-CN do we observe a splitting of these modes or some appreciable

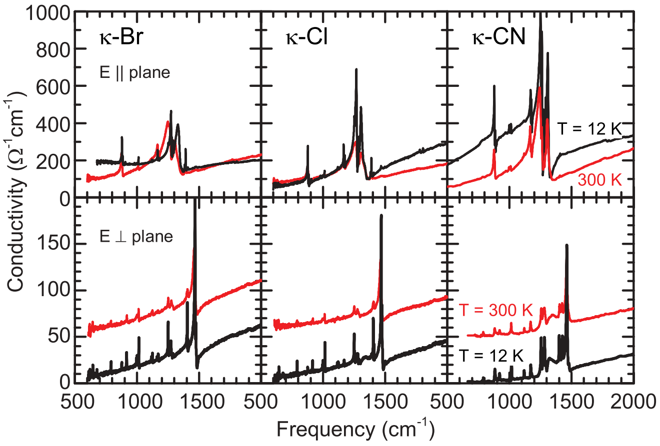

FIG. 3. (Color online) Optical conductivity of κ-(BEDT-TTF)$_2X$ measured within (upper frames) and perpendicular (lower frames) to the BEDT-TTF planes. In the lower row the room-temperature spectra (red lines) are shifted by 50 $(\Omega\,\text{cm})^{-1}$ with respect to the one measured at $T = 12$ K (black curves). For κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, the light was polarized $E \parallel b$ and $E \perp b$, while for κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ the polarizations were $E \parallel b$ and $E \parallel a^*$, respectively.

shift beyond the usual thermal dependence. Note, however, the ν_2 and ν_3 modes are not well suited for infrared determination of the ionicity because they are strongly affected by the electronic coupling strength and location of the midinfrared band. The superior local probe of the molecular charge is the antisymmetric stretching mode $\nu_{27}(b_{1u})$ that involves the outer C=C; its eigenfrequency shifts according to[35]

$$\nu_{27}(\rho) = 1398\ \text{cm}^{-1} + 140(1-\rho)\ \text{cm}^{-1}, \qquad (1)$$

where ρ is the site charge. According to the stacking of the BEDT-TTF molecules in the planes, this mode can be best observed perpendicular to the crystal plane.

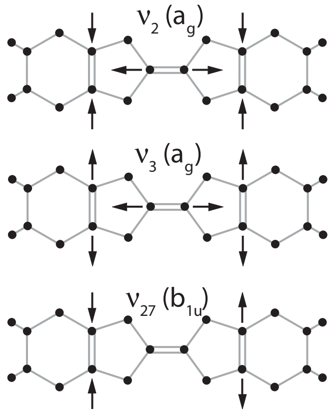

FIG. 4. Sketch of the three most charge-sensitive C=C stretching modes of the BEDT-TTF molecule: $\nu_2(a_g)$, $\nu_3(a_g)$, and $\nu_{27}(b_{1u})$, according to D_{2h} symmetry (Ref. 37).

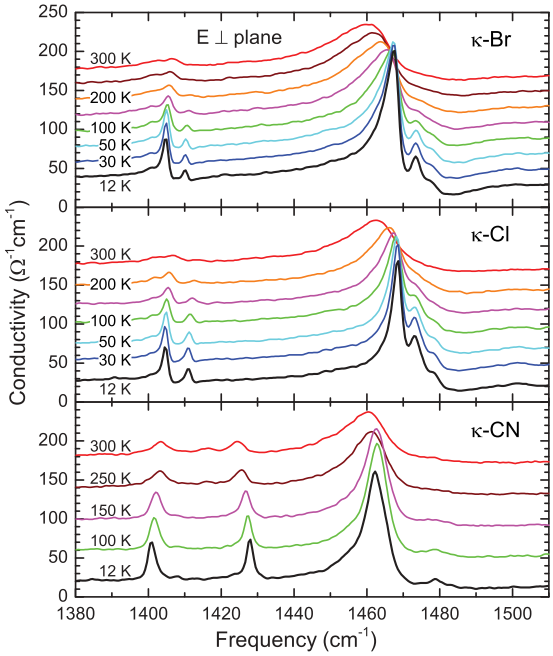

FIG. 5. (Color online) Temperature evolution of the out-of-plane optical conductivity of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, and κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, measured at the small side of crystals with the electric field polarized perpendicular to the BEDT-TTF planes. The dominant vibrational mode $\nu_{27}(b_{1u})$ is a very sensitive local probe of charge per molecule.

In Fig. 5 the midinfrared conductivity ($E \perp$ planes) of κ-Br, κ-Cl, and κ-CN is plotted for different temperatures; at 1460 cm^{-1} we observe the ν_{27} mode right where it is expected for half a hole per BEDT-TTF molecule. With decreasing temperature there is a slight hardening of a few cm^{-1} and a strong narrowing due to the decrease in interaction with low-lying phonons.[33] The reduced width of the ν_{27} feature makes two side bands visible at 1473 and 1478 cm^{-1} in κ-Br and κ-Cl; κ-CN develops a single satellite at 1479 cm^{-1}. Temperature-dependent Raman and infrared experiments on κ-Br confirm our observations: Maksimuk *et al.*[33] could better describe their Raman spectra with two Lorentzians at 1468 and 1475 cm^{-1} (Ref. 71). The reason for the difference lies in the crystallographic inequality among the BEDT-TTF molecules. As depicted in Fig. 1, κ-CN consists of a single conducting layer with two dimers per unit cell, while in κ-Br and κ-Cl the molecules in adjacent layers are tilted in opposite directions.

Similarly the $\nu_{28}(b_{1u})$ mode shows up as a doublet at around 1405–1411 cm^{-1} for the double-layer compounds κ-Br and κ-Cl, while as a single line in κ-CN, the mode slightly softens upon cooling. It is interesting to note that the mode at 1428 cm^{-1}, which hardens with decreasing temperature, is present only in κ-CN.

There is cumulating evidence[55,72–75] that the spin-liquid compound κ-CN undergoes some transition at low temperatures. In order to experimentally verify whether a charge rearrangement happens around the 6 K anomaly, we have performed powder transmission measurements down to temperatures as low as 2.3 K. In Fig. 6 the absorption spectra of κ-CN are plotted for different temperatures. The peak at 1464 cm^{-1} corresponds to the $\nu_{27}(b_{1u})$ mode in accord with the reflectivity data presented in Fig. 5; it slightly hardens by approximately 2 cm^{-1} and becomes narrower as the temperature is reduced. The peak position is plotted in Fig. 6(b) as a function of temperature. There is some tiny increase of the $\nu_{27}(b_{1u})$ frequency for $T \leqslant 8$ K, but the uncertainty of the

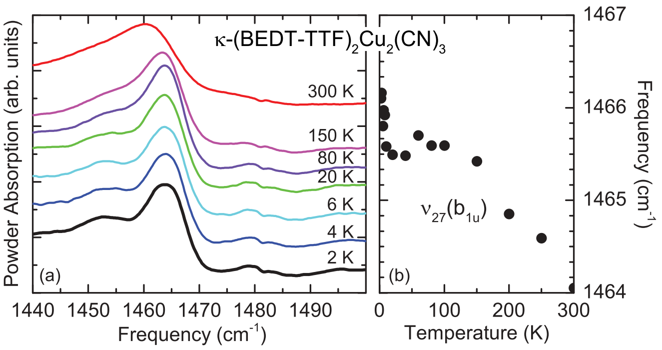

FIG. 6. (Color online) (a) Powder absorption of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ in the range of the C=C molecular vibrations. The curves for selected temperatures are displaced for clarity reasons. (b) Temperature dependence of the center frequency. The vibrational mode $\nu_{27}(b_{1u}) = 1464$ cm^{-1} slightly hardens upon cooling and remains basically unchanged for $T \leqslant 100$ K, in accord with the reflection data.

fit does not allow to make a strong statement about significant changes at the low-temperature anomaly.

V. DISCUSSION

A. Fluctuations

In a typical charge-ordered system such as α-(BEDT-TTF)$_2$I$_3$ the charge imbalance amounts to $2\delta = 0.6e$, which results in a splitting of 80 cm^{-1} for the $\nu_{27}(b_{1u})$ mode, in full accord with our detailed theoretical and experimental investigations.[76–78] This molecular vibration not only shifts strongly with temperature at $T_{\rm CO}$, it also becomes extremely narrow: at 10 K the width $\Delta\nu \approx 2.3$ cm^{-1}.

Nothing like that is found in the systems investigated here; neither in the metal κ-Br, the Mott insulator κ-Cl above or below the antiferromagnetic ordering, nor in Mott insulator κ-CN, which is supposed to be a spin liquid. Our present findings confirm previous temperature- or pressure-dependent Raman and infrared experiments by various groups.[33,53,70,79–82] Also, complementary methods such as nuclear magnetic resonance (NMR) or x-ray scattering do not evidence charge disproportionation in any of these κ-phase compounds.[83] Pictures like Figs. 2(c) and 2(d) with a permanent electric dipole can basically be ruled out. The experimental findings do not depend on whether the dipoles are oriented or disordered; they unambiguously lead to the conclusion that there is no charge imbalance of appreciable magnitude.

From Eq. (1) we can estimate that a charge disproportionation of 1% would correspond to a splitting of about 3 cm^{-1}. Since our data are taken with a frequency resolution of 1 cm^{-1}, we can exclude any charge imbalance of more than $\pm 0.005e$, i.e., $2\delta = 0.01e$.

As seen from Fig. 5, the width of the ν_{27} modes decrease with reduced temperature, discussed quantitatively in the subsequent Sec. V B. Nevertheless they are broader than the correspondent mode observed in α-(BEDT-TTF)$_2$I$_3$: at the lowest temperature $\Delta\nu \approx 6.5$ cm^{-1} in the case of κ-CN. Similar observations were made by Yamamoto *et al.*[82] by looking at the linewidth and temperature dependence of the Raman-active $\nu_2(a_g)$ mode and the infrared active $\nu_{27}(b_{1u})$ mode in κ-CN. The extended width of these molecular vibrations may be caused by inhomogeneities in the environment, or by a distribution of the charge per molecule.

If we imagine the electronic charge fluctuating within the dimer and not remaining static as assumed in common models of charge disproportionation, we can quantitatively estimate the fluctuation rate. Depending on the time scale of fluctuations and probe, this results in either a broadening or a splitting of the mode. Kubo suggested a "two-states-jump model" to describe charge to "jump" stochastically between two molecules.[84] Since the vibrational modes in the charge-ordered state do have very different strengths,[37] the original formula had to be extended to account for the different infrared intensities, frequency, and band shape of the mode in differently charged molecules.[78] The band-shape function is given by the real part of the following function:

$$\mathcal{L}(\omega) = \frac{\mathcal{F}[(\gamma + 2v_{\rm ex}) - i(\omega - \omega_{\rm w})]}{\mathcal{R}^2 - (\omega - \omega_1)(\omega - \omega_2) - 2i\Gamma(\omega - \omega_{\rm av})}. \qquad (2)$$

Here $\mathcal{F} = f_1 + f_2$, with f_1, f_2 being the oscillator strengths of the bands of frequency ω_1 and ω_2 and halfwidth γ. The charge fluctuation velocity is $v_{\rm ex}$, $\Gamma = \gamma + v_{\rm ex}$ is the resulting width, and the abbreviation $\mathcal{R}^2 = 2\gamma v_{\rm ex} + \gamma^2$. Finally, we define the average and weighted frequency, $\omega_{\rm av}$ and $\omega_{\rm w}$, by

$$\omega_{\rm av} = \frac{\omega_1 + \omega_2}{2} \quad \text{and} \quad \omega_{\rm w} = \frac{f_2\omega_1 + f_1\omega_2}{f_1 + f_2}. \qquad (3)$$

If the charge oscillations are slow, $v_{\rm ex} \ll |\omega_1 - \omega_2|/2$, Eq. (2) yields two separated bands centered around ω_1 and ω_2, while if $v_{\rm ex} \gg |\omega_1 - \omega_2|/2$, the motional narrowing will give one single band centered at the intermediate frequency $\omega_{\rm av}$. Finally, when $v_{\rm ex} \approx |\omega_1 - \omega_2|/2$ we shall observe one broad band shifted towards the mode with larger oscillator strength.

We do not see any splitting of the ν_{27} vibrational mode, and the peaks become narrower as the temperature is reduced, instead of broader as expected from a growing charge disproportionation. The width at low temperatures, however, remains about three times larger than observed in α-(BEDT-TTF)$_2$I$_3$, for instance. This can be explained by some minor inhomogeneity in the charge arrangement among the molecules, which is not identical for each dimer. If the charge distribution is not static, the fluctuations have to be at a time scale of 10^{-11} s or faster.

B. Fano shape

In order to more quantitatively analyze the ν_{27} mode displayed in Fig. 5, we have fitted the vibrational bands for each temperature. Surprisingly, the features are rather asymmetric, which might in part be caused by charge fluctuations as discussed in the previous Sec. V A. Since fits by Lorentz oscillators yield unsatisfactory results, we utilized the phenomenological Fano model[85] for which the real and imaginary parts of the conductivity read

$$\sigma_1^{\rm Fano}(\nu) = \sigma_0 \frac{\gamma\nu\left[\gamma\nu(q^2 - 1) + 2q\left(\nu^2 - \nu_0^2\right)\right]}{\left(\nu^2 - \nu_0^2\right)^2 + \gamma^2\nu^2}, \qquad (4a)$$

$$\sigma_2^{\rm Fano}(\nu) = \sigma_0 \frac{\gamma\nu\left[(q^2 - 1)\left(\nu^2 - \nu_0^2\right) - 2\gamma\nu\right]}{\left(\nu^2 - \nu_0^2\right)^2 + \gamma^2\nu^2}, \qquad (4b)$$

where σ_0 is the amplitude of the Fano contribution and q is the phenomenological coupling parameter. Here strong coupling $q = 0$ yields an antiresonance and no coupling $q = \pm\infty$ gives a Lorentzian shape; the negative sign indicates that the maximum in $\sigma_1(\nu)$ occurs at low frequencies, while the minimum is located at high frequencies. We define the linewidth $\gamma = 1/2\pi c\tau$, the resonance frequency $\nu_0 = \omega_0/(2\pi c)$, and the spectral weight $\int |\sigma_1(\nu)|\, d\nu = \nu_p^2/8$, where the absolute value has to be taken because the Fano contribution can also be negative in sign.

The Fano model is commonly employed to describe the interaction of vibrational modes with the electronic background. Here, however, we probe the out-of-plane direction with basically no conductivity present. The tilt of the molecules by about 35° might give some coupling to the in-plane conductivity. Below 50 K the in-plane conductivity of κ-Br and κ-Cl differs by orders of magnitude; nevertheless the ν_{27} modes and their couplings are not that much different. This indicates that it is not the interaction to the conduction electrons that mainly causes the Fano shape.

In the cases of κ-Br and κ-Cl four modes are needed, with one significantly stronger, but all of them follow a very similar temperature dependence. In Fig. 7 the parameters of the dominant peaks for each compound are plotted as a function of temperature. For all three materials the center frequency shifts up as the temperature is reduced to approximately 100 K and then basically saturates. There is a slight downshift observed for κ-Br and κ-CN, but not for κ-Cl. In all cases the spectral weight of the mode is significantly reduced when going to low temperatures [Fig. 7(c)]; κ-Br exhibits some anomaly around 200 K which cannot be unambiguously assigned at this point. We are tempted to relate it to the rearrangement of the ethylene groups that takes place in κ-(BEDT-TTF)$_2X$ salts at elevated temperatures. Interestingly, for κ-CN we observe even a slight increase for very low temperatures. If we consider the peak-to-peak difference $\Delta\sigma$ between the maximum and minimum in conductivity, for all three compounds, we find a continuous increase from $\Delta\sigma = 60\ (\Omega\,\mathrm{cm})^{-1}$ to approximately 150 $(\Omega\,\mathrm{cm})^{-1}$ as the temperature decreases to 12 K. This is related to the Fano coupling q [Fig. 7(d)] and accounts for the asymmetry but also the intensity of the mode and background.

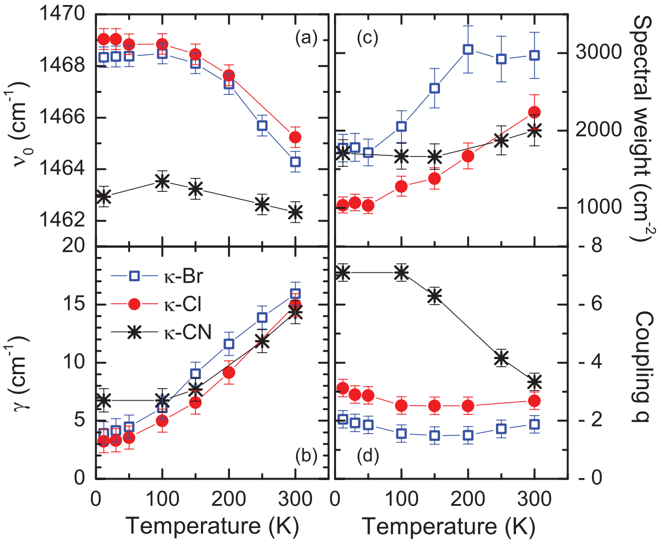

FIG. 7. (Color online) Temperature dependence of the mode parameters obtained from the Fano fit of the $\nu_{27}(b_{1u})$ vibrational features of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, and κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. (a) The resonance frequency ν_0 of the dominant mode, (b) the damping γ, (c) the mode strength, and (d) the Fano coupling parameter q. The error bars indicate the uncertainty of the fits and might be overestimated.

Finally we note that there is basically no change in the ν_{27} mode below 100 K observed for κ-CN, while there is a continuous temperature evolution for the other two compounds. For the linewidth this means that the modes get narrow for κ-Br and κ-Cl. Most interestingly, the damping gets considerably smaller upon cooling with no difference between the metallic or insulating materials as demonstrated in Fig. 7(b); again there seems to be a saturation below 100 K most obvious in κ-CN. The behavior of the curves is monotonous without any discontinuity; the magnitude, however, is higher than expected from the typical narrowing of lattice phonons and molecular vibrations. The overall behavior as described above may be attributed to charge fluctuations which are present at elevated temperatures and become reduced when the temperature is lowered. It is noteworthy that the low-temperature fluctuations are more pronounced in the case of the spin-liquid compound κ-CN compared to κ-Br and κ-Cl.

C. Low-temperature anomaly in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

Thermodynamic,[55,72] transport,[73] dielectric,[74] and lattice[75] properties provide evidence for a low-temperature anomaly of the spin-liquid compound κ-CN near $T = 6$ K that by now has not been explained satisfactorily. Based on a quarter-filled extended Hubbard model with both electron-electron and electron-phonon interaction taken into account, Mazumdar and collaborators[26] propose a paired-electron crystal that includes charge-rich and charge-poor molecules. There is quite some controversy whether the 6 K transition is related to charge order. One idea is that fluctuating dipoles (paired-electron liquid, dipolar liquid) crystallize at that temperature (paired-electron crystal, dipolar solid). This might also influence the magnetic properties.

In our transmission measurements presented in Fig. 6, we do not observe any significant change when cooling κ-CN down to $T = 2$ K, giving evidence that no charge order happens at 6 K or any other temperature. The vibrational mode $\nu_{27}(b_{1u}) = 1464\ \mathrm{cm}^{-1}$ slightly hardens upon cooling and remains basically unchanged for temperatures below 100 K, in accord with the reflection data, displayed in Fig. 5. The smaller feature around 1480 cm^{-1} might correspond to the $\nu_2(a_g)$ mode. No temperature dependence is observed for this feature or for the shoulder at 1452 cm^{-1}.

D. Coupling to anionic layers

We observe two slightly Fano-shaped resonances at 920 and 987 cm^{-1} in the powder absorption spectra as well as in the out-of-plane spectra that become more pronounced as the temperature is reduced to $T = 2$ K, although they do not split. We assign them to the $\nu_7(a_g)$ and $\nu_6(a_g)$ modes which mainly involve the outer ring and the terminating ethylene groups. These modes are rather strong in the Raman response but also observed in infrared spectra previously.[79] The presence of a totally symmetric vibrational feature in the infrared spectra implies that the mode is affected by some asymmetric coupling to the anion layers.

From x-ray diffraction results[32] it is known that with decreasing temperatures the $Cu_2(CN)_3$ network becomes warped, possibly due to the unbalanced interaction with the ethylene groups. The presence of the totally symmetric molecular modes infers a loss of symmetry (loss of inversion centers) although the translation symmetry is still preserved. It also is consistent with the intriguing results of thermal expansion that evidence an anomalous behavior around 6 K. From this point of view it is interesting to note that the dielectric response reported by Abdel-Jawad *et al.* was obtained from experiments perpendicular to the molecular layers of κ-CN.[41] The dielectric constant was found to be rather small ($\epsilon_1 \approx 10$) compared to κ-Cl ($\epsilon_1 \approx 400$).[42] The interaction of positively and negatively charged planes might be the crucial point and requires further consideration. It is of paramount interest to explore the anisotropy we predict for the dielectric properties within the *bc* plane of the triangular lattice of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$.

VI. CONCLUSIONS

We have performed comprehensive measurements of the vibrational features of the dimerized κ-(BEDT-TTF)$_2X$ salts, ranging from the superconducting metal κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br to the Mott insulator κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl and the spin-liquid compound κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. Despite the large differences in electronic and magnetic properties, the vibrational features are remarkably similar. In particular, focusing on the antisymmetric $\nu_{27}(b_{1u})$ mode observed in out-of-plane measurements, we can rule out any sizable charge disproportionation (with an upper bound of 1%; i.e., $2\delta = 0.01e$) within or among the dimers, and charge fluctuations of a moderate rate. No modification in the charge distribution is observed at any temperature; this also holds for the low-temperature anomaly reported for the spin-liquid κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ around $T = 6$ K. Our findings imply that the dielectric relaxation observed in the insulating samples κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl and κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ is not simply due to the formation electric dipoles on the dimers. Spatial and temporal variations of the charge distribution need to be explored in more detail. We further suggest one reconsider the interaction of the molecular layers to the polymeric anion sheet.

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APPENDIX: IN-PLANE POLARIZATION

In Fig. 8 the in-plane conductivity spectra of the three κ-BEDT-TTF salts κ-Br, κ-Cl, and κ-CN are plotted for different temperatures. Even for the insulating state, these optical spectra are dominated by the electronic background that changes strongly with temperature. The most dominant features near 1300 cm^{-1} are the totally symmetric $\nu_3(a_g)$ vibrations of the C=C double bonds, which are normally infrared silent but are activated by electron-molecular vibrational (emv) coupling that involves charge oscillations between the molecules in each dimer pair. The band is rather broad with a width of approximately 50–70 cm^{-1} that mainly depends on the electronic interaction and thus does not change much with temperature. Due to the presence of strong vibrational features in this range, the ν_3 mode does not appear as a smooth band, but exhibits considerable structure as discussed in the following.

Most surprising, the optical properties of κ-CN are significantly more anisotropic than κ-Cl, for instance.[67,69] As shown in Figs. 8(c) and 8(d), there seems to be a much stronger coupling of the $\nu_3(a_g)$ vibrational modes in the *c* direction compared to the *b* direction, resulting in a larger downshift due to emv interaction. Since this is the plane the BEDT-TTF molecules are tilted in, it might be related to the coupling of the molecular vibrations to the in-plane conductivity. As the temperature is lowered, the tilting even increases by approximately 2°, which enhances this effect.[32]

While the $\nu_2(a_g)$ mode is well present in Raman spectra and was intensively discussed by Yamamoto *et al.*,[35] it shows up only as a very weak emv-coupled peak around 1480 cm^{-1}, as expected from quantum chemical calculations.[37] As seen

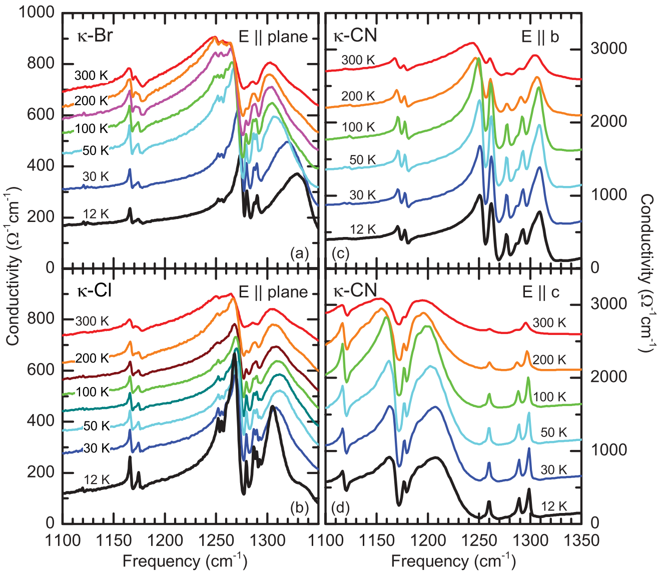

FIG. 8. (Color online) Temperature evolution of the in-plane optical conductivity of (a) κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, (b) κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, and [(c),(d)] κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ in the range of the emv-coupled $\nu_3(a_g)$ mode. For clarity reasons the curves are shifted with respect to each other.

in the out-of-plane spectra (Fig. 5) no significant temperature dependence was observed in any of the compounds under investigation. The mode is also seen in the powder absorption spectra (Fig. 6) with no appreciable modification when the temperature decreases to $T = 2$ K.

For the isostructural compounds κ-Br and κ-Cl, the ν_3 feature is basically centered around the same frequency (1275 cm^{-1} at room temperature). In κ-Br the maximum weakens and shifts to higher frequencies as the temperature decreases, indicating a weaker electronic coupling; this is well understood by the decreasing interband conductivity due to the shift of spectral weight to the Drude contribution. The opposite behavior is observed in the Mott insulator κ-Cl, where the ν_3 strength grows dramatically and the peak frequency decreases as the midinfrared peak grows with the formation of the gap.[53,66] The four dips between 1277 and 1294 cm^{-1} belong to a quartet of $\nu_5(a_g)$ modes and appear as antiresonances within the strong $\nu_3(a_g)$ mode.[86]

In the case of κ-CN [Figs. 8(c) and 8(d)] the vibrational features are quite different for the two polarizations within the conducting plane. For $E \parallel b$ the emv-coupled $\nu_3(a_g)$ shows up around 1280 cm^{-1}, while it is shifted to 1180 cm^{-1} for $E \parallel c$, indicating a much stronger emv coupling. This also agrees with the fact that the optical properties of κ-CN are rather anisotropic compared to κ-Cl.[67,69] It is interesting to see how the dips (antiresonances) in one case become peaks in the other polarization, and vice versa. Note, the quartet of ν_5 dips within the ν_3 modes is degenerated to a doublet for $E \parallel c$. Since it mainly involves the ethylene scissoring motion, it is particularly sensitive to the anion coupling. The tilt of the BEDT-TTF molecules in the c direction breaks the in-plane symmetry and causes the vibrations to become different for $E \parallel b$.

In addition a mode is seen at 1260 cm^{-1} that does not split for $E \parallel b$; it is also present in the other two compounds and can most likely be assigned to $\nu_{46}(b_{2u})$ or $\nu_{29}(b_{1u})$. In all three compounds we find a double peak at 1166 and 1174 cm^{-1} which is labeled as $\nu_{67}(b_{3u})$. A new Fano-shaped structure occurs around 1118 cm^{-1} that might be the $\nu_{47}(b_{2u})$ mode. At lower frequencies the $\nu_{60}(b_{3g})$ vibrations show up as a strong doublet at around 880 cm^{-1}(see Fig. 9). This mode has drawn considerable attention in the past[81,87] and may be regarded as a totally symmetric mode of a distorted BEDT-TTF molecule. For κ-CN it converges to a significant Fano shape in the $E \parallel c$ polarization. This again indicates the anisotropy of κ-CN and the particularity of the c direction in this compound. Most importantly, in our in-plane optical result of κ-Br, κ-Cl, and κ-CN we do not observe a splitting of any of the modes or some appreciable shift beyond the usual thermal dependence.

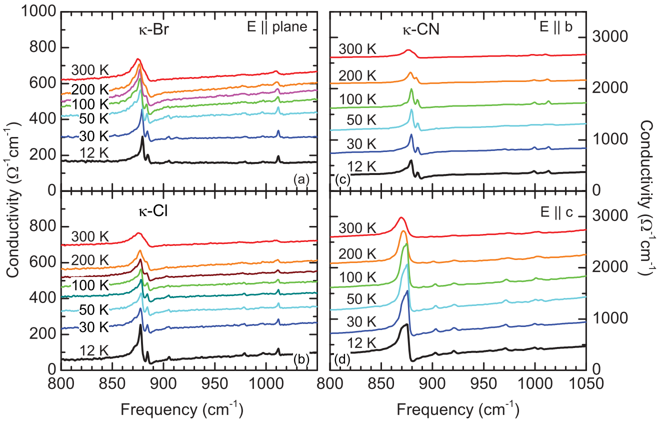

FIG. 9. (Color online) Temperature evolution of the in-plane optical conductivity of (a) κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, (b) κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, and [(c),(d)] κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ in the range of the $\nu_{60}(b_{3u})$ mode.

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