

Understanding the totally symmetric intramolecular vibrations in κ -phase organic superconductors

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We report magnetoinfrared measurements of two quasi-isostructural κ -phase organic molecular solids: κ -(ET)₂Cu[N(CN)₂]Br ($T_c=11.6$ K) and the nonsuperconducting κ -(ET)₂Cu[N(CN)₂]Cl analog. Our results support the contributing role of electron-molecular vibrational coupling to superconductivity in layered organic superconductors, and we identify the most important totally symmetric modes in κ -(ET)₂Cu[N(CN)₂]Br within the nonplanar molecular building block picture.

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I. INTRODUCTION

Understanding superconductivity in layered organic molecular, density wave, and cuprate superconductors is regarded as one of the “grand challenges” in condensed matter science.^{1–4} Critical temperature, magnetic field, and current (T_c , H_c , and J_c) represent important energy scales in the system. Measurements across these energy scales require careful temperature control, large magnetic fields to quench superconductivity, or control of possible heating effects in critical current experiments.^{5–7} Despite theoretical predictions,^{8,9,14} there have been few experimental attempts to probe the role of the lattice in establishing superconductivity in layered organic molecular solids by a direct and microscopic technique, such as infrared spectroscopy.¹⁰ Lattice phonons are already known to be important in the organics.^{11–13} Understanding the contribution of intramolecular vibrational modes and clarifying their coupling to the underlying electronic system is central to progress in this area.^{8,9,14} In order to investigate these effects, we selected two model materials: κ -(ET)₂Cu[N(CN)₂]Br and κ -(ET)₂Cu[N(CN)₂]Cl (abbreviated as κ -Br and κ -Cl, respectively). Here, ET = bis(ethylenedithio)tetrathiafulvalene. They were chosen because of their chemical and structural similarities, the accessible critical field, the overall energy scale of interactions, and their well-studied vibrational response. κ -Br is a superconductor ($T_c=11.6$ K).^{15,16} κ -Cl is an antiferromagnetic insulator at low temperature; it displays partial (not bulk) superconductivity under slight pressure.^{18–21}

In this work, we report magnetoinfrared investigations of κ -Br and κ -Cl. In the κ -Br superconductor, three electron-molecular vibration (EMV)-activated intramolecular modes change substantially with applied magnetic field. The recently developed framework of Girlando and co-workers,^{14,22} which accounts for local distortions of the ET building block molecule in the dynamical response, is the basis of our mode assignments. The nonsuperconducting κ -Cl analog does not display any field-induced changes within our sensitivity, suggesting that the observed magnetoinfrared features in κ -Br

are associated with superconductivity. These experiments complement previous magnetoinfrared studies on κ -(ET)₂Cu(SCN)₂ ($T_c \sim 10.4$ K, abbreviated here as κ -SCN),¹⁷ where field-dependent changes in vibronically activated vibrational modes were recently observed.²³ They also dovetail with recent decoration experiments on natural and deuterated κ -Br solid solutions, where the totally symmetric C=C stretching mode is a sensitive indicator of microtexture,²⁴ and with recent magnetoinfrared work on α -(ET)₂KHg(SCN)₄, which follows a field-induced transition from density wave to metallic states.²⁵ We anticipate that the results will stimulate additional theoretical progress.

II. EXPERIMENT

High-quality single crystals of κ -Br and κ -Cl were grown at Argonne National Laboratory using electrocrystallization techniques.^{15,18,26} Mosaics were prepared with oriented crystals on a brass plate.²³ The cooling rate was ~ 5 K/min. Experiments were carried out at the National High Magnetic Field Laboratory in Tallahassee, FL. Spectra were collected in reflectance mode with a Bruker 113V Fourier transform infrared spectrometer from 30 to 2500 cm⁻¹, with 2 cm⁻¹ resolution at 4.2 K. A superconducting magnet (0–17 T, Faraday geometry, $H \perp$ conducting two-dimensional plane) was employed. Single-beam reflectance spectra were collected between 0 and 17 T, after which the field was swept back for a second 0 T single-beam scan. The applied field allowed us to sweep from the superconducting phase, through H_{c2} , and into the high-field normal state in κ -Br ($H_{c2} \approx 6.2$ T).^{15,16} κ -Cl is an antiferromagnetic insulator at 4.2 K, and the applied magnetic field does not drive any phase transitions.^{18–21}

It is our experience that field-induced changes in vibrational features of organic superconductors are small. As a consequence, they do not appear clearly in the absolute reflectance (or optical conductivity) spectrum. To circumvent this problem, we instead report a reflectance ratio: $R(H)/R(H_0=0$ T). The reflectance ratio is essentially a nor-

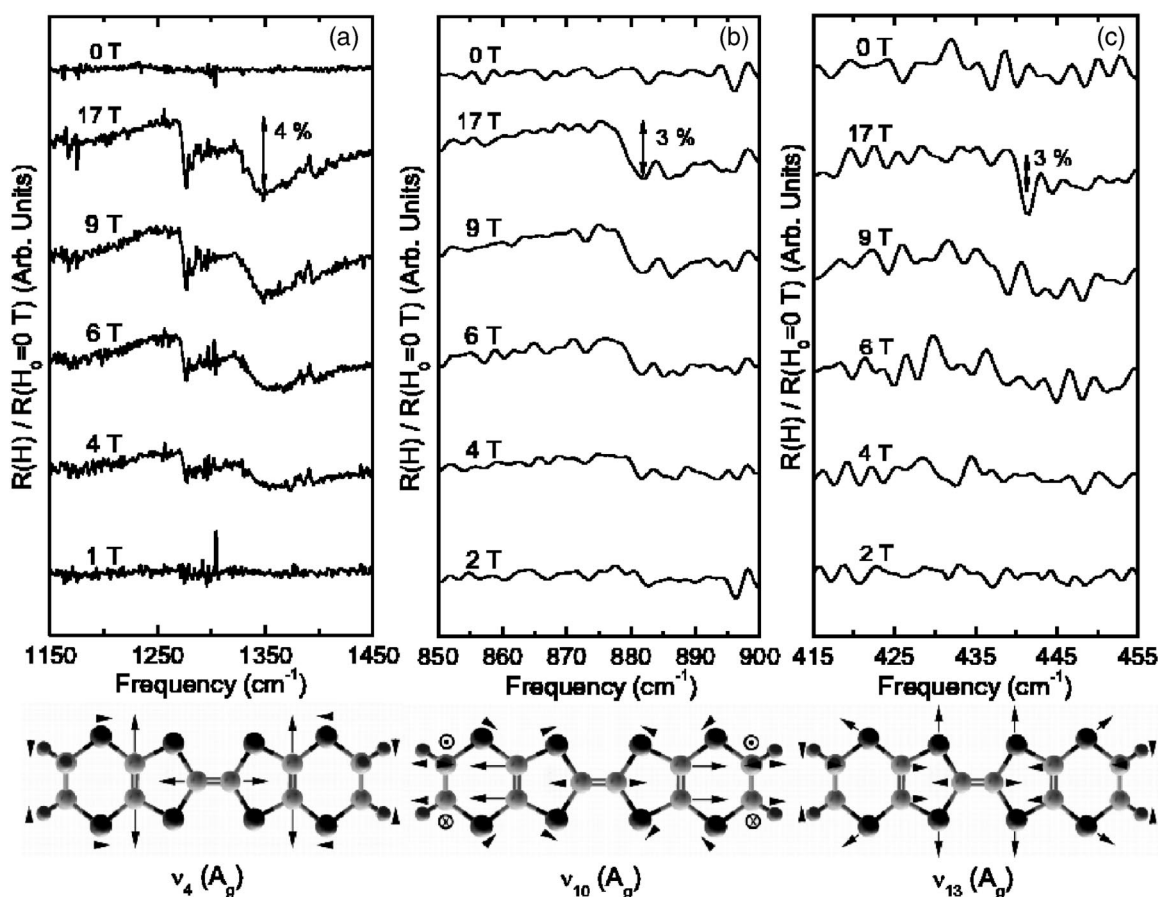


FIG. 1. Reflectance ratio spectra, $R(H)/R(H_0=0\text{ T})$, of (a) the ν_4 (A_g), (b) ν_{10} (A_g), and (c) ν_{13} (A_g) modes of κ -(ET) $_2$ Cu[N(CN) $_2$]Br at 4.2 K. The top curve in each panel shows the reflectance ratio $R(H=0\text{ T})/R(H_0=0\text{ T})$, providing an indication of the overall noise level. The double arrows indicate the size of field-induced changes at 17 T. The reflectance ratio curves have been offset for clarity. The relevant motions in C_{2h} (eclipsed) molecular symmetry (see Refs. 14 and 22) are schematically drawn.

malized response and a purely experimental quantity. We quantify field-induced changes in the reflectance ratio as $\int_{\omega_0}^{\omega_1} |R(H)/R(H_0=0\text{ T}) - 1| d\omega$, where ω_0 and ω_1 define the frequency range of interest. Measurements on the gold reference mirror as well as the $R(H=0\text{ T})/R(H_0=0\text{ T})$ ratio spectra on the samples provide an indication of the overall noise level.

III. RESULTS AND DISCUSSION

The vibrational properties of κ -(ET) $_2X$ -type organic molecular superconductors (X =counterion) are usually interpreted as a superposition of local intramolecular and extended lattice modes.^{4,10–13,27} Intramolecular modes related to the ET building block molecule are observed above 100 cm^{-1} and traditionally assigned using planar (D_{2h}) symmetry,^{10,27,28} an approximation that yields 12 totally symmetric modes which appear in the infrared spectrum due to EMV coupling.² The totally symmetric C=C stretch (ν_3) is the strongest mode in the optical conductivity spectrum.^{10,27,29} Within the D_{2h} picture, the infrared response also includes selected B_g modes as well as normally infrared-active modes of B_u symmetry.^{10,27} Vibrational modes related

to the central tetrathiafulvalene skeleton of the ET molecule seem to be reasonably described within the planar (D_{2h}) approximation. On the other hand, it is well known that distortions of the lateral ethylene groups lower the overall molecular symmetry in the salts.^{14,30–36} The two main deviations from planarity are eclipsed (C_{2h}) and staggered (D_2). κ -Br and κ -Cl display eclipsed (or lower) molecular symmetry, and κ -SCN is staggered (or lower).^{34,37} Note that ethylene group twisting with respect to the ET plane constitutes a local deformity, not a long-range change in the unit cell. Small differences in ethylene group disorder may be present as well.^{37,38}

At this time, only selected molecular dynamics calculations have been carried out in reduced symmetry conformations.^{14,22,30,35,36} In the C_{2h} case, 18 totally symmetric (A_g) modes are predicted, whereas in the D_2 subgroup, 19 totally symmetric (A) modes are anticipated.^{14,22,30,35,36} The conventional numbering scheme goes from highest to lowest frequency. We employ this new framework here. Of particular interest in recent renderings²² is the reassignment of the strong totally symmetric C=C stretching motion as ν_4 and the vibronic activation of the $\sim 890\text{ cm}^{-1}$ “ring breathing” mode (ν_{10}). The strength and sensitivity of the 890 cm^{-1}

mode has recently attracted attention in the organic superconductors.^{10,37,39}

Figure 1 shows the evolution of the 4.2 K reflectance ratio spectrum of κ -Br with applied magnetic field. Systematic modifications are observed in three areas, which, from the perspective of organic materials, are quite substantial. We assign these structures as the modification of EMV-activated totally symmetric intramolecular modes of the ET building block molecule.¹⁰ Within the C_{2h} subgroup picture, the features are attributed to ν_4 (A_g), ν_{10} (A_g), and ν_{13} (A_g). The approximate eigenvector patterns are shown in Fig. 1 and follow the spirit of Girlando's recent work in this area.^{14,22} An important consequence of dynamics simulations in reduced symmetry molecular subgroups is the renumbering of the modes. We emphasize that low-frequency motion involving the outer portion of the ET building block molecule is more strongly affected by local symmetry reductions than motion involving the central portion of the molecule. The sharp features superimposed on the broad totally symmetric C=C stretching mode near 1270 cm^{-1} in Fig. 1(a) are related to the narrow ethylene end-groups antiresonance dips which appear in the absolute reflectance spectrum.¹⁰

Figure 2(a) displays a close-up view of the $R(H=17\text{ T})/R(H_0=0\text{ T})$ reflectance ratio spectrum of κ -Br in comparison with similar data on the two quasi-isostructural compounds κ -SCN and κ -Cl. We assign the broad and complex changes observed in the organic superconductors to field-induced modifications of the totally symmetric C=C stretching mode. Although of different magnitude, the field-induced spectral changes in κ -Br and κ -SCN are similar in character. Interestingly, κ -Cl, the quasi-isostructural antiferromagnetic insulator, does not display any field-induced features within our sensitivity. Considering that the dynamics (and, in particular, the unperturbed A_g modes) of κ -Br and κ -Cl are very similar, we attribute the magnetoinfrared effects to differences in the low-energy electronic state to which the mode is vibronically coupled.

We quantify changes in the totally symmetric C=C mode for the two organic superconductors by plotting the normalized integral area of the field-induced features versus applied magnetic field [Fig. 2(b)]. Strikingly, the magnetoinfrared signature grows substantially with field in the superconducting phase, shows a clear correlation with H_{c2} , and tends toward saturation in the high-field normal state. Modification of these features through H_{c2} is strong evidence for the supposition that the observed vibronic changes below H_{c2} are associated with the superconducting portions of the mixed state.²³ That the EMV-coupled modes show little magnetic field dependence above H_{c2} also connects this effect to the local charge environment and the idea that the low-energy electronic structure is changing with field. Support for such a supposition comes from the recent work of Kimura *et al.*⁴¹ on [2,2]-D- κ -(ET)₂Cu[N(CN)₂]Br, where the charge transfer excitation seems to change with applied field. Isotopic decoration studies on κ -(ET)₂Cu(SCN)₂ (Refs. 27 and 42) show only nascent changes of the C=C stretching mode at T_c and H_{c2} .

Figure 3 displays a close-up view of the 17 T reflectance ratio spectra of κ -Br and κ -SCN in the vicinity of the totally

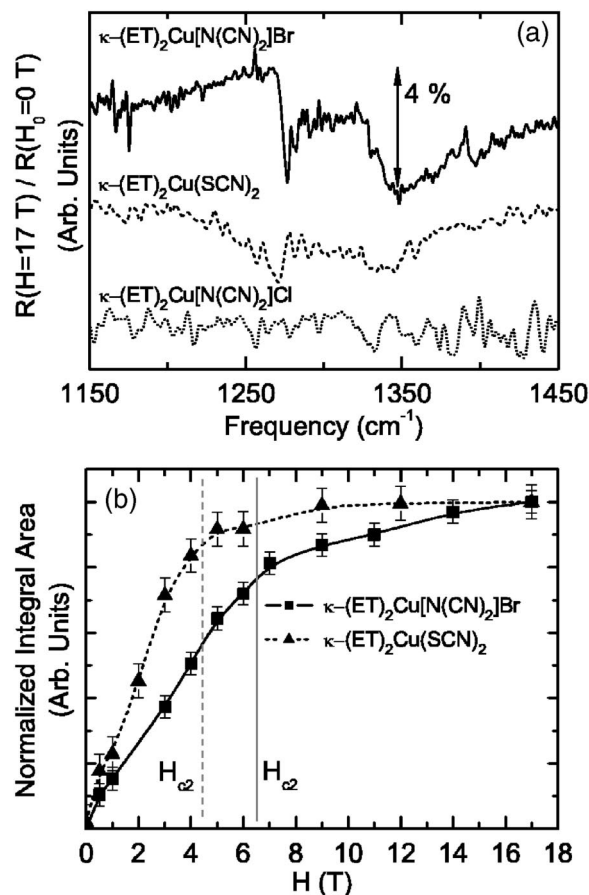


FIG. 2. (a) Reflectance ratio, $R(H=17\text{ T})/R(H_0=0\text{ T})$, of the totally symmetric C=C stretching mode for κ -(ET)₂Cu[N(CN)₂]Br, κ -(ET)₂Cu(SCN)₂, and κ -(ET)₂Cu[N(CN)₂]Cl at 4.2 K. The double arrow shows the size of the field-induced features. The reflectance ratio curves have been offset for clarity. (b) Normalized integral area of the changes in the reflectance ratio of the totally symmetric C=C stretching mode versus applied magnetic field for κ -(ET)₂Cu[N(CN)₂]Br and κ -(ET)₂Cu(SCN)₂. Solid and dashed vertical lines indicate H_{c2} values for the κ -(ET)₂Cu[N(CN)₂]Br and κ -(ET)₂Cu(SCN)₂ superconductors, respectively (see Refs. 16 and 40). Lines connecting the data points guide the eye. Estimated error bars, obtained from a similar analysis of the $R(H=0\text{ T})/R(H_0=0\text{ T})$ ratio spectra are shown.

symmetric 890 cm^{-1} (ν_{10}) breathing mode. The field-induced modification of this feature is much larger in κ -Br ($\sim 3\%$) than in κ -SCN ($\sim 1\%$), a result that seems to correlate with the size of T_c and H_{c2} . This trend is in line with that for ν_4 , discussed above. Comparison of the integrated area of this structure versus magnetic field with the response of other field-dependent vibronic modes in κ -Br demonstrates that although the field-induced response is similar overall to that of the C=C mode (growing in the superconducting phase, changing near H_{c2} , and leveling off in the high-field normal state), the change is more gradual around H_{c2} . Saturation of the effect is also less pronounced.

The fairly clear field-induced spectral changes in κ -Br make it possible to identify an additional, but much smaller, magnetoinfrared feature that is involved in the superconduct-

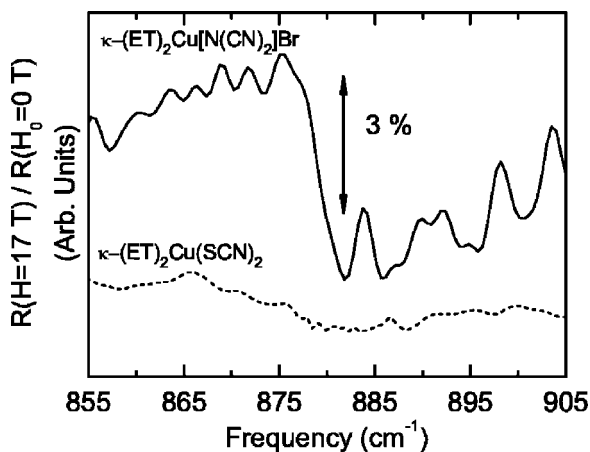


FIG. 3. Reflectance ratio $R(H=17\text{ T})/R(H_0=0\text{ T})$, of the totally symmetric ν_{10} mode for $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$ and $\kappa\text{-(ET)}_2\text{Cu}(\text{SCN})_2$ at 4.2 K. The double arrow shows the magnitude of the field-induced change in the reflectance ratio. The curves have been offset for clarity.

ing to normal state transition [Fig. 1(c)]. Based on dynamics simulations in reduced symmetry point groups,^{14,22} we assign this structure (centered around 440 cm^{-1}) as a totally symmetric intramolecular vibrational mode ν_{13} (A_g). Although changes in this mode were discovered only in $\kappa\text{-Br}$, we suspect that similar (but more modest) modifications are hidden beneath the noise for $\kappa\text{-SCN}$. The field-induced reflectance ratio near ν_{13} (A_g) evolves systematically, albeit with a greater overall noise level than shown previously.

Phonons contribute to superconductivity in a variety of materials.^{43,44} Even in high- T_c superconductors, vibronic effects may be important because of nanoscale phase separation or self-energy scaling effects.^{3,45} The pairing mechanism in κ -phase organic solids is particularly complicated, with evidence for several different contributions. In addition to unconventional electron correlation and/or antiferromagnetic spin fluctuations (implicated in numerous studies),^{46–48} both lattice phonons^{11,12} and vibronically activated intramolecular modes of the ET building block molecule (this work) seem to be involved. Although the EMV-activated modes add a larger

energy scale to the problem, many materials exhibit cooperative effects with coupling over various (sometimes surprising) lengths, energies, and time scales.⁴⁹ Understanding how these interactions combine represents an important challenge.

IV. CONCLUSIONS

Vibronically activated totally symmetric modes are well known to be some of the most sensitive spectral features available, making them ideal for investigating microscopic aspects of the magnetically driven superconducting to normal state transition in organic molecular solids. To this end, we report the 4.2 K magnetoinfrared reflectance of two quasi-isostructural organic solids: $\kappa\text{-Br}$ and $\kappa\text{-Cl}$. We compare our spectral results with previous work on $\kappa\text{-SCN}$. In $\kappa\text{-Br}$, three totally symmetric intramolecular modes change systematically with applied magnetic field. The magnetoinfrared features in $\kappa\text{-Br}$ ($T_c=11.6\text{ K}$) are similar but noticeably larger than those in $\kappa\text{-SCN}$ ($T_c=10.4\text{ K}$), indicating that the strength of the effect may be correlated to T_c (although the exact relationship is probably not simple) or to the locally different (eclipsed versus staggered) molecular distortions. On the other hand, no field-induced features were observed within our sensitivity in the quasi-isostructural reference compound $\kappa\text{-Cl}$. These results support the contributing role of electron-molecular vibrational coupling in the pairing mechanism of layered organic superconductors, and we identify the most important totally symmetric modes in $\kappa\text{-Br}$ within the nonplanar molecular building block picture.

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