

LETTER TO THE EDITOR

**Infrared studies of the organic superconductor
 κ -(BEDT-TTF)₂Cu(SCN)₂ under pressure**

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Abstract. The organic superconductor κ -(BEDT-TTF)₂Cu(SCN)₂ has been investigated at room temperature by polarized mid-infrared (600–7000 cm⁻¹) reflectivity measurements at pressures of up to 1.7 GPa. The optical effective mass, m_{opt} , decreases linearly with pressure, in contrast to the pressure dependence of the effective mass, m^* , determined by magnetic quantum oscillation measurements (Caulfield *J et al* 1994 *J. Phys.: Condens. Matter* **6** 2911–24; Caulfield *J et al* 1995 *Synth. Met.* **70** 815–8). Most phonon modes are seen to exhibit a linear pressure dependence of 0.5–1%/GPa. The stronger pressure dependence of the central C=C mode of the BEDT-TTF molecule is discussed: it is thought to be due to the pressure dependence of the effective Coulomb repulsion in κ -(BEDT-TTF)₂Cu(SCN)₂. These measurements suggest that a change in the electron–electron interaction under pressure could be the relevant factor for the suppression of superconductivity under pressure in κ -(BEDT-TTF)₂Cu(SCN)₂.

κ -(BEDT-TTF)₂Cu(SCN)₂ is one of the best characterized organic molecular metals. At ambient pressure it is a superconductor with a superconducting transition temperature of $T_c \simeq 10.4$ K, which decreases upon the application of pressure, until at pressures exceeding 0.5 GPa superconductivity is fully suppressed [1, 2]. Magnetic quantum oscillation measurements have determined that the Fermi surface (FS) of κ -(BEDT-TTF)₂Cu(SCN)₂ consists of two quasi-one-dimensional (Q1D) sheets and one quasi-two-dimensional (Q2D) pocket [3, 4]. Besides suppressing superconductivity, pressure was also found to decrease the magnetic breakdown gap between the Q1D and Q2D sections of the FS [1]. Recent millimetre wave [5] and NMR measurements [6] indicate evidence for d-wave symmetry of the superconducting groundstate. d-wave superconductivity is also supported by ideas that the antiferromagnetic fluctuations between the Q1D sections of the FS result in superconductivity in these materials [7]. Some phonon modes in κ -(BEDT-TTF)₂Cu(SCN)₂ exhibit a strong correlation with the associated magnetic anomalies [8].

Magnetic quantum oscillation measurements have also been used to determine the pressure dependence of the effective mass, m^* , which decreases linearly with pressure up to 0.5 GPa; above this pressure the magnitude of dm^*/dP is strongly reduced [1]. This ‘kink’ in the pressure dependence of m^* coincides with the pressure above which superconductivity in κ -(BEDT-TTF)₂Cu(SCN)₂ is suppressed. A similarly large m^* with a strong pressure dependence has also been observed in other organic molecular superconductors, whereas non-superconducting organic molecular metals are generally characterized by a smaller m^* [9]

and a small pressure dependence [10]. According to theory [11, 12], m^* , determined using magnetic quantum oscillations, represents the band mass re-normalized by both electron–electron and electron–phonon interactions. Infrared (IR) measurements, on the other hand, probe an optical mass, m_{opt} , that is closely associated with the band structure mass of the material [11]. Infrared measurements have also been used to deduce information about the electron–phonon interactions [13, 14] and electronic structure parameters [13, 15]. Thus, all three relevant factors for m^* are in principle obtainable from IR measurements, which therefore provide a possible tool for identifying the cause of the ‘kink’ in m^* and the suppression of superconductivity in κ -(BEDT-TTF)₂Cu(SCN)₂ under pressure.

Infrared reflectance spectra were measured for a sample placed in direct contact with the top anvil [16] of a wide-angle Mao diamond anvil cell (DAC) [17]. A Bruker IFs66V interferometer equipped with a Bruker microscope was used with a mercury–cadmium–telluride detector and a KBr beamsplitter for the mid-infrared. The measurement resolution was 4 cm^{−1}. The background signal was the diamond–air reflectivity ($\simeq 17\%$). The diamonds in the diamond anvil cell were selected carefully for infrared purposes (type IIa diamonds), and their thickness (1.13mm) was chosen to be as small as possible in order to minimise the intensity of the diamond absorption band in the mid-infrared (≈ 1600 – 2500 cm^{−1}). The samples were single crystals of κ -(BEDT-TTF)₂Cu(SCN)₂ with shiny, flat surfaces of $\sim 200 \times 200$ μm^2 containing the b - and c -axes. CsI was used as a pressure medium inside the cell. The pressure was determined by the conventional method of measuring the pressure-induced shift of the ruby fluorescence line [18]. The pressure in the cell for each measurement could be determined to an accuracy of better than ± 0.05 GPa, a value comparable to the pressure gradient inside the cell.

The pressure dependence of the in-plane dc conductivity at room temperature of a single crystal of κ -(BEDT-TTF)₂Cu(SCN)₂ was measured using a standard piston-cylinder cell with Fluorinert as a pressure medium and an internal calibrated manganin gauge. The in-plane resistance of the crystal was obtained in a 4-point measurement with a constant current of 3.5 μA , making no distinction between the in-plane b -axis and c -axis. The in-plane conductivity was found to increase linearly as $\sigma_0(P) = \sigma_0 \times (1 + 8 \times P(\text{GPa}))$ up to the maximum measured pressure of 0.6 GPa. The ambient pressure room temperature conductivity of κ -(BEDT-TTF)₂Cu(SCN)₂ was taken to be 2000 $\Omega^{-1}\text{m}^{-1}$ [19, 20].

Figure 1 shows the unmodified c -polarized reflectance spectrum of a single crystal of κ -(BEDT-TTF)₂Cu(SCN)₂ in the diamond anvil cell in the frequency range from 600 cm^{−1} to 7000 cm^{−1} for a selection of pressures. Despite the small sample size and the further reduction in signal due to the diamond anvil as a window material, the main features of the spectrum in the frequency range investigated are well resolved. Comparison of the ambient pressure data in these experiments with published measurements at ambient pressure and room temperature [14, 19, 20, 21] reveals the effect of the diamond–sample interface. The inset in figure 1 demonstrates this change by exhibiting the measured spectrum of the same crystal at ambient pressure, once viewed through the diamond anvil and once viewed without a covering material. Whereas the vibrational modes (800 cm^{−1} \rightarrow 1600 cm^{−1}) maintain their general appearance and position, the broad feature around 3500 cm^{−1} changes from a step-like feature (air–sample interface) to a hill-like feature (diamond–sample interface). The interpretation of the data by a modified Kramers–Kronig analysis will be discussed only briefly here. More details about the analysis procedure can be found in [22, 23].

Reflectivity measurements with a diamond–sample interface require a more sophisticated analysis than measurements with an air–sample interface, as the refractive index of the sample can either be larger or smaller than the refractive index of diamond. At the frequency where the indices match, a phase change of 180° is observed. In order to perform Kramers–Kronig analysis on the data obtained during the pressure measurement, the frequency (β)

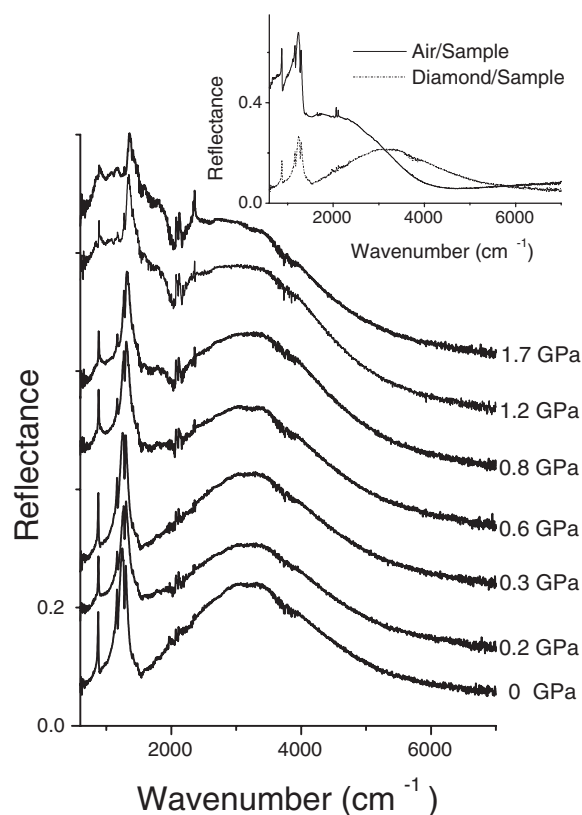


Figure 1. The *c*-polarized reflectance spectrum at room temperature of a single crystal of κ -(BEDT-TTF)₂Cu(SCN)₂ for a selection of pressures. The spectra are offset proportional to their pressure for clarity. A comparison of an ambient pressure reflectance spectrum in the same polarization with an air–sample and a diamond–sample interface is shown in the inset.

at which the sample refractive index is matched by the diamond refractive index has to be determined [22]. β for a representative selection of pressures was obtained by fitting the bare reflectivity data with a Drude–Lorentz model [24]. This model considers the reflectance spectrum to arise from a combination of a Drude term and several Lorentz oscillators describing the individual phonon modes as well as the broad mid-infrared hump. These fits could only provide limited information in the low-frequency limit and were not sufficient to determine the plasma frequency, ω_p , from the Drude term. However, their high frequency limit gave a very good fit so that β could be determined satisfactorily. A linear dependence of β on pressure was found for both polarizations and was used in a modified Kramers–Kronig analysis [23]. The phase of the reflectance and thus the optical conductivity of κ -(BEDT-TTF)₂Cu(SCN)₂ under pressure were obtained.

Figure 2 shows the calculated optical conductivity, $\sigma_{\text{opt}}(\omega)$, under pressure at room temperature. With increasing pressure $\sigma_{\text{opt}}(\omega)$ increases and the mid-IR hump at ~ 3000 (2300) cm^{-1} in the *b*(*c*)-axis polarization becomes less pronounced. Along the *b*-axis polarization this hump is seen to shift to higher energies with increasing pressure;

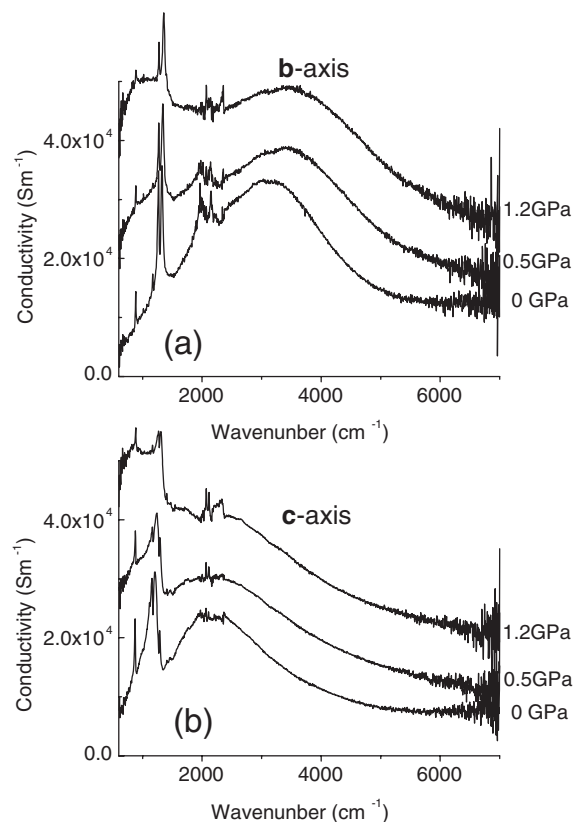


Figure 2. The optical conductivity at room-temperature of κ -(BEDT-TTF)₂Cu(SCN)₂ single crystal for selected pressures in the (a) *b*-axis and (b) *c*-axis polarization as calculated from a modified Kramers–Kronig analysis.

no such clear tendencies can be observed along the *c*-axis polarization (see figure 2). The position of this hump has frequently been taken as a direct measure of the effective Coulomb repulsion in this material [15, 25]. The pressure induced shift of the mid-IR band is thus an indication of an increase in the effective Coulomb repulsion under pressure. The low frequency increase in $\sigma_{\text{opt}}(\omega)$ under pressure at room temperature is similar to the increase observed [20, 21] during cooling of the sample at ambient pressure. The observation of an increasing Drude contribution to the optical conductivity with increasing pressure is consistent with transport measurements which show that κ -(BEDT-TTF)₂Cu(SCN)₂ increases its metallic character under pressure [1, 2, 6]. The relatively high temperature (room temperature) of this measurement had the effect of smearing out the Drude response. Thus, the plasma frequency, ω_p , could not be determined unambiguously from the Drude term. However, an estimate of the overall plasma frequency, ω'_p , was extracted from the optical conductivity by employing the sum rule

$$(\omega'_p)^2 = \int_0^{7000\text{cm}^{-1}} \sigma_{\text{opt}}(\omega) d\omega. \quad (1)$$

Instead of integrating to infinity in equation (1), an upper integration limit of 7000 cm^{-1} was used. In the low frequency limit $\sigma(\omega)$ was extrapolated linearly between $\sigma_{(\omega=600 \text{ cm}^{-1})}(P)$ and the dc conductivity $\sigma_0(P)$ [26]. The effective optical mass, m_{opt} , was determined from ω'_p according to $m_{\text{opt}}(P) = 4\pi n(P) \times e^2 / (\omega'_p)^2$, where $n(P)$ is the carrier density. $n(P)$ was calculated assuming that the charge transfer between the organic molecules and $\text{Cu}(\text{SCN})_2$ does not depend on pressure. At all pressures two BEDT-TTF molecules contribute exactly one hole to the conductivity and the only change in the carrier density is due to the decreasing unit cell volume under pressure. Thus, $n(P) = n_0 \times V_0 / V(P)$, with $n_0 = 1.2 \times 10^{27} \text{ m}^{-3}$ [19, 27], and $V(P) = V_0 \times (1 - 0.065 \times P(\text{GPa}))$ [28]. Note that m_{opt} determined this way contains contributions from the Drude term as well as from the broad mid-IR hump and is thus expected to be an underestimate of the Drude mass.

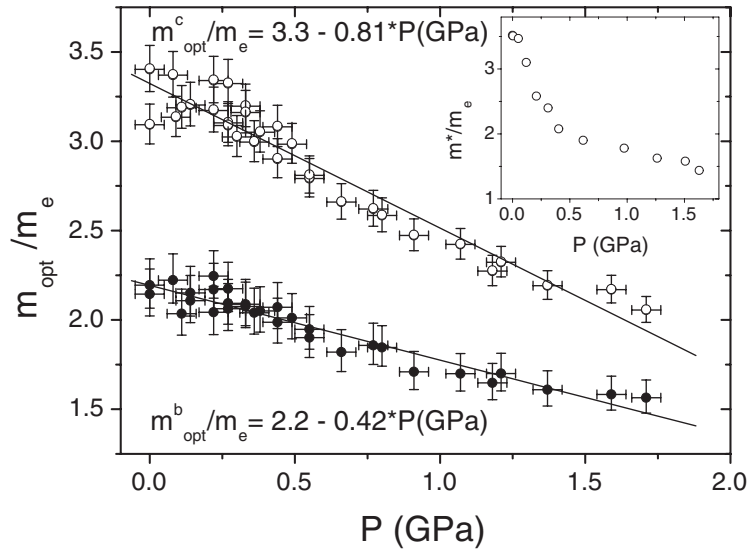


Figure 3. Pressure dependence of m_{opt} for b -axis and c -axis polarization. The inset shows the equivalent variation of m^* (after [1]).

The values of m_{opt} are plotted for both b -axis and c -axis data in figure 3. The exact value obtained depends on the interpretation of the spectra and on the extrapolation procedure below 600 cm^{-1} [26]; however, it should be noted that this will affect all of the data in a similar way. Hence, whilst there is some uncertainty in the absolute values of m_{opt} shown in figure 3, the measured change of m_{opt} with pressure should be robust. The data in figure 3 show that $m_{\text{opt}}(P)$ has a linear pressure dependence of $dm_{\text{opt}}/dP \sim -0.4 - 0.8 m_e/\text{GPa}$ over the whole pressure range investigated. This is similar to the high pressure variation of m^* ($dm^*/dP \simeq -0.4 m_e/\text{GPa}$) at pressures above 0.5 GPa (see inset of figure 3) but much less than the pressure dependence of m^* ($dm^*/dP \simeq -3.3 m_e/\text{GPa}$) at pressures less than 0.5 GPa.

It can be assumed that the vibrational modes of κ -(BEDT-TTF) $_2$ Cu(SCN) $_2$ at ambient pressure [29, 30] retain their identity under pressure since the molecular symmetries and the molecular arrangement are sustained [28]. The diamond-sample interface does not affect the appearance or position of the vibrational modes (see inset figure 1). The following discussion is thus based on the bare reflectivity spectrum.

Two different vibrational features are well resolved in the frequency range investigated:

the mode around 880 cm^{-1} , which has been assigned to the $\nu_{60}(\text{B}_{3g})$ mode [30, 31], and the double (triple) features at $\sim 1300\text{ cm}^{-1}$ in the b -axis (c -axis) polarization that are due to the Fermi resonance between the central C=C vibration and the C-H modes. The 880 cm^{-1} mode exhibits a linear pressure dependence of $\sim 1\%/GPa$.

The pressure dependence of the C=C mode is more difficult to determine and understand. The strong coupling to the C-H modes obscures its direct observation and results in the ‘ragged’ appearance of this feature around 1300 cm^{-1} . Figures 4(a) and (b) show the development of these coupled modes with pressure. The anti-resonance dips in both polarizations are seen to depend linearly on pressure ($\simeq 0.5\text{--}1\%/GPa$). Especially in the c -axis polarization (figure 4(b)), the underlying C=C mode is seen to ripple through the diagram with a much larger pressure dependence of $\simeq 4\%/GPa$ (it moves from 1260 cm^{-1} at ambient pressure to 1340 cm^{-1} at 1.7 GPa). This crossing of the modes under pressure causes the high-frequency ‘peak’ of the C=C mode (at 1300 cm^{-1} at 0 GPa) to exhibit a kink in its pressure dependence at 0.5 GPa, the same pressure above which superconductivity in $\kappa\text{-(BEDT-TTF)}_2\text{Cu(SCN)}_2$ is destroyed. As can be seen in figure 4(b), at higher pressures the pressure dependence of the C=C mode in the c -axis polarization is reflected in the pressure dependence of its high frequency peak. In the b -axis polarization no such crossing of modes can be observed directly; however, the high-pressure peak of the C=C mode exhibits a stronger pressure dependence than the clearly visible anti-resonance dips. By analogy with the observed high pressure behaviour of the c -axis polarization, the pressure dependence of this high frequency peak is assumed to reflect the behaviour of the whole C=C mode.

When discussing the measurements described here one has to keep in mind that they were taken at room temperature and that superconductivity in this material occurs around 10.4 K. Any direct comparison should thus be treated cautiously. However, ambient pressure IR measurements as a function of temperature [19, 20] demonstrated that the main effect of temperature is to sharpen individual features and the Drude contribution to the spectrum. Initial attempts were made to fit the reflectivity spectrum to a Drude–Lorentz model. However, no satisfactory fits with physical significance could be obtained. The discussion of the results above is thus based on the direct observable behaviour or has been extracted via Kramers–Kronig analysis from the measured spectra.

The pressure dependence of m_{opt} reveals that the ‘kink’ in the pressure dependence of m^* is not due to a non-linear pressure dependence of the optical mass. In addition, it is evident that m_{opt} has a similar pressure dependence to that observed for m^* above 0.5 GPa, i.e., once superconductivity has been suppressed by pressure. As m_{opt} is closely related to the bare band mass, we infer that the bare band mass cannot be the determining factor for superconductivity in $\kappa\text{-(BEDT-TTF)}_2\text{Cu(SCN)}_2$.

As mentioned above, the pressure dependence of the C=C mode is very difficult to determine. Fitting attempts did not succeed in separating this mode unambiguously from the C-H modes and thus an estimate of the pressure dependence of this mode was obtained by visual inspection of the spectra shown in figure 4. The pressure dependence of the central C=C mode estimated this way is very large ($\simeq 2\%/GPa$ and $\simeq 4\%/GPa$ for the b -axis and c -axis polarization, respectively).

The C=C mode is only IR active due to its strong electron–phonon coupling [32]. Its IR-activity is thought to originate from the out-of-phase coupling of this mode on the two molecules forming a dimer [33]. The observed softening of the C=C mode depends on its electron–phonon coupling and its closeness to the mid-IR band [33]. This can be seen at ambient pressure: the mode exhibits a stronger softening along the c -axis polarization, where the band occurs at lower energies, than along the b -axis polarization where the mid-IR band is shifted to higher frequencies. Thus a potential pressure induced shift of the mid-IR band

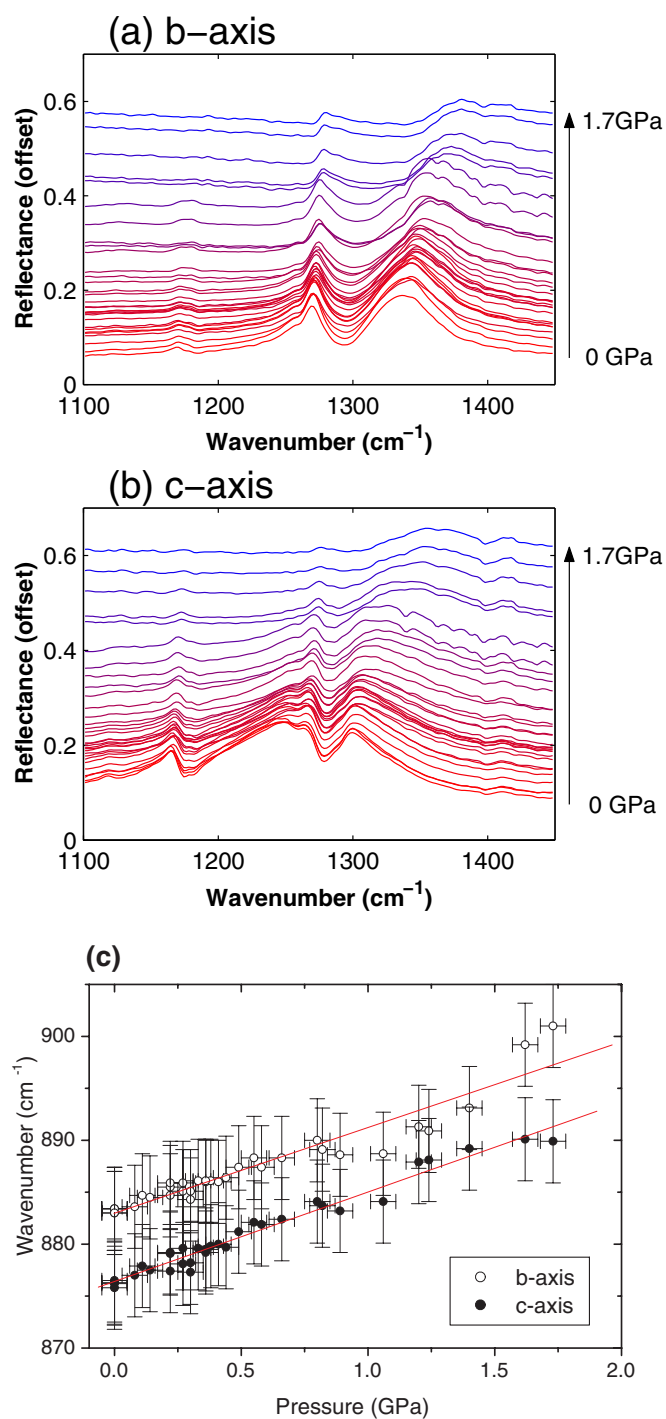


Figure 4. The pressure dependence of the C=C vibration along the *b*- and *c*-polarization and of the 880 cm⁻¹ mode in both polarizations can be seen in (a), (b) and (c), respectively. The reflectance of the spectra in (a) and (b) have been offset proportional to their pressure by $0.15 \times P(\text{GPa})$. The anti-resonant features and the $\nu_{60}(\text{B}_{3g})$ mode all exhibit a linear pressure dependence.

to higher energies is expected to reduce the softening of the C=C mode and will thus cause a shift of this mode to higher frequencies. Whereas the shift of the mid-IR band could not be observed directly in the IR conductivity in the *c*-axis polarization, its shift to higher pressure can be seen in the *b*-axis polarization. Thus, even though we do not know the exact pressure induced shift of the mid-IR band, the observed pressure dependence of the C=C vibration can be understood as originating from the shift of the mid-IR band to higher energies.

The central C=C bond in κ -(BEDT-TTF)₂Cu(SCN)₂ is known to exhibit an unusually large pressure-induced change [28]. However, κ -(BEDT-TTF)₂Cu(SCN)₂ contains two crystallographically independent BEDT-TTF molecules in a dimer [34], of which one stretches its C=C bond under pressure ($\sim +3\%/GPa$) whereas the other contracts ($\sim -6\%/GPa$) [28]. Thus, instead of observing a shift of a singular mode, a splitting or a significant broadening of the mode would be expected under pressure if the strong pressure dependence of the IR vibration is mainly structure based. Neither is observed. Considering that the central C=C mode is due to the identical vibration in the molecules in both polarizations, one can naively expect a similar or the same pressure dependence in both polarizations, if this strong pressure dependence mainly originates in the change in C=C bond length under pressure [35]. Thus, the difference in pressure dependence for both polarizations can be interpreted as another indication that the strong pressure dependence of the C=C modes originates either from a change in electron-phonon interactions or a change of the mid-IR band. The latter and its pressure dependence could not be determined unambiguously due to the mid-IR band's strong overlap with the poorly defined Drude term at room temperature.

In contrast to the infrared activity of the central C=C vibration, the infrared activity of the $\nu_{60}(B_{3g})$ mode at 880 cm^{-1} is thought [30] to originate from the coupling to charge oscillations between BEDT-TTF dimers rather than within dimers. It is to be expected that inter-dimer and intra-dimer charge oscillations are independent of each other in their pressure dependence. Thus, if the $\nu_{60}(B_{3g})$ mode is only IR active due to inter-dimer coupling, then its linear pressure dependence contains no information on the pressure dependence of the electron-phonon coupling of the central C=C vibration. However, there is some uncertainty about the symmetry of the BEDT-TTF molecules in κ -(BEDT-TTF)₂Cu(SCN)₂. In view of this uncertainty, it is possible [30] that this mode is a fully symmetric mode that is IR active due to intra-dimer coupling; some authors have discussed the 880 cm^{-1} feature as a fully symmetric mode with a moderate [13, 30] to strong [14] electron-phonon coupling.

The temperature dependence of the 880 cm^{-1} mode has attracted attention, as it exhibits strong features that can be associated with superconductivity [36] or anti-ferromagnetic fluctuations [8]. However, no anomaly could be observed in its pressure dependence in infrared measurements.

Within the accuracy of our measurements, both the 880 cm^{-1} mode and the central C=C vibration have a linear pressure dependence at low pressures and show no indication of a 'kink' or anomaly around 0.5 GPa making it less likely that it is a pressure induced change in the electron-phonon interaction that causes this 'kink' in m^* . Having found no evidence for an unusual pressure dependence below ~ 1 GPa in either the electron-phonon or m_{opt} and considering the contributing factors to m^* , these measurements could be seen as a suggestion that it is the pressure induced change in the electron-electron interactions that is the main cause for the suppression of superconductivity in κ -(BEDT-TTF)₂Cu(SCN)₂ under pressure.

In conclusion, we have obtained the first infrared reflectance data on an organic superconductor under pressure. The increase in metallic character upon the application of pressure in κ -(BEDT-TTF)₂Cu(SCN)₂ can be seen clearly in the optical conductivity data. The optical mass, m_{opt} , shows a small linear pressure dependence, which is in contrast to the behaviour seen in the effective mass, m^* [1]. Whereas the $\nu_{60}(B_{3g})$ mode exhibits no anomalies

under pressure, the central C=C vibration is characterized by an unusually large pressure dependence. The cause for this strong pressure dependence is thought to originate from the pressure dependence of the mid-IR band. These measurements suggest that a change in the electron–electron interaction under pressure could be the relevant factor for the suppression of superconductivity under pressure in κ -(BEDT-TTF)₂Cu(SCN)₂.

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