Noname manuscript No.
(will be inserted by the editor)

Ultrafast Carrier Dynamics in a Organic Superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br by Spectrally-Resolved Pump-Probe Spectroscopy

Satoshi Tsuchiya · Tomaz Mertelj · Dragan Mihailovic · Jun-ichi Yamada · Yasunori Toda

Received: date / Accepted: date

Abstract In this work, spectrally-resolved optical pump probe measurements were carried out on strongly correlated organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. We find two different types of carrier relaxation dynamics, one of which appears at 1.82 eV and 1.94 eV, and another at 2.17 eV. The former is characterized by short decay time $\sim$ 1 - 2 ps and appears below $\sim$ 60 K. From the comparison with the previous studies, the dynamics arises from the photo-induced pseudogap (PG) formation of the partially-appeared Mott phase. The latter has long relaxation time $\sim$ 9 ps at 5 K and developed as temperature decreases below 30 K. The slow dynamics is consistent with appearance of superconducting (SC) gap. Such separate observation of PG and SC dynamics enables us to proceed further investigation of a relationship between them.

Keywords Organic superconductor · Time resolved spectroscopy · Supercontinuum pulse

PACS 78.47.D- · 74.70.Kn

1 Introduction

Up to now, the coexistence and competition between superconductivity (SC) and other electronic phases have been a major research topic in the field of condensed matter physics. For example, in strongly correlated cuprate superconductors, a relationship between SC and pseudogap (PG)[1,2] have been widely studied. It is of interest to reveal the mechanism of such coexistence and competition in the archetypal multiband superconductor MgB_2[3] and the pressure-induced hydrogen sulfide[4,5] and FeSe superconductor[6].

An organic charge-transfer salt κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (κ-Br) is one of the most commonly studied superconductors[7–9] in terms of their similarity to cuprates. In this system, it is difficult to conduct spectroscopic measurements using high energy photons such as angle-resolved photoelectron spectroscopy (ARPES) because of fragility of organic molecular crystals, so few researches on PG has been reported. Recently, pump probe spectroscopy using near infrared and visible light has revealed that anomalous nonequilibrium carrier dynamics have emerged at $T^* \sim 70$ K, indicating formation of a PG[10,11]. In addition, quasi-particle dynamics which arises from the SC state was observed below $\sim$ 20 K[12]. However, because their signals were overlapping at low temperatures, these dynamics need to be detected separately to investigate further the relationship between PG and SC.

In strongly correlated electron systems, the electronic properties at the Fermi energy relate to those at high-energy scales. In cuprates, a spectrally-resolved pump probe technique has revealed that changes of electronic spectra induced by a formation of PG and SC gap reached to a high energy in the order of eV[13,14]. Moreover, the high-energy spectral change due to the SC transition is found to be different from that due to the PG formation. Thus, this technique enables us to observe the PG and SC dynamics individually in the organic superconductors. In this paper, we report the transient spectral change at high-energy range (1.65 - 2.40 eV) by an optical pump-supercontinuum-probe spectroscopy in κ-Br. The PG and SC dynamics are successfully observed at

S. Tsuchiya · Y. Toda
Department of Applied Physics, Hokkaido University, Hokkaido 060-8628, Japan
Tel.: +81-11-706-6630
Fax: +81-11-706-6630
E-mail: satoshi.tsuchiya@eng.hokudai.ac.jp

T. Mertelj · D. Mihailovic
Complex Matter Department, Jozef Stefan Institute, Jamova 39, Ljubljana, SI-1000, Ljubljana, Slovenia

J. Yamada
Graduate School of Material Science, University of Hyogo, Hyogo 650-004, Japan

1.82 eV and 1.94 eV, and 2.17 eV, respectively as a single component.

2 Experimental

Single crystals of κ-Br was prepared electrochemically[15]. The crystal consists of alternate stacking of the conducting layer of BEDT-TTF molecules and insulating layer of $Cu[N(CN)_2]Br$ along the b axis. κ-Br shows the SC transition at T_c of 12 K[16], on the other hand, the isostructural salt, κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ (κ-Cl) becomes the Mott insulator at low temperatures. Moreover, in κ-Cl, the application of pressure leads to the Mott insulator-to-superconductor transition at low temperatures[17–19]. These results suggest that the chemical substitution from Cl to Br leads to increase of effective electron correlation t/U, where t and U are the transfer integral between the BEDT-TTF dimers and Coulomb repulsion on the dimer, respectively, in the same way as pressure. Thus, the electronic state of κ-Br is located near the Mott insulating phase in the T vs t/U phase diagram[20].

The optical measurements were conducted using 50 fs pulses of 1.53 eV generated from an $Ti:Al_2O_3$ regenerative amplifier seeded with an $Ti:Al_2O_3$ oscillator with a repetition rate of 100 kHz to avoid the heating effect. The pump photons of 3.1 eV were obtained by the standard frequency doubling in a BBO crystal. To conduct spectrally-resolved measurement, we prepared the supercontinuum pulse for a probe by passing the pulse of 1.53 eV through a 2.5-mm-thick Al_2O_3 plate. The spectral density of the probe pulse is ranged from 1.65 eV to 2.40 eV. The polarization of the probe photons was rotated by a broadband half waveplate and the beam was focused on the sample by a pair of achromatic lenses. The reflected beam was dispersed by a transmission grating and entered a 48-channel silicon PIN diode array[21].

In the optical pump-probe experiments, the pump pulse excites electrons from the occupied states to nonequilibrium high-energy states. The photoexcited carriers relax immediately to states near the Fermi energy via electron-electron and electron-phonon scatterings, resulting in a nonequilibrium distribution of phonons as well as carriers. The probe pulse measures transient change of reflectivity (ΔR/R) involved with the nonequilibrium carrier distribution as a function of delay time. In the previous studies[11,12], temperature-dependent dynamics have been observed depending on a polarization of probe photon. In this measurement, we set the polarization parallel to the c axis, where ΔR/R was mostly enhanced[11]. The measurement was carried out with the pump fluence of $\sim$ 184 μJ/cm^2.

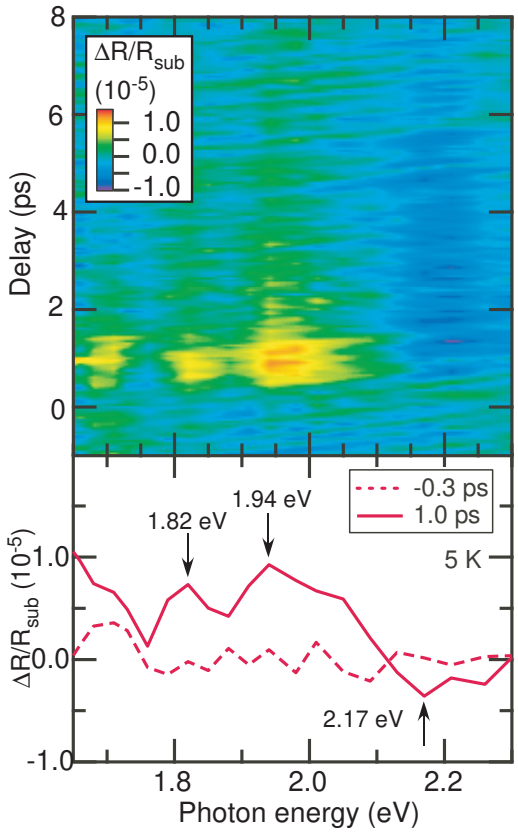

Fig. 1 An intensity plot of transient change of reflectivity ΔR/R$_{sub}$ as a function of probe photon energy at 5 K and probe photon energy spectra of ΔR/R$_{sub}$ at -0.3 ps (dashed line) and 1.0 ps (solid line). Note that ΔR/R$_{sub}$ was obtained by subtracting the data at 122 K.

3 Results and Discussion

Figure 1 shows an intensity plot of ΔR/R$_{sub}$, in which the data at 122 K has been subtracted to show temperature-dependent components[11,12], as a function of probe photon energy at 5 K and energy spectra at -0.3 ps and 1.0 ps. Positive and negative peaks are observed at 1.82 eV and 1.94 eV, and 2.17 eV, respectively.

Figures 2(a) and (b) show ΔR/R$_{sub}$ at 1.82 eV and 1.94 eV, respectively, for various temperatures. These positive components are qualitatively similar to each other. On the other hand, the negative component seems to have a long relaxation time as compared to the positive ones as shown in Fig. 2(c).

Figures 3(a) and (b) show the temperature dependences of signal amplitude $|A|$ and decay time τ, respectively, which are obtained by fitting the data with a single exponential function. Both $|A|$ of the positive components gradually developed with decreasing temperature below $\sim$ 60 K. The increase of $|A|$ indicates formation of an energy gap. Moreover, the τ values in both components are estimated as 1 - 2 ps in the whole temperature range except for 9 K. The

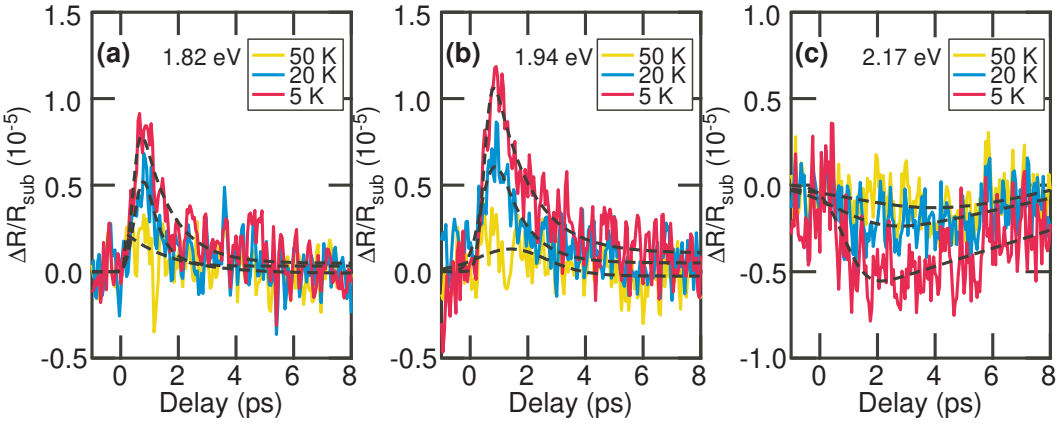

Fig. 2 (a)-(c): $\Delta R/R_{sub}$ at 1.82 eV, 1.94 eV and 2.17 eV for various temperatures, respectively.

anomalous change at 9 K may be related with the SC transition, as will be mentioned later. The similarity of the temperature dependences of |A| and τ between the 1.82 eV and 1.94 eV channels indicates that their carrier dynamics arise from a same origin.

On the other hand, |A| of the negative component of 2.17 eV gradually grows below $\sim$ 30 K and increases steeply at 9K with decreasing temperature. The τ values are quite larger than those of the positive components in the whole temperature range except for anomaly at around 9 K. Typically, at 5 K, the τ value is estimated as $\sim$ 9 ps. These results suggest that an origin of the negative component is different from that of the positive components.

Here, we discuss origins of the fast-decay positive and long-lived negative components. In the previous polarization-resolved pump probe studies, two types of carrier dynamics have been observed in κ-Br at low temperatures[10–12]. One gradually developed at $\sim$ 70 K with $\tau \sim$ 1 - 2 ps as temperature decreases. The gradual variation indicates formation of PG, which is quite similar to that in the cuprate $Bi_2Sr_2CaCu_2O_{8+\delta}$[22]. The other which has long relaxation time appeared at $\sim$ 20 K and strikingly changed at T_c[12], indicating formation of the SC gap.

From comparison with the previous results, the observed fast-decay components at 1.82 eV and 1.94 eV can be assigned to the former PG dynamics. Although, in κ-Br, presence of PG remains controversial so far, the most likely interpretation of PG dynamics is photo-induced metallic-insulator phase separation[10, 11]. When the pump pulse excites carriers, those lead to modulation of the electron correlation *t/U*, which can affect electronic state as negative pressure. Since the electronic state of κ-Br is located near the Mott insulating phase, a part of the electronic states from metal to Mott insulator, opening an energy gap. The quantitative difference of the onset temperature may be due to difficulty of detection of the PG response in this measurement. In the previous study in which the probe pulse of 1.55 eV was used[11], the transient signal of the PG is about 10 times greater than that in this measurement.

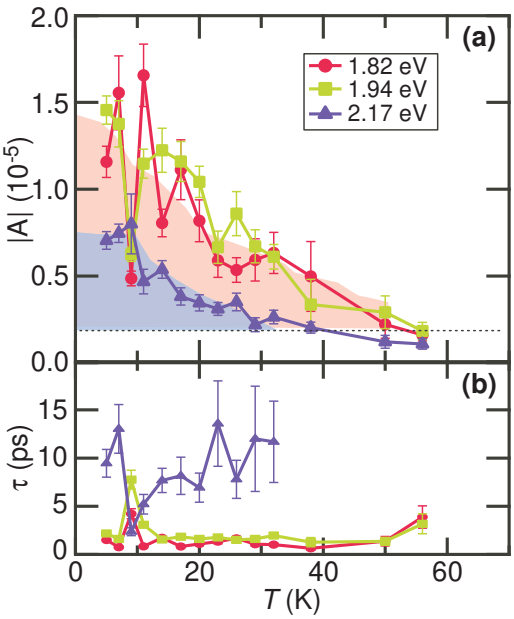

Fig. 3 (a) Temperature dependences of signal amplitude at 1.82 eV, 1.94 eV and 2.17 eV. The dashed line indicates a noise level. (b) Temperature dependences of decay time at 1.82 eV, 1.94 eV and 2.17 eV. A slight enhancement of τ in 1.82 eV and 1.94 eV channels at 56 K is probably an artifact related with the fitting because the signal tends to be buried in the noise.

On the other hand, the long-lived component at 2.17 eV can arise from the SC state. In κ-Br, fluctuating SC (FSC) has been suggested above T_c in various measurements[23–26]. Since the pump probe measurement is sensitive to formation of an energy gap, it is reasonable to observe the SC dynamics above T_c[12]. The onset temperature of the SC dynamics is $\sim$ 30 K, which is somewhat higher than that in the previous measurement in which the probe pulse of 1.55 eV was used[12]. In the conditions, the SC and PG components were overlapped at low temperatures. The SC component was extracted as A_s from the fitting with the function of

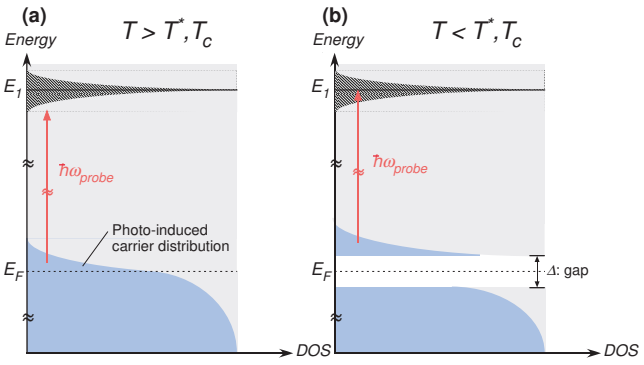

Fig. 4 Schematic illustrations of the optical transition in the probe process at (a) $T > T^*$, T_c and (b) $T < T^*$. T_c. E_1 and E_F denote an intramolecular excitation energy and the Fermi energy, respectively.

$A_f exp(-t/\tau_f) + A_s exp(-t/\tau_s)$ under the assumption $\tau_s \rightarrow \infty$. Because such decomposition by fitting involves ambiguity, it can lead to the difference of the onset temperatures of FSC.

As has been shown in Figs. 3, the amplitude and decay time of the PG dynamics decrease and increase just near T_c, respectively, as temperature decreases. In the SC dynamics, those variations are opposite. The results imply that there is a correlation between the PG and SC states. Indeed, in the cuprate superconductors, the pump probe measurements have suggested the correlation between them[14,27].

Finally, we mention an origin of the resonances in the ΔR/R spectrum at 1.82 eV, 1.94 eV and 2.17 eV. In the organic compounds, several absorptions depending on the directions of the crystal axis at high energy ranges have been reported. For example, in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (κ-NCS), several resonance peaks due to the intramolecular excitation of BEDT-TTF molecule are observed above $\sim$ 1 eV for the in-plane direction in the optical conductivity spectrum[28]. Although there are few high-resolution optical measurements in high energy range in κ-Br so far, similar trends are expected[29,30] because of similarity of the electronic structure in κ-NCS.

In the pump probe measurements, the probing process is dominated by the optical transition between the pump induced occupied states near the Fermi level and the unoccupied states separated from the Fermi energy by the probe photon energy. As shown in Fig. 4(a), the energy E_1 of intramolecular excitation is assumed to be higher than the energy of probe photon $\hbar\omega_{\rm probe}$. When the temperature decreases and an energy gap opens at the Fermi energy as shown in Fig. 4(b), the resonance energy becomes close to $\hbar\omega_{\rm probe}$, leading to enhancement of ΔR/R. Although, in principle, it is difficult to identify the optical transition of the probe, which contributes to ΔR/R, some intramolecular excitations enhance and some suppress, resulting in positive and negative changes in ΔR/R, respectively. This may be the reason why the PG and SC dynamics are observed as resonances.

4 Summary

By performing spectrally-resolved pump probe spectroscopy with supercontinuum pulses in the organic superconductor κ-Br, we observed the PG dynamics probing at 1.82 eV and 1.94 eV, and SC dynamics probing at 2.17 eV. The anomalous changes in the amplitude and decay time of the PG and SC dynamics at $\sim T_c$ imply their mutual interaction.

Acknowledgements One of the authors (S. T.) would like to thank Faculty of Engineering, Hokkaido University for a partial financial support.

References

1. Timusk T., Statt B.: Rep. Prog. Phys. **62**, 61 (1999)
2. Wang Y., Li L., Ong N. P.: Phys. Rev. B **73**, 024510 (2006)
3. Bauer, E., Paul, C., Berger, S., Majumdar, S., Michor, H., Giovannini, M., Saccone A. and Bianconi A., J. Phys.: Condens. Matter, **13**, L487 (2001)
4. Yang, J. Y., and Hu, M., Phys. Chem. Chem. Phys., **20**, 24222 (2018)
5. Jarlborg, T., Bianconi, A., Sci. Rep. **6**, 24816 (2016)
6. Li M., Lee-Hone N. R., Chi S., Liang R., Hardy W. N., Bonn D. A., Girt E. and Brounet D. M., New J. Phys. **18** 082001 (2016)
7. Mori H., J. Phys. Soc. Jpn. **75**, 051003 (2006)
8. Guterding D., Diehl S., Altmeyer M., Methfessel T, Tutsch U., Schubert H., Lang M., Muller J., Huth M., Jeschke H. O., Valenti R., Jourdan M., and Elmers H.-J. Phys. Rev. Lett., **116**, 237001 (2016)
9. Efimov, V. B., Makova, A. M., and Mezhov-Deglin, L. P. Low Temp. Phys. 21, 907 (1995)
10. Toda Y., Mertelj T., Naito T., and Mihailovic D.: Phys. Rev. Lett. **107**, 227002 (2011)
11. Tsuchiya, S., Nakagawa K., Yamada J., Taniguchi H., Toda Y.: Phys. Rev. B **96**, 134311 (2017)
12. Nakagawa K., Tsuchiya, S., Yamada J., Toda Y.: Europhys. Lett. **122**, 67003 (2018)
13. Giannetti C., Cilento F., Conte S. D., Coslovich G., Ferrini G., Molegraaf H., Raichle M., Liang R., Eisaki H., Greven M., Damascelli A., van der marel D., Parmigiani F.: Nat. Commun. **2**, 353 (2011)
14. Coslovich G., Giannetti C., Cilento F., Conte S. D., Abebaw T., Bossini D., Ferrini G.,Eisaki H., Greven M., Damascelli A., Parmigiani F.: Phys. Rev. Lett. **110**, 107003 (2013)
15. Anzai H., Delrieu J. M., Takasaki S., Nakajima S., Yamada J.: J. Cryst. Growth **154** 145 (1995)
16. Kini A. M., Geiser U., Wang H. H., Carlson K. D., Williams J. M., Kwok W. K., Vandervoort K. G., Thompson J. E., Stupka D. L., Jung D., Whangbo M.: Inorg. Chem. **29** 2555 (1990).
17. Ito H., Ishiguro T., Kubota M., and Saito G.,: J. Phys. Soc. Jpn. **65**, 2987 (1996)
18. Mckenzie R. H.: Science **278**, 820 (1997)
19. Lefebvre S., Wzietek P., Brown S., Bourbonnais C., Jerome D., Meziere C., Fourmigue M., Batail P.: Phys. Rev. Lett. **85**, 5420 (2000)
20. Powell B. J., McKenzie R. H.: J. Phys.: Condens. Matter **18** R827 (2006).

21. Mertelj T., Vujicic N., Borzda T., Vaskivskyi I., Pogrebna A., Mihailovic D.: Rev. Sci. Instrum. **85**, 123111 (2014)
22. Toda Y, Kawanokami F, Kurosawa T, Oda M, Madan I, Mertelj T, Kabanov V V, Mihailovic D, Phys. Rev. B **90**, 094513 (2014).
23. Nam M.-S., Ardavan A., Blundell S. J. and Schlueter J. A.: Nature **449**, 584 (2007)
24. Uehara T., Ito M., Taniguchi H. and Satoh K.: J. Phys. Soc. Jpn. **82**, 073706 (2013)
25. Tsuchiya S., Yamada J., Terashima T., Kurita N., Kodama K., Sugii K. and Uji S.: J. Phys. Soc. Jpn. **82**, 064711 (2013)
26. Kobayashi T., Ihara Y., Saito Y. and Kawamoto A.: Phys. Rev. B **89** 165141 (2014)
27. Toda Y., Mertelj T., Kusar P, Kurosawa T., Oda M., Ido M., Mihailovic D.: Physica C **493**, 112 (2013)
28. Sugano T., Hayashi H., Kinoshita M., Nishikida K.: Phys. Rev. B **39**, 11387 (1989)
29. Vlasova R. M., Drozdova O. O., Semkin V. N., Kushch N. D., Zhilyaeva E. I., Lyubovskaya R. N., Yagubskii E. B.: Physics of the Solid State **41** 814 (1999)
30. McGuire J. J., Room T., Pronin A., Timusk T., Schlueter J. A., Kelly M. E., Kini A. M. : Phys. Rev. B **64**, 094503 (2001)