PHYSICAL REVIEW B **81**, 205107 (2010)

Reexamination of ^{13}C-NMR in (TMTTF)$_2$AsF$_6$: Comparison with infrared spectroscopy

Shinji Hirose, Atsushi Kawamoto,* Noriaki Matsunaga, and Kazushige Nomura
Department of Quantum and Condensed Matter Physics, Hokkaido University, Kita-ku, Sapporo, Hokkaido 060-0810, Japan

Kaoru Yamamoto and Kyuya Yakushi
Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan

(Received 15 January 2010; revised manuscript received 31 March 2010; published 10 May 2010)

The charge order (CO) state can be observed by microprobe measurements such as nuclear magnetic resonance (NMR) and infrared spectroscopy. We used the infrared spectroscopy to examine (TMTTF)$_2$AsF$_6$ and confirmed the CO transition seen in previous ^{13}C-NMR studies. However we found the degree of charge disproportionation, $\Delta\rho=0.16$, to be smaller than that obtained from the analysis of T_1 in ^{13}C-NMR and the redistribution of charge density below spin Peierls transition predicted by ^{13}C-NMR was not observed at low temperature. We estimated the degree of spin disproportionation to be 0.11 from the analysis of the NMR shift in previous NMR studies. This small disproportionation does not require the redistribution of charge density at low temperature. The different behaviors of T_1 at charge-rich and charge-poor molecular sites observed by ^{13}C-NMR can be examined by the contribution of the commensurate antiferromagnetic fluctuation with $4k_F$.

DOI: 10.1103/PhysRevB.81.205107 PACS number(s): 71.30.+h, 74.70.Kn, 76.60.−k

I. INTRODUCTION

The CO state has been noted as the new physics in low-dimensional materials, where the off-site coulomb energy, V, plays an important role.[1] Indeed, the CO state has been observed by the nuclear magnetic resonance (NMR), vibrational spectroscopy, and x-ray crystallography in the quasi-two-dimensional organic conductors, α-(BEDT-TTF)$_2$I$_3$ and $\theta-$(BEDT-TTF)$_2$RbZn(SCN)$_4$ (BEDT-TTF =bis-ethylenedithio-tetrathiafulvalene).[2–8] Moreover, in some of these salts, superconductivity was confirmed, suggesting a relationship between superconductivity and charge fluctuations in the CO state.[9–11]

The series of quasi-one-dimensional conductors, (TMTCF)$_2X$ (C=S or Se, TMTTF =tetramethyltetrathiafulvalene, TMTSF=tetramethyltetraselenafulvalene), consists of two equivalent TMTCF molecules, whose position is related at the inversion center, and counter anion X. A ferroelectric anomaly has been observed at 100 K in (TMTTF)$_2$AsF$_6$, suggesting the breaking of the inversion center and a charge imbalance between two donor molecules.[12–15] The CO state is considered to exist on the universal phase diagram.[13] The ratio of charge disproportionation in the CO state was estimated as 3:1, which corresponds to a degree of charge disproportionation of $\Delta\rho=0.5$,[14] or 2:1 ($\Delta\rho=0.33$) (Ref. 15) from the ratio of spin-lattice-relaxation time, T_1, of each splitting peak in ^{13}C-NMR. Moreover, the split spectrum peaks combine into one broad peak below the spin Peierls (SP) transition temperature of 14 K, suggesting a charge redistribution from rich to poor sites.[15,16]

There are two powerful microscopic tools for examining CO state. NMR probes the degree of charge disproportionation, $\Delta\rho$, as a degree of the spin susceptibility. On other hand, vibrational spectroscopy measures the strength of chemical bond, which is ultimately determined by local electron density on the bond. Since chemical bond is much stronger than the intermolecular interactions such as off-site electron-electron repulsions that causes CO, the chemical structure should be unaffected by the CO. Therefore, it would be certain that the vibrational frequency is almost directly related to the molecular charge, ρ, on the bonding or antibonding orbit on the highest occupied molecular orbit (HOMO). Hence, the vibrational spectroscopies are complementary to NMR. To verify anomalous behavior of the charge observed in ^{13}C-NMR, we performed the reconsideration of previous NMR result and the measurement of infrared spectroscopy in (TMTTF)$_2$AsF$_6$.

II. RECONSIDERATION OF CO SYSTEMS IN NMR

A. Basis of NMR on the paramagnetic CO state

The NMR studies and experiments were done by two independent groups previously. Therefore, we discuss here the discrepancies between the vibrational spectroscopies and NMR. Most NMR studies on the paramagnetic CO state have been based on analysis in ^{13}C-NMR on θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$.[2] The previous NMR were performed on the two central carbon substituted by ^{13}C shown in Fig. 1(a). The NMR shift, δ, can be expressed as the sum of the Knight shift, K, and chemical shift, σ. The Knight shift can be also expressed as the product of the hyperfine coupling constant, A, and the spin susceptibility, χ, and the hyperfine coupling constant depends on the position of the ^{13}C

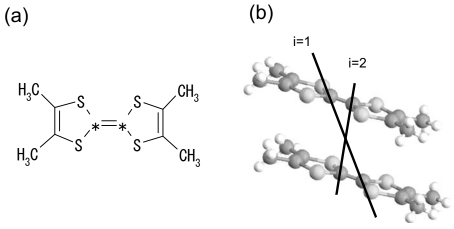

FIG. 1. (a) TMTTF molecule substituted by ^{13}C atom (*: ^{13}C atomic site). (b) ^{13}C nuclear site in TMTTF molecule.

nuclei. This implies that the NMR shift can be expressed as the following equation:

$$\delta_\rho = K_\rho + \sigma_\rho = A\chi_\rho + \sigma_\rho. \tag{1}$$

Here, the subscript denotes the charge status. The splitting of the NMR spectrum in ^{13}C-NMR of $(\mathrm{TMTTF})_2\mathrm{AsF}_6$ was considered to be caused by the splitting of the Knight shift and the chemical shift, depending on the change in ρ in the TMTTF molecule caused by the CO transition. Assuming that (a) the hyperfine coupling constant has the same value in the charge-rich and charge-poor molecular sites and (b) the charge density, ρ, is proportional to the spin density, the relationship between the charge and the Knight shift in charge-poor molecular site and charge-rich molecular site is expressed as

$$\rho_{poor}{:}\rho_{rich} = K_{poor}{:}K_{rich}. \tag{2}$$

The spin-lattice-relaxation time, T_1, in charge-poor molecular site and charge-rich molecular site can be generally expressed as

$$\frac{1}{T_{1,\rho}T} = \left(\frac{\gamma_I}{\gamma_e}\right)^2 \frac{2k_B}{\hbar^2} A^2 \sum_{\mathbf{q}} \frac{\mathrm{Im}\ \chi_\rho(\mathbf{q},\omega)}{\omega}, \tag{3}$$

where γ_e and γ_I are the gyromagnetic ratio of the electron and ^{13}C nuclei, $\hbar$ is Planck's constant, k_B is Boltzmann constant, and Im $\chi_\rho(\mathbf{q},\omega)$ is imaginary part of the dynamical susceptibility with wave vector, $\mathbf{q}$, and NMR frequency, ω. When we include an additional assumption that (c) the sum of imaginary part of the dynamical susceptibility is proportional to the square of the spin density, the relationship between ρ and T_1 can be given as

$$\rho_{poor}^2{:}\rho_{rich}^2 = 1/T_{1,poor}{:}1/T_{1,rich}. \tag{4}$$

Based on this relationship, the ratio of the charge disproportionation was estimated to be 3:1 or 2:1 from the ratio of the T_1 values of the peaks from two sites. According to previous reports, the different temperature dependences of T_1 in the two sites have been observed, whereas K showed similar temperature behavior in these sites.[14,15] The T_1^{-1} in the charge-rich molecular site did not show a significant temperature dependence, while the T_1^{-1} in the charge-poor molecular site drastically decreased with decreasing temperature. One explanation points to how the charge disproportionation changes with temperature. However, this explanation is inconsistent with the finding that the NMR shift is constant above SP transition. The analysis of T_1^{-1} requires the assumptions of at least (a) and (b). Namely, the disproportionation estimated from T_1^{-1} should be same as that from Knight shift. This discrepancy seems to give important information.

B. Estimation of the degree of spin disproportionation

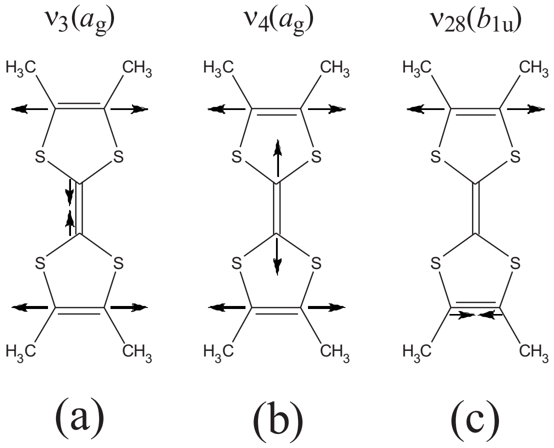

FIG. 2. Symmetric [(a) and (b)] and asymmetric (c) stretching modes of the TMTTF molecule.

To estimate the degree of charge disproportionation from the Knight shift, we need to determine the chemical shift. However, there is no authoritative value of the chemical shift of the partial ionic state. Therefore, the degree of disproportionation is determined not from the Knight shift but from T_1. The key idea is that the chemical shift arises mainly from coherent shielding current and is not much sensitive to the crystal structure. Indeed, when the spin susceptibility vanishes, no difference in the two positions is observed.[2–4] Hence, the NMR shift in the CO state is expressed as

$$\delta_{i,rich(poor)} = K_{i,rich(poor)} + \sigma_{rich(poor)} = A_i\chi_{rich(poor)} + \sigma_{rich(poor)}, \tag{5}$$

at the charge-poor and charge-rich molecular sites of ith nuclear position shown in Fig. 1(b). In ^{13}C-NMR of $(\mathrm{TMTTF})_2\mathrm{AsF}_6$, two local ^{13}C nuclear positions, $i=1,2$, exist. The ratio of the hyperfine coupling constant at the two local atomic positions can be expressed as

$$\frac{A_1}{A_2} = \frac{K_{1,rich(poor)}}{K_{2,rich(poor)}} = \frac{\delta_{1,rich(poor)} - \sigma_{rich(poor)}}{\delta_{2,rich(poor)} - \sigma_{rich(poor)}}. \tag{6}$$

From the values of the four NMR shifts of $\delta_{1,rich}=42$ kHz, $\delta_{1,poor}=36$ kHz, $\delta_{2,rich}=32$ kHz, $\delta_{2,poor}=28$ kHz, and $A_1/A_2=3$, which were evaluated from the slope of the K_1-K_2 plot in the metallic state above T_{CO},[14] the values of chemical shift can be determined to be $\sigma_{rich}=27$ kHz and $\sigma_{poor}=24$ kHz. Using these values, we can estimate $K_{poor}/K_{rich}=0.8$, corresponding to $\Delta\rho$ of 0.11. Working from the results of another group, we also obtained an estimation, $\Delta\rho$ of 0.10.[15] The $\Delta\rho$ values from the Knight shift are smaller than that from T_1.

III. DETERMINATION OF CHARGE DISPROPORTIONATION BY INFRARED SPECTRUM

TMTTF contains three C=C bonds in its molecular structure. Assuming that the donor molecule has D_{2h} symmetry, the normal modes for the stretching motions of the C=C bonds consist of two symmetric modes $\nu_3(a_g)$ and $\nu_4(a_g)$ [Figs. 2(a) and 2(b)] and one asymmetric modes $\nu_{28}(b_{1u})$ [Fig. 2(c)].

It has been known that for the TTF derivatives, including TMTTF, the C=C stretching modes show a large frequency shift which is proportional to the molecular ionicity.[17] The

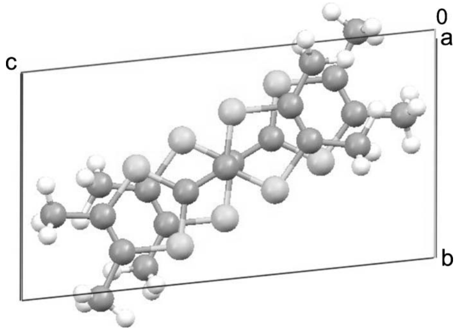

FIG. 3. Crystal structure of (TMTTF)$_2$AsF$_6$ salt along *a* axis.

molecular ionicity dependence allows us to estimate the charge density of TMTTF molecules in radical salts. However, because of the strong vibronic effect the frequencies of the symmetric modes do not show the simple linear dependence.[7] To avoid the complexities relevant to the vibronic effects, we focused in the present study on the asymmetric mode $\nu_{28}(b_{1u})$, which is free from such a vibrancy effect in estimating the degree of charge disproportionation.[18]

The infrared signal of the C═C stretching mode is as weak as other small vibrational signals such as bending modes of C—H bond or overtones of some low-frequency modes. Thus, to detect the signal, it is important to measure the spectrum from a single-crystal sample with properly polarized illumination. From this standpoint, one should measure the *c*-polarized spectrum, since the molecular long axis of TMTTF molecules are oriented along the [011] axis. However, the crystal was too thin to perform such measurement (the axis corresponds of the single crystal). Thus, in the present study, we measured the reflection spectrum for $\mathbf{E} \perp a$ (the one-dimensional axis) on the *ab* plane (parallel to the b' axis, which is about 60° off the molecular long axis shown in Fig. 3) to suppress the inclusion of electronic transition signal (the so-called CT band) that may screen the weak vibrational signals.[19–21]

Figure 4(a) shows the optical-conductivity spectrum calculated by Kramers-Kronig analysis of the reflection spectrum. Since the measurement was performed in air, a number of spike absorptions due to water vapor were overlayered on the reflectivity spectrum. For the close analysis of C═C stretching signals, we have eliminated the spikes absorptions in prior to the Kramers-Kronig transformation. The obtained optical conductivity spectrum exhibited a broad band and narrow peaks in the C═C stretching region. The broad band appearing around 1260 cm^{-1} would be attributable to the vibronically activated signal of $\nu_4(a_g)$ from the exceedingly broad shape.[18] On the other hand, the narrow peaks were assigned to vibrational signals, as shown in Fig. 4(a).[22,23]

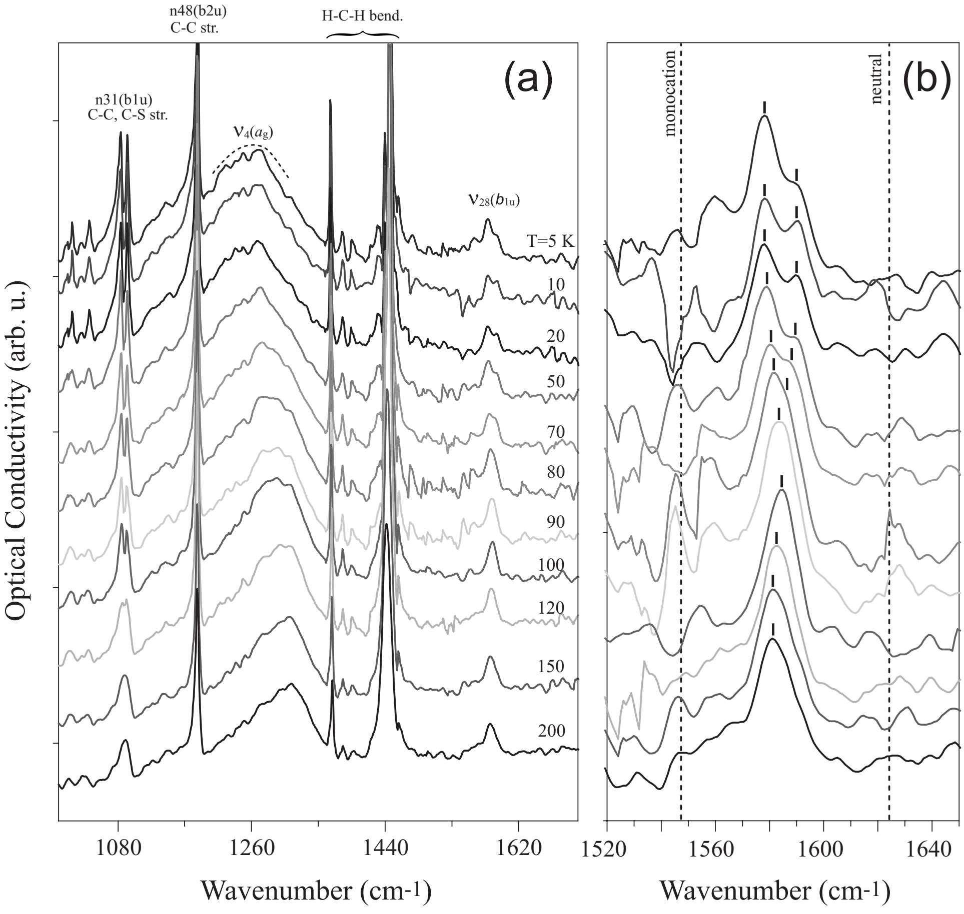

FIG. 4. (a) Temperature dependence of the infrared reflection spectrum of (TMTTF)$_2$AsF$_6$. Peak assignments were given in accordance with Ref. 22. (b) Magnification of $\nu_{28}(b_{1u})$ mode. The dotted lines represent the frequencies of the mode in neutral and monocationic states.

The spectrum shows an exceedingly broad band around 1260 cm^{-1}, which is probably attributable. Among these vibrational signals, we focus on the signals of $\nu_{28}(b_{1u})$, appearing around 1580 cm^{-1}, as this mode shows a simple linear dependence.

Figure 4(b) shows the magnification of the signals. At higher temperatures (for instance, $T=200$ K), there is only one band between the frequencies of $\nu_{28}(b_{1u})$ for the neutral and the monocationic states, as shown by the dotted lines. This indicates that the charge distribution is regarded as uniform within the limit of the spectral resolution. Note that the peak (at $\sim$1580 cm^{-1}) is located almost at the midpoint between the two lines. The peak position suggests that the charge density of the TMTTF molecules was approximately $+0.5e$. This is consistent with the two-to-one stoichiometry of the cation radical salt.

As the temperature decreases, the band exhibits a slight high-frequency shift, which is presumably due to an ordinary thermal contraction of bond length, followed by broadening from $\sim$90 K, then, finally splits into two components. It should be mentioned that, we have measured the Raman spectrum and confirmed that $\nu_3(a_g)$ mode also showed the similar temperature dependence and the degree of charge disproportionation as observed for the infrared signal of $\nu_{28}(b_{1u})$ mode.[24] The splitting of the ν_{28} signal indicates the occurrence of charge disproportionation. Although it is difficult to specify the precise temperature of the onset of the separation, this result appears to be consistent with the argument of the previous reports[14,15] that have proposed the occurrence of CO. However, we found that there is a noticeable difference in the degree of charge disproportionation evaluated by the vibrational frequency in comparison with the value estimated in previous NMR reports.[14,15]

Supposing that the average charge density is kept at $+0.5e$, the degree of charge disproportionation is given by

$$\Delta\rho = \rho_{rich} - \rho_{poor} = \frac{\omega_{rich} - \omega_{poor}}{\omega_{cation} - \omega_{neutral}}, \tag{7}$$

where ρ and ω represent the charge density of the TMTTF molecule and the vibrational frequency of the $\nu_{28}(b_{1u})$ mode, respectively. The subscript denotes the charge status of the TMTTF of interest. From this formula and the positions of the split peaks (at 1578 and 1590 cm^{-1}) as well as the reported frequencies for the neutral and monocationic state (1624 cm^{-1} and 1547 cm^{-1}, respectively), the degree of charge disproportionation ($\Delta\rho$) was calculated to be 0.16, i.e., $\rho_{rich}:\rho_{poor}=+0.58e:+0.42e$. This is less than half degree estimated by the previous NMR studies. It should be also noted that the separation of the two $\nu_{28}(b_{1u})$ peaks observed at $T=6$ K was almost equal to the split at $T=50$ K, whereas the NMR study suggested that the charge separation is diminished in the SP phase.

IV. DISCUSSION

The degree of charge disproportionation estimated from the Knight shift was smaller than that from T_1 in NMR and was comparable to that calculated from the vibrational spectroscopies. And the charge-redistribution behavior predicted by NMR was not observed by the vibrational spectroscopies. When the degree of charge disproportionation is small, the difference between the chemical shift in the charge-poor and charge-rich molecular sites is expected to be small, and the small difference of 3 kHz is consistent with small charge disproportionation. The broad spectrum at low temperatures masks this small splitting from the chemical shift. The single site of the central C═C enriched ^{13}C-NMR, which is free from the influence of Pake doublet, may detect the small difference created by the chemical shift.

We discuss here the small difference in the degree of charge disproportionation between the vibrational spectroscopy and analysis of Knight shift in ^{13}C-NMR. The wave function of the conduction electron in $(\mathrm{TMTTF})_2\mathrm{AsF}_6$ is given as

$$\Psi_{\mathbf{k}} = (c_{\mathbf{k},poor}\phi_{poor} + c_{\mathbf{k},rich}\phi_{rich})e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{8}$$

Here, $c_{\mathbf{k},\rho}$ is linear combination of atomic orbitals coefficient and ϕ_ρ is HOMO of TMTTF molecule. The charge in the charge-poor molecular site and charge-rich molecular sites can be expressed as

$$\rho_{poor} \propto \sum_{\mathbf{k}=unoccu} |c_{\mathbf{k},poor}|^2, \quad \rho_{rich} \propto \sum_{\mathbf{k}=unoccu} |c_{\mathbf{k},rich}|^2. \tag{9}$$

As the charge of on the donor molecule depends on the degree of the hole doping to the neutral molecule, the summation is performed from the hole-occupied band over Fermi energy in $(\mathrm{TMTTF})_2\mathrm{AsF}_6$. On the other hand, the local spin susceptibility in the charge-poor site and charge-rich site can be expressed as

$$\chi_{poor} \propto |c_{\mathbf{k}_F,poor}|^2, \quad \chi_{rich} \propto |c_{\mathbf{k}_F,rich}|^2. \tag{10}$$

If $c_{\mathbf{k},rich(poor)}$ is independent of the wave number, $\mathbf{k}$, we can obtain the relationship

$$\rho_{rich}:\rho_{poor} = \chi_{rich}:\chi_{poor}, \tag{11}$$

and this relationship corresponds to the assumption (b) in Sec. II A. Therefore the small difference in the degree of the disproportionation calculated from the vibrational spectroscopy and Knight shift might be considered to break the assumption (b) in Sec. II A.

We next discuss the behavior of T_1. If the assumption (c) in Sec. II A is broken, the behavior of T_1 need not be the same as that of the Knight shift. In general, the amplitude of the dynamic susceptibility depends on the crystallographically independent sites. For example, the T_1 in a high-T_c cuprate shows different behavior on the ^{63}Cu and ^{17}O sites. The ^{63}Cu site lies on an antinode of the magnetic fluctuation whereas the ^{17}O site sits at a node of the fluctuations. If the charge-rich molecular site is on an antinode and the charge-poor molecular site is on a node of the commensurate magnetic fluctuation as shown in Fig. 5, the spin-lattice-relaxation rate of charge-rich molecular site is expected to show a Curie-type temperature-independent behavior and the nuclear magnetization recovers faster than that of the charge-poor molecular site. As a result, the value of T_1 shows different behaviors on two molecular sites. These behaviors were observed in the ^{13}C-NMR of the quasi-one-dimensional

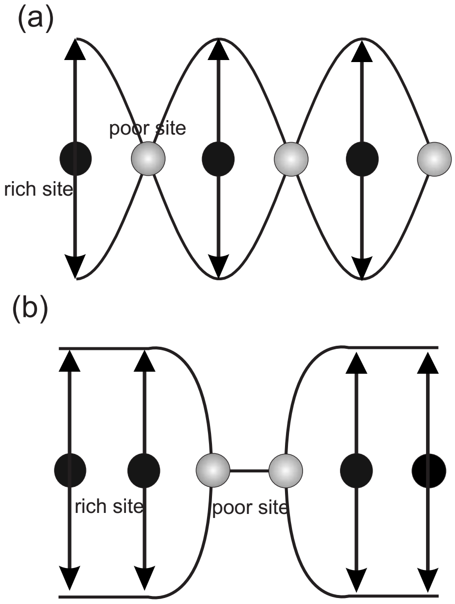

FIG. 5. The magnetic fluctuation at charge-rich and -poor molecular sites in case of (a) rich-poor-rich-poor pattern and (b) rich-rich-poor-poor pattern. Two-headed arrows show the amplitude of the magnetic fluctuation at each molecular site.

organic conductor, $(DI\text{-}DCNQI)_2Ag$.[25] In $(DI\text{-}DCNQI)_2Ag$, T_1 remains constant in the charge-rich molecular site and in charge-poor molecular site increases as the temperature decreases, as it does in $(TMTTF)_2AsF_6$. While the antiferromagnetic transition occurs in low temperature in $(DI\text{-}DCNQI)_2Ag$, in $(TMTTF)_2AsF_6$, the antiferromagnetic transition does not occur, and the SP transition occurs in the low temperature. However, since $(TMTTF)_2AsF_6$ is in the vicinity of the antiferromagnetic phase in the universal phase diagram of $(TMTCF)_2X$, it is likely that the antiferromagnetic fluctuations in $(TMTTF)_2AsF_6$ is exist.

The antiferromagnetic fluctuation reflects not only the temperature dependence of T_1^{-1} but also the magnitude of T_1^{-1}. The value of $T_1^{-1}=25\ \mathrm{s}^{-1}$ in charge-rich molecular site below CO transition is comparable to $T_1^{-1}=15\ \mathrm{s}^{-1}$ at 50 K in $(TMTTF)_2Br$ due to commensurate antiferromagnetic fluctuation.[26] These considerations suggest the existence of commensurate antiferromagnetic fluctuations under the CO state in $(TMTTF)_2AsF_6$ and commensurate antiferromagnetic fluctuation gives the important information about the pattern of the disproportionation. The pattern of disproportionation of CO in TMTTF salt is indistinctive by vibrational spectrum and NMR spectrum. The patterns are expected to be rich-poor-rich-poor ($4k_F$) or rich-rich-poor-poor ($2k_F$) structure along one-dimensional chain. Considering the sinusoidal magnetic fluctuation, the rich-poor-rich-poor structure [Fig. 5(a)] is more suitable than the rich-rich-poor-poor structure [Fig. 5(b)]. Two patterns of dimerization in spin Peierls state are expected. One is intercolumn dimerization and another is intracolumn dimerization. The $4k_F$ structure may suggest the intercolumn dimerization as in $\alpha\text{-}(BEDT\text{-}TTF)_2I_3$ and $\theta\text{-}(BEDT\text{-}TTF)_2RbZn(SCN)_4$. To clarify the pattern, however, the detailed crystal structure studies by x-ray diffraction or the detailed investigation of vibrational spectroscopy including electron-molecular vibration (emv) coupling are desired.

V. CONCLUSION REMARKS

The previous NMR studies of the paramagnetic CO state in $(TMTTF)_2AsF_6$ suggested the existence of a CO state with a large degree of charge disproportionation below 100 K and charge redisproportionation below the SP transition. However, the degree of charge disproportionation indicated by vibrational spectroscopy is much smaller than that from T_1 of NMR and does not show a significant temperature dependence until low temperatures. The analysis of the NMR shift using results from the previous studies is consistent with vibrational spectroscopic study, and the different behaviors of T_1 on charge-rich and charge-poor sites may predict the commensurate antiferromagnetic fluctuations in the CO state.

ACKNOWLEDGMENTS

The authors thank K. Sato and N. Shimohara of Hokkaido University for the sample preparation and K. Hiraki of Gakusyuin University for stimulating discussions on $(DI\text{-}DCNQI)_2Ag$. This study was supported in part by a Grant-in-Aid for Scientific Research (Grant No. 20540338) from the Ministry of Education, Culture, Sports, Science, and Technology.

---

*atkawa@phys.sci.hokudai.ac.jp

[1] H. Seo and H. Fukuyama, J. Phys. Soc. Jpn. **66**, 1249 (1997).
[2] K. Miyagawa, A. Kawamoto, and K. Kanoda, Phys. Rev. B **62**, R7679 (2000).
[3] T. Kawai and A. Kawamoto, J. Phys. Soc. Jpn. **78**, 074711 (2009).
[4] S. Moroto, K. I. Hiraki, Y. Takano, Y. Kubo, T. Takahashi, H. M. Yamamoto, and T. Nakamura, J. Phys. IV **114**, 399 (2004).
[5] Y. Takano, K. Hiraki, H. M. Yamamoto, T. Nakamura, and T. Takahashi, J. Phys. Chem. Solids **62**, 393 (2001).
[6] R. Wojciechowski, K. Yamamoto, K. Yakushi, and A. Kawamoto, Synth. Met. **135-136**, 587 (2003).
[7] K. Yamamoto, K. Yakushi, K. Miyagawa, K. Kanoda, and A. Kawamoto, Phys. Rev. B **65**, 085110 (2002).
[8] T. Kakiuchi, Y. Wakabayashi, H. Sawa, T. Takahashi, and T. Nakamura, J. Phys. Soc. Jpn. **76**, 113702 (2007).
[9] N. Tajima, A. E. Tajima, M. Tamura, Y. Nishio, and K. Kajita, J. Phys. Soc. Jpn. **71**, 1832 (2002).
[10] B. Salameh, A. Nothardt, E. Balthes, W. Schmidt, D. Schweitzer, J. Strempfer, B. Hinrichsen, M. Jansen, and D. K. Maude, Phys. Rev. B **75**, 054509 (2007).
[11] J. Merino and R. H. McKenzie, Phys. Rev. Lett. **87**, 237002 (2001).
[12] P. Monceau, F. Y. Nad, and S. Brazovskii, Phys. Rev. Lett. **86**,

4080 (2001).

[13] D. S. Chow, F. Zamborszky, B. Alavi, D. J. Tantillo, A. Baur, C. A. Merlic, and S. E. Brown, Phys. Rev. Lett. **85**, 1698 (2000).

[14] F. Zamborszky, W. Yu, W. Raas, S. E. Brown, B. Alavi, C. A. Merlic, and A. Baur, Phys. Rev. B **66**, 081103(R) (2002).

[15] S. Fujiyama and T. Nakamura, J. Phys. Soc. Jpn. **75**, 014705 (2006).

[16] T. Nakamura, K. Furukawa, and T. Hara, J. Phys. Soc. Jpn. **76**, 064715 (2007).

[17] A. Girlando, C. Pecile, A. Brillante, and K. Syassen, Solid State Commun. **57**, 891 (1986).

[18] T. Yamamoto, M. Uruichi, K. Yamamoto, K. Yakushi, A. Kawamoto, and H. Taniguchi, J. Phys. Chem. B **109**, 15226 (2005).

[19] M. Dressel, Naturwiss. **94**, 527 (2007).

[20] M. Dumm, M. Abaker, M. Dressel, and L. K. Montgomery, J. Low Temp. Phys. **142**, 609 (2006).

[21] M. Dumm, B. Salameh, M. Abaker, L. K. Montgomery, and M. Dressel, J. Phys. IV **114**, 57 (2004).

[22] M. Meneghetti, R. Bozio, I. Zanon, C. Pecile, C. Ricotta, and M. Zanetti, J. Chem. Phys. **80**, 6210 (1984).

[23] The appearance of the vibronic mode ν_4 in the b' polarization may be caused by the staggered stack along the a axis and/or weak interstack interaction.

[24] K. Yamamoto and K. Yakushi (unpublished).

[25] K. Hiraki and K. Kanoda, Synth. Met. **103**, 1806 (1999).

[26] S. Fujiyama and T. Nakamura, J. Phys. Chem. Solids **63**, 1259 (2002).