PHYSICAL REVIEW B VOLUME 21, NUMBER 1 1 JANUARY 1980

Nuclear-spin-lattice relaxation in the one-dimensional organic conductor acridinium ditetracyanoquinodimethane (Adn $TCNQ_2$)

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(Received 20 July 1979)

Studies of the proton spin-lattice relaxation in the one-dimensional organic conductor acridinium ditetracyanoquinodimethane (Adn $TCNQ_2$) are presented. Using partially deuterated samples the relaxations of the different chains were separated. In the high-temperature region ($50 < T < 300$ K) the relaxation is dominated almost entirely by the TCNQ chains, and the ratio of the different chain-relaxation rates indicates nearly complete charge transfer with an estimate of only $\sim 10^{-3}$ spins per Adn molecule. The dependence of the TCNQ chain-relaxation rate on the proton-resonance frequency was found to follow a $\ln \nu^{-1}$ behavior for $\nu = 7-52$ MHz at room temperature. This frequency dependence together with the observed temperature dependence is accounted for by an anisotropic-spin-diffusion model with small Coulomb interaction. Below ~ 40 K the contribution of the acridinium chains to the relaxation rate increases gradually as the temperature is lowered and at ~ 1.5 K it is comparable to the TCNQ contribution. A characteristic weak maximum of the relaxation rate is observed at about 7–10 K.

I. INTRODUCTION

The organic charge-transfer salts quinolinium (tetracyanoquinodimethane)$_2$ (Qn $TCNQ_2$) and Adn $TCNQ_2$ (Adn = acridinium) are 2:1 TCNQ-based salts possessing very similar physical properties.[1,2] They are considered among the best room-temperature organic conductors ($\sim 100\,\Omega^{-1}$ cm^{-1}) and have similar temperature dependence as well as magnitude of their magnetic susceptibility, thermoelectric power, specific heat, and electrical conductivity. Their crystalline structure[3,4] consists of columns of donor and acceptor molecules, stacked in a plane-to-plane manner. Within each TCNQ column the intermolecular spacing is very short (~ 3.25 Å), giving rise to appreciable overlap of the electronic wave functions and in turn to the high electrical conductivity in the direction of the columns. The columns of the TCNQ acceptors are packed intimately within the crystal; however, because of the planar structure of the TCNQ molecules, there is minimal overlap of the electronic wave functions and much smaller conductivity in the transverse directions. The Adn molecule is bigger than Qn, giving rise to somewhat smaller donor-acceptor column separation in Adn $TCNQ_2$; hence one may expect an anisotropy of the conductivity nearly as large as in Qn $TCNQ_2$ ($\sigma_{\parallel}/\sigma_{\perp} \sim 200$).[5] The longitudinal conductivity[6,7] is metalliclike at room temperature and has a weak maximum at T_m (~ 150 K for Adn $TCNQ_2$ and ~ 240 for Qn $TCNQ_2$), below which it decreases exponentially. The paramagnetic susceptibility,[8] on the other hand, maintains its temperature-independent value (within $\sim 20\%$) down to 40–50 K, below which it rises steeply as the temperature is lowered. Nuclear spin-lattice relaxation in Qn $TCNQ_2$ (Refs. 9 and 10) and thermoelectric power[6,11] in both salts also do not show any evidence for a phase transition at $T \sim T_m$.

The proton spin-lattice relaxation time T_1 in the Qn $TCNQ_2$ system has been extensively studied in recent years. The one-dimensional (1-D) nature of the electronic spin dynamics has been verified through the special frequency dependence of T_1 ($T_1^{-1} \propto \omega^{-1/2}$).[12-14] Both this frequency dependence and the Korringa-like temperature dependence have been analyzed assuming a relatively weak on-site Coulomb repulsion and correlated with the nearly temperature-independent susceptibility[15] and the strongly temperature-dependent longitudinal conductivity.[13,14] No T_1 measurements have been reported so far for Adn $TCNQ_2$. We have therefore studied the temperature and frequency dependence of T_1 in selectively deuterated samples of Adn $TCNQ_2$. We have found that the gross features are similar to those of Qn $TCNQ_2$ but differ in two respects. T_1^{-1} is smaller and is better described by a $\ln \omega^{-1}$ law rather than the $\omega^{-1/2}$ law, which may indicate a stronger interchain coupling in Adn $TCNQ_2$.

II. EXPERIMENTAL RESULTS

Two samples in the form of black microcrystalline powders were used in this study: a nondeuterated Adn $TCNQ_2$ (sample I) and a deuterated sample Adn

TCNQ$_2^*$ (sample II), on which 96% of all TCNQ protons were replaced by deuterium. The deuterium enrichment of this sample was determined by low-resolution mass spectroscopy. The samples were prepared by the reaction of acridinium iodide with a 30% molar excess of TCNQ[16] in acetonitrile using Vycor glassware. The elemental chemical analysis of the recrystallized powders showed them to be chemically pure.

The proton spin-lattice relaxation rates were measured as a function of the temperature between 1.5 and 295 K at several frequencies and at ambient temperature as a function of the proton-resonance frequency between 7.1 and 52 MHz (for sample I). The recovery of the nuclear magnetization after saturation (achieved by one or more $\frac{1}{2}\pi$ pulses) was exponential over more than a decade at all temperatures and frequencies investigated, thus defining a unique spin-lattice relaxation time T_1. The temperature dependence of T_1^{-1} in both samples I and II (denoted hereafter as $T_{1\mathrm{I}}^{-1}$ and $T_{1\mathrm{II}}^{-1}$, respectively) are shown on a log-log plot in Fig. 1 for proton Larmor frequencies $\nu = 52$ and 10.5 MHz. Similar data (not shown here) were obtained at other frequencies. We note the similar behavior of T_1^{-1} in both samples, with T_1^{-1} being roughly proportional to the temperature for $90 < T < 300$ K and the existence of a broad maximum around 6–8 K. The temperature at which this maximum occurs depends only slightly on the proton-resonance frequency (or equivalently on the external magnetic field). The inset of Fig. 1 shows that above ~50 K, T_1^{-1} is nearly three times larger in sample I than in sample II. This demonstrates that the TCNQ protons relax more rapidly than the Adn protons, and thus in this temperature region the main relaxation mechanism originates in the TCNQ chains (see below). The ratio $T_{1\mathrm{II}}^{-1}/T_{1\mathrm{I}}^{-1}$ increases monotonically as the temperature is lowered below ~40 K, and at ~1.5 K the relaxation rate of the protons on the two chains is comparable. Although no measurements were made below 1.5 K, a naive extrapolation of $T_{1\mathrm{II}}^{-1}/T_{1\mathrm{I}}^{-1}$ to lower temperatures indicates that at temperatures below ~1.5 K the Adn protons relax more quickly than the TCNQ protons. The dependence of the relaxation rate of sample I upon the proton-resonance frequency is shown in Fig. 2 in two representations: T_1^{-1} vs $\ln\nu^{-1}$ (circles, lower scale) and T_1^{-1} vs $\nu^{-1/2}$ (crosses, upper scale) appropriate for 2-D and 1-D diffusion process, respectively. Because of the limited range of frequencies investigated, it is difficult from these plots alone to determine the proper description for the electronic spin diffusion in these frequencies. However, an analysis of the data in terms of an anisotropic-spin-diffusion model shows that in the experimental frequency range (electron spin Larmor frequencies $\omega_e = 2.9\times10^{10}$ sec^{-1} to 2.2×10^{11} sec^{-1}), the spin motion is essentially two dimensional (see below).

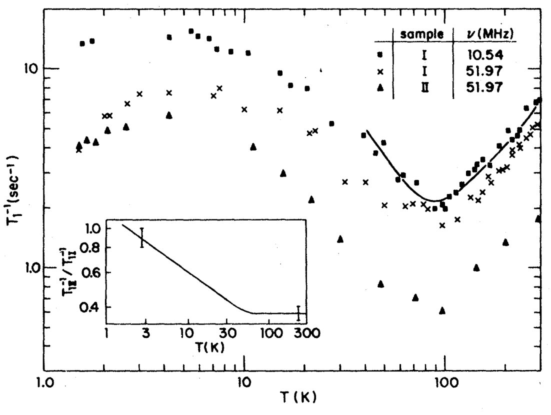

FIG. 1. Temperature dependence of T_1^{-1} in nondeuterated (sample I) and deuterated (sample II) Adn TCNQ$_2$. The solid line through the data points represents a fit of the data to Eq. (12), as explained in the text. The inset shows the ratio $T_{1\mathrm{II}}^{-1}/T_{1\mathrm{I}}^{-1}$ vs T as obtained from the data points. Note the log-log scales.

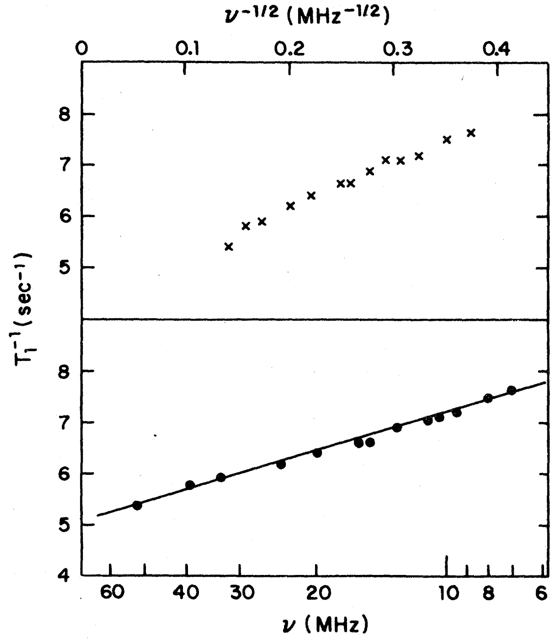

FIG. 2. Frequency dependence of $T_{1\mathrm{I}}^{-1}$ at room temperature plotted as $T_{1\mathrm{I}}^{-1}$ vs $\ln\nu^{-1}$ (full dots) and vs $\nu^{-1/2}$ (crosses).

III. ANALYSIS OF THE RESULTS

Adn TCNQ$_2$ is composed of two distinct subsystems: the TCNQ anion chains and the Adn cation chains. The two chains possess different electronic behavior, and we therefore associate with each chain a different proton spin-lattice relaxation time: T_{1Q} for the TCNQ protons and T_{1A} for the acridinium protons. The dipolar interaction between protons on the two chains ensures a common spin-lattice relaxation time for the undeuterated or partially deuterated samples.[10] The common relaxation rate is a weighted average of the two rates T_{1Q}^{-1} and T_{1A}^{-1}. In Adn $TCNQ_2$ the ratio between the number of Adn chain protons to that of the TCNQ chains is 10:8. Thus, if the degree of deuteration of the TCNQ molecule is x ($x=1$ means fully deuterated molecule), the common relaxation rate is given by

$$T_1^{-1}(x)=\frac{1}{9-4x}[5T_{1A}^{-1}+(4-4x)T_{1Q}^{-1}] \quad . \tag{1}$$

Using this relation and the measured relaxation rate in sample I ($x=0$) and sample II ($x=0.96$), the individual chain relaxation rates T_{1A}^{-1} and T_{1Q}^{-1} are obtained. Thus, for instance, the ratio $T_{1\mathrm{II}}^{-1}/T_{1\mathrm{I}}^{-1}=0.37\pm0.03$ at high temperatures (Fig. 1) implies $T_{1A}^{-1}/T_{1Q}^{-1}=0.18\pm0.02$, which means that the TCNQ spins dominate the relaxation mechanism above $T\simeq50$ K. At this point it is instructive to distinguish between intrinsic and cross-relaxation rates and write

$$T_{1Q}^{-1}=T_{1QQ}^{-1}+T_{1AQ}^{-1} \quad , \tag{2}$$

$$T_{1A}^{-1}=T_{1AA}^{-1}+T_{1QA}^{-1} \quad , \tag{3}$$

where $T_{1\alpha\alpha}^{-1}$ and $T_{1\beta\alpha}^{-1}$ ($\alpha,\beta=Q$ or A) are the α-chain proton-relaxation rates due to the α-chain electrons and the β-chain electrons, respectively. The intrinsic relaxation is caused mainly by the contact and intramolecular dipolar interactions, whereas the cross relaxation is caused by the dipolar interaction between protons and electrons on two different chains and is therefore much weaker ($T_{1\beta\alpha}^{-1} << T_{1\alpha\alpha}^{-1}$). In the high-temperature region we have $T_{1A}^{-1}\simeq\frac{1}{6}T_{1Q}^{-1}$, and thus T_{1AQ}^{-1} in Eq. (2) can be neglected, and one has

$$T_{1QQ}^{-1}\cong T_{1Q}^{-1}=1.9T_{1\mathrm{I}}^{-1} \quad (T\gtrsim50\text{ K}) \quad . \tag{4}$$

The evaluation of T_{1AA}^{-1} requires the knowledge of the contribution of the TCNQ spins to the Adn proton relaxation, since T_{1QA}^{-1} cannot be neglected in Eq. (3). Assuming that the cross hyperfine coupling is purely dipolar, we write for the mean-square coupling of Adn protons to the TCNQ electron spin the expression[14,17]

$$d_{QA}^2=(g\mu_B\gamma_N)^2\frac{1}{10}\sum_{\lambda=1}^{10}\sum_{l}\left(\sum_i\sigma_i r_{il\lambda}^{-3}\right)^2 \quad , \tag{5}$$

where $r_{il\lambda}$ is the distance between the proton λ ($\lambda=1$ to 10) of a given Adn and the atom i of the TCNQ anion l, and σ_i is the spin density of the atom i.. Using the improved self-consistent-field–molecular-orbital (SCF–MO) calculation by Jonkman *et al.*[18] for σ_i and the crystal structure parameters of Adn $TCNQ_2$,[4] we have computed d_{QA}^2, taking into account 72 TCNQ neighbors for each proton.[19] The result is

$$d_{QA}/g\mu_B=0.20\text{ G} \quad .$$

This is of a reasonable magnitude[14] and is considerably smaller than the scalar (contact) TCNQ hyperfine coupling in solids ($|a_Q|/g\mu_B=1.2$ G) (Ref. 20) or from the TCNQ intramolecular dipolar coupling ($d_Q/g\mu_B=0.60$ G).[20]

Both T_{1QA}^{-1} and T_{1QQ}^{-1} involve TCNQ spin fluctuations and can be expressed as follows:

$$T_{1QQ}^{-1}=\frac{3}{5}\left(\frac{d_Q}{\hbar}\right)^2F_Q(\omega_N)+\hbar^{-2}(a_Q^2+\tfrac{7}{5}d_Q^2)F_Q(\omega_e) \quad , \tag{6}$$

$$T_{1QA}^{-1}=\left(\frac{d_{QA}}{\hbar}\right)^2[\tfrac{3}{5}F_Q(\omega_N)+\tfrac{7}{5}F_Q(\omega_e)] \quad , \tag{7}$$

where powder averages were assumed; $F_Q(\omega)$ is the fluctuation spectrum of the TCNQ spins, and ω_N and ω_e are the nuclear and electron Larmor frequencies, respectively. Estimation of T_{1QA}^{-1} requires the determination of $F_Q(\omega)$, which can be done via the measured frequency dependence of $T_{1\mathrm{I}}^{-1}$ and Eq. (4). Assuming that the frequency dependence of T_{1QQ}^{-1} is contained entirely in $F_Q(\omega_e)$, we have analyzed (see Sec. IV) $T_{1QQ}^{-1}(\omega_e)$. From this analysis and the above value of d_{QA}, it turns out that T_{1QA}^{-1} accounts for at least 70% of the total relaxation of the Adn protons. We thus obtain

$$T_{1AA}^{-1}\simeq0.05T_{1QQ}^{-1} \quad (T\gtrsim50\text{ K}) \quad . \tag{8}$$

This small value of T_{1AA}^{-1} is consistent with nearly complete charge transfer from Adn to TCNQ, leaving the cation chain with near zero-spin concentration while the TCNQ spin concentration is $C\cong\frac{1}{2}$. In fact, from Eq. (8) we can estimate the spin concentration on the Adn chain. Assuming a spin distribution for Adn similar to that of NMP (*N*-methylphenazinium) in NMP TCNQ in which the NMP spin concentration was found to be $\simeq$20%,[17] a direct comparison of T_{1AA}^{-1} to the intrinsic NMP relaxation rate T_{1PP}^{-1} ($\simeq$85 $\sec^{-1}$ at ambient)[17] gives an upper estimate of $\simeq1\times10^{-3}$ spins per Adn molecule in Adn $TCNQ_2$. For comparison, the estimate in Qn $TCNQ_2$ is $\simeq5\times10^{-4}$ spins per Qn molecule.[14]

At $T<50$ K the ratio $T_{1\mathrm{II}}^{-1}/T_{1\mathrm{I}}^{-1}$ increases as the temperature is reduced and reaches the value $\simeq1$ at 1.5 K. Equation (1) thus implies that T_{1A}^{-1}/T_{1Q}^{-1} increases towards unity at 1.5 K. Therefore, at low temperatures the contribution of the two chains to the relaxation is comparable, and T_{1AA}^{-1} cannot be ignored in the analysis of the relaxation process. Using Eqs. (3) and (1) together with Fig. 1, it can be shown that $T_{1AA}^{-1}/T_{1QQ}^{-1}$ increases gradually as T decreases (roughly as T^{-1}) even below the maximum at $\simeq$7 K observed both in $T_{1\mathrm{I}}^{-1}$ and $T_{1\mathrm{II}}^{-1}$. We can conclude that at low temperatures the Adn chains play an important role in the relaxation of Adn $(\mathrm{TCNQ})_2$.

IV. DISCUSSION

A. High-temperature region ($T \gtrsim 50$ K)

The similarity of the physical properties of Qn TCNQ_2 and Adn TCNQ_2 noted above is evident also in the temperature and frequency dependence of the nuclear-relaxation data. Recent analyses[13–15] of the nuclear-relaxation data in Qn TCNQ_2 showed this conductor to be a "small-U" case; that is, the effective screened on-site Coulomb interaction on the TCNQ chain is relatively weak, and the electronic spin and charge dynamics are basically the same. We shall attempt therefore to analyze the T_1 data in the present case of Adn TCNQ_2 by a theory which treats the short-wavelength ($q \simeq 2k_F$) spin-response function as coherent and 1-D while the long-wavelength case ($q \simeq 0$) is diffusive.[15,21] The nuclear-relaxation rate can be expressed in terms of the imaginary part of the wave vector and frequency-dependent electronic susceptibility $\chi(\vec{q},\omega)$ both for the contact hyperfine interaction[22] and the dipolar one.[21] Assuming no q dependence of the hyperfine coupling constants, the relaxation rate is given by Eq. (6) with

$$F_Q(\omega) = (2k_BT/g^2\mu_{\mathrm{B}}^2)\sum_q \chi''(\vec{q},\omega)/\omega \ , \tag{9}$$

where $\chi(\vec{q},\omega)$ is calculated at zero external magnetic field. When $ql > 1$ (where l is the electronic mean free path), $\chi''(\vec{q},\omega)$ is given by the usual metallic expression,[22] which for the 1-D case has appreciable values only for $q \simeq 0$, $2k_F$. The contribution of $q = 2k_F$ for this case including the Coulomb enhancement has been dealt with in detail previously[21,23] and found to be frequency independent. For $ql < 1$ the susceptibility is diffusive[24] and is given by

$$\chi(\vec{q},\omega) = \chi_s \frac{Dqq}{Dqq - i\omega} \ , \tag{10}$$

where χ_s is the usual (enhanced) Pauli spin susceptibility, and D is the (anisotropic) diffusion constant. In a purely 1-D system with no interchain hopping[21,24] $D = D_1 = \tau v_F^2(1-\alpha)$, where v_F is the Fermi velocity, $(1-\alpha)$ is the Stoner enhancement factor, and $\tau = l v_F^{-1}$.[25] When the interchain coupling is finite, electrons diffuse slowly in the transverse directions (by hopping between parallel chains), and the diffusion constant in Eq. (10) becomes anisotropic. In this case we write the imaginary part of Eq. (10)

$$\omega^{-1}\chi''(\vec{q},\omega) = \chi_s \left[\sum_i D_i q_i^2 / (\sum_i D_i q_i^2)^2 + \omega^2 \right] \ , \tag{11}$$

where $i = 1$ denotes the chain direction, and $i = 2, 3$ are the two transverse directions. The case $D_2 = D_3 << D_1$ was considered in detail previously.[15] For Adn TCNQ_2 it is appropriate to consider the fully anisotropic case $D_1 >> D_2 > D_3$ (see below). Using Eq. (11) the calculation of $F_Q(\omega)$ in Eq. (9) is straightforward, and the final result is given in the Appendix. It is seen that T_1 is frequency dependent only when $\omega_e > D_3\pi^2 a_3^{-2}$ (a_i is the lattice parameter in the direction i); in this case with $\omega_N = \omega_e/658 << D_3\pi^2 a_3^{-2}$, we have

$$T_{1QQ}^{-1} = \frac{k_BT\chi_s}{\hbar^2(g\mu_{\mathrm{B}})^2}[(a_Q^2 + 2d_Q^2)f_2 + \tfrac{3}{5}d_Q^2 f_1(0) + (a_Q^2 + \tfrac{7}{5}d_Q^2)f_1(\omega_e)] \ , \tag{12}$$

where $f_2 = 2\pi h\chi_s K(\alpha)$ is the contribution of the nondiffusive $q \simeq 2k_F$ part of the response function, and $K(\alpha)$ is the 1-D Coulomb enhancement factor which gives rise to the enhancement of T_1^{-1} with respect to the Korringa relation.[21,23]

The frequency dependence is contained in $f_1(\omega_e)$ and can be compared with the observed frequency dependence at room temperature (Fig. 2). Consistent with our treatment we have assumed moderate Coulomb enhancement, $K(\alpha) \simeq 1–2$ in Eq. (12) and also $\ln D_2/D_3 \sim 2–5$, i.e., moderate to substantial anisotropy in the transverse plane. A two-parameter least-squares fit of the data to Eq. (12) has then been carried out, which yielded $D_1 a_1^{-2} \simeq 3\times10^{13}$ sec^{-1} and $D_2 a_2^{-2} \simeq 2\times10^{11}$ sec^{-1} at room temperature. D_1, χ_s, and the parallel conductivity $\sigma_\parallel$ are all related as follows[1,13]:

$$\sigma_\parallel = \eta(E_F)e^2D_1 = 2\chi_s e^2 D_1/g^2\mu_{\mathrm{B}}^2 \ , \tag{13a}$$

$$D_1 = v_F l(1-\alpha) = (2\pi\hbar\chi_s)^{-1} l/a_1 \ , \tag{13b}$$

where $\eta(E_F)$ is the density of states at the Fermi energy. Using the measured susceptibility and the above estimate for D_1, Eq. (13a) gives for $\sigma_\parallel$ a value which agrees within a factor of 2 with the measured conductivity. Or alternatively, Eq. (13b) yields for the apparent mean free path $l/a_1 \approx 0.2–0.3$, whereas the measured conductivity yields, through the Drude formula, $l/a_1 \approx 0.1–0.2$. (This small value of l/a_1 means that the charge motion is better described by the value of D_1, which is related to the electron hopping, rather than the apparent mean free path l.) We note here that similar results were obtained also for Qn TCNQ_2,[13,25] and TTF TCNQ.[21] With the above value of D_2, we see that in the measured range $\omega_e << \pi^2 D_2 a_2^{-2}$, consistent with the $\ln\omega_e^{-1}$ law shown in Fig. 2. Thus in the measured frequency regime the anisotropic spin diffusion may be regarded as 2-D. Furthermore, attempts to force a $\omega_e^{-1/2}$ fit to the T_1^{-1} data (i.e., 1-D spin diffusion as in Qn TCNQ_2,[13]) yielded a very high intrachain diffusion constant ($D_1 a_1^{-2} = 7\times10^{14}$ sec^{-1} or $l a_1^{-1} \simeq 6$) and unreasonably high anisotropy ($D_1/D_2 > 10^6$). Analyses of the frequency dependence at various temperatures between ambient and ~60 K, assuming a $\ln\omega_e^{-1}$ behavior, are consistent with D_2 being roughly temperature independent (within ~30%) and $D_1 \propto \sigma_{\parallel}$ [Eq. (13)].

Comparing again Adn $TCNQ_2$ with Qn $TCNQ_2$, we note that in Qn $TCNQ_2$ T_1^{-1} was found to follow $\omega_e^{-1/2}$ (i.e., 1-D diffusion) even at the lowest frequency investigated (1.6×10^{10} sec^{-1}), while Adn $TCNQ_2$ shows 2-D spin diffusion at frequencies as high as $\omega_e = 2.2 \times 10^{11}$ sec^{-1}. Thus the transverse diffusion coefficient in Adn $TCNQ_2$ is at least an order of magnitude larger than in Qn $TCNQ_2$. Since the TCNQ column separation in Adn $TCNQ_2$ is not smaller than in Qn $TCNQ_2$ the diffusion among different TCNQ columns in the two conductors is expected to be of the same order. We argue, therefore, that the bigger Adn molecules which are packed closer to the TCNQ's give rise to relatively large probability of electron hopping to the Adn empty states. If the transfer matrix elements for such a process are t_2, then the hopping rate of electrons between the localized Adn states and the TCNQ chain states is $\tau_2^{-1} = t_2/\hbar$. Assuming that D_2 is connected with this process, we have $t_2 = \hbar a_2^{-2} D_a \simeq 2$ meV which is of a reasonable order of magnitude. We note here that this argument is based on the assumption that the Adn and TCNQ levels have the same energy within $\sim k_B T$, which may not be applicable at low temperatures.

We turn now to the temperature dependence of T_1^{-1} which is contained in the temperature dependence of the susceptibility χ_s, and that of the diffusion constant through the function $f_1(\omega)$ in Eq. (12). Using the above room-temperature values for the diffusion constants, assuming as indicated above that D_2 is temperature independent and that the temperature dependence of D_1 follows that of σ and χ_s according to Eq. (13), we have calculated T_{1QQ}^{-1} as a function of the temperature. To compare it with the measured relaxation rate T_{1I}^{-1} we have used Eq. (4), and the results are shown for the 10.54 MHz data as a solid line in Fig. 1. As can be seen good quantitative agreement (with no adjustable parameters!) is obtained in the temperature range 50–300 K. In this range, above ~100 K, where $D_1^{1/2}$ changes only slightly with the temperature, T_1^{-1} is approximately proportional to T ("Korringa-like law") whereas the increase of T_1^{-1} below 100 K is caused by the exponential decrease of $\sigma_{\parallel}(T)$ (and of D_1). We conclude therefore that in this temperature range the spin dynamics (as measured by T_1^{-1}) and the charge dynamics [$\sigma_{\parallel}(T)$] are very similar, indicating relatively weak on-site Coulomb interaction on the TCNQ chain. Below about ~40 K, Eq. (12) predicts much higher relaxation rates than those observed, and cannot therefore be used in this range (see below).

B. Low-temperature region
($1.5 < T < 40$ K)

In this region the spin susceptibility increases as the temperature is decreased ($\chi_s \propto T^{-0.75}$ for $T < 20$ K), compared with a nearly temperature-independent χ_s above ~40 K. This upturn of the susceptibility is likely to arise from magnetically coupled localized electronic states on the TCNQ chains.[1,26] As can be seen in Fig. 1, the ratio T_{1II}^{-1}/T_{1I}^{-1} also starts to increase at about 40–50 K which means that the contribution of the Adn chain to the relaxation rate grows as T decreases (see Sec. III). This Adn chain contribution is probably the result of small amounts of localized spins on the chain (back charge transfer in Adn $TCNQ_2$ was estimated in Sec. III to be of the order 1×10^{-3} spins per Adn molecule). An analysis of the data in Fig. 1 using Eq. (1) shows that both T_{1A}^{-1} and T_{1Q}^{-1} possess similar temperature dependence with maximum at about 7–10 K. It is therefore possible that at low temperatures the two kinds of chains experience a common relaxation mechanism originating from localized electronic states. The maximum observed in T_1^{-1} at ~7–10 K is perhaps characteristic of such a mechanism. Further measurements at various fields and below 1.5 K (Ref. 27) are needed to account in more detail for the nuclear relaxation data in Adn $TCNQ_2$.

V. CONCLUSION

In this study we have measured the proton spin-lattice relaxation rates in Adn $TCNQ_2$ and its deuterated analog Adn $(TCNQ(D_4))_2$. In the high-temperature region the relaxation is dominated by the (low $q_{\parallel}$) diffusive behavior of the TCNQ electron spin susceptibility. This spin diffusion is strongly anisotropic with diffusion constant along the TCNQ chains at least $\sim 10^2$ times larger than those in the transverse directions. The $\ln\omega_e^{-1}$ behavior of the relaxation rate shows that the transverse diffusion is also anisotropic. It is argued that relatively fast hopping between TCNQ chains and Adn chains compared with slower hopping between two TCNQ chains is responsible for the transverse anisotropy of the spin diffusion. The temperature dependence (above ~40 K) of T_1^{-1} shows that the spin and the charge dynamics are similar, indicating a relatively weak effect of the on-site Coulomb correlation.

ACKNOWLEDGMENTS

Stimulating discussions with Professor A. Ron are gratefully acknowledged. We also thank Mr. D. Katmor for his assistance in the measurements. The material preparation work at the University of

Pennsylvania was supported by the NSF MRL Program under Grant No. DMR76-80994.

APPENDIX

Using Eq. (11), one should integrate $\chi''(\vec{q},\omega)$ in Eq. (9) over the diffusive region in the reciprocal space. In the transverse directions (q_3 and q_2) the integration is limited, of course, by the Brillouin zone. In the longitudinal direction $q_1 l < 1$. However, it turns out that the final result is not sensitive to the actual limit of q_1 which may be taken also at the Brillouin zone. Rewriting $F_Q(\omega)$,[13]

$$F_Q(\omega) = (k_B T \chi_s / g^2 \mu_B^2) f_1(\omega) \quad , \qquad \text{(A1)}$$

we may express the frequency dependence of the spin correlations by $f_1(\omega)$.

For $\omega \ll \pi^2 D_3/a_3^2$ ($D_1 > D_2 > D_3$) we find,

$$f_1(\omega) = \frac{a_1 a_2}{2\pi(D_1 D_2)^{1/2}} \ln \frac{4e^2 a_3^2 D_2}{a_2^2 D_3} \quad , \qquad \text{(A2)}$$

i.e., frequency independent.

For $\omega > \pi^2 D_3/a_3^2$ we find,

$$f_1(\omega) = \frac{a_1 a_2}{2\pi(D_1 D_2)^{1/2}} \times \ln \frac{1+(1+\Omega^2)^{1/2}+[2+2(1+\Omega^2)^{1/2}]^{1/2}}{(\Omega^2 + D_3^2 a_2^4 / D_2^2 a_3^4)^{1/2}} \quad , \qquad \text{(A3)}$$

where $\Omega = \omega/\pi^2 D_2 a_2^{-2}$.

The function $f_1(\omega)$, as given by Eq. (A3), has a characteristic frequency dependence

$$f_1(\omega) \propto \omega^{-1/2}, \quad \text{for } \Omega \gg 1 \qquad \text{(A4)}$$

and

$$f_1(\omega) \propto \ln \omega^{-1}, \quad \text{for } D_3/D_2 < \Omega \ll 1 \quad . \qquad \text{(A5)}$$

Thus the anisotropic diffusive-spin-correlation function has a 1-D nature at high frequencies [Eq. (A4)] which gradually changes to 2-D as the frequency decreases [Eq. (A5)] and to 3-D at very low frequencies [Eq. (A2)].

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