

Collisional coalescence of photoexcited midgap states in an MX chain compound

journal or publication title	Physical Review B
volume	59
number	20
page range	12973-12976
year	1999-05-15
その他の言語のタイトル	MX鎖錯体に光生成されるミッドギャップ状態の衝突合体
URL	http://hdl.handle.net/2298/9622

doi: 10.1103/PhysRevB.59.12973

Collisional coalescence of photoexcited midgap states in an *MX* chain compound

N. Kuroda

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Y. Tabata

Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa 920-1181, Japan

M. Nishida*

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

M. Yamashita

Graduate School for Human Informatics, Nagoya University, Nagoya 464-01, Japan

(Received 21 December 1998)

The pumping-power dependence of the time decay of the long-lived photoinduced midgap absorption has been studied in an *MX* chain compound $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$, (*en*) being ethylenediamine. The 476.5 nm light of a cw Ar-ion laser is used as the pumping light source. In addition to an extremely nonexponential time decay, the life time of the midgap band is found to vary as K_0^{-2} with the absorption intensity K_0 induced by the laser pumping. This decay behavior is explained well in terms of the Torney-McConnell survival-probability function, $S(\zeta) = e^{8\zeta} \text{erfc} \sqrt{8\zeta}$ with $\zeta = A_0^2 D t$, peculiar to the geminate coalescence of unequilibrated states in one dimension, where A_0 , D , and t are the initial density of the unequilibrated states, diffusion coefficient, and time, respectively. The observed midgap states are confirmed from this finding to collapse through diffusion-limited mutual collisions in locally disordered PtCl chains. Our previous data on temperature and sample dependencies are reviewed within the framework of this collisional geminate coalescence model. [S0163-1829(99)00919-4]

I. INTRODUCTION

The question how their density varies with time if particles walking in a one-dimensional (1D) medium collapse upon mutual collisions is a basic problem of nonlinear dissipative dynamics of physical and chemical quasiparticle systems. Nagai and Kawasaki^{1,2} have theoretically argued that the spatial distribution profile of the unequilibrated particles changes drastically, depending on interactions among them, with time. Nagai and Kawasaki propose that the sublinear time evolution of the magnetic order in a layered antiferromagnet, which has been observed by Ikeda³ from neutron-scattering experiment, arises from the 1D geminate coalescence of domain-wall kinks. Spectroscopically, photoexcited solitons and polarons in polymers and linear chain compounds are of particular interest, because their unique transient properties are suggestive of their 1D bimolecular^{4,5} reactions. Unfortunately, however, no satisfactory evidence has been obtained for the geminate coalescence to date.

As for polymers, the difficulties originate from defects of conjugated bonds. Measuring the photoinduced absorption as a function of the ultrashort time interval t after picosecond laser pumping in *trans*-polyacetylene, Shank *et al.*⁶ and Vardeny *et al.*⁷ have found a $(t/\tau)^{-0.5}$ power-law decay of photoexcited solitons. On the basis of the finding of a distinctive temperature dependence of the time constant τ , Shank *et al.* have conceived that the charged solitons undergo geminate recombination while executing random walks along the chain. Unsuccessful attempt, on the contrary, to influence the decay behavior with high external electric

fields has led Vardeny *et al.* to claim that the solitons are trapped by defects. Although the disorder of polymer chains might function merely to decelerate the random walks,⁸ Zozulenko⁹ argues that the defects in *trans*-polyacetylene are rather likely to trap solitons. The disorder also governs the dynamics of polarons. Recombination of photoexcited polarons due to randomly distributed recombination centers manifests itself as the large fluctuation of the lifetime, which is indicated by the Kohlrausch form, $\exp\{-(t/\tau)^\beta\}$ with $\beta = 0.20 - 0.33$, of the decay profile.^{10,11}

MX chain compounds comprise another family of 1D conductors. Kuroda *et al.*¹² have recently found that photoinduced long-lived absorption band in $[\text{Pt}(\text{en})_2] \times [\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$, where (*en*) denotes ethylenediamine, also exhibits an extremely nonexponential time decay. There is no doubt from the temperature dependence of the time decay that the photoexcited states perform thermally activated random walks. However, as evident from comparison with the cases of polymers, the observed Kohlrausch form with sample dependent β of 0.27–0.54 or the $t^{-0.5}$ dependence provides only a little information about the nonlinear nature of the recombination process.

In this paper, we present the results of a simple but unconventional pump-and-probe measurement of the long-lived photoinduced midgap absorption in single crystals of $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$. In this experiment, in order to maintain the diffusion coefficient unchanged, we fix the sample temperature at 298 K. Instead, we pay attention to the dependence of the time decay of the photoinduced absorp-

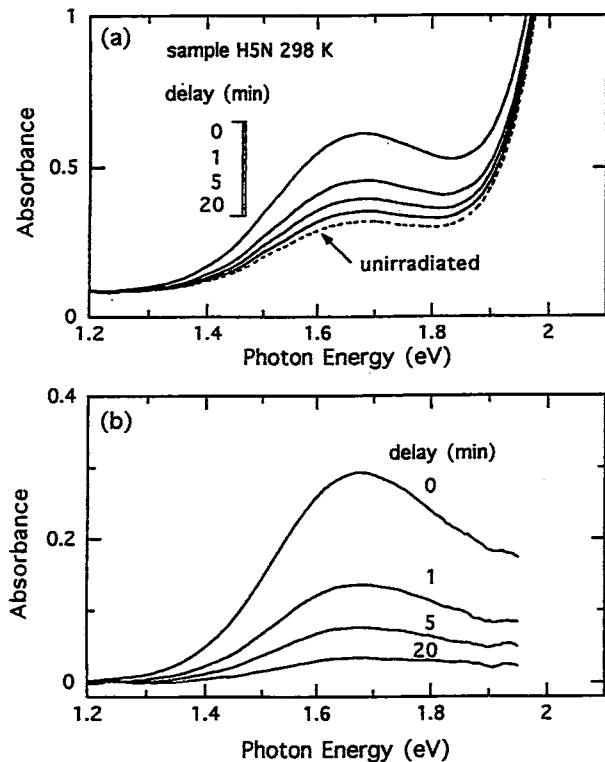


FIG. 1. (a) Stationary absorption spectrum and the spectra measured at several time delays. (b) The photoinduced absorption at the same time delays as (a).

tion on the pumping fluence, that is, the initial density of the photoexcited midgap states. We shall show that this method is crucial to experimentally investigate the nature of the dissipative dynamics of unequilibrated quasiparticle states such as photoexcitations in 1D systems.

II. EXPERIMENT

Planar crystals with the thickness of about 300 μm are used as the samples. The 476.5 nm (2.60 eV) line of a cw Ar-ion laser is used to create the midgap states. The time evolution of the optical-absorption spectrum is measured using a multichannel spectrometer. The light of wavelength longer than 600 nm is obtained with a tungsten halogen lamp and a glass filter. The shutter of the charge-coupled-device detector (Photometrics PM512) is synchronized with the shutter of the light source. The exposure time is chosen to be 0.5 s.

The pumping laser beam is polarized $E \perp$ chain (b axis). Since for the $E \perp b$ polarization the laser beam is absorbed only moderately, the charge-transfer excitons and thus, the midgap states are created almost homogeneously throughout the crystal.¹³ The laser power is changed between 0.05 and 0.5 W/cm^2 . All the measurements are performed at room temperature (298 K).

III. RESULTS AND DISCUSSION

The photoinduced absorption rises sublinearly with irradiation time at any levels of the laser power. The irradiation is discontinued when the intensity of the midgap band becomes almost stationary. Figure 1(a) shows an example of

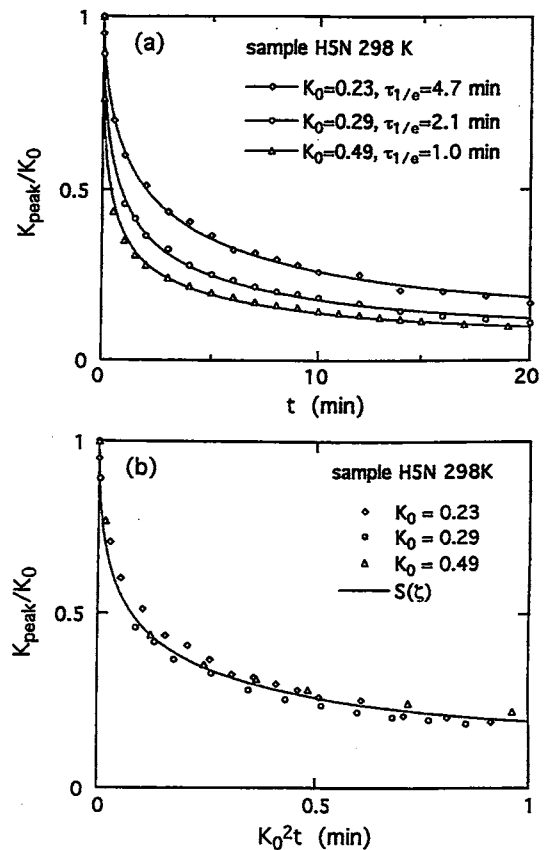


FIG. 2. (a) K_{peak}/K_0 versus time delay for several pumping levels. Markers are the experimental points and the solid lines are guides for the eye. (b) Plot of K_{peak}/K_0 as a function of $K_0^2 t$. The solid line is the theoretical curve of the survival probability calculated from Eq. (1).

the stationary absorption spectrum and the spectra measured at several time delays after discontinuation of irradiation. The absorption spectrum taken before the laser irradiation is also shown for comparison. The probe light is polarized $E \parallel b$. In this sample (sample *H5N*) the subgap tail¹⁴ of the charge-transfer absorption starts to rise at ~ 1.9 eV. In addition, there is a weak absorption at ~ 1.7 eV in the pristine crystal. This is due to the inherent midgap states that are confined in chain segments terminated by large energy barriers. The nature of the energy barriers is mentioned later. Figure 1(b) shows the photoinduced spectra that are obtained by subtracting the preirradiation spectrum from postirradiation spectra.

Figure 2(a) shows the plot of the peak absorbance K_{peak} of the photoinduced band normalized by its initial value K_0 as a function of time delay t . The decay is nonexponential for any levels of pumping intensity. This time evolution cannot be reproduced by the familiar formula of $K_0/(1+ct)$ no matter how the constant c is adjusted. Note, in addition, that the decay time depends on K_0 , showing clearly that the decay is governed by a nonlinear process. The $1/e$ decay time $\tau_{1/e}$ decreases from 4.7 to 1.0 min with increasing K_0 from 0.23 to 0.49. The decreasing rate of $\tau_{1/e}$ is in good accord with the decreasing rate of $1/K_0^2$. Furthermore, as shown in Fig. 2(b), the decay curves converge into a single curve if $K_0^2 t$ is chosen as the variable. The absorbance K_0 measures the initial density N_0 of the photoexcited states and thus, the present

result suggests that the survival probability of the photoexcited states obeys a universal function of a certain variable, which is proportional to $N_0^2 t$.

Torney and McConnell (hereafter abbreviated as TM) have developed the stochastic theory for the diffusion-limited bimolecular chemical reaction, that is, $A + A \rightarrow A_2$ of molecules A , in an infinitely long ring of 1D medium.⁴ The molecules are assumed to be placed randomly in the ring before they start to react. The TM theory shows that the survival probability S of a molecule after the start of reaction is given exactly by

$$S(\zeta) = e^{8\zeta} \operatorname{erfc} \sqrt{8\zeta}, \quad \zeta = A_0^2 D t, \quad (1)$$

where $\operatorname{erfc} x$ is the complementary error function defined as $1 - \operatorname{erf} x$ and A_0 and D are the initial density and diffusion coefficient, respectively, of the reacting molecules. The non-linearity of the reaction is shown by the fact that the survival probability at a given time depends on A_0^2 . In this theory, the medium is implicitly assumed to be continuous. The computer simulation made recently by Tabata and Kuroda¹⁵ assures that as long as A_0 is sufficiently low, Eq. (1) is valid also when molecules move in a discrete medium consisting of periodic lattice sites by hopping. Here we discuss the decay behavior of the midgap states in the present PtCt chain compound in terms of the TM theory. Since the present study is closely related with Ref. 12, Ref. 12 is referred to as paper [I] hereafter.

It is worth recalling that because of the pair-creation constraint, solitons and antisolitons created in a 1D lattice are automatically alternated one by one. In other words, the two nearest neighbors of every soliton are antisolitons against it. Accordingly, they should coalesce whenever they collide with each other. This situation corresponds just to the above-mentioned bimolecular reaction. If we read A_0 as N_0 , Eq. (1) means that the survival probability of solitons is determined by the dimensionless variable $N_0^2 D t$, consistent with the present experiment, and that $N_0^2 D \tau_{1/e} (= \zeta_{1/e})$ is equal to 0.195 ($= \zeta_{1/e}^{\text{TM}}$) regardless of external conditions. In Fig. 2(b), the theoretical curve, which is calculated from Eq. (1) by putting $N_0 = a K_0$ and taking $a^2 D = 0.91 \text{ min}^{-1}$, is shown along with the experimental data. The theoretical curve agrees excellently with the experimental data.

Concerning creation and annihilation of the long-lived photoexcited states in this PtCl compound the following picture has been proposed in paper [I]: The PtCl chains are divided into segments physically by irregular energy barriers due to some local disorder of chain bonds. Through a relaxation mechanism like the charge-separation of the photoexcitations in polymers,¹⁰ some of the photocreated charge-transfer excitons are transformed into kink-antikink pairs of solitons or polarons across the energy barriers. These separated kinks recombine with their antikinks when they collide in the course of the random walk by jumping over the barriers. The barriers, being of the order of 0.5 eV, are so high compared with the thermal energy at a moderate temperature that the lifetime is exceedingly long even if the kinks move freely in any segments.

This picture accords with the TM theory if the observed kinks are assigned to solitons and the chain segments are regarded as the lattice sites of the discrete ring. Presumably,

symmetry lowering at the local disorders causes the optical excitation of charge-transfer excitons to be allowed to some extent for the originally forbidden polarization of $E \perp$ chain axis. Even though a single event of the photoexcitation creates a soliton-antisoliton pair in two consecutive segments, successive events of photoexcitation will sometime create one more soliton in one of the two segments. The two solitons accommodated in the same segment would recombine to collapse instantaneously in the time scale of the present experiment. As a result, in the lattice ring model, the soliton-antisoliton separation is elongated by one lattice constant. The good randomness of the positional arrangement under laser pumping may be produced by the interplay of this process and the selfdiffusion of individual solitons.

As already mentioned, the argument β obtained from the Kohlrausch fit of the experimental data depends on samples, because β is sensitive to the irregularity of the energy barriers. The TM theory presumes a uniform ring as the medium. In the lattice ring model this condition requires energy barriers to be uniform. We note that the curve of Eq. (1) shown in Fig. 2(b) is almost indistinguishable from the Kohlrausch curves with β of 0.4–0.5. According to the numerical simulation,¹⁵ random fluctuation of the barrier height by 25% causes β to be reduced to 0.25. It is safe to say, therefore, that the energy barriers are very uniform throughout the sample crystal (sample *H5N*) used for the present experiment.

Now let us look directly at the role of the diffusion motion within the framework of the TM theory. In Fig. 3(a), the data of the sample *H8W* of [I] in the orthorhombic phase are plotted in the same form as presented in [I]. In the experiment of [I], the sample temperature was changed, whereas the pumping laser power was held at a constant level. We see that K_0 and $\tau_{1/e}$ vary largely with temperature. Nevertheless, if D is permitted to vary with temperature, all the data for $K_{\text{peak}} > 0.03$ can be reproduced well in terms of Eq. (1), as shown in Fig. 3(a). From this result the energy barriers seem uniform also in the sample *H8W*: The significant disagreement between the experimental data and the theoretical curve for $K_{\text{peak}} < 0.03$ may be due to the presence of a small density of annihilation centers. Figure 3(b) shows the Arrhenius plot of $K_0^2 \tau_{1/e}$, and thus of $\zeta_{1/e}^{\text{TM}} / (a^2 D)$, extracted from this analysis. This plot illustrates that the diffusion motion of the photoexcited states is dominated by thermally activated random walks. The slope of the plot gives the mean height E_0 of the energy barriers to be $0.45 \pm 0.05 \text{ eV}$.

If the barrier height is fluctuated around E_0 , collisions of far-separated soliton-antisoliton pairs are still more suppressed, so that $\tau_{1/e}$ is enlarged. In the lattice ring model, this effect can be expressed as $\zeta_{1/e} = g \zeta_{1/e}^{\text{TM}}$ with $D = l^2 \nu$,¹⁵ where $g (> 1)$ is a numerical constant, l is the mean length of chain segments and $\nu = \nu_0 \exp(-E_0/kT)$ is the specific hopping frequency at temperature T . Let the sample thickness be d and the constant that relates the absorption coefficient to N_0 be C . Then, replacing a with $(Cd)^{-1}$, we have $K_0^2 \tau_{1/e} = g(Cd/l)^2 \zeta_{1/e}^{\text{TM}} / \nu$. The factor $g(d/l)^2$ gives rise to the sample dependence of $K_0^2 \tau_{1/e}$. Figure 3(b) shows the experimental values of $K_0^2 \tau_{1/e}$ of the samples *H5N* and *H6N* of [I] along with the data of *H8W*. The good agreement between the data of *H5N* and *H8W* means that these two samples

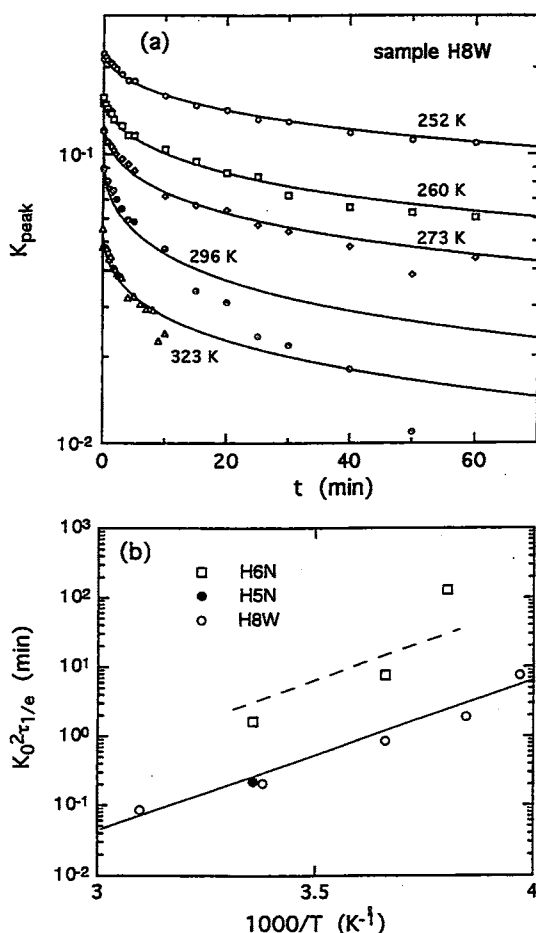


FIG. 3. (a) Plot of the data of the sample H8W of Ref. 12. Solid lines are the best fits of Eq. (1). (b) The Arrhenius plot of $K_0^2 \tau_{1/e}$ of the samples H8W, H5N, and H6N.

have almost the same values of d/l , since $g \approx 1$ in these samples. Our concern is the fact that $K_0^2 \tau_{1/e}$ of H6N is an order of magnitude greater than that of H5N and H8W regardless of temperature, although d ($\approx 150 \mu\text{m}$) of H6N is half of d ($\approx 300 \mu\text{m}$) of H5N. This fact reminds us that β is so small as ~ 0.27 in H6N. According to the computer simulation,¹⁷ g increases almost exponentially with the half width of Gaussian fluctuations of the barrier height, and

amounts indeed to 50–100 in the case of $\beta \approx 0.27$. It appears, therefore, that the observed large values of $\tau_{1/e}$ of H6N is caused by the fluctuations of energy barriers.

Finally, we turn our attention to the difference in the dynamical properties between solitons and polarons. In nondegenerated MX chain compounds such as $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Br}_2](\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, only polarons can be photoexcited.¹⁶ In contrast to solitons, the electron and hole polarons may not necessarily be alternately arranged in the MX chains. The coalescence dissipation of the electron and hole polarons corresponds to another sort of bimolecular chemical reaction, that is, the reaction $A + B \rightarrow AB$ of different species A and B. This reaction is predicted to evolve into the formation of domains of individual species.⁵ Hence, if polarons have no interactions with each other, their $S(\zeta)$ should vary as $\zeta^{-1/4}$ for $\zeta > 1$,^{5,15} differing from the $\zeta^{-1/2}$ -like variation of $S(\zeta)$ of solitons shown in Fig. 2. The experiment on the decay properties of polarons will enable us to study the self-formation process of the electron and hole domains.

IV. CONCLUSIONS

We have examined the pumping-power dependence of the time decay of the long-lived photoinduced midgap absorption in $[\text{Pt}(\text{en})_2][\text{Pt}(\text{en})_2\text{Cl}_2](\text{BF}_4)_4$. The time decay is found to exhibit a nonexponential behavior of which the decay time varies largely with pumping power. The result is explained in terms of the Torney-McConnell geminate reaction theory well, suggesting that the photoexcited solitons collapse through mutual collisions while performing random walks in locally disordered PtCl chains. Previous data on temperature and sample dependencies are consistent with the present interpretation. This study demonstrates that the Torney-McConnell geminate reaction theory is helpful to understand the nonlinear dissipative dynamics of unequilibrated quasiparticle states in one-dimensional materials.

ACKNOWLEDGMENTS

One of the author (N.K.) is grateful to Professor K. Sasaki for illuminating discussions. Part of this work was performed under the interuniversity cooperative research program of the Institute for Materials Research, Tohoku University.

*Present address: Sony Co., Kitashinagawa 6-7-35, Tokyo 141, Japan.

¹T. Nagai and K. Kawasaki, *Physica A* **120**, 587 (1983).

²K. Kawasaki and T. Nagai, *Physica A* **121**, 175 (1983).

³H. Ikeda, *J. Phys. C* **16**, 3563 (1983).

⁴D. C. Torney and H. M. McConnell, *J. Phys. Chem.* **87**, 1941 (1983).

⁵G. Zumofen, A. Blumen, and J. Klafter, *J. Chem. Phys.* **82**, 3198 (1985).

⁶C. V. Shank, R. Yen, R. L. Fork, J. Orenstein, and G. L. Baker, *Phys. Rev. Lett.* **49**, 1660 (1982).

⁷Z. Vardeny, J. Strait, D. Moses, T. C. Tung, and A. J. Heeger, *Phys. Rev. Lett.* **49**, 1657 (1982).

⁸E. Mulazzi and A. Ripamonti, *Synth. Met.* **49-50**, 329 (1992).

⁹I. V. Zozulenko, *Solid State Commun.* **76**, 1035 (1990).

¹⁰B. Kraabel, D. Moses, and A. J. Heeger, *J. Chem. Phys.* **103**, 5102 (1995).

¹¹G. S. Kanner, X. Wei, B. C. Hess, L. R. Chen, and Z. V. Vardeny, *Phys. Rev. Lett.* **69**, 538 (1992).

¹²N. Kuroda, Y. Wakabayashi, M. Nishida, N. Wakabayashi, M. Yamashita, and N. Matsushita, *Phys. Rev. Lett.* **79**, 2510 (1997).

¹³K. Sato, M. S. thesis, Tohoku University, Sendai, 1992.

¹⁴N. Kuroda, M. Nishida, and M. Yamashita, *Phys. Rev. B* **54**, 2390 (1996).

¹⁵Y. Tabata and N. Kuroda, *Synth. Met.* (to be published).

¹⁶N. Matsushita and N. Kuroda, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **256**, 867 (1994).

¹⁷Y. Tabata and N. Kuroda (unpublished).