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Time dynamics of photogrowth and decay of long-lived midgap states in an *MX* chain compound

Noritaka Kuroda and Masato Nishida
Institute for Materials Research, Tohoku University, Sendai 980 8577, Japan

Yoshinori Tabata
Department of Pharmaceutical Sciences, Hokuriku University, Kanazawa 920 1181, Japan

Yusuke Wakabayashi
Department of Physics, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223, Japan

Kazuo Sasaki
Department of Applied Physics, Faculty of Engineering, Tohoku University, Aoba-yama 08, Sendai 980 8579, Japan
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An experimental study on the pumping-power dependence of photogrowth and decay properties of the long-lived midgap absorption band in an *MX* chain compound $[Pt(en)_2][Pt(en)_2Cl_2](BF_4)_4$, (*en*) = ethylenediamine, is reported. The data show that the upper bound of the density of solitonic photogenerated states is determined by autophotobleaching processes. The observed whole course of the photogrowth and decay can be described well on the basis of a lattice ring model, in which intersite energy barriers serve as the particle source as well as barriers against hopping motion.

In conjugated polymers and linear chain compounds a variety of self-localized excited states can be photogenerated. Experiments on transient properties of those unequilibrated random walkers have provided a great deal of information about the decay dynamics peculiar to one-dimensional systems. In most cases, however, equilibration between excitation and relaxation occurs so fast during optical pumping that it is difficult to look into details of the photogeneration process itself. In this respect, neutral solitons in *trans*-polyacetylene,[1] pernigraniline base polymer,[2] and *MX* chain compounds, $[Pt(en)_2][Pt(en)_2Cl_2]Y_4$, where (*en*) = ethylenediamine and $Y = ClO_4$ or BF_4,[3] are of particular interest, because they exhibit a very long growth time. In *trans*-polyacetylene an electron spin resonance (ESR) signal grows in a period of ~0.2 sec under illumination with a visible light.[1] In pernigraniline base polymer it takes several hours to have the photoinduced absorption band be saturated,[4] whereas in *MX* chain compounds, if a crystal is irradiated with a blue light, the midgap absorption band grows gradually in a time scale of 1–10 sec.[5,6] This slow response opens the possibility to investigate the photogeneration dynamics of solitons experimentally.

It has emerged from recent studies on the midgap absorption in the *MX* chain compounds that the chain bonds are likely to have local disorders.[6,7] Soliton-antisoliton pairs appear to be produced across the disorders by an interband optical irradiation. The solitons survive a long time since they have to jump over the disorders to recombine with one another, although they are free to move in any uninterrupted segments. Regarding the individual segments as single lattice sites, Tabata and Kuroda[8] have modeled the chain bond as a lattice ring. In this model the intersite gaps serve as the particle source and barriers against motion simultaneously. What is noteworthy is that in the photogrowth process annihilation, say, autophotobleaching, of pre-existing solitons by photogenerated ones is expected to occur, as speculated originally by Rácz[9] for solitons in *trans*-polyacetylene. Taking this interesting effect into account, Lushnikov[10] has made a theoretical approach to the photogrowth process in a one-dimensional lattice.

In this paper we present the experimental study on the time evolution of the midgap absorption band during the whole course of its photogrowth and decay in single crystals of an *MX* chain compound $[Pt(en)_2][Pt(en)_2Cl_2](BF_4)_4$. In the light of Lushnikov's theory we focus attention on the growth profile and equilibration behavior as well as the decay profile of the midgap absorption. The results show clearly that the excitation of solitons is dominated by a competition of autophotobleaching and diffusion-controlled collision recombination with pair creation by light.

We select appropriate samples for this study, for the energy barriers are irregular more or less, depending on crystals.[7] From recent experimental[6] and theoretical[8] studies it has appeared that if the energy barriers are uniform the decay profile of photogenerated solitons obeys the Torney-McConnell formula[11] well but presence of irregularity causes a significant deviation from the formula. To exclude the fluctuation effects due to the irregularity, we use the crystals in which the energy barriers can be judged to be rather uniform from the decay profile. The 476.5-nm light of a cw Ar-ion laser is used as the illumination light source. The laser beam is loosely focused on the sample. The time-resolved spectrum of midgap absorption of the illuminated crystal is measured at room temperature (297±1 K) with a multichannel spectrometer. The exposure time to take each spectrum is chosen to be 0.3–0.5 sec. The laser beam and the probe light are polarized $E \perp b$ (the chain axis) and $E \| b$, respectively, for the same reasons as described elsewhere.[5–7]

Figure 1(a) shows the absorption spectra in the steady state at various levels of the laser power *I*. Figure 1(b) shows the photoinduced spectra obtained by subtracting the preirradiation spectrum from the postirradiation spectra. This ab-

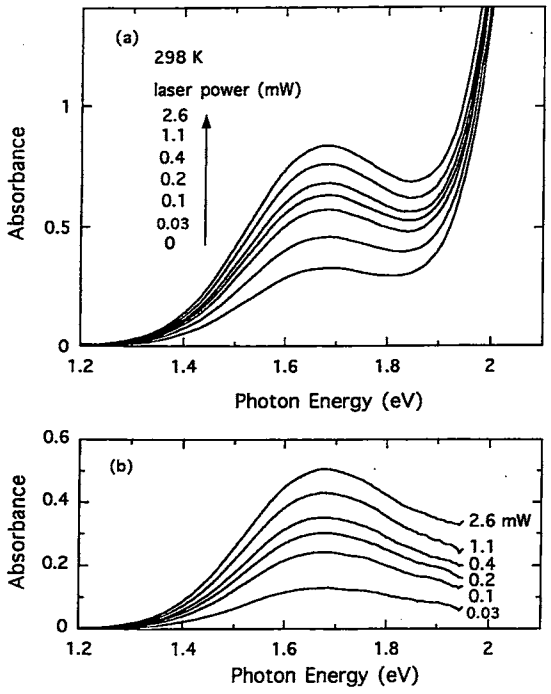

FIG. 1. (a) Stationary absorption spectra at various laser powers. (b) The photoinduced absorption at the same laser powers as (a).

sorption band exhibits pressure and temperature dependencies characteristic of the midgap transition due to neutral solitons.[12] A recent theoretical study on the basic spectroscopic nature of these neutral solitons is reported by Iwano.[13]

As shown in Fig. 2 the steady-state peak absorbance K_s of the midgap band scales quite sublinearly with increasing I. The aforementioned segment picture[6–8] for the chain bond presumes that the uninterrupted segments are much longer than the lattice constant of the chain bond but are still short enough for a pair of solitons put in a segment to recombine almost instantaneously in a time scale of the present experiment. Within the framework of this picture, the long-lived solitons we are observing are those generated in pairs on adjoining segments. They hop each from a segment to one of the next segments, recombining when they meet in a segment. In this situation, the chain bond can be treated as a long lattice ring and the time evolution of the occupation probability P_i at the ith site of the lattice ring satisfies the master equation

$$\frac{dP_i}{dt}=2C(1-2P_i)+\{(P_{i-1}+P_{i+1})(1-2P_i)-2P_i\}W, \tag{1}$$

where C and W are the pair-creation rate on a site and the probability of intersite hopping per unit time, respectively. In the present experiment the laser power is unchanged during illumination, so that C is held at a constant level. The first term on the right-hand side of Eq. (1) consists of contributions from photogeneration, $2C$, and autophotobleaching, $-4CP_i$, whereas the second term represents the density fluctuation caused by hopping. The autophotobleaching results from two processes: (i) If solitons are created on adjoining sites both of which are already occupied, the newly created ones coalesce with pre-existing ones; (ii) if only one of the adjoining sites is preoccupied, while a new soliton is created on the empty site, the other one coalesces with the pre-existing one. The processes (i) and (ii) result in annihilating two solitons and displacing a soliton by one lattice constant, respectively. The remarkable saturation of K_s, which is shown in Fig. 2, illustrates that the photogrowth is decelerated by autophotobleaching.

In a steady state, the interplay of the autophotobleaching process and hopping motion produces a random distribution throughout the lattice ring. Putting $dP_i/dt=0$ into Eq. (1) we obtain the steady-state solution P_s for the mean value P of P_i:

$$P_s=\frac{\sqrt{C}}{\sqrt{C+2W}+\sqrt{C}}. \tag{2}$$

Because of the autophotobleaching effect, P_s cannot exceed 0.5 even in the strong pumping limit of $C/2W\to\infty$. Equation (2) permits us to relate K_s and I to P_s and $C/2W$, respectively. The result is shown in Fig. 2. The theoretical curve of P_s versus $C/2W$, showing a steep rise as $\sqrt{C/2W}$ followed by a strong saturation towards 0.5, accords with the observed behavior of K_s very well.

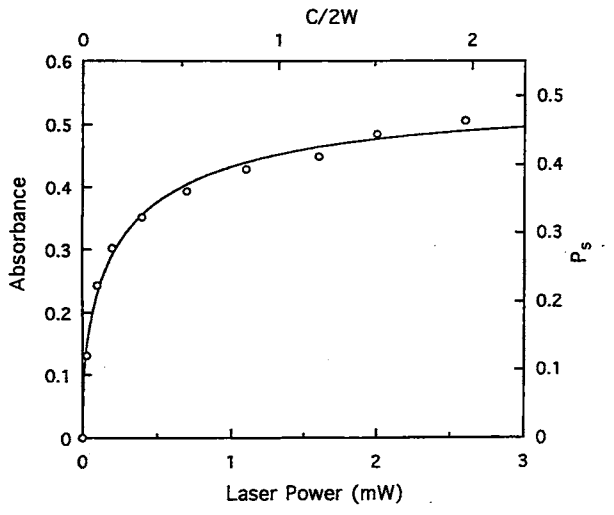

FIG. 2. Peak intensity of photoinduced midgap absorption versus laser power. Open circles show the experimental values and the solid line is the theoretical curve calculated from Eq. (2). The right ordinate and upper abscissa represent P_s and $C/2W$, respectively.

Figures 3(a) and (b) show the time evolution of growth and decay of the peak absorbance K at $I=0.02$ and 2 mW, respectively. These are examples of the contrasting cases of $C/2W\ll 1$ and $C/2W>1$. We note that in the case of $I=0.02$ mW K tends still to increase at $t=10$ min, whereas in the case of $I=2$ mW K is almost saturated at $t=6$ sec. At the early stage of illumination P is expected to rise almost linearly with the laser fluence $2Ct$. Consequently, the rise time of K differs two orders of magnitude between the two cases. When $C/2W>1$, annihilation of particles is governed by autophotobleaching. The system would then be homogeneous regardless of values of $2Ct$, yielding the growth of $P(t)\approx(1-e^{-4Ct})/2$. Accordingly, in the case of $I=2$ mW the time growth of K can be expressed by a single exponen-

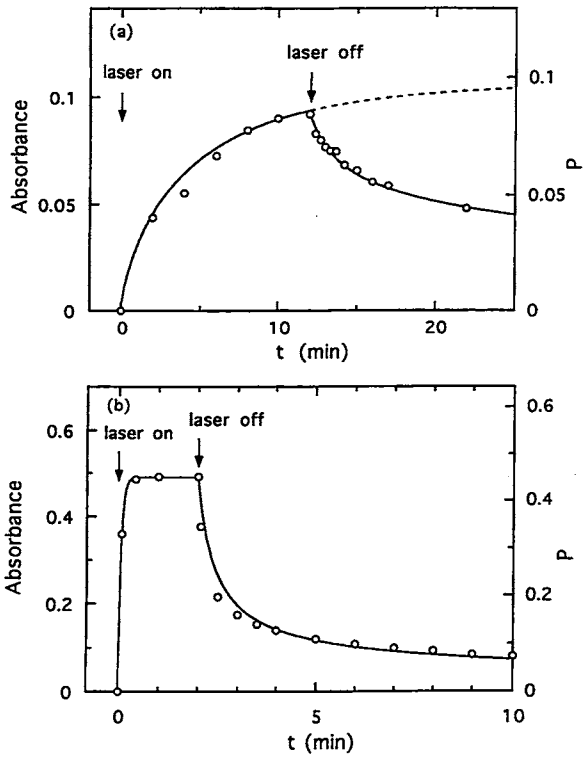

FIG. 3. Time evolution of the peak intensity of photoinduced midgap absorption during illumination at a laser power of (a) 0.02 mW and (b) 2 mW and after discontinuation of the illumination. Open circles show the experimental values and the solid lines are the theoretical curves calculated from Eqs. (3) and (4). The right ordinates of (a) and (b) represent P. The dashed line in (a) is the extrapolation of the theoretical curve for $t \leq 12$ min to longer t.

tial. It is also known that the ESR signal exhibits an exponential growth with fluence if a crystal of the ClO_4 salt is illuminated at 77 K.[14]

When $C/2W<1$, on the other hand, the growth of K deviates from a single exponential. Lushnikov has treated the process of Eq. (1) by the evolution-operator method,[10] arguing that inhomogeneous density fluctuations due to random walks cause a nonexponential time growth:

$$P(t)=\frac{2C}{\pi}\int_0^{\pi/2}\frac{\cos^2 q(1-e^{-4\gamma_q t})}{\gamma_q}dq, \qquad (3)$$

with $\gamma_q=C+2W\sin^2 q$. The steady-state value P_s given by Eq. (2) equals $P(\infty)$. Interestingly, $P(t)$ of Eq. (3) depicts P-t curves of a complementary stretched exponential of $P(t)=P_s[1-\exp\{-(2Ct/\phi)^{\beta}\}]$, where ϕ and β are determined uniquely by $C/2W$. We have $\phi=0.5$ and $\beta=1.0$ to a good approximation for $C/2W\gg 1$, but they are reduced slightly at around $C/2W=1$. As $C/2W$ decreases further, ϕ and β are still more reduced.

To analyze the observed growth data in conjunction with the decay profile we look at the decay properties anticipated from Eq. (1) under $C=0$. The process corresponds to the familiar $A+A\rightarrow 0$ reaction.[6,9] Torney and McConnell[11] have developed the stochastic theory for this reaction in a continuous one-dimensional medium. Balding, Clifford, and Green[15] and very recently Sasaki and Nakagawa[16] have extended the theory to the lattice ring model. According to the treatment of Sasaki and Nakagawa, if the particles are initially populated at random with $P=P_0$, the survival probability $S(t')\equiv P(t')/P_0$ at time t' after the start of reaction is given exactly by

$$S(t')=\frac{2P_0}{\pi}\int_0^{\pi/2}\frac{\cos^2 q\exp(-8Wt'\sin^2 q)}{P_0^2+(1-2P_0)\sin^2 q}dq. \qquad (4)$$

When $P_0\ll 1$, Eq. (4) is reduced to Torney and McConnell's formula $S(\zeta)=e^{8\zeta}\operatorname{erfc}\sqrt{8\zeta}$ with a dimensionless variable $\zeta=P_0^2Wt'$. If P_0 exceeds 0.05, the lattice effect manifests itself as a slowing down of the initial drop of S, while unaltering the gross profile, as described in detail in Ref. 8. The striking difference in the decay rate of K between the cases of $I=0.02$ and 2 mW shown in Figs. 3(a) and (b) reflects the good P_0^{-2} dependence of the $1/e$ decay time. Here we employ Eq. (4) rather than Torney and McConnell's formula in order to take the lattice effect into account explicitly.

It is evident from Eqs. (3) and (4) that the time dependence of growth and decay are quantified by C's at respective levels of I and by the common parameter W. The best theoretical curves are obtained with $C=0.0266$ and 3.32 min^{-1} for $I=0.02$ and 2 mW, respectively, and $W=1.11\ \text{min}^{-1}$. As shown in Figs. 3(a) and 3(b), the theoretical curves reproduce experimental results very well in the whole range of time. The values of $C/2W$ are 0.012 and 1.50 for $I=0.02$ and 2 mW, respectively, in good agreement with the linear relationship between I and $C/2W$ shown in Fig. 2. In the case of $I=0.02$ mW, since in such a low excitation regime random walks govern the annihilation of particles, the growth curve $P(t)$ depicts a complementary stretched exponential of $\phi=0.24$ and $\beta=0.74$. At this illumination intensity, the steady state is not accomplished yet at $t=12$ min, when laser is turned off. However, the good agreement of Eq. (4) with experimental decay data shows that a good randomness of the spatial distribution is established if P attains ~90% of P_s. A small systematic discrepancy is seen between the experimental and theoretical decay curves for $I=2$ mW. It may be induced by some extent of irregularity of energy barriers.[8]

It is suggested by the thermally induced narrowing of ESR signal observed in the ClO_4 salt[17] that neutral solitons are moving rapidly in chain segments. Nevertheless, the observed value of $W=1.11\ \text{min}^{-1}$ is quite low compared with the ordinary intrachain hopping rate ν of $\sim 8\times 10^8\ \text{sec}^{-1}$ at room temperature. The solitons hop from a unit cell to an adjacent unit cell to move in a regular Pt-Cl chain. The hopping between adjacent chain segments is also activated thermally, but the activation energy E_0 is so large as 0.45–0.50 eV.[6,7] With the values of W and E_0 a relationship of $W=W_0\exp(-E_0/kT)$ yields $W_0=8.0\times 10^5-5.7\times 10^7\ \text{sec}^{-1}$, leading us to imagine that every soliton tries to jump over the barriers many times during the stay in a segment. Given the length lb_0 of a segment, since the soliton explores ν unit cells in total a second, it would visit every unit cell ν/l times a second, where b_0 signifies the lattice constant of the chain bond. Provided that the soliton tries to jump over the barrier once on every visit to either end of the segment and that W_0 represents the trial rate, we obtain $l\sim\nu/W_0=1.4\times 10^1-1$

$\times 10^3$. Although the ambiguity is not small, this finding is consistent with the estimation of soliton density based on the oscillator strength of the midgap band.[18]

In conclusion, we have observed the whole course of photogrowth and decay of the midgap absorption in single crystals of an *MX* chain compound as a function of illumination intensity. The results demonstrate that the photogrowth of long-lived neutral solitons is dominated by three competitive processes, that is, photoinduced pair-creation, autophotobleaching, and diffusion-controlled bimolecular recombination, taking place on locally disordered linear chain bonds. In particular, the autophotobleaching effect is found to play a crucial role in the growth process.

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[1] C. G. Levey, D. V. Lang, S. Etemad, G. L. Baker, and J. Orenstein, Synth. Met. **17**, 569 (1987).
[2] S. M. Long, Y. Sun, A. C. MacDiarmid, and A. J. Epstein, Phys. Rev. Lett. **72**, 3210 (1994).
[3] N. Kuroda, M. Ito, Y. Nishina, A. Kawamori, Y. Kodera, and T. Matsukawa, Phys. Rev. B **48**, 4245 (1993), and references therein.
[4] K. A. Coplin, S. Jasty, S. M. Long, S. K. Manohar, Y. Sun, A. G. MacDiarmid, and A. J. Epstein, Phys. Rev. Lett. **72**, 3206 (1994).
[5] N. Kuroda, M. Ito, Y. Nishina, and M. Yamashita, J. Phys. Soc. Jpn. **62**, 2237 (1993).
[6] N. Kuroda, Y. Tabata, M. Nishida, and M. Yamashita, Phys. Rev. B **59**, 12 973 (1999).
[7] N. Kuroda, Y. Wakabayashi, M. Nishida, N. Wakabayashi, M. Yamashita, and N. Matsushita, Phys. Rev. Lett. **79**, 2510 (1997).
[8] Y. Tabata and N. Kuroda, Synth. Met. **101**, 329 (1999); Phys. Rev. B. **61**, 3085 (2000).
[9] Z. Rácz, Phys. Rev. Lett. **55**, 1707 (1985).
[10] A. A. Lushnikov, Zh. Eksp. Teor. Fiz. **64**, 1376 (1986) [Sov. Phys. JETP **64**, 811 (1986)].
[11] D. C. Torney and H. M. McConnell, J. Phys. Chem. **87**, 1941 (1983).
[12] As for pressure and temperature dependencies, see N. Kuroda, M. Nishida, N. Matsushita, and M. Yamashita, Synth. Met. **71**, 1921 (1995), and N. Kuroda, M. Nishida, and M. Yamashita, Phys. Rev. B **52**, 17 084 (1995), respectively.
[13] K. Iwano, J. Phys. Soc. Jpn. **66**, 1088 (1997).
[14] S. Kurita and M. Haruki, Synth. Met. **29**, F129 (1989).
[15] D. Balding, P. Clifford, and N. J. B. Green, Phys. Lett. A **126**, 481 (1988).
[16] K. Sasaki and T. Nakagawa (unpublished).
[17] N. Kuroda, M. Sakai, M. Suezawa, and Y. Nishina, J. Phys. Soc. Jpn. **59**, 3049 (1990).
[18] N. Kuroda, M. Sakai, Y. Nishina, M. Tanaka, and S. Kurita, Phys. Rev. Lett. **58**, 2122 (1987).