Photoexcitations in Pernigraniline: Ring-Torsional Polarons and Bond-Order Solitons

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We report the near-steady-state and long-time photoinduced spectroscopies of pernigraniline base, a novel Peierls ground-state polymer with multiple order parameters. Two kinds of defects are distinguished by differing time domains, ir-active vibrations, and light-induced electron spin resonance (LESR). The short-lived defect has a lifetime of msec scale, defect mass of $\sim 5m_e$, and is spinless; in contrast, the long-lived defect (mass $\sim 300m_e$) has a lifetime of greater than several hours at low temperatures and spin $\frac{1}{2}$. We propose the short-lived excitation is a soliton defect in the bond-length order parameter, while the long-lived excitation is a polaronlike defect in the ring-torsion-angle order parameter.

Soliton and polaron defects in the bond-length alternation of conjugated polymers such as polyacetylene and polythiophene have been extensively studied [1]. Similar excitations have been predicted to be stable in the pernigraniline base (PNB) form of polyaniline, which is suggested to have a Peierls band gap (E_g) with a twofold-degenerate ground state [2], the first such system beyond polyacetylene. However, in contrast to polyacetylene, there is an additional order parameter to be considered, the periodicity in the phenyl ring torsion angle, giving rise to the possibility of ring-torsional polaronic and solitonic defects [3]. Recent calculations have predicted that the two order parameters will act independently, additively contributing to the Peierls gap [4]. The successful synthesis of PNB [5,6] has created the opportunity to test the presence of multiple order parameters and their roles in the Peierls ground and excited states [7].

We report here the photoinduced spectra of PNB. Two types of defect states are observed, namely, long-lived and short-lived defects. The long-lived defect is associated with a 1.5-eV photoinduced-absorption peak and a set of long-lived photoinduced infrared-active vibrational (IRAV) modes, is massive $(\sim 300m_e)$, and has spin $\frac{1}{2}$. This long-lived massive defect can be understood in the picture of ring-torsional dimerization proposed by Ginder and Epstein [3]. In addition, short-lived photoinduced IRAV modes associated with short-lived photoinduced-absorption peaks at 1.0 and 1.3 eV are detected. No corresponding spin is detected by LESR. The estimated defect mass from this photoinduced-absorption spectrum is comparatively small $(\sim 5m_e)$, in agreement with dos Santos and Brédas's calculation of the bond-length changes for solitons [2]. These experimental results demonstrate that PNB indeed has a Peierls gap with multiple independent order parameters including bond order u and ring torsion angle Ψ. The long-lived photoinduced absorption we attribute to a massive ring-torsional pola-

ronlike defect while the short-lived defect is attributed to a low mass bond-length soliton.

The schematic chemical structure of PNB is shown in Fig. 1 as (a) undimerized and (b) dimerized forms. For the undimerized PNB structure, there is one unpaired electron per each repeat unit (N-ring) of projected length a along the chain axis, forming a half-filled metallic energy band. However, as described by the Peierls theorem, the lattice is subject to a spontaneous symmetry breaking, a Peierls gap forms at $k_F = \pi/2a$, and the polymer becomes an insulator. In a way similar to *trans*-polyacetylene, a bond-length order wave (BOW) forms in PNB. Here, the shorter bond is a quinoid structure with a $C=N$ double bond, while the longer bond is a benzenoid structure with a $C−N$ single bond [Fig. 1(b)]. dos Santos and Brédas [2] studied the ground state and the nonlinear excitations in PNB. From their results, the defect mass of the BOW soliton is estimated to be $\sim 5m_e$.

One noticeable difference between pernigraniline base and *trans*-polyacetylene [1] is that the former contains
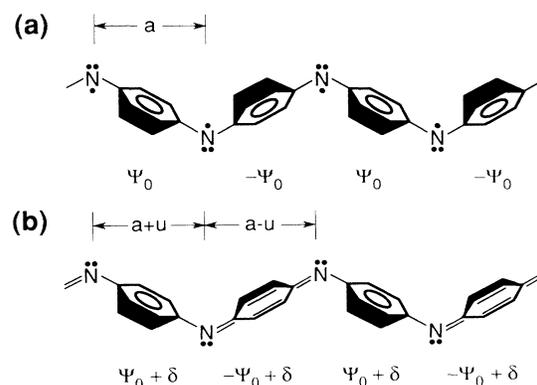

FIG. 1. Schematic chemical structure of (a) undimerized and (b) bond-length and ring-torsion-angle dimerized PNB.

rings while the latter does not. In dos Santos and Brédas's treatment, the rings are renormalized and suppressed into effective bonds. While this simplification makes its possible to describe pernigraniline base in the Su-Schrieffer-Heeger (SSH) model [8], the ring-angle rotation effect is not explicitly described by this simplified model. Recently, the central role of ring-torsion-angle freedom in ring-containing polymers was proposed [3]. In addition to the electron-phonon interaction, it is expected that there are couplings between nitrogen p_π orbitals and the ring π orbitals with a cosine dependence on the ring torsion angle Ψ. The ring torsion angle of the quinoid rings tends to be more planar than that of the benzenoid rings. Instead of alternating angles $\pm \Psi_0$ and $\mp \Psi_0$ as in a leucoemeraldine base (LEB) [3], PNB was proposed [3] to have alternating torsion angles $\pm \Psi_0 \pm \delta$, and $\mp \Psi_0 \pm \delta$, where Ψ_0 is the average ring torsion angle and δ is the deviation from the average ring angle. Typical values for Ψ_0 and δ are all $\sim 30°$ based on quantum chemical calculations [4]. It is anticipated that, due to the large moment of inertia of the rings, the ring-torsional defect is massive ($> 100 m_e$). Therefore, unlike trans-polyacetylene, the Peierls gap of pernigraniline base originates not only from bond-length dimerization (u), but also from ring-torsion-angle dimerization (δ).

The near-steady-state photoinduced-absorption experiments were carried out over a broad probe photon energy range (0.1–3.3 eV) using either a glow bar or tungsten lamp as a probe source, filtered through a grating monochromator. The sample was photoexcited by the output of an argon-ion laser (2.4 eV). The pump beam was mechanically chopped at frequencies between 4 and 400 Hz. Defect lifetimes of millisecond order can be detected by this apparatus. The long-time photoinduced-absorption experiment was carried out on a Nicolet 60SX Fourier-transform infrared (FTIR) spectrophotometer (500–20000 cm^{-1} or 0.06–2.5 eV). In this apparatus, lifetimes longer than a few seconds can be determined. LESR studies utilized a Bruker 300 ESR spectrometer and argon-ion and dye lasers. Long-lived phenomena were studied by recording the difference in the ESR signal before and after illumination; msec studies were carried out by chopping the exciting light at 5–1000 Hz, and monitoring the output through a lock-in amplifier.

Samples used in this experiment were cast from N-methyl pyrrolidinone (NMP) solution as films on either glass or quartz substrates for probe photon energies in the range of 0.5–3.3 eV, or in powder form mixed with KBr and pressed into pellets for probe photon energy in the mid-ir range (500–20000 cm^{-1}) and LESR studies. X-ray-diffraction studies show that PNB is partially crystalline with a coherence length of ~ 50 Å [9].

The near-steady-state photoinduced-absorption spectra of PNB in the range 0.5–3.3 eV at temperatures of 300 and 10 K are in Fig. 2. The 300-K spectrum shows three photoinduced-absorption (PA) features, namely, a low-energy peak (LE) at 1.0, a middle-energy peak (ME) at
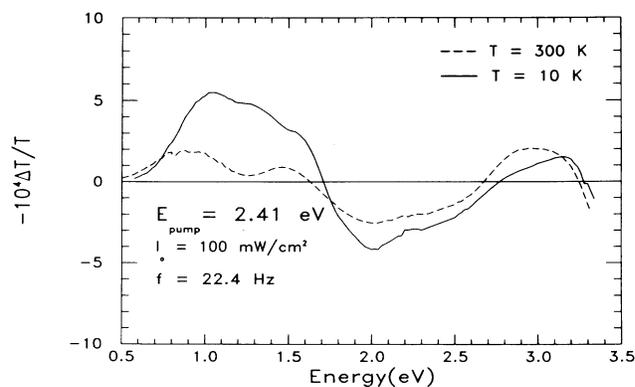

FIG. 2. Near-steady-state photoinduced absorption spectra of PNB cast on quartz substrate.

1.5, and a high-energy peak (HE) at 3.0 eV; and two photoinduced bleaching (PB) features, a broad PB (1.75–2.7 eV) and the onset of PB for energies greater than 3.3 eV. At a temperature of 10 K, the original LE peak is replaced by a peak at 1.0 eV (LE1) and a shoulder at 1.3 eV (LE2). We note that LE1 and LE2 are much stronger than LE, while HE is reduced in strength and shifted to 3.1 eV upon cooling. The crossover energy from photoinduced absorption to photoinduced bleaching is ~ 1.63 eV at 300 K and ~ 1.71 eV at 10 K.

Figure 3 shows the 10-K near-steady-state PA of PNB in powder form in the midinfrared range (1000–12000 cm^{-1} or 0.1–1.5 eV). PA peaks are found at 8000 cm^{-1} (1.0 eV) and 12000 cm^{-1} (1.5 eV). A shoulder is also seen at ~ 10000 cm^{-1} (~ 1.3 eV). Photoinduced IRAV modes are found at 1100, 1220, 1320, and 1580 cm^{-1}. Also shown in Fig. 3 is the long-time PA spectrum of PNB at 80 K in powder form for the same mid-ir range, plotted by reducing its magnitude by a factor of ~ 400. Only one peak was observed in this energy range, at 12000 cm^{-1} (1.5 eV). Two major photoinduced IRAV modes are found at 1153 and 1554 cm^{-1} and photoinduced bleaching peaks are found at 1219, 1323, 1487, and 1591 cm^{-1} [10].

The data support the fact that the origin of the 1.5-eV PA peak and corresponding IRAV modes is very different from that of the 1.0-eV PA peak and associated IRAV modes. First, their defect masses are different. The defect mass can be estimated from the relative oscillator strengths of electronic transitions and IRAV modes utilizing the amplitude mode formalism [11]. The ratio of electronic and IRAV oscillator strengths for the 1.5-eV defect is calculated to be ~ 3000 while this ratio is estimated to be ~ 80 for the 1.0-eV defect. Using a band effective mass of $0.14 m_e$ for PNB [10], the defect masses are estimated to be $\sim 300 m_e$ and $(5–10) m_e$ for the 1.5- and the 1.0-eV defects, respectively. Second, the lifetimes of these two defects are very different. The 1.5-eV peak and associated IRAV (particularly the 1153-cm^{-1} mode) are observed to have effective lifetimes of several
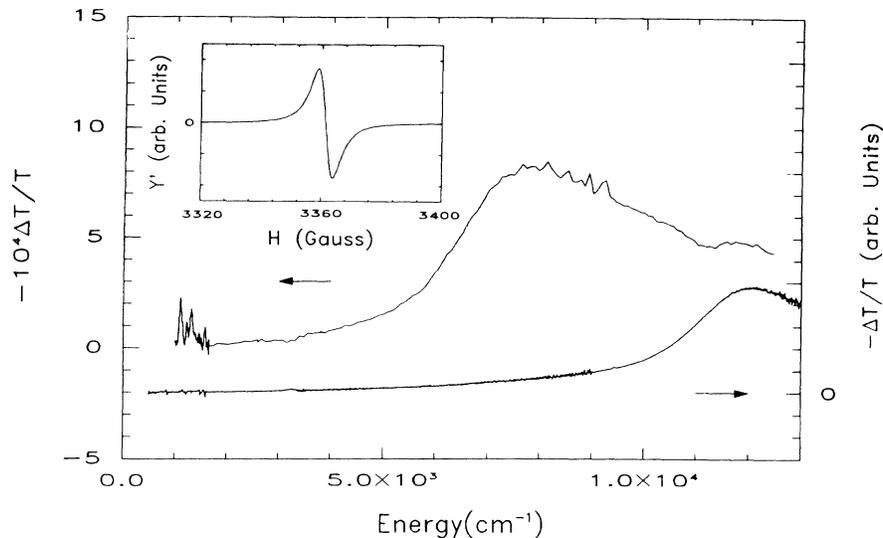
FIG. 3. Photoinduced absorption spectra of PNB as powder mixed with KBr, obtained with pump laser intensity $I_0 = 250$ mW/cm^2. Left scale: Near-steady-state (22.4-Hz light modulation) at 10 K. Right scale: Long-lived (reduced by a factor of ~ 400) at 80 K. Inset: LESR derivative signal after the sample was exposed to a laser beam ($E_{pump} = 2.54$ eV, $I_0 = 100$ mW/cm^2) for 1 h and at 60 K.

hours or longer at 80 K. On the other hand, the 1.0-eV broad peak which is observed in near-steady-state pho-toinduced absorption is completely absent in the long-time experiment. We conclude that the lifetime of the defect associated with the 1.0-eV PA peak is less than 20 sec while the lifetime of that associated with the 1.5-eV PA peak is longer than 3 h at 80 K.

In order to estimate the lifetime of the short-lived de-fect, the chopper-frequency dependence was investigated in a near-steady-state PA experiment. Figure 4 shows to-gether the 1.0 eV (LE1), 1.5 eV (ME), and 1320 cm^{-1} (IRAV) transitions versus the chopper frequency of the pump beam. It is observed that ME has the stronger fre-quency dependence, and, secondly, that LE1 and IRAV follow the same frequency dependence. The saturation of LE1 below 20 Hz indicates that the lifetime of this defect is ~ 100 msec, accounting for the absence of the 1.0-eV feature in the long-time PA experiment. The fact that the IRAV modes follow the same frequency dependence as the 1.0-eV peak especially for chopper frequencies ≥ 30 Hz indicates that these IRAV modes are associated with the short-lived defect. However, no saturation is ob-served for ME (as well as HE) to the lowest chopper fre-quency (4 Hz) available in the near-steady-state PA ex-periment, reflecting that the effective lifetimes of ME and HE are much longer than that of the LE features, con-sistent with the long-time experiment of PNB.

The dependence of PA on the pump laser intensity was also studied. No evidence of saturation is observed in near-steady-state PA as the laser intensity I increases up to 100 mW/cm^2. The magnitude of all PA features fol-low a power law of $I^{\sim 0.7}$, indicating that the defect decay channels are neither purely bimolecular nor unimolecular in nature. For long-lived PA experiments with continu-

ous pump light exposure for over several hours at 80 K, the magnitude of PA for the ME feature is asymptotic to 0.4, corresponding to an estimated concentration of exci-tation of one defect per five to six rings with a pump laser intensity of 250 mW/cm^2.

Based on these experimental results, we propose that LE1 and LE2 originate from bond-length-order soliton levels in PNB. We suggest that LE1 and LE2 correspond to optical transitions from the valence band to the empty type-II soliton level [2] and from the filled type-I soliton
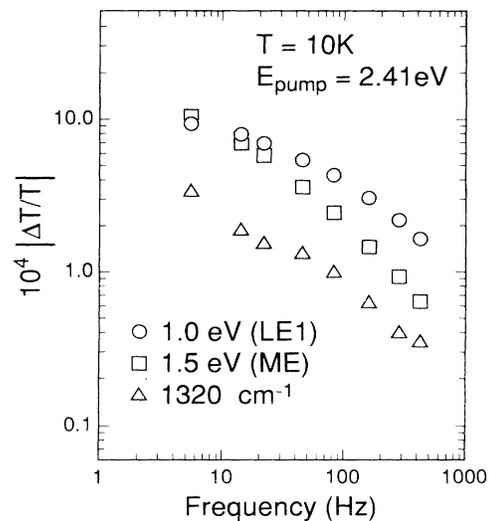

FIG. 4. Chopper-frequency dependence of the 1.0 eV, 1.5 eV, and 1320 cm^{-1} transitions of PNB. The data of the 1.0- and 1.5-eV peaks were taken on thin-film samples with $I_0 = 100$ mW/cm^2; those of the 1320 cm^{-1} transition were taken on a pressed pellet of PNB mixed with KBr and $I_0 = 250$ mW/cm^2.

level [2] to the conduction band, respectively. Optical transition between the filled type-I soliton level to the empty type-II soliton level was not observed, which is consistent with the fact that these two levels correspond to defects centered at different sites. That the energies of LE1 and LE2 are both $\geq E_g/2$ supports that these features correspond to a pair of bond-order solitons [2].

LESR experiments were used to distinguish the spin state of long-lived and short-lived defects [12]. The LESR data (inset in Fig. 3) were taken after exposure of PNB to pump light of 2.54 eV for 1 h at 60 K. Within errors of a factor of 2 in absolute intensities per PNB repeat unit, the data show that the long-lived photoexcitations have spin $\frac{1}{2}$ and are thus polaronlike defects. On the other hand, the double modulation (msec) technique shows that the number of short-lived spins produced are at least 1 order of magnitude less than the number of short-lived defects photoexcited, in accord with spinless soliton excitations.

We propose that the slow relaxation of photoexcited ring-rotational defects is due to constraint of the rings (from rotating), caused by the lack of free volume as suggested by an NMR study [13]. Hence intrachain and interchain steric interactions may make ring-torsional defects metastable. It is likely that short-lived polarons exist in both crystalline and amorphous regions while long-lived polarons are preferentially stabilized in amorphous regions [14] (where there is greater variability in the steric interactions). Solitons in contrast may be preferentially formed in crystalline regions. Long-lived LESR data [12] are consistent with the formation of extended regions of interacting defects, which could be stabilized by ring-torsional conformation changes in the amorphous portions of PNB.

We tentatively assume that the IRAV of the short-lived photoinduced defect present at 1100, 1220, 1320, and 1580 cm^{-1} arise from symmetry breaking of the *para*-disubstituted benzene rings due to formation of bond-length-order solitons. Hence the formerly Raman-active 1163, 1223, 1321, and 1594 cm^{-1} modes [15] become ir active. An effective electron-phonon coupling parameter [11] $2\tilde{\lambda}$ is estimated as ~ 0.66 for the short-lived defect in PNB and ~ 0.9 for the long-lived defects in emeraldine base [10]. A pinning parameter $\alpha \sim 0.58$ is found for PNB, larger than that of polyacetylene (~ 0.06) [11] and polythiophene (~ 0.31) [16].

Two order parameters could be involved in the long-lived massive defect (δ and Ψ_0) while a third (u) is involved with the short-lived less-massive defect. The model used here assumes that the three proposed order parameters are independent. However, our long-time PA involves vibrational modes of the benzenoid and quinoid rings, indicating that there is some coupling between bond-length and ring-rotation parameters. Hence the defect mass associated with the ME feature is an "effective mass" since the corresponding IRAV are coupled to the bond-length parameter. Further work is necessary to study the coupling between these order parameters.

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