π-conjugated polymers have been attracting much attention of many scientists as one of the most promising materials for optoelectronic devices because of high conductivity and light-emitting efficiency. The rational design of novel plastic materials with enhanced functionalities for such devices requires deep insight into their electronic structure, charge and energy transport, and photoexcitation dynamics.

Trans-polyacetylene (t-PA) is the simplest π-conjugated polymer in which a nonlinear excitation, the soliton, is photogenerated, owing to strong electron-phonon coupling with a doubly degenerate ground state.\(^1\)–\(^{12}\) The soliton dynamics after photoexcitation is well investigated both experimentally\(^1\),\(^2\),\(^6\)–\(^8\),\(^12\) and theoretically,\(^9\)–\(^{11}\) motivated by the fact that its high conductivity is based on the soliton dynamics in the polymer chain, which can originate either from self-localized nonlinear excitations in small amount or from charge doping in abundance.\(^5\)

The soliton dynamics in t-PA has been successfully interpreted by the Su-Schrieffer-Heeger (SSH) model about three decades ago.\(^3\) Then several attempts have been made to improve the model.\(^10\),\(^11\) Recently, with the aid of progress in computational technology, quantum chemical approaches such as time-dependent Hartree-Fock calculations also have been implemented.\(^13\),\(^14\) In any cases theoretical models have predicted that a breather soliton is created, owing to the excess energy of photoexcitation and modulates the frequencies of stretching modes of C–C and C=C bonds during the ultrafast relaxation process from a photogenerated electron-hole pair to an unbound charged soliton-antisoliton pair.\(^9\)–\(^{14}\)

In this Brief Report, we revealed the modulated wavepacket real-time dynamics due to the electron-phonon coupling of the breather soliton in t-PA by ultrafast multichannel pump-probe spectroscopy and compared with the theoretical predictions. The sample was fabricated by polymerizing acetylene on a new rhenum catalyst in a highly viscous solution of polyvinyl butyral.\(^2\) Both pump and probe pulses were derived from a noncollinear optical parametric amplifier (Spectra-Physics, Spitfire), whose pulse duration, center wavelength, repetition rate, and average output power were 50 fs, 790 nm, 5 kHz, and 800 mW, respectively. The visible NOPA pulse with 6.2-fs duration covered the photon energy range of 1.69–2.37 eV, with constant spectral phase throughout the whole laser spectrum. Pump-probe signals were detected with a 128-channel lock-in amplifier. Real-time vibration spectra were measured at delay time between the pump (40 nJ) and probe pulses (2 nJ) from −100 to 1100 fs with a 1-fs step.

In the photoexcitation of t-PA in the visible region of the NOPA output, an interband intrachain dipole-allowed π→π* transition can take place. The peak (1.95 eV) in the absorption spectrum corresponds to the \(^1B\_u\) state.\(^17\) Figure 1 shows the two-dimensional display of absorbance change (ΔA) of t-PA traced from −100 to 1100 fs of the pump-probe delay time over the whole probe spectral range. The observed ΔA(ω, t) were decomposed into difference spectra with a set of three corresponding decay time constants, τ\(_1\), τ\(_2\), and τ\(_3\), by a global fitting method as given by the following equation:

\[
\Delta A(\omega, t) = A_1(\omega)\exp(-t/\tau_1) + A_2(\omega)\exp(-t/\tau_2) + A_3(\omega)\exp(-t/\tau_3).
\]

The decay times of the signal were determined by the singular value decomposition method to be τ\(_1\) = 66 ± 20 fs, τ\(_2\) = 565 ± 50 fs, and τ\(_3\) ≈ 2 ps by fitting Eq. (1) to the absorption spectra over the whole probe photon energy region. The shortest time constant, τ\(_1\), is the lifetime of the electron-hole pair, which is in good agreement with values found in the literature.\(^8\)\(^{13}\),\(^14\) The medium length decay time τ\(_2\) corresponds to the lifetime of a charged soliton-antisoliton pair to geminate recombination.\(^8\) The absolute value of the longest time constant τ\(_3\) cannot be determined, with only a lower limit being obtained. However, this time constant is considered to be associated with the thermalization of the system, which does not necessarily have to be described with a single exponential decay constant, but can have complicated decay dynamics including diffusion process. The dynamics then
cannot be described by the rate equation, but by a diffusion
equation considered to be taken place in the time range of
5–10 ps. It is well known that a signal in the “negative”
delay-time range is due to perturbed free-induction de-
cay. Here the “negative” delay means that the probe
pulse comes earlier than probe pulse to the sample position.
From the probe-delay-time dependence of \( \Delta A \) in the negative
time range, the electronic dephasing time is determined to be
61 fs, which is fairly close to the lifetime of the
electron-hole pair 20 fs. In a system with no pure
dehrasing or inhomogeneity the dephasing time is expected
to be two times longer than the population decay time.
Therefore the results indicate that a half of the fraction of
electronic dephasing is induced by the population decay due
to conversion of the electron-hole pair to an isolated charged
soliton-antisoliton pair.

Probe-delay-time \((t)\)-dependent change \([\Delta \Delta \Delta A(\omega, t)]\) in
\( \Delta A(\omega, t) \) is due to the molecular vibration. Figure 2 shows
the two-dimensional (\(\omega, t\)) display of the fast Fourier trans-
form (FFT) power spectra of real-time traces of \( \Delta A(\omega, t) \)
probed at the 128 photon energies in Fig. 1. The peak posi-
tions of the FFT amplitude due to C–C and C=C stretching
modes were 1089 ± 6 and 1487 ± 10 cm\(^{-1}\), respectively. The
full width at half maximum (FWHM) of the peaks of each
mode were 59 ± 2 and 70 ± 3 cm\(^{-1}\), corresponding to the
vibrational dephasing times of 570 ± 24 and 480 ± 14 fs, re-
spectively. The dephasing times of both modes are close to
the above-mentioned recombination time (565 ± 50 fs) of a
charged soliton pair. This indicates that the dephasing of vi-
bational modes is determined partly by the recombination
of the soliton pair and partly by the pure dephasing with nearly
equal degree of contribution.

The result of spectrogram analysis \(^{20-22}\) of the real-time
trace at 1.71 eV is shown in Fig. 3. The probe-delay-time-
dependent Fourier amplitude reveals the time evolution of
C–C and C=C stretching modes with 1100 ± 8 and
1488 ± 8 cm\(^{-1}\), respectively. In addition to the main skeleton
oscillation, there exist four peaks at 305, 757, 1877, and
2254 with ambiguity of ±8 cm\(^{-1}\). The separation between
the main bands and corresponding sidebands is
770 ± 40 cm\(^{-1}\) in all four cases. This frequency separation
corresponds to a modulation period of 43 ± 3 fs, which is
consistent with the breather period theoretically predicted
(33–50 fs) (Refs. 9–11, 13, and 14) and the previously ob-
served (44 ± 3 fs). \(^{2}\) In the present work, these sidebands
were observed in the whole photon energy range from 1.70
to 2.36 eV, which is considered to be the tail of the breather
absorption with a peak located around 1.03 eV. The lifetime
of the sideband amplitude in all cases is about 60 fs, which is
in agreement with the electronic dephasing time of

FIG. 1. (Color online) Two-dimensional real-time absorbance change spectrum of \( t \)-PA. (a) Two-dimensional display of \( \Delta A(\omega, t) \) of \( t \)-PA. (b) The upper three show the real-time traces of \( \Delta A \) at the photon energies of 1.86, 1.96, and 2.12 eV, respectively. The lower three show the photon energy dependencies of \( \Delta A \) at the delay times of 30, 50, and 100 fs, respectively.

FIG. 2. (Color online) Two-dimensional display of FFT power spectra of \( t \)-PA.

FIG. 3. (Color online) Two-dimensional display of spectrogram spectra of \( t \)-PA at 1.71 eV.
to the modulation of the location of potential minimum along the mode. The frequency modulation is considered to be due to vibronic coupling and the electronic coherence is thus dissipated by the breather oscillation. The fast decay or disappearance of the breather is also explained by dephasing and vibrational relaxation channels even on a single chain. This is the observation of the transition state from the electron-hole pair with a breather to charged soliton pair with the localized breather at later delay time.

The modulation inducing the four sidebands to the C–C single and double bonds can be discussed in terms of amplitude and frequency modulations. The amplitude modulation (AM) on the vibrational amplitude \( A(t) \) of C–C single and double bonds with vibrational frequency \( \omega_0 \) can be described as follows:

\[
A(t) = A_0 [1 + m_A(t) \cos \omega_A t] = A_0 \cos \omega_A t + \frac{A_0 m_A(0)}{2} [\cos (\omega_0 + \omega_m) t + \cos (\omega_0 - \omega_m) t],
\]

\[
m_A(t) = m_{A0} \cos \omega_A t.
\]

Here \( m_A(t) \) is modulation function with amplitude \( m_{A0} \) and modulation frequency \( \omega_m \). In the case of frequency modulation (FM), the modulation due to the instantaneous frequency \( m_F(t) \) is given by following equation written as Eq. (3):

\[
A(t) = A_0 \cos (\omega_A t + \int dt m_F) = A_0 \cos \omega_A t + \frac{A_0 m_F(0)}{2} [\cos (\omega_0 + \omega_m) t - \cos (\omega_0 - \omega_m) t],
\]

\[
m_F(t) = m_{F0} \cos \omega_F t.
\]

In frequency modulation the amplitudes of sidebands show opposite phase unlike in the amplitude modulation. The ratio of amplitude fraction of FM to that of AM can be determined by \( m_{F0} / m_{A0} = (I_{\text{higher sideband}} - I_{\text{lower sideband}}) / (1 + I_{\text{higher sideband}}) \).

\[
\begin{align*}
\text{The profile of spectrogram from 0 to 80 fs with a 20 fs step is plotted in Fig. 4(a). The peak FFT amplitude of the C–C stretching mode shifts from 1155 to 1095 cm}^{-1} \text{ with time evolution while that of the C=C stretching mode shifts from 1488.5 to 1503 cm}^{-1}. \text{Our scenario of the primary processes of photoexcitation follows the steps proposed in theoretical works.}^{24,25} \text{The electron-hole pair formed by the photoexcitation associated with a localized breather mode relaxes to a separated pair of charged solitons with a localized breather mode. The observed frequency shifts are interpreted as a consequence of the coupling of the breather with the charged solitons. In the following, SSH Hamiltonian model}^{13,14} \text{ is calculated to describe above scenario. The model Hamiltonian is given as follows:}
\end{align*}
\]

\[
H = - \sum_{n,s} \left[ t_0 + \alpha(u_n - u_{n+1}) \right] \left[ \bar{c}_{n+1,s}^\dagger c_{n,s} + c_{n,s}^\dagger c_{n+1,s} \right] + \frac{K}{2} \sum_n (u_n - u_{n-1})^2 + \frac{M}{2} \sum_n \bar{u}_n^2. \tag{4}
\]

\[
u_n \text{ is the displacement of nth CH group in the polymer chain, } t_0 \text{ is the } \pi \text{-band width, } \alpha \text{ is the electron-phonon coupling, } K \text{ is the spring constant, and } M \text{ is the mass of each CH group. } c_{n,s}^\dagger \text{ and } c_{n,s} \text{ are the creation and annihilation operators of } \pi \text{ electron, respectively, with spin } s \text{ for nth site. Based on the Hamiltonian, classical equations of motion for order parameters } \bar{\eta}_n(t) = (-1)^s u_n / u_0 \text{ and velocities } \bar{\eta}_n \text{ are derived.}^{10} \text{ Here } u_0 = 0.04 \text{ Å, assuming that the change in bond length due to dimerization from the nondimerized structure (that is, all bond orders are 1.5) is 0.08 Å.}^{9} \text{ Frequencies of the single and double bonds are determined experimentally to be 1095 and 1503 cm}^{-1}, \text{ respectively. Calculated results and the observed data are shown in Fig. 4(a), revealing that the peak of the single bond redshifts while the peak of the double bond blueshifts. It is also shown that the initially localized excitation with a peak having an order parameter of } -2 \text{ results in the two peaks being closer to each other. The time trace of bond order is estimated from both experimental and calculated data}^{26} \text{ [Fig. 4(b)]. The figure shows that the bond order of each bond exceeds 1 on the lower order side and is less than 2 on the higher side at the moment of electron-hole pair generation.}
\]

Recently, Tretiak et al. found that the breather mode and C=C stretching mode mainly modulate the intensities (transition dipoles and oscillator strength) and transition energies, respectively. To verify these calculations, the zeroth and first derivatives of } \Delta \Lambda \text{ with respect to photon energy were compared with the probe photon energy dependence of FFT amplitude of spectrogram analysis [Figs. 4(c) and 4(d)]. The zeroth and first derivatives of } \Delta \Lambda \text{ correspond to the modulation of the transition intensity and that of the electronic transition energy, respectively. These results are consistent with the prediction made by Tretiak et al.}^{13,14}
\]

In conclusion, it was directly verified that after photoexcitation, the electron-hole pair relaxes with a breather mode as theory predicts with an electron-hole pair lifetime of 33–50 fs, which is in agreement with the electronic dephasing time. This is evidence of the correspondence between breather and electronic dephasing as predicted in the literature. We could also determine the ultrafast phonon dephasing time.
dynamics induced by the breather in r-PA: amplitude modulation, frequency modulation, and frequency shifts of C–C and C=C stretching modes. Calculation with the SSH Hamiltonian reproduced the time trace of the bond order of the C–C bonds in the polyacetylene. As theoretically predicted, it was found that the breather mode and the C=C stretching mode mainly modulate the transition intensity and transition energy, respectively.

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