PHOTO INDUCED INFRARED ACTIVE PHONONS IN TRANS POLYACETYLENE

Z. Vardeny, J. Orenstein, G. Baker

To cite this version:

HAL Id: jpa-00222716
https://hal.archives-ouvertes.fr/jpa-00222716
Submitted on 1 Jan 1983

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
PHOTO INDUCED INFRARED ACTIVE PHONONS IN TRANS POLYACETYLENE


*Physics Department, Technion-Israel Institute of Technology, Haifa 32 000, Israel
**Bell Laboratories, Murray Hill, N.J. 07974, U.S.A.

Résumé - Nous avons mis en évidence des phonons actifs dans l'infrarouge dans le trans (CH) par une technique d'absorption photoinduite. Il y a une corrélation avec une bande d'absorption photoinduite d'origine électronique. Nos résultats montrent la photoproduction de défauts libres chargés avec un temps de vie long.

Abstract - We measured photogenerated ir active phonons in trans-(CH) by the photoinduced absorption technique. A correlation was found to exist with a photoinduced absorption band in which electronic transitions are involved. Our results show photoproduction of free charged defects with long lifetimes.

In the photoinduced optical absorption technique (PA), the signal arises from the change \( \Delta a \) in the optical absorption spectrum of the semiconductor due to the presence of excited carriers. Recently, Orenstein and Baker** have reported measurements of the PA spectrum in (CH) at a delay time of 10\( \mu \)sec following excitation, in the energy range 0.5eV to 1.6eV. In trans - (CH) they observed two new subgap PA bands at 1.36eV and at 0.5eV. These bands appear to be uncorrelated to each other due to their different decay time and different temperature dependence. Very recently the resultant interband bleaching at 2eV and the PA spectrum from 1.2eV to 1.9eV were measured with picosecond pulse excitation. It was shown that the gap states** and their resultant interband bleaching are produced in less then 10\( ^{-12} \) sec and that the photogenerated carriers are localized but highly mobile.

In this work we report the steady state PA spectrum in trans (CH) in the energy range 0.09 to 1.1 eV, which includes also the phonons energy range. The photoinduced changes in the sample optical absorption spectrum were measured with an incandescent light source dispersed by a monochromator. The light transmitted through the sample(T) and its changes (AT) were measured with a solid state detector having a wide spectral range. The laser beam used for excitation was a CW Ar with photon energy of 2.4eV which is larger than the gap of trans-(CH). Phase detection techniques improved the sensitivity of AT/T to 10\(^{-5}\) for most parts of the spectrum. The sample was in the form of thin film of (CH) grown on NaCl substrate, initially polymerised as cis-(CH) and subsequently isomerized to trans-(CH).

In Fig. 1 the induced absorption (-AT/T) at 10K obtained with a laser absorbed power of 20mWcm\(^{-2}\) is plotted versus the probe photon energy. The PA spectrum consists of an assymetric band peaked at 0.43 eV with a FWHM of 0.35eV and a much narrower doubly peaked feature with maxima at 170meV(1360cm\(^{-1}\)) and 157meV(1256cm\(^{-1}\)) with FWHM of less than 4meV (32cm\(^{-1}\)). At higher temperatures these bands decrease in intensity and shift up in energy (172meV and 0.48eV at 200K). We identify the narrow PA bands as induced ir active phonons, due to their energy location and sharpness. The broader assymetric PA band is due to electron transitions from photoinduced localized states in the gap (with a delta function energy distribution).
To the nearest band edges (with an almost square root singularity in a quasi 1D system like (CH) ) However we note that this band is sharper than half the width of the interband absorption of trans-(CH) (which is about 1.5eV). The lack of induced bleaching (Δα<0) in the whole energy range below the gap shows that the induced localized states cannot be associated with ionization of gap natural impurities. Also the lack of induced bleaching in the energy range of the natural infrared phonons located in trans-(CH)x at 1015 cm⁻¹ and at 3000 cm⁻¹.

The PA bands at 0.43 eV and at 0.15-0.17 eV share a common origin since their absorption strength Δα(=α L ΔT/T, α L is the absorption coefficient at the laser frequency) exhibits similar dependencies on the laser intensity, laser chopping frequency and sample temperature. An example is shown in Fig. 2 where their intensities at 80K are plotted as a function of the laser chopping frequency; the PA strength for each lines saturates at about 200Hz. Since Δα=N σ (where N is the steady state density and σ is the defect absorption cross-section), this frequency dependence shows that steady state condition is reached only at about 5x10⁻⁵ sec, implying that the recombination lifetime is longer than 10⁻³ sec at 80K. We measured the dependence of Δα on the laser intensity-I(Fig.3). Δα for both bands has a I⁰ behaviour, characteristic of bimolecular recombination kinetics, followed by saturation at high intensities. The PA strength for both bands decreases with temperature: a slow decrease up to 150K, where the decrease becomes more pronounced. We conclude therefore that the electronic and the vibronic PA are due to the same photoinduced defects.

We can estimate N shown in Fig. 1 assuming that the doping induced and the photoinduced defects have similar Σ. From the doping induced "midgap" absorption band and the associated impurity density we evaluate the defect integrated absorption cross-section Σ=∫αdE=4x10⁻¹⁶ cm⁻²eV. Integrating the 0.43eV absorption in Fig. 1, we
calculate $N = 6 \times 10^{17} \text{cm}^{-3}$. From this we can estimate the
generation quantum efficiency $\eta$ of these defects, since $N = G \eta$. Taking $t = 5 \times 10^{-10} \text{sec}$, $\eta$ is
of order $10^{-1}$.

This $\eta$ is consistent with the decay in the picosecond time range which
was interpreted as due to
geminate recombination; the
induced signal in trans-(CH)$_x$
decays to $5 \times 10^{-7}$ of its
strength at $t = 0$ in $1.5 \times 10^{-9} \text{sec}$
at $80K$.

The infrared activity in the
phonon range in both photo-
induced and doping induced
cases, proves that the induced
defects are charged. However
there is an important
difference between the induced

spectra in the phonon range obtained by the two different methods. In the earlier
work two strong ir active phonons were observed upon dilute doping in trans-(CH)$_x$:
a narrow (50 cm$^{-1}$) mode at 1370 cm$^{-1}$ and a broader (300 cm$^{-1}$) mode at 900 cm$^{-1}$. In more
recent experiments a third weaker vibration was observed at 1270 cm$^{-1}$. In the case
of photogeneration we observe only the two high frequency vibrations (slightly
shifted at 10K), namely at 1360 cm$^{-1}$ and at 1255 cm$^{-1}$. The 900 cm$^{-1}$ mode is
completely missing from the PA spectrum (see Fig. 1). In their original work 1, Su,Schrieffer
and Heeger interpreted the doping induced ir active vibrations as due
to charged soliton vibrations. However the lower frequency mode at 900 cm$^{-1}$ was
ascribed to vibrations of the soliton against the impurity, and therefore it is a
pinned mode 6,7. Later, some controversy about the origin of this mode appeared in the
literature 6,11. In our case the photoinduced defects are not connected to
impurities and therefore should not be pinned. The failure to observe this mode in
the photoinduced experiment confirms therefore that the 900 cm$^{-1}$ mode is indeed the
pinned mode 6,11.

Based on B. Horovitz general analysis 7, we can tentatively associate each new ir
active mode to phonons lines of C=C stretch character which are observed in Raman
scattering. The 1360 cm$^{-1}$ line is the modified 1470 cm$^{-1}$ C=C mode, the 1255 cm$^{-1}$ is
the modified 1290 cm$^{-1}$ C-C mode 9 (which appears weaker in Raman scattering) and the
strong 1090 cm$^{-1}$ mode observed in Raman scattering is shifted to frequency lower
than 750 cm$^{-1}$ (our experimental lower limit) and is transformed into the pinned mode
of the free defect which theoretically is shifted to $\omega_0$.

Based on our calculation of $N$, we can estimate the defect mass (a more precise
calculation which is not based on $N$ will be published elsewhere). The induced
absorption strength $\Delta \alpha$ at 0.17 eV is about 350 cm$^{-1}$; similar in strength to the
absorption of the natural ir active phonons of trans - (CH)$_x$. Taking
$N = 6 \times 10^{17} \text{cm}^{-3}$, the oscillator strength per induced defect is 8 enhanced by more than
3 order of magnitudes as compared to the natural vibrations of this compound. A
defect (or impurity) mode ir oscillator strength is inversely proportional to its
vibrating mass 12; We conclude therefore that the defect mass should be of order
of $m_e$ (electron mass).

Our results show that supergap light absorption in trans-(CH)$_x$ produces mobile,
light mass charged defects with associated in gap localized states, whose lifetime is
longer than few milliseconds. These findings may show indeed that free charged
solitons are photogenerated in trans-(CH)$_x$, since they fit the expected soliton
properties. However there are yet two unresolved problems in this picture.
connected with our findings: (i) The electronic PA band is located at 0.43eV (with threshold at 0.25 ev), quite far from the expected soliton absorption at midgap (0.7 ev). (ii) The PA strength saturates at high light intensities; we estimate the saturation defect density to be 2-4x10^13 cm^-2. Solitons possess a reverse charge-spin relationship and it was theoretically shown that photoinduced e-h pair decays to charged soliton-antisoliton pair (J.R. Schrieffer, Les Arc conference). Since our experiment definitely shows the existence of photoinduced charged defects, the crucial experiment needed now to prove solitons photogeneration in trans-(CH)x is to measure the unpaired spins photogeneration quantum efficiency. However the saturation at high illumination intensities and the small charged defects quantum efficiency certainly influence the conclusions of this crucial experiment. Preliminary results where these effects were taken into consideration (A. Heeger, Les Arc conference) suggest that this quantum efficiency is indeed small.

On the other hand, our results might fit photoproduction of charged polarons. The energy threshold of the electronic PA at 0.25eV fits well the predicted low energy transition of the charged polaron in trans-(CH)x. However a second correlated transition at higher energy (1.1 to 1.4 ev), which was also predicted for charged polarons was not found in the PA experiments (J. Orenstein et al., Les Arc conference).

A part of this work was done at Brown University while one of us (Z.V.) was supported by the NSF MRL program and by NSF Grant; we thank Prof. J. Tauc for his kindly support, T. Kirst and D. Pfost for technical assistance and B. Horovitz for fruitful discussions.

References