Polariton Induced Transparency at Low Light Level: Polymer Chains Dispersed in a Monomer Single Crystal

Gerhard Weiser
Faculty of Physics and Centre of Material Science, Philipps-Universität 35037 Marburg, Germany

Jeanne Berréhar
Institut des Nanosciences de Paris; Université Pierre et Marie Curie, 75015 Paris, France

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Excitons of polydiacetylene chains, diluted in a 3BCMU monomer single crystal, turn at very low light intensity into a nonabsorbing polariton state once the polymer concentration exceeds 10^{-4} in weight. The transition is evident from a Lorentzian absorption peak which is truncated at an optical density OD ≈ 2 and is consistent with polariton coupling of light to eigenstates of the solid while Rabi coupling of individual chains to light is excluded. The saturated absorption is nearly independent of polymer content and crystal thickness and defines a surface region where photons are converted into polaritons, the corresponding electromagnetic eigenmodes of matter.

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Light in matter excites polaritons, which are characterized by a joint photon-exciton state that is coupled by a transition dipole [1,2]. The energy oscillates between the photon and exciton states representing the quanta of the electromagnetic field and the polarization, respectively, and is absorbed as the inelastic scattering rate γ of the exciton converts polaritons into an incoherent exciton population. Energy dissipation thus competes with the polariton coupling frequency ω_c, which depends on the photon and exciton frequencies ω and Ω and increases with the square root of the oscillator strength f and the density N of exciton states [1,3]:

$$\omega_c = \omega_p \sqrt{\frac{\Omega}{\omega} f}, \qquad \omega_p^2 = \frac{Ne^2}{m\varepsilon_0}. \tag{1}$$

If scattering is negligible, $\omega_c \gg \gamma$, the energy remains stored in the nonabsorbing polariton state and is transmitted without loss even at resonance to the exciton. Such a long living polariton is rarely observed since scattering increases linearly with the density of states and faster than ω_c. Energy dissipation commonly prevails, $\gamma \gg \omega_c$, and reduces light to a perturbation of the electronic states which is absorbed according to Fermi's golden rule. An early violation of that rule was reported for tiny naphthalene crystals where the 50 μeV narrow absorption peak of the weak Davydov component of a molecular exciton increased from 2 to 10 K despite thermal broadening [4]. In other cases, coherent coupling of light and matter was enforced by laser pulses which induced transparency in multiple quantum wells [5], semiconductor bulk material [6], and Rabi oscillations in heterostructures [7].

The close relationship of polariton coupling to the Rabi frequency ω_R [8,9] of an atomic transition in a laser field is revealed if the coherent electric field E is substituted by the density N of photons and the transition dipole μ by the oscillator strength f and frequency Ω of the transition

$$\omega_R = \frac{\vec{\mu} \cdot \vec{E}}{\hbar} = \sqrt{\frac{Ne^2}{m\varepsilon_0}} \sqrt{\frac{\Omega}{\omega} f}. \tag{2}$$

Although coherent coupling increases in either case with the square root of the oscillator strength and density of oscillators, a subtle difference exists. In the case of Rabi coupling a field of many photons forces an electronic system into a periodic motion between the ground and excited state. If this laser field is the resonator mode of a cavity Rabi coupling lifts the degeneracy of a resonant molecular transition and the cavity mode. In the case of polariton coupling the transition dipoles of local excitations combine to a coherent polarization which provides the source for an electromagnetic wave. The local excitons thus play the role of photons in a cavity and drive the emission of photons.

Coherent coupling of light and a strong exciton has recently been inferred from the fluorescence of a single "red" chain of polydiacetylene 3BCMU [10]. Their low concentration of 10^{-8} in weight in a monomer single crystal enabled excitation of a single chain with high fluorescence yield and long lifetime. The identical emission spectrum on a scale of 10 μm proved coherent coupling of excitons over a long chain segment [11]. Resonant excitation of the exciton at 2.28 eV and their scattering by a vibrational mode of the chain generated an incoherent population of vibrational excitons. Their nonresonant emission of light saturated at laser intensities of a few kW/cm^2. This saturation was attributed to coherent coupling of the resonantly excited exciton to the laser field which slowed down the scattering rate to the observed nonresonant state. This experiment observed indirectly Rabi coupling of a single chain exciton to a laser field although the paper referred to polariton-induced transparency. We demonstrate here true polariton coupling of polydiacetylene excitons by direct observation of the absorption of incoherent light. The excitons belong to "blue" chains which exist in the same monomer single crystals at concentrations of some 10^{-5}, much larger than the concentration of red chains. Their transition energy near 2 eV defines the color of the otherwise transparent crystals while their short fluorescence lifetime of 135 fs [12,13] and low fluorescence yield enabled the detection of the small minority of red chains.

Single crystals of 3BCMU ($R - \mathrm{C} \equiv \mathrm{C} - \mathrm{C} \equiv \mathrm{C} - R$, R being $(\mathrm{CH_2})_3 - \mathrm{OCO} - \mathrm{NH} - \mathrm{CH_2} - \mathrm{COO} - \mathrm{CH_4H_9}$) of lateral size of a few mm^2 were grown in the dark at 40 °C from a saturated solution of purified powder in acetone. A fraction η of molecules of density $N_0 = 1.52 \times 10^{21}$ cm^{-3} in the monoclinic crystal [14,15] is transformed into conjugated chains which run parallel to the symmetry axis b creating excitons with transition dipole $\mu \parallel b$ and an absorption constant of 10^6 cm^{-1} at room temperature in fully polymerized samples [16]. Since the surface of the crystal platelets contains the b axis normal incidence of b-polarized light generates always a transverse propagating mode. The samples were placed in the He exchange gas of a cryostat and spectra of the optical density were taken with a Cary double monochromator. The band pass of 2 Å reduced the light intensity on the sample to 3 nW/cm^2 which corresponds to a field $E = 0.15$ V/m. Identical polarizers in probe and reference beams, aligned better than 0.5° to the b axis, and a second set of polarizers in front of the detectors allowed measuring optical densities OD ≈ 4. After recording the absorption spectra at various temperatures the polymer content of the sample was increased *in situ* by UV radiation at room temperature, selecting a wavelength at the absorption edge of the monomer of sufficient penetration depths.

Absorption spectra of an 87 μm thick sample in its pristine state (Fig. 1) resolved at 293 K the exciton E at 1.95 eV and two vibrational satellites D and T resulting from coupling to double and triple bond stretch modes. The peak absorption corresponds to a polymer content of 7.2×10^{-5} and absorption below 1.9 eV is due to chains of unknown origin but identical electronic structure [17]. Decreasing temperature shifts the spectrum to lower energy and resolves more vibronic states and low energy transitions. The inset displays the smoothly increasing peak height of the absorption of the exciton E and its strongest satellite D at decreasing temperature and the integrated absorption remains constant in agreement with Fermi's golden rule. The exciton band matches a 7.7 meV wide Lorentzian of oscillator strength $f = 0.4$ per repeat unit. Two unresolved satellites of 6 and 11 meV energy cause a small asymmetry at high energy and contribute an additional 20% to the strength of the main peak. Similar Lorentzians describe the low energy side of the strong vibronic satellites D and T, but these vibronic satellites show an extended high energy tail which is attributed to free motion of excitons along the chain. Evidence for a 1d density of states is found in fluorescence [13] and electroabsorption spectra [17].

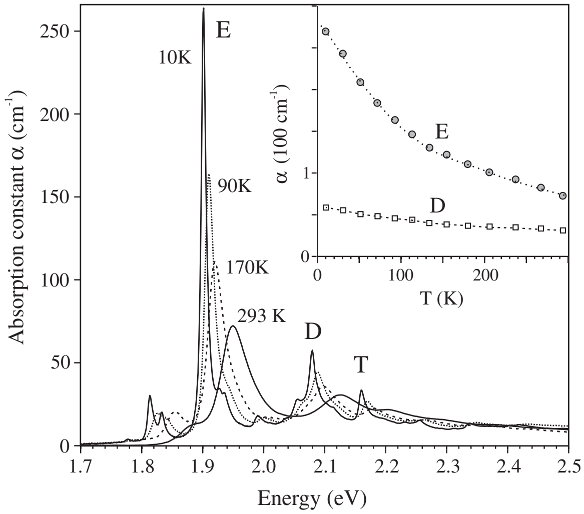

FIG. 1. Absorption spectra of 3BCMU with low polymer content $\eta = 7.2 \times 10^{-5}$. The inset shows the smooth increase of the peak absorption of the exciton E and its strongest satellite D with decreasing temperature.

Exposure to UV light at 279 nm with 3 nm band pass increased within 12 min the polymer content to 2.5×10^{-4}, leaving the spectral shape of the absorption apparently unchanged (Fig. 2). The inset, however, shows that only the vibronic state D rises smoothly with decreasing temperature while the increase of the exciton peak slows down below 150 K and saturates at 50 K. Most of the absorption peak at 10 K still matches the narrow

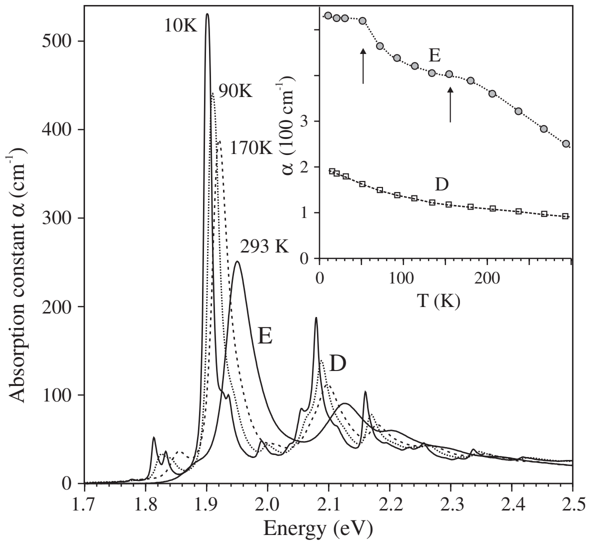

FIG. 2. Absorption spectra of 3BCMU with polymer content $\eta = 2.5 \times 10^{-4}$. Arrows in the inset mark temperatures where the exciton peak changes its temperature dependence.

Lorentzian which has increased in strength by a factor 3.7. The Lorentzian peak should rise to $\alpha = 980\ \mathrm{cm}^{-1}$ but the observed absorption saturates at $\alpha = 500\ \mathrm{cm}^{-1}$ and remains constant over a range of 6 meV.

The truncated peak is evident as the polymer content is increased further to 5.5×10^{-4} by additional 20 min UV exposure. The spectra in Fig. 3 exhibit an exciton peak which increases with decreasing temperature down to 236 K and decreases then rapidly to the same saturation value of $\alpha = 500\ \mathrm{cm}^{-1}$. The wings of the exciton peak at 10 K are still described by a Lorentzian of 7.7 meV width but the saturated range extends now over 11 meV, cutting off a peak that should exceed $\alpha = 2000\ \mathrm{cm}^{-1}$. We emphasize that none of the weaker transitions show such behavior.

All crystals exhibit a truncated exciton absorption once the polymer content exceeds 10^{-4} in weight and the transition temperature to saturation and the saturated range increase with polymer content. Figure 4 compares the optical density of samples with different thickness and polymer content. Spectra 1–3 show the different stages of the 87 μm thick sample (Figs. 1–3) with the shaded area representing the sum of Lorentzians matched to the main peak at lowest polymer content. The dotted line displays the spectrum of a much thicker sample, 350 μm, with $\eta = 1.3 \times 10^{-4}$. The product of η and thickness is similar to the product of the thin sample in its final state (curve 3) and indeed the optical density is almost identical in the range of the vibronic satellites above 1.95 eV. The exciton peak of the thick sample is truncated at OD $\approx$ 2.5 and exhibits a smaller saturation range. The dashed-dotted curve 5 presents the spectrum of another thin sample (88 μm) of much larger polymer content, $\eta = 14 \times 10^{-4}$. The optical density of the vibronic satellites increased accordingly but the exciton peak is truncated at OD $\approx$ 1.5 over a 45 meV broad range which has swallowed the two weak satellites of 26 and 35 meV energies which at lower polymer content are clearly resolved.

The reduced absorbance of excitons at polymer concentration larger than 10^{-4} suggests that a coherent coupling frequency to light exceeds the dissipative scattering rate. The Lorentzian linewidth $\Gamma = 7.7$ meV yields a scattering rate $\gamma = \hbar/\Gamma = 12$ THz, slightly larger than the value estimated from the fluorescence decay time $\tau = 135$ fs. Reduced absorbance may be achieved either by Rabi coupling of each blue chain individually as in case of single red chains [10] or by collective coupling of all excitons to the radiation modes of the crystal. Presuming coherence over 10 μm as in isolated red chains [10] the exciton of such quantum wire combines the strength of 2×10^4 units to the huge oscillator strength $f = 8000$. Nevertheless, the weak field of 0.15 V/m in the spectrometer yields a Rabi frequency $\omega_R = 4$ MHz which is orders of magnitude too small to compete with exciton scattering.

Very different numbers emerge for polariton coupling. The critical polymer concentration $\eta = 10^{-4}$ corresponds to a density $N = 1.5 \times 10^{17}/\mathrm{cm}^3$ of local oscillators arranged in long chains and separated by about 100 nm. That distance excludes exchange coupling and strong dipolar coupling of excitons but it is less than the wavelength $\lambda =$ 420 nm of an electromagnetic wave in a crystal of refractive index $n = 1.5$. Equation (1) applied to a medium of dielectric constant $\varepsilon_b = 2.3$ at $\eta = 10^{-4}$ yields a coupling frequency $\omega_c = 14.4$ THz which just exceeds the scattering rate derived from the linewidth. Since ω_c increases with polymer content, strong coupling should persists for

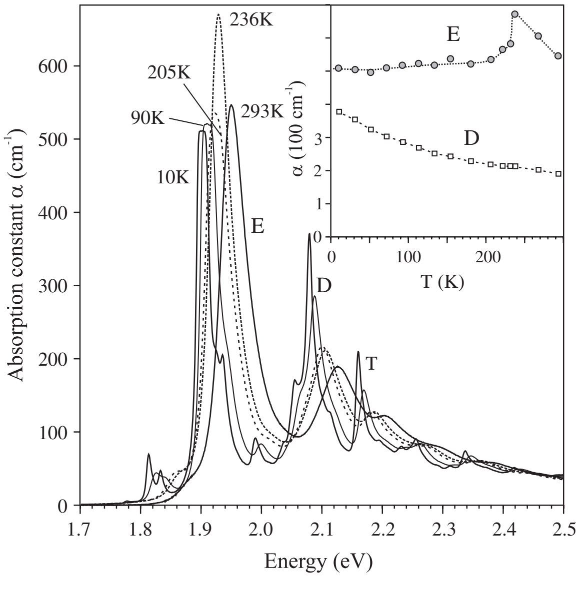

FIG. 3. Absorption spectra of 3BCMU with polymer content $\eta = 5.5 \times 10^{-4}$. The inset shows a narrow temperature change where the exciton absorption peak decreases rapidly.

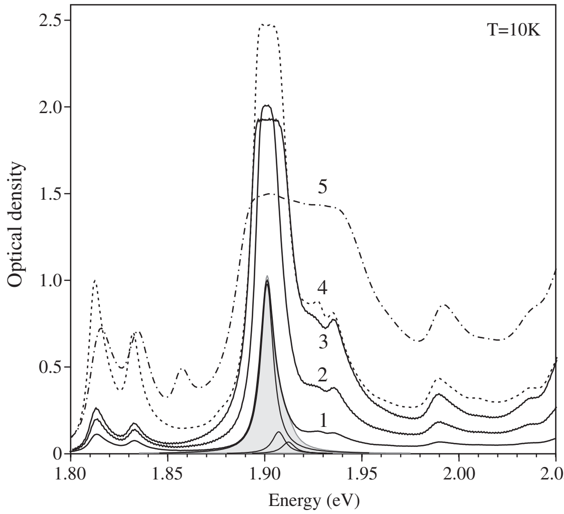

FIG. 4. Comparison of the optical desity of 3BCMU crystals with different thickness d and polymer content η. (1–3) $d = 87\ \mu$m, $10^4\eta = 0.72$, 2.54, 5.5. (4) $d = 350\ \mu$m, $\eta = 1.3 \times 10^{-4}$; (5) $d = 88\ \mu$m, $\eta = 14 \times 10^{-4}$. The shaded area is the Lorentzian fit to spectrum 1.

small detuning $\delta = \omega - \Omega$ of photon and exciton frequencies. The polariton scattering rate $\gamma_{\rm eff}$ defines the rate of absorption and depends on ω_c, the exciton scattering rate γ and on detuning [3]

$$\gamma_{\rm eff} = \frac{\gamma\omega_c^2/2}{\omega_c^2/4 + \gamma^2 + \delta^2}. \tag{3}$$

For strong coupling, $\omega_c \gg \gamma$, the absorption rate at resonance is 2γ and maintains that value for some detuning. Saturated absorption thus extends over about half the coupling frequency ω_c, which is consistent with the observed saturated range Δ in Table I. The only exception is spectrum 5 where due to the large polymer content the coupling strength exceeds the separation of the exciton from its nearest satellites. The disappearance of these weak spectral features suggests that polariton coupling of sufficient strength couples excitons of different transition energy into a common collective state. This effect is beyond the scope of this Letter and will be demonstrated in an extended paper together with more unusual properties of this composite of single crystal and polymer chains in the strong coupling regime.

The saturation value OD ≈ 2 corresponds to 1% transmittance and is quite independent of the sample thickness and polymer content. This observation indicates that energy loss occurs in a surface region where a propagating wave must be generated from the emission of chains excited by the incident light. No coherent polarization exists on the interface to vacuum [18] and the layer needed to generate coherent polarization from spontaneous emission of excitons into the radiation modes of the crystal should shrink with the density of emitters. This build up of coherence defines the region where excitons absorb light and the dependence of its thickness on η explains an optical density which is nearly independent of polymer content and sample thickness. Based on the absorption constant at low polymer content we estimate the absorbing layer to shrink from 50 μm at $\eta = 0.025\%$ to 6 μm at $\eta = 0.14\%$. We emphasize that the diluted chains contribute little to the dielectric properties of the composite. The Lyddane-Sachs-Teller relation predicts even for $\eta = 1\%$ splitting of longitudinal and transverse excitons by less than 1 meV, which is too small to observe spectral features like a polariton gap and a band of high reflectance.

TABLE I. Polariton coupling strength $\hbar\omega_c$ derived from the polymer content η and the width Δ of saturated absorption observed in Fig. 4.

Spectrum	d (μm)	η (10^{-4})	$\hbar\omega_c$ (meV)	Δ (meV)
1	87	0.72	8.0	⋯
2	87	2.54	15.1	6.1
3	87	5.5	22.2	10.8
4	350	1.3	10.8	7.5
5	88	14	52	45

We conclude that parallel aligned π-conjugated chains couple their exciton dipoles of large oscillator strength into a coherent bulk polarization which is stable against exciton scattering. The transition to the nonabsorbing polariton state occurs at surprisingly low density of 10^{-4} in weight and induces transparency at the exciton resonance to incoherent light of low intensity as anticipated in the first presentation of polaritons [1]. Novel observations are the truncation of the exciton absorption over a spectral range that increases with polymer content and the existence of an absorbing surface region where incident photons are converted into polaritons, the eigenstates of electromagnetic waves in matter.

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