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Highly oriented poly(paraphenylene vinylene): Polarized optical spectroscopy under pressure

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We investigate the role of intermolecular interactions in thick highly oriented poly(p-phenylene-vinylene) under applied hydrostatic pressure by polarized reflectance and Raman spectroscopy. Evidence of intramolecular and intermolecular effects is observed. The analysis of the C=C stretching modes and of the optical transition at about 3.7 eV previously assigned to conjugation chain ends indicates that the conjugation length of this highly ordered polymer is weakly affected by the applied pressure. On the other hand, the absorption onset and the spectral shape of the vibronic progression are deeply influenced by pressure, which generates a bathochromic shift joined to a broadening of all the optical transitions. By analyzing the data with a suitable optical model for an anisotropic system, a significant difference between the optical components polarized parallel and perpendicular to the stretching direction is observed. For the parallel component, a low energy gain of the oscillator strength, joined to a correspondent reduction in the high energy spectral range, is observed. For the perpendicular component, an increase in the oscillator strength is instead observed for all wavelengths. These effects are mainly assigned to intermolecular interactions even though a contribution from electron-phonon coupling cannot be excluded to explain the observed broadening.

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I. INTRODUCTION

Intermolecular interactions in conjugated polymers have been widely discussed since the beginning of the field of organic semiconductors and still attract great attention in relation to different physical, chemical, or technological aspects. From the physical point of view, intermolecular interactions turn the dimensionality of the system from ideally one (as for isolated chains) into three (as for a crystal). This leads to changes in the charge transport properties as well as to a modification of the role of electron-phonon (el-ph) coupling, dielectric screening, and electron correlation.[1,2] When disorder intrinsic to organic systems is removed by orientation of polymer chains or by molecular crystal growth, new insight in the electronic structure is also possible since anisotropy of optical and electrical properties can be investigated.[3–5]

From the chemical point of view, intermolecular interactions through noncovalent or secondary bonds play a role in order to control the supramolecular structure of the molecular system giving rise to a variety of structures such as single crystals, *J* aggregates, different mesophases, or simple molecular dimers.[6] Even in the amorphous phase or in solutions, due to thermal treatment and solution processing, conjugated polymers might possess different physical chemical properties caused by specific packing of their skeleton.[2,7]

In several technological applications of conjugated polymers, the control of intermolecular interactions is crucial. Transport properties in transistors or solar cells benefit from such interactions while in light emitting diodes, they have to be carefully balanced in order to provide sufficient carrier mobility without suppressing the radiative recombination pathway of excited states. For these reasons, specific classes of polymers obtained by proper synthetic procedures are used for particular applications, as in the case of regioregular polyalkylthiophenes when charge transport is the relevant parameter to be optimized.[8]

In the field of molecular semiconductors, the "order" of the system often plays a major role in the comprehension of their properties, allowing disentangling between intramolecular and intermolecular effects. Single crystals are of course the optimal system to investigate intermolecular interactions but only molecular semiconductors are available in this form. In the case of conjugated polymers, single crystals exist only for few selected polydiacetylenes (PDAs) due to their peculiar (topochemical) polymerization mechanism[9] while for the most interesting families, such as poly-arilene or poly-arilene-vinylene, this achievement is at present extremely challenging or impossible. In general, polymeric systems are weakly ordered and this makes it difficult to study in detail the fundamental issues masked underneath different forms of "disorder," such as distribution of conjugation length, random distribution of polymer chains, unreacted monomer, catalyst residual, or molecular weight distribution. For this reason, when addressing the topic of intermolecular interactions, the choice of the suitable system to be investigated is essential.

In this work, our interest is mainly devoted to polymeric systems and in particular to highly stretch-oriented poly(p-phenylene-vinylene) (PPV) which has a double advantage with respect to other systems: first, it possesses both a very good optical quality and a high anisotropy, thus allowing for a detailed optical investigation with minor contributions from disorder, as demonstrated in previous papers.[3–5,10] Second, it is a reference system for physics, chemistry, and devices, thus making all information extracted from it particularly interesting for the scientific and technological community working in the field.

For chosen polymeric systems, a way of tuning the intermolecular interaction is the application of a hydrostatic pressure, which changes the interchain separation favoring wavefunction delocalization which can be probed by spectroscopic tools. Since the pioneering work on polyacetylene[11] and polydiacetylenes,[12] the investigation of spectroscopic properties under hydrostatic pressure has become a powerful tool in probing properties of different conjugated polymers, even following the evolution of synthetic approaches. Without claiming here to review all papers published in the field, we would like to remember works on ultrafast relaxation of excited states in PDAs,[13] thiophene derivatives,[14] or other polyarylenes[15] as well as on their optical properties.[16,17] Here, a polarized spectroscopy study on highly oriented conjugated polymers under pressure is reported, which allows us to distinguish between intermolecular and intramolecular effects. We show that backbone planarization, usually observed for other systems, weakly affects our measurements, thus indicating that main effects (redshift of $\pi-\pi^*$ onset and vibronic progression broadening) are related to intermolecular interaction. However, we cannot exclude that an evolution from weak to intermediate el-ph coupling might affect the line broadening. Finally, the analysis of oscillator strength for parallel and perpendicular polarizations shows a complex change in its progression upon applying pressure.

II. EXPERIMENT

Free-standing PPV films oriented by tensile drawing with an elongation ratio up to 5 (Ref. 18) and a thickness of 15–16 μm, as determined by a Mitutoyo comparator, have been investigated. An extended optical and photophysical characterization of the same samples was previously reported.[3–5,10]

Hydrostatic pressure up to 50 kbar was applied by means of a diamond-anvil cell (DAC). Two opposed diamonds with a 1.2 mm diameter culet separated by a spring-steel gasket are the core of the cell. An electrochemically drilled hole (500 μm in diameter) in the center of the gasket is the sample chamber, which is filled with CsI salt as pressure transmitting medium. The sample is mounted in direct contact with one diamond culet in order to assure perfect planarity and to avoid unwanted ethalon effects. The applied pressure is determined via the spectral shift of $BaSO_4$ IR-active vibrational stretching mode at 983.4 cm^{-1}, previously calibrated against the ruby fluorescence up to 50 kbar. The hydrostatic character of the applied pressure was also monitored by the full width at half maximum of such a vibrational mode,[19] which showed only a slight increase at 50 kbar.

Polarized reflectance (R) spectra in the 1.5–4.5 eV spectral range were recorded by a Fourier transform spectrometer (Bruker IFS 66/S) with a spectral resolution of 8 cm^{-1}. The spectrometer was equipped with a homemade microreflectometer that allows collimation and focusing of the incident light that provides a probing spot of 50 μm with an angular divergence of the incident light cone of less than 1°.[20]

The incident light was linearly polarized with a standard Glan-Taylor polarizer operating in the range of 200 nm–2.8 μm and mounted on a rotation stage. The parallel and perpendicular components refer to light polarized parallel and perpendicularly to the polymer chains, which are aligned to the stretching direction.

Nonpolarized Raman measurements were performed with a Dilor Labram spectrometer, using a 10× objective. The excitation was provided by a He-Ne laser ($\lambda_{exc}=632.8$ nm). In this case, even though the laser beam is polarized, no anisotropic Raman response is observed due to the high numerical aperture of the objective combined with diamond optical response, which depolarizes all signals.

A methodological warning on optical data reduction has to be provided in order to clarify the limits of the experimental approach used for polarized reflectance under high pressure. In addition to the optical response of the sample, several other contributions affect the measured spectra, and must be properly considered for a correct data analysis. These are:

(1) The reflection from the front surface of the diamond-anvil cell;

(2) The dielectric contrast between diamond and sample instead of the usual air/sample interface;

(3) The optical transfer function of our DAC, in particular diamond birefringence induced by defects,[21] which can inhomogeneously rotate the plane of polarization of light, introducing a polarization mixing in the sample optical response;

(4) Light scattering from the sample itself, as inferred from previous spectroscopic measurements.[4]

In general, all mentioned contributions exhibit a smooth spectral dependence so the main spectral features characterizing PPV, particularly for the parallel polarization, can be discussed starting from the raw data. Nevertheless, a more detailed discussion and a quantitative evaluation of the relative strengths of the observed spectral features require a more careful inspection of the data due to the problems cited above. A simple model, considering the diamond anvil as a thick transparent layer, allows the calculation of the contributions to reflectance and transmittance of the air/diamond and diamond/sample interfaces, and can easily account for the first two issues. To account for the optical transfer function and the defect-induced birefringence of diamond anvils, we renormalized our results by using a series of calibration measurements performed on the empty diamond cell, which fully characterize both its polarized spectral response and depolarization effects. We notice that the small angular divergence (1°) of our setup minimizes the volume of diamond crossed by the probing beam, thus strongly improving the control on polarization of the incoming beam. As a matter of fact, by inserting the calibration data in the optical model for DAC+PPV, we obtained a reasonable set of renormalized spectra, the one corresponding to ambient pressure being very close to the literature data measured out of the cell.[4,5,10,22] The spectral reliability of polarized data analyzed by our method is guaranteed up to 3.5 eV with the noise increasing for larger energies. Some minor discrepancies, probably ascribed to the last listed issue, still remain and cannot be accounted for without arbitrary assumptions. Moreover, since the normalization procedure is based on data measured at ambient pressure, some caution has to be used to interpret the spectra at higher pressures. Nevertheless, the features we want to discuss do not depend on the adopted procedure, showing a regular evolution with the pressure,

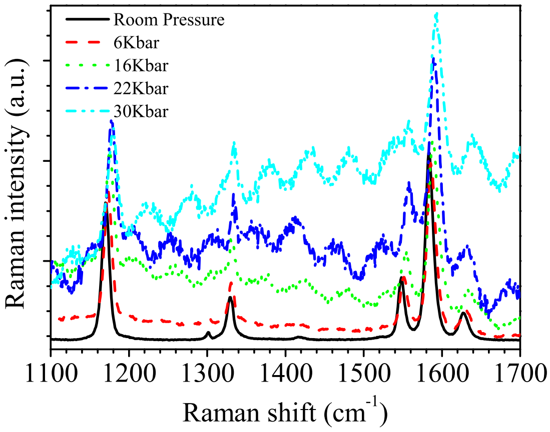

FIG. 1. (Color online) Raman spectra (λ_{exc}=632.8 nm) of highly oriented PPV under applied pressure.

which is not affected by the renormalization. Anyway, some care has to be used in the interpretation of the data related to the perpendicular polarization since these spectra are much less intense than the parallel ones and thus more sensitive to uncertainties. Bearing in mind these observations, whose detailed description will be provided in a separate publication,[23] experimental parallel and perpendicular *R* spectra will be presented and discussed.

III. RESULTS AND DISCUSSION

Preresonant Raman spectra (λ_{exc}=632.8 nm), as recorded (without rescaling) up to 30 kbar, are shown in Fig. 1. At room pressure five modes are clearly detectable (at 1170, 1329, 1548, 1583, and 1627 cm^{-1}), whose assignment is reported in Table I, according to Refs. 24 and 25. Additional very weak modes are also identified but they disappear under applied pressure and they are disregarded in the present discussion. A detailed analysis of such small vibrational features has been reported in Ref. 24.

We notice the appearance of a background in the Raman spectra whose intensity increases upon increasing the applied pressure. This background shows a well resolved interference fringe pattern that resembles the one previously observed and attributed to photoluminescence (PL).[4] By increasing pressure, the excitation at 632.8 nm becomes closer to the absorption onset (vide infra), thus providing a more efficient PL excitation. This emitted light, due to the high optical quality of the sample, is then reflected back and forth from the sample surfaces, thus resulting in Fabry-Perot cavitylike interference fringes.[4] The presence of a weak photoluminescence emission suggests the extremely extended conjugation length of the polymer chain in these samples. Nevertheless, the weakness of the Raman signal and this PL background prevent us the observation of any “resonant” enhancement of the Raman peaks.

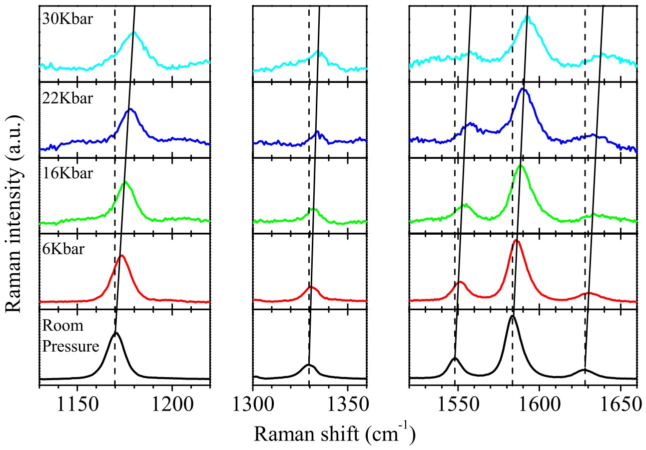

FIG. 2. (Color online) Raman shifts for vibrational modes in highly oriented PPV upon applying pressure. Raman spectra are shown for each applied pressure after smooth background subtraction.

Figure 2 shows Raman spectra after the smooth PL background has been subtracted. This correction does not alter significantly the spectral position of Raman modes. No new bands appear in the Raman spectrum by applying pressure. All observed vibrational modes harden, increasing their frequency upon applying pressure (Fig. 2) with a rate ($d\nu/dP$) ranging from 0.16 to 0.36 cm^{-1}/kbar.

The shift rates as a function of pressure for oriented PPV are compared in Table I with literature data measured for nonoriented PPV films.[26,27] Due to the different synthetic

TABLE I. Assignment of Raman modes of PPV according to Ref. 24 and comparison of $d\nu/dP$ for oriented (this work) and nonoriented (from Refs. 26 and 27) PPV.

		$d\nu/dP$ (cm^{-1}/kbar)		
Raman shift	Main assignment[a]	Nonoriented PPV[b]	Nonoriented PPV[c]	Oriented PPV
1170 (cm^{-1})	C-C stretching+C-H bending of the phenyl ring	0.36	0.26	0.34
1329 (cm^{-1})	C=C stretching+C-H bending of the vinyl group	0.18	0.17	0.16
1548 (cm^{-1})	C=C stretching of the phenyl ring	0.39	0.40	0.33
1583 (cm^{-1})	C-C stretching of the phenyl ring	0.35	0.37	0.28
1627 (cm^{-1})	C=C stretching of the vinyl group	0.35	0.39	0.36

[a] References 24 and 25.
[b] Reference 26.
[c] Reference 27.

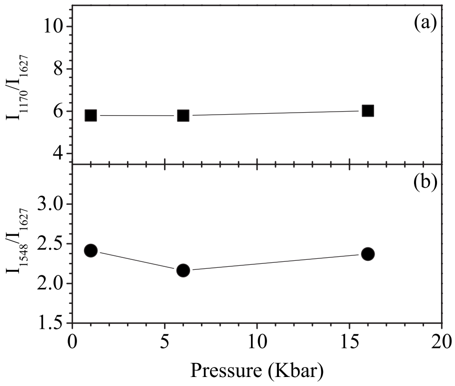

FIG. 3. (a) Intensity ratio I_{1170}/I_{1627} and (b) I_{1548}/I_{1627} vs applied pressure for highly oriented PPV.

procedure used to prepare those polymers and then to their different supramolecular structure, a definite trend of the pressure rates for the shift of vibrational modes of various samples cannot be easily rationalized. However, we notice that, for oriented PPV, the Raman modes assigned to CC phenyl ring stretchings (1548 and 1583 cm^{-1}) show a softer dependence on pressure with respect to those of the nonoriented samples. The lower $d\nu/dP$ rates observed for such modes in oriented PPV could be related to its high crystallinity degree [about 70% (Ref. 28)] and long intrinsic conjugation length. We suggest that in the crystalline regions phenyl rings are better packed and then weakly perturbed in the range of applied pressures. This interpretation is in full agreement with data for polydiacetylenes, where $d\nu/dP$ for crystalline polymers is less pronounced than in amorphous ones.[29]

Additional insight on the photophysical properties of this material can be obtained by analyzing the relative intensities of Raman bands. In particular, the modes at about 1170 (assigned to the C-H bending of the phenyl ring), at 1548 (C=C phenyl stretching), and at 1627 cm^{-1} (C=C vinyl stretching) are relevant for the present discussion [see Table I (Refs. 24 and 25)]. It has been observed[25,30] that the ratio between the bands at 1548 and at 1627 cm^{-1} (I_{1548}/I_{1627}) is greater (less) than the one for long (short) conjugated segments while the ratio I_{1170}/I_{1627} is related to the torsion of the phenyl rings, being greater (less) than the one for planar (twisted) polymer chain conformation.[24,25,30,31] Then, these ratios are fundamental in assessing the planarity of the chains and consequently the conjugation length of PPV macromolecules. Thus, Raman scattering provides a tool for monitoring the geometrical changes induced by pressure in the polymer structure, yielding a qualitative criterion for evaluating the conjugation extension. Similar reasoning have been also previously reported for different conjugated polymers.[30,32]

Our data for highly oriented PPV show that the ratio $I_{1548}/I_{1627} \sim 2.4$ is almost independent of pressure up to 16 kbar (Fig. 3). For higher applied pressure the presence of interference fringes in the background of Raman spectra prevents the determination of band intensity. Similarly, the ratio $I_{1170}/I_{1627} \sim 6$, also plotted in Fig. 3, is almost independent of pressure up to 16 kbar. It is interesting to compare the data for oriented PPV with those for nonoriented PPV (Refs. 26 and 27) and oligophenyl parahexaphenyl (PHP).[17] In nonoriented PPV I_{1543}/I_{1622} grows from 1 to 2.4 upon changing applied pressure up to 80 kbar.[27] In our case the value of 2.4 is already achieved at room pressure and does not change by applying pressure. This indicates that conjugation length of stretch-oriented PPV is not substantially increased by pressure while in standard PPV such a high value is achieved only at very high pressures.

Furthermore, it is worth noticing that the ratio I_{1170}/I_{1627} is also independent of pressure (Fig. 3), i.e., phenyl rings have a very low twisting angle, again, indicating that our PPV is already planar at room pressure. This behavior is dramatically different with respect to that observed both in spin cast PPV (Ref. 27) and PHP (Ref. 17), where, instead, the observed remarkable increase in this ratio up to 50 kbar indicates a progressive planarization of the macromolecules for increasing pressures.

All these observations point out that oriented PPV possesses a high degree of planarity and consequently an exceedingly extended conjugation length, which is not significantly improved by applying pressure. This indicates that, in the investigation of the optical properties of oriented PPV under pressure, minor effects due to the extension of conjugation length are expected.

Finally, we observe in Fig. 2 an apparent broadening of the Raman bands. However, a detailed analysis indicates that the full width at half maximum of Raman peaks is almost constant and the apparent broadening is due to the relative reduction in the signal intensity with respect to the PL background upon increasing pressure. The independence of broadening on applied pressure in oriented PPV indicates that anharmonicity plays a minor role on the vibrational properties of the system. In other conjugated polymers, such as polydiacetylene,[29] which is a highly crystalline system, the broadening of Raman peaks was instead assigned to phonon distribution correlated with intramolecular ordering (flattening) upon increasing pressure. Therefore, we deduce that order in oriented PPV is almost independent of the applied pressure, thus further indicating that the main effects of pressure observed in the optical spectra are due to different reasons.

Measured reflectance spectra for different applied pressures with light polarization parallel to the polymer chains are shown in Fig. 4. At room pressure, the lowest energy peak, assigned to the $\pi-\pi^*$ transition, is located at 2.46 eV (504 nm). The considerably low energy of this purely electronic (0–0) transition further testifies the exceedingly long conjugation length of the polymer chains in this sample, even at room pressure. Well resolved vibronic replicas are also observed at 2.70, 2.90, and 3.09 eV (460, 427, and 401 nm). The clear spectral resolution of these features reflects the high degree of structural order, a fundamental issue in order to deeply investigate the optical and electronic properties of this polymer. Furthermore, another transition can be detected as a shoulder around 3.77 eV [329 nm—so-called peak II (Ref. 4)]. The assignment of this very weak structure, only detected for polarization along the chain axis, was previously provided on the basis of quantum chemical calculations and assigned to conjugation chain ends.[3,4,33] Since the intensity of such a structure is expected to decrease as chain

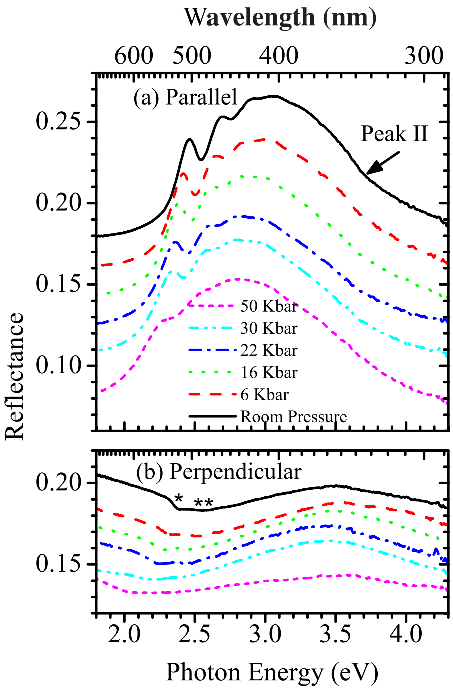

FIG. 4. (Color online) Reflectance spectra of PPV for different applied pressures; (a) parallel polarization; (b) perpendicular polarization. The high-pressure spectra have been vertically translated to improve visibility.

length increases,[4,33] its weakness further confirms the extremely long average conjugation length of macromolecules in these samples.

The overall effect of pressure on the parallel component of R is a rigid redshift of the whole spectrum joined to a broadening of the vibronic transitions. In particular, it is worth noting that the $\pi-\pi^*$ transition shifts to -3.7 meV/kbar, as shown in Fig. 5(a), while the dependence on pressure of peak II (Fig. 5(b)), determined as the zeros of the third derivative of R spectrum, is weaker, -2.7 meV/kbar. Furthermore, the spectra in Fig. 4 also exhibit a broadening of all electronic transitions and vibronic replicas upon increasing pressure. We notice that intramolecular effects probed by Raman and peak II pressure dependences are very weak, and then the deep modification observed for the $\pi-\pi^*$ transition suggests their origin being due to different mechanisms.

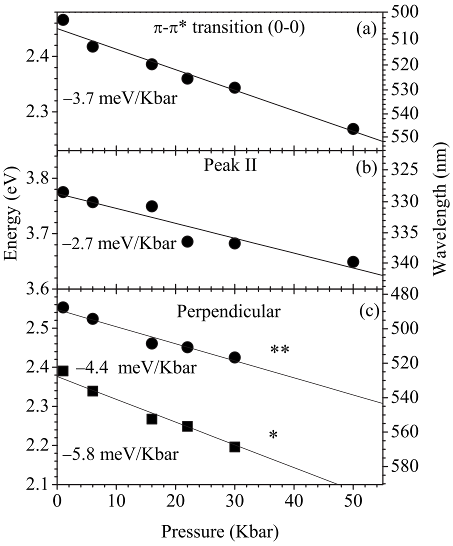

FIG. 5. Shift with applied pressure of $\pi-\pi^*$ transition and peak II. The linear fits are also shown. dE/dP for double structure of perpendicular component of reflectance spectra of oriented PPV.

Figure 4(b) shows the perpendicular component of reflectance spectra for different applied pressures. For this polarization the shape of R spectra exhibits some difference when compared to the ones previously reported, for instance, in Refs. 3 and 5 at room pressure outside the diamond-anvil cell and due to the optical effects described in Sec. II.

Although the lowest energy transition and its vibronic replica between 2.46 and 3.09 eV are hardly detectable, as expected for a highly oriented and thus optically anisotropic sample, some features can be identified. In the low energy region of the R perpendicular spectrum, up to about 2.3 eV, by increasing the photon energy, the signal decreases due to the increasing absorption. This is an effect of chain misalignment, which provides a projection of parallel component into the perpendicular one. Moreover, a weak structure appears around 2.5 eV denoted with asterisks in Fig. 4(b) and for higher energies a maximum is also observed at about 3.5 eV. However, the careful analysis of the optical data previously described shows that this maximum is an artifact due to polarization mixing.

Upon applying pressure, the onset of R perpendicular [marked with * in Fig. 4(b)] shifts toward lower energies at a rate of $dE/dP=-5.8$ meV/kbar, a value close to that observed for the $\pi-\pi^*$ absorption edge transition in the parallel transmittance spectrum, being due to the sum of energy shift and broadening rates of the $\pi-\pi^*$ peak (Fig. 5).[23,34] The feature at about 2.5 eV [marked with ** in Fig. 4(b)] shows a pressure rate of $dE/dP=-4.4$ meV/kbar, which is more similar to that observed for the 0–0 peak of parallel reflectance spectrum, thus suggesting its origin as due to chain misalignment.

In order to provide a deeper understanding of the spectral properties of reflectance so far described, the knowledge of the complex dielectric function $(\varepsilon_1+i\varepsilon_2)$ is a key issue. As a matter of fact, the importance of the complex dielectric function was demonstrated in previous papers, where the assignment of optical transitions was reported.[4,5] In Ref. 4 the dielectric constants of highly oriented PPV were determined via a Kramers-Kronig (KK) transformation of reflectivity spectra joined with ellipsometry while in Ref. 5 a combination of KK analysis and an interferometric method[10] was used. In the present case, the relatively narrow extension of the spectral range and the diamond/sample interface hinder the use of KK transformations to directly obtain the two components of the dielectric function. For these reasons, the complex dielectric constant was obtained according to the following procedure (for further details, see Refs. 22 and 23):

(i) we fit the literature data[4,5,10] (obtained for the same specimen as we used in the present work) of both components of the dielectric function with a series of Gaussian peaks for ε_2 and the related KK consistent function for ε_1;

(ii) with these functions we calculate the normalized reflectance for a diamond/sample interface;

(iii) using the peak positions of the Gaussian curves, their widths, and, as a refinement, their amplitudes as free parameters, we search for the best fit of the experimental spectra, starting from the ambient pressure ones (very similar to the literature results) and moving progressively to high-pressure results.

The advantages of such a procedure are twofold: taking special care of the smooth evolution of the fit parameters from a defined and well-known configuration, namely, the room pressure measurements, we could follow the pressure changes continuously and we obtained an intrinsically KK-consistent set of functions describing ε_1 and ε_2 at different pressures. These optical functions are now used to provide an assignment of observed spectral broadening and shifting.

As we showed before, since planarization effects of macromolecules weakly affect the parallel component of R, we expect the main effects on such a spectrum to be related to intermolecular interactions and/or el-ph coupling. Applied pressure reduces the intermolecular distances, thus favoring the possibility of wave-function delocalization on different chains, which in turns induces a splitting of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the isolated molecules with the overall effect of broadening the optical transitions and vibronic progression. The increased electronic delocalization due to interacting molecules might also reduce the el-ph coupling, hence further contributing to spectral broadening. As a matter of fact, it is well known[35] that changes in el-ph coupling bring a redistribution of the vibronic progression intensity in the absorption spectrum. For better understanding of this point, we compare the intermolecular interaction bandwidth (W_{inter}) with the strength of the electron-phonon coupling ($W_{\text{el-ph}}$), which can be evaluated by the energy separation of the vibronic progression.[36,37] The value of the ratio $W_{\text{inter}}/W_{\text{el-ph}}$ determines the weak ($\ll 1$), intermediate (~ 1), or strong ($\gg 1$) coupling regime in the investigated system and then the correspondent spectral shape. For instance, pioneering papers on molecular dimers[36,38] indicate that, in the extreme limits of weak and strong el-ph coupling, the vibronic progression retains the structure observed for isolated molecules with a bathochromic or hypsochromic spectral shift. Conversely, in the case of intermediate coupling, since the electronic and vibrational wave functions are not separable, a deep modification of the absorption spectral contour occurs, characterized by an apparent broadening of all the electronic transitions. For this reason, it is difficult to disentangle between the two mechanisms which in principle provide a similar optical effect.

At room pressure from the parallel component of ε_2 ($\varepsilon_{2,\parallel}$), we find $W_{\text{el-ph}}=0.18$ eV.[3,4,23] It is very difficult instead to find W_{inter}, which is hidden underneath the full width at half maximum of the 0–0 line and its unavoidable inhomogeneous broadening. A hint in solving such a problem comes from the fitting procedure so far described. As a matter of fact, the R parallel spectrum is best fitted only when the dielectric function (for details, see Ref. 23) is composed of two oscillators for each peak of the vibronic progression. We also notice that this requirement becomes more and more pressing upon increasing hydrostatic pressure. We interpret this fact as a direct proof of the existence of intermolecular interactions.[39] Since the separation of these two oscillators for the 0–0 peak of $\varepsilon_{2,\parallel}$ is 0.035 eV, we assume this as the value of W_{inter}. Then, at room pressure, $W_{\text{inter}}/W_{\text{el-ph}}=0.19$, implying a relatively weak-coupling regime.[36] Upon increasing pressure, from the hardening of phonons detected in $\varepsilon_{2,\parallel}$, we can derive $W_{\text{el-ph}}\sim 0.23$ while the fit of 0–0 transition of optical spectra shows a strong enhancement of W_{inter} to 0.113 eV, which results in $W_{\text{inter}}/W_{\text{el-ph}}=0.5$, i.e., a coupling regime much closer to the intermediate one. As a consequence, we deduce that at 50 kbar intermolecular interactions are important and induce a broadening of the optical spectra of the parallel polarization even though a contribution from el-ph coupling cannot be neglected.

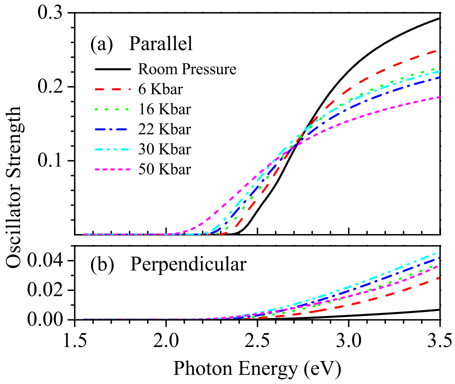

FIG. 6. (Color online) Oscillator strength derived by numerical integration of (a) parallel and (b) perpendicular components of ε_2.

Additional information on the electronic structure of oriented PPV can be obtained by discussing the oscillator strength for parallel and perpendicular polarized transitions. Within the quantum theory of absorption and dispersion, the sum rule for the oscillator strength of optical transitions in a solid is provided by the ε_2 spectrum through the following equation:[40]

$$\left(\frac{m}{2\pi^2 N_C e^2}\right)\int_0^{\omega_x} \omega\varepsilon_2(\omega)d\omega = f(\omega_x), \qquad (1)$$

where N_C is the carbon atom density (sixteen in an orthorhombic crystallographic cell $8.07\times 5.08\times 6.54$ Å^3),[41] e is the electronic charge, and m is its mass. Equation (1) relates the optical constants with the oscillator strength f of the optical response within the frequency ω_x. The plots of the oscillator strength as a function of ω_x are reported in Fig. 6 for the (a) parallel and (b) perpendicular polarizations.

Even though a complicated mathematical treatment has been done on the rough data in order to obtain ε_2 and then some approximations are implicit in our spectra, Fig. 6(a) clearly indicates that for the parallel component an isosbestic point occurs around 2.75 eV (451 nm).[42] The oscillator strength for electronic transitions having energy up to the isosbestic points is conserved for all pressures with a different spectral spread. At room pressure, when the system is closer to a single chain behavior, the oscillator strength is achieved with a sharp structure. Upon increasing pressure the same oscillator strength is distributed in a wider spectral range due to redshift and broadening of transitions. For photon energies above the isosbestic point, the oscillator strength decreases upon applying pressure.

Very different is the case of perpendicular polarization [(Fig. 6(b))]. Even though, for this component of the optical constant, the role of approximation used in the data reduction is more relevant, an unambiguous trend is observed. The oscillator strength increases upon increasing applied pressure. Since the overall oscillator strength should be preserved, we deduce that an oscillator strength transfer from parallel to perpendicular polarization occurs, in particular for the highest energy spectral range. We interpret this transfer as evidence of intermolecular interactions, which increase the system dimensionality. These data clearly show that applied pressure modifies the electronic structure of PPV, increasing the probability of transitions having perpendicular polarization. We notice the internal consistency of our data, for which the overall oscillator strength (calculated as the parallel component plus two times the perpendicular one) is lower than one. This seems quite a reasonable result (the value one should indicate the maximum contribution of all the carbon π electrons), even considering the limited spectral range analyzed with quantitatively reliable anisotropy. As a matter of fact, π electrons in PPV derivatives give rise to optical transitions up to 6–7 eV.[3,4,43]

Comparison with theoretical calculations is at present very difficult since ε_2 spectra are reported only for molecular crystals such as fluorene[44] or para-terphenyl[45] in their different phases. No anisotropic imaginary components of dielectric constant spectra or oscillator strength data have been so far reported. It is also difficult to extrapolate from molecular crystal calculations any information for corresponding polymers due to both different crystallographic structures and role of conjugation length, which was qualitatively elucidated by quantum chemical calculations.[46]

In conclusion, we observed that hydrostatic pressure allows tuning of intermolecular interactions in highly stretch-oriented PPV. While usually the main effect of pressure in amorphous polymeric systems is an increase in intramolecular order due to the extension of the conjugation length, in our case main effects seems to be due to intermolecular interactions, which bathochromically shift the $\pi-\pi^*$ transition. A careful analysis of the complex dielectric constant shows that for parallel polarization electronic transitions below 2.75 eV gain intensity while those at higher energies show a reduced oscillator strength. For perpendicular polarization, a generalized increase in oscillator strength is observed in all the spectra indicating that this component is not only due to chain misalignment but also to intermolecular interactions. The broadening of vibronic progression has been qualitatively assigned to a splitting of electronic states due to intermolecular interactions even though a non-negligible contribution from el-ph interaction in the intermediate coupling regime has to be considered.

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