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Mechanochromic Luminescent Tetrathiazolylthiophenes: Evaluating the Role of Intermolecular Interactions Through Pressure and Temperature-Dependent Raman Spectroscopy

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Abstract

The Raman spectrum of the mechanochromic luminescent tetrathiazolylthiophene has been investigated as a function of pressure and temperature. This study verifies the sensitivity of the Raman spectroscopy as technique to characterize and understand the structural effects causing any mechanochromic changes. Continuous and evident Raman shifts and changes in intensities of the strongest lines in the spectra occur while increasing pressure or lowering temperature. These spectral changes are related with the modulation of intermolecular C-H...N hydrogen bonding previously identified for this system. The Raman bands involved are assigned to collective normal modes associated to the C-C bond stretching of the rings and reveal that the modulation of local hydrogen bonding interaction has indeed an effect which has an impact on the whole conjugated structure of the molecule. Pressure-dependent Raman spectra have been also computed by means of periodic density functional theory calculations of the crystal, giving an accurate prediction of the experimental trends.

Introduction

Organic-based high-pressure sensors are highly demanded in both industrial and scientific communities. They are good alternatives to inorganic sensors due to many advantages, such as good flexibility, low-cost preparation, and large-area fabrication. Up to now, there were only very few organic materials reported to exhibit significant piezochromism, as a result of crystalline structure changes (related to different intermolecular packing)¹⁻⁶. In the particular case of 2,3,4,5-Tetra(2-thiazolyl)thiophene crystals¹, the interplay among a 3-D network of intermolecular N...H-C hydrogen bonds and π - π interactions between stacked molecules forming dimers confers to the crystal a peculiar sensitivity to mechanical stress. Indeed, the material exhibit luminescent chromism, *i. e.* a remarkable shift of the fluorescence emission, induced both by grinding and by modulation of the hydrostatic pressure⁷⁻⁹. Piezochromism is relevant in the perspective of the potential applications, such as memory devices and sensors.

Opposite effects on the luminescence behavior is determined by grinding and by applying hydrostatic pressure, consisting in a blue or red shift of the emission maximum, respectively. These effects have been elucidated in ref. ¹, by means of theoretical modeling, X-rays diffraction data and IR experiments. In particular, the analysis of the infrared CH stretching region provided evidence of a remarkable strengthening of the H-bonds upon applied load, clearly correlated with a geometry change induced by compression and resulting in a shortening of the H bonds. In addition, the IR analysis allowed highlighting the fully reversible nature of the process, because the spectral features observed at ambient pressure are completely recovered after the loading – unloading cycle.

The high sensitivity of the IR spectra to mechanical stimuli inspired the present study in which we aim to conduct a complementary Raman investigation to further understand what inter/intra molecular changes control the pressure induce mechanochromism. In this work we will combine Raman experiments with DFT simulations under the effect of increasing pressure.

The analysis will be focused on the spectral region showing band associated to collective C-C stretching of the conjugated backbone. These modes are responsible of very strong Raman transitions, due to the presence of a sequence of nearly planar rings, which share to a highly polarizable π electrons cloud.

Therefore, the pressure evolution of these bands will be a determinant marker to understand the pressure effect on the π system. Parallel to the pressure dependent experiments, we have performed Raman spectroscopy in a wide range of temperatures. This temperature dependent experiments show that the pressure effect is conveyed by a geometry relaxation of the lattice, due to the thermal shrinking upon cooling.

As already proven by the study of ref. ¹, theoretical calculations can now reach a degree of accuracy suitable for a reliable prediction of crystal structures and spectra. The joint use of experiments and calculations is expected to be a valuable strategy to extract detailed information on the phenomena investigated.

Materials and Methods

Experimental Details

Raman signal were recorded with a Senterra (Bruker) Dispersive Raman spectrometer equipped with a Peltier-cooled CCD detector (-70, -55°C) and a 785 nm diode laser as excitation line. Raman spectra were collect through a 20x objective with a spectral resolution of 3 cm^{-1} . The power of laser source on sample were changed in order to optimize the Raman signal and set to 10 mw and 100 mw respectively for measurements a different temperature and pressure.

The temperature of the sample were controlled by a Linkam temperature Stages (BCS196) and changed in the temperature range from -180°C to 200° with a step of 20°C.

High pressure experiments were conducted in a sapphire anvil cell (SAC), with a diameter culet of 380 μm and a gold gasket. No pressure transmitting medium was used and diamond chips were placed as the pressure calibrant^{10,11}.

Computational Details

Periodic DFT calculations (full optimization + Raman spectra calculation) have been carried out by means of CRYSTAL14 code^{12,13} at PBE0/6-31G(d,p) level of theory including D2 Grimme's correction for dispersion interactions (PBE0-D2)¹⁴. The parameters adopted for the correction have been taken from a previous paper¹⁵. The following cases have been considered for the prediction of the Raman spectra.

- Isolated molecule
- 3D crystal (see Figure 1)
- 3D crystal with application of different hydrostatic pressures up to 5.9 GPa

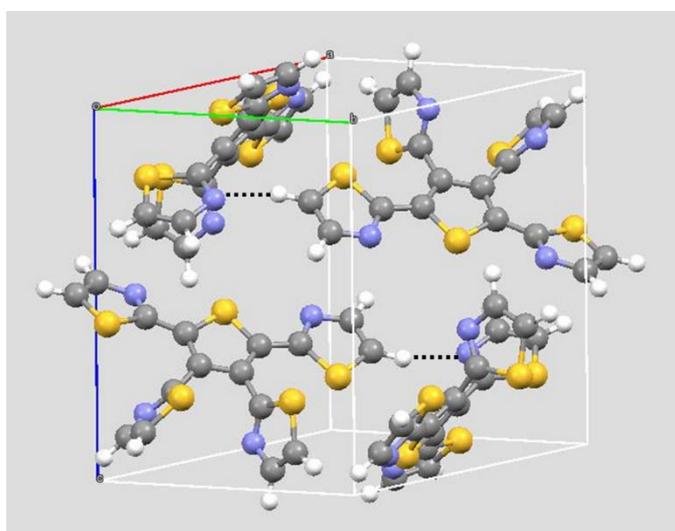


Figure 1: Sketch of the tetrathiazolythiophene crystal: weak C–H...N hydrogen bonds are represented as dotted lines

In the case of the crystal (P21/n space group), the starting input geometry employed to run the full optimization of the crystal have been taken by the experimental data reported by Yamaguchi et al.¹.

In Table 1 the experimental cell parameters are compared to the DFT-D computed ones: a very good agreement is found with very small discrepancies between the two groups of values. Moreover, values of the cell parameters are reported also for the calculations of the cell under pressure, showing the contraction of the cell which follows straightforwardly the application of a pressure as also previously demonstrated¹. Based on the optimized structure so obtained, Raman spectra have been computed for the different pressures and compared to the experimental ones. In the comparison a standard scaling factor of 0.9512 have been adopted, as proposed by Radom et al.¹⁶.

Table 1: Experimental and DFT-D computed values of the cell parameters for varying pressures. The average deviation with respect to the experimental data is reported in brackets for the optimized geometry.

P21/n	Expt. (ref. ¹)	PBE0-D2/ 6-31G(d,p)	PBE0-D2/ 6-31G(d,p) P= 0.736 GPa	PBE0-D2/ 6-31G(d,p) P= 1.471 GPa	PBE0-D2/ 6-31G(d,p) P= 2.207 GPa	PBE0-D2/ 6-31G(d,p) P= 2.942 GPa	PBE0-D2/ 6-31G(d,p) P= 5.884 GPa
a	11.3154	11.2397 (0.67%)	11.1783	11.0940	11.0261	10.9970	10.8602
b	11.9773	11.8305 (1.23%)	11.8034	11.6807	11.5971	11.5711	11.3529
c	12.5982	12.5037 (0.75%)	12.1002	11.9559	11.8002	11.5927	11.1573
β	94.3	95.5 (1.27%)	96.3	96.5	96.3	97.1	97.7

Results

The remarkable response to mechanical grinding of tetrathiazolythiophene was previously investigated, among many other techniques, by means of infrared spectroscopy, focusing on the region characteristic of CH stretching vibrations (from 2900 cm⁻¹ to 3300 cm⁻¹)¹. It is indeed well-known that CH stretchings are highly influenced by the environment that they experience, showing a modulation both in frequency¹⁷ and intensity¹⁸.—This behavior allows excluding any phase transition and suggests that the occurrence of mechanochromism is related to a smooth modulation of the C-H...N hydrogen bond strength, which in turns results in the formation of the excimer responsible for the luminescence¹.

In these sense, it is particularly interesting to verify which contribution could Raman spectroscopy give to the characterization of this class of materials. The reasons for the interest in this characterization technique are manifold. First of all, Raman spectroscopy is a non-destructive characterization technique which can be adopted both in-situ and ex-situ without the need to manipulate and modify permanently the sample. Moreover, Raman spectroscopy is a very powerful method to characterize molecules containing conjugated π electrons, providing many information about the properties of these materials, beyond the simple structural investigation¹⁹⁻²². In addition, by a proper interpretation of the spectra it is possible to get precise information about π electrons, including the effect of weak intermolecular interactions²³. It is thus very interesting to analyze how supramolecular effects mediated by the application of pressure or temperature can affect the Raman spectra.

As a first comparison, in Figure 2 we report the Raman spectrum of the crystal recorded by means of two different excitation lines (1064 and 785 nm). Experiments are compared to DFT-D calculation of the periodic crystal and of the isolated molecule. We first notice, as expected for conjugated materials, that the spectrum is dominated by the bands ranging between 1300 and 1600 cm^{-1} . These bands are directly related to normal modes of vibrations involving collective C-C and C-N bond stretchings involving all the rings and all the molecules in the unit cell. As expected this kind of vibrations are sensitive to the degree of π electrons delocalization into each molecule. In this case, there are five bands in this region showing comparable intensity and the sketches of the DFT-D computed normal modes of vibration, together with the predicted values of Raman shifts and activities are reported in the Supporting Information . Because of the collective character of these modes it is impossible to give a qualitative description of the eigenvectors in terms of individual internal coordinates. Moreover, the sketches of crystal eigenvectors - reported in SI - are rather difficult to analyze because of the complex 3D structure of the cell. In order to better highlight the kind of normal modes involved, we report in Supporting Information also the sketches of the vibrational eigenvectors of the corresponding modes of the isolated molecule. A look to these sketches support the conclusion that strong Raman active modes are collective backbone vibrations.

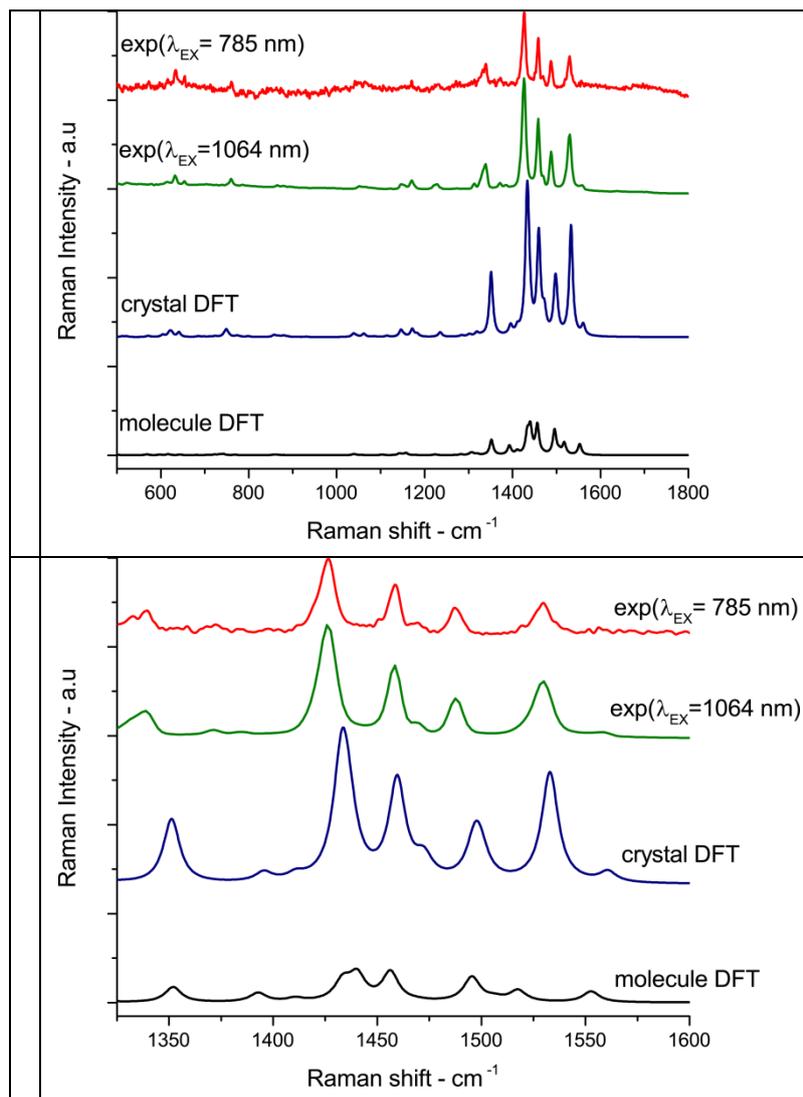


Figure 2: Above: Comparison between the experimental Raman spectra of the single crystal and the DFT-D computed spectra of the crystal and of the isolated molecule. DFT computed Intensities are normalized to the contribution of a single molecule. Below: Comparison in the spectra range 1300-1600 cm^{-1}

The spectra obtained for the excitation at 1064 nm and 785 nm do not show frequency shifts and appreciable changes of the intensity pattern and would exclude any dependence of the spectrum recorded on the exciting line adopted. The reason to choose these two excitation lines is to make sure we are as far as possible of getting into any resonant regime and get rid of any luminescence problems¹

On the other hand, in the DFT-D computed spectra, it can be seen that calculations for the crystal give a very good and accurate description of the experimental one, both in the relative frequencies and intensities and including also all the minor details, such as the shoulder at 1469 cm^{-1} and the weak transitions at 1373 cm^{-1} and 1558 cm^{-1} . Such agreement confirms the reliability of the computational method and of the model adopted in the present case, allowing to extend confidently the calculations to the case of crystals under the application of an external pressure.

Considering again the predicted spectra, it should be noticed that the Raman spectrum computed for the isolated molecule (in black), while giving again a general and good enough assignment of the spectrum, is not however able to describe accurately all the minor details related to relative intensities and frequencies. This is a first indication of the fact that the intermolecular interactions found in the solid state cannot be overlooked, if a detailed interpretation of the spectrum is required. It should be noted that also the effect of the dielectric constant in the crystal could induce a general intensity enhancement, as already shown in the case of infrared spectra of crystalline polymers²⁴.

Figure 3 shows the pressure-dependent Raman spectra for the tetrathiazolythiophene crystal. As anticipated, we have also explored the temperature effect on the intermolecular interactions, in order to study the effect of another external parameter which can affect molecular packing interaction. So figure 4 show the tetrathiazolythiophene Raman spectra as a function of temperature.

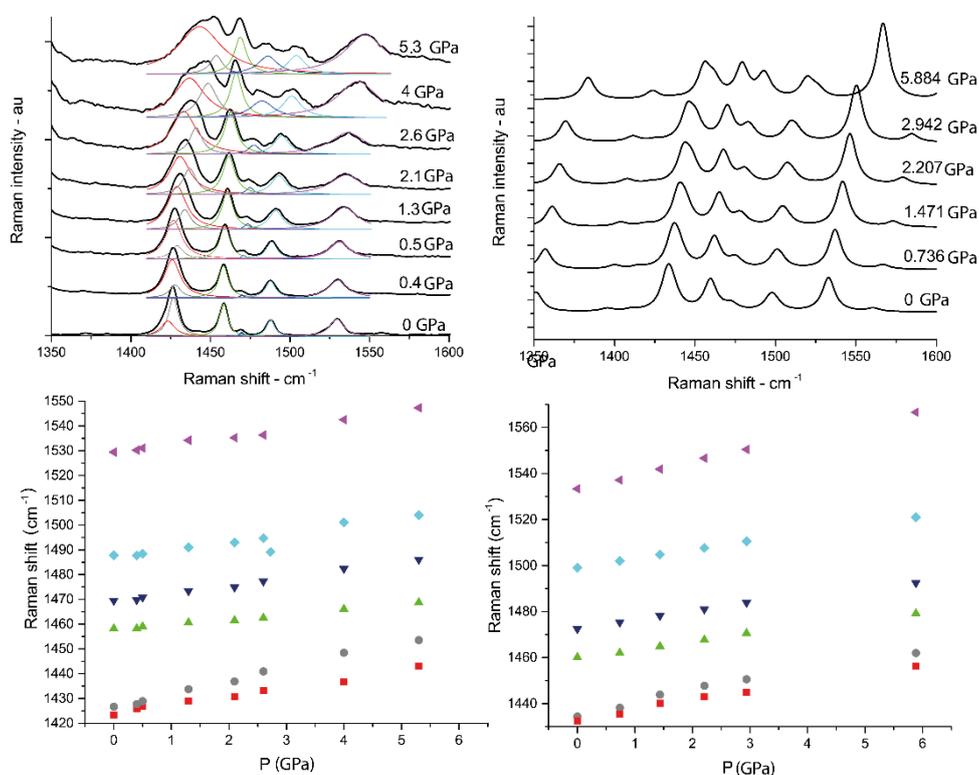


Figure 3: Above: Experimental pressure-dependent Raman spectra from 0 to 5.3 GPa (left) and DFT-computed pressure-dependent Raman spectra from 0 to 5.9 GPa (right). Below: Modulation of the wavenumbers of the strongest Raman bands observed (left) or predicted (right) as a function of pressure.

As reported in figure 3, the four most prominent band between 1400 and 1600 cm^{-1} show all a significant and continuous up-shift for increasing pressure. Up to 4 GPa, the spectra remain well defined and resolved, while for higher pressure, bands become broader and more structured, indicating that, probably, pressure is now introducing a non-negligible structural disorder in the crystalline phase. However, the continuous upshift of the four bands remains well-evident also for higher pressures **both according to experimental**

evidences and predicted spectra above 5 GPa. Moreover, changes in the intensity pattern are observed: in particular, the higher frequency band shows an evident intensity increase with pressure. This intensity behavior can be interpreted in terms of non-negligible changes of the vibrational eigenvectors, i. e. different mixing of internal displacements of the collective modes involved, while varying the applied pressure.

Considering now temperature-dependent spectra (figure 4), very similar trends are observed, with an downshift shift with the temperature decrease from 200°C to -180°C.

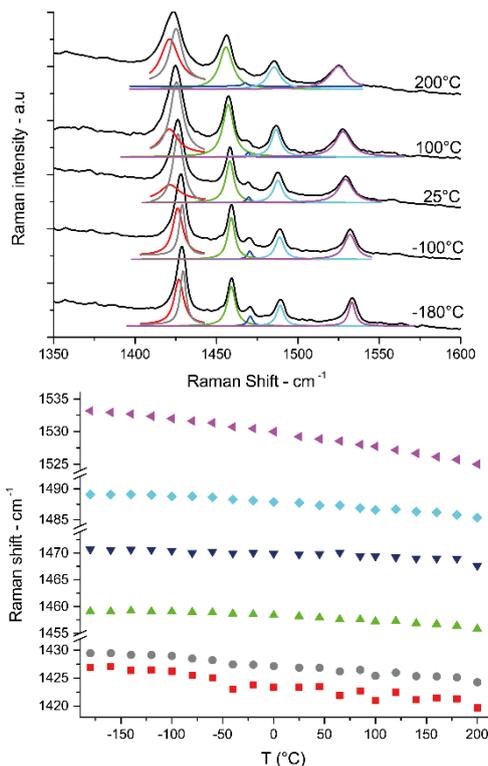


Figure 4: Above: Temperature-dependent Raman spectra recorded from -180°C to 200°C. Below: Modulation of the wavenumbers of the strongest Raman bands observed as a function of temperature.

The trends observed both lowering temperature or increasing pressure are in perfect agreement. The intermolecular packing is increased due to the contraction of the crystal which occur in both cases; moreover, the same effect is predicted by DFT-D calculation by means of the application of a pressure. A modulation by intermolecular interactions of the wavenumber of the Raman bands associated to the stretching vibrations of the conjugated rings has been also observed in the case of unsubstituted oligothiophenes, revealing that the interactions arising from an effective packing can induce a pinning effects which reduce the delocalization of π electrons²².

This effect is not surprising, it is however remarkable the fact that the effect introduced by temperature and pressure acts on the whole molecule and not only locally, as proven by the fact that the structural perturbation due by intermolecular interactions is now affecting normal modes of vibrations which are delocalized on the entire molecules in the crystal. As demonstrated in the paper by Yamaguchi et al., the effects of pressure does not change significantly the conformation of the molecule, since also at ambient

pressure the α -conjugated backbone is formed by the two end thiazole rings which are almost co-planar with the central thiophene ring and this co-planarity is kept for increasing pressure. The distances associated to the π - π stacking are only moderately affected by pressure but the major effect is observed on the geometry of the C-H...N hydrogen bond which is shortened by the application of a pressure. The perturbation induced in the hydrogen bonding network is fully reversible and both pressure- and temperature- dependent Raman spectra are restored to the initial one when going back to the unperturbed condition (see Supporting Information). Since the strength of the hydrogen bonds affects the electronic structure of the molecule as a whole, collective bond stretching vibrations and the related intense Raman lines in the spectrum are also affected, allowing to characterize these phenomena by means of the Raman technique.

In order to support the interpretation given for pressure dependent Raman spectra, in figure 3 we report the DFT-D computed Raman spectra for different values of hydrostatic pressure up to about 6 GPa. The trends observed clearly reveal the upward shift found for the four intense lines in very good agreement with the experimental results.

As a last analysis, we investigated quantitatively the variations of the frequencies of these lines as a function of pressure and temperature. This investigation required a proper curve fitting of the data by using a suitable number of components to obtain a detailed value of the frequency in the different conditions for each relevant component. Since the number of components is a critical choice in any spectral curve fitting, we used the results of DFT-D calculation to orient our choice. Indeed, the DFT-D computed Raman spectrum (see also the Supporting Information for of frequencies and intensities data) reveals that the bands observed in the spectral region 1400-1600 cm^{-1} are due to six different Raman active transitions. Therefore, six lorentzian functions have been employed to carry out the curve fitting of the experimental pressure- and temperature- dependent Raman spectra, as reported in Figure 3. In Figures 3 and 4, the frequency values of these six components are reported as a function of pressure and temperature.

In all the cases, the trends obtained can be fairly fitted by means of a continuous function, which further highlights that there are not abrupt changes, as it was expected in the case of a phase transition. A smooth modulation of the intermolecular interactions can be indicated as the responsible for the mechanochromic behaviour (and spectra changes) of this crystal.

As a function of temperature (see figure 4), DFT-D predicted frequency values of the six main components associated to the experimental one give similar trends. A similar behavior to that displayed by the experimental pressure-dependent frequency values is observed, with an approximate linear trend.

On this basis, by fitting both theoretical and experimental data by linear functions, we can simply compare the angular coefficient of the straight lines obtained. The nice correspondence of the parameters obtained from fitting the experimental data and the theoretical ones is another proof of the quality of the theoretical predictions. The results obtained are reported in Figure S2 of the Supporting Information.

Conclusions

We studied the pressure evolution of the Raman spectrum of a mechanochromic tetrathiazolythiophenes crystal. Several strong Raman bands show a remarkable up-ward frequency shift, which, for the most pressure-sensitive transitions, reaches a value of $\Delta\nu\cong 15\text{ cm}^{-1}$, while passing from ambient pressure to an applied pressure of 5.3 GPa.

The observed frequency shifts follow a nearly linear trend, thus indicating that there are not abrupt changes of the crystal structure at given critical pressure values, in agreement with the hypothesis that no phase transition are induced in the pressure regime considered.

From the point of view of the structural changes, we can ascribe the observed spectra modulation to the increase of packing between molecules, which enhances π - π stacking interactions and significantly shortens N...H-C intermolecular hydrogen bonds. This is also proven by measurements done at increasing temperatures (from -180°C to 200°C), which clearly show that thermal expansion produces frequency shift in the opposite direction.

The analysis presented is supported by a thorough comparison with DFT predictions of the crystal structure and of the Raman spectra, while exploiting PBC implemented in the CRYSTAL code. The results from theoretical modelling:

1. Give a nice prediction of the spectral features. Moreover, they indicate that the description of intermolecular interactions among different molecules arranged according the crystal structure is mandatory for a satisfactory description of the Raman features.
2. Predict the observed Raman frequencies trends, by means of calculations carried out at increasing hydrostatic pressure.
3. Allow a vibrational assignment of the strongest Raman transitions, showing that collective C-C, C-S and C-N stretching modes are affected by the pressure changes. This observation suggests that the perturbation induced by crystal compression is not merely localized on the chemical groups involved in hydrogen bonding, but it affects the whole molecule.

This can be due to the joint effect of two phenomena: (i) the change of the hydrogen bond strength, which is responsible of a modulation of the charge transfer among acceptor and donor moieties, coupled with the π electrons system delocalized on the molecule backbone; (ii) a more tight packing of molecules modifies the π -stacking distances. This fact could enhance the intermolecular π -electron pinning, already observed for polyconjugated materials characterized by an efficient crystalline packing.

In summary, this work demonstrates that Raman spectroscopy is a powerful tool to get precise information about the weak intermolecular interactions that are responsible for the mechanochromic behaviour in organic conjugated crystals.

Acknowledgements

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