

Low-frequency Raman spectroscopy – a versatile technique for material characterization and detection

<https://doi.org/10.51167/ice000016>

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Abstract:

Low-frequency Raman spectroscopy (LFRS) is a branch of vibrational spectroscopy that allows easy interpretation and highly sensitive structural identification of trace amounts of chemicals based on their unique vibrational characteristics. Due to the continuous technical improvement in Raman spectroscopy, advanced development of the device has been achieved and more applications have become possible. This article illustrates the use of LFRS for unique applications such as crystalline phase identification, enantiomeric identification, and enantiomeric separation. We present a general summary of our different research efforts in the field of polarised LFRS. The aim of this article is to highlight potential applications of different types, especially applications developed to characterize organic crystalline materials.

Overview of Raman Spectroscopy

Raman spectroscopy (RS) is an optical means of probing the vibrational modes of materials. The spontaneous Raman effect is a scattering phenomenon where photons, i.e. electromagnetic radiation of a specific wavelength, interact with the analyte i.e. the material under observation in either the ground state or one of the excited rotational-vibrational states. This interaction results in promoting the molecule into a so-called “virtual energy state” for a very short period before an inelastic photon is scattered. The resulting inelastically scattered photon which is “emitted”/“scattered” can be either of higher (anti-Stokes) or lower (Stokes) energy than the incoming photon. The probability of such inelastically scattered photons is much lower than elastically scattered photons, called Rayleigh scattered photons. Upon such

interaction, the resulting rotational-vibrational state of the molecule differs from its original state, before interaction with the incoming photon. The difference in energy between the original state and the new state leads to a shift in the emitted photon's frequency, resulting in a Raman shift [1].

RS displays several advantages over other techniques such as infrared spectroscopy. For example, the quality of the signal collected is barely affected by the presence of water, allowing for its use in many applications where infrared analysis is not reliable. A representative case study is the in-situ monitoring of a fermentative process where Raman techniques outperforms any other spectroscopic approach. Nonetheless, Raman analysis in addition to its intrinsic property of lower signal strength compared to fluorescence or absorption, suffers from some difficulties such as the

Hagit Aviv is a researcher at the Department of Chemistry, Bar-Ilan University and a co-founder of the Center for Energy and Sustainability. Until recently, as the lab manager of the Device Spectroscopy Laboratory, Hagit initiated projects and collaborations to develop spectroscopy techniques using Raman spectroscopy, specifically LFRS. Previously, her post-graduate work was centered on the field of polymers, and her doctoral research dissertation focused on synthesis and characterization of iodinated nano- and macro-particles for CT and MRI imaging.



challenge of developing quantitative robust and trustworthy methods of data analysis. However, many methods have been developed for enhancement of these signals over the years by many research groups. These include chemical, surface, and cavity enhancement techniques that were reported by us [2–4]. Furthermore, the presence of highly active Raman species such as carbon particles can mask the presence of other species. Several studies have been devoted to overcoming these drawbacks. Among these different approaches, it is known that polarized Raman spectroscopy provides information on molecular orientation and bond vibrational symmetry, in addition to general chemical identification [5].

In general, in polarized RS the spectra captured are either parallel or perpendicular to the inherent polarization of the excitation laser. However, Raman optical activity deals with the polarization phenomenon differently by observing the evolution of the Raman spectrum at different polarization angles. Polarization measurements provide useful information about molecular shape and the orientation of molecules in ordered materials, such as crystals, polymers, and liquid crystals.

The RS modes at lower wavenumbers ($< 200\text{ cm}^{-1}$) are called low-frequency Raman (LFR) modes and the technique used to analyse this region of the spectrum is called low-frequency Raman spectroscopy (LFRS); the technique is very similar to spontaneous RS. LFRS is possible due to recent development of much sharper optical filters called volume holographic filters (VHFs). These filters facilitate easy observation of wavenumber shifts that are as low as 5 cm^{-1} away from the laser line. The LFR region is rich in information relating to lattice vibrations, crystallinity, symmetry, and inter-molecular acoustic modes, as well as phonon modes [6].

LFRS for identification of crystalline phases in methylammonium lead iodide

Energy conversion from light to electricity has remained a major research area since the discovery of the photo-electric effect. While many materials and technologies have been developed over the years for this purpose, semiconductor-based solar cells have been spearheading the solar cell world due to their considerably higher efficiencies in spite of being expensive. The higher cost of existing technology has led to the expansion of research beyond conventional crystalline semiconductor materials. Organo-inorganic hybrid perovskites (OHPs) have remained promising in these efforts due to their exceptional performance resulting from their intrinsic properties such as high absorption coefficient, tunable band gap, long charge carrier diffusion, low exciton binding energy etc. Methylammonium lead iodide (MAPbI_3) is the most widely used perovskite solar cell material. While the performance of the perovskite solar cells (PSCs) is commendable, the stability of OHPs remain questionable due to their high sensitivity to humidity, light, and temperature. The instability affects the crystal structure of the material and leads to degradation of crystal structure [7]. Here, we

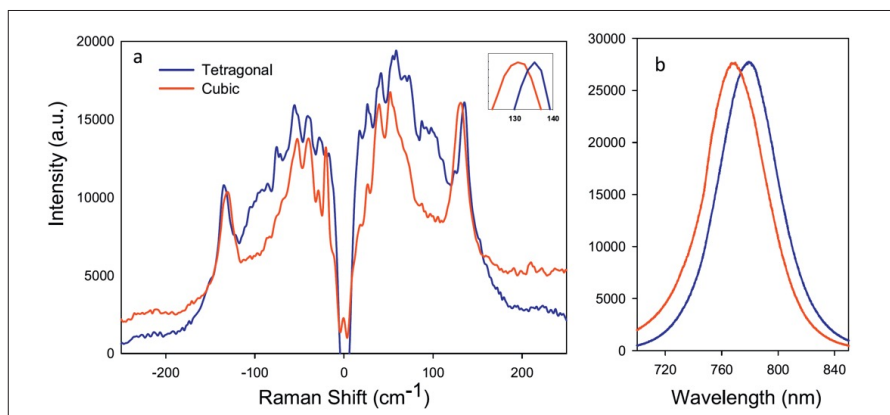


Figure 1. (a) Low-Frequency Raman Spectra and (b) PL spectra of tetragonal and cubic phases of MAPbI_3 confirming laser-induced phase transition.[§]

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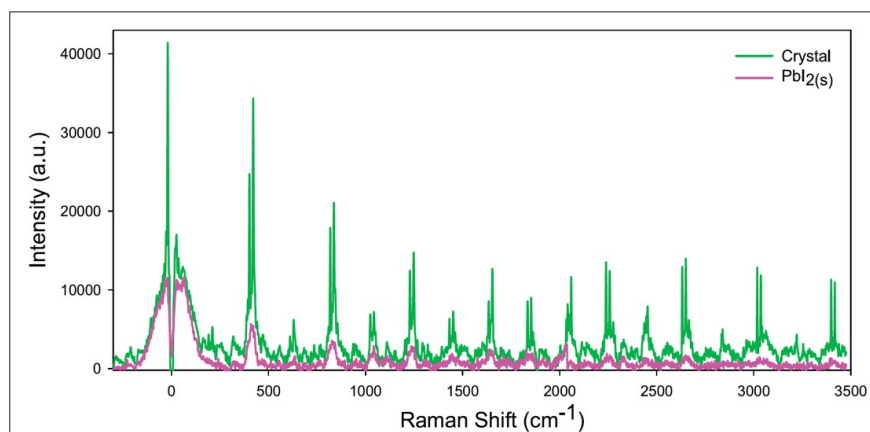


Figure 2. SRS from the resonant vibrational mode when laser power crosses 15 mW (green plot), and RRS obtained from high laser power excitation of Pbl₂(s) (pink plot).

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present LFRS as a handy tool to identify and characterize phase transformations within such highly sensitive materials.

Our preliminary work showed that the LFR modes are dependent on the crystallinity of the analyte material. It was observed that even in-situ changes in the material matrix upon laser excitation can successfully be captured with the right optical set-up and laser power. This was observed in examination of MAPbI₃ single crystals. It is well-known from the literature that MAPbI₃ exhibits different stable crystalline phases at different temperatures. At temperatures below 164 K it is orthorhombic, between 165–330 K tetragonal and at higher temperatures cubic. Additionally, there is a general agreement within the literature on thermally induced phase transitions in MAPbI₃ [8]. In one of our earlier works, we presented a photo-induced phase transition [9]. A mere 2-minute excitation of MAPbI₃ single crystals in the tetragonal phase with a 532 nm laser above 15 mW power resulted in the formation of cubic phase at ambient conditions and this phase transformation was confirmed using the photoluminescence (PL) shift as shown in Figure 1. Such dynamic phase transitions are hard to

capture in conventional crystallographic techniques such as XRD. However, LFRS makes a good candidate for such thermal and photo-induced phase transition observations. When lower laser power can be used for characterizing the former, sufficiently high laser power facilitates both phase transition and detection. In addition to these unique characteristics of phase identification and phase transition detection, the study also revealed some interesting characteristics of the material such as Raman stimulation of iodine vapor signals in addition to stimulated spontaneous Raman signals.

The overlap of the excitation laser with the electronic absorption band of the material results in resonance Raman scattering (RRS). This overlap results in a higher scattering intensity compared to the fundamental spontaneous Raman bands and in many cases leads to appearance of overtone bands [10]. On the other hand, stimulated Raman scattering (SRS) is a third-order nonlinear process that exhibits narrow-line emission from existing Raman shifts. In a regular experimental framework, this process is induced using two synchronized pulsed lasers as single-frequency excitation sources, or a narrowband source synchronized with a broadband source for multiplex excitation [11]. Certain materials under certain specific conditions self-induce SRS when subjected to a high enough laser power, even when the exciting laser is continuous wave (CW). This self-stimulated phenomenon is generally referred to as impulsive stimulated Raman scattering, or cascaded Raman process. Self-induced SRS is extensively investigated for ionic crystals, and it is understood that non-linear Raman gain is governed mainly by large crystal size and ionic radius of the cation; both of which are true for the MAPbI₃ crystals used for this study [12]. Figure 2 represents the SRS from the resonant vibrational modes when the excitation laser power exceeds 15 mW.

Yaakov R. Tischler leads the Device Spectroscopy Laboratory (DSL) at Bar-Ilan's Institute for Nanotechnology and Advanced Materials. The lab is focused on studying and tailoring light-matter interactions in nanoscale devices and nanostructured materials. This involves research on microcavity polaritonic devices, organic-based lasers, near-field scanning microscopy, and applied vibrational spectroscopy. One of the main thrusts of DSL is Raman spectroscopy, which includes development of new spectroscopic techniques and applications thereof. Yaakov opened DSL 12.5 years ago and personally holds 13 US Patents. His former students and post-docs have gone on to make an impact in government, academic and high-tech sectors, particularly in the semiconductor and photonics industries as well as in start-ups.



LFRS for differentiation of enantiopure and racemic chiral molecules

Chiral molecules form the basis of biological systems. Their occurrence is universal in the living world. They are present in the form of basic structures such as sugars and proteins and more complex ones such as amino acids, enzymes, and nucleic acids. The left- and right-handed chiral compounds exhibit different physiological effects and biological activities in biotic systems due to their contrasting interactions with proteins and enzymes [13]. It is therefore important to accomplish separation of enantiopure products from their counterparts. While various forms of chiral chromatography are widely used for enantiomeric separation, the identification of enantiopurity is achieved by studying their optical rotation or different forms of circular dichroism. While these studies are simple, they demand the analyte to be in solution form. Although X-ray diffraction, differential scanning calorimetry,

inelastic neutron scattering etc. enable identification in the solid form, they are much more complex and expensive [14].

Most of the work on LFR for chiral analysis was conceived together with our colleague Prof. Mastai. In these works, we demonstrated that LFRS can be used for crystal chirality investigations, particularly for distinguishing between racemic and enantiopure organic crystals [15]. Enantiopure chiral crystals are those comprising only one type of chiral crystal among the two possible forms. However, when a crystal contains equal amounts of each enantiomer constituting an enantiomeric pair, it is called a racemate. Most racemic mixtures crystallize as racemic crystals; however, in some cases (5% to 10% in nature), racemic compounds crystallize in a conglomerate form that is a mixture of homochiral crystals. It is known from the literature that racemic crystals are denser than the corresponding enantiopure crystals. This is generally explained by the difference in their hydrogen bonding. In the case of an enantiopure material, crystallization is dictated

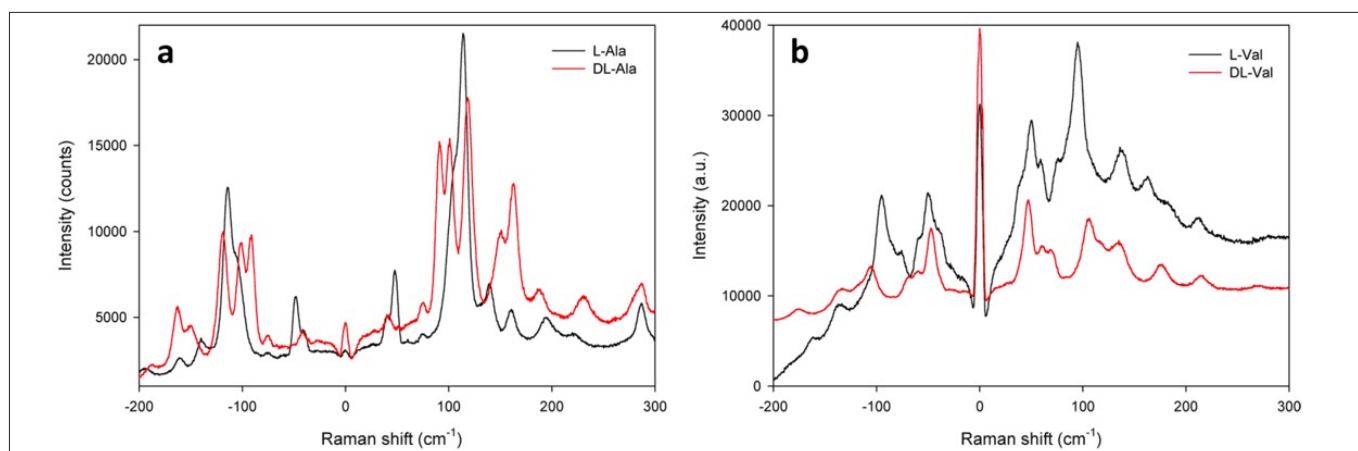


Figure 3. LFR spectra of (a) L-Alanine, DL-Alanine crystals, and (b) L-Valine, DL-Valine crystals[‡].

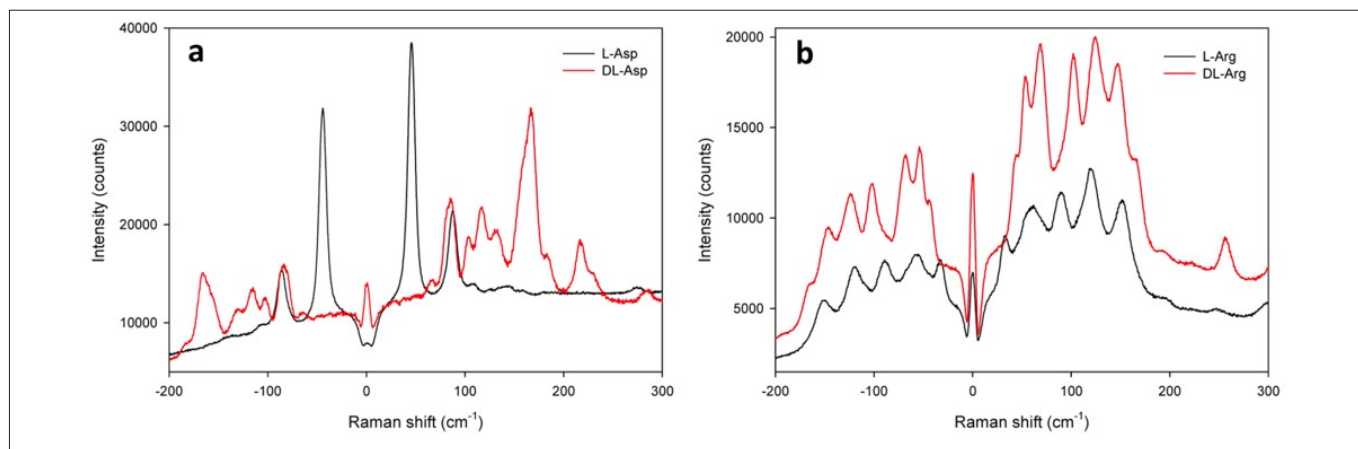


Figure 4. LFR spectra of (a) L-Aspartic acid, DL-Aspartic acid crystals, and (b) L-Arginine, DL-Arginine crystals[‡].

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by the chirality, and thus the hydrogen bond network is limited, whereas for racemic crystals, there is an extremely large availability of hydrogen bonding modes [16]. Hence the structure is stochastically defined. These considerable differences in the crystalline structure result in differences in the intermolecular interactions of racemic and enantiopure crystals. As a result, distinct vibrational modes exist in enantiopure and racemic crystals that are detectable by LFRS. Some examples of enantiomeric differentiation from their racemic mixtures are presented in Figure 3 and 4. Hence, it is observed that LFRS produces completely different spectra for racemic and enantiopure crystals. Moreover, LFRS offers faster and more sensitive chiral characterization in crystals than currently used methods, enabling facile measurements for microcrystals and detection of defects in chiral crystals. More detailed study can be found elsewhere [15].

Polarization dependence of LFRS in organic single crystals

Crystallization is a very unique phenomenon in pure compounds. Post nucleation, under a conducive environment, crystallization results in formation of highly ordered structures and adaptation of a unique three-dimensional orientation. The crystal structure governs physical and chemical properties in materials [17]. Therefore, it is extremely important to investigate and understand the structure and orientations of intermolecular interactions in crystals.

Over the years, many different physical techniques have been used to characterize crystalline structures, such as X-ray diffraction (XRD), thermal analysis, and electron diffraction. In general, each face of a single crystal provides detailed

structural information. The most common experimental method that allows resolution of individual atoms is single crystal X-ray diffraction (SCXRD) [18]. However, it requires a sufficiently large crystal that is at least partially transparent i.e. in general is bright looking, having clear edges and faces, and is free of inclusions. Another method for characterizing crystals that uses X-rays is near-edge X-ray absorption fine structure, a technique which determines the molecular orientation for non-transparent samples. Raman spectroscopy, with established higher sensitivity than XRD in crystal purity investigations, provides information on both covalent bonds based on intramolecular vibrations and intermolecular interactions [19]. At the same time, intermolecular interactions that result in shear modes, breathing modes, and hydrogen bond stretching modes are lower in energy and are observed in LFRS. The LFR modes are generated by weak interactions including molecular degrees of freedom and shear modes, and are observed in the lower range of LFRS, while vibrational modes that are generated by stronger intermolecular interactions such as hydrogen bonds exhibit larger LFR shifts within the LFRS spectral range. Theoretical and computational efforts have successfully assigned these larger LFR modes to hydrogen bond stretching vibrations using density functional theory (DFT) calculations. Previous studies have used polarized Raman spectroscopy for various applications in material characterization. Polarization dependence in Raman, along with transmission electron microscopy, is used to investigate the crystallographic orientation of dark crystals [20].

Polarization-dependent contrast in the interaction cross section of LFR modes was primarily probed in this study. We observe that investigation of crystal structures is indeed possible by studying vibrational modes obtained from each face of a single crystal using LFRS. Unlike other methods,

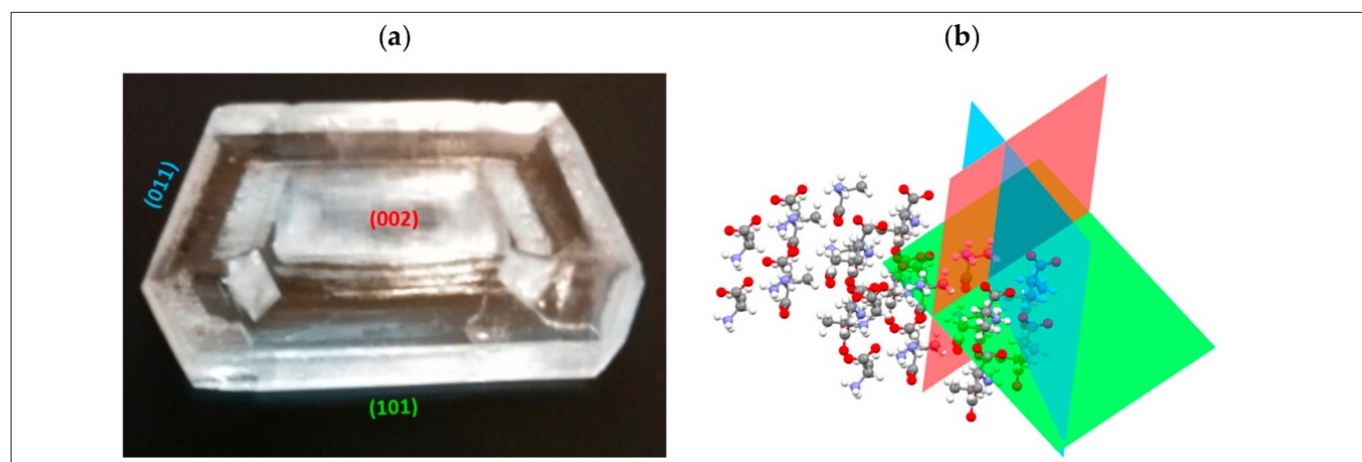


Figure 5. (a) Photo of L-aniline single crystal and measured planes. (b) L-aniline crystal structure constructed using the program "Mercury" along with the measured planes (101), (002), and (011).

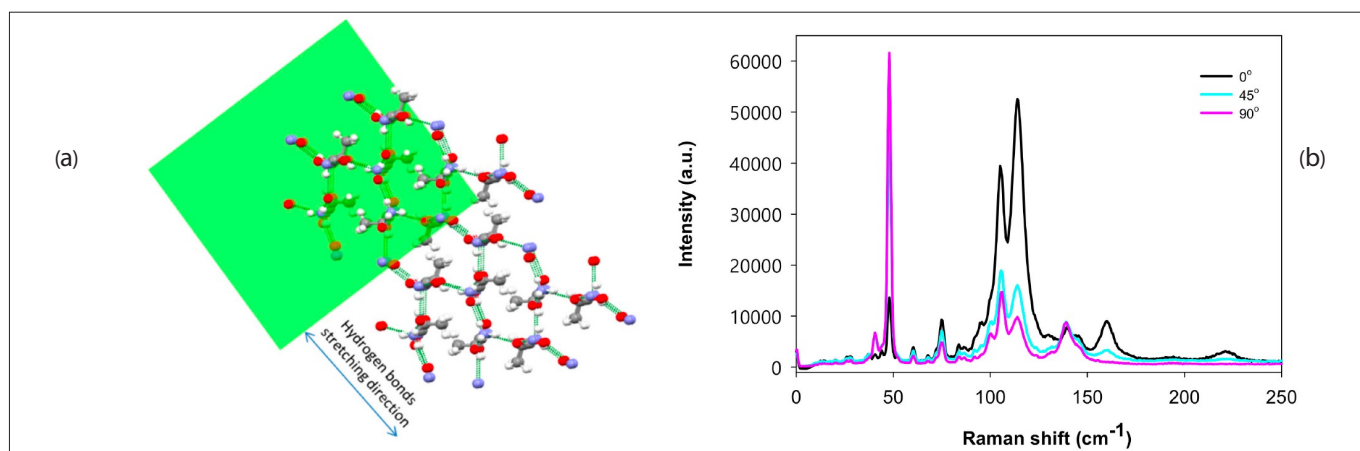


Figure 6. (a) Hydrogen bonds' simulation (dotted lines) in the L-alanine single crystal relative to the (101) plane. (b) LFRS of crystals excited from (101) direction with three different polarization angles.

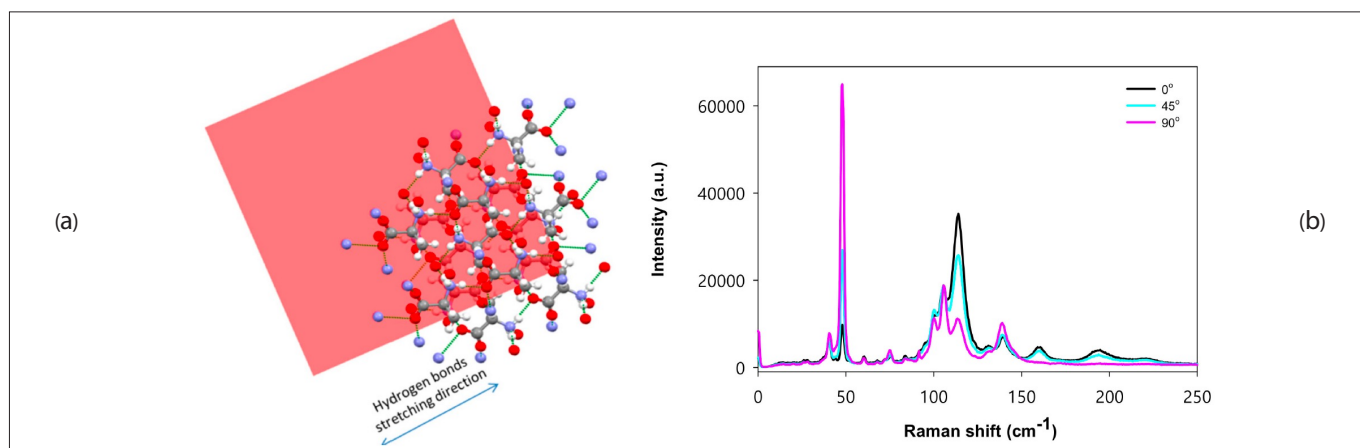


Figure 7. (a) Hydrogen bonds' simulation (dotted lines) in the L-alanine single crystal relative to the (002) plane. (b) LFRS of crystals excited from (002) direction with three different polarization angles.

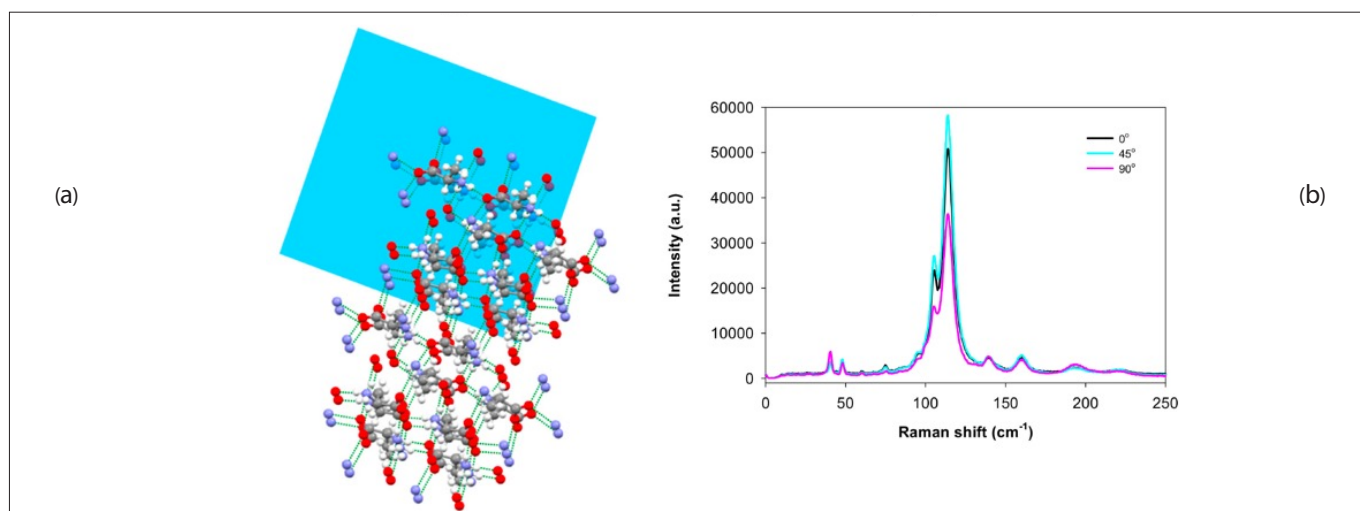


Figure 8. (a) Hydrogen bonds' simulation (dotted lines) in the L-alanine single crystal relative to the (011) plane. (b) LFRS of crystals excited from (011) direction with three different polarization angles.

due to the reflection geometry of the optical set-up, even lack of transparency does not affect the ability to characterize the structural properties of a crystalline material. The only known governing factors for successful characterisation is presence of hydrogen bonds in addition to other low energy modes. The contrast in polarizability of hydrogen bond in the crystal in different directions resulted in characterizability of the structure using LFRS. The variation of polarizability of the hydrogen bonds and resulting spectral contrast is presented in Figures 5–8. A detailed report of this can be found elsewhere [21].

Polarized LFRS for identification of enantiomers

An overview of enantiomers and chirality is presented in earlier sections. Enantiomers being molecules with mirror symmetries have right-handed or left-handed symmetry in their structure. This results in anti-parallel polarizabilities. In other words, when plane-polarized laser excitation along a particular polarization plane is incident on D- and L-enantiomers, the polarizabilities induced in the molecule are opposite to one another [22]. With LFR modes in general being orientation dependent, the LFR interaction cross-section is therefore dependent on the polarization angle of the excitation laser [23]. This counterintuitively results in different scattering cross sections along different polarization directions. Observation of this contrast is impossible in RS systems that have normal angle of incidence.

This work is the realization of a theoretical study of the polarization phenomena with respect to the laser and Raman signal propagation in optically active samples, which was proposed elsewhere [24]. In our work, we engineered an asymmetry into the optical set-up in both excitation and collection geometries and constructed an off-axis excitation collection set-up. In addition to the engineered asymmetry, the excitation and collection geometries were modified to accommodate polarizers to allow capture of orthogonally polarized signals. This resulted in enantio-contrasting interaction cross sections along excitation geometry and enantio-selective LFR spectrum in collection geometry. Figure 9 represents the

schematics of asymmetry induced into the optical system by virtue of modification and resulting asymmetrical interaction cross sections and induced contrast into the collection signal. Experimental details can be found elsewhere [25]. The study was the first of its kind for identification of enantiomers in their solid form using LFRS.

For representation purposes, we present the spectra showing enantioselective contrast between enantiomeric pairs in Figure 10. A detailed explanation of the experimental set-up can be found elsewhere.

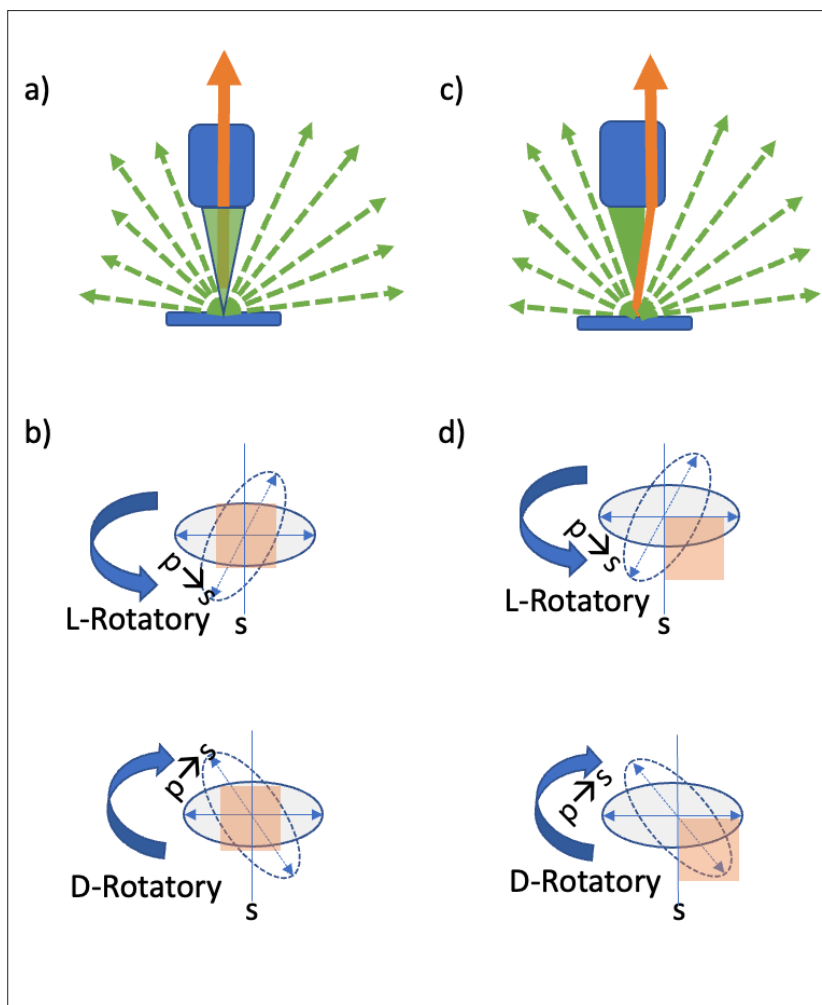


Figure 9. (a) Schematic representation of conventional Raman excitation and collection and (b) its collected focal area. (c) Schematic representation of the modified Raman setup and (d) its collected focal area. The modified Raman collects different intensities from the polarization planes after excitation of optically active materials. The schematics are approximate representations directed to understand the processes. The colored squares are a guide to the eye, representing (a) a symmetric interaction cross section for both D and L enantiomers and (b) relative asymmetric interaction cross section for D and L enantiomers*.

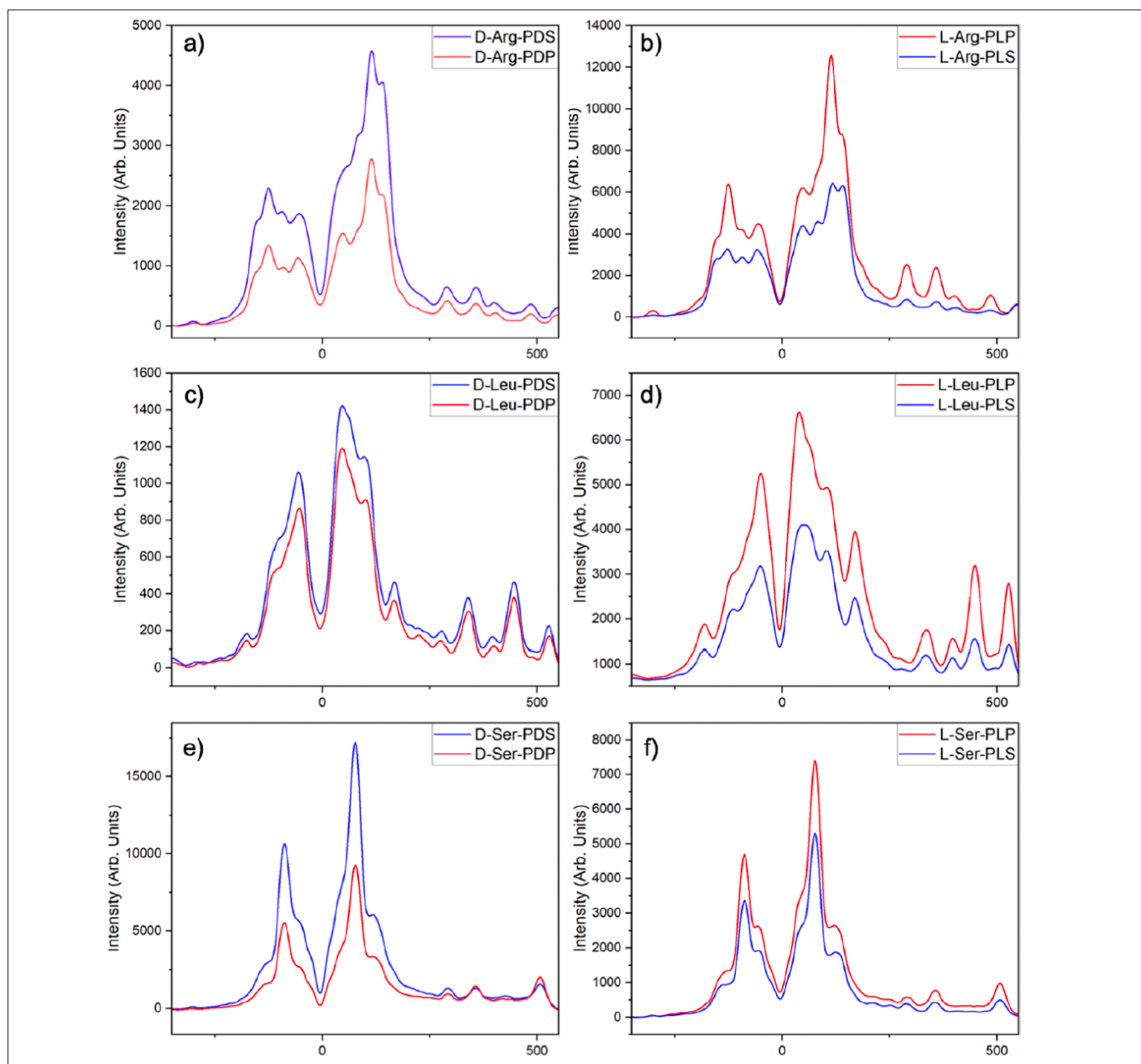


Figure 10. LFR spectra of (a) D-arginine, (b) L-arginine, (c) D-leucine, (d) L-leucine, (e) D-serine, and (f) L-serine. All powders were excited using P-Polarization. Red curves present the signal collected along P-Polarization, and blue curves present the signal collected along S-Polarization*.

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Conclusion

Raman spectroscopy is a well-known powerful analytical tool that has become increasingly important in recent years. More recently, the development of VHF has led to high impact research in LFRS. The main aim of this article is to summarize unique characterization efforts using LFRS and polarized

LFRS, leading to evolution of the technique into a versatile characterisation and material detection tool. In this article, we have summarised four of our distinct research efforts leading to the unique application of LFRS for enantiomeric identification in solid form.

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