



In-situ vibrational optical rotatory dispersion of molecular organic crystals at high pressures



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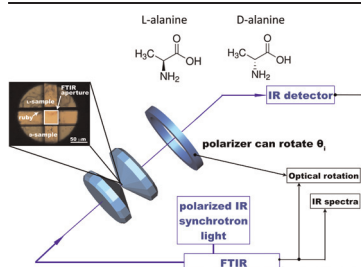
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HIGHLIGHTS

- High pressure synchrotron source vibrational optical rotary dispersion is possible.
- Our method simultaneously collects high-quality polarized FTIR spectra.
- The high resolution of the synchrotron is essential for confident measurements.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic structures respond to pressure with a variety of mechanisms including degradation, intramolecular transformation and intermolecular bonding. The effects of pressure on chiral organic structures are of particular interest because of the potential steric controls on the fate of pressurized molecules. Despite representing a range of opportunities, the simultaneous study of high pressures on different forms of chiral structures is poorly explored. We have combined synchrotron-source vibrational optical rotatory dispersion, micro-Fourier transform infrared spectroscopy and the use of a diamond anvil cell to simultaneously monitor the effects of pressure on the two enantiomers of the simple amino acid, alanine.

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1. Introduction

The responses of molecular organic crystals at high pressures are relevant to a number of scientific fields, ranging from astrophysics [1] to pharmaceuticals [2–5]. Intense effort has been expended to understand the effects of high pressure on organic crystals, using techniques such as X-ray diffraction, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) [6–8]. High pressure applied to organic crystals can result in

polymorphism, intermolecular motion of hydrogen bonds, breaking, distortion, symmetrization of hydrogen bonds and proton transfer [8–13]. The pressure-induced intermolecular bonding often involves hydrogen bonds enhanced by new geometric arrangements and increased intermolecular proximity. High pressure experiments offer a quantitative control over the proximity of atoms and the formation of intermolecular hydrogen bonds [9,13,14].

One aspect of high-pressure polymorphism of particular relevance to molecular organic crystals is absolute conformation, specifically referred to as chirality or handedness. Chirality results from the presence of asymmetric bonds arranged around carbon atoms. It plays a key role in biology, with practical effects in pharmacology, where one enantiomer may be beneficial while another is damaging [15].

Abbreviations: DAC, diamond anvil cell; GPa, gigapascal; ORD, optical rotatory dispersion; VORD, vibrational optical rotatory dispersion.

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In the absence of direct observation of atomic arrangements using X-ray or neutron diffraction, chirality can be measured indirectly via sample interaction with polarized light, either linear or circular, over a range of wavelengths. There are a variety of possible combinations for valid measurements: common techniques include vibrational circular birefringence (circularly polarized light), and Raman optical activity (linearly polarized light) but these have, to some extent, been superseded by chiral chromatographic and X-ray and neutron diffraction techniques [16].

The techniques presently available for the study of molecular organic crystals under high pressure all have individual weaknesses when employed for the determination of molecular conformation. Firstly, classical vibrational spectroscopy, which is routinely performed at high pressures, does not distinguish between enantiomers. Secondly, non-optical techniques currently used for conformational analysis are not easily applied to the small volumes of organic material produced at high pressures, and in any case would offer only static pre- and post-experiment data.

Recent improvements in instrumental capability have led to renewed interest in chiroptical techniques such as optical rotatory dispersion (ORD), which measures the response of a sample to linearly polarized light rotated through a known series of angles. The first comprehensive modern measurements of vibrational ORD (VORD) used infrared active vibrations in place of visible or Raman alternatives, although the effect was first observed in 1836 [17,18].

The immediate advantage of VORD is that one measurement can probe the vibrational structure (e.g., chemical bonds) and the conformation (chirality) simultaneously. The benefits of using a diamond anvil cell (DAC) when seeking to monitor any changes in chirality at high pressure include the possibility of continuous real-time monitoring, the wide window of infrared transparency of Type II diamonds, and the simultaneous visual observation of the sample.

In order to directly observe the effect of pressure on chiral molecules, we have combined the high-pressure capability of the diamond anvil cell with the benefits provided by a synchrotron-source FTIR spectroscopy beamline [19] to measure high-pressure vibrational optical rotatory dispersion for the first time. For these unprecedented chiral experiments we chose to avoid complications involving multiple stereocenters (i.e., chiral carbons) and performed our measurements with L- and D-alanine. We chose alanine because it is the simplest chiral amino acid, containing only

one chiral carbon center, thereby providing interpretative simplicity. Crystalline L-alanine has been studied isothermally at pressures up to 15 GPa using X-ray diffraction (powder and single-crystal), neutron diffraction, Raman and optical microscopy [20–24]. Prior to our work, crystalline D-alanine had not been studied under static high pressures. Indeed, only two studies of D-isomers of amino acids (methionine and threonine) appear in the literature, and investigation of two enantiomers of the same amino acid exists only in the case of methionine albeit in two separate studies [25–27]. Our approach of simultaneously examining the effects of high pressure in-situ on two optical isomers of the same organic molecule in solid state is therefore unprecedented.

2. Materials and methods

2.1. Materials

Single crystals as tabular cleavage fragments of L-alanine and D-alanine (typically $\sim 0.1 \text{ mm} \times 0.05 \text{ mm} \times 0.01 \text{ mm}$) were taken from large grains (Fluka 5130 and 5140) and used in this study.

2.2. Instruments

2.2.1. Diamond anvil cell

To reach high pressures we used a membrane-type diamond anvil cell containing Type II diamonds with 0.5 mm culets (Fig. 1). A stainless steel gasket with a 0.25 mm diameter sample chamber and a pre-indented thickness of 0.1 mm depth was placed between the diamonds. Samples of the two enantiomers measuring approximately $0.1 \text{ mm} \times 0.05 \text{ mm} \times 0.01 \text{ mm}$ were loaded on to a precompressed cesium iodide (CsI) window with good spatial separation. A small (0.020 mm) piece of ruby was also placed on the window before the diamond anvil cell was closed. Pressure was monitored throughout the experiments using the ruby fluorescence technique [28].

Since CsI and diamond are stable and optically isotropic up to far higher pressures than those encountered in this study, they have no effect on the measurement of the VORD. CsI is IR-transparent over the range of wavelengths used, so it will not add noise to the collected spectra. CsI acts as a pressure transmitting medium and fills the sample chamber, allowing a thinner sample to be used thereby guaranteeing sufficient light transmission.

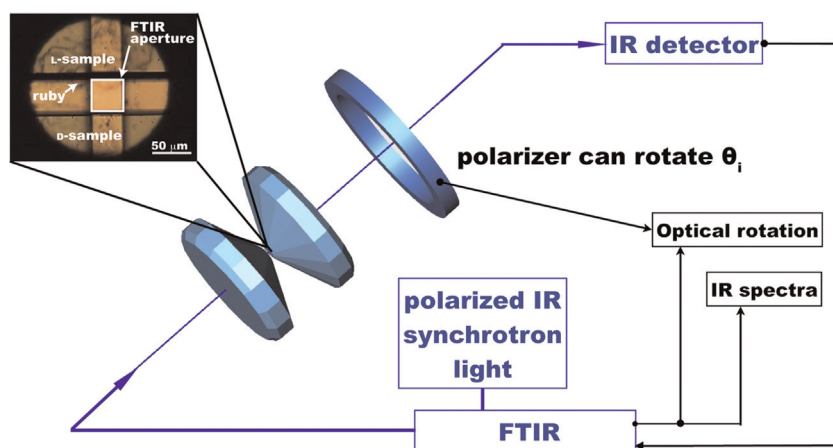


Fig. 1. Experimental setup: schematic of the infrared optical rotatory dispersion high pressure experimental setup using synchrotron light. The inset (upper left) micrograph shows two samples loaded into the gasket hole of the diamond anvil cell, along with the ruby and CsI window. The main panel illustrates the optical path: polarized synchrotron light is modulated by the FTIR spectrometer, steered and focused by Cassegrain optics (optical elements not shown for clarity) into the sample chamber of the DAC, collected by further Cassegrain optics (not shown), steered to the motorized polarizer and focused (not shown) to the IR detector. The FTIR bench spectrometer delivers IR spectra. By combining the angular information, as described in the text, vibrational optical rotatory dispersion spectra are obtained.

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