

The Raman Effect

Light from a laser source is used to excite the vibrational, rotational, and electronic states of a sample. Light emitted from the sample having same energy as the incident light is said to be elastically scattered. Inelastic scattering occurs when the sample scatters the light in such a way that the difference in energy between the incident and emitted light is not zero. This is termed the Raman Effect, whereas the elastic process is called Rayleigh scattering.

Raman Shift

The interaction of the incoming light with the molecule increases the energy of the vibration to a certain virtual energy state. When the energy of the vibration falls back down, it can either reach an energy state that was lower or higher than the initial state. The difference in energy between the initial and final states defines the Raman shift, and is expressed in units of wavenumber (cm^{-1}).

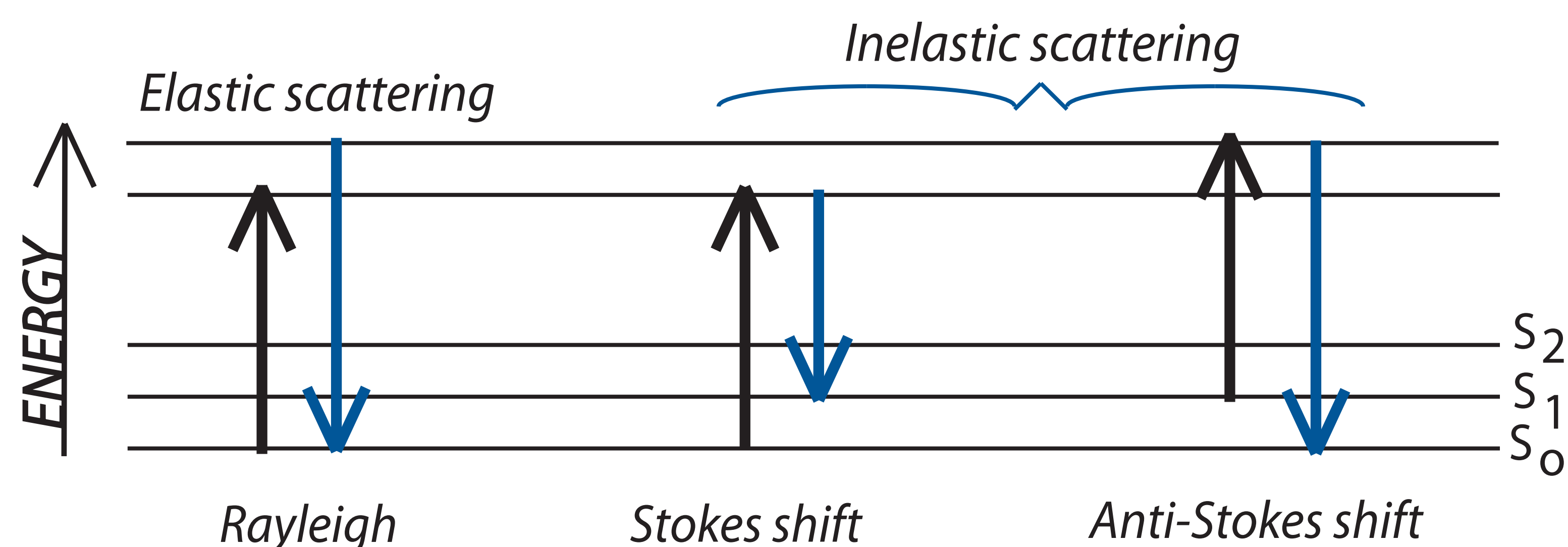


Figure 1. Corresponding energetic transitions of Rayleigh, Stokes, anti-Stokes scattering.

Raman shift is defined as:

$$\bar{\nu} = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}}$$

Vibrational Modes

Linear molecules have $3N-5$ normal modes ($N = \#$ of atoms); non-linear molecules have $3N-6$. These modes include stretching and bending between atoms as well as out-of-plane vibration. The following figure shows some of the Raman active modes of $(\text{Mg,Fe})\text{CO}_3$.

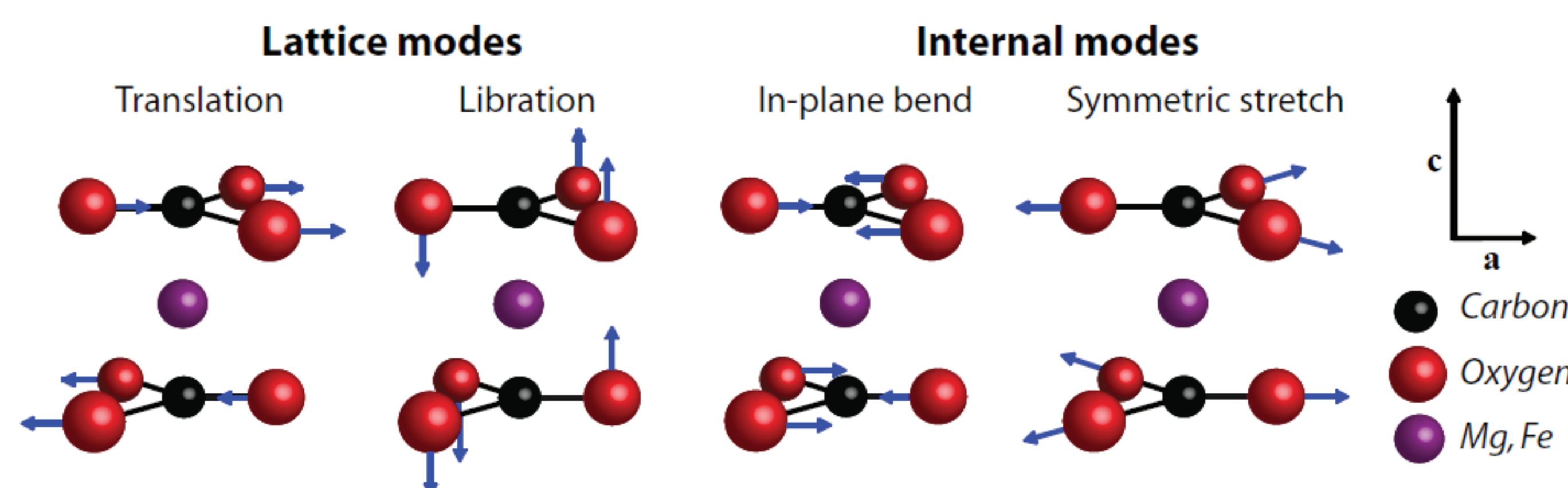
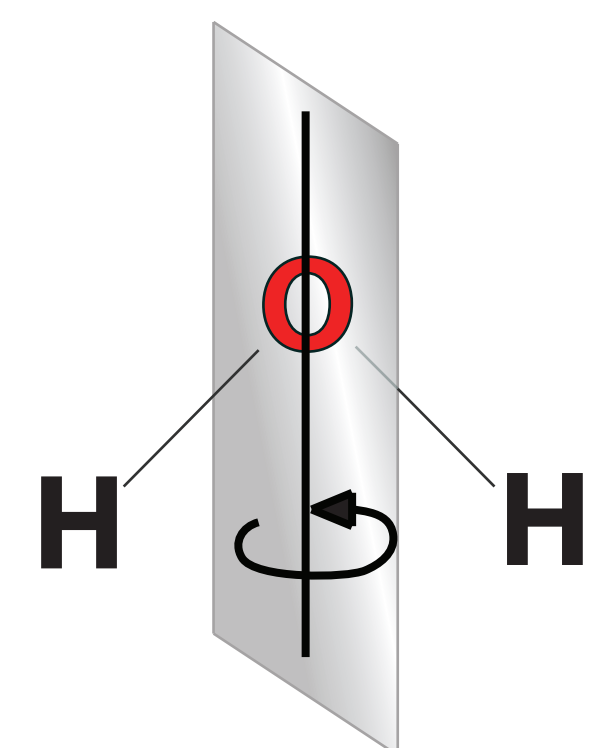


Figure 2. Lattice and internal modes of ferromagnesite, as described in Lin *et al.* (2012).

Lattice vibrational modes involve molecular vibration relative to other molecules. Internal vibrational modes refer to atomic movement relative to other atoms.

Group Theory

Group theory is based on mathematical reduction, which assigns a point group to molecules of the same fundamental symmetry. Point groups hold important implications for many of the properties, including spectral, of molecules. Take for example water:



Geometry: Bent
Point group: C_{2v}
of normal modes: $3(3)-6=3$
3 peaks in Raman spectrum

Figure 3. Symmetry operations of water, showing vertical mirror plane and rotation axis.

The point group of water is derived from its symmetry: one cyclic (C) 2-fold rotation, and one vertical mirror plane. Water has two symmetric stretching modes and one asymmetric mode. Group theory is used to predict the number of observed spectral bands.

Instrumentation

Raman spectroscopy uses a monochromatic laser source in the near-UV to near-IR range (200-2500 nm) of the electromagnetic spectrum. The set-up in the Mineral Physics lab at UT-Austin uses a Verdi V2 532 nm laser and an Andor iCCD detector.

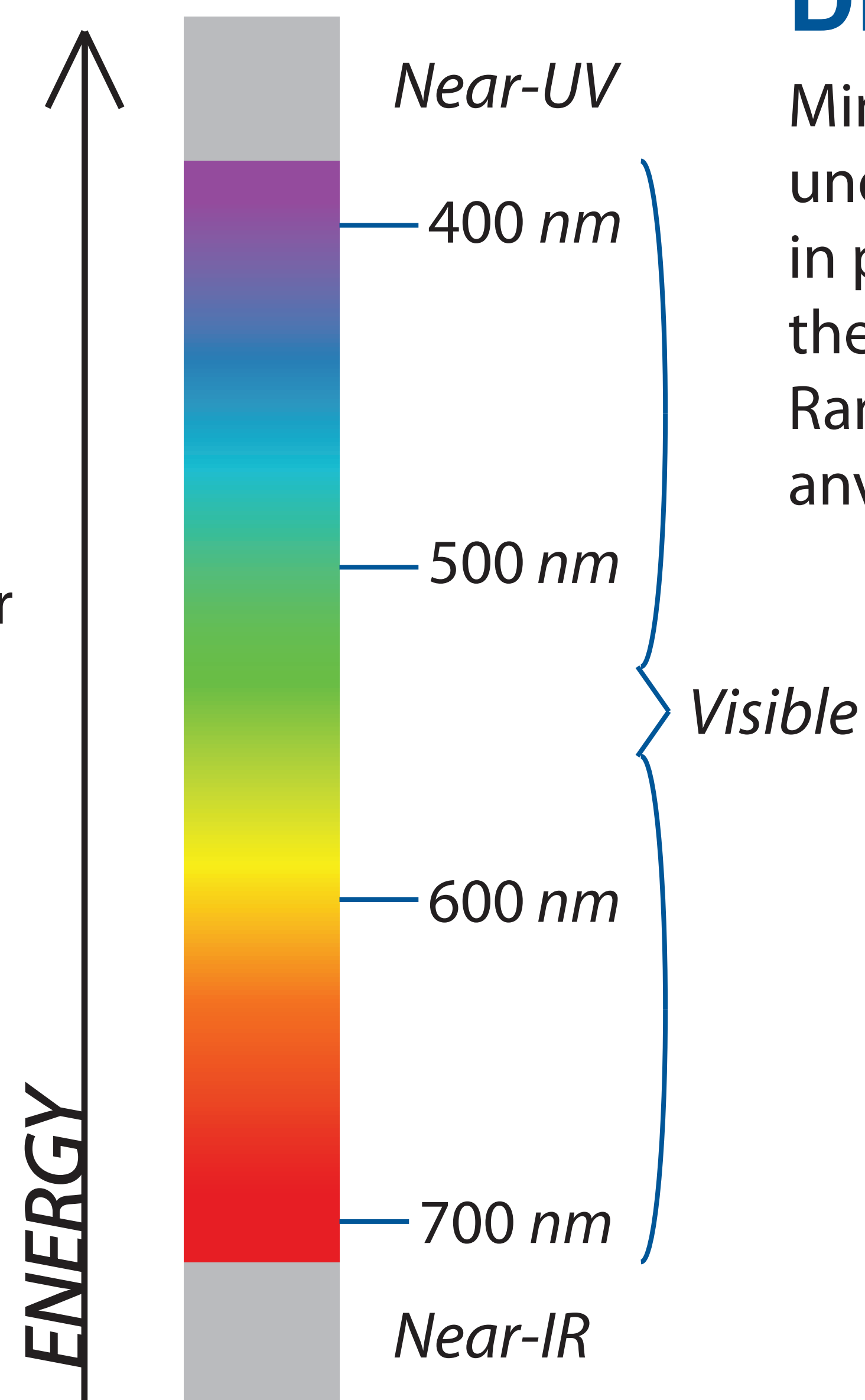


Figure 4. Near-UV to near-IR portion (200-2500 nm) of the electromagnetic spectrum.

Diamond Anvil Cell

Minerals found in the deep Earth can undergo changes under an increase in pressure and temperature. Some of these changes can be observed using Raman spectroscopy in a diamond anvil cell (DAC).

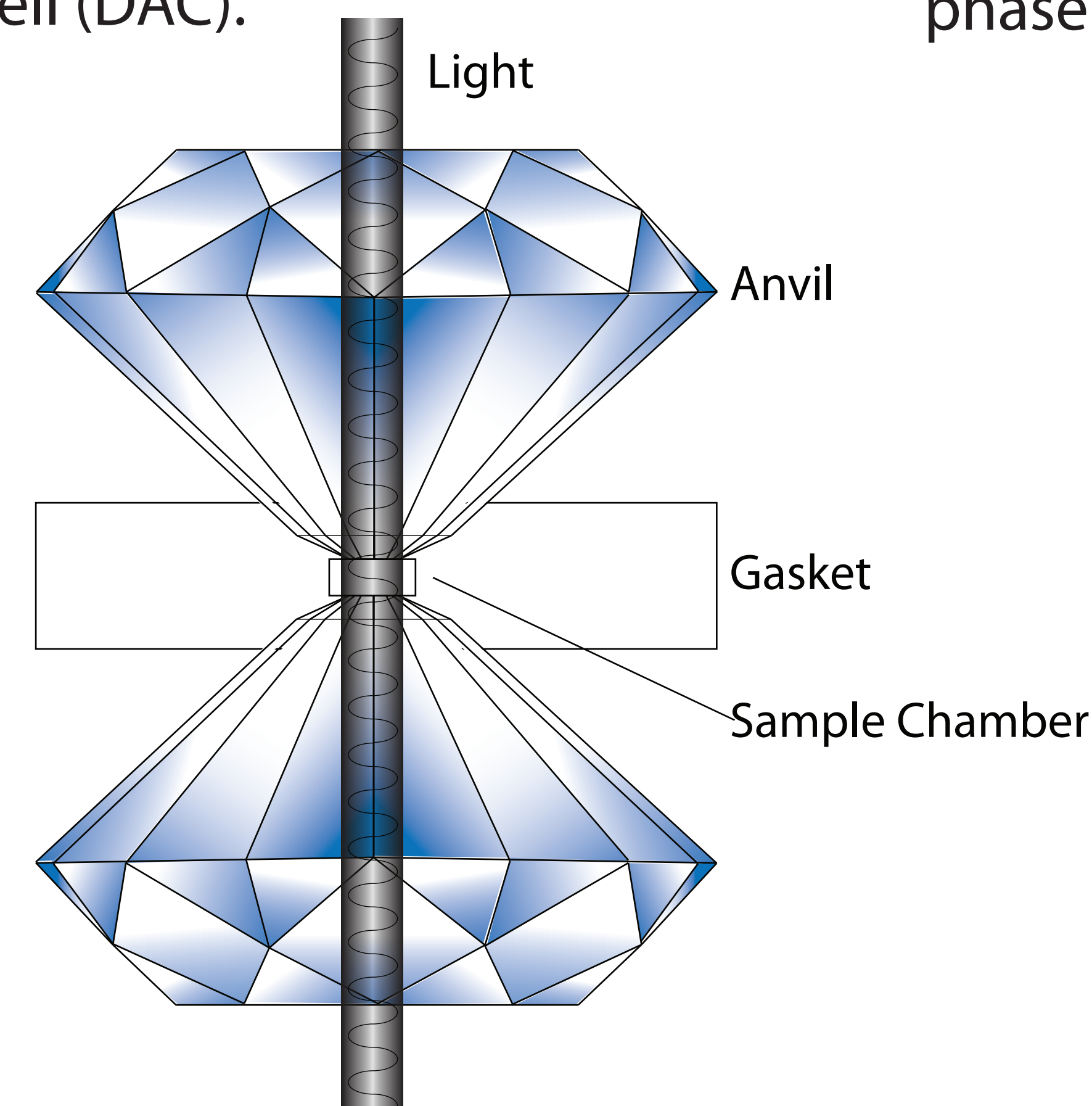


Figure 5. Diamond anvil cell schematic.

Lin *et al.* (2012), *Am. Mineral.*

Vibrational and elastic properties of magnesian siderite across the electronic spin-pairing transition of iron

A Raman and X-ray diffraction study of the electronic and vibrational properties of magnesian siderite ($\text{Mg}_{0.35}\text{Fe}_{0.65}\text{CO}_3$) shows a spin-pairing transition at around 45 GPa in a DAC. The observed Raman shifts result from an $\sim 8\%$ decrease in unit cell volume and a 10% increase in bulk modulus.

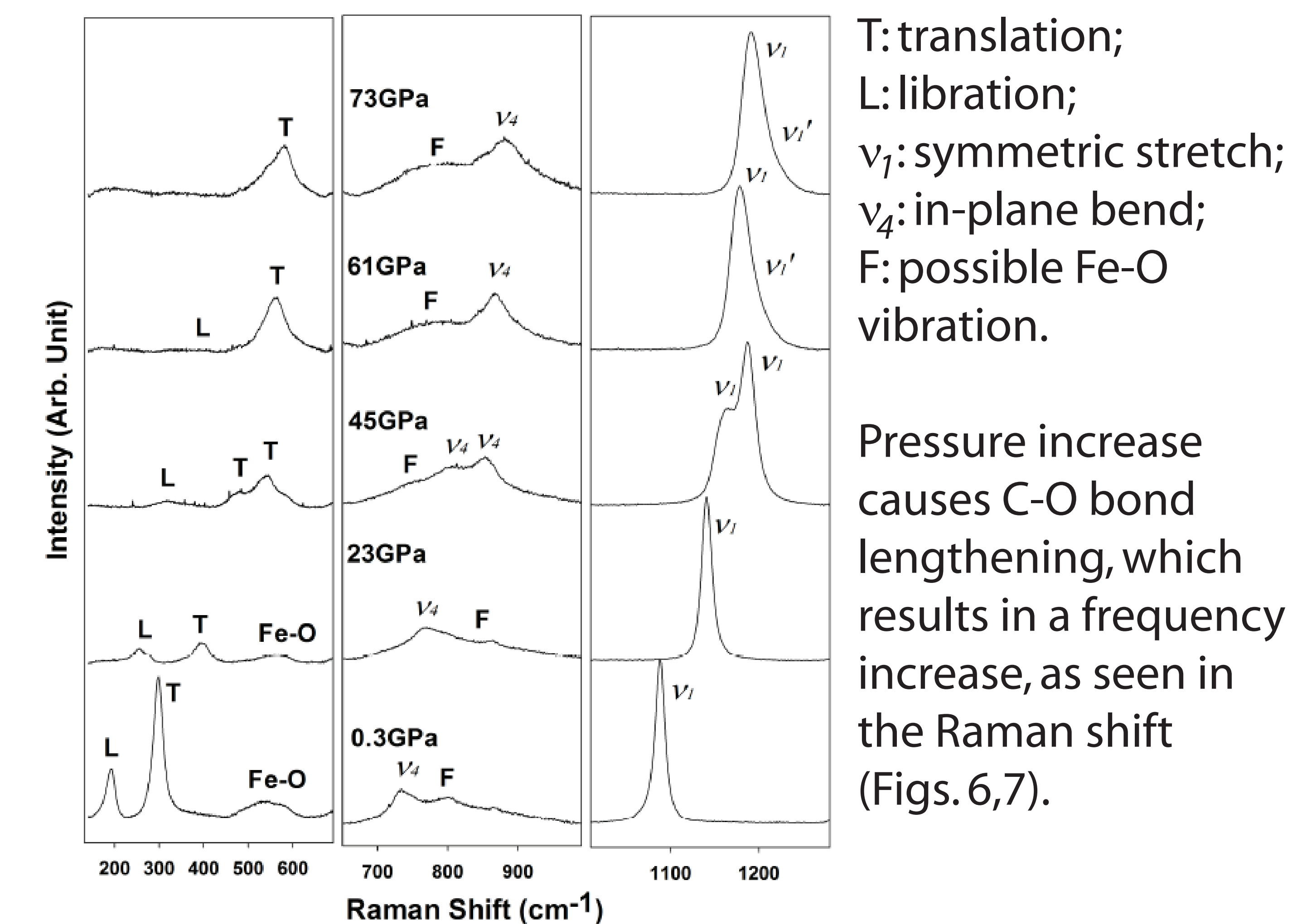


Figure 6. Raman spectra of magnesian siderite over pressure increase.

Increases in unit cell stiffness and bulk modulus, and decrease in unit cell volume contribute to frequency increase in all modes except for the symmetric stretch. The symmetric stretch shows splitting presumably due to the in-phase and out-of-phase vibration of adjacent CO_3^{2-} units.

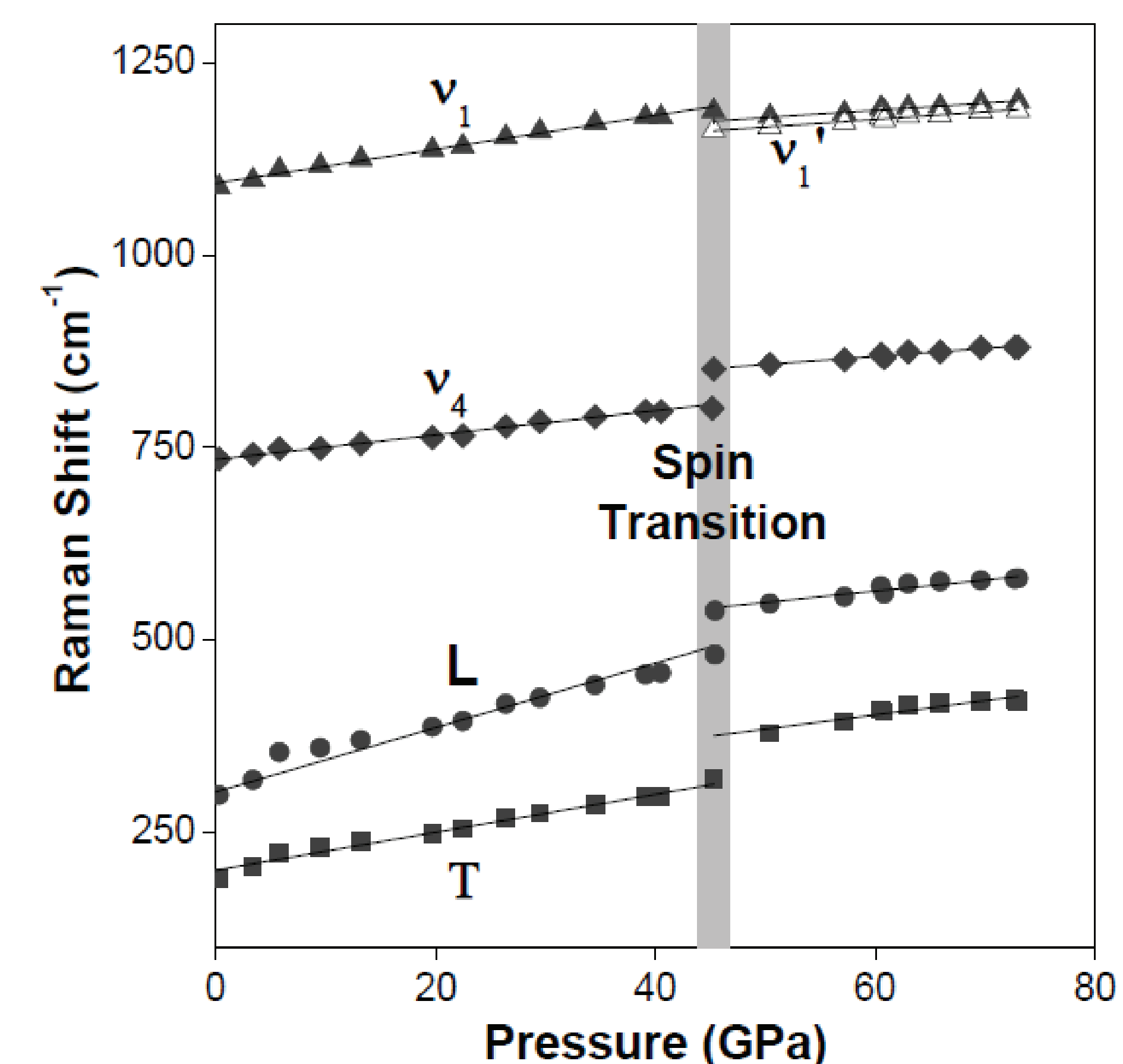


Figure 7. Increase in Raman shift at the spin transition, except in symmetric stretch.