Invited keynote lecture:

High-pressure Raman spectroscopy: Vibrational constraints on polymorphism, structural distortions and thermodynamic properties at extreme conditions

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Since the first Raman spectra were collected in high-pressure anvil devices in the late 1960's, Raman spectroscopy has been a primary mechanism for constraining bonding changes associated with pressure-induced polymorphism, progressive distortions and shifts in bonding environments with compression and, through pressure-induced mode shifts, the pressure dependence of anharmonicity (and hence of thermodynamic properties). Because of both the tranparency of anvils, and the broad pressure range that can be accessed, the general tool of choice for such experiments has been the diamond (or, less commonly, sapphire) anvil cell.

In terms of pressure-induced mineral polymorphism, examples illuminated by Raman spectral measurements within the diamond anvil cell include comparatively subtle changes in mineral symmetry induced by pressure, such as a transition that we have characterized in $MgSO_4$ near 15 GPa. This transition is manifested by the coalescence of sulphate symmetric stretching and bending bands. In this instance, a second-order shift to higher symmetry is induced by compaction within this material, and its polymorphism is in general accord with the systematics of ABO_4 compounds under compression. Similarly, moderate changes in the orientation of the water molecules in $CaSO_4 \cdot 2H_2O$ gypsum coupled with minor distortions in the sulphate ions have been observed at ~5 GPa utilizing Raman spectroscopy (Knittle et al. 2001). In each of these sulphates, the nearest-neighbor bonding environments within the crystals are only subtly altered by pressure, but the manifestations of these changes are readily apparent in the Raman spectra. At the other extreme, first-order, kinetically-impeded transitions have been characterized in aragonite-structured carbonates such as $BaCO_3$-witherite near 10 GPa: transitions which require laser-heating to activate (e.g., Townsend et al. 2013), and are associated with marked shifts in the splittings and frequencies of Raman-active bands. Indeed, Raman spectroscopy has been pivotal in the characterization of the complex (and geologically important) high-pressure phase diagrams of the carbonates.

A more extreme molecular solid, the polycyclic aromatic hydrocarbon naphthalene, has been identified as converting to a dense, carbon-hydrogen amorphous material when pressurized above about 45 GPa; in this instance, the Raman spectrum weakens considerably above about 20 GPa, while characteristic infrared bands of naphthalene persist (albeit broadened and weakened) until the amorphization pressure. Particular challenges associated with such high-pressure Raman spectroscopic studies include the sensitivity of Raman spectroscopy to comparatively symmetric vibrations (relative to infrared spectroscopy). Hence, pressure-induced losses of local symmetry, such as those associated with amorphization (whether of oxide-based minerals or hydrocarbons), are characterized by dramatic decreases in Raman scattering intensity. Moreover, the magnitude of pressures that can be accessed within the diamond anvil cell can cause electronic transitions to shift such that they overlap with the excitation laser at high pressures: this phenomenon is frequently observed in very high pressure studies of hydrocarbons.

Despite the relative Raman scattering weakness of amorphous materials relative to their crystalline equivalents, there is considerable motivation for utilizing Raman spectroscopy to probe the structure of liquids at simultaneous high pressures and temperatures. In particular, the coordination number of silicon has long been inferred to increase at high pressures from four-fold to six-fold (or perhaps higher) with respect to oxygen, with implications for the buoyancy forces on melts within the deep planet. Indeed, such structural changes are, for the most part, unquenchable on decompression from high pressures (e.g., Manghnani et al. 2011). Raman spectral results on amorphous sodium silicate and germanate (with varying degrees of hydration) heated above their glass transition (~500 °C) while held at high pressure clearly illustrate a shift in coordination of the tetrahedral cations, as manifested by the pressure-induced increase in amplitude of a band that can be associated with octahedrally coordinated silicon or germanium. Complementary Brillouin measurements (measuring acoustic waves via laser-mediated optical spectroscopy) at simultaneous high pressures and temperatures illustrate the magnitude of compression associated with these structural changes (~25% volume compaction over 5 GPa: Tkachev et al., 2005). Such measurements of Raman spectra of liquids at simultaneous high-pressures and high-temperatures pose challenges that are primarily associated with both the chemical reactivity of liquids and the low signal-to-noise associated with Raman spectra at these conditions.

Raman spectroscopy under pressure also provides critical insights into the thermochemical properties of materials under extreme pressures. The pressure-induced mode shifts observed using Raman spectroscopy at high pressures (which, for hard modes, have typical magnitudes of 0.1–10 cm^{-1}/GPa for most geologic materials) can, when coupled with the corresponding infrared pressure shifts, be utilized to constrain the Grüneisen parameter. This parameter is of key geophysical importance, as it dictates the adiabatic thermal gradient within Earth's convecting interior. The Grüneisen parameter can either be expressed thermodynamically as equal to $\alpha K/\rho C_p$, where α is the thermal expansion, K the bulk modulus, ρ the density, and C_p the heat capacity, or from a vibrational perspective as $\Sigma(d\omega_i/\omega_i)/(dV/V)$, where ω_i is the frequency of an individual vibrational mode, V is volume, and the sum is over the i vibrational modes of a crystal. Hence, the variation in mode frequencies with the shifting volumes of pressurized crystals provides insights into not only their bulk thermochemical properties. Compilations of pressure-induced mode shifts for the high-pressure phases present within Earth's mantle emphasize the key role of low-frequency lattice vibrations in contributing disproportionately, through their comparatively large mode shifts, to the sum that defines the vibrational Grüneisen parameter.

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