

Listening to metallic oxygen

How high-performance single-frequency lasers unlocked one of high-pressure spectroscopy's most challenging measurements.

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For more than three decades, the vibrational properties of metallic oxygen have remained inaccessible to Raman spectroscopy because of weak scattering, high reflectivity, and the challenges of high-pressure experiments. By combining diamond anvil cell techniques with highly stable single-frequency lasers, it was possible to obtain clear Raman spectra over a broad pressure range, opening new possibilities for studying matter under extreme conditions.

Pressure is a powerful thermodynamic parameter for probing and tuning interactions in condensed matter. In molecular systems, compression reduces intermolecular distances, driving profound electronic and structural transformations. Under extreme pressures, insulating molecular gases can become metallic and ultimately transform into close-packed atomic solids. Such conditions are routinely achieved using diamond anvil cells (DACs, **Fig. 1**), which generate pressures comparable to those at the Earth's center while providing optical access across a broad spectral range, from X-rays to the far infrared. This makes the DAC an ideal “window to extremes”, enabling the in situ investigation of materials using a wide variety of spectroscopic techniques.

One of the most celebrated goals of high-pressure physics is the creation of metallic hydrogen, predicted in 1935 and anticipated to exhibit remarkable properties including high-temperature superconductivity. While its synthesis re-



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mains elusive due to the vast pressures required, oxygen (a molecular analogue of hydrogen) metallizes at 96 GPa and has been reported to become superconducting below 0.6 K [1][5]. Despite its accessibility, the structure and vibrational properties of metallic oxygen (ζ -O₂) remain poorly understood [2].

Raman spectroscopy is uniquely suited to DAC experiments because

it can probe the minute sample volumes, typically only a few tens of cubic micrometers, at extreme pressures. It has played a central role in establishing phase diagrams and identifying crystal structures through their lattice vibrations, while also providing a direct means of testing computational models that predict energetically favorable molecular configurations.

However, high-pressure Raman measurements remain intrinsically challenging because of optical aberrations and reflections arising from the diamond anvils.

Metallic samples present an even greater challenge because strong electronic screening limits optical penetration depths and severely weakens the Raman response. Consequently, the vibrational spectrum of metallic oxygen has remained elusive for more than three decades, representing one of the most demanding outstanding problems in high-pressure spectroscopy.

Results and discussion

Oxygen was cryogenically loaded as a liquid into a diamond anvil cell (DAC) at 100 K and 10 bar and sealed within a laser-machined rhenium gasket (Fig. 1). High-purity type IIa diamonds were used to minimize fluorescence and maximize optical clarity. Using culets of approximately 100 μm and a sample chamber measuring about 30 μm in

diameter, pressures exceeding one million atmospheres were achieved, driving oxygen into its metallic phase. Raman measurements were performed in a confocal back-scattering geometry using 532 nm, 660 nm, and 785 nm excitation. The laser beam was focused to a spot size of approximately 2 μm with a high-numerical-aperture microscope objective. The scattered light was filtered using ultra-narrow notch gratings, dispersed by a spectrometer, and detected with a CCD camera.

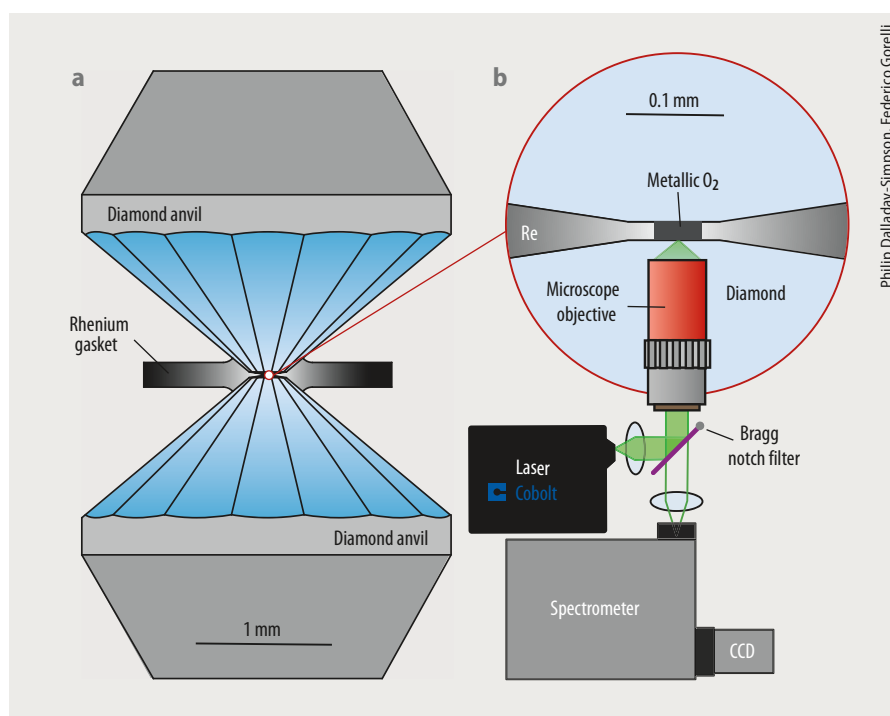
Under compression, oxygen undergoes a sequence of molecular phase transitions as increasing orbital overlap gradually closes the bandgap. A notable feature of this evolution is the formation of O_8 molecular units, consisting of four O_2 molecules arranged in a distinctive quartet-like structure (Fig. 2c) [3]. Above 96 GPa, oxygen develops a metallic luster and becomes visually indistinguishable from the surrounding rhenium gasket. Despite decades of study, however, the structure

and vibrational properties of this metallic phase have remained unresolved because of extremely weak Raman signals and phase coexistence.

Here, we report the first unambiguous vibrational signature of metallic oxygen obtained using multiple excitation wavelengths. The spectra reveal a rich phonon response spanning the range from 50 to 800 cm^{-1} (Fig. 2a). After correction for the Bose thermal population factor, which otherwise distorts spectral line shapes below approximately 200 cm^{-1} , all three excitation wavelengths yield consistent peak positions at 150 GPa. The Raman response is extraordinarily weak: the mode near 400 cm^{-1} is approximately 10^{12} times weaker than the excitation line (Fig. 2a), requiring exposure times of up to 10 minutes at laser powers approaching 30 mW.

The observation of anti-Stokes scattering (Fig. 2c) confirms the first-order Raman origin of the signal, while wavelength-dependent intensity variations point to reso-

Fig. 1 Experimental Setup for high-pressure Raman spectroscopy. Opposed diamond anvils are used to generate extreme pressures (a). Pressure amplification is achieved by the substantial reduction in surface area from the millimeter-sized anvil base to the micrometer-scale tip. The enlarged drawing (b) shows the anvil tip together with the optical layout of the Raman spectroscopy system. Single-frequency lasers provide the excitation light, which is focused onto the sample through a microscope objective. The back-scattered Raman signal is filtered by holographic Bragg notch filters and subsequently dispersed and detected using a spectrometer coupled to a CCD camera.



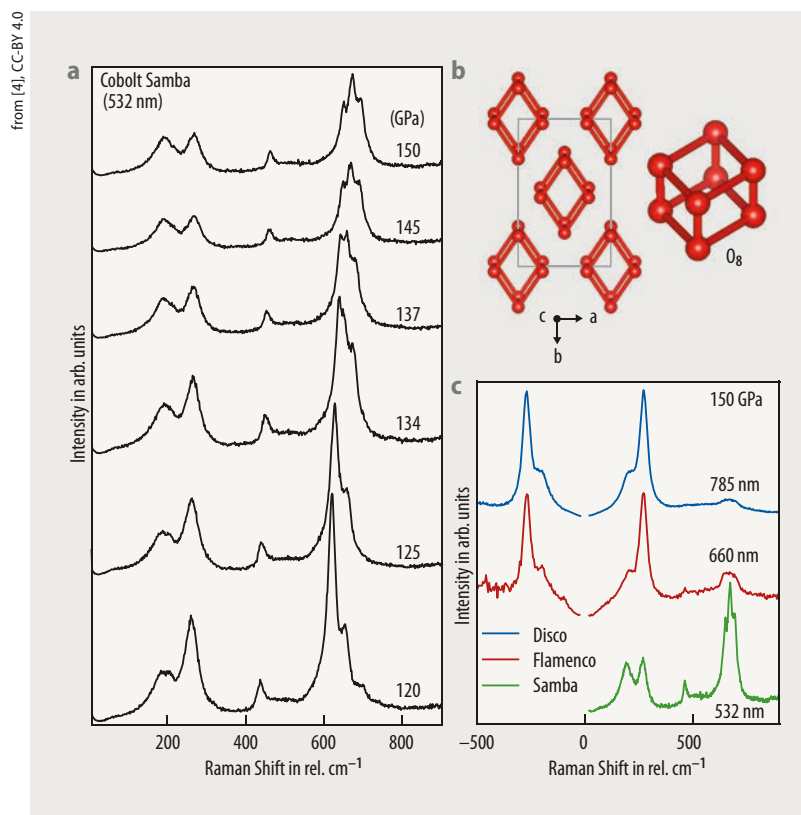


Fig. 2 Characterizing metallic ζ -oxygen with Raman spectroscopy: The low-frequency Raman modes (a) provide a fingerprint of the candidate crystal structure shown in panel (b). The proposed C2/m crystal structure (b) consists of layered O_8 molecular units. The Raman spectra of metallic oxygen (c) were recorded at 150 GPa using Cobolt Samba™ (532 nm), Cobolt Flamenco™ (660 nm), and Cobolt Disco™ (785 nm) lasers with between 5 – 30 mW output power.

nance effects associated with the electronic structure.

Comparison with theoretical predictions enables a definitive structural assignment of metallic oxygen. The results identify a crystal structure that retains the distinctive O_8 molecular units already present in the dense insulating precursor phase (Fig. 2b) [4].

Lasers for low frequency Raman

Obtaining observable Raman signals in the fingerprint region under high-pressure conditions places stringent demands on the excitation source. First, exceptional spectral purity is required to detect the low-frequency Raman features located close to the laser line. In addition, excellent beam-pointing

stability, output-power stability, and wavelength accuracy are essential, as the inherently weak Raman signal necessitates long acquisition times and a tightly focused beam within the diamond anvil cell, increasing the risk of misalignment.

The compact single-frequency Cobolt Samba™ 532 nm, Cobolt Flamenco™ 660 nm, and Cobolt Disco™ 785 nm lasers are ideally suited to meet these demanding requirements. They combine excellent spectral purity (> 80 dB suppression close to the main peak) with ultra low wavelength drift (<1 pm) and a TEM₀₀ beam ($M^2 < 1.1$), enabling detection of Raman shifts as low as a few 10's cm⁻¹ even with several minutes of acquisition time. Furthermore, these diode-pumped solid-state lasers deliver outstanding beam-pointing stability (5 μ rad/°C) with power stability better than 2 per-

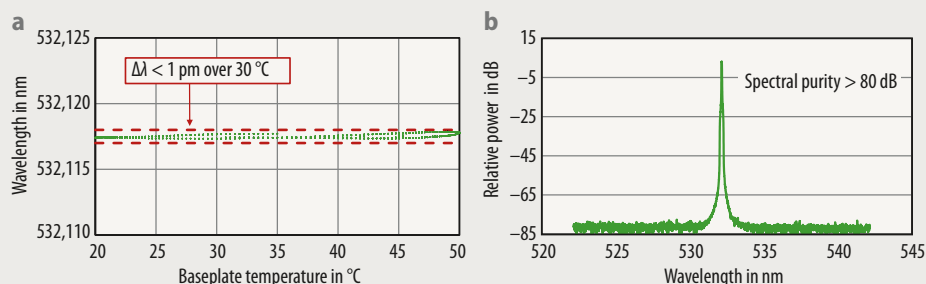


Fig. 3 The wavelength stability (a) remains better than 1 pm over a temperature range of 30 °C. The spectral purity (b) exceeds 80 dB. The Cobolt Samba™ 532 nm laser (c) used in this study is shown.

cent. Together, these characteristics make Cobolt lasers well suited for high-pressure Raman spectroscopy applications.

Outlook

While the vibrational Raman signature of metallic oxygen is of fundamental scientific interest, the broader significance of this work lies in overcoming a challenge that had long been considered beyond the practical reach of Raman spectroscopy. Measurements once thought impossible have now become achievable through advances in high-performance single-frequency laser technology with excellent spectral purity and exceptionally low wavelength drift. This breakthrough opens the door to the investigation of a wide range of systems with intrinsically weak Raman responses, including electronic

Raman scattering, superconducting excitations, and amorphous materials. By pushing beyond this long-standing technical barrier, researchers can now access previously hidden information about matter under extreme conditions. The present work highlights how modern single-frequency lasers are enabling new frontiers in spectroscopy, demonstrating that even the faintest material responses can now be detected with confidence.

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