

## Anomalous optical emission in hot dense oxygen

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### Abstract

We report the observation of unusually strong, broad-band optical emission peaked between 590 and 650 nm when solid and fluid oxygen are heated by a near infrared laser at pressures from 3 to 46 GPa. *In situ* Raman spectra of oxygen were collected and corresponding temperatures were measured from the Stokes/anti-Stokes intensity ratios of vibrational transitions. The intense optical emission overwhelmed the Raman spectrum at temperatures exceeding 750 K. The spectrum was found to be much narrower than Planck-type thermal emission, and the intensity increase with input power was much steeper than expected for the thermal emission. The result places an important general caveat on calculating temperatures based on optical emission spectra in high-pressure laser-heating experiments. The intense emission in oxygen is photo-induced rather than being purely thermal, through multiphoton or multi-step single photon absorption processes related to the interaction with infrared radiation. The results suggest that short lived ionic species are induced by this laser–matter interaction.

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Among simple molecular systems, whose high-pressure induced transformations are of paramount importance, oxygen has unique features by virtue of its spin ( $S = 1$ ). Spin–spin Heisenberg-type interactions assist the formation of dimers in the fluid phases [1]. Shock wave studies on the hot dense fluid have found evidence for metallization [2], and it is predicted that spin fluctuations play a key role, and molecules dissociate [3]. Spin–spin interactions stabilize anti-ferromagnetically ordered solid phases such as  $\alpha$ -O<sub>2</sub> ( $C2/m$ ), to 6 GPa and in the range 23–190 K, and  $\delta$ -O<sub>2</sub> ( $Fmmm$ ), in the range 6–11.5 GPa and 0–365 K [1,4–8]. At pressures up to 16 GPa, and in the range 23–650 K, a frustrated anti-ferromagnetic solid phase,  $\beta$ -O<sub>2</sub> ( $R\bar{3}m$ ), is also encountered [1,5].

Above 10 GPa, at room temperatures, oxygen transforms to the  $\epsilon$  phase [9] ( $A2/m$  [10–12]), that is stable up to the point of metallization in the solid (96 GPa). Since its discovery, this phase was thought to be characterized by relevant changes in the electronic structure due to dramatic colour changes from deep red to brown [9]. Recently, structural studies have demonstrated that the  $\epsilon$  phase is made of O<sub>8</sub> units that are held together by weak chemical bonds [13,14]. A magnetic collapse was also suggested in a recent neutron diffraction study [8]. The origin of stability of the (O<sub>2</sub>)<sub>4</sub> clusters is still unclear, though new insight has been obtained from X-ray Raman spectroscopy [15].

Profound modifications of the electronic structure in solid oxygen are encountered above 96 GPa, where metallization and superconductivity were observed [16,17]. It also appears that the molecular units survive in the metallic phase [18]. Therefore, remarkable changes in the electronic structure of oxygen are evident under different values of pressure. The extent to which there are intriguing changes in the excited electronic states of oxygen at high pressures is also of interest.

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Here we report a strong optical emission which is observed when oxygen was heated by an intense near infrared laser (NIR), starting from the fluid,  $\beta$  and  $\varepsilon$  phases. We suggest that this is a multiphoton or multi-step single photon excited luminescence, involving short lived ionic molecular species.

Oxygen samples (stated purity  $\geq 99.99\%$ ) were loaded cryogenically in symmetric diamond anvil cells (DAC) with type Ia diamonds having culet sizes ranging from 200 to 400  $\mu\text{m}$ . Rhenium gaskets with sample chambers ranging from 100 to 200  $\mu\text{m}$  in diameter, and of about 30  $\mu\text{m}$  in thickness were used. No signs of impurities (e.g.,  $\text{N}_2$  or  $\text{CO}_2$ ) were found by careful Raman measurements after loading. The pressure was determined by the ruby luminescence technique [19], before and after the heating and did not change appreciably during the heating cycle. In the first two experiments, a metallic coupler (Pt foil) was inserted in the sample chamber to improve the absorption of the NIR laser energy, as it was done for other molecular samples [20–24]. However, it was found that most of the IR radiation was absorbed by the sample directly and further experiments were conducted without using a metallic coupler. The intense absorption present in dense oxygen at lower pressures, in the fluid and in the  $\beta$  phase, is due to the tuning between the lowest electronic excitations [5] and the NIR laser radiation (1053 nm). This tuning is still present in the  $\varepsilon$  phase, due to the low-frequency wing of the broad optical absorption bands, which extend through the visible spectral region toward the UV [9,5].

A Nd:YLF laser operating in a continuous donut mode ( $\text{TEM}_{01}^*$ ) at 1053 nm with a maximum power of 80 W was used to heat the sample from one side by focusing the beam through a Mitutoyo (10  $\times$ ) micro-objective to a 10  $\mu\text{m}$  spot at the sample surface. Raman spectra were measured *in situ* (e.g. simultaneously with the IR laser irradiation) from the same side of the DAC in a back-scattering geometry. An  $\text{Ar}^+$  laser with a maximum power of a few hundred mW (457, 488, or 514 nm lines) was used as the Raman excitation source, and Raman signals were dispersed by the high throughput-single grating Jobin-Yvon HR460 monochromator, using a 300 groves/mm grating, and collected by a Roper-Princeton CCD detector. The diameter of the focused laser beam was as small as a few microns; the small beam spot insured that the Raman signal was measured within the region that was irradiated by the IR laser. The temperature-dependent asymmetry of the Raman spectra (i.e. the intensity ratio between Stokes and anti-Stokes pairs of spectral lines) therefore was used to determine the average temperature of the heated samples. This method relies on the principle of detailed balance. Further details of the *in situ* high  $P$ – $T$  laser-heating Raman system are provided elsewhere [20–22].

Fig. 1 shows selected *in situ* Raman spectra measured along a typical, approximately isobaric heating run, at 23.7 GPa. When the IR laser power was gradually increased the sample temperature rose smoothly while the background exhibited a highly non-linear increase. At above 650–750 K the optical emission became exceptionally strong, with the sample emitting intense radiation in the visible range easy detectable by eye and, as a result, completely overwhelmed the Raman signal. This phenomenon appears not to have been reported

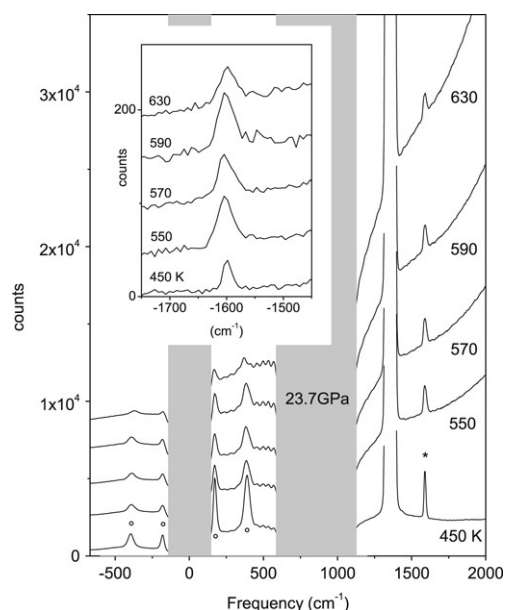


Fig. 1. Selected *in situ* Raman spectra measured using the green (514.5 nm) laser line in a typical laser-heating run, at 23.7 GPa. Suppression of the optical signals between  $-140$  and  $+145$   $\text{cm}^{-1}$  and between  $+590$  and  $+1130$   $\text{cm}^{-1}$  was produced by the super-notch laser filters used for filtering out the  $\text{Ar}^+$  and Nd:YLF laser beams, respectively. Dots and star identify oxygen peaks. The inset shows the anti-Stokes spectrum of the oxygen vibration at  $-1600$   $\text{cm}^{-1}$ , where the intensity scale was magnified by about two orders of magnitude.

in laser-heating experiments of oxygen or other materials at high pressure. When oxygen was investigated in the same range of pressures with high temperatures reached by the resistive heating, such a strong emission in the visible range was never observed [25]; on the other hand, during the Nd:YLF laser heating of other simple molecular systems such as  $\text{CO}_2$  or nonmolecular nitrogen, thermal radiation from the sample overwhelmed the Raman signal at much higher temperatures (e.g., above 1700 K) [22,24]. The observed emission in laser heated oxygen is quite different in nature than thermal radiation and is observed over a wide range of  $P$ – $T$  conditions.

The spectra reported in Fig. 1 are measured in the  $\varepsilon$  phase. All Stokes/anti-Stokes pairs of sharp peaks are assigned to internal modes of the molecular clusters [26]. Specifically, the two pairs of peaks lying in the spectral range between  $-550$  and  $+550$   $\text{cm}^{-1}$  are assigned to internal modes of the  $(\text{O}_2)_4$  units (i.e. to fluctuations of the intermolecular bonds among the constituent  $\text{O}_2$  molecules) while the pair at  $\pm 1600$   $\text{cm}^{-1}$  corresponds to the  $\text{O}_2$  stretching mode [13]. All of the pairs were taken into account for calculating the temperatures. The increase of the emission background with temperature is very similar at the other investigated pressures, between 3 and 46 GPa, both when the starting sample was in the solid and in the supercritical fluid states. Some corrosion of the diamond anvils was observed after several heating runs, specifically when the runs were performed in fluid oxygen.

To further explore the origin of the intense emission, we present the intensity of the background to the Raman spectra measured at a fixed wavelength of 573.5 nm (Raman shift of 2000  $\text{cm}^{-1}$ ) against temperatures, at three different pressures, and compare this behaviour to what is expected for thermal

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