

High-pressure Raman spectroscopy of solid oxygen

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High-pressure Raman spectroscopy of solid oxygen has been carried out at room temperature up to 110 GPa in order to study the recently observed structural transition at 96 GPa. The vibron and lattice phonons in the ε -O₂ phase corresponding to the transition became undetectable, although the vibron wave number in the ε -O₂ phase has shown a linear pressure dependence with a coefficient of 2.33 cm⁻¹/GPa and reached 1753 cm⁻¹ at 94 GPa. Several bands have been recently observed above 25 GPa, and three of them we assigned to higher-order bands. [S0163-1829(96)50946-X]

At present, pressure-induced insulator-metal transition and molecular dissociation of homo-nuclear molecular solids of light elements H₂, N₂, and O₂, have attracted special interest with a view to understanding the fundamental effect of chemical bonding.¹⁻⁷ Recently, our high-pressure x-ray diffraction study up to 116 GPa has revealed a structural phase transition of solid oxygen.¹ The transition, which was observed at 96 GPa at room temperature, was interpreted as an isostructural one between monoclinic phases. The volume reduction at the transition is too small to consider it to be molecular dissociation to the monatomic phase observed in I₂ (Ref. 8) and Br₂.⁹ Because the critical pressure corresponds to metallization reported by Desgreniers *et al.*,² the high-pressure phase has been considered to be a molecular metal. Although such a metallic state is widely accepted, there is still no clear picture of the exact mechanism of the metallization.

The aim of this study was to research the high-pressure behavior of the molecular bonds in solid O₂ around this structural transition. We have performed high-pressure Raman spectroscopy of solid oxygen in a range of pressure beyond the 72 GPa achieved in previous studies.¹⁰ This paper will discuss the pressure dependence of the Raman-active bands of solid oxygen to 110 GPa.

With increasing pressure at room temperature, three solid phases successively appear in O₂ on the order of 10 GPa,¹¹ β -O₂ ($R\bar{3}m$) (Refs. 12 and 13) at 5.4 GPa, δ -O₂ ($Fmmm$) (Ref. 13) at 9.3 GPa, and ε -O₂ ($A2/m$) (Refs. 14 and 15) at 9.9 GPa, and further, the ε -O₂ phase transforms to the ζ phase (monoclinic) at 96 GPa.¹ However, the structure refinement of the ε and ζ phases has been imperfect up to now. The vibrational feature of these phases has been studied by Raman scattering^{11,16} and infrared absorption¹⁷ experiments and the pressure dependence of the stretching mode (vibron) of O₂ has been reported up to 72 GPa previously.^{10,18} These studies have suggested the presence of a strong intermolecular interaction between O₂ molecules. Optical absorption spectra of ε -O₂ have confirmed band-gap narrowing with pressure.^{2,19} Recently, Drude-type metallic behavior has been observed in reflectivity spectra above 95 GPa.²

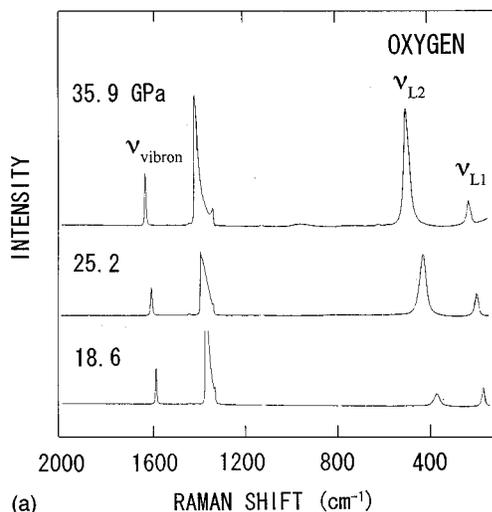
The high-pressure experiments were performed with the use of a diamond anvil cell (DAC). Liquid oxygen, which was prepared from high-purity oxygen gas (99.9999% up) passing through a liquid N₂ trap, was loaded in the high-

pressure cell inside a cryostat at 77 K by rotating the control shaft connected to the advancing screw of the DAC from the exterior.

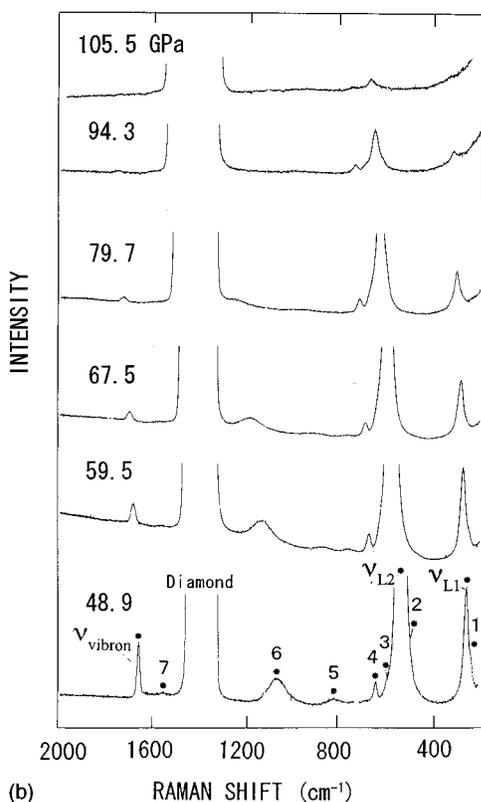
High-pressure Raman spectroscopy at room temperature was carried out using the micro-optical system of a JASCO Model NR-1800 spectrometer equipped with a triple monochromator and a liquid-nitrogen-cooled charge-coupled device (Princeton Instrum. Inc.) multichannel detector. The 514.5 nm line from an Ar ion laser with a maximum power of 2 W was used for excitation. The system, which was equipped with a periscope for viewing the sample image, enables us to position the laser spot (focused down to about 5 μ m in diameter) on a small area of the sample. We can measure the same spot in the sample. Low-fluorescence diamonds were specifically selected for Raman spectroscopy. In order to improve the spatial resolution, that is, to reduce the luminescence from the diamond, a pinhole aperture of 50 μ m diameter was placed in the scattering light pass. Pressure was increased at room temperature and measured by the ruby fluorescence method. Because both the R1 and R2 ruby lines were clearly resolved in all of our fluorescence spectra up to the maximum pressure of 110 GPa, the pressure was determined by the quasihydrostatic ruby scale.²⁰

Raman spectra of solid O₂ over a wave-number range between 100 and 2000 cm⁻¹ were measured near 298 K at pressures up to 110 GPa. Figures 1(a) and 1(b) represent the pressure change in the Raman spectra of solid O₂ in lower and higher pressure regions, respectively. A strong broad band around 1330–1550 cm⁻¹ comes from the diamond used for the anvil. The ε -O₂ at 18.6 GPa shows three Raman-active bands; an internal stretching model (vibron: ν_{vibron}) of O₂ molecules around 1600 cm⁻¹ and two librational bands (librons: ν_{L1} and ν_{L2}) at a lower wave number. These bands are already known from earlier low-temperature measurements.^{16,21} The ν_{L1} may be assigned to a doublet of two libron models, viz., librations around two crystallographic axes perpendicular to the molecular axis of O₂, as is analogized from the low-temperature phase of α -O₂.^{22,23} The much broader band, ν_{L2} , of which the character is not yet established, was observed at room temperature in the present study.

The scattering intensity of these bands increases with increasing pressure and exhibits a maximum around 35 GPa. After that, it undergoes abrupt dumping. The anomalous be-



(a)



(b)

FIG. 1. Raman spectra of solid O₂ at 298 K at pressure up to 105 GPa (a) in a lower-pressure region and (b) in a higher-pressure region.

havior of the intensity is illustrated in Fig. 2. The ν_{L2} band is more remarkable. At the same time, several Raman-active bands were newly observed at about 25 GPa and grew with pressure. The typical Raman spectra of ϵ -O₂ at higher pressure are shown in Fig. 1(b). The new bands are labeled by numbers. Three broad bands 5, 6, and 7, at 790, 1040, and 1530 cm⁻¹ are due to a higher-order process and assigned to a combination tone or overtones of $\nu_{L1} + \nu_{L2}$, $2\nu_{L2}$, and $3\nu_{L2}$, respectively. The pressure dependence of these bands also satisfies the relations well. Possible interpretation of bands 1–4 is as follows: bands 3 and 4 are due to two phonon combinations of the librions and low-frequency lattice modes, and bands 1 and 2 may be due to

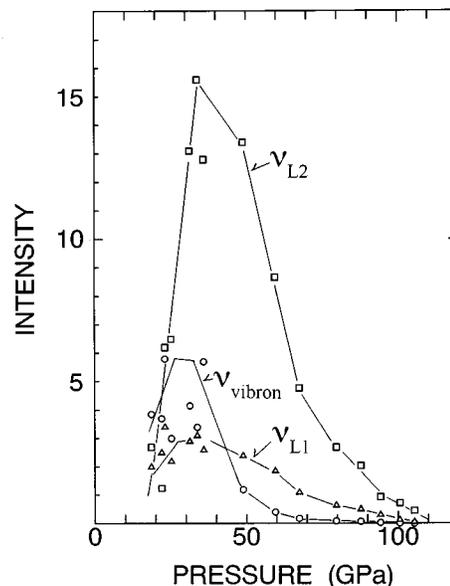


FIG. 2. The pressure dependence of the scattering intensity of original Raman bands ν_{vibron} , ν_{L1} , and ν_{L2} , in solid O₂. The curves serve as a guide for the eye.

splitting of librations ν_{L1} and ν_{L2} because the structure of ϵ -O₂ ($A2/m$, $Z=8$ molecules) allows four Raman-active librational modes. The observation of higher-order bands suggests resonance enhanced Raman scattering. The rapid decrease in the intensity of the original peaks above 50 GPa is due to the increase in the absorption coefficient of light by narrowing of the energy gap with pressure.

At pressures higher than 100.7 GPa, the vibron peak merged into the background and became undetectable. Other bands also became undetectable above 110 GPa. It should be noted that the disappearance of these Raman-active bands of ϵ -O₂ coincides with the structural transition from the ϵ to the metallic ζ phase.¹ The distinct Raman band of librions observed above 96 GPa might be due to the coexistence of low- and high-pressure phases, because a recent x-ray study has pointed out the coexistence between 88 and 106 GPa.¹ Also a thermal effect by laser heating near the phase boundary may lead the coexistence. However, the possibility that the spectra of the ζ phase are quasicontinuous to those of the ϵ -O₂ phase still remains, because the observed structural transition from the ϵ to ζ phase has been explained as an isostructural transition with a discontinuous change in lattice constants in a monoclinic cell with smaller volume reduction.

A possible interpretation of the result that the Raman bands became undetectable is derived from the fact that the transition corresponds to metallization. Because the overlapping of an energy gap results in an abrupt increase in the absorption coefficient of the light, this may make the vibron of the ζ phase undetectable. Actually, the previous study by Desgreniers *et al.*² has reported an increase in not only the near-infrared reflectivity but also in the baseline level of the reflectivity spectra at a higher pressure than around 96 GPa, though the estimated plasma energy $\hbar\omega_p$ from the reflectivity spectrum at 118 GPa was 0.89 eV and seems too low as compared with 2.4 eV of the excitation light. But their reflectivity spectra, which also showed an increase in reflectiv-

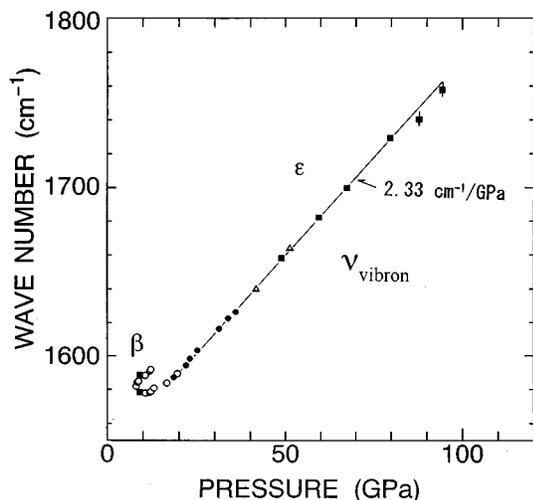


FIG. 3. The pressure dependence of the vibron wave number, ν_{vibron} , of solid O_2 .

ity in the near-UV range at very high pressure, have not yet been fully explained. Anyway, more detailed studies of near-infrared and visible optical properties are needed to clarify the reason for the disappearance.

Figure 3 shows the pressure dependence of the wave number of the vibron. Each set of symbols corresponds to a separate experimental run. Except between 10 and 15 GPa, the wave number of the vibron in the ϵ - O_2 phase increased linearly with increasing pressure with a coefficient of $2.33 \text{ cm}^{-1}/\text{GPa}$ and reached 1753 cm^{-1} at 94.3 GPa. The linear increase is significant for understanding the intramolecular bond of O_2 . The previous results^{10,18} were in good agreement with the present data, considering the difference of the pressure scale. The pressure dependence of ν_{vibron} between 15 and 94 GPa provided no evidence of another phase transition. This result is consistent with that from the recent x-ray study.¹

We know that other homonuclear diatomic molecular solids of light elements, H_2 ,³ D_2 ,³ and N_2 ,^{3,4} show a turnover of the vibron wave-number shift and have a maximum in the pressure dependence curve around 30, 40, and 80 GPa, respectively. Softening of the vibron occurs. The linear dependence of solid oxygen is different from those. The increase from 1556 cm^{-1} for an isolated molecule to 1753 cm^{-1} for ϵ - O_2 at 94 GPa is equivalent to 57% of the difference between the vibrations of the doubly bonded O_2 and the O_2^+ ion whose formal bond order is 2.5. The dependence of solid O_2 may come from the delocalization of π^* electrons discussed by Syassen and Nicol.¹⁸

The pressure dependence of the librions and the other bands is plotted in Fig. 4. A remarkably large shift in the wave number is observed in ν_{L1} and ν_{L2} at lower pressure. The result suggests a rapid increase in the intermolecular interaction. The increase tends to saturate at higher pressure. The dependence was different from that of the vibron. The splitting of the ν_{L1} band is clearly detected above 35 GPa. Each doublet was resolved using two Lorentzian curves. As a result, the ν_{L1} band gradually separated into two peaks above 25 GPa. The wave number of the peaks increased continuously with pressure. As mentioned earlier, the two

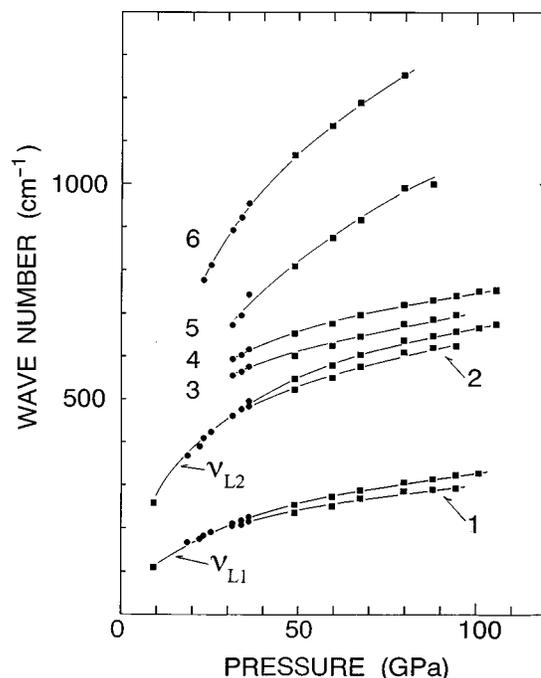


FIG. 4. The pressure dependence of the librions and the other bands. The curves serve as a guide for the eye.

peaks may be assigned to the former two librational modes. A similar splitting was also observed in the ν_{L2} band. The splitting has also been observed in the ϵ - O_2 phase at low temperature by Carter *et al.*²¹ The split observed by them occurred discontinuously at 25 GPa and 20 K by about 10 cm^{-1} . They have attributed the splitting to a phase transition. However, the splitting observed in the present study at room temperature is rather continuous with pressure and differed from the results reported by Carter *et al.*

The anomalous behavior of the intensity of the vibron and the librions and the appearance of the higher-order bands may suggest a certain resonant effect. Actually, previous optical-absorption spectroscopies^{2,13} have revealed that an allowed-type strong absorption band moves from the ultraviolet through the visible with increasing pressure. The band edge at 35 GPa coincides with the energy of the excitation light, 2.4 eV. Pressure-tuned resonant Raman scattering²⁴ seems to be a plausible interpretation for these results.

In conclusion, the present Raman study revealed the disappearance of Raman-active modes corresponding to the structural transition to the ζ phase. The result was significantly related to the metallization. The linear increase in the vibron wave number of the ϵ - O_2 phase observed between 15 and 94 GPa was peculiar and suggested strengthening of the intramolecular bonding of O_2 molecules by compression. Higher-order bands above 25 GPa indicated a certain resonant effect. Further research on the optical character of the metallic phase is needed to clarify the disappearance of the Raman-active modes in the ζ phase.

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