Raman and UV absorption studies on supercritical fluid of oxygen

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Summary

The intermolecular interaction in high-density fluid O$_2$ was investigated by high-pressure Raman scattering and UV absorption experiments. From the pressure evolutions of the Raman vibrational frequency and its linewidth, an appreciable contribution of the attractive interaction to the vibrational frequency was suggested for the fluid. From the UV absorption spectra of molecular oxygen at pressure up to 1.5 GPa and room temperature, an absorption band was observed in an UV region between 4.5 and 7 eV and showed an appreciable enhancement in the intensity with pressure. The observed UV absorption band of high-density oxygen was attributed to the two-molecule process by an antiferromagnetic O$_2$ pair.

I. Introduction

Molecular oxygen, O$_2$, with its characteristic magnetism, exhibits unique behavior under high-pressure. Many high-pressure phases with fascinating physical properties occur in its pressure-temperature phase diagram (Nicol, 1979 and Akahama, 1995&2001). One of its notable features is an abnormally high freezing pressure, 5.9 GPa, at room temperature (Nicol, 1979), which is 3.5 GPa higher than that of N$_2$. As a result, the supercritical state is stable in a wide range of pressure and temperature. Formation of O$_4$ or (O$_2$)$_2$ molecular units in this high-pressure fluid or liquid has been argued (Lewis, 1924, Dianov-Klokov, 1964, Shardamand, 1969 and Oda, 2002). Namely, intermolecular interactions are expected to play an important role in the properties of this high-pressure fluid as well as these high-pressure phenomena. Therefore, a detailed spectroscopic study for condensed oxygen is indispensable to understand these phenomena from the viewpoint of the electronic structure of molecules.

Raman spectroscopy is available to probe the intermolecular interaction in question, which depends on the local environment, and to investigate the dynamics of molecular fluids. High-pressure Raman scattering has been studied by Nicol et al. (1979) for the vibrational band of O$_2$. They discovered the phase relation among fluid and solid phases near room temperature from the pressure dependence of its frequency. However, there is no detailed report on the intermolecular interactions in the high-density fluid O$_2$ by vibrational Raman spectroscopy. On the other hand, there has been no report on the electronic spectra for high-density oxygen in the UV region above a few tens of MPa. High-pressure optical absorption experiments using a diamond anvil cell have also been limited to the photon energy of 3.5 eV (Nicol, 1983 and Desgreniers, 1990).

In this paper, the vibrational Raman spectra and UV absorption spectra of high-density fluid O$_2$ are investigated from the viewpoint of molecular interactions.
II. Experimental

High-pressure Raman scattering experiments of O\textsubscript{2} at 296 K were carried out at pressures up to 10 GPa. The measurements were made with the backscatter arrangement using a diamond anvil high-pressure cell (DAC) and a micro-optical system of the JASCO Model NR-1800 spectrometer. Liquid oxygen with 99.999 \% purity was loaded in the sample chamber of the DAC at 77 K and used as the sample. The sample pressure was regulated at 300 K with a ruby pressure scale (Mao, 1986) with an accuracy of ±0.05 GPa. The Raman spectra were collected by a triple polychromator using a liquid-nitrogen-cooled CCD detector (Princeton Instruments Inc.). The 514.54 nm line from an Ar ion laser was used for an excitation source. A typical beam power was 100 mW, but the spectra around the fluid-solid boundary were collected below 10 mW to prevent sample heating by the laser beam. The emission lines of Ne were used as an internal standard for determination of absolute Raman frequencies. The resolution of the system was estimated to be \( \approx 1.0 \text{ cm}^{-1} \). At each pressure, two Raman spectra were collected at different places of the sample chamber, and the frequency and linewidths (the full-widths at half-maximum) of the Raman band were averaged. The errors in the data were estimated from the difference between the two values measured at each pressure. The errors in the frequency in the fluids fell within 0.13 cm\textsuperscript{-1}. The spectra were fitted using the Voigt function for precise estimation of the peak positions. As a result, the frequency was determined with ±0.2 cm\textsuperscript{-1}.

For the UV absorption measurements, a Merrill-Bassett typed high-pressure cell with sapphire anvils was used. The Raman shift due to the intramolecular vibration (vibron) was also used to monitor the sample pressure. Typical thickness and diameter of the sample chamber were about 46 and 250 μm, respectively. The UV absorption measurements were carried out in the range from 0.02 - 1.5 GPa using an UV source on the BL-B1 beam line, at the UVSOR Facility in the Institute of Molecular Science (IMS). Since the critical temperature, \( T_c \), and pressure, \( P_c \), of molecular oxygen are 154.56 K and 5.05 MPa, respectively, the sample oxygen in this pressure range was the supercritical fluid at room temperature. Transmitted light through the oxygen sample was detected by a photomultiplier tube placed in a vacuum at 2x10\textsuperscript{3} Pa.

An X-ray diffraction experiment of the supercritical fluid of oxygen in a diamond anvil cell was carried out at 300 K by an angle-dispersive method using a monochromatic SR X-ray (\( \lambda = 0.4956 \text{ Å} \)) on a BL10XU beam-line at SPring-8. Diffraction X-rays were detected by an image plate.

III. Results and discussion

3.1. Raman spectra

Experimental runs were carried out twice for each sample to guarantee accurate determination of the pressure dependence of the Raman spectra for O\textsubscript{2}. Obtained data in both runs agreed satisfactorily. The pressure changes are shown in Fig. 1. With increasing pressure, the vibrational band for O\textsubscript{2} exhibited a high-frequency shift and a line broadening. An abrupt decrease in the linewidth, observed at 5.9 GPa, is ascribed to the phase transition from fluid to solid. This transition was confirmed independently by visual observation with a microscope. The transition pressure also agreed well with the previous report (Nicol, 1979). In the β-O\textsubscript{2} solid phase, the frequency increased with pressure.
Fig. 1. Pressure changes of vibrational Raman spectra of O\textsubscript{2} at 296 K.

Fig. 2. The frequency, \( \nu \), of the vibrational Raman band of O\textsubscript{2} as a function of pressure up to 10 GPa at 296 K together with previous data. The present data for the fluid and solid phases are represented by solid and open circles, respectively. Solid lines show the least-squares fitting to the data for both phases. Broken and doted lines correspond to the previous data for the fluid and solid phases by Nicol et al. (1969). Symbols denote values of the atmospheric pressure gas (diamond), the liquid at 90 K at ambient pressure (star) and calculated data using the Herzberg potential (cross). The inset represents the contribution, \( \nu_a \), of the attractive force to the frequency.

The vibrational frequency, \( \nu \), of O\textsubscript{2} is shown in Fig. 2 as a function of pressure together with the previous data. The frequency of the fluid and \( \beta \)-O\textsubscript{2} phases, represented in units of \( \text{cm}^{-1} \), exhibits a slight nonlinear-dependence on pressure (in GPa), as determined from the
following least-squares fitting:

\[ \nu = 1551.9(2) + 4.08(15)P - 0.084(0.28)P^2, \tag{1} \]

where uncertainties enclosed in parentheses represent standard deviations. The value at 0.3 GPa is 1553.0 cm\(^{-1}\) and corresponds to 1552.56 cm\(^{-1}\) of the liquid O\(_2\) at atmospheric pressure (Kleutz, 2003). Since the molar volume of liquid O\(_2\) is nearly equal to that of the supercritical fluid at 296 K and 0.3 GPa, this correspondence seems reasonable. The values obtained here are smaller by \(\approx 3\) cm\(^{-1}\) than those by Nicol et al. (1979) in all pressure range, and the present values below 1 GPa are less than 1556.22 cm\(^{-1}\) of the gas at atmospheric pressure (Herzberg, 1950). This behavior can be ascribed to the attractive intermolecular interaction to be discussed below. As a result, a sharp decrease in the frequency is suggested at pressures below 0.2 GPa. Actually, the low-frequency shift has been reported by a previous experiment of the density change along the coexistence line of gas and liquid from the triple point to the critical point (Clouter, 1980).

The pressure dependence of \(\nu\) for the \(\beta\)-O\(_2\) solid phase is also determined as

\[ \nu = 1549.60(9) + 5.196(2)P - 1.66533(4)P^2. \tag{2} \]

From both dependences, the frequency change in the fluid-solid transition at 5.9 GPa is estimated to be 0.8±0.2 cm\(^{-1}\). This value is consistent with the previous report (Nicol, 1979) and the dependence joins well with our previous data at pressures above 8 GPa (Akahama, 1996).

This pressure dependence of the frequency can be explained as the solvent shift (Schweizer, 1982). In diatomic-molecular liquids, the pressure dependence of vibrational frequency is generally interpreted as the result of competition between repulsive and attractive forces. The former is an external force by surrounding molecules and results in a high-frequency shift. The physical source of the latter, which causes a low-frequency shift, is largely the dispersive force through polarization interaction. The exerted force on one molecule along the axial direction by surrounding molecules at pressure \(P\) is approximately equal to \(P/[V_m(P)]^{2/3}\), where \(V_m\) is the molar volume. From the pressure dependence of \(V_m\) (shown in Fig. 6), the changes in the equilibrium bond distances and the frequencies of O\(_2\) at high pressure were calculated using the Morse function and the Herzberg potential parameters (Herzberg, 1950). The calculated frequency, \(\nu_{\text{cal}} = \nu_b + \nu_r\), is a sum of the frequency of an isolated molecule, \(\nu_b\), and the shift caused by the external repulsive force, \(\nu_r\), those for O\(_2\) are plotted in Fig. 2. For the fluid, \(\nu_{\text{cal}}\) is higher by 4-7 cm\(^{-1}\) than the present experimental data, \(\nu\). Thus the difference between \(\nu\) and \(\nu_{\text{cal}}\) may be interpreted as a contribution of the attractive force, \(\nu_a = \nu - \nu_{\text{cal}}\). The estimated values of \(-\nu_a\) for O\(_2\) are illustrated in the insets of Fig. 2. The pressure dependence of \(\nu_a\) seems to increase sharply below 0.4 GPa. This increase implies that the \(\nu_a\) depends strongly on the density. From the present findings, the contribution of the attractive interaction to the frequency change appears to be comparable to that of the repulsive interaction around 1 GPa.
The observed pressure evolution of the linewidth, \( \Gamma \), for O\(_2\) is shown in Fig. 3. The instrumental width of the spectroscopic system, 1.0 cm\(^{-1}\), was subtracted from the measured linewidth beforehand. The prominent feature of the result is a sharp increase in the linewidth with pressure; the linewidth for O\(_2\) reaches 2.2 cm\(^{-1}\) at 5.9 GPa. Sudden drops in the linewidth at the transition to solid phases are observed. This drop may be attributed to the translational coupling in solid phases, as suggested by Kroon et al. (1989).

The linewidth is related to the relaxation processes in vibrational excitation. In highly condensed fluids, the main contribution to the linewidth is possibly associated with adiabatic perturbations of the excited vibrational state arising from fluctuations in the density of the fluid medium. As a result, the linewidth, \( \Gamma \), corresponds to the dephasing rate, \( T_2^{-1} \), given by (Lcouter, 1977 and Oxtoby, 1978)

\[
\Gamma = (\pi c T_2)^{-1} = \langle (\Delta \omega_i)^2 \rangle \tau_c / \pi c,
\]

where the mean-square frequency fluctuation, \( \langle (\Delta \omega_i)^2 \rangle \), is a measure of the strength of coupling between the oscillator and the bath, and \( \tau_c \) is the correlation time. The sharp increase in the linewidth for the fluid with pressure may be related to an increase in \( \langle (\Delta \omega_i)^2 \rangle \).

3.2. UV absorption spectra

Figure 4 shows the absorption spectra of oxygen at pressures up to 1.5 GPa at 300 K. The absorption coefficient, \( \alpha = \ln(I_0/I)/x \), was estimated from the thickness, \( x \), of recovered metal gasket, which approximately equals to the sample thickness under pressure. At pressure below 0.13 GPa, the onset of the absorption is located above 6.5 eV and agrees with that of the absorption spectrum of low-pressure gas phase at \( \approx 1 \) Pa. The absorption band corresponds to the Schumann-Runge system of the \( ^3\Sigma_g^{-} \rightarrow ^3\Sigma_u^{-} \) transition. With increasing pressure, an absorption band appeared in the region between 4.5 and 7 eV and showed an increase in the intensity. The band edge energy, \( E_g \), was estimated to be 4.5 eV, being independent of pressure. The pressure dependences of \( \alpha \) at photon energies, \( E \), of 5.0
and 5.5 eV are shown in Fig. 5(a). The coefficient, $\alpha$, increased linearly with increasing pressure. The results suggest that the spectra can be described with a similar function of $E$. An empirical function, $A(\E - E_g)^{5/2}/E$, obtained by analogy with the forbidden transition between a direct band gap in solids, explained the spectra near the edge as shown in Fig. 4.

Fig. 4. UV absorption spectra of high-density oxygen at various pressures at RT. The spectra near edge except for spectrum a at 0.02 GPa could be described by a function of photon energy ($E$), $\alpha=\frac{A(\E - E_g)^{5/2}}{E}$ with the edge energy, $E_g$, of 4.5 eV. The broken line shows the fitting curve to the spectrum g at 0.83 GPa with the parameter, $A$, of 3350 cm$^{-1}$ [eV]$^{-3/2}$.

Fig. 5. (a) Pressure change of the absorption coefficient at 5.0 and 5.5 eV. (b) Pressure dependence of the absorption cross-section, $\sigma_{\text{eff}}$, of condensed oxygen at 5.0 and 5.5 eV. The slope of the solid line corresponds to that of the previous report (Shardanand, 1969).

The absorption coefficient of one molecule was calculated by estimating the pressure
dependence of the molar volume, $V_m$, of the supercritical phase by X-ray diffraction experiment. Diffraction data were collected in the range of 0.22 and 5.42 GPa. The 2θ-intensity profiles exhibited a halo pattern, reflecting the short-range order between the oxygen molecules. Under the assumption that the $d$-value of the halo peak is proportional to the mean intermolecular distance and the coordination between the molecules is independent of pressure, we determined the fitting parameter, $A = V_m/d^3$ so as to connect $V_m$ smoothly with the data at lower pressures (Washburn, 1928). The obtained $V_m$ is plotted as a function of pressure in Fig. 6 together with the previous data and our data for the solid β phase (Uemura, 2002). The present data link to those of the solid β phase. From these results, we obtained the following pressure dependence of $V_m$:

$$V_m = 22.53(P/P_0)^{-1/4.32} - 0.4024,$$

where $P_0$ is 1 GPa. The units of $V_m$ and coefficients are cm$^3$ mol$^{-1}$ and $P$ is in GPa. This formula suggests that the repulsive interaction between molecules is dominant in this pressure region due to the contact between molecular orbitals.

![Fig. 6. Molar volume of oxygen as a function of pressure at RT, □: Ref. (Washburn, 1928), ◇: our data for the β-O$_2$ phase (Uemura, 2002), and ○: the present data. The solid and broken lines represent Eq. (5) and the $P$-$V$ relation of the ideal gas, respectively, at RT.](image)

The absorption cross-section, $\sigma_{\text{eff}} = \alpha V_m/N_A$, where $N_A$ is the Avogadro constant, was calculated from the pressure dependence of the $V_m$. The values of $\sigma_{\text{eff}}$ at 5.0 and 5.5 eV are plotted in Fig. 5(b). The $\sigma_{\text{eff}}$ increases monotonically with pressure. The value of $\sigma_{\text{eff}}$ for 5.5 eV at 1.5 GPa, 4x10$^{-20}$ cm$^{-2}$, exceeds that measured previously at 1.0 MPa, 5x10$^{-23}$ cm$^{-2}$ (Shandanand, 1969) by three orders of magnitude, while the pressure coefficient is consistent.
with the earlier data reported by Shardanand (1969) up to 2.0 MPa. The $\sigma_{\text{eff}}$ corresponds to the absorption coefficient of one molecule and is basically independent of pressure according to Beer’s law. Therefore, the presently observed large enhancement of $\sigma_{\text{eff}}$ cannot be explained by the single molecule transition process and requires a much stronger interaction between oxygen molecules in the absorption process.

The band energy of the newly found UV absorption corresponds to that of the Herzberg band. However, the Herzberg system of $^3\Sigma_g^+ \rightarrow ^3\Sigma_u^+$ or $^3\Delta_u, ^1\Sigma_u^-$ transitions is naturally forbidden by the selection rule of the orbital angular momentum or parity. Its absorption is extremely weak and is independent of pressure (Herzberg, 1950). Many investigators have studied the origin and the transition process of this UV absorption band (Lewis, 1924, Dianov-Klokov, 1964, Shardamand, 1969 and Fujiwara, 1974). One probable explanation of the origin is the transition to the Herzberg system through the two-molecule process. The formation of (O$_2$)$_2$ molecular units may convert it to an allowed transition via an intermediate state through the charge-transfer interaction. In fact, the absorption band due to two-molecule transition: $2^3\Sigma_g^+ \rightarrow 2^1\Delta_g$ was clearly observed in the $\alpha$-O$_2$ solid phase at 17 K at 2.2 eV. The mean intermolecular distance between molecules, which was estimated from the $d$-value of the halo peak at 1.0 GPa, is close to 3 Å. The Coulomb interaction, $-e^2/4\pi\varepsilon_0 r$, between the molecules at this distance is as strong as 4.8 eV. We estimate 6.8 eV for the charge-transfer excitation energy from the ionization energy of 12.08 eV and the electron affinity of 0.43 eV. This value cannot be disregarded when we consider the two-molecule process.

The $\alpha$-O$_2$ phase belongs to a monoclinic lattice with two molecules in the unit cell (Barrett, 1967) and shows collinear antiferromagnetic order (Collins, 1966 and Alikhanov, 1967). The spin arrangement between the nearest-neighbor molecules is antiparallel. The fact that the two-molecule absorption and the UV band were observed in the $\alpha$-O$_2$ phase suggest that the basic character of the (O$_2$)$_2$ molecular units is an antiferromagnetic O$_2$ pair.

It has recently been revealed that ozone, O$_3$, is created by 248 nm (5.0 eV) excimer laser irradiation to the $\alpha$-O$_2$ solid at ambient pressure, and the initiation process of this ozone formation is proposed to be the excitation in the Herzberg states by one-photon absorption (Schriver-Mazzuoli, 1995). Therefore, the UV band is significantly related to the mechanism of the ozone formation. Further experimental studies are needed to clarify the process of the UV absorption and the mechanism of ozone formation.

IV. Conclusions

Pressure dependences of the vibrational Raman frequency and the linewidth of O$_2$ have been measured and analyzed in terms of intermolecular interaction. The dependence of the frequency of the supercritical fluid was interpreted as competition between repulsive and attractive interactions, and an appreciable contribution of the attractive interaction is manifested for the fluid O$_2$. A low-frequency shift, with a minimum below 0.2 GPa, is also suggested. Enhancement of the intermolecular interaction with pressure is reflected in a sharp increase in the linewidth of the Raman band in fluid O$_2$.

An absorption band was observed in an UV region between 4.5 and 7 eV in the supercritical phase of oxygen. The origin of the observed UV absorption can be ascribed to the two-molecule process with an antiferromagnetic O$_2$ pair. The pairing is considerably enhanced with increasing pressure. It has also been confirmed that the excitation state of the
UV absorption forms the valence band of solid oxygen. These results demonstrated that intermolecular interaction certainly plays an important role in the optical properties of high-density oxygen under high-pressure through its electronic structure.

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