PHYSICAL REVIEW B
CONDENSED MATTER

THIRD SERIES, VOLUME 28, NUMBER 3 1 AUGUST 1983

# High-pressure optical spectra of condensed oxygen

Malcolm Nicol
*Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024*

Karl Syassen
*Physikalisches Institut III, Universität Düsseldorf, D-4000 Düsseldorf, West Germany*

(Received 15 March 1983)

Optical-absorption spectra (1.5–3.5 eV) of the fluid and three solid phases of $O_2$ have been recorded up to 40 GPa near 298 K. The principal feature of the spectra of the fluid and rhombohedral $\beta$-$O_2$ is the $2\,{}^1\Delta_g \leftarrow 2\,{}^3\Sigma_g^-$ band; in $\beta$-$O_2$, it is polarized perpendicular to the *c* axis of the hexagonal cell. The energies of this and other transitions among the ${}^3\Sigma_g^-$, ${}^1\Delta_g$, and ${}^1\Sigma_g^+$ states increase with increasing pressure. The spectra and visual observations of the transformation between orthorhombic and $\epsilon$-$O_2$, whose structure has not been determined, suggest that $\epsilon$-$O_2$ has a layered structure. Absorption spectra of orthorhombic and $\epsilon$-$O_2$ for light propagating perpendicular to the layers are dominated by a moderately strong band which moves from the uv through the visible with increasing pressure and a very strong ultraviolet band. These bands can be assigned as excitations from $\pi^4$-$\pi^{*2}$ states to $\pi^3$-$\pi^{*3}$ states which are mixed with intermolecular-charge-transfer excitations. Both bands move toward longer wavelengths at high pressures. At pressures above 13 GPa, absorption features for light propagating in the planes of the $\epsilon$-phase structure can be assigned as $2\,{}^1\Delta_g \leftarrow 2\,{}^3\Sigma_g^-$. However, between 10 and 13 GPa, this feature is absent, and the pressure dependence of the Raman spectrum also is unusual. Both observations suggest that, between these pressures, the molecules reorient with respect to the crystallographic axes.

## I. INTRODUCTION

The occurrence of three solid phases of oxygen near room temperature and the intense colors of these phases were first described by Nicol, Hirsch, and Holzapfel.[1] These colors mean that with $O_2$, in contrast to other light homonuclear diatomics which are transparent in the visible and ultraviolet at similar pressures, one can study the very significant ways by which compression of intermolecular separations perturb the electronic states of a simple molecular solid. Structures of two of the solid phases have been determined by x-ray crystallography by d'Amour *et al.*[2] and by Schiferl *et al.*[3,4] Single crystals grown from the fluid have the rhombohedral ($R\bar{3}m$) structure of $\beta$-$O_2$.[2,3] Near 9.6 GPa, $\beta$-$O_2$ transforms to an orthorhombic structure with space group $F_{mmm}$.[4] Both the $\beta$ and orthorhombic structures can be viewed as stacks of approximately close-packed planes of $O_2$ molecules whose axes are normal to the plane. The anisotropies of the optical spectra of these solids are consistent with this model. Pink facets of $\beta$-$O_2$ crystals transform to dark orange facets of orthorhombic crystals while other facets of crystals of both phases are only faintly colored under appropriately polarized light. Near 10 GPa, orthorhombic crystals transform to $\epsilon$-$O_2$, whose structure has not been determined but appears to be closely related to those of $\beta$-$O_2$ and orthorhombic $O_2$ by virtue of the changes of optical spectra of the facets and the relatively minor changes of grain structures during the transformation.

This paper describes details of electronic spectra of solid $O_2$ between 1.5 and 3.5 eV. These spectra were obtained at

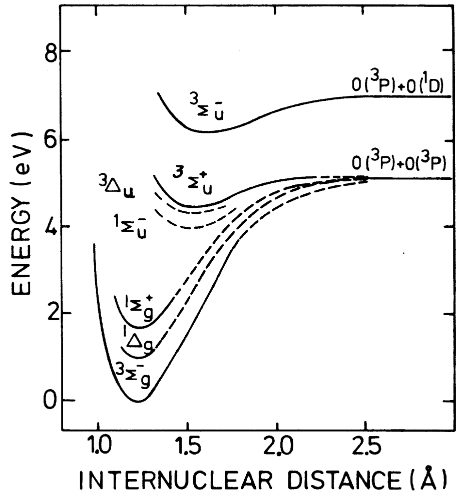

FIG. 1. Potential-energy diagram of the $O_2$ molecular states relevant to this study [after Krupenie (Ref. 5) and Herzberg (Ref. 6)].

room temperature with several oriented single crystals of $\beta$-$O_2$ grown from the melt and samples of orthorhombic and $\epsilon$-$O_2$ grown by compression of $\beta$-$O_2$ crystals that had different crystallographic orientations. Thus spectra could be recorded for light propagating along different crystalline axes. These absorption spectra can be interpreted in terms of exciton bands derived from the several low-energy states of the $O_2$ molecule included in Fig. 1.[5] The three lowest states derive from the same $\pi^4$-$\pi^{*2}$ configuration but differ with respect to correlations between the two $\pi^*$ electrons. These three states have similar equilibrium bond distances (0.12 nm) and stretching frequencies (1555 $cm^{-1}$). Transitions among the ${}^3\Sigma_g^-$, ${}^1\Delta_g$, and ${}^1\Sigma_g^+$ states are forbidden by spin, orbital angular momentum, and parity selection rules, and thus can be detected only for long path lengths or high densities. At high densities, vibronically induced excitations of $O_2$ pairs are detected such as the $2\,{}^1\Delta g \leftarrow 2\,{}^3\Sigma_g^-$ bands that make liquid oxygen blue. Excitation of a $\pi$ electron to a $\pi^*$ orbital gives rise to the ${}^3\Sigma_u^+$, ${}^3\Delta_u$, and ${}^3\Sigma_u^-$ states in which the molecule is single bonded (length ~0.16 nm, vibrational frequency 7–800 $cm^{-1}$). Transitions between the ${}^3\Sigma_g^-$ state and these excited states vary from weakly to strongly allowed and give rise to the characteristic oxygen spectra in the far and vacuum ultraviolet at atmospheric pressure.

The absorption spectra of single crystals of $\beta$-$O_2$ are dominated by the $2\,{}^1\Delta_g \leftarrow 2\,{}^3\Sigma_g^-$ system with an origin near 2 eV and two or three components of a vibrational progression of about 0.2 eV. This absorption band is polarized normal to the unique axis of the $\beta$-$O_2$ structure, and the (1-0) component of the progression is most intense. With increasing pressure, this band moves to shorter wavelengths. Weaker bands corresponding to excitation of the ${}^1\Sigma_g^+$ on one molecule or ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ on two molecules also are seen in some $\beta$-$O_2$ spectra. These bands also move to shorter wavelengths with increasing pressure.

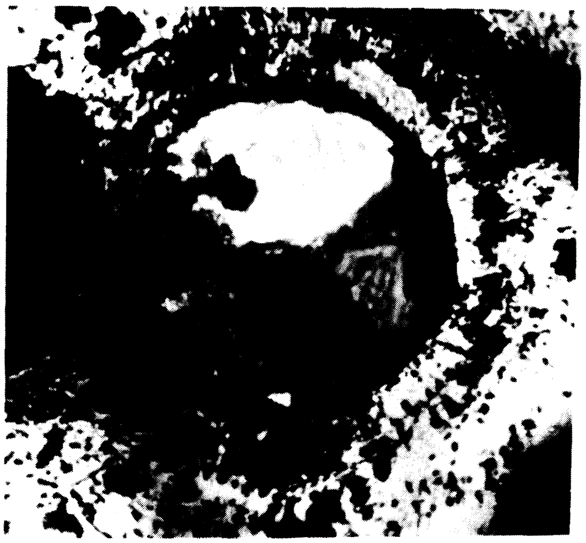

FIG. 2. Transmission photomicrograph under polarized illumination of the $\epsilon$-$O_2$ sample prepared (Ref. 7) by compressing the sample used by Schiferl *et al.* (Ref. 4) to determine the structure of orthorhombic $O_2$. The approximately 0.2-mm-diam sample in the center of this approximately 0.4-mm×0.4-mm field of view is surrounded by a cylindrical steel gasket. The polarization was selected to maximize the contrast between the light and colored parts of the sample which correspond to different orientations of the crystals relative to the optical axis of the cell. The sample used to record the $\epsilon$-$O_2$ spectra reported here was similarly divided.

Two characteristic settings of orthorhombic and $\epsilon$-$O_2$ crystals can be identified visually and by absorption spectra. This is illustrated in Fig. 2 which shows the $O_2$ sample used by Schiferl *et al.*[4] to determine the structure of the orthorhombic phase after the sample had been transformed to the $\epsilon$ phase.[7] This photograph was taken with polarized light, and the polarization direction was selected to maximize the contrast between the two parts of the sample. Before transformation the orthorhombic sample had a similar grain structure and "colored" (orange) and "light" facets. The orange facets were normal to the *c* axis of the orthorhombic structure; thus, the strong visible absorption is polarized in the layers (*ab* planes) of that structure. That the resulting $\epsilon$-$O_2$ has a similar polarization pattern suggests that it also has a layered structure.

The spectra of the colored facets of orthorhombic and $\epsilon$-$O_2$ are dominated by a band that shifts from the ultraviolet to longer wavelengths and led Nicol *et al.*[1] to describe them as "orange" and "red" oxygen. This band is interpreted in terms of closing the gap between the ground and $\pi$-$\pi^*$ excited states of the $O_2$ molecule such as the ${}^3\Delta_u$ or ${}^3\Sigma_g^-$ that appear to be strongly mixed with intermolecular charge-transfer excitations by the crystal field. Rotation of the plane of polarization had little effect on the intensity of the absorption spectra of the colored facets in these samples. Reflection spectra of a colored facet of $\epsilon$-$O_2$ at pressures near 35 GPa locate a strongly allowed transition in the near ultraviolet whose molecular parent is the ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ Schumann-Runge band. The principal features of the spectra of the light facets of $\epsilon$-$O_2$ are the two-molecule excitations and a strong absorption band in the ultraviolet which becomes apparent above 20 GPa.

## II. EXPERIMENTAL SETUP

The micro-optical double-beam system and diamond-anvil high-pressure cell used to obtain the absorption and reflectance spectra reported here have been described in detail elsewhere.[8] Pressures were measured by recording the fluorescence spectrum of a small ruby chip embedded in the sample and converting the shift of the wavelength of the $R_1$ line to pressure with the factor +0.365 nm/GPa.[9] Raman measurements[1,10] were used to confirm the visual identification of the $O_2$ phases whose spectra were being recorded.

The oxygen samples were prepared from liquid $O_2$ of nominal 99.9% purity by the method described by Nicol *et al.*[1] Large crystals of $\beta$-$O_2$ were grown by a three-step cycle. First, a polycrystalline sample of $\beta$-$O_2$ was grown and compressed to about 9 GPa in order to reduce the gasket to an appropriate thickness. The pressure was then reduced to the melting pressure [about 5.5 GPa (Refs. 3 and 11)], and all but one or two seed crystals melted. The sample was then recompressed slowly to fill the cell with one or two large crystals. With appropriate manipulation of the applied pressures, the process could be repeated until large crystals with specific orientations were obtained. The resulting samples typically are 0.08(±0.02)-mm thick and are subsequently thinned to less than 0.05 mm at the highest pressure (~40 GPa) studied. However, path lengths were not determined precisely, and relative absorbances at different pressures are known only approximately. It should be noted that the absolute values of optical densities reported below are approximate. Since the $\beta$, orthorhombic, and $\epsilon$ phases are optically anisotropic, light scattering at strain-induced cracks also may reduce the transmitted intensity.

$\beta$-$O_2$ crystals often could be compressed to 7 GPa without shattering, and well polarized spectra were obtained with such samples. However, before they transformed to the orthorhombic phase, all $\beta$-$O_2$ crystals developed strain-induced cracks with prevented quantitative polarization work. Cracked samples, nevertheless, could be used to compare polarizations of spectra of different phases by observing color changes that accompany the transformations through a microscope illuminated by transmitted polarized light. Such observations suggested that all three phases have layered structures.

One preparation yielded two crystals of $\beta$-$O_2$ of similar volumes but with different orientations: The orthorhombic and $\epsilon$-$O_2$ samples prepared from it consisted of colored and light regions similar to those depicted in Fig. 2. Raman spectra demonstrated that both regions were at the same pressure; thus, the regions correspond to different facets of crystals with the same structure. The collection optics of the absorption spectrometer could be focused to diameters smaller than 0.04 mm so that absorption spectra of both facets could be determined.

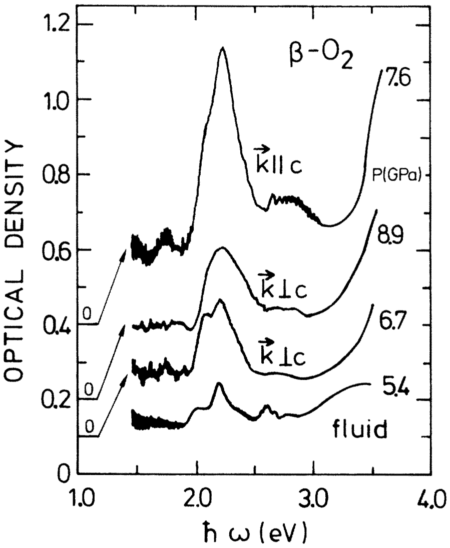

FIG. 3. Unpolarized optical-absorption spectra of $O_2$ in the liquid phase at 5.4 GPa and in the crystalline $\beta$ phase. Spectra at 6.7 and 8.9 GPa were measured with the $c$ axis parallel to the diamond culets (wave vector $\vec{k} \perp c$), while for the 7.6 GPa spectrum the $c$ axis is essentially perpendicular to the diamond culets ($\vec{k} \parallel c$). The spectra are corrected for all but the reflection loss at the two diamond-oxygen surfaces and have been displaced vertically for clarity. Transmission interferences created by reflections at the four diamond faces appear as noise and distort the weaker absorption bands. The sample thickness was approximately 0.1 mm.

## III. RESULTS AND DISCUSSION

### A. Fluid and $\beta$-phase oxygen

The absorption spectrum of fluid oxygen at 5.4 GPa and about 295 K is compared in Fig. 3 with spectra of two $\beta$-$O_2$ crystals at higher pressures. The spectrum at 7.6 GPa was obtained with a crystal whose unique axis (the $c$ axis of the hexagonal unit cell) was approximately perpendicular to the culets of the diamonds; thus, the light was propagating parallel to the axes of the $O_2$ molecules. The $c$ axis of the crystal used to obtain the spectra at 6.7 and 8.9 GPa was parallel to the culets and perpendicular to the propagation direction. Five features can be seen in one or more of the spectra of Fig. 3, although reflections at the diamond facets distort some weak features. The five features are the following: the prominent $2\,{}^1\Delta_g \leftarrow 2\,{}^3\Sigma_g^-$ (0-0) band, and an even more intense (1-0) member of a vibrational progression; the weak, near-infrared ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ band; one other double excitation, ${}^1\Sigma_g^+ + {}^1\Delta_g \leftarrow 2\,{}^3\Sigma_g^-$; and the edge of a much stronger band that moves into this region from the mid uv at higher pressures.

The $2\,{}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ origin near 2 eV and the more intense (1-0) vibronic band near 2.2 eV appear in all of the spectra. With increasing pressure, these bands move to higher energies by approximately 0.03 eV/GPa. The bands broaden and could not be resolved from each other at the higher pressures. Whether this broadening is inherent to the $O_2$ or resulted from inhomogeneities in the applied stress was not determined. The pressure dependence of the transition energy can be understood in terms of the molecular basis of the splitting between the ${}^1\Delta_g$ and ${}^3\Sigma_g^-$ states; that is, the repulsion between the two $\pi^*$ electrons. The magnitude of this repulsion should increase as these electrons are compressed into a smaller volume, thereby increasing the separation between these states.

In each $\beta$-$O_2$ sample the intensities of the bands remain constant within the precision of these measurements from the melting pressure to 9 GPa. Although the intensity of the transition depends upon intermolecular interactions, this weak pressure dependence is not particular surprising since this compression decreases the nearest-neighbor separation by at most 5%. However, in the 7.6-GPa spectrum, these bands are about twice as intense as in the 6.7 or 8.9-GPa spectrum which clearly demonstrates that these bands are strongly polarized perpendicular to the molecular axes.

These polarizations cannot be explained on purely electronic terms. Tsai and Robinson[12] have demonstrated that the intensity induced by mixing with the ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ or ${}^1\Delta_u \leftarrow {}^1\Delta_g$ transitions is zero for pairs of $O_2$ molecules in the same layer of the $\beta$-$O_2$ structure. However, the polarizations and relative intensities of the 0-0 and 1-0 components are consistent with a vibronic mechanism[13] in which, for a pair of parallel $O_2$ molecules, the transition is

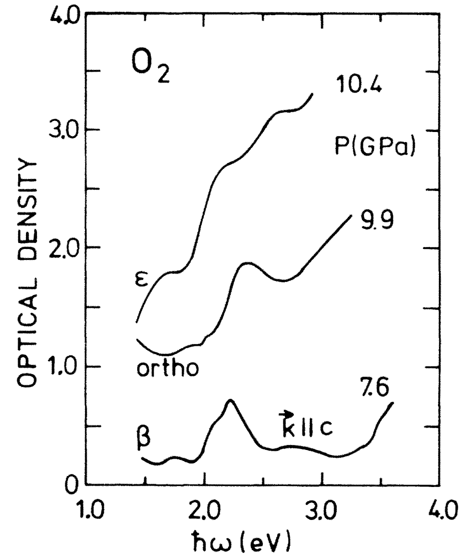

FIG. 4. Absorption spectra of $\beta$-, orthorhombic, and $\epsilon$-$O_2$ in the region of the phase transformation. The $c$ axes of the $\beta$-$O_2$ sample (7.6 GPa) and the orthorhombic sample (9.9 GPa) were preferentially oriented parallel to the propagation direction of the light. This orientation of the $\epsilon$-$O_2$ sample exposes the colored facets to the transmitted light.

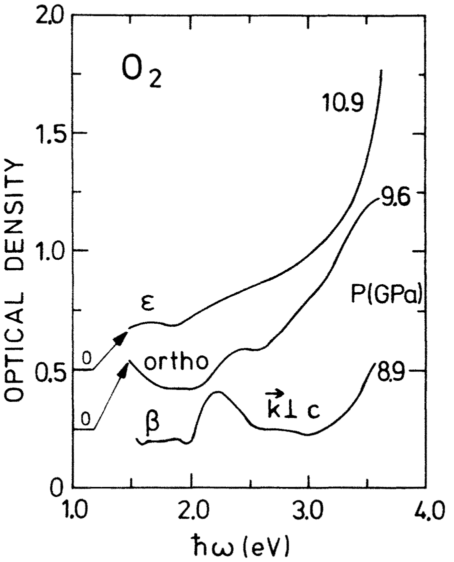

FIG. 5. Sequence of absorption spectra of solid $O_2$ in the region of the $\beta$-, orthorhombic, and $\epsilon$-phase transformations taken with the same sample. The initial $\beta$ crystal (8.9 GPa) was preferentially oriented with its $c$ axis perpendicular to the propagation direction. Successive spectra have been displaced for clarity. Note the change of absorbance scale from Fig. 4.

induced by the antisymmetric combination of the O-O stretching vibrations. In this context, Brus's high-resolution spectra of $O_2$ dimers in solid Ne suggest that the 0-0 band in the spectra of $\beta$-$O_2$ may be a false origin.

On melting, the integrated intensities of the two $2\,{}^1\Delta_g \leftarrow 2\,{}^3\Sigma_g^-$ bands decrease by a factor of 5 relative to the 7.6-GPa spectrum from the combined effects of reduced intermolecular orientational order and random orientation relative to the photon field. In the fluid the intensities of the spectra vary with pressure to a greater degree as might be expected from quadratic density dependence of these intensities observed at low pressures.[14] Indeed, the intensity near the melting line is about 4 times greater than would be calculated by extrapolating the low-pressure behavior and using the density of $\beta$-$O_2$ near the melting line[2] to approximate the density of the fluid. Changes in the orientational correlations between the solid and dense fluid could explain the difference.

The remaining features of the $\beta$-$O_2$ spectra could not be studied in detail. Weaker bands can be seen in several spectra near 1.7 eV, 2.7 eV, and in the fluid spectrum 3.4 eV. All three bands move to higher energies with increasing pressure; however, the transmission interferences and the strong uv edge prevented a precise determination of the pressure dependences of these transitions. These weak features can be consistently interpreted by assigning them as the ${}^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$, ${}^1\Delta_g + {}^1\Sigma_g^+ \leftarrow 2\,{}^3\Sigma_g^-$, and $2\,{}^1\Sigma_g^+ \leftarrow 2\,{}^3\Sigma_g^-$ transitions, respectively. The ultraviolet edge is attributed to the Herzberg system.

### B. Orthorhombic oxygen

Absorption spectra of $\beta$-, orthorhombic, and $\epsilon$-$O_2$ in the region of the phase transformation are compared in Figs. 4 and 5. Spectra for the colored and light facets of an $\epsilon$-$O_2$ sample at higher pressures are reproduced in Figs. 6 and 7, respectively. The $c$ axes of the $\beta$ and orthorhombic crystals whose spectra are reproduced in Fig. 4 were oriented parallel to the direction of propagation. This orientation exposes to the spectrometer a colored facet of orthorhombic $O_2$ and, after transformation to $\epsilon$-$O_2$, a colored facet of the $\epsilon$ phase. Spectra of these facets are shown in Figs. 4 and 6, respectively. The spectra shown in Figs. 5 and 7 were obtained with $\beta$ and orthorhombic crystals whose $c$ axes were perpendicular to the propagation direction and with the light facets of the $\epsilon$-$O_2$ crystal produced by further compression of this sample.

At least three features are obvious in the spectra of the orthorhombic phase. The spectra of colored facets (Fig. 4) can be interpreted in terms of one- and two-molecule triplet-singlet bands sitting on top of a broad band of moderate intensity that extends across the visible and becomes more intense with increasing energy. For light facets (Fig. 5) the triplet-singlet bands in the visible are more clearly separated from the edge of a stronger band that rises in the near uv. The number of triplet-singlet bands that can be identified in these spectra depends upon how one separates these spectra into bands. The tail of an infrared-absorption band appears in both polarizations; this probably is the ${}^1\Delta_g \leftarrow {}^3\Sigma_g^-$ band. The corresponding double-excitation transition occurs as an unresolved band peaked at 2.4±0.1 eV in both polarizations, but comparison with the spectra of $\beta$-$O_2$ suggests that the origin is closer to 2.1 eV. This band is roughly 3 times stronger for light propagating along the $c$ axes; thus, as in the $\beta$ phase, this transition is polarized in the oxygen layers. The energies of these bands are consistent with the pressure depen-

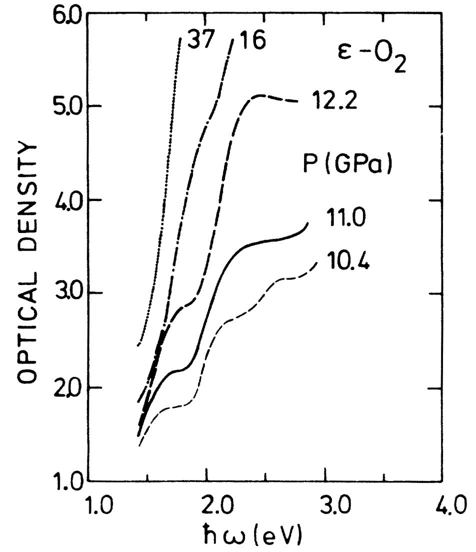

FIG. 6. Absorption spectra of a colored facet of an $\epsilon$-$O_2$ sample at several pressures. The thickness of the sample was roughly 0.05 mm.

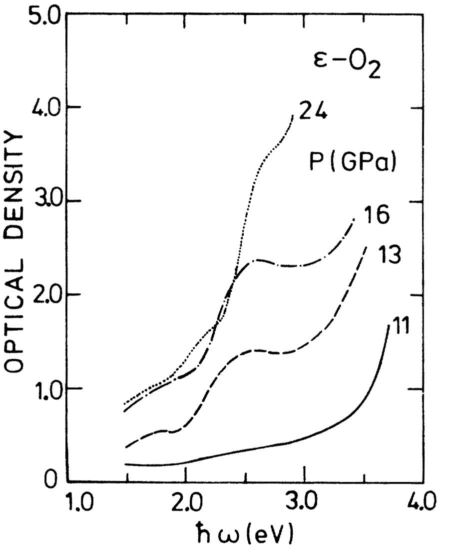

FIG. 7. Absorption spectra of a light facet of an $\epsilon$-$O_2$ sample at several pressures. Note the change of absorbance scale from Fig. 6.

dences of the corresponding bands of $\beta$-$O_2$. A weak hump near 1.8 eV in the spectrum of the colored facets might be the $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$ band, which would place the $^1\Sigma_g^+ + {}^1\Delta_g \leftarrow 2\,{}^3\Sigma_g^-$ transition near 3 eV; however, no band is obvious in that part of either spectrum.

The precise relationships among the broad band in the spectra of the colored facets, the ultraviolet feature in the spectra of the light facets, and the ultraviolet bands of the $\epsilon$-$O_2$ spectra are uncertain. A plausible interpretation involves associating them with the Herzberg band $^3\Delta_u \leftarrow {}^3\Sigma_g^-$ which involves a $\pi$-$\pi^*$ excitation. With increasing pressure, coupling of $\pi$ and $\pi^*$ orbitals on neighboring oxygen molecules will increase, and stable bonds will form that should both decrease in energy and broaden the $\pi$-$\pi^*$ spectra. In the $\beta$ structure the separation between the six nearest neighbors in the same (001) plane is identical with the smallest atom-atom separation between nearest neighbors in adjacent (001) planes. However, in the orthorhombic structure, four atoms on the nearest neighbors in the same (001) plane come 0.006 nm closer than two atoms on the next-nearest neighbors in the adjacent (001) plane.[4] Thus, in the orthorhombic structure, bond formation within (001) planes should be more important than between planes. This may explain the orientation dependence of the intensity and the breadth of the $\pi$-$\pi^*$ bands in the absorption spectrum, but detailed calculations are needed to test this interpretation.

### C. $\epsilon$-phase oxygen

The transformation from the orthorhombic to the $\epsilon$ phase changes the spectra of both light and colored facets. Near 10 GPa, three weak features occur at 1.6, 2.1, and 2.6 eV in the colored spectra (Fig. 4), but the tail of the infrared band of the orthorhombic spectrum is absent. These features appear to be 1.6 eV, $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$; 2.1 eV, $2\,{}^1\Delta_g \leftarrow 2\,{}^3\Sigma_g^-$; and 2.6 eV, $^1\Sigma_g^+ + {}^1\Delta_g \leftarrow 2\,{}^3\Sigma_g^-$. In the light spectra at similar pressures (Fig. 5) the triplet-singlet features are either absent or, at least, very weak and broad. If this assignment is correct, the energies of the maxima of the $^1\Delta_g$ and $^1\Sigma_g^+$ bands decrease by from 0.15 to 0.25 eV between the orthorhombic phase at 9.9 GPa and the $\epsilon$ phase at 10.4 GPa. A plausible interpretation of this shift is that the structural transformation changes the intermolecular coupling mechanism and the coupling mechanism in the $\epsilon$ phase induces more intensity in the (0-0) components of these bands than in the (1-0) and higher components. It thus appears that neighboring $O_2$ molecules are not parallel in the layers of $\epsilon$-$O_2$.

At slightly higher pressures, the 2.1 and 2.6 eV features broaden into a single band near 2.3 eV (Fig. 6, 11.0 GPa), and both the 1.6- and 2.3-eV features appear in the spectra of the light facets (Fig. 7, 13 GPa). The 1.6- and 2.3-eV features move toward higher energies with increasing pres-

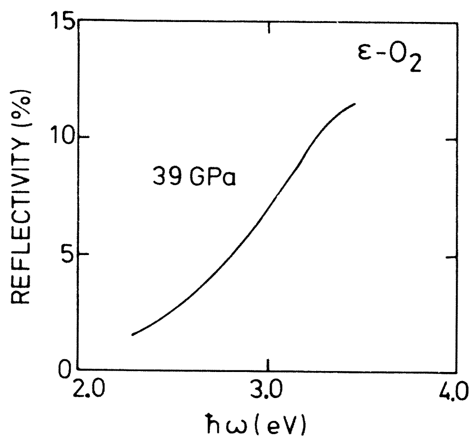

FIG. 8. Reflection spectrum of a colored facet of an $\epsilon$-$O_2$ sample at 37 GPa.

sure by $\sim 0.03$ eV/GPa which identifies them as triplet-singlet transitions. Between 10 and 13 GPa, the pressure dependence of the vibrational stretching frequency also is unusual.[1] These observations imply the following: (1) Near 10 GPa, the molecular axes in the $\epsilon$ structure are not in the parallel orientation of $\beta$-$O_2$ or orthorhombic $O_2$ and the O-O stretch is somewhat hindered, and (2) the initial compression of the structure occurs by further reorienting molecular axes to remove the stress on the O-O stretch.

A major change in the spectra of $\epsilon$-$O_2$ above 11 GPa is the appearance of an intense absorption band edge is the spectra of the colored facets (Fig. 6). With increasing pressure, this band edge moves to low energies such that at 37 GPa the absorbance at 1.4 eV exceeds 2.4 eV and changes the appearance of the colored facets from red to black. Reflection spectra indicate, however, that the corresponding transition is only weakly allowed which suggest that the molecular parent of this transition is the spin allowed but orbitally forbidden $^3\Delta_u \leftarrow {}^3\Sigma_g^-$.

Another feature of the $\epsilon$-$O_2$ spectra at very high pressures is a strong ultraviolet band that is suggested by the high-energy end of the light spectra (Fig. 7) and confirmed by the reflection spectrum of a colored facet at 39 GPa shown in Fig. 8. The reflectivity scale in this figure was calibrated by assuming that the reflectivity of the diamond—stainless-steel gasket surface is 50%. The high ultraviolet reflectivity clearly demonstrates that this is an allowed transition. If it is a one-molecule transition, the most likely assignment is the $^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ band which should be polarized along the molecular axis. If it is not an artifact of the very high stresses to which this solid had been subjected, the strength of the transition in spectra of the "in-plane" polarization means that, in $\epsilon$-$O_2$, the molecular axes are not perpendicular to layers as they are in the $\beta$ and orthorhombic structures, or the transition is strongly mixed with intermolecular excitations, e.g., charge transfer, which are polarized in the layers.

This latter interpretation is supported by the observation of two strong O-O stretching bands in the infrared spectrum of $\epsilon$-$O_2$.[15] The strengths of these bands suggest that ungerade combinations of the stretching vibrations of the $O_2$ molecules in the primitive cell significantly change the character of the ground state by mixing with a low-energy rate of ionic ($O_2^+$-$O_2^-$) character. As isolated species, $O_2^-$ is slightly more stable and has a slightly longer bond than $O_2$: $O_2^+$ is slightly shorter but much more ($\sim 10$ eV) energetic than $O_2$. However, the proximity of the ion pair in the solid and the compression and extension of adjacent molecules by the ungerade bond-stretching modes combine to lower the charge-transfer excitation energy and to increase the ionic character of the ground state. The vibrational frequencies of both $O_2^+$ and $O_2^-$ are less than that of the $^3\Sigma_g^-$ state of the $O_2$ molecule. Thus introduction of ionic character into the ground state of $\epsilon$-$O_2$ will tend to reduce its vibrational stretching frequencies below those that $\beta$-$O_2$ and orthorhombic $O_2$ would have at the same pressure, as the spectra show.[1,15] Thus, effects of low-energy charge-transfer excitations are evident in both vibrational and electronic spectra of $\epsilon$-$O_2$.

## IV. SUMMARY

We have measured optical spectra of solid oxygen near 298 K in three of its high-pressure phases. Most of the absorption bands in the (1.5—3.5)-eV photon energy range have been assigned to one- or two-molecule excitations. The relationship between optical-absorption features and crystal structure has been discussed. Further insight into the electronic structure of compressed solid oxygen should be obtained from low-temperature absorption measurements and from recent advances in electronic structure calculations.

## ACKNOWLEDGMENTS

It is a pleasure to acknowledge valuable conversations with Dr. Basil Swanson and with Dr. David Schiferl, who graciously provided access to his sample of orthorhombic oxygen. Partial support for this work was provided by National Science Foundation Grants Nos. DMR-77-27428 and DMR-80-25620 and NATO Travel Grant No. 1952.

---

[1] M. Nicol, K. R. Hirsch, and W. B. Holzapfel, Chem. Phys. Lett. 68, 49 (1979).

[2] H. d'Amour, W. B. Holzapfel, and M. Nicol, J. Phys. Chem. 85, 131 (1981).

[3] D. Schiferl, D. T. Cromer, and R. L. Mills, Acta Crystallogr. Sect. B 37, 1329 (1981).

[4] D. Schiferl, D. T. Cromer, L. A. Schwalbe, and R. L. Mills, Acta Crystallogr. 39B, 153 (1983).

[5] For a thorough discussion of the spectra of molecular oxygen, see P. H. Krupenie, J. Phys. Chem. Ref. Data 1, 423 (1972).

[6] G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950).

[7] D. Schiferl and M. Nicol (unpublished).

[8] K. Syassen and R. Sonnenschein, Rev. Sci. Instrum. 53, 644 (1982).

[9] G. J. Piermarini and S. Block, Rev. Sci. Instrum. 46, 973 (1975) and references therein.

[10] K. Syassen and M. Nicol, in *Physics of Solids under High Pressure,* edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), pp. 33—38.

[11] T. Yagi, K. R. Hirsch, and W. B. Holzapfel (private communication).

[12] S. C. Tsai and G. W. Robinson, J. Chem. Phys. 51, 3559 (1969).

[13] J. Goodman and L. E. Brus, J. Chem. Phys. 67, 4398 (1977).

[14] R. P. Blickensderfer and G. E. Ewing, J. Chem. Phys. 51, 5284 (1969).

[15] B. Swanson, S. Agnew, L. H. Jones, R. L. Mills, and D. Schiferl, J. Phys. Chem. (in press).

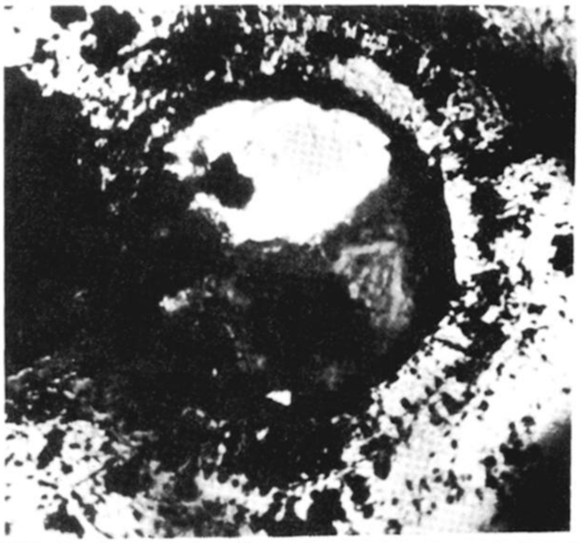

FIG. 2. Transmission photomicrograph under polarized illumination of the $\epsilon$-$O_2$ sample prepared (Ref. 7) by compressing the sample used by Schiferl *et al.* (Ref. 4) to determine the structure of orthorhombic $O_2$. The approximately 0.2-mm-diam sample in the center of this approximately 0.4-mm × 0.4-mm field of view is surrounded by a cylindrical steel gasket. The polarization was selected to maximize the contrast between the light and colored parts of the sample which correspond to different orientations of the crystals relative to the optical axis of the cell. The sample used to record the $\epsilon$-$O_2$ spectra reported here was similarly divided.