Interpretation of the visible and near-infrared absorption spectra of compressed oxygen as collision-induced electronic transitions

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The intensity profiles of some of the broad continuous absorption bands of oxygen in the near-infrared and visible regions were measured in the compressed gas over a range of pressures and temperatures. Three single electronic transitions (12 600, 10 600, 7620 Å) and three double transitions (6290, 5770, 4770 Å) were studied in detail. The asymmetry of the band profiles is shown to arise from a Boltzmann relation between the intensity distributions in the high and low frequency wings when the band origin is properly chosen. By assuming an appropriate rotational structure and broadening each rotational transition by a Boltzmann-modified dispersion curve the profiles of the bands could be reproduced with only minor discrepancies. These criteria, along with the well-known quadratic density dependence of the intensity, show that the bands are properly interpreted as collision-induced electronic transitions. The large width of the translational broadening functions required in the analysis indicates that the induction must be predominantly due to overlap interaction. No specific effects of \((\text{O}_2)_2\) complexes are identifiable in the spectra.

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I. Introduction

The distortion of the electron distribution of molecules in binary and higher order collisions gives rise to a dipole moment which permits optical transitions which are forbidden in the free molecule. The induced dipole moment is modulated by the rotation and vibration of the colliding molecules and by their relative translational motion. Thus, pressure-induced infrared spectra involving rotational, vibrational, and translational transitions, alone and in combination, are known for several simple molecules of high symmetry. On the other hand, no pressure-induced electronic transitions have yet been definitely identified. However, certain symmetry-forbidden electronic band systems of oxygen in the near infrared and visible regions show some of the characteristics of induced spectra. Although these absorption bands have often been ascribed to \((\text{O}_2)_2\) molecules, that is, binary complexes of \(\text{O}_2\) molecules held together by Van der Waals forces, it seems probable that they are more properly described, especially at higher temperatures, as originating in collision pairs. The present investigation is an attempt to ascertain to what extent, if any, the agency of quasi-stable \((\text{O}_2)_2\) molecules must be invoked in explaining these spectra.

In the next paragraphs we give a short description of (a) the oxygen band systems in question, (b) the basic properties of pressure-induced infrared absorption, and (c) the known effects of Van der Waals complexes on the pressure-induced absorption of homopolar molecules.

\textit{(a) The Oxygen Electronic Bands in the Region 12 000 Å – 3300 Å}

These band systems involve transitions between the three lowest electronic states of the oxygen molecule, \(3\Sigma^+, \Delta^\text{e}, \text{and } \Sigma^+\), and are:

the infrared system,

\[ ^1\Delta_e \leftarrow ^3\Sigma_g^- \]

the red system,

\[ ^1\Sigma_g^+ \leftarrow ^3\Sigma_g^- \]

and the combination systems

\[ ^1\Delta_e + ^1\Delta_g \leftarrow ^3\Sigma_g^- + ^3\Sigma_g^- \]
\[ ^1\Sigma_g^+ + ^1\Sigma_g^- \leftarrow ^3\Sigma_g^- + ^3\Sigma_g^- \]

All five systems have been extensively studied. A comprehensive bibliography of earlier work has been given by Dianov-Klokov (1966).

For the free molecule the infrared and red systems are forbidden as electric dipole but allowed as magnetic dipole and electric quadrupole radiation (Van Vleck 1934); the observed rotational structure is in accordance with the magnetic dipole selection rules (Babcock and Herzberg 1947; Herzberg and Herzberg 1947).

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The absorption due to the allowed transitions depends linearly on the density but is important only at very low densities. At pressures above about 1 atm the change in the absorption with density requires that a term quadratic in the density be added; this latter term becomes predominant as the pressure is increased (Fahrenfort 1955), and at very high pressures still higher order terms become non-negligible (Robin et al. 1956; Cho et al. 1963).

For the combination systems there is no linear term in the dependence of absorption on density (Salow and Steiner 1936). Ellis and Kneser (1933) interpreted these systems as simultaneous transitions in two oxygen molecules with the absorption of a single photon and suggested that the absorption takes place in loosely bound (O₂)₂ complexes.

(b) Pressure-Induced Absorption

The distinctive properties of the collision-induced absorption of homonuclear diatomic molecules, which have been deduced for the most part from the infrared spectrum of compressed hydrogen, can be summarized as follows:

(i) In the pure gas the integrated absorption coefficient corresponding to a given transition varies essentially as the square of the density in the density range in which binary collisions predominate.

(ii) The rotational selection rules, ΔJ = 0, ±2, are the same as for Raman scattering, which is also an induction effect.

(iii) Double transitions are a common occurrence; in these, both molecules of a collision pair simultaneously undergo the same or different transitions with the absorption of a single photon.

(iv) Induced transitions are greatly broadened as a consequence of the short duration of the collisions; this can be construed as a consequence of the Heisenberg uncertainty principle.

(v) The broad induced transition is, in effect, a continuum of summation and difference tones of the molecular frequency with the continuous distribution of relative kinetic energies of the colliding pairs. The intensities in the low and high frequency wings at frequencies equally displaced from the molecular frequency are related by the Boltzmann factor, e⁻\(\frac{\Delta E}{kT}\), and this imparts a characteristic asymmetry to the bands (Kiss and Welsh 1959).

(vi) The intensity distribution in the high frequency wing has, to a good approximation, a dispersion shape (Kiss and Welsh 1959). However, in some cases a dispersion shape with an exponential tail gives a better reproduction of the experimental data (Bosomworth and Gush 1965).

The theory of pressure-induced absorption has been developed principally by Van Kranendonk (1957, 1958). In his exp-4 model the induced dipole moment, μ, is a sum of two contributions:

\[ μ = \left( A/r^4 \right) + \xi \exp \left( -r/ρ \right) \]

where \( r \) is the intermolecular separation and \( A, \xi \), and \( ρ \) are constants. The first term is due to quadrupolar interaction and has a relatively long range; the induction is strongly orientation dependent and the rotational selection rule is ΔJ = 0, ±2 for homonuclear diatomic molecules. The second term is due to overlap forces and has a shorter range; in hydrogen this interaction is highly isotropic and produces mainly transitions with ΔJ = 0.

(c) Some Remarks on Van der Waals Complexes

General arguments, as well as the results of some recent experiments, delineate to some extent the part played in induced absorption by the bound states of complexes of nonpolar molecules. The magnitude of the binary absorption coefficient depends essentially on the law of induction, eq. [1], and the molecular pair distribution function, \( g_0(r) \). In the low density classical limit g₀(r) depends only on the pair potential, and the integrated intensity of a given transition is independent of whether or not there are molecular pairs in bound states. Thus, the increased intensity of the \( ^1Σ_u^- \rightarrow ^3Σ_u^- \) transition of oxygen, observed by Blickensderfer and Ewing (1967) as the temperature of the gas is lowered from 194 °K, is evidence that the Lennard–Jones constant \( ε/κ \) (≈ 118 °K for oxygen) is of the order of the gas temperature, but does not constitute a proof of the existence of (O₂)₂ complexes. On the other hand, the intensity distribution in an induced band, which depends on the relative translatory motion of the molecular pair, can be profoundly affected if there is an appreciable population of bound states and if these states are sufficiently long-lived. Thus, fine structure accompanying the induced fundamental band of hydrogen gas at 20 °K (Watanabe and Welsh 1965) and hydrogen–argon mixtures at 80 °K (Kudian et al. 1966) is interpreted as arising from transitions between bound states of (H₂)₂ and H₂–Ar complexes. In the case of H₂–N₂ complexes...
and \text{H}_2\text{-CO} mixtures only the envelope of such a fine structure appears to be present; this can be understood in terms of a shortening of the lifetime of the complex by a type of predissociation when the rotational energy of the \text{N}_2 or \text{CO} component exceeds the dissociation energy of the complex. The shortening of the lifetimes of complexes such as \((\text{O}_2)_2\) and \((\text{N}_2)_2\), presumably by this mechanism, has been directly demonstrated in the mass spectrometric studies of Leckenby and Robbins (1966).

Although \((\text{O}_2)_2\) complexes undoubtedly exist even at room temperature, the above considerations make it appear unlikely that transitions between bound states will be directly observed by spectroscopic means. If the lifetimes of the complexes are very short, induced transitions involving complexes will be scarcely distinguishable from transitions in ordinary collision pairs. A detailed study of the band shapes should therefore distinguish between a situation in which the complexes are quasi-stable and one in which they effectively constitute collision pairs; this is the aim of the present investigation.

II. Experimental Methods and Observations

Six strong bands representing four of the five band systems listed above were selected for observation: the 0-0 and 1-0 bands of the \(^1\Delta_g \leftrightarrow ^3\Sigma_g^+\) system at 12 600 \text{ Å} and 10 600 \text{ Å}, respectively, the 0-0 band of the \(^1\Sigma_g^+ \leftrightarrow ^3\Sigma_g^+\) system at 7620 \text{ Å}, the 0-0 and 1-0 bands of the \(^1\Delta_g + ^1\Delta_e \leftrightarrow ^3\Sigma_g^+ + ^3\Sigma_g^+\) system at 6290 \text{ Å} and 5770 \text{ Å}, respectively, and the 0-0 band of the \(^1\Sigma_g^+ + ^1\Delta_g \leftrightarrow ^3\Sigma_g^+ + ^3\Sigma_g^+\) system at 4770 \text{ Å}.

(a) Experimental Details

The absorption cell used was described by Cho et al. (1963) and provided an absorption path length of \(\sim 60\) cm. It was mounted in an insulated container which could be filled with either an ice-water bath or powdered solid carbon dioxide; thermocouples on the cell body indicated the cell temperature.

Commercial grade oxygen was compressed to densities of 100 to 300 amagat by means of a thermal compressor; the pressures were read on a bourdon gauge calibrated against a Hart pressure balance. The amagat densities corresponding to the experimental temperatures and pressures were derived from the tables of Stewart (1966). Since the primary purpose of the investigation was the determination of band shapes the observations on each band were limited to that density range in which the absorption intensity was suitable for the purpose. Since a cell of fixed length was used the density range and the number of densities at which measurements were made differed from band to band.

Experiments were performed at 297 \(^\circ\)K, 273 \(^\circ\)K, and temperatures in the range 220–205 \(^\circ\)K. The temperature in this low range, obtained with solid carbon dioxide, was not precisely the same in different experiments and could not be held constant over long periods. The uncertainty in the gas temperature in a given experiment carried out under these conditions was \(\sim 4\) \(^\circ\)K.

A Jarrell–Ash model 78–480 scanning spectrometer equipped with a 300 line/mm plane grating in an Ebert mount and a collimating mirror of 1.83 cm focal length was used. Because of difficulties due to stray light in the higher orders near the blaze angle (Watanabe and Tabisz 1967), observations were made in the first order where the reciprocal linear dispersion at the exit slit was 9.0 Å/mm. Various filters were used to limit the spectral region entering the absorption tube.

Several detectors were used to cover the wavelength region studied: an EMI \# 6255B photomultiplier for the visible bands, a Phillips 150 CVP photomultiplier cooled by liquid nitrogen for the 7620 Å and 10 600 Å bands, and an Infratron lead sulfide cell \# B3-SA3 for the 12 600 Å band. Since accurate band profiles were required the spectral slit width was kept as small as possible consistent with a satisfactory signal-to-noise ratio and varied from 1.1 \text{ cm}^{-1} for the infrared band to 7.9 \text{ cm}^{-1} for the 4770 Å band.

Examples of the observed profiles are shown below in Figs. 1, 4–9. From these, certain characteristics already noted in previous investigations can be seen. The bands are broad, the double electronic transitions being considerably broader than the single electronic transitions. With the exception of the 7620 Å band, they show no resolved structure. All are asymmetric, the intensity falling off more rapidly on the low frequency side of the maximum than on the high frequency side. When the temperature is lowered, the density remaining the same, the width at half-intensity decreases and the bands become more asymmetric (Fig. 1). The widths of the bands increase slightly with increasing density but the behavior of different bands in this respect is not uniform (Fig. 2).
Fig. 1. (a) Dependence of absorption on density. Absorption coefficient vs. frequency for the 5770 Å band at 273 °K and three different densities. (b) Dependence of band shape on temperature. Shape of the 12 600 Å band for the same gas density at temperatures of 297 °K and 215 °K.

Some variation of width with density was observed also by Dianov-Klokov (1962, 1964) but he seemed to attribute it to experimental error. The frequency, \( \sigma_0 \), shown in the diagrams is that of the band origin calculated from the constants of the free molecule (Herzberg and Herzberg 1947; Babcock and Herzberg 1947). The shift of the intensity maximum from \( \sigma_0 \) is small in all cases (Table II). Above 200 amagat the 6290 Å and 5770 Å intensity maxima begin to shift to higher frequencies, moving 10 to 20 cm\(^{-1}\) in the 200 to 300 amagat range. Previously, Dianov-Klokov (1962) noted a 30 cm\(^{-1}\) shift in the 5770 Å peak but over a much greater density range.

Although the purpose of the experiment was not the precise determination of integrated absorption coefficients, these were evaluated at each temperature and density used. When the density dependence of these integrated absorption coefficients was expressed as a power series,

\[
\int \sigma \, d\sigma = A\rho + B\rho^2 + C\rho^3 + \ldots
\]

the quadratic term was predominant as expected. The linear term was measurable only for the 7620 Å band. This term is due to the allowed magnetic dipole transition in single molecules, and is known to be much smaller in the 12 600 Å and 10 600 Å bands than in the 7620 Å band (Cho et al. 1963); it is of course absent in the double transition bands. Even at the highest density used the cubic term in [2] amounted to only about 10% of the total absorption; terms of higher order than this were therefore neglected.

The values of the coefficients \( A, B, C \) in [2] at 297 °K are given in Table I. For the 12 600 Å and 10 600 Å bands there is good agreement with the \( B \) and \( D \) coefficients of Cho et al. (1963). The values of \( A \) and \( B \) for the 7620 Å band are probably more accurate than the earlier values since the light power of the apparatus was greater and a much narrower spectral slit width was used.

The integrated absorption coefficient at constant density appeared to decrease slightly with temperature. The variation differed from band to band and was never much greater than the uncertainty in the experimental value.
TABLE I
Values at 297 °K of the coefficients in the expansion $\alpha = A + B\sigma^2 + C\sigma^3$

<table>
<thead>
<tr>
<th>Band (Å)</th>
<th>A (cm⁻² amagat⁻¹)</th>
<th>B (cm⁻² amagat⁻²)</th>
<th>C (cm⁻² amagat⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 600</td>
<td>(0)</td>
<td>3.0 x 10⁻⁶</td>
<td>2.6 x 10⁻⁷</td>
</tr>
<tr>
<td>10 600</td>
<td>(0)</td>
<td>2.3 x 10⁻⁶</td>
<td>1.1 x 10⁻⁷</td>
</tr>
<tr>
<td>7 620</td>
<td>5.4 x 10⁻³</td>
<td>5.2 x 10⁻⁵</td>
<td>1.5 x 10⁻⁷</td>
</tr>
<tr>
<td>6 290</td>
<td>—</td>
<td>2.5 x 10⁻⁴</td>
<td>1.5 x 10⁻⁷</td>
</tr>
<tr>
<td>5 770</td>
<td>—</td>
<td>3.3 x 10⁻⁴</td>
<td>4.7 x 10⁻⁸</td>
</tr>
<tr>
<td>4 770</td>
<td>—</td>
<td>1.5 x 10⁻⁴</td>
<td>8.0 x 10⁻⁸</td>
</tr>
</tbody>
</table>

*(0) indicates that the coefficient could not be determined because of the small value of the term involved.

III. Methods Used in the Analysis of the Band Shapes

(a) The Boltzmann Relation in the Intensity Distribution

The Boltzmann relation which has been found to hold between the intensities in the high and low frequency wings of a pressure-induced band has the form

$$\alpha(\sigma_m + \Delta\sigma)/\alpha(\sigma_m - \Delta\sigma) = \exp(h\epsilon\Delta\sigma/kT)$$

where $\sigma_m$ cm⁻¹ is the frequency of the molecular transition and $\alpha(\sigma_m + \Delta\sigma)$ and $\alpha(\sigma_m - \Delta\sigma)$ are the absorption coefficients at frequencies displaced from $\sigma_m$ by $+\Delta\sigma$ and $-\Delta\sigma$ cm⁻¹, respectively. This relation holds for each molecular transition. It should also hold for the overall contour of a band arising from a large number of unresolved transitions if the translational broadening is large compared with the frequency range covered by the component transitions.

The first step in the analysis of the oxygen band shapes was a test to see to what extent the overall profile of each band satisfied the Boltzmann relation [3]. Since the frequency of the molecular transition is unknown, a trial and error method was used to find the “Boltzmann origin”, $\sigma_B$, this frequency is defined as that for which [3] is best satisfied, and is later identified with $\sigma_m$, the frequency of the molecular band origin.

Various frequencies near the intensity maximum were taken as trial values of $\sigma_B$, and

$$\ln \alpha(\sigma_B + \Delta\sigma)/\alpha(\sigma_B - \Delta\sigma)$$

was plotted against $\Delta\sigma$ in each case. Figure 3 illustrates this procedure for the 6290 Å band at 297 °K. The line drawn has a slope equal to $h\epsilon/kT$ with $T = 297$ °K. It is apparent that a change of only 4 cm⁻¹ in $\sigma_B$ makes an obvious change in the fit of the experimental points to the line and that $\sigma_B$ is determined within narrow limits by this procedure. Confirmation is provided by the fact that the same value of $\sigma_B$ is obtained at all three temperatures. Deviations of the experimental points from the line at large values of $\Delta\sigma$ are to be expected since the absorption coefficient on the low frequency side becomes so small that errors in the background matching are serious.

(b) Calculated Band Profiles

As an aid to the interpretation of the bands, profiles based on an assumed character of the transition, and hence on the underlying rotational
structure, were calculated. We recall that there is a close analogy between pressure-induced infrared spectra and Raman spectra. This is not surprising since in induced absorption the electric dipole is produced by the intermolecular force field, whereas in Raman scattering it is induced by the field of the light wave. We assume that this analogy is also present for collision-induced electronic transitions. It will therefore be necessary to consider some of the properties of electronic Raman scattering.

In the theory of Raman scattering (Placzek 1934), the matrix elements of the transition moment give a "scattering tensor" which can be split into three terms corresponding to isotropic, anisotropic, and antisymmetric scattering. The J dependence of the spectra predicted by the anisotropic and antisymmetric terms is the same as for electric quadrupole and magnetic dipole transitions, respectively. The types of scattering which are important in a given case are determined by the symmetry properties of the initial and final states. On this basis, it can be shown that the symmetry selection rules for the transitions \( ^1\Delta_g \leftrightarrow ^3\Sigma_g^- \) and \( ^1\Sigma_g^+ \leftrightarrow ^3\Sigma_g^- \) are the same as for the free molecule, i.e., both electric quadrupole and magnetic dipole transitions are allowed. In the case of the free molecule the magnetic dipole transition is much the stronger; electric quadrupole transitions are as yet undetected. It will be assumed that this is true also for the induced bands, that is, antisymmetric induction is predominant.

In order to calculate the band profiles, a stick spectrum using the frequencies and the relative intensities appropriate to the assumed nature of the transition was first plotted. To simulate the translational broadening each stick was then replaced by a Boltzmann-modified dispersion-exponential line shape (Kiss and Welsh 1959; Bosomworth and Gush 1965; Shapiro and Gush 1966), centered at the stick frequency and having an intensity equal to the height of the stick. The broadening shape may be specified as:

\[
I^+(\sigma) = I(\sigma_b + \Delta\sigma) = I_0/[1 + (\Delta\sigma/\delta)^2]
\]

for \( \sigma_b < \sigma < \sigma_b + 1.75\delta \)

\[
I^+(\sigma) = A \exp (-B\Delta\sigma)
\]

for \( \sigma > \sigma_b + 1.75\delta \)

\[
I^-(\sigma) = I^+(\sigma) \exp (-hc\Delta\sigma/kT)
\]

for \( \sigma < \sigma_b \)

where \( \delta \) is the half-width at half-height and \( A \) and \( B \) are chosen to make \( I \) and its first derivative continuous at \( \sigma_b + 1.75\delta \). When broadened in this way the rotational lines overlap and the band contour is obtained by summing the intensities at regular, small frequency intervals. It is then either area-normalized or least square fitted to the observed profile. This procedure was applied to each band in turn and the results are discussed below.

In the case of the double electronic transitions each molecule can probably make a rotational transition independently of the other. Thus the rotational structure for a double transition is the combination of all pairs of possible rotational transitions. This simple approach may include transitions forbidden by conservation of angular momentum, but detailed considerations of this problem are very involved.

IV. Results of the Analysis of the Band Profiles

The results of the application of the criteria discussed in section III will now be given individually for each of the bands studied.

(a) The Single Electronic Transitions

(i) The 0-0 Band of the \( ^1\Delta_g \leftrightarrow ^3\Sigma_g^- \) System at \( \sim 12600 \text{ Å} \)

When \( \sigma_b = 7895 \pm 5 \text{ cm}^{-1} \) was chosen as the origin, the Boltzmann criterion (as in Fig. 3) was fulfilled over most of the band at all temperatures and pressures; some deviation was apparent within \( \pm 75 \text{ cm}^{-1} \) of the maximum.

A spectrum was constructed using the frequencies of Herzberg and Herzberg (1947) and the magnetic dipole matrix elements of Van Vleck (1934), and broadening each transition with a translational profile of the form [4]. With dispersion half-widths of \( 130 \pm 10 \text{ cm}^{-1} \) and \( 110 \pm 10 \text{ cm}^{-1} \) the experimental profiles at \( 297^\circ \text{K} \) and \( 215^\circ \text{K} \), respectively, could be fitted very well except in the immediate neighborhood of the maximum (Fig. 4). Although there are nine branches \( (\Delta J = 0, \pm 1, \Delta K = 0, \pm 1) \) in the assumed spectrum, the close spacing of the \( \Delta K = 0 \) transitions, \( ^2Q, ^2P \), and \( ^2R \), combined with the wide broadening function makes the calculated profile insensitive to all others.

The "extra" intensity which lies outside the calculated profile near the maximum amounts to only about 5% of the total. It may signify the presence of a weak component of much smaller half-width than the main component and hence due to a longer range interaction. The shape of
Fig. 4. Contour of the 0–0 band of the $^1\Delta_g \leftarrow ^3\Sigma_g^+$ system. Comparison of calculated and observed profiles at 297 °K and a density of 132 amagat.

this weak component cannot be determined accurately, but its intensity maximum appears to be at a frequency lower than that of the main maximum; this shift apparently accounts for the failure of the Boltzmann relation in this region.

We note that a satisfactory analysis of this band can also be obtained by assuming that the $\Delta K = 0$ transitions are split and/or broadened to give a “core” intensity of $\sim 8 \text{ cm}^{-1}$ overall width before the translational broadening is applied. The profile calculated in this way fits over the whole band for broadening functions of half-width 120 cm$^{-1}$ and 100 cm$^{-1}$ at 297 °K and 215 °K, respectively. That the Q branch should be broadened in this way can be explained qualitatively as an effect of the relative orientation of the molecules in the collision or, equivalently, in terms of an anisotropy of the interaction which removes the degeneracy of the upper electronic state of the collision pair.

(ii) The 1–0 Band of the $^1\Delta_g \leftarrow ^3\Sigma_g^-$ System at $\sim 10 \text{ 600 } \AA$

A deviation from the Boltzmann relation observed in a considerable portion of this band was clearly associated with the presence of a shoulder on the higher frequency side of the profile (Fig. 5). A satellite component in this position was observed by Cho et al. (1956) in the liquid and assigned to the double transition in which one molecule makes the electronic transition and the other the 1–0 vibrational transition in the ground electronic state.

In the present case the weak component was extracted by forcing the appropriate Boltzmann relation on the main component with the assumption that the low frequency wing of the band contained no contribution from the weak component. For a given trial origin, $\sigma_0$, the high frequency intensities were calculated from [3], and the “correct” value of $\sigma_0$ taken as that which gave the best agreement of the calculated and observed intensities in the high frequency tail of the band. The profile of the main component is similar to that of the 0–0 band. The profiles of the major and minor components have similar asymmetry but overall half-widths of 210 cm$^{-1}$ and 66 cm$^{-1}$, respectively.

Analyses of this type were carried out for all three temperatures and for a number of densities; all gave frequencies of the maxima in the range $9375 \pm 3 \text{ cm}^{-1}$ for the major and $9447 \pm 4 \text{ cm}^{-1}$ for the minor component. These represent identical shifts from the calculated frequencies, 9366 for the single transition and 9439 cm$^{-1}$ for the double transition. The integrated intensity of each component increased as the square of the density.

The narrowness of the double transition indicates that a longer range interaction is involved in its production, as in the case of the weak component near the peak of the 0–0 band.
(iii) The 0–0 Band of the $^1\Sigma_g^+ \leftarrow ^3\Sigma_g^-$ System at $\sim 7620 \AA$

This is the only band studied for which [2] was found to contain a linear term corresponding to absorption in individual molecules, and the structure observed (Fig. 6) is due to this magnetic dipole contribution. The magnetic dipole component of the band was removed from the total profile by the following procedure: A stick spectrum was constructed using the relative intensities calculated by Schlapp (1932, 1937), and each transition broadened by a dispersion line shape. Since, to our knowledge, no measurements of collision broadening in this band have been made,
the $K$ dependence and the pressure dependence of the half-widths were taken from the results of Jammu et al. (1966) on the collision broadening in the rotational Raman effect of oxygen. The area under the resultant curve was then adjusted to that demanded by the linear term in [2] for the density in question.

Figure 6 shows the observed profile for a density of 180 amagat at 297 °K and the calculated magnetic dipole spectrum for these conditions. When the latter is subtracted from the observed band, the induced component is obtained as shown. Although this component shows qualitatively the asymmetry typical of an induced band, the Boltzmann relation was found to hold only between the low and high frequency tails of the band ($\Delta \sigma > 125 \text{ cm}^{-1}$). This is apparently a consequence of the absence of all $\Delta K = 0$ transitions, which are forbidden by symmetry since $I = 0$ for the oxygen atom. The rotational structure concealed in the induced band was assumed to be the same as for the magnetic dipole spectrum. When each transition was translationally broadened with a half-width, $\delta$, equal to $113 \pm 5 \text{ cm}^{-1}$ at 297 °K, a very good fit to the induced spectrum as derived from the experimental band resulted (Fig. 6). The slight discrepancy in the region of the peak is probably due to inaccuracies associated with the removal of the allowed magnetic dipole component.

This is the only band studied for which the relative importance of the antisymmetric and anisotropic contributions to the induced absorption could be well assessed (Section III(b)). If anisotropic induction were prominent $\Delta K = \pm 3$ branches should occur. The inclusion of such branches in the stick spectrum would not result in as successful a reconstruction of the observed profile as that shown and only the antisymmetric contribution, therefore, appears to be of importance.

(b) The Double Electronic Transitions

(i) The 0–0 Band of the $^1\Delta_g + ^1\Sigma_g^+ \leftrightarrow ^3\Sigma_g^- + ^3\Sigma_g^-$ System at $\sim 4770$ A

The Boltzmann criterion is satisfied for this band at all temperatures and pressures when $\sigma_B$ is taken as 20 930 $\pm 5 \text{ cm}^{-1}$. In contrast to all the other bands studied, $\sigma_B$ in this case is at a frequency lower than the band maximum.

As suggested in Section III(b) it was assumed that the underlying rotational structure is a convolution of the structures of the 0–0 bands of the corresponding single transitions. When the origin of the resulting structure was taken as $\sigma_B$ and each transition was translationally broadened, a good reproduction of the observed profile could be obtained (Fig. 7). The dispersion half-width of the broadening function was $150 \pm 5 \text{ cm}^{-1}$ for 297 °K and $130 \pm 5 \text{ cm}^{-1}$ for 218 °K.
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(ii) The 0–0 Band of the $^1\Delta_g + ^1\Sigma_g \leftarrow ^3\Sigma_g^- + ^3\Sigma_g^-$ System at $\sim 6290$ Å

This band poses problems in analysis which have not been met with in any of the previous cases; this is immediately evident from its very large half-width, namely, 350 cm$^{-1}$ at 297 °K. Nevertheless, the Boltzmann relation holds very well over the whole profile if $\sigma_B$ is taken as 15 822 ± 5 cm$^{-1}$, i.e., 57 cm$^{-1}$ higher than $\sigma_O$. However, all attempts to reproduce the shape of the band by the same procedure as was used for the other bands have been unsuccessful. The convolution of two ' $^3\Sigma_g^- \leftarrow ^3\Sigma_g^-$ rotational structures gives a large number of intense transitions near the band origin; hence, the profile obtained when a broadening function is applied has nearly the same shape as the broadening function itself. The wings conform when the dispersion half-width is taken as 200 cm$^{-1}$ at 297 °K, 180 cm$^{-1}$ at 273 °K, and 165 cm$^{-1}$ at 210 °K; the first of these is illustrated in Fig. 8. Within a range of about ±100 cm$^{-1}$ about $\sigma_B$ the observed intensity falls considerably below that of the broadening function which fits the wings; in other words, the experimental profile is too flat-topped. The “missing” intensity forms, curiously enough, a relatively narrow component with a Boltzmann-modified dispersion curve centered at $\sigma_B$. Two possible explanations could be advanced for this effect, but both must be considered rather improbable. Firstly, if the upper state has a relatively deep Van der Waals minimum and is long-lived, one can imagine a fluorescence (or perhaps, more correctly, phosphorescence) process which cancels some of the absorption by emission. As a second possibility, brought to mind by a well-known property of infrared absorption induced by overlap interaction, the center of the band might be partially removed by an intercollisional interference effect; the theory of this effect has been given recently by Van Kranendonk (1968). However, we do not advance either of these explanations with conviction.

It should be recognized that the actual physical situation is more complex for this band than in any of the previous cases. The upper electronic state of each molecule is $^1\Delta_g$, so that the combined upper state is highly degenerate. Presumably the degeneracy can be removed by the intermolecular interactions to give the band a “core” of different electronic–vibrational energies on each of which a rotational spectrum is superimposed. We have attempted to find the shape of the core by deconvoluting the band by an appropriate translational broadening function, but with indifferent success.

(iii) The 1–0 Band of the $^1\Delta_g + ^1\Sigma_g \leftarrow ^3\Sigma_g^- + ^3\Sigma_g^-$ System at $\sim 5770$ Å

The Boltzmann relation could not be made to fit this band and its failure probably indicates the presence of more than one component. The high frequency tail of this band and that of the 0–0 band are identical; consequently it was assumed that the major component has the same shape as the 0–0 band. Profiles of the two bands, observed at the same temperature and pressure, were matched in the high frequency wing and the difference curve determined (Fig. 9). Consistent results were obtained from profiles observed under different experimental conditions. The Boltzmann origin $\sigma_B$ of the main component was displaced 79 ± 7 cm$^{-1}$ above $\sigma_O$, the peak of the minor component by 35 ± 5 cm$^{-1}$ above $\sigma_O$. The intensities of the two were in the ratio 15:1; the weak component was narrower and appeared more symmetrical than the strong component but its precise shape could not be determined because of its low intensity. In the absence of a detailed explanation of the shape of the peak it is impossible to affirm that it should be the same for the 1–0 as for the 0–0 band. However, the failure of the Boltzmann relation in this band lends support to the suggestion that there is a weak second component with a different half-width and produced by a longer range interaction.
FIG. 9. Separation of the 1-0 band of the $^{1}\Delta_{g} + ^{1}\Delta_{g} \rightarrow ^{3}\Sigma_{g}^{-} + ^{3}\Sigma_{g}^{-}$ system into two components. Curve shown is for a temperature of 273 °K and a density of 173 amagat.

V. Discussion and Conclusions

The general conclusions which can be drawn from the results of the analyses of IV can be summarized as follows:

1) The Boltzmann relation holds with rather high accuracy for all of the bands examined. In the cases in which it shows deviation it has been necessary to postulate the presence of a second component in the band, but the second component never involves more than a small fraction of the total intensity. The validity of the Boltzmann relation in itself constitutes a convincing proof that the oxygen bands in question arise essentially from collision-induced electronic transitions.

2) The Boltzmann origin, $\sigma_B$, can be identified with the band origin, that is, the frequency of the electronic-vibrational transition. The values of $\sigma_B$ obtained from the analyses are summarized in Table II: these values were found to be independent of pressure and temperature within the error limits given. The electronic-vibrational frequencies, $\sigma_e$, calculated from the constants of the free molecule, allow us to calculate the frequency shifts, $\sigma_B - \sigma_e$, in the induced transitions. The shifts have one order of magnitude for the single transitions and another (apart from sign) for the double transitions. They are remarkably small, especially when they are presented as percentages of the absolute frequencies of the transitions; for the single transitions the average frequency shift is 0.1% and for the double transitions 0.4% of the transition frequency. The frequency shifts obtained from the Boltzmann analysis thus form a consistent pattern, whereas the frequency shifts of the band maxima are much more haphazard.

The frequency shifts obtained here are of the same order as those obtained by a different kind of analysis in solid $\alpha$-oxygen (Landau et al. 1962); in the latter both the single and the double transitions are shifted by about 0.4% from the calculated values. The anomalous negative shift for the 4770 Å band appears in the spectrum of the gas and the solid.

3) Our attempts to fit the band profiles by assuming a rotational structure and broadening each transition by a translational broadening function can be described as moderately successful. Table III summarizes the dispersion half-widths, $\delta$, of the broadening functions for the cases in which comparable results at different temperatures were obtained. The dispersion half-width varies as the square root of the temperature as is usual for pressure-induced absorption. The half-widths are greater for the double transitions than for the single transitions, but both are of the order of magnitude expected for the short-range overlap interaction.

4) Although the two criteria used in the analysis account for most of the intensity of the bands, in some cases there was a small residual
TABLE II

Comparison of observed and calculated band frequencies

<table>
<thead>
<tr>
<th>Band (Å)</th>
<th>Observed peak frequency ( \sigma_{\text{max}} ) (cm(^{-1} ))</th>
<th>Calculated band origin ( \sigma_0 ) (cm(^{-1} ))</th>
<th>Boltzmann origin ( \sigma_\text{B} ) (cm(^{-1} ))</th>
<th>( \sigma_\text{B} - \sigma_0 ) (cm(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>7.897 ± 7</td>
<td>7.882.4</td>
<td>7.895 ± 5</td>
<td>+13 ± 5</td>
</tr>
<tr>
<td>10600</td>
<td>9.390 ± 10</td>
<td>9.365.9</td>
<td>9.376 ± 3</td>
<td>+ 9 ± 3</td>
</tr>
<tr>
<td>7620</td>
<td>13.105 ± 5</td>
<td>13.120.9</td>
<td>13.137 ± 3</td>
<td>+16 ± 3</td>
</tr>
<tr>
<td>6290</td>
<td>15.875 ± 20</td>
<td>15.764.8</td>
<td>15.822 ± 5</td>
<td>+57 ± 3</td>
</tr>
<tr>
<td>5770</td>
<td>17.327 ± 10</td>
<td>17.248.3</td>
<td>17.327 ± 7</td>
<td>+79 ± 7</td>
</tr>
<tr>
<td>4770</td>
<td>20.964 ± 20</td>
<td>21.003.3</td>
<td>20.930 ± 5</td>
<td>-73 ± 5</td>
</tr>
</tbody>
</table>

TABLE III

Variation of the half-width of the broadening function with temperature

<table>
<thead>
<tr>
<th>Band (Å)</th>
<th>Temperature (K)</th>
<th>Half-width ( \delta )</th>
<th>( \delta ) ( \sigma_1/\sigma_2 )</th>
<th>( (T_1/T_2)^{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12400</td>
<td>297</td>
<td>120</td>
<td>1.2</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>215</td>
<td>100</td>
<td>1.16</td>
<td>1.17</td>
</tr>
<tr>
<td>4770</td>
<td>218</td>
<td>130</td>
<td>1.16</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>297</td>
<td>200</td>
<td>1.2</td>
<td>1.20</td>
</tr>
<tr>
<td>6290</td>
<td>206</td>
<td>165</td>
<td>1.2</td>
<td>1.20</td>
</tr>
</tbody>
</table>

intensity. In general, the extra intensity is in the form of a component of much smaller half-width which, if it is indeed real, must originate in a longer range interaction. The half-widths of these subsidiary components are of the order of those found for quadrupole-induced infrared transitions.

(5) No specific features of the spectra can be assigned to transitions between bound states of \((O_2)_2\) complexes. Although such complexes undoubtedly exist at any temperature at the concentration expected from statistical mechanics, their lifetimes are probably too small to be spectroscopically observable.

In conclusion it may be stated that the present experimental investigation has shown that the electronic band systems of oxygen observed in the compressed gas in the near-infrared and visible regions conform to all the known criteria for collision-induced spectra as far as these can be applied to these systems; they are therefore properly designated as pressure-induced electronic absorption spectra. Probably not much more can be done experimentally in the further elucidation of the production mechanism; a set of broad unresolved (and apparently unresolvable) bands does not leave much scope for the experimental physicist once the density and temperature dependences of the intensities and band profiles have been ascertained. The main requirement is of course a detailed theoretical study of the possible induction mechanisms which are operative during \(O_2-O_2\) collisions and a dynamical treatment of the collisions themselves. This may be more difficult than the parallel case of pressure-induced translational-rotational-vibrational spectra but the results would be of considerable interest.

REFERENCES