Physical Chemistry

Cumulative Exam
January 13, 2005
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This cumulative exam is about the oxygen diatomic molecule. Many aspects of the electronic structure of the O_2 molecule are revealed by its molecular spectra. Demonstrate your understanding of some fundamental concepts in physical chemistry by answering the questions on page 5.

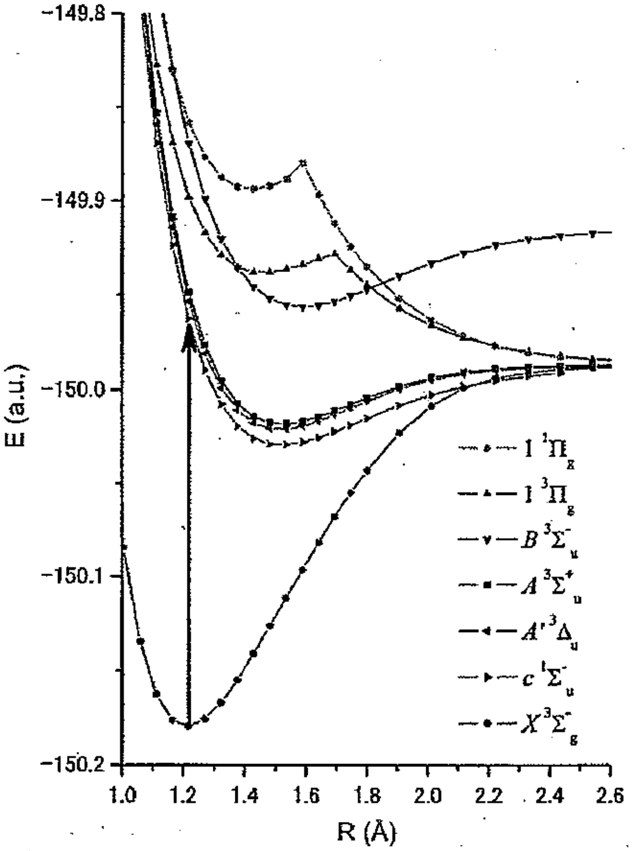
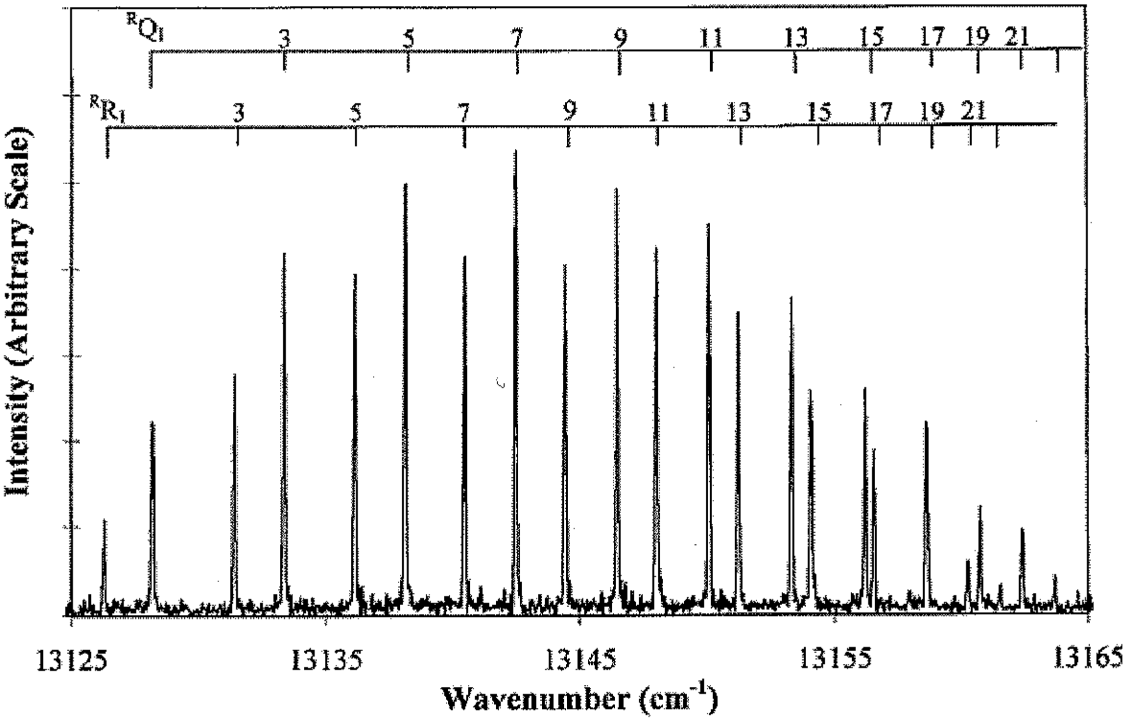


Fig. 1 The calculated potential energy curves of the O_2 molecule. Shown are, from the lowest one, $X^3\Sigma_g^-$, $c^1\Sigma_u^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$, $B^3\Sigma_u^-$ $1^3\Pi_g$, $1^1\Pi_g$. Not shown are $b^1\Sigma_g^+$ and $a^1\Delta_g$ which are just above the ground $X^3\Sigma_g^-$; also not shown are other higher energy electronic states.
The $B^3\Sigma_u^-$ dissociates into $O(^3P)+O(^3D)$, whereas the $b^1\Sigma_g^+$, $a^1\Delta_g$, $A^3\Sigma_u^+$, and the ground $X^3\Sigma_g^-$ dissociate into $O(^3P)+O(^3P)$ atoms.

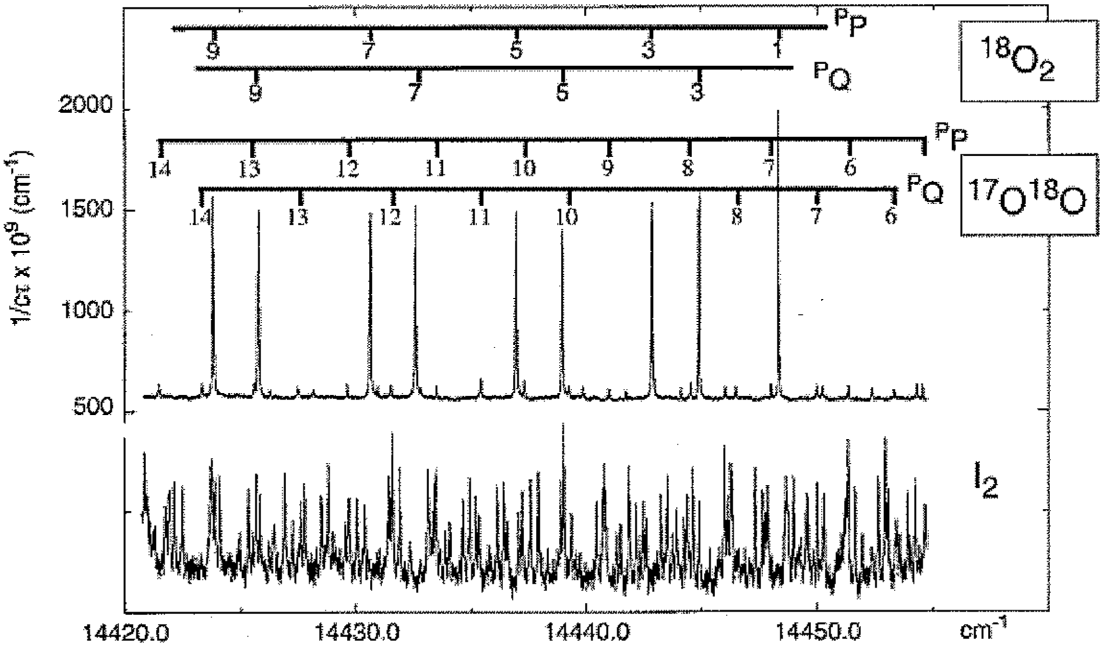
The O_2 molecule is a well studied system because of its importance to the atmospheric chemistry on Earth. Its importance comes from the great abundance, reactivity, and photosensitivity in the atmosphere, and detailed spectroscopic information is available. In recent years, several experimental and theoretical groups have re-investigated this molecule. The figure given above is from a theoretical study of the spectral band system associated with the electronic transition shown by the arrow in the figure taken from this paper [R. Takegami and S. Yabushita, *J. Mol. Spectrosc.* 229, 63-77 (**2005**)].

Some of the very well studied spectral band systems are the Schumann-Runge bands in the wavelength region 175 to 205 nm $\{B^3\Sigma_u^- \leftrightarrow X^3\Sigma_g^-\}$ sections of which are shown in ***Fig. 4-5***, and the so-called "atmospheric bands" which are weak forbidden transitions, $\{b^1\Sigma_g^+ \leftrightarrow X^3\Sigma_g^-\}$ but are easily observed because of the long path lengths available, sections are shown in ***Fig. 2-3***, thus they are an important component of the Earth's atmospheric absorption spectrum. Examples of sections of spectra from these band systems are shown below:

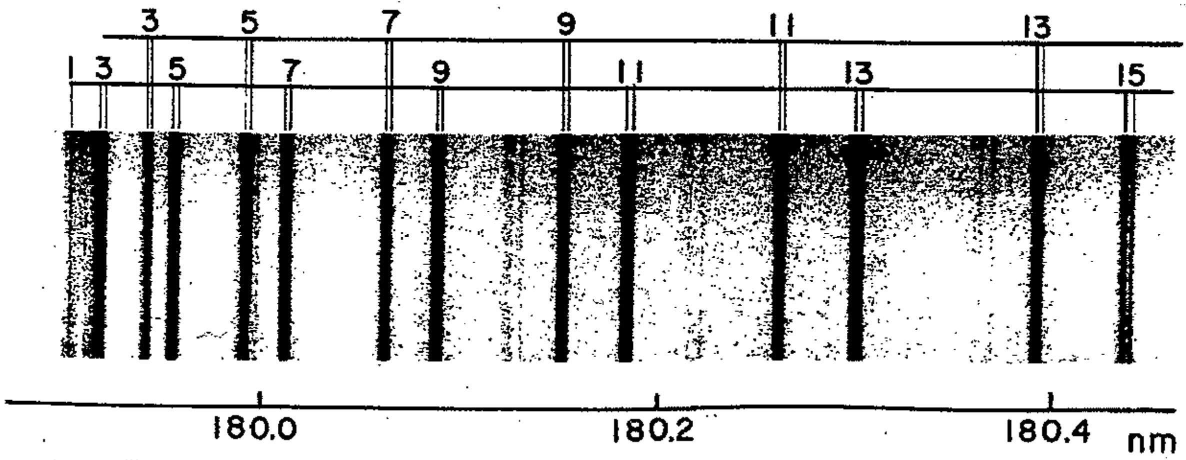
(a) ***Fig. 2*** The R branch of the 0-0 band of the atmospheric bands, recorded in emission: [*J. Mol. Spectrosc.* 184, 162-166 (**1997**)]:



(b) ***Fig. 3*** The spectrum from a (95%) $^{18}O_2$-enriched sample at 31.6 Torr (top) and a simultaneously recorded I_2 absorption spectrum (for calibration, bottom). $^{18}O_2$ lines, as indicated, are saturated. This spectrum was used to determine line positions of $^{17}O^{18}O$ which exists as a very minor component: [*J. Mol. Spectrosc.* 192, 162-168 (**1998**)]



(c) ***Fig. 4*** The (v'=12 →v"=0) Schumann-Runge absorption band of $^{18}O_2$ [J. Mol. Spectrosc. 131, 96-112 (**1988**)]:



(d) ***Fig. 5*** The earlier Schumann-Runge spectra shown below are absorption traces of the v'=2 →v"=0 and v'=3→v"=0 taken at pressures 40 and 25 cm Hg respectively [*J. Opt. Soc. Am.* 58, 1621 (**1968**)]:

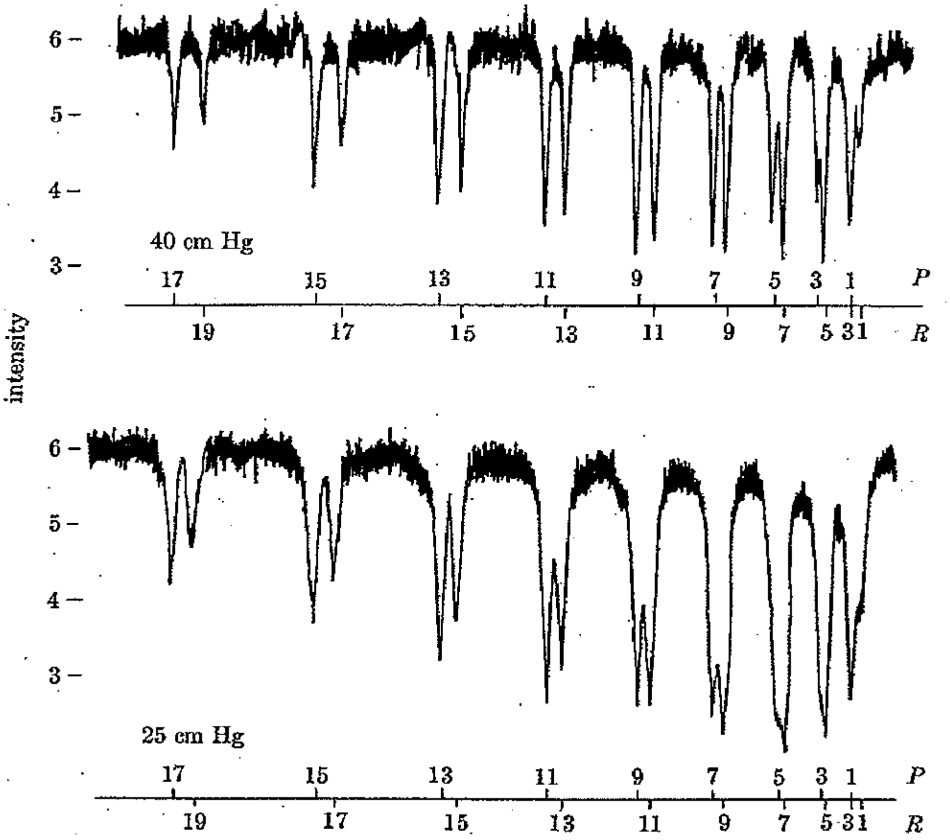
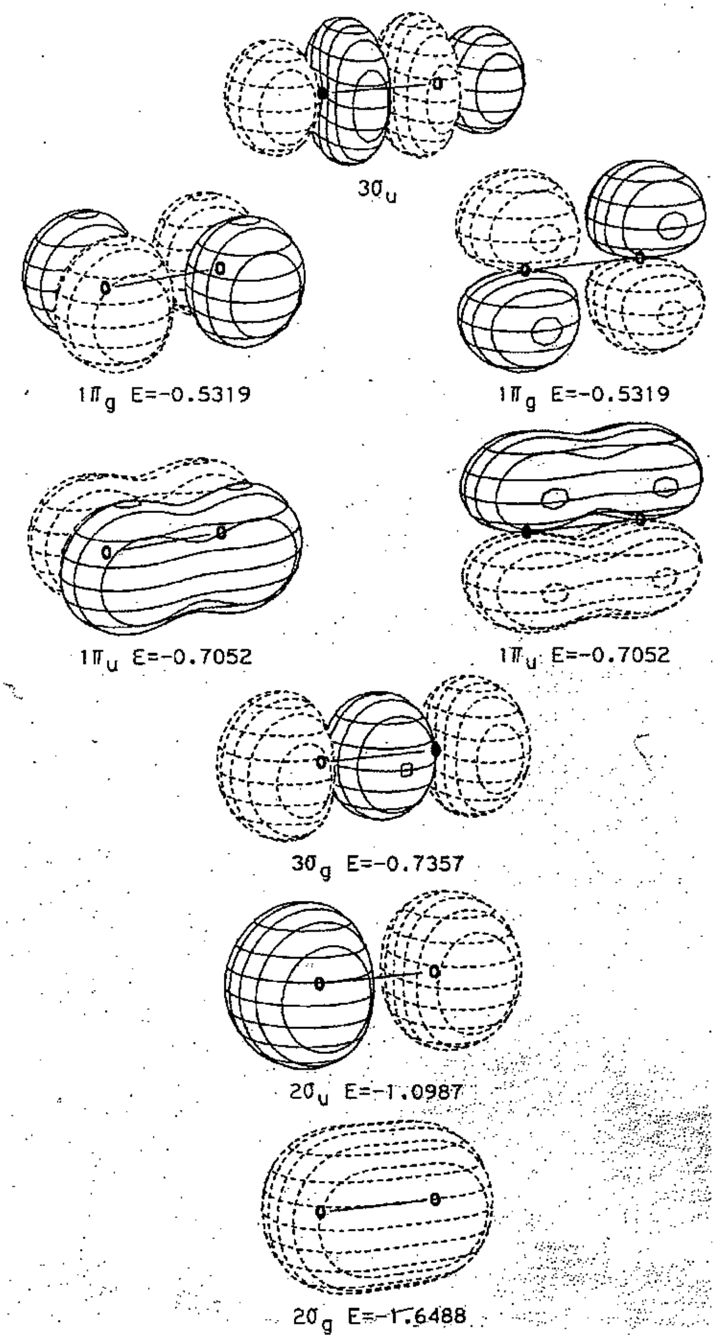


Fig. 6 Some of the molecular orbitals of the O_2 molecule are shown below:



Questions: *Do not attempt to answer the following questions before you have digested the previous 4 pages. Although there is much to read and comprehend, the required answers are short and require no computations beyond addition and subtraction.*
(1) What is the ground state electronic configuration of O_2 molecule?

(2) Several terms (electronic states) are associated with the ground state electronic configuration. Determine these terms and order them in energy according to Hund's rules. Note that these electronic states should all dissociate to ground state oxygen atoms, since the lowest valence orbitals are used in the formation of the molecular orbitals in the ground electronic configuration, and the lowest molecular orbitals are involved in the ground state electronic configuration of O_2. (In other words, check the states you have arrived at against the experimental information given to you!)

(3) State the principle or approximation which forms the basis for discussions of "potential energy surfaces such as those given in ***Fig. 1***. Write out, in a reasonably compact but explicit form, the equation to be solved in order to obtain the values corresponding to the points appearing in ***Fig. 1***. Suppose this equation is solved and the potential energy surfaces such as those shown in the lowest part of ***Fig. 1*** are found. Which energy terms have not been included in finding the potential energy surfaces? In the light of (at least a part) of your answer to that question, provide a plausible explanation of why the potential functions for states $1^3\Pi_g$ and $1^1\Pi_g$ in ***Fig. 1*** possess what appear to be uncharacteristic maxima. Observed spectroscopic transitions between electronic states can be interpreted with the help of potential energy surfaces such as shown in Fig. 1, and you should refer to Fig. 1 while examining the spectra in Figures 2-5.

(4) The "atmospheric band system", a small section of which is shown in ***Fig. 2***, corresponds to very weak transitions so the spectrum shown, for example, had to be obtained by accumulating 320 scans. This particular electronic transition is said to be "triply forbidden". Which three selection rules are violated in observing the "atmospheric band system"?

(5) Note in ***Fig. 4*** the labels such as P(13) and R(15). Which transition does the standard notation P(13) correspond to? Which transition does the standard notation R(15) correspond to? The spectral resolution in ***Fig. 4*** is sufficient to show that the P(13) and R(15) lines (for example) are split into three components, as are the other lines. The wavenumbers (cm^{-1}) are as follows:

P(13) : 55 434.08, 55 435.00, 55.435.10
R(15) : 55 419.92, 55 420.98, 55 421.40

Explain (with the help of simple equations, quantum numbers, whatever) why there are 3 of each in the case of O_2.

(6) Usually, only the P ($\Delta J=-1$) and R ($\Delta J=+1$) branches of a vibrational band can be observed in an electronic transition of a diatomic molecule, and no Q branch ($\Delta J=0$). Give an explanation for the observation of lines of the Q branch for oxygen molecule, for example, note the labels ^RR and ^RQ, for example as seen in ***Fig. 2***, and ^PP and ^PQ in ***Fig. 3*** for oxygen molecule and figure out which transitions these labels stand for.

(7) In ***Fig. 3***, the lines that have been assigned to different isotopomers of the oxygen molecule are labeled with numbers, for example $^{P}Q(9)$, $^{P}Q(7)$. Which quantum number of which state do you think the number 7 in the label corresponds to? Such spectra are taken by using isotopically labeled compounds, of course. Explain, with the help of equations, specifically why the $^{P}Q(7)$ line for $^{18}O_2$ is offset from the $^{P}Q(7)$ line for $^{17}O^{18}O$ in ***Fig. 3***, despite the fact that both sets of lines, those for $^{18}O_2$ and those for $^{17}O^{18}O$ correspond to transitions between the same two electronic potential energy surfaces?

(8) ***Fig. 5*** gives a low-resolution early absorption spectrum, which shows for the naturally abundant oxygen molecules (nearly all $^{16}O_2$), that only the odd-numbered lines are present in the P and R branches. This is not a mistake in assignment of Schumann-Runge spectral lines by the authors. To confirm, notice in the "atmospheric band system" spectrum in ***Fig. 3***, that lines that have been assigned to $^{18}O_2$ have corresponding lines that have been assigned to $^{17}O^{18}O$, with one set offset with respect to the other set, as already explained why in question 7, however, every other line (the even-numbered ones) in the spectrum of the $^{18}O_2$ isotopomer is missing, while all lines (odd <u>and</u> even) are present in the $^{17}O^{18}O$. Give an explanation of this phenomenon. We see this here in two different electronic transitions. Do you expect all even-numbered lines to be completely absent from <u>all</u> electronic spectra of the $^{18}O_2$ isotopomer? Explain if and when <u>only</u> odd-numbered lines can be present.

(9) The v"=0 and v"=1 levels of the ground electronic state are very well characterized from Raman spectroscopy (no spectra shown here), so the spectroscopic constants may be considered accurately known for these levels. Given that this is the case, which spectroscopic constants can then be obtained from analysis of the lines in ***Fig. 2***? Explicitly identify which constants (that is, name them in addition to providing the standard symbols), and for which states.

$$E = U_\alpha(R_e) + (v+½)\nu_e - x_e\nu_e\,(v+½)^2 + y_e\nu_e\,(v+½)^3 +$$
$$B_eJ(J+1) - D_e[J(J+1)]^2 - \alpha_e(v+½)J(J+1) + Y_{00}$$

where all spectroscopic quantities are expressed in energy units (or the corresponding frequency or wavenumbers). In energy units, the following are positive quantities:

$B_e \equiv \hbar^2 / 2\mu\, R_e^2$ B_e rotational constant

$$h x_e\nu_e \equiv ¼\, B_e^2 / (h\nu_e)^2 \cdot \{ ({}^{10}/_3)B_e[U'''(R_e)R_e^3]^2 / (h\nu_e)^2 - U^{iv}(R_e)R_e^4 \}$$

$x_e\nu_e$ anharmonicity constant

$$D_e \equiv 4\, B_e^3 / (h\nu_e)^2$$

D_e centrifugal distortion constant

$$\alpha_e \equiv -\,2\, B_e^2 / h\nu_e \cdot \{3 + 2\, B_e[U'''(R_e)R_e^3]^2 / (h\nu_e)^2\}$$

α_e vibrational rotational coupling constant

$$Y_{00} \equiv B_e^2 / 16(h\nu_e)^2 \cdot \{ U^{iv}(R_e)R_e^4 - ({}^{14}/_9)B_e[U'''(R_e)R_e^3]^2 / (h\nu_e)^2 \}$$

$h\nu_e \equiv (h/2\pi)[\,U''(R_e) / \mu\,]^{½}$ ν_e harmonic frequency

μ reduced mass $1/\mu = 1/m_A + 1/m_B$

R_e equilibrium bond length

Rotational constant for the v<u>th</u> vibrational state is B_v

$$B_v = B_e - \alpha_e\,(v+½)$$

Y_{00} same anharmonic correction to <u>every</u> vibrational level

Since Y_{00} is a constant for the electronic state, it is usually put together with $U(R_e)$.

Answers:

1. The ground state electronic configuration of O_2 molecule:
From Fig. 6 we can use the molecular orbital designations and orbital energy ordering. The inner core orbitals are not shown but we know which ones they are. There are 16 electrons in the molecule. $(1\sigma_g)^2(1\sigma_u{}^*)^2(2\sigma_g)^2(2\sigma_u{}^*)^2(3\sigma_g)^2(1\pi_u)^4\,(1\pi_g{}^*)^2$

2. The terms (electronic states) which are associated with the ground state electronic configuration can be obtained by considering the orbital and the spin angular momentum components. Closed shells have net zero orbital and zero spin angular momentum because all components (+ and -) are represented equally. Thus, we just have to consider $(1\pi_g{}^*)^2$. π means the component of the electron orbital angular momentum along the line of centers is $\lambda = \pm 1$.

	electron 1	electron 2	net	Λ	S	Term
g or u	g	g	g			
λ, m_s	+1, +½	+1, -½	λ=+2,M_s=0	Δ	0	$^1\Delta_g$
λ, m_s	-1, +½	-1, -½	λ=-2,M_s=0			
λ, m_s	+1, ±½	-1, ±½	λ=0,M_s=±1,0,0	Σ	1, 0	$^3\Sigma^-{}_g$, $^1\Sigma^+{}_g$
λ, m_s	-1, ±½	+1, ±½	λ=0,M_s=±1,0,0	Σ	1, 0	

$^3\Sigma^+{}_g$, $^1\Sigma^-{}_g$, $^3\Delta_g$ are forbidden by Pauli exclusion principle. The only allowed electronic functions are:

$\{\pi^+(1)\bullet\pi^-(2) + \pi^-(1)\bullet\,\pi^+(2)\}\,[\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)]$: $^1\Sigma^+{}_g$ and
$\{\pi^+(1)\bullet\pi^-(2) - \pi^-(1)\bullet\,\pi^+(2)\}\,\{\alpha(1)\bullet\alpha(2)$, or $\beta(1)\bullet\beta(2)$, or $[\alpha(1)\bullet\beta(2) + \beta(1)\bullet\,\alpha(2)]$: $^3\Sigma^-{}_g$ and
$\{\pi^+(1)\bullet\pi^+(2)$ or $\pi^-(1)\bullet\,\pi^-(2)\}\,[\alpha(1)\bullet\beta(2) - \beta(1)\bullet\alpha(2)]$: $^1\Delta_g$

According to Hund's rules, the electronic state of higher spin angular momentum is lower in energy; and for the same spin angular momentum, the electronic state of higher orbital angular momentum is lower in energy. Thus, energy order is

$$U(^3\Sigma^-{}_g) < U(^1\Delta_g) < U(^1\Sigma^+{}_g)$$

3. The Born-Oppenheimer separation of electronic motion problem from the nuclear motion problem makes it possible to have the concept of potential energy surfaces for molecular states. The values corresponding to the energy values at specific fixed values of the internuclear distance R_{AB} are the eigenvalues $U(R_{AB})$ of the Schrödinger equation for the electronic motion problem:

$$\Big\{\Sigma_i\,\{-(h^2/2m_e)\nabla^2{}_i - Z_Ae^2/r_i - Z_Be^2/r_i + \Sigma_j\,e^2/r_{ij}\} + Z_AZ_Be^2/R_{AB}\Big\}\,\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots)$$
$$= U(R_{AB})\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots)$$

At specific RAB values, crossing between potential curves may occur, that is, two different $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots)$ for the same value of $U(R_{AB})$ (that is, degeneracy).The energy terms that have been neglected in doing the Born-Oppenheimer separation are the interaction terms between electronic and vibrational motion. When these neglected terms in the Hamiltonian are put back as a perturbation ***h***, then the degenerate functions become mixed (if they are the same symmetry) and the energies split away from the original equal values. Such mixing has clearly occurred in the two potential surfaces ($1^3\Pi_g$ and $1^1\Pi_g$) that exhibit cusps or maxima where the "avoided crossing" would have occurred. There must exist two other potential surfaces $^3\Pi_g$ and $^1\Pi_g$ that exhibit minima close to these avoided crossing points.

4. The transition $b^1\Sigma_g^+ \leftrightarrow X^3\Sigma_g^-$ is triply forbidden in that the electric dipole selection rules $\Delta S = 0$, $g \leftarrow\times\rightarrow g$, $\Sigma^+ \leftarrow\times\rightarrow \Sigma^-$ are violated.

5. P(13) corresponds to the transition (v'', $J_{rot}''=13$) $\leftrightarrow$ (v', $J_{rot}'=12$).
R(15) corresponds to the transition (v'', $J_{rot}''=15$) $\leftrightarrow$ (v', $J_{rot}'=16$).
There are three of each in the case of O_2 because the ground state $X^3\Sigma_g^-$ has spin angular momentum S=1 which has components M_S = 1, -1, 0. Thus, the net angular momentum is $J_{net} = J_{rot}+1$, $J_{rot}-1$, $J_{rot}+0$, respectively. Each of these three states is capable of transitions to the upper state $B^3\Sigma_u^-$, which also has M_S = 1, -1, 0.

6. When there is a non-vanishing electron angular momentum, here S = 1 in the ground $X^3\Sigma_g^-$ state, in addition to the molecular rotational angular momentum J_{rot}, the transitions $\Delta J = 0$ are no longer forbidden. The notation in Fig. 2 & 3 for the ($b^1\Sigma_g^+ \leftrightarrow X^3\Sigma_g^-$) bands is
$^PP(7)$ corresponds to (v'', $J_{net}''=7$, $J_{rot}''=7$, $M_S=0$) $\leftrightarrow$ (v', $J_{net}'=J_{rot}'=6$).
$^RR(7)$ corresponds to (v'', $J_{net}''=7$, $J_{rot}''=7$, $M_S=0$) $\leftrightarrow$ (v', $J_{net}'=J_{rot}'=8$).
$^PQ(7)$ corresponds to (v'', $J_{net}''=7$, $J_{rot}''=8$, $M_S=+1$) $\leftrightarrow$ (v', $J_{net}'=J_{rot}'=7$).
$^RQ(7)$ corresponds to (v'', $J_{net}''=7$, $J_{rot}''=6$, $M_S=-1$) $\leftrightarrow$ (v', $J_{net}'=J_{rot}'=7$).

7. The $^PQ(7)$ corresponds to (v'', $J_{net}''=7$, $J_{rot}''=8$, $M_S=+1$) $\leftrightarrow$ (v', $J_{net}'=J_{rot}'=7$), as already mentioned in the answer to 6. The difference between the positions of corresponding $^PQ(7)$ lines for $^{18}O_2$ and $^{17}O^{18}O$ arises from the fact that the v" vibrational energy for $^{18}O_2$ and $^{17}O^{18}O$ differ in that the harmonic frequency is $(1/2\pi)[k/\mu]^{1/2}$. While k is independent of mass since it is the second derivative of the electronic energy U at R_{equil}, $1/\mu$ = 1/18+1/18 versus $1/\mu$ = 1/17+1/18 for the two isotopomers. The vibrational frequencies of both the lower and upper electronic states are lower for $^{18}O_2$ than for $^{17}O^{18}O$. Thus, the transitions, which are centered around $v'' \leftrightarrow v'$ will correspond to non-identical energy differences for $^{18}O_2$ and $^{17}O^{18}O$.

8. Both even and odd J_{rot} states are possible for $^{17}O^{18}O$ since there are no symmetry restrictions associated with the nuclear spin states. On the other hand for each of $^{18}O_2$ and $^{16}O_2$ molecules, the nuclei are exchangeable since they are identical isotopes. Pauli exclusion principle states that the total wavefunction of a molecule has to be symmetric with respect to interchange of any equivalent <u>bosons</u>, such as ^{18}O or ^{16}O (which have zero spin). Thus,

$$P_{AB}\{\Psi_{electronic}\bullet\Psi_{vibr}\bullet\Psi_{rot}\bullet\Psi_{nuclear\ spin}\} = +\Psi_{electronic}\bullet\Psi_{vibr}\bullet\Psi_{rot}\bullet\Psi_{nuclear\ spin}$$

Since nuclear spins are zero, the only nuclear spin state in the $^{18}O_2$ or $^{16}O_2$ molecule is $\gamma(A)\bullet\gamma(B)$ where γ corresponds to $M_I=0$. This does not change sign upon interchange of A and B.

$P_{AB}\Psi_{vibr} = +\Psi_{vibr}$ since there is no dependence of this function on the coordinates of A and B, only a dependence on the distance R_{AB}.

$P_{AB}\Psi(X^3\Sigma_g^-)_{electronic} = -\Psi(X^3\Sigma_g^-)_{electronic}$, the product g•— is minus

$P_{AB}\Psi(b^1\Sigma_g^+)_{electronic} = +\Psi(b^1\Sigma_g^+)_{electronic}$, the product g•+ is plus

$P_{AB}\Psi_{rot} = P_{AB}Y_{JM}(\theta,\phi) = (-1)^J Y_{JM}(\theta,\phi)$ since odd J spherical harmonic functions change sign upon interchange of A and B, while even J functions do not.

Thus, overall, only the Ψ_{rot} functions with <u>odd J can exist in the ground</u> $X^3\Sigma_g^-$ electronic state, while only the Ψ_{rot} functions with <u>even J can exist in the upper</u> $b^1\Sigma_g^+$ electronic state for $^{18}O_2$ molecule or for $^{16}O_2$ molecule. Indeed, we find that the even J″ lines are missing in all the absorption spectra of these isotopomers in Fig. 2, 3, 4 and 5! All transitions involving the ground electronic state will exhibit only odd J″ lines for $^{18}O_2$ molecule or for $^{16}O_2$ molecule.

On the other hand, if we observe those electronic transitions to a <u>lower</u> electronic state of the type Σ_g^+ or Σ_u, only the even J″ lines will be observed, since only even J″ states can exist for $^{18}O_2$ molecule or for $^{16}O_2$ molecule in these electronic states.

9. Fig. 2 involves $b^1\Sigma_g^+(v' = 0) \rightarrow X^3\Sigma_g^-(v'' = 0)$ emission lines for $^{16}O_2$ molecule. If all the lower level spectroscopic constants are well known, then it should be possible to determine the spectroscopic constants for the $b^1\Sigma_g^+(v' = 0)$ state. From the given equation,

$$\begin{aligned} E = {} & U_\alpha(R_e) + (v+\tfrac{1}{2})\nu_e - x_e\nu_e\,(v+\tfrac{1}{2})^2 + y_e\nu_e\,(v+\tfrac{1}{2})^3 + B_eJ(J+1) - D_e[J(J+1)]^2 \\ & - \alpha_e(v+\tfrac{1}{2})J(J+1) + Y_{00} \end{aligned}$$

we find by difference,

$$\begin{aligned} \Delta E = {} & U_\alpha(R_e)' - U_\alpha(R_e)'' + (v'+\tfrac{1}{2})\nu_e' - (v''+\tfrac{1}{2})\nu_e'' - x_e\nu_e'(v'+\tfrac{1}{2})^2 + x_e\nu_e''(v''+\tfrac{1}{2})^2 \\ & + y_e\nu_e'(v'+\tfrac{1}{2})^3 - y_e\nu_e''(v''+\tfrac{1}{2})^3 + B_e'J'(J'+1) - B_e''J''(J''+1) \\ & - D_e'[J'(J'+1)]^2 + D_e''[J''(J''+1)]^2 \\ & - \alpha_e'(v'+\tfrac{1}{2})J'(J'+1) + \alpha_e''(v''+\tfrac{1}{2})J''(J''+1) \end{aligned}$$

We apply the specific case v′ = 0 and v″ = 0 to get,

$$\begin{aligned} \Delta E = {} & U_\alpha(R_e)' - U_\alpha(R_e)'' + Y_{00}' - Y_{00}'' \\ & + \tfrac{1}{2}(\nu_e' - \nu_e'') - \tfrac{1}{4}(x_e\nu_e' - x_e\nu_e'') + \tfrac{1}{8}(y_e\nu_e' - y_e\nu_e'') \\ & - \tfrac{1}{2}[\alpha_e'J'(J'+1) - \alpha_e''J''(J''+1)] + B_e'J'(J'+1) - B_e''J''(J''+1) \\ & - D_e'[J'(J'+1)]^2 + D_e''[J''(J''+1)]^2 \end{aligned}$$

We can determine the values of the constants $U_\alpha(R_e)' - U_\alpha(R_e)'' + Y_{00}' - Y_{00}''$ and $\tfrac{1}{2}\nu_e' - \tfrac{1}{4}x_e\nu_e' + \tfrac{1}{8}y_e\nu_e'$ and α_e' and D_e'.