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The Visible Spectrum of Liquid Oxygen in the General Chemistry Laboratory

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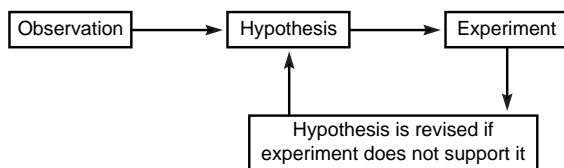
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One great success of MO theory championed at the general chemistry level is that it correctly predicts O_2 to be paramagnetic. In fact, many instructors illustrate this paramagnetic behavior as a demonstration in lecture (1). While the “Evans” Johnson Matthey balance has greatly simplified measurements of magnetic susceptibility (2)¹ of solid and liquid samples at or near room temperature, it is difficult to extend this to liquid oxygen with a normal boiling point of $-183\text{ }^\circ\text{C}$.

A less exploited feature of MO theory of O_2 is its ability to explain the visible spectrum of liquid oxygen. Unlike magnetic susceptibility measurements, the optical spectrum of liquid oxygen is relatively easy to obtain. The spectral features of liquid oxygen have been known for a long time (3, 4) and continue to be investigated (5). The purpose here is simply to share the viability and the highly instructive nature of this experiment at the general chemistry level.

Although general chemistry textbooks have some form of the following diagram to illustrate how science works, few experiments incorporate a meaningful revision of hypothesis. In this experiment, the instructor guides the student through three hypotheses, the third of which explains the spectrum of liquid oxygen.



In examining the spectrum of liquid oxygen, students (i) come to better understand molecular orbital energy levels and the effect of spin on the energy; (ii) learn how to make spectroscopic assignments to measured transitions; (iii) learn and verify that each electronic state has equally spaced vibrational energy subdivisions (the vibrational energy differences are used to calculate the bond force constant); (iv) are introduced to the idea that not all transitions are observed with the same intensity and that in some cases the transitions are not observed at all. Most importantly, the above points are examined in the context of a clear demonstration of the process of science.

The valence electronic configuration of the O_2 molecule is $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2(\sigma_{2p}^*)^0$. According to Hund's rule, the electrons in the π_{2p}^* reside in different molecular orbitals with unpaired (parallel) spins. This is the paramagnetic ground state called the triplet state. The two other ways the electrons can be accommodated in the two π_{2p}^* molecular orbitals are (see Fig. 1) (i) antiparallel electrons in different π_{2p}^* molecular orbitals (diamagnetic and called the singlet state) and (ii) antiparallel electrons in one orbital (diamagnetic and also called the singlet state). Since there are two singlet states, we recommend the use of singlet-1 and singlet-2. Term

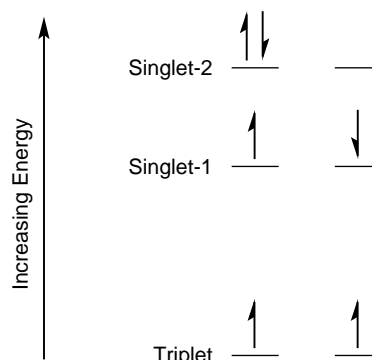


Figure 1. Triplet and singlet states of O_2 .

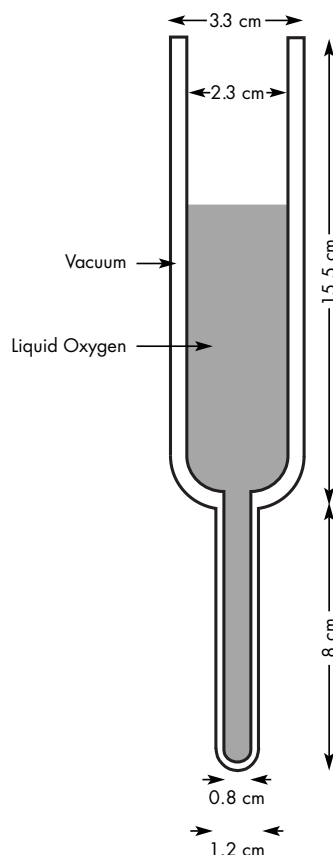


Figure 2. Finger-Dewar cuvette for liquid oxygen spectral measurements.

symbols are beyond the scope of a typical general chemistry curriculum. The current discussion excludes transitions into the σ_{2p}^* that occur in the UV region, since our discussion here is limited to the visible region.

Formulation of Hypothesis 1

Based on Figure 1, predict how many peaks you will see in the spectrum. Given that liquid oxygen is blue, where do you expect to see the major absorption peak or peaks? Answer: Two, 570 to 630 nm.

Hypothesis 1 is the only one written into the laboratory manual. The idea is to have the student seriously evaluate hypothesis 1 without the knowledge that other hypotheses will be considered.

Experimental Procedure

Materials and Equipment

Finger-Dewar (Fig. 2, path length = 0.80 cm)² with liquid oxygen, Hewlett-Packard 8452A UV-vis diode array spectrophotometer, Dewar flask, liquid nitrogen.

Procedure

Liquid oxygen was prepared by condensation using liquid nitrogen according to published procedure (1) and poured into the finger-Dewar. It was stored in the liquid nitrogen Dewar to keep it from boiling away.³ Before recording the spectrum (range 320–750 nm),⁴ the lower portion of the finger-Dewar was de-iced with room-temperature water and wiped dry. The vacuum compartment in the finger-Dewar allows up to three minutes before the liquid oxygen starts boiling. The finger-Dewar was immediately returned to the liquid-nitrogen storage Dewar. The peak wavelengths were then identified⁵ and marked, and the spectrum was printed.

Hazards

Avoid spilling the liquid oxygen and liquid nitrogen.⁶ Liquid oxygen and liquid nitrogen are very cold (−183 and −196 °C, respectively). Secure the liquid-nitrogen Dewar and use the thick gloves (winter gloves work well too) when transferring the finger-Dewar from the liquid-nitrogen storage Dewar to the spectrophotometer and back. Both the nitrogen and oxygen liquids should be open to the atmosphere at all times to avoid pressure buildup. There should be no open flames or heated plates in the laboratory during this experiment.

Results and Discussion

Testing of Hypothesis 1

Although the two major peaks are in the expected region, the number of peaks in the absorption spectrum (see Fig. 3) does not fit hypothesis 1. Peaks are located at 630, 578, 534, 478, 446, 380, 362, and 344 nm. If more than two peaks are observed, some other energy level subdivision must come into play. Our students have previously been exposed to the idea that molecular energy levels have vibrational energy subdivisions. Students are asked to add four small, equally spaced vibrational energy levels as dotted lines to the singlet-1 and singlet-2

states and number these $v = 0$ to $v = 3$. In the ground triplet state, only $v = 0$ is occupied at −183 °C, and since transitions originate from this state, no vibrational lines are shown. In Figure 4, the “A” transitions go from the triplet state into singlet-1 state and the “B” transitions go from triplet state into singlet-2 state. The letters A and B are followed by a number that denotes the excited state vibrational quantum number.

The two hypotheses formulated below require the following assumptions: the vibrational energy gaps are equal to each other, and the absorptions into the singlet-1 and the absorptions into the singlet-2 states do not overlap.

Formulation and Testing of Hypothesis 2

From the assumptions above and Figure 4, all but one of the energy intervals (energy difference between neighboring peaks) observed in the spectrum will be equal to the vibrational energy gaps. The unique energy interval represents a switch from singlet-1 (λ_A 's) to singlet-2 absorptions (λ_B 's). Energy gaps in the spectrum are calculated according to the formula $\Delta E = hc[(1/\lambda_1) - (1/\lambda_2)]$, where $h = 6.62608 \times 10^{-34}$ J s; $c =$

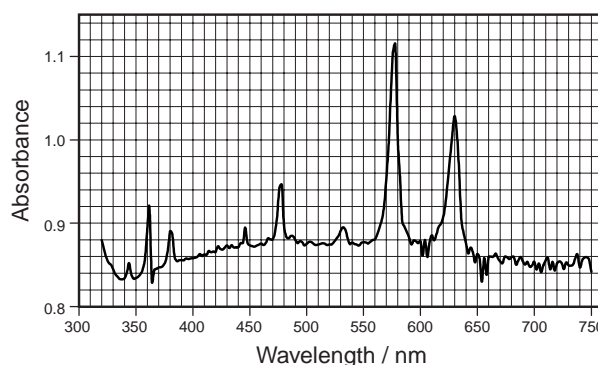


Figure 3. Spectrum of liquid oxygen.

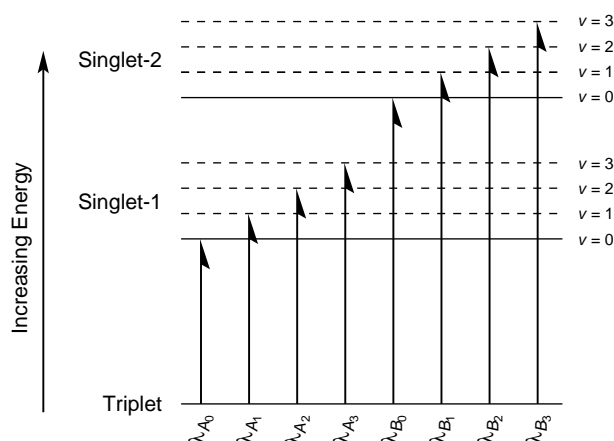
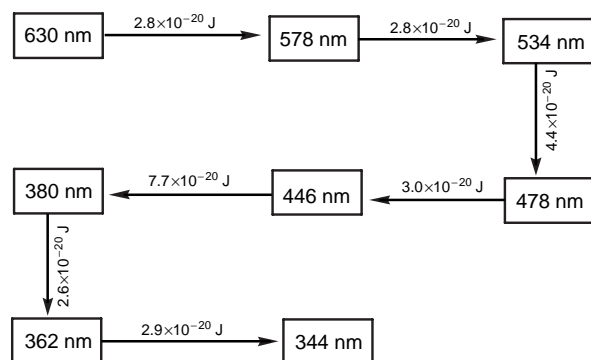


Figure 4. One-molecule-one-photon absorptions. Vibrational energy states are indicated by the dotted line and vibrational quantum numbers $v = 0, 1, \dots$

$2.9979 \times 10^8 \text{ m s}^{-1}$; λ_1, λ_2 are neighboring peaks; and $\lambda_2 > \lambda_1$. The energy gaps are



Hypothesis 2 does not fit the recorded spectrum because there are two intervals that differ from the rest. In other words, there must be three sets of transitions rather than two. Absorptions as noted in Figure 4 actually occur in the infrared (6, 7).

Finally, the class is introduced to two-molecule-one-photon absorptions. The two molecules that absorb the photon are not bound to each other but are simply a colliding pair. There is a distance requirement ($\sim 3.6 \times 10^{-10} \text{ m}$) as well as a parallel orientation requirement (5–8). Figure 5 illustrates the transitions.

Formulation and Testing of Hypothesis 3

From the assumptions above and Figure 5, all but two of the energy intervals (energy difference between neighboring peaks) observed in the spectrum will be equal to the vibrational energy gap. The two that differ are $hc[(1/\lambda_{D_0}) - (1/\lambda_{C_2})]$ and $hc[(1/\lambda_{E_0}) - (1/\lambda_{D_1})]$. The energy gaps have been calculated and indeed there are two that are different from the rest.

We also calculate the bond force constant of O_2 (see below). A value for this constant obtained from Raman spectroscopy is available (9). If our value compares favorably with the known value, it lends further support to hypothesis 3.

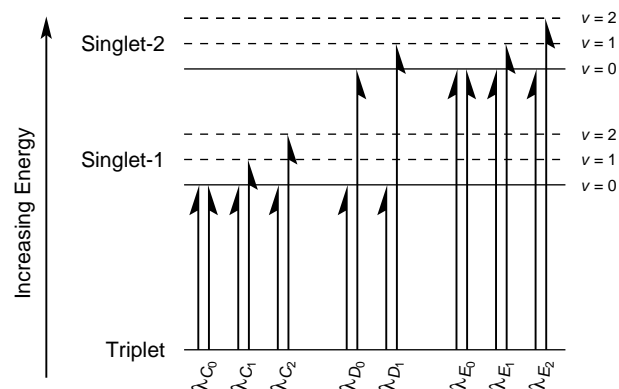


Figure 5. Two-molecule-one-photon absorptions. Paired arrows indicate final state of each of the two excited molecules.

Questions

In conclusion, the class is asked to answer the following questions.

Question 1: Assign all the peaks to the transitions. *Answer:* $\lambda_{C_0} = 630 \text{ nm}$, $\lambda_{C_1} = 578 \text{ nm}$, $\lambda_{C_2} = 534 \text{ nm}$, $\lambda_{D_0} = 478 \text{ nm}$, $\lambda_{D_1} = 446 \text{ nm}$, $\lambda_{E_0} = 380 \text{ nm}$, $\lambda_{E_1} = 362 \text{ nm}$, and $\lambda_{E_2} = 344 \text{ nm}$.

Question 2: Does the visible spectrum of liquid oxygen account for the blue color of liquid oxygen? *Answer:* λ_{C_0} and λ_{C_1} are the most intense peaks and they are located in the yellow to red spectral region (630 and 578 nm, respectively). The complementary color is blue.

Question 3: Identify the most intense peak and use this to calculate the molar absorptivity of liquid oxygen. Assume the density is 0.6 g cm^{-3} at -183°C and the path length is 0.8 cm . *Answer:* Using λ_{C_1} and calculating the concentration of liquid oxygen to be 19 M , students calculate a molar absorptivity between 0.7×10^{-2} and $1.8 \times 10^{-2} \text{ M}^{-1} \text{ cm}^{-1}$.

Question 4: Calculate ΔE_{C_0} on a per molecule basis ($\Delta E_{C_0} = hc/2\lambda_{C_0}$). Similarly, calculate ΔE_{E_0} . *Answer:* $\Delta E_{C_0} = 1.576 \times 10^{-19} \text{ J}$; $\Delta E_{E_0} = 2.62 \times 10^{-19} \text{ J}$.

Question 5: Calculate the vibrational energy gaps in the singlet-1 state $\{hc[(1/\lambda_{C_1}) - (1/\lambda_{C_0})], hc[(1/\lambda_{C_2}) - (1/\lambda_{C_1})]\}$. Is the spacing between vibrational energies constant? Similarly, calculate vibrational energy gaps in the singlet-2 state $\{hc[(1/\lambda_{E_1}) - (1/\lambda_{E_0})], hc[(1/\lambda_{E_2}) - (1/\lambda_{E_1})]\}$. *Answer:* $0.28 \times 10^{-19} \text{ J}$ in both. $0.26 \times 10^{-19} \text{ J}$, $0.28 \times 10^{-19} \text{ J}$.

Question 6: Calculate the O_2 bond force constant (k) in N m^{-1} from the following equation:

$$\Delta E_{\text{vib}} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}}$$

where $\Delta E_{\text{vib}} = \Delta E_{\text{vib}}(\text{av})$ and μ is the reduced mass [$\mu = m_1 m_2 / (m_1 + m_2)$, $m_1 = m_2 = \text{mass of the oxygen molecule in kg}$].⁷ Compare your calculated value with a literature value (9). *Answer:* O_2 (calcd) = $9.9 \times 10^2 \text{ N m}^{-1}$, O_2 (lit.) = $11.4 \times 10^2 \text{ N m}^{-1}$. The literature value is recorded in the ground state and so is expected to be slightly higher than in either of the excited states.

Question 7: Using the triplet state as zero, draw an energy level diagram to scale indicating the $v = 0$, $v = 1$, and $v = 2$ vibrational energy levels of the singlet-1 and singlet-2 states.

Question 8: (a) Assign $\Delta v = 0$, $\Delta v = 1$, and $\Delta v = 2$ labels to the transitions in Figure 5. (b) Which of these gives the largest peaks within the C and E group of transitions, $\Delta v = 0$, $\Delta v = 1$, or $\Delta v = 2$? *Answer:* $\Delta v = 1$. (c) The λ_{C_3} , λ_{D_3} , and λ_{E_3} transitions are not included in Figure 5. Explain why this is reasonable. *Answer:* There is a large drop in intensity going from $\Delta v = 1$ to $\Delta v = 2$. A similar drop in intensity from $\Delta v = 2$ to $\Delta v = 3$ would make the peak undetectable under the present experimental conditions.

Question 9: What contribution do you expect the two-molecule-one-photon absorptions to have in the gas phase? *Answer:* None. In the gas phase the oxygen concentration is low compared to that in the liquid state. The probability of obtaining the colliding complex (two oxygen molecules plus photon) is extremely low.

Recording the spectrum of liquid oxygen takes about 2 minutes per measurement. An instructor could use the typical three-hour laboratory period to go through the pre-laboratory and use the time remaining after the measurement of the spectrum to go through the post-laboratory exercise.

An interesting way to finish this discussion is with a demonstration of a chemiluminescent reaction in which O_2 in the excited singlet-2 emits a red photon as it returns to the ground state (6). A grand finale would be to measure this emission wavelength and by comparison with Figure 5 to establish the emission transition occurring.

We have run this experiment for eight successive quarters for more than 3000 students. While our students find this experiment is easy to execute, they find the formulation and testing of the hypothesis challenging and rewarding.

^wSupplemental Material

Instructions for students and notes for the instructor are available in this issue of *JCE Online*.

Notes

1. Alfa Aesar, 30 Bond Street, Ward Hill, MA; <http://www.alfa.com/> (accessed Jan 2002).
2. The finger-Dewar was made by our glassblower. Pope Scientific used to make such a Dewar many years ago.
3. Cooled by liquid nitrogen, the liquid oxygen evaporates slowly. We have been able to use the same liquid oxygen sample for multiple laboratory sessions from 8:30 a.m. to 9:30 p.m.
4. Since the finger-Dewar is not tight fitting in the cuvette holder, the blank scan is a function of position. In some cases, this

variation in the blank can make the liquid oxygen spectrum have negative absorbance. To avoid this problem, we recommend the use of air as the blank, although this makes for a less clean spectrum.

5. Manual reading of the wavelength yields unacceptable error.
6. The liquid oxygen is more a low-temperature hazard than an explosion hazard.
7. Some brief introduction of the equation may be necessary for those students who have not taken general physics.

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