720. *The Far-ultraviolet Absorption Spectrum of* $^{18}O_2$, $^{17}O^{18}O$, *and* $^{16}O^{18}O$.

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The Schumann–Runge bands of $^{18}O_2$, $^{17}O^{18}O$, and $^{16}O^{18}O$ in the 1800—1950 Å region have been measured under moderate resolution. Frequency shifts of the vibrational absorption band-heads and rotational lines are consistent with theoretical expectations. The intensity of the absorption bands of $^{18}O_2$ is two-thirds that of the corresponding bands of $^{16}O_2$. The spectrum of oxygen gas in the 1900 Å region can be used to determine its isotopic composition when the oxygen-18 concentration is high.

THE discovery of the isotopes oxygen-18 and oxygen-17 was due to the detection, in the solar spectrum, of the weak bands of $^{16}O^{18}O$ and $^{16}O^{17}O$ in the 7600 Å region.[1] The intense absorption bands of oxygen in the Schumann–Runge region below 2000 Å have been measured many times,[2-7] but no results have been reported on the corresponding bands of the isotopic oxygen molecules.

Vibrational Structure.—The absorption spectra of normal oxygen and of highly enriched $^{18}O_2$ are presented in Fig. 1. Comparison of the spectra shows that the vibrational band system of the heavier oxygen molecules is shifted to lower frequencies. The numbering of the vibrational band-heads in Fig. 1(*a*) is taken from the literature.[4,5] Assignment of the corresponding vibrational band-heads for the isotopic oxygen molecules in Fig. 1(*b*) was made by using the formula of Knauss and Ballard[5] describing the origins of absorption bands of normal oxygen, and applying the factor ρ to account for the effect of mass on vibrational levels.[7] Thus, the predicted band-origin (in cm.$^{-1}$) is given by

$$\nu(v',0) = 49{,}014{\cdot}93 + 700{\cdot}36 \, \rho \, (v' + \tfrac{1}{2})$$
$$- 8{\cdot}0023 \, \rho^2 \, (v' + \tfrac{1}{2})^2 - 0{\cdot}3753 \, \rho^3 \, (v' + \tfrac{1}{2})^3 \qquad (1)$$

where ρ^2 is the ratio of the reduced masses[8] of normal and isotopic oxygen molecules. In Table 1 the frequencies of the observed absorption *band-heads* of $^{16}O_2$, $^{16}O^{18}O$, $^{17}O^{18}O$, and $^{18}O_2$ are listed, and are compared with the corresponding values for the *band-origins* calculated by means of eqn. 1. The agreement is within the experimental error of ± 25 cm.$^{-1}$.

Rotational Structure.—The effect of isotopic substitution in a diatomic molecule on the rotational term F is expressed by the change in the rotational constant B'. The rotational term is given by $F = B'J \, (J + 1)$ for the normal molecule, and by $F^i = \rho^2 B'J(J + 1)$ for the isotopic molecule, where J is the rotational quantum number.[9] Thus, the spacing of rotational lines in the spectrum of $^{18}O_2$ should be decreased by the factor ρ^2 ($= 0{\cdot}88863$) compared with the spacing in $^{16}O_2$. The rotational structures of the (11,0) and (6,0) vibrational bands of $^{18}O_2$ are shown in Figs. 1(*c*) and 2(*b*), respectively. The $P(J)$ and $R(J + 2)$ lines overlap for transitions to the lower vibrational levels,[6] such as the (6,0) band, but are resolved from the (9,0) band onwards, and are clearly seen for the (11,0) band [Fig. 1(*c*)]. The rotational constants for $^{18}O_2$ were derived by dividing the observed spacings, $\Delta F'(J)$, of rotational lines by various values of $(J + \tfrac{1}{2})$, until a set

[1] Giauque and Johnston, *J. Amer. Chem. Soc.*, 1929, **51**, 1436.
[2] Birge and Sponer, *Phys. Rev.*, 1926, **28**, 259.
[3] Mulliken, *Phys. Rev.*, 1928, **32**, 880.
[4] Curry and Herzberg, *Ann. Physik*, 1934, **19**, 800.
[5] Knauss and Ballard, *Phys. Rev.*, 1935, **48**, 796.
[6] Brix and Herzberg, *Canad. J. Phys.*, 1954, **32**, 110.
[7] Herzberg, " Molecular Spectra and Molecular Structure, Vol. I, Spectra of Diatomic Molecules," Van Nostrand, New York, 2nd edn., 1950, p. 162.
[8] Cameron and Wichers, *J. Amer. Chem. Soc.*, 1962, **84**, 4182.
[9] Ref. 7, p. 143.

of $\Delta F'(J)/(J + \frac{1}{2})$ values was obtained, the average of which gave the best fit with that calculated from eqn. 2: [5]

$$\Delta F'(J)/(J + \tfrac{1}{2}) = 4\rho^2 B' \qquad (2)$$

Here, B' is the known rotational constant of $^{16}O_2$ for the particular vibrational state, and $\rho^2 B'$ is the corresponding calculated constant for $^{18}O_2$. In Table 2, observed and calculated
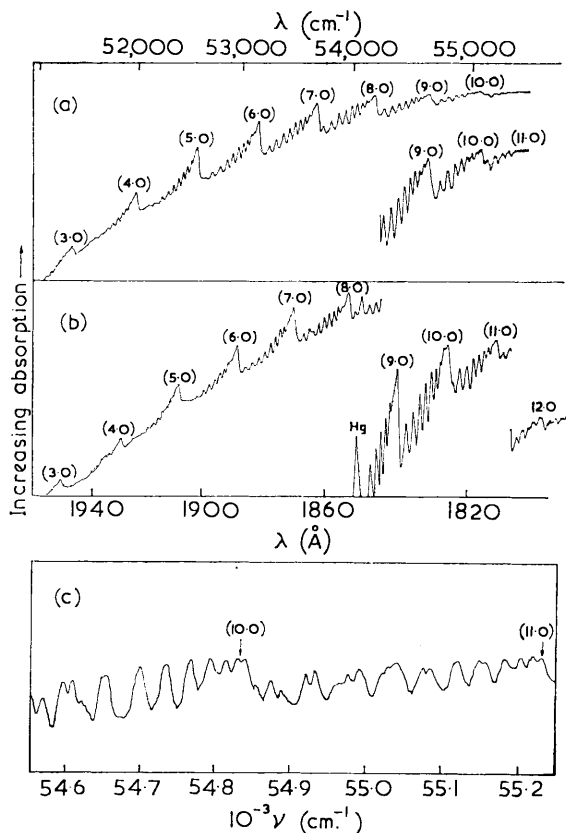

Fig. 1. Schumann–Runge absorption bands of oxygen. Pressure, 1 atm.; optical path-length 5·000 cm. Single-beam technique of recording. Vibrational band-heads are identified as $(v', 0)$.

(*a*) Normal oxygen in the 1960—1800 Å region. Scan-speed, 230 cm.$^{-1}$ min.$^{-1}$.

(*b*) $^{18}O_2$ (92 mole %) + $^{16}O^{18}O$ (6 mole %) in the 1960—1800 Å region. Scan-speed, 230 cm.$^{-1}$ min.$^{-1}$.

(*c*) $^{18}O_2$ (98 mole %) in the 1830—1810 Å region. Slit-width, 0·015 mm.; scan-speed, 12 cm.$^{-1}$ min.$^{-1}$.

TABLE 1.

Observed absorption band-heads and calculated band-origins for isotopic oxygen molecules (in cm.$^{-1}$).

	$^{16}O_2$		$^{16}O^{18}O$		$^{17}O^{18}O$		$^{18}O_2$	
$(v'v'')$	Obs.	Lit.[4]	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
(3,0)	51,337	51,352·2		51,318		50,479	51,257	51,225
(4,0)	51,947	51,969·8	51,890	51,931		51,889	51,837	51,821
(5,0)	52,544	52,561·6	52,470	52,502		52,453	52,407	52,379
(6,0)	53,125	53,122·8	53,030	53,055	52,980	52,999	52,950	52,920
(7,0)	53,647	53,656·8	53,565	53,579	53,500	53,518	53,473	53,434
(8,0)	54,143	54,158·9	*	54,072	54,005	54,008	53,962	53,920
(9,0)	54,619	54,624·4	54,510	54,533	54,470	54,466	54,411	54,376
(10,0)	55,039	55,053·3	54,940	54,959	54,890	54,891	54,825	54,800
(11,0)	55,437	55,441·5	55,320	55,348	55,280	55,280	55,220	55,190
(12,0)		55,786·9		55,699	*ca.* 55,610	55,633	*ca.* 55,600	55,543

* The strong line observed at 54,060 cm.$^{-1}$ may be partly due to absorption by mercury vapour (54,066 cm.$^{-1}$) present in the samples.

values of B' for $^{18}O_2$ are listed for the vibrational bands (5,0) to (11,0), and are compared with the values for $^{16}O_2$.

Absorption Intensities.—The intensities of Schumann–Runge absorption bands are pressure-dependent.[10-12] With increasing gas pressure, the bands are broadened.[10] The
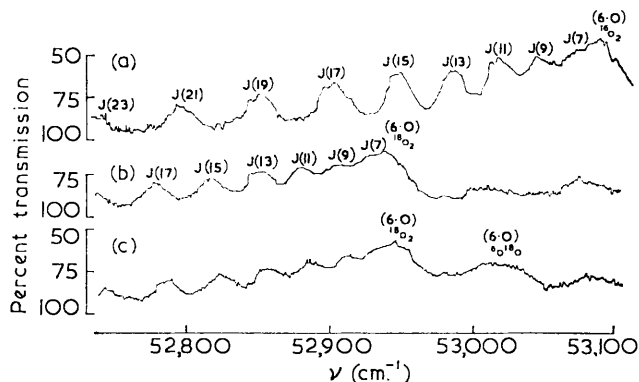

FIG. 2. Absorption band (6,0) of oxygen. Pressure, 1 atm.; optical path-length, 5·000 cm.; scan-speed, 12 cm.$^{-1}$ min.$^{-1}$. "Compensated" technique of recording. Rotational bands are identified as $P(J)$.

(*a*) Normal oxygen. (*b*) Pure $^{18}O_2$ (98·4 mole %) + $^{16}O^{18}O$ (0·2 mole %) + $^{16}O_2$ (0·2 mole %) + N_2 (1·2 mole %). (*c*) Isotopic mixture: $^{18}O_2$ (73·4 mole %) + $^{16}O^{18}O$ (22·9 mole %) + $^{16}O_2$ (2·3 mole %) + N_2 (1·5 mole %).

TABLE 2.

Rotational constants for the upper-state vibrational levels in Schumann–Runge absorption bands of $^{18}O_2$ and $^{16}O_2$.

(v',v'')	(5,0)	(6,0)	(7,0)	(8,0)	(9,0)	(10,0)	(11,0)
$B'(^{18}O_2)$ (obs.)	0·65	0·64	0·59	0·59	0·58	0·55	0·52
$B'(^{18}O_2)$ (calc.)	0·658	0·642	0·623	0·602	0·579	0·553	0·525
$B'(^{16}O_2)$ [5]	0·741	0·722	0·701	0·677	0·651	0·622	0·591

determination of integrated absorption coefficients requires either very high resolution[11] or broadening of bands by high pressures.[12] Since neither technique was available in the present work, only relative absorption intensities for bands of $^{16}O_2$ and $^{18}O_2$ could be

TABLE 3.

Intensities of Schumann–Runge absorption bands of $^{16}O_2$ and $^{18}O_2$. Absorption coefficients, k (in cm.$^{-1}$ atm.$^{-1}$), are given for band-heads. The integrated absorption coefficient, K (in cm.$^{-2}$ atm.$^{-1}$), is given for the (6,0) vibrational transition.

(v',v'')	k			K		
	$^{16}O_2$	$^{18}O_2$	$k(^{16}O_2)/k(^{18}O_2)$	$^{16}O_2$	$^{18}O_2$	$K(^{16}O_2)/K(^{18}O_2)$
(5,0)	0·081 ± 0·006	0·050 ± 0·005	1·6 ± 0·2			
(6,0)	0·113 ± 0·01	0·068 ± 0·008	1·65 ± 0·2	24·8	17·0	1·45
(7,0)	0·158 ± 0·007	0·128 ± 0·007	1·2 ± 0·2			
(8,0)	0·205 ± 0·04	0·137 ± 0·02	1·5 ± 0·4			

obtained. Although the Beer–Lambert Law is not observed, it seems that measurements of *relative* absorption coefficients, carried out at the same pressure for both isotopic oxygen molecules, should be valid.

All the measurements reported in Table 3 were made with oxygen gas at atmospheric

[10] Watanabe, Inn, and Zelikoff, *J. Chem. Phys.*, 1953, **21**, 1026.
[11] Ditchburn and Heddle, *Proc. Roy. Soc.*, 1954, *A*, **226**, 509.
[12] Bethke, *J. Chem. Phys.*, 1959, **31**, 669.

pressure; the results are given as absorption coefficients, k (in cm.$^{-1}$ atm.$^{-1}$) $= (\ln I_0/I)/pl$, where p is the oxygen pressure in atm. at 0°, l is the path-length in cm., and I_0/I is the ratio of incident to transmitted radiation intensities. Integrated absorption coefficients, K (in cm.$^{-2}$ atm.$^{-1}$), defined by $K = \int k d\nu$, are given for the (6,0) vibrational transition of $^{16}O_2$ and $^{18}O_2$. All measurements of absorption coefficients for band-heads were made at least twice, and in the case of the (6,0) band-head of $^{18}O_2$, six different gas samples were used.

The observed integrated absorption coefficient for the (6,0) vibrational transition of $^{16}O_2$ at atmospheric pressure was 25 cm.$^{-2}$ atm.$^{-1}$. In previous reports on this transition, where the spectra were broadened by very high pressures of added argon, the value 41·2 cm.$^{-2}$ atm.$^{-1}$ was obtained.[12] Since at decreased pressures lower absorption coefficients were found, the value 25 cm.$^{-2}$ atm.$^{-1}$ at atmospheric pressure seems reasonable.

That the intensity of the $^{18}O_2$ bands is considerably lower than that of the $^{16}O_2$ bands is evident from Fig. 2(*a*) and (*b*) for the (6,0) vibrational system. Table 3 shows that both the absorption coefficients for several band-heads and the integrated absorption coefficient for the (6,0) band system of $^{16}O_2$ are 1·5 $\pm$ 0·2 times as large as those for $^{18}O_2$.

The absorption intensity for bands of $^{16}O^{18}O$ may be expected to be the average of those for $^{16}O_2$ and $^{18}O_2$. Thus the absorption coefficient, k_2, for the (6,0) band-head of $^{16}O^{18}O$ should be (0·113 + 0·068)/2 = 0·09 $\pm$ 0·01 cm.$^{-1}$ atm.$^{-1}$). Since pure $^{16}O^{18}O$ was not available, its absorption coefficient could not be directly measured, but the results obtained from isotopic mixtures indicated that $k_2 = 0·085 \pm 0·01$ cm.$^{-1}$ atm.$^{-1}$. Therefore, the ratio of the absorption coefficient of $^{16}O_2$ to that of $^{16}O^{18}O$ is $k_1/k_2 = 0·113/0·085 = 1·33 \pm 0·1$.

This now makes it possible to understand the precise results of earlier workers,[13] who found that the ratio, D, of the intensity of the atmospheric absorption band at 7596 Å of $^{16}O_2$ to that of $^{16}O^{18}O$ is $D_1/D_2 = 630$. They suggested that this is also the ratio of isotopic abundances, C_1/C_2, assuming that the absorption coefficients are independent of isotopic substitution, *i.e.*, $k_1 : k_2 = 1$. However, isotopic-abundance measurements by means of mass spectrometry give an appreciably different result. Recent data[8] give $C_1/C_2 = 99·759/0·2039$. Since $k_1/k_2 = C_2D_1/C_1D_2$, we obtain $k_1/k_2 = 0·2039 \times 630/99·759 = 1·29$. The ratio $k_1 : k_2$ for the red absorption bands of oxygen is similar to that reported above for the ultraviolet bands, 1·33 $\pm$ 0·1.

Application to Isotopic Analysis.—An ultraviolet absorption method should be a convenient alternative to mass spectrometry for non-destructive isotopic analysis of oxygen gas. However, since the band-heads of $^{18}O_2$ and of $^{16}O^{18}O$ are at the long-wavelength side of the $^{16}O_2$ band-heads, and thus coincide with the rotational lines of the $^{16}O_2$ system, it is not easy to use the Schumann–Runge bands for the determination of *small* concentrations of oxygen-18 in oxygen. On the other hand, it should be possible to measure the isotopic composition of oxygen gas containing more than *ca.* 50% of oxygen-18, because in this case the band-heads of $^{16}O^{18}O$ occur at the absorption minima of the $^{18}O_2$ system. The (6,0) vibrational band-heads (at *ca.* 1880Å) seem most convenient, because the bands at shorter wavelengths are superimposed on the absorption continuum due to predissociation,[12] while the longer-wavelength bands are of lower intensity.

Experimental

Oxygen Gas Enriched in Oxygen-18 or Oxygen-17.—This enriched gas was obtained from the thermal-diffusion plant of this laboratory, and was analysed mass spectrometrically.

Far-ultraviolet Absorption Measurements.—The measurements were made by using a specially sealed Zeiss PMQ II spectrophotometer with Suprasil quartz optics, which was completely flushed with nitrogen. Absorption cells of Suprasil quartz, fitted with stopcocks and conical joints, were filled with oxygen to atmospheric pressure. Slit-widths of 0·015 to 0·18 mm., corresponding to band-widths of 5 to 20 cm.$^{-1}$, were used.

[13] Mecke and Childs, *Z. Physik.*, 1931, **68**, 362.

Wavelengths were calibrated against the 1849·6 Å mercury line, using a mercury lamp as the light-source. Spectra were scanned by using a wavelength drive motor, and the spectral intensity was recorded (as in Fig. 1).

In order to derive integrated absorption intensities with this single-beam instrument, the " compensated " technique of recording was devised. Use was made of the " 100 Point Automatic " attachment to the monochromator, which brought the slit, within *ca.* 1 sec., to the position required for 100% transmission, whenever the reference cell was brought in the light-beam. The sample holder was pushed manually back and forth, keeping it for *ca.* 2 sec. with the reference cell, and for *ca.* 8 sec. with the sample cell, before the slit. Using a slow rate of scan, a trace similar to that of a double-beam instrument was recorded (as in Fig. 2). In order to obtain the integrated absorption intensities, results were then replotted as optical density against wave-number.