New Fine Structure in Neutral Oxygen*

LEE W. PARKER AND JOHN R. HOLMES
University of Southern California, Los Angeles, California
(Received December 19, 1952)

Untabulated fine structure in O I has been resolved in the triplet multiplets λ8446($3s\,^3S_1-3p\,^3P_{210}$), λ2884($3p\,^3P_{21}-3d'\,^3P_2$), and λ4368 ($3s\,^3S_1-4p\,^3P_{210}$). Interferometer patterns of these lines were analyzed to obtain splittings and relative intensities. Listed as a doublet, λ8446 has three components whose relative intensities allowed establishment of the $3p\,^3P_{210}$ anomalous splitting as follows: $J=1$ lies 0.559(±0.003) cm^{-1} below $J=2$, and $J=0$ lies 0.158(±0.002) cm^{-1} above $J=2$, in agreement with Edlén. λ2884, heretofore found single, has two components, separated by 0.558(±0.002) cm^{-1}. Two components of λ4368, previously considered single, were resolved and found to have a separation of 0.300(±0.001) cm^{-1}, the weaker component having the shorter wavelength. From the relative intensities it is deduced that $J=0$ lies above the degenerate $J=2$, 1 level of the state $4p\,^3P_{210}$, which, like $3p\,^3P_{210}$, is perturbed by an unobserved state in the displaced (^3D) system.

THERE are many levels of O I whose spin-orbit splittings are so small that the associated multiplet lines have remained unresolved or only partially resolved.[1] During a recent survey of isotope shift in the O I spectrum[2] new fine structure was uncovered in λλ8446, 4368, and 2884 with the use of a Fabry-Perot interferometer crossed with a large prism spectrograph. The source was a helium (2–5 mm Hg)—oxygen (about 0.1 mm Hg) mixture excited by a 10-Mc oscillator and cooled with liquid nitrogen. Plate calibrations were made for each of the three multiplets. Silvered interferometer plates were used for λ8446 and λ4368, and aluminized plates for λ2884. The density contours of the interferometer patterns were reproduced by a Zeiss microphotometer connected to a Speedomax Leeds and Northrup recorder. The fine structure splittings were determined by measuring the relative positions of pattern maxima.

λ8446:[3] Two spacers, 5 mm and 6 mm, were used to obtain interferometer patterns which show all three fine structure components clearly separated. This triplet was very strong. The background of the I-N plate used was quite clean, as Fig. 1 indicates. Because of the overlapping wings of the two strongest components, the weakest is spuriously shifted toward the nearer of its neighbors, i.e., toward the second strongest component in the 6-mm pattern. The 5-mm spacer, on the other hand, shifts the weakest component toward the strongest one. Therefore, the value for the displacement of the weakest component from the strongest, given in Table I as $^3P_2-{}^3P_0$, was obtained as a weighted average of the values obtained from the 5-mm and 6-mm traces.

λ2884: A 4-mm spacer placed the weaker component of this doublet almost exactly midway between orders. About 30 minutes were required for an exposure on a II-O plate. Molecular band background was present.

λ4368: The strength of this doublet (incompletely resolved triplet) was such that about 90 seconds were required for an exposure on a II-O plate.

RESULTS

Table I shows the splittings and relative intensities for the three transitions studied. The figures in parentheses are probable errors. Ten orders were used to obtain data for λ8446, twelve for λ2884, and twelve for λ4368. Relative intensities within a multiplet were obtained by drawing a smooth curve through each set of peaks and obtaining the average of several determinations of relative intensities in different places along the nearly flat central portions of these curves.[4] The heights, converted of course to intensities by means of the calibration, were taken with respect to the back-

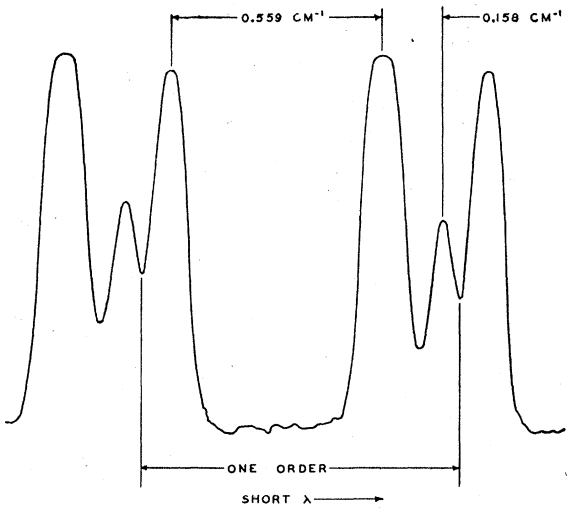

FIG. 1. Fabry-Perot fringes (6-mm spacer) showing all three components of λ8446 clearly resolved. The center of the fringe system is toward the left.

* Supported by the U. S. Office of Naval Research.

[1] B. Edlén, Kl. Svenska Vetenskapsakad. Handl., Series 3, Vol. 20, No. 10 (1943).

[2] L. W. Parker and J. R. Holmes, J. Opt. Soc. Am. 43, 103 (1953).

[3] D. O. Davis and K. W. Meissner have reported the complete structures of λλ8446, 7254, and 6046 in J. Opt. Soc. Am. 42, 871 (1952). Our measurements on λ8446 agree closely with theirs.

[4] S. Tolansky, *High Resolution Spectroscopy* (Pitman, New York, 1947), p. 270.

ground level, which was very uniform over the entire photographic plate in all cases. The values $^3P_2-^3P_1$ for λ8446 and $^3P_2-^3P_1$ for λ2884 should be equal since the same two fine structure levels are involved (Fig. 2). The error in intensity measurements is estimated to be 15 percent.

DISCUSSION

The complete anomalous structure of the $3p\,^3P$ level was inferred from its combination with $3s'\,^3D$ by Edlén with the sum rule. The corresponding complex multiplet is λ7982–95. Although the doublet structure of λ7982.41, which ends on $^3P_{20}$, was not resolved directly by Edlén, be determined the splitting $^3P_2-^3P_0$ (0.16 cm^{-1}) by noting that the splitting of the line pair $^3P_{20,1}-^3D_1$ was measurably greater than that of the pair $^3P_{1,2}-^3D_2$. There have remained, however, about a dozen lines involving the $3p\,^3P$ level which are incompletely resolved with respect to this level and which are expected to have splittings based on the known structure of $3p\,^3P$. Two of these are λ8446.35 and λ2883.78, the former wavelength determined by Edlén, the latter by Runge and Paschen.[5] Complete resolution of the λ8446

TABLE I. New fine structure in O I.

Wavelength	Transition	Splittings (cm^{-1})	Intensity ratio of components
8446	$3s\,^3S_1-3p\,^3P_{210}$	$^3P_2-^3P_1=0.559(\pm0.003)$ $^3P_2-^3P_0=-0.158(\pm0.002)$	1:0.64:0.30
2884	$3p\,^3P_{21}-3d'(^2D)\,^3P_2$	$^3P_2-^3P_1=0.558(\pm0.002)$	1:0.66
4368	$3s\,^3S_1-4p\,^3P_{210}$	$^3P_{21}-^3P_0=-0.300(\pm0.001)$	1:0.26

triplet, as well as of the λ2884 doublet, confirms the structure of $3p^3P$ proposed by Edlén. The relative intensity ratio found for the three components of λ8446, 1:0.64:0.30, was used to associate J-values of $3p\,^3P$ with individual components. This ratio deviated slightly from the theoretical ratio expected for pure Russell-Saunders coupling without configuration interactions, i.e., 1:0.60:0.20. The discrepancy may be due to an error in the relative intensity measurement since it is well known that instrumental background between orders in interferometer patterns can sometimes increase the apparent relative intensity of weak components by an order of magnitude.[6] One may examine the effect on λ2884 of band background, which is definitely present in addition to the instrumental background. In this case the relative intensity of the two components, ending on $J=2$ and $J=1$ of $3p\,^3P$, respectively, is found to be 1:0.66 whereas the theoretical ratio is 1:0.60. The corresponding ratio found for λ8446, 1:0.64, is negligibly different. There is a distinct possibility, then, that the deviation of the λ8446 relative intensity ratio from the theoretically expected ratio may be due at least in part to a perturbation effect.[7] Edlén has shown that the entire $np\,^3P$ series is perturbed by $3p'\,^3P$ in the "displaced" (^2D) system. This level, expected at a position above the ionization limit of the "normal" (^4S) system, is missing due to a strong autoionization effect in which $3p'\,^3P$ interacts with the continuum above the $np\,^3P$ series limit.[1]

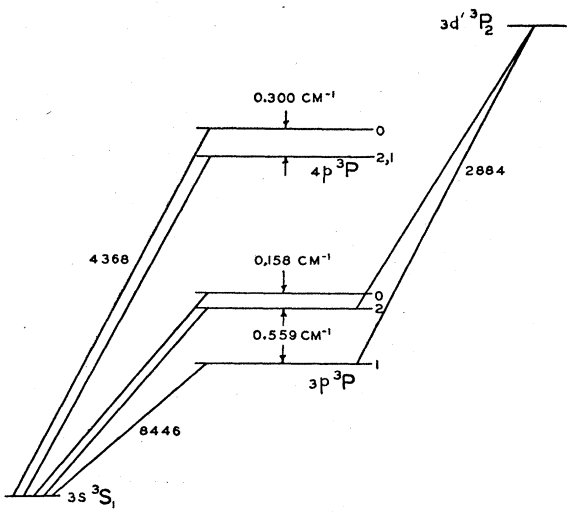

FIG. 2. Energy level diagram of states involved in the transitions studied, showing the deduced structures of $3p\,^3P_{210}$ and $4p\,^3P_{210}$. The energy scale is purposely distorted for clarity.

The structure found for λ4368 is interesting since this line originates on $4p\,^3P$ of the same perturbed series. Since only two components were resolvable, there remained the problem of deciding which two of the three levels $J=0, 1, 2$ coincide. The choice made was based on the relative intensity ratio, found to be 1:0.26. The three possibilities of coincidence were as follows: $J=0$ and $J=1$, $J=0$ and $J=2$, and $J=1$ and $J=2$, which would give relative intensity ratios 1:0.80, 1:0.50, and 1:0.125, respectively. The last possibility is most reasonable, since the presence of instrumental background would require that 0.26 be considered an upper limit. Figure 2 indicates the inferred structure of $4p\,^3P$, which is anomalous. It is to be expected that higher terms of the $np\,^3P$ series, lying closer to the perturbing level, should be even more distorted.

The same perturbation is probably responsible for the very appearance of lines such as λ7982 and λ2884, which connect terms formed by addition of the optical electron to different terms of the parent ion. Such transitions are otherwise forbidden.[8]

[5] C. Runge and F. Paschen, Ann. Phys. Chem. **61**, 641 (1897).
[6] See reference 4, p. 272.
[7] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), pp. 218 and 367.
[8] See reference 7, p. 245.