NBS CIRCULAR 541

A Spectrophotometric Atlas of the ²Σ⁺—²∏ Transition of OH

$$^2\Sigma^+ - {}^2\Pi$$

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Arnold M. Bass and Herbert P. Broida

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1. Introduction

Until recently the standard method of studying the intensity distributions in atomic spectra and among rotational lines of electronic band spectra was to photograph the spectrum and then to make a densitometer record of the line density from the photographic plate. Line intensity could be measured, using carefully determined calibration curves. For the most part these procedures are used in such applications as quantitative chemical analysis in which the intensities of a few outstanding lines are compared with certain standards, and in which a detailed record of the entire spectrum in the form of a densitometer tracing is not required.

The direct recording of spectra in the form of intensity as a function of frequency, or wavelength, has been done for some time in the infrared spectral region. However, similar developments in the visible and ultraviolet regions have been more recent because of the reasonable adequacy of existing photographic techniques and the lack of suitable detectors. With the development of sensitive photoelectric multiplier tubes it has been feasible to use the direct-recording techniques in conjunction with high-resolution spectrometry between 1800 and 7000 A. In the past 7 or 8 years a number of recording grating spectrometers have been constructed that employ multiplier phototubes as receivers and present the spectral data directly as curves of intensity against wavelength, or frequency. There is a growing interest in these scanning high-resolution instruments, which results from the rapid, accurate, and highly reproducible intensity measurements that may be obtained with their use. The versatility of these instruments, together with their other highly desirable characteristics, indicates that they will probably be widely used in coming years both as research tools and for industrial applications.

In laboratories where the emphasis in spectroscopic research is primarily on photographic measurements of wavelength, the various photographic spectral atlases and charts that have been published [1] are valuable aids in the identification of unknown spectra. Most of these charts have been prepared for atomic spectra, although there is available a collection of molecular spectra [2] photographed under widely varying conditions, but mostly at medium and low dispersion. To the best of our knowledge there is not available a comprehensive collection of spectra—either of atomic or molecular origin—presented in the form of a curve of intensity against wavelength, as the data are received from a densitometer or from a recording photoelectric spectrometer.

There has been developing in recent years a greater interest in the study of intensity relationships in spectra. For example, a necessary part of the program of radiation researches on high-temperature gases and flames which has been established at the National Bureau of Standards [1] is the detailed identification of the spectra and the measurement of intensity distributions in these gases. From the relative intensities of the spectral lines it is possible to determine the distributions of rotational, vibrational, and electronic energies for the different chemical species that exist in the hot gases and to use this information for studying the processes of reaching equilibrium. The most outstanding features of the ultraviolet and visible radiation of flames are the emission spectra of the molecules OH, CH, C_2, CN, NH, NO, and O_2.

The importance of radiation studies as a tool for increasing knowledge of combustion and flame propagation makes it desirable to have atlases showing clearly the structure of the spectra of these molecules. Of course there are other types of spectroscopic studies in which such atlases would be of great benefit. This spectrum of OH has been prepared as a trial to learn whether it is desirable to present spectral atlases showing relative intensities, as well as wavelengths.

We would be interested to receive any comments and suggestions which would help us in the preparation of other atlases of this kind. Should the response on this first trial indicate sufficient general interest, we shall endeavor to prepare similar spectra for the other diatomic radicals which occur in flames, and perhaps in time to extend this work to other important molecules.

2. Arrangement of the Atlas

All notation, assignments and wavelengths are those given in the complete work on OH of Dieke and Crosswhite [3]. The identification of the O_2 Schuman-Runge band ($^3\Sigma_u^- - {^3\Sigma_g^+}$) in the region 3370 to 3430 A was taken from the paper of Lochte-Holtgreven and Dieke [4].

The spectra are arranged so that an overall view of the $^2\Sigma^+ - {^2\Pi}$ electronic transition of OH from 2610 to 3520 A is given in figure 2. This spectrum was obtained from the hot gases above a hydrogen-oxygen flame. Outstanding features of the spectrum are labeled. Following this the

1

spectrum is given in detail in figures 3 to 19 with resolution sufficient to separate lines as close together as 0.1 A. The rotational and vibrational assignments are clearly marked above each spectrum. For convenience, an intensity scale is placed on each graph to show the relative intensity of the lines as compared to the intense Q_2 head of the 0,0 transition. It should be noted that the stronger lines have an emissivity of the order of 0.25 and therefore, the peak heights of strong lines will be considerably decreased by self absorption compared to weak lines.

Since the relative intensities of the various lines and bands are dependent upon temperature, it is necessary to use with care an atlas such as this to identify lines from different sources. Figure 20 shows the marked difference between the appearance of a small region at the 0,0 head (A) from a flame source, (B) from a high-frequency electrodeless discharge through water vapor, and (C) from a discharge through a mixture of water vapor and argon.

In figure 21, the emission from the flame, for a small region in the 0,0 band, is compared with absorption in the same flame as observed with the use of a xenon high-pressure lamp.

3. Experimental Arrangement

The flame source for figures 2 to 21 was a 3.5-mm thickness of hot gas approximately 3 mm above the tip of the inner cone of a flame of a stoichiometric mixture of hydrogen and oxygen. An ordinary welding burner with a port diameter of 0.5 mm was used. Previous studies have indicated that the measured rotational and vibrational distributions of OH in this part of the flame correspond to a temperature of 2,700° K, or 400° less than the calculated adiabatic temperature. Spectral intensities are reproduced to better than 3 percent with this source.

The source for figure 20 (B) was a 150-Mc electrodeless discharge through a stream of water vapor of about 1-cm Hg pressure; in figure 20 (C) the discharge was maintained through a flowing mixture of argon and water vapor at a partial pressure of H_2O of 3 mm Hg and a total pressure of 3 cm Hg. The discharge tube was a clear-quartz tube of 10-mm inner diameter and was water-cooled. The rotational distribution of this source is nearly a Maxwell-Boltzmann distribution for the lower rotational states, indicating a temperature of the order of 680° K. In figure 20 (C) higher rotational levels are populated somewhat in excess of a thermal distribution at this temperature.

The spectral dispersing system used to obtain the charts for this atlas is an experimental high-resolution grating monochromator that was constructed by the Research Department of Leeds & Northrup Co. and loaned to the Heat and Power Division at the National Bureau of Standards on a field-trial arrangement. This equipment is a special adaptation for laboratory use of a more general instrument designed for industrial metallographic analysis. Detailed descriptions of this equipment are given elsewhere [5].

A schematic diagram of the light path is shown in figure 1. Light from the flame, F, is focused by the front surface concave mirror, M_1, on the entrance slit, S_1, of the monochromator. Light passes through the slit to one side of the 8-inch-diameter concave mirror, M_2, at the focal distance (30 inches) from the slit and is reflected in a parallel beam to the grating, G. G is a plane reflection grating with 91,440 lines on a 3-by 3-inch flat of aluminum-coated glass. It is blazed for strong second-order diffraction in the region of 3,000 A. The diffracted beam is refocused by the other side of mirror M_2, to the exit slit, S_2, and then to a 1P28 photomultiplier tube, T. The signal from the photomultiplier is amplified and is fed into a pen recorder. Linear intensity is recorded along one axis of the chart and wavelength along the other.

A resolving power, $\lambda/\Delta\lambda$, in excess of 55,000 can be obtained. However, for this OH atlas such resolution has been sacrificed in order to obtain more intensity. Slit widths of 10 microns have been used; in the second order this width corresponds to 0.05 A. The spectra in figures 20 and 21 were made at a scanning rate of 1.18 A per minute, whereas the remaining spectra were scanned at 5.9 A per minute.

The spectra have been recorded on blank paper, and the figures are photographs of the original records. Positions of all lines of the main branches have been marked, but only resolved lines of the satellite branches have been indicated. Where possible, the assignments of Dieke and Crosswhite were extended either by use of the known energy levels or by a consideration of the spacing of the observed spectrum lines. Lines for which such identification seems reasonable, but not entirely certain, are indicated by dashed lines.

References

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    A. Gatterer and J. Junkers, Atlas der Restlinien, Specola Vaticana, Castel Gandolfo, Italy (1937).
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[2] R. W. B. Pearse and A. G. Gaydon, Identification of molecular spectra, John Wiley & Sons, New York, N. Y., (1950).

[3] G. H. Dieke and H. M. Crosswhite, The ultra violet bands of OH, fundamental data, Bumblebee Series Report No. 87, Nov. 1948.
[4] W. Lochte-Holtgreven and G. H. Dieke, Ann. Physik 3, 937 (1929).
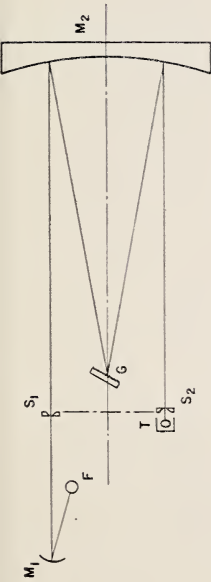[5] W. G. Fastie, J. Opt. Soc. Am. 42, 641 (1952).

Figure 1. *Schematic representation of optical system.*

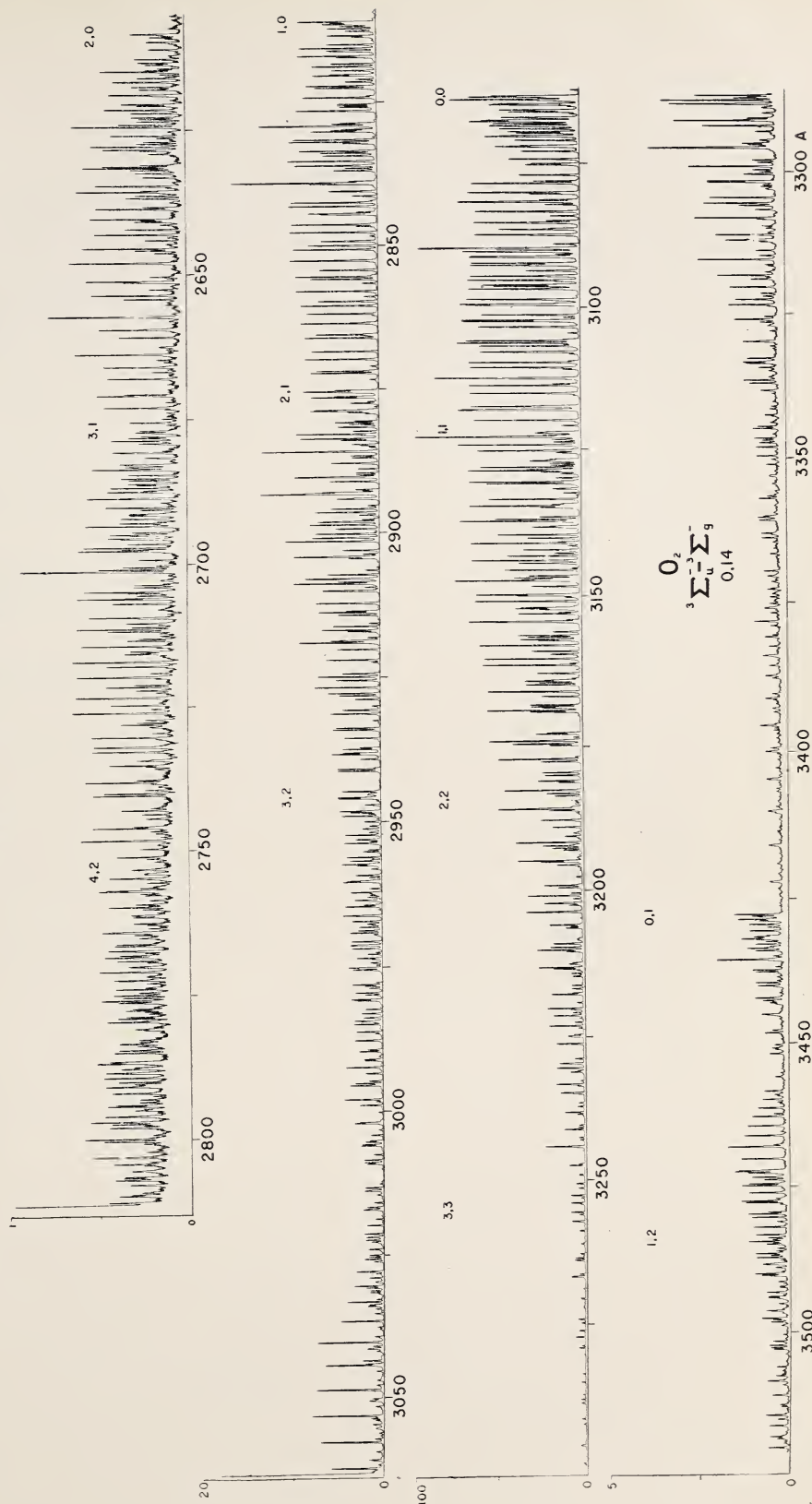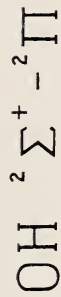F, Flame; M₁ and M₂, concave mirrors; S₁ and S₂, slits; G, grating; T, detector.

OH ²Σ⁺ - ²Π
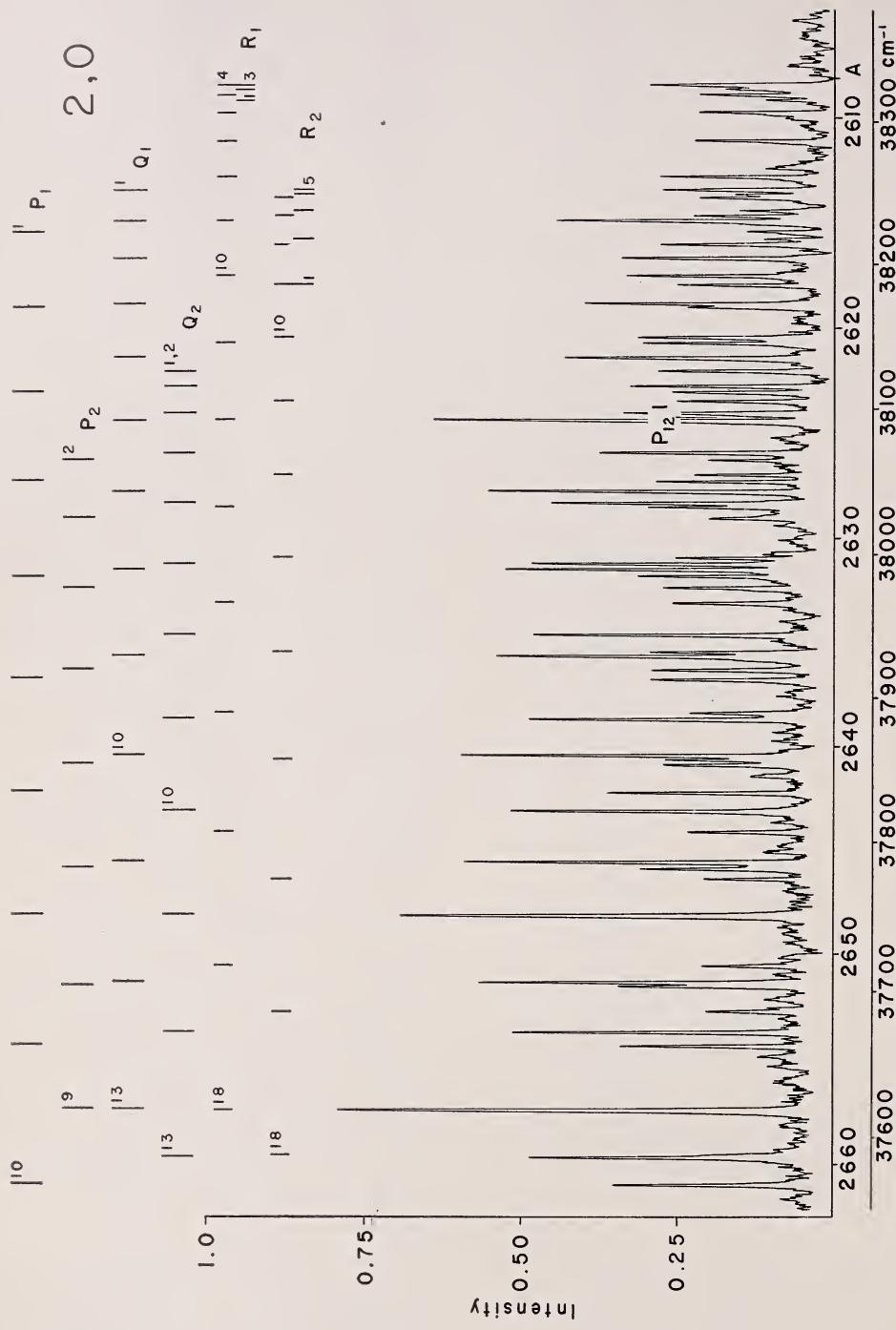
O₂
³Σ⁻ᵤ - ³Σ⁻g
0,14

Figure 2.

3

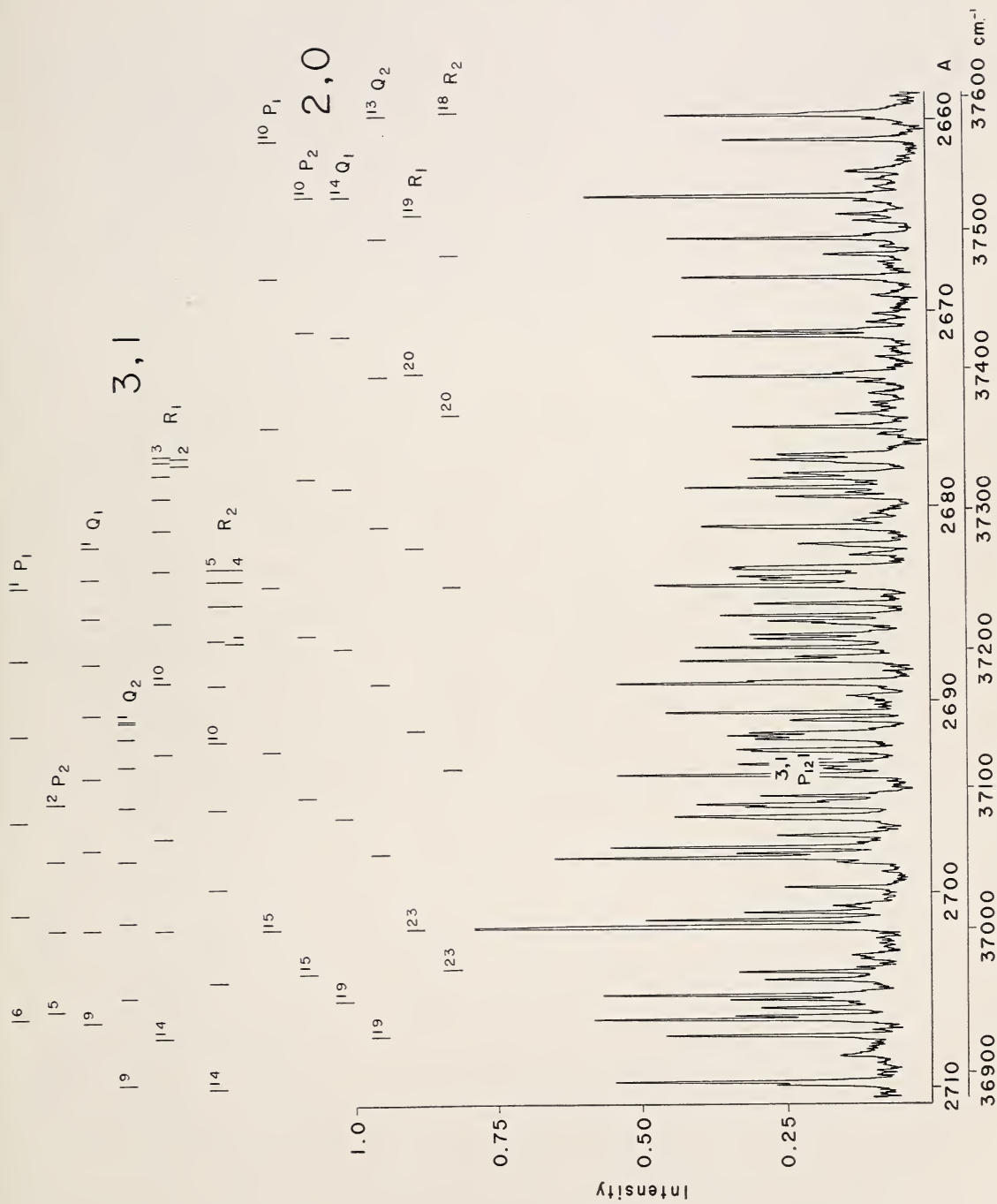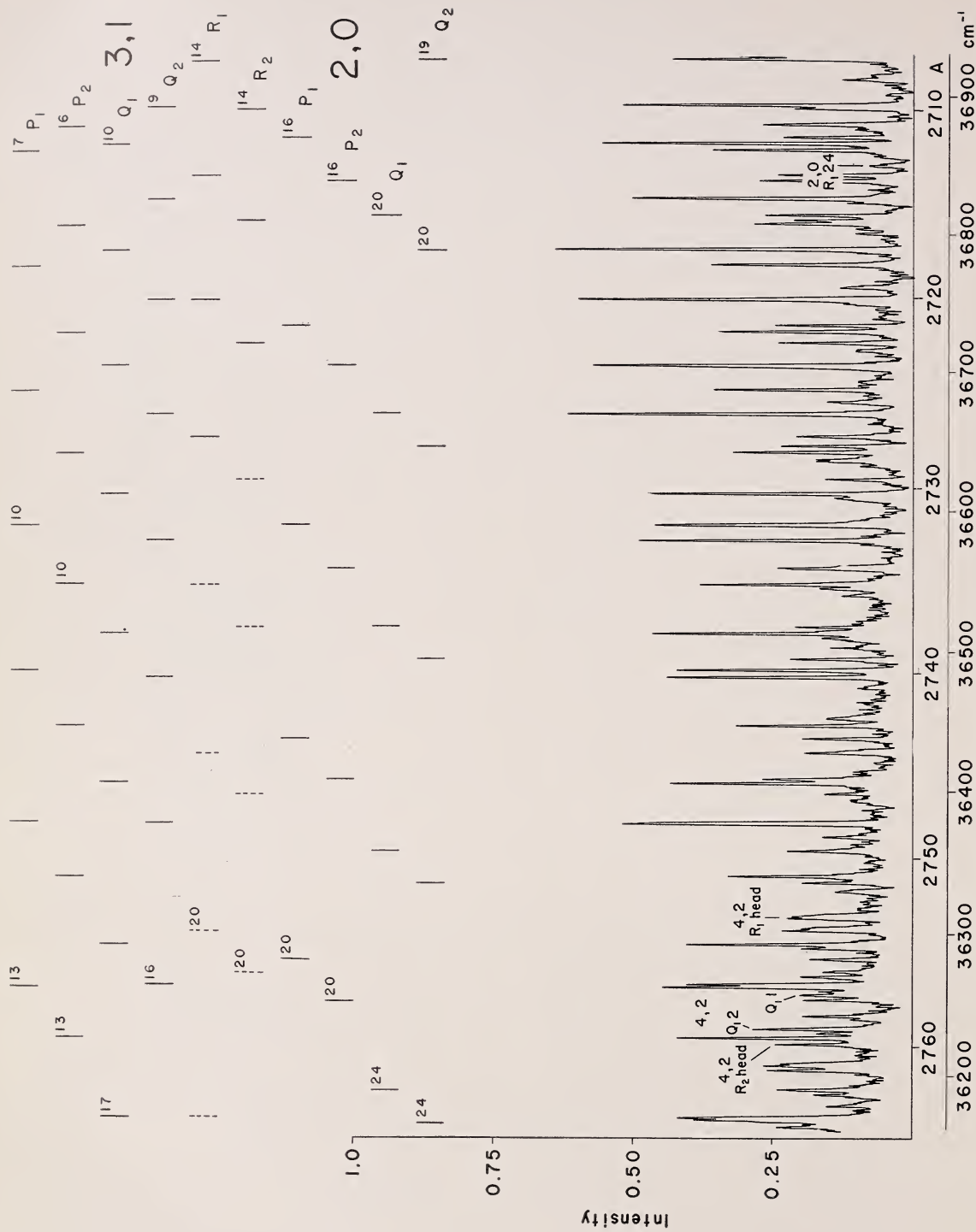FIGURE 3. OH emission in spectral region 2610 to 2660 A

4

FIGURE 4. OH *emission in spectral region 2660 to 2710 A.*

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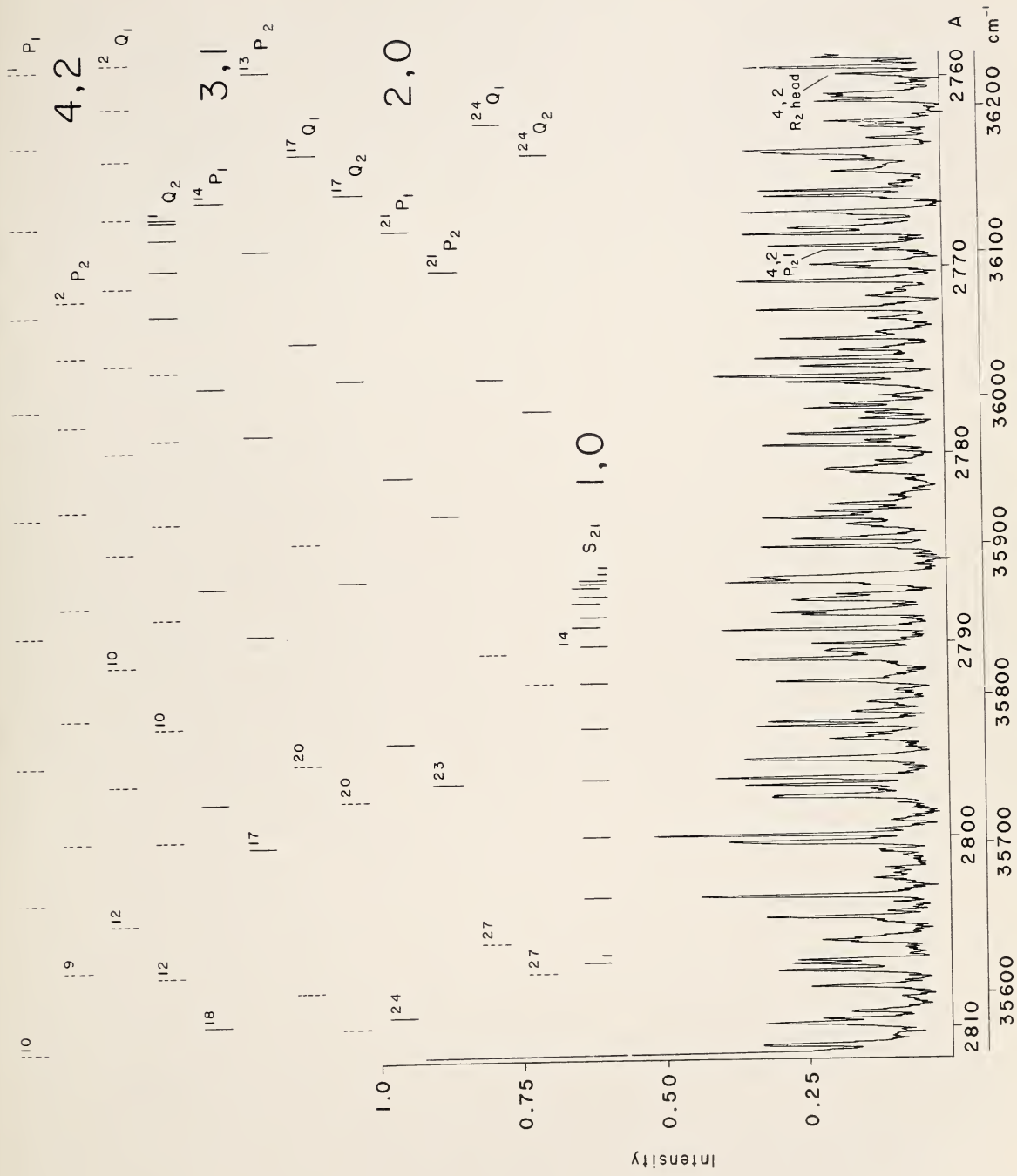FIGURE 5. *OH emission in spectral region 2710 to 2760 A.*

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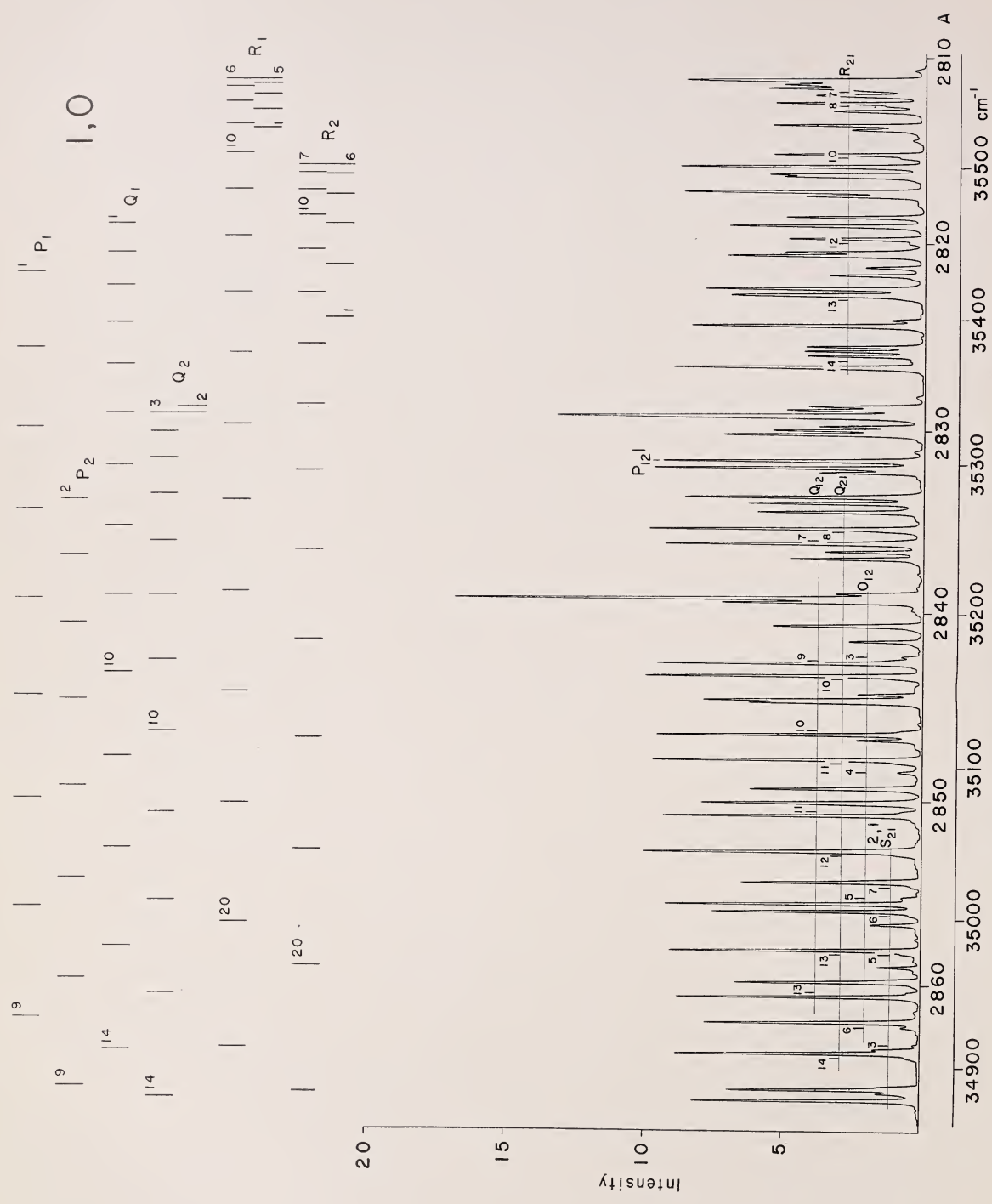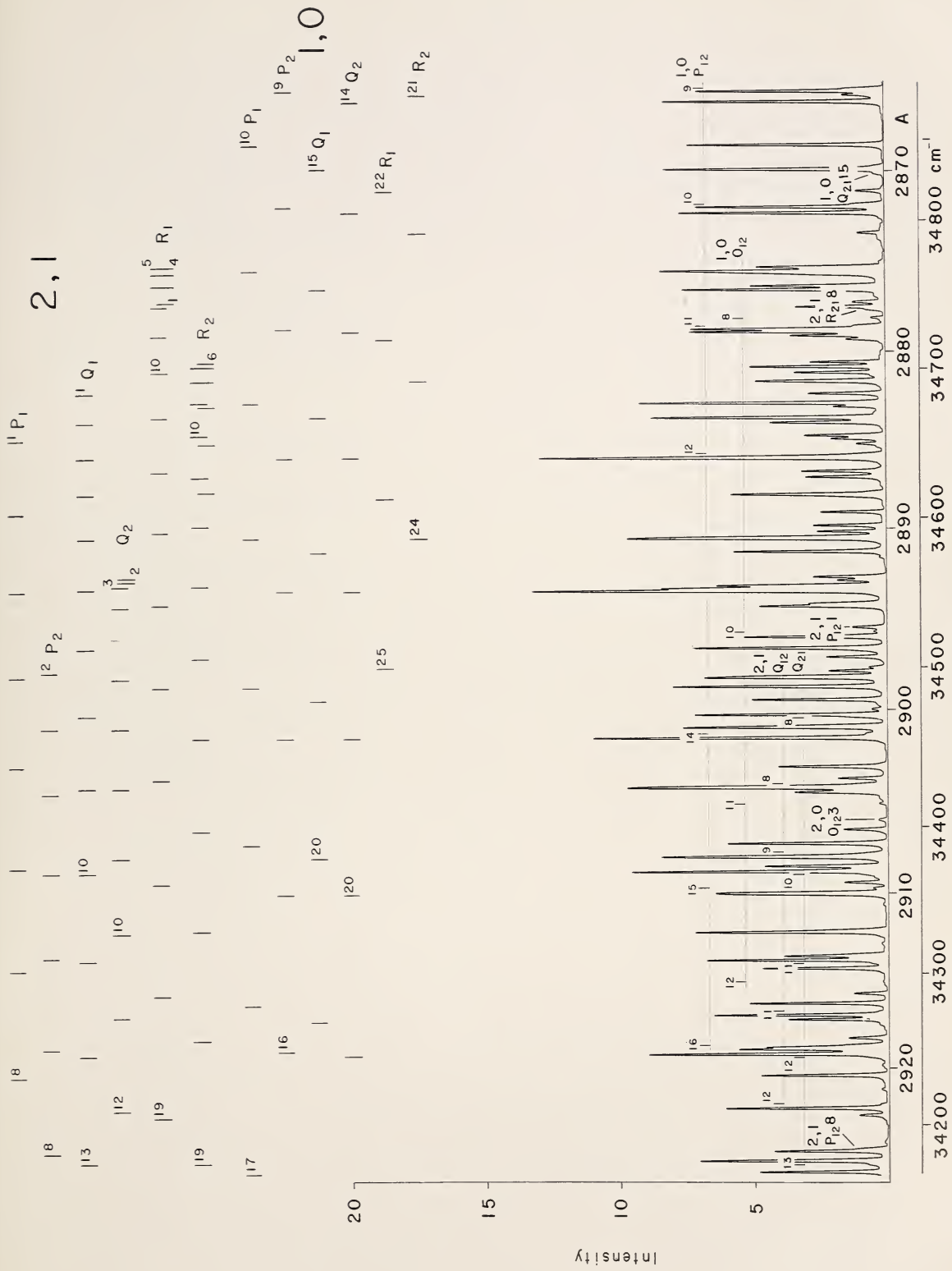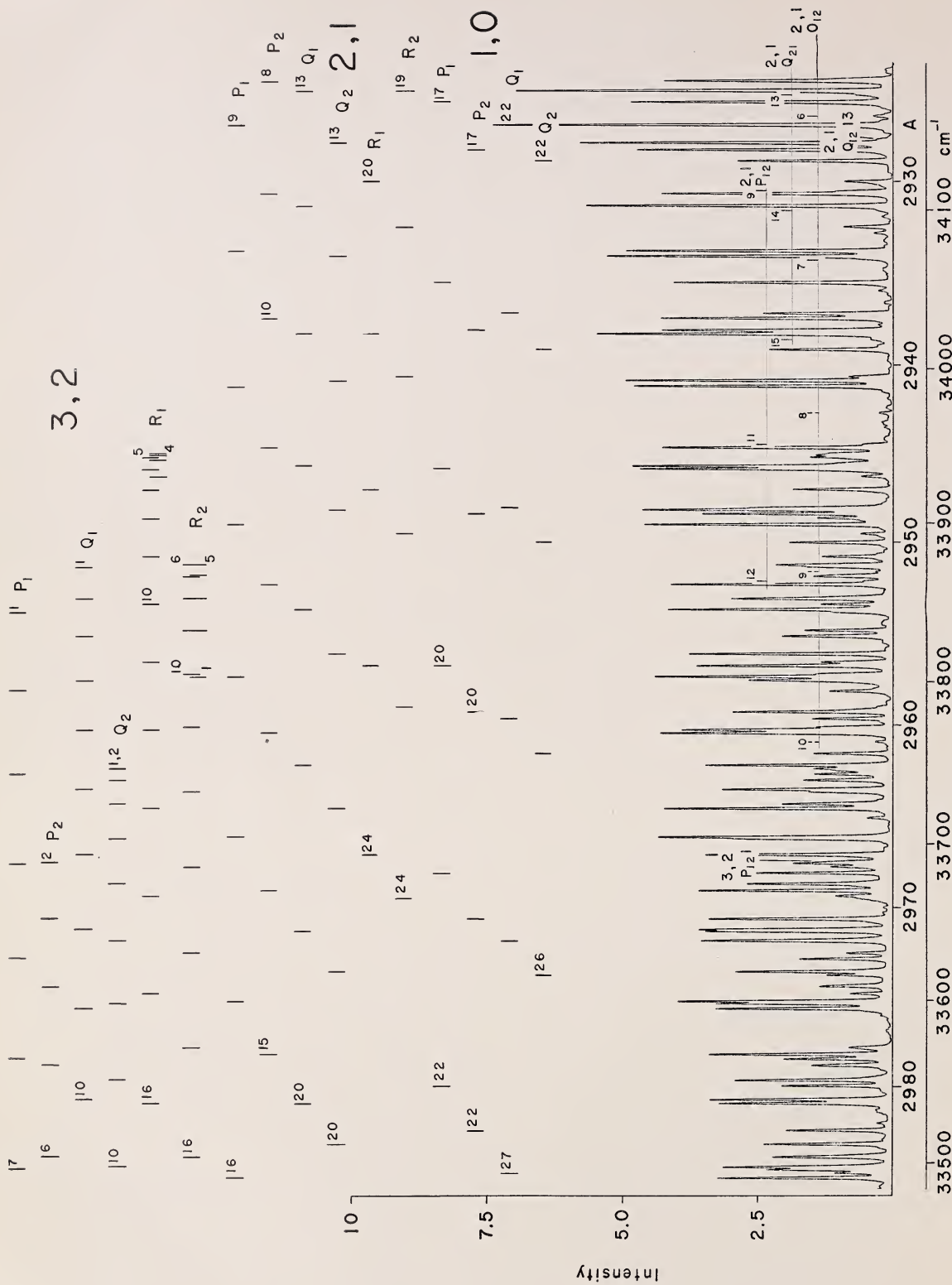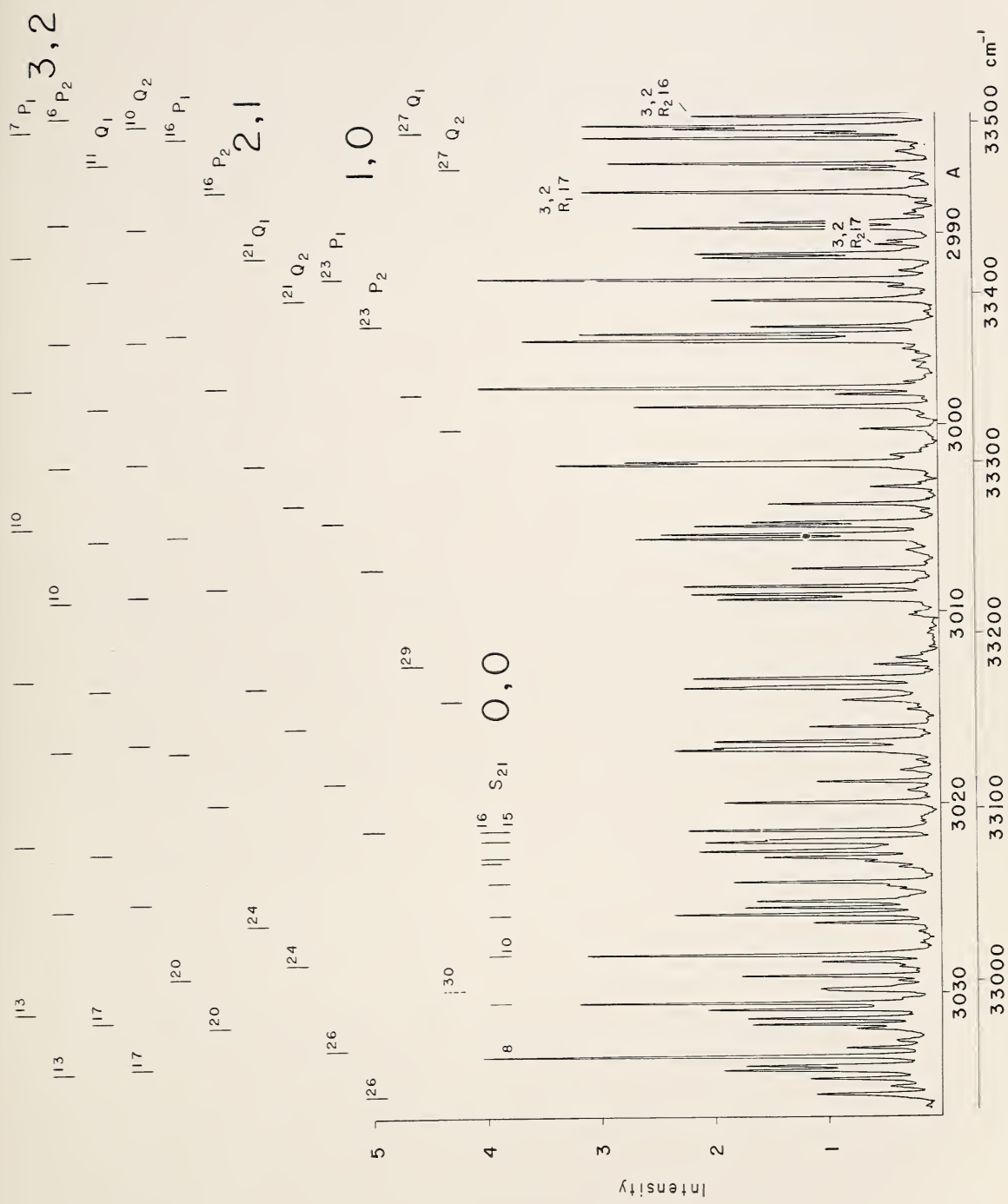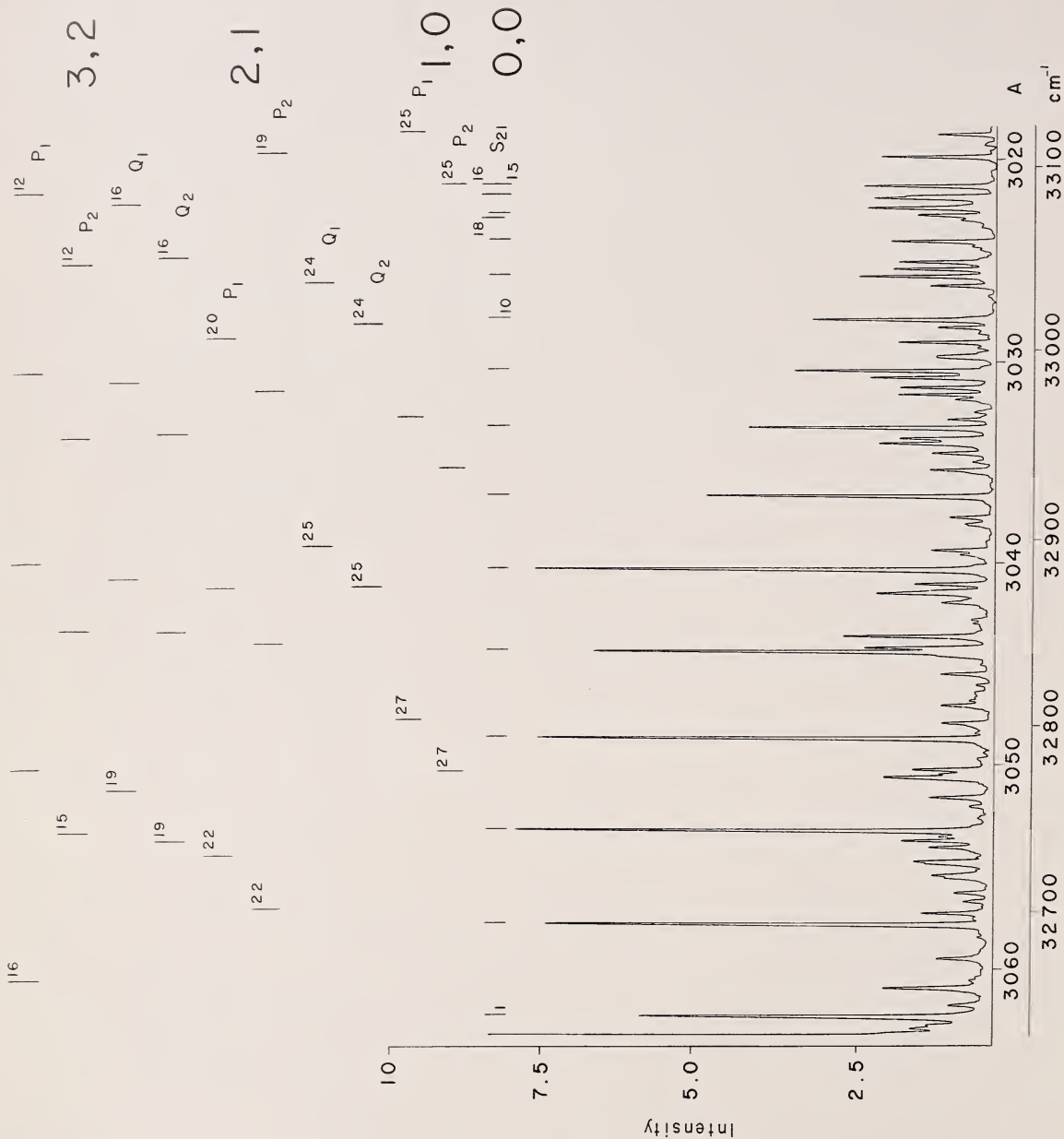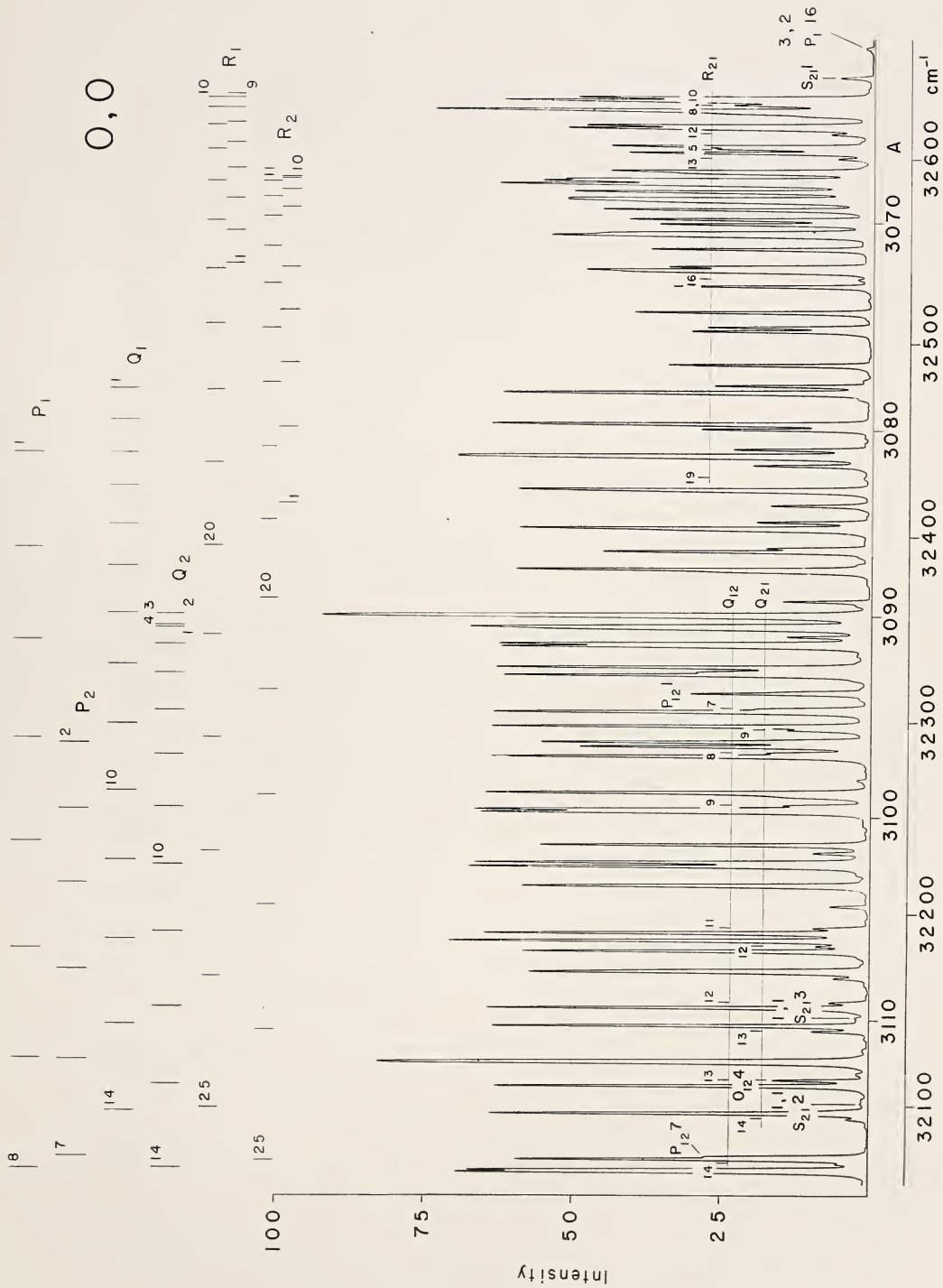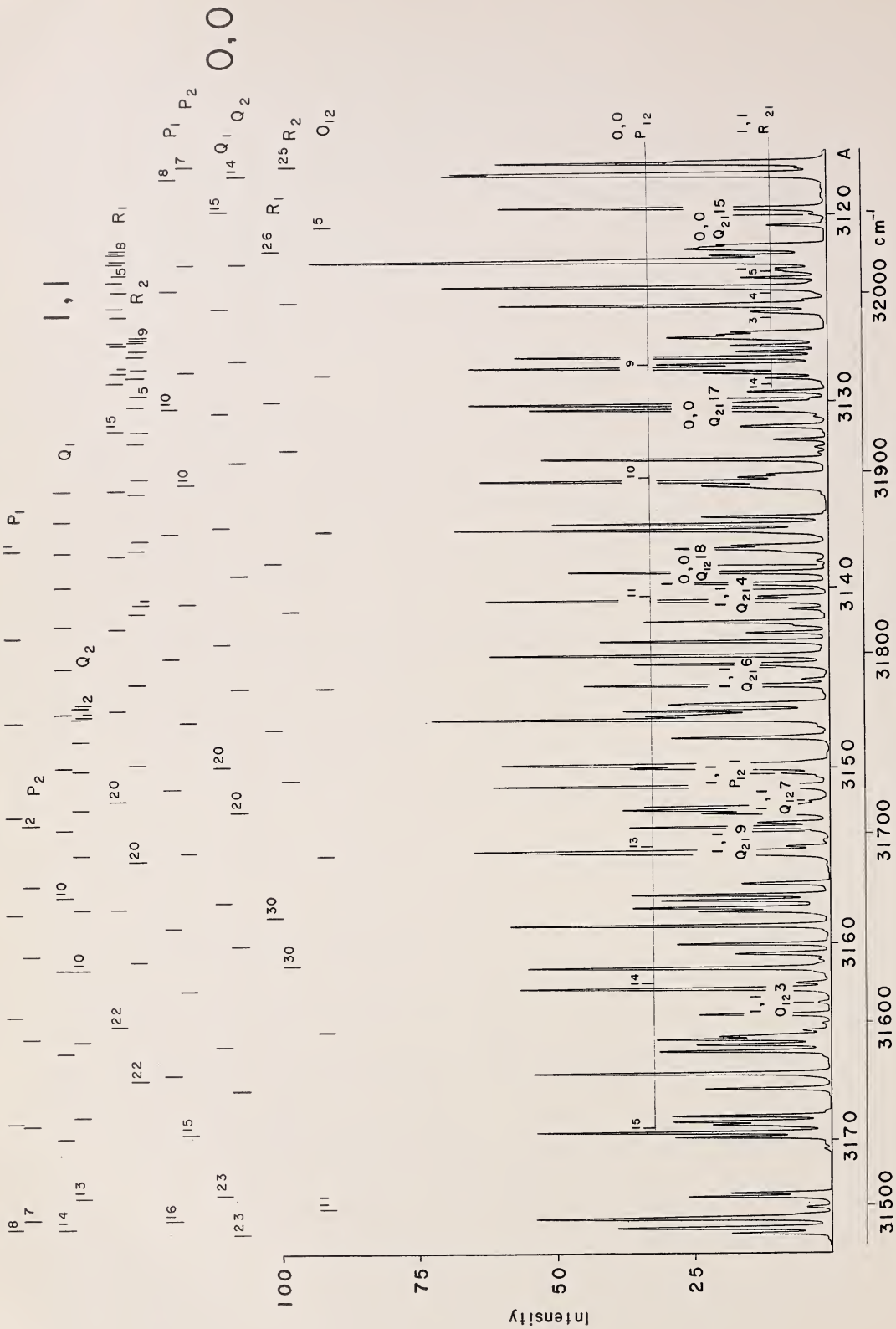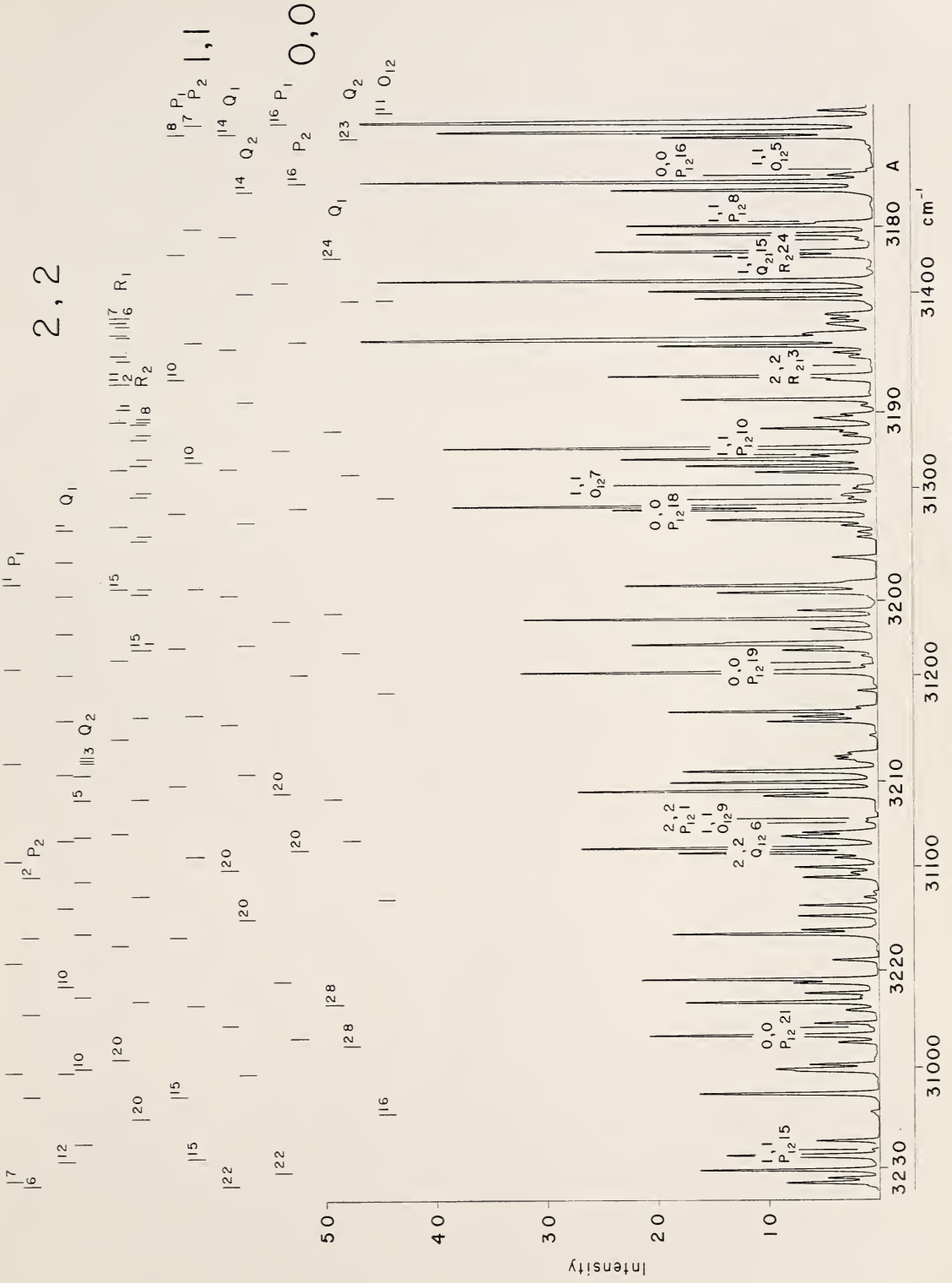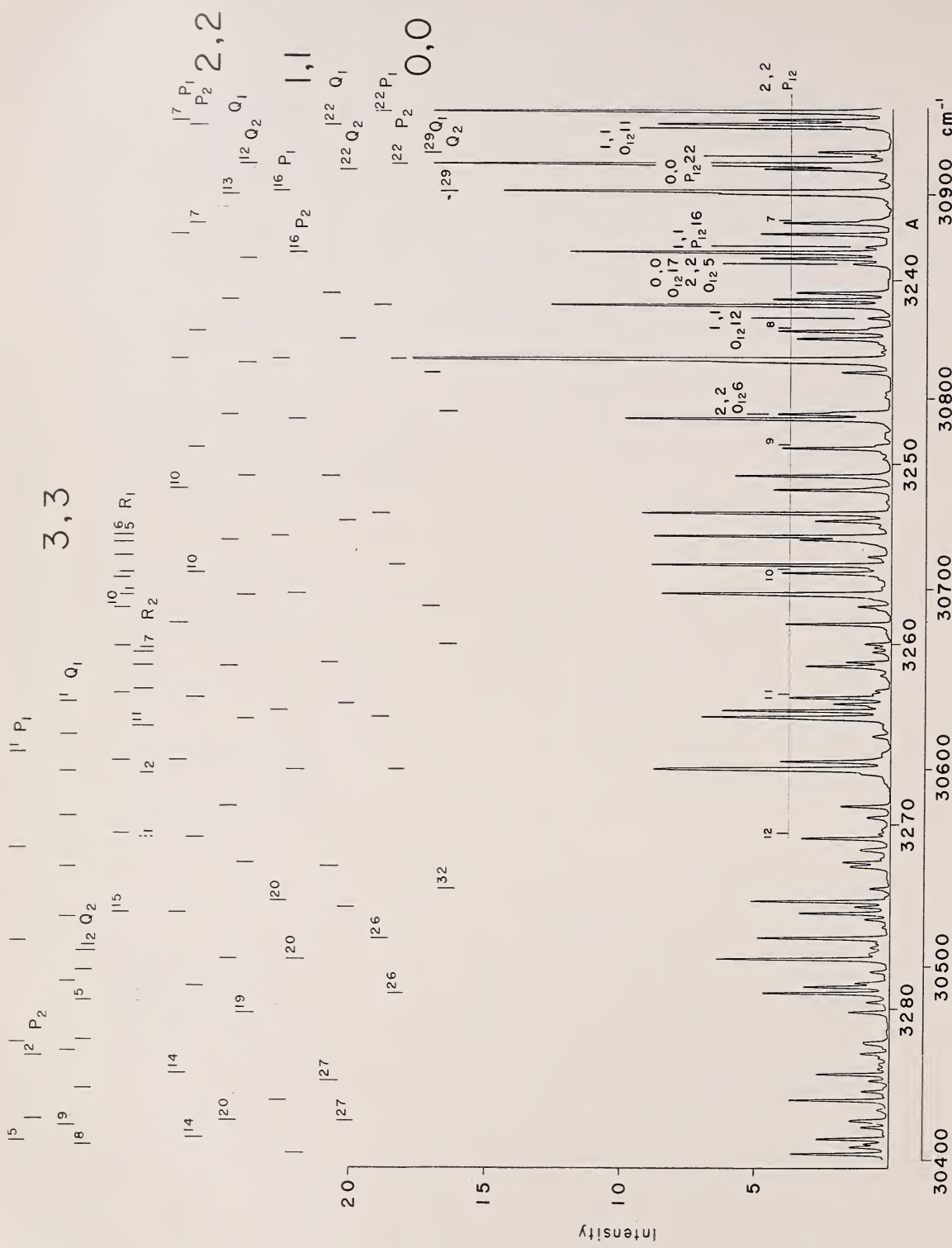FIGURE 6. *OH emission in spectral region 2760 to 2810 A.*

Figure 7. *OH emission in spectral region 2810 to 2860 A.*

8

Figure 8. OH emission in spectral region 2870 to 2920 A.

9

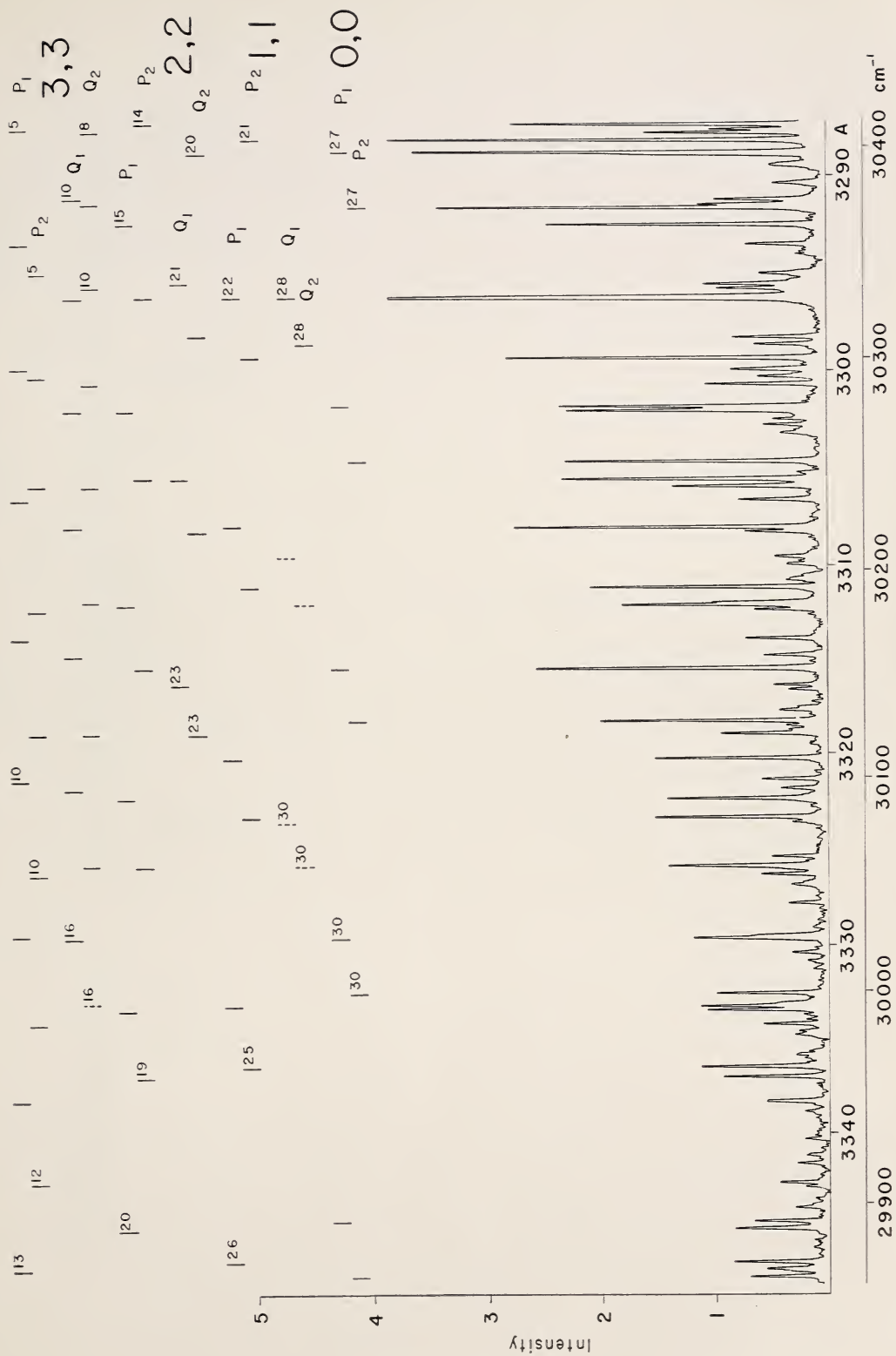FIGURE 9. OH *emission in spectral region 2930 to 2980 A.*

Figure 10. *OH emission in spectral region 2990 to 3030 A.*

11

Figure 11. OH *emission in spectral region 3020 to 3060 A.*

12

FIGURE 12. OH emission in spectral region 3070 to 3110 A.

13

FIGURE 13. OH *emission in spectral region 3120 to 3170 A.*

14

FIGURE 14. OH emission in spectral region 3180 to 3230 Å.

15

Figure 15. *OH emission in spectral region 3240 to 3280 A.*
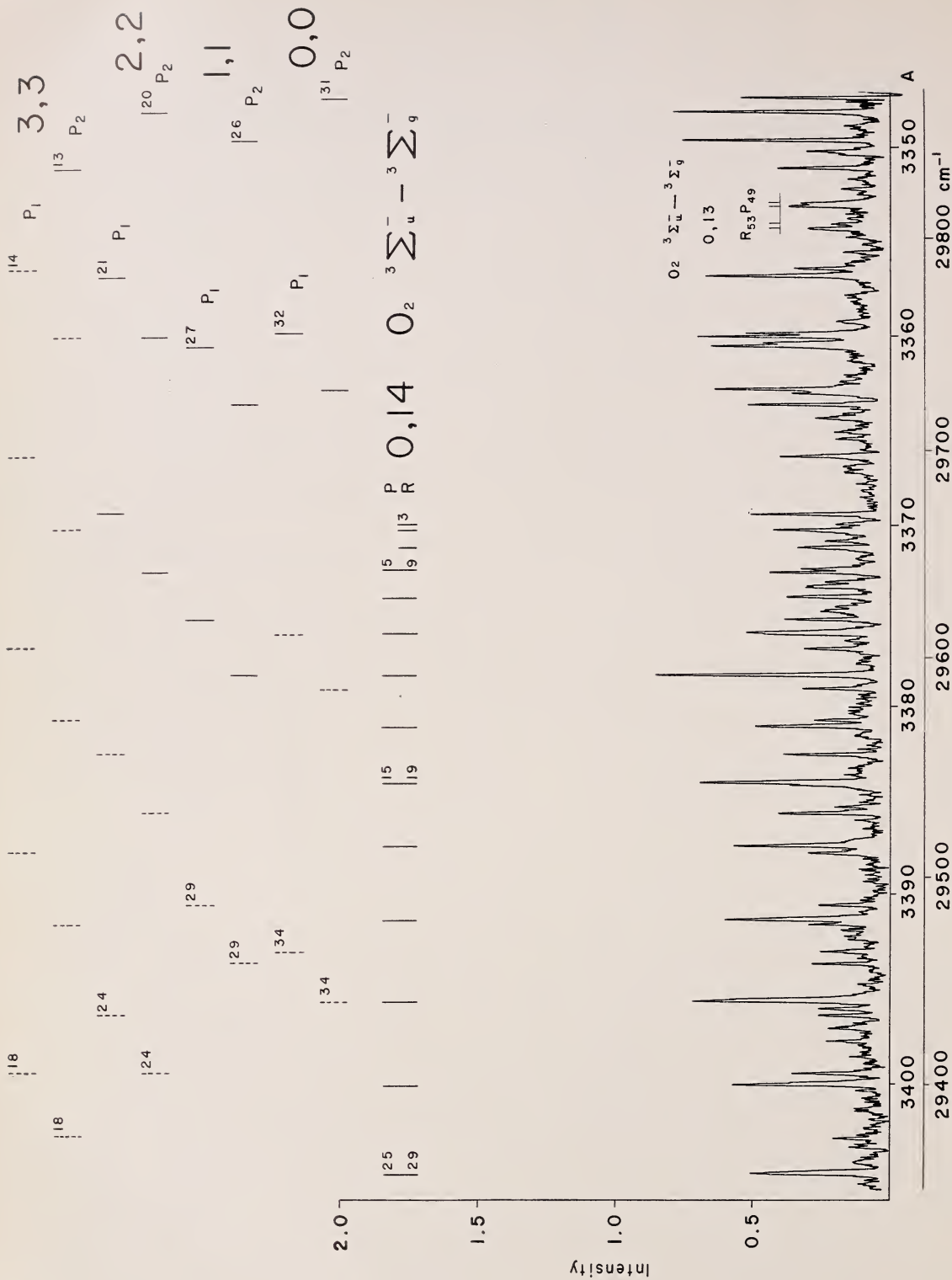
16

FIGURE 16. OH emission in spectral region 3290 to 3340 A.

17

FIGURE 17. OH emission in spectral region 3350 to 3400 A.

18

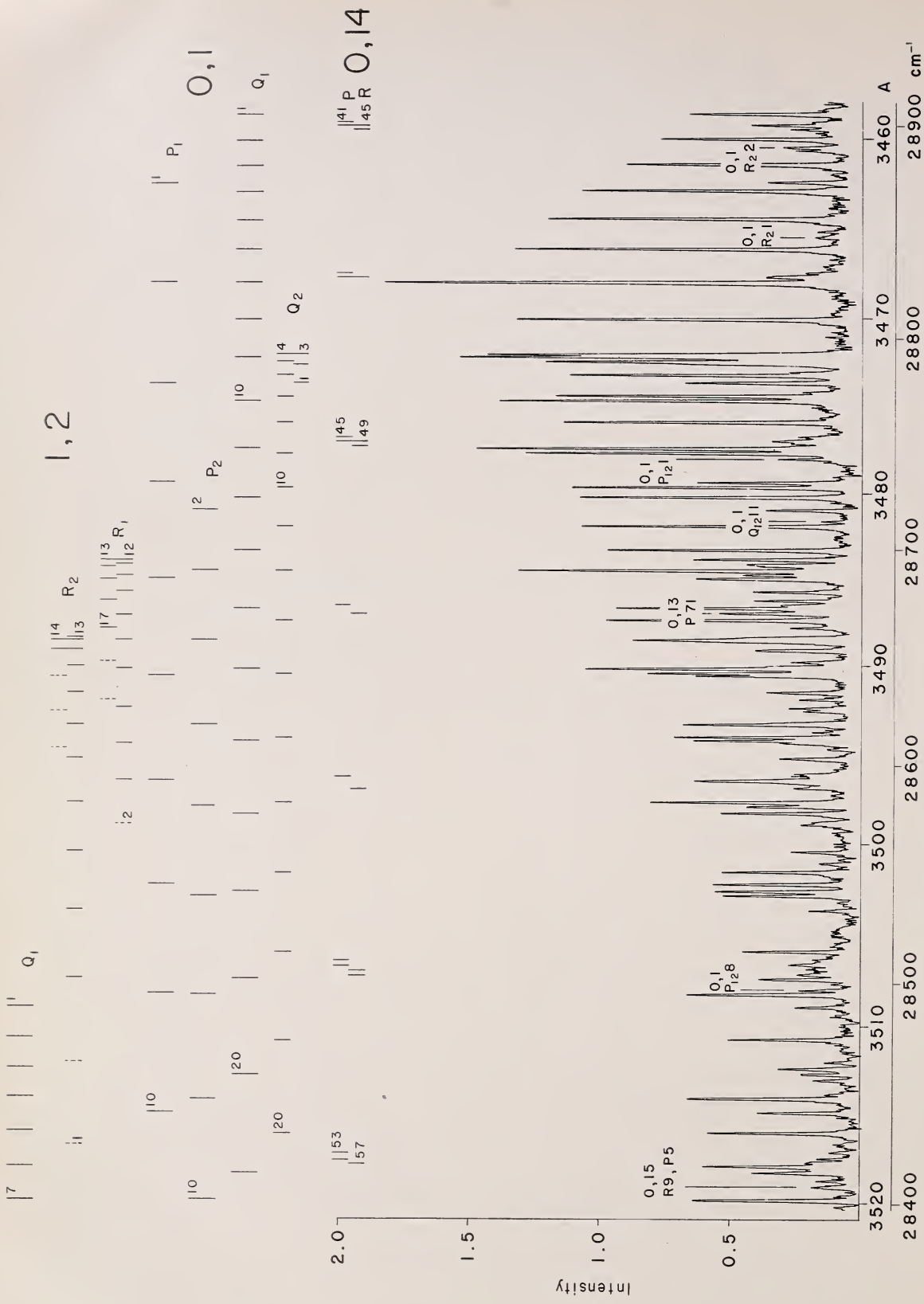FIGURE 18. OH emission in spectral region 3410 to 3460 Å.

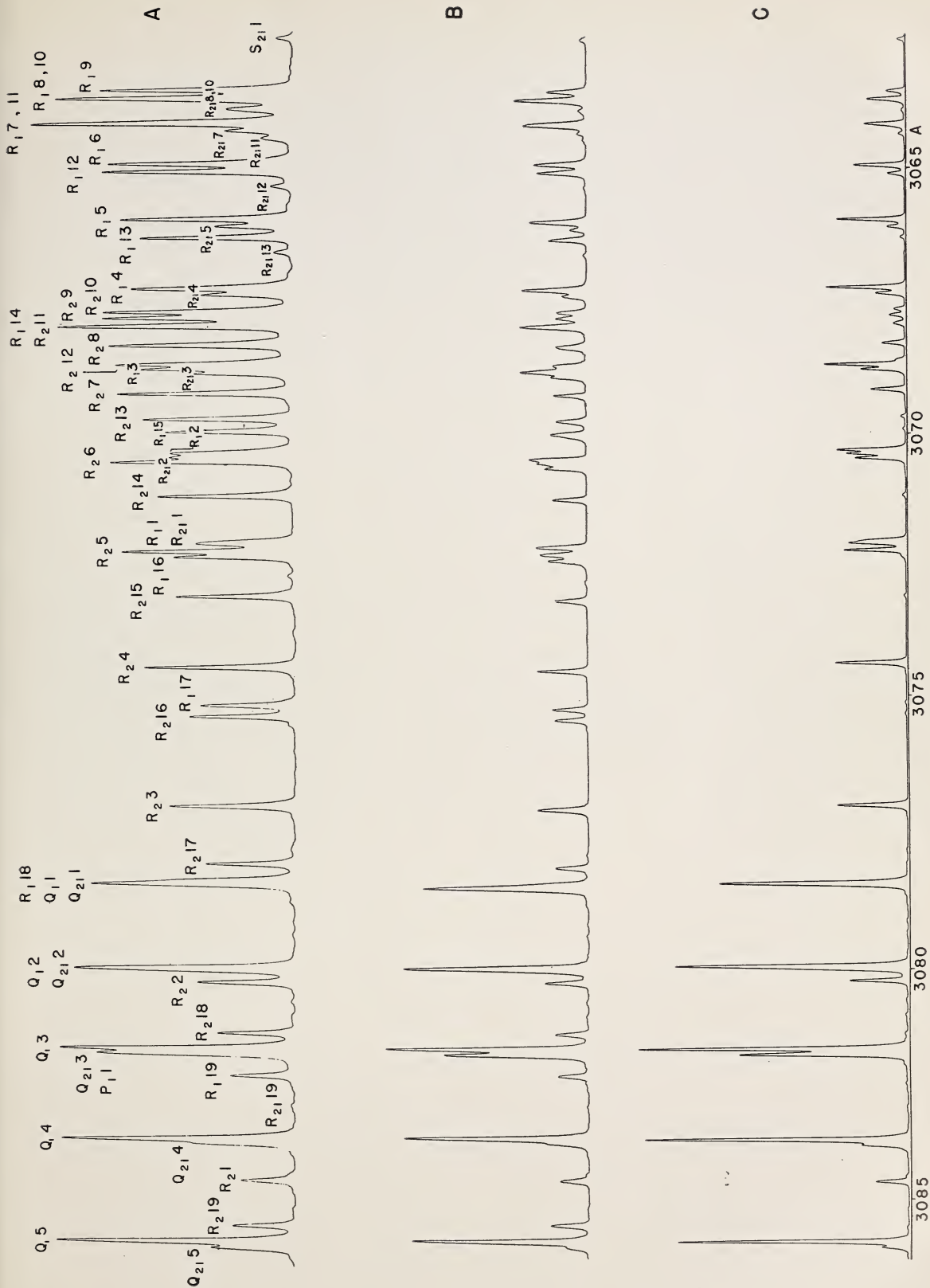FIGURE 19. OH *emission in spectral region 3460 to 3520 A.*

FIGURE 20. *Effect of excitation conditions on spectrum of OH.*

A, Flame source; B, 150-megacycle electrodeless discharge in water vapor at 1-cm Hg pressure; C, 150-megacycle electrodeless discharge in water plus argon; H₂O pressure, 3 mm Hg; total pressure, 3 cm Hg.
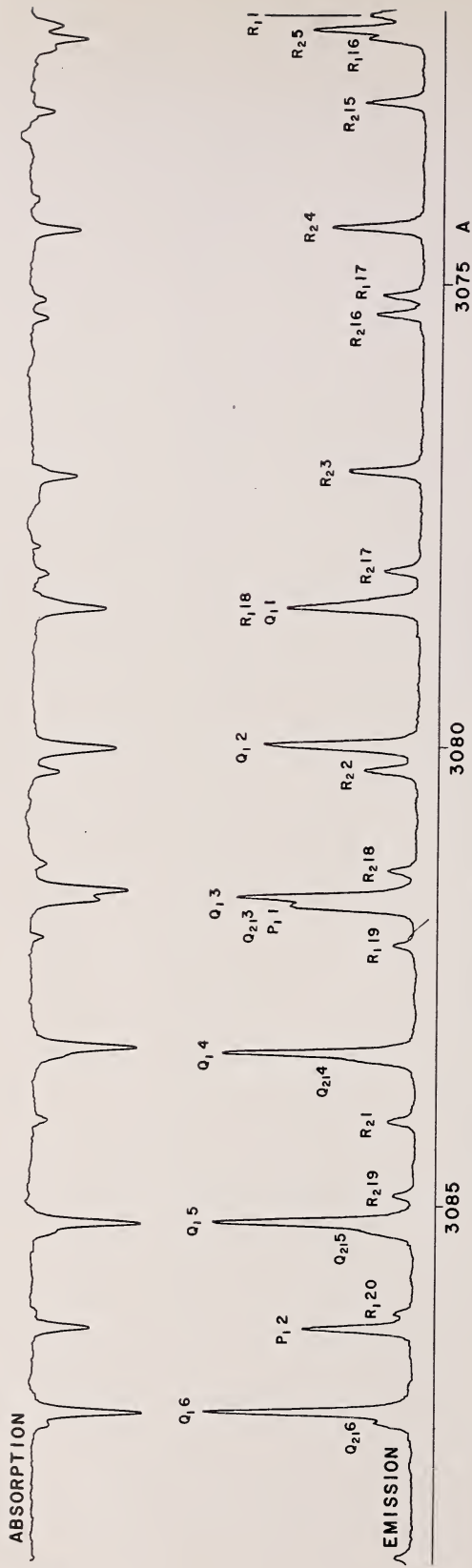
FIGURE 21. *Emission and absorption spectra of OH in hydrogen-oxygen flame.*