# INFRA-RED SPECTRA OF HELIUM 

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#### Abstract

Employing Xenocyanine photographic plates to explore the infra-red spectra of helium emitted by a Geissler tube used "end-on" about 120 new lines were recorded in the spectral interval 8,361 to 11,045 A. Analysis of these data shows that 32 of the lines belong to the arc spectrum of neutral He atoms ( He I ) and the remainder are ascribed to the band spectrum of the $\mathrm{He}_{2}$ molecule. The He $\mathbf{r}$ lines are accounted for as combinations of previously known terms and as extensions to the fundamental series, while the $\mathrm{He}_{2}$ lines for the most part represent hitherto lacking intercombinations between groups of terms which account for the visible bands of helium.


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## I. INTRODUCTION

The spectra of helium have been investigated ${ }^{2}$ so extensively that they would appear to have been exhausted. However, the recent discovery of a remarkable new infra-red sensitizer, Xenocyanine, by the Eastman Kodak Research Laboratories ${ }^{3}$ has greatly extended the photographic range of spectra, and use of these plates at the Bureau of Standards has revealed many new lines in the emission spectra of chemical elements. Up to the present, the longest published wave length observed photographically from helium was 7,281 A, but with Xenocyanine plates 120 lines have been recorded in the infra-red between 8,361 and $11,045 \mathrm{~A}$. In this range, only the reasonance line at 10,830 A was known, since its detection radiometrically by Paschen ${ }^{4}$ in 1908. Analysis shows that 32 of the above lines belong to the He i spectrum, while the remainder are ascribed to the band spectrum of the $\mathrm{He}_{2}$ molecule.

## II. EXPERIMENTAL

The source of the infra-red He spectra described in this paper was a Geissler tube made by Robert Goetze in Leipzig. It had a narrow capillary and was designed for end-on projection of the light into the

[^0]spectrograph. The tube was operated with uncondensed discharges from a 40,000 -volt transformer, the primary of which was fed by 5 or 6 amperes, 60 cycle, alternating current, 110 volts.

A concave grating spectrograph in Wadsworth mounting ${ }^{5}$ was employed in recording the spectra on Xenocyanine plates, the He exposure being made in the first order spectrum in which the dispersion is 10.26 A per millimeter. Comparison spectra of the iron are were photographed in the second order of the grating, above and below the He exposure, and wave-length measurements were based on the internationally adopted secondary standards. ${ }^{6}$ The duration of exposure averaged 16 hours for He and 2 minutes for Fe.

The appearance of such a large number of new lines in the He exposures first suggested the presence of impurities or spurious lines, but careful examination showed that the O I triplet at 9,260.9, $9,262.8$, and $9,266.1 \mathrm{~A}$ was the only impurity, and no evidence of Lyman ghosts was found. It was immediately suspected that most of the lines in this region must be due to the $\mathrm{He}_{2}$ molecule, but the production of this band spectrum under the conditions of excitation employed was somewhat surprising. It is well known that the ordinary Geissler tube of He excited by uncondensed discharges shows only the so-called are spectrum, He r. The band spectrum of the $\mathrm{He}_{2}$ molecule is excited with great intensity by using a higher pressure of He in a discharge tube with a large bore in place of the usual capillary, and passing through it discharges from an induction coil or transformer with a condenser in parallel and a small spark gap in series with the tube, ${ }^{7}$ but it appears also with uncondensed discharges in tubes with a very fine constriction in the bore. ${ }^{8}$ The latter conditions are approximated by the tube described above, and probably account for the production of the observed mixture of He I and $\mathrm{He}_{2}$ spectra.

## III. RESULTS

## 1. THE He I SPECTRUM

The Bohr model of a neutral He atom consists of a nucleus and two electrons so that its characteristic spectrum must resemble that of alkaline earths with two valence electrons. Its energy states must comprise a system of singlet terms and a system of triplet terms, among which singlet $S\left(1^{1} S_{0}\right)$ represents the normal state of the atom.

Analysis of the structure of the He i spectrum has been summarized in treatises on spectral series ${ }^{9}$ in which singlet and doublet systems are described. In the last treatise, it is shown that the doublet system is in reality a triplet system in which the level separations are so small that they are difficult to detect. Partial resolution of the ${ }^{3} \mathrm{P}$ terms gave the impression of doublets in the spectrum. Since the new infra-red (He I) lines are all accounted for as combinations of known terms or extensions of known series we are presenting our results in Table 1 in Grotrian's modern notation. Table 1 may,

[^1]however, be regarded as an extension to the He tables in any of the above-mentioned reports.

Table 1.-He I
Fundamental series $3^{1} \mathrm{D}=12,205.09$. $3^{1} \mathrm{D}-m^{1} \mathrm{~F}$

| $\lambda_{\text {air }}$ | $\begin{aligned} & \text { In- } \\ & \text { ten- } \\ & \text { sity } \end{aligned}$ | $\nu$ マac | $m$ | $m^{15}$ |
| :---: | :---: | :---: | :---: | :---: |
| 18,693. 4 | 2 | 5,348. 0 | 4 | 6,857. 1 |
| 12,792. 2 | 1 | 7,815. 1 | 5 | 4,390. 0 |
| 10, 917.0 | 3 | 9,157. 5 | 6 | 3,047. 6 |
| 10, 031. 16 | 15 | 9,966. 20 | 7 | 2, 038.9 |
| 9,529. 27 | 4 | 10, 491. 10 | 8 | 1,714.0 |
| 9, 213.1 | 1 | 10,851. 1 | 9 | 1,354. 0 |

Fundamental series $3^{3} D=12,209.10 . \quad 3^{3} \mathrm{D}-m^{3} \mathrm{~F}$

| $18,684.2$ | 3 | $5,350.71$ | 4 | $6,858.39$ |
| :---: | :---: | :---: | :---: | :---: |
| $12,784.6$ | 1 | $7,819.89$ | 5 | $4,389.21$ |
| $10,912.95$ | 6 | $9,160.92$ | 6 | $3,049.82$ |
| $10,027.73$ | 40 | $9,969.61$ | 7 | $2,239.49$ |
| $9,526.17$ | 10 | $10,494.52$ | 8 | $1,714.58$ |
| $9,210.28$ | 6 | $10,854.46$ | 9 | $1,354.64$ |
| $8,996.7$ | 2 | $11,112.1$ | 10 | $1,097.0$ |
| $8,845.0$ | 1 | $11,302.7$ | 11 | 906.4 |

Combinations

| $\lambda_{\text {a ir }}$ | $\begin{aligned} & \text { In- } \\ & \text { ten- } \\ & \text { sity } \end{aligned}$ | $\nu$ | $\begin{gathered} \text { Combina- } \\ \text { tion } \end{gathered}$ |
| :---: | :---: | :---: | :---: |
| 10,233. 0 | 2 | 9,769.6 | $3^{1} \mathrm{P}-71 \mathrm{~S}$ |
| 9,682. 4 | 1 | 10, 325.2 | $3^{1 \mathrm{P}}$ - $8^{1 / S}$ |
| 11, 045.1 | 1 | 9, 051. 3 | $3^{1} \mathrm{P}-6^{1} \mathrm{D}$ |
| 10, 138. 50 | 10 | 9, 860.69 | $3^{1} \mathrm{P}-7^{1} \mathrm{D}$ |
| 9, 625.80 | 3 | 10, 385.90 | $3^{12} \mathrm{P}-8^{1} \mathrm{D}$ |
| 9,303.2 | 2 | 10,746.0 | $3^{1} \mathrm{P}-91 \mathrm{D}$ |
| 9, 085.6 | 1 | 11, 003.4 | $3^{1 \mathrm{P}}-10^{1} \mathrm{D}$ |
| 11, 013.1 | 1 | 9, 077.6 | $31 \mathrm{~S}-5^{1 \mathrm{P}}$ |
| 9,603. 50 | 6 | 10,410. 11 | $31 \mathrm{~S}-6^{1 P}$ |
| 8,914. 7 | 2 | 11, 214.4 | $31 \mathrm{~S}-7^{1 \mathrm{P}}$ |
| 10, 667. 62 | 4 | 9, 371. 60 | $3^{3} \mathrm{P}-6^{3} \mathrm{~S}$ |
| 9,702. 66 | 10 | 10, 303. 63 | $3^{3} \mathrm{P}-7^{3} \mathrm{~S}$ |
| 9, 346.2 | 2 | 10,896. 6 | $3^{3} \mathrm{P}-8^{3} \mathrm{~S}$ |
| 10, 311. 32 | 40 | 9, 695.43 | $3^{3} \mathrm{P}-6^{3} \mathrm{D}$ |
| 9, 516. 70 | 30 | 10, 504.9? | $3^{3} \mathrm{P}-7^{3} \mathrm{D}$ |
| 9, 063.40 | 6 | 11, 030.36 | $3^{3} \mathrm{P}-8^{3} \mathrm{D}$ |
| 10, 072. 10 | 2 | 9, 925. 70 | $3^{3} \mathrm{D}-7^{3} \mathrm{P}$ |
| 9, 552.8 | 1 | 10, 465.3 | $3^{3} \mathrm{D}-8^{3} \mathrm{P}$ |
| 9, 463. 66 $8,361.7$ | 60 3 | $10,563.84$ $11,956.0$ | $\begin{aligned} & 3^{3} S-5^{3} \mathrm{P} \\ & 3^{3} S-6^{3} \mathrm{P} \end{aligned}$ |

The so-called fundamental (hydrogenlike) series of He have been extended from 2 to 6 members in the singlet system and from 2 to 8 in the triplet system, the first two lines of each series representing the radiometric observations of Paschen, so that the intensities of these are not to be compared with the photographic estimates of the remainder. The third line of each series lies close to $11,000 \mathrm{~A}$, and to compensate for declining photographic sensitivity their estimated intensities should be multiplied by 10 or more to make them comparable with the succeeding lines.

## 2. THE $\mathrm{He}_{2}$ BANDS

The known energy levels of the helium molecule ${ }^{10}$ may be regarded as originating from a single valence electron and may therefore, be classified as $s \Sigma, p \Sigma, p \Pi, d \Delta$, etc., levels in which the $s, p, d$ mean, as in atomic spectra, that the orbital moment of the valence electron is $0,1,2$, whereas the symbols $\Sigma, \Pi, \Delta$ designate the component $\Lambda$ of this orbital momentum along the internuclear axis. The low levels which are the final states in the transitions which give rise to the visible helium bands are $2 s \Sigma, 2 p \Pi$, and $2 p \Sigma$. The negative $s$ and $d$ levels combine with the $2 p \Sigma$ and $2 p \Pi$ levels, whereas the positive $p$ levels combine with the $2 s \Sigma$ level. This fact divides the terms of the helium molecule into two groups, the $2 s \Sigma$ level and those terms which combine with it on the one hand and the $2 p \Sigma$ and $2 p \Pi$ levels and those terms which combine with them on the other hand. The relative term values in each group can be determined with the accuracy of the wave-length measurements, but the relative position of the two groups can only be determined by calculating the limits of two Rydberg series. This is due to the fact that all the intercombinations between the two groups which are allowed by the selection rules must fall in the infra-red and were not observed so far.

The new lines in the infra-red given in the present paper are partly due to just such transitions. ${ }^{11}$ The most prominent band in this region has its head at $9,123 \mathrm{~A}$ and is due to a transition $2 p \Sigma \rightarrow 2 s \Sigma$. (See Table 2.)

Table 2.- $\mathrm{He}_{2}$
Band at $9,123 \mathrm{~A} \quad 2 p \Sigma \rightarrow 2 s \Sigma$

| K | P branch |  |  | R branch |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\lambda$ | J | $\nu$ | $\lambda$ | I | $\nu$ |
| 1 | 9,193. 55 | 4 | 10,874. 21 | 9, 158. 92 | 7 | 10, 915. 32 |
| 3 | 9, 222.96 | 10 | 839.53 | 42.23 | 12 | 935. 25 |
| 5 | 57.50 | 20 | 799. 09 | 30.66 | 10 | 949.11 |
| 7 | 97.14 | 20 | 753.05 | 24. 29 | 8 | 956.75 |
| 9 | 9,341. 91 | 15 | 701.51 | 23. 17 | 6 | 958.10 |
| 11 | 91. 90 | 10 | 644.55 | 27. 34 | 5 | 953.09 |
| 13 | 9, 447. 12 | 8 | 582.34 | 37. 00 | 5 | 941.51 |
| 15 | 9, 507. 74 | 8 | 514.86 | 52. 23 | 5 | 923.30 |
| 17 | 73.90 | 7 | 442.20 | 73. 18 | 5 | 898.36 |
| 18 | 9,645. 68 | 7 | 364.49 | 9,200.00 | 5 | 866. 59 |
| 21 | 9, 723. 33 | 6 | 281.72 | 33. 03 | 3 | 827.71 |
| 23 | 9, 807. 13 | 5 | 183.87 | 72.60 | 2 | 781.50 |
| 25 | 97.47 | 3 | 100.82 |  |  |  |
| 27 | 9,994.6 | 1 | 002.7 |  |  |  |

Band at $9,346 \mathrm{~A} \quad 2 p \Sigma^{1} \rightarrow 2 s \Sigma^{1}$

| 1 |  |  |  | 9, 376.6 | 1 | 10.661. 9 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3 | 9,441.6 | 2 | 10,588. 5 | 60.67 | 2 | 680.07 |
| 5 | 77.72 | 3 | 548.17 | 50.50 | 2 | 691.69 |
| 7 | 9, 519. 39 | 3 | 501. 89 | 46.2 | 2 | 696.6 |
| 9 | 67.08 | 3 | 449.64 | 48.0 | 2 | 694.5 |
| 11 | 9,620. 88 | 2 | 391.21 | 55. 70 | 2 | 685. 74 |
| 13 | 80.54 | 2 | 327. 17 | 69.8 | 1 | 669.7 |
| 15 | 9, 746. 64 | 2 | 257.13 | 90.3 | 1 | 646.4 |
| 17 | 9, 819.18 | 2 | 181. 36 |  |  |  |
| 19 | 98. 67 | 2 | 099.60 |  |  |  |
| 21 | 9,985. 43 | 1 | 011.85 |  |  |  |

[^2]Both the initial and the final state of this band are already known. The final state is that of the so-called main series ${ }^{12}$ ( $2 s-n p$ in the old notation) which contains the most prominent bands of the spectrum. The initial state $2 p \Sigma$ is the final state of a group of bands, the first of which was discovered by Merton and Pilley ${ }^{13}$ and which are described in full elsewhere. ${ }^{14}$

The combination relations given in Table 3 prove the identity of the band. The second column (marked new) gives the rotational differences of the final state

$$
R(K-1)-P(K+1)=2 s \Sigma(K+1)-2 s \Sigma(K-1)
$$

The next column gives the average of the same differences obtained from the bands of the main series. ${ }^{15}$ The agreement is very good which proves that $2 s \Sigma$ must be the final state of the band.

In the same way we prove from the agreement of the differences

$$
R(K)-P(K)=2 p \Sigma(K+1)-2 p \Sigma(K-1)
$$

given in column 7 for the new band and in column 8 for the previously known bands which have $2 p \Sigma$ as final state that $2 p \Sigma$ is the initial state of the new band. The band has only a $P$ and $R$ branch as must be expected for a $\Sigma \rightarrow \Sigma$ transition.

There is a fainter band of exactly the same structure with its head at $9,346 \mathrm{~A}$. (See Table 2.). It is the $2 p \Sigma^{1} \rightarrow 2 s \Sigma^{1}$ band which has the same electronic transition as the band at 9,123 A mentioned above, but a $1 \rightarrow 1$ vibrational transition (instead of $0 \rightarrow 0$ for $\lambda 9,123$ ). The columns 4 and 5 of Table 3 prove in the same way as explained above for the main band that $2 s \Sigma^{1}$ is actually the final state. The initial state $2 p \Sigma^{1}$ was not known before.

Table 3.-Combination relations

| $K$ | $2 s \Sigma(K+1)-2 s \Sigma(K-1)$ |  |  |  | $K$ | $2 p \Sigma(K+1)-2 p \Sigma(K-1)$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $v=0$ |  | $\theta=1$ |  |  | $v=0$ |  | $p=1$ (new) |
|  | New |  | New |  |  | New |  |  |
| 2 | 75. 79 | 75.80 | 73.4 | 73.39 | 1 | 41. 11 | 41.07 |  |
| 4 | 136. 16 | 136.20 | 131.90 | 131.87 | 3 | 95. 72 | 95. 69 | 91.57 |
| 6 | 196.06 | 196. 06 | 189.70 | 189.84 | 5 | 150. 02 | 150.00 | 143. 52 |
| 8 | 255. 24 | 255. 22 | 247.0 | 247.08 | 7 | 203. 70 | 203. 69 | 194. 61 |
| 10 | 313. 55 | 313.49 | 303.3 | 303.47 | 9 | 256. 59 | 256.61 | 248.86 |
| 12 | 370.75 | 370.76 | 358. 57 | 358. 63 | 11 | 308. 54 | 308.56 | 294.53 |
| 14 | 426. 65 | 426. 63 | 412.6 | 412.60 | 13 | 359.17 | 359. 14 | 342. 53 |
| 16 | 481.10 | 481.07 | 465.0 | 465.03 | 15 | 408.44 | 408.22 | 389. 27 |
| 18 | 533.87 | 533.85 |  |  | 17 | 456. 16 | 456.45 |  |
| 20 | 584.87 | 584.91 |  |  | 19 | 502. 10 |  |  |
| 22 | 633.84 | 633 |  |  | 21 | 545.99 |  |  |
| 24 | 680.68 | 680 |  |  | 23 | 587.63 |  |  |

Besides the two bands given above, we must expect in this region the bands $3 s \Sigma \rightarrow 2 p \Sigma$ and the whole $3 d \rightarrow 2 p \Sigma$ complex. Only a few lines of the $3 s \Sigma \rightarrow 2 p \Sigma$ band could be identified near 10,400 A. The sensitiveness of the photographic plate in this region is already too

[^3]weak to allow also the weaker lines to be recorded. The $3 d \rightarrow 2 p \Sigma$ complex is completely present, it is given in Table 4. The calculated frequencies are obtained with the help of the known differences between the $2 p \Sigma$ and the $2 p \Pi$ states. This band complex shows the same characteristics as the $4 d \rightarrow 2 p \Sigma$ complex. ${ }^{16}$ The $P$ branch of $3 d \Sigma \rightarrow 2 p \Sigma$ is practically absent, and the $R$ branch of $3 d \Pi \rightarrow 2 p \Sigma$ can not be found at all. This is due to the decoupling of the orbital momentum. The band $3 d \Delta \rightarrow 2 p \Sigma$ is entirely absent. It is forbidden if the orbital momentum is coupled to the internuclear axis, as $\Lambda$ would change by two units. For the $3 d \Delta$ states the decoupling is still very small. For the $4 d \Delta$ and $5 d \Delta$ states it is much bigger, and, therefore, the transitions from these states to the $2 p \Sigma$ state are present, though with faint intensity.

Also the $5 p$ П, $6 p \Pi$, etc., $\rightarrow 3 s \Sigma$ transitions have to be expected in this region. But they are apparently much weaker than the bands mentioned above and were not found.

Table 4.
3d $\Sigma \rightarrow 2 p \Sigma$

| K | P branch |  |  | R branch |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\nu_{\text {calc }}$. | I | $\nu_{\text {obs }}$. | $\nu$ calc. | I | $\nu_{\text {obs }}$. |
| 0 |  |  |  | 10, 667.76 | 1 | 10,667. 6 |
| 2 | 10, 626.67 |  |  | 71.75 | 3 | 71. 58 |
| 4 | 576.05 | 12 d | 10, 576.3 | 65.26 | 4 | 65.17 |
| 6 | 515.25 | 28 | 514.86 | 53.90 | 5 | 53.72 |
| 8 | 450.20 | ${ }^{3} 3$ | 449.64 | 40.11 | 4 | 40.09 |
| 10 | 383.51 | 1 | 383.38 | 26. 02 | 4 | 26.03 |
| 12 | 317.47 | 1- | 317.5 | 12.13 | 3 | 12.05 |
| 14 | 252.97 | 1- | 252.8 | 599.29 | 2 | 599.03 |
| 16 | 190.86 |  |  | 87.44 | 2 | 87.6 |
| 18 |  |  |  |  | 2 | 76.3 |

${ }^{1}$ Confused with $R_{18}$.
${ }^{2}$ Masked by $P_{15}$ of 9,123 .
${ }^{3}$ From $P_{9}$ of $\lambda 9,346$.
$3 d \Pi \rightarrow 2 p \Sigma$

| K | P branch |  |  | Q branch |  |  | R branch |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\nu_{\text {calo }}$. | I | $\nu_{\text {obs }}$. | $\nu$ calc. | I | $\nu_{\text {obs }}$. | $\nu_{\text {calc }}$. | I | $\nu_{\text {obe }}$. |
| 0 |  |  |  |  |  |  | 10,897. 18 |  |  |
| 2 | 10, 853.09 |  |  | 10, 863.77 | 2 | 10, 863.8 | 932.61 |  |  |
| 4 |  | 1 | 10, 837.14 | 60.16 54.84 | ${ }_{2}^{2}$ | 60.02 54.46 | 990.40 $11,050.84$ |  |  |
| 8 | 46.96 | 2 | 46.8 | 48.36 | 2 | 48.32 | 11, 110.86 |  |  |
| 10 | 54.42 | 26 | 54.46 | 41.57 | 1 | 41.2 | 169.68 |  |  |
| 12 | 60.98 | 1. | 60.9 | 34.69 | 1 | 34.44 | 226. 19 |  |  |
| 14 | 67.05 |  | ${ }^{(3)}$ | 28.43 | 1 | 28.4 | 280.75 |  |  |
| 16 | 72.10 | 1 | 71.9 | 23.17 | , | 23.2 | 333.25 |  |  |
| 18 |  |  |  |  | 1 | 19.2 |  |  |  |

${ }_{1}$ Too close to $P_{3}$ of $\lambda 9,123$.
${ }^{2} P_{10}, Q_{6}$, and $3^{3} D-9^{3} F$.
${ }^{3}$ Too close to $R_{19}$.

## 3. CONSTANTS

The constants wnich can be calculated from the bands at 9,123 and 9,346 A are

$$
\begin{array}{ll}
\lambda 9,123: 2 s \Sigma \rightarrow 2 p \Sigma & \nu_{0}=10,889.59 \\
\lambda 9,346: 2 s \Sigma^{1} \rightarrow 2 p \Sigma & \nu_{0}=10,637.8
\end{array}
$$

[^4]From these values for the origins of the bands it follows that the difference between the first and second vibrational state of the initial electronic level is

$$
\text { for } 2 p \Sigma \quad \omega=1,481.0
$$

if the value of $\omega$ for $2 s \Sigma$ is $1,732.8$.
The rotational constants are

$$
\begin{array}{rlrl}
2 p \Sigma v & =0 & B & =6.851 \\
v & =1 & B=5.42 .10^{-4}
\end{array}
$$

in which $B$ and $\beta$ are the constants in the formula

$$
B(K+1 / 2)^{2}-\beta(K+1 / 2)^{4}
$$

for the rotational energy.
It is interesting to note that the values $B$ and $\omega$ for the $2 p \Sigma$ state are the smallest of all levels observed so far. This means that the bond which holds the two atoms together is weakest for the $2 p \Sigma$ state. It is weaker than for the $\mathrm{He}_{2}{ }^{+}$ion for which the constants are

$$
\begin{aligned}
& B=7.10^{17} \\
& \omega=1,627.2^{1819}
\end{aligned}
$$

As stated above it is possible now with the help of the $2 p \Sigma \rightarrow 2 s \Sigma$ band to calculate all the relative term values of the triplet system with the accuracy of the wave-length measurements. In order to obtain the absolute energy values it is necessary to calculate the limit of one Rydberg series. We take

$$
2 s=34,301.8
$$

which is the value which Curtis and Long ${ }^{20}$ calculated from the limit of the series $n p \Pi \rightarrow 2 s \Sigma .{ }^{21}$ Then we get for the other low terms

$$
\begin{aligned}
& 2 p \Pi=29,533.7 \\
& 2 p \Sigma=23,412.2
\end{aligned}
$$

All other terms can then be easily calculated from the zero lines of the bands which have the level in question as initial level.

The $2 p \Pi$ term can also be directly calculated as head of the ns $\Sigma \rightarrow$ $2 p \Pi$ series. The value obtained in this way is $2 p \Pi=29,530.7 .^{22}$ The difference of only $3 \mathrm{~cm}^{-1}$ between this value and the value given above shows how well the terms can be represented by a Rydberg series.

Finally, all of the infra-red He lines observed photographically are presented in order of increasing wave length in Table 5, in which the column headings are either self-explanatory or given by the key to the classifications.

[^5]Table 5.-Infra-red He spectra
Key to the classification of the $\mathrm{He}_{2}$ lines:

A: $2 p \Sigma \rightarrow 2 s \Sigma$.
B: $2 p \Sigma 1 \rightarrow 2 s \Sigma 1$.
C: $3 d \Pi \rightarrow 2 p \Sigma$.
D: $3 d \Sigma \rightarrow 2 p \Sigma$.


Table 5.-Infra-red He spectra-Continued

| Intensity | $\lambda_{\text {air }}$ I. A. | $\nu_{\mathrm{vac}} \mathrm{Cm}^{-1}$ | He 1 | $\mathrm{He}_{2}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | A | B | C | D | E |
| 10 | 9,391. 90 | 10,644. 55 |  | $\mathrm{P}_{11}$ |  |  |  |  |
| 4 | 9, 395. 84 | 640.09 |  |  |  |  | $\mathrm{R}_{8}$ |  |
| 4 | 9,408. 27 | 626. 03 |  |  |  |  | $\mathrm{R}_{10}$ |  |
| 1 | 17.73 20.67 | 615.36 612.05 |  |  |  |  |  |  |
| 3 | 20.67 | 612.05 |  |  | - |  | $\mathrm{R}_{12}$ |  |
| 2 | 32.24 | 599. 03 |  |  |  |  | $\mathrm{R}_{14}$ |  |
| 2 | 41.6 | 588.5 |  |  | $\mathrm{P}_{3}$ |  | P |  |
| 8 | 42.4 47.12 | 587.6 582.34 |  | $\mathrm{P}_{13}$ |  |  | $\mathrm{R}_{16}$ |  |
| 2 | 52.5 d | 576.3 |  | Pı |  |  | $\mathrm{P}_{4} ; \mathrm{R}_{18}$ |  |
| 60 | 63.66 | 563.84 | $3^{3} \mathrm{~S}-5^{3} \mathrm{P}$ |  |  |  |  |  |
| 3 | 9, 477. 72 | 548.17 |  |  | $\mathrm{P}_{5}$ |  |  |  |
| 8 | 9,507. 74 | 514.86 |  | $\mathrm{P}_{15}$ |  |  | $\mathrm{P}_{6}$ |  |
| 30 3 | 16.70 19.39 | 504.97 501.99 | $3^{3} \mathrm{P}-7^{3} \mathrm{D}$ |  | $\mathrm{P}_{7}$ |  |  |  |
| 10 | 26. 17 | 494.52 | $3^{3} \mathrm{D}-8^{3} \mathrm{~F}$ |  |  |  |  |  |
| 4 | 29. 27 | 491.10 | $31 \mathrm{D}-81 \mathrm{~F}$ |  |  |  |  |  |
| 1 | 52.8 | 465. 3 | $3^{3} \mathrm{D}-8^{3} \mathrm{P}$ |  |  |  |  |  |
| 3 | -67.08 | 449.64 |  | $\mathrm{P}_{17}$ | $\mathrm{P}_{9}$ |  | $\mathrm{P}_{8}$ |  |
|  |  |  |  |  |  |  |  |  |
| 6 | 9,603. 50 | 410.01 | $3{ }^{15}{ }^{-61 P}$ |  |  |  |  |  |
| 2 | 20. 88 | 391.21 <br> 385 | $31 \mathrm{P}-81 \mathrm{D}$ |  | $\mathrm{P}_{11}$ |  |  |  |
| 1 | 28. 14 | 383. 38 | 3P-81 |  |  |  | $\mathrm{P}_{10}$ |  |
| 7 | 45. 68 | 364.49 |  | $\mathbf{P}_{1}$ |  |  |  |  |
| 2 | 80.54 | 327.17 |  |  | $\mathrm{P}_{18}$ |  | $\sim$ |  |
| 1 | 82.4 $9,687.6$ | 325.2 317.5 | $3^{1} \mathrm{P}-8^{1} \mathrm{~S}$ |  |  |  | P12 |  |
| 10 | 9, 702.66 | 303. 63 | $3^{3} \mathrm{P}-7{ }^{3} \mathrm{~S}$ |  |  |  | $\mathbf{P}_{12}$ |  |
| 6 | 23.33 | 281.72 |  | $\mathrm{P}_{21}$ |  |  |  |  |
| 2 | 46. 64 | 257.13 |  |  | $\mathrm{P}_{15}$ |  |  |  |
| 1 | 50.8 | 252.8 |  |  | P15 |  | $\mathrm{P}_{14}$ |  |
| 1 | 9,782.7 | 219.3 |  |  |  |  |  |  |
| 5 2 | $9,807.13$ 19.18 | 193.87 181.36 |  | $\mathrm{P}_{23}$ | $\mathrm{P}_{17}$ |  |  |  |
| 3 | 97.47 | 100.82 |  | $\mathrm{P}_{25}$ |  |  |  |  |
| 2 | 9, 898. 67 | 099.60 |  |  | $\mathrm{P}_{19}$ |  |  |  |
| 1 | 9,985. 43 | 011.85 |  |  | $\mathrm{P}_{21}$ |  |  |  |
| 1 40 | $9,994.6$ $10,027.73$ | $10,002.7$ $9,969.61$ | $33 \mathrm{D}-73 \mathrm{~F}$ | $\mathrm{P}_{27}$ |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
| 15 | 31.16 | 966.20 | $31 \mathrm{D}-71 \mathrm{~F}$ |  |  |  |  |  |
| 2 | 72. 10 | 925. 70 | $3^{3} \mathrm{D}-7^{3} \mathrm{P}$ |  |  |  |  |  |
| 10 | 10, 138. 50 | 860.69 | $3{ }^{1} \mathrm{P}-71 \mathrm{D}$ |  |  |  |  |  |
| 2 | 10, 233. 0 | 769.6 | $3^{1} \mathrm{P}-7{ }^{1} \mathrm{~S}$ |  |  |  |  |  |
| 1 | , 258.8 | 745.1 |  |  |  |  |  | $\mathrm{R}_{12}$ |
| 40 | 10,311. 32 | 695.43 | $3^{3} \mathrm{P}-6^{3} \mathrm{D}$ |  |  |  |  |  |
| 1 | - 50.9 | 658.4 |  |  |  |  |  | $\mathrm{R}_{8}$ |
| 1 | 393. 3 | 618.9 |  |  |  |  |  | $\mathrm{R}_{6}$ |
| 1 | 10, 433. 1 | 582.2 |  |  |  |  |  | $\mathrm{R}_{4}$ |
| 1 | 10,599. 2 | 432.1 |  |  |  |  |  | $\mathrm{P}_{4}$ |
| 4 | 10, 667. 62 | 371.60 | $3^{3} \mathrm{P}-6^{3} \mathrm{~S}$ |  |  |  |  |  |
| 2 | 10, 714.4 | 330.7 |  |  |  |  |  |  |
| 100 | 10, 829.09 | 231.86 | $2^{2} \mathrm{~S}-2^{3} \mathrm{P}_{0}$ |  |  |  |  |  |
| 500 | 10,830. 30 | 230.83 | $2^{3} \mathrm{~S}-2^{3} \mathrm{P}_{1}, 2$ |  |  |  |  |  |
| 6 | 10,912.95 | 160.92 | $3^{3} \mathrm{D}-6^{3} \mathrm{~F}$ |  |  |  |  |  |
| 3 | 1917.0 | 157.5 | $3{ }^{1} \mathrm{D}-6{ }^{1} \mathrm{~F}$ |  |  |  |  |  |
| 1 | 11,013.1 | 077.6 | $3^{1} \mathrm{~S}-5^{1} \mathrm{P}$ |  |  |  |  |  |
| 1 | 11, 045.1 | 9,051.3 | $31 \mathrm{P}-61 \mathrm{D}$ |  |  |  |  |  |

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    ${ }^{21}$ If we assume the value calculated in the usual way from the head of a Rydberg series we assume that the actual levels which have half a quantum of vibrational energy follow the Rydberg law. It looks more plausible to assume that the actual electronic levels; that is, the levels extrapolated to no vibrational energy are the ones which obey the Rydberg formula more closely. Imanishi (see footnote 19) has calculated the limit of the $n p \Pi \rightarrow 2 s \Sigma$ series under this assumption and found a somewhat different value for $2 s \Sigma$. But also this procedure is open to objections as the different orientation for the orbital momentum cause a shift and splitting up of the levels. (The $s \Sigma$ terms would be free from this objection.) On account of this complication, and because the absolute values of the energies are of very little importance for most purposes anyway, we have chosen the old value of Curtis and Long rather than that of Imanishi.
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