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INFRARED SPECTRA OF NOBLE GASES (10500 TO 13000 A)

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ABSTRACT

The first spectra of helium, neon, argon, krypton, and xenon, excited by uncon- densed discharges in Geissler tubes, have been explored in the infrared (10500 to 13000 A) with Eastman I-Z photographic plates. In each spectrum new lines have been recorded, most of which are accounted for as combinations of established terms, thus confirming the structural analyses of the spectra. Two missing 28 terms are revealed for xenon and possibly one new *I-type* term each for neon and for argon. Among the stronger lines those which involve accurately determined relative terms may serve as preliminary standards of wave length in the infrared.

CONTENTS

1. INTRODUCTION

On account of the "closed-shell" electron configurations in atoms of the noble gases, these elements are chemically inert, the atoms have exceptional stability, and their characteristic spectra extend over a very large range of wave lengths. For example, lines associated with neutral atoms of helium have been recorded photographically in the extreme ultraviolet down to 515 A, and radiometrically in the infrared to 20582 A. Neutral neon gives lines in the extreme ultraviolet (587 to 744 A), but the majority of its lines are distributed throughout the near ultraviolet, visible, and infrared.

The first spectra of the noble gases have been investigated intensively both for theoretical reasons connected with spectral and atomic structure, and for practical purposes, such as the use of monochromatic radiations as wave-length standards in spectroscopy and as standards of length in metrology. Most of this work has been done photographically since this is the best method for studying the details of a spectrum, but it was greatly handicapped by the limited range of infrared sensitiveness of photographic materials. A great advance was made several years ago when the discovery of new photosensitizing dyes 1 displaced this practical limit from about 9000 to approxi-

¹ C. E. K. Mees, J.Opt.Soc.Am. 22, 204 (1932); 23, 229 (1933).

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mately 11000 A. Now the recent success of the research laboratory of the Eastman Kodak Co., in the preparation of still better infrared sensitizers,<sup>2</sup> makes it practicable to photograph the spectra of ordinary laboratory sources to 13000 A.

The results obtained by employing Eastman I-Z plates for the photography of the first spectra of the noble gases are presented in this paper. Most of the new data represent combinations of spectral terms already established. They thus confirm the structural analyses, and lines involving accurately known relative terms may serve as temporary standards in the infrared.

## II. WAVE-LENGTH MEASUREMENTS

Geissler tubes of the type supplied by Robert Goetze in Leipzig were used as light sources. They have been described in other publications,<sup>3</sup> and it is hardly necessary to repeat that by using them end-on an enormous intensity increase is obtained. The tubes were operated in the 40,000-volt secondary circuit of a transformer, the primary of which was connected to a 110-volt source and supplied with 4 to 5 amperes alternating current. Light from the end-on capillary was projected on the slit of a stigmatically mounted concave grating  $4$  having a radius of curvature of  $21\frac{1}{2}$  feet, 7,500 lines per inch, and a scale of 10.2 A per millimeter in the first-order infrared spectrum.

The infrared radiation was filtered into the spectrograph with a sheet of Jena RG 5 glass, 2 millimeters thick, after the first exposure showed that the selenium red glass used heretofore was not safe beyond 12200 A. No second-order spectra or Lyman ghosts were found on any of the following spectrograms, but Rowland ghosts accompanied some of the strongest infrared lines. An indication of the infrared sensitivity of I-Z plates is given by the fact that the helium line at 10830 A was flanked by Rowland ghosts to the 12th order, although the grating employed shows no trace of such ghosts with moderately overexposed lines.

Exposures to the Geissler tubes ranged from 20 to 24 hours. Wave lengths of lines thus recorded in the first-order spectrum were derived from measurements relative to iron-arc standards photographed. in the third-order spectrum. An exposure of one second sufficed to impress the iron spectrum. The first-order spectrum lines were measured and calculated as if they belonged to the third order, and then these values were multiplied by 3 to convert them to their true values. The corrections for standard density of air were neglected since they were always less than 0.01 A, while the average probable error of the infrared wave-length measurement is several times larger.

#### III. RESULTS

Preliminary exposures of Eastman I-Z plates to metallic-arc spectra in which a continuous background from white-hot electrodes and oxides was visible, immediately gave the impression that the sensitizing resembled that of I-Q (xenocyanine) plates, except that the maximum was displaced toward longer waves. In both cases the

 $^2$  C. E. K. Mees, J.Opt.Soc.Am.  $\bf 25,80$  (1935). 3 W. F. Meggers and C. J. Humphreys, BS J.Research 10, 428 (1933) RP540. • W. F. Meggers and Keivin Burns, BS Sci.Pap. 18, 191 (1922) 8441.

sensitizing band is very broad, in Q the maximum action is at 9700 A, while in  $\widetilde{Z}$  it is near 10900 A. The Z plates were found inferior to  $\widetilde{Q}$ for wave lengths below 10300 A, but they run well ahead at 10500 A, and appear to be more sensitive at 13000 A than the latter are at  $12000$  Å. Since no new lines short of 10500 Å were detected with I-Z plates, the results are given only for lines of greater wave length. The data are presented in the following tables, in which successive columns contain estimates of relative intensity, measured wave lengths, wave numbers in vacuum, term combinations, and numerical differences of the terms. The intensity estimates are not corrected for variations in the photographic spectral sensitivity and as usual are comparable only over more or less limited regions.

In each table, the vacuum wave number (column 3) is derived from the observed wave length (column 2) by converting the wave length in air to vacuum value by means of the atmospheric-dispersion formula of Meggers and Peters,<sup> $5$ </sup> and then calculating its reciprocal.

The modern quantum notation for spectral terms is used for helium, while for the remaining noble gases the notation is that first employed by Paschen<sup>6</sup> for the representation of neon terms.

#### 1. HELIUM

Previous knowledge of the first spectrum of helium has been summarized in treatises on spectral series,<sup>7</sup> and in a paper on the infrared spectra photographed with xenocyanine.<sup>8</sup> Observations for the longer waves are displayed in table 1. For the sake of completeness, some lines probably due to  $He<sub>2</sub>$  molecules are included, but no attempt has been made to classify them. Values for the  $2 \text{ }^{8}S-2 \text{ }^{3}P$  group at 10830 A are quoted from another paper;<sup>9</sup> they represent interferometer comparisons with neon standards.

 $^5$  W. F. Meggers and C. G. Peters, BS Sci.<br>Pap. 14, 722 (1918) 8327. <br> $^8$  F. Paschen, Ann.<br>Physik 64, 405 (1919). <br> $^1$  A. Fowler, Series in Line Spectra, page 91 (Fleetway Press, London, 1922). F. Paschen and R. Goetz



TABLE *I.- Infrared spectra of helium* 

#### 2. NEON

To Paschen's 10 description and analysis of the neon spectrum a considerable extension was made when mesocyanine and xenocyanine plates were employed 11 in 1932. Additional lines have been found with  $I-Z$  plates (table 2), but these represent for the most part, combinations of established terms. Possibly one new term (3068.9) of *6f* type is revealed, but a few lines of very low intensity remain unclassified in this and in the preceding lists of neon lines.

<sup>10</sup> F. Paschen, Ann. Physik  $60$ ,  $405$  (1919).<br><sup>11</sup> W. F. Meggers and C. J. Humphreys, BS J. Research 10,  $430$  (1933) RP540.

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TABLE *2.-Infrared spectrum of neon-Continued* 

### 3. ARGON

Former knowledge of the first spectrum of argon is contained in papers published by Meissner 12 and in the infrared data presented 13 in 1933. A considerable extension of the latter IS now given in table 3. Most of the new lines are accounted for as combinations of the known terms, and with the possible exception of  $4W = 5458.10$ , no new terms have been revealed. However, a few lines still await classification.





12 K. W. Meissner, Z. Physik 37, 238 (1926); 39, 172 (1926); 40, 839 (1927).<br><sup>13</sup> W. F. Meggers and C. J. Humphreys, BS J.Research 10, 437 (1933) RP540.





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TABLE *3.-Infrared spectrum of argon-Continued* 

#### 4. KRYPTON

Complete information concerning the first spectrum of krypton 14 was summarized in 1933, when an extension to the infrared data was published.<sup>15</sup> Some additional lines (table 4) have been found on spectrograms made with I-Z plates, but most of them represent combinations of terms already known. In a few cases, the differences between observed and calculated wave numbers suggest a slight revision of term values. The term  $2 s_5 (=13287.96)$ , previously proposed on the basis of a single transition of the type  $(p-s)$ , is now confirmed by double-electron  $(s-f)$  transitions, but two of the lines beyond 12000 still remain unclassified.

<sup>14</sup> W. F. Meggers, T. L. DeBruin, and C. J. Humphreys, BS J. Research 7, 643 (1931) RP364. <sup>15</sup> W. F. Meggers and C. J. Humphreys, BS J. Research 10, 443 (1933) RP540.

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TABLE *4.- Infrared spectrum of krypton* 

#### 5. XENON

The most complete description and analysis of the first spectrum of xenon is that published by Humphreys and Meggers 16 in 1933. With xenocyanine (I-Q) plates, it was impossible to record lines beyond 11141 A, but with I-Z plates, 21 lines of greater wave length have been measured (table 5). Here also the majority of new lines is accounted for by known terms, but two new terms of 28 type are suggested. If the last observed line 12623.40 A is assumed to represent the transition  $2p_{10}-2s_5$ , the faint line at 11175.5 A is explained as the combination  $2s_5-5p_8$ , and the term  $2s_5$  acquires a value of 12645.09. The line at 12235.24 A is similarly assumed to represent  $2p_{10}$ -2s<sub>4</sub>, giving the term  $2s_4$  a value of 12393.87, but unfortunately no lines remain with which to check it.

<sup>16</sup> C. J. Humphreys and W. F. Meggers, BS J. Research 10, 139 (1933) RP521.



TABLE 5.-Infrared spectrum of xenon

#### 6. IMPURITIES

A small number of impurity lines were found on some of the spectrograms. Mercury and oxygen are fairly common contaminants of gases in Geissler tubes, and it happens occasionally that the glass becomes overheated to such a degree that sodium and potassium lines appear in the discharge. These impurity lines are listed in table 6. They are possibly of interest as additional or accidental standards in further infrared investigations of Geisslertube spectra. In this table, the classification and calculated wave numbers are quoted from Atomic Energy States.<sup>17</sup> If the sodium and potassium lines observed here in low-pressure sources are compared with values reported for arcs at atmospheric pressure<sup>18</sup> they will be seen to be 0.41 A smaller, or 0.31 greater in wave number This difference may be regarded as a reasonable measure of the displacement due to one atmosphere of pressure.

<sup>&</sup>lt;sup>17</sup> R. Bacher and S. Goudsmit, (McGraw-Hill, New York, 1932). <sup>18</sup> W. F. Meggers, BS J. Research **10, 669** (1933) RP558.

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TABLE 6.-Infrared spectra of impurities

WASHINGTON, January 21, 1935.