THE

PHYSICAL REVIEW

A Journal of Experimental and Theoretical Physics

VOL. 47, NO. 10 | MAY 15, 1935 | SECOND SERIES

Some Bands in the Extreme Ultraviolet Spectrum of Helium

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(Received March 18, 1935)

The band at λ600 in the extreme ultraviolet spectrum of helium, first observed by Lyman and first attributed to the helium molecule He_2 by Sommer, has been investigated under various discharge conditions. Low voltage arc, Schüler hollow cathode and uncondensed capillary discharges have been used as sources with a one-meter vacuum spectrograph. The helium used was circulated from the spectrograph back to the discharge tube through the purifying system of a misch metal arc and a chabazite trap in liquid air. The band at λ600 appeared under those conditions of purity which favored the appearance of the visible bands of helium and under such conditions that there can be little doubt that it is due to helium. The intensity of this λ600 band varied directly with the first power of the current in the discharge, whereas the visible bands are known to vary as the square of the current. This suggests a difference of mechanism in the two cases, and in the light of this, various explanations of the origin of the λ600 band are considered but none found satisfactory. A possible explanation of the diffuse structures appearing at λ647 and λ662 is advanced.

THE ultraviolet spectrum of helium as obtained by Lyman[1] contained a prominent line at λ600.3±0.6 which was of a diffuse character and occasionally showed a suggestion of a prolongation toward the regions of long wavelengths. Its persistence of occurrence and intensity relative to the $1^1S_0-m^1P_1{}^0$ series, as the impurity of the gas decreased, made it doubtful whether it was carbon λ600.2 or other impurity, while its diffuse width λ599.9−λ601.3 not falling over the region of the forbidden line of helium, $1^1S_0-2^1S_0$, at λ601.4 was not consistent with its being a helium line. Further doubts about its being the forbidden line were raised by the fact that it occurs in discharges with steady currents while the forbidden transitions are made more probable by disruptive discharges where the fields are stronger. Lyman also observed diffuse structures at λ647 and at λ662. These shaded toward the regions of short wavelengths and were said to be due to impurities although the actual impurity was not stated.

The line λ600 was next discussed by Dorgelo and Abbink[2] who suggested that it was not any of the possibilities advanced by Lyman but was the $1p-4s_2$ $(2p^1S_0-5s^1P_1{}^0)$ of neon excited by collisions of the second kind with metastable helium atoms. This conclusion is based on the appearance on their plates of a line at λ600.03, which is within the limit of experimental error of the calculated position of the neon line, and the observation that in neon (with a trace of helium) the higher energy levels are less strongly developed than in helium (with a trace of neon). This is taken to indicate that the higher states of neon are excited by impacts of the second kind with helium metastable atoms.

It was suggested by Sommer[3] that λ600.03 is a

[1] T. Lyman, Astrophys. J. **60**, 1 (1924).

[2] H. B. Dorgelo and J. H. Abbink, Zeits. f. Physik **37**, 667 (1926).

[3] L. A. Sommer, Proc. Nat. Acad. Sci. **13**, 213 (1927).

helium band because of its bandlike appearance and its association with helium of reasonable purity.

In the work of Compton and Boyce[4] the structure at λ600.03 had none of the bandlike appearance described by Sommer and was enhanced by the addition of a further trace of neon to the helium in the discharge. Consequently they incline to the view of Dorgelo and Abbink but suggest there are possibly two or three causes which independently give radiation near λ600 and that the experimental conditions determine which cause predominates.

Paschen[5] mentions the structure at λ600.019 which appears on plates taken by P. G. Kruger[6] and states definitely that it originates in helium and is not the forbidden transition, which is found at λ601.418. The structure at λ600.019 is distinctly bandlike being sharp on the short wavelength edge and shading away toward the red.

The present work was carried on at Princeton University in an attempt to determine the origin of the band at λ600. Spectrograms in the extreme ultraviolet were made of the low voltage arc, Schüler hollow cathode, and uncondensed capillary discharges. The vacuum spectrograph, used formerly by Compton and Boyce,[4] had a one-meter grating ruled fifteen thousand lines to the inch, and covered the region from the zero order to λ1250 with a dispersion of about 12A/mm. This investigation was made at pressures above 2 mm of mercury in order to favor the appearance of the visible bands of helium and it was found that λ600 appeared strongly when the gas purity was sufficient to give the visible bands. Purification of the gas was difficult. The system had several wax seals and since a volume equivalent to several hundred cubic centimeters of gas at atmospheric pressure was in circulation, the purifying system had to be efficient. The best method was circulation of the gas through a misch metal arc using heavy currents and through a chabazite trap immersed in liquid air. These processes removed the inert gases neon and argon and the more active gases, including even hydrogen after long running. However, as hydrogen provided good standards for some regions of the plates it was not always completely removed. This was satisfactory providing Hα (λ6563) was kept less in intensity than the neighboring red line of helium (λ6678), otherwise mild excitation particularly with the uncondensed capillary discharge gave the hydrogen band spectrum very strongly. Occasionally it was necessary to use liquid air traps filled with glass beads to remove mercury vapor. Circulation of the gas at pressure from 2 mm to 12 mm was maintained by one Langmuir pump which kept a pressure ratio of 5 : 1 between the discharge tube and the body of the spectrograph. Purification of the gas for several days in a misch metal arc was always a necessary preliminary to circulation. The increase of strength of the λ600 band with continued purification is strong support for the identification of its origin.

A $94\frac{1}{2}$-hour exposure of a 40-volt arc in helium was obtained. The plate current was 0.3 ampere and the gas pressure 8.8 mm. The filament of the arc consisted of a 15-mil tungsten wire wound in a helix of eight turns on a 30-mil wire as mandrel. The plate was a one-inch diameter circular disk of nickel with its plane 3 mm from the filament. Here, as in all other cases, the metal parts were baked out by the induction furnace while the pumps were running to remove gas contamination. The filament was parallel to the slit and just out of the direct line from it to the grating. This exposure showed the helium band at λ600 but not with extreme intensity. For quick and easy production of the band this method was not suitable, the long exposure time making it very difficult to keep the gas pure. There is a slight continuum observed which extends from λ600 to approximately λ900. This was observed by Hopfield.[7] In plates by the other methods the development of this continuum is not so well marked although the λ600 band appears more readily.

A series of Schüler hollow cathodes were next investigated. These cathodes were made of sheet tungsten bent into hollow cylinders varying from 25 to 50 mm in length and from 6 to 10 mm in internal diameter. The anode was a one-inch

[4] K. T. Compton and J. C. Boyce, J. Frank. Inst. **205**, 497 (1928).
[5] F. Paschen, *Sitzungberichte der Preussischen Akademie der Wissenschaften*, Berlin, p. 662, 1929.
[6] P. G. Kruger, Phys. Rev. **36**, 855 (1930).
[7] J. J. Hopfield, Phys. Rev. **35**, 1133 (1930).

diameter nickel disk. The cathode axis was directly in line with the slit of the spectrograph. With this source a typical exposure was produced in 48 hours from a Schüler cathode discharge in helium at 2.5 to 3-mm pressure. The plate current was 0.2 ampere and the voltage applied 700 d.c. The helium band at λ600 was but poorly developed. The conclusion from several plates was that this method of excitation was not favorable to the strong excitation of the band at λ600.

In order to make intensity comparisons of the band under different current densities, it was desirable to have short exposure under constant conditions of pressure and purity. The most satisfactory type of discharge was the one finally used, the uncondensed capillary type which enables one to have good exposures within an hour. The capillary was a Pyrex tube 8.8 cm long and 3.2 mm internal diameter lined up with, and its near end 4 mm from the slit. The discharge was produced by a 15,000-volt, 8-kilowatt transformer controlled by a resistance in the primary making it possible to vary the discharge current from 10 ma to 350 ma. Considerable care was taken to prevent overheating, air blasts being turned on the discharge tube continuously, and with the higher currents the discharge was intermittent, one second on and one second off, the intervals being timed by a motor-driven interrupter. During any one set of observations for intensity comparisons the same rate of intermittency was maintained. Approximate photometry was attained by a series of carefully timed and regulated exposures with the gas pressure and purity constant. The latter was judged by visual observations and by photographs taken in the visible region simultaneously with those in the vacuum region. In a typical run, for example, a forty-minute exposure with a discharge current of 150 ma was followed by two exposures, one of ten minutes and the other of twenty minutes, both of these with the doubled discharge current of 300 ma. Lines whose excitation depended on the square of the discharge current would then be expected to show equal blackening in the first and second of these exposures while those for which the excitation depends on the first power of the current would be equally blackened in the first and third exposure. The assumption of approximate reciprocity between current and time in producing plate darkening was checked by the variation of the helium resonance series members from one exposure to another, an excitation process known to depend directly on the first power of the current.

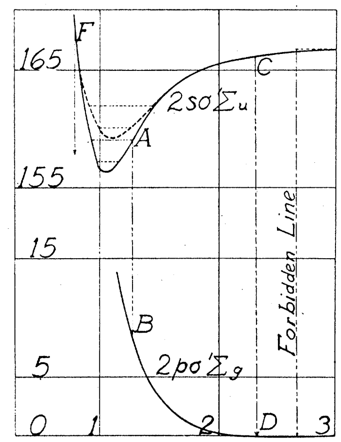

FIG. 1. Energy curves for the helium molecule. Energy in thousands of wave numbers plotted against the internuclear distance in Angstrom units.

From a number of sets of exposures and current ratios of 2/1 and 3/1 it is found that the band at λ600 varies more nearly with the first power of the current[8] than with the square of the current. It was also observed that the diffuse structures at λ647 and λ662 occur in all cases where the gas is quite pure and the current density relatively large.

In seeking an explanation of the band at λ600 one observes that the conditions of gas purity and type of discharge favor the presence of metastable helium atoms (atoms in the $1s2s\,{}^1S_0$ state). Kruger[6] has found that this band is frequently accompanied by the forbidden line $(1^1S_0-2^1S_0)$, and that the line never appears without the band although the band sometimes appears alone. This suggests an association of the band with the forbidden line. That the band edge at 166,660 cm^{-1} represents 385 cm^{-1} greater energy than the forbidden line at 166,275 cm^{-1} raises a difficulty, which will be considered in the remainder of this paper.

Variation of the intensity of a band with the square of the current indicates a process involving two electron impacts, producing either two

[8] J. L. Nickerson, Phys. Rev. **38**, 1907 (1931).

excited atoms which unite to form a molecule, or one electron impact producing a metastable atom which unites with a normal atom to form a molecule and a further electron impact raising that molecule to a higher state. Such variation with the square of the current has been observed by Weizel for the visible bands of He_2.[9] Variation with the first power of the current would indicate that the process involves a normal atom and an excited atom, which, in the case we are considering, may be the 2^1S_0 metastable state. The molecular state so formed, $2S\sigma^1\Sigma_u$, has allowed transitions to the ground state, $2p\sigma^1\Sigma_g$, which is formed by the union of two normal atoms.[10]

The potential energy curve of the ground state is known with considerable accuracy in the region concerned in this problem. This is found in the work of Lennard-Jones, Slater, Slater and Kirkwood, and Margenau.[11] Slater's curve in Fig. 1 shows the energy relations to be expected. The depth of the minimum is less than 20 cm^{-1} with its lowest point at an internuclear distance of 2.9A.

For the upper state the potential energy curve was obtained in the form of Morse's function:[12]

$$U(r)=166{,}275+10{,}000\,e^{-6.9(r-r_0)}-20{,}000\,e^{-3.45(r-r_0)}$$

where $r_0=1.05$A.[13]

The determination of the constants of this equation depended on the estimation of the heat of dissociation for the state. The value assumed, namely $D\sim 10{,}000$ cm^{-1} is reasonable from three viewpoints:

(1) Using the data of Imanishi[14] and of Dieke, Takamine and Suga[15] in the rotational energy relation of Kratzer:

$$\omega_0=2(B_0{}^3/\beta_0)^{\frac{1}{2}}\quad \text{gives}\quad D=8600.$$

(2) Considering the extent of the development of the rotational levels for $2s\sigma^1\Sigma_u$ in the work of Imanishi it can be found that D must be greater than 6500 to prevent dissociation before the higher rotational states are reached.

(3) For the level $3p\pi^3\Pi_g\,D\sim 20{,}000$ has been estimated[16] and this would allow a value of the same order for $2s\sigma^1\Sigma_u$. Transitions from the upper to the lower state will produce diffuse bands because of the steep slope of the ground state potential energy curve in the regions to which transitions occur, see C–D in Fig. 1, and this together with transitions discussed in the next section will account for some of Hopfield's continuum[7] which extends from λ600 to about λ900. It is impossible to obtain from this type of radiation sufficient energy to account for the high frequency edge of the λ600 band. A glance at the curves in Fig. 1 will show that they are nowhere else as far apart in ordinates as at complete dissociation. It is hence impossible to obtain, from any transitions between these two states, bands of higher frequency than that associated with the forbidden line λ601.418.

Besides radiation from this definite molecular state there may be radiation from the temporary states formed momentarily during impact. Born and Franck[17] have shown that for two atoms on collision to form a stable molecule there is necessarily present a third body, wall or atom, in order to have conservation of energy and momentum. Very frequently a third body will not be at hand, and in the present problem, when a stable molecule is not formed, there is with decreasing radius of collision an increasing probability of electron transition from the metastable state accompanied by the radiation of energy. Two-body collisions have been used by Kuhn and Oldenberg[18] and by Finkelnburg[19] to describe the origin of bands appearing in the spectra of mixtures of argon and mercury. In Fig. 1 transitions from point F to the ground state are illustrative of this process as applied to the present problem. However, it is again obviously impossible to have frequencies greater than the forbidden line because of the position of the ground state potential energy curve. Sufficient energy could be obtained if the electronic transitions were probable at internuclear distances of the order of 2.5A or

[9] W. Weizel, Zeits. f. Physik **59**, 320 (1930).
[10] F. Hund, Zeits. f. Physik **63**, 719 (1930).
[11] J. E. Lennard-Jones, Proc. Roy. Soc. **A107**, 157 (1925); J. C. Slater, Phys. Rev. **32**, 349 (1928); J. C. Slater, Kirkwood, Phys. Rev. **37**, 682 (1931); H. Margenau, Phys. Rev. **38**, 747 (1931).
[12] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[13] W. Weizel, *Bandenspektren*, p. 268.
[14] S. Imanishi, Inst. Phys. and Chem. Res. Tokyo **10**, 250 (1929).
[15] G. H. Dieke, T. Takamine and T. Suga, Zeits. f. Physik **49**, 637 (1928).
[16] W. Weizel, *Bandenspektren*, p. 255.
[17] M. Born and J. Franck, Zeits. f. Physik **31**, 411 (1925).
[18] H. Kuhn and O. Oldenberg, Phys. Rev. **41**, 72 (1932).
[19] W. Finkelnburg, Zeits. f. Physik **81**, 781 (1933).

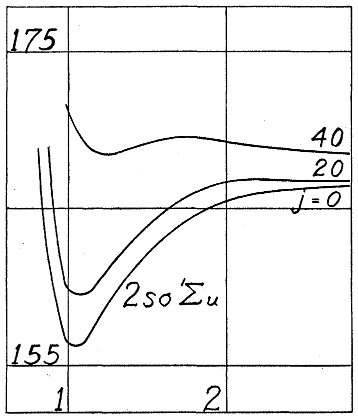

FIG. 2. Energy curves E_n+E_j for the j values indicated.

greater. This would be so if on the approach or recession of the two atoms there were a slowing of their motion in that region. This would occur if the upper state potential energy curve was shaped as in Fig. 2. Such a form of curve actually appears[20] when the combined energy of vibration and rotation is plotted against the internuclear distance. Such curves may be calculated, but the large energies involved in these processes make it very unlikely that in an ordinary gas discharge, where the mean kinetic energy is of the order of 600 to 800 cm^{-1}, the number of high energy atoms would be sufficient to provide the excess 385 wave numbers of energy with the intensity observed. Further since the levels involved are Σ levels there would be only R and P branches and they would be of about equal intensity. One would expect therefore a symmetric distribution of radiation about the forbidden line but one observes that with short exposures the band shades away from λ600.019 but does not always cross λ601.418.

There remains another possibility to be considered:—

That the potential energy curve in the upper state has, for $j=0$, a rise of a few hundred wave numbers above the horizontal asymptote thus producing a potential barrier at large internuclear distances and enabling larger energy contributions to the radiation to be associated with smaller values of j. This rise in the curve would indicate repulsion at large internuclear distances but changing to attraction as the internuclear distance decreases. This would require a nearby perturbing level in the atomic state. The nearest level that combines with 2^1S_0 is $2^1P_1{}^0$ which lies 4829 cm^{-1} above it, and there are no lower lying levels which combine with 2^1S_0. Now the effect of these perturbing levels is to act repulsively on each other, the higher one being raised and the lower one lowered. Thus clearly there is nothing to make one anticipate a rise in the molecular potential energy curve.

There seems to be then no simple explanation of λ600 considering it as a helium band originating in the molecular $2s\sigma^1\Sigma_u$ level, the only reasonable electronic assignment. One point of interest remains. The appearance of the diffuse structures at λ647 and λ662 (sharper edges at λ648.73 and λ663.23, corresponding to 154,450 cm^{-1} and 150,800 cm^{-1}, approximately) both shading toward the short wavelength side occur only when the gas is pure and when the current density is relatively large. These structures could be transitions from the two known vibrational levels of $2s\sigma^1\Sigma_u$ to the ground state, since the accuracy in the position of these curves is small. One of these is $A-B$ in Fig. 1. The dotted curve in the figure shows the order of change in the upper state necessary to give good agreement in frequency. The observed shading toward short wavelengths would also be expected from the shape of the curves. It is significant that associated plates of the visible region show the helium bands in the region of λ4723 strongly developed only when these two structures appear in the ultraviolet. The bands that appeared were identified with the $4s\sigma^{1,\,3}\Sigma_u$ to $2p\pi^{1,\,3}\Pi_g$. The lower of the singlet levels can radiate further only by going into the $2s\sigma^1\Sigma_u$ level which is the upper state suggested for the diffuse structures at λ647 and λ662.

In conclusion grateful acknowledgment is made to Dr. K. T. Compton for suggesting this problem, and to Dr. J. C. Boyce and Professor E. U. Condon for encouragement and criticism, and to the Carnegie Institution of Washington for financial assistance.

[20] O. Oldenberg, Zeits. f. Physik **56**, 563 (1929).