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THE BROADENING OF THE RESONANCE ATOMIC LINE OF HELIUM

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ABSTRACT

The asymmetric broadening of the resonance atomic line of helium is explained by the shape of the potential energy curves of the two center systems consisting of two helium atoms. The broadened atomic lines account for some of the unstable electronic levels of the helium molecule (He_2), which have hitherto not been found.

THE width of atomic emission and absorption lines, is known to be appreciably affected by pressure. If the radiation process is affected by other gases, there is a slight effect only. In alkali, mercury and cadmium spectra, however, lines of great width have been observed, the broadening resulting from the vapor pressure of the metal itself in most cases. This kind of broadening is not at all symmetrical, enlargements to the long wavelength side prevailing.

Some features of the pressure effect may be explained on the basis of a shortening of the life time caused by resonance and by means of the Heisenberg uncertainty principle. This gives an uncertainty of the energy of the levels, but it seems very difficult to account for the asymmetry of the broadening in this way. On the other hand, it seems obvious, that a system of two colliding atoms can be treated as a two-body system—a method very familiar in the theory of molecules—which suggests a connection between molecular spectra and the pressure effect on the width of atomic lines.

In a recent paper Hopfield[1] reported some work on the far ultraviolet spectrum of helium. Besides a continuous spectrum, due to the He_2 molecule, there are some photographs of the He atom resonance line and some other lines of the main series, which show some remarkable features. In an arc discharge they are all reversed and as a matter of fact quite distinctly broadened to the ultraviolet (short wave-length) side. No intensity measurements and no measurements of the shape of the lines have been made, but as I will show later, the mere fact that there is an enlargement to the ultraviolet side will be a sufficient clue to connect the resonance line with the molecular spectrum. It seems furthermore worth while to remark that Hopfield's plates indicate that the intensity and perhaps also the broadening of the resonance line (not the higher lines of the main series) is smaller in the oscillatory discharge than in the arc. Conceding that it is very difficult to compare intensities under such different conditions as arc and oscillatory discharge without exact measure-

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[1] J. J. Hopfield, Astrophys. J. **72,** 133 (1930).

ments, we will try to give an explanation for the supposed quenching of the resonance line in the oscillatory discharge.

To simplify our considerations, we will limit them to the resonance line of the helium atom at 585A, which is the $2^1P \rightarrow 1^1S$ line of the atomic spectrum. We now investigate the molecular terms derived from a helium atom in the normal state and another helium atom in the states 1^1S, 2^1S, 2^1P, 2^3S and 2^3P. If both atoms are in the 1^1S state, they will give only one molecular term, $^1\Sigma_g$. The index g indicates, that the term is even with respect to a reflection at the center of mass. This $^1\Sigma$ state is the lowest state of the He_2 system, but since two normal He atoms give no stable compound, it must be an unstable continuous term. Perhaps a very shallow minimum could occur at very high internuclear distances r, but this would not affect our considerations. From the atomic states 1^1S+2^1S two molecular states are derived, a $^1\Sigma_u$ and a $^1\Sigma_g$ term. Similar terms $^3\Sigma_u$ and $^3\Sigma_g$ are connected with the atomic states 1^1S+2^3S. The atomic combination 1^1S+2^1P gives 4 molecular terms $^1\Pi_g$, $^1\Sigma_g$, $^1\Pi_u$ and $^1\Sigma_u$ and the analogous triplet atomic combination 4 quite analogous triplet terms. In all we get 12 possible molecular terms derived from a combination having one atom of principal quantum number two. In fact, from the analysis of the He_2 band spectrum only five molecular states are known, which could dissociate into such atomic configurations.

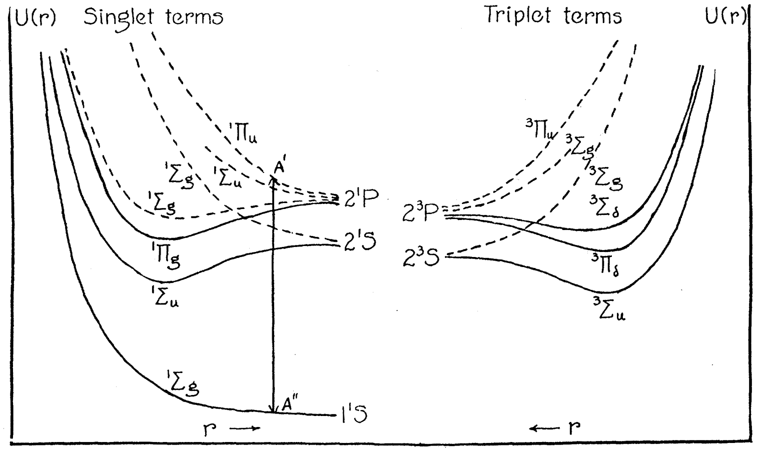

Fig. 1. Solid curves show presumable potential energy of the known levels of He_2. Broken curves show presumable potential energy of the unknown levels of He_2. $A'A''$ shows resonance line broadened to short wave-length side.

The $^1\Sigma_u$ state, derived from the 1^1S+2^1S atoms, certainly must be identified with the $2^1s \equiv (1s\sigma)^2 2p\sigma 2s\sigma {}^1\Sigma_u$ state[2] of the molecule and the $^1\Pi_g$, coming from 1^1S+2^1P, with the $2^1p \equiv (1s\sigma)^2 2p\sigma 2p\pi {}^1\Pi_g$ molecular level. Quite analogous identifications have to be made for the analogous triplet states (see Fig. 1). In the molecular triplet system, there is an additional state $3^3u = (1s\sigma)^2 2p\sigma 3p\sigma {}^3\Sigma_g$ and according to Hund,[3] this state has to be identified with the

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[2] See W. Weizel, Zeits. f. Physik **56**, 727 (1929) for these states.

[3] F. Hund, Zeits. f. Physik **63**, 19 (1930).

$^3\Sigma_g$ state, dissociating into 1^1S+2^3P. A similar singlet molecular term has not been found in the He_2 band spectrum, but probably exists.

Now let us consider the potential energy curves of the 5 singlet molecular terms dissociating into the atomic combinations 1^1S+2^1S and 1^1S+2^1P. Two of the curves connected with the latter combination increase with r at high values of r, the other two decrease. Since there are two stable molecular levels $^1\Pi_g$ and $^1\Sigma_g$, the curves of these two terms are the ones which increase and the curves of $^1\Pi_u$ and $^1\Sigma_u$ have to decrease. The resonance atomic line, in terms of the two-body system, then has to be written as $^1\Pi_u \rightarrow {}^1\Sigma_g$ and $^1\Sigma_u \rightarrow {}^1\Sigma_g$, since there is a selection rule allowing only transition from u states to g states and vice versa. This leads to the important conclusion that in the upper state of the resonance line the electronic energy always increases on the approaching of another helium atom.

According to the reproductions of Hopfield's plates the lines are enlarged to the ultraviolet side about 500 cm^{-1}. There can be no question, that the average translational energy of the excited He atoms in the arc may be high enough to accout for such an effect. It is certain, that an electron in exciting an atom will transfer to it a translational momentum and energy, so that the average kinetic energy of the He atoms in the 2^1P states may be much higher, than the average temperature energy. It is interesting that this argument would not hold for the long lived metastable states.

The eigenfunctions of a two-center system in an unstable state will have the largest amplitudes at r values corresponding to the turning point of the particles in the classical model, that is, at the point where the whole kinetic energy is converted into electronic (potential) energy. According to the Franck-Condon principle the change of the distance between the nuclei during the electronic jump must be small. Consequently the frequency radiated during a collision is proportional to the energy difference between the potential energy curves of the upper and lower states at the special value of r, which is the internuclear distance when the radiation process occurs. (Length of the line $A'A''$ in Fig. 1). The question, whether the line is broadened to the ultraviolet or to the red, now depends on whether the potential energy curve of the upper or the lower state is steeper.

Since in the helium resonance line, we observe a broadening to the ultraviolet, we must conclude, that the upper potential curve is steeper.

But the real case is a little more complicated. There are two upper molecular states participating in the emission of the resonance line. The $^1\Pi_u$ state has twice the statistical weight of the $^1\Pi_u$ state. Its influence therefore is probably stronger. Our assumption that the upper state has the steeper potential energy function is only made *ad hoc* and further evidence for that would be desirable. The eigenfunctions of a normal He atom have appreciable values only in the near neighbourhood of the nucleus. In consequence there should be only a very small interaction between two normal He atoms at larger internuclear distances. This means that the potential energy function is very flat indeed. In excited states however, the eigenfunctions have greater amplitude at larger distances from the nucleus, so that there is a more appreciable overlapping at larger r values. This means a larger interaction energy, which gives an increase of the electronic energy for these terms, as we stated above.

In this way, we have not only got a very simple explanation of the fact that the resonance line shows a pressure broadening to the ultraviolet, we have also accounted for two of the missing electronic terms in the helium molecular spectrum. It is obvious that the other lines of the main series of the helium atom will account for the missing electronic states of the molecule derived from the atomic configurations 1^1S+n^1P.

Finally we will try to account for the relative weakness of the resonance line in the oscillatory discharge compared with the arc. In the arc the density of the current is rather small, and therefore there is only a very small amount of metastable atoms and He_2 molecules in the gas. In the oscillatory discharge however, the instantaneous current density is high, and consequently the percentage of metastable atoms and molecules is higher. This difference is known to explain the enhancement of the He_2 band spectrum in the oscillatory discharge. Since metastable atoms and He_2 molecules do not require much energy for further excitation, it seems probable that the presence of these atoms and molecules reduces the velocity of the electrons in the discharge. Now it is known from measurements of Hanle[4] and Schaffernicht,[5] that the yield of excited singlet states starting from a fundamental singlet state is the greatest if the velocity of the electrons is about twice as high as the excitation voltage. The reduction of the velocity of the electrons would therefore also cause a quenching of the excitation of singlet states and this would easily account for the quenching of all singlet lines. To explain why only the resonance line is quenched, we have to consider the possibility, that excitation of higher singlet states starting from metastable atoms occurs. Such processes could compensate sufficiently for the loss of excitation of the higher singlet states, but could never make up for the great decrease of excitation of the resonance line.

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[4] W. Hanle, Zeits. f. Physik **56,** 94 (1929).

[5] W. Schaffernicht, Zeits. f. Physik **62,** 106 (1930).