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New Absorption Band of Alkalis in the Presence of Foreign Gases*

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In the presence of foreign gases, a narrow and structureless absorption maximum was observed on the short wave-length side of certain members of the principal series of alkali metals. A résumé of the results obtained so far is given. It is suggested that the band is due to the increase in the energy of the optical electron through the process of collision with a foreign gas atom when the electron is at that energy level whose orbital radius is close to the distance of optical collision.

INTRODUCTION

THE influence of surrounding atoms on the frequency of the absorbing or emitting atoms as exhibited by broadening, asymmetry, and shift is well known and gives a new way to study the perturbations of energy levels; but during the study of the intensity distribution of the line due to pressure broadening, the narrow diffuse band[1,2] appearing very close to certain members of the principal series is very easily overlooked, yet it appears to be of considerable importance. Ny and the author first observed the band on the short wave-length side of the second member of the rubidium principal series in absorption.[1] Later on the corresponding band was also observed for caesium.[2] It was found that the width of the band and its position with respect to the corresponding series member depend on the nature of both the colliding and the absorbing atoms. The lighter the colliding or the absorbing atoms the greater the width and the separation between the series line and the band. In the investigation of the pressure effects of foreign gases on spectral lines the concentration of the foreign gas is always sufficiently high for the band to appear, even when the temperature of the absorption tube is rather low. The corresponding phenomenon was also studied for sodium.[3] It is very interesting to note that, for sodium, this sort of absorption band appears only in the neighborhood of the third member of the principal series. Very recently the phenomenon was also observed by the author and his collaborators for potassium. The narrow and structureless absorption maximum was observed on the short wave-length side of the second member of potassium principal series, and no bands of this kind were observed in the vicinity of the other members of the series. It is the purpose of this paper to present the results newly obtained for sodium and potassium and to give a résumé of the results obtained so far with a theory to account for the phenomenon.

EXPERIMENT

The experimental arrangement was essentially the same as that previously described.[4] Nitrogen and hydrogen were used as foreign gases in the presence of sodium and potassium. Pure nitrogen was prepared by decomposing ammonium nitrite. Hydrogen was prepared by the electrolysis of water whose contained air was first removed by repeated boiling and cooling in "vacuum." Several stages were also used to remove various kinds of possible impurities. Before the admission of hydrogen or nitrogen to the absorption tube, the gas was allowed to pass through a vapor trap of the same alkali as that whose absorption spectrum was to be studied, so that the residue of impurities (especially water vapor and oxygen) present in the gas were removed. A high intensity tungsten filament lamp and a hydrogen discharge tube were employed as light sources for the visible and the ultraviolet parts of the spectrum. A Hilger E-316 and a 10-foot grating spectrograph were used to register the entire absorption series of the alkali. The appearance of the band was studied by means of an automatic recording microphotometer.

Spectra were taken when the absorption tube

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* In memory of the author's mother.

[1] Ny Tsi-Zé and Ch'en Shang-Yi, Nature **138**, 1055 (1936).

[2] Ny Tsi-Zé and Ch'en Shang-Yi, J. de phys. et rad. **9**, 169 (1938).

[3] Ke T'ing-Sui and Ch'en Shang-Yi, Chinese J. Phys. **5**, publication delayed by the war.

[4] Ny Tsi-Zé and Ch'en Shang-Yi, Phys. Rev. **51**, 567 (1937).

was heated to various temperatures. Great care was taken, so that the possibility that weak lines were overlooked owing merely to improper exposures is very small.

RESULTS AND DISCUSSION

Table I gives a résumé of the data obtained so far on the absorption bands of alkalis in the presence of foreign gases. It has been found that the pressure of the foreign gas does not appreciably affect the appearance of the band as long as the pressure is much higher than that of the alkali vapor. The pressure of the foreign gas is not so important and, therefore, is not listed in the table. In fact, for potassium the pressure in the absorption tube was 34 and 45.5 cm Hg for nitrogen and hydrogen, respectively. The corresponding values for sodium were 48 and 30 cm Hg, and for all the rest of the data the pressures were about one atmosphere.

TABLE I. New absorption bands of alkali metals in the presence of foreign gases.

Foreign gas	Alkali	Wave-length of band	Width of band	Separation between the band and the series member	Temperature of absorption tube
		A	*A*	*A*	°C
H_2	Na	2811.2	83	41.7 (3rd member)	544
	K	4007.2	42	38.5 (2nd member)	450
	Rb	4178.7	38	23.1 (2nd member)	300
	Cs	4541	30	14 (2nd member)	280
He	Rb	4182.5	35	19.3 (2nd member)	220
	Cs	4543	27	12 (2nd member)	200
N_2	Na	2818	70	34.8 (3rd member)	522
	K	4018.7	39	27.0 (2nd member)	484
	Rb	4183	24	18.8 (2nd member)	240
	Cs	4544	21	11 (2nd member)	210
Ne	Rb	4194.5	16	7.3 (2nd member)	220
	Cs	4549	12	6 (2nd member)	190
A	Rb	no band			
	Cs	no band			

The last column of Table I gives the most favorable temperatures of the absorption tube for observation of these bands. Certainly the lowest temperatures to render the band perceptible are much lower than those listed. For potassium, the lowest temperatures at which the band became visible were 410°C for hydrogen and 380°C for nitrogen. In all cases the temperatures were rather low, so that no molecular bands of alkalis or of alkali-foreign-gas compounds appeared.

The readings in the fifth column of Table I show in each case the distance between the maximum of the band and the $^2P_{3/2}$ component of the member of the series. The readings for the width (i.e., the half-width) of the band are only approximate.

Oldenberg, Kuhn, and others[5] have studied some bands which may conceivably be a similar phenomenon in emission spectra. They used various other metals and observed one or more bands appearing near all spectral lines. Obviously owing to the many complicating factors, such as the non-uniformity of the temperature of the discharge and of the vapor pressure of the metal, the pressure of ions, dipoles, etc., the condition for the production of these bands in emission is not so simple as that in absorption. The bands were interpreted by Oldenberg, Kuhn, and others as due to loosely bound molecules resulting from close collisions. According to their theory, bands of this type would occur with all metal lines, in agreement with their results.

Their theory is evidently not confirmed in the present work, in that this type of band appears only in the neighborhood of certain spectral lines. Nor is there any obvious rule for selecting these lines, as illustrated by the fact that in the series of sodium the absorption maximum appears by neither of the first and second members nor by its weaker members, except the third, $3^2S_{1/2}-5^2P_{3/2}$. Again for K, Rb, and Cs, the band appears only beside the second member of the principal series. Another fact also unexpected is that argon produces no band for Rb and Cs. Whether the bands observed by Oldenberg and Kuhn are of the same nature as those observed here is quite doubtful.

In the light of a systematic observation of this phenomenon as shown in Table I, it is easy to single out five points:

(1) The lighter the absorbing or perturbing atoms, the greater the separation between the band and the series line. Hence for a certain foreign gas the separation corresponding to Cs has the lowest value while that corresponding to Na possesses the highest value. For a certain absorbing alkali the separation corresponding to the lightest gas has the highest value and that corresponding to the heaviest gas has the lowest value. Consequently the separation correspond-

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[5] Oldenberg, Zeits. f. Physik **47**, 184 (1928); **55**, 1 (1929). Kuhn and Oldenberg, Phys. Rev. **41**, 72 (1932). Krefft and Rompe, Zeits. f. Physik **73**, 681 (1932). Preston, Phys. Rev. **51**, 298 (1937).

ing to H_2-Na has the highest value of all and that corresponding to Ne – Cs has the lowest value of all; as to the extreme case of argon and Rb or Cs, no band can be resolved.

(2) The lighter the absorbing or perturbing atoms, the greater the width of the band. Examples given in (1) can be similarly applied here.

(3) The wider the band, the higher the temperature of the absorption tube or the concentration of absorbing atoms that is needed to render the band perceptible.

(4) For heavier alkalis, *viz.*, K, Rb, and Cs, the band appears on the short wave-length side of the second member of the principal series, while for a lighter alkali, Na, the band appears on the short wave-length side of the third member of the series. It can be predicted without hesitation that the corresponding band for lithium will appear on the short wave-length side of the third or still higher member of the principal series.

(5) The band observed is narrow, structureless, and much fainter than the intensity of the series lines.

One more point should also be mentioned here.[6]

(6) When the pressure of the perturbing gas is very large in comparison with that of the absorbing vapor, the intensity of the band depends only upon the concentration of the absorbing vapor. If the pressure of the perturbing gas is reduced so that the concentration of the absorbing vapor becomes comparable with that of the perturbing gas, the intensity of the band will decrease with the decrease of concentration of either the absorbing or the perturbing atoms.

The production of the band may be suggested as due to the increase in the energy of the optical electron through the process of collision with the foreign gas atoms when the electron reaches that energy level whose orbital radius is close to the distance of optical collision. Foreign gas atoms can be regarded as evenly distributed in the surroundings of the absorbing atom. It is the effect, say the polarization effect, of the introduction of the foreign atoms within the space of the possible orbits of the optical electron of the alkali that contributes certain features of the well-known "pressure effects." As the spacing between foreign atoms is quite large, and the foreign atoms are moving with an enormous speed, the chance of collision between the excited electron and the foreign gas atom is rather small. But the chance of collision becomes considerable when the foreign gas atom reaches the location where collision between the foreign gas atom and the absorbing atom takes place because the colliding atom will spend the major part of its time around the district of closest collision. If that distance of closest collision happens to be near a certain energy level of the alkali atom, only the electron at that state will have appreciable chance to change energy. With this picture in mind the above six points can be accounted for without difficulty.

The magnitude of the separation between the band and the series line is a measure of the energy change of the optical electron at the instant of collision with the foreign gas atom. The lighter the colliding particle, the higher the relative speed of collision; consequently more energy will be given to the electron when it is excited to the energy level whose orbital radius is close to the distance of collision. For heavier alkalis, Rb and Cs, and a heavier gas, say argon, the separation might be so small that no band is perceptible. This is illustrated in point (1). The distribution of velocities has a wider range for lighter absorbing or perturbing particles, so the structureless band is wider for lighter atoms. This explains point (2). Point (3) is simply a matter of photometry because the amount of absorption depends only upon the concentration of the absorbing atom. For a broader band the energy is distributed over a wider range, thus a higher concentration of the alkali vapor is required to obtain the perceptible intensity.

Point (4) tells the approximate distance of optical collision. By applying the quantum mechanics expression for the average value of the electron nuclear distances at various energy levels, it is possible to tell the approximate value of the distance of collision between the nuclear and the colliding atom. The value for the third member of Na principal series, $3s-5p$, is 19A. For the second members of K($4s-5p$), Rb($5s-6p$), and Cs($6s-7p$) series the values are 19A, 28A, and 38A, respectively. Points (5) and (6) are simply a reflection of the probability of this kind of transition.

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[6] Cf. references 1 and 2.