The Positive Ion Excitation of Mercury Vapor

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Mercury vapor was bombarded by Li^+ and K^+ ions and the resulting spectra photographed with a quartz spectrograph and the plates photometered to give an approximate intensity-velocity curve. Voltages used ranged from 150 to 1500 volts. The results indicate that the velocity rather than the energy is the important factor to be considered in the mechanism of the collision process. A preference seems to exist for the excitation of levels of higher L values. The spark lines 2847, 2260 and 2224 appear at 1000 volts for Li^+ ions. A powerful source of positive ions has been developed.

EXPERIMENTS on the effect of positive ion impact in gases[1] have usually been directed toward measuring the resulting ionization as a function of the kinetic energy of the ions. The purpose of the present investigation is to study the somewhat more general problem of the probabilities of excitation of an atom to its various energy states by positive ion impact.[2] The excitation of the spectrum lines of the mercury atom by impact with the positive ions of lithium and potassium was the specific problem attacked.

Source of Positive Ions

A first essential was the development of a copious and constant source of the ions. The material which proved most satisfactory was the alkali aluminum silicates. Hundley was the first to use these compounds in studying the emission of lithium ions from spodumene. In the present work the system $Li_2O \cdot Al_2O_3 \cdot SiO_2$ was studied and a mixture of the composition $3Li_2O \cdot Al_2O_3 \cdot 3SiO_2$ proved to be most satisfactory. A similar mixture $3K_2O \cdot Al_2O_3 \cdot 3SiO_2$ was used as a source of potassium ions. With these sources it was possible to maintain a remarkably constant current of about 4×10^{-4} amp./cm^2 for periods of forty hours. The mixtures were prepared from pure chemicals by heating the constituents on a platinum gauze. A further study[3] is in progress concerning the whole problem of emission of alkali ions from their corresponding aluminum silicates.

Apparatus

Fig. 1 gives the plan of the experimental tube and the arrangement of the electrodes and is self-explanatory. It was evacuated by a two-stage diffusion pump. The tube was placed in the magnetic field of a pair of Helmholtz coils which have a field of about 150 gauss parallel to the direction of observation. This field was ample to prevent any electrons from entering the region under observation.

The spectrograph was a medium size Hilger quartz instrument. The slit width was 0.5 mm. A Zeiss step filter covered the slit and allowed the photographic plate to be calibrated for intensities. The plates used were Seed 23 and were developed 5 minutes at 16°C.

Procedure

An exposure time of eight hours was chosen as standard. Each exposure was made on a sepa-

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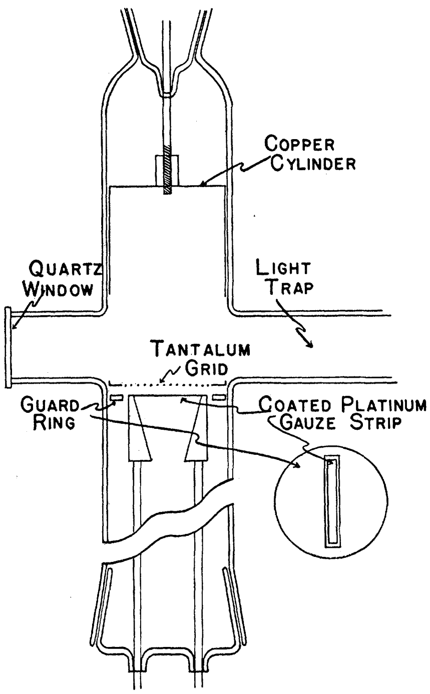

FIG. 1. A diagram of the apparatus.

rate plate. While this procedure made photometric comparison of one exposure with another less accurate, it was adopted to facilitate the taking of a large number of plates. For each exposure a time record of the ionic current was made with a recording microammeter. The current was of the order of 3×10^{-4} amp. and was held to this value as closely as possible by adjusting the temperature of the filament. From the integrated value of the positive ion current it was possible to reduce the intensity measurements to a comparable basis. The photometric measurements were made with a photoelectric photometer. The transmission of the clear part of the plate on each side of the line and of the line itself was obtained for each step of the step filter. The characteristic curve of the plate was obtained by plotting the logarithm of the blackening against the logarithm of the intensity.

RESULTS

A series of exposures from 150 to 1500 volts for lithium positive ions and from 300 to 1500 volts for potassium positive ions was taken as described. (Below 300 volts, for K^+ ions, space charge made it impossible to obtain currents of the magnitude chosen as a standard.) The plates were then measured and the blackening of each line relative to that of the line 2537 was calculated. To obtain the intensities relative to a fixed standard it is necessary to compare exposures taken on different plates. However, the plates were all from the same batch and were developed in exactly the same way. The curves showing the variation of the intensity of 2537 with both voltage and velocity are given in Figs. 2 and 3. In Fig. 4 are plotted the intensities of various other

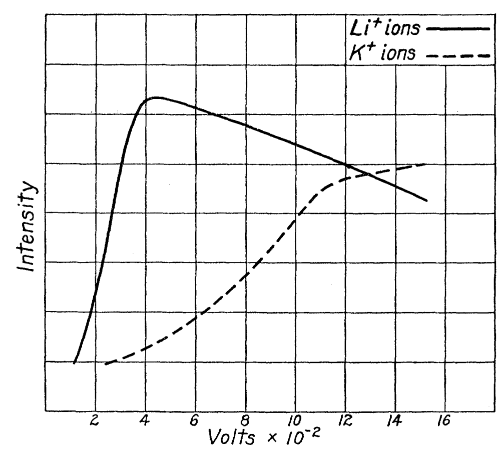

FIG. 2. The intensity of 2537 (arbitrary scale) as a function of voltage.

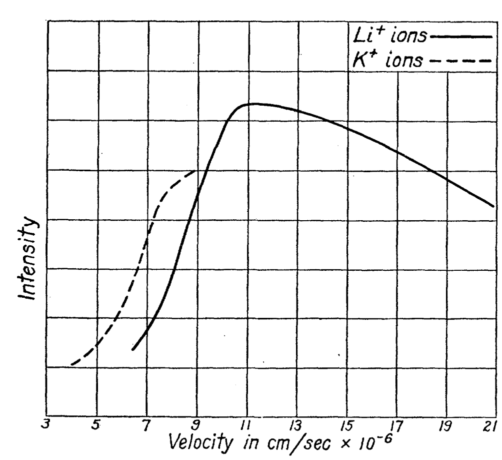

FIG. 3. The intensity of 2537 (arbitrary scale) as a function of velocity of the impacting ion.

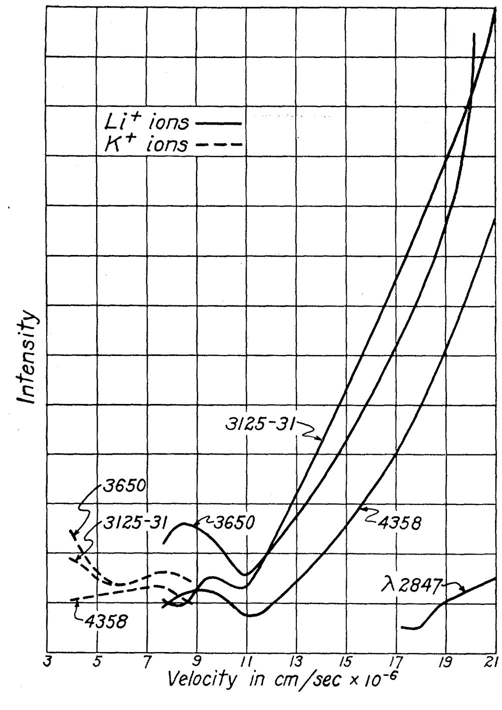

FIG. 4. The absolute intensities (arbitrary scale) of the prominent mercury lines as a function of the velocity.

mercury lines. These intensities were calculated by multiplying the intensities of each line relative to 2537 by the corresponding intensity of that line. The effect of the magnetic field in preventing stray electrons from exciting mercury vapor is seen in Fig. 5. In exposure A the magnetic field failed for 90 minutes. As may be seen the spectrum has the familiar appearance of that of the ordinary arc. An interesting feature which is illustrated in these photographs is the appearance of 2857 of the arc spectrum and 2847 of the spark spectrum in A while in B (pure positive ion excitation) only the spark line 2847 appears.

The following characteristic differences between the mercury spectrum excited by positive ion impact and the spectrum excited by electron impact may be pointed out. The most conspicuous of these is the relatively great intensity of the line 2537 in positive ion bombardment. Up to 1500 volts this line is more than three times as intense as any other line on the plate. This effect is, of course, not due to any lack of energy on the part of positive ions.

Another interesting feature of positive ion excitation is that the lines do not appear in the order of the energy necessary for their excitation. Table I illustrates this point. It will be noted that

TABLE I. *Order of appearance of Hg levels by positive ion excitation.*

Term	Energy	Order of appearance	Term	Energy	Order of appearance
2^3P_1	4.9	1	3^1S	9.2	absent
2^3S	7.7	3	4^1D & ^3D	9.3	4
2^1S	7.9		4^1S	9.7	absent
3^1D & ^3D	8.8	2	Hg II		
3^3S	9.1	7	$2S$	22	5
			$3d$	23	6

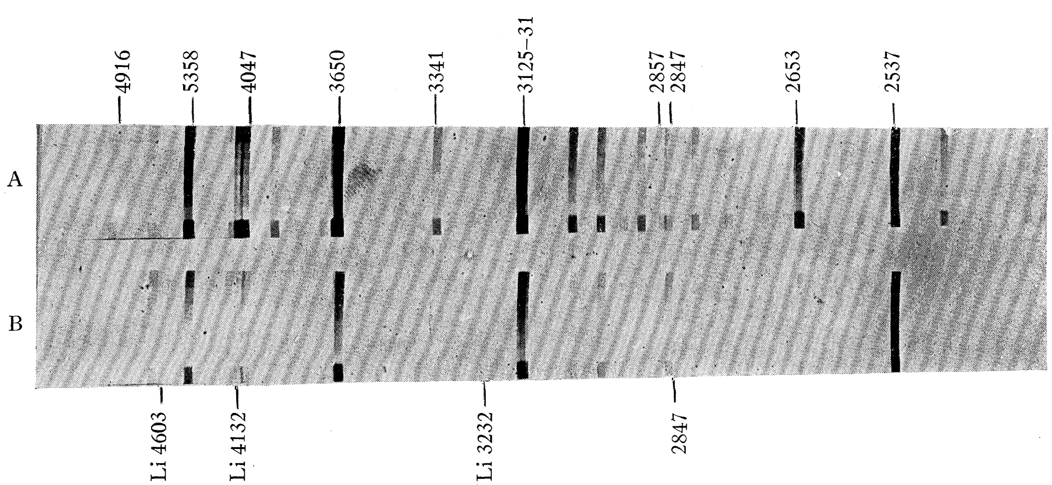

FIG. 5. Plate showing the effect of secondary electrons; A, magnetic field off $1\frac{1}{2}$ hours. Total exposure time 8 hours. B, magnetic field on 8 hours.

there is a preference for levels of higher L values and this suggests the possibility that in collisions of this type there is a preference for the transfer of larger amounts of angular momentum.

Attention should be drawn also to the early appearance of the spark lines. Some of them appear before lines of the arc spectrum which appear early in electronic excitation. Lithium arc lines appeared on the plates and their presence is probably due to the bombardment of lithium vapor arising from the lithium compounds by lithium ions. Capture of an electron by a lithium ion to yield the arc spectrum seems to be ruled out.

Finally, it is apparent from Figs. 2 and 3 that for this type of excitation the velocity of the ions rather than their energy is the variable which reduces the excitation produced by different ions to a comparable basis.

Acknowledgment

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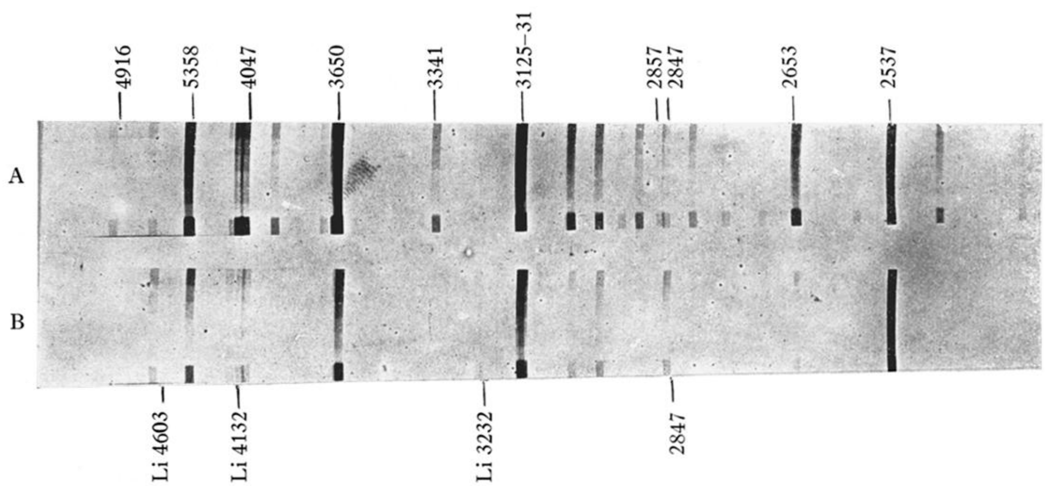

FIG. 5. Plate showing the effect of secondary electrons; *A*, magnetic field off 1½ hours. Total exposure time 8 hours. *B*, magnetic field on 8 hours.