Absorption of NaCl, KCl and KI in the Far Ultraviolet

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With a normal incidence concave grating vacuum spectrograph with a hot spark for a light source and oiled photographic films, qualitative absorption curves for NaCl, KCl, and KI between 190A and 1550A have been obtained. The absorbing film of the alkali halide was distilled directly onto the ruled surface of the grating. The positions of maximum absorption as read from the three curves presented are: for NaCl, 655A, 535A, 350A, and 890A; for KCl, 705A, 530A, 320A, and 1120A; for KI, 825A, 625A, and 510A, all accurate to 6 percent. These results are at variance with early theoretical extrapolations from the known form of the dispersion curves for rocksalt and silvite in the near infrared.

I. INTRODUCTION

HERZFELD and Wolf,[1] from the dispersion curves for NaCl and KCl in the near infrared, have calculated three principal positions of maximum absorption for these halides at wavelengths shorter than 2000A. For NaCl the positions were: weak absorption at 1584A, and strong bands at 1085 and 347A.

The absorption in the 1600A region was verified by Pfund[2] who observed the metallic reflection from cleavage planes of NaCl and KCl. Hilsch and Pohl[3] with a vacuum fluorite spectrograph investigated in detail the absorption between 1600 and 2600A of the remaining alkali halides.

Recently Hilsch[4] has used the scattering of electrons from thin films of the alkali halides as a qualitative means of determining the positions of maximum absorption. He was able to check the results of Hilsch and Pohl excellently but no new regions of maximum absorption were observed at shorter wave-lengths despite the fact that his curves are continuous down to electron energies corresponding to 450A.

The present investigation has for its purpose the qualitative determination of the general form of the absorption curved for NaCl, KCl and KI

between 190 and 1550A. The method and preliminary observations on NaCl have already been briefly described.[5]

II. APPARATUS AND METHOD

A normal incidence vacuum spectrograph, designed for use with a one-meter grating, together with a hot spark for a light source, was used. The general arrangement is shown in the schematic diagram of Fig. 1. The hot spark is of the conventional type, having in series with it an auxiliary gap in air. It is excited by transformer and condenser in the manner described by O'Bryan.[6] The water-cooled electrodes were of tungsten or copper. The discharge was run intermittently, every two seconds, for $\frac{1}{4}$ of a second duration during which time the transformer drew 45 amperes at 125 volts and 60 cycles.

The grating was especially ruled for this investigation on a spherically figured concave flint glass blank with 15,000 lines to the inch. The ruling, which covers about 25 square centimeters, was intentionally made very light. The reflecting power of glass is far superior to that of speculum metal for these short wave-lengths; moreover, in the spectral region studied, it was found that glass gratings always gave more intense spectra than speculum ones. The dispersion of the grating was 17A per mm.

The spectrum was recorded on oiled Commercial Safety film which was wrapped around the

[1] K. F. Herzfeld and K. L. Wolf, Geiger-Scheel Handbuch der Physik **20**, 480 to 634.

[2] A. H. Pfund, Phys. Rev. **32**, 39 (1928).

[3] R. Hilsch and R. W. Pohl, Zeits. f. Physik **59**, 812 (1930).

[4] R. Hilsch, Zeits. f. Physik **77**, 427 (1932).

[5] A. Smith, Phys. Rev. **39**, 1013 (1932).
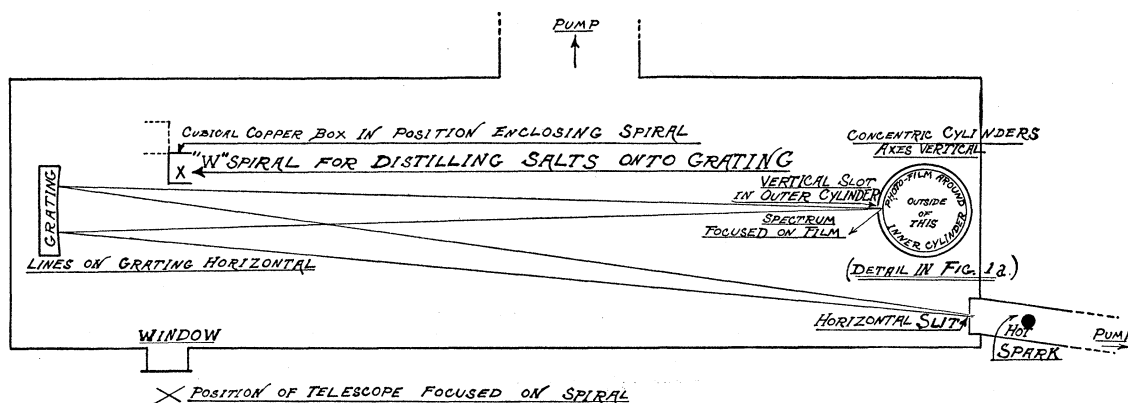
[6] H. M. O'Bryan, Phys. Rev. **38**, 32 (1931).

FIG. 1. Schematic diagram of vacuum spectrograph.

outside of a blackened metallic cylinder (Fig. 1a). It was manipulated as described by Pfund.[2] As many as 36 spectra could be obtained on a single film without opening the apparatus.

In the extreme ultraviolet the absorption is so strong that very thin layers of the salts must be used. To avoid the necessity of a supporting film the salts were distilled directly onto the ruled surface of the grating. This is accomplished by vaporizing a small fused bead of the alkali halide from an electrically heated conical tungsten spiral placed about 13 cm from the grating and just far enough to one side to be out of the path of the light.
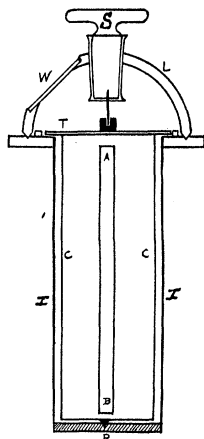

FIG. 1a. Detail of film holder. Vertically projected spectrum passed through slot AB, in outer cylinder I striking inner cylinder C about which is wrapped photographic film. Stopcock S permits rotation of cylinder C for successive exposures. Amount of rotation is observable by graduations on C at T through window W in hemispherical dome L.

A small cubical copper box, with one side missing, was supported from one corner by a rod so pivoted that it could be rotated from the outside so as to enclose the spiral and shield the grating. The whole procedure was viewed through a glass window with a small telescope. In manipulation, the heating current to the spiral was turned on, and, a few seconds later, when the halide was being freely distilled from the spiral onto the interior of the copper box, the box was swung out of the way for a second or two so as to deposit a thin coating of the halide on the grating.

In making a complete run with the apparatus, therefore, the procedure was first to take several spectrograms of the source of different exposure times with the grating clean; then, after distilling a very thin layer of the halide onto the grating, to repeat these same exposures. The quantity of the salt on the grating is at all times so small that it is scarcely detectable when the grating is removed and examined visually.

As the thickness of the absorbing film is increased an interesting sequence of changes in the appearance of the spectrograms is noted. For the thinnest films the region of maximum absorption, around 675A for NaCl, becomes apparent. Next the 675A region broadens and an absorption maximum at about 900A appears. This is followed by the appearance of absorption at about 1600A while the structure in the absorption below 1000A is gradually wiped out. Finally with increasing salt thickness the absorption at 1600A is replaced by a reflection maximum displaced about 85A to 1685A. There is an analogous phenomenon in the
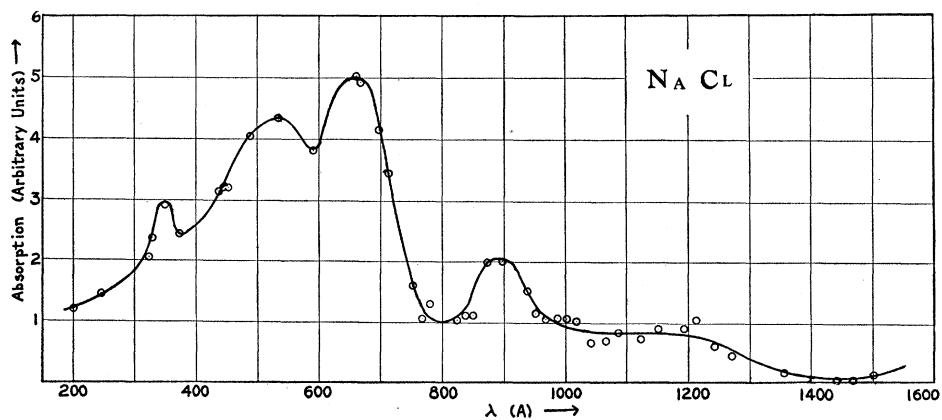
FIG. 2. Absorption curve for NaCl, showing absorption maxima at 655A, 535A, 350A, and 890A.
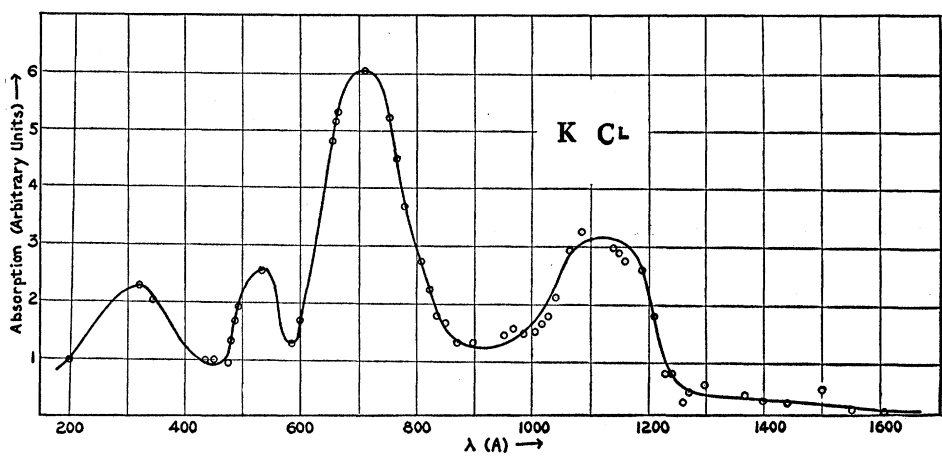
FIG. 3. Absorption curve for KCl, showing absorption maxima at 705A, 530A, 320A, and 1120A.
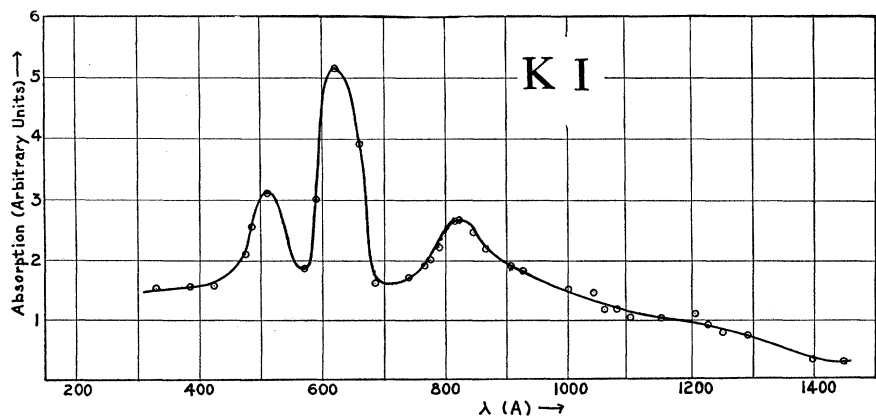
FIG. 4. Absorption curve for KI showing absorption maxima at
825A, 625A, and 510A.

visible spectrum which is easy to observe for certain dyes, such as methyl aniline violet. In the spectral range between 190 and 1550A no reflection maxima were ever observed by the experimental method of this paper. It is thought probable that the increasing roughness of the surface due to deposition of the salt film or its increasing cloudiness with increasing thickness, may account for the fact that we find no reflection maxima at these shorter wave-lengths.

At the conclusion of each run, the grating was cleaned by dabbing it with absorbent cotton wetted first with distilled water and then with acetone. The grating is considered clean when the film of acetone dries without leaving any noticeable stain or "contour" lines.

Precautions were taken to be sure that the alkali halide distilled onto the grating was free from any contamination or decomposition. Distillation was carried out at as low a temperature as possible. Further, the same tungsten spiral has been used for distilling the various halides for the last twenty-eight runs with but slight evidence of deterioration, all of which is thought to have taken place at the end of the runs, when the tungsten is made to glow at a much higher temperature in order to clean out all traces of the halide.

III. INTERPRETATION OF SPECTROGRAMS

To determine the absorption of the films, the spectrograms taken with various thicknesses, including zero, were run through a Moll microphotometer. (Since the thicknesses were not measured only relative absorptions could be determined.) The logarithm of the ratio of the microphotometer readings for a given spectrum line with and without salt film at the same exposure time gives the ratio of the intensities of the light in the two cases and hence the absorption in the salt film. This is true provided the blackening of the photographic film is proportional to the light intensity. Care was taken, by comparing absorptions measured on spectrum lines of very different intensities, that the exposures were in the range in which this proportionality held. From an intercomparison of the data taken with tungsten and with copper sparks it is estimated

that the relative magnitudes of the absorption are accurate to within 40 percent and the positions of the maxima to 6 percent.

IV. RESULTS AND DISCUSSION

Figs. 2, 3, and 4 show the form of the absorption curves found for NaCl, KCl and KI, respectively. Considerable difficulty is experienced in procuring a salt film on the grating of the requisite thickness to give such curves, for quite frequently the film is so thick that it is opaque below 1000A, while at other times it is so thin that the position of maximum absorption is just beginning to appear. In the curves of Figs. 2, 3, and 4, the thickness was such as to absorb about 90 percent of the incident energy at the wave-length of maximum absorption. Twenty-one separate runs were taken in obtaining the three useful photographic films from which these graphs were obtained. These curves, which were all obtained with the aid of the tungsten spectrum are typical ones. The reason for extending the curves so far up towards the 1600A region is to show that, with the film thickness of halide used for these particular curves, there is but little absorption of this longer wave-length region.

By referring to Figs. 2 and 3, it is seen that there is striking similarity between the absorption of the NaCl and KCl. The maxima at 655A, 535A, and 350A for NaCl seem but slightly shifted when we pass to KCl, while, on the other hand, the maximum at 890A for NaCl shifts to 1120A for KCl. This suggests that for these two halides absorption below 800A is more dependent on the negative than on the positive ion of the lattice. The curve for KI, Fig. 4, where we have now changed the negative ion, seems to bear out this statement, since the maxima have shifted to considerably longer wave-lengths.

From a consideration of the proper frequencies of absorption as here experimentally determined, it is hoped that a theoretical calculation of the refractive index for these alkali halides will be made.