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Extreme Vacuum Ultraviolet Absorption Spectra of Silver Chloride and Silver Bromide Films*

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The absorption spectra of silver chloride and silver bromide films have been extended to shorter wavelengths than in previous studies, in order to locate the maxima and any associated structure and to find the magnitude of the absorption coefficient. Measurements in the region 800–1600 A were made by using a grazing-incidence vacuum spectrograph with a Lyman discharge tube as source. Overlapping of orders was avoided by using the noble gases as filters. Sample films of the order of 100 A thick were vacuum evaporated onto very thin (100–150 A) celluloid supports. The silver halide film thicknesses were measured by channeled spectra. Silver chloride shows its greatest absorption in the region 900–1200 A, with some structure. Silver bromide has a broad absorption maximum about 1500 A, with some structure at shorter wavelengths. With the films used, both compounds showed absorption coefficients at maxima of approximately 1.5×10^6 cm^{-1}.

I. INTRODUCTION

THE absorption spectrum of a crystalline substance reveals data on the relative positions and structure of the bands of initial states and excited states. In the soft x-ray and extreme ultraviolet region initial states are narrow[1] enough so that observed structure can be associated with structure of the excited states.

The absorption spectra of the silver halides have been studied in the near and far ultraviolet by Fesefeldt,[2] Fesefeldt and Gyulai,[3] Schneider and O'Bryan,[4] and Milliman.[5] For silver chloride the curves show an absorption coefficient which generally increases with decreasing wavelength and has a small bump at 2600 A. Schneider and O'Bryan observed the absorption from 2000 A down to 1050 A of silver chloride films evaporated onto lithium fluoride. The absorption was observed to rise as wavelength decreased, but no maximum was reached.

The silver bromide absorption measured by Fesefeldt and Gyulai also showed a general increase with decreasing wavelength with a bump at 3150 A.

The purpose of the work reported here was to extend the absorption measurements on silver chloride and silver bromide to shorter wavelengths, to locate the absorption maxima in each material along with any associated structure, and to find the magnitude of the absorption coefficients in the regions of strong absorption.

II. EXPERIMENT

A description of the grazing-incidence spectrograph used in this research was given by Givens and Siegmund.[6] It is fashioned after one described by Skinner and Johnston[7]; the source was a Lyman discharge tube similar to that described by Rathenau.[8]

Samples were thin films vacuum-evaporated rapidly onto celluloid supports. The transmissions of two different thicknesses of silver halide were compared so that the calculated absorption was independent of reflection and high absorption[9] at the interfaces. Film thicknesses were measured by utilizing fringes of equal chromatic order.[10]

An attempt was made to study with an electron microscope the physical structure of the evaporated thin halide films. In particular it was desired to learn whether or not the films were continuous, and if not, what was the percentage of open area. The attempt was unsuccessful for, even with low beam intensity, the film quickly sublimed and agglomerated.

After a series of exposures the spectroscopic plates (Kodak SWR) were developed and then microphotometered on a radiometer-type instrument described by Leighton, Smith, and Henson.[11] From the microphotometer traces a plate characteristic curve was constructed as described by Woodruff and Givens.[12] The exposures, E_n, through the thin film, and E_k, through the thick film, were read from the curve and the approximate absorption coefficient, α, was computed from the relation $RE_n/E_k = e^{\alpha T}$, where T is the difference in average thickness of the pair of films, and

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[1] H. W. B. Skinner, in *Reports on Progress in Physics* (The Physical Society, London, 1938), Vol. 5, p. 257.

[2] H. Fesefeldt, Z. Physik **64**, 741 (1930).

[3] H. Fesefeldt and Z. Gyulai, Nachr. Gess. Wiss. Göttingen, Math.-physik. Kl., p. 226 (1929).

[4] E. G. Schneider and H. M. O'Bryan, Phys. Rev. **51**, 293 (1937).

[5] P. D. Milliman, thesis, Cornell University, 1953 (unpublished).

[6] M. P. Givens and W. P. Siegmund, Phys. Rev. **85**, 313 (1952).

[7] H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. (London) **A161**, 420 (1937).

[8] G. Rathenau, Z. Physik **87**, 32 (1933).

[9] D. H. Tomboulian and E. M. Pell, Phys. Rev. **83**, 1196 (1951).

[10] S. Tolansky, *Multiple-beam Interferometry of Surfaces and Films* (Oxford University Press, New York, 1948), Chaps. 8 and 9.

[11] Leighton, Smith, and Henson, Rev. Sci. Instr. **5**, 431 (1934).

[12] R. W. Woodruff and M. P. Givens, Phys. Rev. **97**, 52 (1955).

R is the ratio of number of sparks in the thick-film exposure to the number in the thin-film exposure.

It was necessary to take into account effects due to reciprocity failure, change in characteristic curve with wavelength, and scattered light. The steps are described elsewhere.[13] The corrected exposure values, e_n and e_k, were used to compute the absorption coefficient, μ, according to the equation $Re_n/e_k = e^{\mu T}$.

III. THEORY

In the silver halides there are several possible electronic transitions which could result in strong absorption in the region 500–1500 A. Allen[14] studied theoretically the absorption of silver bromide using a model consisting of a bromide ion in a cavity in a uniform dielectric. The predicted absorption due to excitation of a bromide $4p$ electron shows a gradual increase with increasing energy from the edge (estimated at 6.25 ev) to the maximum value of 1.4×10^6 per cm at about 14.6 ev (850 A), with a gradual decrease at higher energy. Presumably, the principal results would be similar for silver chloride, that is, a rather diffuse absorption with the maximum value the order of 10^6 per cm occurring at an energy well above that at the edge.

Another process to be considered is excitation of a bromide $4s$ or chloride $3s$ electron. The energies of these levels are not directly available. However, the energy difference between the isolated chloride ion levels $3p$ and $3s$ can be estimated as follows. Consider two different excitations of an isolated chloride ion, $3s^2\,3p^6 \rightarrow 3s^2\,3p^5 + e$, and $3s^2\,3p^6 \rightarrow 3s^1\,3p^6 + e$, where the electron in each case is just free. The difference in energy required is obviously equal to the energy of the *atomic* transition $3s^2\,3p^5 \rightarrow 3s^1\,3p^6$. This in turn can be estimated from the screening doublet law[15] for the isoelectronic sequence Cl I, A II, K III, Ca IV, Sc V, T VI, V VII. A plot of term values for the $3s\,3p^5$ states *vs* atomic number for A II through V VII gives a straight line. Extrapolated to atomic number 17 the line yields 10.7 ev for the energy difference between Cl I $3s\,3p^6$ and $3s^2\,3p^5$. Therefore, if in the solid there are states to which either a chloride $3p$ or $3s$ electron can be excited (such as ionization states), then the transition from $3s$ would be expected at an energy the order of 11 ev greater than that of the $3p$ transition. The corresponding transitions for the bromide $4s$ electron should involve less energy, but quantitative information is not available.

In silver chloride there are some states beginning about 3 ev above the Cl^- $3p$ band and strong absorption, possibly due to the formation of excitons, at about 5 ev. If $3s$ electrons can be excited to these states or states with nearly the same energy, then we would expect absorption structure to occur in the region 13 to 16 ev.

A third process to be considered is excitation of a silver ion $4d$ electron. In the isolated ion there are three $5p$ states to which transitions are permitted by the selection rule, ($\Delta J = \pm1$, 0, but not $J=0 \rightarrow J=0$). They are:

$^3P_1$, 10.32 ev above ground state;
$^1P_1$, 11.10 ev above ground state;
$^3P_1$, 11.14 ev above ground state.

Of these, only the $^1P_1$ state also satisfies the rules ($\Delta S = 0$) and ($\Delta L = \pm1, 0$).

In the solid there are undoubtedly available to a silver ion $4d$ electron, states whose wave functions, ψ_i, near the silver ion are made up in part of $5p$ wave functions of an isolated ion. It is to be expected, then, that transitions from the $4d$ levels to states ψ_i will occur and that the excited levels will be broadened by overlap of the wave functions. The energy associated with these transitions is expected to be lower than that for the corresponding transitions in the isolated ion, for as

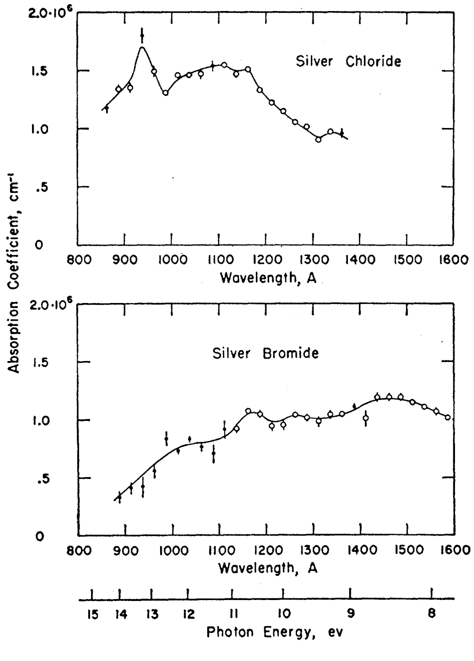

FIG. 1. Absorption spectra of silver chloride and silver bromide film. Each circled point is the average over a 25 A interval of two independent determinations. Other points are averages over 25 A intervals of absorption measured in one run only.

Average film thicknesses	Thin film	Thick film	Difference
Silver chloride sample *A*	149 A	186 A	37 A
Silver chloride sample *B*	7 A	63 A	56 A
Silver bromide sample *A*	43 A	128 A	85 A
Silver bromide sample *B*	130 A	207 A	77 A

Probable error of the mean for the difference was 6 A.

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[13] C. J. Koester, thesis, University of Rochester Library, 1955 (unpublished).

[14] J. R. Allen, Can. J. Phys. **31**, 218 (1953).

[15] H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934), pp. 316, 337, 348; G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, Inc., New York, 1944), second edition, p. 63.

Seitz points out,[16] an excited electron can take advantage of the lattice fields to reduce its energy.

The ground state of a halogen atom is a doublet, the separation for chlorine and bromine being 0.11 and 0.45 ev, respectively. In the alkali bromides the doublet structure shows clearly in absorption[17] except in lithium bromide. In the chlorides this structure is not resolved. O'Bryan and Skinner[18] have shown by soft x-ray emission studies that in silver bromide the bromide $4p$ band is wider than the corresponding bands in all the alkali bromides except lithium bromide. Therefore, the wide $4p$ band may hide the doublet structure in silver bromide.

IV. RESULTS

Curves of absorption coefficient, μ, *vs* wavelength for silver chloride films and silver bromide films are given in Fig. 1. Each is the average of two independent determinations. The shapes of the curves are more certain than the absolute magnitude of the absorption which could be in error by as much as 30%.

For silver chloride the general features are the gradual rise with decreasing wavelength at long wavelength, punctuated by a relatively narrow absorption peak at 1165 A. There are broader maxima at about 1120 and 950 A.

For silver bromide the absorption has a broad maximum centered at about 1470 A with two narrower bands at 1260 and 1170 A. The absorption coefficient remains high to about 1000 A. There was some evidence for narrow peaks at 1035 and 975 A, but the scatter of experimental points was too great to permit confidence in their reality.

V. INTERPRETATION

It seems likely that the peaks at about 1170 A which appear in both the silver chloride and silver bromide absorption curves, result from excitation of the silver ion. Table I gives a summary of the pertinent data.

Without the relatively narrow peaks the curves suggest the type of absorption predicted by Allen for silver bromide. The agreement is not complete, however, for Allen's calculation predict a maximum absorption at 850 A for silver bromide, whereas the present work shows it to be about 1470 A.

Table I. Observed peaks in silver halide absorption curves compared to silver ion levels.

	λ (A)	Photon energy (ev)	λ (A)	Photon energy (ev)
AgCl	1165	10.6		
AgBr	1170	10.6	1260	9.8
Average		10.6		
Isolated Ag^+	(^3D,^1P)	11.1		(^3P)10.3
Difference		0.5		0.5

The strong absorption at shorter wavelengths, around 950 A in silver chloride and between 950 and 1150 A in silver bromide may be due in part to excitation of the chloride $3s$ and bromide $4s$ electrons, respectively.

The measurements on silver chloride agree with Schneider and O'Bryan's curve[4] to the extent that the absorption generally rises with decreasing wavelength down to their limit of 1100 A. However, the sharp rise at 1200 A which they report is not observed in the present data.

VI. CONCLUSIONS

The experimental procedure yielded results which were largely reproducible and which showed a definite difference between the absorption of silver chloride and that of silver bromide. Some of the structure is of the type expected for excitation of the halide valence electrons, and some of the structure appears to be related to the excitation of the silver ion $4d$ electrons.

More information about the location of the conducting states relative to the silver ion levels can probably be obtained by absorption measurements in the region 100–170 A, since the silver atom $N_{\text{II,III}}$ edge is at about 158 A and the N_{I} edge, about 133 A.

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[16] F. Seitz, Revs. Modern Phys. **23**, 330 (1951).

[17] R. Hilsch and R. W. Pohl, Z. Physik **59**, 812 (1930).

[18] H. M. O'Bryan and H. W. B. Skinner, Proc. Roy. Soc. (London) **A176**, 229 (1940).