

Structure of the L Absorption of Sodium Metal and Its Halides*

H. M. O'BRYAN

Georgetown University, Washington, D. C.

(Received March 15, 1940)

The structure of the soft x-ray absorption of thin films of sodium metal, NaF, NaCl, NaBr, and NaI has been photographed in the region between 250A and 430A with a plane grating vacuum spectrograph having a resolving power of 0.1 electron volt. The structure is much narrower and more complicated than found in the K -absorption spectra for the same compounds. The sodium halides have narrow intense absorption "lines" beginning near 380A and extending toward shorter wave-lengths. These absorption "lines" of these crystals have widths at half-maximum intensity as small as 0.3 ev and almost the same wave-length as the emission of NaII in the vacuum spark. Sodium metal has a sharp edge at 405A and relatively faint structure at shorter wave-lengths. Continuous absorption in the halides starts near 45 ev corresponding to the ionization potential of the free ion at 47 ev and probably is due to transitions to the conduction states of the crystal lattice. These similarities between the energy levels of the sodium ion in these crystalline solids and in the free ions indicate a highly ionic character of the halides and surprisingly little broadening and displacement by neighboring ions in the crystals.

INTRODUCTION

ALTHOUGH the effect of chemical combination on the structure of the x-ray absorption edges has been studied by many, very slow progress has been made in unraveling the energy levels of even the simplest of salts. The advantages of soft x-ray spectra over ordinary x-ray spectra for this purpose have been summarized and illustrated by Skinner.¹ More recently Parratt² has examined the K absorption of a monatomic gas (argon) and finds a width at half-maximum intensity of 0.58 electron volt while in the soft x-ray region Skinner³ finds that the emission edge of a solid can be as narrow as 0.05 electron volt. These examples show directly an inherent limitation of x-ray absorption spectra of wave-lengths less than 5 angstroms as a source of information on the effect of chemical combination on the energy levels of atoms. Instrumental limitations can be more or less overcome through refinements in apparatus or by corrections but there is a more fundamental limitation which cannot be eliminated in the ordinary x-ray region.

This factor which determines the minimum

widths of structures in the region of hard x-rays and which is negligible in the soft x-ray region depends directly on the reciprocals of the lifetimes of the initial and final states involved in the transition. Unless the effects of the crystalline lattice, chemical combination, and temperature are as large or larger than that described above little progress can be made in the use of x-ray absorption structure for the study of these phenomena. At present it appears that only wave-lengths longer than 20 angstroms will reveal structures as narrow as 0.1 electron volt.

This paper presents the structure of the absorption by the $L_{2,3}(2p)$ electrons of sodium metal and its halides. This metal has its electrons almost completely free from the influence of the lattice and closely described by the simple Sommerfeld theory while the valence electrons of the sodium halides are tightly bound to their respective ions with almost no freedom to move about. The absorption of the valence electrons of the halide ions starting near 2000A and becoming less intense below 1100A has been studied previously.⁴ The outer electrons of the sodium ion of the halides have little effect on this absorption and it is not until below 400A that their absorption appears. While it is not possible to make certain what fraction of the

* Presented at the meeting of the American Physical Society, New York, New York, February 23-24, 1940.

¹ H. W. B. Skinner, "The soft x-ray spectroscopy of the solid state," Reports on Progress in Physics, Vol. 5, 1938 (The Physical Society London).

² L. G. Parratt, Phys. Rev. **56**, 295 (1939).

³ H. W. B. Skinner, Nature **142**, 432 (1938).

⁴ R. Hilsch and R. W. Pohl, Zeits. f. Physik **59**, 812 (1930); E. G. Schneider and H. M. O'Bryan, Phys. Rev. **51**, 293 (1937).

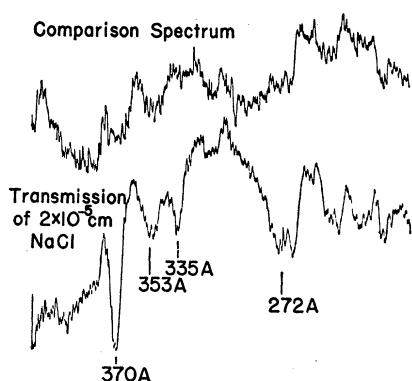


FIG. 1. Microphotometer curves showing the absorption of NaCl evaporated on a Formvar film.

width of their absorption structure is due to the various contributing factors, more is due to the final excited states than the initial states.

EXPERIMENTAL

The vacuum spectrograph was of the Thibaud type using a 600-line per mm plane grating with a plate to grating distance of 15 cm. The slit widths were determined according to the equations of Bisacre⁵ giving a resolving power of 0.1 electron volt at 300A. A hot spark between alloy electrodes produced a many-lined spectrum sufficiently continuous in appearance for detecting the important structure in the absorption in this spectral region. Ilford Q plates were used and exposure times varied from a few seconds to several minutes.

The very high absorption coefficients of nearly all substances in this spectral region require absorbing films which are less than 10^{-4} cm thick. This requirement and others concerning purity and perfection of the surfaces were satisfied by distilling the absorbing material onto "Formvar" films within the vacuum spectrograph and photographing their absorption spectra without exposing them to the atmosphere. The films of Formvar (a plastic of the Shawinigan Products Corporation) were prepared according to the instructions of Germer.⁶ These were about 200A thick and transmitted about 50 percent of wavelength 300A. At shorter wave-lengths this material becomes more transparent and has a maximum absorption near 900A. In order to

obtain good quality films of sodium metal and prevent re-evaporation within a few minutes it was necessary to cool the Formvar film to about -80°C . The sodium metal films suitable for obtaining absorption spectra near 400A were completely opaque to visible light. As judged from interference colors suitable films of the halides were about 1000A thick.

Alternate exposures were made through uncoated and coated films inserted in the path of the light beam about halfway between the first slit and the grating slit. No impairment of definition of the spectral lines resulted from insertion of the absorbing films at this position. Microphotometer curves of the spectrum transmitted by NaCl on a Formvar film and the comparison spectrum transmitted by a similar but uncoated Formvar film are shown in Fig. 1. From these and similar microphotometer curves with various exposure times on several thicknesses of NaCl films the absorption curve in Fig. 2 has been constructed. Due to the uncertainty in determining the thickness of the salt films the absolute magnitude of the absorption coefficients can only be estimated. For NaCl the maximum absorption coefficient in the center of a band is about 15×10^4 per cm and in the more transparent region near 300A about 3×10^4 per cm. No estimate of the absorption coefficient for sodium metal can be made at present. The structure of the NaF absorption was not as definite as that of the other halides due to the intense overlapping absorption of the six $2p$ and two $2s$ electrons of the fluorine ion.

DISCUSSION

The absorption curves in Fig. 2 show the types of absorption expected from two widely different classes of solid crystals; one a metal in which the valence electrons move about the crystal almost as freely as gas molecules and the other an extremely ionic compound in which the electrons are tightly bound to their respective ions and have no freedom to move about the crystal. The differences between energy states of the singly charged atomic ion as obtained from vacuum spark spectra⁷ are shown in Fig. 2 on the same energy scale as the absorption of the

⁵ F. F. P. Bisacre, *Phys. Soc. Proc.* **47**, 948 (1935).

⁶ L. H. Germer, *Phys. Rev.* **56**, 58 (1939).

⁷ R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, New York, 1932), p. 309.

same ions in the crystals. Only transitions involving the ground state $1s^2 2s^2 2p^6$ and the lower excited states $1s^2 2s^2 2p^5 3p$ and $1s^2 2s^2 2p^5 3s$ are shown. Examination of the absorption curves for the chloride, bromide, and iodide show probably the existence of about four separate bands whose widths at half-maximum intensity vary from 0.2 to 0.5 eV. Tentatively these can be identified with transitions from the ground state of the ion to the lower excited states although final assignment requires better separation of the bands which probably can be obtained at reduced temperatures. The differences in structure and relative separation of these lower excited states found in the chloride, bromide, and iodide can be associated with the allowed Brillouin energy bands whose position is a function of the lattice distance. Table I lists the energy values of these bands together with tentative identifications with atomic transitions. The basis of this identification is that the strongest absorption is due to the resonance line and the remaining three probably are the intercombination triplet. The ionization potential corresponds to removal of the electron from the sodium ion to the conduction band of the crystal.

In order to use the structure in Fig. 2 to draw conclusions regarding the various effects causing the absorption widths it is necessary to evaluate their contributions. The instrumental resolving power as determined by the definition of emission spark lines and sharpness of the Na metal contributes little to the observed structure. It also appears certain that the ground state is broadened much less by the interaction of neighboring atoms and lattice vibrations than the excited state in which the electron orbit is larger and consequently more influenced by its surroundings. Thus it appears that the widths of the observed structure are very closely the widths of the excited states of the ion in the

TABLE I. Tentative identification of *L* absorption of sodium, energies in electron volts.

ABS. TRANS.	IN FREE ION	NaF	NaCl	NaBr	NaI
1S to 1P	32.83	33.7	33.3	33.2	33.1
	32.66		34.5	34.2	33.8
1S to 3P	32.75	33.7	35.1	35.5	35.8
	33.14		36.8	36.5	
ionization	47		45	44	42

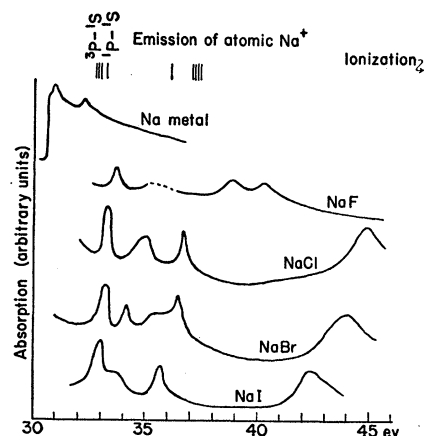


Fig. 2. Emission of the atomic sodium ion and the absorption of the same ion in the metal and halide crystal lattice.

lattice. It is apparent from the sharpness of the emission lines of the sodium ion in the vacuum spark and the absorption edge of the metal that the lifetime of the excited states are sufficiently long, probably more than 10^{-11} second, so as to make the uncertainty of the energy of the excited state due to this cause negligibly small compared with the widths of the absorption structure. Hence the widths of the observed structure must be due to collisions of the excited atoms with the lattice vibrations and interaction with neighboring ions and both of these effects produce widths not greater than 0.3 eV in some levels of the alkali halide crystals.

It can be expected that the contribution of temperature to the widths of this structure will be of the order of magnitude of that energy characteristic of room temperature or about several hundredths of an electron volt. This means that cooling of the absorbing film to liquid-air temperature may sharpen appreciably the absorption structure and such experiments with the instrumental resolving power increased to 0.06 eV are planned for the near future. Very fruitful results can be expected in this region as preliminary studies show considerable structure in selenium, and its compounds as well as in both the ferrous and ferric chlorides. At reduced temperatures it will be possible to study the energy levels in the solid state of many of the simplest chemical compounds which are gaseous at room temperature.