Attempts to Observe an Electron Affinity Spectrum

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The failure of previous attempts to observe an electron affinity spectrum (emitted by the combination of neutral, electronegative atoms and electrons) is explained by inadequate experimental methods. On the basis of recent results regarding combination spectra of positive ions and electrons, new attempts have been made to observe the electron affinity spectrum of atomic iodine by using three methods (hollow cathode, positive column with addition of a rare gas, glowing filament). No new spectrum was observed. This failure is discussed theoretically. It seems that the capture of electrons by halogen atoms is an improbable process as compared with the combination of positive ions and electrons.

I. PROBLEM AND PREVIOUS WORK

THE *electron affinity* of the halogen atoms, i.e., their ability to form negative ions, is known from various observations: the existence of polar molecules and crystals, the low mobility of the negative particles in their vapors, the negative values of e/m in the "positive ray." The *value* of the electron affinity (i.e., the energy difference between the atom and electron separated and the negative ion) has first been derived by Born[1] from the grating energy of the alkali halogen crystals. Another determination of the electron affinity of the iodine atom, based on the thermal equilibrium at high temperature of CsI vapor, has been made by J. E. Mayer.[2] The iodine atom has an electron affinity of 74.2 ± 1.5 k cal.

These results establish the *existence* of the negative ions and its *energy of formation*. They do not give evidence, however, by what process this ion is formed. Franck[3] suggested that a neutral gas atom as well as a positive ion, capturing a free electron, might radiate the energy of formation plus the kinetic energy the electron had before this process. The corresponding spectrum, therefore, would consist of a continuous band starting from the frequency given by the energy of electron affinity, spreading to short waves. The intensity distribution within this continuous band would depend upon the kinetic energy distribution of the electrons (modified by some probability factor for the capture also depending on the kinetic energy). The observation of this spectrum would be important in that it would give evidence of the elementary process, and in addition yield by its long wave-length limit a straightforward determination of the energy of electron affinity.

All previous attempts to observe electron affinity spectra of gaseous atoms or molecules have failed. Two continuous bands observed in the *positive column of the electric discharge* through iodine vapor have been ascribed to the process under discussion. Both of them turned out later to belong to the band spectrum of the iodine molecule.[4] These failures in observing the electron affinity spectrum in the positive column can be understood on the basis of more recent information. In this source of light even the combination of *positive ions* and electrons—in spite of the Coulomb force acting—does not play an important part, the reason being that only *very slow electrons* have an appreciable chance to be caught by ions.[5] By analogy we conclude that in the positive column most electrons are too fast to be captured by *neutral iodine atoms*.

Von Angerer and Mueller[6] investigated *absorp-*

[1] M. Born, *Problems of Atomic Dynamics*, Cambridge, 1926, p. 170.

[2] J. E. Mayer, Zeits. f. Physik **61**, 798 (1930); J. E. Mayer and Lindsay Helmholz, Zeits. f. Physik **75**, 29 (1932).

[3] J. Franck, Zeits. f. Physik **5**, 428 (1921); cf. K. Fajans, Verh. d. D. Phys. Ges. **21**, 714 (1919).

[4] W. Steubing, Ann. d. Physik **64**, 673 (1921); J. Franck, Zeits. f. Physik **5**, 428 (1921); W. Gerlach and F. Gromann, Zeits. f. Physik **18**, 239 (1923); O. Oldenberg, Zeits. f. Physik **25**, 136 (1924).

[5] R. Seeliger, Phys. Zeits. **30**, 346 (1929).

[6] E. von Angerer and A. Müller, Phys. Zeits. **26**, 643 (1925) and L. A. Müller, Ann. d. Physik **82**, 64 (1927).

tion spectra of alkali halogen compounds. In their vapors at high temperature a considerable concentration of negative halogen ions is to be expected. The neutralization of these negative ions ($I^- \rightarrow I + \epsilon$) requires the energy of electron affinity. The question is: does the neutralization take place by the action of light? Continuous bands were observed, which the authors interpreted later, however, as belonging to the neutral alkali halogen molecules. Their failure to observe electron affinity spectra might be due to the masking of a faint absorption by another stronger one.

Franck and Scheibe[7] have interpreted continuous absorption bands observed in the solutions of the alkali halogen compounds in water as electron affinity spectra of the negative halogen ion losing the excess electron under the influence of light. This hypothesis has recently been modified, however, by Franck and Haber.[8] They assume that the electron is not *liberated* but that it *jumps* from the halogen ion to a water molecule which in the same process splits up into H and OH^-. The spreading of the continuous spectrum, therefore, is not related to the velocity distribution of the electrons liberated but is the same phenomenon as the broadening of all spectral lines in liquids. This result does not solve the original, simple problem: the electron affinity spectrum of the undisturbed atom. This can be solved only by observing the gaseous state.[9]

So we come to the conclusion that as yet the problem has been attacked under conditions that from our present standpoint seem to be unfavorable. Therefore, the failure to observe the spectrum under discussion is not necessarily to be interpreted as due to the *nonexistence* of this spectrum. It will be worth while to search for it under more favorable conditions.

II. Experiments

(a) Hollow cathode method

Recent successes in producing combination spectra of *positive ions* and electrons[10] suggest various methods for producing the electron affinity spectrum of *neutral halogen atoms*. In the inside of a hollow cathode of a discharge tube containing helium Paschen[11] discovered marked continuous spectra connected with well developed line series of the helium atom. As only slow electrons are able to recombine with ions it must be concluded that the concentration of slow electrons in the hollow cathode is considerable. This is largely due to the fact that no rapid acceleration exists, because, from symmetry, the electric field will be small along the axis of the hollow cathode. The corresponding experiment carried through with iodine vapor completely dissociated by heat should give a chance to observe the electron affinity spectrum—slow electrons being present due to the properties of the hollow cathode, and iodine atoms due to the thermal dissociation of the vapor.

The iodine atom is particularly suited for this experiment, because iodine is the only halogen vapor that can be dissociated to nearly 100 percent at easily accessible temperatures.[12] Any new spectrum, therefore, that might come out under special conditions will be likely to belong to the iodine *atom*. The only remainder of the *molecular* spectrum that is known to appear in spite of complete dissociation is the band with the long

[7] J. Franck and G. Scheibe, Zeits. f. physik. Chemie (A) Haberband **22** (1928); G. Scheibe, Ber. d. Dtsch. Chem. Ges. **59**, 1321 (1926).

[8] J. Franck and F. Haber, Ber. d. preuss. Ak. d. Wiss; Phys. math. Klasse **XIII**, 8 (1931).

[9] In this argument it has been assumed that the electron affinity spectrum consists only of the continuous band without showing sharp lines, in other words that the negative ion has no definite excited states. As the electron affinity is understood on the basis of the great stability of a completed group of electrons, there seems to be no reason to assume a *stable* negative ion with the excess electron in an *excited* state. It might be as stable as the negative ion of any other atom having no pronounced electron affinity. No corresponding atomic spectrum (line spectrum of a negative ion) has been observed. Bartlett (Nature **125**, 459 (1930)) estimates that the Cl^- ion has no stable excited states at all below its neutralized state. Since he applies an extrapolation method, it might be safer to conclude that excited states, if there are any, should be very near the ionized state and therefore almost unstable. This result does not agree with Mecke's tentative interpretation of certain intense band spectra of BeH and MgH as due to negative molecular ions (Zeits. f. Physik **72**, 155 (1931)).

[10] A survey has been given by R. Seeliger, Phys. Zeits. **30**, 329 (1929).

[11] F. Paschen, Sitzungsber. d. Preuss. Akad. d. Wiss., p. 207 (1927); cf. R. A. Sawyer, Phys. Rev. **36**, 44 (1930).

[12] G. E. Gibson and W. Heitler, Zeits. f. Physik **49**, 465 (1928); cf. W. G. Brown, Phys. Rev. **38**, 708 (1931).

wave-length limit 3460A. This is well outside the region between 3740 and 3910A in which, according to Mayers determination, we must search for the spectrum under discussion. It happens that this spectral range is appreciably free from intense bands even for a large concentration of molecules.

The discharge tube was made of quartz with tungsten electrodes.[13] Care has been taken that the inside of the hollow cathode was observed not against the glowing wall of the oven as a background but, instead, against a quartz window. As it is known to be difficult to keep the iodine pure in the electric discharge, a continuous flow of iodine vapor was supplied. Iodine vapor reservoirs with different pressures were attached one on each side of the discharge tube. The resulting flow of vapor washed all impurities away from the region of the electrodes and discharge. From time to time the whole system was evacuated after freezing the iodine.

The *results* have been negative. Under no conditions (pressure varied up to 8 mm, current up to 90 m.a.) has a new continuous spectrum been observed. The plates showed mainly the line spectrum of the iodine atoms with faint traces of tungsten lines. In addition the I_2 band 3460 came out with high intensity. It will be discussed in another note. Several plates showed traces of the known diffuse bands of the I_2 molecule.

An argument against the hollow cathode method is that it might fail under the present conditions, because most of the free electrons might be captured by the atomic iodine immediately after leaving the cathode so that no free electrons would be present near the axis. In order to test this possibility, all parts of the hollow cathode discharge, particularly those parts in the neighborhood of the metal, have been carefully investigated by the spectrograph without any positive result. Only intensity differences within the line spectrum appeared.[14]

The presence of free electrons was checked by another method. Their disappearance by immediate capture would produce a fundamental change in the discharge, as compared, for example, with the discharge through hydrogen or nitrogen. The conductivity is largely due to ionization by impacts of *free electrons*. This process cannot be simply replaced by impacts of *ions* only, particularly at high pressure. The reason for this is that only the light electrons keep their kinetic energy in the numerous *elastic* impacts not leading to excitation and ionization and thus can gradually gain energy from the electric field. The heavy ions, on the other hand, give up some kinetic energy in every elastic impact. In order to store up in a heavy ion the kinetic energy required for ionization in spite of collisions, enormous fields are necessary particularly at high pressure. Moreover for ionizing an atom by impact, the heavy ion must have a much larger kinetic energy than the electron which requires just the limiting value of the ionization energy.[15] Hence the potential difference between the electrodes in a discharge tube from which all free electrons are taken away will be very large compared with the potential difference, e.g., in the hydrogen or nitrogen discharge. The comparison of potential differences, therefore, for atomic iodine and hydrogen or nitrogen will give evidence whether or not an appreciable number of free electrons still exist in the iodine discharge. In the same discharge tube for the same pressure (5 mm) and temperature (1000°C), the current-potential-curve for iodine yielded even smaller values of potential difference than in hydrogen. We must conclude that there was some concentration of free electrons left. It is true that this observation was concerned not only with the potential drop in the positive column itself but that in the measurement the cathode drop was included. Actually in the positive column the potential drop in iodine (although mainly molecular) has been found[16] to be somewhat higher than in nitrogen but of the same order (75 instead of 43 volts/cm). Hence it seems certain that in the discharge through atomic iodine the concentration of free electrons might be reduced by the formation of negative ions, but it cannot be very small as compared with the better known discharges through hydrogen or

[13] For technical detail of the electric discharge in iodine cf. H. F. Fruth (Phys. Rev. **31**, 614 (1928). Special stopcock grease has been used as advised by M. Bodenstein.

[14] E. Müller (Ann. d. Physik **14**, 851 (1932)) proved that glowing platinum in iodine vapor emits electrons, not negative ions.

[15] J. Franck, Zeits. f. Physik **25**, 312 (1924); G. Joos and H. Kulenkampf, Phys. Zeits. **25**, 258 (1924).

[16] Matthies, Ann. d. Physik **18**, 493 (1905).

nitrogen.[17] The failure to observe the electron affinity spectrum cannot be due to the complete absence of free electrons.

(b) Positive column in a mixture with helium

It still might seem questionable whether the negative results of the experiments just discussed is due to the nonexistence of the electron affinity spectrum or to unknown properties of the hollow cathode discharge in the halogens. It is desirable, therefore, to search for the same spectrum under other widely different conditions that are also known to be favorable for recombination spectra of ions and electrons. Intense spectra of this kind have been discovered recently by Krefft[18] in the positive column of the electric discharge through metallic vapors with the addition of rare gases. For a group of metals Krefft was able to compare the probability with which they emit the recombination spectra. Under most conditions the radiation emitted from the positive column of the ordinary discharge is known to be due to previous *excitation* by electron impact but not to *recombination* of ions and electrons,[19] the reason being that the concentration of *slow* electrons, which alone have a good chance to recombine, is too small. Under the conditions of Krefft's experiment, however, it is not easy to understand the large concentration of *slow* electrons indicated by the intense combination spectra of ions and electrons (continuous bands connected with series limits). It seems possible that with He added the conditions are particularly favorable for the slowing down of electrons, because, as Sommermeyer[20] found out, the energy input in the electric discharge through He is largely used up for the numerous purely elastic collisions between the electrons and He atoms.[21] In the present experiments, therefore, He of 7 mm pressure has been added to atomic iodine (iodine vapor heated to 1050°C). The positive column was projected "end on" on the slit of the spectrograph. The pressure of the iodine was varied between 0.2 and 1.1 mm. Not a trace of a new continuous spectrum was observed although the exposure was long enough to bring out some traces of the bands of molecular iodine. This negative result points again to a low intrinsic probability of the combination of the neutral iodine atoms with free electrons taking place with radiation.

(c) Glowing filament method

In order further to test the negative result of the experiments discussed it seemed desirable to try still another experiment. A straightforward method for producing electrons with very low velocity at a considerable concentration has been very successfully applied by Mohler.[22] He observed recombination spectra in the close neighborhood of a glowing filament, where the velocity distribution of the electrons is mainly determined by the temperature of the metal from which they have just been evaporated without being accelerated as yet by the electric field. In a quartz tube with iodine vapor heated to 1000°C a glowing tungsten filament was used; tungsten interferes least with the atomic iodine and, therefore, gives the purest conditions.

Again no new continuous spectrum came out. This observation, however, does not give as good evidence as the hollow cathode method because the exposure could not be extended to a considerable length of time because of the superimposed spectrum of the glowing filament. It is not possible to screen it off so completely that in a very

[17] This conclusion is supported by the small probability of the formation of negative ions in (molecular) iodine derived from electrical measurements by W. Hey and A. Leipunski (Zeits. f. Physik **66**, 669 (1930)); cf. F. L. Mohler, Phys. Rev. **26**, 614 (1925) and L. B. Loeb, J. Frank. Inst. **197**, 45 (1924).

[18] H. Krefft, Phys. Zeits. **32**, 948 (1931); Zeits. f. Physik **77**, 752 (1932).

[19] Cf. J. Franck and P. Jordan, *Anregung von Quantenspruengen durch Stoesse*, Berlin, 98 (1926).

[20] Sommermeyer, Ann. d. Physik **13**, 315 (1932); cf. H. Kessel, Zeits. f. Physik **70**, 614 (1931).

[21] Results of Mohler (Bull. Am. Phys. Soc. **7**, No. 7, p. 8 (1932)) just published suggest another reason for the slowing down of electrons in the positive column. Mohler observed combination spectra of positive ions and electrons in the positive column of a discharge through pure caesium at a considerable pressure. It might be that the exceptionally low value of the excitation potential of caesium (1.38 volts) together with the large probability of the lowest quantum transition in the alkali atoms is responsible for a large concentration of slow electrons. Also from this point of view it seems worth while to investigate the positive column in atomic iodine at various pressures because the iodine atom has an excitation potential as low as 0.94 volts (L. A. Turner, Phys. Rev. **27**, 406 (1926)) although with a much smaller probability of transition.

[22] F. L. Mohler, Phys. Rev. Sup. **1**, 221 (1929).

long exposure it gives no continuous background even in the near ultraviolet.

From the three groups of experiments discussed it will be concluded that the neutral iodine atom has a smaller chance than a positive ion to capture a free electron and radiate the energy liberated although the energy value of this process is about the same as the ionization energy of caesium whose ions show an intense recombination spectrum. It must be admitted, however, that this negative result cannot be proved by experiments with the same certainty as a positive observation. The mechanism of the discharge is not known so completely that we can with full certainty predict the most favorable condition for a certain elementary process. In particular it might be that still slower electrons than those appearing in the discharges just discussed show a larger tendency of combining with neutral halogen atoms.[23]

III. Theoretical Discussion

In order to explain the failure in all attempts to observe the electron affinity spectrum two reasons will be discussed, one dealing with the velocity of the electrons in the discharge, the other with the process of combination itself.

A great difference between the two cases of combination—positive ions and neutral halogen atoms capturing electrons—will be due to the long range over which the Coulomb force of the *ion* affects free electrons, whereas the *halogen*, being a neutral atom, is surrounded by a field which, although unknown in detail, certainly becomes negligible within a very small distance. Therefore classically the electron to be captured must approach the halogen atom much more closely than the positive ion with the result that the group of electrons which can be captured by the halogen atoms will be comparatively small.

This comparison, however, between combination processes, the energy of which is radiated, must take into account the selection rules. According to these rules the angular momentum of the electron can change in the radiation process only by the quantized amount $h/2\pi$. Let us consider electrons with the average value of the kinetic energy. The capture of an electron by a *positive ion* will frequently happen over a comparatively large distance because of the long range of the Coulomb field. In this case the electron will have a large angular momentum with regard to the ion. After emitting the quantum $h/2\pi$ it will still retain an appreciable value and, therefore, go to a quantum orbit of the neutralized atom with large azimuthal quantum number. A frequency will be emitted belonging to a high *subordinate* series. The continuum connected with a *principal* series, however, will be emitted by the smaller group of electrons passing the ion with smaller angular momentum, i.e., at a smaller distance. This smaller number of processes will give rise to a fainter spectrum. This argument holds only if we deal with electronic temperatures such that the electrons have angular momenta of the order of magnitude $h/2\pi$ when passing the ions at distances of the order of magnitude of atomic dimensions. Actually for an electron temperature of 5000°C, an electron which has the most probable velocity and an angular momentum with respect to the ion of $h/2\pi$, will pass the ion at a distance of 2×10^{-8} cm; this is well within the range of atomic dimensions. On this basis we understand the fact, reported by Krefft, that in the combination spectra of *positive ions* and electrons the continuum connected with the principal series is much less intense than the one connected with the first subordinate series.

In the electron affinity spectrum of the halogen atoms, as discussed in Section I, we expect to observe only the continuum representing the *principal* series. It is not surprising that because of the more constricted field of force of the halogen atoms, the probability of this process comes out still smaller than for the positive ions, although the energy with which the halogen keeps the electron is of the same order.

This interpretation, based on the velocity distribution of electrons in the discharge, does not preclude the inverse process, the separation of the excess electrons from the negative ions by absorption of light, provided the ions are produced in sufficient concentration. For the initial state of this process, the negative ion, is independent of

[23] Recombination spectra of positive iodine ions and free electrons were not observed either. This is not surprising as Krefft, too, failed to observe this type of spectrum for certain groups of elements.

the velocity distribution of electrons. Therefore, it does not contradict the theory that in *absorption* in solutions the electron affinity spectrum has actually been observed by Scheibe, although modified by the water to such an extent that no conclusion can be drawn regarding the same absorption process (its wave-length and its probability) in the vapor. The concentration brings in another difference between vapors and solutions in water. For example, in a 1/100 normal solution of KI the I^- ions have a partial pressure of 1/4 atmosphere; that is a very large pressure as compared with the value in electric discharges.

The theoretical result discussed, regarding the halogen atom in the gaseous state, might be modified in one respect by a recent result derived from wave mechanics by Jen.[24] As yet it has been assumed from analogy with the behavior of *positive ions* that the electron affinity spectrum of certain *neutral atoms* it if exists at all will have a large intensity near its long wave-length limit. A different result, however, has been derived by Jen. In any case (positive ion or neutral atom) the effective cross section for the capture of electrons approaches infinity as a limit with decreasing kinetic energy of the electrons; the *concentration* of slow electrons, however, approaches zero as a limit. The *intensity observed* (product of probability factor and concentration factor) comes out with a finite limiting value. For the electron affinity spectrum of hydrogen—contrary to the spectrum of combination of positive ions—the theoretical *intensity* curve shows a pronounced maximum at a considerable distance from the limit. Hence it might be difficult to observe the theoretical long wave-length limit (defined by the energy of electron affinity) and to identify the spectrum, even if the maximum were intense enough to be photographed.

Jen's theory certainly does not lead to the result that the capture of an electron by a neutral atom resulting in radiation is a "forbidden" process. It seems hardly possible, however, to estimate from wave mechanics the actual intensity of the electron affinity spectrum of *hydrogen;* and we certainly must not correlate Jen's theoretical results quantitatively with observations in the *halogen* vapors.

The main result is that the chance for observing electron affinity spectra in certain parts of the electric discharge seems to be a great deal smaller than the chance for observing combination spectra of positive ions and electrons.[25]

[24] C. K. Jen, Phys. Rev. **42**, 588 (1932). Cf. the following paper. His results are partly supported by the probability for the formation of negative ions as derived from electrical measurements by W. Hey and A. Leipunski (Zeits. f. Physik **66**, 669 (1930)). Their results, however, do not apply directly because their experiments were performed with molecular iodine vapor.

[25] It is interesting to compare the negative result of the present spectroscopic investigation with the results of Hogness and Harkness (T. R. Hogness and R. W. Harkness, Phys. Rev. **32**, 784 (1928)), who investigated the ionization processes of iodine by the mass-spectrograph. Working with molecular iodine they had no chance to investigate the atomic process under discussion ($I+\epsilon \rightarrow I^-$). They found out, however, that negative atomic ions I^- are formed by neutral molecules capturing electrons and breaking up at the same time into a neutral atom and a negative ion ($I_2+\epsilon \rightarrow I+I^-$). Not even I_2^- ions are formed simply by neutral molecules I_2 capturing free electrons but by a more complicated process.