# THE LINE SPECTRA OF THE ISOTOPES OF MERCURY AND CHLORINE

By Francis A. Jenkins[1]

Abstract

**Comparison, for Hg and Cl, of wave-lengths and relative intensities in line spectra from samples of varying isotopic composition.**—Two sample-pairs of mercury with atomic weight differences of 0.124 and 0.180 and one sample pair of chlorine with a difference of 0.097 were examined spectroscopically. An echelon (resolving power about 400,000) and a plane grating (resolving power 478,000 in the fifth order) were used. The spectra of the mercuries with the smaller atomic weight separation showed for the lines λλ5461, 4359, 4078 and 4047 no wave-length differences greater than the error of measurement ($3\times10^{-4}$A). The first two of these lines, obtained, with the use of a special source from the mercuries of the greater atomic weight separation, were studied to see if differences in the relative intensities of the satellites could be brought out. None was found. The results, therefore, do not favor the isotopic origin of the satellites. The spectra of the two chlorine samples, when examined with the echelon showed distinct evidence of differences in wave-length. The heavier chlorine almost invariably gave the smaller wave-length. The displacements were of the order of 0.001A, and only two or three times the error of their determination. A convenient source of the chlorine spectrum is described.

THE only direct experimental evidence of a difference in the electronic spectra of isotopes is that first brought forward by Aronberg,[2] who found the line λ4058 in the arc spectrum of ordinary lead to have a wave-length 0.0043A shorter than the same line in the spectrum of lead extracted from a uranium ore. This result has since been confirmed and extended to other lead lines in later independent investigations.[3] It is important that the effect observed by Aronberg was a distinct shift of the line, and not a mere broadening on one side, which we should expect if ordinary lead were a mixture of isotopes of mass 206 and 208. The latter effect was noted, however, by Grebe and Konen[4] in their comparison of the lines of the lead band spectrum. Even if we assume ordinary lead to be a third isotope, it is difficult to explain Aronberg's result, since his uranium lead was not free from ordinary lead. Although the shift which we observe in a line when the relative proportions of the isotopes are altered is most reasonably ascribed to a re-distribution of

[1] National Research Fellow.

[2] Aronberg, Astrophys. J. **47,** 96 (1918).

[3] Comprehensive reviews of the subject of isotope spectra have been given by Aston, "Isotopes," 2nd ed., Ch. X (1924) and by Joos, Phys. Zeits. **26,** 357 (1925).

[4] Grebe and Konen, Phys. Zeits. **22,** 546 (1921).

intensities in a close multiplet whose components arise in the several isotopes, it has not been experimentally proven to be due to this effect.

The results of other investigations of the spectra of the lead isotopes agree as to the direction of the shifts (the lines from the heavier lead always had the smaller wave-length), and fairly well as to their magnitude. Discrepancies in the latter were attributed to the different purity of the samples of radioactive lead, and correspond roughly with the atomic weight data. Merton[5] compared the wave-lengths of several of the brighter arc lines, and found that the shifts varied, sometimes by as much as 50 percent, for different lines. Recent work by Mlle. Pierette,[6] however, has failed to confirm this: the displacements were found to be constant over the range of wave-lengths studied.

The circumstance that we have been unable completely to separate the isotopes of other non-radioactive elements in appreciable quantities has left the theoretical interpretation of these results in a rather unsatisfactory state. The simple Bohr equation[3] for the change of the Rydberg constant with the nuclear mass, although strictly accurate only for an atom having one planetary electron, was thought to give an upper limit for the actual shift for complex atoms. However, as Bohr has pointed out,[7] the equation is probably not at all valid for lines involving *S*-states, since the electron in these orbits penetrates the shells of other electrons and passes very near the nucleus. The energy of the orbit would be largely determined during this close approach, and a difference in the distribution of the nuclear field of force in the isotopes might thus account for the unexpected magnitude of the shift observed for some lead lines.

In order to obtain further information on these uncertain points, the writer has made a comparison of the spectra of samples of mercury of different atomic weight, which were made available for this investigation through the kindness of Professor W. D. Harkins. A similar comparison has also been made for chlorine, which was likewise obtained from him.[8] The atomic weight difference for both elements was brought about by long-continued fractional diffusions, and in both cases represents an appreciable change in the proportions of the isotopes.

[5] Merton, Proc. Roy. Soc. **100A,** 84 (1921).

[6] Pierette, Comptes rendus **180,** 1589 (1925).

[7] Bohr, Nature **109,** 745 (1922).

[8] This separation of the mercury isotopes was obtained by using the extremely rapid and efficient method devised by Mulliken (Jour. Am. Chem. Soc. **45,** 1592 (1923)). The results have not yet been published. The chlorine samples were produced by independent work on the heavy fraction from the diffusion of HCl (Harkins and Hayes, Jour. Am. Chem. Soc. **43,** 1803 (1921)), and on the light fraction (Harkins and Jenkins, Jour. Am. Chem. Soc. **48,** 58 (1926)).

The mercury spectrum in particular has interested those searching for spectroscopic evidence of isotopes, since the numerous satellites of its lines were thought to be related to its complex composition.[9] While it is now generally conceded that the satellites have no direct connection with the isotopes,[10] the results of Nagaoka, Sugiura, and Mishima,[9] which they held to demonstrate such a relation, can be tested by investigating the "partially separated" isotopes, as Nagaoka suggested later.[11] Although the separation for mercury is small in terms of the atomic weight change, we might expect a considerable difference in the relative proportions of the lighest and heaviest isotopes in the two fractions because of the large atomic weight interval. Assuming the more accurate isotopic constitution recently reported by Aston,[12] the exact changes in the proportions of all isotopes, corresponding to a given atomic weight change, may be calculated. This has been done for the two best samples, which differed by 0.18 atomic weight units, using the equations of Mulliken and Harkins.[13] The results show that, while the proportions of most of the isotopes are nearly the same in each, the fraction of isotope 198 in the heavier mercury is 20 percent smaller than in the lighter mercury, and the fraction of isotope 204 is 27 percent greater. A comparison of the intensities of the satellites of a given line from the two samples thus affords an experimental test of the theories mentioned above.

The separation for chlorine, expressed as an atomic weight difference, was less than that for mercury. However, because of its smaller atomic weight, the *relative* difference for chlorine is three times that for mercury. We may suppose that, although the components of the hypothetical isotopic chlorine doublets should show smaller changes in relative intensity than should be found in the isotopic components for mercury, their frequency difference should be much greater than the differences for mercury. Since, in the absence of a quantitative theory for this effect, it is impossible to say what difference should exist between the spectra of these isotopic samples, and how it will manifest itself at the dispersion

[9] See, for example, Nagaoka, Sugiura, and Mishima, Nature **113,** 459 (1924); Jap J. Phys. **2,** 121, 167 (1923) and McLennan, Ainslie and Cale, Proc. Roy. Soc. **102A,** 33 (1922). These theories have lost some force since Aston's recent discovery (Ref. 12), of the absence of an isotope of mass 197, and neither is supported by the intensity relations among the satellites. The work of Metcalfe and Venkatesachar (Nature **115,** 15 (1925); Proc. Roy. Soc. **105A,** 520 (1924)), on the long-column radiation and absorption of the mercury lines seems to favor the isotopic origin of some of the satellites.

[10] Runge, Nature **113,** 781 (1924); Joos, Ref. 3.

[11] Nagaoka, Nature **114,** 245 (1924).

[12] Aston, Nature **116,** 208 (1925).

[13] Mulliken and Harkins, Jour. Am. Chem. Soc. **44,** 37 (1922).

used, the comparison of wave-lengths and intensities has been made as accurate and complete as possible for both mercury and chlorine.

### Comparison of the Mercury Lines

The spectra of two small mercury arcs containing the isotopic mercury were compared using a 30-plate Michelson echelon, and later an 8-inch plane grating in the fifth order. Owing to its greater dispersion, the echelon gave more accurate wave-length comparisons, although its resolving power was slightly less than that of the grating. The optical system for the echelon photographs consisted of a collimator, the echelon, a large glass prism, and a lens of 4 m focal length to form the image. The slit was horizontal, and was fitted with a slide which could expose either of two adjacent portions 1 mm long. The collimator passed a beam of parallel light directly into the echelon, which was placed so that its steps ascended toward the collimating lens. After leaving the echelon, the light passed through the prism, which was in the usual position and hence crossed with the echelon—a very convenient arrangement for isolating the individual lines of a spectrum when they are not too numerous. The lens and plate-holder were mounted at either end of a light-tight metal pipe.

It is well known that the relative intensities of the satellites of the mercury lines vary somewhat with the conditions in the source. In order to minimize this effect, the two mercury arcs were made with identical dimensions, operated with the same current, and connected with the same vacuum line. They were placed close together in a rectangular jar of running water, and one could be lowered slightly so that a comparison photograph could be made without moving the condensing lens. A heavy metal box surrounded the echelon, and the apparatus was mounted on solid piers in a constant-temperature room. These precautions were necessary to avoid false shifts of the adjacent spectra. The time of exposure was short (3 to 5 minutes for the brightest lines), with these mercury arcs. The arc is established between two small pools of mercury and passes through a short horizontal length of tubing 3 mm in diameter. The light from the constriction is very intense, while the definition of the lines is still very good owing to the efficient cooling.

Other mercury sources giving very sharp lines were used later, and are worthy of mention. For the grating photographs, a water-cooled arc lamp constructed from the figure shown by Wood[14] proved very satisfactory, though its lack of intensity necessitated long exposures. In examining the mercury with the largest atomic weight difference, it

[14] Wood, Phil. Mag. **50**, Fig. 1, 765 (1925).

was found convenient to excite the spectrum in a Geissler tube discharge through helium at 1 cm pressure, with a droplet of mercury in the tube. The lines from this source, when it was operated with a small current from a transformer, were bright and extremely sharp, and the method had the advantage of requiring only a trace of the valuable mercury. The spectra of Fig. 1 (*B*) were taken in this way.

Fig. 1 (*A*) shows one of the comparison plates for the green mercury line. Several plates of this kind were taken for each of the lines λλ5461, 4359, 4078 and 4047, all of which involve *S*-terms in the series notations. The most accurate wave-length comparisons were obtained with these plates. Relative measurements were made for all of the satellites, as well as the central components. With a Gaertner comparator graduated

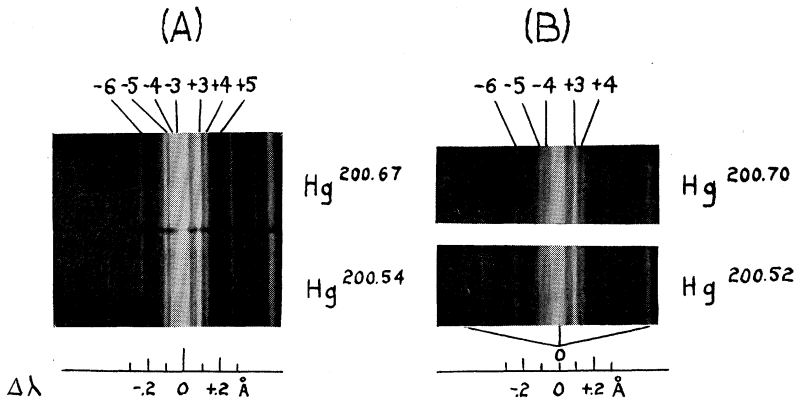


Fig. 1. Comparison of green mercury line from isotopic sources. (A) From vacuum arcs. This illustrates the method of wave-length comparisons. The slight haziness in the upper pattern was due to a droplet of mercury which condensed in the constriction of the arc. (B) From Geissler tubes containing helium and mercury. Note the identical intensity distribution among the satellites.

These photographs were taken with the echelon. The central band may be seen in 2 and 3 orders, respectively, in (A) and (B). The three in (B) are marked below. The atomic weight of the mercury giving the line is indicated at the right in each case. The satellites are numbered outward from the central band, which consists of five unresolved lines. Lines not marked are ghosts, which always appeared on the high-frequency side of the brighter lines. The wave-length separations are indicated by the scales drawn below.

in .001 mm, settings were made alternately on the same line in the two spectra, and the difference in the two readings could be reproduced to within a few ten-thousandths of an angstrom. All the shifts measured were $3\times10^{-4}$A or less, and were about equal to the probable error of measurement in each case. As typical of these results, the values obtained for the brighter components of λ5461 may be quoted: −6, 0.0000A

$\pm 0.0001$; $-5$, $-0.0003 \pm 0.0002$; $-4$, $-0.0002 \pm 0.0002$; central component, $-0.0001 \pm 0.0003$; $+3$, $+0.0001 \pm 0.0002$; $+4$, $0.0000 \pm 0.0002$. A positive sign indicates that the line from the heavier mercury gave the smaller wave-length. A survey of all the data indicates a random distribution in regard to both sign and magnitude, and it is evident that all the wave-lengths resolved are very exactly equal in these isotopic samples of mercury (atomic weight difference 0.124 units). If the shift for mercury were similar to that for lead, and proportional to the atomic weight difference, we should expect the shifts to be $+0.0007$.

The relative intensities of the satellites were always visually the same in the two patterns. Some preliminary photometric measurements were made, but failed to show any consistent variation. The two spectra were so nearly alike that in some cases, where the patterns were particularly well matched, it was very difficult to distinguish the dividing line. Further confirmation of the identical intensity distribution was obtained from the spectra of the mercury with the larger separation (atomic weight difference 0.180 units), using the helium-mercury sources mentioned above (see Fig. 1 (*B*)). Plates were taken for the lines λλ5461 and 4359. For these, a small comparison prism was employed, so that they were not as suitable for the determination of wave-length differences. The spectra were adjacent, however, and the relative intensities of the satellites could be accurately compared. No difference could be detected for either line, whereas, if the satellites of a line were given out by the isotopes, those corresponding to 198 and 204 should show intensity differences of 1/5 and 1/4, as has been explained. It is possible, as McLennan has suggested for λ5461, that the real isotopic satellites lie within the central group ($-3$ to $+3$), which was not resolved with these instruments.[15] The entirely negative results obtained here would be expected if this were the case. They are, however, certainly contrary to any hypothesis attributing the *outer* satellites to the isotopes.

## Comparison of the Chlorine Lines

For studying the chlorine lines, a special discharge tube was used, provided with a trough-shaped platinum cathode. Silver chloride prepared from the isotopic chlorine was fused on the surface of the cathode. The tube was then highly evacuated and filled with purified hydrogen to a pressure of 1 mm. This was necessary to maintain the constant radiation of the chlorine spectrum required for long exposures. When it was excited by a large induction coil, the chlorine lines appeared in the bright green glow above the cathode, which was viewed end-on.

[15] But see Ref. 9.

The only hydrogen line in the region investigated, H$\beta$, was easily distinguished by its diffuseness in the high-dispersion spectra. It is interesting to note that the chlorine lines from this source have an intensity distribution remarkably different from that given by a tube containing chlorine gas.[16]

Here again the echelon proved best adapted to an accurate comparison of wave-lengths. The exposures were of from 5 to 7 hours duration, so that the spectra were necessarily photographed simultaneously. This was accomplished with a small total-reflection prism placed as near as possible to the slit. The latter was set vertical, and the echelon placed so that its dispersion was horizontal and in the same direction as that of the prism which followed. The image was formed by a lens of much shorter focus (1 m), which increased the intensity and possessed the added advantage that the whole visible spectrum could be photographed on the same plate. The sources were operated in series from the same induction coil, and plates were taken where they were interchanged, to bring out any artificial shifts.

In the first few trials a difficulty was experienced in accurately comparing the positions of a line in the two spectra, since, with the small image, the lines had a marked curvature. This was met by superimposing a comparison spectrum of mercury, so that measurements could be made from a point in a sharp mercury line to the corresponding point in a chlorine line. The mercury lines were exposed by placing a mercury lamp for a few seconds in the positions which had been occupied by the two chlorine sources, without moving either condensing lens.

Fig. 2 shows one of the plates which were taken in this way. No attempt has been made to ascertain the fine-structure of the chlorine lines from these photographs, but it is evident from the reproduction that most of them are relatively simple. The wave-length designations in the echelon spectra are somewhat arbitrary, but probably most of them are correct. A bright line in the echelon spectrum, appearing in two or more orders, was usually found in the approximate position of a line in the spectrum with the prism alone, and was designated by the wave-length of the latter.

The coincidences of twelve of the brighter lines were measured by the method mentioned above. The sharp satellites in the superimposed mercury patterns were used as reference lines. Four plates served for these comparisons. For two of these, the light from the heavier chlorine had passed into the collimator directly, while that from the lighter

[16] For instance, as shown by Hagenback and Konen, "Atlas of Emission Spectra," (1905) chart 249. The chlorine was used at a fairly high pressure.

chlorine was reflected by the comparison prism. For the other two, the position of the sources was interchanged. If, as before, the shift is given a positive sign when the heavier sample showed the shorter wave-length, the four brightest lines gave the following results: λ5392, $+0.0012$A $\pm 0.0007$; 5218, $+0.0008 \pm 0.0006$; 4741, $+0.0011 \pm 0.0003$; 4133, $+0.0001 \pm 0.0002$. All four plates gave the shift as positive for λ4741, the line which gave the most definite indications of a displacement. A further series of measurements was made for these four lines, averaging a large number of settings on each line. The values thus obtained were (in the same order as above), $0.0006 \pm 0.0005$; $0.0008 \pm 0.0003$; $0.0012 \pm 0.0002$, and $-0.0004 \pm 0.0003$. This is typical of the accuracy with which the results could be reproduced. Although it is true that the shifts for the first three lines are not far above the probable error of their determination, the writer considers that they represent a real difference in these spectra. It seems significant that a large majority of the values obtained were positive, the direction of shift required by the Bohr theory. The negative shifts were always small and the lines among the faintest.

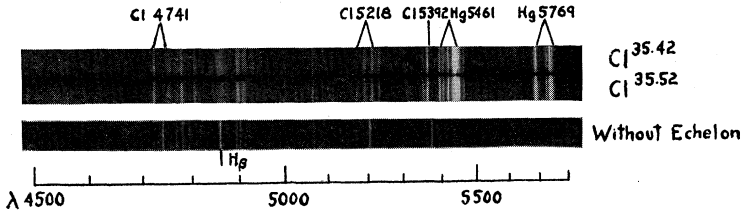


Fig. 2. Comparison of chlorine lines from isotopic sources. The upper strip shows echelon spectra of the chlorine samples, the atomic weight of which is given at the right. Three of the lines which gave the best measurements are marked above; two of them appear in two orders. The green and yellow lines of mercury were here superimposed to furnish reference lines. Most of the measurements in this region were made from the satellite $-6$ of the green line. A prism spectrum of the chlorine lines in this region is shown in the lower strip, and the wave-lengths are roughly indicated by the scale.

The lines λλ5078 and 4133, however, could be measured accurately and the results for each appeared to be equally distributed about zero. No difference in the character of the lines, or in their relative intensities, could be found on any of the plates.

A further increase in the precision of the measurements would be necessary if conclusions are to be drawn from the numerical values of the shifts. This would require a low-temperature source to decrease the intrinsic width of the lines. The spectra of the mercury isotopes deserve further study: it would be of great value to compare the lines with instruments capable of resolving the closer components, and to carry

out more accurate photometric measurements of the intensities of the satellities in these isotopic samples. The separation for mercury obtained by Harkins and his collaborators is almost twice that hitherto reported, while that achieved for chlorine (one part in 365 of the atomic weight), is by far the largest relative change that has been given for any element. Unless new methods of separation are devised, it seems improbable that material much better than that used for the present investigation will be available for some time.

The writer wishes to express his indebtedness to Professor Harkins, who kindly furnished the isotopic chlorine and mercury for this work, and to Professor H. B. Lemon, who made many valuable suggestions during its progress. The experiments were carried out in the Chemistry and Physics departments of the University of Chicago.

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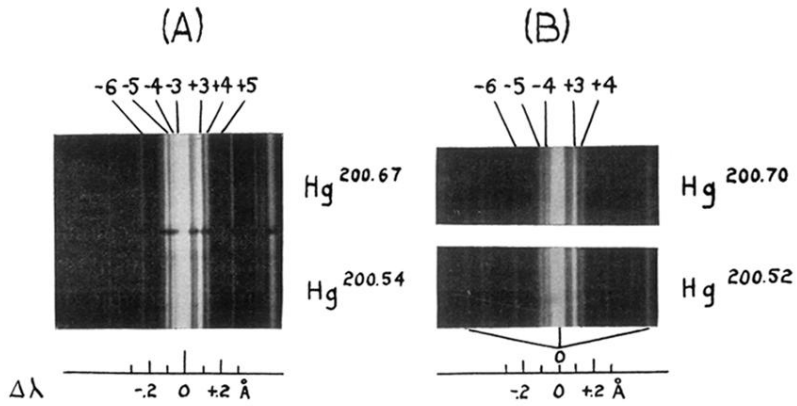
August 20, 1926.

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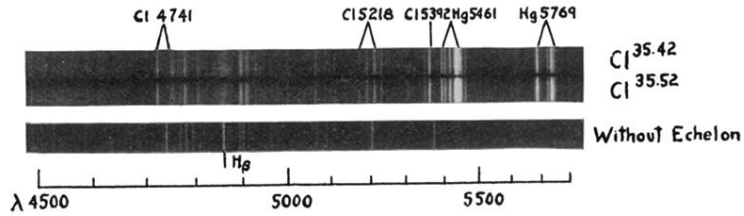


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