Hyperfine Structure of the Quadrupole Line 2815A and of Some Other Lines of Ionized Mercury

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(Received December 1, 1939)

The structure of many lines of ionized mercury is investigated by means of apparatus of high resolving power. Most of them have been found to possess complex structure. The components of the lines 2815, 3984 and 2848A are measured and the structure analyzed in terms of isotope shift and hyperfine structure. It is shown that in the case of a forbidden line of quadrupole character like the line 2815A the intensities of the hyperfine components must be computed from the formulas given by Rubinowicz (replacing J, L and S by F, J and I). The hyperfine structure splittings of the levels $6s^2S_{1/2}$, $5d^96s^2\ ^2D_{5/2}$ and $6p^2P_{3/2}$ found experimentally are in agreement with Goudsmit's formulas and allow in the case of the $6s^2S_{1/2}$ level a very accurate evaluation of the nuclear g factors for the isotope 199. The isotopic shifts in Hg II levels are discussed.

IN connection with investigations of the nuclear isotopic shift in the band spectra of ionized mercury hydride and deuteride, the results of which will be reported in the near future, it became necessary to study the structure of the forbidden line 2815A of Hg II. It could be inferred from the figure given by Schüler and Jones[1] that there should be a very large isotope shift of about 0.5 cm^{-1} between the lines of the even mercury isotopes, but in the light of the results of my work on the HgH^+ band spectrum this seemed improbable. In order to go farther and to get the energy level shifts it was necessary to study the structure of other lines of Hg II, because there have previously been made only a few incidental and insufficiently exact investigations of some lines by other workers. The structures of the following lines had been measured: 6150,[1, 2] 4797[3] and 3984A;[1, 2, 4] the lines 7945[1] and 2848A[1, 2] were reported to be single. In view of such meager data it seemed worth while to examine the whole spark spectrum of mercury for hyperfine structure and isotope shifts, furnishing at the same time a basis for a future classification of many intense spark lines found long ago by Paschen[5] and Naude,[6] but for which until now there has been found no place in the level scheme.

The spectrum of ionized mercury was excited in a hollow cathode discharge tube. The cathode was of copper and was cooled with running water. Liquid-air cooling, for reasons of expense, was only used for a few of the photographs. The whole tube was very similar in design to one previously used by Ritschl[7] and has proved very efficient for producing intense spectra. It will be described in detail in a later paper. The structure of the lines was investigated by the use of two different Fabry-Perot etalons. The reflecting surfaces of one pair of plates were of Hochheim amalgam, and were very kindly made for the author some years ago by Dr. E. Hochheim, while those of the other pair were of silver. Different plate separations, varying from 1 to 30 mm were used. The spectra were photographed by the use of two spectrographs, one a Hilger Large Interchangeable Spectrograph of 1.5-m focus, with a very fast quartz optical system, the other a medium Leiss glass spectrograph. Ilford Monarch and Gevaert panchromatic plates were generally used for the ultraviolet and the visible parts of the spectrum, respectively.

The intensity of the lines of ionized mercury depends chiefly on two factors: the current density and the helium pressure. With increase of current the intensity of all lines is appreciably greater; the lowering of helium pressure has no

[1] H. Schüler and E. G. Jones, Zeits. f. Physik **76**, 14 (1932).
[2] K. Murakawa, Scient. Papers of the Institute of Phys. and Chem. Research, Tokyo **18**, 299 (1932).
[3] S. Tolansky, Proc. Phys. Soc., London **43**, 545 (1931).
[4] B. Venkatesachar and L. Sibaya, Naturwiss. **52**, 1041 (1931).
[5] F. Paschen, Berichte der Preussischen Akad. der Wiss. **32**, 536 (1928).
[6] S. M. Naudé, Ann. d. Physik **3**, 1 (1929).
[7] R. Ritschl, Zeits. f. Physik **79**, 1 (1932).

influence on the intensity of the forbidden line 2815A, produces a slight increase of the intensity of the lines originating from lower energy levels (for example 3984A), but enormously strengthens the lines originating from higher energy levels. This effect is no doubt connected with the longer mean free path of the electrons at the lower gas densities. Therefore in the case of the line 2815A the photographs were taken using a helium pressure of 1–1.5 mm, and a current of about 250 ma. The exposures were of about one-half hour. These conditions were also quite satisfactory for studying many lines of lower excitation energy. All the other experiments were performed by starting the discharge at about 1.5 mm helium and 250 ma, then pumping off most of the helium until the current fell to 120–150 ma. Under such conditions many spark lines are very intense and the structure of some of them (4797, 5129, ···) can be easily seen by visual observations with a magnifying glass. Although the dispersion of the larger spectrograph was nearly $2\frac{1}{2}$ times that of the spectrograph used by Naudé[6] in his classification experiments and although exposures did not exceed one hour, it was possible to study about 130 lines of ionized mercury in the range from 2200–6000A in which range nearly 50 lines are unclassified. About 70 lines were found to show isotope shift or hyperfine structure, or both. Only three of them (see Fig. 3) were measured and analyzed by the author for the purpose of getting the isotope shifts in the states $5d^96s^2\ ^2D_{5/2}$ and $6s^2S_{1/2}$. The results of these measurements are reported here; we hope to be able to measure all other lines in the near future. It will then be possible for the isotope shifts in a great number of energy levels to be determined. Anticipating the publication of these results it is perhaps worth while to mention that in the line 4797A a new component was found which enables one to correlate the components found by Tolansky[3] with the different mercury isotopes: 0 (202), −420 (201), −645 (200), −1165 (199 +198). We then see that in conformity with Tolansky's[3] supposition, this line shows the unusually large isotope shift of nearly 0.65 cm^{-1} between the two even mercury isotopes 200 and 202. But 23 lines are found which show still greater shifts—in 17 of them about 0.75 cm^{-1}—these being the largest isotope shifts found in

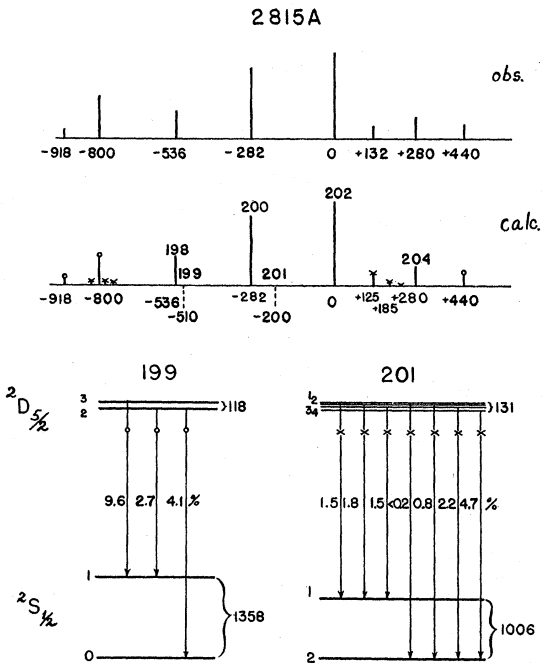

FIG. 1. Structure of the line 2815A. The broken lines give the calculated positions of the centers of gravity of the hyperfine multiplets for the isotopes 199 and 201. The intensities of the components in both term schemes are given in percentage of the total intensity of the line 2815A. All separations are given in 10^{-3} cm^{-1}.

atomic spectrum at the present time. The explanation of the cause of these shifts cannot be given now, because most of these lines are not yet classified and a large part of the classifications which have been given seem to be erroneous.[8]

The results of the measurements in the case of the forbidden line 2815A are presented in Fig. 1. The distances of the components were calculated from the measured values, taking into account the nonlinear variation of the dispersion in the interference pattern.[9] The heights of the components indicate rough estimate of the intensities. In order to interpret this relatively complicated structure, we must investigate the cause of the violations of the selection rules in the case of this line. There are only two possibilities: a quadrupole or a forced electric dipole radiation. The second possibility is ruled out at once by the fact that the strong electric fields producing the violations of the selection rules

[8] One of these, λ2982 can even be found classified in the most reliable work on the spectrum of Hg II by I. C. McLennan, A. B. McLay and M. F. Crawford, Proc. Roy. Soc. **134**, 41 (1932).

[9] S. Mrozowski, Zeits. f. Physik **112**, 223 (1939).

will cause a broadening of the line, thus making the hyperfine structure unobservable.[10] The sharpness of the components in this case shows without doubt that the line is a quadrupole line. Therefore the components must have intensities proportional to the concentration of isotopes, as in normal electric dipole radiation.[11] The distribution of intensities in Fig. 1 permits one to find at once the components belonging to the even isotopes.[12] The remaining components must belong to the two odd isotopes, including eventually components overlapping those of the even isotopes.

In order to correlate the observed components with certain hyperfine multiplet transitions, the selection rules for the hyperfine quantum number F and the intensity rules for the transitions must be found. I am indebted to Mr. W. Opechowski for calling my attention to the fact that these rules in a case of a quadrupole line can be easily obtained (as can be seen on very general argument involving the group properties of coupled vectors) from the formulas given by Rubinowicz[13] by merely replacing the quantum numbers L, S and J, by J, I and F, a procedure formerly applied in obtaining the h.f.s. intensity rules from the Hönl-Kronig formulas. The allowed transitions and their relative intensities thus computed are entered in the level diagrams of Fig. 1. The proper correlation was found using the Fisher-Goudsmit[14] graphical method. All three components of the isotope 199 are observed with the correct intensities and their measured separations allow us to determine exactly the splittings of both electronic states.[15] For the isotope 201 the splittings are calculated from the data found for the isotope 199, using the very accurate value of the ratio of the magnetic moments of the two nuclei given by Schüler and Schmidt.[16] The large difference in splittings in the lower level originates from the factor $(2I+1)/I$ in the formula for the total width of a h.f.s. multiplet. The calculated pattern for the isotope 201 was arranged in Fig. 1 in such a way as to obtain overlapping of the three long wave-length components with the 9.6 percent component of the isotope 199 and at the same time to have a near coincidence of the 4.7 percent component with the measured line +132. The relatively great half-width of the lines does not permit resolution of the four components lying near −800; thus one obtains the impression of a single line at −800 of greater intensity. Taking into consideration also the fact that the presence of the 2.2 percent component at +185 has apparently shifted the measured position of the 4.7 percent component, we can say that there is a perfect agreement of the calculated positions and intensities of the components with the observed ones. This agreement shows the applicability of the selection rules and intensity formulas of Rubinowicz to h.f.s. multiplet and constitutes one of the few general proofs of these formulas, or conversely it can be regarded as a proof of the quadrupole nature of the line 2815A. At the same time it furnishes another method, in addition to the Zeeman effect, of distinguishing electric quadrupole from the magnetic dipole radiation. In the latter case the normal dipole selection rule for the quantum number J is operative, so that in the first case not only a different intensity distribution, but also a greater number of hyperfine structure components would

[10] This was pointed out to the author by Professor W. Rubinowicz some years ago in a private conversation.

[11] It has been shown by the author that there are forbidden lines in which the intensity ratios of components are not proportional to the concentration of isotopes (see S. Mrozowski, Zeits. f. Physik **108**, 204 (1938) and W. Opechowski, Zeits. f. Physik **109**, 485 (1938), also R. Einaudi, Rend. Accad. dei Lincei **17**, 552 (1933)).

[12] In spite of the figures given by Schüler, reference 1, the separations of these components are only about 0.3 cm^{-1} instead of 0.5 cm^{-1}. It is difficult to find a reason for his erroneous results. It seems possible that he did not observe the 2815A line at all, and that his statement that in the line 2815A the component of the isotope 204 lies on the violet side was merely inferred from the results on other lines. However the reproduction of the whole energy level diagram in his article (H. Kallmann and H. Schüler, Ergebn. d. exakt. Naturwiss. **11**, 134 (1934)) seems to indicate that he observed this line. His remark, reference 1, that the sign of the isotope shift changes in going from Tl II to Tl I spectrum is not significant, because the sign depends on the electron configuration chosen, by definition, as the state of zero shift. If in all the spectra, Hg, Tl and Pb, the state of zero shift is properly defined, the levels of the heavier isotopes would in all cases lie higher, as one would expect from the theory of Rosenthal and Breit (Phys. Rev. **41**, 459 (1932)).

[13] See for instance E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Camb. Univ. Press, 1935), p. 253, 1935. [My attention has been called to a typographical error in the ninth entry of this table, which should read $+J(L+1)$ in place of $-J(L+1)$.]

[14] R. A. Fisher and S. Goudsmit, Phys. Rev. **37**, 1057 (1931).

[15] I was not certain whether the F values in the $^2D_{5/2}$ state were in the proper order, but Dr. L. I. Schiff has kindly assured me that the order of the h.f.s. levels in the cases of inverted D doublets should be not inverted; a result that can be easily seen by considering the interaction of a hole in the shell of 10 d electrons with the nucleus.

[16] H. Schüler and Th. Schmidt, Zeits. f. Physik **98**, 239 (1935).

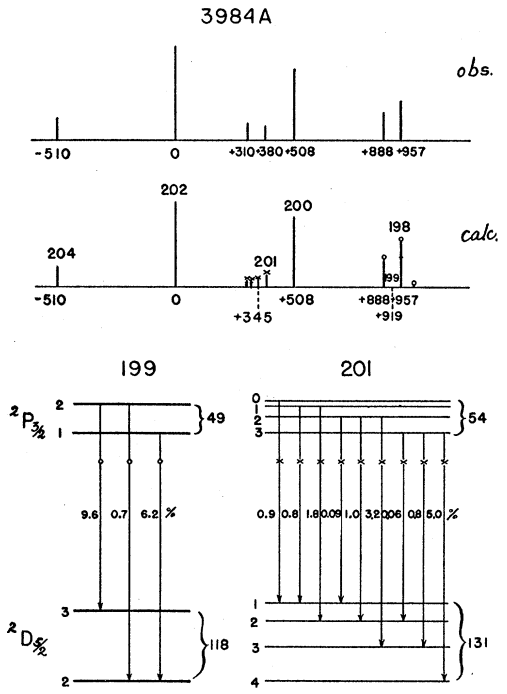

FIG. 2. Structure of the line 3984A. The designations are similar to those in Fig. 1.

be observed. Therefore it would be very interesting to investigate and compare the hyperfine structures of quadrupole, of magnetic dipole and of mixed type forbidden lines. This seems to be possible for instance in the spectrum of lead.[17]

The results of the measurements for the line 3984A are presented in Fig. 2. This line, thanks to its great intensity, could also be studied by means of two Lummer-Gehrcke plates (6.89 and 3.92 mm thickness). The structure found diverges in some points from the results of former investigations.[2, 4] A careful search for the very weak component +1950 reported by Murakawa[2] led to a negative result, in his experiments it was probably due to a foreign line. It may possibly have been a line of mercury hydride which is often present in small amounts in the hollow-cathode discharge. The analysis of the structure in the case of the isotope 199 again presents no difficulties and gives the splitting of the $^2P_{3/2}$ state. From this the splitting for the isotope 201 was calculated and all transitions were arranged in Fig. 2 so as to have overlapping of the calculated 5 percent component with the measured +380. It appears, then, that the component +310 is complex; this is supported by the fact that with greater resolving power the measured position shifted in the long wave-length direction. The fact that the intensity of the component +310 is greater than that of +380 seems to indicate that the 3.2 percent component does not lie at the calculated position +345, but is shifted in the direction of long wave-lengths. This effect is probably caused by the influence of the quadrupole moment of the nucleus.

The splittings of the states $6p^2P_{3/2}$ and $5d^96s^2\ ^2D_{3/2}$ found differ widely from the values formerly given by Murakawa (1578 and 992).[2] It is clear that the latter values are in error, because in cases when there are no s electrons outside closed shells the splitting can only be very small. The values given in Figs. 1 and 2 are in excellent agreement with the requirements of the theoretical formulas.[18] Furthermore the value for the $6s^2S_{1/2}$ state gives the possibility of a very exact evaluation of the magnetic moments of both isotopes. From the splitting in the case of the isotope 199, using the Goudsmit formula and the latest values of the constants M/m and α kindly given me by Professor Birge,[19] and using the value $n_{\text{eff}}=1.7034$, we find $g_{199}=1.0944$. This value is much more exact than those formerly calculated from data on the Hg I spectrum, because it is only to this case of one electron outside closed shells that the formula of Goudsmit applies exactly and that the number n_{eff} can be accurately calculated. For the magnetic moments of the nuclei we obtain:

$$\mu_{199}=0.547\pm0.002$$
$$\mu_{201}=0.607\pm0.003,$$

the latter value being calculated from the first using the value of the ratio of the magnetic moments given by Schüler and Schmidt.[16] The limits of error are estimated by allowing an error in the splitting of $\pm5\times10^{-3}$ cm^{-1} and by taking into consideration a possible error in the Schüler-Schmidt value. Naturally they do not include the uncertainty contained in the theoretical formula, which may be considerable.

The results concerning the isotope shifts are

[17] H. Niewodniczanski, Acta Phys. Polonica **2**, 375 (1934).

[18] S. Goudsmit, Phys. Rev. **43**, 636 (1933); E. Fermi and E. Segrè, Zeits. f. Physik **82**, 729 (1933).

[19] R. T. Birge, "A consistent set of Values of the General Physical Constants," August, 1939 (mimeographed sheets).

represented in Fig. 3. There is practically on isotope shift in the $6p^2P_{3/2}$ level (defining as the zero shift configuration the case of the closed shell $5d^{10}$ without outer electrons), as the structure of lines of the type $6p^2P_{3/2}-6d^2D_{3/2,\ 5/2}$ and $6d^2D-nf^2F$ has shown, all these lines being single and very sharp. The big shifts in the two lower levels originate from the interaction of the $6s$ electrons with the nuclei; the shift for two $6s$ electrons is a little more than twice the shift for one $6s$ electron, probably because the interaction is strengthened by the presence of a hole in the $5d$ shell. But the $7s$ electron gives only a quite small shift, as is shown by the small broadening of the line 2848A. In this case besides the slightly broadened main component only a diffuse and much weaker component near -70 was found, a result quite in agreement with expectations. Calculating the splittings of the level $7s^2S_{1/2}$ for the isotopes 199 and 201 with the aid of the formula of Goudsmit[12] we find that the strongest component of the isotope 199 falls on the short wave-length side of the main component, thus giving an impression of broadening, and a group of components of the isotope 201 of a total intensity also about 8 percent lies a little farther away on the opposite side, thus giving the impression of a single diffuse component near -70. Other weaker components lying farther away (at about 200) have not been observed. Probably they merge into the continuous blackening of the plate spreading out from the main component in both directions. The isotope shift in the level $7p^2P_{3/2}$ given in Fig. 3 was obtained by using the results of Murakawa's[2] measurements on the structure of the line 6150A.

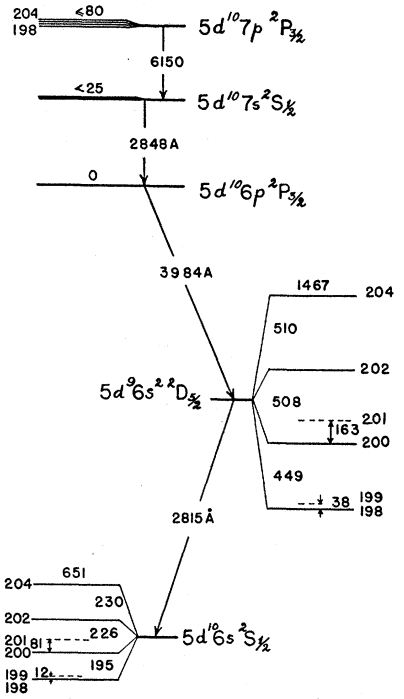

FIG. 3. Scheme of isotope shifts in energy levels of Hg II. The over-all width of each group (i.e., the shift of 204 against 198) is given above it.

In the light of these results the origin of the very large isotope shifts previously mentioned in some of the lines of Hg II seems to be rather mysterious. The big shifts belong to the upper levels, as can be seen from the intensity distribution among the components in these lines. These levels, showing an over-all isotope shift of over 2000, would have to correspond to states with at least two electrons in the $6s$ shell (i.e., only 8 electrons in the $5d$ shell); but it is hard to understand how the lowering of the number of $5d$ electrons and the resulting presence of one electron in a higher s state (as we have seen, these electrons give only small shifts) could have such a strong influence as to increase the shift from two to more than three times that caused by one $6s$ electron. The difficulty would disappear if these lines could be ascribed to a spectrum of Hg III, because in this case two $6s$ electrons would give shifts of such a magnitude. The second $6s$ electron gives an over-all shift of about 480 in Hg I and 800 in Hg II an increase of about 65 percent. In the case of Hg III an over-all shift of more than 2000 would be expected for transitions of the type $5d^86s^2\rightarrow 5d^{10}$ or $5d^9n\,p$, etc. But it would be surprising that in a hollow cathode discharge the more highly ionized spectra could be excited with such intensities.

My best thanks are due to Professor C. Bialobrzeski for his kind interest in this work and to Mr. W. Opechowski for discussions clarifying some important points connected with the forbidden line studied.

This paper was written, and some final calculations made, during the early part of a year's stay at the University of California. I am very much indebted to Professors E. O. Lawrence and F. A. Jenkins for extending to me the facilities of their laboratories, and to the latter for the kind help he has given me in the writing of this paper.