The Spectrum and Ionization Potential of Radium

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A new interpretation of the connection between the two groups of terms in Ra I found by Rasmussen is suggested and confirmed by new observations which he has courteously communicated. Certain term-designations are altered. The first ionization potential is 5.252 volts.

 $R^{
m ASMUSSEN,\ in\ his\ admirable\ analysis\ of}_{
m the\ arc\ spectrum\ of\ radium^1\ has\ con-}$ clusively identified two groups of lines-one resulting from transitions from ^{3}D and ^{1}D terms to higher odd levels and the other from ${}^{3}P^{0}$ and ${}^{1}P^{0}$ to higher even levels and the groundterm ${}^{1}S_{0}$. Absolute term-values for the first group are well determined from a series of four ${}^{3}F^{0}$ terms. The only series available in the other consists of two ³S terms, and gives but a rough limit. Connection between the two groups should occur through the ultraviolet line λ 3101.80 which must arise from the ${}^{1}S$ level. Rasmussen assigns this as $1^{1}S_{1} - 3^{1}P_{1}$.² The combination $3^{1}D_{2} - 3^{1}P_{1}$ should lie in the red and he adopts the strongest unclassified line at 6336.90. All terms are thus referred to an accurately known limit, giving $1^{1}S_{0} = 41,949.19$ and 5.176 volts for the ionization potential: but this arrangement is not confirmed by any other combinations. An independent determination of the term-values for the P^0 terms and those which combine with them may be made by combining the low ${}^{1}S$ and the two higher ${}^{3}S$ terms in a single series. This apparently crazy method-first suggested to the writer some time ago by Professor A. G. Shenstone in connection with another spectrumworks very well, as is illustrated by Table I which gives the Rydberg denominators n^* for the other alkaline earths.

The progression of these values is very regular and leads to the estimates for Ra I given in the corresponding line. The estimated tolerances represent the probable limit of error provided that the progression remains regular. The "observed" values are discussed below. With Rasmussen's value ${}^{1}S_{0} = 41,950$ the values of Δn^{*}

TABLE I. Rydberg denominators for alkaline earths.

| Term | $1^{1}S_{0}$ | | 2 ³ S ₁ | | 33S1 |
|---------------------------------------|---|--|---|--|---|
| Element Be Mg Ca Sr Ba | <i>n</i> * 1.208 1.334 1.492 1.546 1.616 | $\begin{array}{c} \Delta n^{*} \\ 0.971 \\ 0.981 \\ 0.993 \\ 1.003 \\ 1.014 \end{array}$ | <i>n</i> * 2.179 2.315 2.485 2.549 2.630 | $\begin{array}{r} \Delta n^{*} \\ 1.026 \\ 1.031 \\ 1.040 \\ 1.044 \\ 1.045 \end{array}$ | <i>n</i> * 3.205 3.346 3.525 3.593 3.675 |
| Ra(est.) | | 1.025 ± 0.005 | | 1.050 ± 0.003 | |
| Ra(obs.) | 1.605 | 1.028 | 2.633 | 1.047 | 3.680 |
| | | | | | |

come out 1.070 $({}^{1}S - {}^{3}S)$ and 1.145 $({}^{3}S - {}^{3}S)$. Increasing the assumed limit by 500 reduces these to 1.036 and 1.066; by 200 more, to 1.024 and 1.036. The two estimated values of Δn^* for Ra I therefore require the additions of 683 ± 80 and 606 ± 20 to Rasmussen's limit,—or, in the mean, 630 ± 30 . With the new value of ${}^{1}S_{0}$, the term which combines with it to give $\lambda 3101$ comes out $10,350 \pm 30$.

Now Rasmussen has already identified a level $dp^{3}D_{1^{0}}$ at 10,347.38. The corresponding level in Ba I combines strongly with ${}^{1}S_{0}$, and it appears very probable that the radium line is homologous. Upon communicating this suggestion to Dr. Rasmussen the writer received a cordial letter stating he had found upon his plates another ultraviolet line which confirms the new arrangement; $\lambda 2955.65$, intensity 2. As the further investigation upon this spectrum, which he plans, may take some time, he generously suggested that this evidence should be presented in the present paper. The new combination, together with some others whose interpretation has been altered, are exhibited in Table II. The intensities are given before the wave numbers, and the differences of the observed and computed values below. It is evident that the true connection between the two parts of the spectrum has been found. Retaining Rasmussen's values for the

¹ Rasmussen, Zeits. f. Physik **87**, 607 (1934). ² These serial numbers are "Lautzahlen" beginning with 1, 2, 3, 4 for the S, P, D and F series. They are retained here for comparison with Rasmussen's tables.

H. N. RUSSELL

| | | $3^{1}D_{2}$ 25495.95 | $3^{3}D_{3}$ 27870.00 | $\begin{array}{c} 3^{3}D_{2} \\ 28583.38 \end{array}$ | $3^{3}D_{1}$ 28861.50 | $1^{1}S_{0}$ 42577.35 |
|---------------------|----------|--------------------------|--|--|--|-------------------------|
| $dp^{3}D_{1}^{0}$ | 10347.38 | $(3) 15148.55 \\ -0.02$ | | $(8) 18236.03 \\ +0.03$ | $(10) \ 18514.07 \\ -0.05$ | (6) 32230.02 +0.05 |
| $dp^{3}P_{2^{0}}$ | 8194.44 | $(5) 17301.40 \\ -0.11$ | $\begin{array}{c} (6) & 19675.58 \\ +0.02 \end{array}$ | $\begin{array}{r} (4) \ 20389.00 \\ +0.06 \end{array}$ | $(3) \begin{array}{c} 20667.06 \\ 0.00 \end{array}$ | |
| ${}^{3}P_{1}{}^{0}$ | 8753.65 | -0.11 | -0.02 | (5) 19829.62 | (5) 20107.96 | (2) 33823.65 |
| ${}^{3}P_{0}{}^{0}$ | 8794.94 | | | -0.11 | $ \begin{array}{c} +0.11 \\ (4) 20066.56 \\ (0.00) \end{array} $ | -0.05 |

TABLE II. Term values in Ra I.

first set $(3^3D, \text{ etc.})$ those of his second set (given in his Table IV) should be increased by 627.66. The corresponding values of n^* for the S terms are given in the last line of Table I.

The ionization potential corresponding to the new data is 5.252 volts.

The adoption of the term $dp^{3}P_{1}^{0}$, as here given, accounts for the unclassified line at $\lambda 4982$ (${}^{3}D_{1} - {}^{3}P_{0}$) and removes from the list Rasmussen's doubtful level at 5431.68 combining with $2^{3}P^{0}$. His levels at 10,702.91 and 11,014.06 may then be interpreted as $3^{3}P_{2}^{0}$ and $3^{3}P_{1}^{0}$. The isolated line at λ 5755.45 ($\nu = 17,370.03$) then gives $3^{3}P_{0}^{0} = 11,491.47$. This interpretation differs from Rasmussen's mainly in the choice between alternatives which he mentioned as possible. It puts $dp^{3}P^{0}$ higher than $dp^{3}D^{0}$, as in the case of Ca, Sr and Ba, and $3^{3}P^{0}$ between $dp^{3}F^{0}$ and $dp^{3}D^{0}$, as is true in Ca and Sr (but not in Ba, where the limits of the normal and displaced series are closer together). Apart from some effects of this difference, the similarity of the spectra of the alkaline earths is remarkably detailed. For example, $dp^{1}D^{0}$ is superposed on $dp^{3}F^{0}$ in all four spectra, and the separation $dp({}^{3}P_{1}{}^{0} - {}^{3}P_{0}{}^{0})$ is abnormally small in every case.

Some revision of the assignments of the high level even terms appears also to be desirable. Table III gives the new and old term-values and

TABLE III. Term values and designations.

| | Old | New | | |
|---|---|--|---|--|
| $2^{3}P_{0}\ 2^{3}P_{1}\ 2^{3}P_{2}$ | 28,871.25 27,950.31 25,261.15 | $\begin{vmatrix} 2^{3}P_{0}^{0} \\ 2^{3}P_{1}^{0} \\ 2^{3}P_{2}^{0} \end{vmatrix}$ | 29,498.91 28,577.97 25,888.81 | |
| $2^{1}P_{1}$ | 21,233.98 | $2^{1}P_{1}^{0}$ | 21,861.64 | |
| ${dd^{3}P_{1}\over 4^{3}D_{2}\over 4^{3}D_{3}}$ | 9948.87 9956.28 9752.41 | ${4^{3}D_{1} \over 4^{3}D_{2} \over 4^{3}D_{3}}$ | $\begin{array}{r} 10,576.53\\ 10,583.94\\ 10,380.07\end{array}$ | |
| $4^{3}D_{1}$ | $\begin{array}{r} 10,701.08\\9008.56\\9734.85\end{array}$ | $p^{2} \ {}^{3}P_{1} \ p^{2} \ {}^{3}P_{2} \ p^{2} \ {}^{1}D_{2}$ | $\begin{array}{r} 11,328.74\\9636.22\\10,362.51\end{array}$ | |

designations. The slight inversion of $4^{3}D_{1}$ appears preferable to the very large interval demanded by the old assignment. The outstanding levels are attributed to the p^{2} , rather than the d^{2} , configuration, since the former is lower in Ca and Sr (which resemble Ra more closely than Ba does). Which of the last two levels is ${}^{3}P_{2}$ is doubtful: the present assignment assumes that the difference ${}^{3}P_{2} - {}^{3}P_{1}$ is likely to be large. Further identifications must be postponed till the fainter lines have been more fully observed.

In conclusion, the writer desires to express his hearty thanks to Dr. Rasmussen for his generous communication of the new data and his permission to refer to them here.