A Plausible Explanation of the Alkali Inverted Doublets

It is well known that the $^2D_{3/2,5/2}$ and $^2F_{5/2,7/2}$ terms of the heavier alkali atoms are inverted. For these doublets the term with the largest J-value lies deepest. In view of the well-known perturbation-resonance phenomenon that occurs between similar energy levels, treated quantum mechanically by Heisengberg, Darwin, Pauli, Slater, Condon, Langer, and others, and of the recent paper by Shenstone and Russell on "Perturbed Series in Line Spectra" (Phys. Rev. **39**, 415, 1932) a plausible explanation of the inverted doublets suggests itself. The $^2D_{3/2,5/2}$ (*even*) and the $^2F_{5/2,7/2}$ (*odd*) terms in the alkalies should not only be normal, i.e., smallest J-value deepest on an energy level diagram, but very narrow as well. If in the neighborhood of the $^2D_{3/2,5/2}$ (*even*) terms other $^2D_{3/2,5/2}$ (*even*) terms occur and these latter terms are inverted there will be an interaction between the two sets of levels, (i.e., between levels having the same J-values) tending (1) to invert the normal doublet, and (2) to right the inverted doublet. In general this tendency to invert the normal doublet will decrease with the distance between the two sets of levels and will increase with the doublet separation of the perturbing levels. If this perturbing inverted doublet has a large separation the effect will be to invert the normal $^2D_{3/2,5/2}$ terms. Such a wide inverted ^2D term occurs in potassium for example by the excitation of a $3p$ electron from the completed $3p^6$ subshell to a $4p$ state. Even though the resultant electron configuration $3p^54s4p$ should lie somewhere between 50,000 to 100,000 cm^{-1} above the perturbed levels, the wide separation of the inverted ^2D terms makes the inversion of the perturbed levels seem probable. By making certain justifiable approximations the magnitude of the interactions can be calculated on the quantum mechanics. This work is now being carried on in this laboratory by Miss M. Phillips.

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The Ionization Potential of Radon

Because of the rarity of the inert gas radon formed from the radioactive disintegration of radium, it was thought that the experimental determination of the ionization potential of the element would be impossible. Hence, estimates of the value of this constant were made by extrapolating different functions correlating the spectral properties of the noble gases. Turner[1] suggested a value of 27.5 ± 1.5 volts based on a linear relationship which he had observed between the atomic number of the elements and their quantum defects. By applying Eve's rule[2] that the product of the ionization potential V and the ionic radius r is roughly a constant for the members of a periodic sub-group, Glocker[3] deduced that the ionization potential of radon is 10.0 ± 0.9 volts by evaluating the radius of the atom (2.80 ± 0.25A) from the measurements of the diffusion coefficient of the gas in air. In a critique on Glocker's assumptions, Struwe[4] concluded that a probable value of the ionization potential is 9 volts. Independently, Piccardi[5] calculated a value which was equal to 11.96 volts on the basis of a generalization which he had observed by plotting the difference between the ionization potentials of the elements of adjacent groups having the same total quantum number n against their atomic numbers. Biswas[6] suggested that the ionization potential of radon will exceed that of xenon, as the last member of practically all the other periodic groups exhibits a similar behavior with respect to the progression of the ionization potentials of the atoms within the group. By assuming an inverse proportionality between the ionization potential and the square of the mean atomic radius, he secured a value equal to 14.0 ± 0.5 volts depending upon the magnitude of the radius which he estimated as 1.8 ± 0.03A from the known viscosity and critical constants of the gas.

The spectrum of radon has recently been

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[1] L. A. Turner, Phil. Mag. **48**, 384, 1010 (1924).

[2] A. S. Eve, Nature **107**, 552 (1921); Phys. Rev. **27**, 515 (1926).

[3] G. Glocker, Phil. Mag. **50**, 997 (1925).

[4] F. Struwe, Zeits. f. Physik **37**, 859 (1926).

[5] G. Piccardi, Atti. accad. Lincei (6) **6**, 305, 428, 621 (1927).

[6] S. C. Biswas, Phil. Mag. (7) **5**, 1094 (1928).

analyzed into its terms by Rasmussen.[7] His analysis reveals that the ionization potential of the neutral radon atom is 10.689 volts. Shortly afterwards Holweck and Wertenstein[8] measured the ionization potential of the gas by applying the well-known method of Hertz for the study of excitation potentials to 300 millicuries of radon in a tube where its pressure amounted to about 0.8 bar. Their value of 10.6 volts establishes the true magnitude of this constant, as experiments with equally small quantities of krypton and xenon also yielded ionization potentials that were in good agreement with the accepted values.

In a communication to the Physical Review the present writer[9] has evaluated the energy levels of the 1^2S and m^2P_j terms of the neutral atom of atomic number 87 and those of the singly ionized radium atom with the aid of a rule stating that within a periodic sub-group the quantum defect of a spectral level is approximately a linear function of the total quantum number of the valence electron. As the ionization potential can be calculated directly from the normal term, the quantum defect rule is also applicable to the coordination of the ionization potentials of the elements. In Table I the calculated quantum defects and ionization potentials of the noble gases are compared with the observed values. The quantum defects were estimated from the relationship: (1) $Q=an+b$, in which the coefficients a and b were evaluated by the method of average points on the data for only neon, argon, krypton and xenon. The calculated values of helium and radon therefore represent extreme extrapolates of Eq. (1), and the fair agreement with the observed constants proves the general validity of the equation.

In view of the researches of Rasmussen and of Holweck and Wertenstein there is little doubt but that the ionization potential of the neutral radon atom is 10.7 volts. The fact that this value follows the normal trend of the ionization potentials of the noble gases is surprising, since most of the spectroscopic properties of the atoms occurring in the seventh period exhibit anomalous behavior in this respect. Thus in the case of the singly ionized radium atom, the doublet separations, the wave-numbers of the principal series spectrum and the term values as arranged by Hicks[10] have properties which are considerably different from those expected from a simple extrapolation of the corresponding values for the other alkaline earth atoms. Indeed, to account for the 1^2S, 2^2P_2 and 2^2P_1 levels of Ra II it was found necessary to introduce a corrective term ϵ in the formula employed for their evaluation.[9] A more complete analysis of the arc and spark spectra of the radium atom than is at present available is desirable for the better understanding of the unusual behavior of seventh-period atoms.

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TABLE I. *Quantum defects and ionization potentials of the noble gases.*

$$Q = 0.9196n - 0.6607 \qquad (1) \qquad\qquad V = \frac{300hcR}{e(n-Q)^2} = \frac{13.538}{(n-Q)^2} \qquad (2)$$

Element	n^*	n	Quantum defect calc. (1)	Quantum defect obs.	Ionization potential calc. (2)	Ionization potential obs.
Helium	0.7438	1	0.259	0.256	24.7	24.47[a]
Neon	0.7941	2	1.179	1.206	20.1	21.47[b]
Argon	0.9292	3	2.098	2.071	16.6	15.68[b]
Krypton	0.9858	4	3.018	3.014	14.0	13.940[c]
Xexon	1.0591	5	3.937	3.941	12.0	12.078[c]
Radon	1.1254	6	4.857	4.875	10.4	10.689[d]

[a] T. Lyman, Nature **110**, 278 (1922).

[b] Landolt-Börnstein Physikalisch-Chemische Tapellen, 5th ed., vol. 2, table 152f, Berlin (1931).

[c] Meggers, de Bruin and Humphreys, Bur. Stand. J. Research **3**, 129, 731 (1929).

[d] E. Rasmussen, Zeits. f. Physik **62**, 494 (1930).

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[7] E. Rasmussen, Zeits. f. Physik **62**, 494 (1930).

[8] F. Holweck and L. Wertenstein, Nature **126**, 433 (1930).

[9] H. Yagoda, Phys. Rev. **38**, 2298 (1931).

[10] W. N. Hicks "Analysis of Spectra", pg. 276 Cambridge University Press 1922. A. Fowler "Report on Series in Line Spectra", p. 138, London 1922.