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AUTO-IONIZATION IN THE ALKALINE EARTH METALS AND THE INERT GASES

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Abstract

The atomic process of auto-ionization put forward by Shenstone[1] is discussed in connection with the alkaline earth metals, calcium, strontium, and barium, and the inert gases, krypton and xenon. The phenomenon is quite similar to the Auger[2] effect in x-rays and analogous with the predissociation of molecules in band spectra put forward by Kronig.[3] Certain characteristics of energy levels in Ca and Sr, known to lie above the first series limit and to give rise, in combination with lower levels, to sharp and nebulous lines, are attributed to the process of auto-ionization. In a similar manner the cutting off at the first or second member of certain series of lines in krypton and xenon and the continuance of other series of the same electron configurations to five, six, seven and eight members is attributed to the process of auto-ionization in those atomic states of the neutral atom which lie above the first series limit.

The process of *auto-ionization* put forward by Shenstone[1] to account for the ultraionization potentials observed in mercury vapor is of considerable importance in that it clears up a great many of the difficulties previously unaccounted for in atomic spectra. One of the well-known anomalies that may be accounted for, as pointed out by Shenstone and to be given later,[1] is the diffuseness of certain lines in the arc spectrum of copper. The observation of sharp lines and of broad diffuse lines in the same multiplet finds a plausible explanation in this process, auto-ionization.

Above the series limit of any series lies a continuum of possible energy states. This continuum is characterized by the same quantum numbers as the series of discontinuous levels below the limit, i.e. the same L, S, J, and the same odd or even sign of the electron configurations involved. An electron configuration or term is said to be *odd* when Σl_i is *odd*, and *even* when Σl_i is *even*, (i.e. *odd* for an *odd* number of $p, f, h, \cdots$ electrons, otherwise *even*). An atom excited to a discrete energy state above the first ionization potential and into a region accompanied by a continuum characterized by the same L, S, J, and *sign* is in a condition for auto-ionization. The transition from the discrete energy state into the continuum may be interpreted as a "resonance" phenomenon between two states of the same energy, which results in the spontaneous ejection of an electron with kinetic energy and the return of the atom to a lower series limit. Several good examples of this process of auto-ionization are to be found in the alkaline earth elements.

[1] Shenstone, Phys. Rev. **38**, 873 (1931).
[2] Auger, Comptes Rendus **187**, 1141 (1928); **188**, 447, 1287 (1929); **192**, 672 (1931).
[3] Kronig, Zeits. f. Physik **62**, 300 (1930).

In the early development of complex spectrum analysis Russell and Saunders[4] found in calcium a series of triplet p' terms which are now famous. These terms, then designated as $2p'_{1,2,3}$, $3p'_{1,2,3}$, $4p'_{1,2,3}$ and $5p'_{1,2,3}$ with term values $T=741$, -5000, -8334, and -10086 cm^{-1} respectively, are now designated as ${}^3P_{2,1,0}$ and are attributed by Russell[5] to the electron configurations $3dmd$. All but the first member of this series, see Fig. 1, lie above the first series limit $4^2s_{1/2}$ of the four chief series of singlets and triplets. The continuum above these four chief series corresponds to *even* S and D terms and to *odd* P and F terms. The ${}^3P_{2,1,0}$ terms being characteristically *even* enables the electron to have in this state a mean-life sufficiently great to combine normally with lower odd terms and to give the respectably sharp spectrum lines observed.

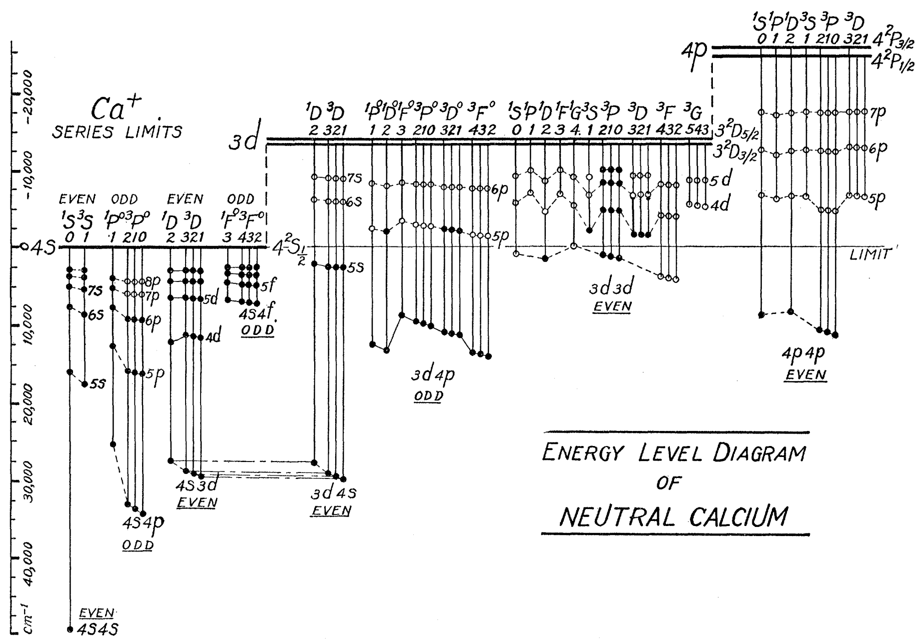

Fig. 1. Energy level diagram of calcium.

The *even* ${}^3S_1$ term in calcium ($T=-2266.9$ cm^{-1}, and attributed by Russell[3] to $3d4d$) because it is found to combine with other *odd* terms at all, would be expected to have a short mean-life, and to give, as a result, diffuse lines. This level ${}^3S_1$, $3d4d$, combining with ${}^3P^0_{2,1,0}$, $4s4p$, in a double electron jump gives rise to three hazy lines $\lambda 2757.40$, $\lambda 2749.34$, and $\lambda 2745.49$.

In strontium a ${}^3F^0$ term, $4d6p$, (the corresponding term in calcium, see Fig. 1, is ${}^3F^0$, $3d5p$,) lies above the $5^2S_{1/2}$ limit and, as in calcium, is in a continuum of ${}^3F^0$ terms, $5smf$. These negative ${}^3F^0_{4,3,2}$ terms, $4d6p$, with term

[4] Russell and Saunders, Astrophys. J. **61,** 38 (1925).
[5] Russell, Astrophys. J. **66,** 1 (1927).

values $T=3729.4$, 3621.6 and 3473.3 cm^{-1}, if they are observed to combine with lower terms at all, would also be expected to have a short mean-life and to give rise to extremely diffuse lines. Combining with the $^3D_{3,2,1}$ terms, $5s4d$, with term values $T-27606.0$, 27706.6, and 27766.6 cm^{-1} respectively, these $^3F^0$ terms give rise to five very diffuse lines.[4]

STRONTIUM[4]

Int.*	λ	ν	Designation
4*n*	3189.23	31346.5	$^3D_3-{}^3F_4{}^0$
3*n*	3189.93	31339.6	$^3D_2-{}^3F_3{}^0$
2*n*	3198.99	31250.9	$^3D_1-{}^3F_2{}^0$
2*n*	3200.22	31238.9	$^3D_3-{}^3F_3{}^0$
1*n*	3205.13	31191.0	$^3D_2-{}^3F_2{}^0$

* The letter *n* indicates that the lines are "nebulous" in appearance.

In barium these same $^3F^0{}_{4,3,2}$ terms, $5d7p$, with term values $T=4558.6$, 4747.5, and 4966.3 cm^{-1} respectively, lie below the first limit $6^2S_{1/2}$ and in combination with the corresponding terms, $6s5d$, with term values $T=$ 32433.0, 32814.1 and 32995.6 cm^{-1} respectively, give rise to six relatively sharp lines as expected.

BARIUM[4]

Int.	λ	ν	Designation
10	3586.50	27874.4	$^3D_3-{}^3F_4{}^0$
10	3561.94	28066.6	$^3D_2-{}^3F_3{}^0$
10	3566.66	28029.2	$^3D_1-{}^3F_2{}^0$
15	3610.96	27685.6	$^3D_3-{}^3F_3{}^0$
3	3589.95	27847.6	$^3D_2-{}^3F_2{}^0$
2	3639.72	27466.9	$^3D_3-{}^3F_2{}^0$

It is suggested in what follows that an extension of the process of auto-ionization to the spectra of the inert gases where *jj*-coupling, rather the *LS*-coupling, predominates may account for certain apparent anomalies. In the noble elements neon, argon, krypton and xenon all observed series approach, as limits, the inverted $^2P_{1/2,3/2}$ terms of the corresponding ions Ne II, A II, Kr II and Xe II respectively. With almost perfect *jj*-coupling in krypton[6] and xenon[7] each series of energy levels arising from the electron configurations p^5ms, p^5mp, p^5md, and p^5mf, consists of two distinct groups of series. From the energy level diagram for xenon, shown in Fig. 2, it may be seen that in each configuration there is one group of terms approaching the lower limit $^2P_{3/2}$ of the ion, and another group of terms approaching the upper limit $^2P_{1/2}$.

The circles, representing unobserved terms, Fig. 2, and the dots, representing observed terms, indicate that transitions from negative levels to lower levels seldom occur, if at all. It is seen that series built upon the lower

[6] Meggers, de Bruin, and Humphreys, Bur. Stand. Jour. Res. **3,** 129 (1929).
[7] Meggers, de Bruin, and Humphreys, Bur. Stand. Jour. Res. **3,** 731 (1929).

limit ${}^2P_{3/2}$ are in general observed for some five to eight members, whereas, the series built upon the upper limit ${}^2P_{1/2}$ are observed for only one or two members. It is reasonable to expect any one of the series arising from the electron configurations $5p^5mp$, for example, to be observed for as many members as any other series belonging to these same configurations. In cases such as this the explanation has been that excitation energies somewhat greater than the first ionization potential ionize the atom rather than excite it to an energy level above the first ionization potential. The process of auto-ionization put forward by Shenstone,[1] however, is a plausible explanation of what happens,

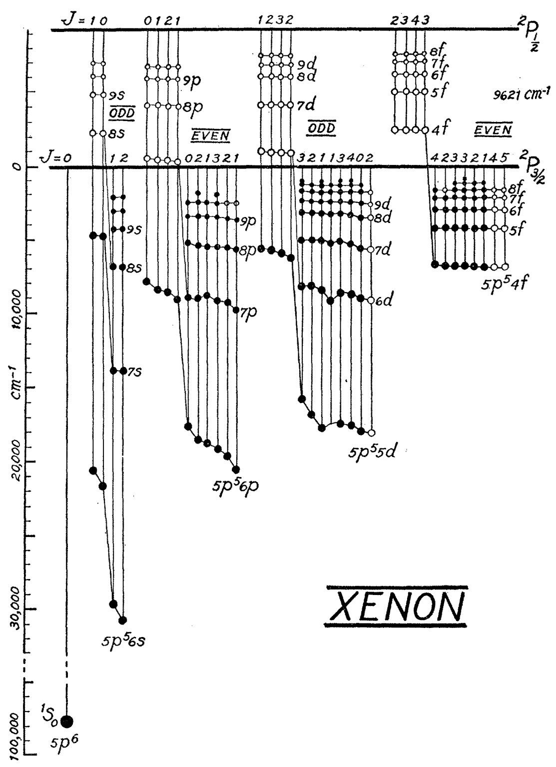

Fig. 2. Energy level diagram of xenon.

and would indicate that excitation into these negative atomic states takes place first and that ionization without radiation is a secondary process.

The energy level diagram for krypton, being so nearly like that of xenon, may be obtained from Fig. 2, by lowering the ${}^2P_{1/2}$ limit and the series built thereon, about half-way to the ${}^2P_{3/2}$ limit (${}^2P_{3/2}-{}^2P_{1/2}=5371$ cm^{-1}). This drops one more member of each upper limit series below ${}^2P_{3/2}$ in a region where its mean-life is sufficiently great to combine normally with lower terms, as observed.

With *jj*-coupling in krypton and xenon the quantum conditions necessary for auto-ionization should be somewhat different than for *LS*-(*Russell-*

Saunders) coupling. For every *odd* state above $^2P_{3/2}$ there is an *odd* continuum characterized by the same J value. It would appear from observation that these conditions might be sufficient for auto-ionization. In some cases, however, the small j's are found to be the same for the two states in "resonance." For example, for the electron configuration $5p^5mp$ there are two *even* terms $J=1$, and $J=2$ above $^2P_{3/2}$, accompanied by *even* continua with $J=1$, and $J=2$, from the same configuration. In addition the discrete states have $j_1=\frac{1}{2}$, $(5p^5)$, and $j_2=3/2$, (mp), and the continua have $j_2=\frac{1}{2}$, (mp), and $j_1=3/2$, $(5p^5)$. Similarly there are two *odd* states $J=1$, and $J=2$, $(5p^5md)$, with $j_1 - \frac{1}{2}$, $(5p^5)$, and $j_2=3/2$, (md) in the *odd* continua characterized by $J=1$ and $J=2$ respectively, $(5p^5ms)$, with $j_2=\frac{1}{2}$, (ms), and $j_1=3/2$, $(5p^5)$. This is not the case for all discrete states. In every case, however, *odd* continua do exist where the resultant J's, and the relative directions of the electron spins s_1 and s_2, are the same as in the *odd* discrete states. This is also true for *even* states. The quantum conditions for the so-called "resonance" between two states having approximately the same energy values in jj-coupling should be determined on the quantum mechanics.