ULTRA-IONIZATION POTENTIALS IN MERCURY VAPOR

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Abstract

It is shown that Takamine's new $^3P_2{}^0$ level in Hg I is probably the lowest level from the structure d^9s^2p. The positions of the other levels are discussed and it is shown that some of them will be negative. The phenomenon of auto-ionization is described and its effect on the negative terms is suggested as the cause for the existence of ultra-ionization potentials. Some remarks are made regarding perturbed series.

The discovery of a new $^3P_2{}^0$ term in the spectrum of Hg I by Takamine and Suga[1] and its verification by Paschen[2] leads to a probable explanation of the hyper-ionization potentials in mercury, first found by Lawrence[3] and afterwards extended by a number of others. The results are collected and compared with his own by P. T. Smith.[4] The explanation depends on the identification of the new term as $5d^96s^26p\,^3P_2{}^0$ and the observation that auto-ionization is effective in atomic spectra.

The new term $X^3P_2{}^0$ is at $\nu = 15295$. If it is due to the structure mentioned above, its value, measured from its own ion is $\nu = 15295 + 35514 = 50809$, since the difference $d^{10}s - d^9s^2$ of Hg II is 35514. A comparison with spectra in which similar structures occur, for instance Cu II, Au II, Ni I, Pd I, Pt I, shows that the value is a very reasonable one. The Rydberg denominator is 1.4692.

Some idea of the positions of the other levels of d^9s^2p may be obtained by an examination of d^9p of Au II.[5] The levels in both cases include$^{3,1}P^0$, D^0, F^0. The total span should be somewhat greater than twice the $d^9s^2\,{}^2D$ difference, i.e. about 30,000, so that the highest levels of the group will extend to about -15000. The lowest level is almost certainly the $^3P_2{}^0$ already found and above it by quite closely 2000 units should be $^3F_3{}^0$. In the neighborhood of 10,000 higher should come $^3F_4{}^0$, $^3D_3{}^0$, $^3D_2{}^0$, $^3P_1{}^0$. The remaining levels including the singlets and the last levels of the triplets should extend from about zero to -15000. In combination with known terms, $^3F_3{}^0$, $^3F_4{}^0$, $^3D_3{}^0$ and $^3D_2{}^0$ can produce only lines of very long wave-length. $^3P_1{}^0$, on the other hand, will have a combination with $^3S_1$ of wave-length around λ6000 to 7000. Its value is possibly 7272, calculated from the two possible combinations λ6868 $2^3S - X^3P_1{}^0$ and λ18127.5 $3^3D_2 - X^3P_1{}^0$. Of the higher group, $^1D_2{}^0$ and $^3D_1{}^0$, in combination with ^3D and ^1D, should give lines in the region around λ4500 to

[1] Takamine and Suga, Sci. Pap. Inst. Phys. and Chem. Res. Tokio **13**, 1 (1930).
[2] Paschen, Ann. d. Physik **6**, 47 (1930).
[3] Lawrence, Phys. Rev. **28**, 947 (1926).
[4] P. T. Smith, Phys. Rev. **37**, 808 (1931).
[5] McLennan and McLay, Proc. Roy. Soc. Canada **22**, 103 (1928).

λ6000; but it is doubtful whether the high F^0 and P^0 levels can be found, as will appear from the following discussion of the effect of auto-ionization.

AUTO-IONIZATION

There is a well-known effect in band spectra which is called predissociation. The effect is an automatic dissociation of a molecule when the sum of its vibrational and electronic energies exceeds the energy necessary for dissociation in some lower electronic system. Kronig has shown theoretically[6] that such radiationless transitions can take place only under very stringent quantum conditions.

Professor Wigner has suggested to me that certain peculiarities of the copper arc spectrum may be logically explained on the assumption that a parallel action can take place in an atom.

Beyond the ionization limit of any ion, there lies a continuum of possible energy states. That continuum may be considered to be composed of a set of continua, each one of which corresponds to an extension of an ordinary term sequence and retains the characteristic quantum numbers of that sequence i.e. for Russell-Saunders coupling the numbers L, S, J and the parity. But it is possible for an atom, by the excitation of two electrons, to exist in a state of energy-content more than sufficient to ionize it by the removal of the first electron. In such a state, there is the possibility of a radiationless transition carrying the excited atom into the state where it exists as an ion plus an electron. A comparison of this case with that of predissociation, dealt with theoretically by Kronig, makes it very probable that such transitions from a given state can occur if there exists a continuum characterized by the same L, S, J and parity as the state in question. This effect has been referred to as the Auger effect from its analogy to the effect in x-rays discovered by Auger; but I believe that it could much more logically be called auto-ionization. In the spectrum Cu I, the effect is very marked and it will be discussed more fully in a later paper in connection with the experimental results obtained in that and other spectra.

From the discussion of the terms from the structure d^9s^2p of Hg I, it will be seen that $^1P_1{}^0$, $^1D^0$, $^1F^0$, $^3D_1{}^0$, $^3F_2{}^0$, $^3P_0{}^0$ all probably lie above the ordinary ionization limit of the spectrum. They are therefore energetically in a position to show the effect of auto-ionization. But the continua following the limit correspond to *odd* P and F terms and *even* D terms. Therefore, we would expect the D^0 levels to possess lives of the ordinary magnitude, and the P^0 and F^0 levels to exist for much shorter times and to pass over into ionization automatically. The effect on the spectrum will be that lines from the negative P^0 and F^0 levels will be extremely diffuse, if they exist at all. By analogy with Cu I, it would be expected that the lines would be emitted only at very high vapour densities.

ULTRA-IONIZATION POTENTIALS

In experiments on ultra-ionization potentials, the observation is that ions

[6] Kronig, Zeits. f. Physik **62**, 300 (1930).

are detected when the bombarding electrons attain certain particular velocities greater than that corresponding to the ordinary series limit. I suggest that those ions are not a direct result of the electron impact, but that the primary process is one of excitation to a negative level, followed by auto-ionization. One would expect such a critical potential for each possible negative S, P^0, D, F^0, etc., level. The potentials observed near the ordinary I. P. are probably due to the terms from the structure d^9s^2p but many higher ones could exist. For instance, d^9s^2s $^3D_1{}^1D$, the lowest even terms based on the ^2D ion, should show the effect. On the other hand $d^{10}p^2$ ^3P should not give any ultra-ionization potentials and d^{10} p^2 ^1S and ^1D should.

It should be noticed that, on this explanation, the observation of ultra-ionization potentials cannot be of much aid in the discovery of new levels because such potentials correspond to levels which are very unlikely to produce spectrum lines.

The $d^{10}p$ $^3P^0$ sequences of Hg I show marked irregularities. The $^3P_0{}^0$ sequence is quite "Ritzian" but the $^3P_1{}^0$ shows a marked perturbation about the 4th and 5th terms and the $^3P_2{}^0$ sequence at the second term. The cause is not far to seek. The $^3P_2{}^0$ sequence is perturbed by $X^3P_2{}^0$ and $^3P_1{}^0$ by the corresponding $^3P_1{}^0$ which possibly has the value 7272. In the former case, the perturbation is of such a magnitude that it is impossible and perhaps meaningless to assign one of the levels to the ordinary sequence and the other to d^9s^2p. The evidence of the line intensities, such as it is, would indicate that possibly the present choice is the less reasonable.

R. M. Langer has shown[7] that the quantum mechanics leads, in such a case as that under consideration, to a series formula in which $n^*=n+\mu+p/(\nu_0-\nu_n)$, in which p is a constant and ν_0 is the wave-number of a term foreign to the sequence. The $^3P_2{}^0$ sequence may be fitted to such a formula with reasonable accuracy, using either one of the possible levels as the second member. Such perturbations are closely analogous to the phenomenon of auto-ionization, and should be governed by similar quantum conditions i.e. the terms must all have the same L, S, J and parity. Kronig, in the paper referred to above, has dealt with the parallel case in band spectra.

Langer remarks in his letter that 'The chief contribution of this work is the satisfaction one gets from the elimination of an apparent flaw in our notions of line spectra.' Professor H. N. Russell and I have indeed felt that relief while recently making a survey of all the known preturbed series which have been so troublesome in the past.

[7] R. M. Langer, Phys. Rev. **35**, 649 (1930).