Plasma-induced broadening of atomic levels of shifted terms lying below the ionization boundary

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The broadening of the levels of shifted terms in the VV and TiIV ions below the ionization boundary has been derived theoretically and observed experimentally in the plasma of a vacuum arc. The results are evidence that a new manifestation of a configurational interaction has been observed in atomic spectra.

The crossing of the $3d^{10}$ ionization boundary by the doubly excited $3d^9\,4p^2$ configuration in ions of the copper isoelectronic sequence, BrVII–AsV, was studied in Ref. 1. An autoionization width appeared beyond the ionization boundary for several of the levels, in accordance with the selection rules. It was also found, however, that these levels become broader even when they lie below the ionization boundary. The known mechanisms (Stark broadening, autoionization, or tunneling due to a lowering of the ionization potential in external fields) do not explain this behavior of the levels. In the present letter we report theoretical calculations and experimental data which show that the observed effect is a new manifestation of a configurational interaction in atomic spectra: The broadening results from an interaction of the levels of shifted terms with the levels of Rydberg series which have undergone a Stark broadening in the plasma.

The configurational interaction is known to cause a mutual shift of levels and a mixing of their wave functions. These effects are manifested in violations of the regular variation through the series in the energies of the levels, in the fine-structure intervals, and in the intensities. Furthermore, for the levels of mixed terms which lie above the ionization boundary a mixing with the continuum is manifested as an autoionization. When the levels of the mixed terms instead lie below the ionization boundary, their wave functions mix with those of Rydberg levels. A broadening of the latter levels in a plasma should thus lead to a simultaneous broadening of the levels of shifted terms.

Let us consider the two-level problem in which the unperturbed position of a level of a shifted term and of the nearest level of a Rydberg series are denoted by E_1 and E_2, respectively, while V_{12} is the matrix element of their electrostatic interaction. If the level E_2 is quasicontinuous because of broadening in the plasma, the width of level E_1 is given[2] by the relation $\Gamma_1 = 2\pi|V_{1E(2)}|^2$, where $V_{1E(2)}$ is the interaction matrix element normalized to a unit interval of the width of level E_2. Assuming, for definiteness, a Lorentzian lineshape for level E_2, with a half-width Γ_2, we can write

$$\Gamma_1 = \frac{|V_{12}|^2\,\Gamma_2}{(E_2 - E_1)^2 + \Gamma_2^2/4} \quad . \tag{1}$$

Curve 1 in Fig. 1 shows Γ_1 as a function of Γ_2 according to (1). Curve 2 shows a qualitative generalization of this behavior to the case of an interaction with a real Rydberg series. The limiting values of Γ_1 here can be used without carrying out any additional calculations. Under the condition $\Gamma_n \ll E_n - E_1$ we have

$$\Gamma_1 = \sum_n \frac{|V_{1n}|^2}{(E_n - E_1)^2}\,\Gamma_n.$$

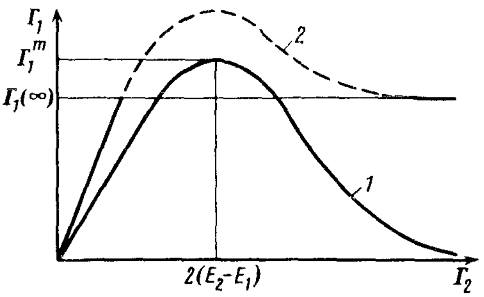

FIG. 1. 1—Width of a level of a shifted term, Γ_1, versus the width of the closest level of a Rydberg series, $\Gamma_1^m = |V_{12}|^2/(E_2 - E_1)$; 2—generalization to the case of an interaction with the complete Rydberg series.

In the other limit, we have $\Gamma_1(\infty) = 2\pi|V_{1E}|^2$. The normalization should be carried out[3] by dividing the square of the interaction matrix element, $|V_{12}|^2$, by the average distance between the levels of the Rydberg series, $2RZ_c^2|(n^*)^3$, where R is the Rydberg constant, Z_c is the charge of the atomic core, and n^* is the effective quantum number of level E_2; i.e.,

$$\Gamma_1(\infty) = \pi(n^*)^3\,|V_{12}|^2/RZ_c^2\ . \tag{2}$$

The intermediate region is shown by the dashed line in Fig. 1, since the particular shape of the curve depends on the arrangement of levels and the strength of the interaction. Furthermore, complex calculations involving the interaction of the quasi-continua of Rydberg levels would have to be carried out.

In the present experiments we used VV and TiIV ions of the *K*I isoelectronic sequence ($3p^63d$ ground state) and the experimental method of Ref. 1. In the case of the VV ions we studied transitions to the ground state from the $3p^53d\,4s$ configuration, two terms of which, $(^3D)^2D$ and $(^1F)^2F$, lie near the $3p^610f\,2F$ Rydberg term, with an energy of 498790 ± 60 cm^{-1} according to a prediction of the quantum-defect theory. The VV ionization energy is[4] 526532 cm^{-1}. The spectrum was measured under cold conditions, with $T \sim 15\times10^4$ K and $N_e \sim 6\times10^{16}$ cm^{-3}, and also under hot conditions, with $T\sim25\times10^4$ K, and $N_e = 1.7\times10^{18}$ cm^{-3}. The temperature was estimated from the Doppler broadening of the lines of the ions OIII–OIV, present as an impurity in the spectrum. The electron density was found from the Stark broadening of the lines of the transitions $3p^63d$–$3p^6nl$, $nl = 6p$, $(5-7)f$ (Ref. 5).

Under cold conditions, the highest observed level of the nf series ($n = 9$) has a width of 35 cm^{-1}. An estimate for $10f$ yields 50 cm^{-1}. The width expected for the $(^1F)^2F$ levels here is ~ 1 cm^{-1} and cannot be observed at the instrumental width of our apparatus, 24 cm^{-1}. In the spectrum under the cold conditions, all the lines of transitions from the $3p^53d\,4s$ configuration have the instrumental width. Under hot conditions, the last detected level of the nf series, $7f$, has a width of 210 cm^{-1}, and we simultaneously observe a significant broadening of the lines of the transitions from both levels of the $(^1F)^2F$ term and from one level of the $(^3D)^2D$ term. For the given plasma parameters, the primary mechanism for the broadening of the $9f$ and $10f$ levels is the static broadening due to the linear Stark effect.[6] Estimates show that the Stark widths of these levels overlap, and for the widths of the levels of the $3p^53d\,4s$ configuration we should expect the limiting values according to (2). Table I shows that this expectation is confirmed. The composition of the wave functions in Table I and the interaction matrix elements required for the calculations were found by the Hartree-Fock method. It should be noted that in certain cases simply an understanding of the mechanism for the broadening of the levels of mixed terms makes it possible to unambiguously test the validity of an identification of a spectrum. For example, in the case of the VV $(^3D)^2D$ levels, whose configurational interaction with the $3p^6nl$ Rydberg series is zero, only a level with a noticeable presence of the ^2F or ^2P term could undergo a broadening. Table I shows that this property is exhibited only by the level with $J = 5/2$. This result means that the level of energy 500502 cm^{-1} which undergoes a broadening in VV should be identified as $(^3D)^2D_{5/2}$, not $(^3D)^2D_{3/2}$, as was done erroneously in Ref. 4.

TABLE I

Term	JE, cm^{-1}		Composition	Γ, cm^{-1}	
				Theo.	Expt.
$(^1F)^2F$	7/2	497 556	$0.928(^1F)^2F$	70	65^{+8}_{-19}
$(^1F)^2F$	5/2	496 296	$0.762(^1F)^2F + 0.430(^3D)^2D$	47	42^{+6}_{-14}
$(^3D)^2D$	5/2	500 502	$0.864(^3D)^2D + 0.456(^1F)^2F$	17	20^{+3}_{-9}
$(^3D)^2D$	3/2	500 117	$0.992(^3D)^2D$	0	< 3

In the case of TiIV, in the course of analyzing the spectrum (the results will be published separately), we observed a broadening of lines of the transitions $3p^63d$–$3p^53d^2(^1G)^2F$. The $(^1G)^2F$ levels with an energy of 283055 cm^{-1} and $J = 7/2$ and with an energy of 281812 cm^{-1} and $J = 5/2$ lie ~7000 cm^{-1} above the $3p^65f$ levels. For the values of the plasma parameters which we have, the maximum width of the $5f$ levels is 87 cm^{-1}. The relation between the width and the level spacing shows that in this case the broadening should have a linear dependence. Measurements at two points yield $\Gamma[(^1G)^2F] \sim 0.3\Gamma(5f)$. The coefficient in the linear dependence agrees with estimates of the interaction of levels based on an analysis of the quantum defect of the series.

In an analogous way, we could work from Fano's theory[2] to derive an expression for the shift of a level of a mixed term due to the broadening of levels of a Rydberg series. In the cases which have been studied experimentally, no shift has been observed, but the possibility of such a shift should be taken into account in precise measurements of the energies of levels of mixed terms.

Finally, we note that Garton *et al.*[7] have also observed a broadening, in the plasma in a shock tube, of the levels of a doubly excited BaI configuration lying below the ionization boundary. The broadening was interpreted as an autoionization due to a lowering of the ionization boundary and led to the introduction of the term "forced autoionization." Estimates show, however, that the static electric fields which would be possible in the plasma of a shock tube and also the charged-particle densities would be insufficient for the necessary lowering of the ionization boundary. The most probable explanation is that a line broadening corresponding to the model described above was observed in Ref. 7, and forced autoionization was observed only in recent laser-spectroscopy studies of the Rydberg states of atoms in external fields (see Ref. 8 and the bibliography there).

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