Broadening of a valence autoionization resonance in electric fields

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We have observed a doubly excited autoionization resonance to broaden with increasing electric field. This broadening is consistent with the quadratic field dependence predicted by a simple perturbative model, but the magnitude of the observed broadening is about four times larger than predicted. Possible reasons for this discrepancy are discussed.

We have observed a relatively narrow autoionizing (AI) resonance to broaden monotonically as an applied dc electric field is increased. We have compared our results to a simple model which predicts that the width should increase quadratically with the field. At sufficiently high fields this effect should be able to broaden a narrow resonance up to widths of several hundred inverse centimeters. Such a large effect could provide a new tool for plasma diagnostics.

The observed state is broadened when the electric field mixes (dipole couples) it with a broader state of opposite parity. Figure 1 illustrates the case for our experiment. A very broad odd-parity $^1P_1^o$ strontium AI resonance rises above the first ionization threshold. The zero-field width of the nearby $^1D_2$ level is 350 times narrower than the broad $^1P_1^o$ resonance. As an external electric field is applied, the narrow level mixes with the broad one (eigenstates in the field will have mixed parity), thus sharing its AI decay channels with the broader level and broadening accordingly.

A simple perturbative model for this phenomenon, presented by Jacobs and Davis,[1] states that the field-induced width in an electric field F of a state "i" which is AI metastable in zero field is

$$\Gamma_i = \sum_j \frac{|p_{ij}|^2 F^2}{|E_i - E_j|^2 + \frac{1}{4}\Gamma_j^2} \Gamma_j \ , \tag{1}$$

plus interference terms, where the Γ_j are the zero-field AI rates (widths) of the j levels which are coupled to the opposite-parity i level by the field. The dipole coupling is given by $p_{ij} = e\langle i \mid r\cos\theta \mid j\rangle$. We show below that if the narrow level i has a non-negligible width Γ_0 in zero field, then one can replace $\Gamma_i \rightarrow \Delta\Gamma_i = \Gamma_i - \Gamma_0$ in the above expression.

This is analogous to the line broadening by field mixing of bound levels. For example, in hydrogen the bound metastable $2s$ level field mixes with the relatively broad $2p$ levels.[2,3] As the electric field is increased, the $2s$ will increasingly mix with the $2p$ levels; it radiative decay rate, and thus its width, will increase quadratically with the field. Indeed, Eq. (1) is equivalent to Eq. (76) of Lamb and Retherford[3] for the field quenching of the $2s$ by field mixing with the $2p$. The mixing effect, however, will begin to saturate when the field is high enough that the width of the narrow level becomes comparable to that of the broad one (i.e., when complete mixing is approached). Then a nonperturbative theory must be used. Validity cri-

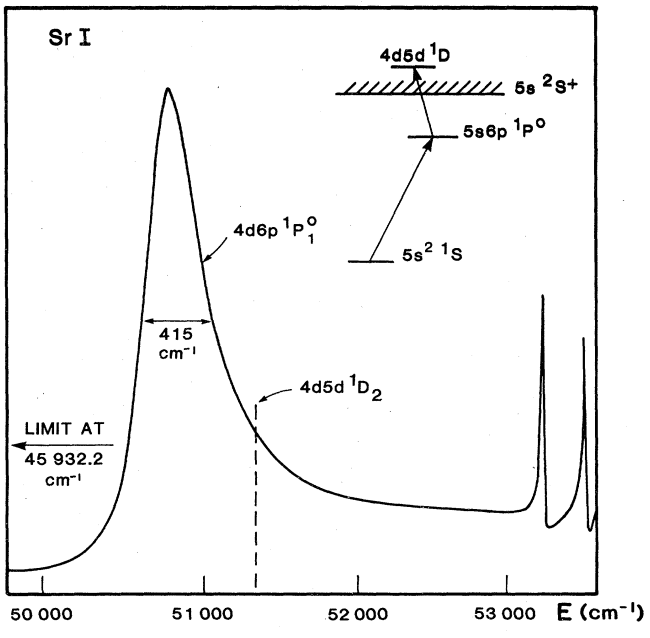

FIG. 1. Spectrum above the ionization threshold of neutral strontium. The solid line indicates the odd-parity spectrum derived from Ref. 21. The dashed line indicates the position of the narrow even-parity $4d\,5d\ ^1D_2$ resonance. The inset depicts the laser excitation scheme.

teria for use of the perturbation theory will be discussed below.

To put our experiment in context, we briefly recall some previous studies of Stark effects on AI resonances: Stark and Zeeman quenching of metastable AI resonances in alkali-metal atoms were observed by Feldman and Novick.[4] In a relativistic H^- beam, the sharp $^1P^o$ resonance was observed to form a triplet whose splitting increased linearly with the field;[5] this Feshbach resonance is quasidegenerate with the 200 times broader ^1S shape resonance, and theoretical interpretations of this effect have used degenerate models.[5–7] Freeman and Bjorklund[8] observed an apparent broadening of Rydberg AI levels at level anticrossings; this effect has since been studied in detail by others.[9,10] Field effects observed for alkali metals[11–15] below and near the zero-field-ionization threshold have been treated in a theory by Harmin.[16] Doubly excited states below the zero-field threshold have been observed to broaden[17–19] ("forced autoionization") when the electric field exceeds that required to lower the ionization threshold below the energy of the level.

The present experiment concerns the effect of electric fields on valence (relatively tightly bound, low-n) doubly excited resonances which lie near to but above the zero-field threshold. For atoms with more than one valence electron, this spectral region frequently contains very broad AI resonances with which narrow resonances of opposite parity can be field mixed. The field-induced width increases monotonically with electric field, in contrast to the cases of forced autoionization or level anticrossing. This effect can broaden a resonance by up to 3 orders of magnitude, depending on the relative widths of the levels being mixed.

Our experiment was performed with an atomic beam of Sr using multistep laser excitation. A thermal beam was passed through two parallel electric field plates where it intersected two overlapping laser beams. A frequency-doubled pulsed dye laser (polarized perpendicular to the dc field) with 0.1-cm^{-1} bandwidth excited the Sr ^1S ground state to the $5s6p$ $^1P^o$ level ($E=34098$ cm^{-1}). The second dye laser (polarized parallel to the dc field) with 0.1-cm^{-1} bandwidth was scanned over the region of the $4d5d$ $^1D_2$ resonance ($E=51345$ cm^{-1}),[20] which lies in the near wing of the broad $4d6p$ $^1P_1^o$ resonance ($E=50770$ cm^{-1}).[21] See Fig. 1. Ions produced by AI passed through a fine wire mesh in one field plate and impinged on a linear-focused electron multiplier. Careful linearity checks demonstrated the necessity of keeping the power density of the scanning laser very low to avoid broadening by depletion of the intermediate level. The field plates were held at a separation of 0.25 cm by "C-shaped" ceramic pieces on the outside of the plates, which allowed fields up to 130 kV/cm.

We observed the width of the Sr $4d5d$ ^1D level to increase monotonically with the electric field. After subtracting the measured zero-field width, $\Gamma_0=1.2$ cm^{-1}, a least-squares fit yielded $(\Gamma-\Gamma_0)=6.5\times10^{-10}F^m$, where F is the electric field in V/cm and $m=1.8(4)$. (Quoted uncertainties correspond to two standard deviations.) Due to technical limitations, shift measurements were not made. The best-fit quadratic field dependence ($m=2$) is indicated in Fig. 2. Comparing our data with Eq. (1), we obtained $p=5.8(9)ea_0$ for the dipole matrix element between the two AI resonances in Fig. 1.

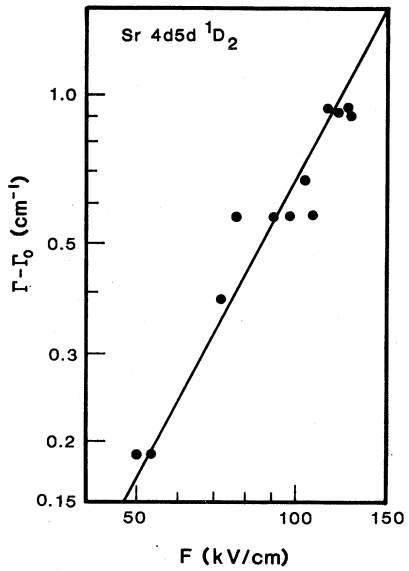

FIG. 2. Field-induced width (with zero-field subtracted) of the $4d5d$ $^1D_2$ line of Sr. The solid line represents the best-fit quadratic field dependence.

A frozen-core multiconfiguration Hartree-Fock (MCHF) calculation yields a value of $p=3.0ea_0$ (the Coulomb approximation yields $4.5ea_0$), a factor of 2 less than the value derived by applying a two-level bound-bound field-mixing model [e.g., Eq. (1)]. An error of this size in the atomic dipole would be unexpectedly large. The MCHF energies agree with the experimental ones to within 0.04% and adding more configurations to the seven used in the calculation

$$\psi_{^1P_1^o}=0.850\psi_{4d6p}-0.119\psi_{4d4f}-0.513\psi_{5p6s}\ ;$$

$$\psi_{^1D_2}=0.962\psi_{4d5d}+0.187\psi_{5p^2}-0.162\psi_{4f5p}-1.112\psi_{4d6s}$$

did not significantly change the value of p.

We have only included one level in the sum of Eq. (1), but from Fig. 1 it is clear that the "$4d6p$ $^1P_1^o$" is the only significant perturbing P level, and our analysis indicates no significant perturbing F levels. According to Ref. 20, the next-nearest perturbing odd-parity levels are the $4d6p$ $^3P_2^o$ at 49 731.7(1) cm^{-1} and the $4d4f$ $^3F_2^o$ ($^1D_2^o$) at 53 184.65(8) cm^{-1}. The energy uncertainties are those quoted by the authors,[20] and presumably reflect the width of these levels. For both levels, the product $\Gamma_0/|E_i-E_j|^2$ is much smaller than for the $4d6p$ $^1P_1^o$ level, and therefore it appears safe to neglect them.

Above we have mentioned the sources of error in the atomic physics quantities (dipole matrix element, inclusion of sufficient perturbing levels) which are put into the simple model given in Eq. (1). Below we discuss briefly the possible shortcomings of the model itself. These fall primarily in two categories. First, the model represents a lowest-order perturbation approach and one might ask whether this is valid if the observed level falls energetically in the near wing of the broad level (see Fig. 1). Second, the model considers only the field mixing of

the discrete part of the AI wave functions, and the question arises as to whether continuum-continuum mixing can play a role in the observable.

A validity criterion for using perturbation theory for the effect of discrete-discrete field mixing on the narrow level can be shown[22] to be roughly given by $2pF < \Delta E$ where ΔE is the energy separation between the levels. If this condition is satisfied, the results predicted by the simple perturbative model for both the shift and the broadening of the narrow level are reasonably close to the "exact" theory's predictions, even when the energy difference is small compared to the width of the broad level. We emphasize that this is not true at all for the broad level, for which interference effects predominate and the perturbative model is not even qualitatively correct,[22,23] as is also the case with the narrow level outside the above validity criterion. In the present experiment $2pF/\Delta E = 0.08$, so the above condition is satisfied.

Up to this point, we have treated the autoionizing levels as though they were simply broadened discrete levels with symmetric Lorentzian profiles. In fact the wave function for autoionizing resonances is a superposition of "discrete" (ϕ) and continuous (ψ) parts[24]

$$\psi_E = a_E\phi + \int b_{E,E'}\psi_{E'}dE' \,. \tag{2}$$

The width of a resonance ψ_E is given by its autoionizing decay rate (ignoring the radiative decay rate) and is equal to[24] $\Gamma = 2\pi |\langle \phi | r_{12}^{-1} | \psi_{E'} \rangle^2|$ where r_{12}^{-1} is the electron-electron interaction which is responsible for the configuration interaction between the discrete and continuous parts. Equation (1) accounts only for the *bound-bound* coupling of two resonances by the electric field.

Let us consider a perturbative model which attempts to account for continuum mixing by an electric field. If we apply an electric field, we couple states of opposite parity. Three types of dipole coupling arise: bound-bound $\langle \phi^o | p_z | \phi^e \rangle$, bound continuum $\langle \phi^{o,e} | p_z | \psi^{e,o} \rangle$, and continuum-continuum $\langle \psi^o | p_z | \psi^e \rangle$. The bound-bound coupling gives rise in lowest order to Eq. (1). The bound-continuum dipole coupling is zero in the uncorrelated electron approximation because a one-electron operator "p_z" cannot couple two states that differ in two electrons (e.g., $Sr^{**} \rightarrow Sr^+ + e^-$). To include the continuum-continuum coupling, we use a perturbation expansion for the wave functions in a field F, assuming for simplicity that we have only one continuum of each parity

$$\phi_m^{(e)}(F) = \phi_m^e + F \sum_{n \neq m} \langle \phi_n^o | p_z | \phi_m^e \rangle \phi_n^o (E_m - E_n)^{-1} \,,$$

$$\psi_E^{(e)}(F) = \psi_E^e + F \int \langle \psi_{E'}^o | p_z | \psi_E^e \rangle \psi_{E'}^o (E - E')^{-1} dE' \,,$$

with analogous expressions of $\phi^{(o)}$ and $\psi^{(o)}$. (One takes the principal value of the above integral when $E \simeq E'$. The superscripts in parentheses indicate the parity of the level in zero field.) We wish to evaluate the autoionization decay widths of the resonances associated with each of the discrete levels, which are prediagonalized to lowest order by the above equations. (For a more general treatment, see Ref. 22.) We refer to Sec. IV of Fano's paper,[24] where he showed that the energy configuration-interaction matrix elements $V_n = (\phi_n | H | \psi_E)$ add quadratically for different continua, yielding in this case

$$\Gamma^{(e)} = |\langle \phi^{(e)} | H | \psi_E^{(e)} \rangle|^2 + |\langle \psi^{(e)} | H | \psi_E^{(o)} \rangle|^2 \,, \tag{3}$$

where $H = H_0 + \mathbf{p}\cdot\mathbf{F}$. ($\Gamma^{(e)}$ refers to the resonance which is even parity in zero field.) An analogous expression holds for $\Gamma^{(o)}$. Evaluating the change in width due to a field, $\Delta\Gamma^{(e)} = \Gamma^{(e)} - \Gamma^e$, with the aid of the above expressions and the substitution $\bar{p}_n = p_n/(E_m - E_n)$, we obtain

$$\Delta\Gamma_m^{(e)}(F) = 2\pi F^2 \left\{ |\Sigma \bar{p}_n V_n^o|^2 + \left| \int \bar{p}_{E'} V^e dE' \right|^2 + \left[\left\{ \Sigma \bar{p}_n^* V_n^{o*} \int \bar{p}_{E'} V^e dE' + \Sigma \bar{p}_n^* V^{e*} \int \bar{p}_{E'} V_n^o dE' \right\} + \text{c.c.} \right] \right\} + O(F^4) \,. \tag{4}$$

The first term in Eq. (4) is equivalent to Eq. (1); it represents the effect of bound-bound mixing. The second term represents continuum-continuum mixing, and the final two terms arise from interference. These three types of terms scale as Γ^o, Γ^e, and $(\Gamma^e\Gamma^o)^{1/2}$, respectively. In our experiment $\Gamma^o = 415\ \text{cm}^{-1}$,[21] $\Gamma^e = 1.2\ \text{cm}^{-1}$, and thus $\Gamma^o/\Gamma^e \simeq 350$. In this case the first term clearly dominates since this ratio is so large, and since the spacing ΔE is only about three times the half-width ($\Gamma^o/2$) of the broad line; also, bound-bound dipole matrix elements are generally larger than free-free. Thus, according to this perturbative model, it appears continuum mixing effects are small in this case, and cannot account for the discrepancy between measured and computed values of $\Delta\Gamma^{(e)}$. This conclusion is consistent with the fact that the electron-electron interaction that gives rise to the bound-continuum coupling occurs in the atomic core, where the external electric field has negligible influence.

In conclusion, the reason(s) for the factor of 4 discrepancy between our measured field-induced width and the model of Eq. (1) are presently unclear. The possibilities we know of are the following: an unknown systematic error in the experiment, an unknown perturbing odd-parity level, an error of a factor of 2 in the dipole matrix element in Eq. (1), continuum-continuum mixing effects, or the marginal validity of the perturbative model due to the fact that $|E^e - E^o| \gg \Gamma/2$ is not satisfied (see Fig. 1). As discussed above, none of the above theoretical possible explanations appears particularly likely. Further studies, perhaps in barium, are certainly warranted. Any future measurements should be done in a regime where careful shift measurements can be performed as well.

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