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Effects of configuration interaction between autoionization and Stark-state resonances

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Strong interference effects have been found in the electric-field-induced autoionization signal of an isolated, doubly excited bound state in Ba. These interferences arise from interaction with narrow, long-living Stark resonances, which exist degenerately with a quasicontinuum of rapidly ionizing Stark states in the neighboring channel. By comparison with a theoretical model we conclude that the configuration interaction is energy dependent and increases by about a factor of 2 in the center of each Stark resonance.

Atomic states in the presence of an external electric dc field (Stark states) are profoundly different from their zero-field counterparts, particularly if the Coulomb binding energy is at all comparable with the potential energy in the electric field. In this case, initially bound states may even field ionize at an appreciable rate, forming a quasicontinuum of Stark states once their width becomes larger than the energy separation between the states. This continuum, however, differs from a regular Coulomb continuum by its structure in energy, i.e., isolated, long-living Stark resonances (having a large amplitude near the center of Coulomb attraction) can exist degenerately with the rapidly ionizing Stark states which add up to the quasicontinuous background.[1,2] These resonances have been observed by the modulation they introduce in the energy dependence of the photoabsorption matrix element. In this paper, we report the first observation and theoretical interpretation of the strong energy dependence in the *configuration interaction* between the Stark resonances and an autoionizing state, leading to characteristic, field-dependent interference structures in the autoionization line shape. We have observed these interferences in the photoabsorption of the Ba $5d7d\,^1D_2$ state, which, at zero field, lies about 200 cm^{-1} ($\frac{1}{40}$ eV) below the first ionization limit Ba$^+6s_{1/2}$. At field strengths above $\sim$1 kV/cm, the Stark quasicontinuum in the Ba$^+6s_{1/2}$ channel extends below the $5d7d$ state and its presence causes the state to autoionize, a phenomenon which has previously been called "forced autoionization."[3]

To illustrate the experimental procedure first, we show in Fig. 1(a) a zero-field photoabsorption spectrum of neutral Ba in the energy region of interest. As in previous experiments,[4] the photoabsorption signal in our two-step laser excitation was obtained by collecting the Ba$^+$ ions resulting from forced autoionization, or, in the zero-field case, pulsed-field ionization. The first laser drives the $6s^2\,^1S_0\rightarrow 5d6p\,^3D_1^0$ transition; thus we excite in the second step mainly discrete members of series converging to one of the Ba$^+5d_{3/2,5/2}$ ionization limits. Configuration interaction with the neighboring Ba$^+6s_{1/2}$ continuum (autoionization) causes the width of the structures above the Ba$^+6s_{1/2}$ ionization limit I_0 (at 42 035 cm^{-1}). Interaction with the discrete $6snd\,^1D_2,{}^3D_2$ Rydberg series gives rise to the discrete absorption structures in the vicinity of our particular state of interest, $5d7d\,^1D_2$ at 41 841 cm^{-1}.[5] A second Rydberg state perturber (at 41 933 cm^{-1}) can be seen, but will be disregarded in this paper.

Figure 1(b) shows the absorption in the same energy region, at an applied field strength of 7.5 kV/cm.

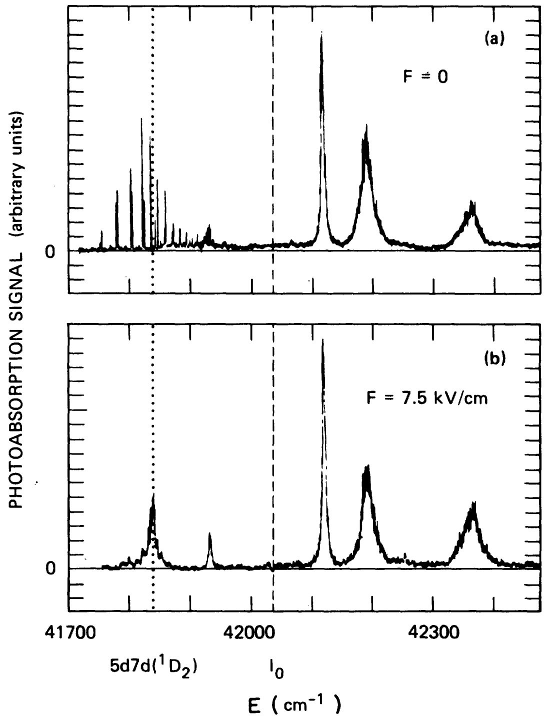

FIG. 1. Two-step photoexcitation signal of atomic Ba via the $5d6p\,^3D_1$ intermediate state at (a) zero field, and (b) an external electric field of 7.5 kV/cm.

As expected, the structures above and below I_0 are now qualitatively equal, since the classical ionization limit (saddle point) in the $Ba^+6s_{1/2}$ potential is now as low as about 41 500 cm^{-1}. We do not expect the autoionization lines to move in energy, since they are far (>5000 cm^{-1}) below the ionization limit of the series to which they belong. We are interested in the structure around 41 841 cm^{-1}, an expanded view of which is given in Fig. 2(a). This spectrum is again taken at 7.5 kV/cm; however, only $|m| = 1$ states have been excited by the appropriate choice of laser polarization. We find a smooth, slightly asymmetric line, which has negligible instrumental broadening because of the high-spectral resolution (~ 1 cm^{-1}) of our lasers.

The line shape observed in Fig. 2(a) implies that under these experimental conditions the $6s$ Stark continuum is essentially smooth and, hence, the forced autoionization may, to a first approximation, be viewed like zero-field autoionization. This suggests the use of a Beutler-Fano[6] profile to fit to the experimental signal [cf. Fig. 2(b)], yielding most importantly the numerical values for the resonance energy $E = 41\,846.3 \pm 2$ cm^{-1}, and the width $\Gamma = 15.5 \pm 1$ cm^{-1}, which is a direct measure of the interaction strength between the $5d7d\,^1D_2$ state and the smooth, fast ionizing $|m| = 1$ Stark continuum in the $Ba^+6s_{1/2}$ channel. Much like in a previous, low-resolution study,[7] these values indicate an interaction very similar to the interaction with a pure Coulomb continuum, as can be seen from the "zero-field prediction" shown in Fig. 2(b). This model absorption profile has been constructed using zero-field multichannel quantum defect theory (MQDT) parameters.[5,8] It is essentially what the $5d7d$ state would look like if the zero-field $6s$ ionization limit lay below it. Despite the good agreement, we note a slight difference in the resonance energies, and, more significantly, a difference in the width of the two lines, indicating that autoionization in an electric field is somewhat slower than comparable zero-field autoionization into a pure Coulomb continuum.

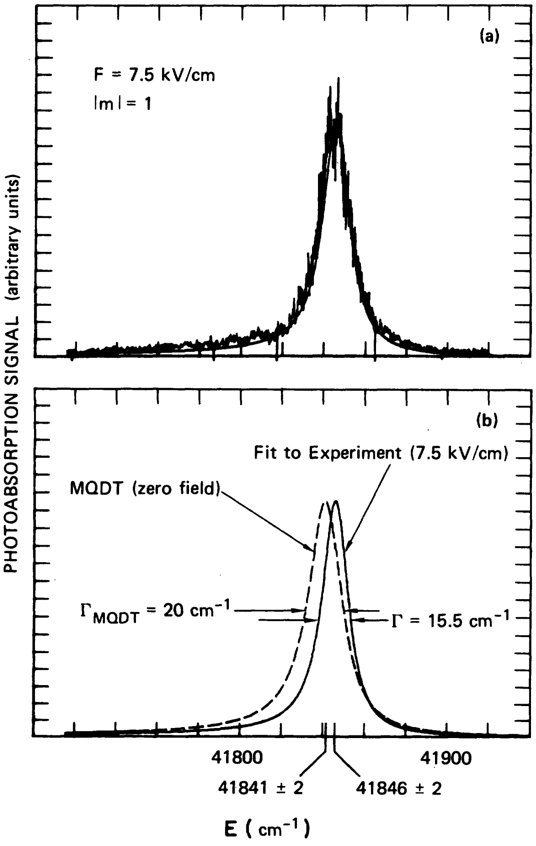

FIG. 2. (a) $|m| = 1$ state "forced-autoionization" signal at 7.5 kV/cm around the $5d7d\,^1D_2$ energy, showing practically no structures arising from Stark resonances. Solid line is the Beutler-Fano fit line. (b) Comparison between the fit-line and the "zero-field prediction" (dashed curve), constructed from MQDT parameters.

The breakdown of this model calculation can be demonstrated most drastically if we apply a field of 4.8 kV/cm and excite only $m = 0$ states (by polarizing both lasers parallel to the electric field). As shown in Fig. 3(a), the signal is now highly structured, though the overall shape still follows the line shape obtained with the $|m| = 1$ states at 7.5 kV/cm [Fig. 2(b)]. This can be seen more clearly by subtracting the fit curve of Fig. 2(b) from the experimental signal in Fig. 3(a). We obtain a difference signal which is mostly zero, except for certain, well-localized Stark resonances, which are expected to occur under these experimental conditions[4] [solid line in Fig. 3(b)]. However, the amplitude of the structures exhibits a conspicuous, dispersionlike behavior near the center energy of the autoionization resonance, $E_0 = 41\,846.3$ cm^{-1}. To display and investigate this behavior in more detail, we have varied the field strength in small (90 V/cm) steps between the values of 4.8 and 3.3 kV/cm. Three typical spectra, with the fit curve from Fig. 2(b) being subtracted, are shown in Figs. 3(b)–3(d) (solid lines). To a good approximation, the Stark-resonance positions varied linearly with the electric field strength. The amplitude, and also the width of the structures, changed dramatically as the Stark resonances moved across the autoionization resonance, as can be seen by the one Stark resonance marked by an (×) in Figs. 3(b)–3(d).

The observed interferences are solely caused by the non-Coulombic properties of the Stark continuum; hence their theoretical description is outside the scope of current atomic MQDT treatments. Therefore, our theoretical description[9] of the observed structure is based on Fano's configuration-interaction theory.[6] Our basic assumption is that both the direct photoexcitation matrix element T_{iE} from the inter-

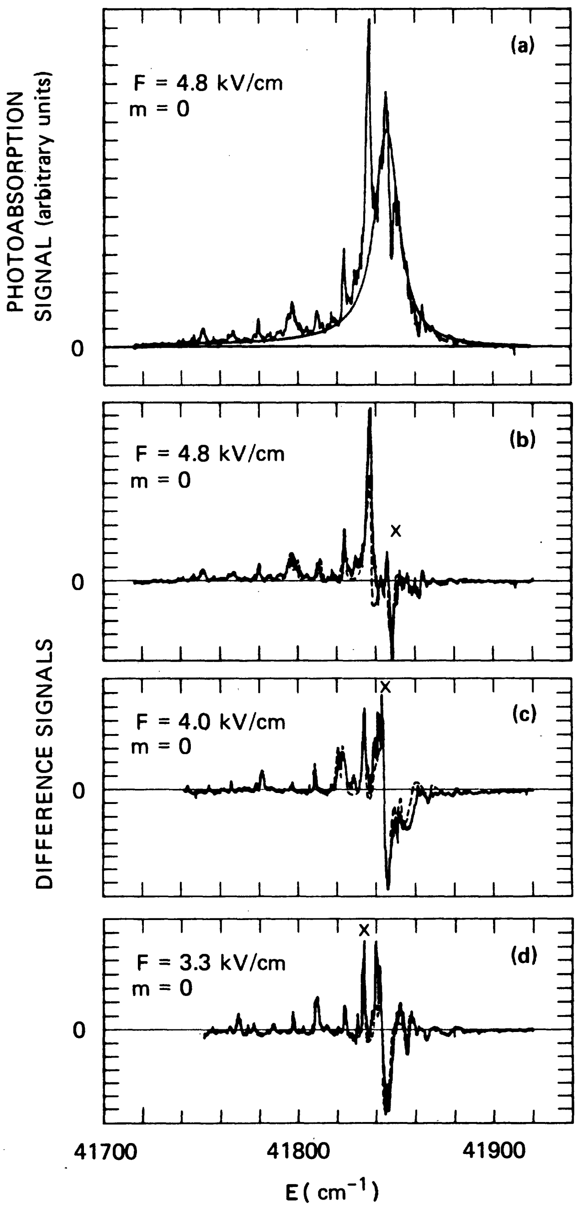

FIG. 3. (a) Signal at 4.8 kV/cm and excitation of $m = 0$ states, showing narrow Stark resonances on top of autoionization resonance. Solid line is the Beutler-Fano curve from Fig. 2(a). (b)–(d) Difference between the experimental signal and the Beutler-Fano curve at three values of electric field strength. Dashed lines: theoretical curves with $C = 2$. The position of one particular Stark resonance is marked by an × in all three figures, showing the dispersionlike behavior of the amplitude.

mediate state i to the $6s$ Stark-state wave functions, and the configuration-interaction matrix element V_E between the $5d7d$ bound state and the same $6s$ states, are strongly energy dependent. This establishes a sharp contrast to practically all previous zero-field studies of atomic autoionization, where both matrix elements are usually considered to be almost constant (ultimately allowing the familiar simple parametrization of a Beutler-Fano autoionization profile in terms of real, constant parameters[6]). In our model, the energy dependence of both matrix elements follows the energy dependence of the *density of Stark states near the nucleus* ($r \rightarrow 0$), which has recently been calculated for a hydrogenic model.[2] Using this result, we were able to obtain an exact expression for the theoretical signal intensity which contains only the energy dependence of the interaction matrix element V_E as a free parameter. The analytical form of V_E deviates from a constant value V_E^0 only in the region of the Stark resonances, where it may reach a maximum value CV_E^0 ($C \geq 0$, C is tentatively assumed to be the same for all Stark resonances). $|V_E^0|^2$ is immediately obtained from the width of Γ of the Beutler-Fano profile in Fig. 2(b).

The parameter C is obtained by fitting the dispersionlike behavior of the amplitudes in the region near the $5d7d$ term energy, between 41 800 and 41 900 cm^{-1} [cf. Figs. 3(b)–3(d)]. A fit curve, which follows closely the experimental signal, is shown as a dashed line in Figs. 3(b)–3(d). The good agreement between theory and experiment could only be obtained by assuming $C = 2 \pm 0.3$; i.e., the interaction between the $5d7d$ state and the center of a typical Stark resonance is about *twice as strong* as between the same $5d7d$ state and the smooth part of the Stark continuum. This result is, of course, consistent with the qualitative argument that the Stark resonances are characterized by their long lifetime in the vicinity of the nucleus, where the $5d7d$ state is also localized. Hence these states are expected to exhibit a stronger interaction than the rapidly ionizing Stark states which make up the smooth part of both the $m = 0$ and $|m| = 1$ Stark continuum.

We conclude that we have observed interference effects caused by a strongly energy-dependent configuration interaction between an autoionizing state and a "structured" Stark continuum. We note that the observed interferences are fundamentally different from possible asymmetries in the Stark resonances themselves, arising from their interaction with their own Stark continuum.[10] These asymmetries are due to an *intrachannel* interaction within the $6s$ channel and have been neglected in the present theory of a particular case of *interchannel* interaction. We also note that we have observed the strong resonance-resonance interaction in a "forced-autoionization" case, displaying most dramatically the limits of a previous approach using zero-field MQDT parameters to describe the observed line shapes.[7] However, since Stark resonances are known to occur even above the first ionization limit,[1,2] this phenomenon should, in principle, be observable also in some cases of normal autoionization.

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