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# Observation of Interferences between Discrete Autoionizing States in the Photoexcitation Spectrum of Barium

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(Received 17 July 1979)

Asymmetric satellites corresponding to interferences between $6p_{1/2}15d_{5/2}$ and $6p_{1/2}nd_{5/2}$ states ($n \neq 15$) in the autoionization spectrum of Ba for the transition $6s15d\,{}^1D_2 \rightarrow 6p_{1/2}$-$15d_{5/2}$ are observed. A simple line-shape theory based on first principles allows us to measure "two-electron" transition-matrix elements in terms of one-electron dipole-transition matrix elements. These values are compared to those calculated using a quantum-defect model which also explains the sign of the observed asymmetries.

The spectroscopy of doubly excited "two-electron" heliumlike atoms is frequently done by single-photon–absorption spectroscopy from the ground state to the autoionizing states lying within the continuum above the lowest ionization threshold. Therefore, the transition to the doubly excited autoionization state is necessarily a weak two-electron transition, comparable in strength to the direct "one-electron" photoionization transition at the same frequency. The interference between these two possible excitations yields asymmetric absorption lines commonly referred to as Beutler-Fano profiles. The asymmetries were first successfully explained by Fano,[1] who pointed out that the discrete autoionizing states are modified by the presence of the continuum through configuration mixing and that the existence of the two channels leads to interference effects. Fano's theory parametrizes each profile and determines for each level the position, the autoionization rate $\Gamma$, and a parameter $q$, which provides an estimate of the transition probability to the modified discrete state in terms of the transition probability to the unperturbed continuum. Although this theory is the cornerstone for analysis of autoionization measurements, it is, in practice, very difficult to check the validity of the extracted parameters by any alternative means.

We describe here the first observation, to our knowledge, of asymmetric Beutler-Fano profiles which are due to interferences between photoexcitations to different *discrete autoionizing states*.[2] Specifically, the observed interferences are between the $6s15d \rightarrow 6p_{1/2}15d$ and the $6s15d \rightarrow p_{1/2}nd$ ($n \neq 15$) excitations in the autoionization spectrum of Ba where $n$ ranges from 13 to 19 as shown in Fig. 1. The weak "two-electron" ($6s15d \rightarrow 6p_{1/2}nd$, $n \neq 15$) transitions[3] occur because the outer electron $nd$ orbital with the excited $6p_{1/2}$ core is not orthogonal to the $15d$ orbital with the $6s$ core. This measurement is of particular interest since

 

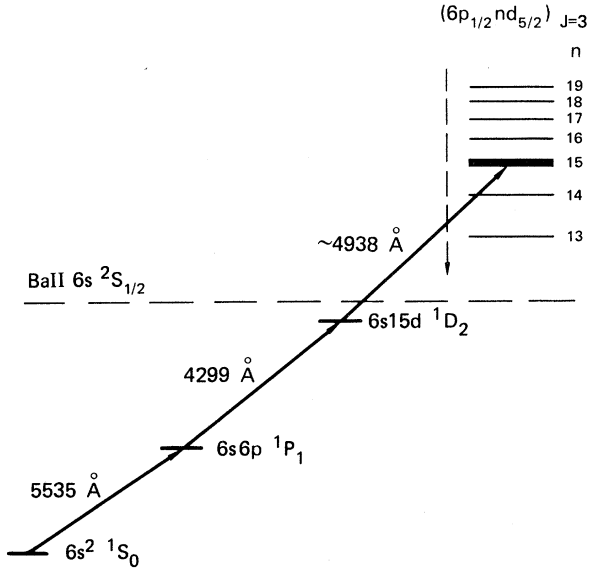


FIG. 1. Level diagram showing the states involved in the experiment. All lasers are $\sigma^+$ polarized to select one initial and one final state for each final $n$ level. The third laser at about 4938 Å is swept as indicated by the dashed arrow across the autoionizing Rydberg series.

we can independently measure the relative positions and autoionization widths of the $6p_{1/2}nd$ states and calculate in a straightforward way the relevant transition-matrix elements. With only these parameters we are able to calculate the interference line shape and compare it with our observations, in a sense the first independent confirmation of the Fano theory.

Since the $6s15d \rightarrow 6pnd$ ($n \neq 15$) transitions are weak, to observe them the laser must be intense enough that it saturates the strong $6s15d \rightarrow 6p15d$ transition; thus the saturation effects must be taken into account in calculating the line shape. Here we present only an outline of the line-shape calculation to convey the essence of the idea.

The total probability amplitude, $a(\nu)$, for excitation and subsequent autoionization of the initial $6s15d$ state by radiation of frequency $\nu$ is written as the sum of the amplitudes, $a_n(\nu)$, for autoionization through a given $6p_{1/2}nd$ state. The direct photoionization amplitude is estimated to contribute $\lesssim 1\%$ to $a(\nu)$, reflecting the strength of the $6s15d \rightarrow 6p15d$ transition, and is therefore ignored. Separating the largest amplitude, $a_{15}(\nu)$, we obtain

$$a(\nu) = a_{15}(\nu) + \sum_{n \neq 15} a_n(\nu). \quad (1)$$

$a_{15}(\nu)$ is determined by assuming that $a_n(\nu) = 0$ ($n \neq 15$) and solving the two-level problem using the rotating-field approximation[4] which takes into account saturation effects of the main transition. Once we solve the two-level problem, the $a_n(\nu)$ are obtained by using lowest-order time-dependent perturbation theory. The line shape $s(\nu)$ is then obtained by squaring Eq. (1),

$$s(\nu) = |a_{15}(\nu)|^2 + \sum_{n \neq 15} 2\,\mathrm{Re}[a_{15}^*(\nu) a_n(\nu)] + \sum_{n \neq 15} |a_n(\nu)|^2, \quad (2)$$

where we ignore terms of order $a_n^*(\nu) a_{n'}(\nu)$. Let us consider for a moment the correspondence of the terms of Eq. (2) with the observed line shape. For example, for $\nu$ in the vicinity of the $6s15d \rightarrow 6p16d$ transition, the first term corresponds to the wing of the saturated strong $6s15d \rightarrow 6p15d$ transition. The only important part of the second term is the dispersion term from the interference of the $6s15d \rightarrow 6p15d$ and $6s15d \rightarrow 6p16d$ amplitudes. The third term corresponds to the $6s15d \rightarrow 6p16d$ transition. From Eq. (2) it is apparent that observable asymmetries will only occur when $a_{15}(\nu) \sim a_n(\nu)$. The sign of the dispersion term depends upon both the signs of $a_{15}(\nu)$ and $a_n(\nu)$ and upon the sign of the detuning from the strong transition. As mentioned above, the probability amplitudes $a_n(\nu)$ may be calculated using the easily measured positions and widths of the states (the measurements will be described shortly) and the calculated transition-matrix elements $H'$ for the $6s15d \rightarrow 6pnd$ excitation followed by the $6pnd \rightarrow 6s\epsilon l$ autoionization. The transition-matrix element $H'$ may be written as

$$H' = \langle 6s\epsilon l | H | 6p\overline{nd} \rangle \langle 6p\overline{nd} | \mu | 6snd \rangle. \quad (3)$$

The bar indicates that the final $nd$ states have a $6p$ ion core. The first matrix element $\gamma_n = \langle 6s\epsilon l | H | 6p\overline{nd} \rangle$ is simply related to the autoionization rate $\Gamma_n$ by $\Gamma_n = \gamma_n^* \gamma_n$. The $6s15d \rightarrow 6pnd$ transition can be regarded as a transition of the $Ba^+$ core with the outer $15d$ electron making a slight readjustment in its orbit. Thus we may write the second matrix element $V_n = \langle 6p\overline{nd} | \mu | 6snd \rangle$ of Eq. (3), as the product of the ionic dipole matrix element and an overlap integral for the Rydberg electron in the $15d$ and $\overline{nd}$ states:

$$V_n = \langle 6p | \mu | 6s \rangle \langle \overline{nd} | 15d \rangle. \quad (4)$$

Since the ionic dipole moment $\langle 6p | \mu | 6s \rangle$ is independent of $n$, we have reduced the problem to calculating the overlap integrals $\langle \overline{nd} | 15d \rangle$ which,

since they are determined primarily by the contributions from the large radii of the Rydberg orbitals, may be calculated using the Coulomb approximation of Bates and Damgaard.[5] The method consists of using hydrogenic radial wave functions with a phase shift, $\Phi$, at the origin to account for the finite-sized ionic core. The phase shifts are determined for each state by measuring the binding energy $W$ of the state relative to an ion limit expressed as $W = -\frac{1}{2}(n-\delta)^{-2}$ where $\delta$ is the quantum defect of the state, a slowly varying function of $n$, the principal quantum number.[1] Since $\Phi = \pi\delta$, it is not surprising that the overlap integral depends only on the change in quantum defect, $\Delta$, between the $15d$ and $\overline{nd}$ state, and in particular if $\Delta$ changes sign so does the overlap integral. If we adopt the usual phase convention that for $r = 0$ the derivative of the radial wave function is positive, then we find that $\gamma_n$ has the same sign for all $n$. Therefore the line-shape theory predicts that the sign of the dispersion term in Eq. (2) and thus the sign of the profile asymmetry is totally determined by the sign of $\Delta$, the change in quantum defect, and the sign of the detuning from the strong $6s15d \rightarrow 6p15d$ transition.

The experimental apparatus has been described in detail elsewhere.[6] As indicated in Fig. 1, a beam of $6s^2$ Ba atoms is excited by two simultaneous laser pulses at 5535 and 4299 Å to produce the initial $6s15d\,{}^1D_2$ state. The third laser is delayed by 5 nsec and is used to drive the core to the $6p_{1/2}$ state. The spectrum shown in Fig. 2 is obtained by sweeping the frequency of the third laser near 4938 Å and detecting the ejected electrons from the autoionizing barium atoms. In general the satellite spectrum is complicated by transitions to $6pns$ states allowed by configuration mixing. However, by circularly polarizing all three lasers we force the $\Delta m_J = 1$ selection rule for each transition, thereby restricting the intermediate state to be ${}^1D_2(m_J = 2)$ and the final state to have $J = 3$. Since we are tuned to the $6p_{1/2}nd_j$ states, we reach only $6p_{1/2}nd_{5/2}$ states with $J = 3$, $m_J = 3$.

Next, by changing the initial state of our system to $6snd$ ($n \neq 15$) we drive the $6snd \rightarrow 6p_{1/2}nd$ ion transitions, as described above, at reduced laser power to avoid power-broadening effects. Since the lines show no evidence of direct photoionization (Fano $q$ parameters estimated to be $\gtrsim 10^4$) we can independently measure the linewidths, relative positions, and the quantum defects of the $6p_{1/2}nd$ states unambiguously. Equation (2) is then used to fit the spectra such as the one shown in Fig. 2 with the measured widths and positions of the satellite profiles fixed and the matrix elements $V_n$ varied to achieve the best fit. The fit to the spectrum of Fig. 2 is indistinguishable from the data at the scale of the figure. The inset in Fig. 2 shows a vertical expansion of the $n = 14$ and $n = 13$ profiles with the calculated fit given by the open circles. The dashed curve in Fig. 2 shows the Lorentzian curve of the $6s15d \rightarrow 6p15d$ transition in the absence of the satellites. If Fano's line shape[1] is applied to these satellite profiles, we obtain $q$ values in the range 1.85–2.76. These values should not be confused with the normal interpretation of $q$ as mentioned earlier; rather they provide us with a number which can be understood in the context of Fano's theory. We note in Fig. 2 that the satellites on both sides of the main transition have the same asymmetry. The line-shape theory then implies that $V_n/V_{15}$ changes sign from negative to positive as we tune across the strong transition toward the red.

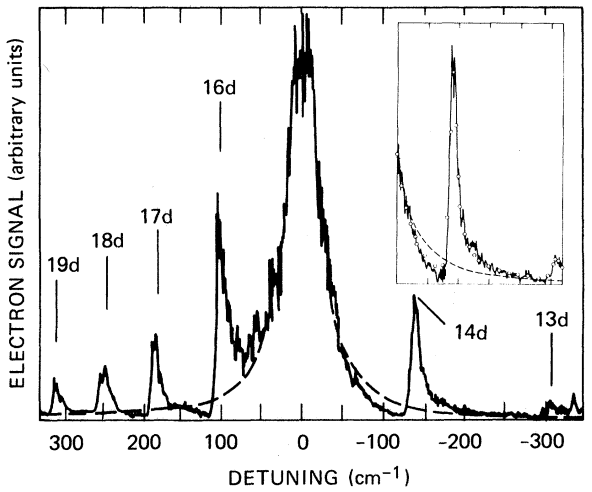


FIG. 2. Power-broadened spectrum of the $6s15d\,{}^1D_2 \rightarrow (6p_{1/2}15d_{5/2})_{J=3}$ transition in Ba showing asymmetric profiles. The dashed line shows the power broadened line in the absence of interferences. The sharp feature to the red side of the $13d$ profile is a Ba two-photon resonance at 4947 Å. The inset is a vertical expansion of the $14d$ and $13d$ profiles showing the theoretical fits to the data as open circles. Each division along the abscissa corresponds to 50 cm$^{-1}$. In the main figure the fit is indistinguishable from the data.

The test of the line-shape calculation is the comparison shown in Fig. 3 of the values of $V_n/V_{15}$ determined by fitting the observed line shape with those determined from the Bates-Damgaard

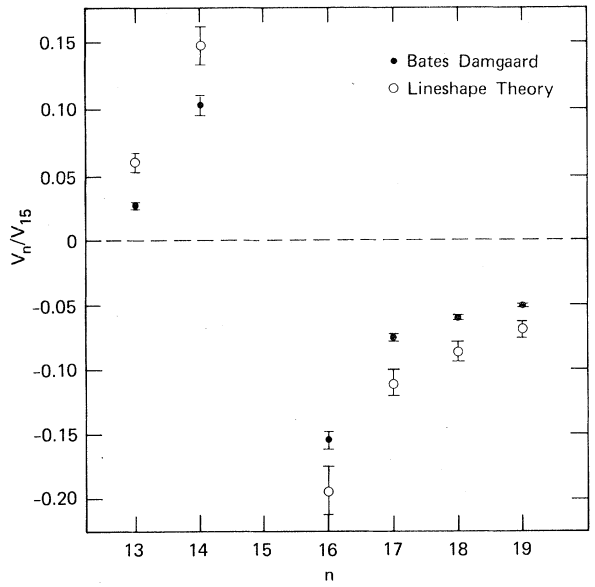


FIG. 3. Comparison of ratios of "two-electron" to one-electron matrix elements using the line-shape theory and the Bates-Damgaard procedure. The ratio at $n=15$ is unity.

calculation. The error bars on the experimental values for $V_n/V$ reflect the random scatter in the ratios of four line shapes such as Fig. 2 with the laser power varied to produce widths of the strong $6s15d \rightarrow 6p15d$ transition from 40 to 52 $cm^{-1}$. The agreement both in sign and magnitude between the calculated and observed matrix-element ratios strongly supports the line-shape theory and the accuracy of the Bates-Damgaard calculations, at least for $\Delta \sim -0.1$.

According to the line-shape theory, if $\Delta<0$, then on the red side of the main transition the profile asymmetries have the sign shown in Fig. 2, but should have the other sign if $\Delta>0$. In fact, as indicated by Table I, the Ba $6s14d$ state has an anomalous quantum defect due to the presence of the $5d7d$ perturber. Thus the $6s14d \rightarrow 6p13d$ transition, to the red of the strong $6s14d \rightarrow 6p14d$ transition, has $\Delta=+0.1$, and, in fact, we have observed experimentally that its asymmetry is reversed from those of Fig. 2, as predicted by the theory.

To our knowledge this is the first observation of Beutler-Fano profiles due to interference between discrete states where one can calculate the line shapes from first principles in terms of measurable quantities and compare the line-shape theory with an alternate physical model (quantum-defect theory in this instance). The success of the line-shape theory in explaining the observed spectra supports the two-step picture of autoionization as excitation followed by nonradiative decay.

In the cases studied here, where $|\Delta| \sim 0.1$, the Coulomb approximation accurately gives the sign of the matrix element. Since the asymmetry of the profile provides a sensitive test of this sign, it will be interesting to investigate the accuracy of the Coulomb calculations for small values of $|\Delta|$, $\sim 0.01$.

TABLE I. Autoionization widths and quantum defects of the $(6p_{1/2}nd)_{J=3}$ states and quantum defects of the $6snd\,^1D_2$ series of Ba.

| $n$ | $\Gamma$ ($cm^{-1}$) | $\delta[(6p_{1/2}nd)_{J=3}]$ | $\delta(6snd\,^1D_2)$[a] |
|---|---|---|---|
| 13 | 16.0(20) | 2.7038(50) | 2.66378 |
| 14 | 11.9(8) | 2.7622(50) | 2.7847 |
| 15 | 10.4(9) | 2.7766(50) | 2.6490 |
| 16 | 9.1(9) | 2.7893(50) | 2.6668 |
| 17 | 8.4(9) | 2.7874(50) | 2.6762 |
| 18 | 7.9(8) | 2.8143(50) | 2.6834 |
| 19 | 7.4(8) | 2.8393(50) | 2.6891 |

[a]See Ref. 7.

We would like to acknowledge helpful discussions with D. L. Huestis, D. C. Lorents, W. E. Cooke, and G. A. Ruff. This work was supported by the National Science Foundation under Grant No. PHY76-24541.

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