PHYSICAL REVIEW A VOLUME 30, NUMBER 1 JULY 1984

Enhancement of the autoionization rate of two-photon excited states of Ba $(6d_{5/2}nd_{5/2(3/2)})_{J=4}$ near the Ba^+ $6d_{3/2}$ limit

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(Received 13 March 1984)

We report the excitation of highly excited $6d_{5/2(3/2)}nd(ns)$ states of barium, which lie ~ 5.6 eV above the first ionization limit of Ba, using two-photon excitation from the bound $6snd(ns)$ Rydberg states. The two-photon excitation scheme requires rather modest laser power (~ 0.5 mJ), and the $(6d_{5/2}nd_j)_{J=4}$ states exhibit a sharp enhancement in the autoionization rate beyond $n=25$ which is accompanied by the onset of ejection of very-low-energy electrons (< 0.02 eV). We observe that the $6d_{5/2}nd_j)_{J=4}$ $(n > 25)$ states predominantly autoionize to the nearly degenerate $6d_{3/2}$ state of Ba^+. This result has important implications for the development of autoionization lasers and the phenomenon of dielectronic recombination.

Historically, autoionizing levels of metal atoms played a central role in understanding the phenomenology of autoionization.[1,2] Recent interest in autoionizing states of metal atoms[4–7] is motivated by interest in unraveling the short-range electron-core interaction, modeling energy loss due to dielectronic recombination in tokamak plasmas, and developing new lasers. Recent purely optical spectroscopy of the low-lying Ba $6pns$, $6pnd$, and $5dnd$ states have suggested that autoionization occurs predominantly to excited states of Ba^+. It was later shown explicitly by electron spectroscopy that 60–70% of the autoionization of the $(6p_{3/2}ns_{1/2})_{J=1}(n \geq 12)$ states that lie above the Ba^+ $6p_{1/2}$ ionization limit is to the $6p_{1/2}$ state of Ba^+.[8] In fact, this population inversion in the ion was used to develop the Ba^+ autoionization pumped laser.[9] While the details of the dynamical process leading to this observed autoionization phenomenon is yet unclear, it is evident that if this observation is more generally applicable to the higher-lying Ba autoionizing states then this will have important implications for the development of autoionization pumped lasers and the modeling of dielectronic recombination. Unfortunately it is experimentally difficult to use the resonant laser stepwise excitation scheme to pump high-lying autoionizing states via the low-lying series of autoionizing states[10] due to the inherently short lifetime of these states ($\sim 10^{-11}$ s).

In this Rapid Communication we report the excitation of high-lying autoionizing $6dnd(ns)$ states of Ba (5.6 eV above the first ionization limit) by a two-photon excitation process from the bound $6snd(ns)$ Rydberg states similar to that used by Jopson, Freeman, Cooke, and Bokor.[11] From the measurement of the linewidth of the two-photon excited $Ba(6d_{5/2}nd_{5/2(3/2)})_{J=4}$ states, we observe an enhancement in the autoionization rate for states that lie energetically above the $6d_{3/2}Ba^+$ limit $(n > 25)$. This enhancement in the autoionizing linewidth is accompanied by the onset of ejection of low-energy electrons (< 0.025 eV) from the $(6d_{5/2}nd_j)_{J=4}$ states with $n \geq 26$. From an energy analysis of the ejected electrons we infer that this enhancement is primarily due to the large autoionization rate of the $(6d_{5/2}nd_j)_{J=4}$ states to the $6d_{3/2}$ state of Ba^+.

Figure 1 shows the relevant energy levels of Ba. First, the $6snd\,^1D_2$ Rydberg state is populated by stepwise laser excitation through the $6s6p\,^1P_1$ state. In the second step, a third laser pulse excites the bound Ba Rydberg state to a doubly excited $6d_{5/2(3/2)}nd_j$ autoionizing state by a two-photon transition.

The experimental arrangement consists of a Ba atomic beam, which effuses from a resistively heated oven with a 0.14-cm-diam hole and passes between two parallel plates separated by 1 cm where the Ba atoms are excited to the $6d_{5/2(3/2)}nd$ states by the three lasers as shown in Fig. 1. All three dye lasers are pumped by the harmonics of the same Quanta Ray Nd:YAlG laser operating at 10 Hz. The first two dye-laser pulses with ~ 10-GHz linewidths (full width at half maximum) have typical energies of 50 μJ/pulse. The third dye laser has a 28-GHz linewidth and a typical energy of 2 mJ/pulse. The relative wavelength scale of the third laser is recorded by observing the transmission through a 3.52-cm^{-1} free-spectral-range etalon and the two-photon excitation of some low-lying autoionizing states via the $6s6p$-$6sns(nd)$ transition provides the absolute calibration (the second dye laser plays no role in populating these autoionizing states.) All three laser beams propagate collinearly and cross the Ba beam at right angles near the center of the plates. The electrons ejected following the excitation of these states can be energy analyzed by a 127°

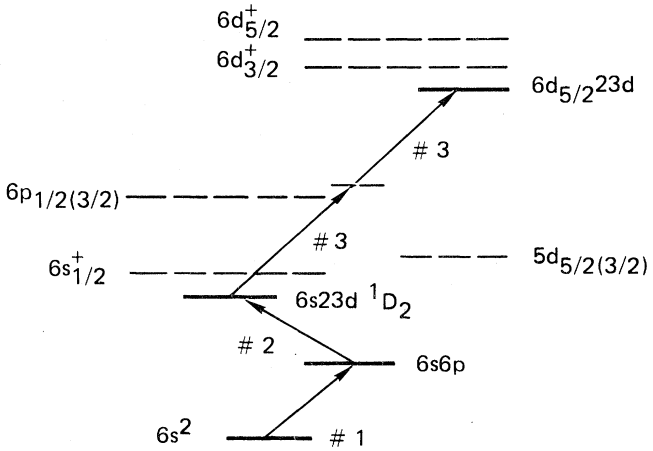

FIG. 1. Ba level diagram showing the relevant energy levels and laser pumping scheme. The first and the second dye lasers at 5535 Å, and populate the bound $6s23d\,^1D_2$ state. The third laser drives the $6s23d$-$6d_{5/2}23d$ two-photon transition.

electrostatic energy analyzer which is fixed below the 1-mm slot in the lower plate. The total ionization is determined by detecting the ions, which are extracted from the interaction region through a grid in the upper plate by applying a 400-V pulse to the upper plate and detecting with an electron multiplier.

A typical plot of the ion signal as the third laser wavelength is scanned, with no selectivity as regards to the final state of the Ba^+ ion, is shown in Fig. 2. In this scan the second laser is resonant with the $6s6p\,^1P_1 \rightarrow 6s23d\,^1D_2$ transition in Ba. The resonance in the ion signal seen in Fig. 2 is due to the two-photon excitation $6s23d\,^1D \rightarrow 6d_{5/2}23d_{5/2(3/2)}$ and subsequent autoionization. This ion resonance signal varies quadratically as the power of the third laser implying that the last laser drives a two-photon transition. The background varies linearly with the third laser power indicating that it arises from single photon absorption as expected.

To confirm that we are indeed exciting the $6d_{5/2(3/2)}nd(ns)$ states we perform the energy analysis of the electrons that result from autoionization. The solid trace in Fig. 3 shows the electron energy distribution when the third laser is tuned to the center of the resonance shown in Fig. 2, and the broken trace in Fig. 3 is a similar plot with the third laser tuned 10 cm^{-1} away from the two-photon resonance. In Fig. 3 the electron energy spectrum of the off-resonant excitation (broken trace) shows peaks at ~ 2.7 and 2 eV corresponding to single photon excitation at 4330 Å to the Ba^+6s and $5d$ continua, respectively. The electron energy spectrum of the on-resonant excitation (solid trace) is quite different. It exhibits a peak at 5.6 eV due to the autoionization of the $6d_{5/2}nd_j$ state to the $6s$ state of Ba^+, while the second peak at 4.9 eV is a result of autoionization to the $5d$ ion state. These two peaks are absent in the off-resonant excitation. In addition, we note a strong peak at

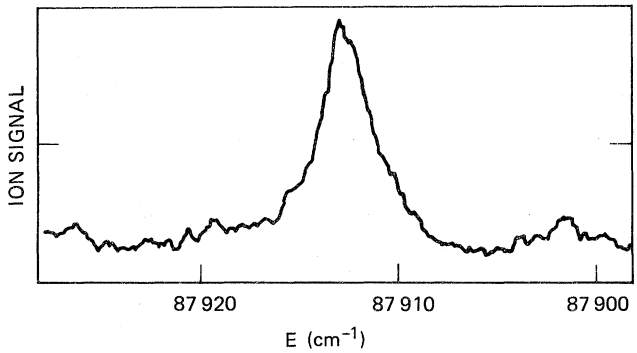

FIG. 2. Ion signal recorded as the third laser frequency is scanned. The first two lasers excite the Ba atoms to the $6s23d\,^1D_2$ state. The peak in the ion signal is a result of the two-photon excitation to the autoionizing $6d_{5/2}23d$ state.

2.9 eV due to autoionization to the $Ba^+\,6p_{3/2}$ state. This peak clearly overlaps the single photon peak at 2.7 eV which is actually diminished in the on-resonant excitation. In sum, the electron spectra confirm that the resonance seen in Fig. 2 is indeed a high-lying $6d_{5/2}23d_{5/2(3/2)}$ state.

One of the most interesting and fundamental aspects of the high-lying autoionizing states is the dynamics of their decay. The starting point of such an investigation is the measurement of the linewidth or the total autoionization rate of the $6d_{5/2}nd_j$ states as a function of n. Since the $6d_{5/2}nd_j$ states of several J values can be excited, we concentrate on substates of this series with $J=4$ by suppressing the excitation to states with $J \neq 4$ by circularly polarizing all the dye lasers. The width of the $(6d_{5/2}nd_j)_{J=4}$ states is determined by sweeping the frequency of the third laser, at low laser power, and recording an ion spectrum similar to the one shown in Fig. 2.

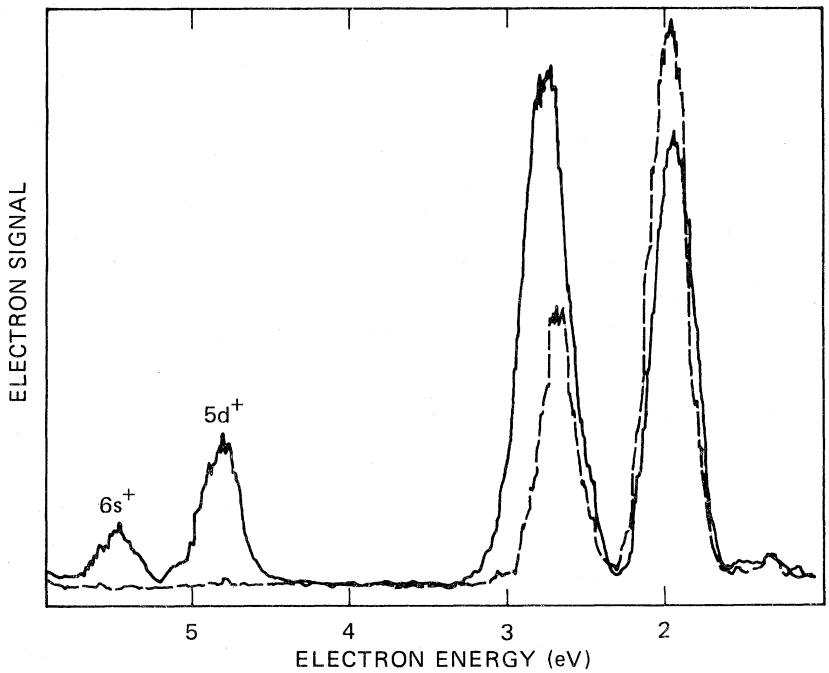

FIG. 3. Energy analysis of the electrons ejected from the autoionization of the $6d_{5/2}23d$ state (solid trace). The broken trace shows electron signal recorded with the third laser tuned 10 cm^{-1} off the two-photon resonance, and shows the extent of the background signal (see text).

TABLE I. Quantum defect (relative to the $Ba^+ 6d_{5/2}$ limit) and widths of the $Ba(6d_{5/2}nd_j)_{J=4}$ levels.

n	Quantum defect	width (cm^{-1})
16	3.050(10)	5.14
17	3.050(10)	4.26
18	3.055(10)	3.73
19	3.060(6)	3.70
20	3.072(5)	2.65
21	3.077(10)	1.96
22	3.075(10)	1.8
23	3.083(10)	1.8[a]
24	3.075(5)	1.7[a]
25	3.075(10)	1.7[a]
26	3.108(5)	2.60
27	3.070(10)	2.35
28	3.075(10)	2.30

[a]The widths of these states are laser-linewidth limited.

The observed quantum defect μ and the reduced width of the $(6d_{5/2}nd_j)_{J=4}$ states Γ are listed in Table I. In Fig. 4 (and Table I) we have obtained the reduced linewidth Γ from the actual observed linewidth Γ_{obs} by assuming that $4\Gamma_{obs}^2=\Gamma^2+4\Gamma_L^2$, where Γ_L is the third laser linewidth ($\Gamma_L=0.95\ cm^{-1}$). The accuracy of the quantum defect measurements is primarily limited by the error in the measurement of wavelength using the etalon, while the accuracy in the width measurements is primarily limited by $2\Gamma_L$. The most interesting aspect of our measurements is the behavior of the width of the $(6d_{5/2}nd_j)_{J=4}$ states as n is increased. Figure 4 shows the linewidths Γ plotted as a function of $(n^*)^3$ on a log-log scale ($n^*=n-\mu$ is the effective quantum number and μ is the quantum defect ~ 3.0). The broken line in Fig. 4 shows that the linewidth decreases as $(n^*)^{-3}$ from $n=16$ to 22 and again from $n=26$ and beyond. For an unperturbed autoionizing series the quantum defect is constant, while the linewidth scales as $(n^*)^{-3}$, a reflection of the fact that the Coulomb interaction between the Rydberg electron and the core electron scales as $(n^*)^{-3}$. For states with $n=23$ to 25 the linewidths Γ are clearly limited by the laser linewidth. Beyond $n=25$ the linewidth of the $(6d_{5/2}nd_j)_{J=4}$ states increases dramatically by almost 45%. In fact, the increase is perhaps higher than 45% because the measurement for the $(6d_{5/2}25d_j)_{J=4}$ state, for instance, is laser-linewidth limited. Since the linewidth of the states is proportional to the total autoionization rate, it is evident that at $n=26$, the autoionization rate increases dramatically. The most likely explanation for this increase in the total autoionization rate is an opening up of a new autoionization channel at $n=26$. To investigate this hypothesis we analyze the energy of the ejected electrons with the energy analyzer. The most interesting aspect of the electron energy analysis, similar to one shown in Fig. 3, is

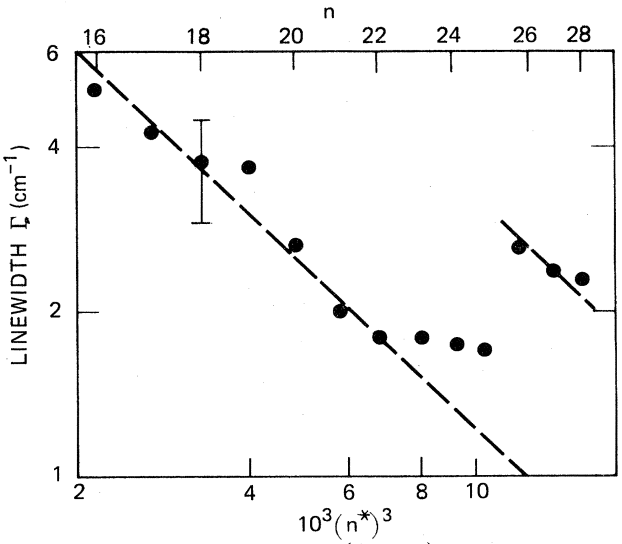

FIG. 4. Reduced width Γ of the $(6d_{5/2}nd)_{J=4}$ states plotted vs $(n^*)^3$ on a log-log scale. The width of the states with $n=22$–25 is laser-linewidth limited. The dashed line has a slope of -3.

the propensity of electrons ejected with very small energy <0.025 eV. Furthermore, electrons of this energy are not observed for the $(6d_{5/2}nd_j)_{J=4}$ states with $n<26$ or for any state of the $(6d_{3/2}nd_j)_{J=4}$ series. Using the value of quantum defect listed in Table I for the $(6d_{5/2}nd_j)_{J=4}$ series, it is evident that states with $n\geq 26$ lie energetically above the $6d_{3/2}$ limit of Ba^+. The autoionization of the $(6d_{5/2}nd_j)_{J=4}$ states to the $6d_{3/2}$ ion state thus becomes energetically allowed for $n\geq 26$. Our measurements not only indicate that the autoionization channel to the $6d_{3/2}$ state of Ba^+ opens up but show that this is a predominant channel (branching ratio $\geq 30\%$).

It has previously been observed in low-lying Ba autoionizing states that Ba states lying above the lower fine-structure level of a Ba^+ state and converging to the upper fine-structure level of the same Ba^+ state autoionize to the lower fine-structure level of Ba^+. These measurements reported here indicate the generality of this process. The generality of this process is important for at least two practical applications. First, this fine-structure autoionization should be included in modeling of dielectronic recombination. Second, nearly all of the energy put into the Ba autoionizing state resides in electronic excitation of the resulting Ba^+ ion. Thus the energy input is efficiently channeled into electronic excitation where it can be used, for example, to make a short-wavelength laser.

This work is supported by National Science Foundation Grant No. PHY-8306082.

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