Electron correlation in three-body Coulomb states of barium

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We excited a special class of states of a three-body Coulomb system, populating double Rydberg states of the type $Ngng$ [$N=5$–9, $n \gg N$ where N (n) is the principal quantum number of the inner (outer) valence electron] in Ba with both valence electrons in non-core-penetrating orbits with the same orbital angular momentum. Electron correlation effects manifest themselves by the appearance of additional $Nhnl$ resonances, a rapid increase of the observed quantum defects with N, as well as a significant decrease of the autoionization rate for $N=9$. [S1050-2947(96)50807-3]

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The three-body Coulomb problem of two excited electrons moving in the field of an ion still is an important issue in physics. Since Madden and Codling's pioneering single-photon absorption experiment [1], the doubly excited helium atom has become the prototype system for investigating the correlated motion of two electrons. Although most efforts in helium involve theoretical studies, important experimental progress has also been achieved by, e.g., Domke *et al.* [2] Many experimental studies of electron correlation in two-electron systems, however, have been performed on alkaline-earth atoms such as calcium, strontium, and barium. The reason for this is that the total binding energy of the two valence electrons of the heavier alkaline-earth atoms is relatively low (≈ 15 eV for Ba) when compared to He (≈ 80 eV). Their highly excited, autoionizing states are therefore accessible for resonant multiphoton laser excitation. The alkaline-earth atoms differ from helium because of their spatially extended 2^+ core. When a valence electron penetrates the core it experiences an incomplete screening of the nucleus, resulting in large quantum defects for states with low orbital angular momentum l ($l \leqslant 3$ for Ba). The l degeneracy, leading to the SO(4) symmetry, which is a characteristic of heliumlike systems [3], is thus removed. However, for high-l orbitals there is no significant overlap of the valence electron's wave function and the 2^+ core, due to the centrifugal barrier effect. Therefore, to excite three-body Coulomb states in alkaline-earth atoms, both valence electrons have to be promoted to high-l orbitals.

In recent years several groups reported on multistep pulsed laser excitation of $Nlnl'$ double Rydberg states of alkaline-earth atoms [N (n) is the principal quantum number of the inner (outer) valence electron] with both valence electrons in core-penetrating orbits [4–7]. Others investigated double Rydberg states with a non-core-penetrating inner [8] or outer valence electron [9]. The only true three-body Coulomb system having both valence electrons in non-core-penetrating orbits was realized by Eichmann, Lange, and Sandner [10] in a five-laser experiment on Sr. They observed so-called *planetary states*, for which the wave functions of the two valence electrons do not have significant overlap due to the large difference in their orbital angular momenta ($l=3$ for the inner and $l \geqslant 9$ for the outer electron). Here we report on observations of a different class of three-body Coulomb states in barium with two non-core-penetrating electrons in orbits with the same orbital angular momentum ($l=4$ for both electrons). In a systematic survey both the principal quantum numbers N and n were varied.

Double Rydberg $Ngng$ states of barium were excited, from the $6s^2$ ground state, in a multistep pulsed laser experiment following an isolated-core-excitation scheme [11]. The energy range studied (13–14.5 eV) includes states pertaining to the lowest Ba^+ level representing a non-core-penetrating inner valence electron ($N=5$, $l=4$), as well as states with a higher principal quantum number for this electron, up to $N=9$, for which the number of nearly degenerate ionic levels has increased to five. According to electric dipole transition rules eight photons (and therefore eight dye lasers) would be required to excite $Ngng$ states from the ground state. However, by making use of configuration interaction in the bound intermediate states, the final $Ngng$ states could be excited in a four-photon process in the sequence $6s^2 \rightarrow 5d6p \rightarrow 5dn''g \rightarrow 4fn'g \rightarrow Ngng$. For this excitation process four linearly polarized tunable pulsed dye lasers were used, pumped by two synchronized neodymium-doped yttrium aluminum garnet (Nd:YAG) lasers. All four (5-ns duration) laser pulses were temporally and spatially overlapped in the interaction region, where they perpendicularly intersected an effusive beam of barium atoms. During the laser excitation the interaction region is free of electric fields. The problem of l mixing in intermediate Rydberg states due to stray electron fields in so-called Stark switching experiments [12] was thus avoided. A detailed description of the first three steps of the excitation process, the experimental setup, and the detection method is reported elsewhere [13]. For the final excitation step the wavelength of a fourth laser was tuned in the range 370–700 nm around Ba^+ $4f \rightarrow Ng$ transitions with $N=5$–9. To suppress parasitic Ba^{2+} signal, produced by subsequent photoionization of Ba^+ ions produced in the autoionization process of the intermediate $4fn'g$ states, the method of excitation through zeros in the continuum [14] has been applied.

Figure 1 shows a typical example of a $6gng$ excitation spectrum, probed via an intermediate $5d26g$ state. The

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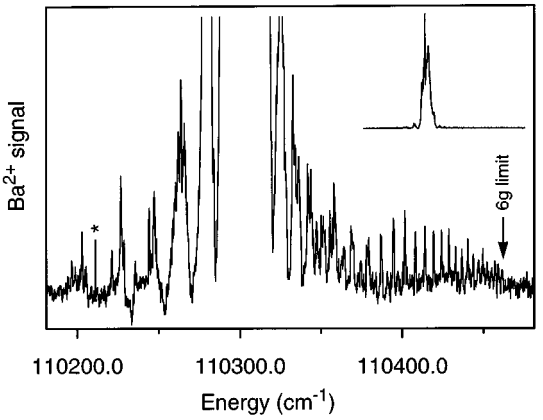

FIG. 1. Excitation spectrum of $6ln'l'$ states, recorded after near-resonant two-photon excitation from $5d_{5/2}26g$ $J=2$. The Ba^{2+} signal is plotted versus total excitation energy with respect to the $6s^2$ ground state. In the upper right-hand corner the full (saturated) spectrum is shown. The resonance denoted by an asterisk is a parasitic two-photon transition in the Ba^+ ion ($6p_{3/2}\rightarrow 8p_{3/2}$).

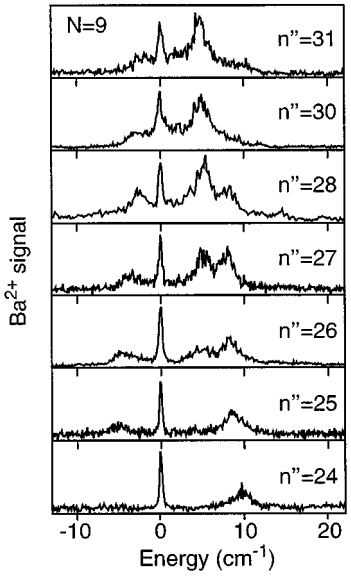

FIG. 2. Excitation spectra $5d_{5/2}n''gJ=2\rightarrow 9lnl'$ with $n''=24$–31. The sharp resonances correspond to Ba^+ $5d_{5/2}\rightarrow Ng$ transitions and are used for energy calibration. The energy scale is relative to the ionic transitions.

modulation in the central region of the excitation spectrum is determined by the Rydberg electron overlap integral for the ($5dn''g\rightarrow 4fn'g\rightarrow 6gng$) near-resonant two-photon transition [15]. At the high-energy side of the spectrum of Fig. 1 we observe a regular Rydberg series of narrow resonances. Assuming a constant quantum defect along this series the ionization limit is determined at 110 508.8(5) cm^{-1}, which is in excellent agreement with a calculated value for the $6h$ limit of 110 508.63 cm^{-1}. This value was obtained by calculating the quantum defect of the Ba^+ $6h$ level using experimental values for the dipole and quadrupole polarizabilities of the Ba^{2+} core determined by Jones and Gallagher [16] and hydrogenic wave functions for the (non-core-penetrating) valence electron. The experimental value for the quantum defect of the $6hnl$ series is found to be $\mu=0.98$ (mod 1). Observation of these states, $6hnl$ in the language of the independent-electron model, in excitation from $5dn''g$ via $4fn'g$ is a signature of the breakdown of this model and a proof for correlated motion of the two valence electrons. The $6hnl$ Rydberg series disappears when it reaches the $6g$ ionization limit at 110 460.77 cm^{-1} [17] for $\nu\approx 48$ (ν is the effective principal quantum number). This is ascribed to a large increase in the autoionization rates of the $6hnl$ resonances as a result of a strong dipole coupling to $6g\epsilon l'$ continua once this channel is open. Below 110 380 cm^{-1} the excitation spectrum starts to show an irregular behavior that cannot be interpreted straightforwardly in terms of $6gng$-$6hnl$ interaction. A similar observation was made by Eichmann, Lange, and Sandner [10] in excitation spectra of planetary states in Sr and was interpreted as a transition between a region in which an ''induced'' and a region in which a ''permanent'' electric dipole moment is formed in the ionic core by the outer electron. The resemblance between the excitation spectrum of Fig. 1 and the planetary spectrum of Sr [10] is remarkable, since our doubly excited system is not planetary at all, as both electrons move in an orbit with the same orbital angular momentum. The irregular behavior continues towards the low-energy side of the excitation spectrum of Fig. 1. Several narrow resonances appear on top of broad structures coinciding with the maxima of the overlap integral of the Rydberg electron. In the framework of the independent-electron model these features may be considered to be low-n members of $6hnl$ Rydberg series observed for various values of l.

A systematic study of doubly excited $Ngng$ states involves a variation of the principal quantum number of one of the valence electrons while keeping the other constant. In a first experiment n was varied by selecting different intermediate $5dn''g$ states. The result for $N=9$ is shown in Fig. 2. Excitation spectra are shown from $5dn''g$ states, with n'' varying from 24 to 31. In the excitation spectra for $n''=24$, 25, 30, and 31 a single resonance is observed, while in the spectra for $n''=26$–28 additional resonances appear. These observations can be interpreted to be the result of interaction between channels converging to the closely spaced $9h$ and $9g$ ionization limit ($E_{9h}-E_{9g}\approx 16$ cm^{-1}) and may be analyzed using a phase-shifted multichannel quantum defect theory (MQDT) model [18]. The Lu-Fano plot of Fig. 3, in which experimental data points and an analytical solution of a simple two-channel phase-shifted MQDT model for an interaction parameter $R_{12}=0.42$ and single-channel quantum defect parameters $\delta_{9g}=0.42$ and $\delta_{9h}=0.83$ are plotted, shows a remarkable agreement between experiment and model calculations. The large value of R_{12} indicates a strong interaction between series converging to the $9g$ and $9h$ ionization limits and is a signature of electron correlation. Similar phenomena of additional Rydberg series were observed for excitation spectra with $N=6$ and $N=8$, but the energy positions of the observed resonances were much less shifted, indicating significantly weaker interaction. For $N=9$ the Ba^+ g and h levels lie closest in energy, resulting in strongest channel interactions; also ionic levels with a higher value of l may become important. In the excitation spectra of Fig. 2 we did not observe states converging to the $9i$ ionization limit, but since the $9i$ level is close to the $9h$ level

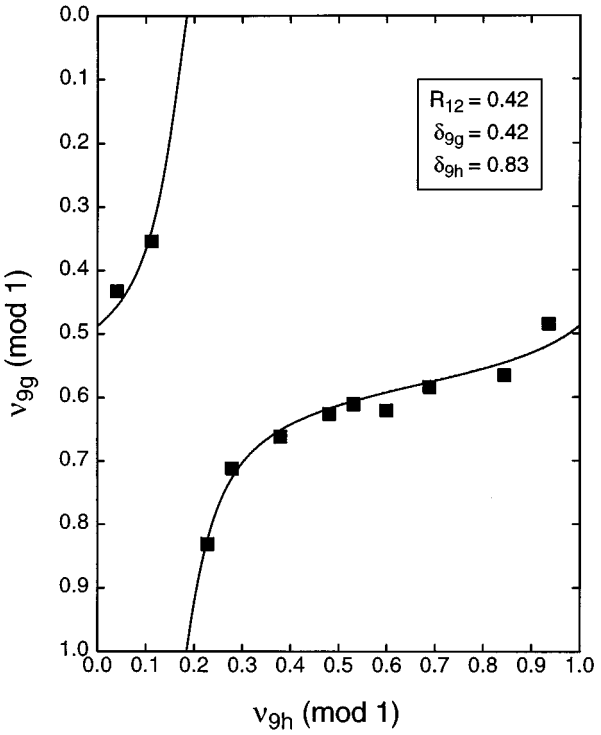

FIG. 3. Lu-Fano plot for the $9gng$-$9hn'l$ channel interaction. Pairs of effective principal quantum numbers (ν_{9h}, ν_{9g}) are derived from experimental energy positions of observed resonances and given by black squares. The values of ν_{9h} are determined using a calculated value for the $9h$-ionization limit of 117 295.00 cm^{-1}. The full line shows the analytical solution of a two-channel phase-shifted MQDT model with fitted parameters.

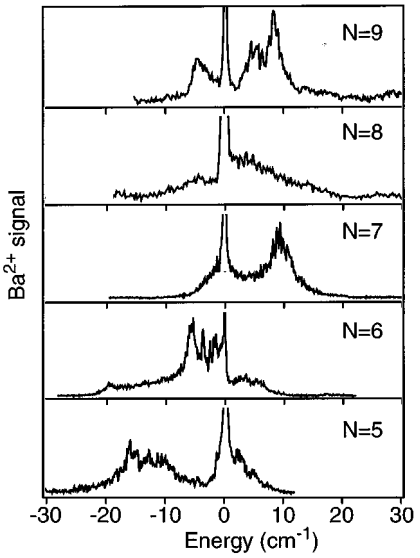

FIG. 4. Excitation spectra $5d_{5/2}26g$ $J=2\rightarrow Nln'l'$ with $N=5$–9. The final states were reached via near-resonant two-photon excitation through zeros in the intermediate continuum. Note that the $N=5$, 6 spectra were recorded with the third laser at a red-shifted zero (with respect to the $5d\rightarrow 4f$ ionic transition) in the intermediate $4f_{7/2}n'g$ spectrum, while for the $N=7$–9 spectra a blue-shifted zero was used. The narrow resonances correspond to Ba^+ $5d_{5/2}\rightarrow Ng$ transitions. The energy scale is given with respect to the ionic transitions.

(≈ 7 cm^{-1}), they may be part of the observed resonances.

In a second experiment the principal quantum number N of the inner valence electron was varied by scanning the wavelength of the dye laser, inducing the final excitation step around other Ba^+ $4f_{7/2}\rightarrow Ng$ transitions with $N=5$–9. This experiment was carried out for several values of the principal quantum number of the outer electron within the range $n=16$–31. Figure 4 shows excitation spectra of $Ngng$ states probed via the same intermediate $5d26g$ $J=2$ state. For $N=5$ and $N=7$ the excitation spectra show two maxima having effective quantum numbers with respect to the Ng ionization limit differing by 1. The $N=5$ spectra show some substructure that may be ascribed to fine structure. The observed quantum defects remain constant when n is varied. For the average value of the quantum defects we find $\mu=0.9$ (mod 1) for $N=5$ and $\mu=0.24$ (mod 1) for $N=7$. For $N=6$ we observe several states belonging to a Rydberg series converging to the $6g$ ionization limit and having a constant quantum defect $\mu=0.42$. For $N=8$ two series of resonances are observed having quantum defects $\mu=0.4$ (mod 1) and $\mu=0.9$ (mod 1). The spectra recorded after excitation from $5dn''g$ states with $n=29$–31 show several additional weak resonances belonging to series converging to the $8h$ ionization limit.

Although the absolute value of the quantum defect cannot be determined in our experiment, it is expected to increase with the size of the Ba^+ core and thus with the principal quantum number N. For $Nsnl$ states in Ba [4] and Ca [6] (with $l\leqslant 2$) a linear increase of the quantum defect μ with the principal quantum number N was reported, with a slope $\partial\mu/\partial N=0.32$. Here, assuming that the increase of the quantum defects of the $Ngng$ states with N is minimal, we also find a linear relation between μ and N. However, the value we find for the slope is twice as large $[\partial\mu/\partial N=0.62(3)]$. This can be ascribed to the large value of the polarizability of the Ba^+ Ng core (due to its near degeneracy with levels with $l>4$), which itself rapidly increases with N. The strong dependence of the quantum defect on N is a second signature of electron correlation.

For Ba $Nsnl$ states having two core-penetrating valence electrons the scaled linewidth Γ ($\Gamma=\nu^3\Gamma$) was reported to be either constant for $l=0$ or increasing with N for $l=2$ [4]. In our experiment the observed linewidths of the $Ngng$ states, which have two non-core-penetrating valence electrons, show a different behavior. Initially, the scaled linewidth increases rapidly with N [$\Gamma=0.16(4)$ a.u. for $N=6$, $\Gamma=0.34(7)$ a.u. for $N=7$, and $\Gamma=0.42(8)$ a.u. for $N=8$], an increase much stronger than for $Nsnd$ states [4]. The observed scaled linewidth for $N=9$, however, is nearly a factor of 3 lower than for $N=8$ [$\Gamma_{N=9}=0.17(5)$ a.u.]. In an independent-electron model the autoionization rates, and therefore the linewidths, are mainly determined by dipole coupling to nearby continua and therefore (for fixed n) approximately proportional to the square of matrix elements of the type $\langle Ng|r|Nf\rangle$ and $\langle Ng|r|(N-1)h\rangle$. An evaluation of these matrix elements using hydrogenlike wave functions shows a strong increase of the autoionization rates with N. The significant decrease in the scaled autoionization rate for $N=9$ indicates a breakdown of the independent-electron

model and is a third signature of electron correlation in this type of three-body Coulomb state.

In conclusion, we have investigated a special class of three-body Coulomb states in the barium atom, having two non-core-penetrating valence electrons. Unlike planetary atoms for which the orbital angular momentum of the outer electron is much larger than that of the inner electron, the states excited here have equal values of l. This implies that the electrons move in orbits having approximately the same classical inner turning point, allowing for transfer of energy and orbital angular momentum at relatively short range. This is illustrated by the fact that a simple MQDT model can be used to fit the energy positions of the observed resonances for $N=9$. It opens up the possibility for eigenchannel R-matrix calculations, which have been shown to reproduce experimental excitation spectra of alkaline-earth atoms in energy ranges near lower ionization limits [19] and recently also of planetary states [20]. We have shown that the effects of electron correlation manifest themselves by the appearance of additional $Nhnl$ resonances in the $Ngng$ excitation spectra, a rapid increase of the observed quantum defects with N, as well as a significant decrease of the autoionization rate for $N=9$.

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