PHYSICAL REVIEW A VOLUME 38, NUMBER 1 JULY 1, 1988

Laser spectroscopy of doubly excited 9sns ($11 \leqq n \leqq 20$) and 8dns ($10 \leqq n \leqq 20$) states of Ca

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(Received 10 March 1988)

Doubly excited *mlns* (*ml* = 9*s* and 8*d*) states of Ca have been produced by multistep laser excitation via 4*sn's* Rydberg states, and the states in which n is from 20 down to $m+2$ have clearly been observed by detecting photoionization current of Ca^{2+}. In some states, remarkable interference patterns and considerable line narrowing caused by the interaction with other autoionizing Rydberg series have been observed. The quantum defects of the observed states have also been obtained and discussed. In addition, we have seen some resonance peaks which are likely to be interpreted as transitions to the states with $n=m+1$ and $n=m$, although they have not definitely been assigned.

The importance of the electron correlation effect in doubly excited states of atoms has been pointed out by many authors.[1] In particular, when two electrons are excited into the same shell with a large principal quantum number, it has been predicted that a high degree of electron correlation causes a remarkable cooperative motion of electrons, and that the energy spectrum of such states has a particular structure equivalent to the rotation-vibration spectrum of a linear flexible *X-Y-X* triatomic molecule.[2] This kind of state is often called a "Wannier state."[3] Using Ba atoms, some experimentalists have been trying to observe this state through multistep laser excitation. They, however, have not yet been successful in this observation, although they have observed a number of doubly excited *mlnl'* states with $m+3 \lesssim n$ and have found various interesting properties.[4-10] Some authors have pointed out the difficulty in the laser excitation of the Wannier state in comparison with other excitation methods, such as electron-impact excitation.[11] With the latter method, however, it is still difficult to resolve high-lying excited states. Therefore, we believe that the laser spectroscopic study should be further advanced in this research. From this viewpoint, we also have started the laser investigation of doubly excited states of atoms in order to study the electron correlation effect. We have chosen Ca atoms as the object of study because it is preferable for the precise theoretical analysis to choose atoms as small as possible. Considering the present technology of lasers, this choice may be the best. As a consequence, we have clearly observed some series of doubly excited *mlns* states in which n is down to $m+2$. Moreover, we have also observed some states that may be assigned to the states with $n=m+1$ and $n=m$, although more data and analysis are required for the confirmation of their assignment. In this Rapid Communication, we present the first results obtained for the 9*sns* and 8*dns* states.

The excitation process of high-lying doubly excited states is the same as that developed by Cooke *et al.*,[12] and is shown in Fig. 1. Two blue lasers excite one of the valence electrons into an *n's* Rydberg state via 4*p* state, then a third uv laser drives the $4s \to ml$ transition of the ionic core through two-photon absorption. The lasers used are all pulsed dye lasers pumped by *Q*-switched yttrium aluminum garnet (YAG) lasers, and the pulse width of each dye laser is 6–7 ns. A uv pulse is a second harmonic of a dye laser pulse and is generated by a recently devised nonlinear crystal, β-BaB_2O_4. The uv pulse is focused into the interaction region through a $f=50$-cm lens. Typical energy of each blue laser pulse is 150 μJ and that of the uv pulse is 1.5 mJ at the interaction region. Two blue lasers excite Ca atoms simultaneously, then the uv laser drives the core transition after 20 ns. The doubly excited states produced are quickly autoionized into some excited states of Ca^+ and then photoionized into Ca^{2+} by the uv laser. We detected the ion current of Ca^{2+} by a tandem multichannel plate detector through a time-of-flight mass spectrometer. The core-excitation spectra

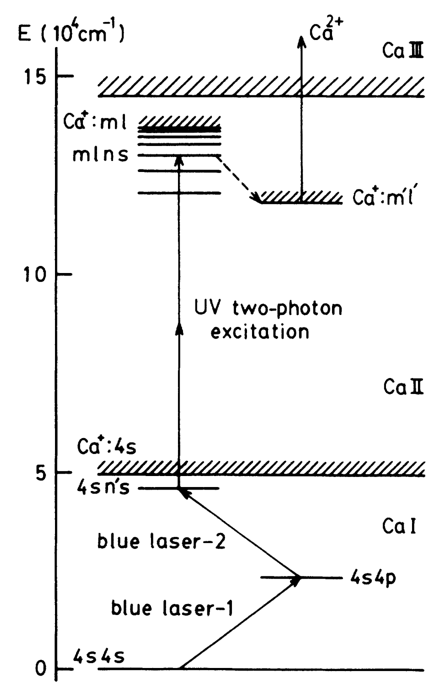

FIG. 1. Relevant energy levels and excitation process for doubly excited states.

were obtained by measuring the ion current as a function of the uv wavelength.

Figure 2 shows a typical core-excitation spectrum obtained when the initial state is $4s18s$. The central feature is a $4s \rightarrow 9s$ transition of Ca^+ and broader resonance peaks at its both sides are $4s18s \rightarrow 9sns$ core transitions. The ionic resonance appears because of the presence of $Ca^+(4s)$ as a by-product of the laser excitation. As seen in Fig. 2, the resonance peak of the core transition appears only in the vicinity of the Ca^+ resonance line corresponding to the core transition, and the transition probability is maximal when n is a little different from n'. The latter fact reflects the difference of the quantum defects between the initial and final states. Figure 2 also shows a theoretical curve calculated by assuming the absence of electron correlation and a nonperturbed autoionizing Rydberg series. The experimental and theoretical curves are best fitted when the quantum defect and the scaled autoionization rate are 3.89 and 0.077, respectively. This good agreement of both curves means that the electron correlation does not play an important role in the doubly excited $mlns$ states with $n \gg m$, as is seen for Ba.[4-8]

We observed the spectra around the $4s \rightarrow 9s$ and $4s \rightarrow 8d$ resonance lines of Ca^+ for many initial $4sn's$ Rydberg states. Figure 3 shows the entire spectra observed. These spectra are all obtained using a linearly polarized uv laser. Some sharp features are resonances of Ca^+, and only $4s \rightarrow 9s$ and $4s \rightarrow 8d$ resonances are of importance in these core-excitation spectra, while others play roles of frequency markers. Broader resonances appearing in a pair around each $4s \rightarrow ml$ line are $4sn's \rightarrow mlns$ core transitions, and the one at the left side is interpreted as a $4sn's \rightarrow ml(n'+1)s$ transition and the other a $4sn's \rightarrow ml(n'+2)s$, as will be noted later.

As seen in Fig. 3, these series of doubly excited states exhibit much variation: a remarkable interference pattern is seen in $8d14s$ and $8d13s$, and considerable line narrowing is seen in $9s16s$ and $9s15s$. Although a precise analysis is currently in progress, it is obvious that the former is due to the interaction with $7fn''l''$ and $7gn''l''$ Rydberg series. The latter is also due to the interaction with some states, which are likely to be $8dn''d$ states.

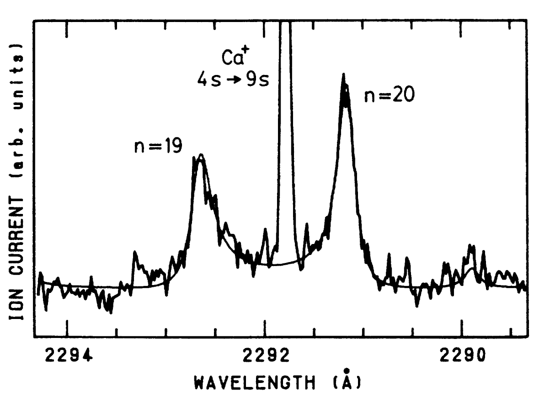

FIG. 2. Excitation spectrum of the $4s18s \rightarrow 9sns$ two-photon transitions; the observed trace is drawn in a heavy line and the theoretical curve fitted to it is drawn in a thin line.

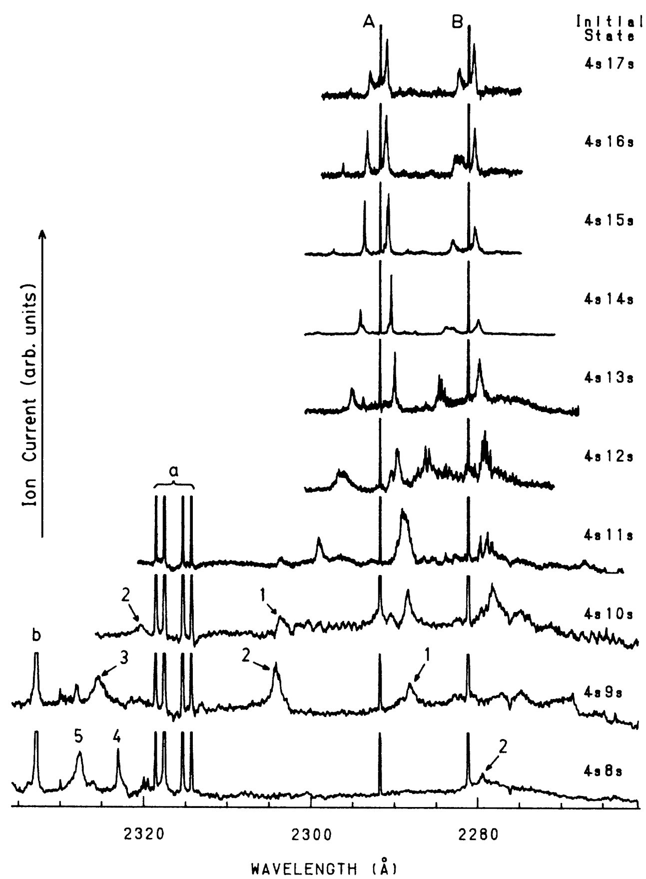

FIG. 3. Excitation spectra observed when the initial state is changed from $4s17s$ down to $4s8s$. The narrow features denoted by A, B, a, and b are the $4s \rightarrow 9s$, $4s \rightarrow 8d$, $3d_{3/2,5/2} \rightarrow 4d_{3/2,5/2}$, and $4p_{1/2} \rightarrow 4f$ resonances of Ca^+, respectively. See text concerning the features numbered 1–5.

In this work, we concentrated on the observation of the states in which n is as close to m as possible. Consequently, we have succeeded in the observation of some resonance peaks denoted by 1–5 in Fig. 3. In obtaining the traces including these peaks, we repeated the scan of the laser wavelength about ten times and averaged the traces in order to improve the signal-to-noise ratio. We note that there is a very broad resonance with an asymmetric shape at 2300–2270 Å, which is a two-photon transition from the $4s^2$ ground state to a low-lying autoionizing state. This resonance causes the traces to be somewhat complicated. A dip seen at 2276 Å is due to a ground-state population depletion caused by a resonance between $4s^2$ and $4s6p$. The peaks denoted by the same number in Fig. 3 can be interpreted as the resonances that have the same final doubly excited state, because they shift exactly corresponding to half the frequency difference of the initial states changed. This fact confirms that they are two-photon resonances. All numbered peaks appear only in the presence of both excitations of two blue lasers. This confirms that these peaks are not due to the transition from the $4s^2$ ground state nor from the $4s4p$ intermediate state. Moreover, when a circularly polarized uv laser was used, only the peaks 2 and 4 appeared with their intensity increased, while others disappeared. Considering all these facts, we can conclude that the final states of the resonances denoted by 1 and 2 are 9*s*11*s* and 8*d*10*s*, respectively. We note that an interference pattern is seen also in the 9*s*11*s* state and is due to the interaction with 8*pn''p* Rydberg series. On the other hand, the assignment of the peaks 3–5 is not clear at present. This is partly because it has not yet been confirmed that they are two-photon resonances. However, according to the result obtained by using a circularly polarized uv laser, the resonance peaks 3 and 5 should be interpreted as two-photon transitions to final states with $J=0$; otherwise, they would be dipole-forbidden one-photon transitions. Although we cannot similarly speculate concerning the peak 4, it is also likely that this resonance is interpreted as a two-photon transition to a final state with $J=2$. Taking these discussions into account, it is not impossible that the final states of the resonance peaks 3, 4, and 5 are assigned to 9*s*10*s*, 8*d*9*s*, and 9*s*9*s*, respectively. Further discussion, however, requires reliable theories on such states of Ca atoms, which do not seem to exist at present.

In order to understand more quantitative properties of these series of doubly excited state, we obtained their quantum defects, which are summarized in Table I. As seen in Table I, the quantum defects do not change significantly when $n \geqq m+3$. This result is similar to that obtained for Ba.[4-8] The quantum defects averaged over the states with $n \geqq m+3$ are 3.96 and 4.01 for 9*sns* and 8*dns* series, respectively. The former quantum-defect value for the 9*s* core is considerably smaller than 5.22 obtained for the 9*s* core of Ba by Bloomfield *et al.*[4] This difference is considered to reflect the difference of the closed-shell core between Ca and Ba. The value 3.96 and those obtained for 4*sns*, 7*sns*, 8*sns*, and 10*sns* series[13] are linearly dependent on *m*, as is that given for Ba.[4] The same result has been obtained for *mdns* series. We note that this fact confirms the correctness of our assignment of the states observed. On the other hand, the quantum defects are considerably increased in the states with $n=m+2$. This trend, however, is not in agreement with the result obtained for the 11*sns* series of Ba in Ref. 6, in which they stated that the energy spacings tend to be equal in the lowest states observed and that this behavior is an evidence of the electron correlation. Although we have not found the exact reason, this difference might be due to the insufficient correlation effect in 9*s*11*s* and 8*d*10*s* states in comparison with the effect by the Ca^{2+} core.

TABLE I. Quantum defects of the doubly excited states observed.

	Quantum defect	
n	9*sns*	8*dns*
20	3.89(2)	3.96(6)
19	3.89(2)	3.93(4)
18	3.99(2)	3.97(3)
17	3.993(28)	4.03(2)
16	3.945(10)	3.975(25)
15	3.938(15)	4.03(3)
14	3.985(20)	4.01(4)
13	3.99(4)	4.06(6)
12	4.055(15)	4.10(3)
11	4.13(2)	4.05(2)
10	4.577(8)[a]	4.276(6)
9	4.200(4)[b]	4.314(2)[c]

[a]Value obtained for the resonance denoted by 3 in Fig. 3.
[b]Value obtained for the resonance denoted by 5 in Fig. 3.
[c]Value obtained for the resonance denoted by 4 in Fig. 3.

In Table I, we also show the quantum defects of the final states of the resonances denoted by 3–5 in Fig. 3, assuming the assignment mentioned before. While the quantum defect is further increased in the $n=m+1$ states, it is considerably decreased in the $n=m$ state. The latter behavior agrees not only with the trend seen in the 11*sns* states of Ba, but also with what is predicted and interpreted as the correlation effect by some theoretical works.[14,15] As stated before, however, there is little theory concerning these states of Ca, although a theoretical work on relatively lower autoionizing states has very recently been presented.[16] Therefore, we cannot discuss these states anymore at present. We believe that it will be an interesting future work to analyze these states, whether their tentative assignment is correct or not.

We have presented here the first results obtained for 9*sns* and 8*dns* states of Ca, and we are carrying on the theoretical analysis of these results.

We would like to thank Professor E. Hirota for lending us the dye laser.

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