Resonance excitation of bound and autoionization states of the ytterbium atom in the course of three-photon ionization

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Three-photon single ionization of the ytterbium atom in the wavelength interval 430–472 nm has been studied for the first time. The plot of the yield of Yb^+ ions versus the laser wavelength has a large number of resonance peaks, which stem from the excitation of bound and autoionization states. These results are evidence that transitions involving the excitation of the $4f^{14}$ inner subshell play an extremely important role in the ionization of the ytterbium atom.

Research on the multiphoton ionization of alkaline-earth atoms has shown that certain particular features of their spectra (the presence of dielectronic bound and autoionization states) make the interaction of laser light with these atoms substantially more complex than the interaction with alkali metals.[1] Rare-earth elements are of considerable interest in this connection. They too have two *s* electrons in the outer shell, but they differ from alkaline-earth atoms in having an incomplete $4f$ subshell.[2] Our purpose in the present study was to learn about the particular features of the excitation of the $4f^{14}$ and $6s^2$ subshells during three-photon ionization of the ytterbium atom by laser light in the wavelength interval 430–472 nm.

The experiments were carried out in an apparatus with intersecting laser and atomic beams. Ions produced in the multiphoton ionization were extracted from the beam intersection volume by a static magnetic field, separated by mass and charge in a time-of flight mass spectrometer, and detected by a electron multiplier. The source of ionizing radiation was a tunable pulsed dye laser with an output spectral width $\sim 0.5\ \text{cm}^{-1}$. Experiments were carried out in linearly polarized light. The field in the beam intersection volume was $\sim 4\times 10^4$ V/cm.

Figure 1 shows the yield of Yb^+ ions versus the laser wavelength, $N_i(\lambda)$. A characteristic feature of this plot is the presence of a large number of clearly expressed resonance peaks. Analysis of the data available[3,4] on the spectrum of the ytterbium atom shows that we can think of these peaks as belonging to three groups. The first group consists of resonance peaks due to two-photon excitation of electrons of exclusively the $6s$ outer subshell. Included in this group are peaks 1–4, which correspond to the following transitions:

$$1—4f^{14}6s^2\ {}^1S_0+2h\omega-4f^{14}6s8d\ {}^3D_2\,,$$

$$2—4f_{14}6s^2\ {}^1S_0+2h\omega-4f^{14}6p^2\ {}^3P_2,$$

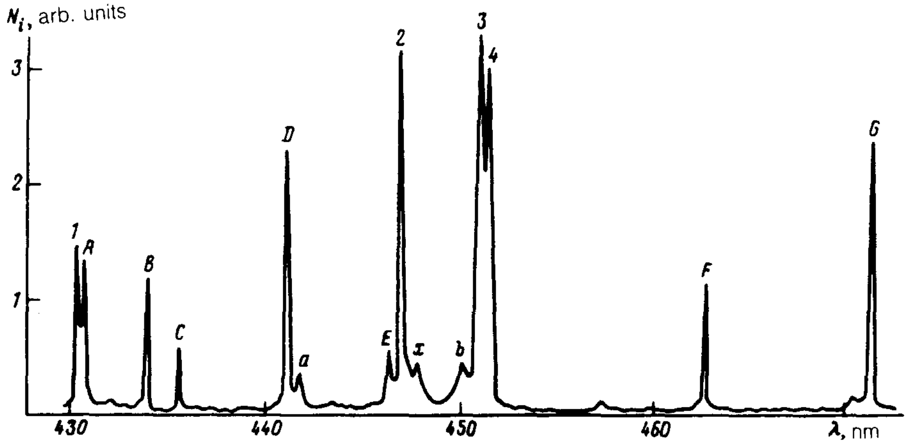

FIG. 1. Yield of Yb^+ ions versus the laser wavelength.

3—$4f^{14}6s^2\ {}^1S_0+2\hbar\omega-4f^{14}6s7d\ {}^1D_2$,

4—$4f^{14}6s^2\ {}^1S_0+2\hbar\omega-4f^{14}6s7d\ {}^3D_{2.1}$.

Transitions *1*, *2*, and *4* stem from the excitation of triplet states of the ${}^3P$ and ${}^3D$ terms and are intercombinational transitions. The heights of peaks *2* and *4* are comparable to that of peak *3*, which is due to the excitation of the ${}^4f^{14}6s7d^1D_2$ singlet state. Peak *1* is roughly half the size of peak *3*. Peak *4* consists of two unresolved peaks, with close-lying ${}^4f^{14}6s7d^3D_2$ and $4f^{14}6s7d^3D_1$ states. The difference between the energy positions of these states is $\Delta E=2\ \mathrm{cm}^{-1}$.

The peaks of the second group are related instead to the excitation of the deeper-lying $4f$ subshell. Included in this group are peaks *A*–*G*, which correspond to the following two-photon transitions:

A—$4f^{14}6s^2\ {}^1S_0+2\hbar\omega-4f^{13}5d6s6p(7/2,3/2)_2$,

B—$4f^{14}6s^2\ {}^1S_0+2\hbar\omega-4f^{13}5d6s6p(7/2,7/2)_0$,

C—$4f^{14}6s^2\ {}^1S_0+2\hbar\omega-4f^{13}6s^26p_{3/2}(5/2,3/2)_2$,

D—$4f^{14}6s^2\ {}^1S_0+2\hbar\omega-4f^{13}5d6s6p({}^2D_{5/2})(7/2,5/2)_2$,

E—$4f^{13}6s^2\ {}^1S_0+2\hbar\omega-4f^{13}6s^26p_{3/2}(5/2,3/2)_1$,

F—$4f^{14}6s^2\ {}^1S_0+2\hbar\omega-4f^{13}5d6s6p({}^4F_{5/2})(7/2,5/2)_2$,

G—$4f^{14}6s^2\ {}^1S_0+2\hbar\omega-4f^{13}5d6s6p(7/2,5/2)_1$,

In the energy region of the two photons corresponding to the position of resonance peak *G*, there is a state in addition to that mentioned: the $4f^{14}6p^{2\,3}P_0$ state. Because these peaks are close together ($\Delta E=0.2\ \mathrm{cm}^{-1}$), however, they are not resolved; they are seen as a single peak. The two-photon transition associated with the excitation of the $6p^{2\,3}P_0$ triplet is an intercombinational transition.

Among all the bound states in the spectrum of the Yb atom which lie in the wavelength region studied, and for which two-photon excitation is allowed by the selection rules, the following are not seen as resonance peaks: $4f^{14}6s8d\,^3D_1$, $4f^{14}6s9s\,^3S_1$, $4f^{14}6p^{2\,3}P_1$, $4f^{13}6s^26p_{1/2}(5/2,\ 1/2)_2$, and $4f^{13}5d6s6p(7/2,\ 7/2)_1$. A possible reason for the absence of resonance peaks due to the excitation of the first three of these states is that these are triplet states, and the corresponding two-photon transitions are intercombinational. As has been shown in a study of alkaline-earth atoms,[5] such transitions are manifested with different intensities and not in all parts of the spectrum. Why we do not see resonance peaks associated with the two-photon excitation of the $4f^{13}5d6s6p(7/2,\ 7/2)_1$ and $4f^{13}6s^26p_{1/2}(5/2,\ 1/2)_2$ states is not clear at this point.

The third and final group of peaks consists of peaks *a* and *b*, which are due to three-photon excitation of autoionization states:

a—$4f^{14}6s^2\,^1S_0+3h\omega-4f^{14}5d6f\,^1P_1^0$,

b—$4f^{14}6s^2\,^1S_0+3h\omega-4f^{13}6s^28d[3/2]_1^0$.

Both *a* and *b* lie near resonance peaks due to two-photon excitation of bound states (peaks *D* and *3*, respectively). Whether this is a general trend or simply a coincidence we cannot say for sure at this point. We would simply point out that a similar situation has been observed for the three-photon ionization of the barium atom.[6]

Analysis of the existing data[4] on the spectrum of autoionization states of the ytterbium atom shows that successive resonances can be realized in the case of peaks *B*, *E*, and *G*: two-photon resonances with the specified bound states and three-photon resonances with autoionization states. Thus three photons can excite the following autoionization states: $4f^{14}5d6p\,^1P_1^0$, $4f^{14}6p6d\,^1P_1^0$, and $4f^{13}6s6p^2[k]_1^0$ in the case ofpeak *B*; $4f^{13}5d6s6d[k]_1^0$ and $4f^{13}5d6s[5/2]_{7/2}^0$ in the case of peak *E*; and $4f^{13}5d6s6d[k]_1^0$ and $4f^{13}5d6s[3/2]_{3/2}^0 6d[3/2]_1^0$ in the peak *G*. The asymmetry of resonance peak *2* on the side of peak *X* may be due to three-photon excitation of the $4f^{13}5d6s7s[k]_1^0$ autoionization state.

The wavelength region which we studied includes about 40 autoionization states whose three-photon excitation is allowed by the selection rules. It follows from the plot of $N_i(\lambda)$ that many of these states are not manifested as resonance peaks. Just why is not clear at this point. One possible reason is a low probability for three-photon excitation of autoionization states: a probability comparable to that for direct three-photon ionization into the continuum. Another possible reason is a pronounced broadening of the autoionization states in the field $\sim 4\times 10^4$ V/cm.

On the plot of $N_i(\lambda)$ we observed peak *X*, which we mentioned earlier, which could not be identified with transitions in the spectrum of either bound or autoionization states. In terms of position and shape, this peak is very reminiscent of peaks *a* and *b*, which are due to the excitation of autoionization states. On this basis it might be suggested that peak *X* is also due to the three-photon excitation of an unknown autoionization state, with an energy $\sim 66980\ \mathrm{cm}^{-1}$. The results of this study demonstrate unambiguously that resonance transitions involving the excitation of both the $6s^2$ outer subshell and the $4f^{14}$ inner subshell play important roles in the three-photon ionization of the ytterbium atom. It can also be asserted that the presence of the $4f^{14}$ subshell of the Yb atom leads to a new (*i.e.*, not seen in the case of the alkaline-earth atoms) and effective ionization mechanism, involving the excitation of one electron of this inner shell.

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