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NEW AUTOIONIZING STATES NEAR THE FIRST IONIZATION LIMIT OF RARE EARTH ELEMENT Dy

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This paper describes the investigation of autoionizing states near the first ionization limit of rare-earth element Dy. The 62, 51, 97 and 25 new autoionizing states resulting from the states of $4f^{10}(^5I_8)6s6p(^3P_2^0)^3I_7^0$, $4f^9(^6H^0)5d^2(^3F)(^8G^0)6s^9G_7^0$, $4f^9(^6F^0)5d6s^2\,^7H_7^0$ and $4f^95d6s^2\,^7K_7^0$, respectively, were found by using a laser resonance ionization time-of-flight mass spectrometer (LRI-TOFMS). The photoionization efficiencies for different channels were compared with each other. In addition, the Shore-Fano parameters of autoionizing states were determined by a nonlinear fitting program.

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I. INTRODUCTION

The study of atomic high-lying excited states nowadays is well developed by physicists. The complicated electronic structures of rare-earth elements, especially the mixing of configurations, have a serious influence on their high-lying excited states. In recent years the development of laser resonance ionization spectroscopy (LRIS) employing several dye lasers to realize multi-step photoionization of atoms has promoted systematic studies of high-lying excited states including autoionizing states of atoms[1]. Using this method, we can find autoionizing states and determine their positions according to a relevant theory. In addition, the mechanism of an autoionizing process might be studied by analyzing the profile and intensity[2].

Investigations of the autoionizing states near the first ionization limit of Dy are not only of significance in atomic physics but also of great practical value in ultrasensitive analysis. For example, in searching for mines, the LRIS ultrasensitive analysis method is becoming a more and more convenient way. The autoionizing states obtained in this experiment provide very important data for resource exploitation.

In section **II** of this paper we describe the LRIS method and the experimental results. The data analysis and discussion are given in section **III**. We draw our conclusions in the last section.

II. EXPERIMENTAL METHOD AND RESULTS

The experimental setup includes a resonance ionization time-of-flight mass spectrometer, a laser system and a data acquisition system. These systems are all controlled by a synchronous trigger pulse. The experimental arrangement and detailed conditions can be found in Refs. [3] and [4]. The measurement of autoionizing states of Dy will be described below.

The ground state ($4f^{10}6s^2\,{}^5I_8$) of Dy I can be excited to autoionizing states by two-step resonance excitation. We have selected four different intermediate states as exciting channels:

$$(1)\quad 4f^{10}6s^2\,{}^5I_8 \xrightarrow{\lambda_{11}} 4f^{10}({}^5I_8)6s6p({}^3P_2^0)\,{}^3I_7^0 \xrightarrow{\lambda_{12}} \text{autoionizing states;}$$

$$(2)\quad 4f^{10}6s^2\,{}^5I_8 \xrightarrow{\lambda_{21}} 4f^9({}^6H^0)5d^2({}^3F)({}^8G^0)6s\,{}^9G_7^0 \xrightarrow{\lambda_{22}} \text{autoionizing states;}$$

$$(3)\quad 4f^{10}6s^2\,{}^5I_8 \xrightarrow{\lambda_{31}} 4f^9 5d6s^2\,{}^7K_7^0 \xrightarrow{\lambda_{32}} \text{autoionizing states;}$$

$$(4)\quad 4f^{10}6s^2\,{}^5I_8 \xrightarrow{\lambda_{41}} 4f^9({}^6F^0)5d6s^2\,{}^7H_7^0 \xrightarrow{\lambda_{42}} \text{autoionizing states.}$$

Here λ_{11}, λ_{21}, λ_{31} and λ_{41} are 5423.32Å, 5395.57Å, 5451.31Å and 5301.58 Å (in air) respectively. In selecting intermediate states we took into account the optical selection rules, and λ_{12}, λ_{22}, λ_{32} and λ_{42} were scanned from 3330Å to 3460Å. In order to ensure the saturated excitation of the first-step and a tolerable background, the pulse energy of the laser $\lambda_{k1}(k = 1, 2, 3, 4)$ were adjusted to about 1mJ and that of $\lambda_{k2}(k = 1, 2, 3, 4)$ about 2–3 mJ. The linewidths of the lasers used in the experiment were $0.2\,\mathrm{cm}^{-1}$ which was narrow enough to meet the requirements in our experiment.

Ignoring $\lambda_{k1}(k = 1, 2, 3, 4)$ and varying λ_2 of the second dye laser from 3330Å to 3460Å, we have not found any peaks, so it can be concluded that in this scan range the influence of two-photon background is negligible. Calibration of wavelength can be referred to Ref. [3]. After carrying out the correction of the refractive index of air, we have obtained the calibrated wavelengths $\lambda_{k2,\mathrm{expt.}}(k = 1, 2, 3, 4)$, as listed in the second column in Tables 1, 2 and 3. The data for channel 4 can be found also in Ref. [3].

Table 1. Autoionizing states of Dy found by excitation of the $4f^{10}(^5I_8)6s6p(^3P_2^0)^3I_7^0$ state.

I	Wavelength(Å)	Energy(1/cm)	Width(1/cm)
1	3391.92	47915.8	1.0
2	3391.23	47921.8	2.4
3	3389.44	47937.4	0.8
4	3388.98	47941.4	3.2
5	3387.97	47950.2	0.8
6	3386.14	47966.1	1.6
7	3385.87	47968.5	1.6
8	3385.36	47972.9	1.2
9	3382.94	47994.1	0.8
10	3382.11	48001.3	1.2
11	3381.56	48006.1	0.4
12	3381.15	48009.7	1.2
13	3380.19	48018.1	3.6
14	3379.27	48026.2	0.8
15	3377.53	48041.4	0.8
16	3377.21	48044.2	0.8
17	3376.34	48051.8	5.6
18	3374.74	48065.9	0.8
19	3371.98	48090.2	0.8
20	3370.91	48099.6	2.0
21	3370.42	48103.9	0.8
22	3370.20	48105.8	0.8
23	3366.86	48135.3	0.8
24	3364.14	48159.2	0.8
25	3362.32	48175.4	1.2
26	3361.74	48180.5	2.0
27	3361.12	48186.0	1.6
28	3360.94	48187.6	0.8
29	3359.87	48197.0	1.2
30	3358.09	48212.8	2.4
31	3357.15	48221.1	0.8
32	3356.58	48226.3	1.2
33	3355.73	48233.8	2.4
34	3354.77	48242.7	3.3
35	3354.04	48248.8	1.2
36	3353.86	48250.4	0.8
37	3353.15	48257.1	1.6
38	3352.55	48262.5	1.6
39	3352.36	48264.1	1.6
40	3352.04	48267.0	0.8
41	3350.89	48276.8	2.5
42	3350.61	48279.3	1.7
43	3350.38	48281.4	1.7
44	3350.04	48284.4	1.5
45	3349.62	48288.1	1.3

Continued

46	3349.29	48291.0	1.7
47	3348.82	48295.2	0.4
48	3348.54	48297.7	0.8
49	3348.31	48299.8	0.8
50	3347.82	48304.1	0.8
51	3347.41	48307.8	0.8
52	3346.94	48312.0	1.0
53	3346.53	48316.1	1.2
54	3346.29	48317.8	1.7
55	3345.63	48323.7	1.3
56	3345.18	48327.8	1.2
57	3342.81	48348.9	0.4
58	3342.11	48355.2	0.8
59	3341.83	48357.8	1.7
60	3333.42	48433.2	0.4
61	3328.83	48474.6	0.8
62	3326.50	48495.6	3.4

Table 2. Autoionizing states of Dy found by excitation of the $4f^9(^6H^0)5d^2(^3F)(^8G^0)6s\ ^9G^0_7$ state.

I	Wavelength(Å)	Energy(1/cm)	Width(1/cm)
1	3400.94	47932.5	0.5
2	3400.75	47934.1	0.6
3	3400.39	47937.2	2.1
4	3399.48	47945.1	3.0
5	3397.68	47960.7	2.6
6	3397.45	47962.6	—
7	3394.93	47984.5	1.1
8	3394.03	47992.3	1.6
9	3393.07	48000.6	1.9
10	3392.05	48009.5	2.9
11	3391.17	48017.1	1.1
12	3389.32	48033.3	0.7
13	3388.89	48037.0	0.2
14	3388.37	48041.5	2.6
15	3388.20	48043.0	—
16	3386.27	48059.8	0.7
17	3382.86	48089.6	2.6
18	3381.78	48099.0	1.0
19	3380.91	48106.6	5.4
20	3378.23	48130.1	0.6
21	3375.44	48154.6	1.0
22	3374.70	48161.1	3.5
23	3373.41	48172.4	0.9
24	3372.94	48176.5	1.5
25	3371.71	48187.3	0.9
26	3370.79	48195.4	0.9

Continued

27	3368.82	48212.8	1.0
28	3367.83	48221.5	1.0
29	3367.74	48222.3	0.8
30	3366.33	48234.7	2.1
31	3365.46	48242.4	0.4
32	3365.19	48244.8	1.3
33	3363.86	48256.5	0.8
34	3363.42	48260.4	0.9
35	3358.47	48304.2	1.5
36	3357.93	48309.0	0.9
37	3357.50	48312.8	0.9
38	3357.01	48317.2	0.8
39	3356.23	48324.1	0.6
40	3355.99	48326.3	0.9
41	3355.61	48329.6	1.1
42	3354.94	48335.6	0.8
43	3354.56	48339.0	0.8
44	3354.00	48343.9	1.1
45	3353.68	48346.8	0.8
46	3353.13	48351.7	2.7
47	3352.75	48355.0	2.5
48	3352.00	48361.7	0.9
49	3351.81	48363.4	1.0
50	3351.60	48365.3	0.8
51	3351.09	48369.9	0.8

Table 3. Autoionizing states of Dy found by excitation of the $4f^9 5d6s^2\ ^7K_7^0$ state.

I	Wavelength(Å)	Energy(1/cm)	Width(1/cm)
1	3381.24	47915.0	0.6
2	3380.21	47924.0	0.9
3	3378.40	47939.9	2.9
4	3377.17	47950.6	3.0
5	3375.58	47964.6	2.5
6	3374.18	47976.9	2.6
7	3373.15	47985.9	1.7
8	3374.67	47993.3	0.7
9	3371.49	48000.5	0.6
10	3370.94	48005.3	0.4
11	3370.25	48011.4	0.9
12	3369.62	48017.0	0.9
13	3369.22	48020.5	2.6
14	3368.70	48025.1	0.5
15	3368.19	48029.5	2.6
16	3367.41	48036.4	0.9
17	3360.99	48093.2	0.7
18	3360.99	48095.6	—

Continued

19	3360.53	48097.2	—
20	3359.94	48102.5	—
21	3359.36	48107.6	0.5
22	3359.18	48109.2	0.5
23	3358.24	48117.5	0.9
24	3357.65	48122.7	0.9
25	3357.46	48124.5	0.9

III. DATA ANALYSIS AND DISCUSSION

A. Spectra of autoionizing states

In the experiment we scanned the tunable laser in a wide range of wavelength from 47900 to 48700 cm^{-1} near the first ionization limit of 47915 cm^{-1} of Dy in four different channels, and autoionizing states have been found in every channel, that is, in channel 1, 62 autoionizing states; in channel 2, 51; in channel 3, 25; and in channel 4, 97. This means that Dy atom is rich in autoionizing states. In addition, there are differences in intensity among autoionizing states in different channels. Detailed comparisons between different channels will be described later. All the autoionizing spectra obtained in the experiment show obviously that most profiles of the autoionizing state are unsymmetric.

The total cross-section from the initial to an autoionizing state is given by[5]

$$\sigma_{\rm tot} = [B(\Gamma/2) + A(E - E_0)]/[(\Gamma/2)^2 + (E - E_0)^2] + \sigma_{\rm nr} ,$$

where $\sigma_{\rm tot}$ represents the total and $\sigma_{\rm nr}$ the non-resonant cross-section for photoionization, $\Gamma = h/\tau$ the linewidth with a lifetime τ of the autoionizing state, E_0 the transition energy; and A, B are the Shore-Fano parameters. Some of the resulting parameters E_0, Γ and A/B of the autoionizing states are obtained.[3]

After fitting to Shore-Fano formula for all the autoionizing states obtained, we get the transition energies E_0 and the linewidths Γ, as shown in the third and fourth columns in Tables 1, 2 and 3, respectively (data for channel 4 can be found in Ref. [3]). The linewidths for most of the autoionizing states are greater than 0.5 cm^{-1}.

B. Comparisons of the autoionizing states in different channels

(1) In the excitation of $4f^9(^6F^0)5d6s^2\,^7H_7^0$ with tunable laser in wavelength range from 3350Å to 3460Å (channel 4), we observed 97 autoionizing states. The resonances of these states are strong in general. The states obtained in channel 2 (by exciting the intermediate state of $4f^9(^6H^0)5d^2(^3F)(^8G^0)6s^9G_7^0$) are also in good resonance. Compared with channel 1 and channel 3, the autoionizing states found in channel 2 and channel 4 are more efficient.Among the autoionizing states obtained in channel 2 and channel 4, we have selected some as reference data for the ultrasensitive analysis of Dy. By means of these states, higher

photoionization yields can be obtained. They are listed in Table 4 (also in Ref. [3]).

Table 4. Reference autoionizing states for measurement of Dy by excitation of the intermediate state $4f^9(^6H^0)5d^2(^3F)(^8G^0)6s\,^9G^0_7$.

I	Wavelength(Å)	Energy(1/cm)
1	3399.48	47945.1
2	3391.17	48017.1
3	3382.86	48089.6
4	3375.44	48154.6
5	3358.47	48304.2

(2) By analyzing all the data in four channels, we find that a few autoionizing states in different channels are coincident, but the linewidths are different evidently. Table 5 gives some examples about this.

Table 5. Linewidths (in cm^{-1}) for some coincident autoionizing states in different channels.

Energy	Channel 1	Channel 2	Channel 4
47915.8	1.0	—	0.2
47937.4	0.8	2.1	—
47992.3	—	1.6	0.6
48041.4	0.8	2.6	—
48226.3	1.2	—	0.6
48369.9	—	0.8	2.4

IV. CONCLUSIONS

This is the first time, as far as we know, to make a comparison between the autoionizing states near the first ionization limit of Dy. It is shown that resonance ionization mass spectroscopy is a very effective tool for the investigation of autoionizing states. By excitation of $4f^{10}(^5I_8)6s6p(^3P^0_2)\,^3I^0_7$, $4f^9(^6H^0)5d^2(^3F)(^8G^0)6s\,^9G^0_7$, $4f^9(^6F^0)5d6s^2\,^7H^0_7$ and $4f^95d6s^2\,^7K^0_7$, 62, 51, 97 and 25 autoionizing resonances have been found respectively. Their resonance profiles can be fitted to Shore-Fano formula. The resonances for some states are very strong which can be used in resonance ionization spectroscopy with time-of-flight mass spectrometer (RIS-TOFMS) for ultrasensitive analysis of Dy to improve the detecting sensitivity.

Most of the linewidths of autoionizing states obtained are, in general, large with $\Gamma \geq 0.5 cm^{-1}$. The ionization efficiencies are quite different for different channels, and the linewidths of some coincident states for different channels are quite different too. Further work on analyzing the spectra and determining the configurations of these autoionizing states is needed.

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