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Photoionization of samarium in the threshold region

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The ground level of samarium was determined by Albertson[1,2] to be $4f^6 6s^2\,{}^7F_0$. The six higher levels of the ${}^7F$ ground-state term lie within 4021 cm^{-1} of the ${}^7F_0$ level. By identification of the terms in the $4f^6 6s6p$ configuration, he derived an ionization potential of 5.6 eV for samarium. Reader and Sugar[3] have calculated the ionization potential to be 5.63 eV (45 410 cm^{-1}), corresponding to a wavelength of 2213 Å. In the present work, we studied the wavelength region from below ionization onset to 1950 Å by use of a photoionization mass spectrometer, described previously.[4,5] A high-temperature source and a light source, described previously,[6] were used to generate an atomic beam and to provide the ionizing radiation.

Figures 1(a) and 1(b) show the photoionization-efficiency curves for samarium at two different temperatures and slightly different wavelength resolutions. The data in Fig. 1(a) were taken with the temperature of the atomic-beam source at about 1100 K and a monochromator bandpass of 2 Å. The data in Fig. 1(b) were taken with the temperature of the atomic-beam source at about 1270 K and a monochromator bandpass of 3 Å.

Both curves show that autoionization is a principal cause of ionization in the measured wavelength region. Because of the temperature of the atomic-beam source, the low-lying levels of the ground-state multiplet are thermally excited. For example, at a temperature of 1270 K the ${}^7F_4$ level at 2273.09 cm^{-1} has about 8% of the total population, the ${}^7F_3$ state at 1489.55 cm^{-1} has about 18%, ${}^7F_2$ at 811.92 cm^{-1} and ${}^7F_1$ at 292.58 cm^{-1} each have about 28% of the total and ${}^7F_0$ about 15% of the total. Even though the higher energy levels are significantly less populated, the line strengths may be greater; hence transitions that arise from them may appear with intensities comparable to the transitions that arise from the lower energy states.

Thermal excitation gives rise to autoionizing lines that appear at an energy less than the ionization potential; as a consequence an abrupt ionization onset is not observed. The transitions giving rise to the observed autoionizing lines are most likely due in part to transitions from the $4f^6 6s^2$ ground configuration to states of the $4f^6 5d7p$ configuration. The $6s^2 \rightarrow 5dnp$ transitions have been observed to be intense in other lanthanide photoionization spectra.[6,7] In samarium, the $4f^6({}^7F)5d6p$ levels are still bound and should be at about 27 000 $cm^{-1} \pm 4000$ cm^{-1}.[8] The series limit for the various $5dnp$ type series is the $4f^6 5d$ configuration of Sm II. The lowest of these Sm II levels are from about 7000 cm^{-1} to 21 000 cm^{-1} above the Sm II $4f^6 6s\,{}^8F_{1/2}$ ground level with the center of gravity of the octet levels at about 11 000 cm^{-1} and the center of gravity of the sextet levels at about 17 000 cm^{-1}. The lower terms of the $4f^6({}^7F_J)5dnp$ configuration would be expected to have as their limits the octet levels of Sm II. With a Rydberg denominator of 3.2, these lower terms of the $4f^6({}^7F_J)5d7p$ configuration that have as their limits the sextet levels of Sm II should then lie around 52 000 cm^{-1}. These estimates compare favorably with the corresponding configurations of Eu.[6] The autoionization observed below 48 000 cm^{-1} is probably in part due to the $4f^6({}^7F_J)5d7p$ terms that have as their limits the octet levels of Sm II, and the intense lines above 48 000 cm^{-1} are due in part to the terms of the $4f^6({}^7F_J)5d7p$ configuration that have as their limits the sextet levels of Sm II. It is uncertain, from this work alone, what the

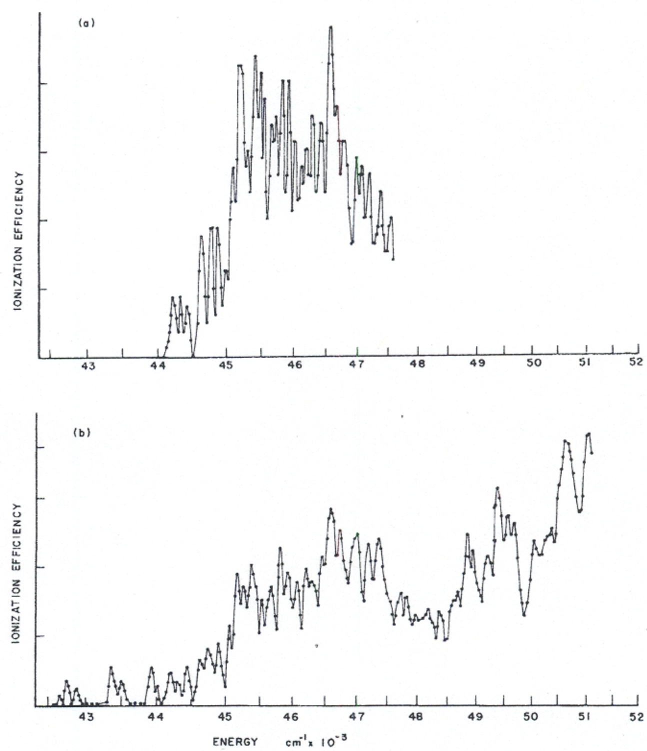

FIG. 1. (a) Photoionization efficiency of samarium, plotted versus energy expressed in cm^{-1}. The data were taken with the high-temperature source of 11 000 K. (b) Photoionization efficiency of samarium plotted versus energy expressed in cm^{-1}. The temperature of the source was 1270 K.

TABLE I. Autoionizing lines observed in samarium near ionization threshold. The table gives the energy and relative intensity of the lines as resolved in Fig. 1(b). The energies are taken at the maxima of the peaks.

Energy (cm^{-1})	Intensity	Energy (cm^{-1})	Intensity
42 650	1	46 210	15.5
42 740	3	46 290	14
42 890	2	46 430	17
43 350	4	46 580	22
43 500	2.8	46 750	20
43 920	4	47 040	19
44 000	2	47 210	18.5
44 200	3.5	47 390	19
44 280	2.5	47 740	12.5
44 430	4	47 830	12
44 620	5	48 380	10.5
44 750	6	48 720	12.5
44 850	7	48 880	19.5
45 060	9	48 970	17.5
45 170	15	49 220	17
45 300	13.5	49 410	24
45 410	16	49 740	20.5
45 550	12	50 060	19
45 660	13.5	50 400	20
45 820	18	50 670	30
45 930	15	51 070	31
46 120	14		

exact designation of the measured levels should be. The coupling scheme of the $4f^6(^7F_J)5d\,np$ configurations undoubtedly will change with increasing n, and the configuration interactions that provide the forbidden double-electron transitions need to be evaluated.

The autoionizing lines, as resolved in Fig. 1(b) are listed in Table I. The energy is in cm^{-1} and the intensity in arbitrary units. The energies are taken as the energies of the peak maximum and are given to the nearest 10 cm^{-1}. It is clear from a comparison of Figs. 1(a) and 1(b) that some of the lines listed in Table I are unresolved combinations of several lines. For example, the line at 45 410 cm^{-1} is resolved into 3 lines in Fig. 1(a), where the resolution is slightly better.

The first three lines observed are probably due to transitions from the $^7F_5$ level. If the three transitions are taken to be members of a multiplet with $J=4, 5, 6$, then several other lines can be fitted into such a sequence. The line at 43 500 cm^{-1} would then be a transition from the $^7F_4$ level to the $J=4$ upper level. The line at 44 280 cm^{-1} would then be a transition from the $^7F_3$ to the $J=4$ upper state.

It is possible for other configurations to lie in the energy region that we measured; they may contribute to the autoionization observed. The determination of the precise configurations and appropriate designations of lines observed requires further experimental and theoretical work.

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