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Possible additions to the spectra of core-excited neutral potassium, rubidium, and cesium

E. Veje
Physics Laboratory, Hans Christian Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark

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Some halides and hydroxides containing either potassium, rubidium, or cesium have been bombarded with 80-keV Ar^+ ions. The light emitted from sputtered particles has been studied in the wavelength range 200–900 nm. In each case some spectral lines, which cannot be identified as previously observed transitions, have been seen. They are tentatively classified as transitions among core-excited levels in the neutral potassium, rubidium, or cesium atoms. A discussion of possible assignments is given.

I. INTRODUCTION

We have bombarded a series of solid compounds containing either potassium, rubidium, or cesium with 80-keV Ar^+ ions and studied the light emitted from sputtered particles, as part of our attempts to systematically study atomic excitation phenomena in sputtering processes. In addition to several well-established optical transitions among levels in the neutral alkali-metal atoms (K I, Rb I, and Cs I) and singly ionized alkalis (K II, Rb II, and Cs II), some other lines showed up in the spectrograms. For each alkali metal, the same set of lines occurred when compounds containing different electronegative elements were used as target materials. The lines could not be related to impurities. Therefore, they are most presumably related to transitions among levels in the neutral or singly ionized alkali metals, because no transitions in K III, Rb III, or Cs III were seen at all by us, ruling out doubly and higher charged atoms. However, they cannot be identified as previously observed transitions in neutral or singly ionized alkalis.

The level schemes of the neutral alkali atoms with completed cores are very well established,[1–5] and so are those of the singly ionized alkali metals,[2,4,5] but little is known about the structure of core-excited terms of the neutral alkali metals studied here. Thus, the new lines may well be due to transitions among core-excited levels. However, transitions in negative ions cannot be ruled out in principle.

The core-excited configurations give rise to a doublet system as well as a quartet manifold. Part of the doublets have been established by means of absorption spectroscopy,[4,5] but information about the quartets is extremely sparse.[2,4–8] Therefore, and also because there is presently some interest in core-excited alkali metals, because of their possible use for vuv lasers,[6] we find it justified to communicate our observations despite our poor wavelength determinations.

Our results and conclusions concerning the excitation mechanism in sputtering are being published elsewhere, where also references to previous sputtering studies can be found.[9]

II. EXPERIMENTAL PROCEDURE

Our experimental equipment is described in detail in Ref. 10. Briefly, some high-grade-purity solid halides and hydroxides containing either potassium, rubidium, or cesium were bombarded with 80-keV Ar^+ ions at normal incidence to the target surface. Photons emitted from sputtered species were analyzed with a one-meter scanning monochromator (McPherson model No. 2051A, working in air, with grating blazed at 500 nm), and detected with a photomultiplier (EMI 9659 QB, S20 cathode). For all targets, the wavelength range 200–900 nm was scanned and the output from the photomultiplier was recorded on a strip chart recorder.

All spectral lines observed were identified as far as possible with the use of the spectral line tables given in Refs. 3 and 11 for potassium, in Refs. 3 and 12 for rubidium, and in Refs. 3, 11, and 13 for cesium. In each case a search was made for impurity lines using the tables of sensitive lines of all elements given in Ref. 14, but no impurities were observed, with the exception that some of the potassium compounds contained traces of sodium and also that some Balmer lines repeatedly showed up, the presence of hydrogen clearly being related to crystal water. Some molecular bands from the OH radical were seen with low intensities and identified using Ref. 15. Generally, only very weak or no radiation was seen from the electronegative elements and argon. The absence of excitation of electronegative elements in sputtering has been noted and discussed before.[16] The wavelengths of the spectral lines which could not be identified, and which repeatedly showed up when different compounds with one and the same alkali element in common were used, were determined using some close-lying, well-established spectral lines as calibration points.

The overall, relative quantum efficiency of the optical device has been determined using a calibrated deuterium discharge lamp (Cathodeon type C80-10V-SMFF) in the wavelength region 200–400 nm and a calibrated coiled-coil filament lamp standard of spectral irradiance (Optronic model 245C) in the wavelength interval 350–900 nm, as described in Ref. 17. For all of the new lines, their

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TABLE I. The table presents the wavelengths (in nanometers) of the new spectral lines of potassium together with relative intensities corrected for change in the overall quantum efficiency of the detecting device and tentative assignments, as discussed in the text.

Wavelength (nm)	Relative intensity (arbitrary units)	Tentative assignment Lower level	Upper level
285.0±0.2	15		
313.1±0.3	13		
445.8±0.3	7		
471.7±0.3	7		
498.0±0.4	3	$3p^5 4s4p\ {}^4S_{3/2}$	$3p^5 4s5s\ {}^4P^\circ_{1/2}$
515.1±0.4	4	$3p^5 4s4p\ {}^4S_{3/2}$	$3p^5 4s5s\ {}^4P^\circ_{3/2}$
546.1±0.4	5	$3p^5 4s4p\ {}^4S_{3/2}$	$3p^5 4s5s\ {}^4P^\circ_{5/2}$
604.5±0.4	7	$3p^5 4s4pJ=\frac{1}{2}$ or $\frac{3}{2}$	$3p^5 4s3d\ {}^4D^\circ_{1/2}$
611.7±0.3	11	$3p^5 4s4pJ=\frac{1}{2}$ or $\frac{3}{2}$	$3p^5 4s3d\ {}^4D^\circ_{3/2}$

average heights on the charts per incoming projectile flux unit were measured and divided by the relative quantum efficiency. Such intensities corrected for change in the quantum efficiency are given together with the wavelengths.

III. CONFIGURATIONS AND METASTABILITY OF LOW-LYING CORE-EXCITED TERMS

The core-excited levels of the neutral alkalis have excitation energies above the first ionization limits. Therefore, energetically they may autoionize. For a large number of levels, their autoionization rates are much larger than their electric dipole transition probabilities, implying that they will autoionize rather than decay through photon emission. Some of the lower-lying levels of quartet nature will, however, be stable or metastable against autoionization as well as against transitions to any doublet with completed core configuration. The only decay mode left for such levels will be possible electric dipole transitions to lower-lying quartet levels. Selection rules for stability or metastability of quartet levels in the neutral alkali-metal atoms has recently been discussed.[6,7] For the heavy alkali metals there are two classes of levels which can be expected to be metastable against autoionization. First are those quartets which have the largest possible value of J within a given configuration, and this is simply because, irrespective of the extent to which the LS coupling holds, there is no doublet level in the same configuration with which that quartet can couple. The second class of levels are those for which $|J-L|=\frac{3}{2}$, with parity and orbital angular momentum both even or both odd.

In each configuration, for the level with highest value of J, all orbital angular momenta and spins must couple parallel. That implies that for these levels, the core must be $p^5\,{}^2P^\circ_{3/2}$ which for all three elements is below ${}^2P^\circ_{1/2}$ (Refs. 4 and 5).

The lowest-lying core-excited term is of configuration $np^5(n+1)s^2$, with $n=3$ for potassium, $n=4$ for rubidium, and $n=5$ for cesium, respectively.[4,5] Both levels of this configuration are true doublets and the level with $J=\frac{3}{2}$ is below the $J=\frac{1}{2}$ level. The positions of the levels are well established.[4,5] The lowest-lying even configuration with quartets will be $np^5(n+1)s(n+1)p$. The three configurations $np^5(n+1)snd$, $np^5(n+1)s(n+2)s$, and $np^5(n+1)p^2$ have odd parity and can therefore combine with the $np^5(n+1)s(n+1)p$ configuration with electric dipole transitions involving one-electron jumps. The np^5nd^2 configuration also has odd parity but cannot combine with $np^5(n+1)s(n+1)p$ with a transition of one electron only. Therefore, the np^5nd^2 configuration is disregarded in the following discussion.

All of the new lines are in the following discussed as

TABLE II. The table presents the wavelengths (in nanometers) of the new spectral lines of rubidium together with relative intensities corrected for change in the overall quantum efficiency of the detecting device and tentative assignments, as discussed in the text.

Wavelength (nm)	Relative intensity (arbitrary units)	Tentative assignment Lower level	Upper level
372.9±0.3	5		
407.4±0.5	4		
411.1±0.4	1	$4p^5 5s5p\ {}^4S_{3/2}$	$4p^5 5s6s\ {}^4P^\circ_{1/2}$
424.8±0.2	18		
442.9±0.3	5		
466.5±0.3	12		
481.0±0.3	7		
495.9±0.3	10		
522.3±0.3	9		
550.6±0.4	1	$4p^5 5s5p\ {}^4S_{3/2}$	$4p^5 5s6s\ {}^4P^\circ_{3/2}$
754.9±0.3	21		

TABLE III. The table presents the wavelengths (in nanometers) of the new spectral lines of cesium together with relative intensities corrected for change in the overall quantum efficiency of the detecting device.

Wavelength (nm)	Relative intensity (arbitrary units)
358.7±0.3	2
435.0±0.2	13
664.9±0.3	2
709.2±0.5	2
715.4±0.5	2
717.2±0.5	2
738.8±0.3	16
763.7±0.2	68

being transitions among core-excited quartets in the neutral alkali-metal atoms. However, in principle, one or more of them might be due to transitions among doublets or in the negative ions.

IV. RESULTS AND DISCUSSION

A. Potassium

The lines observed with potassium targets are given in Table I, together with their relative intensities. According to Ref. 7, the $3p^54s4p\,^4S_{3/2}$ level is located at 161 426 cm^{-1}±60 cm^{-1}. The $3p^54s5s\,^4P^\circ_{1/2}$ and $^4P^\circ_{3/2}$ level values are 181 517 and 180 850 cm^{-1}, respectively,[4] indicating that the $^4P^\circ_{5/2}$ level will be approximately at 179 738 cm^{-1}, using the Landé interval rule. The wave numbers of the three transitions seen at 498.0, 515.1, and 546.1 nm agree within uncertainty limits with the energy differences from the $3p^54s4p\,^4S_{3/2}$ level to the $^4P^\circ_{1/2}$, $^4P^\circ_{3/2}$, and $^4P^\circ_{5/2}$ levels of the $3p^54s5s$ configuration, suggesting the assignments given in Table I for these three lines.

The $3p^54s3d\,^4D^\circ_{1/2}$ and $^4D^\circ_{3/2}$ levels are at 172 800 and 172 623 cm^{-1}, respectively.[4] The difference in wave numbers (195 cm^{-1}) between the lines seen at 604.5 and 611.7 nm agrees with the difference between the $^4D^\circ_{1/2}$ and $^4D^\circ_{3/2}$ level values (177 cm^{-1}), indicating that these two lines may be transitions from the $^4D^\circ_{1/2}$ and $^4D^\circ_{3/2}$ levels to a common lower level which thus has $J=\frac{1}{2}$ or $\frac{3}{2}$, is located at 156 266 cm^{-1}, and belongs to the $3p^54s4p$ configuration. Possible transitions from the $3p^54s5s$ configuration to such a level should occur at 396.0, 406.8, and 426.0 nm. We observed lines at these positions, which however also agree with known transitions in potassium in all three cases, precluding any confirmation of the above.

The remaining new potassium lines cannot be identified at present. The two lines with shortest wavelengths cannot be from the $3p^54s5s$ configuration, because that would place part of the $3p^54s4p$ configuration below the $3p^54s^2$ level.

B. Rubidium

The lines observed from rubidium are given in Table II. The two tentative assignments given are based on energy data for the $4p^55s5p\,^4S_{3/2}$ level given in Ref. 7, and for the $4p^55s6s\,^4P^\circ_{1/2}$ and $^4P^\circ_{3/2}$ levels in Ref. 5. The positions of the latter two levels indicate that the $^4P^\circ_{5/2}$ level of that configuration will be so low lying that its transition to the $4p^55s5p\,^4S_{3/2}$ level will be in the infrared.

C. Cesium

The new cesium lines are shown in Table III. Identification problems are worse for this element, partly because less information is available from absorption studies, and partly because cesium is not well described with the *LS*-coupling approximation. The fine-structure splitting of the $5p^56s^2$ term is large, and the data given in Refs. 7 and 8 indicate that the $5p^56s5d\,^4P^\circ_{3/2}$ and $^4P^\circ_{5/2}$ levels are located in between the $5p^56s^2\,^2P^\circ_{1/2}$ and $^2P^\circ_{3/2}$ levels, and also that the $5p^56s7s\,^4P^\circ_{5/2}$ level comes close to the $5p^56s^2\,^2P^\circ_{1/2}$ level. These data indicate that some of the quartet levels of the $5p^56s7s$ and the $5p^56s5d$ configurations will be below some of the quartets of the $5p^56s6p$ configuration, precluding at present to give tentative assignments for the transitions in Table III.

At the end, we mention that in the wavelength tables by Striganov and Sventitskii,[11] some lines are ascribed to Cs II, but with unknown upper levels, these being given with reciprocal centimeters only. We observed some of these lines with intensities noticeably larger than other Cs II lines. Maybe this indicates that some of these lines are due to transitions among core-excited levels in Cs I rather than among Cs II levels.

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