K\(\beta_1\) Line in Compounds of Elements of the Third Period

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It is shown that the K\(\beta_1\) line in compounds of the elements of the third period with elements of the second period is connected with levels for which the energy is determined principally by the 2s states of the second period atoms. The presence and absence of the line in compounds, magnitude of the K\(\beta_1\)-K\(\beta\) separation, shifts of the K\(\beta_1\) lines, and relative intensities are explained.

The K\(\beta_1\) line in the x-ray spectrum of an element arises from the K-M\(_{II}\) transition, and in the spectra of compounds of the third-period elements it gives rise to the idea of dispersion of 3p electrons in the molecule or crystal. At the present time, two theories have been put forward to explain the long-wave satellite K\(\beta\). The first theory explains the K\(\beta\) line by the K-M\(_I\) transition [1], and the second connects it with a transition from a ligand level [2]. As yet, however, a detailed analysis of results of both theories is lacking. From comparison of the respective L-spectrum and K\(\beta_1\)-band transition energies, it follows that the K\(\beta_1\) and L\(_{II}\) bands of aluminum in Al\(_2\)O\(_3\), magnesium in MgO, and silicon in SiO\(_2\) and SiC take up the entire upper level [3, 4], since the K\(\beta\) line cannot arise from the K-M\(_I\) transition and must be caused by a transition from a level lying deeper than the M\(_I\). In [5] it was shown that the K\(\beta\) lines in sulfates and chloride compounds which contain oxygen arise from transitions from molecular orbitals (1\(\pi_2\) in the cases of sulfate and perchlorate) to the K level of the central atom. This orbital corresponds essentially to the 2s orbital of oxygen. We shall show that the principal experimental results with respect to the K\(\beta_1\) lines can be explained by proceeding from the premise that the K\(\beta\) line is connected with transitions from molecular orbitals which are essentially 2s orbitals of the second-period element or other orbitals which lie somewhat below the 3p level of the third-period element. It should be emphasized that in compounds of the type Al\(_2\)O\(_3\), SiO\(_2\), SiC, etc., it is impossible to speak of 3p and 3s levels of the metal (or metalloid) or 2s levels of oxygen, in contrast to compounds of the type SiF\(_6^{2-}\), SO\(_4^{2-}\), etc., since in the first type of compounds the valence electrons form bands. However, results which are valid for levels will also be qualitatively valid for bands. We shall make the provision that by K\(\beta_1\) is understood the maximum of the intensity of the band.

Principal experimental results in regard to the K\(\beta_1\) lines are contained in the following discussion.

1. The K\(\beta\) line is practically absent in the spectrum of the element, but appears in compounds of the elements of the second period [6-8]. The K\(\beta\) line is absent in the spectra of sulfides, chlorides, Ti\(_2\)Si\(_3\), Mo\(_2\)S\(_3\), and Si\(_2\)B\(_6\), but is present in the spectra of SO\(_4^{2-}\), Cl\(_4^-\), SiO\(_2\), SiC, etc.

2. The K\(\beta_1\)-K\(\beta\) separation for like neighboring atoms decreases slightly with increase of atomic number of the third-period element, and for a given atom of the third period decreases noticeably in proportion to the decrease of atomic number of the neighboring atom of the second period. This phenomenon can be seen from this series: KClO\(_4\) 12, SO\(_4^{2-}\) 14.3-13.9, P\(_2\)O\(_5\) 14.4-13, SiO\(_2\) 13.8, Al\(_2\)O\(_3\) 15.3, Si\(_2\)N\(_4\) 11, SiC 8.3-9.2 eV. (Experimental values are taken from [2b, 3, 6-9].)

The K\(\beta_1\) displacement upon the transition from element to compound proceeds in the long-wave direction for atomic numbers 11 to 14, increases with increasing ionicity of the bond and decreases with increase of Z. For sulfate, this displacement is small and, in comparison with sulfide, even proceeds in the short-wave direction, and for ClO\(_4^-\) (where x = 2 to 4) a well-expressed short-wave displacement is observed which increases from 0.6 to 3.3 eV with increase in x [6-10]: NaF 7.8, NaCl 7.5, NaBr 6.4, NaI 5.7, MgO 5.3-6.3, Al\(_2\)O\(_3\) 4.1-4.5, SiO\(_2\) 4.3-3.3, SiC 0-1.1 eV. The effect of ionicity of the bond on the displacement has been especially well studied for aluminum compounds.

4. The ratio of the intensities I(K\(\beta\))/I(K\(\beta_1\)) increases with increase of atomic number of the third-period element for like neighboring atoms, and with increase of ionicity of the bond [6, 2a]. This ratio is \(1/3\) for ClO\(_4^-\).
These rules agree with results of calculations by the molecular orbital method for the $K\beta_1\beta^*$ lines in $SO_4^{2-}$ and $ClO_4^-$ and are explained in the following manner.

1. The appearance of the $K\beta^*$ line in the spectrum agrees with the assumption of the presence of a level which lies below the 3p level, which in this particular case is the 2s level of the second-period element. Calculation gives the correct $K\beta_1-K\beta^*$ separations and relative intensities for sulfate and perchlorate [6].

2. The $K\beta_1-K\beta^*$ separation is determined principally by the 2s–2p separation, and decreases proportionately with decrease of Z of the second-period element. The 2s–2p separation is about 16 eV for oxygen; with increase in Z of the third-period element, interaction of the 2p and 3p levels increases and leads to slight lowering of the 2p level of oxygen, so that the $K\beta_1-K\beta^*$ separation decreases slightly from $Al_2O_3$ to $SO_4^{2-}$. This decrease is particularly great for the transition to $ClO_4^-$, for in that case the energy of the 3p orbital of chlorine is greater in absolute value than the energy of the 2p orbital of oxygen, so the 2p draws the 3p noticeably toward the 2s level of oxygen and the $K\beta_1$ line is formed as a result of a transition from a level genetically related to the 3p level of the central atom. This process causes a difference from the compounds of other third-period elements, where the $K\beta_1$ line arises from a transition from levels preferentially connected with the 2p levels of oxygen.

3. As was noted above, in compounds of the elements up to Z = 16 inclusive, the $K\beta_1$ line is connected with a level whose energy is determined, for example, by the 2p level of oxygen, and the difference between its energy and the energies of the 3p levels of the third-period element causes the long-wave displacement of the $K\beta_1$ line, which increases with ionicity of the bond, of the compound with respect to the line of the element. However, the energy of transition depends equally on the change of the energy of the K level as a result of increase in the charge of the atom of the third-period element in the compound. This change increases with increase in Z and results in short-wave displacement of the $K\beta_1$ line, as can be seen from the following series, which was calculated from the charge on the atom of the third-period element on the basis of values of [12-13]: $SiO_2$ 21.6, $PO_4^{3-}$ 25.6, $SO_4^{2-}$ 32.2, $ClO_4^-$ 34.6 eV. This displacement is essentially compensated by the field of the surrounding atoms and for sulfate, for example, is 5.5 eV [6]. If the charge on oxygen in compounds of these elements in their highest oxidation states is calculated, then it also decreases with increase in Z [13]; therefore, the uncompensated short-wave displacement of the K level increases with Z. In regard to this conclusion, the overall long-wave displacement decreases proportionately with increase in Z, and the short-wave contribution to the displacement of the $K\beta_1$ line is so large for the chlorine compound that it determines the magnitude and tendency of increase of displacement as a function of atomic charge.

4. The contribution of the 3p states to the wave function describing the level closest in energy to the 2s level of oxygen increases as a result of the increase in orbital energy of the 3p level with increase in atomic number. (Owing to the rough determination of the non-diagonal elements, this conclusion was not obtained by calculation[5].) The decrease of $I(K\beta_1\beta^*)/I(K\alpha_{1,2})$ was explained in [11] by the decrease in density of valence electrons in the inner regions of the atoms in the compound. Within the framework of the molecular orbital method, an equivalent explanation is contained in the decrease of $\Sigma \alpha_3p^2$, where $\alpha$ is the coefficient of the 3p function in the molecular orbital, and the sum is distributed in all orbitals which contain the 3p function. If it is assumed that the total decrease in the number of 3s and 3p electrons in the atom in comparison with the sulfur and chlorine compounds, as determined on the basis of displacement of the $K\alpha_{1,2}$ line, is equivalent to the decrease in the number of 3p electrons, and if it is considered that the charges of chlorine and sulfur in NaCl, NaClO3, NaClO4, Na2SO3, and Na2SO4 are equal, respectively, to −1.00, + 1.72, + 2.27, + 1.95, and + 2.34, then for the ratios of intensities we get $I_{NaCl}: I_{NaClO_3}: I_{NaClO_4}: I_{Na_2SO_3}: I_{Na_2SO_4}$ = $1: 1.71: 0.62$ and $1: 0.81$. Experiment [11, 6] gives, respectively, $1: 0.74-0.81: 0.49-0.54$ and $1: 0.83$. For comparison, a compound is taken for which the molecular orbital concept is well justified, since the 5-charge chlorine in NaCl cannot be greatly different from −1. However, it must be emphasized that the change in charge of the 3p function plays an important role which is of the same order as the change of $\Sigma \alpha_3p^2$ and tends to compensate the decrease in intensity of the $K\beta_1\beta^*$ line. This effect is especially important for elements with small Z. An estimation indicates that the effect can still be neglected for chlorine and sulfur compounds.

It should also be noted that the behavior of the long-wave satellite in the K spectra of $B_2O_3$ and BN [14], as well as the direction of displacement of the principal maximum, agrees completely with the rules set down here; consequently, the origin of the satellite can be explained by a transition to the K level of boron from a level described essentially by the 2s functions of oxygen or nitrogen.