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The Raman Spectra of Dioxane

On occasion of an investigation of Raman spectra of oxomium association compounds we studied the Raman spectra of dioxane. The results obtained show some discrepancies from those of Villars,[1] who probably used a set of less aperture and worked without light-filter. Dioxane, prepared from ethylene-glycol according to Favorsky,[2] and having the boiling-point at 96–102°C was investigated in a Raman apparatus described elsewhere.[3] The exposure was one hour. We obtained 29 Raman lines while Villars obtained 21, and all the lines of Villars were reproduced except 20,214 cm^{-1}(00). The spectra taken with a quinine filter according to Warburg and Nezelein with an exposure of two hours show some errors in the readings of Villars, who found the following Raman frequencies (in cm^{-1}):

291(5)(i,k); 434(00)(e); 519(0)(e); 837(4)(e,i,k); 1117(1)-(g,i,k); 1214(1)(k); 1442(2)(e,k); 2720(00)(e,k); 2864(3)-(e,i,k); 2967(3)(e,i,k).

Instead of these frequencies we obtained the following: 427(3)(e,k); 487(3)(e,k); 836(10)(e,f,i,k); 940(2)(e,f,k); 1017(5)(e,k); 1115(5)(e,k); 1213(3)(e,k); 1306(5)(e,k); 1450(6)(e,f,k,m); 2862(10)(e,k); 2971(10)(e,k,p,q).

It is interesting to note the close resemblance between the Raman spectra of dioxane and of ether. We obtained for the latter the following frequencies, which do not largely differ from the data of Bär.

440(5)(e,f,g,i,k,m); 497$(i)(e,i,k)$; 843(8)(e,f,i,k); 928(3)-(e,i,k); 1152(1)(k); 1276(2)(e,k); 1456(5)(e,f,g,k,m); 2694-(4)(k); 2807(5)(k,g); 2872(10)(e,k,g); 2935(10)(e,k,g); 2983(10)(e,k,o,p,q). We did not find the line 2730(1) of Bär and observed a new line 497(1).

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[1] Villars, J. Am. Chem. Soc. **52**, 4612 (1930); K. W. Kohlrausch, *Der Smekal-Raman Effect*, p. 338.
[2] Favorsky, J. Russ. Chem. Soc. **38**, 741 (1906) (Russian).
[3] Syrkin und Wolkenstein, Acta Phys. Chim. URSS **2**, 303 (1935).
[4] Warburg and Nezelein, Zeits. f. physik. Chemie **106**, 191 (1923).
[5] K. W. F. Kohlrausch, reference 1, p. 311.

Surface Ionization of Potassium Iodide on Tungsten

It has been shown by Rodebush and Henry[1] that positive ions are formed when molecular rays of alkali halides strike a hot oxygen-coated tungsten surface. We have made a further study of this phenomenon; in particular we have observed, as a function of the surface temperature, the positive ion current obtained when a constant ray of KI molecules struck a tungsten filament, first oxygen-coated and then stripped of its oxygen (by flashing at a high temperature). In the region of temperature in which the oxygen layer is stable the positive ion current was constant. A similar constancy was observed by Langmuir and Kingdon[2] for alkali metals on an oxygen-coated surface, and was interpreted by them as indicating complete ionization.

When the wire was flashed and the oxygen removed, the positive ion current was found to be lower at all temperatures than before flashing, and was observed to decrease with increasing temperature. This behavior after flashing was the same as that reported by the authors[3] for potassium atoms. The fact that metal and salt showed the same behavior suggests that the essential ionization process in both cases is the same: namely, the ionization of a potassium atom on the surface. This would imply a preliminary dissociation of the adsorbed salt molecule into atoms on the surface. Making this assumption, we have calculated values of the ratio of the numbers of potassium ions to potassium atoms evaporating from the clean wire at temperatures in the region 1700° to 2200°K.

It has been shown theoretically[2] that in the case of potassium atoms the following relation should hold: ·

$$\log_{10}\frac{i_+}{i_a}=\log_{10}C+\frac{(\phi-I)\epsilon}{2.303k}\cdot\frac{1}{T},$$

where i_+/i_a is the ion-atom ratio, ϕ is the work function of the surface, I is the ionization potential of the atom, and C is a constant for a given surface and atom. When a plot of the logarithm of the ion-atom ratio for the salt case was made against $1/T$, a straight line was obtained whose slope and intercept were found to agree within experimental error with those observed[3] for potassium metal. This agreement confirms the suggested mechanism.

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[2] Langmuir and Kingdon, Proc. Roy. Soc. **A107**, 61 (1925).
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