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The strong Raman line from solutions of cadmium, silver and lead nitrates has been re-measured at varied concentrations, and the results of Grassmann confirmed, namely that the frequency shift diminishes with increasing concentration for lead and silver, and varies little for cadmium. A qualitative explanation of this behavior and that of sodium nitrate is suggested in the effect of the cations on the structure of water, and attention is drawn to the similar order of these nitrates in x-ray diffraction phenomena.

THE Raman effect in solutions of nitrate has been studied by a number of observers, and from various standpoints. One of these has been the question of the dependence of the magnitude of the frequency shift on concentration, cation, and temperature. Gerlach[1] found for $NaNO_3$ and $LiNO_3$ slight, barely measurable, increases in the frequency shift with concentration, but larger changes in various nitrate crystals. Grassmann[2] found variations in both directions, depending on the cation. Franklin[3] confirmed the increase in frequency shift for $NaNO_3$ solutions from 1048.0 ± 1 cm^{-1} at 1.25 N to 1050 cm^{-1} at 8 N and to 1068 cm^{-1} in the crystal. On the other hand, a change of 12.5 cm^{-1} reported by Embirikos[4] for solutions of magnesium sulphate was not confirmed by Woodward and Horner[5] nor by Coon.[6] It seemed, hence, worth while to repeat some of Grassmann's experiments, and for this the nitrates of silver, cadmium, and lead were chosen.

The source of illumination was a glass mercury arc, the spectrograph a Hilger D78, the Raman tube of the jacketed horn form, with the horn and the circle around the window painted black. It was placed under the arc, and so that the light scattered from the farthest portion would just fill the collimator lens of the spectrograph without use of lens between the tube and slit. Water was ordinarily used in the jacket, but for some of the long exposures a solution of praseodymium neodymium sulphate was used as filter. Times of exposure varied from three hours to thirty. The slit width was such as to give a slit image somewhat narrower than the Raman line. An iron arc comparison spectrum was put on most of the plates at the end of the exposure.

Measurements were made on a Hilger measuring micrometer. Earlier experience had shown that the use of a comparison iron arc in determining wave-lengths was unsatisfactory, as shifts between this spectrum and the unmodified Hg lines sometimes appeared. These were suspected to be due to changes in temperature or barometric pressure during exposure. The room temperature was controlled by a thermostat, and thermograph records showed a variation of less than 2°F, but there was no way of controlling the pressure. While the effect of variations in pressure and temperature on the mercury lines would be to broaden them, but not to shift the relative center of gravity by a measurable amount, the iron spectrum put on in a few seconds might be measurably shifted, and by different amounts at different parts of a plate. Hence it was decided to use the mercury lines only, with the Hartmann formula, in computing, and to make a correction curve for the Hartmann formula from some test plates where both the mercury and iron spectra were recorded with short exposures. Any slight error in determining this correction would affect all the measurements equally, and not alter comparative values. During the progress of the work the paper of Teal and MacWood[7] appeared giving data on the effect of changes in barometric pressure even

* Skinner Fellow in Physics, 1935–36.
[1] Gerlach, Ann. d. Physik **5**, 196 (1930).
[2] P. Grassmann, Zeits. f. Physik **77**, 616 (1932).
[3] Franklin and Laird, Phys. Rev. **45**, 738 (1934).
[4] Embirikos, Zeits. f. Physik **65**, 266 (1930).
[5] Woodward and Horner, Proc. Roy. Soc. **144**, 129 (1934).
[6] Coon and Laird, Phys. Rev. **47**, 889 (1935).

[7] Teal and MacWood, J. Chem. Phys. **3**, 760 (1935).

over a period of three hours. The mercury lines 4916.0A, 4339.23A, and either 4108.08A or 4077.83A were used as standards. The deviations of the other mercury lines measured as checks were of the order of 0.03A.

The results reduced to vacuum are shown in Table I; they have been computed from measurements on the strong Raman line excited by the Hg line 4358A. The corresponding line excited by 4047A was also measured but the accuracy was not so great. The dispersion in the neighborhood of 4566A is 25A/mm. The table of wavenumber differences compiled by P. L. Bayley was used in checking. All but one of the silver nitrate plates were measured twice, and all but three of the lead plates, the $\frac{1}{2}N$ lead plates were measured four or more times on different days and at different points on the lines. The average was taken for each plate as the measurement of that plate, and the deviations shown are the deviations of these from the final average. In the case of lead nitrate there is also shown the average deviation of the separate measurements. The last column shows Grassmann's values.

It will be seen that in a general way the results are in agreement with those of Grassmann. His assumption that for silver nitrate the shift increases with dilution is confirmed, and it is shown that for cadmium nitrate the shift, if any, is very slight. For lead nitrate the variation found looks smaller than his, but the difference is within the sum of the estimated errors. Combining these results with those obtained earlier for sodium nitrate, one may arrange the four nitrates in the order sodium, cadmium, silver, lead, in that the effect of increasing concentration is with sodium to slightly increase the shift of the Raman line, with cadmium to change it very slightly if at all, and with silver and lead to diminish it, possibly more for the lead at the same concentration of the cation, also, the difference between the frequency shift in the crystal and in the dissolved state is larger for sodium nitrate than for cadmium nitrate, and for lead and silver is questionable.

In the observations of Prins[8] on x-ray diffraction by nitrate solutions a somewhat parallel order is found. Prins distinguishes the cases

where a diffraction ring is found, the diameter of which increases with concentration, and inside of which, the diffraction diminishes as the angle approaches 0°, and the cases where the position of maximum diffraction does not change with concentration. He finds a mobile maximum in the case of cadmium nitrate but not for either lead or silver nitrates. He attributes the mobile ring to a kind of super-arrangement of the heavy ion, and the lack of it to an irregular gas-like distribution. Sodium is too light in comparison with the other atoms present for the method to be applied with success, and Prins found no small angle scattering of importance for sodium nitrate solution, but a pattern which he attributed to an arrangement that the water molecules assume in the electric field of the cations. As he notes that the phenomenon of super-arrangement decreases in the series K, Rb, Cs, one might infer that it would be large for sodium, although the experimental method does not show it directly.

Prins attributed the lack of superarrangement in the case of lead and silver to nondissociated molecules. One finds no support for this in the electrolytic conductivities of these nitrates, and measurements of the intensity of the Raman line at different concentrations by several observers has shown that for sodium, cadmium, and lead nitrates it is proportional to the concentration of the NO_3 ion. It has been argued that this is not an evidence of dissociation as the NO_3 constituent would be present in either case. But as in all cases the frequency shift in the crystal is different from that in the dilute solution, there should also be a difference for light scattered from associated

[8] Prins, J. Chem. Phys. 3, 72 (1935); Physica 3, 1016 (1935).

TABLE I.

SUBSTANCE	NOR-MALITY	No. PLATES	$\Delta\nu$ IN CM^{-1}	$\Delta\nu$ IN CM^{-1} GRASSMANN
Pb(NO₃)₂	4	5	1044.1±0.4±0.6	1043.8±0.6
	2.7			1046.0
	2	5	1045.7±0.6±0.9	
	1	2	1045 ±1	
	0.5	3	1046.7±0.4±1.0	1048.0±1.0
Crystals		1	1044.3	1045
AgNO₃	7	2	1043.2 ±0.1	1042.3 ±0.8
	3	4	1045.4 ±0.4	
	1	2	1046.1 ±0.4	
Crystals				1045 (Gerlach)
Cd(NO₃)₂	8	4	1047.4 ±0.3	1047.4 ±0.4
	2	3	1047.7 ±0.3	
Cd(NO₃)₂·4H₂O Crystals		1	1052.2	

molecules. The photometric curves of the Raman lines from the concentrated solutions appear however those of single lines. If one concludes that dissociation is complete, one may still find in the ideas concerning the structure of water of Bernal and Fowler,[9] used also by Prins, a qualitative explanation of the difference with respect to Raman scattering between the behavior of the nitrates of sodium and cadmium on the one hand and silver and lead on the other. The sodium and silver ions are singly charged, but the sodium being smaller exerts a greater influence in maintaining or increasing a certain regularity in structure in the water. The cadmium and lead ions are doubly charged, so that although the cadmium ion is as large as silver it produces an effect more like that of sodium, but the still larger lead ion again has a smaller directing effect, and its presence may lead to a weakening

of the structure. This might be tested in a study of the water bands of small frequency shift referred to by Hibben[10] as surely due to intermolecular interaction.

The NO_3 ion is considered to be plane, with the nitrogen at the center of an equilateral triangle, and the oxygen atoms at the corners. The Raman line studied here is ascribed to the radial vibration. The effect of the cations on this vibration would be indirect according to the point of view suggested here. Where there is a super-arrangement of the cations, there are crystal-like groupings of molecules, and the symmetry makes for a higher vibration frequency, but if the water structure is weakened, and the cations are more at random, the central forces in the NO_3 ion may be weakened, and the frequency lowered.

Our thanks are due to Dorothy Franklin, who assisted considerably in measuring the plates.

[9] Bernal and Fowler, J. Chem. Phys. 1, 515 (1933).

[10] Hibben, J. Chem. Phys. 5, 166 (1937).

Temperature Scale and Thermionic Emission from Rhodium

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When rhodium is heated to incandescence in an atmosphere of air or oxygen, a coating forms on its surface. This is shown by a change in the emissivity. When the temperature is increased sufficiently this coating suddenly disappears, and when the temperature is lowered it reappears. This coating is probably an activated adsorption of oxygen, or an oxide of rhodium. It is found experimentally that the temperature and partial oxygen pressure at which the coating disappears are related by the Clausius-Clapyron equation:

$$(d \log_e P)/dT = L/RT^2.$$

P is the partial oxygen pressure, T the absolute temperature, and L the heat of vaporization of the surface. The electron work function of a clean rhodium surface is found to be $\varphi = 4.80$ volts, and $A = 33$ amp./cm^2/degree^2.

EMISSIVITY AND TEMPERATURE SCALE

THE peculiarities of rhodium surfaces described below were first encountered when measurements of spectral emissivity were being taken.[1] A specimen of rhodium in the shape of a V wedge 6 cm long, 4 mm wide on a side, and about 0.04 mm thick was mounted inside a brass

chamber which was evacuated to a pressure of $1–2 \times 10^{-6}$ mm. The true temperature was measured by an optical pyrometer sighted inside the wedge, and the apparent temperature by another pyrometer sighted on the outside surface.

A typical sequence of readings is shown in Fig. 1. When the temperature was first raised, a series of values shown by the lower curve was found. Upon lowering the temperature there was

[1] L. V. Whitney, Phys. Rev. 48, 458 (1935).