Raman Effect in Samarium Nitrate Solutions

Rasetti\(^1\) has adduced evidence for the possibility of an electronic Raman effect in the case of the diatomic molecule NO, where the Raman band corresponds to the transition \(\Pi_{1/2} \rightarrow \Pi_{3/2}\). While all attempts at discovering an electronic Raman effect in \textit{atoms} by one of us (L. Sibaiya) in thallium vapor (after a suggestion by Jevons\(^2\)) failed, it was surmised that samarium ion, \(\text{Sm}^{++}\), with a ground state \(\Pi\), was perhaps more suitable for the study of such an effect because of the ease with which the ions could be had at high concentrations in solution. But the examination of the Raman spectrum (Fig. 1.4) of a dilute solution of samarium nitrate (about 8 percent) revealed no new features except the nitrate frequency at 1047 cm\(^{-1}\), the water bands and the characteristic fluorescent bands of samarium with intensity maxima at \(\lambda = 5600, 5950, 6030\) and 6390 A (Fig. 2). When the investigation was, however, repeated at a higher concentration (about 40 percent), three entirely new bands made their appearance (Fig. 1.3). Since even the Raman band of water arising from \(\lambda = 4047\) A is here completely absent due to the strong absorption of the solution for this radiation, the three new bands have to be ascribed to the incident radiation \(\lambda = 858\) A. As no trace of these bands is seen in the dilute solution, it follows first, that the new bands do not arise from fluorescence and second, that they appear because of the increased concentration of samarium ions in solution. No such effect arising from an increased concentration of the nitrate ion in the case of potassium nitrate, for instance, could be observed. The new bands therefore with approximate frequency shifts of 950, 680 and 2770 cm\(^{-1}\) at their maxima from the incident line \(\lambda = 858\) A have been \textit{tentatively} ascribed to an electronic Raman effect in samarium ions. A calculation of the frequency separation between \(\Pi_{1/2}\) and \(\Pi_{3/2}\) from Goudsmit's formula yields a value 932 cm\(^{-1}\), which agrees fairly satisfactorily with the observed Raman shift of 950 cm\(^{-1}\); the band at 2770 cm\(^{-1}\) requires the assumption of a transition from \(\Pi_{1/2}\) to \(\Pi_{3/2}\). The width of these bands, however, remains to be explained. An analysis of the absorption spectrum of samarium salts at low temperatures by Spedding and Bear\(^3\) has shown that the ground level \(\Pi_{1/2}\) is a close group of about five levels with a total separation of about 250 cm\(^{-1}\). Frank\(^4\) concludes that the ground level can split only into one doublet in an ionic field with cubic symmetry; this possibly explains the existence of another band at 680 cm\(^{-1}\). If it is assumed that the larger number of low lying levels postulated by Spedding and Bear is correct, Van Vleck\(^5\) sees no other possibility of explaining them but as an interaction between vibration and electronic states. The sharpness of these close levels observed at such low temperatures as 20°K-78°K cannot obtain at ordinary temperatures and to this cause is traced the bandlike appearance of what ought to have been Raman "lines." The provisional explanation here put forth for the new bands observed at greater concentration of samarium ions is being tested with other salts of samarium and europium. In Fig. 2 the Raman band of water in concentrated solution (B) is seen to be widened out as compared with the same band in dilute solution (A); this possibly arises from an interaction of the ionic fields with the OH bond.

Another very interesting feature in Fig. 1 is the rotational wing accompanying the incident radiation \(\lambda = 858\) A present only in the Raman spectrum of the dilute solution and entirely absent in the spectrum of the concentrated solution brought about by an enormous increase of fluid viscosity. Attention to this point has been recently drawn by Raman and Venkataraman\(^6\) who have worked with four liquids of increasing viscosity; we have in the present instance a case where the increase in concentration of the same solution suppresses the wings on account of enhanced viscosity.

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\(^{6}\) Raman and Venkataraman, Nature 133, 795 (1939).