

followed on the average by two gamma-rays. It follows also that the disintegration leads to an excited state of  $\text{Sn}^{116}$ .

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<sup>1</sup> M. V. Brown and A. C. G. Mitchell, *Phys. Rev.* **50**, 593 (1936).  
Gaertner, Turin and Crane, *Phys. Rev.* **49**, 793 (1936).

<sup>2</sup> Langer, Mitchell and McDaniel, *Phys. Rev.* In press.

### Raman Effect in Samarium Nitrate Solutions

Rasetti<sup>1</sup> has adduced evidence for the possibility of an electronic Raman effect in the case of the diatomic molecule  $\text{NO}$ , where the Raman band corresponds to the transition  ${}^2\Pi_{1/2} - {}^2\Pi_{3/2}$ . While all attempts at discovering an electronic Raman effect in *atoms* by one of us (L. Sibaiya) in thallium vapor (after a suggestion by Jevons<sup>2</sup>) failed, it was surmised that samarium *ion*,  $\text{Sm}^{++}$ , with a ground state  ${}^6H$ , 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. 1A) of a dilute solution of samarium nitrate (about 8 percent) revealed no new features except the nitrate frequency at  $1047\text{ cm}^{-1}$ , the water bands and the characteristic fluorescent bands of samarium with intensity maxima at  $\lambda\lambda 5600, 5950, 6030$  and  $6390\text{A}$  (Fig. 2). When the investigation was, however, repeated at a higher concentration (about 40 percent), three entirely new bands made their appearance (Fig. 1B). Since even the Raman band of water arising from  $\lambda 4047\text{A}$  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  $\lambda 4358\text{A}$ . 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  $2770\text{ cm}^{-1}$  at their maxima from the incident line  $\lambda 4358\text{A}$  have been *tentatively* ascribed to an electronic Raman effect in samarium ions. A calculation

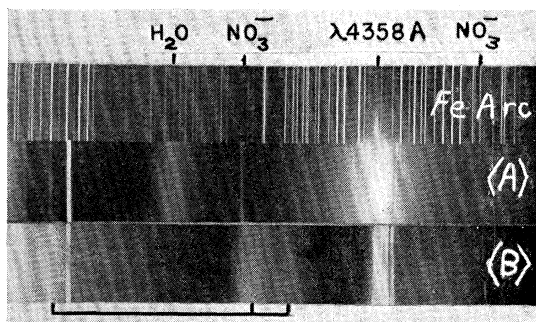


FIG. 1.

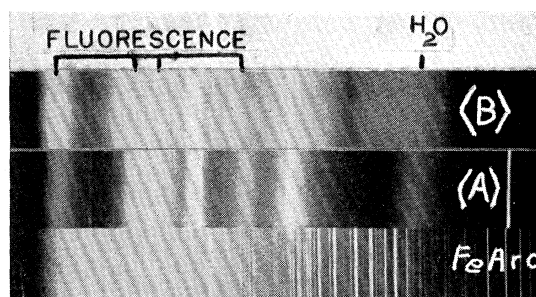


FIG. 2.

of the frequency separation between  ${}^6H_{5/2}$  and  ${}^6H_{7/2}$  from Goudsmit's formula yields a value  $932\text{ cm}^{-1}$ , which agrees fairly satisfactorily with the observed Raman shift of  $950\text{ cm}^{-1}$ ; the band at  $2770\text{ cm}^{-1}$  requires the assumption of a transition from  ${}^6H_{7/2}$  to  ${}^6H_{11/2}$ . 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<sup>3</sup> has shown that the ground level  ${}^6H_{5/2}$  is a close group of about five levels with a total separation of about  $250\text{ cm}^{-1}$ . Frank<sup>4</sup> concludes that the ground level can split only into a doublet in an ionic field with cubic symmetry; this possibly explains the existence of another band at  $680\text{ cm}^{-1}$ . If it is assumed that the larger number of low lying levels postulated by Spedding and Bear is correct, Van Vleck<sup>5</sup> 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  $20^\circ\text{K} - 78^\circ\text{K}$  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  $\lambda 4358\text{A}$  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 Venkateswaran<sup>6</sup> 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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<sup>1</sup> F. Rasetti, *N. Cimento*, **7**, 261 (1930).

<sup>2</sup> Jevons, *Report on Band-Spectra of Diatomic Molecules* (1932), p. 246.

<sup>3</sup> F. H. Spedding and R. S. Bear, *Phys. Rev.* **46**, 975 (1934).

<sup>4</sup> A. Frank, *Phys. Rev.* **48**, 765 (1935).

<sup>5</sup> J. H. Van Vleck, *J. Phys. Chem.* **41**, 67 (1937).

<sup>6</sup> Raman and Venkateswaran, *Nature* **143**, 798 (1939).

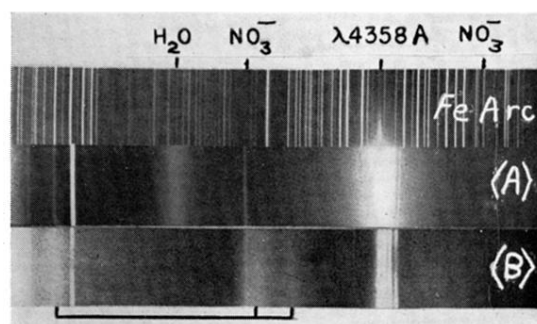


FIG. 1.

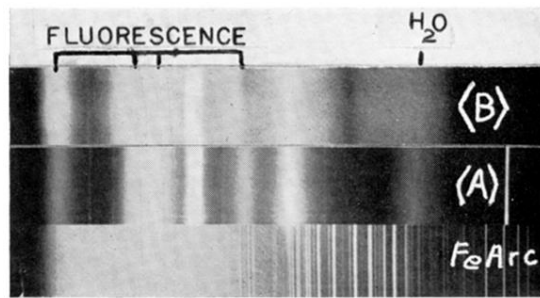


FIG. 2.