

The Polarization of the Absorption Lines of Single Crystals of Rare Earth Salts

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The Polarization of the Absorption Lines of Single Crystals of Rare Earth Salts

The absorption spectra of rare earth salts of the type $M_2(SO_4)_3 \cdot 8H_2O$ have been studied in great detail, at different temperatures, by Spedding and his collaborators.¹ From a preliminary analysis of these spectra they have concluded that the electric fields acting on the rare earth ions in these crystals, which are responsible for the splitting of the energy levels of the ions, should be nearly cubic in symmetry. Since the absorption spectra of these crystals are complicated and their analysis difficult, it would be desirable to verify this conclusion by an independent method. One direct result of such a cubic symmetry for the electric fields is that the crystals should be magnetically isotropic.

But actually many of these crystals are strongly anisotropic,² showing that the fields should deviate considerably from cubic symmetry.

The purpose of the present note is to show that some of the features of the absorption spectra themselves point to such a deviation from cubic symmetry in the internal electric fields. From a study of the absorption spectra of single crystals of these salts in polarized light, it is found that many of the absorption lines are strongly polarized, some of them being confined almost wholly to vibrations along one or another of the principal axes of the optical ellipsoid of the crystal, and that these variations in the direction of polarization occur even among the lines of the same group; in other words, among the Stark components

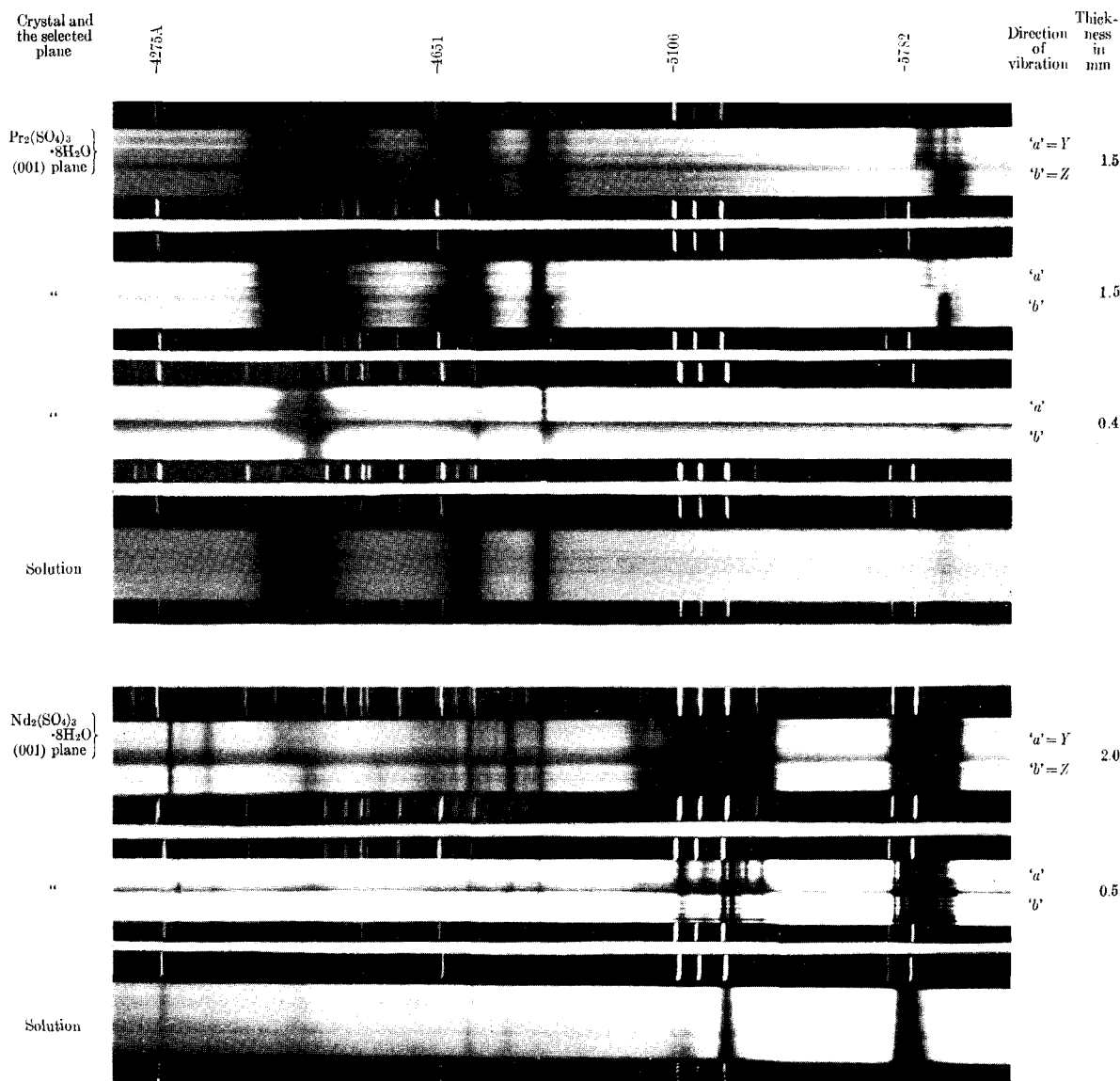


FIG. 1.

which originate from the same absorption line of the free ion, some are polarized strongly in one direction and some strongly in another.

We reproduce in Fig. 1 some typical absorption photographs which show the polarization. The crystals are monoclinic, and the upper and the lower halves in each photograph correspond to light vibrating respectively along the two extinction lines in the particular crystal plane selected for study.

The strong polarization, and the variation in its direction, observed among the members of a Stark group, show that the electric fields which produce the Stark splitting should be strongly asymmetric. Since there are 8 rare earth ions in the unit cell of the crystal, and the principal axes of the electric fields acting on these 8 ions may not be all parallel, the noncubic parts of the fields may be even much larger than the observed polarizations would suggest.

We are studying the polarization of the lines in some detail in the hope that the results may be helpful in the analysis of these complicated spectra.

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January, 24, 1938.

¹ Several papers in this journal, 1937.

² K. S. Krishnan and A. Mookherji, *Nature* **140**, 549 (1937), and paper in course of publication in *Phil. Trans. Roy. Soc. A*.

The Infra-Red Absorption Spectrum of Nickel, Carbonyl Vapor

We have examined the infra-red absorption spectrum of nickel carbonyl between 1 and 20 μ . The bands observed are shown in Table I, and compared with the Raman spectrum as observed by Duncan and Murray.¹

The figures in parentheses indicate two complex and extended regions of absorption near 7.5 and 10 μ ; the former appears to have six or seven peaks at intervals of approximately 20 cm⁻¹.

The question at once arises as to whether free CO was present. The fundamental band of this substance as determined with a fluorite prism² has its center at 2146, with *P* and *R* branches easily resolvable at a separation of some 46 cm⁻¹; the Raman line³ lies at 2155 10 cm⁻¹. A weak frequency in the Ni(CO)₄ infra-red spectrum shows as a side maximum at 2134 on the 2051 band. We found no trace of structure in the side band but cannot definitely say that it is not due to carbon monoxide. We propose to examine the effect of additions of small quantities of the gas on the spectrum in this region.

Evidence from electron diffraction measurements favors a tetrahedral model;⁴ in this case the numbers of frequencies and their spectral characteristics are:

*A*₁: Two; Raman active, polarized;
E: Two; doubly degenerate, Raman active, depolarized;
*F*₁: One; triply degenerate, inactive in both Raman and IR;
*F*₂: Four; triply degenerate, active in both Raman and IR, depolarized.

TABLE I. The Raman and infra-red spectrum of Ni(CO)₄.

Raman	Intensity Polarization Frequency	100 <i>P</i> 82	20 <i>P</i> 382	8 <i>D</i> 463	—	4 601	—
IR	Frequency Intensity	—	—	—	542 <i>m</i>	—	655, 669, 684 <i>w</i>
Raman	Intensity Polarization Frequency	0	—	—	2	2	2
IR	Frequency Intensity	718	—	—	833	872	913
Raman	Intensity Polarization Frequency	—	—	—	—	0	—
IR	Frequency Intensity	(983) <i>m</i>	(1340) <i>m</i>	1589 <i>m</i>	—	1609	1677 <i>w</i>
Raman	Intensity Polarization Frequency	30 <i>P</i> 2043	5 2132	1 2223	—	—	—
IR	Frequency Intensity	2051 <i>v.s.</i>	2134 <i>w</i>	—	2326 <i>m</i>	2476 <i>s</i>	—

The coincidence of the high frequencies at 2043 and 2051 cm⁻¹ would make it necessary to attribute these to the out-of-phase CO motions in *F*₂; the in-phase motion might then be 2223 cm⁻¹ but this line should be powerful in the Raman effect and highly polarized. Further inspection of the data will show that other difficulties exist.

The plane square model was discussed by Bright Wilson⁵ who showed that there should be 7 active Raman lines and 6 infra-red with no coincidences. Although those observed lie in the shorter wave region of the spectrum where one might anticipate their chance occurrence in combination tones due to many fundamentals, on the whole the evidence seems to support the tetrahedral model.

An approximate estimate of the Ni-C and C-O bond force constants gives 2.35 and 17.35 × 10⁸ dynes/cm.

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The Sir William Ramsay and Ralph Forster Laboratories,
University College, London, England,
February 15, 1938.

¹ J. Chem. Phys. **2**, 636 (1934).

² E. von Bahr, *Verhand. Deutsch. Physikal. Gesell.* **15**, 710 (1913).

³ F. Rasetti, *Proc. Nat. Acad. Sci.* **15**, 234 (1929).

⁴ L. O. Brockway and P. C. Cross, *J. Chem. Phys.* **3**, 828 (1935).

⁵ J. Chem. Phys. **3**, 59 (1935).

Low and High Raman Frequencies for Water

I have read with some delay the remarks of I. Ramakrishna Rao and P. Koteswaran published by this journal¹ on "Low and High Raman Frequencies for Water." These authors state that of the Raman bands of water: 172, 510, 780, 1645, 2150, 3990 cm⁻¹, observed since 1933 by different workers using as exciting line the 2537A of the mercury arc, only the band 1645 cm⁻¹ is genuine.² The authors consider all other bands as excited by lines of the mercury arc excepting 2537A, with an average shift of 3400 cm⁻¹, corresponding nearly to the center of gravity of the well-known very intense group of frequencies 3200, 3435, 3620 cm⁻¹.