

¹⁵ E. Schrödinger, *Ann. Physik*, **82**, 265-272 (1927); in particular p. 270. •

¹⁶ P. Jordan and E. Wigner, *Z. Physik*, **47**, 1928, 631; G Q, § 44.

Correction made on the proofs (March 4, (1929)).—The calculation of the action density \mathbf{m} contains an error which should be corrected as follows. The spacial components $\alpha = 1, 2, 3$ of $l(\alpha)$ are pure imaginary and the temporal component $l(0)$ real, not the opposite as I had assumed. In the definition of \mathbf{m}' we must therefore divide the right-hand side by $2i$. But this has as consequence that the $\mathbf{H} = \mathbf{m} + \mathbf{m}'$ obtained from the calculation is practically real and not composed of a real and an imaginary part. We therefore obtain but *one* invariant action density for matter: $\mathbf{m} + \mathbf{m}'$. To the tensor density of energy arising from \mathbf{m} must naturally be added the term arising from \mathbf{m}' .

RAMAN SPECTRA OF SOLUTIONS OF SOME IONIZED SUBSTANCES

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A new type of secondary radiation has recently been found¹ to be present in the light scattered by liquids. If a medium is illuminated with a monochromatic radiation for which it is largely transparent, the scattered light is found to contain in addition to light of the original frequency, lines of altered frequency which do not arise from fluorescence. A characteristic of this phenomenon, the Raman Effect, is that the changes in frequency on scattering are independent of the frequency of the incident radiation. The changes in frequency are, however, specifically dependent on the nature of the scattering substance and, indeed, are often found to agree with previously known infra-red frequencies of the substance. There is little doubt that the frequency changes on scattering measure differences in the energy contents of stationary states of the molecules of the scattering substance.

The change in frequency accompanying the scattering of light has been measured for the case of the crystal calcite, CaCO_3 , by Wood,² and by Landsberg and Mandelstam.³ Landsberg and Mandelstam found strong scattered lines corresponding to the frequency change $\Delta\nu = 1095 \text{ cm.}^{-1}$, and somewhat weaker ones corresponding to $\Delta\nu = 291 \text{ cm.}^{-1}$; Wood reported the values 1087.0 and 280.2 for these shifts and in addition a faint shift with⁴ $\Delta\nu = 730.2 \text{ cm.}^{-1}$. In the light scattered by an aqueous solution of sodium nitrate, NaNO_3 , Carrelli, Pringsheim and Rosen,⁵ found shifted lines having $\Delta\nu = 1044 \text{ cm.}^{-1}$.

Water has been found by various observers to give no sharp lines in the spectrum of its scattered light. The line given by sodium nitrate solution,

and also present in the spectrum⁵ from nitric acid solution, is presumably to be attributed to the nitrate ion. The close agreement between the strongest lines of the Raman spectra of calcite and of sodium nitrate solution might be entirely fortuitous; however, the supposed similarity in the electronic structures of carbonate ion, CO_3^- , and nitrate ion, NO_3^- , as well as the similarity of these ions in masses and size, suggest that this is not the case.

In order to obtain more satisfactorily comparable data we have photographed the spectrum of the radiation scattered by an aqueous solution of potassium carbonate, K_2CO_3 . The liquid was contained in a water-jacketed glass tube, and was strongly illuminated by a mercury arc, both tube and arc being placed within a cylinder nicked on the inside. Two different spectrographs were employed—a Hilger type E2 quartz instrument and a glass instrument of lower dispersion but greater speed. The frequencies of the shifted lines were evaluated with the aid of copper arc

TABLE 1
RAMAN SPECTRA FROM NaClO_3 SOLUTION

FREQUENCY OF SHIFTED LINE CM. ⁻¹	INTENSITY OF SHIFTED LINE	WAVE-LENGTH OF EXCITING LINE Å	FREQUENCY OF EXCITING LINE, CM. ⁻¹	FREQUENCY CHANGE, CM. ⁻¹
24226	Medium	4046.6	24705	479
22460	Medium	4358.3	22938	478
24092	Weak	4046.6	24705	613
22330	Weak	4358.3	22938	608
23772	Strong	4046.6	24705	933
22582	Weak	4077.8	24516	934
22008	Strong	4358.3	22938	930

lines recorded on the same plate. With potassium carbonate solution shifted lines corresponding to $\Delta\nu = 1063 \text{ cm.}^{-1}$ were readily obtained; weaker lines, if present, would probably have been obliterated by the continuous background which we have thus far been unable to eliminate in the case of this solution. On the other hand, with sodium nitrate solution not only a strong shift with $\Delta\nu = 1050$ but also a weaker shift with $\Delta\nu = 717 \text{ cm.}^{-1}$ was found.

We have also photographed Raman spectra from solutions containing the ions ClO_3^- , BrO_3^- , IO_3^- , SO_3^- , and HCO_3^- , as well as from solutions containing SO_4^- , and ClO_4^- . As regards the fainter lines of the spectra, our measurements are probably incomplete. However, since considerable time will probably be consumed before the continuous background can in all cases be suppressed, it has seemed desirable to call attention to the unexpected regularity of at least the strong lines of the spectra of all of these solutions.

Details of the assignment of exciting lines to the shifted lines are given in table 1 for the sample case of NaClO_3 solution. The magnitudes of

the frequency shifts together with an estimate of their relative prominence are summarized for the various substances in table 2.

From the results given in table 2 it appears that the magnitude of the frequency changes are uninfluenced by the nature of the positive ion; thus sodium, calcium, and ammonium nitrates yielded frequency changes which are identical⁶ within the error of our measurements. Nitric acid solution has been found⁵ to give a slightly more complicated spectrum than has been obtained with the nitrates; but, according to our observations, by far the strongest line given by nitric acid solution has $\Delta\nu = 1047$ in agreement with the nitrates. There is, moreover, considerable evidence⁷ that strong nitric acid solutions contain other molecular species beside the simple ions. Although the spectra of the solutions in table 2 appear to

TABLE 2
RAMAN SPECTRA FROM VARIOUS IONIZED SUBSTANCES

SCATTERING MATERIAL	CONCENTRATION OF SOLUTION	FREQUENCY CHANGE (CM ⁻¹) AND INTENSITY			OBSERVER
CaCO ₃	Calcite crystal	1087 (v. st.)	730 (f.)	280 (st.)	Wood ²
		1095 (v. st.)		291 (st.)	L. and M. ³
K ₂ CO ₃	52%	1063			D. and D.
KHCO ₃	26%	1035			D. and D.
NaNO ₃	47%	1050 (st.)	717 (w.)		D. and D.
Ca(NO ₃) ₂	41%	1052 (st.)	723 (w.)		D. and D.
NH ₄ NO ₃	52%	1050 (st.)	(723) (w.)		D. and D.
K ₂ SO ₃	52%	988			D. and D.
(NH ₄) ₂ SO ₄	43%	987 (st.)	624 (m.)	458 (m.)	D. and D.
NaClO ₃	51%	932 (st.)	611 (w.)	479 (m.)	D. and D.
HClO ₄	60%	935 (st.)	634 (m.)	470 (m.)	D. and D.
NaBrO ₃	26%	810 (st.)		367 (m.)	D. and D.
HIO ₃	45%	800 (st., broad)		329 (m., broad)	D. and D.

arise from the negative ions, it is not unlikely that other, especially more complex, positive ions, might well give rise to spectra of their own.

It may be observed that in all the cases in table 2 the spectra are characterized by one line considerably stronger than any others. For this line the frequency change is very little different for the solutions containing the ions CO₃⁻, HCO₃⁻, and NO₃⁻. Also the frequency change is substantially the same for SO₃⁻ as for SO₄⁻, and the same for ClO₃⁻ as for ClO₄⁻, and accordingly is in these cases, independent of the number of oxygen atoms associated with the central atom. Indeed, except for the relative intensities of the weaker lines, the spectra of sodium chlorate and perchloric acid are scarcely distinguishable. Finally (omitting the somewhat irregular case of HCO₃⁻) the frequency change corresponding to the strong line decreases with increase in atomic number of the central atom of the negative ion. This fact seems rather surprising if the magnitude

of the shift can, when suitable corrected for the masses involved, be taken as a measure of the stiffness of binding.

We are indebted to Professor Ira S. Bowen for valuable advice relative to the present measurements.

¹ Raman, *Indian J. of Phys.*, **2**, 387 (1928); Raman and Krishnan, *Ibid.*, **2**, 399 (1928).

² Wood, *Phil. Mag.*, **6**, 742 (1928).

³ Landsberg and Mandelstam, *Z. Phys.*, **50**, 769 (1928).

⁴ There appears to be a misprint in the original paper.

⁵ Carrelli, Pringsheim and Rosen, *Z. Phys.*, **51**, 511 (1928).

⁶ Carrelli, Pringsheim and Rosen, loc. cit., reported somewhat lower values for ammonium nitrate (mean 1014) than for sodium nitrate.

⁷ Mellor, *Treatise on Inorganic and Theoretical Chemistry*, vol. VIII, p. 566.

THE CRYSTAL STRUCTURE OF STRONTIUM

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The crystal structure of strontium has been recently determined by Simon and Vohsen¹ from the powder spectrogram obtained in an ingenious low-temperature x-ray diffraction camera which was designed for the study of the alkali metals. They have assigned a face-centered cubic lattice with a unit cube edge, $a_0 = 6.03$ A.U. The small resolution of their camera, however, limited the accuracy of their results, so that it was thought advisable to publish the results obtained under more ideal conditions in our study of the alkaline earth metals and their alloys.

Strontium was obtained for this measurement by the sublimation of the metal from a mixture of pure strontium oxide and aluminum² in a high vacuum at 1000°C. This product was further purified by resublimation at 700°C. in vacuum. The metal resulting from this final treatment was silvery white, quite soft and contained over 99.9 per cent strontium.

The samples for x-ray analysis were prepared by the same method as was used in the study of barium.³

The powder spectrograms were obtained with a quadrant camera, $r = 20.32$ centimeters, using the MoK radiation from a Coolidge tube. Due to an exceptionally strong fogging of the film, it was found necessary to introduce a heavy ZrO₂ filter into the cassette in addition to the filter which was supplied with it, since the latter was not sufficient to remove the intense secondary radiation. That this fogging is due to a secondary radiation from strontium and not to impurities is apparent from the