NOTE ON MR. KING'S PAPER: "THE CRYSTAL STRUCTURE OF STRONTIUM"

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In No. 4 of this periodical King stated that on redetermining the crystal structure of strontium he found a cubic face-centered lattice in agreement with our measurements,[1] but that the unit cubic edge ($a_0 = 6.075 \pm 0.004$ A.U.) was 0.7% greater than ours, which figured 6.03 A.U. King believes that this rather considerable discrepancy is due to the fact that his measurements, which were carried out with a view to obtaining very accurate results, were more exact than ours. We feel bound to point out that this is not the reason, but that our spacing applies to liquid air temperature— a fact that King has apparently overlooked—whereas his value holds for room temperature. The difference in question cannot be calculated accurately but can be gauged at 0.03 A.U. $\pm$ 10% by the usual approximation as shown in our paper. Computed for room temperature our result would thus be 6.06 A.U. The difference between this value and King's is within the limits of our experimental error. We will not discuss the question whether our value or King's is the more accurate, but we may mention that in a recent paper Ebert[2] gives the unit cubic edge of strontium as 6.05 A.U. at room temperature.

[1] *Zeit. phys. Chemie*, **133**, 165, 1928.
[2] *Zeit. anorg. Chemie*, **179**, 4, 1929.

THE RAMAN SPECTRUM OF GYPSUM

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In an investigation of the Raman spectra of some ionized substances in aqueous solution, it was found[1] that the frequency shift given by a solution of potassium carbonate was in fairly close agreement with the strongest shift given by calcite. Data for such a comparison in other cases do not appear to exist, for change of frequency on scattering has been measured for only a few crystalline substances. In addition to calcite,[2,3,5] these are quartz,[2,3,4,6] ice,[5] and topaz.[6] No modified frequencies were found in the light scattered by halite,[2] NaCl, fluorite,[5]

CaF_2, or by the salts[7] LiF and NaF. In the present paper are described the results of measurements on gypsum, $CaSO_4.2H_2O$, and a comparison of these with data on ammonium sulfate solution.

The crystal used was a clear, colorless specimen internally free from cleavage cracks. It was about 15 cm. long and had a cross-section of about 2 cm.[2]; the long edges of the prism faces were parallel to the *c*-axis. The crystal was placed in a water-jacketed glass tube with an end window and irradiated with light from a mercury arc. The arc was placed parallel

TABLE 1

RAMAN SPECTRA FROM GYPSUM

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.$^{-1}$
24291.5	Weak	4046.56	24705.5	414.0
24085.0	Very weak (broad)	4046.56	24705.5	620.5
24033.6	Very weak	4046.56	24705.5	671.9
23985.7	Medium (broad)	3650.15	27388.4	3402.7
23949.3	Weak (broad)	3654.83	27353.3	3404.0
23896.1	Strong (very broad)	3650.15	27388.4	3492.3
		(3663.27)	(27290.5)	(3394.4)
23861.4	Medium weak (broad)	3654.83	27353.3	3491.9
23798.1	Medium weak (broad)	3663.27	27290.5	3492.4
23697.8	Strong	4046.56	24705.5	1007.7
23569.3	Medium	4046.56	24705.5	1136.2
23507.2	Very weak	4077.8	24516.1	1008.9
23351.5	Very faint	4358.34	22938.1	−413.4
22523.0	Medium weak	4358.34	22938.1	415.1
22445.2	Very weak	4358.34	22938.1	492.9
22318.6	Weak (broad)	4358.34	22938.1	619.5
22267.3	Weak	4358.34	22938.1	670.8
21987.1	Very weak	4347.50	22995.3	1008.2
21929.9	Very strong	4358.34	22938.1	1008.2
21803.3	Medium strong	4358.34	22938.1	1134.8
21303.2	Medium strong (broad)	4046.56	24705.5	3402.3
21215.2	Strong (broad)	4046.56	24705.5	3490.3

to the *c*-axis of the crystal, and scattered light from the crystal was taken off in the direction of the *c*-axis. Since the end of the crystal was quite irregular, the crystal was submerged in chlorobenzene which has a refractive index close to those of gypsum. To insure that no scattered lines had reached the spectrograph from the liquid, carbon tetrachloride, which gives a quite different Raman spectrum from chlorobenzene, was used in one case with no change in the observed scattered lines. The glass tube containing the crystal was painted black around the ends of the crystal. The light from the crystal was converged with lenses and thrown on the spectrograph slit with the aid of a reflecting prism.

The spectrograph was a two-prism glass instrument arranged with interchangeable camera lenses so as to give either a dispersion of about

100 cm.$^{-1}$ per mm. with an aperture of f 8, or a smaller dispersion and higher speed corresponding to an aperture of f 3. A comparison spectrum of the iron arc was recorded on each plate, and the plates measured on a Gaertner comparator. The frequencies of the shifted lines were computed by linear interpolation between the frequencies of closely neighboring iron lines.

The measured frequencies and estimated intensities of the modified lines are given in the first two columns of table 1. The wave-lengths and frequencies of the corresponding exciting lines are given in the third and fourth columns, respectively, while the frequency shifts are given in the last column. As a control on the assignment of exciting lines to the various observed lines, we have made a photograph while flowing through the water-jacket an alkaline solution of potassium chromate of a concentration such that considerable light of wave-length λ 4358 was trans-
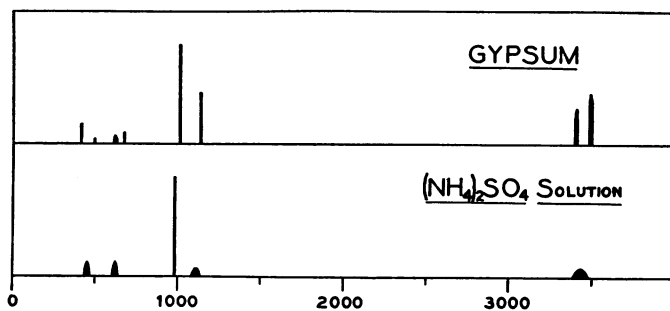

FIGURE 1

mitted, while that of shorter wave-length was largely absorbed. All of the modified lines appearing on this photograph were ones for which excitation by λ4358 is indicated in table 1, and all lines thus indicated appeared on the photograph with the exception of the very faint anti-Stokes line.

The data of table 1 indicate eight different frequency shifts; the best values of these are summarized in table 2.

TABLE 2

FREQUENCY SHIFTS GIVEN BY GYPSUM

Frequency shift (cm.$^{-1}$)	414.2	492.9	620.0	670.4	1008.2	1135.5	3403.0	3491.5
Intensity	Med. weak	Very weak	Weak (broad)	Weak	Very strong	Med. strong	Med. strong (broad)	Strong (broad)

We have also rephotographed the spectrum from ammonium sulfate solution using higher dispersion than previously.[1] The new measurements yield the following values for the frequency shifts of the Raman lines pre-

viously reported: 451, medium (broad); 620, medium (broad); 980.3, strong. In addition there appears to be a very broad shift with $\Delta\nu \simeq$ 1113 as well as the still broader band due to water with $\Delta\nu$ equal to about 3430. With this higher dispersion it is especially evident that the strongest line is far sharper than the others. A comparison of this spectrum with that of gypsum is shown in figure 1.

The two largest frequency shifts given by gypsum are presumably due to water of crystallization while the smaller shifts are very likely due to sulfate ion. Schaefer and Schubert[8] measured residual rays from a variety of sulfates and concluded that all sulfates possess prominent maxima of reflection in the neighborhood of 9 and 16μ which are to be attributed to the sulfate ion. In the case of gypsum, the maxima occurred at 8.74 and 14.84μ with a weak maximum at 8.62μ, and another weak one at about 3μ due to water of crystallization. The two prominent maxima correspond to frequencies of 1143 and 674 cm.$^{-1}$, respectively, in reasonable agreement[9] with the values 1135.5 and 670.4 which we have found. The two smallest Raman shifts do not fall in the range of the residual ray measurements. The absence of any maximum corresponding to the strongest Raman line ($\Delta\nu = 1008.2$) suggests that the initial and final states of the transition producing it are without electric moment, as Carelli, Pringsheim and Rosen[10] have suggested for an analogous line in the case of calcite. This appears to afford a reasonable explanation of the sharpness of this line in aqueous sulfate solution; for absence of electric moment would presumably minimize the interaction between sulfate ion and water molecules.

If the symmetry of the sulfate ion in aqueous solution may be taken as tetrahedral, Brester's[11] considerations concerning the multiplication of characteristic frequencies consequent upon removal of symmetry afford one possible explanation of the multiplicity of lines found from gypsum. The point group symmetry of this crystal is monoclinic holohedral. The space groups symmetry has been reported by Onorato[12] to be C_{2h}^3 with $8CaSO_4.2H_2O$ in a unit of structure that employs a face-centered lattice; if an end-centered lattice is used, the number of $CaSO_4.2H_2O$ becomes four. If the sulfur atoms occupy equivalent positions, the sulfate ion can, strictly speaking, have only either a center of symmetry, a two-fold axis, or a plane of symmetry in this crystal although it may approximate to a higher symmetry. If the sulfur atoms are not all in equivalent positions, a multiplication of lines could result for this reason. In any case, it is also possible that the weaker Raman lines do not represent fundamental frequencies.

[1] Dickinson and Dillon, *Proc. Nat. Acad. Sci.*, 15, 334 (1929).

[2] R. W. Wood, *Phil. Mag.*, 6, 729 (1928).

[3] Gr. Landsberg and L. Mandelstam, *Zeit. Phys.*, 50, 769 (1928).

[4] P. Pringsheim and B. Rosen, *Zeit. Phys.*, **50**, 741 (1928).

[5] I. R. Rao, *Indian J. Physics*, **3**, 123 (1928).

[6] H. Nisi, *Proc. Imp. Acad. of Japan*, **5**, 127 (1929).

[7] C. Schaefer, *Zeit. Phys.*, **54**, 153 (1929).

[8] Schaefer and Schubert, *Ann. Phys.*, **50**, 283 (1916).

[9] This agreement may be fortuitous because of the fact that maxima of reflection and absorption are not quite coincident and are sometimes very appreciably removed from each other. See, for example, Havelock, *Proc. Roy. Soc.* **105A**, 488 (1924).

[10] Carelli, Pringsheim and Rosen, *Zeit. Phys.*, **51**, 511 (1928).

[11] Brester, *Ibid.*, **24**, 324 (1924).

[12] E. Onorato, *Zeit. Krist.*, **66**, 504 (1928).

RAMAN SPECTRA FROM ACETONE

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Measurements of Raman spectra from acetone have been published in a recent paper.[1] These measurements were so interpreted that out of thirteen modified lines, twelve corresponded to frequencies of observed infra-red absorptions, the thirteenth lying outside the range of the infra-red measurements. This result is surprising; for the occurrence of frequency shifts in Raman effect without the appearance of the corresponding infra-red absorptions is a very common phenomenon. We have examined Raman spectra from acetone; and as both our measurements and our interpretation disagree with those mentioned above, it seems desirable to report them.

The acetone used was Merck's "C.P." It was distilled through a 30 cm.-Eastman fractionating column the product used all coming over within 0.05° of 55.7° at 746 mm. It is important to use materials of reasonable purity; we have, for example, found it possible to bring out the strongest benzene lines from a carbon tetrachloride solution containing only 0.46% benzene.

The acetone was irradiated with light from a glass mercury arc, and the spectra photographed with a glass spectrograph having a dispersion of about 100 cm.$^{-1}$ per mm. in the blue. The iron arc was used as a standard.

The measured frequencies of the shifted lines together with their intensities are given in the second and third columns of table 1. Comparison of these measurements with those which have already been reported[1] shows considerable disagreement even among the strongest lines. Apparently seven lines are concerned in the production of these Raman lines. The wave-lengths and frequencies of these mercury lines are: