THE RAMAN AND INFRA-RED SPECTRA OF SOME SOLID HYDROXIDES

Part I. Raman Effect Data

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1. INTRODUCTION

A STUDY of the Raman spectra of the hydroxides of the alkali and alkaline earth group of metals is inherently of interest in view of the simplicity of their chemical composition. There have been comparatively few investigations regarding them and the results reported refer only to the frequency shifts in the $3\,\mu$ region. This paucity of data is attributable to the experimental difficulties of the subject; these substances are available only in the form of small crystals, polycrystalline masses or fine powders, and when the radiations of the mercury arc in the visible region are used for the excitation of the Raman spectra, the parasitic illumination entering the spectrograph is so strong as to obliterate any low-frequency shifts that might be observable in the vicinity of the exciting radiation. When the technique of exciting the Raman effect by the $\lambda\,2536\cdot5$ resonance radiation of mercury is employed, these difficulties are minimized and it becomes possible to record the low-frequency spectra at least in those cases where the material exhibits some measure of crystallinity and transparency. Since several of the hydroxides are also available as hydrates, it is of interest to study the Raman spectra of these hydrates as well. The first part of the present memoir deals with the facts of observation emerging from the experimental studies made with these substances.

Since the crystal structures of most of these substances have been determined already by X-ray diffraction methods and sometimes even through neutron-diffraction studies, the details of the spectra recorded are amenable to interpretation by the application of group theoretical methods and the second part of the memoir concerns itself with this. As all these substances crystallize in the holohedral class of their respective crystal systems, the rule of mutual exclusion is operative and hence the results of the Raman effect studies are complementary to those derived from infra-red studies and the latter do not therefore render the former superfluous.

The few infra-red investigations so far reported on these substances have all been restricted to the high-frequency region of $3\,\mu$ to $15\,\mu$, evidently because of the experimental difficulties in the study of the far-infra-red region of the spectrum. That the present Raman effect data also afford a satisfactory explanation of the complex infra-red absorption spectra, reported in some cases in the $3\,\mu$ region, will emerge in the third part of the memoir wherein we shall consider the infra-red data in relation to the Raman spectra of these substances.

2. EXPERIMENTAL TECHNIQUES

The spectra were recorded with a Hilger medium quartz spectrograph and in some cases with a Hilger Littrow spectrograph of higher resolving power. The general details regarding the experimental set-up and about the water-cooled magnet-controlled quartz mercury arc emitting the intense $\lambda\,2536\cdot5$ resonance radiation which was used for the excitation of the Raman effect have already been described in an earlier paper by the author (1957). It is pertinent to emphasize here that the results to be reported have been achieved chiefly because of the advantages inherent in the use of $\lambda\,2536\cdot5$ excitation, *viz.*, the intense scattering power in the ultra-violet region and the effective suppression by a filter of mercury vapour inside the spectrograph of the parasitic resonance radiation reaching the slit of the spectrograph, thereby enabling us to record the low-frequency spectrum clearly even in the cases of coarse crystals and polycrystalline masses. The large reactivity of these substances with the atmospheric moisture and carbon dioxide necessitated that they be sealed up in quartz tubes before recording their spectra.

With a slit width of $0\cdot05$ mm. exposures of the order of ten hours were found to be usually adequate to record the spectra with reasonable intensity and contrast. With increased exposures only the weaker mercury lines and the continuous background accompanying the spectrum of the mercury arc became prominent and any weak Raman lines recorded were masked by the general background intensity. Sometimes a few weak mercury lines appeared on the anti-Stokes side of the spectrum and care has been taken not to identify any of them as frequency shifts unless Raman lines of the same frequency shifts were present on the Stokes side as well. As a particular case of this, mention may be made of a group of lines noticed on the anti-Stokes side of the spectrum of $Ba\,(OH)_2\cdot8H_2O$, and which were not identified as Raman frequency shifts.

The following is a brief description of the several substances whose spectra were recorded in the present investigation:

(i) *Lithium hydroxide (anhydrous).*—The sample, made available through the kindness of a friend, was in the form of porous granules and exhibited no visible crystallinity. The sample actually contained a good proportion of LiOH.H$_2$O as was revealed by the spectrum which exhibited the Raman lines due to pure LiOH.H$_2$O also.

(ii) *Lithium hydroxide monohydrate.*—The material in the form of small lumps containing minute cyrstals was kindly provided by the Head of the Department of General Chemistry, Indian Institute of Science, Bangalore.

(iii) *Sodium hydroxide (anhydrous).*—The sodium hydroxide used in the study was the translucent polycrystalline mass commercially available in the form of sticks and manufactured by British Drug Houses, Ltd., and was of analytical reagent quality.

(iv) *Sodium hydroxide monohydrate.*—The monohydrated compound of NaOH was prepared by cooling a hot concentrated solution of the substance. The monohydrate is formed between 12·3° C. and 64·3° C. (Mellor, 1946).

(v) *Potassium hydroxide (anhydrous).*—In the case of KOH, the commercially available substance was found to be of the hydrated variety. Therefore, the pure substance (manufactured by the firm Merck & Co.) was heated in a nickel crucible in an attempt to drive out the water. The substance thus prepared was a white mass of fine texture. In spite of the heating, however, it was found that the spectrum continued to exhibit the hydroxyl frequency shift due to the hydrate by the side of that due to the anhydrous substance.

(vi) *Potassium hydroxide monohydrate.*—Near room temperature there are two hydrates of KOH, *viz.*, the dihydrate and the monohydrate. The dihydrate is stated to melt at about 35° C. or slightly below and pass over into the monohydrate which is stable up to 143° C. (Mellor, 1946). The substance used in the present investigation was prepared by cooling a highly concentrated hot solution of KOH and the stability of this substance was checked up to 50° C. and was identified as the monohydrate.

(vii) *Calcium hydroxide.*—This is normally available only in the form of a fine powder. Crystals of this substance were grown by slowly evaporating a large volume of a saturated solution of Ca (OH)$_2$ at about 80° C. inside a thermostat. Owing to the very low solubility of the substance, the crystals obtained were quite small, being only a fraction of a millimetre in size. The material thus prepared contained a small proportion of calcium carbonate formed by the action of atmospheric carbon dioxide, as was revealed by the presence (faintly) of the principal frequency shift of the CO$_3$ group in the spectrum recorded.

(viii) *Magnesium hydroxide.*—The compound in the form of a colloidally fine powder was prepared by precipitation and was kindly made available by the Head of the Department of General Chemistry, Indian Institute of Science, Bangalore.

(ix) *Strontium hydroxide octahydrate.*—The substance in the form of small crystals, manufactured by Merck & Co., was used directly as such to record the spectra. The tetragonal crystal forms and the uniaxial nature of the crystal served to confirm their identification as the common octahydrate of Sr (OH)$_2$.

(x) *Barium hydroxide octahydrate.*—Small crystals of this substance (manufactured by Johnson & Sons) were used directly as such to record the spectra. That they were the common octahydrate of Ba (OH)$_2$ was confirmed by their biaxial nature and by the small optic axial angle exhibited by them (Winchell, *Microscopic Characters of Artificial Minerals*, pp. 187).

(xi) *Aluminium hydroxide.*—'Dry' aluminium hydroxide manufactured by British Drug Houses Ltd., in the form of fine powder, was used to obtain the spectra.

3. RESULTS

The frequency shifts observed in the case of the different substances are shown in Table I. The following are the principal features exhibited by the spectra of the several hydroxides. The observed frequency shifts group themselves and naturally fall into two specific regions, *viz.*, (a) a region of low-frequencies from about 75 cm.$^{-1}$ to 400 cm.$^{-1}$ and (b) a region between 3300 to 3700 cm.$^{-1}$ and which can readily be recognized as respectively the range of lattice frequencies and of hydroxyl frequencies. It is noteworthy that no frequency shifts have been observed in the region intermediate to the above ranges. The extremely fine texture and near opacity of some of the materials used in the study, *viz.*, LiOH, KOH, Mg (OH)$_2$ and Al (OH)$_3$, and the intense parasitic illumination consequent thereon reaching the slit of the spectrograph made it impossible to observe any low-frequency shifts in their cases. The spectra recorded have been grouped to form two Plates (II and III) and reproduce respectively the low and the high frequency regions.

In the majority of cases the high-frequency region exhibits only a single intense and sharp frequency shift contrary to our experience of the broad and diffuse bands observed with water and water of crystallization in the case of hydrated crystals. It is a surprising fact that in the cases of LiOH·H$_2$O, NaOH·H$_2$O and KOH·H$_2$O the Raman bands due to water of crystallization
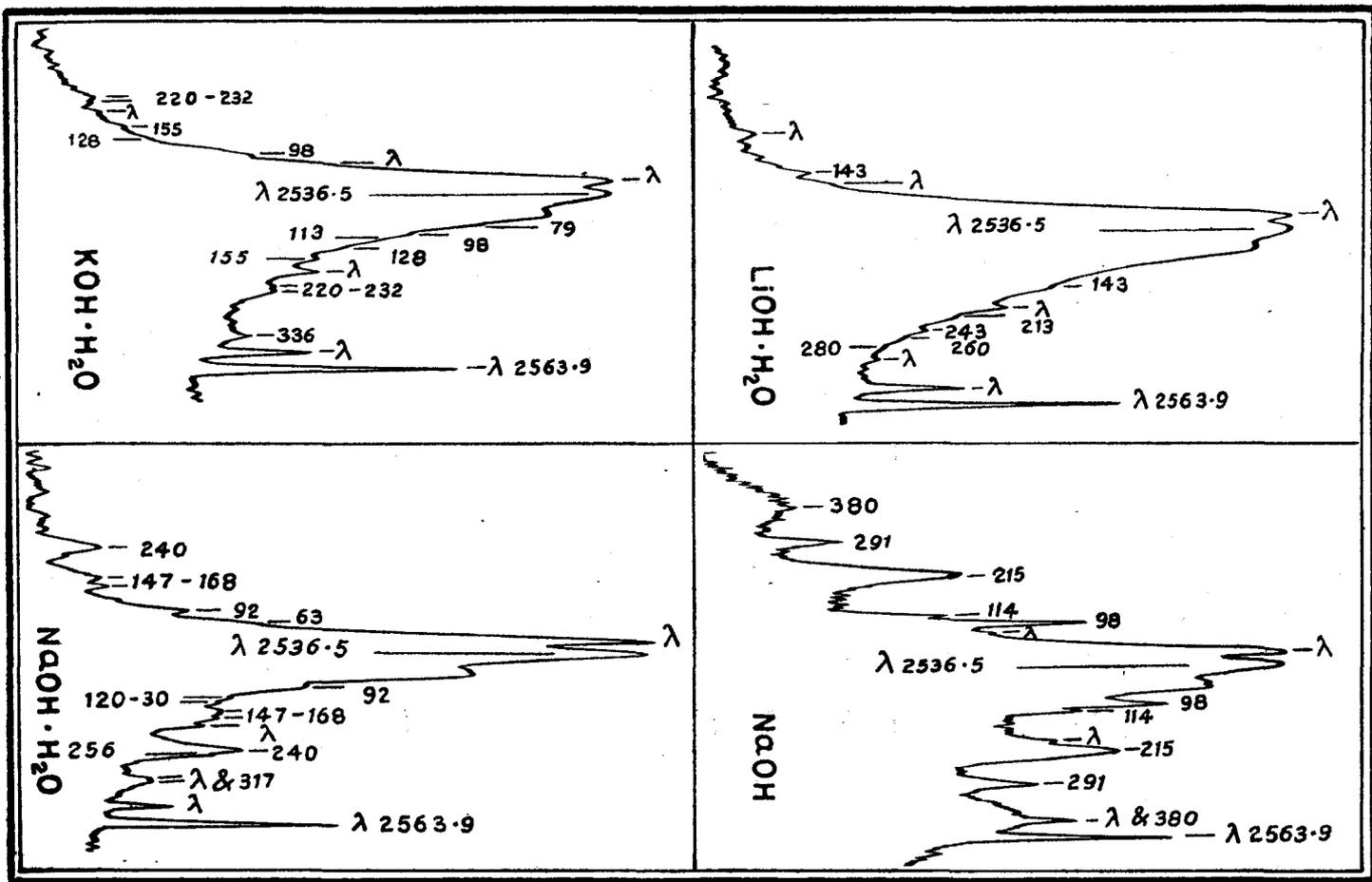
FIG. 1

TABLE I

Observed Raman frequency shifts in cm.$^{-1}$

Substance	Lattice frequencies	Internal frequencies
LiOH	..	3664 (*v.s.*)
LiOH.H$_2$O	143 (*s.*), 213 (*m.*), 243 (*m.*), 260 (*w.*), 280 (*w.*)	3563 (*v.s.*)
NaOH	98 (*v.s.*), 114 (*m.*), 215 (*v.s.*), 291 (*s.*), 380 (*w.b.*)	3632 (*v.s.*)
NaOH.H$_2$O	63 (*s.*), 92 (*s.*), 120 (*w.*), 130 (*w.*), 147 (*m.*), 168 (*m.*), 240 (*v.s.*), 256 (*w.*), 317 (*m.*)	3568 (*v.s.*)
KOH	..	3597 (*s.*)
KOH.H$_2$O	79 (*m.*), 98 (*s.*), 113 (*s.*), 128 (*s.*), 155 (*m.*), 220 (*m.*), 232 (*m.*), 336 (*m.*)	3501 (*v.s.*)
Mg (OH)$_2$	..	3651 (*s.*)
Ca (OH)$_2$	247 (*m.*), 282 (*m.*), 359 (*s.*)	3616 (*v.s.*)
Sr (OH)$_2$.8H$_2$O	106 (*m.*), 132 (*s.*), 155 (*w.*), 173 (*m.*), 199 (*w.*), 230 (*v.s.*), 297 (*m.*), 328 (*w.*)	3302 (*m.b.*) 3393 (*m.b.*) 3488 (*v.s.*) 3536 (*w.*) 3593 (*w.*)
Ba (OH)$_2$.8H$_2$O	106 (*s.*), 139 (*m.*), 156 (*m.*), 173 (*w.*), 205 (*v.s.*), 220 (*m.*), 276 (*m.*), 287 (*m.*), 328 (*w.*)	3335 (*w.b.*) 3481 (*v.s.*) 3529 (*s.*)
Al (OH)$_3$	..	3369 (*s.*) 3431 (*m.*) 3521 (*s.*) 3583–3602 (*m.*)

s. = strong; *w.* = weak; *m.* = moderate intensity; *v.s.* = very strong; *b* = broad.

have not been recorded even though the hydroxyl frequency shift appears with large intensity. Even in the case of Sr (OH)$_2$.8H$_2$O and Ba (OH)$_2$.8H$_2$O the water bands appear only weakly in comparison with the large intensity of the shifts due to the hydroxide.

It may be noticed that the hydroxyl frequency shift (in anhydrous compounds) is generally higher in the case of substances with metallic ions of
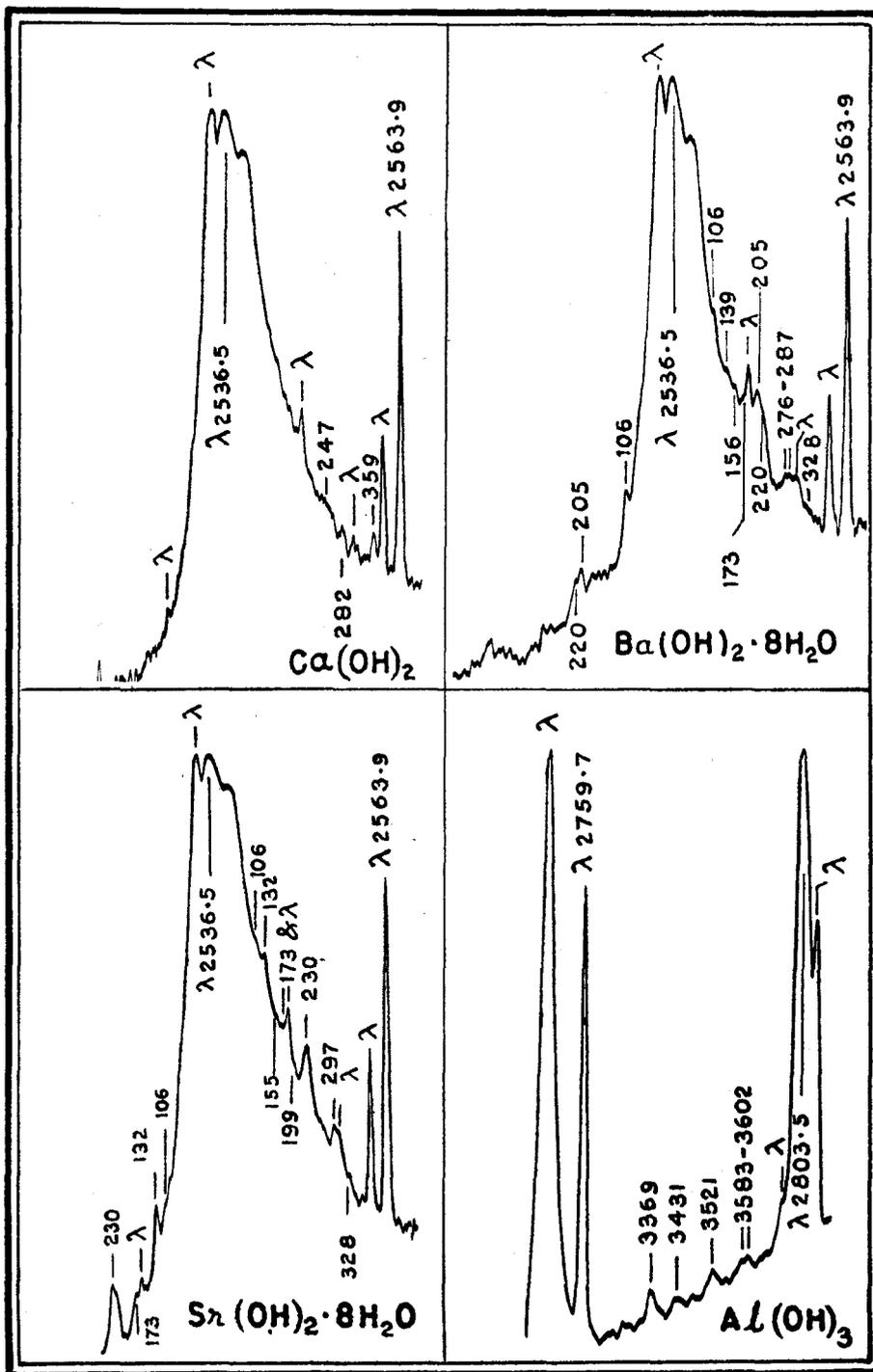
FIG. 2

lower atomic weight. The hydroxyl frequency shifts in the cases of the hydrated hydroxides also form a similar sequence and are considerably lower (and less sharp) than the frequency shifts observed with the corresponding anhydrous compounds.

The lattice frequency shifts in the several cases exhibit diverse features with regard to their number, intensity and sharpness, all of which evidently have their origin in the differences in their crystal structures. To a discussion of these facts we shall return in the next part of the memoir.

The frequency shift of 282 cm.$^{-1}$ observed with Ca(OH)$_2$ coincides with the value of one of the lattice frequencies of calcite. The spectrum of the slightly impure Ca(OH)$_2$, as already mentioned, showed weakly the principal frequency 1086 cm.$^{-1}$ of calcite. However, the 282 cm.$^{-1}$ shift in calcite is relatively weaker than the 1086 cm.$^{-1}$ shift and it is highly improbable that the impurity of CaCO$_3$ was responsible for the 282 cm.$^{-1}$ shift. The identification of the shift as genuinely due to the Ca(OH)$_2$ is vindicated by the infra-red data as we shall see in Part III.

In order to exhibit several of the frequency shifts which were recorded rather faintly, microphotometer records of different cases (for the lattice frequency region) appear in the text. Figure 2 in the text includes also the microphotometer record of the spectrum of Al(OH)$_3$ in the hydroxyl frequency region since the spectrum recorded was too weak for reproduction.

Some of the frequency shifts shown in Table I, viz., 3632 cm.$^{-1}$ in the case of NaOH, and 3302, 3393 and 3488 cm.$^{-1}$ in the case of Sr(OH)$_2$.8H$_2$O and 3481 and 3529 cm.$^{-1}$ in the case of Ba(OH)$_2$.8H$_2$O have been reported by the earlier investigators, with minor differences in the observed values (Krishnamurti, 1930; Theimer, 1950; Busing, 1955).

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4. SUMMARY

The paper reports the results of an investigation on the Raman spectra of eleven solid hydroxides using the λ 2536·5 resonance radiation of mercury arc for the excitation of the Raman effect. The cases studied (most of them for the first time) consist of the hydroxides of Li, Na and K and their monohydrates, the hydroxides of Ca, Mg and Al, and the octahydrated hydroxides of Sr and Ba. The facts of observation are discussed in relation to the crystal structure and the infra-red absorption data of these crystals in two separate parts following this paper.
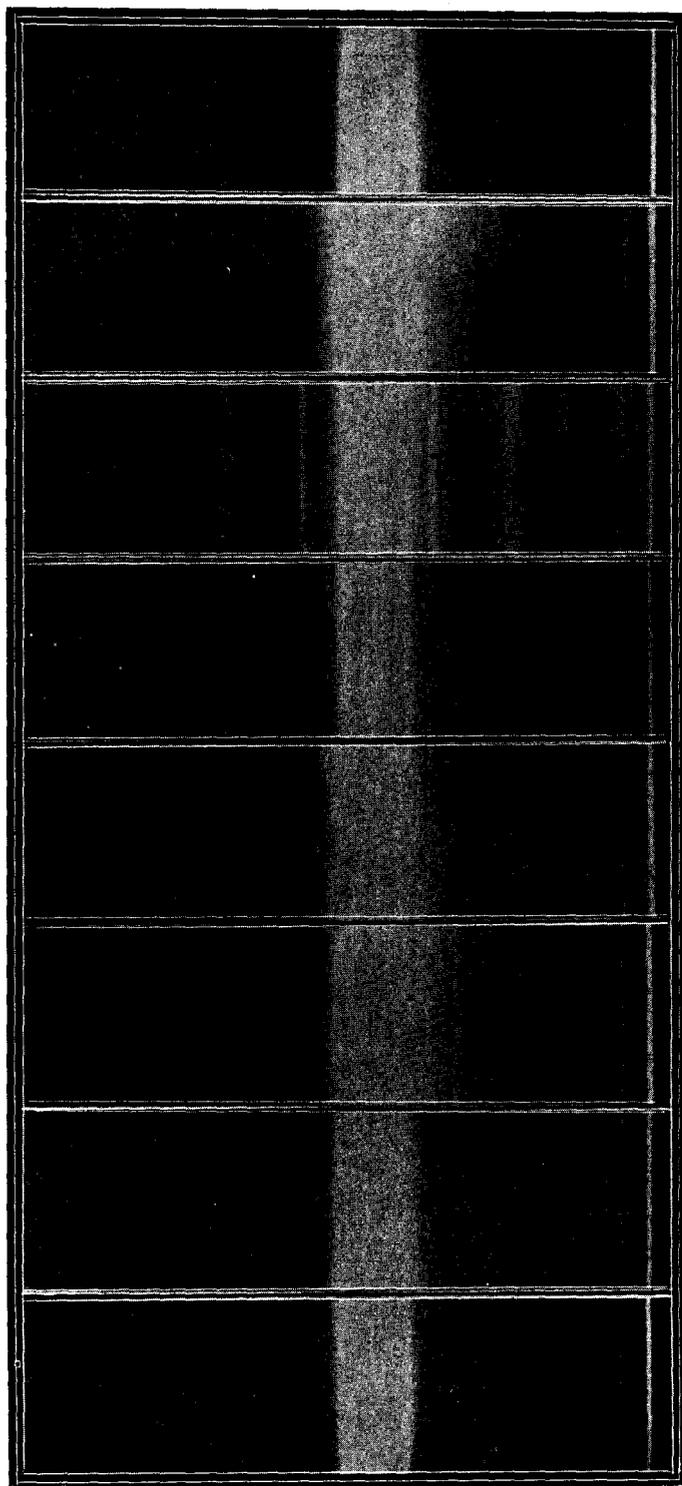
Hg arc

LiOH·H$_2$O

NaOH

NaOH·H$_2$O

KOH·H$_2$O

Sr (OH)$_2$·8 H$_2$O

Ba (OH)$_2$·8H$_2$O

Hg arc
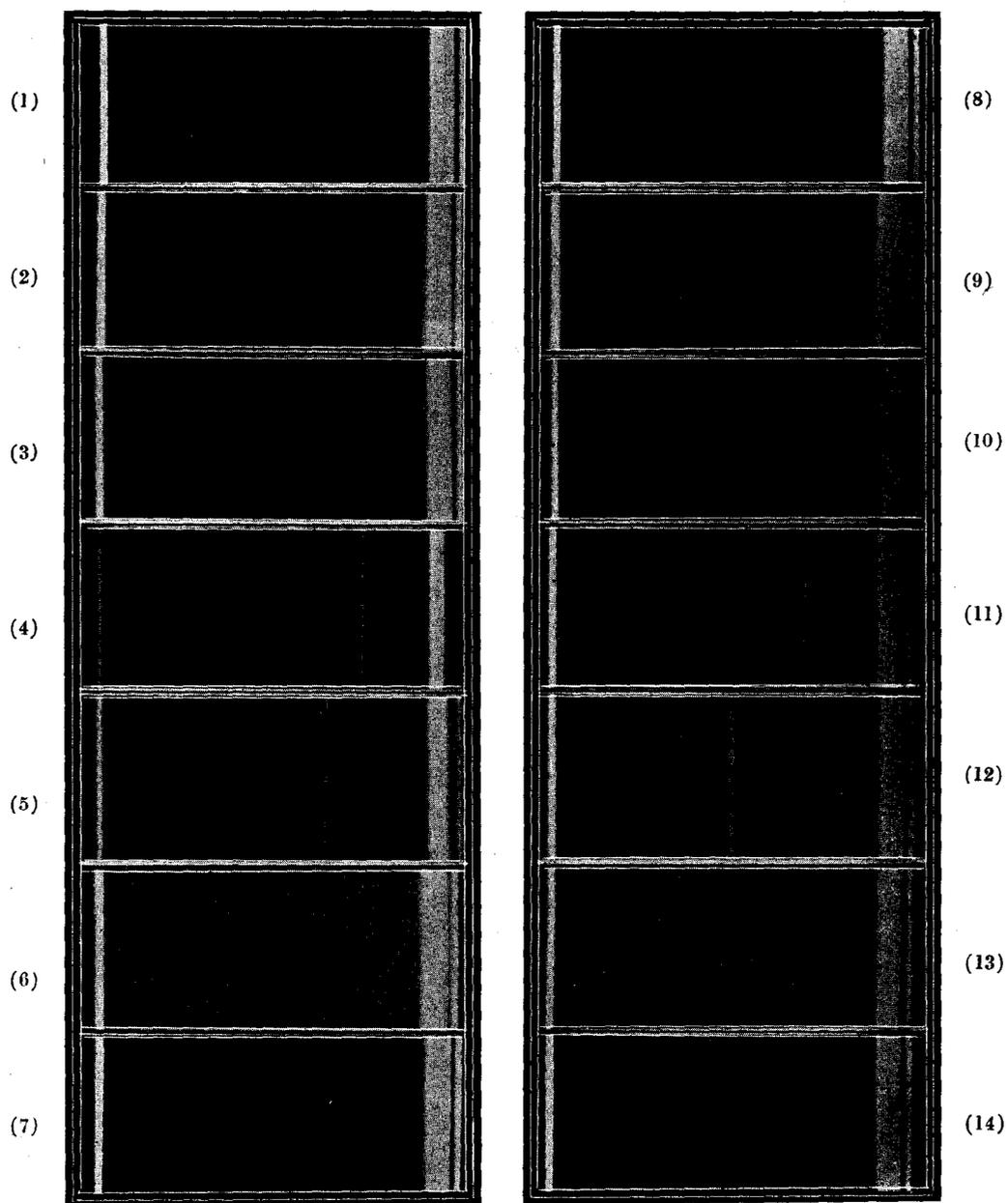
FIGS. 1–14

Fig. 2. LiOH and LiOH F₂O; Fig. 3. LiOH·H₂O; Fig. 4. NaOH; Fig. 5. NaOH·H₂O;
Fig. 6. Mg (OH)₂; Fig. 9. KOH and KOH·H₂O; Fig. 10. KOH·H₂O; Fig. 11. Ca (OH)₂;
Fig. 12. Sr (OH)₂·8 H₂O; Fig. 13. Ba (OH)₂·8 H₂O. Figs. 1, 7, 8 and 14. Mercury spectrum.

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