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On the Physical Validity of the LANE-EMDEN Equation in $(y;z)$-Plane

LANE-EMDEN equation of index n[1]:

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2\frac{d\theta}{d\xi}\right) = -\theta^n, \qquad (1)$$

in $(y;z)$-plane, takes the form

$$y\frac{dy}{dz} + (2w-1)y + w(w-1) + z^n = 0; \qquad (2)$$

where equations connecting $(y;z)$- with $(\xi;\theta)$ are

$$z = \xi^w\theta; \quad w = \frac{2}{n-1} \qquad (3)$$

$$y = \frac{dz}{dt} = -\xi^{w+1}\frac{d\theta}{d\xi} - wz; \quad \xi = e^{-t}. \qquad (4)$$

It has generally been believed that all parts of the solution-curves which correspond to $\theta \geqq 0$, $z \geqq 0$ have astrophysical validity. This gives the impression that every point on the y-axis is of interest. But, actually, only points on the positive y-axis have a relevancy.

Equation (3) shows that z vanishes for either $\theta = 0$ or $\xi = 0$. In other words, the neighbourhood of $z = 0$ in $(y;z)$-plane maps two different regions in $(\xi;\theta)$-plane: the regions being the neighbourhood of $\xi = 0$ and that of $\xi = \xi_1$, where solutions of (1) have their first zero at $\xi = \xi_1$. Further equation (4) clears that the former region, in $(\xi;\theta)$-plane, corresponds to the neighbourhood of the origin $y = z = 0$ and the latter one to the immediate neighbourhood of the y-axis. The author has shown recently[2] that in a complete polytrope, whatever be the index of the polytrope, the immediate neighbourhood of the origin is an interfacial region and at the origin solutions for $n = 0$ and $n = -1$ only are relevant. Hence the point $y = z = 0$ cannot have any relevancy when discussion of solution curves for general values of n is made. When $z = 0$ corresponds to $\xi = \xi_1$, equation (4) shows that y remains positive, since $d\theta/d\xi$ is negative in every part lying in the configuration. Thus we see that the point $y = z = 0$ and the negative y-axis have no physical validity[3].

Zusammenfassung. Es wird bewiesen, dass die Lösungen der Emden-Gleichung nur für $y > 0$ eine physikalische Bedeutung haben.

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[3] The author is indebted to Dr. B. BASI LAL, Head of the Department of Mathematics, K.N. Government College, Gyanpur, for his guidance, and to the University Grants Commission for the award of a Junior Fellowship.

Infrared Spectrum of Strontium Hydroxyapatite

The apatites form a group of structurally very closely related substances and hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, is well known. Relatively little is known about the strontium hydroxyapatite, $Sr_{10}(PO_4)_6(OH)_2$. The ionic radii ('crystal' radii of PAULING, in Å) of Sr(1.13) and Ca(0.99) are very close together[1] and strontium can substitute for calcium in the $Ca_{10}(PO_4)_6(OH)_2$ lattice. The X-ray powder diffraction patterns confirm the isomorphous substitution of strontium for calcium; the resulting strontium hydroxyapatite crystallizes in hexagonal lattice. Measurements of the unit cell dimensions of strontium hydroxyapatite are given in Table I and are compared with those of hydroxyapatite.

The sample of this investigation was prepared according to the method described by CHRISTENSEN[7]. The X-ray powder diffraction pattern resembled that reported by COLLIN[6]. As far as we know, this is the first IR-spectroscopic study on strontium hydroxyapatite.

The IR-spectrum was recorded on Beckman IR-12. The instrument parameters on the chart legend were: diluent, sample CsI, reference air; concentration, 1.0 mg; phase, solid; gain, 3.0%; ordinate scale, % T; SB/DB energy ratio, 1; speed, 80 cm^{-1}/min.

Under the conditions used, the spectrum resolution was approximately 2–3 cm^{-1} throughout most of the region. The sample was prepared as a cesium iodide pellet using the following procedure. A small amount of the sample was hand ground in an agate mortar and pestle. 1.0 mg of the powdered sample was transferred to a small polystyrene vial containing approximately 300 mg of Harshaw IR quality cesium iodide powder (100–200 mesh) and 3 steel balls. The mixture was shaken for 1 min on a Wig-L-Bug. The mixture was transferred to a 5 · 25 mm rectangular pellet die and was pressed 3 times for 5 min using a 15,000 lb load. Multiple pressing was used to minimize, as much as possible, the scattering of short wave-length radiation which is quite typical of pellets prepared from cesium iodide. The spectrum obtained was of high quality with little indication of scattering. Several fairly intense bands were observed in the extended wave-length region. The frequencies and assignment for absorption bands are given in Table II.

The hydroxyl ion is linear and has $3N - 5$, where N is 2, normal modes, i.e. one normal mode. This corresponds to the stretching of the O–H bond with frequency near 3600 cm^{-1}. The O...O distance between the OH^- ion and the nearer of the phosphate oxygens is 3.068 Å and it has been shown[8] that an empirical relationship exists between O–H...O bond length and νs OH, from which, for 3.068 Å, a value of 3578 cm^{-1} was predicted for the stretching frequency. The OH^- ions in hydroxyapatite[9] give rise to a single sharp absorption band whose frequency 3578 cm^{-1} is the same as predicted by NAKAMOTO et al.[8]. In the case of strontium hydroxyapatite, the free O–H stretching mode appears at 3590 cm^{-1}.

Table I. Unit cell dimensions of strontium hydroxyapatite

Sample	a-axis, Å	c-axis, Å	c/a	Reference
$Ca_{10}(PO_4)_6(OH)_2$	9.43	6.88	0.730	2
$Sr_{10}(PO_4)_6(OH)_2$	9.74	7.20	0.739	3
	9.76	7.27	0.745	4
	9.76	7.27	0.746	5
	9.76	7.28	0.746	6

The enlargement of the unit cell dimensions of strontium hydroxyapatite may result from the larger ionic radius of strontium.

Table II. IR-frequencies of strontium hydroxyapatite

Frequency cm^{-1}		Assignment
235	s	$\nu_2 PO_4$
330	vs	
432	w	$\nu_3 - \nu_4$, $1030 - 595 = 435$
458	w	$\nu_3 - \nu_4$, $1030 - 572 = 458$
545	sho	?
560	vs	$\nu_4 PO_4$
572	sho	
595	vs	
652	vw	νL OH ?
672	vw	?
700	w	adsorbed CO_3 ?
878	w	adsorbed CO_3 ?
946	vs, sha	$\nu_1 PO_4$
1015	vs	$\nu_3 PO_4$
1030	vs	
1075	vs	
1410	w	adsorbed CO_3 ?
1435	w	
1452	w	
1495	vw	
1630	br, w	OH
1968	w	$\nu_3 + \nu_1$, $1030 + 946 = 1976$
2868	vw	?
3460	br	OH
3590	w, sha	νs OH

s, strong; vs, very strong; w, weak; sho, shoulder; vw, very weak; sha, sharp; br, broad; νL, librational; νs, stretching.

Hydroxyapatite has another peak at 635 cm^{-1} which has recently been assigned to the librational mode of the hydroxyl group in hydroxyapatite. It is found to arise from proton motion due to the shift by about $^1/_{\sqrt{2}}$ upon deuteration, from 635 cm^{-1} to 450 cm^{-1}. The librational motion is basically an oscillatory or hindered rotational motion of the protons[10]. A second assignment for 635 cm^{-1} absorption was recently based[11] on a Fermi resonance effect between a combination of the 2 components of ν_2, $350 + 270 = 620$ cm^{-1}, coinciding with a band of the partially split ν_4 at about 620 cm^{-1}. This would result in 1 band at 603 cm^{-1} and 1 band at 633 cm^{-1} in hydroxyapatite.

The ideal symmetry of the tribasic orthophosphate ion in the free or undistorted state is tetrahedral, i.e. it is a member of the T_d point group. The frequencies and normal modes are given in Table III.

The lowering of the symmetry of the phosphate ion in strontium hydroxyapatite causes the normal mode ν_2 at 363 cm^{-1} to become IR-active. The symmetric stretching frequency ν_1 at 980 cm^{-1} also becomes IR-active and appears at 946 cm^{-1} in strontium hydroxyapatite. The triple degeneracies of ν_3 and ν_4 are lost and the phosphate absorbance bands are observed near 1075–1015 cm^{-1} and 595–560 cm^{-1} region.

Table III. The normal modes of the orthophosphate ion[12]

Normal mode	Frequency cm^{-1}	IR-activity
The symmetric P-O stretch ν_1	980	inactive
The symmetric P-O bending ν_2 doubly degenerate	363	inactive
The antisymmetric P-O stretch ν_3 triply degenerate	1082	active
The antisymmetric P-O bending ν_4 triply degenerate	515	active

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Two bands between 460 and 430 cm^{-1} appear consistently in strontium hydroxyapatite. These bands are not as intense as the other 2 members of ν_4. The numerical value of their frequency, however, is close in magnitude to the difference between ν_3 and ν_4, suggesting them to be difference tones[12,13].

Zusammenfassung. Es wird über eine Methode berichtet, die es erlaubt, Apatide zu unterscheiden, in denen anstelle des Calciums Strontium eingetreten ist.

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Fisk University, Nashville (Tennessee, USA),
29th March 1967.

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[14] This investigation was supported by Research Grant DE-02102-02 of the U.S. Public Health Service. I thank Prof. N. Fuson for his interest, encouragement and many helpful suggestions throughout apatite investigation. The IR-spectrum of the sample was run by Mr. K. E. Stine at Beckman Instruments Inc., Fullerton, California, and the X-ray diffraction pattern was done by Dr. R. L. Collin of the University of Rochester, Rochester, New York. The sample was prepared at the Infrared Spectroscopy Institute, Fisk University, Nashville, Tennessee, and the results and discussion parts were completed at Kentucky State College, Frankfort, Kentucky.

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Isolation and Structure of Caerulein, an Active Decapeptide from the Skin of *Hyla caerulea*[1]

Methanol extracts of the skin of some South-American and Australian amphibians contain a polypeptide, or closely related polypeptides, which displays a potent and relatively long-lasting hypotensive action in the dog, potently stimulates some extravascular smooth muscles and possesses a remarkable action on several external secretions of the digestive tract[2,3].

The polypeptide, called caerulein, has been obtained for the first time in a pure form from methanol extracts of the skin of *Hyla caerulea*, an Australian amphibian.

In this communication the procedures used for the isolation of caerulein and the elucidation of its structure are briefly reported.

Isolation procedure. Crude methanol extracts of the dry skin of *H. caerulea* were submitted to a short counter-current distribution between petroleum ether and aqueous 80% ethanol and then to a single distribution in a separatory funnel between 50 ml each of the aqueous and solvent phases of the system: chloroform ml 62, methanol ml 35, and acetic acid 0.5*M* ml 40. The active material was collected in the aqueous phases freed of the fat soluble contaminants and of a large part of the pigments.

Further purification of the defatted material was obtained with a counter-current distribution of 80 transfers using the solvent system *n* butanol-acetic acid-ethanol-water (800:160:160:1280) in which caerulein showed a distribution coefficient of about 1.6. This step was repeated twice.

The partially purified material was then adsorbed on a small column of DEAE Sephadex in the OH$^-$ form and eluted with ammonium carbonate solutions of concentrations increasing from 0.05*M* to 1*M*. Caerulein emerged with the higher concentration of carbonate while the bulk of contaminants emerged with the first fractions of the effluent.

The appropriate samples were finally passed through a small column of Amberlite CG-50 in the H$^+$ form and eluted with water. Caerulein emerged unretarded in the first fractions while the ammonium ion and the small amounts of less acidic contaminants still present were retained on the resin. The active fractions were pooled and freeze-dried.

Caerulein purified with the above procedures was homogeneous on paper electrophoresis and chromatography giving a single biologically active peptide spot which was negative to ninhydrin and positive to the Ehrlich reagent for tryptophan, to the α-nitrose-β-naphthol reagent for tyrosine and to the jodoplatinate reagent for sulphur amino acids.

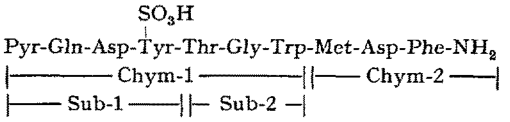
On ascending thin-layer chromatography on silica gel caerulein had an Rf of 0.2 with the solvent system *n* butanol-acetic acid-water (4:1:1) and of 0.7 with 80% aqueous ethanol. On high-voltage electrophoresis the caerulein spot migrated toward the anode at neutral and acidic pHs, its position being 0.43 relative to glutamic acid at pH 5.8 and 0.53 relative to cysteic acid at pH 1.9.

Structure. The results of the experiments summarized below were consistent with the following structure for caerulein:

$$\text{Pyr-Gln-Asp-Tyr}(SO_3H)\text{-Thr-Gly-Trp-Met-Asp-Phe-NH}_2$$

On total acid hydrolysis pure preparations gave 2 moles each of glutamic acid and aspartic acid and 1 mole each of tyrosine, threonine, glycine, methionine and phenylalanine. Tryptophan was recovered in a low yield. On alkaline hydrolysis with N $Ba(OH)_2$ tryptophan was obtained in a 1:1 ratio with respect to the other neutral amino acids and tyrosine was found in the form of a tyrosine *O*-sulphate ester.

The sequence of caerulein was deduced by the analysis of the fragments obtained upon digestion with the enzymes chymotrypsin and subtilisin which split the molecule as shown below:



$$\text{Pyr-Gln-Asp-}\overset{\displaystyle SO_3H}{\overset{|}{\text{Tyr}}}\text{-Thr-Gly-Trp-Met-Asp-Phe-NH}_2$$

Chymotrypsin hydrolysed rapidly a single bond at the carboxylic side of tryptophan, splitting the molecule into

[1] Supported in part by a grant from the Consiglio Nazionale delle Ricerche, Roma.

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