

FORCE CONSTANTS OF SOME ZINC
BLLENDE TYPE CRYSTALS

THE analysis of optically active lattice vibrations on the basis of GF matrix method as enunciated by Shimanouchi *et al.*¹ has recently been applied to some of the zinc blende type crystals.² In the present study a similar analysis has been carried out for Gallium and Indium compounds of zinc blende type structure to determine the force constants.

A zinc blende type crystal belongs to the space group $Td^2-F\bar{4} 3m$. Each Bravais unit cell of this type of crystals contains one formula unit—one zinc atom and one sulphur atom. The group theoretical considerations show that for zinc blende type there is only one fundamental lattice vibration, which is triply degenerate and active in both Raman and infrared absorption. The normal coordinate analysis gives only a combination of force constants.

$$k = K + 4H + 4H'$$

where K is the stretching force constant and H and H' are the S-Zn-S and Zn-S-Zn bending force constants. The values of k obtained are given in Table I along with the lattice frequencies. H and H' having only very small values will be negligible compared to K .

The stretching force constant K was calculated using Gordy's relation³ for Gallium and Indium compounds,

$$K = 2.25 (\chi_A \chi_B / d^2)^{\frac{2}{3}} - 0.20$$

where χ_A and χ_B are the electronegativity factors and d the bond length. These values are also given in Table I. The values of K calculated agree well within the value of k showing that the values of the bending force constants H and H' are negligible. An inspection of the values in Table I also indicates that

TABLE I
Force constants

Crystals	Frequencies cm^{-1}	k $\text{md}/\text{\AA}$	K stretching force constant calculated from Gordy's relation $\text{md}/\text{\AA}$
Ga P	367*	1.277	1.197
Ga As	273†	1.190	1.080
Ga Sb	231†	1.046	0.852
In P	307†	1.016	1.050
In As	219†	0.961	0.952
In Sb	185†	0.895	0.763

* Ref. 4.

† Ref. 5.

the force constants decrease in the order $P \rightarrow As \rightarrow Sb$ in both Gallium and Indium compounds. This indicates that as the electronegativity of the atom decreases, the force constant decreases.

One of us (V. U. N.) is grateful to C.S.I.R., New Delhi, for the award of a Junior Research Fellowship.

Dept. of Physics, V. UNNIKRISSNAN NAYAR.
Kerala Univ. Centre, G. ARULDHAS.
Ernakulam,
Kerala, November 7, 1968.

1. Shimanouchi, T., Tsuboi, M. and Miyazawa, T., *J. Chem. Phys.*, 1961, 35, 1957.
2. Tsuboi, M., *Ibid.*, 1964, 40, 1326.
3. Gordy, W., *Ibid.*, 1946, 14, 305.
4. Krishnan, R. S. and Krishnamoorthy, N., *Le J. De. Physique*, 1965, 26, 630.
5. Hass, M. and Hennis, B. W., *Bull. Am. Phys. Soc.*, 1962, 7, 78; *J. Phys. Chem. Solids*, 1962, 23, 1099.

SPECTROPHOTOMETRIC ESTIMATION
OF URANIUM WITH 2-HYDROXY-
1-NAPHTHALDOXIME

DURING the investigations on *o*-hydroxyoximes as inorganic analytical reagents the author found that 2-Hydroxy-1-Naphthaldoxime^{1,2} gave the following reactions with: (a) uranium, an orange red colour at pH 9 to 11; (b) palladium, a pale yellowish precipitate in acid solution (pH 1), (c) vanadium, a green colour in acid medium (pH 2 to 4), (d) molybdenum, yellow colour in neutral as well as in acid medium (pH 2 to 7) and (e) iron, green colour at pH 3 to 5. The uranyl ions formed a stable orange red complex with the reagent in alkaline solution (pH 9 to 11) and the limit of identification was 3.6 γ at a dilution of 1 : 277,700 (cf. salicylaldoxime, 5 γ and 1 : 200,000).

REAGENTS AND APPARATUS

1. *Uranyl Nitrate Solution*.—Uranyl Nitrate (A.R.—B.D.H.) (ca. 1.2 gm.) was dissolved in water, acidified with dilute nitric acid and the solution diluted to 500 ml. and standardised.

2. A 0.05 M solution of the oxime in 95% alcohol was used as the reagent.

3. Absorption measurements were made with Hilger U.V. Speck Spectrophotometer with 1 cm. quartz cells. All pH measurements were made with Elico pH meter (Model LI-10A).

ABSORPTION SPECTRUM OF THE COMPLEX

4 ml. of the uranyl solution was treated with 5 ml. of the reagent solution and the pH maintained at values ranging from 7.0 to 11.0 by adding 0.1N ammonia. The solution was diluted in a measuring flask to 25 ml. with 50% alcohol. Optical densities were measured at different wavelengths for each pH value and the values plotted in a graph. The region of maximum absorption was indistinct and the curve was flat between 470–475 m μ . Optical density was maximum and constant in the region of pH 9.0 to 11.0 at 470–475 m μ .

STANDARD CURVE FOR ESTIMATION OF URANIUM

A series of uranylaldoxime complex solutions in 50% alcohol was prepared having different concentrations of uranium by adding the reagent in excess (4 ml.). The pH was adjusted to be in between 9.0 and 11.0 with (0.1N) ammonia and made up to 25 ml. The reagent treated with ammonia (light yellow solution) was used as the blank. Optical densities of these solutions were measured at 470 m μ . Beer's Law was obeyed in the concentration range, 0.5 to 5 mg./25 ml. (Fig. 1).

MOLAR COMPOSITION OF THE COMPLEX

Job's Method of Continuous Variation.—Equimolar solutions (4.25×10^{-3} M) of uranyl ions and the ligand were prepared. A series of solutions was prepared by mixing x ml. of ligand with $(10-x)$ ml. of uranyl solution (x varies from 1 to 10). The optical densities of these solutions were determined at 470 m μ . The absorption due to the component parts was negligible and therefore the corresponding densities were taken. The readings are given in Table. I.

TABLE I

S. No.	Vol. of uranyl solution (ml.)	O.D. at 470 m μ
1	1.0	0.180
2	2.0	0.221
3	3.0	0.227
4	4.0	0.224
5	5.0	0.190
6	6.0	0.150

The above results plotted in a graph (Fig. 2) show that the ratio of the metal to ligand is 1 : 2.

The author expresses his grateful thanks to Prof. K. Neelakantam for his guidance.

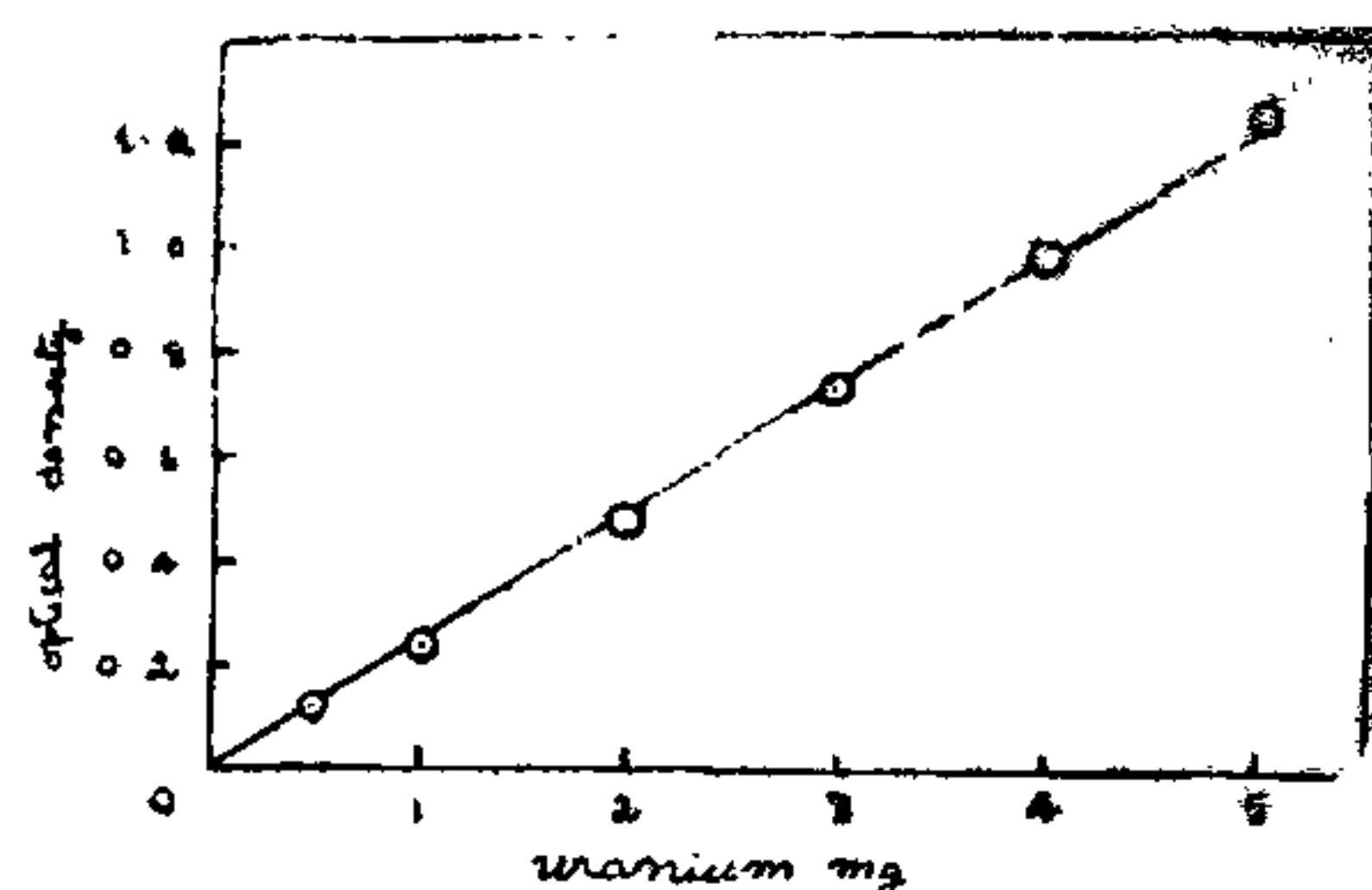


FIG. 1

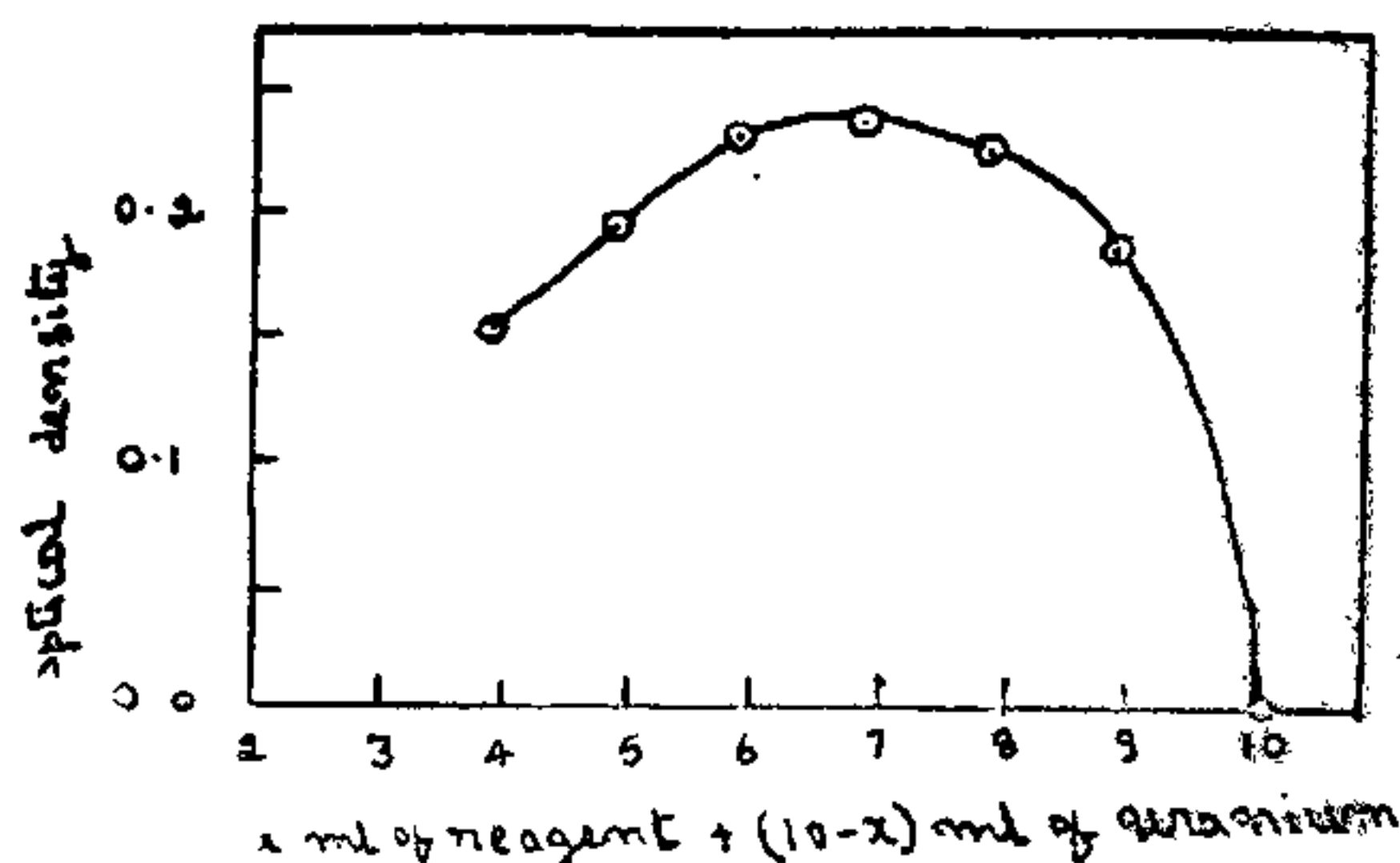


FIG. 2

Dept. of Chemistry,
Sri Venkateswara

G. RAJA REDDY.

University College,
Tirupati (A.P), October 23, 1968.

1. Ephraim, F., *Ber.*, 1930, 63, 1928.
2. Juitsu Endo and Michio Mashima, *C.A.*, 1954, 48, 2507.

THE KINETICS OF THE OXIDATION OF BENZYL ALCOHOL BY N-BROMO SUCINIMIDE

ALTHOUGH NBS is known to be a versatile oxidising agent, very little kinetic work has earlier been listed.¹ We have shown recently that the kinetics of the NBS oxidations in aqueous acid solutions is generally complicated due to the liberation of Br₂ *in situ* and that this can be circumvented and pure NBS oxidation studied in the presence of added mercuric acetate.² The kinetics and mechanism of the oxidation of secondary alcohols have been the subject of a recent study.³ We present in this communication certain interesting results on the NBS oxidation of benzyl alcohol. The oxidation was carried out in aqueous acetic acid-perchloric acid mixtures and the kinetics was investigated by following the rate of disappearance of NBS by iodometry. The reaction