

LETTERS TO THE EDITOR

MEAN AMPLITUDES OF VIBRATION:
PYRAMIDAL XYZ₂ TYPE MOLECULES

THE pyramidal XYZ₂ type molecules have the symmetry C_s and give rise according to selection rules 4a' + 2a'' type vibrations, all active in Raman and infrared spectra. The symmetry co-ordinates and the elements of the kinetic energy matrices used in the present investigation are the same as given by Venkateswarlu and Rajalakshmi.¹ In the present work, an attempt has been made to study the mean amplitudes of vibration for NH₂D, NHD₂, NF₂H and NF₂D molecules at 298° K. using Cyvin's² secular equation method. While computing the mean amplitude elements proper account has been taken of the appropriate equilibrium bond lengths of the molecule.

The harmonic wave-numbers for NH₂D, NHD₂, NF₂H and NF₂D have been calculated using the observed fundamentals and the anharmonic constants. The anharmonic constants x_{ii} and x_{ii}' are obtained for the a' and a'' species using the method suggested by Dennison.³ The harmonic wave-numbers and the anharmonic constants are given in Table I, along with the observed fundamentals.

TABLE I
Harmonic wave-numbers (cm.⁻¹) and anharmonic constants

Type of vibration	Observed				Calculated				Anharmonic constants			
	NH ₂ D	NHD ₂	NF ₂ H	NF ₂ D	NH ₂ D	NHD ₂	NF ₂ H	NF ₂ D	NH ₂ D x _{ii} *	NHD ₂ x _{ii}	NF ₂ H x _{ii}	NF ₂ D x _{ii} '
a'	3307 ⁴	3378 ⁴	3193 ⁵	2333 ⁵	3465	3495	308	2235
	2444	2389	1307	1008	2561	2173	1231	965	0.0434	..	0.0227	..
	1609	1255	972	972	1686	1299	916	931	..	0.0349	..	0.0166
a''	994	905	500	500	1042	937	471	479
	3378	2500	1424	1042	3320	2500	1456	1059	0.0039	0.0029	-0.0580	-0.0424
	1393	1476	888	888	1398	1480	908	903

The molecular parameters used in the calculations are given in Table II.

TABLE II
Molecular parameters of pyramidal XYZ₂ type molecules

Molecule	R (Å)	r (Å)	α	β	Ref.
NH ₂ D NHD ₂	1.014	1.014	110°	110°	4
NF ₂ H NF ₂ D	1.026	1.400	99.9°	102.9°	5

Using the principle suggested by Cyvin,² the secular equations giving the normal frequencies

in terms of the mean-square amplitude quantities σ at 298° K. were constructed with the help of Σ and G^{-1} matrix elements. The mean amplitudes of vibration for both the bonded and non-bonded atom pairs for the molecules are listed in Table III.

TABLE III
Mean amplitudes of vibration for pyramidal XYZ₂ type molecules (Å)

Atom pair	NH ₂ D	NHD ₂	NF ₂ H	NF ₂ D
X-Y	0.06482	0.07295	0.07379	0.06460
X-Z	0.07224	0.06469	0.04797	0.04787
Z..Z	0.13480	0.11060	0.06656	0.06573
Y..Z	0.12900	0.13020	0.12190	0.11090

The following conclusions may be drawn from the results presented in Table III.

1. The mean amplitude of vibration is the same for the N-H atom pair in NH₂D, NHD₂ and NF₂H.
2. The mean amplitude of vibration for the N-D bond is also the same for the molecules NH₂D, NHD₂ and NF₂D.
3. The N-F mean amplitude quantity is found to be the same in NF₂H and NF₂D.
4. The F...F non-bonded mean amplitude value is almost the same in NF₂H and NF₂D.

These mean amplitude values may be useful in electron diffraction measurements of these molecules.

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COMPLEXES OF CUPRIC ION

STUDIES on formation and properties of complexes between cupric ions and various ligands like halide ions, anions from various acids, etc., in aqueous solution especially by spectrophotometry are limited. Mc Connel and Davidson¹ and Kruh² have reported different values for the formation constant, K for the complex CuCl^+ . The former have also reported under conditions of very high chloride concentration formation of an ion pair CuCl_4^- which has absorption peak in the visible ($\lambda = 380 \text{ m}\mu\text{-}440 \text{ m}\mu$). We have investigated by spectrophotometry complexes between cupric ions and chloride ions, anions from various acids—(formic; acetic; propionic; lactic; β -hydroxy propionic; itaconic, etc.), as ligands with a view to determine the formation constants and associated thermodynamic functions and to investigate the photosensitizing properties of these complexes.

Cupric perchlorate in aqueous solution has been used as the source of cupric ions. Analar acids have been used as sources for ligands. All absorbancy measurements have been made in a Hilger U.V. spectrophotometer under conditions of constant ionic strength, pH range, temperature, etc. A typical study is briefly described: Optical density vs. Wavelength

curves are constructed for 1:1, 1:2, 1:3, 1:4 mixtures (by molarity) of cupric ion and ligand acid respectively to determine the wavelength region for absorption and to get a rough idea of number of complexes formed from the shape of these curves. Composition of each complex is determined by Job's method³ extended by Vosburgh and Cooper.⁴ The data are treated to Mole ratio method⁵ also to check the composition and stability of the complex. Effect of pH on the stability of each complex is also studied. From measurements of optical densities of a series of dilutions of the composition of the complex and from a knowledge of extinctions for cupric ion and the complex, the dissociation constant of the ligand acid and pH, the formation constant for the complex has been evaluated.

We report briefly the following results:—

(i) Our values for CuCl^+ at 25°C ., and $\mu = 1$, $K = 0.297$ litre/mole and $\Delta H = 4834$ calories, $\Delta S = 15.979$ calories per degree. The divergence between our value for K and those by Mc Connel and Davidson (1.296 litre per mole) and Kruh (0.27 litre per mole) is attributed to the fact that small differences in the optical density values reflect large differences in the K values. We find that there is no initiation of vinyl polymerisation on irradiation of the system CuCl_4^- -Vinyl monomer, (with $\lambda = 365 \text{ m}\mu\text{-}546 \text{ m}\mu$), which indicates that the dark

back reaction in $\text{CuCl}_4^- \xrightarrow{h\nu} \text{CuCl}_3^- + \text{Cl}$ is quite

fast. (ii) (a) Optical density vs. λ curves for 1:1, 1:2, 1:3, 1:4 mixtures of cupric ion and ligand acid indicate that the effective wavelength region is between 250–350 $\text{m}\mu$ for $\lambda > 3500 < 6000 \text{ \AA}$ there is negligible absorption. With each ligand the curves for various mixtures have similar shape and therefore formation of one type of complex only is concluded in each case. Job's method of continuous variation extended by Vosburgh and Cooper, has given a maximum of 0.5 mole fraction and therefore formation of 1:1 complex in each case is concluded. (iii) Application of Mole ratio method does not give a sharp break at 1:1 mole ratio for any acid. Beyond 1:1 ratio the optical density continues to increase. Degree of dissociation of the complex⁶ $\alpha = (E_m - E_s)/E_m$ for each complex has however been evaluated and the values are: 0.89 (formate ligand); 0.94 (propionate); 0.90 (isobutyrate); 0.92 (lactate); 0.84 (itaconate); 0.84 (β -hydroxypropionate). E_m , the maximum extinction for the 1:1 complex has been evaluated from optical density for a solution in which

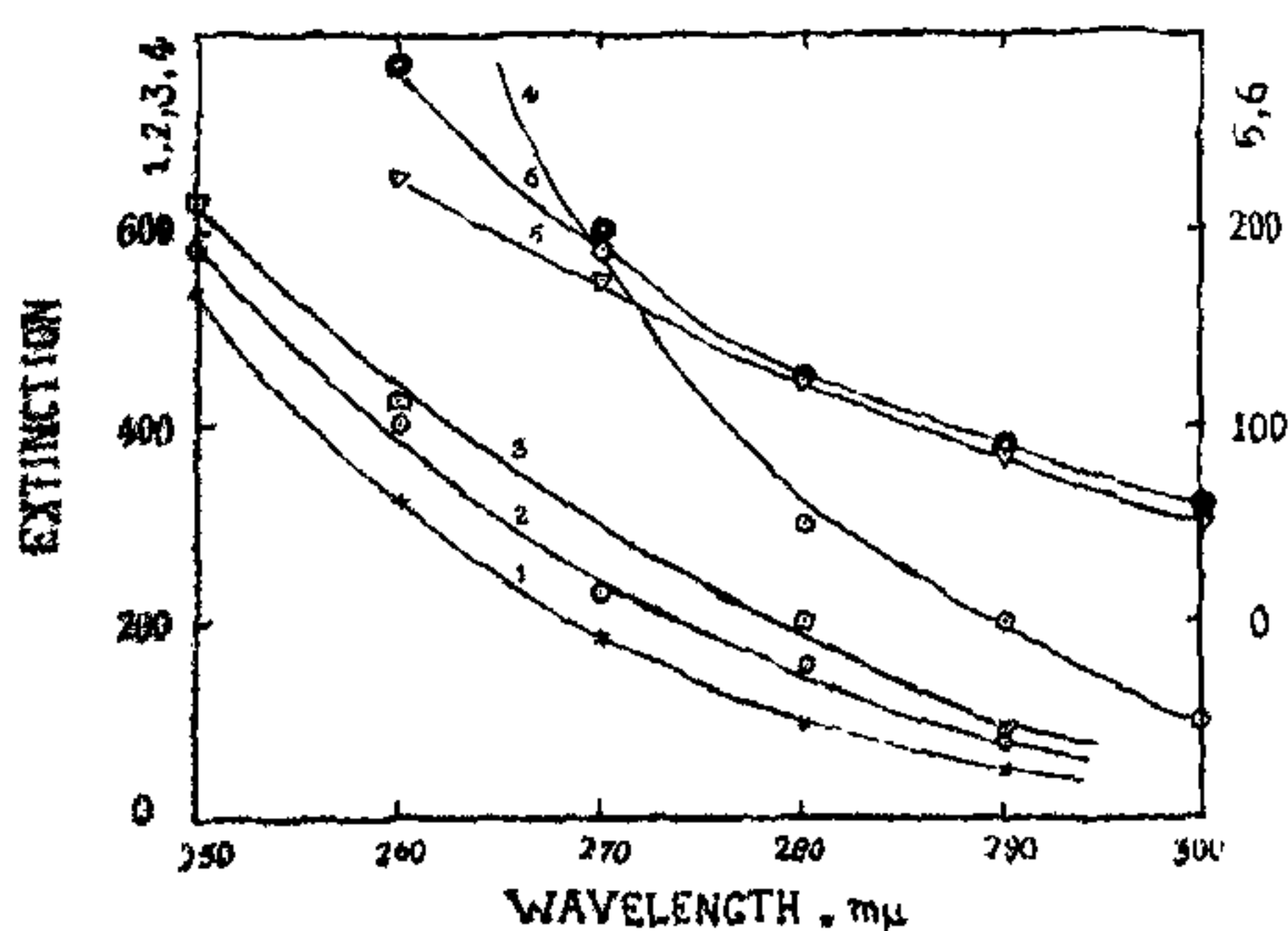


FIG. 1. Curve (1) Copper formate; (2) Copper propionate; (3) Copper iso-butyrate; (4) Copper lactate; (5) Copper itaconate; (6) Copper β -hydroxy propionate.