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# The Infrared Spectrum of Matrix Isolated Cuprous Chloride

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*The infrared spectrum (500-33 cm$^{-1}$) of cuprous chloride has been studied using the matrix isolation technique. The observed bands were assigned to the polymeric species $Cu_3Cl_3$ and $Cu_4Cl_4$. The principal bond stretching force constants were calculated as 1.52 mdyn/Å and 1.1 mdyn/Å for the trimer and tetramer respectively, assuming for the former a planar six membered ring of alternate copper and chlorine atoms with bond angles Cl–Cu–Cl 150° and Cu–Cl–Cu 90°, and for the latter a distorted cube with an angle Cl–Cu–Cl 68°24′.*

## Introduction

The infrared spectrum of cuprous chloride vapor at approximately 1000°C was studied by Klemperer and co-workers.[2] They interpreted their data on the basis of a distorted cyclic trimer, in accordance with the vapor density measurements reported by Brewer and Lofgren.[3] However, recent mass-spectrometric work by Guido *et al.*[4] indicates that the vapor in equilibrium with condensed cuprous chloride consists of trimer and tetramer with small amount (0.5%) of pentamer. The average bond energies of these species are 2.8 eV and 1.9 eV respectively.[4] Since there is a rough correlation between bond stretching force constant and bond energy, one would expect the tetramer to abosrb at lower frequency than the trimer.

It seems useful, therefore, to extend the IR spectrum of gaseous cuprous chloride to lower frequency (33 cm$^{-1}$), using the matrix isolation technique, which has the advange of yielding sharp bands.

The present paper reports the infrared spectrum between 500 and 33 cm$^{-1}$ of matrix isolated cuprous chloride which resulted in the determination of some of the vibrational frequencies of the trimer and tetramer.

## Experimental Section

The experimental apparatus was that used previously.[5,6] The range below 200 cm$^{-1}$ was investigated using a Beckman IR-11 Spectrophotometer; cesium iodide and polyethylene were used as window materials. Argon and nitrogen were employed as inert gas matrices. Degassed CuCl was vaporized at approximately 400°C from a pyrex cell and temperature was measured with a chromel-alumel thermocouple.

## Results and Discussion

The Spectrum was observed using a Perkin Elmer 225 and a Beckman IR-11 instruments. Results were identical over the common range scanned (500-200 cm$^{-1}$). Argon was preferable to nitrogen as the matrix gas because of its better transparency below 250 cm$^{-1}$; however no significant shifts were observed between the two matrices in the high frequency region.

The observed spectrum showed many absorption peaks, whose frequencies are reported in the Table I. Most of the bands show multiplet structure and broadening, the latter being unusual at 20°K. These two effects are probably due respectively to matrix splitting of the degenerate modes and to partially substituted species absorbing very close to each other. The assignment, therefore, appears to be quite difficult and it was done assuming the trimer and tetramer as the main vapor species, in accordance to the mass-spectrometric data.[4] In fact neither $^{35}$Cl $^{37}$Cl isotopic substitution nor variation of deposition conditions could be used to check the assignments since bands half-widths are too broad to show isotopic shifts and the enthalpies of vaporization of the two polymers are nearly the same.[4]

Assignment of the frequencies to each polymer was made assuming for the trimeric molecule a planar six-membered ring of alternate copper and chlorine atoms ($D_{3h}$) with bond angles Cl–Cu–Cl 150° and Cu–Cl–Cu 90° as inferred from electron diffraction data[7] and solid-vapor structural relationship advanced by Shelton;[8] this relationship can be extended to the tetramer suggesting a cubic structure ($T_d$) for this molecule, as for the tetrameric oxides of the IV B group elements.[5,9,10]

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**Table I.** Observed and Calculated Frequencies ($cm^{-1}$) for Cuprous Chloride.

| In Argon | In Nitrogen | Calculated [a] | Assignment |
|---|---|---|---|
| Trimer | | [b] | |
| 393.5±0.5 (s) [d] | 393±0.5 | 393.6 | $Cu_3Cl_3$ E′ |
| 383 ±0.5 (m) | 382±0.5 | | [c] |
| 285 ±1 (m) | | 286.4 | $Cu_3Cl_3$ E′ |
| 101 ±1 (m) | | 101.3 | $Cu_3Cl_3$ E′ |
| Tetramer | | [c] | |
| 324 ±1 (m) | | 324.1 | $Cu_4Cl_4$ $F_2$ |
| 248 ±1 (w) | | | [e] |
| 234 ±1 (w) | | 234.5 | $Cu_4Cl_4$ $F_2$ |
| 218 ±1 (w) | | | [e] |

[a] Frequencies are calculated for the most abundant isotopic species. [b] Assuming $f_r = 1.52$ mdyn/Å $f_\theta/R^2 = 0.065$ mdyn/Å and angle Cl-Cu-Cl 150°. [c] Assuming $F_R = 1.1$ mdyn/Å and angle Cl-Cu-Cl = 68°24′. [d] s: strong; m: medium; w: weak. [e] Matrix split bands.

On the basis of these assumed structures, the trimeric molecule has three doubly degenerate in plane modes (E′) and one out-of-plane mode ($A''_2$) which are infrared active; the latter mode will have a very low vibrational frequency (below 100 $cm^{-1}$).

Calculations of in plane frequencies were made using a two parameter potential function:[5]

$$2V = f_r(\Delta r_1^2 + \Delta r_2^2 + \Delta r_3^2 + \Delta r_4^2 + \Delta r_5^2 + \Delta r_6^2) + f_\theta/R^2(\Delta\theta_1^2 + \Delta\theta_2^2 + \Delta\theta_3^2 + \Delta\theta_4^2 + \Delta\theta_5^2 + \Delta\theta_6^2)$$

The observed frequencies are reproduced by setting $f_r = 1.52$ mdyn/Å and $f_\theta/R^2 = 0.065$ mdyn/Å.

For the tetramer we assumed a distorted cubic structure ($T_d$ symmetry). The normal vibrations for this system are $2A_1 + 2E + F_1 + 3F_2$ and only the $F_2$ modes are IR active. Two of these lie in the Cu–Cl stretching region and the third is expected at much lower frequency.

For the calculation we assumed, in this case, a very simplified field analogous to that reported by Ogden and Ricks:[9]

$$2V = F_R(\Delta R_{15}^2 + \Delta R_{16}^2 + \Delta R_{18}^2 + \Delta R_{38}^2 + \Delta R_{48}^2 + \Delta R_{47}^2 + + \Delta R_{46}^2 + \Delta R_{26}^2 + \Delta R_{27}^2 + \Delta R_{37}^2 + \Delta R_{35}^2 + \Delta R_{25}^2).$$

if one assumes $F_R = 1.1$ mdyn/Å the observed frequencies are reproduced. In the latter calculations the angle Cl–Cu–Cl, which is an extra variable, was set at 68°24′ to give the best fitting.

It is interesting to observe that the ratio between the bond stretching force constants of trimer and tetramer is equal to the ratio of the average bond energies of the two molecules, being 1.4.

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