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On the Geometry of the $CuCl_2$ Molecule

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A recent paper in this journal[1] drew attention to the need to define the geometry of molecular $CuCl_2$ in its ground electronic state. It was suggested that the problem might best be resolved "by measuring the EPR spectrum", presumably in a cryogenic matrix. However, gas phase studies of this moderately volatile molecule would be much more informative. Difficulties would arise in obtaining bond lengths and geometries from electron diffraction experiments on $CuCl_2$ because of dissociation to form $(CuCl)_n$ and chlorine. On the other hand, gas phase studies of $CuCl_2$ can be carried out using laser-induced-fluorescence (LIF) spectroscopy at high resolution. By use of a narrow-band source such as a CW tunable dye laser (line width 3×10^{-5} cm^{-1}), rotationally resolved excitation spectra may be obtained by recording the total fluorescence signal from a seeded molecular beam (giving rotational temperatures of the order of 10 K);[2,3] alternatively, using a hot cell with excitation of a selected rovibronic transition, the laser-induced-fluorescence spectrum can be studied at rotational resolution, using a Fourier transform spectrometer.[4−7] Recently, these two approaches (molecular beam and FT spectrometer) have been combined into one experiment.[8] In principle, both ground and excited state constants can be obtained from such measurements. However, a limiting factor for exploring electronic energy levels is the requirement that the molecule should undergo an appropriate transition by emitting fluorescence. Several papers have also been published on the rotationally resolved excitation spectra of $NiCl_2$ produced in a molecular beam.[9−11]

Table 1. Equilibrium Vibrational and Rotational Constants for Different Isotopomers of $CuCl_2$ in Its Ground Electronic State[a]

parameter	$^{63}Cu^{35}Cl_2$ (1783 lines)	$^{63}Cu^{37}Cl_2$ (1872 lines)	$^{65}Cu^{37}Cl_2$ (1675 lines)
ω_1	371.693(2)	361.553(1)	361.5395(4)
ω_2	95.807	94.60	93.81
ω_3	525.897(4)	519.113(1)	514.791(1)
x_{11}	−0.5066(4)	−0.4788(2)	−0.4810(1)
x_{33}	−1.212(1)	−1.1798(2)	−1.1545(2)
x_{13}	−2.577(2)	−2.4590(6)	−2.4481(2)
y_{113}	$-4.13(20) \times 10^{-3}$	$-5.16(10) \times 10^{-3}$	$-3.216(4) \times 10^{-3}$
y_{133}	$8.14(20) \times 10^{-3}$	$6.867(9) \times 10^{-3}$	$5.724(5) \times 10^{-3}$
y_{333}	$8.6(8) \times 10^{-4}$		
B_e	0.058188(1)	0.055053(1)	0.055046(1)
α_1	$1.234(2) \times 10^{-4}$	$1.127(2) \times 10^{-4}$	$1.1348(2) \times 10^{-4}$
α_2	-1.1×10^{-4}	-1.0×10^{-4}	$-.991 \times 10^{-4}$
α_3	$1.978(2) \times 10^{-4}$	$1.8634(2) \times 10^{-4}$	$1.828(1) \times 10^{-4}$
D_e	$5.8(1) \times 10^{-9}$	$5.0(2) \times 10^{-9}$	$5.4(2) \times 10^{-9}$
rms error	0.013	0.009	0.009

[a] All quantities are quoted in cm^{-1}. The uncertainties (2 SD error) are given in parentheses, in units of the last digit, for all of the floated parameters.

The purpose of this paper is to report the vibrational and rotational constants of gaseous $CuCl_2$ in its ground state, establishing its electronic configuration and geometry. We have analyzed high-resolution data from three symmetric isotopomers: $^{63}Cu^{35}Cl_2$, $^{63}Cu^{37}Cl_2$, and $^{65}Cu^{37}Cl_2$. In each case, a series of LIF data recorded with isotopically enriched samples of copper and chlorine provided information on many low-lying vibrational levels of this molecule, particularly for the stretching vibrations. The rotational structure observed and the fact that the bending vibration is not easily excited already suggest that $CuCl_2$ is linear, but by careful extraction of the equilibrium stretching wavenumbers, we can derive the bond angle 2θ for $CuCl_2$ in the vapor phase from these data. The $^{63}Cu^{35}Cl_2$ molecule has also been investigated by laser excitation spectroscopy,[2,3] providing high-quality data pertaining to the (000) and (100) levels of the lower electronic state. These data were merged with laser-induced-fluorescence transitions observed to the lowest vibrational levels ($v_1 \leq 6$, $v_2 = 0$, $v_3 \leq 6$) with $J'' < 80^1/_2$, avoiding regions known to contain local perturbations.[7] Values for the equilibrium parameters are obtained independently for each isotopomer from a least-squares fit to rovibrational energies in the ground state:

$$T_{vJ} = G(v) + F(J)$$

where the vibrational energy $G(v)$ is given by

$$\begin{aligned} G(v) = {} & \omega_1(v_1 + {}^1/_2) + \omega_2(v_2 + 1) + \omega_3(v_3 + {}^1/_2) + \\ & x_{11}(v_1 + {}^1/_2)^2 + x_{33}(v_3 + {}^1/_2)^2 + y_{333}(v_3 + {}^1/_2)^3 + \\ & x_{13}(v_1 + {}^1/_2)(v_3 + {}^1/_2) + y_{113}(v_1 + {}^1/_2)^2(v_3 + {}^1/_2) + \\ & y_{133}(v_1 + {}^1/_2)(v_3 + {}^1/_2)^2 + ... \end{aligned}$$

and the rotational energy $F(J)$ is given by

$$\begin{aligned} F(J) = {} & [B_e - \alpha_1(v_1 + {}^1/_2) - \alpha_2(v_2 + 1) - \\ & \alpha_3(v_3 + {}^1/_2)][J(J + 1) - \Omega^2] - D_e[J(J + 1) - \Omega^2]^2 \end{aligned}$$

The results of these fits are presented in Table 1. The values of ω_2 and α_2 for $^{63}Cu^{35}Cl_2$ and $^{63}Cu^{37}Cl_2$ are derived from analyses of the Renner−Teller structure in the (020) vibrational level of the ground state[6,8] and are only approximate because

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they ignore anharmonicity. The values of ω_2 and α_2 for $^{65}Cu^{37}Cl_2$ were obtained by isotopic scaling.[12]

In a symmetrical XY_2 molecule, the antisymmetric (or asymmetric) stretching vibrational wavenumber ω_3 varies with isotopic substitution as

$$\left(\frac{\omega_3}{\omega_3^{(i)}}\right)^2 = \frac{\left(1 + \frac{2m_Y}{m_X}\sin^2\theta\right)m_Y^{(i)}}{\left(1 + \frac{2m_Y^{(i)}}{m_X^{(i)}}\sin^2\theta\right)m_Y}$$

so ratios of ω_3 values for different isotopomers may be used to determine the bond angle 2θ without a knowledge of the force field. This approach leads to the following angles:

$$^{63}Cu^{35}Cl_2 / {}^{63}Cu^{37}Cl_2: \quad 2\theta = 173°$$

$$^{63}Cu^{37}Cl_2 / {}^{65}Cu^{37}Cl_2: \quad 2\theta = 171°$$

$$^{63}Cu^{35}Cl_2 / {}^{65}Cu^{37}Cl_2: \quad 2\theta = 176°$$

We also have a large amount of information on the excitation of the symmetric stretching vibration for the different isotopomers of $CuCl_2$. These results can also be used to estimate the bond angle of the molecule if it is assumed that the symmetric stretching and bending vibrations are not significantly coupled. In this situation

$$\left(\frac{\omega_1}{\omega_1^{(i)}}\right)^2 = \frac{\left(1 + \frac{2m_Y}{m_X}\cos^2\theta\right)m_Y^{(i)}}{\left(1 + \frac{2m_Y^{(i)}}{m_X^{(i)}}\cos^2\theta\right)m_Y}$$

Using combinations of ω_1 from different isotopomers leads to the following angles:

$$^{63}Cu^{35}Cl_2 / {}^{63}Cu^{37}Cl_2: \quad 2\theta = 173°$$

$$^{63}Cu^{37}Cl_2 / {}^{65}Cu^{37}Cl_2: \quad 2\theta = 175°$$

$$^{63}Cu^{35}Cl_2 / {}^{65}Cu^{37}Cl_2: \quad 2\theta = 172°$$

To eliminate the possibility that the value actually determined ($2\theta = 173°$) suggests that the molecule is slightly bent, we have estimated the barrier to linearity implied by such a bond angle. This barrier is found to be less than 10% of the zero-point energy for the bending motion, so that $CuCl_2$ shows linear behavior in all its accessible energy levels. (In fact, we would prefer to attribute the small difference between the value determined for 2θ and 180° to neglect of some of the anharmonic corrections, such as terms involving x_{12}, x_{22}, and x_{23} which have not been determined.) Consequently, we have shown that the molecule is linear, with a $^2\Pi_{g(3/2)}$ ground electronic state.[2] This conclusion is supported by the shortness of the bending progressions and the absence of any K structure in the detailed rotational analyses.[2−4,7] For a linear symmetrical molecule, the rotational constant B_e is related to the equilibrium Cu−Cl bond distance r_e by

$$B_e = \frac{h}{16\pi^2 c m_Y r_e^2}$$

With a bond angle of 180°, the rotational constants in Table 1 lead to bond lengths of $r_e(^{63}Cu^{35}Cl_2) = 203.53$ pm, $r_e(^{63}Cu^{37}Cl_2) = 203.51$ pm, and $r_e(^{65}Cu^{37}Cl_2) = 203.53$ pm.

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