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Laser-induced fluorescence spectra of the non symmetrical isotopomers of CuCl_2

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Abstract

Investigations of the ground state of CuCl_2 have been pursued recording laser induced fluorescence spectra on a BOMEM DA3 Fourier transform spectrometer in the range $10000\text{--}16500\text{ cm}^{-1}$. In this work, we specially extend the study to the non symmetrical isotopomers $^{35}\text{Cl}^{63}\text{Cu}^{37}\text{Cl}$ and $^{35}\text{Cl}^{65}\text{Cu}^{37}\text{Cl}$. Band-by-band and polynomial fits allowed us to determine rotational and vibrational constants in the range $v''_1=0\text{--}9$, $v''_3=0\text{--}6$ that will be compared to the constants of the main symmetrical isotopomers $^{63}\text{Cu}^{35}\text{Cl}_2$. An approximate Valence Force Field model is tested and discussed.

Introduction

CuCl_2 is one of the simplest molecule to be found among the transition metal dihalides and is a good candidate for testing ligand field theory on d electron systems. After a few works, thirty years ago /1/, recently this molecule became again very attractive. First, the ab initio calculations of Bauschlicher and Roos /2/ was a useful framework for the spectroscopic exploration of this molecule. Then, Yoshida /3,4/ suggested that this molecule was responsible of very strong red and infra-red emissions during a chemical reaction with energy transfer between $\text{O}_2^1\Delta_g$, Cl_2 and heated copper (200°C). This molecule has also another chemical interest for the formation of polyvinylchloride /5/.

In several contributions /6,7/ we presented a high resolution spectroscopic study of the ground state of CuCl_2 using the combined Fourier Transform Spectrometry (F.T.S) and Laser Induced Fluorescence (L.I.F) techniques. The last paper /7/ gave a global treatment for the four symmetrical isotopomers of copper dichloride, assuming a Valence Force Field linear XY_2 molecule model for isotopic shifts. A simple polynomial expression for the v_1 , v_3 and J rovibrational levels of the observed ground state allowed to obtain a complete set of molecular parameters, force constants and Cu-Cl bond length.

In this work, we try to extend the study to the non symmetrical isotopomers of CuCl_2 . In natural CuCl_2 , their abundance is respectively 25.14% and 11.83%. Obtaining extensive data proved difficult and the data base is still reduced. However, we will give our preliminary results. We have determined the effective

spectroscopic constants for the two states $2\Pi_u$ and $X^2\Pi_{g3/2}$ of the red transition using band-by-band fit. Then, we separately used polynomial expressions for vibrational and rotational energies to obtain their inherent constants. We took $^{63}\text{Cu}^{35}\text{Cl}_2$ as a test molecule to verify the simplified Valence Force Field model relative to the non symmetrical isotopomers /8/.

Experiments

The sources are sealed quartz cells containing copper wire and enough Cl_2 to react stoichiometrically to produce CuCl_2 . The cells are ended by two Brewster windows to minimize the reflection of the laser polarized light, and equipped with a sidearm. A cell is heated in a dual temperature electric oven. For isotopic studies of the non symmetrical molecule, we need to use natural CuCl_2 . To increase rotational relaxation processes, we can introduce a few torrs of argon before sealing. The fluorescence of CuCl_2 is excited with a CW ring dye laser (Spectra Physics 380-D), pumped by an argon ion laser, operating single mode with DCM, Rh6G or Kiton Red dye. The laser mode is monitored by a 2Ghz confocal interferometer and for high resolution, a reference extra-cavity of 500MHz, free spectral range, (Spectra Physics 388) is used. Backwards, L.I.F. is collected and focused into a fused silica optical fiber. L.I.F. arrives to the entrance iris of the Michelson interferometer (BOMEM DA3). The spectra are recorded using a silicon avalanche detector. A Fizeau wavemeter controls continuously the laser wavelength. An optical filter is used to attenuate the laser line and protect the detector. The access to the anti-Stokes side of the L.I.F. spectrum is possible when the level of scattered light from the ring laser is low enough. The spectrum is recorded at low resolution (30 cm^{-1}) to choose accurately the laser wavelength; then, we record the spectrum at high resolution (0.070 cm^{-1}) : a good compromise between convenient recording time (2 hours) and the Doppler width of CuCl_2 .

Results

The spectra we obtained are illustrated in figure 1. Several isotopes are present and it is generally the case for all the spectra recorded with a good signal to noise ratio. The wavenumber of any fluorescence line can be represented by a difference in term energies for the upper and lower electronic states:

$$\nu_{\text{measured}} = T'_{\nu'}(J') - T_{\nu_1\nu_3}(J)$$

Table I			
isotopomers	T' (cm ⁻¹)	B' (cm ⁻¹)	D' (cm ⁻¹).10 ⁹
A	15547.713(25)	0.050521(16)	7.9(2)
B	15979.890(25)	0.050353(17)	7.5(2)
C	16125.394(6)	0.049882(11)	7.0
C'	16127.549(4)	0.049882	7.0
35 - 63 - 37 D	16251.031(55)	0.049882	7.0
D'	16251.897(4)	0.04920(3)	7.0
D''	16250.643(5)	0.0492	7.0
E	16647.745(227)	0.0542(1)	7.0
A	15548.270(48)	0.050485(22)	10.0
B	15978.53(17)	0.05047(9)	22(1)
D	16244.960(48)	0.049889(21)	10.0

where, $T'_{v'}(J') = T'_{v'} + B'_{v'}J'(J' + 1) - D'_{v'}J'^2(J' + 1)^2$,

is the total vibration energy populated by the laser and J' the rotational quantum number of the $2\Pi_u$ state. For the ground state, we used a similar expression. The table I shows the complexity of the $2\Pi_u$ state. We cannot assign a vibrational numbering. The tables II and III present the effective rovibrational constants obtained using a band-by-band fit for $X^2\Pi_{g3/2}$ state for $^{35}\text{Cl}^{63}\text{Cu}^{37}\text{Cl}$ and $^{35}\text{Cl}^{65}\text{Cu}^{37}\text{Cl}$ ($0 \leq v''_1 \leq 9$ and $0 \leq v''_3 \leq 6$). The R.M.S. deviation of the global fit is generally of a few 10^{-3} cm^{-1} except for perturbed vibrational levels, for example ($v''_1=8-9$, $v''_3=0$), ($v''_1=5$, $v''_3=2$). Using these accurate results we take separate polynomial developments function of v_1 , v_2 and v_3 for $G(v_1, v_2, v_3)$, $B(v_1, v_2, v_3)$ and $D(v_1, v_2, v_3)$.

$$G(v_1, v_2, v_3) = \sum_{j=1,2,3} \omega_j (v_j + d_j/2) + x_{11}(v_1 + 1/2)^2 + x_{33}(v_3 + 1/2)^2 + x_{13}(v_1 + 1/2)(v_3 + 1/2) + x_{111}(v_1 + 1/2)^3 + x_{113}(v_1 + 1/2)^2(v_3 + 1/2) + x_{133}(v_1 + 1/2)(v_3 + 1/2)^2 + x_{333}(v_3 + 1/2)^3$$

$$B(v_1, v_2, v_3) = B_e - \sum_{j=1,2,3} \alpha_j (v_j + d_j/2)$$

$$D(v_1, v_2, v_3) = -D_e - \sum_{j=1,2,3} \beta_j (v_j + d_j/2)$$

The bending vibration did not appear or appeared so weakly that we neglected the terms including ω_2 . We obtained spectroscopic constants using a least squares fitting code MINUIT 9/ (table IV).

Table II

^{63}Cu	v''_1	v''_3	$T_v'' (\text{cm}^{-1})$	$B_v'' (\text{cm}^{-1})$	$D_v'' (10^{-9} \text{ cm}^{-1})$	Nb lines	R.M.S (cm^{-1})
1	0	0	363.92(2)	0.05648(2)	12(3)	6	0.009
2	0	0	727.262(7)	0.056323(5)	6.8(9)	37	0.012
3	0	0	1089.559(4)	0.056212(4)	7.2(6)	63	0.013
4	0	0	1450.864(4)	0.056096(3)	7.9(5)	69	0.011
5	0	0	1811.207(3)	0.055959(3)	5.8(5)	72	0.01
6	0	0	2170.503(5)	0.055835(6)	7.5(1.0)	61	0.014
7	0	0	2528.822(8)	0.055707(8)	11(1)	48	0.021
8	0	0	2886.08(1)	0.055564(4)	10(F)	38	0.038
9	0	0	3242.55(2)	0.05557(2)	10(F)	4	0.017
0	2	0	1035.23(1)	0.05617(1)	4.9(2.0)	14	0.016
1	2	1	1394.511(8)	0.056063(8)	7.2(1.2)	34	0.018
2	2	1	1752.778(5)	0.055965(5)	13.1(8)	42	0.015
3	2	1	2110.041(5)	0.055846(4)	13.7(7)	46	0.014
4	2	1	2466.303(6)	0.055672(9)	11.5(2.8)	27	0.007
5	2	1	2821.580(9)	0.055647(8)	20(1)	24	0.014
6	2	1	3176.03(8)	0.05540(3)	2(3)	7	0.005
7	2	1	3528.977(7)	0.055368(4)	9.6(6)	7	0.004
0	4	0	2061.314(4)	0.0557(F)	10.0(F)	2	0.004
1	4	0	2415.544(8)	0.055710(7)	12(1)	10	0.007
2	4	0	2768.875(9)	0.055582(7)	10(1)	12	0.009
3	4	0	3121.19(3)	0.05542(3)	14(7)	8	0.006
4	4	0	3472.375(3)	0.0553(F)	10.0(F)	2	0.003
2	6	0	3775.51(10)	0.05525(4)	17.1(4.8)	7	0.0046
3	6	0	4122.91(9)	0.05509(4)	15(4)	6	0.003

Table III

^{65}Cu	v''_1	v''_3	$T_v'' (\text{cm}^{-1})$	$B_v'' (\text{cm}^{-1})$	$D_v'' (10^{-9} \text{ cm}^{-1})$	Nb lines	R.M.S (cm^{-1})
1	0	0	362.983(7)	0.05645(F)	10(F)	2	0.001
2	0	0	726.11(4)	0.05641(2)	18(2)	7	0.003
3	0	0	1088.68(9)	0.05617(4)	5.2(4.0)	8	0.004
4	0	0	1449.79(3)	0.056120(15)	12.4(1.5)	10	0.007
5	0	0	1809.96(2)	0.05605(1)	18.20(12)	14	0.006
6	0	0	2169.38(2)	0.05580(14)	8.4(2)	10	0.002
7	0	0	2527.27(14)	0.05594(8)	36.8(11.2)	12	0.087
8	0	0	2884.22(3)	0.05592(2)	50.3(2.5)	10	0.019
0	2	0	1026.09(7)	0.05613(2)	10.0(F)	4	0.012
1	2	1	1385.03(3)	0.056120(16)	15.7(1.9)	14	0.0081
2	2	1	1743.24(4)	0.05605(2)	19.4(3.3)	10	0.0037
3	2	1	2100.64(3)	0.055860(9)	10.0(F)	8	0.008
4	2	1	2456.17(3)	0.05611(4)	57.1(8.1)	8	0.017
5	2	1	2811.63(3)	0.05587(2)	34.7(3.0)	8	0.019
6	2	1	3165.80(3)	0.05576(2)	36.6(3.3)	6	0.014
7	2	1	3519.62(5)	0.05537(9)	10.0(F)	4	0.0039
8	2	1	3872.06(1)	0.05515(F)	23.7(6)	4	0.0076
0	4	0	2043.184(3)	0.0559(F)	10(F)	2	0.0032
1	4	0	2397.22(4)	0.05608(2)	52.9(3.3)	8	0.021
2	4	0	2750.61(3)	0.05596(2)	51.6(2.6)	8	0.017
3	4	0	3102.95(3)	0.05583(2)	51.0(3.0)	8	0.019
2	6	0	3751.14(1.58)	0.0551(3)	10.0(F)	5	0.61
3	6	0	4103.3(8)	0.0541(2)	10.0(F)	6	0.36
4	6	0	4436.99(1.57)	0.0569(4)	10.0(F)	5	0.2
5	6	0	4781.8(2.0)	0.0570(5)	10.0(F)	4	0.2

Discussion

In table V we compared the main constants B_e , ω_1 , ω_3 with constants of $^{63}\text{Cu}^{35}\text{Cl}_2$ previously determined 7/. For non symmetrical, CuCl_2 the moment of inertia has been calculated for two hypothesis : the copper is not superposed to the center of mass and is equidistant from the two different chlorines ; we found a

good agreement between the ratio of the constants B_e and of moments of inertia. Formulae for the isotopic effect in unsymmetrical linear triatomic molecules, assuming a small mass difference, might be available because $(\Delta m_y/m_y)^2 = 0.003 \ll 1$ in our case /10/. In fact the agreement is good enough for $\Delta\omega_1/\omega_1$ but not satisfying for $\Delta\omega_3/\omega_3$.

Table IV

$G_{v_1v_3} \text{ cm}^{-1}$	$B_{v_1v_3} \text{ cm}^{-1}$	$D_{v_1v_3} \text{ cm}^{-1}$
^{63}Cu		
ω_1 366.79(24)	B_e 5.6715(38). 10^{-2}	D_e 1.1(9). 10^{-8}
ω_3 522.11(46)	α_1 1.1621(531). 10^{-4}	β_1 0.75(1.3). 10^{-9}
x_{13} -2.538(253)	α_3 1.8626(752). 10^{-4}	β_3 0.16(19). 10^{-8}
^{65}Cu		
ω_1 366.10(32)	B_e 5.677(4). 10^{-2}	D_e 1.6(2). 10^{-8}
ω_3 517.88(11)	α_1 1.03(25). 10^{-4}	β_1 1.4(2.8). 10^{-9}
x_{13} -2.442(24)	α_3 1.67(27). 10^{-4}	β_3 4.4(4.3). 10^{-9}

Table V

	^{63}Cu	^{65}Cu
$\frac{B_{e,35-35}}{B_{e,35-37}}$	1.02759(30)	1.02946(5)
$\frac{I_{29-37}}{I_{29-35}}$	1.0281304	1.0281366
$\frac{\Delta\omega_1}{\omega_1}$	$1.31(77)10^{-2}$	$1.50(1)10^{-2}$
$\frac{\Delta m_y}{4(m_e + \Delta m_y)}$	$1.35 \cdot 10^{-2}$	$1.35 \cdot 10^{-2}$
$\frac{\Delta\omega_3}{\omega_3}$	$6.79(87)10^{-2}$	$1.48(45)10^{-2}$
$\frac{m \Delta m_y}{4(m_e + 2m_y)(m_e + \Delta m_y)}$	$3.64 \cdot 10^{-3}$	$3.59 \cdot 10^{-3}$

Conclusion

Results concerned the ground state of the two non symmetrical isotopomers of CuCl_2 . Effective spectroscopic constants have been determined for all the observed vibrational levels. Rotational constants B_e , α_1 , α_3 , D_e , β_1 , β_3 and vibrational constants ω_1 , ω_3 , x_{13} have also been obtained. The validity of the simplified Valence Force Field model seems to give agreement for ω_1 . But we need to get a more important data base to confirm the disagreement concerning ω_3 . Perturbations have been clearly shown both in the upper and lower vibrational levels of $2\Pi_u$ and $2\Pi_{g3/2}$. They are certainly due to several possible perturbers $2\Sigma_g^+$, $2\Pi_{g1/2}$, $2\Delta_g$, $2\Pi_{u1/2}$, $2\Sigma_u^+$ but they have yet to be treated. We have also to understand the vibrational structure of the upper state $2\Pi_u$.

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