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EMISSION SPECTRA FROM THE CHEMICAL REACTION OF HEATED Cu WITH METASTABLE OXYGEN AND Cl₂, COMPARISON WITH LASER INDUCED FLUORESCENCE AND ABSORPTION SPECTRA OF CuCl₂

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Abstract

We present the results of a spectroscopic investigation of CuCl₂ vapour obtained from laser induced fluorescence recorded by Fourier transform spectrometry, and give preliminary spectroscopic constants for the ²Π_u and ²Π_g states of Cu³⁵Cl₂. Coupled with data obtained from absorption experiments on CuCl₂, this work brings us closer to understanding the mechanism of the reaction of copper with chlorine in the presence of singlet oxygen (¹Δ_g), which is accompanied by an intense red flame. This emission has been proposed as a possible candidate for the production of a visible or infrared chemical laser. We consider this question in view of lifetime measurements on the ²Π_u state of the CuCl₂ molecule, now accepted to be the emitting species, and also compare the infrared and visible spectra of CuCl₂ with the chemiluminescence recorded around 1.2 and 0.7 μm.

Introduction

Since it was discovered that the reaction of heated copper with Cl₂ in the presence of O₂ (¹Δ_g) produces a bright red flame, there has been interest in this system as a potential chemically pumped visible laser. The emitting species has been identified as the ²Π_u state of CuCl₂ /1/, and the red emission ascribed to the ²Π_u - ²Π_g transition. There were no high resolution experimental data available in the literature for CuCl₂, although high quality ab initio calculations have been performed recently which include both ligand field and spin orbit splittings in the electronic states of CuCl₂ derived from the Cu 3d atom /2/, so we set out to derive reliable spectroscopic constants for the low-lying electronic states with a view to refining this assignment, and to understanding the reaction mechanisms and reaction rates involved in the chemiluminescence.

Obtaining high resolution spectra of CuCl₂ proved difficult. We wanted to work at about 700 °C to guarantee a reasonable vapour pressure of CuCl₂, but the molecule tends to reduce to CuCl + 1/2 Cl₂ on heating - and CuCl is known to form a stable, cyclic trimer in the gas phase. Even when CuCl₂ is isolated, its spectrum is complicated by the presence of two isotopes of Cu and of Cl. Because both the absorption and the chemiluminescent emission spectra were too congested to allow us to attempt a full analysis, we studied gaseous CuCl₂ by laser induced fluorescence, recording the emission on a Fourier transform spectrometer. We could thus populate a single level of the excited state, and study a much simpler emission spectrum.

To discover whether or not CuCl_2 was likely to produce a chemical laser, we went on to measure the lifetime of the excited state involved in the laser induced fluorescence experiment. A priori, visible laser action seems unlikely, as it will be difficult to maintain a population inversion from the ground state of CuCl_2 , even though the lower level can be chosen to be a thermally unpopulated vibrational level. Although attempts to reproduce the reported /3/ laser oscillation at 700 nm have failed, there is still a second candidate for laser action: the infrared transition around 1.2 μm .

Experiment

We produced CuCl_2 for absorption, laser induced fluorescence and lifetime measurements in a sealed quartz cell, containing 10 mg CuCl_2 powder plus a few torr Cl_2 to drive the equilibrium $\text{CuCl}_2 \rightleftharpoons \text{CuCl} + 1/2 \text{Cl}_2$ to the left. The cell was maintained at 700°C. The absorption and laser induced fluorescence spectra were recorded on a Bomem Fourier transform spectrometer in the infrared (around 1.2 μm) on an InGaAs detector, and in the visible/near infrared on a silicon avalanche detector. Fluorescence was excited by a series of laser frequencies around 15500 cm^{-1} from a cw single mode DCM ring dye laser (Spectra Physics 380) and by the red lines of a Kr^+ laser. The radiative lifetime of the $^2\Pi_u$ state of CuCl_2 was measured by detecting the decay of fluorescence at 700 nm after excitation by a pulsed laser source. We excited CuCl_2 with DCM ($\lambda = 635 \text{ nm}$) pumped by a copper vapour laser (repetition rate 6 kHz) and found a lifetime of 90 ns for the $^2\Pi_u$ state.

To record the chemiluminescence associated with the reaction between heated copper and chlorine in the presence of O_2 ($^1\Delta_g$), we used a microwave discharge to produce O_2 ($^1\Delta_g$), which was mixed with Cl_2 and allowed to react with hot Cu metal, as an alternative to the cumbersome setup required to produce O_2 ($^1\Delta_g$) in a chemical reaction /4/. This arrangement yielded lower concentrations of O_2 ($^1\Delta_g$), and thus weaker emission, but produced stable emission for about 2 hours, which was far more satisfactory for the Fourier transform spectrometer than the shorter run times achieved with the chemical generator of O_2 ($^1\Delta_g$). Spectra were again recorded by Fourier transform spectrometry.

Results

The spectra we obtained are illustrated in figures (1) and (2). Figure 1 shows the visible / near infrared spectrum obtained a) in the chemical reaction, and b) a typical laser induced fluorescence spectrum. Curve b is a series of P,R doublets sitting on a continuous band. The simplicity of the discrete part of the spectrum suggests that the molecule is linear and that only one mode of vibration (symmetric stretch) is observed. Treating the molecule as though it were strictly linear, we used a linear least squares fit of 177 lines (corresponding to transitions to 8 vibrational levels of the ground state) to obtain the following parameters (in cm^{-1}) for the $^2\Pi_g$ state of CuCl_2

$$\begin{array}{llll} Y_{00} = 0.0 & Y_{10} = 372.2667 & Y_{20} = - 0.4759 & Y_{30} = 1.190 \times 10^{-3} \\ Y_{01} = 0.05845 & Y_{11} = - 1.148 \times 10^{-3} & Y_{21} = - 1.337 \times 10^{-5} & \\ Y_{02} = - 8.81 \times 10^{-9} & Y_{12} = 4.32 \times 10^{-10} & & \end{array}$$

The standard deviation of the fit was 0.008 cm^{-1} .

For the ${}^2\Pi_u$ state we find :

$$\begin{array}{lll} T_v = 16474.4 \text{ cm}^{-1} & B_v = 0.05183 \text{ cm}^{-1} & D_v = 3.0 \times 10^{-9} \text{ cm}^{-1} \\ T_{v+1} = 16809.8 \text{ cm}^{-1} & B_{v+1} = 0.05175 \text{ cm}^{-1} & D_{v+1} = 5.1 \times 10^{-9} \text{ cm}^{-1} \end{array}$$

At present, we cannot specify which spin-orbit components of the ${}^2\Pi$ states are observed. From preliminary Franck-Condon calculations, we believe $v = 0$.

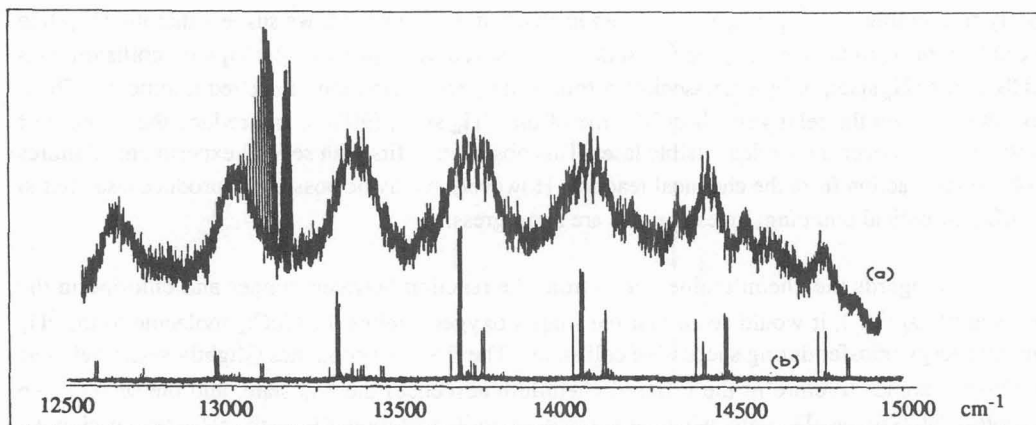


Figure 1 Visible / near infrared spectra.

- Chemiluminescence from the reaction $\text{Cu} + \text{Cl}_2 + \text{O}_2 ({}^1\Delta_g)$ at 350°C . Resolution = 0.25 cm^{-1} . The sharp bands at 13100 cm^{-1} correspond to $\text{O}_2 ({}^1\Delta_g \rightarrow {}^3\Sigma_g^-)$.
- Laser induced fluorescence. The laser gave 340 mW at 15502.06 cm^{-1} . The spectrum was recorded for 4 hours at a resolution of 0.08 cm^{-1} .

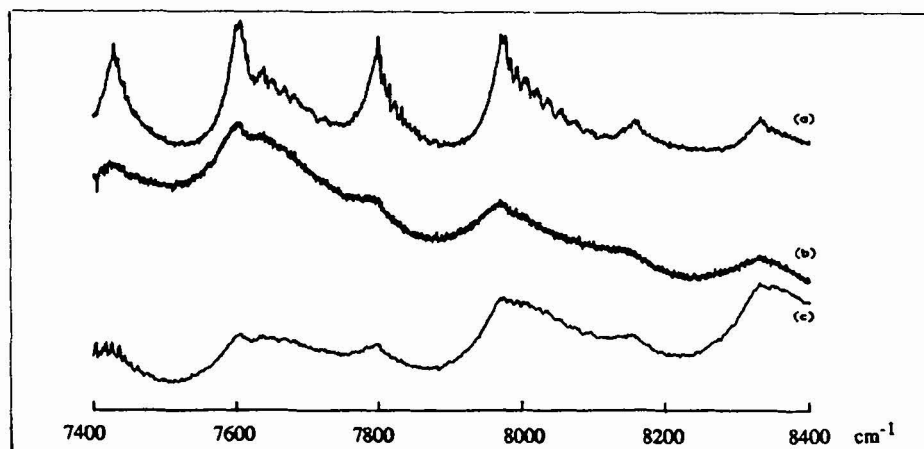


Figure 2 Infrared spectra, recorded at 0.5 cm^{-1} resolution.

- Chemiluminescence from the reaction $\text{Cu} + \text{Cl}_2 + \text{O}_2 ({}^1\Delta_g)$ at 350°C .
- Laser induced fluorescence, after subtraction of the blackbody contribution from the oven. This spectrum was totally insensitive to the choice of laser wavelength.
- The absorbance spectrum of CuCl_2 at 700°C (cell $l=10\text{cm}$)

Discussion

The most striking feature is the similarity between the three IR spectra. Analysis of the laser induced fluorescence spectra revealed that the upper state was ${}^2\Pi_u$ - and we expected to see a similar discrete system, with P, Q and R branches in the infrared, corresponding to the ${}^2\Pi_u$ - ${}^2\Delta_g$ system (predicted by ab initio calculations to lie around 8000 cm^{-1}). Instead of this, we obtained a spectrum closely resembling the ${}^2\Delta_g$ - ${}^2\Pi_g$ system seen in absorption. At present, we suspect that the ${}^2\Pi_u$ state of CuCl_2 returns to the lower lying ${}^2\Delta_g$ state by a non-radiative process, perhaps by collision with CuCl_2 in the ${}^2\Pi_g$ state, or by predissociation followed by recombination of excited fragments. These processes explain the relatively short lifetime of the ${}^2\Pi_u$ state, (90 ns), and reduce the chances of being able to produce a chemical visible laser. This observation fits with several experimental failures to obtain laser action from the chemical reaction. However, it may be possible to produce laser action in CuCl_2 by optical pumping: investigations are in progress.

As regards the chemiluminescence from the reaction between copper and chlorine in the presence of O_2 (${}^1\Delta_g$), it would seem that the singlet oxygen excites the CuCl_2 molecule to the ${}^2\Pi_u$ state by energy transfer during successive collisions. The first step populates (slightly selectively - as we observe some structure in the infrared chemiluminescence) the ${}^2\Delta_g$ state, and the second step promotes CuCl_2 to the ${}^2\Pi_u$ state, which apparently re-emits preferentially to the ${}^2\Pi_g$ state, giving the characteristic red emission first observed by Yoshida.

Conclusions

We have attributed the visible and infrared luminescence observed in the $\text{Cu} + \text{Cl}_2 + \text{O}_2$ (${}^1\Delta_g$) reaction to the ${}^2\Pi_u$ - ${}^2\Pi_g$ and ${}^2\Delta_g$ - ${}^2\Pi_g$ systems in CuCl_2 . We have used laser techniques in spectroscopy to obtain preliminary constants for the ${}^2\Pi_u$ and ${}^2\Pi_g$ states of $\text{Cu}^{35}\text{Cl}_2$, and to measure the lifetime of the ${}^2\Pi_u$ state. From our observations, we deduce that CuCl_2 is unlikely to become a visible chemically pumped laser.

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