

# Single vibronic level emission spectroscopy and fluorescence lifetime of the $\tilde{B}^1A'' \rightarrow \tilde{X}^1A'$ system of CuOH and CuOD

Chong Tao, Calvin Mukarakate, Scott A. Reid \*

Department of Chemistry, Marquette University, Milwaukee, WI 53201-1881, USA

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## Abstract

We report new studies of the  $\tilde{B}^1A'' \leftrightarrow \tilde{X}^1A'$  system of CuOH/CuOD, generated in a pulsed discharge source under jet-cooled conditions. Single vibronic level (SVL) emission spectra obtained from the  $0_0^0$  and  $2_0^1$  levels of the  $\tilde{B}^1A''$  state reveal new information on the bending and Cu–O stretching frequencies in the ground state. The derived vibrational parameters are in good agreement with recent high level *ab initio* calculations. Rotationally resolved laser induced fluorescence excitation spectra of the  $2_0^1$  band were obtained, and a rotational analysis performed for the  $^{63}\text{CuOD}$  isotopomer. Additionally,  $\tilde{B}^1A''$  state fluorescence lifetimes are reported.

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## 1. Introduction

Transition-metal hydroxides have been subjected to extensive experimental and theoretical studies because of their importance in catalytic and electro-chemistry, as well as in the interactions of water with metal surfaces [1]. The reaction of transition metals with  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}_2$  has been an effective approach to generate the hydroxides, and CuOH is responsible for the green color of flames containing copper salts [2]. The green emission, due to the  $\tilde{B}^1A'' \rightarrow \tilde{X}^1A'$  system, was recorded in several early studies [3–5], and in 1983, the first rotationally resolved laser induced fluorescence (LIF) spectra of the origin band of the  $\tilde{B}^1A'' \leftarrow \tilde{X}^1A'$  system of CuOH and CuOD near 540 nm were recorded and analyzed by Trkula and Harris for  $K'_a \leq 1$  [6]. The molecule was found to be bent in both the ground and excited states with bond angles of  $111^\circ$  and  $119^\circ$ , respectively. Emission was observed to the  $2_1$  level, giving anharmonic bending frequencies of  $743\text{ cm}^{-1}$  for CuOH and  $537\text{ cm}^{-1}$  for CuOD.

Bernath and co-workers reported high resolution spectra of these bands, extending the analysis up to  $K'_a = 9$

for CuOH and  $K'_a = 12$  for CuOD [7]. Later, the same group measured under high resolution a second band system near 640 nm, which was assigned to the  $\tilde{A}^1A' \leftarrow \tilde{X}^1A'$  transition [8]. These studies yielded very accurate rotational constants and improved structural parameters for the three lowest-lying singlet states. However, these observations were limited to the origin band of the  $\tilde{A}$  and  $\tilde{B}$  states due to small Frank–Condon factors for vibrationally excited states, and thus limited experimental information is available on the vibrational structure of the ground state.

Recently, new high level calculations of the ground and two lowest lying singlet states of CuOH have been reported by Schaefer and co-workers [9]. Their calculations call into question the assignment of the 640 nm system, as the predicted position of the  $1^1A'$  state is much farther to the blue, and they suggest that the  $\tilde{B}^1A''$  state might actually be the first excited singlet state. Their calculations also predict the barrier to linearity in the  $\tilde{X}^1A'$  state ( $11.0\text{ kcal mol}^{-1}$ ), and vibrational frequencies and equilibrium rotational constants were reported for all three singlet states.

Motivated by this recent theoretical work, in this study we report new single vibronic level (SVL) emission spectroscopy of the  $\tilde{B} \rightarrow \tilde{X}$  transition for CuOH and CuOD. Based upon an emission spectrum from the origin band,

\* Corresponding author. Fax: +1 414 288 7066.

E-mail address: [scott.reid@mu.edu](mailto:scott.reid@mu.edu) (S.A. Reid).

it was clear that the  $2_0^1$  band should appear with reasonable intensity, and we subsequently found this band for both isotopomers. SVL emission spectra from  $2_0^1$  show an extensive progression in the bending mode which extends up to 3 (for CuOH) and 5 (for CuOD) quanta of excitation. In addition, the Cu–O stretching frequency was determined for the first time. Our results concerning the vibrational structure of the  $\tilde{X}^1A'$  state are compared with recent high level *ab initio* calculations. Additionally, we report our results of rotational analysis of the CuOD  $2_0^1$  band, and fluorescence lifetime measurements for both isotopomers.

## 2. Experimental

The apparatus used in this work is essentially the same as in previous studies [10–13], except for a slight modification of the pulsed discharge source. Briefly, CuOH/CuOD were produced using a pulsed discharge nozzle with two copper ring electrodes, through a  $\sim 3\%$  mixture of  $\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$  in Ar with a total backing pressure of  $\sim 2$  bar. A 2.5 cm flow channel followed the second electrode, allowing collisions between Cu atoms and discharge fragments from methanol to form copper hydroxide. The discharge was initiated by a  $-1$  kV pulse of  $\sim 100$   $\mu\text{s}$  duration, through a current limiting 2 k $\Omega$  ballast resistor. The high peak current of several hundred mA is important in stabilizing the sputtering of Cu atoms, and thus the CuOH/CuOD signals. We also tried  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  as precursors; however, these gave a smaller CuOH LIF signal and larger discharge background compared with  $\text{CH}_3\text{OH}$ .

Fluorescence excitation spectra were obtained by pumping the molecules to the  $\tilde{B}$  state with a Nd:YAG laser (Continuum Powerlite 7010) pumped dye laser (Lambda-Physik Scanmate 2E), and collecting total fluorescence via a photomultiplier tube detector (Oriel) held at typically  $-700$  V. The spectra were calibrated using optogalvanic spectroscopy with a Fe:Ne hollow cathode lamp. In acquiring the SVL emission spectra, the laser wavelength was fixed, and emission was dispersed by a spectrograph (Acton SR303i with ISTAR intensified CCD) equipped with a 600 lines/mm grating blazed at 500 nm, with typical accumulation over 10000 laser shots. Calibration of the spectrograph was carried out using Ne I lines from a Fe:Ne hollow cathode lamp.

## 3. Results and discussion

We first obtained SVL emission spectra from the origin level of the  $\tilde{B}$  state for both CuOH and CuOD. Fig. 1a displays an example spectrum for CuOH obtained by pumping  $K'_a = 1$ , which shows significant intensity for the origin transition and weak transitions to excited bending states. Note that the fundamental of the Cu–O stretch, which had previously been observed in an Ar matrix [15] is observed here for the first time in a gas-phase experiment. The anharmonic frequencies are: 625(1)  $\text{cm}^{-1}$  (CuOH), 635(1)  $\text{cm}^{-1}$  (CuOD).

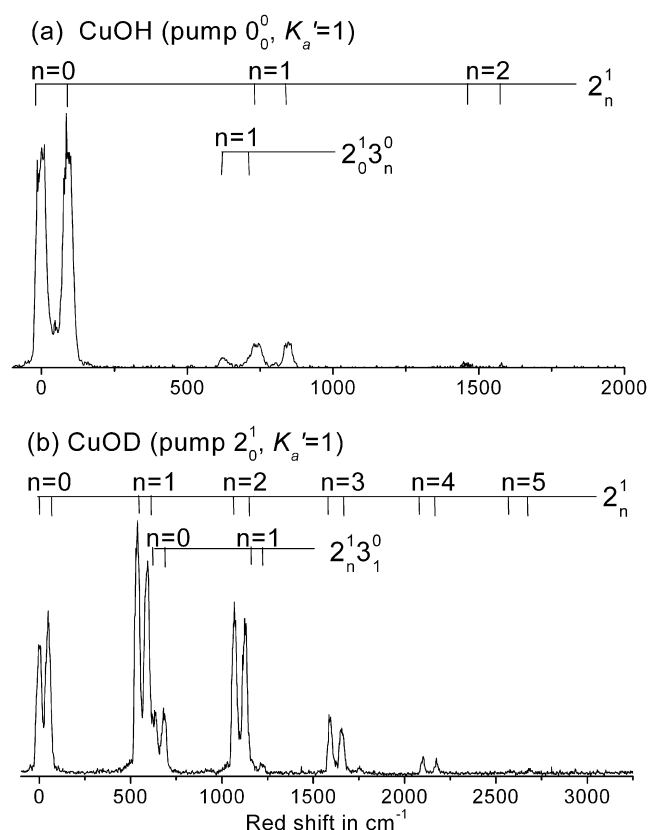


Fig. 1. Single vibronic level (SVL) emission spectra of: (a) CuOH obtained by pumping the  $K'_a = 1$  sub-band of the  $0_0^0$  band, and (b) CuOD obtained by pumping the  $K'_a = 1$  sub-band of the  $2_0^1$  band. Each spectrum represents an average over 10000 laser shots, and the vibrational assignments are noted.

We were encouraged by the emission spectrum of Fig. 1a to look for excited bending levels in the  $\tilde{B}$  state, which had not previously been observed. In their studies of the  $\tilde{B}$  state origin [7], Bernath and co-workers reported a parallel band lying to the blue, which was tentatively assigned to the  $\tilde{C}^1A'$  state. Scanning to higher energies for CuOH, we found a complicated structure arising from an overlap of the  $\tilde{B}2_0^1$  band with the parallel band observed by Bernath. We did not observe additional parallel bands to lower energy, and thus the probable assignment for this band is the  $\tilde{C}^1A'$  state origin. For CuOH, these bands strongly overlap, precluding a rotational analysis; however, SVL emission spectra could be obtained from the  $2_0^1$   $K'_a = 1$  level, which was free of overlap. For CuOD, the two bands were well separated, and a survey scan of the  $2_0^1$  band is shown in Fig. 2. At our resolution, the isotope and asymmetry splittings were not completely resolved. A fit of the transitions for the major  $^{63}\text{CuOD}$  isotopomer yielded the following parameters (in  $\text{cm}^{-1}$ , quoted uncertainties represent three standard deviations):  $T_{00} = 18831.66(8)$ ,  $A = 17.10(5)$ ,  $(B + C)/2 = 0.3544(5)$ ,  $\Delta_K = 0.031(5)$ . These results indicate a 20% increase in the  $A$  rotational constant upon bending excitation, and give an anharmonic  $\tilde{B}$  state bending frequency of 409.33(8)  $\text{cm}^{-1}$ .

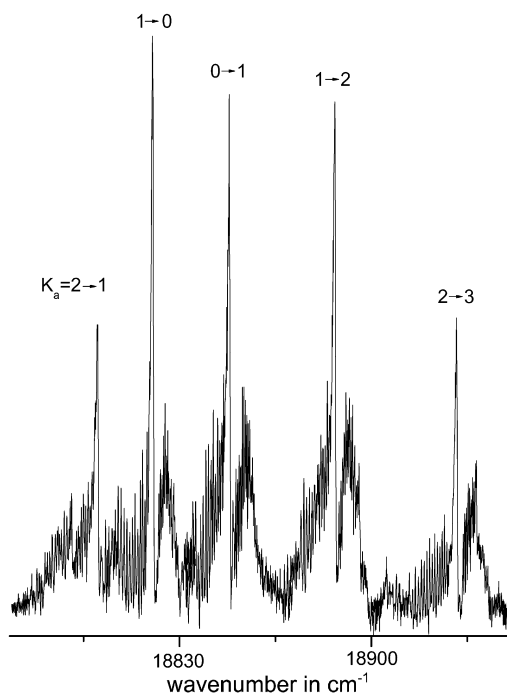


Fig. 2. Fluorescence excitation spectrum of the  $2_0^1$  band of CuOD. The  $K_a$  sub-band assignments are noted.

SVL emission spectra from the  $2_0^1$  band (Fig. 1b) reveal a pronounced bending progression extending up to 3 quanta for CuOH and 5 quanta for CuOD. The dependence of the vibrational intervals for the bending levels of CuOH and CuOD are shown in Fig. 3. Within a simple anharmonic model, where the vibrational term energies are given by:  $G^0(v_2) = v_2\omega_2^0 + v_2^2x_{22}^0$ , the intervals are given by:  $\Delta G^0 = G^0(v_2 + 1) - G^0(v_2) = (\omega_2^0 + x_{22}^0) + 2v_2x_{22}^0$ , and therefore a plot of  $\Delta G^0$  vs.  $v_2$  should be linear. As is clear from Fig. 3, a linear dependence is not observed, which can be understood from the small ( $\sim 11$  kcal mol $^{-1}$ ) barrier to linearity in the  $\tilde{X}^1A'$  state. As described theoretically by Dixon [16] and observed experimentally in a number of triatomics with low barriers to linearity [10,12–14,17], the vibrational intervals initially decrease, reach a minimum at the barrier, and increase above it. In this case, the data does not extend to the region of the barrier. Efforts were made to find the  $2_0^2$  band in order to probe higher vibrational levels in the  $\tilde{X}^1A'$  state; unfortunately this band was too weak to be observed. The data were thus modeled by including a third order anharmonic correction:  $G^0(v_2) = v_2\omega_2^0 + v_2^2x_{22}^0 + v_2^3x_{222}^0$ , so that the vibrational intervals are given by:  $\Delta G^0 = G^0(v_2 + 1) - G^0(v_2) = (\omega_2^0 + x_{22}^0 + x_{222}^0) + (2x_{22}^0 + 3x_{222}^0)v_2 + 3x_{222}^0v_2^2$ . A fit of the data to a second order polynomial yielded the following vibrational parameters (in cm $^{-1}$ ):  $\omega_2^0 = 744.0(41)$ ,  $x_{22}^0 = -6.2(26)$ ,  $x_{222}^0 = -1.6(5)$  for CuOH;  $\omega_2^0 = 537.02(33)$ ,  $x_{22}^0 = 0.78(23)$ ,  $x_{222}^0 = -0.95(5)$  for CuOD.

The approach to the barrier to linearity is also evidenced in the vibrational state dependence of the  $A$  rotational constant, which we determined from the  $K$ -splittings in SVL emission spectra obtained from excited state levels with

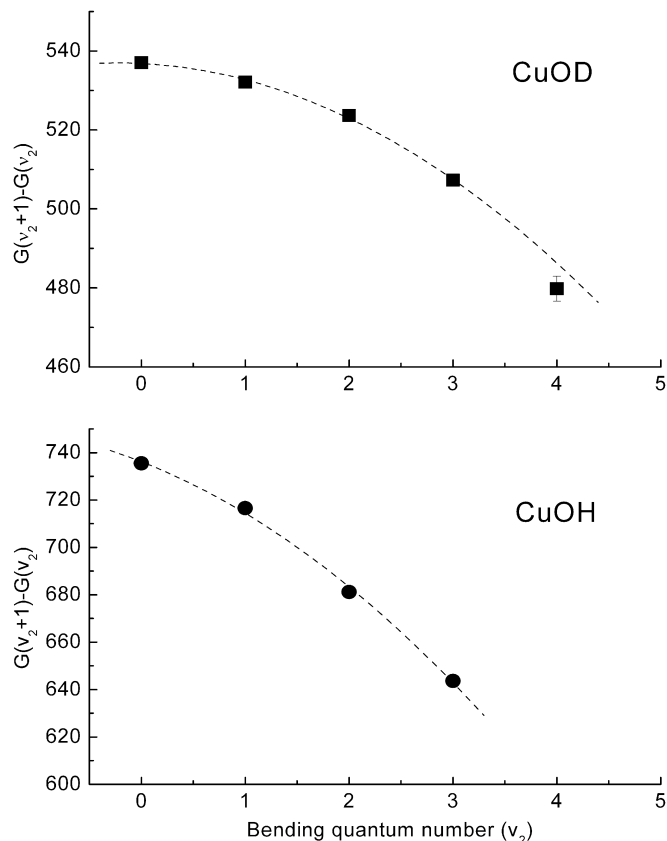


Fig. 3. Dependence of the vibrational intervals  $\Delta G^0 = G(v_2 + 1) - G(v_2)$  on quanta of bend for CuOH (lower panel) and CuOD. The symbols represent experimental data, while the lines are fits to a second order polynomial, as described in the text. Where error bars are not shown, the uncertainty is smaller than the symbol size.

$K'_a \geq 1$ . The dependence for CuOD is shown in Fig. 4. Typically, a linear dependence of the  $A$  constant vs. bending quanta is observed; however, as the barrier is approached a large increase in the  $A$  constant can be seen, similar to that observed in, e.g., the  $\tilde{A}^1A''$  state of CHF [10,12,17]. This increase can be attributed to a coupling of bend and  $a$ -axis rotation [17].

The vibrational frequencies determined in this work are in good agreement with the recent *ab initio* predictions of Schaefer and co-workers [9]. For example, their calculations at the QZVPP CCSD(T) level give harmonic  $\tilde{X}^1A'$  state frequencies (in cm $^{-1}$ ) of:  $\omega_2 = 737$ ,  $\omega_3 = 624$ .

Finally, we measured fluorescence lifetimes for different  $K'_a$  sub-bands in the  $0_0^0$  band for both CuOH and CuOD. The lifetimes were recorded using a 1 GHz digital storage oscilloscope, and represent an average of five measurements. Within the uncertainty of our measurements, there was no dependence of lifetime on  $K'_a$ , and therefore the results were also averaged over this quantity. The measured  $\tilde{B}^1A''$  state fluorescence lifetimes are (in ns): 612(10) for CuOH, 607(17) for CuOD. Note that the CuOH  $\tilde{B}^1A''$  state is thought to correlate primarily with the  $\tilde{B}^1\Sigma^+$  state of CuF [18,19], which has a fluorescence lifetime of  $\sim 1.5$   $\mu$ s [20].

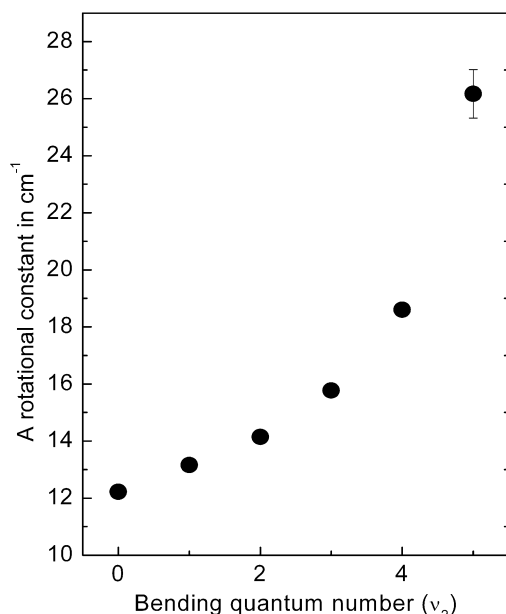


Fig. 4. Dependence of the  $A$  rotational constant for CuOD on quanta of bend. The  $A$  constants were determined from the  $K_a$  sub-band splitting in SVL emission spectra from excited state levels with  $K'_a \geq 1$ . Where error bars are not shown, the uncertainty is smaller than the symbol size.

#### 4. Conclusions

We have reported new single vibronic level (SVL) emission spectra of the  $\tilde{B}^1A'' \rightarrow \tilde{X}^1A'$  system of CuOH/CuOD, generated in a hollow cathode pulsed discharge source under jet-cooled conditions, which reveal new information on the bending and Cu–O stretching frequencies in the ground state. The derived vibrational parameters are in good agreement with recent high level *ab initio* calculations. Rotationally resolved laser induced fluorescence excitation spectra of the  $2_0^1$  band were obtained, and a rotational analysis was performed for the  $^{63}\text{CuOD}$  isotopomer. The fluorescence lifetime of the  $\tilde{B}^1A''$  state was determined to be 612(10) ns for CuOH, and 607(17) ns for CuOD.

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