Copper Fluoride Luminescence during UV Photofragmentation of Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) in the Gas Phase

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Gas phase 308 and 350−370 nm photolysis of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II), Cu(hfac)$_2$, produces CuF as well as copper atoms and dimers. These metal-containing fragments, identified by luminescence spectroscopy, are studied under a variety of gas phase conditions ranging from 1 bar in a static chamber to 10^{-4} mbar in a collision-free molecular beam. Copper atom and dimer luminescence is observed at the higher pressures, whereas at low pressures (total pressure no greater than the vapor pressure of the sample) exclusively CuF emission is observed. The a, A ($\omega = 0, 1, 2$), B, and C excited states at 681.0, 567.6, and 505.1, and 491.7 nm are observed. The $^3\Pi_0{}^-$ component of the A state is observed for the first time. The CuF luminescence obeys a quadratic power law with 308 nm excitation. The partitioning of excess energy into fragment degrees of freedom is determined from the intensities of the emission lines. The vibrational and rotational temperatures of the CuF fragment are in excess of 1700 K. Mechanisms of CuF formation, comparisons with the free ligand and with other volatile copper complexes, and the implications for laser-assisted chemical vapor deposition are discussed.

Introduction

Laser-assisted metal organic chemical vapor deposition (CVD) relies on the use of volatile organometallic compounds to deliver material to a substrate where the compound is photodecomposed, leaving behind the material to be deposited (and possibly undesired contaminants). Both gas phase and surface reactions can cause deposition. Our interest in this area was sparked by CVD precursor molecules (or fragments) that exhibit luminescence under the conditions of laser-assisted CVD.[1,2] It is our aim to gain an understanding of the photodeposition process by examining this luminescence. One issue we investigate is that of surfaces versus gas phase components of the CVD process. The CVD precursor can produce metal atoms directly in the gas phase, or it can deposit in a partially fragmented form before undergoing further fragmentation, resulting in the metal deposit. Luminescence spectroscopy can identify the nascent gas phase photoproducts in the deposition process. This understanding of the fundamental nature of the CVD process may lead to improved film properties and better growth rates. If the photofragmentation mechanism involves an intermediate that is likely to incorporate contaminants, this knowledge can be used to redesign the molecule to make a CVD precursor that yields higher purity films. Toward this end of understanding the photofragmentation process, we address the fundamental questions of metal−ligand bond formation and cleavage, as well as the partitioning of excess energy into fragment degrees of freedom.

The focus of this paper is bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II), Cu(hfac)$_2$, which has been studied extensively because of its potential for copper and copper oxide CVD.[3−5] Modern applications include metallization for semiconductor interconnects[3] and preparation of high-T_c superconducting films.[4] The use of fluorinated CVD precursors increases volatility and improves mass transport characteristics. Fluorinated precursors for copper oxide CVD cause fluorine incorporation, significantly degrading superconducting film performance.[5] Similarly, photolytic CVD of copper shows measurable fluorine incorporation.[6,7] An important issue is whether this incorporation is due to the gas phase portion of the deposition process or if it is a result of surface chemistry. Our focus is on the initial gas phase photochemistry of Cu(hfac)$_2$ under deposition conditions.

In ethanol solution, irradiation of Cu(hfac)$_2$ into the ligand-to-metal charge transfer band at 253.7 nm causes ligand loss with a quantum yield of 0.036.[8] No solution phase ligand loss is observed upon 312 nm excitation into the $\pi-\pi^*$ ligand centered transition leading to the conclusion that photoreduction of the metal is required for ligand loss.[8]

In this paper we report the luminescence spectra and use the spectra to identify the photofragments resulting from photolysis of Cu(hfac)$_2$ in the gas phase. These studies focus on the purely gas phase photofragmentation without involvement of a surface. We compare the luminescence from 308 nm excitation of Cu(hfac)$_2$ under "high pressure" conditions (~1 bar), low pressure conditions (~1−10 mbar), and collision free conditions (molecular beam, 10^{-4} mbar). This comparison gives information about the photofragmentation process and the role of molecular collisions in photofragmentation to form metal deposits. Surprisingly under collision free conditions only CuF luminescence is observed. The vibrational and rotational temperatures of the CuF fragment are determined from the spectra.

Experimental Section

The light source for our spectroscopic investigations is a Lambda Physik EMG 201 MSC XeCl excimer laser coupled with a Lambda Physik FL2001 excimer-pumped dye laser operating with DMQ as the dye. The pulse width is typically 12 ns. The 308 nm pulse energy used for excitation of the CVD precursors is varied from approximately 0.3 to 30 mJ.

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Our "deposition simulation" experiments are carried out in an evacuated glass spectroscopy cell. A sample of the CVD precursor is placed in the sample chamber and is leaked into the photolysis chamber with a Teflon valve. Buffer gases are introduced via a separate inlet. The entire cell is heated using thermostated heating tape. The excimer laser is focused with a $\varnothing = 2$ in., $f = 500$ mm CaF lens. The resulting fluence is typically ~ 3 MW/cm^2. The focused output of the laser excites the gaseous sample, and the emitted light is collected by $f/4$ optics and directed into a 0.32 m single monochromator, where it is dispersed by a 300 or a 600 groove/mm holographic grating and detected by a UV-intensified diode array detector (Princeton Applied Research 1024 × 1). Resolution is limited by grating dispersion due to the spatially discrete nature of the detector. The spectral widths of a pixel are ~0.24 and ~0.12 nm for the 300 and 600 groove/mm gratings, respectively. The UV intensifier allows time-resolved grating of the detector with a resolution of 10 ns.

Our molecular beam experiments are carried out in a cubic stainless steel vacuum chamber (30 cm edge length). A mechanical pump and a directly connected 12 in. diffusion pump are used to evacuate the chamber. Background pressures of 6×10^{-5} and 5×10^{-6} Torr are typical of operation with and without the molecular beam, respectively. The seeded carrier gas (Ar or He at 50–1000 mbar stagnation pressure) expands continuously through a ~ 100 μm pinhole into the chamber. The excimer laser is focused with a $\varnothing = 1$ in., $f = 1000$ mm quartz lens. The resulting fluence is typically 2 MW/cm^2. The molecular beam is intersected by the focused output of the laser 1.5 cm downstream. The light is collected by $f/5$ optics and directed into a 0.67 m single monochromator, where it is dispersed by a 600 or an 1800 groove/m holographic grating and detected by a liquid-nitrogen-cooled CCD detector (Princeton Instruments 1024 × 256). Resolution is limited by the grating dispersion due to the spatially discrete nature of the detector. The spectral widths of a pixel are ~0.066 and ~0.019 nm for the 600 and 1800 groove/mm gratings, respectively.

Results

The emission spectrum from $Cu(hfac)_2$ excited at 308 nm at "high" pressure (sample + argon = ~1 bar) is shown in Figure 1a. There are sharp peaks at 493.0, 510.5, 515.0, 521.8, 578.2, and 589.2 nm and a broad feature with irregular but reproducible structure at 468.6 nm.

Under 308 nm excitation and low-pressure conditions (sample pressure less than or equal to its vapor pressure), we observe the spectrum in Figure 1b. We observe no sharp lines between 310 and 425 nm. There are peaks at 426.7, 437.9, 449.5, 461.7, 473.6, 476.8, 491.7, 505.1, 519.3, 545.6, 564.7, 567.6, 579.3, and 681.0 nm. The peaks at 491.7, 505.1, 567.6, and 681.0 nm have poorly resolved but regular structure. Similar results are observed for excitation at 360 nm.

Under the collision-free conditions of the molecular beam and 308 nm excitation, the spectral features present under the low-pressure conditions resolve into distinct structured bands (Figure 2). The upper two panels were acquired using the 1800 groove/mm grating; the lower two were acquired using the 600 groove/mm grating. Molecular beam fluorescence excitation spectra taken in the range 350–370 nm show no sharp features, but the dispersed fluorescence is the same as that observed with 308 nm excitation. In the molecular beam, we observe that the features at 449.5, 491.7, 505.1, and 567.6 nm display quadratic power dependencies, as shown in the Inserts of Figure 2. Power laws were not determined in the static chamber because of the possibility that multiple-shot excitation of the molecule could obscure the analysis.

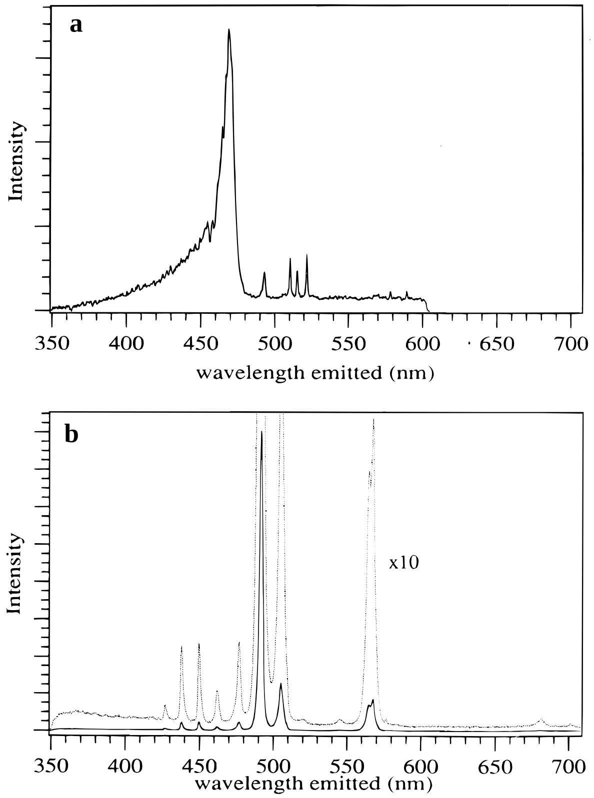

Figure 1. Emission spectra observed from 308 nm excitation of $Cu(hfac)_2$ in the gas phase: (a) spectrum observed using a static chamber at a pressure of 1 bar; (b) spectrum observed at a pressure of no greater than the vapor pressure of $Cu(hfac)_2$.

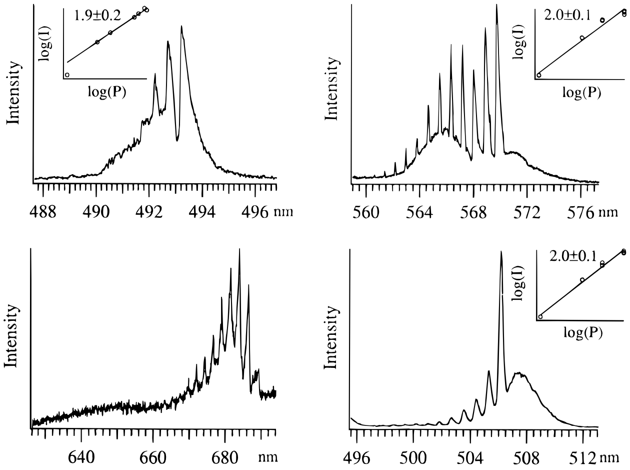

Figure 2. Emission spectra of CuF arising from 308 nm excitation of $Cu(hfac)_2$ in a molecular beam. The inserts in each panel show the laser power dependence of the spectrum shown in that panel.

Discussion

Copper Atom and Cluster Emission. The sharp lines in the high-pressure 308 nm excited luminescence spectra are Cu atomic transitions $4s^2$ 2D → $4p^2\ ^2P^0$ at 510.5 nm, $4p^2\ ^2P^0$ → $4d^2\ ^2D$ at 515.0 nm, $4p^2\ ^2P^0$ → $4d^2\ ^2D$ at 521.8 nm, and $4s^2\ ^2D$ → $4p^2\ ^2P^0$ at 578.2 nm.[9] The broad feature at 468.6 nm includes contributions from Cu_2. A similar broad feature is observed by ablating OFHC copper under similar conditions, leading us to the conclusion that this feature is due at least in part to Cu_n clusters. Residual unquenched CuF appears at 493.0 nm (C → X) and at 589.2 nm (A → X).

Production of luminescent copper atoms from laser excitation of copper complexes is well-known.[10,11] Wehry found that three 193 nm photons are required to produce bare fluorescent Cu from $Cu(hfac)_2$ (i.e. that two 193 nm photons (103 600 cm^{-1})

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Table 1. Assignments of the Emission Bands of CuF Resulting from the Photolysis of Cu(hfac)$_2$

electronic	vibrational	wavelength, nm
C $^3\Delta_1 \rightarrow$ X $^1\Sigma^+$	$\Delta v = -5$	426.7
D $^1\Pi \rightarrow$ X $^1\Sigma^+$	$\Delta v = 0$	437.9
C $^3\Delta_1 \rightarrow$ X $^1\Sigma^+$	$\Delta v = -4$	449.5
C $^3\Delta_1 \rightarrow$ X $^1\Sigma^+$	$\Delta v = -3$	461.7
C $^3\Delta_1 \rightarrow$ X $^1\Sigma^+$	$\Delta v = -2$	473.6
C $^3\Delta_1 \rightarrow$ X $^1\Sigma^+$	$\Delta v = -1$	476.8
C $^3\Delta_1 \rightarrow$ X $^1\Sigma^+$	$\Delta v = 0$, $v = 0-4$	491.7
B $^1\Sigma^+ \rightarrow$ X $^1\Sigma^+$	$\Delta v = 0$, $v = 0-15$	505.1
B $^1\Sigma^+ \rightarrow$ X $^1\Sigma^+$	$\Delta v = 1$	519.3
A $^3\Pi_0{}^- \rightarrow$ X $^1\Sigma^+$	$\Delta v = 0$	545.6
A $^3\Pi_0{}^+ \rightarrow$ X $^1\Sigma^+$	$\Delta v = 0$	564.7
A $^3\Pi_1 \rightarrow$ X $^1\Sigma^+$	$\Delta v = 0$, $v = 0-12$	567.6
A $^3\Pi_2 \rightarrow$ X $^1\Sigma^+$	$\Delta v = 0$	579.3
a $^3\Sigma^+ \rightarrow$ X $^1\Sigma^+$	$\Delta v = 0$, $v = 0-18$	681.0

are insufficient to produce bare metal). Thus, even three 308 nm photons would be insufficient to produce bare metal from the complex in the gas phase. In contrast, Mikami et al. determined the threshold for bare metal atom production from the nonfluorinated complex to be two 308.6 nm photons or 8.03 eV using multiphoton dissociation/ionization (MPD/MPI).[12] These authors postulated that direct loss of both of the acetylacetonate ligands results from the coherent two-UV-photon excitation of a superexcited state at 8.03 eV.

CuF Emission. We assign all of the 308 nm excited features in the low-pressure chamber and the molecular beam to CuF luminescence (see Table 1). The observation of the $^3\Pi_0{}^-$ component of the A state[13] at 545.6 nm is, to our knowledge, the first reported observation of this state. Dufour et al. calculated an energy of 18 250 cm^{-1} for this component.[14] Our observation of a band at 545.6 nm (18 330 cm^{-1}) confirms the theoretical predictions of both the symmetry and energies involved in the A state of CuF.

Excitation at 361 nm also results exclusively in CuF luminescence under low-pressure conditions and in the molecular beam. The fluorescence excitation spectra from 350 to 370 nm is unstructured. If the CuF fragment luminescence were arising from resonant excitation of ground state CuF by our fragmentation laser, we would expect to see structure in the fluorescence excitation spectrum because the signal would be proportional to the product of the unstructured fragmentation cross section and the structured CuF absorption cross section. Therefore we conclude that CuF is ejected from Cu(hfac)$_2$ in an electronically excited state and is not being resonantly excited by our fragmentation laser.

The laser power dependence of the intensity of the CuF bands at 449.5, 491.7, 505.1, and 567.6 nm is quadratic. Two 308 nm photons have enough energy (64914 cm^{-1}) to break all four metal−oxygen bonds. Because we are using a high-fluence excitation source (~2 MW/cm^2), however, transitions could be saturated so this luminescence should be viewed as being a result of *at least* two 308 nm photons. Saturation effects may, in general, complicate the interpretation of experimentally derived power laws.

Our comparisons between the low- and high-pressure studies of Cu(hfac)$_2$ show that there are multiple pathways for photofragmentation of this complex. When collisions are present, bare metal atoms and metal dimers are produced in an excited state. These channels do not appear under low-collision and collision-free conditions, implying that the production of bare metal at 308 nm is not a strictly unimolecular photodissociation reaction.

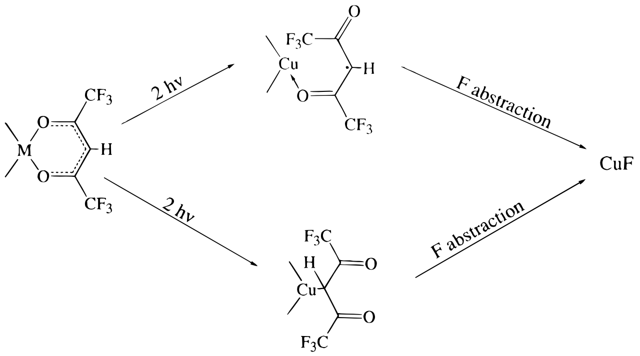

Figure 3. Intramolecular rearrangements that could bring Cu and F into proximity.

The formation of CuF is endoergic with respect to the formation of Cu for ground state Cu(hfac)$_2$. Interestingly, under collision-free conditions, we only observe luminescence from CuF. The cleavage of the four metal−oxygen bonds requires 157 kcal/mol[15] of the 185.5 kcal/mol available from two 308 nm photons, leaving just enough energy (28 kcal/mol) to cleave the C−F bond and form the Cu−F bond. However, the CuF fragment has up to 66.4 kcal/mol of electronic excitation. There are two possible explanations for this discrepancy. The first is that the ligand fragments combine or rearrange to provide the required energy. The second, and simpler, explanation is that a third photon is exciting a saturated transition, giving an apparent quadratic power law.

Fragmentation patterns from 70 eV electron impact mass spectra have shown precedent for the elimination of metal fluorides from fluorinated metal acetylacetonates, but no evidence for formation of CuF from Cu(hfac)$_2$ was observed.[16] Reichaert et al. postulated that the absence of CuF was a result of the CuF bond being 25−30 kcal/mole weaker than the C−F bond.[16] Recently metal fluoride production from metal fluoroalkoxides has been observed in 15 eV electron impact mass spectra.[17]

Using 193 nm excitation Schendel et al. observed extensive fragmentation of Cu(hfac)$_2$ to CO, CH, and CC diatomic ligand fragments.[11] They did not report any luminescence characteristic of CuF. Mikami et al. did not observe any ions from Cu(acac)$_2$ other than Cu$^+$ under one color mpd/mpi conditions at 280.5 nm.[12] The different behavior we observe in the case of fluorinated copper acetylacetonates may be a result of the strong metal fluorine bond that provides a driving force that a metal hydride bond cannot.

Using a 282 nm dissociation laser with a 125 nm ionization laser, Bartz et al. observed extensive fragmentation of the fluorinated complex and a three 282 nm photon power law for the production of Cu atoms.[18,19] These mass resolved fragmentation spectra show a very small peak barely resolved from the noise at CuF (mass = 82).[20] The ionization potential of CuF is 10.15 eV[21] and the photoionization energy available in that study was 9.9 eV, so the relative contribution of this channel to the overall photochemistry remains in question.

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Table 2. Spectroscopy Parameters Used in the Intensity Fits To Determine the Vibrational and Rotational Temperatures of CuF

state	ref	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	B_e	$10^{-3}\alpha_e$	$10^{-9}D_e$	r_e, pm	$\boldsymbol{T}_{\mathbf{rot}}$	$\boldsymbol{T}_{\mathbf{vib}}$
X	24	0	620.87	3.365	0.0	2.8	0.379403	3.229	565.5	174.493		
a	25	14 580.5	674.2	4.14	0.07	−2	0.38248	2.98	495.3	173.79	**1300**	**3060**
A1	24, 25	17 543.4	647.63	3.458	0.0492	−0.096	0.37729	2.97	509	177.3	**1200**	**1700**
A0	24, 25	17 571.1	647.63	3.458	0.0492	−0.096	0.37609	2.91	509	177.3	**1200**	**1700**
B	25	19 717.5	657	3.92			0.3716	3.2	480	176.32	**1600**	**1800**
C	24	20 258.1	643.83	3.75	0.0149	−0.46	0.3756	2.8766	533	176.32	**2400**	**2200**

Mechanisms for Formation of CuF. CuF appears under the collision-free conditions of the molecular beam. This implies that the formation of this photoproduct is a unimolecular process. However, it is also possible that in the cold molecular beam a polymolecular complex can form which allows intermolecular copper−fluorine contact, facilitating the formation of CuF. This mechanism can be ruled out due to the formation of CuF in the low-pressure bulb at ~320 K, where clusters are not expected and the observation of CuF from the six-coordinate Cu(hfac)$_2$(H$_2$O)$_2$ complex that is not expected to form polymolecular complexes as readily as the coordinatively unsaturated complex. Additionally, Bartz et al. found that polymolecular complex formation generally occurred at stagnation pressures above 500 mbar.[20] It was our observation that the CuF signal intensities were much smaller for the colder beam conditions generated by stagnation pressures in excess of 350 mbar. Therefore, we conclude that the appearance CuF under collision-free conditions is due to an intramolecular process and not a polymolecular complex.

Intramolecular fluorine atom abstraction by the copper could occur by two simple mechanisms. The first mechanism involves metal migration as illustrated in the bottom pathway in Figure 3. Alternate binding modes of metals to β-diketonates are known, including binding through the π system of the acetylacetonyl moiety or binding in a σ manner to the α-carbon of the acetylacetonyl moiety.[22,23] If the metal migrates onto the π system or is bound thrugh the α-carbon, it is much closer to the fluorines on the CF$_3$ groups than it would be in the standard bidentate binding mode. A second and more likely mechanism illustrated in the top pathway in Figure 3 is that one photon excites the $\pi \rightarrow \pi^*$ system on the ligand and another photon excites a LMCT, breaking a M−O bond. The resulting half free ligand is bound through one oxygen. The unbound side can then rotate about the (now) formally C−C single bond, placing the CF$_3$ group in direct contact with the metal. The metal abstracts the fluorine, and the resulting CuF chemiluminesces. If a collision occurs before the abstraction takes place, free copper can be produced. This mechanism involves the least motion of the atoms in the molecule. The single-photon absorption at 308 nm has been assigned as a $\pi \rightarrow \pi^*$ ligand-centered transition.[24] Additionally, the fluorinated complex exhibits a strong VUV absorption band at ~65 000 cm^{-1}, which is approximately twice the 308 nm photon energy.[25] Calculations have indicated that this absorption band has a component of ligand σ to copper charge transfer. This supports the least motion mechanism of how this complex could produce a CuF fragment.

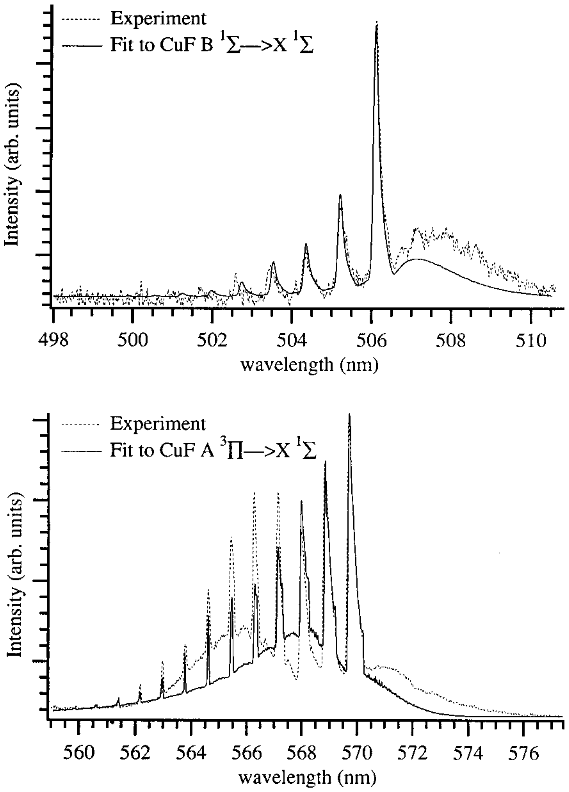

Figure 4. Calculated (solid lines) and experimental (dotted lines) luminescence spectra of CuF produced from Cu(hfac)$_2$ photofragmentation illustrating the deviation of the population of the excited state vibrational levels from statistical Boltzmann populations.

Partitioning of Excess Energy. Fits to the individual bands were obtained by using literature values[26,27] for diatomic molecular parameters to calculate the excited and ground state vibrational and rotational energy levels. The fitting parameters were the Boltzmann temperatures used to determine the populations of rotational and vibrational levels in the excited states. The resulting sticks were convoluted with a Lorenzian line shape and integrated for each pixel element of the detector.

The energy levels are $E = T_e + G(\nu) + F(J,\nu)$ where

$$G(\nu) = \omega_e(\nu + {}^1/_2) - \omega_e x_e(\nu + {}^1/_2)^2 + \omega_e y_e(\nu + {}^1/_2)^3 + \omega_e z_e(\nu + {}^1/_2)^4 + ...$$

$$F(\nu,J) = [B_e - \alpha_e(\nu + {}^1/_2) + ...](J(J + 1)) + [D_e - \beta_e(\nu + {}^1/_2) + ...](J(J + 1))^2 + ...$$

The parameters used for the fits to the various states of CuF are summarized in Table 2. Figure 4 shows fits to states A and B of CuF. The experimental intensities of these states exhibit the least (B state) and greatest (A state) deviation from Boltzmann fits of the observed states of CuF.

Boltzmann fits to the spectra from our molecular beam studies show that the ejected CuF is both rotationally and vi-

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brationally hot. The observed temperatures are on the order of 1700 K. The amount of energy disposed of in electronic and vibrational excitation is approximately 27 000 cm^{-1}. Nonstatistical vibrational populations are observed and can be explained in part by internal conversion of electronic excitation to vibrational excitation. For example the lowest vibrational levels of the C state could transfer population to the $\Omega = 1$ component of the A state's $v > 4$ levels, resulting in an observed intensity distribution different from that calculated by using the Boltzmann distribution, as shown in Figure 4 (bottom). The $^1\Sigma$ B state ($\Omega = 0$), which does not interact as strongly with the other nearby states ($\Omega = 1$) has an intensity distribution much closer to that calculated using a Boltzmann distribution, Figure 4 (top).

Fragmentation of Related Compounds. Excitation of (η-2,2-butyne)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(I), CuLhfac, at 308 nm under low-pressure conditions results in structured emission. Under high-pressure (~1 bar) conditions, a variety of luminescences can be observed. These include peaks for the Cu atoms and Cu_2 and a broad peak that we have tentatively assigned to Cu_n clusters. The low-pressure signal was not reproducible in a molecular beam unless the sample chamber was heated 20 °C above the sublimation temperature of 30 °C. This result convinced us that the structured emission was a result of fragmentation of $Cu(hfac)_2$ that was produced by thermal disproportionation, $2CuLhfac \rightarrow Cu(hfac)_2 + Cu + 2L$. The spectrum was identical to that obtained from pure $Cu(hfac)_2$.

It is interesting to contrast the emission of the free ligand and its fragments to that of $Cu(hfac)_2$ under the low-pressure conditions. At low fluence, the spectrum shows a single broad band centered at 425 nm that we tentatively assign as emission from the intact ligand molecule. At higher fluences, many intense bands from CC and CH emission appear. These bands are not observable in the copper-containing-complex spectra under our fluence and wavelength conditions.

Conclusions

The results of our characterization of the UV photofragmentation of $Cu(hfac)_2$ under a range of gas phase conditions with no surface interactions imply that CuF is formed by intramolecular fluorine abstraction by Cu. The CuF molecule is both rotationally and vibrationally hot ($T \sim 1700$ K). Although the one-photon transition at 308 nm has been assigned as ligand-centered $\pi \rightarrow \pi^*$, there is likely some metal contribution to the orbitals involved in the two-photon transition. Collisions are required for metal production from $Cu(hfac)_2$. The free ligand shows CC and CH emission. Photochemically derived deposits of copper from $Cu(hfac)_2$ are expected to show fluorine incorporation due to the gas phase component of the deposition process; however, the contributions of surface reactions will also be important.

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