

Spectroscopy of jetcooled YCu

Caleb A. Arrington, Dale J. Brugh, Michael D. Morse, and Mats Doverstål

Citation: *The Journal of Chemical Physics* **102**, 8704 (1995); doi: 10.1063/1.468973

View online: <http://dx.doi.org/10.1063/1.468973>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/102/22?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Jet-cooled laser spectroscopy of the cyclohexoxy radical](#)

J. Chem. Phys. **120**, 10579 (2004); 10.1063/1.1701618

[Vibrational spectroscopy and photodissociation of jet-cooled ammonia](#)

J. Chem. Phys. **116**, 4955 (2002); 10.1063/1.1450550

[Electronic spectroscopy of jet-cooled vinyl radical](#)

J. Chem. Phys. **115**, 10738 (2001); 10.1063/1.1416495

[Fourier transform infrared absorption spectroscopy of jetcooled radicals](#)

Rev. Sci. Instrum. **66**, 2430 (1995); 10.1063/1.1145641

[Spectroscopy of jetcooled tyrosine derivatives](#)

J. Chem. Phys. **94**, 5826 (1991); 10.1063/1.460466



Spectroscopy of jet-cooled YCu

Caleb A. Arrington, Dale J. Brugh, and Michael D. Morse
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Mats Doverstål
Department of Physics, Stockholm University, Vanadisvägen 9, 11346 Stockholm, Sweden

(Received 9 January 1995; accepted 3 March 1995)

Optical spectra of jet-cooled diatomic YCu have been recorded using resonant two-photon ionization spectroscopy in a supersonic expansion of helium. The ground state is shown experimentally to be of $^1\Sigma^+$ symmetry, with a measured bond length of $r_e'' = 2.6197(6)$ Å and a vibrational frequency of $193.21(24)$ cm $^{-1}$ for $^{89}\text{Y}^{63}\text{Cu}$. Five excited electronic states are identified as the $[10.2]^1\Sigma^+$ state, the $[11.8]^3\Pi_{0+}$ state, the $[12.0]^3\Pi_1$ state, the $[14.0]^1\Pi$ state, and, with the help of *ab initio* theory, the $[12.2]^1\Pi$ state. No evidence whatever for participation of the $3d$ orbitals of copper in the chemical bonding is found, and the electronic structure of YCu is found to exhibit a striking similarity to that of YH. © 1995 American Institute of Physics.

I. INTRODUCTION

In recent work from this group we have reported predisociation threshold measurements of the bond dissociation energies of several mixed early-late transition metal diatomics, specifically YCo, YNi, ZrCo, ZrNi, NbCo, and NbNi.¹ Our study of these molecules was initiated with the goal of finding interpretable spectra, which would provide insight into the electronic structure and chemical bonding in the mixed early-late transition metal diatomics. The chemical bonding in such species had been suggested to result from a transfer of s electron density from the early transition metal to the late transition metal atom, with a concomitant transfer of d electron density from the d electron rich late transition metal atom to the d electron poor early transition metal atom.² Despite our attempts, however, none of the diatomic metals listed above displayed discrete features in the visible spectrum. Instead, the high density of electronic states caused a nearly continuous adsorption spectrum, even in the jet-cooled molecules.

Another study of the mixed early-late transition metal diatomics ScNi, YPd, and ZrCo initiated by this group led to the observation of discrete vibronic features in the near-infrared which could be grouped into vibronic progressions.³ Unfortunately, the available laser linewidth of 0.04 cm $^{-1}$ was insufficient for the resolution of rotational structure in these molecules, and no measurements of bond lengths were possible. In another attempt to gain insight into the electronic structure of the mixed early-late transition metal diatomics, the present study of YCu was begun. In this molecule the closed $3d$ subshell of copper leads to a relatively low density of electronic states, which in turn results in an uncongested molecular spectrum. In addition, because the $3d$ subshell of copper almost certainly lies too low in energy and is too contracted to take part in the chemical bonding, spectroscopic results on YCu will provide an important base line measurement which may be used to evaluate the importance of d -orbital backbonding in related molecules such as YNi and YCo, once these molecules succumb to rotationally resolved investigation.

The experimental method is described in Sec. II, and

results are presented in Sec. III. Section IV discusses the chemical bonding and electronic structure of YCu and makes comparisons to what is known about the isovalent molecule, YH. Section V then concludes the paper with a summary of our most important findings.

II. EXPERIMENT

Diatomic YCu was studied using a resonant two-photon ionization instrument which has been previously described.⁴ In the present study, production of the diatomic species was accomplished by pulsed laser ablation (Nd:YAG, 532 nm, 20 mJ/pulse) of an equimolar YCu alloy disk, which was rotated and translated on a cam assembly to prevent the pulsed Nd:YAG laser from drilling holes in the sample, and to continually present a fresh surface for ablation. The metal plasma was entrained in helium carrier gas, which was pulsed over the metal target surface from a reservoir pressure of 120 psi. The metal-containing plasma was then collisionally cooled during its passage through a channel 3 cm in length and 2 mm in diameter before undergoing rapid cooling during supersonic expansion into vacuum from the 2 mm orifice. In this final step, metal clusters formed in the expansion achieve rotational temperatures of 6–10 K.

Rough collimation of the molecular beam was accomplished by a 5 mm skimmer, which separated the source chamber from the ionization region of a reflection time-of-flight mass spectrometer (TOFMS). In this region the molecular beam was spectroscopically investigated with a Nd:YAG-pumped tunable dye laser. The resonant states populated by the dye laser radiation were one-photon ionized by an excimer laser operating on a KrF gas mixture (248 nm, 5.00 eV). The photoions were then mass separated by TOFMS and detected with a dual microchannel plate detector, which permitted the optical spectra of $^{89}\text{Y}^{63}\text{Cu}$ and $^{89}\text{Y}^{65}\text{Cu}$ to be separately recorded by scanning the dye laser while monitoring the ion signal at masses 152 and 154, respectively.

Rotationally resolved studies were performed by insertion of an intracavity étalon into the grating cavity of the dye laser, narrowing the laser linewidth to 0.04 cm $^{-1}$. The cavity

was then evacuated and the dye laser was pressure scanned from 0 to 1 atm with CCl_2F_2 (Freon 12, DuPont). Simultaneous recording of an I_2 transmission spectrum allowed the rotationally resolved scans to be calibrated using the I_2 atlas of Gerstenkorn and Luc.⁵ This external calibration of the dye laser permitted absolute line positions to be reported for all rotationally resolved bands. In order to perform the spectroscopy and simultaneously record an I_2 spectrum we found it necessary to Raman shift the output of the dye laser by focusing the dye laser radiation through a high pressure (500 psi) H_2 cell, as described by Clouthier and Karolczak.⁶ The stimulated Raman scattering which results occurs only on the $Q(1)$ line, leading to a shift of the laser wave number by 4155.163 cm^{-1} . Spectra of YCu were then recorded using either the first Stokes Raman light or the fundamental radiation of the dye laser, while the I_2 transmission spectrum was recorded using either the fundamental output or the first anti-Stokes Raman radiation. In all cases the experimental configuration demanded that the dye laser frequency be corrected for the Doppler shift experienced by the molecular beam as it approached the radiation source at the beam velocity of helium ($1.77 \times 10^5\text{ cm/s}$). The correction was approximately 0.07 cm^{-1} for the energy region covered in this study.

Another experimental capability of this instrument is the measurement of excited state lifetimes. The measurement is performed by scanning the delay between the excitation and ionization lasers and measuring the ion signal as a function of this delay. The resulting decay curves were fit to an exponential decay function through the use of a nonlinear least-squares algorithm,⁷ allowing the $1/e$ decay lifetime to be extracted.

III. RESULTS

The present spectroscopic study of diatomic YCu covers the frequency range from $8\,830$ to $24\,090\text{ cm}^{-1}$. The low energy portion of the optical spectrum contains three distinct excited state regions near $10\,000$, $12\,000$, and $14\,000\text{ cm}^{-1}$. Survey scans performed to the blue of these regions also revealed vibronic bands, but assignment of discrete band systems proved impossible. In the remainder of this section we present a description of the band systems found in the three low frequency regions listed above. Wave numbers for the various bands and measured upper state lifetimes are provided in Table I; the results of rotational analyses of 15 different bands are given in Table II.

A. Low energy region: The $[10.2]\Omega'=0 \leftarrow X\Omega''=0$ band system

Figure 1 displays the lowest frequency band system found for YCu, which was recorded using the Stokes radiation from H_2 Raman shifted laser dyes LDS 698 and DCM to excite the molecule and KrF excimer radiation for photoionization. This band system shows three groups of bands separated by roughly 200 cm^{-1} , with bands within each group separated from one another by approximately 20 cm^{-1} . Within each group of bands a similar pattern of diminishing band intensities is found as one moves to the red. As is verified from the rotationally resolved work reported below,

TABLE I. Vibronic bands of $^{89}\text{Y}^{63}\text{Cu}$.^a

| System | Band | Measured frequency (cm^{-1}) | Isotope shift (cm^{-1}) ^b | Lifetime (μs) |
|---|------------------|--|--|-------------------------------|
| $[10.2]^1\Sigma^+ \leftarrow X^1\Sigma^+$ | 4-5 | 9 947.453(-0.311) | | |
| | 3-4 | 9 967.053(0.194) | | |
| | 2-3 | 9 985.840(-0.035) | -2.743 | |
| | 1-2 | 10 004.799(-0.014) | -2.050 | |
| | 0-1 | 10 023.633(-0.040) | -1.770 | |
| | 5-5 | 10 116.015(0.124) | | |
| | 4-4 | 10 136.280(0.232) | -1.827 | |
| | 3-3 | 10 156.043(-0.085) | -1.153 | |
| | 2-2 | 10 176.290(0.161) | -0.205 | 0.904(136) |
| | 1-1 ^c | 10 196.133(0.080) | -0.272 ^c | 0.852(187) |
| | 0-0 ^c | 10 215.799(-0.099) | -0.087 ^c | 0.730(62) |
| | 5-4 | 10 304.451(0.277) | +0.476 | |
| | 4-3 | 10 324.580(-0.738) | +0.026 | |
| | 3-2 | 10 346.454(0.072) | +0.890 | |
| | 2-1 ^c | 10 367.586(0.217) | +1.441 | 0.717(81) |
| $[11.8]^3\Pi_{0+} \leftarrow X^1\Sigma^+$ | 1-0 ^c | 10 388.243(-0.034) | +1.459 ^c | 0.758(50) |
| | 0-1 | 11 629.564 | -1.646 | 1.152(53) |
| | 0-0 ^c | 11 821.916 | +0.058 ^c | 1.342(13) |
| | 1-0 ^c | 12 025.635 | +1.901 ^c | 1.335(370) |
| $[12.0]^3\Pi_1 \leftarrow X^1\Sigma^+$ | 2-0 ^c | 12 229.555 | | 1.164(53) |
| | 0-1 ^c | 11 828.438(0.001) | -1.699 ^c | 1.373(73) |
| | 0-0 ^c | 12 020.555(-0.001) | +0.035 ^c | 1.475(38) |
| | 1-0 ^c | 12 224.035(0.000) | +1.451 ^c | 1.451(120) |
| | 2-1 ^c | 12 229.871(-0.001) | +1.741 ^c | |
| $[12.2]^1\Pi_1 \leftarrow X^1\Sigma^+$ | 2-0 ^c | 12 421.992(0.001) | +2.874 | 1.420(61) |
| | 0-0 ^c | 12 209.352 | +0.307 ^c | |
| $[14.0]^1\Pi_1 \leftarrow X^1\Sigma^+$ | 1-1 | 13 982.215(0.122) | -0.549 | |
| | 0-0 ^c | 14 001.266(0.284) | -0.054 ^c | 0.865(394) |
| | 2-1 | 14 155.736(0.162) | +2.162 | |
| | 1-0 ^c | 14 174.227(-0.973) | +1.548 ^c | 0.859(34) |
| | 3-1 | 14 328.037(-0.284) | +2.468 | |
| | 2-0 | 14 349.370(0.689) | +3.772 | |

^aVibronic bands were fitted to the formula $\nu = \nu_{00} + \omega'_e v' - \omega'_e x'_e (v' + v'^2) - \omega''_e v'' + \omega''_e x''_e (v'' + v''^2)$ for the $[10.2]^1\Sigma^+ \leftarrow X^1\Sigma^+$ system and to the formula $\nu = \nu_{00} + \omega'_e v' - \omega'_e x'_e (v' + v'^2) - \nu'' \Delta G''_{1/2}$ for the remaining band systems. Residuals ($\nu - \nu_{\text{calc}}$) are given following each entry in parentheses. Fitted constants for $^{89}\text{Y}^{63}\text{Cu}$ (and their 1σ errors, quoted in terms of the last digits) are $[10.2]^1\Sigma^+ \leftarrow X^1\Sigma^+$, $\nu_{00}=10\,215.90(19)$; $\omega'_e=173.44(24)$; $\omega'_e x'_e=0.53(4)$; $\omega''_e=193.21(24)$; $\omega''_e x''_e=0.49(4)\text{ cm}^{-1}$. $[11.8]^3\Pi_{0+} \leftarrow X^1\Sigma^+$, $\nu_{00}=11\,821.916$; $\omega'_e=203.518$; $\omega'_e x'_e=-0.101$; $\Delta G''_{1/2}=192.352\text{ cm}^{-1}$. $[12.0]^3\Pi_1 \leftarrow X^1\Sigma^+$, $\nu_{00}=12\,020.556(2)$; $\omega'_e=209.003(9)$; $\omega'_e x'_e=2.762(3)$; $\Delta G''_{1/2}=192.119(2)\text{ cm}^{-1}$. $[14.0]^1\Pi_1 \leftarrow X^1\Sigma^+$, $\nu_{00}=14\,001.0(9)$; $\omega'_e=174.9(16)$; $\omega'_e x'_e=0.37(39)$; $\Delta G''_{1/2}=193.1(9)\text{ cm}^{-1}$.

^bIsotope shifts are calculated as $\nu(^{89}\text{Y}^{63}\text{Cu}) - \nu(^{89}\text{Y}^{65}\text{Cu})$.

^cData obtained from rotationally resolved spectra, calibrated with the aid of the I_2 atlas.

there is little change in bond length upon electronic excitation in this band system, leading to a pattern of Franck-Condon intensity which favors the $\Delta v=0$ sequence. Accordingly, the bands near $10\,200\text{ cm}^{-1}$ are assigned to the $\Delta v=0$ sequence, those near $10\,400\text{ cm}^{-1}$ are assigned as the $\Delta v=+1$ sequence, and those near $10\,000\text{ cm}^{-1}$ are assigned as the $\Delta v=-1$ sequence. These assignments are confirmed by isotope shift measurements between the $^{89}\text{Y}^{63}\text{Cu}$ and $^{89}\text{Y}^{65}\text{Cu}$ isotopic modifications.

When this spectrum was recorded ablation conditions were hot enough that several vibrational quanta of the ground electronic state were populated in the molecular beam (as high as $v''=5$), an unusual circumstance in a jet-

TABLE II. Fitted spectroscopic constants for the band systems of YCu. All values are reported in wave numbers (cm⁻¹), with 1σ error limits given in parentheses.^a

| System | Band | ⁸⁹ Y ⁶³ Cu | ⁸⁹ Y ⁶⁵ Cu |
|--|------|----------------------------------|----------------------------------|
| [10.2] ¹ Σ ⁺ ←X ¹ Σ ⁺ | 1-1 | $\nu_0=10\,196.133(2)$ | $\nu_0=10\,196.405(3)$ |
| | | $B'_1=0.064\,79(9)$ | $B'_1=0.063\,67(16)$ |
| | | $B''_1=0.066\,32(10)$ | $B''_1=0.065\,24(17)$ |
| | 0-0 | $\nu_0=10\,215.799(2)$ | $\nu_0=10\,215.886(2)$ |
| | | $B'_0=0.065\,00(6)$ | $B'_0=0.063\,90(6)$ |
| | | $B''_0=0.066\,51(5)$ | $B''_0=0.065\,34(6)$ |
| | 2-1 | $\nu_0=10\,367.586(4)$ | |
| | | $B'_2=0.064\,47(18)$ | |
| | | $B''_1=0.066\,24(17)$ | |
| | 1-0 | $\nu_0=10\,388.243(1)$ | $\nu_0=10\,386.784(2)$ |
| [11.8] ³ Π ₀ +←X ¹ Σ ⁺ | 0-0 | $\nu_0=11\,821.916(1)$ | $\nu_0=11\,821.858(1)$ |
| | | $B'_0=0.070\,41(3)$ | $B'_0=0.069\,16(3)$ |
| | | $B''_0=0.066\,41(3)$ | $B''_0=0.065\,22(3)$ |
| | 1-0 | $\nu_0=12\,025.635(1)$ | $\nu_0=12\,023.734(1)$ |
| | | $B'_1=0.070\,25(2)$ | $B'_1=0.068\,98(5)$ |
| | | $B''_0=0.066\,56(3)$ | $B''_0=0.065\,36(5)$ |
| | 2-0 | $\nu_0=12\,229.555(1)$ | |
| | | $B'_2=0.069\,95(4)$ | |
| | | $B''_0=0.066\,58(4)$ | |
| | 0-1 | $\nu_0=11\,828.438(2)$ | $\nu_0=11\,830.137(3)$ |
| [12.0] ³ Π ₁ ←X ¹ Σ ⁺ | 0-0 | $\nu_0=12\,020.555(1)$ | $\nu_0=12\,020.520(2)$ |
| | | $B'_0=0.070\,26(8)$ | $B'_0=0.069\,32(9)$ |
| | | $B''_0=0.066\,12(8)$ | $B''_0=0.065\,32(9)$ |
| | 1-0 | $\nu_0=12\,224.035(1)$ | $\nu_0=12\,222.584(1)$ |
| | | $B'_1=0.070\,36(4)$ | $B'_1=0.069\,05(6)$ |
| | | $B''_0=0.066\,52(4)$ | $B''_0=0.065\,28(6)$ |
| | 2-1 | $\nu_0=12\,229.871(2)$ | $\nu_0=12\,228.130(1)$ |
| | | $B'_2=0.069\,81(16)$ | $B'_2=0.068\,48(6)$ |
| | | $B''_1=0.066\,28(19)$ | $B''_1=0.064\,97(6)$ |
| | 2-0 | $\nu_0=12\,421.992(1)$ | |
| [12.2] ¹ Π←X ¹ Σ ⁺ | 0-0 | $\nu_0=12\,209.352(1)$ | $\nu_0=12\,209.045(1)$ |
| | | $B'_0=0.072\,30(9)$ | $B'_0=0.070\,49(9)$ |
| | | $q'_0=-0.000\,532(12)$ | $q'_0=-0.000\,522(12)$ |
| | | $B''_0=0.066\,94(10)$ | $B''_0=0.065\,28(10)$ |
| | | | |
| [14.0] ¹ Π←X ¹ Σ ⁺ | 0-0 | $\nu_0=14\,001.266(1)$ | $\nu_0=14\,001.320(2)$ |
| | | $B'_0=0.064\,94(4)$ | $B'_0=0.063\,71(10)$ |
| | | $B''_0=0.066\,66(4)$ | $B''_0=0.065\,32(10)$ |
| | 1-0 | $\nu_0=14\,174.227(1)$ | $\nu_0=14\,172.679(1)$ |
| | | $B'_1=0.064\,69(6)$ | $B'_1=0.063\,49(6)$ |
| | | $B''_0=0.066\,63(6)$ | $B''_0=0.065\,39(6)$ |

^aAll line positions have been calibrated with the aid of the I₂ atlas.

cooled spectrum. A fit of the individual band positions to the formula

$$\begin{aligned} \nu = & \nu_{00} + \omega'_e v' - \omega'_e x'_e (v'^2 + v') \\ & - \omega''_e v'' + \omega''_e x''_e (v''^2 + v'') \end{aligned} \tag{3.1}$$

gives ground state vibrational constants of $\omega''_e = 193.21(24)$ cm⁻¹ and $\omega''_e x''_e = 0.49(4)$ cm⁻¹ and excited state vibrational constants of $\omega'_e = 173.44(24)$ cm⁻¹ and $\omega'_e x'_e = 0.53(4)$ cm⁻¹ for ⁸⁹Y⁶³Cu. Band positions and residuals ($\nu_{\text{calc}} - \nu_{\text{obs}}$) are given in Table I, along with the results of lifetime measurements.

Three of the bands displayed in Fig. 1 were rotationally resolved, and all were found to display a similar rotational structure. A rotationally resolved scan over the most intense of these bands, the 0-0 band centered at 10 215.799 cm⁻¹, is displayed in Fig. 2. This spectrum shows clear *R* and *P* branches, but the absence of a *Q* branch is indicative of an $\Omega' = 0 \leftarrow \Omega'' = 0$ transition. The appearance of a band head at rather high *J* values indicates similar bond lengths in the ground and excited states, as was confirmed by a fit of the rotational line positions to the standard expression

$$\nu = \nu_0 + B'_v J'(J' + 1) - B''_v J''(J'' + 1). \tag{3.2}$$

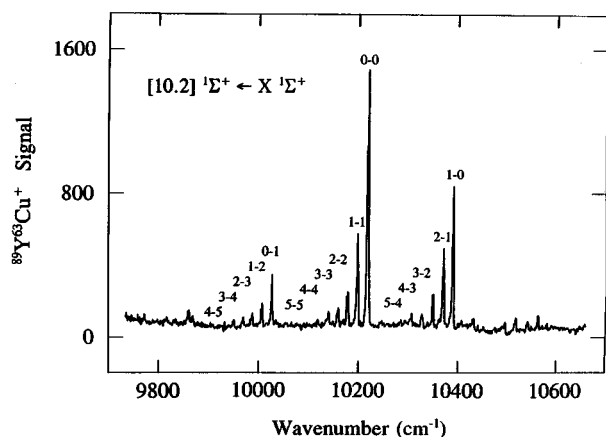


FIG. 1. Low resolution R2PI spectrum of the $[10.2]1\Sigma^+ \leftarrow X 1\Sigma^+$ band system of jet-cooled $^{89}\text{Y}^{63}\text{Cu}$, recorded using the Raman shifted Stokes radiation of laser dye LDS 698 in conjunction with KrF excimer radiation for photoionization. Hot vaporization conditions produce significant populations in several vibrationally excited levels of the ground state which are seen as hot bands up to $v''=5$.

Measured and fitted line positions for both $^{89}\text{Y}^{63}\text{Cu}$ and $^{89}\text{Y}^{65}\text{Cu}$ isotopic modifications, for this and all other rotationally resolved bands, are available from the Physics Auxiliary Publication Service (PAPS) of the American Institute of Physics⁸ or from the author (M.D.M.). Fitted values of the rotational constants are $B''_0 = 0.066\,51(5)\text{ cm}^{-1}$ and $B'_0 = 0.065\,00(5)\text{ cm}^{-1}$ for $^{89}\text{Y}^{63}\text{Cu}$, which convert to $r''_0 = 2.6227(10)\text{ \AA}$ and $r'_0 = 2.6530(10)\text{ \AA}$.

As indicated in Table I, the decay lifetime of the upper state displays little dependence on the vibrational quantum number, giving an average value of $\tau = 792\text{ ns}$. Assuming the decay is dominated by fluorescence to the ground electronic state, this corresponds to an absorption oscillator strength of $f \approx 0.02$, indicating a strongly allowed band system.

B. The $12\,000\text{ cm}^{-1}$ group of band systems

A low resolution scan over the portion of the YCu spectrum near $12\,000\text{ cm}^{-1}$ is displayed in Fig. 3. Although this spectrum appears simple at first glance, isotope shift measurements comparing $^{89}\text{Y}^{63}\text{Cu}$ and $^{89}\text{Y}^{65}\text{Cu}$ indicate the presence of three distinct origin bands in this energy region. Adding to this complexity is the fact that vibrational hot bands are observed. These are particularly troublesome because the upper state vibrational frequency nearly matches the ground

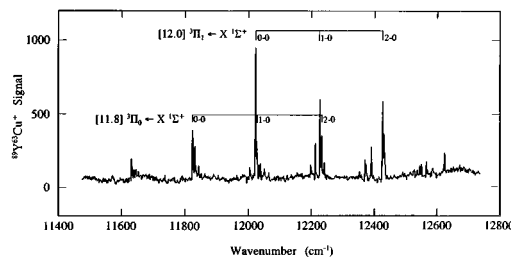


FIG. 3. Low resolution R2PI spectrum of the excited states in the $12\,000\text{ cm}^{-1}$ region of $^{89}\text{Y}^{63}\text{Cu}$, recorded using the Raman shifted Stokes radiation of DCM, rhodamine 640, and rhodamine 610 laser dyes in conjunction with KrF excimer radiation for photoionization.

state frequency, placing the $v'-1$ hot bands close in frequency to the $(v'-1)-0$ cold bands. In addition, these vibrational intervals very nearly match the separation between two excited electronic states in this region, leading to numerous overlapping bands near $11\,820$, $12\,020$, $12\,230$, and $12\,420\text{ cm}^{-1}$. In the remainder of this section the band systems which are identified are individually described.

1. The $[11.8]\Omega' = 0 \leftarrow X\Omega'' = 0$ band system

Figure 4 displays a rotationally resolved scan over the $11\,822\text{ cm}^{-1}$ band of $^{89}\text{Y}^{63}\text{Cu}$, which displays an isotope shift of only 0.058 cm^{-1} [$\nu_0(^{89}\text{Y}^{63}\text{Cu}) - \nu_0(^{89}\text{Y}^{65}\text{Cu})$]. Based on the negligible isotope shift it is apparent that this is an origin band. Further, the band possesses obvious *R* and *P* branches but the *Q* branch is absent, again identifying the transition as $\Omega' = 0 \leftarrow \Omega'' = 0$. The $0-0$ band of the $[11.8]\Omega' = 0 \leftarrow X\Omega'' = 0$ system shown in Fig. 4 possesses a band head in the *P* branch at approximately *P*(17), indicating a bond length decrease in the excited state. This bond length shortening is quantified when the rotational constants are extracted from a fit of the line positions to Eq. (3.2). The $^{89}\text{Y}^{63}\text{Cu}$ isotope yields values of $B''_0 = 0.066\,41(3)$ and $B'_0 = 0.070\,41(3)\text{ cm}^{-1}$, which correspond to $r''_0 = 2.6247(6)\text{ \AA}$ and $r'_0 = 2.5490(5)\text{ \AA}$. The similarity in the lower state rotational constant obtained for this band and that obtained for the $0-0$ band of the $[10.2]\Omega' = 0 \leftarrow X\Omega'' = 0$ band system implies that both transitions originate from the same lower state.

The small positive isotope shift of the origin band indicates that the vibrational frequency of the upper state is slightly larger than that of the ground state. Ignoring anharmonicity, the shift of 0.058 cm^{-1} corresponds to

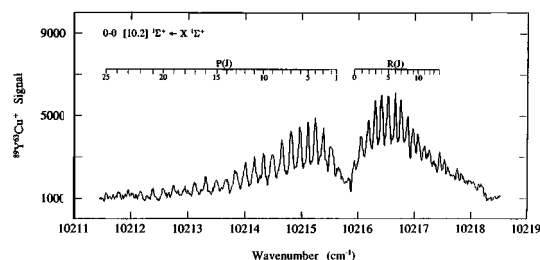


FIG. 2. Rotationally resolved scan over the $0-0$ band of the $[10.2]1\Sigma^+ \leftarrow X 1\Sigma^+$ system of $^{89}\text{Y}^{63}\text{Cu}$, recorded as described in Fig. 1 and the text.

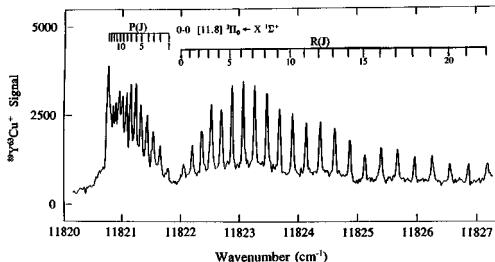


FIG. 4. Rotationally resolved scan over the $0-0$ band of the $[11.8]1\Pi_0 \leftarrow X 1\Sigma^+$ system of $^{89}\text{Y}^{63}\text{Cu}$, recorded as described in Fig. 3 and the text.

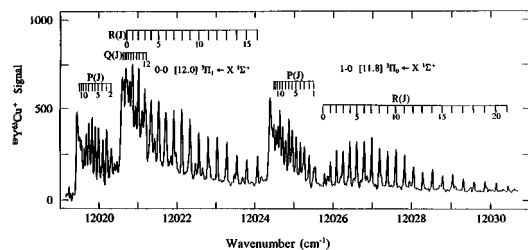


FIG. 5. Rotationally resolved scan over the 0–0 band of the $[12.0]^3\Pi_1 \leftarrow X^1\Sigma^+$ system and over the 1–0 band of the $[11.8]^3\Pi_0 \leftarrow X^1\Sigma^+$ system of $^{89}\text{Y}^{63}\text{Cu}$, recorded as described in Fig. 3 and the text.

$\omega_e' - \omega_e'' \approx 13 \text{ cm}^{-1}$. Given that $\Delta G_{1/2}''$ has been established by high resolution work on the $[10.2]\Omega' = 0 \leftarrow X\Omega'' = 0$ system to be 192.11 cm^{-1} , this implies $\Delta G_{1/2}' \approx 205 \text{ cm}^{-1}$ for the present system.

Indeed, a second $\Omega' = 0 \leftarrow \Omega'' = 0$ band with a substantial isotope shift [$\nu_0(^{89}\text{Y}^{63}\text{Cu}) - \nu_0(^{89}\text{Y}^{65}\text{Cu}) = 1.901 \text{ cm}^{-1}$] is observed 203.719 cm^{-1} to the blue of the origin band displayed in Fig. 4. This 1–0 band is shown in Fig. 5, along with the 0–0 band of another system, the $[12.0]\Omega' = 1 \leftarrow X\Omega'' = 0$ system, which is discussed below. In addition to the 0–0 and 1–0 bands displayed in Figs. 4 and 5, the 2–0 band at $12\,229.555 \text{ cm}^{-1}$ has also been rotationally resolved and analyzed. This band, displayed in Fig. 6, unfortunately overlaps rather severely with the 2–1 band of the $[12.0]\Omega' = 1 \leftarrow X\Omega'' = 0$ system, which is discussed below. Nevertheless, it has been possible to obtain excellent fits for all of these overlapping bands, with fitted values of the spectroscopic constants which are consistent and reasonable.

Excited state lifetimes measured for the various vibrational levels of the $[11.8]\Omega' = 0$ state are listed in Table I. No significant dependence of lifetime on vibrational level is observed, suggesting that predissociation is not occurring in this system. The average of the measured lifetimes is $1.25 \mu\text{s}$. If one assumes that the excited $[11.8]\Omega' = 0$ state decays entirely by fluorescence to the ground electronic state (a fact which is by no means certain), this would imply an absorption oscillator strength of $f \approx 0.008$.

2. The $[12.0]\Omega' = 1 \leftarrow X\Omega'' = 0$ band system

As mentioned in the preceding subsection, Fig. 5 displays another band in addition to the 1–0 band of the

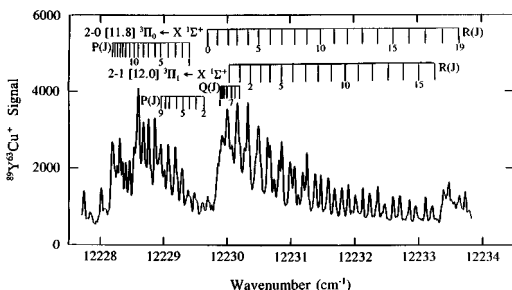


FIG. 6. Rotationally resolved scan over the 2–0 band of the $[11.8]^3\Pi_0 \leftarrow X^1\Sigma^+$ system and the 2–1 band of the $[12.0]^3\Pi_1 \leftarrow X^1\Sigma^+$ system of $^{89}\text{Y}^{63}\text{Cu}$.

$[11.8]\Omega' = 0 \leftarrow X\Omega'' = 0$ system. This blue-shaded band is located near $12\,020.6 \text{ cm}^{-1}$, and displays R , Q , and P branches. Assuming that the band originates from the same $\Omega'' = 0$ state that is the lower state of the $[10.2]\Omega' = 0 \leftarrow X\Omega'' = 0$ and $[11.8]\Omega' = 0 \leftarrow X\Omega'' = 0$ systems, this implies that the upper state must possess $\Omega' = 1$. Furthermore, there is a negligible isotope shift in this band, with $\nu_0(^{89}\text{Y}^{63}\text{Cu}) - \nu_0(^{89}\text{Y}^{65}\text{Cu}) = 0.0380 \text{ cm}^{-1}$. This implies that the $12\,020.6 \text{ cm}^{-1}$ band is vibrationally an origin band, so the band system corresponding to this transition is designated the $[12.0]\Omega' = 1 \leftarrow X\Omega'' = 0$ system.

The assignment of the $12\,020.6 \text{ cm}^{-1}$ band as an $\Omega' = 1 \leftarrow \Omega'' = 0$ transition is borne out by the observation of the first lines $R(0)$, $Q(1)$, and $P(2)$, and by a fit of the line positions to Eq. (3.2). From this fit rotational constants of $B_0'' = 0.066\,12(8)$ and $B_0' = 0.070\,26(8) \text{ cm}^{-1}$ are obtained, corresponding to bond lengths of $r_0'' = 2.6304(16) \text{ \AA}$ and $r_0' = 2.5518(15) \text{ \AA}$. The nearly identical values of B_0' obtained for the $v' = 0$ levels of the $[11.8]\Omega' = 0$ and $[12.0]\Omega' = 1$ states suggests strongly that these states are spin–orbit components of a common Hund’s case (a) state.

Further evidence that both the $[11.8]\Omega' = 0$ and $[12.0]\Omega' = 1$ states derive from a common Hund’s case (a) state is obtained when one searches for higher vibrational quanta of the $[12.0]\Omega' = 1$ state. At a frequency 203.48 cm^{-1} to the blue of the 0–0 band of the $[12.0]\Omega' = 1 \leftarrow X\Omega'' = 0$ system one finds another $\Omega' = 1 \leftarrow \Omega'' = 0$ band, with an isotope shift (1.451 cm^{-1}) which is characteristic of a 1–0 band. This is the 1–0 band of the $[12.0]\Omega' = 1 \leftarrow X\Omega'' = 0$ system. The vibrational interval of the $[12.0]\Omega' = 1$ state ($\Delta G_{1/2}' = 203.48 \text{ cm}^{-1}$) is so close to the vibrational interval of the $[11.8]\Omega' = 0$ state ($\Delta G_{1/2}'' = 203.72 \text{ cm}^{-1}$) that the assignment of these states as spin–orbit components of a common Hund’s case (a) state cannot be avoided.

A final piece of evidence that the $[11.8]\Omega' = 0$ and $[12.0]\Omega' = 1$ states derive from a common Hund’s case (a) state comes from the lifetimes of these excited states. The average of the measured lifetimes for the $[11.8]\Omega' = 0$ state is $1.25 \mu\text{s}$, which compares to an averaged value of the measured lifetimes for vibrational levels of the $[12.0]\Omega' = 1$ state of $1.43 \mu\text{s}$. These values are equal to the limit of our ability to measure them, suggesting similar fluorescence pathways for the two states.

In addition to the 0–0 and 1–0 bands of the $[12.0]\Omega' = 1 \leftarrow X\Omega'' = 0$ system, located at $12\,020.555$ and $12\,224.035 \text{ cm}^{-1}$, rotationally resolved spectra have also been recorded for the 0–1, 2–0, and 2–1 bands of this system at $11\,828.438$, $12\,421.992$, and $12\,229.871 \text{ cm}^{-1}$, respectively, for $^{89}\text{Y}^{63}\text{Cu}$. The 2–1 band of this system severely overlaps with the 2–0 band of the $[11.8]\Omega' = 0 \leftarrow X\Omega'' = 0$ system, as shown in Fig. 6, but an analysis has nevertheless been possible.

3. The $[12.2]\Omega' = 1 \leftarrow X\Omega'' = 0$ 0–0 band

All of the bands in the $12\,000 \text{ cm}^{-1}$ energy region described to this point appear to be transitions from the $X\Omega'' = 0$ state to two upper states of $\Omega' = 0$ and $\Omega' = 1$ symmetry. Furthermore, these $\Omega' = 0$ and $\Omega' = 1$ states seem to be

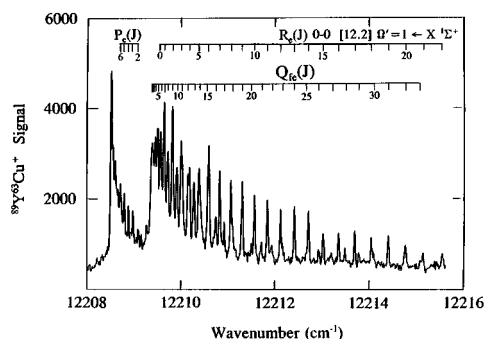


FIG. 7. Rotationally resolved scan over the 0-0 band of the $[12.2] \Omega'=1 \leftarrow X^1\Sigma^+$ system of $^{89}\text{Y}^{63}\text{Cu}$, which demonstrates a lambda doubling in the excited state.

spin-orbit levels of the same excited Hund's case (a) state. In addition to these major contributors to the spectrum in this region, another band with a small isotope shift has also been observed. This is located at $12\,209.352\text{ cm}^{-1}$ in $^{89}\text{Y}^{63}\text{Cu}$, and the rotationally resolved spectrum is shown in Fig. 7. The small isotope shift of $\nu_0(^{89}\text{Y}^{63}\text{Cu}) - \nu_0(^{89}\text{Y}^{65}\text{Cu}) = 0.307\text{ cm}^{-1}$ measured for this band strongly suggests that it is a $\Delta v = 0$ band.

The $12\,209\text{ cm}^{-1}$ band is quite similar in appearance to the other $\Omega'=1 \leftarrow \Omega''=0$ bands in this energy region, with intense Q and R branches and a slightly weaker P branch with a bandhead near $P(13)$. An attempt to fit the rotational line positions to Eq. (3.2), however, leads to substantial errors in the Q lines which increase with increasing J . In order to fit the lines of this spectrum to the same accuracy as was achieved for the other bands of this study a lambda doubling parameter for the $\Omega'=1$ upper state was required. Because the $\Omega''=0$ ground state of YCu is nondegenerate and possesses only e or f levels, however, this lambda doubling manifests itself as a J -dependent offset of the Q lines (as compared to the R and P lines), rather than as a doubling of all the lines at high J .

Assuming for the moment that the ground state is of 0^+ symmetry, it will possess only e levels. In transitions to the upper $\Omega'=1$ state, P and R lines will lead to levels of e parity in the upper state, while Q lines will lead to levels of f parity.⁹ The rotational levels of the $\Omega'=1$ upper state are then given by $B'J'(J'+1) \mp (q'_v/2)J'(J'+1)$,¹⁰ where the upper sign corresponds to e levels and the lower sign to f levels. With the inclusion of lambda doubling, Eq. (3.2) is then modified to read

$$\nu = \nu_0 + B'_v J'(J'+1) \mp (q'_v/2)J'(J'+1) - B''_v J''(J''+1), \quad (3.3)$$

where the upper sign is used for the P and R lines, and the lower for the Q lines.

The fit of the spectrum yields a lambda doubling parameter for the excited state of $q'_0 = -0.000\,532(12)\text{ cm}^{-1}$, with rotational constants of $B''_0 = 0.066\,94(10)\text{ cm}^{-1}$, $r''_0 = 2.6143(20)\text{ Å}$ for the ground state and $B'_0 = 0.072\,30(9)\text{ cm}^{-1}$, $r'_0 = 2.5155(16)\text{ Å}$ for the excited state. This upper state rotational constant is significantly

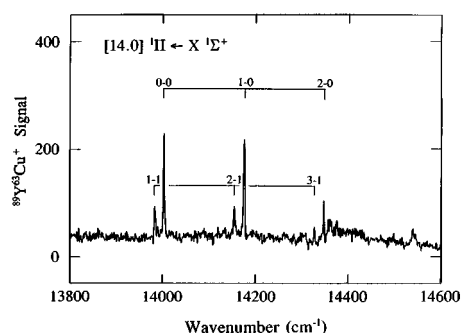


FIG. 8. Low resolution RPI spectrum of the $[14.0] 1\Pi_1 \leftarrow X^1\Sigma^+$ band system of $^{89}\text{Y}^{63}\text{Cu}$, recorded using LDS 698 and DCM laser dyes in conjunction with KrF radiation for photoionization. A strong progression originating from $v''=0$ is exactly mimicked by a less intense hot band progression originating from $v''=1$.

larger than that of either the $[11.8]\Omega'=0$ or the $[12.0]\Omega'=1$ state, indicating that this excited state is of a completely different origin than either of those previously found in this spectral region. In the absence of compelling evidence to the contrary, we assume that the band is vibrationally an origin band due to the small isotope shift.

C. The $[14.0]\Omega'=1 \leftarrow X\Omega''=0$ band system

The highest energy band system of YCu rotationally resolved in this study is the $[14.0]\Omega'=1 \leftarrow X\Omega''=0$ system shown in Fig. 8. The 0-0 and 1-0 bands of this system have been rotationally resolved, with the 0-0 band displayed in Fig. 9. The ground state rotational constant, obtained from an average of the 0-0 and 1-0 bands, is in agreement with the $X\Omega=0$ rotational constant found for the other transitions in this investigation, with $B''_0 = 0.066\,65(3)\text{ cm}^{-1}$. Also in agreement with the other measured ground state constants is the vibrational interval, $\Delta G''_{1/2} = 193.1\text{ cm}^{-1}$, which is measured in low resolution from the progression of hot bands lying slightly to the red of the main progression in Fig. 8. As is evident in Fig. 9, a prominent Q branch identifies the transitions as perpendicular $\Omega'=1 \leftarrow X\Omega''=0$ transitions. The rotational analysis of these bands is simplified by the nearly symmetrical fanning out of the R and P branches which permits the low J lines to be easily identified. This unfortunately leads to an unresolved Q branch because all of the Q

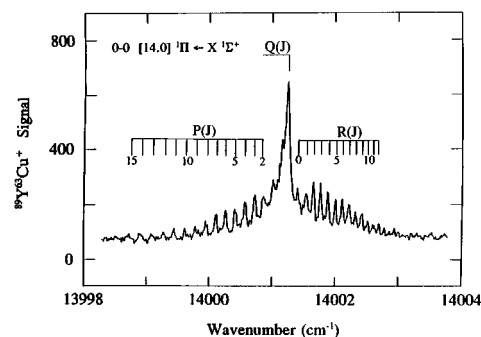


FIG. 9. Rotationally resolved scan over the 0-0 band of the $[14.0] 1\Pi_1 \leftarrow X^1\Sigma^+$ band system of $^{89}\text{Y}^{63}\text{Cu}$.

TABLE III. Observed electronic states of $^{89}\text{Y}^{63}\text{Cu}$.

| State | T_0 (cm^{-1}) | ω_e (cm^{-1}) | $\omega_e x_e$ (cm^{-1}) | B_e (cm^{-1}) | α_e (cm^{-1}) | r_e (\AA) | τ (μs) |
|---------------------|----------------------------|---------------------------------|-------------------------------------|----------------------------|---------------------------------|------------------------|--------------------------|
| [14.0] $^1\Pi$ | 14 001.266(1) | 174.9(1.6) | 0.37(0.39) | 0.065 07(7) | 0.000 25(7) | 2.6517(14) | 0.86 |
| [12.2] $^1\Pi$ | 12 209.352(1) | | | $B_0=0.072\ 30(9)^a$ | | $r_0=2.5155(16)^a$ | |
| [12.0] $^3\Pi_1$ | 12 020.555(1) | 209.003 | 2.762 | 0.070 71(6) | 0.000 30(4) | 2.5436(11) | 1.43 |
| [11.8] $^3\Pi_0^+$ | 11 821.916(1) | 203.518 | -0.101 | 0.070 55(4) | 0.000 22(2) | 2.5465(7) | 1.25 |
| [10.2] $^1\Sigma^+$ | 10 215.799(2) | 173.44(0.24) | 0.53(0.04) | 0.065 11(9) | 0.000 19(6) | 2.6507(17) | 0.79 |
| $X\ ^1\Sigma^+$ | 0.000 | 193.21(0.24) | 0.49(0.04) | 0.066 66(3) | 0.000 23(5) | 2.6197(6) | |

^aFor the [12.2] $^1\Pi$ state, only the $v'=0$ level was rotationally resolved, so only B_0 and r_0 are reported.

lines occur at nearly the same frequency. Consequently we are completely unable to estimate the lambda doubling parameter in the upper state of this system.

The nearly equal spreading out of the P and R branches in Fig. 9 is a result of the similar bond lengths of the ground state, $r_e''=2.6197(6)$ \AA , and excited state, $r_e'=2.6517(14)$ \AA . The lifetime of the [14.0] $\Omega'=1$ state shows no apparent vibrational dependence, and the measured average value of $\tau=0.86$ μs leads to an absorption oscillator strength of $f\approx 0.009$ if it is assumed that the decay is governed by fluorescence to the ground electronic state. This is similar to the other excited electronic states found for YCu.

IV. DISCUSSION

The spectroscopic data presented in the preceding section is summarized in Table III, where Hund's case (a) labels are provided. In the following subsection, justifications for the Hund's case (a) assignments are presented. Following this assignment of Hund's case (a) labels, a discussion of the electronic structure of YCu is presented and comparison to related molecules is made.

A. Hund's case (a) labels

All of the rotationally resolved spectra recorded for YCu originate from a lower state with $\Omega''=0$. The fact that no other Ω'' values are observed suggests that the ground state is of $^1\Sigma$ symmetry, because any other source of an $\Omega''=0$ state would have spin-orbit levels. This argument is particularly compelling because the molecule has been investigated under vibrationally hot conditions, and under these circumstances one would expect low-lying spin-orbit levels to be populated. For example, in the [10.2] $\Omega'=0\leftarrow X\Omega''=0$ spectrum displayed in Fig. 1 vibrational levels as high as $v''=5$ are observed to be populated. The $v''=5$ level lies 951 cm^{-1} above the ground level, suggesting strongly that if the ground state possessed spin-orbit levels, they would be populated and observed. On this basis the ground state is assigned as $X\ ^1\Sigma$. Further, the two lowest separated atom limits¹¹ of $\text{Y}+\text{Cu}$ generate no $^1\Sigma^-$ states, and a ground state of $^1\Sigma^-$ symmetry would be unprecedented in diatomic molecule spectroscopy, so the ground state of YCu may be confidently assigned to be $^1\Sigma^+(0^+)$.

The assignment of the ground state as $^1\Sigma^+$ allows definite assignments of Hund's case (a) labels for most of the remaining excited electronic states to be easily made. Both the [10.2] $\Omega'=0$ and [14.0] $\Omega'=1$ excited states show strong transitions from the ground state and a complete absence of

other spin-orbit levels. These characteristics are indicative of singlet states, so these are assigned as the [10.2] $^1\Sigma^+$ and [14.0] $^1\Pi$ states, respectively.

As discussed in the results section above, the [11.8] $\Omega'=0$ and [12.0] $\Omega'=1$ states are thought to be spin-orbit components of the same Hund's case (a) state, based on the similar rotational constants, vibrational frequencies, and lifetimes. As such, they must derive from a triplet state, and it is not reasonable for a $^3\Sigma$ state to have an interval between the $\Omega=0$ and $\Omega=1$ levels as large as the 198 cm^{-1} that is observed. A triplet state with $\Lambda>1$ possesses no $\Omega=0$ component, so these levels must correspond to substates of a $^3\Pi$ term. Accordingly, they are labelled the [11.8] $^3\Pi_0^+$ and [12.0] $^3\Pi_1$ states. Presumably these states gain oscillator strength for absorption from the ground $X\ ^1\Sigma^+$ state by spin-orbit mixing with the [10.2] $^1\Sigma^+$ and [14.0] $^1\Pi$ states, respectively. The decay lifetimes of these states are not dramatically longer than those of the [10.2] $^1\Sigma^+$ and [14.0] $^1\Pi$ states, suggesting that the decay is dominated by fluorescence to low lying triplet states, rather than to the $X\ ^1\Sigma^+$ ground state. Presumably these states correspond to components of a $^3\Pi$ state which derives from the first excited separated atom limit of $\text{Y}(5s^25p^1,^2P^0)+\text{Cu}(3d^{10}4s^1,^2S)$, or from the slightly higher limit of $\text{Y}(4d^25s^1,^4F)+\text{Cu}(3d^{10}4s^1,^2S)$.¹¹ Fluorescence is then probably dominated by emission to the triplet states deriving from the ground state separated atom limit of $\text{Y}(4d^15s^2,^2D)+\text{Cu}(3d^{10}4s^1,^2S)$.¹¹

Finally, the one remaining band system requiring explanation is the [12.2] $\Omega'=1\leftarrow X\Omega''=0$ system, which was found to display lambda doubling in the upper state. It is clearly speculative to suggest a Hund's case (a) identity and separated atom parent for this state, but the major possibilities are $^1\Pi_1$, $^3\Sigma_1^+$, $^3\Sigma_1^-$, $^3\Pi_1$, and $^3\Delta_1$. *Ab initio* calculations by Ricca and Bauschlicher strongly suggest that the observed state is of $^1\Pi$ symmetry, and on this basis an assignment as the [12.2] $^1\Pi$ state is adopted.¹² The large magnitude of the observed lambda doubling [$q'_0 = 0.000\ 562(6)$ cm^{-1}] indicates that a perturber state of either $\Omega=0^+$ or 0^- symmetry is located quite close in energy. The most likely candidates for this perturber are $^1\Sigma^-$, $^3\Sigma^+$, or $^3\Sigma^-$ states, which may lack sufficient oscillator strength to be observed and which possess only a single 0^+ or 0^- level, thereby causing a differential perturbation of the e vs f levels. Based on the preliminary *ab initio* results, the most likely perturber appears to be a $^1\Sigma^-$ state, which is calculated to lie within 300 cm^{-1} of the [12.2] $^1\Pi$ state.

B. General aspects of the chemical bonding in YCu and comparisons to YH

The chemical bonding in the diatomic transition metals has proven to be exceedingly complicated in general, requiring the combination of many different ideas for even a qualitatively accurate description.¹³ Three of the most important determinants of the chemical bonding are (1) the energetics of the separated atom asymptotes which are most suitable for chemical bonding, (2) the degree of interaction of the atomic orbitals, which is governed by the amount of overlap between the orbitals and their relative energy, and (3) the acute competition between exchange stabilization of high spin states vs formation of two-electron bonds. In the bonding of YCu the first two considerations are quite important, while the closed shell structure of copper and the presence of only one 4d electron on yttrium diminishes the importance of exchange effects in the determination of the ground state electronic state.

1. The $X^1\Sigma^+$ ground state of YCu and its comparison to YH

The $X^1\Sigma^+$ ground state of YCu must derive from the ground separated atom limit of $Y4d^15s^2 + Cu3d^{10}4s^1$, simply because the lowest excited separated atom asymptote lies more than 10 000 cm^{-1} higher in energy. Given that the net bond strength of the molecule is estimated to be 2.22 eV (17 900 cm^{-1})¹⁴ in an atomic cell model and our own measurements of the ground state ω_e and $\omega_e x_e$ values provide a Morse potential prediction of the bond strength of 2.36 eV (19 000 cm^{-1}), it is simply not possible to recoup the 10 000 cm^{-1} required to excite one of the atoms in the form of enhanced chemical bonding. With this in mind, it becomes pertinent to ask why the $^1\Sigma^+$ state deriving from the $Y4d^15s^2 + Cu3d^{10}4s^1$ separated atom limit is more strongly stabilized than the $^1\Pi$, $^1\Delta$, $^3\Sigma^+$, $^3\Pi$, or $^3\Delta$ states deriving from this limit.

If the 4d orbitals of yttrium were uninvolved in the chemical bonding, one could understand the electronic structure of YCu in its ground state simply by considering the σ bonding and σ^* antibonding orbitals which are formed as linear combinations of the $5s_Y$ and $4s_{Cu}$ atomic orbitals. This would lead to a ground state electronic configuration of $4d_Y^1 3d_{Cu}^{10} \sigma^2 \sigma^{*1}$ with a net bond order of 1/2. In such a scenario, however, one would expect a high spin coupling of the $4d_Y$ electron and the σ^* electron, resulting in a triplet ground state. The fact that this is not observed argues in favor of some involvement of the 4d orbitals of yttrium in the bonding.

The prototypical example of the interaction between yttrium and an s^1 atom is the YH diatomic molecule, which has been investigated both computationally^{15,16} and experimentally.^{17–19} Both theoretical studies find a $^1\Sigma^+$ ground state for YH, but the initial experimental study identified the ground state as $X^3\Delta$.¹⁷ The two subsequent spectroscopic investigations^{18,19} have proven that the ground state is $X^1\Sigma^+$, as found in the theoretical work on YH and the present experimental investigation of YCu. An unpublished theoretical investigation of YCu also finds a $^1\Sigma^+$ ground state.¹² A most important contribution of the theoretical stud-

ies of YH is an explanation for the emergence of $^1\Sigma^+$ as the ground state. In YH a full two-electron σ^2 bond occurs between the $4d\sigma_Y$ and $1s\sigma_H$ orbitals, leading to a significantly enhanced stabilization of the $^1\Sigma^+$ state over the other states deriving from the $Y4d^15s^2 + H\ 1s^1$ separated atom limit.¹⁶ One would ordinarily think that the $5s^2$ electrons would prevent a close approach of the hydrogen atom to the $4d\sigma_Y$ orbital, but this deleterious effect is mitigated by the high polarizability of the $5s^2$ pair of electrons. In the early transition metals there is a strong tendency to form $4d-5s$ hybrid orbitals.¹⁶ In the example of YH this allows the $5s$ electron density to be shifted off the axis of the molecule, permitting $4d\sigma_Y-1s_H$ bonding to occur. This polarization of the $5s$ electron density off of the molecular axis is further enhanced by a significant configuration interaction between the $5s^2$ and the $5p\pi^2$ electron configurations,^{15,16} leading again to a removal of $5s^2$ electron density from the internuclear axis.

The observation of a $^1\Sigma^+$ ground state in the isovalent YCu molecule suggests that a similar mechanism is at work in this molecule. The calculated results on YH place the remaining electronic states deriving from the $Y\ 4d^15s^2 + H\ 1s^1$ ground separated atom limit 7000 cm^{-1} or more above the $^1\Sigma^+$ ground state. It would be very interesting to determine whether the polarizability of the $5s_Y$ orbital leads to a comparable stabilization of the $^1\Sigma^+$ ground state in the case of YCu. Unfortunately, insufficient experimental data exists on either molecule to make a significant comparison at the present time.

2. Excited electronic states of YCu and their comparison to YH

The $[10.2]^1\Sigma^+$, $[11.8]^3\Pi_0$, $[12.0]^3\Pi_1$, and $[14.0]^1\Pi$ states of YCu appear to correspond directly with theoretically predicted or experimentally known states of YH. The corresponding $^1\Sigma^+$, $^3\Pi$, and $^1\Pi$ states in YH are calculated to lie 15 050, 20 510, and 21 991 cm^{-1} above the $^1\Sigma^+$ ground state using a complete active space self-consistent field (CASSCF) method followed by second order configuration interaction (SOC) and relativistic configuration interaction (RCI).¹⁵ These theoretical T_e values are in close correspondence to the experimentally measured $v'=0$ term energies of the $C^1\Sigma^+$ state ($T_0=14\,295.3956\ \text{cm}^{-1}$)¹⁹ and the $D^1\Pi$ state ($T_0=19\,601.53\ \text{cm}^{-1}$).¹⁷ Further, these term energies fall into an appropriate range for the states to derive from the excited $Y(5s^25p^1,^2P^0) + H(1s^1,^2S)$ separated atom limit.

If one could assume that the only important distinction between YH and YCu concerned the effectiveness of the $1s_H$ or $4s_{Cu}$ atomic orbital in its bonding with the σ framework of yttrium, then one might imagine that the separation between states in YCu would be given by a constant factor times the corresponding separation between states in YH. If such a factor could be found, it would provide support for the assignment of corresponding states in the two molecules. Comparing the energies required to excite YH and YCu to the $^1\Sigma^+$ state, we find the excitation in YCu at 10 215.8 cm^{-1} corresponds to 71.5% of the excitation energy required for YH (14 295 cm^{-1}). A similar examination for the $^1\Pi$ state shows that the excitation energy in YCu (14 001 cm^{-1}) is

71.4% of the YH excitation energy ($19\,601\text{ cm}^{-1}$). Although the bond strengths of the two molecules are poorly known, one might also expect the same factor to pertain to them as well. A comparison of the theoretical estimate of $D_0(\text{YH})$ ($3.5 \pm 0.2\text{ eV}$)¹⁵ to that estimated for YCu (2.22 eV)¹⁴ gives the YCu bond strength as roughly 63% of that of YH. Considering that the bond strengths are probably only known to an accuracy of 20%, this represents essentially the same decrease in going from YH to YCu as was found for the excitation energies. It also suggests that the analog of the $[12.2]^1\Pi$ state of YCu may be found near $17\,100\text{ cm}^{-1}$ in YH. The analog of this $^1\Pi$ state of YCu appears to be still unknown in YH.

C. Comparison to other diatomic transition metals

The strongest evidence that the $3d$ orbitals of copper are uninvolved in the chemical bonding in YCu comes from comparisons of YCu with other transition metal diatomics, such as YNi and YCo. Bond strengths of YNi and YCo have been recently measured by the abrupt onset of predissociation in a congested electronic spectrum, resulting in values of $D_0^\circ(\text{YNi}) = 2.904(1)\text{ eV}$ and $D_0^\circ(\text{YCo}) = 2.591(1)\text{ eV}$.¹ These lie substantially higher in energy than the bond strength of YCu, which is estimated to be 2.22 eV on the basis of Miedema's atomic cell model,¹⁴ and 2.35 eV based on a Morse potential extrapolation of the ground $X\ ^1\Sigma^+$ state.

In addition, *ab initio* calculations on YNi by Faegri and Bauschlicher lead to an assignment of the YNi ground state as $^2\Sigma^+$, with a bond length of 2.29 \AA .²⁰ Given the tendency of *ab initio* calculations to err on the side of predicting bond lengths which are longer than experimental results, this short bond length calculated for YNi establishes that the nature of the bonding in YCu [with $r_e = 2.6197(6)\text{ \AA}$] is very different from that of YNi. A similar conclusion is reached when the calculated vibrational frequency of YNi (285 cm^{-1}) is compared to the measured value for YCu [$193.21(24)\text{ cm}^{-1}$].

All of these comparisons demonstrate that it is correct to think of the copper $3d$ orbitals as inert core orbitals in the YCu molecule. In contrast, the $3d$ orbitals in nickel and cobalt become active participants in the bonding in the YNi and YCo molecules. Thus it is correct to use YCu as a benchmark molecule to evaluate the importance of d orbital interactions in the remaining YM molecules, where M belongs to the $3d$ transition metal series.

In many intermetallic molecules previously investigated in this research group, nickel has behaved similarly to copper, indicating that the $3d$ orbitals of either Ni or Cu are uninvolved in the chemical bonding. Thus, for example, the bond strengths and bond lengths of Ni_2 [$2.042(2)\text{ eV}$, 2.155 \AA],²¹ NiCu [$2.05(10)\text{ eV}$, 2.235 \AA],^{22,23} and Cu_2 [$2.03(2)\text{ eV}$, 2.220 \AA]²⁴ are all nearly identical. Likewise, the bond strengths and bond lengths of AlNi [$2.29(5)\text{ eV}$, 2.321 \AA]²⁵ and AlCu [$2.315(12)\text{ eV}$, 2.339 \AA]²⁶ are again nearly the same. The present investigation of YCu, in comparison to previous theoretical and experimental results on YNi, provides the most potent demonstration to date that nickel and copper can display very different bonding mechanisms, given the proper partner in bonding.

There are two major reasons why yttrium is capable of engaging in strong bonding with the $3d$ orbitals of nickel. First, yttrium has the largest and most accessible d orbitals of any of the $3d$, $4d$, or $5d$ metals (with the exception of the lanthanides), with a radial expectation value of $\langle r_{4d} \rangle = 1.33\text{ \AA}$ in the $4d^1 5s^2\ ^2D$ state.²⁷ Second, although the $5s$ orbital of yttrium is quite large, it can be easily polarized out of the way, either by $5s-4d\sigma$ or $5s-5p\sigma$ hybridization. These two properties combine to make yttrium one of the transition metals which is most capable of d orbital bonding. Nevertheless, the present investigation shows that the $3d$ orbitals of copper remain untouched by the $4d$ orbitals of yttrium. This indicates that the $3d$ orbitals of copper may be expected to remain essentially inert in all of the intermetallic compounds of copper. The intermetallic compounds of copper therefore provide an ideal reference point for the evaluation of d -orbital bonding contributions in related intermetallic molecules.

V. CONCLUSIONS

Resonant two-photon ionization spectroscopy has been employed to investigate jet-cooled diatomic YCu. The ground state is demonstrated to be $X\ ^1\Sigma^+$, deriving from the ground separated atom limit of $\text{Y } 4d^1 5s^2\ ^2D + \text{Cu } 3d^{10} 4s^1\ ^2S$. From rotationally resolved results the ground state bond length is given as $r_e'' = 2.6197(6)\text{ \AA}$, and the ground state vibrational frequency is $\omega_e'' = 193.21(24)\text{ cm}^{-1}$ for $^{89}\text{Y}^{63}\text{Cu}$. Five excited electronic states have been observed, and are identified through rotationally resolved spectroscopy as the $[10.2]^1\Sigma^+$ state, the $[11.8]^3\Pi_0^+$ state, the $[12.0]^3\Pi_1$ state, the $[14.0]^1\Pi$ state, and, with the aid of *ab initio* theory, the $[12.2]^1\Pi$ state. The observed singlet states show a strong resemblance to the corresponding states of YH, although it is evident that copper binds somewhat less strongly to yttrium than does hydrogen. The lack of participation of the $3d$ orbitals of copper in the bonding is shown to account for the dramatic differences in bond strength, bond length, and vibrational frequency between YCu and YNi. On this basis it is argued that the $3d$ orbitals of copper will remain essentially inert in all intermetallic compounds of copper.

ACKNOWLEDGMENTS

Research support from the National Science Foundation under Grant No. CHE-9215193 is gratefully acknowledged. The donors of the Petroleum Research Fund, administered by the American Chemical Society, are also acknowledged for partial support of this research.

¹C. A. Arrington, T. Blume, M. D. Morse, M. Doverstål, and U. Sassenberg, *J. Phys. Chem.* **98**, 1398 (1994).

²N. Engel, *Acta Metall.* **15**, 557 (1967); L. Brewer, *ibid.* **15**, 553 (1967); *Science* **161**, 115 (1968).

³C. A. Arrington, M. D. Morse, and M. Doverstål, *J. Chem. Phys.* **102**, 1895 (1995).

⁴Z.-W. Fu, G. W. Lemire, Y. Hamrick, S. Taylor, J.-C. Shui, and M. D. Morse, *J. Chem. Phys.* **88**, 3524 (1988).

⁵S. Gerstenkorn and P. Luc, *Atlas du Spectre d'Absorption de la Molécule d'Iode* (CNRS, Paris, 1978); *Rev. Phys. Appl.* **14**, 791 (1979).

⁶D. J. Clouthier and J. Karolczak, *Rev. Sci. Instrum.* **61**, 1607 (1990).

- ⁷P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), CURFIT program, pp 235–245.
- ⁸See AIP document no. PAPS JCPSA-102-8704-17 for 17 pages of absolute line positions. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, Carolyn Gehlbach, 500 Sunnyside Boulevard, Woodbury, New York 11797–2999. Fax: 516-576-2223, e-mail: janis@aip.org. The price is \$1.50 for each microfiche (98 pages) or \$5.00 for photocopies of up to 30 pages, and \$0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.
- ⁹H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, Orlando, 1986).
- ¹⁰R. S. Mulliken and A. Christy, *Phys. Rev.* **38**, 87 (1931).
- ¹¹C. E. Moore, *Natl. Bur. Stand. Circ. No. 467* (U.S. GPO, Washington, DC, 1949, 1952, 1971).
- ¹²A. Ricca and C. Bauschlicher, *J. Chem. Phys.* (submitted).
- ¹³S. P. Walch and C. W. Bauschlicher, Jr., in *Comparison of Ab Initio Quantum Chemistry with Experiment*, edited by R. J. Bartlett (Reidel, Dordrecht, 1985), p. 17.
- ¹⁴A. R. Miedema, *Faraday Symp. Chem. Soc.* **14**, 136 (1980).
- ¹⁵K. Balasubramanian and J. Z. Wang, *J. Mol. Spectrosc.* **133**, 82 (1989).
- ¹⁶S. R. Langhoff, L. G. M. Pettersson, C. W. Bauschlicher, Jr., and H. Partridge, *J. Chem. Phys.* **86**, 268 (1987).
- ¹⁷A. Bernard and R. Bacis, *Can. J. Phys.* **55**, 1322 (1977).
- ¹⁸B. Simard, H. Niki, W. J. Balfour, and P. A. Hackett, presentations RC11 and RC12 in the 45th Ohio State University Symposium on Molecular Spectroscopy, June 11–15, 1990, Columbus, Ohio; also B. Simard (personal communication).
- ¹⁹R. S. Ram and P. F. Bernath, *J. Chem. Phys.* **101**, 9283 (1994).
- ²⁰K. Faegri, Jr. and C. W. Bauschlicher, Jr., *Chem. Phys.* **153**, 399 (1991).
- ²¹J. C. Pinegar, J. D. Langenberg, C. A. Arrington, E. M. Spain, and M. D. Morse, *J. Chem. Phys.* **102**, 666 (1995).
- ²²Z. Fu and M. D. Morse, *J. Chem. Phys.* **90**, 3417 (1989).
- ²³E. M. Spain and M. D. Morse, *J. Chem. Phys.* **97**, 4633 (1992).
- ²⁴M. D. Morse, *Adv. Metal Semiconduct. Clusters* **1**, 83 (1993).
- ²⁵J. M. Behm, C. A. Arrington, and M. D. Morse, *J. Chem. Phys.* **99**, 6409 (1993).
- ²⁶J. M. Behm, C. A. Arrington, J. D. Langenberg, and M. D. Morse, *J. Chem. Phys.* **99**, 6394 (1993).
- ²⁷J. P. Desclaux, *At. Data Nucl. Data Tables* **12**, 311 (1973).