Spectroscopic studies of jet-cooled CuAg

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Resonant two-photon ionization spectroscopy has been applied to jet-cooled diatomic CuAg. Four band systems have been observed, three of which have been rotationally resolved and analyzed. The ground state is $X\,^1\Sigma^+$ in symmetry, deriving from the $3d_{Cu}^{10} 4d_{Ag}^{10}\sigma^2$ molecular configuration. Its bond length has been determined as $r_0 = 2.3735 \pm 0.0006$ Å (1σ error limits). Based on an analysis of the possible separated atom limits, three of the excited states observed ($A\,0^+$, $A'\,1$, and $B'\,0^+$) are assigned as primarily $3d_{Cu}^9 4d_{Ag}^{10}\sigma^2\sigma^*$ in character. The observation of unusually large electronic isotope shifts in the $A-X$, $A'-X$, and $B'-X$ band systems, similar in magnitude to those previously observed in the $A-X$ and $B-X$ systems of Cu_2 and the $s\leftarrow d$ excitations in atomic copper, provides further confirmation that these excited states derive from the $3d_{Cu}^9 4d_{Ag}^{10}\sigma^2\sigma^*$ molecular configuration. Finally, the highest energy state observed in this work is argued to be primarily ion pair in character, and is expected to have significant contributions from both the Cu^+Ag^- and Cu^-Ag^+ ion pair states.

I. INTRODUCTION

The diatomic copper group molecules Cu_2, Ag_2, Au_2, CuAg, CuAu, and AgAu are in many ways the simplest of the transition metal dimers, because all six diatomics are formed from atoms with filled d subshells. In their ground electronic states all are expected to possess the electronic configuration of $d_A^{10}d_B^{10}\sigma_{(g)}^2$, giving a $^1\Sigma_{(g)}^+$ ground molecular term. Furthermore, because the d orbitals are quite contracted at the right-hand side of the Periodic Table, and the d subshells are filled in the copper group elements, there can be no net d-orbital contributions to the chemical bonding in these molecules. Accordingly, these molecules will be bound only by the outer σ electrons, giving a net bond order of one. This makes the coinage metal dimers the transition metal analogs of H_2. As such, they provide an important standard of comparison which may be used to evaluate the magnitude of d-orbital contributions to the chemical bonding in the more complicated open d-subshell transition metal dimers. For this reason we have undertaken a program to study these species, so that a set of benchmarks may be obtained against which the bond lengths and bond strengths of other transition metal dimers may be judged.

Although a considerable number of gas-phase and matrix isolation spectroscopic studies have been performed on Cu_2 (Refs. 1–27), and to a lesser extent on Ag_2 (Refs. 2, 3, 10, 12, 28–38) and Au_2 (Refs. 2, 3, 39–42), rather little is spectroscopically known about the mixed coinage metal diatomics CuAg,[43,44] CuAu,[45] and AgAu. In this paper we report analyses of the $A-X$, $A'-X$, $B'-X$, and $B-X$ band systems of CuAg, observed using the resonant two-photon ionization (R2PI) spectroscopic technique. The following paper presents the results of a related study of CuAu, and the last of this series of three papers presents results on AgAu and Au_2.

The present study of CuAg was motivated principally by the need to have spectroscopic data for the filled d-sub-shell transition metal molecule CuAg for comparison with corresponding data for the open d-subshell molecules. Data for CuAg is particularly relevant to the mixed $3d-4d$ open d-subshell transition metal molecules, such as the previously investigated NiPd.[46] With such data in hand it will become possible to estimate the d-orbital contributions to the bonding in NiPd and related molecules. Section II briefly describes the experimental method employed in this work, while Sec. III presents our results. Section IV then provides a discussion of these results, identifies an unusual electronic isotope effect, and shows the importance of ion pair states in the spectroscopy of CuAg. Section V concludes the paper with a summary of our most important findings.

II. EXPERIMENT

This gas-phase spectroscopic investigation of CuAg was performed using the identical apparatus described previously in our reports on the spectroscopy of Al_3,[47] NiCu,[48] NiPd,[46] and NiPt,[49] among others. A metal target consisting of an equimolar alloy of copper and silver was prepared by melting the weighed metals in an electric arc. After cooling, the light yellow alloy was pressed flat and polished to give a disk-shaped sample 1 mm in thickness and 2.5 cm in diameter, which was suitable for pulsed laser vaporization using a rotating disk mount similar to that described by O'Brien et al.[50] Pulsed laser vaporization of the sample was achieved using the frequency-doubled output from a Q-switched Nd:YAG laser (532 nm, 15 mJ/pulse, focused to a diameter of approximately 0.5 mm). The ejected atoms were then entrained in a pulsed flow of helium (120 psi), which carried them through a channel 2 mm in diameter and 2 cm in length. Experiments were then performed with various extension channels, which were added to lengthen this channel prior to the final supersonic expansion into vacuum to improve the production of the diatomic CuAg. Ultimately, an extension channel 6 mm in length, tapering from a 5 mm

initial inside diameter down to a 1.5 mm exit orifice was chosen. The small exit orifice also promoted excellent supersonic cooling, so that low rotational temperatures were achieved.

The resulting molecular beam was then skimmed (5 mm skimmer) prior to its entrance into a reflectron time-of-flight mass spectrometer, where excitation was accomplished with a pulsed dye laser counterpropagating along the molecular beam path. Ionization was then achieved with a pulsed excimer laser operating on ArF (193 nm, 6.42 eV), which crossed the molecular beam at right angles. Ions were extracted with a Wiley–McLaren extraction assembly, traveled through a drift tube, were reflected in a second electrostatic field, traversed a second drift tube, and were detected with a dual microchannel plate detector. The optical spectra of $^{63}Cu^{107}Ag$, $^{63}Cu^{109}Ag/^{65}Cu^{107}Ag$, and $^{65}Cu^{109}Ag$ were then obtained by separately monitoring the ion signals at mass 170, 172, and 174, respectively, as a function of dye laser frequency.

The output of a side-pumped Hänsch configuration dye laser was narrowed for high resolution (0.03 cm^{-1}) studies by the insertion of an air-spaced intracavity etalon, which was then pressure scanned with SF$_6$. Absolute line positions were then obtained using the simultaneously recorded I$_2$ absorption spectrum in conjunction with the I$_2$ atlas of Gerstenkorn and Luc.[51] A difficulty in obtaining this absolute calibration arose because the observed band systems of CuAg all lie in the range from 20 800–26 600 cm^{-1}, while the I$_2$ atlas only covers the range up to about 20 000 cm^{-1}. This problem was overcome by Raman shifting the dye laser output radiation in high-pressure H$_2$ (≈ 500 psi). The dye laser fundamental radiation could then be used to obtain the spectrum of CuAg in high resolution while the first Stokes radiation was used to record the I$_2$ absorption spectrum. Since the Raman shifting process occurs only on the Raman line with the highest gain [in this case $Q(1)$, corresponding to a Raman shift of 4155.264 cm^{-1} according to the published[52] spectroscopic constants of H$_2$], the Stokes shifted output light appears at a precisely defined frequency relative to the fundamental, and the useful range of the I$_2$ atlas as a calibration may be extended about 4155 cm^{-1} to the blue. Finally, the Doppler shift experienced by the CuAg molecules as they travel toward the radiation source at the beam velocity of helium (1.77×10^5 cm/s) was included to provide accurate absolute line positions for all of the rotationally resolved bands.

Excited state lifetimes were measured by the time-delayed resonant two-photon ionization method, in which the delay between the excitation and ionization lasers is varied, and the ion signal is measured as a function of this delay. The resulting decay curves were fitted to exponential decay functions by a nonlinear least-squares algorithm,[53] allowing the upper state lifetimes to be extracted. For upper states with short lifetimes (below 200 ns) a convolution of a pure exponential decay with a Gaussian instrument function (FWHM of 15 ns) representing the convoluted dye and excimer laser pulses was included in the fitting function. This was required to obtain a reasonable fit to the data.

III. RESULTS

A. The $A\,0^+ \leftarrow X\,^1\Sigma^+$ system of CuAg

Figure 1 displays the low resolution resonant two-photon ionization spectrum of the A–X band system of CuAg, which was previously observed in emission from a King furnace by Ruamps.[43] The higher frequency bands of this system continue into Fig. 2, which displays the next band system ($A\,'$–X) as well. Although scans were performed as far to the red as 18 000 cm^{-1}, the A–X system is the lowest frequency band system which has been found. The long progression observed (up to the 11–0 band) is indicative of a large change in bond length upon electronic excitation, and high resolution studies confirm that the internuclear separation increases substantially in this transition. Frequencies of
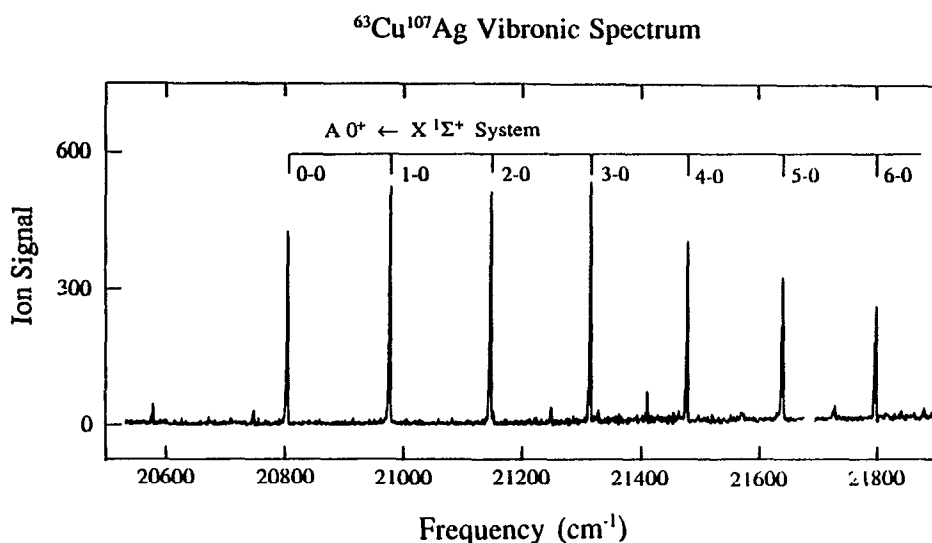

$^{63}Cu^{107}Ag$ Vibronic Spectrum

FIG. 1. Low-resolution spectrum of the $A\,0^+ - X\,^1\Sigma^+$ system of $^{63}Cu^{107}Ag$, recorded using coumarin 480 and 460 dye laser radiation in combination with an ArF excimer laser for photoionization. The weak features near 20 600, 20 750, 21 250, and 21 400 cm^{-1} are the 0–1, 1–1, 4–1, and 5–1 vibrational hot bands, respectively.

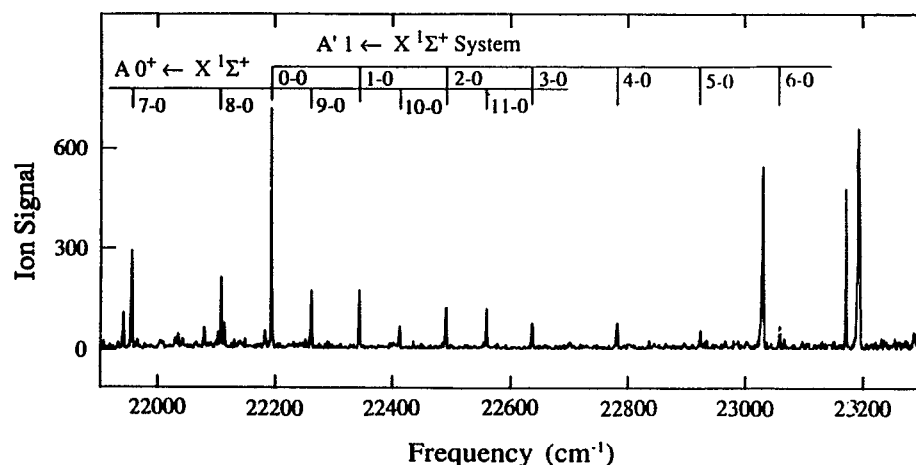## $^{63}Cu^{107}Ag$ Vibronic Spectrum

FIG. 2. Low-resolution spectrum of the A' $1-X$ $^1\Sigma^+$ system of $^{63}Cu^{107}Ag$, recorded using coumarin 460, 440, and stilbene 420, in combination with an ArF excimer laser for photoionization. Also evident in this figure are the higher vibrational bands of the A 0^+-X $^1\Sigma^+$ system, which are labeled up to the 11–0 band. Near 23 000 cm^{-1} the B' 0^+-X $^1\Sigma^+$ system begins, as is shown in more detail in Fig. 5.

the observed vibrational bands for $^{63}Cu^{107}Ag$ and the other isotopic modifications are given in Table I for all of the observed band systems. Excited state lifetimes, measured by the time-delayed R2PI technique, are given there as well. If the A state of CuAg decays solely by fluorescence to the ground X $^1\Sigma^+$ state, the measured lifetime of 32 ns corresponds to an absorption oscillator strength of $f\approx0.12$, making the $A-X$ system very strongly allowed. The observed vibrational levels of the $A-X$ system have been least squares fitted to obtain $\omega'_e = 173.16 \pm 0.02$ cm^{-1}, $\omega_e x'_e = 1.117 \pm 0.004$ cm^{-1}, and $\Delta G''_{1/2} = 229.2 \pm 0.3$ cm^{-1} for $^{63}Cu^{107}Ag$, in close agreement with the values reported by Ruamps[43] of $\omega'_e = 171.5$ cm^{-1} and $\omega_e x'_e < 0.50$ cm^{-1}.

High resolution scans were also performed over the 0–0, 1–0, 2–0, and 4–0 bands of the $A-X$ system, and fitted constants are provided in Table II. Absolute line positions are available through the Physics Auxiliary Publication Service (PAPS) of the American Institute of Physics[54] or from the author (M.D.M). As shown in Fig. 3, which displays the A–X 0–0 band for the predominant isotopic form $^{63}Cu^{107}Ag$, the rotationally resolved spectra show only P and R branches, implying an $\Omega' = 0 \leftarrow \Omega'' = 0$ transition. Given that the ground state must be described as X $^1\Sigma^+$ deriving from the $3d^{10}_{Cu}4d^{10}_{Ag}\sigma^2$ molecular configuration, this then implies that the $A-X$ band system is an $\Omega' = 0^+ \leftarrow X$ $^1\Sigma^+$ transition. In addition, the early bandhead in the R branch confirms that the bond lengthens considerably under electronic excitation. Fitting of the 0–0, 1–0, 2–0, and 4–0 bands to the formula

$$v = v_0 + B'J'(J' + 1) - B''J''(J'' + 1) \qquad (3.1)$$

then allows accurate values of v_0, B'', and B' to be obtained for each band. From the fits of these bands, B'_e and α'_e are obtained, and r'_e (A 0^+) is then accurately determined from the data for $^{63}Cu^{107}Ag$ as r'_e (A 0^+) = 2.522 $\pm$ 0.002 Å (1σ error limit).

B. The A' $1\leftarrow X$ $^1\Sigma^+$ system of CuAg

Figure 2 displays the next higher frequency band system found in CuAg, which has not previously been observed.[43,44] In order to retain the $A-X$ and $B-X$ labels previously assigned by Ruamps[43] this new system is assigned as $A'-X$. As is evident from the much longer lifetime of the A' state ($\approx3.8\mu s$) as compared to the A state (32 ns), the A' state is a relatively poor radiator and may well have been deactivated by collisional processes under the conditions of Ruamps' experiments. Again, assuming that the A' state decays entirely by fluorescence to the ground X $^1\Sigma^+$ state, the measured lifetime corresponds to an absorption oscillator strength of $f\approx0.001$, indicating that the $A'-X$ system is a much weaker band system than is the $A-X$ system. Nevertheless, the 0–0 through 6–0 vibrational bands have been observed in the present studies, and the 0–0 and 1–0 bands have been rotationally resolved and analyzed. Absolute line positions for these bands are provided through the Physics Auxiliary Publication Service (PAPS) of the American Institute of Physics[54] or the author (M.D.M.), and fitted constants are given in Table III.

Figure 4 displays the $A'-X$ 0–0 band of the $^{63}Cu^{107}Ag$ isotopic combination. Although the signal quality is not as good as that found for the $A\leftarrow X$ system, the obvious Q-branch identifies the A' state as having $\Omega' = 1$, and least-squares fitting of the observed lines to formula (3.1) allows accurate values of B'_e and α'_e to be obtained. The equilibrium internuclear separation $r'_e(A'$ $1)$ is then determined for $^{63}Cu^{107}Ag$ as $r'_e(A'$ $1)$ = 2.497 $\pm$ 0.004 Å (1σ error limit).

C. The B' $0^+\leftarrow X$ $^1\Sigma^+$ system of CuAg

Slightly further to the blue another new band system is found (see Fig. 5), which again was unobserved in previous King furnace emission studies.[43,44] To differentiate this new system from the previously assigned $B-X$ system,[43] it is proposed that the new system be labeled $B'-X$. It is somewhat

TABLE I. Vibronic bands of ^{63}Cu^{107}Ag.[a]

System	Band	Observed frequency (cm^{-1})[a,b]	Isotope shift (cm^{-1})[c]			Lifetime[d]
			^{63}Cu^{109}Ag	^{65}Cu^{107}Ag	^{65}Cu^{109}Ag	
$A–X$	0–0	* 20 807.20(− 08)	* + 0.087	+ 0.09	* + 0.324	39.9 ± 7.2 ns
	1–0	* 20 978.10(− 07)	* − 0.480	* − 1.397	* − 1.892	29.3 ± 2.7 ns
	2–0	* 21 146.82(09)	* − 1.043	* − 3.013	* − 4.032	29.7 ± 0.5 ns
	3–0	21 313.35(37)	− 1.41	− 4.24	− 6.12	⋯
	4–0	* 21 477.48(57)	* − 2.118	* − 6.061	* − 8.207	⋯
	5–0	21 637.76(− 76)	− 1.95	− 6.49	− 9.09	⋯
	6–0	21 797.48(− 33)	− 3.25	− 9.09	− 13.74	⋯
	7–0	21 954.92(14)	− 3.38	− 10.15	− 13.53	⋯
	8–0	22 109.15(− 28)	− 4.06	− 10.82	− 14.12	⋯
	9–0	22 261.91(15)	− 4.12	− 12.38	⋯	⋯
	10–0	22 412.50(73)	− 6.19	− 14.44	⋯	⋯
	11–0	22 558.96(− 50)	− 5.50	− 17.19	⋯	⋯
	0–1	20 578.47(37)	+ 1.33	+ 1.33	+ 3.54	30.9 ± 2.7 ns
	1–1	20 748.44(− 55)	+ 0.45	+ 0.44	+ 1.34	⋯
	4–1	21 247.49(− 25)	− 1.41	− 3.29	− 4.70	⋯
	5–1	21 409.78(43)	− 2.35	− 4.76	− 8.46	⋯
$A'–X$	0–0	* 22 195.56(− 14)	* + 0.121	+ 0.12	* + 0.441	4.27 ± 0.27 μs
	1–0	* 22 346.48(17)	* − 0.389	* − 0.854	* − 1.507	3.38 ± 0.09 μs
	2–0	22 495.08(32)	− 2.06	− 2.06	− 3.44	⋯
	3–0	22 640.50(− 56)	− 2.43	− 3.43	− 3.60	⋯
	4–0	22 785.38(19)	− 2.26	− 6.58	− 7.30	⋯
	5–0	22 927.20(02)	− 2.88	− 7.20	− 9.36	⋯
$B'–X$	0–0	23 031.22(61)	+ 0.75	+ 0.75	+ 0.75	⋯
	1–0	* 23 194.99(− 32)	* − 0.443	* − 1.305	* − 1.751	53.6 ± 2.4 ns
	2–0	23 356.59(− 89)	* − 2.113	− 1.20	− 3.44	57.3 ± 0.4 ns
	3–0	23 516.73(− 41)	− 1.49	− 2.26	− 5.97	⋯
	4–0	23 674.84(56)	− 2.35	− 5.48	− 7.82	⋯
	5–0	23 830.49(158)	− 3.38	− 7.08	− 9.42	⋯
	6–0	23 979.88(− 114)	− 3.36	− 9.38	− 12.52	⋯
$B–X$	0–0	25 826.62(− 98)	− 0.02	− 0.02	+ 0.26	12.2 ± 0.9 ns
	1–0	25 989.26(07)	− 0.36	− 0.36	− 2.19	⋯
	2–0	26 150.49(159)	− 1.02	− 2.95	− 2.95	16.4 ± 0.1 ns
	3–0	26 307.74(100)	− 1.50	− 3.70	− 5.07	⋯
	4–0	26 460.70(− 201)	− 1.97	− 5.23	− 7.46	14.9 ± 1.9 ns
	5–0	26 617.14(33)	− 2.87	− 6.74	− 8.67	⋯
	0–1	25 598.48(05)	+ 0.62	+ 0.62	+ 2.29	⋯
	2–1	25 921.09(136)	+ 0.36	− 0.36	− 1.19	10.9 ± 0.4 ns
	3–1	26 076.03(− 154)	− 0.26	− 1.64	− 1.64	⋯
	4–1	26 232.72(− 82)	− 0.53	− 1.91	− 3.56	14.0 ± 0.4 ns
	5–1	26 388.00(36)	⋯	⋯	⋯	⋯
	6–1	26 540.44(58)	⋯	⋯	⋯	⋯

[a] Bands indicated by asterisks were measured in high resolution using the I_2 atlas for calibration (Ref. 51). Vibronic bands for ^{63}Cu^{107}Ag were fitted to the formula $\nu = \nu_{00} + \omega'_e v' - \omega'_e x'_e (v'^2 + v') - v'' \Delta G''_{1/2}$ for $v'' = 0,1$, resulting in the following values, with errors given in parentheses corresponding to 1σ in the least-squares fit: $A–X$: $\nu_{00} = 20\,807.197(15)$; $\omega'_e = 173.157(23)$; $\omega'_e x'_e = 1.117(4)$; $\Delta G''_{1/2} = 229.17(30)$ (ν_{00}, ω'_e, and $\omega'_e x'_e$ obtained from band origins of the 0–0, 1–0, 2–0, and 4–0 bands; $\Delta G''_{1/2}$ obtained from a fit of all observed bands. The rms error in the fit of the accurately measured 0–0, 1–0, 2–0, and 4–0 band origins was only 0.008 cm^{-1}.) $A'–X$: $\nu_{00} = 22\,195.560(2)$; $\omega'_e = 152.76(41)$; $\omega'_e x'_e = 1.08(7)$. $B'–X$: $\nu_{00} = 23\,030.61(103)$; $\omega'_e = 167.21(93)$; $\omega'_e x'_e = 1.26(13)$. $B–X$: $\nu_{00} = 25\,827.60(93)$; $\omega'_e = 163.46(79)$; $\omega'_e x'_e = 0.94(12)$; $\Delta G''_{1/2} = 229.17(80)$.
[b] Following each observed frequency in the table, the residual $\nu_{obs} - \nu_{calc}$ is given in units of 0.01 cm^{-1} in parentheses.
[c] Isotope shifts are defined as ν(isotopic modification) $- \nu(^{63}$Cu^{107}Ag).
[d] Errors reported for lifetimes correspond to 1σ in the nonlinear least-squares fit.

surprising that the $B'–X$ system was not previously observed, because the upper state decays rapidly, having a measured lifetime of about 55 ns. If the B' state decays primarily by fluorescence to the ground $X\,^1\Sigma^+$ state, this corresponds to an absorption oscillator strength of $f \approx 0.05$. Perhaps fluorescence from the B' state was not observed in previous studies because of the near degeneracy between the B' and A' states, which could possibly lead to rapid collisional deactivation. A similar collisional process is known to occur in Cu$_2$, leading to efficient conversion of Cu$_2$ from its long-

lived $C\,1_u$ state ($\tau \approx 800$ ns) to the short-lived $B\,0_u^+$ state, which then radiates efficiently ($\tau \approx 40$ ns).[15,21] In any event, the 0–0 through 8–0 bands of the $B'–X$ system of CuAg have now been observed, and the 1–0 and 2–0 bands have been rotationally resolved and analyzed. Line positions are available through the Physics Auxiliary Publication Service of the American Physical Society[54] or the author (M.D.M), and fitted constants are given in Table IV. Absolute line positions are provided for the 1–0 band; only relative line positions are provided for the 2–0 band, however, because

TABLE II. Fitted constants for the $A\ 0^+ \leftarrow X\ ^1\Sigma^+$ system of CuAg.[a]

Band	$^{63}Cu^{107}Ag$	$^{63}Cu^{109}Ag$	$^{65}Cu^{107}Ag$	$^{65}Cu^{109}Ag$
0-0	$\nu_0 = 20\,807.198(2)$	$\nu_0 = 20\,807.285(2)$		$\nu_0 = 20\,807.533(3)$
	$B_0' = 0.066\,92(14)$	$B_0' = 0.066\,52(9)$		$B_0' = 0.065\,74(17)$
	$B_0'' = 0.075\,38(12)$	$B_0'' = 0.074\,85(9)$		$B_0'' = 0.073\,93(18)$
1-0	$\nu_0 = 20\,978.105(3)$	$\nu_0 = 20\,977.625(3)$	$\nu_0 = 20\,976.708(2)$	$\nu_0 = 20\,976.213(1)$
	$B_1' = 0.066\,25(16)$	$B_1' = 0.066\,11(14)$	$B_1' = 0.065\,63(15)$	$B_1' = 0.065\,12(8)$
	$B_0'' = 0.075\,14(19)$	$B_0'' = 0.074\,89(14)$	$B_0'' = 0.074\,48(18)$	$B_0'' = 0.073\,47(9)$
2-0	$\nu_0 = 21\,146.815(2)$	$\nu_0 = 21\,145.773(3)$	$\nu_0 = 21\,143.802(3)$	$\nu_0 = 21\,142.783(6)$
	$B_2' = 0.066\,21(9)$	$B_2' = 0.065\,18(25)$	$B_2' = 0.065\,96(18)$	$B_2' = 0.064\,55(43)$
	$B_0'' = 0.075\,48(8)$	$B_0'' = 0.074\,76(32)$	$B_0'' = 0.074\,49(22)$	$B_0'' = 0.073\,80(36)$
4-0	$\nu_0 = 21\,477.480(3)$	$\nu_0 = 21\,475.362(2)$	$\nu_0 = 21\,471.419(2)$	$\nu_0 = 21\,469.273(3)$
	$B_4' = 0.065\,77(14)$	$B_4' = 0.064\,72(9)$	$B_4' = 0.063\,76(21)$	$B_4' = 0.064\,03(15)$
	$B_0'' = 0.075\,91(13)$	$B_0'' = 0.074\,87(9)$	$B_0'' = 0.074\,01(26)$	$B_0'' = 0.073\,57(18)$

[a]All constants are given in units of wave numbers (cm^{-1}), with the 1σ error limits given in parentheses following each entry. These are obtained by fitting the measured line positions to the formula $\nu = \nu_0 + B'J'(J'+1) - B''J''(J''+1)$.

the I_2 calibration spectrum proved to be unassignable in this region.

Figure 6 displays a high resolution ($0.03\ cm^{-1}$) scan over the $B'-X$ 2-0 band of $^{63}Cu^{109}Ag$. The obvious lack of a Q branch again implies that both the upper and lower states are of 0^+ symmetry, and the presence of a bandhead in the R branch shows that the internuclear separation increases upon electronic excitation, although not as severely as in the $A-X$ system. A fit of the observed rotational lines for the 1-0 and 2-0 bands to formula (3.1) yields a bond length of $r_e'(B'\ 0^+) = 2.463 \pm 0.008$ Å for $^{63}Cu^{107}Ag$.

D. The $B\,(0^+?) \leftarrow X\,^1\Sigma^+$ system of CuAg

Finally, Fig. 7 shows the highest frequency band system thusfar observed for CuAg, the $B-X$ system. This band system has been previously observed in emission by Ruamps[43] in a King furnace. Joshi and Majumdar[44] have also observed a band system in CuAg or a related molecule in the same region, but the 0-0 band observed by them lies 25 cm^{-1} to the blue of the 0-0 band observed in the present investiga-

tion. Moreover, the vibrational constants found for the B state in the present study ($\nu_{0-0} = 25\,826.6\ cm^{-1}$, $\omega_e = 163.46 \pm 0.79\ cm^{-1}$, $\omega_e x_e = 0.94 \pm 0.11\ cm^{-1}$ for $^{63}Cu^{107}Ag$) differ substantially from those reported by Joshi and Majumdar[44] ($\nu_{0-0} = 25\,851.6\,cm^{-1}$, $\omega_e = 178.5\,cm^{-1}$, $\omega_e x_e = 0.50\ cm^{-1}$) but are only slightly different from those reported by Ruamps[43] ($\nu_{0-0} = 25\,825\ cm^{-1}$, $\omega_e = 166\ cm^{-1}$, $\omega_e x_e \simeq 1.5\ cm^{-1}$). The discrepancy with the results of Ruamps[43] may be explained by the fact that his measurements were taken from bandheads in a rotationally hot system, while ours are obtained under jet-cooled conditions and should be closer to the band origins. The results of Joshi and Majumdar,[44] however, probably correspond to either a different molecule altogether or result from an erroneous analysis.

The ability of Ruamps to observe the $B \rightarrow X$ system in emission in a King furnace results from the highly efficient radiative decay of the B state ($\tau \approx 14$ ns). Assuming that the B state decays exclusively by fluorescence to the $X\ ^1\Sigma^+$ ground state, this radiative lifetime implies an absorption
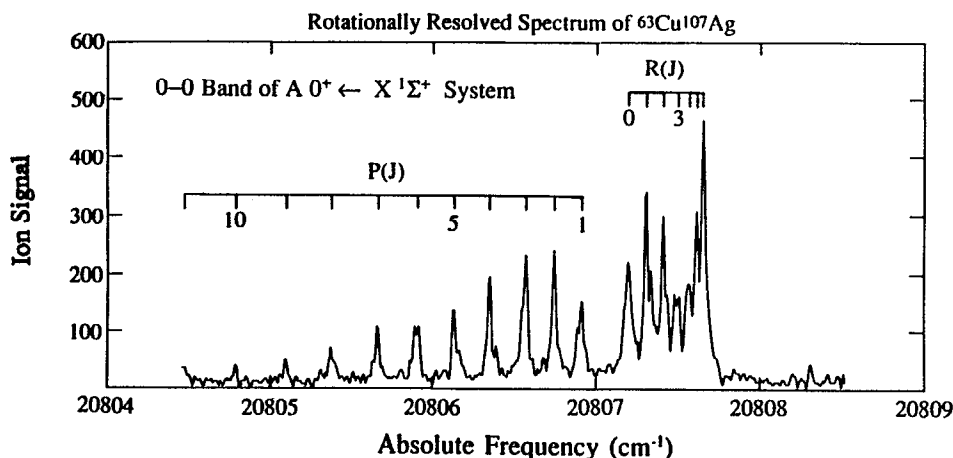

FIG. 3. High-resolution scan over the 0-0 band of the $A\ 0^+-X\ ^1\Sigma^+$ system of $^{63}Cu^{107}Ag$. The spectrum was recorded with an absolute calibration established by the absorption spectrum of I_2, as described in the text. The absence of a Q branch identifies the band system as $\Omega' = 0 \leftarrow \Omega'' = 0$ in character, and the severe R-branch head shows that the bond length increases substantially upon electronic excitation.

TABLE III. Fitted constants for the A′ 1←X $^1\Sigma^+$ system of CuAg.[a]

Band	$^{63}Cu^{107}Ag$	$^{63}Cu^{109}Ag$	$^{65}Cu^{107}Ag$	$^{65}Cu^{109}Ag$
0–0	$\nu_0 = 22\,195.560(2)$	$\nu_0 = 22\,195.681(3)$		$\nu_0 = 22\,196.001(2)$
	$B_0' = 0.067\,88(13)$	$B_0' = 0.067\,44(18)$		$B_0' = 0.065\,57(23)$
	$B_0'' = 0.075\,80(14)$	$B_0'' = 0.075\,23(22)$		$B_0'' = 0.073\,16(28)$
1–0	$\nu_0 = 22\,346.484(3)$	$\nu_0 = 22\,346.095(4)$	$\nu_0 = 22\,345.629(4)$	$\nu_0 = 22\,344.976(3)$
	$B_1' = 0.067\,11(24)$	$B_1' = 0.067\,16(30)$	$B_1' = 0.065\,38(36)$	$B_1' = 0.065\,13(31)$
	$B_0'' = 0.075\,94(30)$	$B_0'' = 0.075\,98(36)$	$B_0'' = 0.076\,14(47)$	$B_0'' = 0.073\,88(39)$

[a] All constants are given in units of wave numbers (cm^{-1}), with the 1σ error limits given in parentheses. These are obtained by fitting the measured line positions to the formula $\nu = \nu_0 + B'J'(J'+1) - B''J''(J''+1)$.

oscillator strength of $f \approx 0.16$, which corresponds to a very strongly allowed transition. We have not been able to rotationally resolve this system, for reasons that are not obvious, but we have reason to believe that the B state is also an $\Omega' = 0^+$ state. As will become clear in the remaining papers in this series, the excited states of the coinage metal dimers with $\Omega' = 0^+$ all tend to have some ion-pair character, which derives from the separated ion asymptote M_A^+ ($d^{10}s^0$, $^1S_0$) + M_B^- ($d^{10}s^2$, $^1S_0$), from which only one 0^+ state arises. For unlike atoms another ion-pair state of 0^+ symmetry derives from the $M_A^- + M_B^+$ separated ion limit. Of course, for like atoms these limits lie at the same energy, and the two molecular states correlating to them are of 0_g^+ and 0_u^+ symmetry. In any case, the transition from the $X\,^1\Sigma_{(g)}^+$ ground state to the $0_{(u)}^+$ ion pair state is a charge-transfer transition and should be extremely intense. All $0_{(u)}^+$ excited states have the possibility of borrowing intensity from this transition, in principle, and this correlates with the observation that the lifetimes of the $0_{(u)}^+$ excited states of the coinage metal diatomics tend to be substantially less than

those of the $\Omega' = 1$ excited states. For this reason we believe that a future investigation of the B state of CuAg will show it to be of $\Omega' = 0^+$ symmetry, with very significant ion-pair character.

Although we have not been able to rotationally resolve the B–X band system, it is nevertheless possible to estimate the B state bond length by a Franck–Condon analysis of the intensities of the vibrational bands. In general, we do not attempt to accurately record band intensities when we collect low-resolution spectra, and usually our spectra suffer to some degree from saturation effects. That is surely the case in the spectra of the B–X system shown in Fig. 7, particularly because this system is so strongly allowed. However, the hot bands originating from $v'' = 1$ of the $X\,^1\Sigma^+$ state show an interesting pattern, with the 0–1, 2–1, 3–1, 4–1, 5–1, and 6–1 bands present, but the 1–1 band missing. In general, the Franck–Condon pattern of intensities arising from a $v'' = 1$ vibrational level should exhibit a single node, and the placement of this node may be used to derive the difference in bond lengths of the two states. For the pattern just described (with the 1–1 band absent) this implies a bond length increase of 0.097 Å upon electronic excitation, thereby giving the B state bond length of $r_e'\,[B(0^+?)] = 2.467$ Å. Furthermore, the 1–1 band would surely be observed if it had 1/2 of the intensity of the 0–1 band or 1/3 of the intensity of the 2–1 band. These constraints allow us to set error limits on the quoted value as $r_e'\,[B(0^+?)] = 2.467 \pm 0.028$ Å.

IV. DISCUSSION

A. The $X\,^1\Sigma^+$ ground state of CuAg

The major new piece of information about the ground state of CuAg obtained through this study is an accurate measurement of the bond length. Because seven bands have been rotationally resolved and analyzed, with absolute frequency calibrations from the I_2 absorption spectrum, the value of $B_0''(X\,^1\Sigma^+)$ has been multiply determined, and the error in the measurement is reduced considerably. The resulting values are: $B_0''(^{63}Cu^{107}Ag) = 0.075\,562(51)$ cm^{-1}, $B_0''(^{63}Cu^{109}Ag) = 0.075\,046(50)$ cm^{-1}, $B_0''(^{65}Cu^{107}Ag) = 0.074\,477(103)$ cm^{-1}, and $B_0''(^{65}Cu^{109}Ag) = 0.073\,534(69)$ cm^{-1}, where the 1σ error limits are given in parentheses. These may be converted to bond lengths to give $r_0''(^{63}Cu^{107}Ag) = 2.3732(8)$ Å, $r_0''(^{63}Cu^{109}Ag) = 2.3734(8)$ Å, $r_0''(^{65}Cu^{107}Ag) = 2.3671(16)$ Å, and
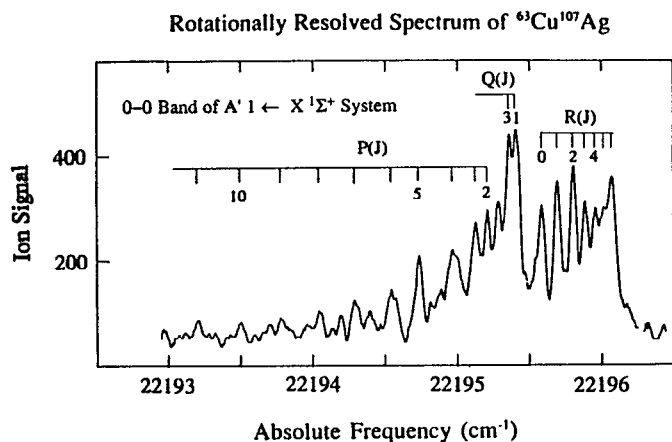
Rotationally Resolved Spectrum of $^{63}Cu^{107}Ag$

FIG. 4. High-resolution scan over the 0–0 band of the $A′\,1$–$X\,^1\Sigma^+$ system of $^{63}Cu^{107}Ag$. The spectrum was recorded with an absolute calibration established by the absorption spectrum of I_2, as described in the text. The presence of a Q branch identifies the band system as an $\Omega' = 1 \leftarrow \Omega'' = 0$ transition. Again, the R-branch head is indicative of an increase in bond length upon electronic excitation. Some of the unlabeled, weaker features in the P branch are due to a poor signal-to-noise ratio, and are probably not real transitions in the molecule.
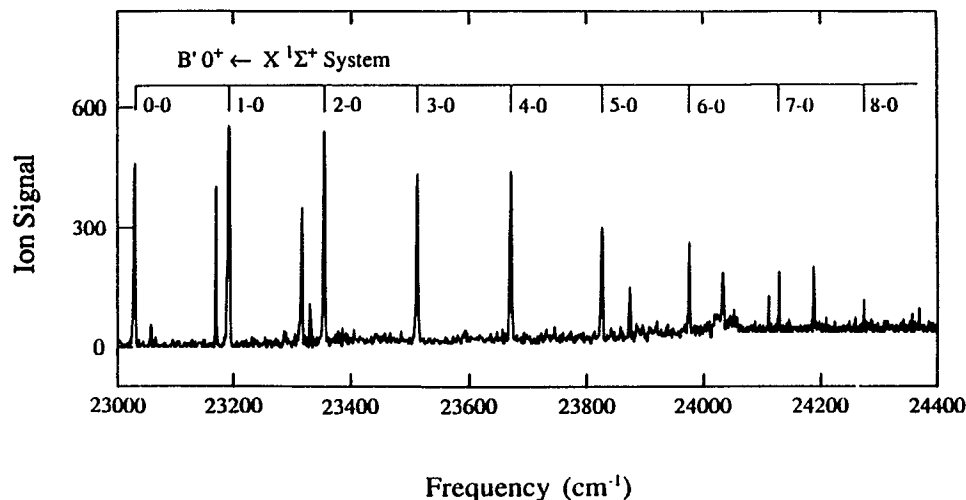
$^{63}Cu^{107}Ag$ Vibronic Spectrum

FIG. 5. Low-resolution spectrum of the $B' 0^+ - X^1\Sigma^+$ system of $^{63}Cu^{107}Ag$, recorded using coumarin 440 and stilbene 420 dye laser radiation with an ArF excimer laser for photoionization. This system is strongly allowed, and some of the unassigned features near the 1–0, 2–0, 5–0, and 6–0 bands may result from other vibronic levels of 0^+ electronic symmetry borrowing intensity from the intense $B' 0^+ - X^1\Sigma^+$ system. The unassigned band near 24 200 cm^{-1}, however, is strongly observed even in the absence of ArF radiation, and therefore must result from a three-photon process involving dye laser radiation alone. This is also true for some of the extraneous features near 22 100 cm^{-1} in Fig. 2, and is reminiscent of similar processes which we have observed in pure silver clusters. These features may possibly result from photofragmentation of larger clusters.

$r_0''(^{65}Cu^{109}Ag) = 2.3740(11)$ Å. The large discrepancy for the $^{65}Cu^{107}Ag$ isotopic modification no doubt reflects the fact that this species occurs at the same mass (172 amu) as the more prevalent $^{63}Cu^{109}Ag$ (33.3%) combination, and overlapping lines from the two species have made the analysis somewhat difficult, particularly for the less abundant species $^{65}Cu^{107}Ag$ (16.0%). With this in mind the best value of $r_0''(CuAg)$ may be obtained from the results for the isotopically pure mass features corresponding to $^{63}Cu^{107}Ag$ and $^{65}Cu^{109}Ag$, giving $r_0''(CuAg) = 2.3735(6)$ Å. This value is very near to the average of the r_0'' values for Cu_2 (2.2228 Å)[4] and Ag_2 (2.5335 Å),[37] which is 2.3782 Å. This would seem to indicate that covalent bond radii of about 1.111 Å for Cu and 1.267 Å for Ag are appropriate for intermetallic compounds of these elements.

High-temperature Knudsen effusion mass spectrometry has been used to estimate the bond strength of CuAg as $D_0^0(CuAg) = 1.76 \pm 0.10$ eV.[55] This was determined by the third-law method, however, and erroneous estimates of the vibrational frequency and bond length (estimated as 250 cm^{-1} and 2.51 Å, respectively) were used. Using the correct values as determined in the present work leads to a slight revision, giving $D_0^0(CuAg) = 1.74 \pm 0.10$ eV.

Finally, we note that in unpublished work[56] James, Lemire, and Langridge-Smith have used two tunable dye lasers in a resonant two-photon ionization scheme to determine the ionization potential of CuAg as IP(CuAg) = 7.7806 $\pm$ 0.0004 eV. As might be expected, this is intermediate between the ionization potentials of the homonuclear diatomics Cu_2 (IP = 7.899 $\pm$ 0.007 eV)[57] and Ag_2 (IP = 7.56 $\pm$ 0.02 eV).[58] Together with the revised bond strength of CuAg given above and the atomic ionization potentials [IP(Cu) = 7.726 380(12) eV[59] and IP(Ag) = 7.574 eV[60]], this implies bond strengths for CuAg$^+$ of $D_0^0(Cu-Ag^+) = 1.54 \pm 0.10$ eV and $D_0^0(Cu^+-Ag) = 1.69 \pm 0.10$ eV.

B. The $d_{Cu}^9 d_{Ag}^{10} \sigma^2 \sigma^*$ excited states of CuAg

Table V summarizes the spectroscopic constants derived in the work described above, and Fig. 8 presents experimentally derived potential energy curves for the ground and

TABLE IV. Fitted constants for the $B' 0^+ \leftarrow X^1\Sigma^+$ system of CuAg.[a]

Band	$^{63}Cu^{107}Ag$	$^{63}Cu^{109}Ag$	$^{65}Cu^{107}Ag$	$^{65}Cu^{109}Ag$
1–0	$\nu_0 = 23\,194.986(2)$	$\nu_0 = 23\,194.543(2)$	$\nu_0 = 23\,193.680(3)$	$\nu_0 = 23\,193.235(3)$
	$B_1' = 0.067\,46(16)$	$B_1' = 0.067\,83(14)$	$B_1' = 0.066\,42(18)$	$B_1' = 0.065\,06(32)$
	$B_0'' = 0.075\,49(20)$	$B_0'' = 0.076\,09(16)$	$B_0'' = 0.074\,45(22)$	$B_0'' = 0.072\,77(41)$
2–0	$\nu_0 = 7.214(3)$[b]	$\nu_0 = 5.101(2)$[b]		
	$B_2' = 0.065\,69(14)$	$B_2' = 0.065\,62(11)$		
	$B_0'' = 0.075\,85(14)$	$B_0'' = 0.075\,69(10)$		

[a] All constants are given in units of wave numbers (cm^{-1}), with the 1σ error limits given in parentheses. These are obtained by fitting the measured line positions to the formula $\nu = \nu_0 + B'J'(J'+1) - B''J''(J''+1)$.

[b] Absolute line positions (and an absolute value for ν_0) could not be obtained for the 2–0 band, since the I_2 absorption spectrum proved to be unassignable in this region. Accordingly, the values of ν_0 for this band are meaningless.
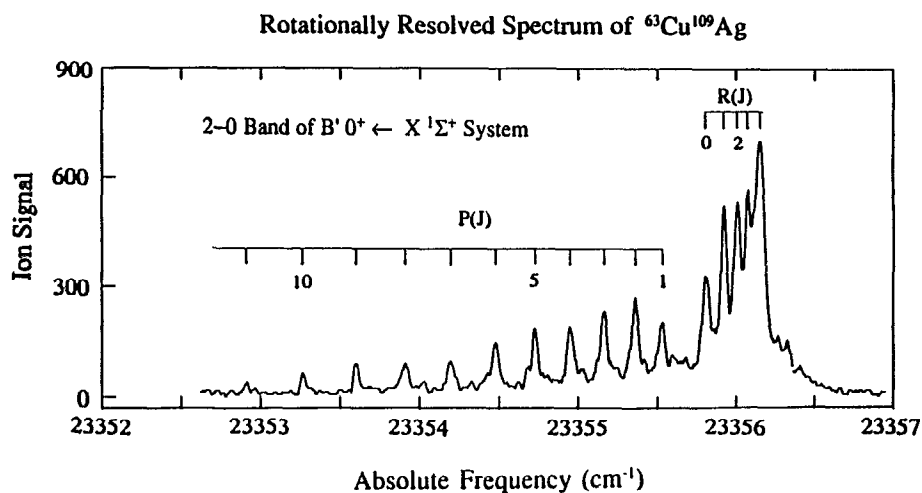
Rotationally Resolved Spectrum of $^{63}Cu^{109}Ag$

FIG. 6. High-resolution scan over the 2–0 band of the $B'\,0^+ - X\,^1\Sigma^+$ system of $^{63}Cu^{109}Ag$. This spectrum was recorded without an absolute calibration established by the absorption spectrum of I_2, since the I_2 spectrum proved to be unassignable in this region. Nevertheless, the absence of a Q branch identifies the band system as $\Omega' = 0 \leftarrow \Omega'' = 0$ in character, and the severe R-branch head shows that the bond length increases substantially upon electronic excitation.

excited states of CuAg. From the data presented in Table V the well depths, D_e, of the four observed excited states of CuAg may be estimated by assuming that they follow a Morse function behavior, giving $D_e = \omega_e^2/4\omega_e x_e$. This may be converted to D_0 by subtracting the excited state zero-point energy, and from this value the energy of the separated atom limit of the excited state, E_{SA}, may be derived by adding the frequency of the origin band, ν_{00}, and subtracting the bond strength of the ground state, D_0, to give

$$E_{SA} = \omega_e^2/4\omega_e x_e - \omega_e/2 + \omega_e x_e/4 + \nu_{00} - D_0. \quad (4.1)$$

This very approximate analysis places the dissociation limits of the excited states of CuAg 1.66, 1.67, 1.79, and 2.33 eV above ground state atoms, for the $A\,0^+$, $A'\,1$, $B'\,0^+$, and B (0^+?) states, respectively. Fortunately, the atomic spectroscopy of copper and silver is well known,[60] and excited separated atom limits lie at 1.39 eV ($3d^9 4s^2$, $^2D_{5/2}$ Cu + $4d^{10}5s^1$,

^2S Ag), 1.64 eV ($3d^9 4s^2$, $^2D_{3/2}$ Cu + $4d^{10}5s^1$, ^2S Ag), 3.66 eV ($3d^{10}4s^1$, ^2S Cu + $4d^{10}5p^1$, $^2P_{1/2}$ Ag), and at higher energies. From these values it seems likely that the excited states of CuAg observed in the present work must correlate to states in which an electron has been removed from the $3d$ subshell of copper and placed in a σ^* orbital, giving excited molecular configurations of $3d^9_{Cu}\,4d^{10}_{Ag}\,\sigma^2\sigma^*$.

Further evidence that these excited states correspond asymptotically to $s \leftarrow d$ transitions on the copper atom is provided from the high-resolution data presented above. From these data absolute band origins have been obtained for the various isotopic combinations of $^{63,65}Cu^{107,109}Ag$, and these may be used to evaluate the magnitude of any electronic isotope effects which may be present. It has previously been observed that excitations changing the number of $3d$ electrons on a copper atom lead to rather large electronic isotope shifts (≈ 0.07 cm^{-1}) in both the free atom[25,61-65] and in Cu_2.[25] The observation of significant electronic isotope ef-
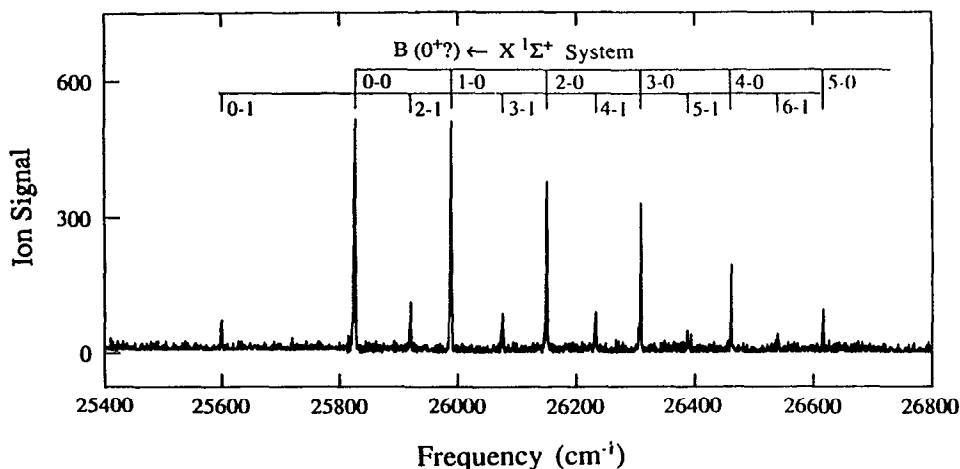
$^{63}Cu^{107}Ag$ Vibronic Spectrum

FIG. 7. Low-resolution spectrum of the $B\,(0^+?) - X\,^1\Sigma^+$ system of $^{63}Cu^{107}Ag$. This system is strongly allowed ($\tau \approx 14$ ns), and probably corresponds to a charge transfer band system in which the B state has significant ion pair character. For this reason it is thought that the B state is of 0^+ symmetry, even though attempts to rotationally resolve the system have been unsuccessful.

TABLE V. Electronic states of $^{63}Cu^{107}Ag$.[a]

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 (Å)	Lifetime (μs)
$B(0^+?)$	25 827.63(93)	163.46(79)	0.94(12)	$\cdots$	$\cdots$	2.467(28)[b]	0.014(2)
$B'0^+$	23 030.61(103)	167.21(93)	1.26(13)	0.070 15(46)	0.001 79(21)	2.463(8)	0.055(3)
$A'1$	22 195.560(2)	152.76(41)	1.08(7)	0.068 26(23)	0.000 77(27)	2.497(4)	3.83(63)
$A0^+$	20 807.198(2)	173.157(23)	1.117(4)	0.066 90(12)	0.000 27(5)	2.522(2)	0.032(5)
$X^1\Sigma^+$	0.00	$\Delta G''_{1/2} = 229.17(28)$		$B_0 = 0.075\ 56(5)$		$r_0 = 2.3732(8)$	$\cdots$

[a] Uncertainties are given in parentheses, and correspond to 1σ in a least-squares fit. For the lifetime measurements the calculated standard deviations were unreasonably small, and were reestimated by examining the spread in lifetimes reported in Table I. D_0^0(CuAg) = 1.74(10) eV (as re-evaluated in the text); IP(CuAg) = 7.7806(4) eV (Ref. 56); D_0^0(Cu$^+$–Ag) = 1.69(10) eV; D_0^0(Cu–Ag$^+$) = 1.54(10) eV.

[b] The r_e value for the B state is estimated from a Franck–Condon analysis, as discussed in Sec. III D. The error estimate is based on the assumption that the 1–1 band possesses less than 1/2 the intensity of the 0–1 band, and less than 1/3 of the intensity of the 2–1 band.

fects may therefore be used as evidence that the electronic transitions involve $s \leftarrow d$ promotion on the copper atom.

To consider the possibility of electronic isotope shifts in CuAg, we note that the frequency of the v'–v'' band origin for isotopic species i is given by[66]

$$\nu_{v'-v''}(i) = \nu_e^{(i)} - (v'' + 1/2)\omega_e''(i)$$
$$+ (v'' + 1/2)^2\omega_e''x_e''(i)$$
$$+ (v' + 1/2)\omega_e'(i)$$
$$+ (v' + 1/2)^2\omega_e'x_e'(i). \quad (4.2)$$

The frequencies ω_e', ω_e'', and anharmonicities $\omega_e'x_e'$, $\omega_e''x_e''$ for two different isotopic modifications labeled i and j are related by

$$\omega_e(j) = \omega_e(i)\rho_{ij}$$

and $\qquad\qquad\qquad\qquad\qquad\qquad (4.3)$

$$\omega_e x_e(j) = \omega_e x_e(i)\rho_{ij}^2,$$

where $\rho_{ij} = (\mu_i/\mu_j)^{1/2}$, and μ_i, μ_j represent the reduced masses of the i, j isotopic combinations, respectively. Taking the difference of expression (4.2) for the isotopic combinations i and j, and simplifying using Eq. (4.3), we obtain

$$\nu_{v'-v''}(i) - \nu_{v'-v''}(j)$$
$$= \nu_e^{(i)} - \nu_e^{(j)} - (v'' + 1/2)\omega_e''(i)(1 - \rho_{ij}) + (v''$$
$$+ 1/2)^2\omega_e''x_e''(i)(1 - \rho_{ij}^2) + (v' + 1/2)\omega_e'(i)$$
$$\times(1 - \rho_{ij}) - (v' + 1/2)^2\omega_e'x_e'(i)(1 - \rho_{ij}^2). \quad (4.4)$$

This expression may finally be solved for the electronic isotope shift, $\nu_e^{(i)} - \nu_e^{(j)}$, giving

$$\nu_e^{(i)} - \nu_e^{(j)} = \nu_{v'-v''}(i) - \nu_{v'-v''}(j) + (v'' + 1/2)\omega_e''(i)$$
$$\times(1 - \rho_{ij}) - (v'' + 1/2)^2\omega_e''x_e''(i)(1 - \rho_{ij}^2)$$
$$- (v' + 1/2)\omega_e'(i)(1 - \rho_{ij})$$
$$+ (v' + 1/2)^2\omega_e'x_e'(i)(1 - \rho_{ij}^2). \quad (4.5)$$

Normally one would expect the electronic isotope shift, $\nu_e^{(i)} - \nu_e^{(j)}$, to be close to zero. When the transition takes a copper d electron into an s orbital, however, it has been observed that spectroscopic features in the ^{65}Cu isotope fall

0.03–0.07 cm^{-1} to the red of where they would otherwise be expected. A discussion of the various contributions leading to this phenomenon has been previously given.[25] In the present study we choose the $^{63}Cu^{107}Ag$ isotopic combination as a reference point, and evaluate the electronic isotope shifts as $\nu_e^{(63-107)} - \nu_e^{(j)}$ using Eq. (4.5). The results, along with 1σ
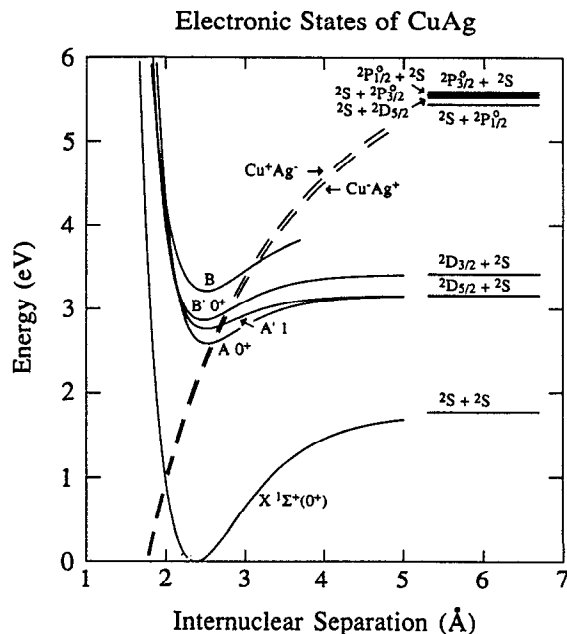

FIG. 8. Qualitative potential energy curves for the experimentally known electronic states of CuAg. Bond lengths, vibrational frequencies, and electronic energies are taken from Table V. Potential curves are plotted as Morse potentials, with anharmonicities adjusted to force dissociation to the appropriate separated atom limits. An exception to this is the B state, which is plotted with the experimentally observed anharmonicity. The ion pair curves for Cu$^+$Ag$^-$ and Cu$^-$Ag$^+$ are plotted as dashed lines, without any corrections to account for the polarizability of one ion in the field of the other, or for Pauli repulsions at short distances. The position of the experimental curve for the B state suggests strongly that it cannot dissociate to Cu(^2D) + Ag(^2S), and its nearness to the estimated ion pair curves suggests that it may be best described as an ion pair state itself.

TABLE VI. Measured electronic isotope shifts in CuAg (cm⁻¹).[a]

Band		$\nu_e^{63-107} - \nu_e^{63-109}$	$\nu_e^{63-107} - \nu_e^{65-107}$	$\nu_e^{63-107} - \nu_e^{65-109}$
A–X	0–0	0.0108(30)	···	0.0414(43)
	1–0	0.0021(38)	0.0330(38)	0.0451(36)
	2–0	0.0052(38)	0.0507(39)	0.0212(68)
	4–0	0.0063(33)	0.0306(43)	0.0420(50)
	Average	0.0067(17)	0.0385(23)	0.0407(23)
A'–X	0–0	0.0109(39)		0.0699(47)
	1–0	0.0146(58)		0.0615(102)
	Average	0.0120(32)		0.0684(43)
B'–X	1–0	−0.0025(61)	0.0343(151)	0.0301(504)

[a]Calculated from the data of Tables I–IV and Eq. (4.5), assuming $\omega_e''(^{63}Cu^{107}Ag) = 229.2(3)$ cm⁻¹ and $\omega_e''x_e''(^{63}Cu^{107}Ag) = 0$. By ignoring the unknown anharmonicity of the ground state, systematic overestimates of the electronic isotope shifts result. These overestimates are probably about 0.003, 0.010, and 0.013 cm⁻¹ for $\nu_e^{63-107} - \nu_e^{63-109}$, $\nu_e^{63-107} - \nu_e^{65-107}$, and $\nu_e^{63-107} - \nu_e^{65-109}$, respectively, assuming a ground state $\omega_e''x_e''$ of 1 cm⁻¹.

errors derived by treating the errors in each term of Eq. (4.5) as uncorrelated, are given in Table VI. Although the observed electronic isotope shifts are quite small (typically at or below the limit of our dye laser linewidth of 0.03 cm⁻¹), the statistical errors in their determination are generally smaller than this, particularly for the A–X system where ω_e' and $\omega_e'x_e'$ are well determined. It is clear from Table VI that the electronic isotope shift is quite small (no larger than 0.01 cm⁻¹) and possibly not statistically significant for the replacement of ^{107}Ag by ^{109}Ag. On the other hand, the electronic isotope shift observed for the replacement of ^{63}Cu by ^{65}Cu is about 0.04 cm⁻¹ for the A–X system, 0.07 cm⁻¹ for the A'–X system, and 0.03 cm⁻¹ for the B'–X system. These values are statistically different from zero, and are comparable to those found for the A–X and B–X systems of Cu₂, which are 0.068 and 0.063 cm⁻¹, respectively.[25] This tends to confirm the assignment of the excited states of CuAg observed in this work as $d_{Cu}^9 d_{Ag}^{10}\sigma^2\sigma^*$ in electronic character.

Table VII lists the molecular electronic states which arise from the first few separated atom limits in CuAg, in both Hund's case (a) and (c) nomenclature. If the upper states are well described in case (a), the only states deriving from the $3d^94s^2$, ^2D Cu + $4d^{10}5s^1$, ^2S Ag separated atom limit which are accessible from the ground $^1\Sigma^+$ state are one $^1\Sigma^+$ ($\Omega' = 0^+$) state and one $^1\Pi$ ($\Omega' = 1$) state. On the other hand, if the states deriving from this separated atom asymptote are thoroughly mixed by spin–orbit interactions, two states with $\Omega' = 0^+$ and four states with $\Omega' = 1$ will be optically accessible from the ground $^1\Sigma^+$ ($\Omega' = 0^+$) state. Our observation of two $\Omega' = 0^+$ states and one state with $\Omega' = 1$ is intermediate between the two limits. As Table VII shows, the two $\Omega' = 0^+$ states (the A and B' states) must correlate to the two separated atom limits $3d^94s^2$, $^2D_{5/2}$ Cu + $4d^{10}5s^1$, ^2S Ag and $3d^94s^2$, $^2D_{3/2}$ Cu + $4d^{10}5s^1$, ^2S Ag, since no other 0^+ states arise from separated atom limits below 29 552 cm⁻¹. Because of the similar intensities of the $\Omega' = 0^+ \leftarrow X^1\Sigma^+$ transitions, the two $\Omega' = 0^+$ states must be described as strongly mixed $^1\Sigma^+(\Omega' = 0^+)$ and $^3\Pi_{0+}$ ($\Omega' = 0^+$) states, which are probably also strongly mixed with the $^1\Sigma^+$ states deriving from the separated ion pair limits of Cu⁺Ag⁻ and Cu⁻Ag⁺. Indeed, the ion pair states expected in this energy region provide the source of the oscillator strength in transitions from the ground state, and thereby account for the great disparity in transition intensities for the strong $\Omega' = 0^+ \leftarrow X^1\Sigma^+$ systems as compared to the much weaker $\Omega' = 1 \leftarrow X^1\Sigma^+$ system. With this in mind, it would seem that state mixing may be less severe in the $\Omega' = 1$ manifold of states, so that the A' 1 state can be assigned as primarily $^1\Pi_1$ in character, and the other $\Omega' = 1$ states arising from the $3d^94s^2$, ^2D Cu + $4d^{10}5s^1$, ^2S Ag separated atom limit may be relatively pure, remaining optically inaccessible under electric dipole selection rules.

C. Ion-pair states of CuAg

As mentioned in Sec. III D, ion pair states deriving from ground state Cu⁺ (^1S) + Ag⁻ (^1S) and Cu⁻ (^1S)

TABLE VII. Separated atom limits in CuAg.

Separated atom limit Copper	Silver	Energy (cm⁻¹)[a]	Case (c) states[b]	Case (a) states[b]
Cu⁺ ($^1S_0$)	Ag⁻ ($^1S_0$)	51 816	0⁺	$^1\Sigma^+$
Cu⁻ ($^1S_0$)	Ag⁺ ($^1S_0$)	51 184	0⁺	$^1\Sigma^+$
$d^{10}s^1$, $^2S_{1/2}$	d^9s^2, $^2D_{3/2}$	34 714.16	0⁺,0⁻,1,1,2	$\{\,^1\Sigma^+, ^3\Sigma^+, ^1\Pi,$
$d^{10}s^1$, $^2S_{1/2}$	d^9s^2, $^2D_{5/2}$	30 242.26	0⁺,0⁻,1,1,2,2,3	$^3\Pi, ^1\Delta, ^3\Delta\,\}$
$d^{10}p^1$, $^2P_{3/2}^0$	$d^{10}s^1$, $^2S_{1/2}$	30 783.69	0⁺,0⁻,1,1,2	$\{\,^1\Sigma^+, ^3\Sigma^+,$
$d^{10}p^1$, $^2P_{1/2}^0$	$d^{10}s^1$, $^2S_{1/2}$	30 535.30	0⁺,0⁻,1	$^1\Pi, ^3\Pi\,\}$
$d^{10}s^1$, $^2S_{1/2}$	$d^{10}p^1$, $^2P_{3/2}^0$	30 472.71	0⁺,0⁻,1,1,2	$\{\,^1\Sigma^+, ^3\Sigma^+,$
$d^{10}s^1$, $^2S_{1/2}$	$d^{10}p^1$, $^2P_{1/2}^0$	29 552.05	0⁺,0⁻,1	$^1\Pi, ^3\Pi\,\}$
d^9s^2, $^2D_{3/2}$	$d^{10}s^1$, $^2S_{1/2}$	13 245.42	0⁺,0⁻,1,1,2	$\{\,^1\Sigma^+, ^3\Sigma^+, ^1\Pi,$
d^9s^2, $^2D_{5/2}$	$d^{10}s^1$, $^2S_{1/2}$	11 202.56	0⁺,0⁻,1,1,2,2,3	$^3\Pi, ^1\Delta, ^3\Delta\,\}$
$d^{10}s^1$, $^2S_{1/2}$	$d^{10}s^1$, $^2S_{1/2}$	0.00	0⁺,0⁻,1	$^1\Sigma^+, ^3\Sigma^+$

[a]From Ref. 60.
[b]From Ref. 66.

+ Ag$^+$ (^1S) separated ion limits are expected to be important in the excited states of CuAg which are of 0^+ symmetry. To illustrate this possibility, Fig. 8 shows dashed potential curves which display the Coulomb attraction experienced by these ion pairs as they are brought together from the appropriate asymptotic limits. The curves correspond to a pure Coulomb ($-e^2/R$) attraction, and do not include the possibility of stronger attractions due to the polarizability of the ions. Neither do they include repulsive interactions arising from the Pauli repulsions of the filled orbitals as the ions approach one another. Because of the neglect of such repulsive interactions, the curves display the unphysical behavior of going to $-\infty$ as the ions approach, while in reality they would turn up as repulsive forces become more important.

It is clear from Fig. 8 that these ion pair states will pass near to the observed excited electronic states of CuAg. In particular, it appears that the B state of CuAg is located too high in energy to correlate to either of the Cu(^2D) + Ag(^2S) separated atom limits. Given the revised bond strength of D_0^0(CuAg) = 1.74 $\pm$ 0.10 eV, the known energetics of the copper atom,[60] and the value of ν_{00} for the B–X system, the B state potential curve would have to be only about 1450 cm^{-1} deep for this state to dissociate to the $3d^94s^2$, $^2D_{3/2}$ Cu + $4d^{10}5s^1$, ^2S Ag separated atom limit. Since vibrational levels have been observed up to an energy of 943 cm^{-1} for the CuAg B state, it is unlikely that dissociation will abruptly occur within another 500 cm^{-1}. Therefore it may be assumed that the B state dissociates to a higher energy state of the separated atoms. However, if the B state dissociates to one of the next higher separated atom limits, its bond strength must be about 50% greater than that of the ground state. This is difficult to understand, since these separated atom limits correspond to promotion of either a silver $4d$ electron to a $5s$ orbital (giving a $3d^{10}4s^1$ Cu + $4d^95s^2$ Ag separated atom limit) or a silver $5s$ electron to a $5p$ orbital (giving a $3d^{10}4s^1$ Cu + $4d^{10}5p^1$ Ag separated atom limit). The former case cannot explain the great bond strength of the B state, since this separated atom limit gives only $\sigma^2\sigma^*$ configurations, with bond orders of 1/2, which should be more weakly bound than the ground state. The latter possibility does give states with a net bond order of one, but the bond should nevertheless be weaker than that of the ground state because the $5p$ orbital of silver is diffuse and expected to be almost nonbonding.

In light of these difficulties, and in view of the nearness of the estimated ion pair curves, the B state of CuAg is probably best described as an ion pair state, particularly at large internuclear separations where its potential curve parallels the ion pair curves of Cu$^+$(^1S) + Ag$^-$(^1S) and Cu$^-$(^1S) + Ag$^+$(^1S). Such an interpretation is enticing because the short lifetime of the B state (14 ns) is quite reasonable for a charge-transfer system with good wave function overlap between the two centers.

For CuAg the similarity in the ionization potentials [IP(Cu) = 7.726 380(12) eV;[59] IP(Ag) = 7.574 eV[60]] and electron affinities [EA(Cu) = 1.228(10) eV; EA(Ag) = 1.302(7) eV][67] of the two metals makes it diffi-cult to guess whether the B state corresponds primarily to Cu$^+$ + Ag$^-$ or Cu$^-$ + Ag$^+$, since the predicted ion pair curves lie so close in energy. In reality the two ion pair curves probably mix strongly, leading to two 0^+ excited states with small net permanent dipole moments. In the process one state increases its oscillator strength in transitions to the ground state, while the oscillator strength of the second state is reduced. In the ultimate limit of two identical atoms, the two ion pair states become 0_g^+ and 0_u^+ in symmetry, and only the 0_u^+ state may be reached in optical transitions from the ground $^1\Sigma_g^+$ (0_g^+) state of the homonuclear dimer. In contrast to CuAg, the disparity in electronic properties between Cu and Au allows the excited 0^+ states of CuAu observed in the next paper to be characterized as having substantial Cu$^+$Au$^-$ electronic character. In the present example of CuAg it seems definite that the lifetimes of the excited states of 0^+ symmetry are shortened substantially by an admixture of ion pair character in their electronic wave functions.

V. SUMMARY

Spectra of jet-cooled CuAg in the 20 000–27 000 cm^{-1} range have been recorded and analyzed. Four band systems have been observed, and three have been rotationally resolved and analyzed. The ground state has been determined to be $^1\Sigma^+$ in character, corresponding to a molecular configuration of $3d_{Cu}^{10}4d_{Ag}^{10}\sigma^2$, with a bond length of r_0''(CuAg) = 2.3735(6) Å. The third-law determination of the bond strength has been slightly revised using the experimentally determined vibrational frequency and bond length, to give D_0^0(CuAg) = 1.74 $\pm$ 0.10 eV.

The excited electronic states observed in the 20 000–27 000 cm^{-1} range correlate primarily to $3d_{Cu}^9 4d_{Ag}^{10}\sigma^2\sigma^*$ states of the molecule. In part, this is established simply by considering the possible atomic limits lying in the appropriate energy range. Additional evidence has been found, however, in the form of anomalous electronic isotope effects associated with the replacement of ^{63}Cu by ^{65}Cu. Such electronic isotope effects have been previously observed in atomic copper and in Cu$_2$, and seem to be associated with transitions changing the number of $3d$ electrons on the copper atom.

Finally, ion pair states are shown to be important in the excited states of CuAg of 0^+ symmetry, and it is argued that the B state may be best described as an ion pair state. The short lifetime of this state (14 ns) is indicative of a strongly allowed charge-transfer transition, as would occur between a covalent and an ion pair state. Moreover, the B state lies somewhat too high in energy to correlate to the Cu(^2D) + Ag(^2S) separated atom limit, and is in the region where an ion pair state might well be expected to occur. It is also argued that all of the $3d_{Cu}^9 4d_{Ag}^{10}\sigma^2\sigma^*$ states of 0^+ symmetry borrow intensity from the ion pair states, thereby accounting for the much shorter lifetimes of these 0^+ states as compared to the $\Omega = 1$ excited state, which is located in the same spectral region.

ACKNOWLEDGMENTS

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