Spectroscopic analysis of jet-cooled AlCu

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Diatomic AlCu has been interrogated using resonant two-photon ionization spectroscopy in a supersonic expansion of helium. The ground state is shown to be $X\ ^1\Sigma^+$, deriving from the $3s^2_{Al}3d^{10}_{Cu}\sigma^2$ configuration, in agreement with theoretical predictions. The closed-shell nature of this molecule results in a low density of electronic states, allowing the chemical bonding and electronic structure to be investigated in detail. Five excited electronic states have been observed and characterized, leading to a potential energy diagram based solely on experimental results. Constants experimentally determined for AlCu include a ground state bond length (r_0) of 2.3389 ± 0.0004 Å, a dissociation energy, D°_0, of 2.315 ± 0.012 eV, and an ionization potential of 7.065 ± 0.014 eV.

I. INTRODUCTION

In this manuscript we report the results of a resonant two-photon ionization (R2PI) spectroscopic study of jet-cooled diatomic AlCu. This represents the first of a series of investigations of the $3d$ transition metal aluminides, which will be followed by reports on the spectra and electronic structure of AlNi (Ref. 1), AlZn (Ref. 2), and AlCa (Ref. 3) (and possibly others). The purpose of these studies is to obtain experimental results which probe the chemical bonding between p-block and d-block metals, thereby gaining insight into the roles of $s\sigma$–$p\sigma$, $d\sigma$–$p\sigma$, and $d\pi$–$p\pi$ bonding in these mixed main group transition metal molecules. It will be particularly interesting to determine whether the atomic configuration of the transition metal atom ($d^m s^2$ or $d^{m+1}s^1$) has an influence on the preferred orientation of the lone $3p$ electron of aluminum ($p\sigma$ vs $p\pi$).

Significant effort has been expended, both theoretically and experimentally, to determine the extent of d orbital participation in the chemical bonding of the d-block transition-metal diatomics. Experimentally, the importance of such contributions has been evaluated by comparison of the open d subshell diatomics to their closed d subshell analogs. Similarly, the p-block metal dimer, Al_2,[4] has been investigated to study the competition between $p\sigma$ and $p\pi$ bonding in a molecule with a deficiency of valence electrons. In the series of studies initiated by this article we hope to shed light on the importance of both effects: the contribution of the d orbitals of the transition metal to the chemical bonding, and the competition between $p\sigma$–$s\sigma$, $p\sigma$–$d\sigma$, and $p\pi$–$d\pi$ bonding in a mixed main group transition metal molecule, as exemplified by the transition-metal aluminides.

The $4d$ transition metal aluminides AlPd (Ref. 5) and AlAg (Ref. 6) have been previously investigated and shown to have $3s^2_{Al}4d^{10}_{Pd}\sigma^1$, $^2\Sigma^+$ and $3s^2_{Al}4d^{10}_{Ag}\sigma^2$, $^1\Sigma^+$ ground states, respectively. Likewise, AlAu has been shown to have a $3s^2_{Al}5d^{10}_{Au}\sigma^2$, $^1\Sigma^+$ ground state.[7] In addition, unclassified emission bands attributed to AlPt have been observed in the region $16\,700–18\,300$ cm^{-1}.[8] Apart from these studies of the $4d$ and $5d$ transition metal aluminides, however, the only other transition metal alu-

minide to our knowledge to have received any attention is the $3d$ metal aluminide, AlCu.[9] The A–X, B–X, and D–X band systems of this molecule have been observed in a laser-induced fluorescence (LIF) investigation by Cai et al.,[9] and theoretical studies have been performed by the NASA-Ames group[10,11] and by Bär and Ahlrichs.[12] The theoretical calculations predict a two-electron σ bond between the $3p$ electron of aluminum and the $4s$ electron of copper, resulting in a $3s^2_{Al}3d^{10}_{Cu}\sigma^2$, $^1\Sigma^+$ ground state that is analogous to the ground states of AlAg and AlAu. Finally, several Knudsen cell mass spectrometric determinations of the AlCu bond strength have been made,[13–16] resulting in values ranging from 2.14 to 2.19 eV.

The present study reports five band systems in diatomic AlCu, three of which are new. In addition to vibrational information, the resonant two-photon ionization technique has allowed specific members of each of the five band systems to be rotationally resolved and analyzed, thereby demonstrating that the ground state is indeed $^1\Sigma^+$ in symmetry, with a bond length (r_0) of 2.3389 ± 0.0004 Å. The direct determination of the Ω' values for each excited state, along with bond lengths, dissociation energies, and vibrational constants, has permitted the construction of a potential energy diagram for the low-lying states of AlCu. The ionization potential of AlCu is also determined in the present study.

Section II contains a brief description of the experimental technique employed in this investigation, while Sec. III presents the results obtained for AlCu. These are discussed in terms of the electronic structure and chemical bonding in AlCu, and are compared to previous studies in Sec. IV. Section V then concludes the paper with a presentation of our most important findings.

II. EXPERIMENT

The resonant two-photon ionization spectrometer employed in these studies has been described previously in detail[17] and has ben extensively used for studies reported in other publications from this laboratory. Diatomic AlCu was produced by laser vaporization (Nd:YAG, 532 nm) of a target disc composed of an equimolar alloy of the two

constituent metals in the throat of a pulsed supersonic nozzle, which was rotated and translated to prevent the vaporization laser from drilling a hole through the sample. Following supersonic expansion into vacuum, the cold AlCu molecules entrained in helium carrier gas (typical backing pressure of 40–80 psi) were collimated by a 5 mm skimmer prior to their entrance into the ionization region of a reflectron time-of-flight mass spectrometer. In this region, excitation of the molecules was accomplished with a pulsed Nd:YAG-pumped tunable dye laser counterpropagating along the molecular beam path. The second, ionizing photon was provided by a pulsed excimer laser operating on KrF (248 nm, 5.00 eV) or ArF (193 nm, 6.42 eV) which crossed the molecular beam at right angles, or by frequency doubled dye light. In the latter case, frequency doubled dye laser radiation [generated by a servo-tracked, angle-tuned potassium dihydrogen phosphate (KDP) doubling crystal] was used to both excite the AlCu molecule and to supply the ionization photon. Ions thus created were mass separated via time of flight and detected with a dual microchannel plate detector. The optical spectra of $^{27}Al^{63}Cu$ and $^{27}Al^{65}Cu$ were collected by individually monitoring the ion signals at masses 90 and 92, respectively, as a function of dye laser frequency.

Rotationally resolved spectra were recorded under high resolution (0.04 cm^{-1}) via insertion of an air-spaced intracavity etalon into the dye laser, which was pressure scanned from 0 to 1 atm with Freon 12 (CCl$_2$F$_2$, DuPont). Absolute line positions were obtained using the simultaneously recorded I$_2$ transmission spectrum in conjunction with the I$_2$ atlas of Gerstenkorn and Luc.[18] For the low-energy band system of AlCu near 14 900 cm^{-1} and the high energy band systems of AlCu above 25 000 cm^{-1}, the fundamental of the dye laser radiation was Raman shifted in 500 psi of H$_2$, and the first anti-Stokes or second Stokes output, respectively, was used to record the transmission spectrum of I$_2$ concurrently with the AlCu spectrum. As described by Clouthier and Karolczak,[19] the H$_2$ Raman shifting process occurs exclusively on the Q(1) line, and at 500 psi this results in a Raman shift of 4155.162 cm^{-1}, allowing for a precise calibration of the spectrum. A final correction for the Doppler shift experienced by the AlCu molecules as they traveled toward the radiation source at the beam velocity of helium (1.77×10^5 cm/s), amounting to less than 0.18 cm^{-1}, then completed the calibration of the rotationally resolved data.

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,[20] allowing upper state lifetimes to be extracted.

III. RESULTS

A. Low energy region: The $^1\Pi(1) \leftarrow X\ ^1\Sigma^+$ band system

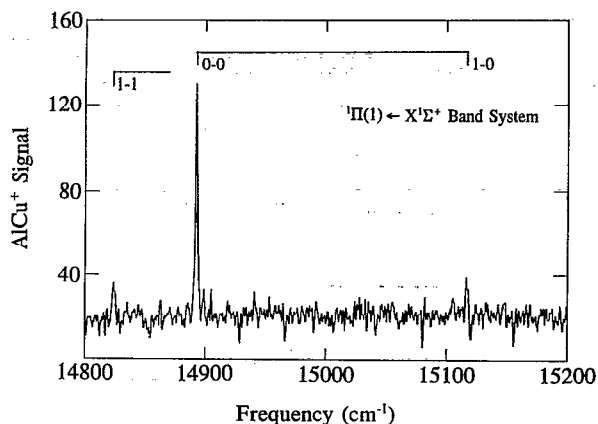The spectral region from approximately 13 900 to 17 500 cm^{-1} was scanned in search of the theoretically

FIG. 1. Low resolution R2PI spectrum of the $^1\Pi(1) \leftarrow X\ ^1\Sigma^+$ band system of jet-cooled $^{27}Al^{63}Cu$, recorded using LDS 698 laser dye in conjunction with ArF excimer radiation for photoionization. The intensity of this band system is much weaker than the other observed band systems, consistent with the $^1\Pi(1)$ state lifetime of 71 ± 3 μs.

predicted[10] low-lying $^3\Pi$ state and the $^1\Pi$ state which also arises from the ground separated atom limit of Al($3s^23p^1$, $^2P^o$) + Cu($3d^{10}4s^1$,^2S). Throughout this entire region only one moderately intense feature at 14 892 cm^{-1} was discovered (assigned as a 0-0 band), accompanied by two very weak features at 14 824 cm^{-1} (thought to be the 1-1 band) and 15 116 cm^{-1} (identified as the 1-0 band) as shown in Fig. 1 and reported in Table I. Although the weak intensity of the 1-0 and 1-1 bands prevented rotational analysis and the measurement of precise band origins, approximate vibrational intervals have been determined as $\Delta G''_{1/2} = 292.4$ cm^{-1} for the ground state and $\Delta G'_{1/2} = 224.1$ cm^{-1} for the excited state. This ground state vibrational interval, $\Delta G''_{1/2}$, compares well with the value of 290.7 cm^{-1} obtained in a previous LIF study[9] (as calculated from the reported values of ω''_e and $\omega''_e x''_e$).

The 0-0 band of this system was investigated under high resolution, enabling the rotational structure to be resolved and analyzed. As shown in Fig. 2, the P and R branches fan out in a nearly symmetrical manner, indicating that the bond length is only slightly changed upon electronic excitation. This has the effect of putting most of the Franck–Condon intensity in the 0-0, 1-1, 2-2, etc. bands, thereby explaining the low intensity of the 1-0 band and the absence of higher v'-0 bands in the spectrum. A fit of the measured rotational line positions to the formula

$$\nu = \nu_0 + B_0' J'(J'+1) - B_0'' J''(J''+1) \qquad (3.1)$$

confirmed that the ground state of AlCu is indeed an $\Omega'' = 0$ state (which must be the $\Omega'' = 0^+$, $^1\Sigma^+$ ground state predicted by *ab initio* quantum chemistry). The observation of a Q branch then shows that $\Omega' = 1$. The fitted rotational constants, B_0' and B_0'', were inverted to obtain bond lengths of $r_0' = 2.3531 \pm 0.0008$ Å and $r_0'' = 2.3389 \pm 0.0004$ Å for the upper and lower states, respectively. It should be noted that this value for the ground state represents a weighted average of the bond lengths $r_0(X\ ^1\Sigma^+)$ obtained for all of the rotationally resolved bands which

TABLE I. Vibronic bands of $^{27}\text{Al}^{63}\text{Cu}$. Vibrational bands were fitted to the formula $\nu = \nu_{00} + \omega'_e v' - \omega'_e x'_e (v'^2 + v') - v'' \Delta G''_{1/2}$ for $v'' = 0,1$, except for the $C-X$ system, where a term $\omega'_e y'_e (v'^3 + 3v'^2/2 + 3v'/4)$ was added to account for higher anharmonicities. Fitted constants are $^1\Pi(1) \leftarrow X$, $\nu_{00} = 14\,892.2744(20)$; $\Delta G'_{1/2} = 224.15$; $\Delta G''_{1/2} = 292.40$ cm^{-1}. $A\,0^+ \leftarrow X$, $\nu_{00} = 25\,574.96(75)$; $\omega'_e = 178.47(53)$; $\omega'_e x'_e = 1.957(64)$; $\Delta G''_{1/2} = 294.06(59)$ cm^{-1}; $A'\,0^+ \leftarrow X$, $\nu_{00} = 25\,920.187$; $\omega'_e = 312.18$; $\omega'_e x'_e = -5.81$ cm^{-1}; $B\,0^+ \leftarrow X$; $\nu_{00} = 26\,372.37(1.91)$; $\omega'_e = 208.11(74)$; $\omega'_e x'_e = 3.747(53)$ cm^{-1}; $C\,1 \leftarrow X$; $\nu_{00} = 28\,401.29(0.57)$; $\omega'_e = 112.50(28)$; $\omega'_e x'_e = 2.999(31)$; $\omega'_e y'_e = 0.0298(10)$ cm^{-1}.

System	Band	Measured frequency (cm^{-1})[a]	Isotope shift (cm^{-1})[b]	Lifetime (μs)[c]
$^1\Pi(1) \leftarrow X\,^1\Sigma^+$	0-0	14 892.2744[d]	+0.1720(30)[d]	71(3)
	1-0	15 116.42		
	1-1	14 824.02	−0.39	
$A\,0^+ \leftarrow X\,^1\Sigma^+$	0-0	25 576.2194[d](1.26)	0.2519(35)[d]	0.016(1)
	1-0	25 750.0402[d](0.53)	−0.5312(36)[d]	0.016(2)
	2-0	25 920.4324[d](0.27)		0.024(3)
	3-0	26 086.5157[d](−0.37)	−1.9941(40)[d]	0.016(1)
	4-0	26 248.08(−1.62)	−2.97	0.028(1)
	5-0	26 407.48(−1.12)	−2.89	0.017(1)
	6-0	26 564.91(1.32)	−3.07	0.010(1)
	7-0	26 714.39(−0.27)	−3.82	0.014(3)
	0-1	25 279.95(−0.94)	1.33	
	1-1	25 454.01(−1.45)	1.60	
	2-1	25 626.81(0.71)	−0.52	
	3-1	25 793.51(0.68)	−0.83	
	5-1	26 115.97(1.42)	−1.97	
	6-1	26 269.61(0.08)	−3.01	
	7-1	26 420.10(−0.50)	−3.10	
$A'\,0^+ \leftarrow X\,^1\Sigma^+$	0-0[e]	25 920.1868[d]	−3.05	0.188(7)
	1-0[e]	26 243.99	−4.29	0.100(5)
	2-0[e]	26 579.41	−2.34	0.091(20)
$B\,0^+ \leftarrow X\,^1\Sigma^+$	0-0	26 371.0068[d](−1.36)	0.1757(32)[d]	0.020(2)
	1-0	26 569.12[f]		0.033(2)
	2-0	26 765.65(−0.46)	−1.82	0.022(12)
	3-0	26 952.81(1.07)	−2.47	
	4-0	27 131.60(1.73)	−2.78	
	5-0	27 302.07(1.56)	−3.24	
	6-0	27 465.10(1.44)	−4.58	
	7-0	27 618.28(−1.04)	−4.25	
	8-0	27 766.05(−1.43)	−5.77	
	9-0	27 905.36(−2.78)	−5.57	
	10-0	28 038.04(−3.28)	−4.59	
	11-0	28 170.76(3.77)		
	12-0	28 285.97(0.79)		
$C\,1 \leftarrow X\,^1\Sigma^+$	0-0[g]	28 399.90(−1.39)	−1.68	0.118(6)
	1-0[g]	28 508.76(0.87)	−4.49	
	2-0[g]	28 608.93(0.16)	−2.76	
	3-0[g]	28 704.79(0.70)	−2.76	
	4-0[g]	28 794.66(0.62)	−2.15	
	5-0[g]	28 879.31(0.50)	−4.04	
	6-0[g]	28 958.45(−0.10)	−3.10	
	7-0[g]	29 032.90(−0.56)	−3.10	
	8-0[g]	29 103.61(−0.11)	−3.50	
	9-0[g]	29 169.34(−0.15)	−3.50	
	10-0[g]	29 229.75(−1.23)	−3.18	
	11-0[g]	29 287.82(−0.52)	−4.48	
	12-0[g]	29 341.25(−0.51)	−3.52	
	13-0[g]	29 392.15(0.74)	−4.16	
	14-0[g]	29 437.46(−0.30)	−2.24	

TABLE I. (*Continued.*)

System	Band	Measured frequency (cm^{-1})[a]	Isotope shift (cm^{-1})[b]	Lifetime (μs)[c]
$C1 \leftarrow X^1\Sigma^+$	15-0[g]	29 480.88(0.71)	−2.88	
	16-0[g]	29 519.93(0.31)	−2.30	
	17-0[g]	29 556.68(0.66)	−2.30	
	18-0[g]	29 590.25(0.70)	−3.61	
	19-0[g]	29 619.11(−1.29)	−0.33	
	20-0[g]	29 648.65(−0.09)	−1.31	

[a]Following each measured frequency, the residual $\nu_{obs} - \nu_{calc}$ for the least-squares fit is given in parentheses.
[b]The isotope shift is reported as $\nu(^{27}Al^{65}Cu) - \nu(^{27}Al^{63}Cu)$. In cases where this was measured in high resolution, the 1σ error limit is reported in parentheses.
[c]Errors reported for lifetimes correspond to 1σ in the nonlinear least-squares fit.
[d]Measured in high resolution, with calibration based on the I_2 atlas.
[e]Vibrational numbering of $A'-X$ system is hypothetical; see text for details.
[f]The $B-X$ 1-0 band is omitted from the fit because the $B,v=1$ level is perturbed by $A,v=6$ and especially by $A',v=2$.
[g]The vibrational numbering of the $C-X$ system is uncertain, due to poor Franck–Condon factors at low v' and numerous perturbations, which make isotope shifts meaningless.

were free of obvious perturbations. By taking a weighted average, the uncertainty in the quoted value (which represents one standard deviation) is reduced significantly. Measured and fitted line positions for both the $^{27}Al^{63}Cu$ and $^{27}Al^{65}Cu$ isotopic modifications, for this and all other rotationally resolved bands of AlCu, are available from the Physics Auxiliary Publication Service (PAPS) of the American Institute of Physics[21] or from the author (M.D.M.). The final fitted rotational constants and their 1σ standard errors are reported in Table II.

The fluorescence lifetime of this state has been measured by the resonant two-photon ionization technique to be 71 ± 3 μs. Assuming this decay lifetime is entirely due to fluorescence to the ground electronic state, this long lifetime corresponds to an absorption oscillator strength of $f \approx 1 \times 10^{-4}$, consistent with the meager intensity of the band.

The low energy of the upper state of this band system suggests strongly that it derives from the ground separated atom limit, particularly when it is compared to

the bond strength of the AlCu molecule, determined below as $D_0^o(AlCu) = 2.315 \pm 0.012$ eV $(18674 \pm 100$ $cm^{-1})$. Assuming the upper state of this system derives from ground state separated atoms, this implies that it is bound by $D_0 \approx 3782$ cm^{-1}. From the $Al(3s^23p^1,^2P^o)$ $+Cu(3d^{10}4s^1,^2S)$ ground separated atom limit only four electronic states arise: the $X^1\Sigma^+$ ground state and $^3\Sigma^+$, $^1\Pi$, and $^3\Pi$ states. Candidates for the $\Omega = 1$ upper state are then the $^1\Pi_1$, $^3\Sigma_1^+$, and $^3\Pi_1$ states. The $^3\Sigma^+$ state, which corresponds to a $\sigma^1\sigma^{*1}$ configuration, seems unlikely to be bound sufficiently or to have a short enough bond length to account for the upper state of this system. The analogous $\sigma_g^1\sigma_u^{*1},^3\Sigma_u^+$ state of Cu_2, for example, is bound by only 1000–1500 cm^{-1} and has a bond length 0.26 Å greater than that of the ground state.[22] In addition, high level quantum chemical calculations predict the $^3\Sigma^+$ state of AlCu to be repulsive.[11] The $^1\Pi$ and $^3\Pi$ states of AlCu, on the other hand, derive from a $\sigma^1\pi^1$ configuration in which the σ electron (and possibly the π electron as well) possess some degree of bonding character, in keeping with the well
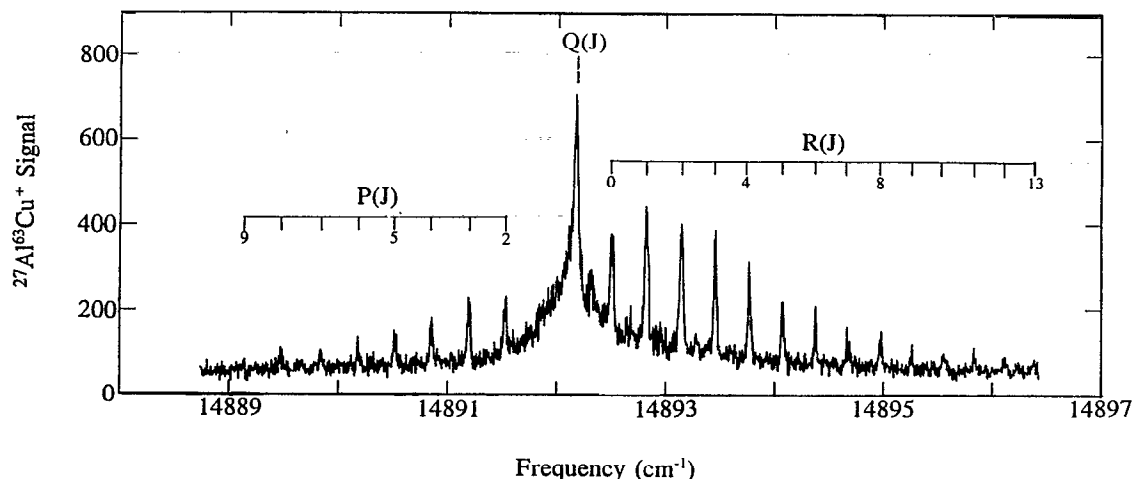

FIG. 2. Rotationally resolved scan of the 0-0 band of the $^1\Pi(1) \leftarrow X^1\Sigma^+$ system of $^{27}Al^{63}Cu$, recorded as described in Fig. 1 and the text.

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

System	Band	^{27}Al^{63}Cu	^{27}Al^{65}Cu
$^1\Pi(1) \leftarrow X\,^1\Sigma^+$	0-0	$\nu_0 = 14\,892.2744(20)^a$	$\nu_0 = 14\,892.4464(23)^a$
		$B_0' = 0.161\,22(11)$	$B_0' = 0.160\,00(12)$
		$B_0'' = 0.162\,88(13)$	$B_0'' = 0.161\,65(13)$
$A\,0^+ \leftarrow X\,^1\Sigma^+$	0-0	$\nu_0 = 25\,576.2194(24)^a$	$\nu_0 = 25\,576.4713(25)^a$
		$B_0' = 0.134\,36(14)$	$B_0' = 0.133\,27(15)$
		$B_0'' = 0.163\,11(17)$	$B_0'' = 0.161\,71(18)$
	1-0	$\nu_0 = 25\,750.0402(22)^a$	$\nu_0 = 25\,749.5090(28)^a$
		$B_1' = 0.132\,47(16)$	$B_1' = 0.131\,95(20)$
		$B_0'' = 0.162\,93(19)$	$B_0'' = 0.162\,14(22)$
	2-0^c	$\nu_0 = 25\,920.4324(39)^{a,b}$	
		$B_2' = 0.163\,50(19)^b$	
		$B_0'' = 0.163\,29(17)^b$	
	3-0	$\nu_0 = 26\,086.5157(23)^a$	$\nu_0 = 26\,084.5216(33)^a$
		$B_3' = 0.128\,86(13)$	$B_3' = 0.128\,23(30)$
		$B_0'' = 0.162\,93(16)$	$B_0'' = 0.161\,92(40)$
$A'0^+ \leftarrow X\,^1\Sigma^+$	0-0^{b,c}	$\nu_0 = 25\,920.1868(30)^{a,b}$	
		$B_0' = 0.154\,23(16)^b$	
		$B_0'' = 0.164\,24(15)^b$	
$B\,0^+ \leftarrow X\,^1\Sigma^+$	0-0	$\nu_0 = 26\,371.0068(15)^a$	$\nu_0 = 26\,371.1825(28)^a$
		$B_0' = 0.141\,01(10)$	$B_0' = 0.139\,73(27)$
		$B_0'' = 0.163\,63(11)$	$B_0'' = 0.162\,42(31)$
$C\,1 \leftarrow X\,^1\Sigma^+$	0-0^d	$\nu_0 = 28\,399.88$	$\nu_0 = 28\,398.22$
		$B_0' = 0.108\,18(67)$	$B_0' = 0.106\,43(10)$
		$B_0'' = 0.161\,71(58)$	$B_0'' = 0.157\,39(37)$

[a] Accurate band origins established with the aid of the I$_2$ atlas.

[b] The $A',v=0$ and $A,v=2$ levels perturb one another strongly, making analysis difficult for the A–X 2-0 and A'–X 0-0 bands. The analyses reported here employed the known B_0 value for the $X\,^1\Sigma^+$ state and a combination differences method of analysis.

[c] Vibrational numbering of the A' state is hypothetical.

[d] Vibrational numbering of the $C1$ state may be in error, due to serious Franck–Condon difficulties at low v', and perturbations which render the isotope shifts erratic and meaningless. Moreover, the absolute frequency of this band is imprecisely known due to difficulties in absolute calibration.

depth ($D_0 \approx 3782$ cm^{-1}) and bond length ($r_0' = 2.3531 \pm 0.0008$ Å) found for the upper $\Omega' = 1$ state. One would expect a $^3\Pi_1$ state to exhibit a long radiative lifetime, consistent with the value of $\tau = 71 \pm 3$ μs obtained for the upper state of this system. On the other hand, subbands terminating on the $^3\Pi_0$ ($\Omega = 0^+$) substate should be observed, particularly since this substate can be mixed by spin–orbit coupling with the $^1\Sigma^+$ ion-pair state (Al$^+$ + Cu$^-$), which carries a tremendous oscillator strength in the analogous coinage metal diatomics. The fact that these $\Omega' = 0^+ \leftarrow X\,^1\Sigma^+$ transitions are not found then argues in favor of an assignment of the upper state as $^1\Pi$. However, if the upper state is the $^1\Pi$ state, it is difficult to explain the long fluorescence lifetime of 71 ± 3 μs, since the $^1\Pi \rightarrow X\,^1\Sigma^+$ emission should be fully allowed.

On the basis of extensive *ab initio* calculations[11] on the ground and excited states of AlCu, however, this predicament is solved: The upper state is indeed the $\sigma^1\pi^1$, $^1\Pi$ state deriving from ground state atoms. In a highly correlated calculation, the $^1\Pi$ state is predicted to lie 13 602 cm^{-1} above the ground $X\,^1\Sigma^+$ state, and is calculated to have a 92 μs fluorescence lifetime,[11] in excellent agreement with the experimental results reported above. In addition, the calculated[11] r_0 and $\Delta G_{1/2}$ are 2.437 Å and 184 cm^{-1}, re-

spectively, in fair agreement with experiment. The long lifetime of this excited state may be rationalized if one considers the π orbital as localized on the aluminum, and the σ orbital as having very little $3s_{Al}$ character. The band system therefore corresponds to the $3p\pi \leftarrow 3p\sigma$ excitation on an isolated aluminum atom, which is rigorously forbidden under electric dipole selection rules. As a result, one may take the low oscillator strength of the $(1)^1\Pi \leftarrow X\,^1\Sigma^+$ transition as evidence that the $3s$ orbital of aluminum fails to form an sp hybrid with the $3p\sigma$ orbital in diatomic AlCu.

B. High energy region: $A\,0^+$–$X\,^1\Sigma^+$ and $A'\,0^+$–$X\,^1\Sigma^+$ band systems

Higher energy regions were investigated using coumarin dyes (24 200–17 000 cm^{-1}), exalite dyes (27 200–24 700 cm^{-1}), and frequency doubled LDS dyes (31 200–25 000 cm^{-1}). Contained in this energy region were four band systems, two of which are presented in this subsection.

The A–X band system reported previously by Cai *et al.*[9] was observed in the region between 25 600 cm^{-1} and 27 000 cm^{-1} using both the exalite and doubled dye
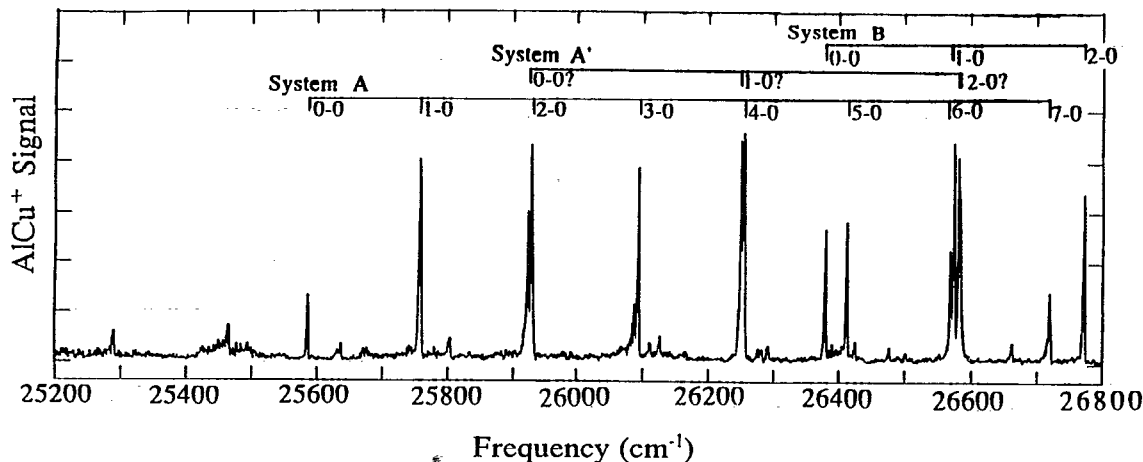
FIG. 3. Low resolution R2PI spectrum of the $A\,0^+ \leftarrow X\,^1\Sigma^+$ band system of $^{27}\text{Al}^{63}\text{Cu}$, recorded using Exalite 398, 389, 384, and 376 laser dyes in conjunction with KrF excimer radiation for photoionization. The 0-0 through 2-0 bands of the B–X system are likewise found in this energy region along with the previously unobserved $A'\,0^+ \leftarrow X\,^1\Sigma^+$ system, which is only detected when the $A'0^+$ state borrows intensity from the $A\,0^+$ or $B\,0^+$ states.

schemes. The low resolution spectrum of this band system obtained with the exalite dyes is displayed in Fig. 3, along with a new system (designated the A'–X system) and a portion of the B–X system (previously observed by Cai *et al.*[9]). The measured spectroscopic constants of $\Delta G''_{1/2}$, ω'_e, and $\omega'_e x'_e$, and band positions for the A–X system are given in Table I. The measured ground state vibrational interval, $\Delta G''_{1/2}=294.1$ cm^{-1}, is in good agreement with that obtained from the analysis of the $(1)^1\Pi \leftarrow X\,^1\Sigma^+$ band system ($\Delta G''_{1/2}=292.4$ cm^{-1}) and is in fair agreement with the results of the previous laser-induced fluorescence study ($\Delta G''_{1/2}=290.7$ cm^{-1}).[9]

Three unperturbed bands of the A–X system, the 0-0, 1-0, and 3-0 bands, were examined in high resolution and rotationally analyzed. Figure 4 displays the 3-0 band of the $^{27}\text{Al}^{63}\text{Cu}$ isotopic combination. The absence of a Q branch immediately identifies the system as an $\Omega'=0\leftarrow\Omega''=0$

transition, and the presence of a head in the R branch indicates that the bond length increases upon electronic excitation. Assuming that the ground state is indeed the $^1\Sigma^+$ state predicted by theory and expected on the basis of qualitative molecular orbital considerations, the selection rules of $0^+\leftrightarrow0^+$, $0^-\leftrightarrow0^-$, and $0^+\leftrightarrow0^-$ dictate that the A state must be an $\Omega'=0^+$ state as well. A least squares fit of the observed rotational transitions then provides the values of $B'_v(A\,0^+)$ listed in Table II, which are further analyzed to give $B'_e(A\,0^+)=0.135\,25\pm0.000\,15$ cm^{-1}, $\alpha_e(A\,0^+)=0.001\,83\pm0.000\,06$ cm^{-1}, and $r_e(A\,0^+)=2.569\pm0.001$ Å. Excited state lifetimes of the unperturbed $v'=0$, 1, 3, and 5 levels, measured by the method of time-delayed resonant two photon ionization (with deconvolution of the instrument function), fall in the range of 16 ± 2 ns. Assuming the decay is dominated by fluorescence to the ground electronic state, this corresponds to an absorption oscilla-
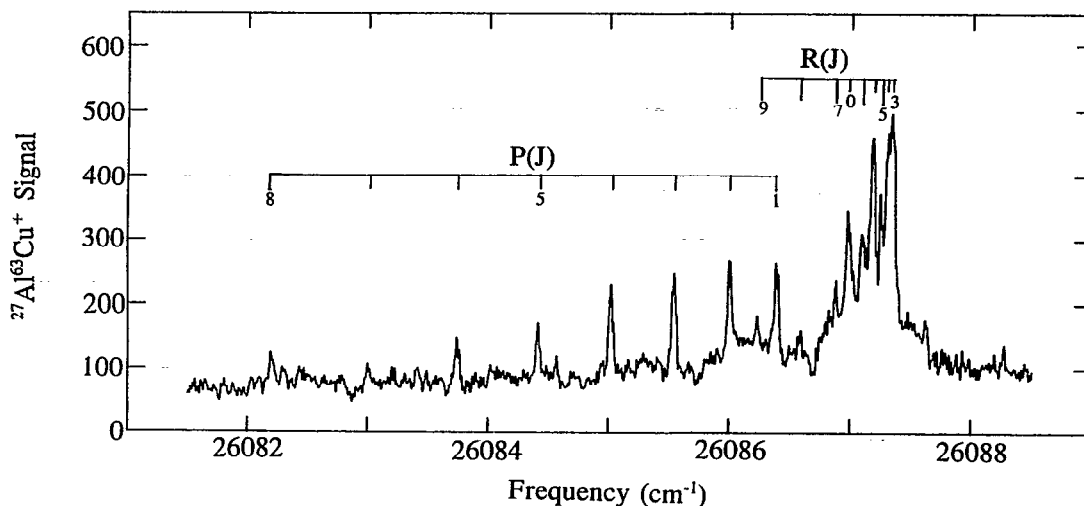

FIG. 4. Rotationally resolved scan of the 3-0 band of the $A\,0^+ \leftarrow X\,^1\Sigma^+$ system of $^{27}\text{Al}^{63}\text{Cu}$, recorded using KrF excimer laser radiation for photoionization.
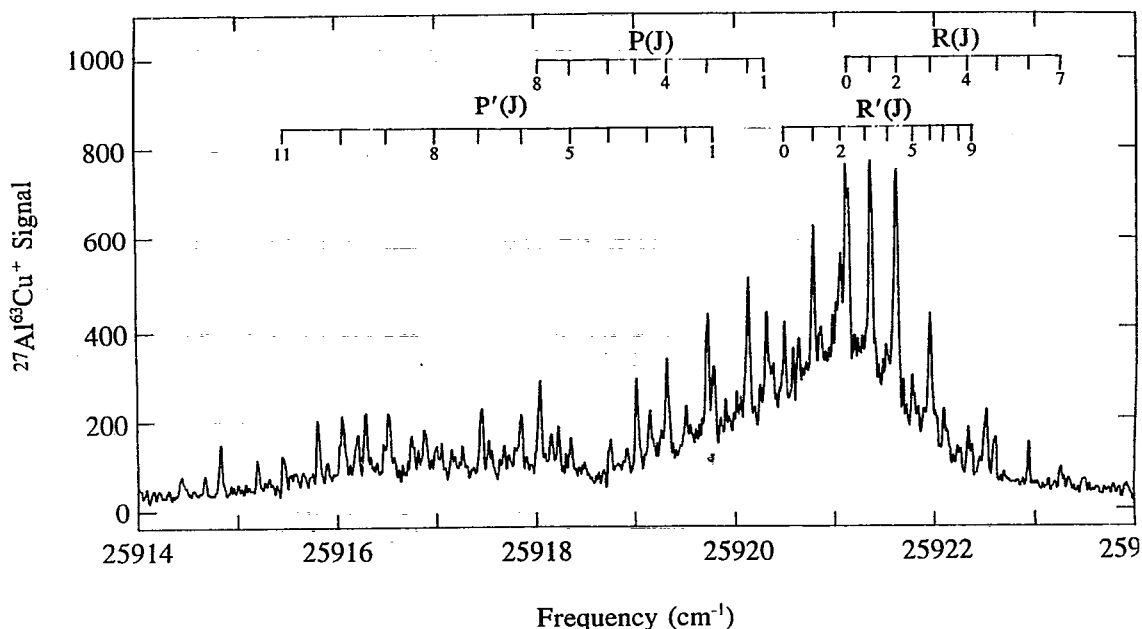
FIG. 5. Rotationally resolved scan over the 2-0 A–X and the supposed 0-0 A'–X bands. The upper levels of these bands perturb one another, making analysis of the spectrum difficult. The complexity of the spectrum demanded the use of combination differences in its analysis and the assignment is rather tentative, as described in the text. The lines labeled $P(J)$ and $R(J)$ are assigned to the 2-0 A–X band, while those labeled $P'(J)$ and $R'(J)$ are assigned to the supposed 0-0 band of the A'–X system.

tor strength of $f \approx 0.14$, indicating a very strongly allowed electronic transition.

Closer examination of the 2-0, 4-0, and 6-0 bands of the A–X system reveals that these bands are actually split into two peaks (three peaks in the case of the 6-0 band, which lies close in frequency to the 1-0 band of the B–X system as well). Excited state lifetimes, given in Table I, were obtained for the $v'=0$–7 levels of the A state, the $v'=0$–2 levels of the B state, and for the extra levels observed near the $v'=2$, 4, and 6 levels of the A state. Although the $v'=0$, 1, 3, and 5 levels of the A 0^+ state show nearly identical lifetimes of 16 ± 2 ns, the $v'=2$ and 4 levels show significantly longer lifetimes, suggesting that the extra levels are borrowing intensity from them. Indeed, the extra levels show significantly longer lifetimes than those measured for the A 0^+ state, and these vary from state to state. Moreover, the intensities and excited state lifetimes measured for the extra bands are related to their proximity to the bands of the A 0^+–X $^1\Sigma^+$ system, in a manner consistent with intensity borrowing: When the frequency interval between the extra band and the corresponding band of the A–X system is small, the measured lifetime of the A state vibrational level is lengthened, and the extra band is more intense.

It is somewhat more problematic to determine whether the perturber is homogeneously coupled to the A state (making it the A' 0^+ state) or heterogeneously coupled (making it the A' 1 state). However, if a heterogeneous coupling mechanism were operative, the coupling matrix element would have the form of $-CB_{vv'}\sqrt{J(J+1)}$, where C is a small constant (typically 1–5).[23] Given an average J value populated in the jet-cooled molecular beam of about

5, and the maximum possible value of $B_{vv'}$ of roughly 0.164 (based on the ground state B value), the maximum possible heterogeneous coupling element would be expected to lie in the range of 1–5 cm^{-1}, if the A and A' states were both primarily singlet in character. If the A' state were primarily triplet in character, this matrix element would be reduced according to the amount of singlet character in the A' state.

To account for the amount of intensity borrowing that is observed, particularly in the B 0^+, $v=1 \sim A'$,$v=2$ perturbation, where the two states are separated by roughly 10 cm^{-1}, the perturbation matrix element must have a magnitude of roughly 1–2 cm^{-1}, consistent with the maximum possible value for a heterogeneous coupling mechanism. This would imply that the A' state is primarily singlet in character, and would have to be a $^1\Pi$ state. However, it is difficult to understand why a $^1\Pi$ state would only be observable when it borrows intensity from a 0^+ state. On the other hand, if the A' state were an $\Omega=0^+$ state, primarily triplet in character, spin–orbit coupling could readily account for the magnitude of the homogeneous perturbation matrix element. Although a heterogeneous coupling mechanism has not been rigorously excluded, it seems more likely that the A' state is another state of 0^+ symmetry, homogeneously coupled to the A 0^+ and B 0^+ states. Accordingly, we label this previously unobserved perturber state as the A' 0^+ state of AlCu.

It is interesting that the only vibrational levels of the A state to be perturbed by the A' 0^+ state are the $v'=2$, 4, and 6 levels, suggesting that the vibrational frequency of the A' 0^+ state is roughly twice the frequency of the A state. Assuming that the three A' 0^+ levels that are ob-
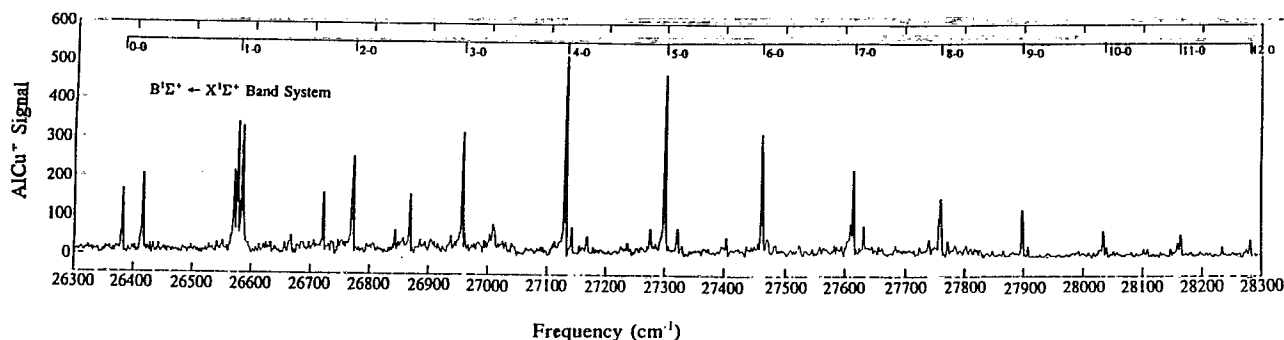
FIG. 6. Low resolution R2PI spectrum of the $B\,0^+ \leftarrow X\,^1\Sigma^+$ band system of jet-cooled ^{27}Al^{63}Cu, recorded using the frequency doubled dye laser radiation produced using LDS 698, 750, and 751 laser dyes, in conjunction with KrF excimer radiation for photoionization. The 11-0 and 12-0 bands are tentatively assigned to this band system although they could be v'-0 bands of the C–X system corresponding to low values of v'. Extraneous bands in the low energy region of the spectrum are vibronic bands of the A–X and A'–X systems.

served have sequential values of v' (such as $v'=0,1,2$), this leads to an estimated vibrational frequency for the $A'\,0^+$ state of 312 cm^{-1}, which is comparable to $\Delta G_{1/2}$ of the ground state (≈ 294 cm^{-1}). Alternatively, the observed levels could possess v' values which differ by 3 (such as $v'=0,3,6$), giving an A' state vibrational frequency of about 104 cm^{-1}. The possibility that only alternate levels (such as $v'=0,2,4$) are observed is unlikely, since unobserved levels would then fall near the $v'=3$ and 5 levels of the $A\,0^+$ state, where we see no evidence of perturbations.

The split feature located at 25 920 cm^{-1}, which comprises the 2-0 band of the A–X system and the supposed 0-0 band of the A'–X system, has been investigated under high resolution as shown in Fig. 5. The spectrum is quite congested due to the overlapping A–X and A'–X features, and is difficult to assign. Only by using the method of combination differences, in conjunction with the now well-established rotational constant of the ground state, could any progress be made in analysis. Using combination differences, $P(J+1)$ and $R(J-1)$ lines were tentatively identified by locating pairs of lines separated by

$$R(J-1)-P(J+1)=[4J+1]B_0''. \qquad (3.2)$$

One such pairs of lines were located, a least squares fit of the lines to Eq. (3.1) was attempted, resulting in the rotational constants listed in Table II for the A 2-0 and A' 0-0 bands. Unfortunately, many unexplained lines remain in the spectrum, indicating that either a third state is present in this region, or perhaps another spin–orbit component of the A' state is gaining intensity through mixing with the $A\,0^+$ or $A'\,0^+$ state. In addition, certain lines failed to fit the expectations of Eq. (3.1), in a manner suggestive of additional perturbations in the upper state. For example, both the $R(0)$ and $P(2)$ lines are displaced approximately 0.15 cm^{-1} to the blue of their expected positions, while $R(1)$ and $P(3)$ are displaced 0.07 cm^{-1} to the blue, and $R(4)$ and $P(6)$ are also displaced approximately 0.07 cm^{-1} to the blue of their expected locations. These results are suggestive of additional perturbations in the $J=1,2$, and 5 levels of the upper state, and are consistent with the fact that many unexplained lines remain. Because of these additional perturbations, not much signif-

icance should be placed on the precise values of B_v' reported for the $v=2$ level of the $A\,0^+$ state and the $v=0$ level of the A' state, except to note that both values are much greater than those reported for the $v=0$, 1, or 3 levels of the $A\,0^+$ state. This strongly suggests that the $A'\,0^+$ state has a much shorter bond length than the $A\,0^+$ state, which in turn supports the high vibrational frequency (312 cm^{-1}) of the A' state derived assuming that sequential vibrational levels are observed.

A recent *ab initio* calculation[11] provides a possibility as to the identity of the A' state that is consistent with all of these observations. The (1) $^3\Sigma^-$ state of AlCu is calculated to have a bond length 0.15 Å shorter than the ground state, a vibrational frequency of 320 cm^{-1}, and a T_e of 22 172 cm^{-1} [5000 cm^{-1} below the (2)$^1\Sigma^+$ state, which we believe corresponds to the observed $A\,0^+$ state]. The $\Omega=0^+$ component of this (1)$^3\Sigma^-$ state could quite possibly perturb the $A\,0^+$ and $B\,0^+$ states, gaining intensity through a homogeneous coupling mechanism. Although this assignment is quite speculative, especially given the difficulties in adequately calculating the states of AlCu deriving from excited separated atoms, it is nevertheless the most credible assignment currently available.

C. High energy region: $B\,0^+$–$X\,^1\Sigma^+$ and $C\,1$–$X\,^1\Sigma^+$ band systems

Spectra to the blue of approximately 27 000 cm^{-1} were investigated using frequency-doubled LDS 698, 750, and 751 laser dyes. The B–X system, previously reported by Cai *et al.*,[9] was also investigated in this study; its low resolution spectrum is similar to that previously obtained and is displayed in Fig. 6. Measured band positions are listed in Table I, along with the results of lifetime measurements for the $v'=0$, 1, and 2 levels. In addition to these measurements, a high resolution scan over the 0-0 band was conducted, leading to the rotationally resolved spectrum displayed in Fig. 7. Lifetimes were measured for the $v=0$, 1, and 2 levels of the B state, with the $v=0$ and 2 levels having essentially identical lifetimes of 20 ± 2 and 22 ± 12 ns, respectively. The $v=1$ level displayed a markedly longer lifetime of 33 ± 2 ns. This was expected because of its perturbation by the $A'\,v=2$ level, which borrows inten-
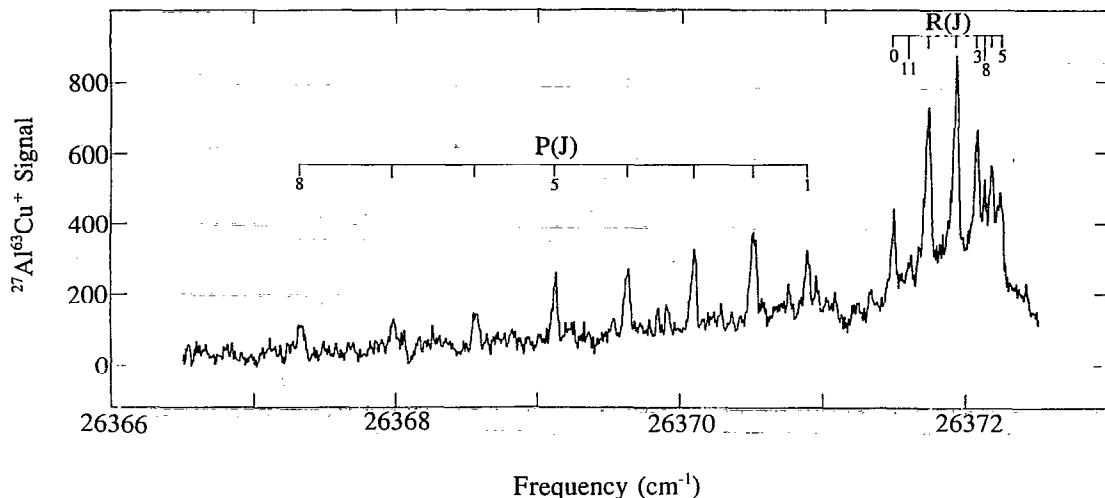
FIG. 7. Rotationally resolved scan of the 0-0 band of the $B\,0^+\leftarrow X\,^1\Sigma^+$ band system of ^{27}Al^{63}Cu.

sity from it. Assuming the decay is dominated by fluorescence to the ground electronic state, these measured lifetimes indicate an absorption oscillator strength of $f\approx0.11$, making the $B\leftarrow X$ system very strong indeed.

The rotationally resolved scan over the 0-0 band of the B–X system clearly shows the absence of a Q branch, conclusively demonstrating that the band corresponds to an $\Omega'=0\leftarrow\Omega''=0$ transition. Along with the $A\,0^+$ and $A'\,0^+$ states, this identifies the B state as possessing $\Omega'=0^+$ as well. Furthermore, rotational analysis of the line positions of this band leads to the rotational constants listed in Table II, which may be inverted to provide $r_0(B\,0^+)=2.5160 \pm0.0009$ Å. Other bands of the B–X system were not investigated with rotational resolution because they required frequency-doubled dye laser radiation; in contrast, the 0-0 band was resolved using the fundamental radiation produced by a dye laser operating on exalite 376 laser dye.

To the blue of 28 300 cm^{-1}, another series of vibronic bands was encountered. Considerably more spectral congestion was present at these energies, and the bands converged toward the blue end of the optical spectrum. Initially these bands were thought to be higher v'-0 bands of the B–X system and were fit as such, however, the supposed 11-0 and 12-0 bands were very weak and not always observable when attempts were made to reproduce the data. Furthermore, when viewed in its entirety the band system appeared to display two broad regions of intensity, which is inconsistent with the Franck–Condon principle for transitions originating from $v''=0$. The energy interval from 28 000–28 400 cm^{-1} was scanned time and time again, however, the signal-to-noise ratio was consistently low. Ultimately, it was concluded that the 11-0 and 12-0 bands should be reported as belonging to the B–X band system; poor Franck–Condon factors prevented the observation of B–X bands with $v'\geqslant13$, however. Bands to the blue of 28 300 cm^{-1} were assigned to a new system, designated as the C–X system, as labeled in Fig. 8. The assignment of these features to a new band system was supported by the measured lifetime of the upper state of the band near 28 400 cm^{-1}, which was 118$\pm$6 ns. Unfortu-
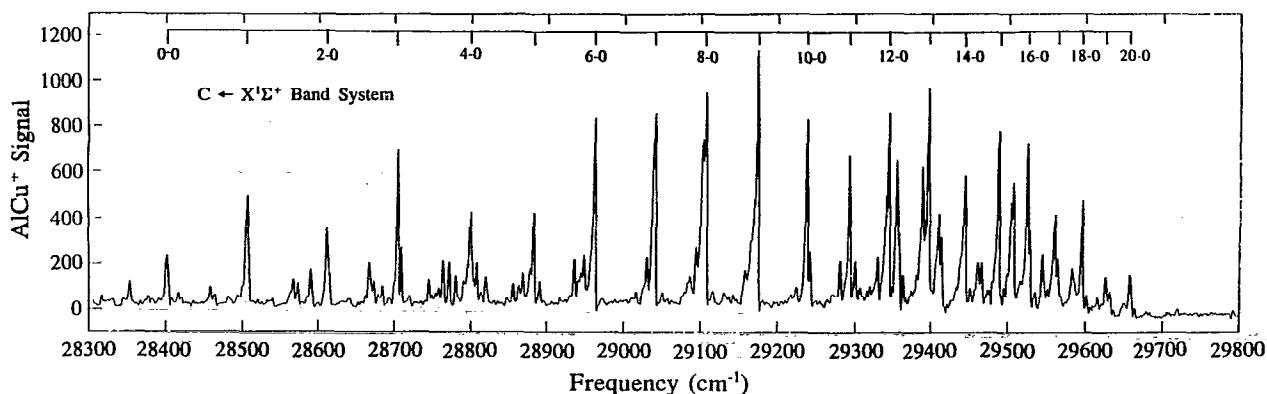

FIG. 8. Low resolution R2PI spectrum of the $C\,1\leftarrow X\,^1\Sigma^+$ band system of ^{27}Al^{63}Cu, obtained using frequency doubled LDS 698 and DCM laser dyes in conjunction with KrF excimer radiation for photoionization. The convergence of these bands as one approaches 29 700 cm^{-1} permits an accurate Birge–Sponer extrapolation to derive the ground state dissociation energy of D_0^0(AlCu) =2.315$\pm$0.012 eV.

nately, lifetimes of higher frequency members of this progression could no be measured, since the higher vibrational levels of the C state lie at energies where absorption of a second near UV photon can ionize the molecule, leading to a one-color ionization pathway that prevents effective use of the time-delayed resonant two photon ionization method for measuring lifetimes. In any case, the measured lifetime of the C state is significantly greater than that measured for the B state, and assuming the decay is dominated by fluorescence to the ground electronic state corresponds to an absorption oscillator strength of $f \approx 0.012$.

Although the vibrational numbering is uncertain due to the poor intensity of the band at $\approx 28\,400$ cm^{-1}, this band is nevertheless assigned as the 0-0 band of the C–X system for the purpose of labeling the bands and reporting vibrational constants. It was originally hoped that the isotope shifts between the ^{27}Al^{63}Cu and ^{27}Al^{65}Cu isotopic modifications could help to clarify the vibrational numbering, but the presence of numerous perturbations and extra bands in the vicinity of the C–X system made the isotope shifts erratic and useless as a tool for vibrational assignment. Nevertheless, with the assignment of the $\approx 28\,400$ cm^{-1} band as the 0-0 band of the C–X system, bands through the 20-0 band could be assigned, leading to the vibrational constants reported in Table I. It should be noted that although numerous unassigned spectral features are present in this region, the vibronic fit was obtained using the bands with the greatest intensities, and the fit which was obtained including ω_e', $\omega_e'x_e'$, and $\omega_e'y_e'$ was excellent, with a root-mean-square error of only 0.7 cm^{-1} and a maximum error of 1.4 cm^{-1}. The resulting constants were used to extrapolate to the convergence limit of the C state, which was determined to lie at $29\,876 \pm 100$ cm^{-1}, where the error limit represents $\approx \frac{1}{2}$ of the energy difference between the last observed band and the extrapolated convergence limit. The detection of the last observed band within 230 cm^{-1} of the predicted convergence limit makes for a very short extrapolation indeed. Assuming that the convergence limit corresponds to production of a ground state aluminum atom $(3s^2 3p^1, ^2P_{1/2}^o)$ and an excited copper atom $(3d^9 4s^2, ^2D_{5/2})$ at a separated atom energy of $11\,202.565$ cm^{-1},[24] this in turn implies that the ground state bond strength is given as $D_0^o(\text{AlCu}) = 2.315 \pm 0.012$ eV $(18674 \pm 100$ cm$^{-1})$.

Although it proved impossible to obtain an accurate calibration based on the I$_2$ absorption atlas in the case of the C–X system, several C–X bands were nevertheless investigated in high resolution. Only the band near $28\,400$ cm^{-1} (designated as the 0-0 band, despite the uncertainty of the vibrational numbering) led to an interpretable spectrum, however. A scan over this band is displayed in Fig. 9. The spectrum displays a rather clean P branch, and the corresponding R branch lines could be readily located using combination differences and the now well-known ground state B_0'' value. Extra features were evident, however, which could only be explained by a Q branch. Since there is no perturbing state that is obvious in the low-resolution spectrum within 10 cm^{-1} of this band, and the lines cannot be explained as returning R lines, we are led to
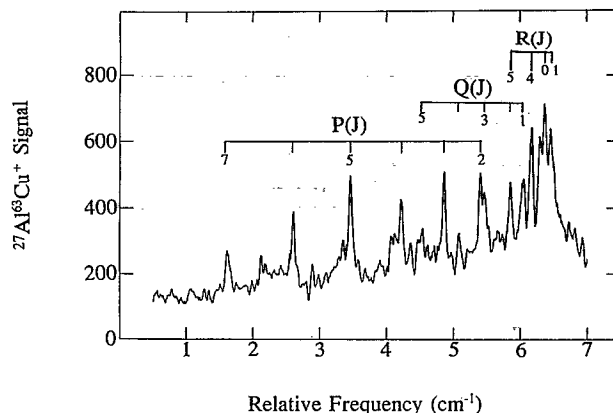

FIG. 9. Rotationally resolved scan of the C–X band located near $28\,400$ cm^{-1}, labeled as the 0-0 band in Fig. 8. The Q branch is much weaker than one would expect for an $\Omega'=1 \leftarrow \Omega''=0^+$ transition, but the band system is tentatively assigned as $C\,1 \leftarrow X\,^1\Sigma^+$.

the assignment of the band as an $\Omega'=1 \leftarrow \Omega''=0$ transition. The immediate head in the R branch shows that the bond lengthens substantially upon electronic excitation, as was confirmed by a detailed analysis, providing $r_0' = 2.8726 \pm 0.089$ Å. The measured rotational constants are given in Table II.

An unusual aspect of this band is the weakness of the Q branch features, which varied in intensity from scan to scan. This initially made it difficult to decide whether the C state corresponded to $\Omega'=1$ or 0. A possible explanation for the weakness of the Q branch features and their variable intensity from scan to scan is that the upper states reached in the Q branch of this system are selectively predissociated, while this may be impossible for the upper states accessed in the P and R branches. If the levels reached through the excitation of the Q branch predissociated on a time scale of ≈ 10 ns, their intensity in the spectrum would depend critically on the interval between the excitation and the ionization lasers. Because it is difficult to keep this separation constant to within ± 5 ns, it is easy to imagine that variations in the excitation-ionization time delay from scan to scan translate into a variation in the apparent intensity from scan to scan. Such a possibility can occur because the states accessed by excitation in the Q branch are of f symmetry, while those accessed in the P and R branches are of e symmetry. This results from the assignment of the ground state as $^1\Sigma^+$ (which possesses only e levels) and the selection rules that for P and R branches $e \leftrightarrow e$ and $f \leftrightarrow f$, but $e \not\leftrightarrow f$, while for Q branches $e \leftrightarrow f$, but $e \not\leftrightarrow e$ and $f \not\leftrightarrow f$.[23] A repulsive state which could be responsible for the selective predissociation of the f levels would be an $\Omega = 0^-$ state. Such a state possesses only f levels, and is therefore incapable of affecting the e levels. The most likely candidate for this state is the $\Omega = 0^-$ component of the $^3\Sigma^+$ state correlating to ground state atoms, which has been calculated to be repulsive through the methods of *ab initio* quantum chemistry.[11] The potential curve for this state could easily cross the C state potential, causing predissociation of the f levels. A conclusive dem-
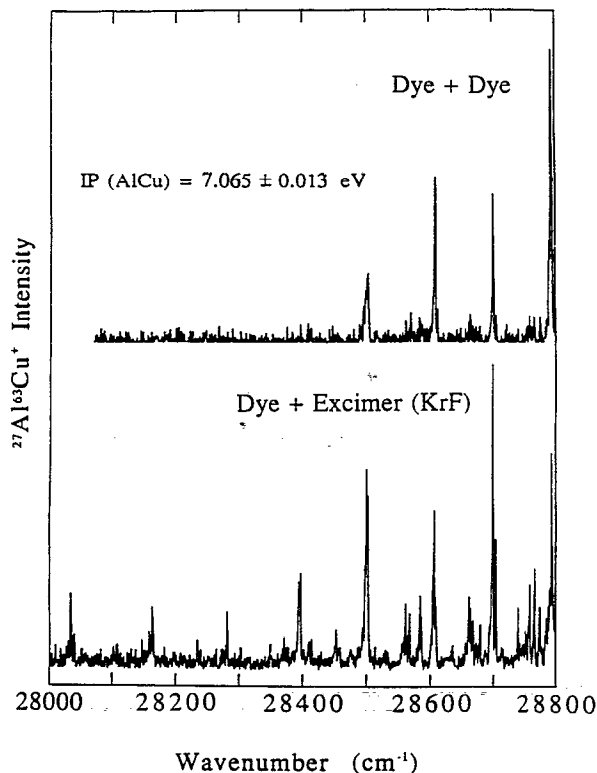
FIG. 10. Determination of the ionization threshold of AlCu. The upper panel displays a scan using frequency-doubled dye light near 28 400 cm^{-1} for both excitation and ionization, while the lower panel displays a scan in which KrF excimer radiation (248 nm, 4.997 eV) is used for ionization of the excited states. The last band observed using the frequency-doubled dye light occurs at 28 400 cm^{-1}, placing the ionization potential of AlCu at 7.065±0.014 eV.

onstration of this possibility will require further experimental (and theoretical) study, however.

D. Ionization potential determination

Resonant two-photon ionization studies can be performed either as a one-color process (in which the tunable dye laser radiation is utilized both to excite and to ionize the molecule) or, more commonly, as a two-color process wherein the ionizing photon is produced by a second laser, which in our group is usually supplied by a fixed frequency excimer laser. Thus, by simply determining the frequency of dye laser radiation required to photoionize the molecule in a two-photon process it is possible to determine the ionization potential, assuming there are no Franck–Condon restrictions on the ionization step. For AlCu this frequency occurred somewhere between the 0-0 and 1-0 bands of the C–X band system, as illustrated in Fig. 10. In the upper panel of Fig. 10, ionization was achieved by absorption of two photons of frequency near 28 500 cm^{-1}, while in the lower panel an excimer laser operating on KrF (248 nm, 4.997±0.003 eV) was used as an ionization source. The observation of the $C\,1\leftarrow X\,^1\Sigma^+$ 1-0 band in both traces places the ionization potential of AlCu below 7.069 eV, while the inability to observe the $C\,1\leftarrow X\,^1\Sigma^+$ 0-0

band in the upper trace places the ionization potential above 7.042 eV. With these results the ionization potential of AlCu may be reliably estimated as I.P.(AlCu) = 7.065 ±0.014 eV, where the error limits include the range spanned by the 0-0 and 1-0 bands of the $C\,1\leftarrow X\,^1\Sigma^+$ system, and a correction of 0.009 eV (75 cm^{-1}) has been included to account for the field ionization shift due to the electric field of the time-of-flight electrodes.

The experimental determination of both the bond strength and the ionization potential of AlCu allows the bond strength of the cation AlCu$^+$ to be obtained by referencing the atomic ionization potentials of Al (5.985 77 eV) (Ref. 25) and Cu (7.726 380 eV) (Ref. 26) and by completing the appropriate thermodynamic cycles:

$$D_0^\circ(\text{Al}^+-\text{Cu}) = D_0^\circ(\text{Al}-\text{Cu}) + \text{I.P.}(\text{Al}) - \text{I.P.}(\text{AlCu}) \quad (3.3)$$

and

$$D_0^\circ(\text{Al}-\text{Cu}^+) = D_0^\circ(\text{Al}-\text{Cu}) + \text{I.P.}(\text{Cu}) - \text{I.P.}(\text{AlCu}), \quad (3.4)$$

thereby providing $D_0^\circ(\text{Al}^+-\text{Cu}) = 1.236\pm0.018$ eV and $D_0^\circ(\text{Al}-\text{Cu}^+) = 2.976\pm0.018$ eV.

IV. DISCUSSION

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

Diatomic AlCu was chosen as the first of the 3d transition metal aluminides to be investigated by resonant two-photon ionization spectroscopy because of its conceptual simplicity and the existence of previous experimental and theoretical studies on this molecule. The ground state is precisely as expected from *ab initio* theory, an $s_{\text{Al}}^2 d_{\text{Cu}}^{10}\sigma^2,{}^1\Sigma^+$ state. Moreover, the measured values of $r_0(X\,^1\Sigma^+) = 2.3389\pm0.0004$ Å, $\Delta G_{1/2}(X\,^1\Sigma^+) = 294$ cm^{-1}, and $D_0^\circ(\text{AlCu}) = 2.315\pm0.012$ eV are in excellent agreement with the values obtained in high-level quantum chemical calculations. For example, Bär and Ahlrichs report calculated values of $r_e(X\,^1\Sigma^+)$, $\omega_e(X\,^1\Sigma^+)$, and $D_0^\circ(\text{AlCu})$ of 2.328±0.026 Å, 285±10 cm^{-1}, and 2.22±0.05 eV, respectively,[12] while Bauschlicher, Langhoff, and Partridge report $r_0(X\,^1\Sigma^+) = 2.337$ Å, $\Delta G_{1/2}(X\,^1\Sigma^+) = 295$ cm^{-1}, and $D_0^\circ(\text{AlCu}) = 2.319$ eV in a highly correlated calculation including both inner shell correlation and relativistic effects.[11]

The bond strength of AlCu, $D_0^\circ(\text{AlCu})$, has been previously measured using Knudsen effusion mass spectrometry, giving values of 2.14±0.15,[13] 2.19,[14] 2.17±0.13,[15] and 2.17±0.18 eV.[16] All of these values are smaller than that deduced from our extrapolation of the vibronic levels of the $C\,1$ state, $D_0^\circ(\text{AlCu}) = 2.315\pm0.012$ eV. A possible error in our procedure is the assumption that the $C\,1$ state dissociates to Al($3s^23p^1,{}^2P^o$) + Cu($3d^94s^2,{}^2D_{5/2}$). If the C state were to dissociate to the higher spin–orbit level of Al($3s^23p^1,{}^2P^o$) + Cu($3d^94s^2,{}^2D_{3/2}$), our value would be revised to $D_0^\circ(\text{AlCu}) = 2.062\pm0.012$ eV. This leads to a marginal improvement in agreement with the Knudsen effusion measurements, but gives a more serious disagreement

with the value of $D_e = 2.250 \pm 0.012$ eV (from which we derive $D_0^\circ(\text{AlCu}) = 2.232 \pm 0.012$ eV), obtained by Cai *et al.*[9] by Birge–Sponer extrapolation of the levels of the A and B states (again, with the assumption that they dissociate to $\text{Al}(3s^23p^1,{}^2P^o) + \text{Cu}(3d^94s^2,{}^2D_{5/2})$. In support of our value, we note that the observed levels of the $C\,1$ state take us to within 230 cm^{-1} of the extrapolated dissociation limit, while the extrapolations of Cai *et al.* for the $A\,0^+$ and $B\,0^+$ states are based on observed levels that lie more than 2100 and 750 cm^{-1} away from the extrapolated dissociation limits, respectively.[9] Furthermore, the dissociation energy for production of $\text{Al}(3s^23p^1,{}^2P^o) + \text{Cu}(3d^94s^2, {}^2D_{5/2})$ proposed by Cai *et al.*[9] (when corrected for the zero-point energy of the $X\,{}^1\Sigma^+$ state) corresponds to a convergence limit of approximately 29 200 cm^{-1}. Figure 8 demonstrates that the $C\,1 \leftarrow X\,{}^1\Sigma^+$ band system shows no irregularities or peculiarities at 29 200 cm^{-1}, but instead shows a regular convergence toward a limit near 29 850 cm^{-1}. Unless the $C\,1$ state possesses a barrier to dissociation, it would seem that our value of the bond strength is more accurate than that proposed by Cai *et al.*[9] The disagreement with the Knudsen effusion results is not so serious, since these values have error limits which come close to encompassing our value.

Further justification for our value of $D_0^\circ(\text{AlCu}) = 2.315 \pm 0.012$ eV [as opposed to the value of $D_0^\circ(\text{AlCu}) = 2.062 \pm 0.012$ eV which results if we assume the $C\,1$ state dissociates to the $\text{Al}(3s^23p^1,{}^2P^o) + \text{Cu}(3d^94s^2,{}^2D_{3/2})$ separated atom limit] may be found by comparison to the bond strength of AlNi. In the following paper[1] we observe a sharp predissociation threshold in AlNi at an energy of 2.459 eV (19 836 cm^{-1}), which is interpreted as dissociation to the first separated atom limit generating repulsive curves. As discussed in that paper, this probably places the bond strength of AlNi in the range of $D_0^\circ(\text{AlNi}) = 2.29 \pm 0.05$ eV. In previous work it has been found that the bond strengths of diatomics containing nickel or copper are very similar, indicating that the $3d$ orbitals of these atoms are tightly contracted and generally incapable of contributing to the chemical bond in the diatomic metals. As an example, the molecules Ni_2, NiCu, and Cu_2 have bond strengths of $D_0^\circ(\text{Ni}_2) = 2.068 \pm 0.010$ eV, $D_0^\circ(\text{NiCu}) = 2.05 \pm 0.10$ eV, and $D_0^\circ(\text{Cu}_2) = 2.03 \pm 0.02$ eV.[27] With this similarity in mind, it is unlikely that AlCu would have a bond strength as low as 2.062 eV, since the bond strength of AlNi is thought to be 2.29 ± 0.05 eV.

B. Excited states of AlCu

The first excited state of AlCu is undoubtedly the $3s^2_{\text{Al}}3d^{10}_{\text{Cu}}\sigma^1\pi^1,{}^3\Pi$ state that correlates to ground state separated atoms, $\text{Al}(3s^23p^1,{}^2P^o) + \text{Cu}(3d^{10}4s^1,{}^2S)$. This state has been predicted to lie 8874 cm^{-1} above the ground state in a highly correlated calculation,[11] far below the spectroscopic region probed in the present experiments. Given the poor oscillator strength observed for the ${}^1\Pi(1) \leftarrow X\,{}^1\Sigma^+$ transition ($f \approx 1 \times 10^{-4}$), it is unlikely that the ${}^3\Pi \leftarrow X\,{}^1\Sigma^+$ transition could be observed, even if this low energy region were searched quite carefully. Spin–orbit coupling between the $3s^2_{\text{Al}}3d^{10}_{\text{Cu}}\sigma^1\pi^1$, ${}^3\Pi$ and $3s^2_{\text{Al}}3d^{10}_{\text{Cu}}\sigma^1\pi^1$,

${}^1\Pi$ states, which would ordinarily provide the best opportunity for lending oscillator strength to the ${}^3\Pi \leftarrow X\,{}^1\Sigma^+$ transition, will be insufficient to make the ${}^3\Pi \leftarrow X\,{}^1\Sigma^+$ transition observable.

The next excited electronic state of AlCu is almost certainly the $3s^2_{\text{Al}}3d^{10}_{\text{Cu}}\sigma^1\pi^1$, ${}^1\Pi$ state observed at $T_0 = 14\,892$ cm^{-1}. As mentioned in Sec. III A, the measured properties of this state are in excellent agreement with those obtained in a highly correlated calculation by Bauschlicher, Langhoff, and Partridge.[11] Apart from the very long lifetime of this excited state, perhaps its most surprising property is the combination of a low bond strength ($D_0 \approx 3780 \pm 100$ cm^{-1}) and a short bond length ($r_0[{}^1\Pi(1)] = 2.3531 \pm 0.0008$ Å). Given that the singly occupied π orbital is apparently localized on the aluminum atom in this molecule, it is probably best to consider this orbital to be nonbonding. Accordingly, the measured bond length of 2.353 Å for the ${}^1\Pi(1)$ state is probably also close to the bond length of the $3s^2_{\text{Al}}3d^{10}_{\text{Cu}}\sigma^1,{}^2\Sigma^+$ state of the AlCu$^+$ cation.

Above the ${}^1\Pi(1)$ state must lie the $3s^2_{\text{Al}}3d^{10}_{\text{Cu}}\sigma^1\sigma^{*1},{}^3\Sigma^+$ state that dissociates to ground state atoms, but no trace of this state appeared in our spectra. Most probably it is unobserved because it is unbound, as predicted theoretically.[11]

Above these states correlating to ground state separated atoms we find a set of states (the $A\,0^+$, $A'\,0^+$, $B\,0^+$, and $C\,1$ states) that are difficult to describe accurately by *ab initio* quantum chemical methods.[11] Presumably all of these states arise from the $\text{Al}(3s^23p^1,{}^2P^o) + \text{Cu}(3d^94s^2,{}^2D)$ separated atom limit, from which the following Hund's case (a) states arise: ${}^1\Sigma^+(2)$, ${}^1\Sigma^-$, ${}^1\Pi(3)$, ${}^1\Delta(2)$, ${}^1\Phi$, ${}^3\Sigma^+(2)$, ${}^3\Sigma^-$, ${}^3\Pi(3)$, ${}^3\Delta(2)$, and ${}^3\Phi$. It would be tempting to assign the $A\,0^+$ and $B\,0^+$ states as the two ${}^1\Sigma^+$ states arising from this separated atom limit, and to assign the $C\,1$ state as one of the three ${}^1\Pi$ states expected. This assignment finds some support in preliminary *ab initio* calculations[11] which place two ${}^1\Sigma^+$ states at $T_e = 27\,159$ and 30 741 cm^{-1}, with vibrational frequencies of 226 and 295 cm^{-1}, bond lengths of 2.47 and 2.30 Å, and excited state lifetimes of 5 and 17 ns, respectively. Likewise, a ${}^1\Pi$ state is calculated at $T_e = 31\,033$ cm^{-1}, with $\omega_e = 213$ cm^{-1}, $r_e = 2.47$ Å, and a lifetime of 50 ns. Although these values (particularly r_e and ω_e) differ substantially from the measured properties, at least the state symmetries and lifetimes are in reasonable accord with our measurements. Likely candidates for the A' state are ${}^3\Sigma^-$ or ${}^3\Pi$ states, either of which possesses an $\Omega = 0^+$ substate, which can gain intensity by mixing with the $A\,0^+$ or $B\,0^+$ states. Of these, the ${}^3\Sigma^-$ state seems more likely, since it will possess an $\Omega = 1$ substate at a similar energy as the 0^+ substate, thereby providing a potential explanation for the extra lines in the rotationally resolved spectrum of Fig. 5. The *ab initio* calculations[11] also predict that the $(1){}^3\Sigma^-$ state has properties similar to those deduced from our investigation. Specifically, a high vibrational frequency of 320 cm^{-1} and a short bond length (0.15 Å shorter than that of the ground state) are predicted.[11]

It is interesting to note that the A and B states possess

short lifetimes of roughly 15 and 20 ns, respectively, while the $^1\Pi(1)$ and $C\,1$ states have much longer lifetimes of 71 μs and 118 ns, respectively. We have noted similar effects in the spectra of the diatomic coinage metals Cu_2,[27,28] Au_2,[27,29] $CuAg$,[27,30] and $CuAu$,[27,31] where states of $0_{(u)}^+$ symmetry have generally much shorter lifetimes than do states of $1_{(u)}$ symmetry. In these systems we have suggested that the ion pair states M^+M^- (corresponding to $d^{10}s^0$,$^1S+d^{10}s^2$,^1S separated ion states) only generate states of $^1\Sigma^+$ ($\Omega=0^+$) symmetry, and these strongly attractive ion pair states lie energetically quite low in these metallic molecules due to the rather low atomic ionization potentials and the significant electron affinities of the metals. Indeed, the Coulomb attraction of the ions causes the ion pair potential curves to slice through the high energy covalent potential curves, causing avoided crossings with all states of 0^+ symmetry. Mixing of covalent states with these ion pair states then allows all of the states of 0^+ symmetry to gain some of the tremendous oscillator strength associated with the charge transfer transition from the covalent ground state to the ion pair excited state. This mechanism then provides a unifying explanation for the general observation that $\Omega=1_{(u)}$ excited states have much longer lifetimes than do excited states with $\Omega=0_{(u)}^+$.

A similar effect is undoubtedly present in AlCu, where states of 0^+ symmetry again have short lifetimes compared to those measured for the $\Omega=1$ states. In this case, the Al^++Cu^- separated ion limit lies only 4.758 ± 0.010 eV above the ground state separated atom limit,[32] and the strong Coulomb attraction again causes the $Al^+(3s^23p^0$,$^1S)+Cu^-(3d^{10}4s^2$,$^1S)$ ion pair state to drop rapidly in energy with decreasing ion separation. As in the coinage metal diatomics, mixing of this ion pair state (which must be $^1\Sigma^+$, $\Omega=0^+$ in symmetry) with other states of $\Omega=0^+$ symmetry provides a mechanism for lending some of the large oscillator strength of the $Al^+Cu^-\leftarrow Al-Cu$ charge transfer transition to other $0^+\leftarrow X\,^1\Sigma^+$ transitions. To illustrate the potential of the ion pair state, Fig. 11 displays Morse oscillator approximations to the known electronic states of AlCu (with anharmonicities adjusted to force dissociation to the appropriate separated atom limits) along with the potential of Coulomb attraction for the ion pair Al^+Cu^-. This ion pair curve is generated by simply adding a $-e^2/R$ attractive term to the energy of the separated ions and, therefore, displays the unphysical behavior of approaching $-\infty$ as the internuclear separation, R, goes to zero. In reality, of course, the finite size of the ions would eventually cause the curve to become repulsive at small R. Given that the radial expectation values, $\langle r\rangle$, for the $3s$ orbital of atomic aluminum and the $4s$ orbital of atomic copper are 1.373 and 1.726 Å, respectively,[33] one would expect a minimum in the zeroth-order ion pair curve at an internuclear separation greater than 3.1 Å (1.373+1.726 Å). Thus, the predicted zeroth-order ion pair curve is expected to lie very close to the curves of the $A\,0^+$ and $B\,0^+$ states, providing compelling evidence for its importance in the description of these states.
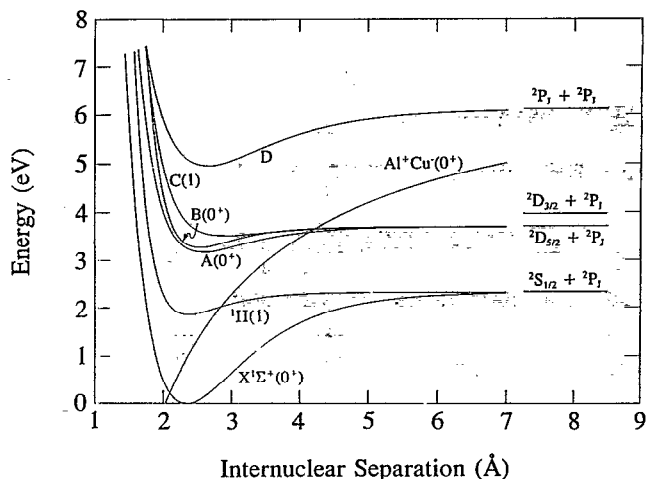

FIG. 11. Qualitative potential energy curves for the experimentally known electronic states of AlCu, constructed as Morse potentials employing the experimentally derived values of ω_e, r_e, and T_e, and a value of $\omega_e x_e$ adjusted to force dissociation to the appropriate separated atom limit. Separated atom limits corresponding to the $Al(3s^23p^1$,$^2P)+Cu(3d^{10}4s^1$,$^2S)$, $Al(3s^23p^1$,$^2P)+Cu(3d^94s^2$,$^2D_{5/2})$, $Al(3s^23p^1$,$^2P)+Cu(3d^94s^2$,$^2D_{3/2})$, and $Al(3s^23p^1$,$^2P)+Cu(3d^{10}4p^1$,$^2P)$ are drawn as solid lines at the right of the figure. The well depth of the $C\,1$ state is based on the tentative vibrational numbering, and may be in error. For reference, the ion pair curve for Al^+Cu^- is also plotted, without corrections for the polarizability of one ion in the field of the other, or for Pauli repulsion of the filled orbitals at short distances. When included, these effects should cause the curve to become repulsive at an intranuclear separation greater than 3.1 Å.

C. The AlCu$^+$ cation

As discussed in the Sec. III D, the determination of the dissociation energy of neutral AlCu in combination with its ionization potential has allowed the dissociation energy of the cationic species to be calculated as $D_0^\circ(Al^+-Cu)=1.236\pm0.018$ eV and $D_0^\circ(Al-Cu^+)=2.976\pm0.018$ eV. Given the ionization potentials of aluminum (5.985 77 eV) (Ref. 25) and copper (7.726 380 eV) (Ref. 26), it seems rather certain that the ground state of the AlCu$^+$ ion must derive from an aluminum cation interacting with a neutral copper atom. One possibility for the ground state is that the $Al^+(3s^23p^0$,$^1S)$ cation combines with a ground state Cu atom $(3d^{10}4s^1$,$^2S)$ to give a $3s_{Al}^23d_{Cu}^{10}\sigma^1$,$^2\Sigma^+$ radical. Assuming that the $3s_{Al}$ and $3d_{Cu}$ electrons remain corelike, this would have a formal bond order of $\frac{1}{2}$, thereby explaining the reduction in bond strength upon ionization from $D_0^\circ(AlCu)=2.3215\pm0.012$ eV to $D_0^\circ(Al^+-Cu)=1.236\pm0.018$ eV. Alternatively, however, the $Al^+(3s^23p^0$,$^1S)$ cation could combine with an excited copper atom in the $3d^94s^2$,$^2D_{5/2}$ state. Although 11 202 cm^{-1} of energy is required to promote the atom to this state,[24] we have seen that in the neutral molecule a two electron σ bond gives a bond strength of 18 674$\pm$100 cm^{-1} (2.315$\pm$0.012 eV), while the one electron σ bond of the $^1\Pi(1)$ state only provides a bond strength of $D_0\approx3780\pm100$ cm^{-1}. With this gain in bond strength associated with the formation of a two electron σ bond in mind, one may perhaps expect the ground state of AlCu$^+$ to derive from the $3s_{Al}^23d_{Cu}^9\sigma^2$ con-

TABLE III. Electronic states of $^{27}Al^{63}Cu$. 1σ error limits are provided in parentheses following each entry in the table. In addition, $D_0^0(AlCu)=2.315$ ±0.012 eV, I.P.(AlCu)$=7.065\pm0.014$ eV, $D_0^0(Al^+-Cu)=1.236\pm0.018$ eV, and $D_0^0(Al-Cu^+)=2.976\pm0.018$ eV.

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)	τ (μs)
D	39 909.26[a]	187.92(63)[a]	−0.455(88)[a]			2.64[d]	
$C\,1$	28 399.90[b]	112.50(28)[b]	2.999(31)[b]	B_0=0.108 18(67)		2.8726(89)	0.118(6)
$B\,0^+$	26 371.0068(15)	208.11(74)	3.747(53)	B_0=0.141 01(10)		2.5160(9)	0.020(2)
$A'\,0^+$	25 920.1868(30)[b]	312.19[b]	−5.81[b]	B_0=0.154 23(16)[c]			
$A\,0^+$	25 576.2194(24)	178.47(53)	1.957(64)	0.135 25(15)	0.00183(6)	2.5691(14)	0.015(1)
$^1\Pi(1)$	14 892.2744(20)	$\Delta G_{1/2}$=224.15		B_0=0.16122(11)		2.3531(8)	71(3)
$X\,^1\Sigma^+$	0.0000	$\Delta G_{1/2}$=2.94.06(59)		B_0=0.16318(6)		2.3389(4)	

[a]From a fit of the data presented in Ref. 9.

[b]Vibrational numbering of the C state may be substantially in error, due to poor Franck–Condon factors at low v' and numerous perturbations, making isotope shifts meaningless. The vibrational numbering of the A' state is likely to be wrong, since this state is only observed when intensity is borrowed from the A or B states.

[c]The $v=0$ level of the A' state is strongly perturbed by the $v=2$ level of the A state. Therefore, its B_0 value should be viewed with caution. For this reason, inversion of B_0 to give r_0 has not been done, since the resulting value would be erroneous.

[d]The bond length of the D state of AlCu is based on the Franck–Condon analysis of band intensities (Ref. 9), corrected for the bond length of the $X\,^1\Sigma^+$ state, which is now known.

figuration that arises from the $Al^+(3s^23p^0,^1S)$ $+Cu(3d^94s^2,^2D_{5/2})$ separated atom limit. If this is so, it is likely that the ground state of AlCu$^+$ is $^2\Delta_{5/2}$, as has been determined for the isoelectronic molecule AlNi in the following paper.[1] A similar decrease in bond strength upon ionization is found in CuH, where the bond strengths are $D_0^0(CuH)=2.65\pm0.17$ eV (Ref. 34) and $D_0^0(Cu^+-H)$ $=0.92\pm0.13$ eV (Ref. 35). In this case of CuH$^+$ it is rather clear that the ground state is $3d_{Cu}^{10}\sigma^1,^2\Sigma^+,^{36}$ but the inability of matrix isolation electron spin resonance experiments[37] to observe AlCu$^+$ suggests that this molecule may indeed possess the $3s_{Al}^23d_{Cu}^9\sigma^2,^2\Delta_{5/2}$ ground state, which would be invisible to this technique.

V. CONCLUSION

Resonant two-photon ionization spectroscopy has been used to investigate diatomic AlCu, and has confirmed the ground state to be $^1\Sigma^+$, as predicted by *ab initio* quantum chemistry. The ground $X\,^1\Sigma^+$ state possesses a bond length, r_0, of 2.3389 ± 0.0004 Å and a bond strength, D_0^0 of 2.315 ± 0.012 eV. Both values are in excellent agreement with the results of quantum chemical calculations.

Five electronic band systems have been identified, three of which are new. A thorough investigation of these systems has been completed, and a concise summary of the results is given in Table III. Future work will involve a systematic study of the rest of the $3d$ transition metal aluminides beginning with the neighboring molecule, AlNi, which is discussed in the following article.[1] As the $3d$ subshell is opened, spectral complexity will increase and as one moves to the left in the transition metal series it is possible that the $3d$ orbitals will begin to play a role in the chemical bonding. In contrast, investigations of molecules in which either a d^0s^2(Ca) or a $d^{10}s^2$(Zn) metal is bound to aluminum are also underway to determine the preferential orientation of the Al $3p$ electron in the presence of a stable s^2 configuration. By a systematic analysis of the $3d$ transition metal aluminides we hope to discover the underlying

periodic trends and draw general conclusions regarding the interaction of a $3d$ transition metal atom with a main group p-block metal.

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