Identification of a new low energy 1_u state in dicopper with resonant four-wave mixing

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The low energy electronic structure of the copper dimer has been re-investigated using non-linear four-wave mixing spectroscopy and high level *ab initio* calculations. In addition to the measurement of the previously reported A, B, and C electronic states, a new state denoted A' is identified with $T_0 = 20\,100.4090(16)\text{ cm}^{-1}$ ($^{63}\text{Cu}_2$). Rotational analysis of the A'–X (0,0) and (1,0) transitions leads to the assignment of A' 1_u . *Ab initio* calculations present the first theoretical description of the low energy states of the copper dimer in Hund's case (c) and confirm the experimental assignment. The discovery of this new low energy excited state emphasizes that spin-orbit coupling is significant in states with d-hole electronic configurations and resolves a decades-long mystery in the initial assignment of the A state. Published by AIP Publishing. <https://doi.org/10.1063/1.5006107>

I. INTRODUCTION

The copper dimer is one of the most studied transition metal (TM) diatomics due to its alkali-metal like electronic shell structure, strongly bound ground state, and chemical reactivity. The high electronic promotion energy in the copper atom leads to a dearth of low-lying electronic states compared to TM dimers with d-hole electronic configurations. An extensive study of Cu_2 has led to the discovery of numerous excited electronic states; however, few of these states have been investigated at high resolution or have been assigned term symbols or dissociation limits.¹

The system has also held numerous surprises for experimentalists. The assignment of both the low lying A and B states to $^1\Sigma_u^+$ defied the expectations of researchers and forced consideration of both the influence of ion-pair states and Hund's case (c) coupling.² The appearance of Q-branch lines in the original rotationally resolved spectrum of the A state remains a mystery.^{3,4} Both A and B states exhibit anomalously large electronic isotope shifts, which have been correlated with the specific mass shift in the d-hole (^2D) levels of Cu_2 .² Homogeneous perturbations of the $v = 0$ levels of the A and B states have also been reported, though it is difficult to identify a perturber given the paucity of states in this energy region. The potential curve of the A state in the region of $v = 2$ is steeper than expected from the vibrational frequency. The lifetime of the $v = 2$ level is shorter even than the $v = 0$ level and it is suggested that the homogeneous perturber is an ion pair state.^{5,6} Finally, the observation of a bound low energy triplet state correlating to the ground state separated atom limit has been explained by ferromagnetic type no-pair bonding mechanisms

with bond energies far exceeding those of the alkali metal dimers.^{7,8}

The spectroscopic methods that have been used to investigate the copper dimer until now have not possessed sufficient *spectral* selectivity, which has complicated the analysis of the often overlapping transitions. Laser induced fluorescence (LIF) measurements are also limited to transitions that couple optically to lower states within the temporal detection window in a molecular beam. Resonance enhanced multiphoton ionisation (REMPI) studies have provided mass resolution to the optical spectra but require significant wave-function overlap of the state probed and a low energy state in the ionised species.

Resonant four-wave mixing (RFWM) is a non-linear absorption based spectroscopic method.⁹ In favorable cases, the two-colour version (TC-RFWM) enables purely optical species selective spectral measurements in a mixed molecular beam. Additionally, by labeling individual rotational levels in the common intermediate state, the spectra are dramatically simplified—often to few well separated transitions, which can be easily assigned from the pump transition. We have previously used this technique in the study of C_2 ,^{10–13} C_2^- ,¹⁴ C_3 ,¹⁵ HC_2S ,¹⁶ HC_4S ,¹⁷ H_2CO ¹⁸ and have very recently demonstrated its application to the A–X and B–X transitions in the copper dimer in a molecular beam expansion.¹⁹

In this work, we report the discovery of a new low energy electronic state of Cu_2 , dubbed A', using resonant four-wave mixing techniques. The identification of this state confirms Hund's case (c) coupling of the d-hole set of states, which has interesting implications for theoretical chemists. A case (a)–(c) assignment based on previous experimental theoretical studies is presented. Finally, this work solves the long standing mystery of the observation of Q-branch lines in the earlier work

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of Pesic and Weniger.^{3,4} Explanations for the difficulties in the observation of the A' state are also examined.

II. EXPERIMENT

The experimental setup has been described previously²⁰ with the current configuration including a metal cluster source covered in a recent publication.¹⁹ In brief, a home built metal cluster laser vaporisation source is used to prepare copper dimers in the gas-phase. Helium (6.0, Messer Schweiz AG) carrier gas is introduced into the source using a pulsed valve (Series 9 General Valve, Parker-Hannifin). Vaporisation of the copper target (99% purity) is performed with the second harmonic of a Nd:YAG laser (Continuum, NY81) (≈ 100 mJ/pulse) focused through a 500 mm focal length lens. Electric motors (Maxon) are used to translate and rotate the target to provide careful control of the rate that fresh surface is sampled. Subsequently, the copper dimers exit the source in a near supersonic expansion and are probed with four-wave mixing techniques 5 mm downstream from the nozzle.

The spectroscopic setup has been described in detail recently and is only briefly described here.¹⁵ For TC-RFWM measurements, the pump and probe beams are produced by two dye lasers (NarrowScan, Radiant Dyes) (Coumarin 47 and 307, Radiant Dyes) pumped by the third harmonic output of a single Nd:YAG laser (QuantaRay Pro 270-10, Spectra-Physics). The dye lasers are operated without amplifier cuvettes and the output is typically attenuated using neutral density filters to avoid saturation. In these measurements, the pump energy is held to ≈ 50 nJ/pulse to avoid saturation of the extremely strong B–X transition, while the probe energy is typically ≈ 3 μ J/pulse. The bandwidth specified for the dye lasers is ≈ 0.04 cm⁻¹. A wavemeter (WS6, HighFinesse, specified accuracy is 600 MHz) is employed to measure the absolute wavelength for each scan step.

The optical setup consists of a forward BOXCARS configuration that is covered in detail in a previous study.²¹ In short, three parallel propagating input beams are focused into the cluster beam using a 1000 mm focal length lens achromatic objective. The beams form the three main diagonals of a parallelepiped and cross at an angle of $\approx 1^\circ$. Doppler broadening of the spectra is eliminated by probing the molecular beam orthogonally to the direction of propagation. Satisfaction of phase-matching conditions occurs for the following combination of wavevectors ($\mathbf{k}_i$):

$$\mathbf{k}_1 + \mathbf{k}_3 = \mathbf{k}_2 + \mathbf{k}_4.$$

For the current experiments, the PUMP beams, $\mathbf{k}_2 + \mathbf{k}_4$, were scanned with one PROBE beam, $\mathbf{k}_1$, fixed, and the signal beam generated along the fourth (or dark) diagonal. The signal beam is collimated with a second achromatic objective and is separated from scattered light over a path length of ≈ 2 m. Further separation of the signal beam is achieved using a 30 mm focal length lens and 50 μ m pinhole situated directly before a photomultiplier detector.

The experiment is operated at 10 Hz with the appropriate timings provided by a set of delay generators (Stanford Research, DG353). Spectra are recorded with an oscilloscope

(Wavepro 950, LeCroy) and stored using a home-made software (LABVIEW). Typically, 200 pulses are averaged per scan step (5×10^{-4} nm/step) of the dye laser on the oscilloscope to improve the signal-to-noise ratio.

III. THEORY

In this work, we report theoretical results on the ground state X $^1\Sigma_g^+$ and the following excited states: the lowest two $^1\Sigma_u^+$ and $^3\Sigma_u^+$ levels, the lowest $^1\Pi_u$, $^3\Pi_u$, $^1\Delta_u$, and $^3\Delta_u$ levels.

Potential energy functions were calculated at the internally contracted multi-reference configuration-interaction (briefly MRCI) level of theory,^{22–24} using single and double excitations, an estimation for corrections due to higher order excitations from the Davidson formula for cluster correction (MRCI+Q) and the aug-cc-PVQZ-DK (AVQZ-DK) basis as implemented in the MOLPRO programme suite.²⁵ The Douglas-Kroll-Hess Hamiltonian^{26,27} was used at order four to estimate relativistic corrections beyond spin-orbit interactions. The AVQZ-DK basis has originally been optimized using the coupled cluster method with perturbational inclusion of triple excitations [CCSD(T)].²⁸ Test calculations have shown that it is possible to use the AVQZ-DK basis at the MRCI level.

An important step prior to the MRCI+Q calculations is the determination of an optimal active space. The best choice has proven to be the calculation of optimal orbitals from a state averaged multi-state self-consistent field calculation (MCSCF) using a reduced active space involving all 22 valence electrons in 18 orbitals, a (22,18)-RAS. The active orbital space comprises the 3d, 4s, and 4p orbitals. Calculations in a (22,18) complete active space (CAS) are too costly to be run efficiently. Instead, we have optionally removed all double excitations of 3d orbitals from the active space, defining in this way a reduced active space of states.

The states included in the MCSCF calculation were the 23 singlet states that can be obtained from the (22,18)-RAS and that correlate with the two lowest dissociation asymptotes. The lowest asymptotes correspond to the $(3d)^{10}(4s)^1 + (3d)^{10}(4s)^1$ electronic configurations of separated copper atoms, which we call the ss separated atom limit. The next lowest asymptotes correlate with the $(3d)^{10}(4s)^1 + (3d)^9(4s)^2$ configurations—also referred to as “d-hole” configurations, which compose the sd separated atom limit. In (22,12)-CAS calculations, which have also been investigated in the course of this work, a third type of asymptotic channels is possible, if double excitations from 3d orbitals are considered: $(3d)^9(4s)^2 + (3d)^9(4s)^2$ configuration, the dd separated atom limit. Each channel may contain singlet (S) or triplet (T) levels, which may additionally be distinguished as neutral (N) or charged (C) levels, where a charge separation into $\text{Cu}^+ + \text{Cu}^-$ occurs asymptotically. These states may be named charge transfer states and are also referred to as ion-pair states; the corresponding separated ion limits are indicated as ss, sd, dd, respectively, in Table I, which summarizes the partition of the $\binom{22}{12} = 276$ valence states that can be obtained from a MCSCF or MRCI calculation in the (22,12)-CAS.

TABLE I. Number of singlet (S) and triplet (T) states in the (22,12)-CAS per irreducible representation of the D_{2h} point group, and their distribution as neutral (N) or charge transfer states (C), and whether the dissociation corresponds to the $(3d)^{10}(4s)^1 + (3d)^{10}(4s)^1$, the ss separated atom limit, or to the $(3d)^{10}(4s)^1 + (3d)^9(4s)^2$, the sd separate atom limit, or to the $(3d)^9(4s)^2 + (3d)^9(4s)^2$, the dd separate atom limit. Separated ion limits in the case of charge transfer states are indicated correspondingly. All states of the lines given in italics correspond to the latter dissociation channel and were excluded from the (22,18)-RAS.

Limit		A_g	B_{3u}	B_{2u}	B_{1g}	B_{1u}	B_{2g}	B_{3g}	A_u	Tot
N	ss	1S	...	...	...	1T	...	...	...	1S+1T
	sd	2S+2T	1S+1T	1S+1T	1S+1T	2S+2T	1S+1T	1S+1T	1S+1T	10S+10T
	dd	<i>6S+1T</i>	<i>3S+3T</i>	<i>3S+3T</i>	<i>3S+3T</i>	<i>1S+6T</i>	<i>3S+3T</i>	<i>3S+3T</i>	<i>3S+3T</i>	<i>25S+25T</i>
C	ss	1S	...	...	...	1S	...	...	...	2S
	sd	2S+2T	1S+1T	1S+1T	1S+1T	2S+2T	1S+1T	1S+1T	1S+1T	10S+10T
	dd	<i>6S+1T</i>	<i>3S+3T</i>	<i>3S+3T</i>	<i>3S+3T</i>	<i>6S+1T</i>	<i>3S+3T</i>	<i>3S+3T</i>	<i>3S+3T</i>	<i>30S+20T</i>

For the (22,18)-RAS calculations, only states belonging to the ss and sd separated atom limits in Table I were considered. States indicated by dd belong to double excitation from 3d orbitals and were excluded in the RAS-calculations. Indeed, electronic correlation inferred from double excitations of the 3d orbitals has been found to be less important than that inferred from excitation into additional 4p orbitals. It is known that the inclusion of 3d orbitals, or orbitals alike, the so-called 3d' orbitals, is necessary to improve on the calculation of the electronic correlation in transition metals.^{29,30}

It is also known that the MCSCF levels of copper are inverted with respect to experiment:³¹ dd levels (see Table I) lie below the sd and below the ss levels at the MCSCF level of theory. Therefore, in a (22,12)-CAS, the reference level giving rise to the dominant $d^{10}s^1$ configuration of the $^1\Sigma_g^+$ ground state is level number 9, from Table I. In the (22,18)-RAS reported in the present work, state number 3 is the reference level that correlates with the expected ground state configuration. Charge transfer states are not involved in this inversion of states.

One has therefore to calculate at least 3 states of symmetry 1 (A_g) in the MRCI program in order to grasp this level correctly. Similarly, one has to calculate at least 3 states of symmetry 5 (B_{1u}) in the MRCI program to grasp the lowest $^3\Sigma_u^+$ ($^3B_{1u}$) level. Even though charge transfer states are not involved in the inversion of states at the MCSCF level of theory, their inclusion into the set of states to be calculated at the internally contracted MRCI level of theory has shown to yield a clear improvement of the energy of the levels reported in this work. Specifically, the following number of roots was calculated at the internally contracted MRCI level: Four in 1A_g , three in singlet and triplet B_{1u} , one in each of singlet and triplet B_{3u} , B_{2u} , and A_u .

Following this rationale, it was possible to obtain the whole set of levels pertaining to the neutral ss and sd asymptotes. Because of the complete disorder between MCSCF reference and MRCI states, the Davidson cluster correction needs to be calculated with respect to the rotated reference state (i.e., use the MOLPRO variable `energdd3` for energies referring to relaxed coefficients in the rotated reference state).

While Table I is of practical relevance for theoreticians, it does not directly convey the information relevant to the spectroscopic states in the $D_{\infty h}$ point group. The corresponding neutral states in the ss separate atom limit decompose as

$^1\Sigma_g^+(^1A_g) + ^3\Sigma_u^+(^3B_{1u})$. In the sd separate atom limit, the corresponding states are $\Sigma_g^+(A_g) + \Sigma_u^+(B_{1u}) + \Pi_g(B_{2g} + B_{3g}) + \Pi_u(B_{3u} + B_{2u}) + \Delta_g(A_g + B_{1g}) + \Delta_u(B_{1u} + A_u)$, each as one singlet and one triplet state. Other important states in the present study stem from the ss limit of separate ions, i.e., charge transfer states with configurations of the type $(3d)^{10}(4s)^0 + (3d)^{10}(4s)^2$: $^1\Sigma_g^+(^1A_g) + ^1\Sigma_u^+(^1B_{1u})$. The latter will in particular be relevant for the assignment of the G state in Cu_2 , as will be discussed below.

Spin-orbit levels are finally computed from diagonalization of the Breit-Pauli operator represented in the basis of MRCI wavefunctions as implemented in the MOLPRO program package.²⁵ The latter exclude cluster corrections. In order to estimate the effect from cluster corrections on the spin-orbit levels, we noticed that the Davidson correction leads to an energy shift of the MRCI spin-eigenfunctions which can be simply related to an energy shift of corresponding spin-orbit eigenfunctions. Davidson corrected spin-orbit energies have hence been obtained by the formula

$$E_{MRCI+Q}^{(SO)} = E_{MRCI}^{(SO)} - E_{MRCI} + E_{MRCI+Q}, \quad (1)$$

where E_{MRCI} and E_{MRCI+Q} are the spin-eigenstates obtained at the MRCI level of theory without and with the Davidson correction, $E_{MRCI}^{(SO)}$ is the energy obtained from diagonalization of the Breit-Pauli operator, and $E_{MRCI+Q}^{(SO)}$ contains the estimated Davidson correction to the latter.

Relevant spin-orbit levels in this report are 0_u^+ and 1_u levels, in Hund's case (c) notation, as these are the only states accessible from the $X^1\Sigma_g^+$ ground state via optical excitation in the electric dipole approximation. Spin-orbit to spin-eigenstate correspondences used in connection with Eq. (1) and verified from inspection of the output of the MOLPRO program are given in the correlation Table II.

In addition to the 0_u^+ and 1_u levels, spin-orbit calculations involving the ungerade states in the ss and sd separated atom limits yield 0_u^- , 2_u , and 3_u levels. When all neutral and charge transfer states considered in the present calculation are included, the spin-orbit matrix has rank 28. These states separate as 4 A_g and 6 of each B_{3u} , B_{2u} , B_{1u} , and A_u irreducible representations of D_{2h} . Among the B_{3u} states, one finds one component of the 1_u and 3_u levels (the other component being among the B_{2u} states), among the B_{1u} states, one finds 0_u^+ and one component of the 2_u levels, and curve crossings may

TABLE II. Correspondence of the ungerade spin-orbit levels [in Hund's case (c) notation, right-hand side] to spin-eigenstates using notations from the $D_{\infty h}$ point group (left-hand side). Reported are all ungerade states belonging to the ss separated atoms and ions limits, as well as those belonging to the sd separated atom limit (see the text and Table I). Electronic term values T_e are given in units of cm^{-1} and were evaluated at the MRCI+Q level of theory at the interatomic distance of 220 pm, where the reference is the minimum of the $X^1\Sigma_g^+$ ground state.

Spin eigenstates		Spin-orbit states	
$2^1\Sigma_u^+$	34 567	34 611	30_u^+
$2^3\Sigma_u^+$	31 758	31 867	20_u^-
		31 867	41_u
$1^1\Delta_u$	27 325	28 005	32_u
$1^3\Delta_u$	26 886	27 785	31_u
		26 249	22_u
		26 051	13_u
$1^1\Pi_u$	23 177	23 264	21_u
$1^1\Sigma_u^+$	22 672	22 935	20_u^+
$1^3\Pi_u$	21 750	22 145	10_u^-
		21 925	10_u^+
		21 552	11_u
		21 267	12_u
$a^3\Sigma_u^+$	17 404	17 404	$a0_u^-$
		17 404	$a1_u$

occur. The correct assignment of levels and manual crossing was indeed necessary at several values of the inter-atomic distance r and carried out by inspection of the eigenvectors of the spin-orbit matrix, which vary as functions r . Only the relevant lowest states in each irreducible representation are finally reported in Sec. IV.

Table II is in line with the correlation diagram for the AgF molecule presented in Ref. 32 but for the position of the $^1\Sigma^+$ level, which lies below $^3\Pi$ in AgF. Also, the signs of the relative shifts of the spin-orbit states with respect to the spin-eigenstates are somewhat different in AgF.

IV. EXPERIMENTAL RESULTS

The production of copper dimers with the laser vaporisation source was first optimized using time of flight mass spectrometry combined with femtosecond ionization. One-colour (degenerate, DFWM) and TC-RFWM spectroscopy was subsequently performed on the known transitions of Cu_2 in the visible region, proving the efficacy of the non-linear spectroscopic methods.¹⁹

Transitions to the A' state were too weak to be observed with DFWM at the Cu_2 density present in the expansion. The low resolution scan of the (0,0) $A'-X^1\Sigma_g^+$ band shown in Fig. 1 was performed using the UP (or hole-burning) scheme of TC-RFWM (inset of Fig. 1) with the probe transition fixed close to the (0,0) $B^1\Sigma_u^+(0_u^+)-X^1\Sigma_g^+$ R-branch band head. The large strength of the $B^1\Sigma_u^+(0_u^+)-X^1\Sigma_g^+$ transition lends intensity to the four-wave mixing signal and enables the measurement of the $A'-X^1\Sigma_g^+$ transition. Double-resonance selection rules impose that only transitions are observed that originate from

FIG. 1. TC-RFWM of Cu_2 . The double-resonance spectrum is observed by tuning the probe laser close to the band head in the R-branch of the (0,0) $B^1\Sigma_u^+(0_u^+)-X^1\Sigma_g^+$ band at $21\,748.28\text{ cm}^{-1}$. Only lines originating from $J'' = 9 - 13$ are observed by scanning the pump lasers in the wavenumber region of the $A'-X^1\Sigma_g^+$ transitions. A dip in the branches occurs at $J = 12$ due to a strong saturation of the R(12) line by the probe laser.

labeled ground state rotational levels in the R-branch. The probe laser power was increased in order to saturate the transition and label as many rotational states as possible ($J = 6 - 13$). The adverse effects of such a saturation can be observed in the intensity distribution of rotational branches which show a dip³³ at $J = 12$. This rotational level is affected predominantly since the probe laser is centered at the R(12) line of the (0,0) $B^1\Sigma_u^+(0_u^+)-X^1\Sigma_g^+$ band.

To ensure that the A' state was one-photon accessible from the ground state (UP scheme), the scan was also performed with the probe laser fixed to rotational transitions in the (1,0) $B^1\Sigma_u^+(0_u^+)-X^1\Sigma_g^+$ and (0,0) $C(1_u^+)-X^1\Sigma_g^+$ bands. Rotational level selective scans at a much higher effective resolution were measured for the (0,0) and (1,0) bands of the $A'-X^1\Sigma_g^+$ electronic transition by fixing the probe laser to isolated transitions in the (1,0) $B^1\Sigma_u^+(0_u^+)-X^1\Sigma_g^+$ band. Transitions to $v' = 2$ and higher vibrational levels proved too weak to observe.

In Fig. 2(a), a typical DFWM scan of the (1,0) $B^1\Sigma_u^+(0_u^+)-X^1\Sigma_g^+$ band is plotted against a simulation of the transition using molecular constants from Ram *et al.*³⁴

The simulation is split into two components representing the contribution from both, the $^{63}\text{Cu}_2$ (green) and $^{65}\text{Cu}^{63}\text{Cu}$ (red) isotopologue to aid the dissemination of the experimental spectrum. Many transitions are found to overlap with other transitions in one or the other isotopologue.

To ensure spectral selectivity of the TC-RFWM scans of A' , the more widely spaced P-branch lines in the (1,0) $B^1\Sigma_u^+(0_u^+)-X^1\Sigma_g^+$ spectrum were used to label the individual rotational states [Fig. 2(a)]. Nevertheless, owing to the dense spectrum, often two rotational states (one in each isotopologue) were labeled simultaneously. The pump transition for each example in Figs. 2(b)–2(d) is marked with an arrow in Fig. 2(a), where $P(J'')$ denotes a transition within the $^{63}\text{Cu}_2$ isotopologue and $iP(J'')$ a transition within the $^{63}\text{Cu}^{65}\text{Cu}$ isotopologue. The minor isotopologue $^{65}\text{Cu}_2$ was not observed in this study due to the inherent squared dependence of the signal on the number density for four-wave mixing.

FIG. 2. Four-wave mixing spectra of Cu₂. (a) depicts a DFWM spectrum of the (1,0) B ¹Σ_u⁺(0_u⁺) - X ¹Σ_g⁺ band. Inverted, a simulated spectrum for ⁶³Cu₂ and ⁶³Cu⁶⁵Cu is shown in green and red, respectively. Simplified TC-RFWM spectra are obtained by intermediate labeling of specific rotational transitions (b)–(d). See the text for details.

Figure 2(b) is obtained by tuning the probe laser to P(13) in the (1,0) B ¹Σ_u⁺(0_u⁺) - X ¹Σ_g⁺ band of the ⁶³Cu₂ isotopologue at 21 984.66 cm⁻¹. This rotational transition coincides with P(9) of the ⁶⁵Cu⁶³Cu isotopologue and is denoted as iP(9) in Fig. 2(a). In the TC-RFWM spectrum, a ¹P₂₁(13), ¹Q₂₁(13), and ¹R₂₁(13) line of the A' - X ¹Σ_g⁺ transition is observed. Three more transitions are observed owing to the overlapping iP(9) line in the probe laser: ¹P₂₁(9), ¹Q₂₁(9), and ¹R₂₁(9). The rotational transitions define the term energies for J = 12, 13, and 14 for A' of the ⁶³Cu₂ isotopologue and J = 8, 9, and 10 for ⁶⁵Cu⁶³Cu.

In Figs. 2(c) and 2(d), additional TC-RFWM scans are shown for intermediate labeling of ground state rotational levels by the overlapping pairs iP(17)/P(20) and P(29)/iP(27) at

21 980.87 and 21 974.33 cm⁻¹ in the (1,0) B ¹Σ_u⁺(0_u⁺) - X ¹Σ_g⁺ band, respectively. Each spectrum shows clearly resolved lines that are easily assigned to transitions within each isotopologue. The spectra show the clear presence of a Q-branch, thus leading to the assignment of A' to 1_u in Hund's case (c). The plots shown inverted in this figure are simulations employing the molecular constants determined in this work for A' and the work of Ram *et al.*³⁴ for the ground state. Accurate simulation of four-wave mixing signal strengths requires careful control of the input laser intensities. For this work, however, no attempt was made to model the spectral intensity distribution in detail because results are obtained from line positions. Line intensities are however used as a guide for the assignment. The individual TC-RFWM spectra were analyzed and

TABLE III. Optimized molecular constants for the A' state. All values are given in cm⁻¹. T is relative to the X, v = 0 state. Uncertainties are one standard deviation.

Parameter	⁶³ Cu ₂ , v = 0	⁶³ Cu ₂ , v = 1	⁶⁵ Cu ⁶³ Cu, v = 0	⁶⁵ Cu ⁶³ Cu, v = 1
T _v	20 100.409 0(16)	20 333.481 3(30)	20 100.491 1(14)	20 331.796 8(27)
B _v	0.105 764 0(44)	0.105 032(14)	0.104 160 7(45)	0.103 345(10)
Observations	50	53	75	38
RMS	0.008	0.011	0.009	0.011

peak positions were determined using the peak finding algorithms in PGOPHER.³⁵ The spectroscopic constants for A' are presented in Table III. The RMS values of all the fits are less than the linewidths of the dye lasers. Statistical uncertainties are given in units of the last significant figure. No allowance is given for systematic errors in the calibration. A complete line list is included in the [supplementary material](#). Considering the T_v values in Table III, the vibrational term differences $\Delta G_{1/2}^{36} = T_1 - T_0 \approx \omega_e - 2\omega_e x_e \approx \omega_e$, one obtains an estimation for the equilibrium constants ω_e and ω'_e for the two isotopologues $^{63}\text{Cu}_2$ and $^{63}\text{Cu}^{65}\text{Cu}$ of 233.0723 cm^{-1} and 231.3057 cm^{-1} , respectively. Similarly, an estimation for B_e (and B'_e) is obtained by $B_e \approx B_0 + \alpha/2$, where $\alpha \approx B_0 - B_1$ which results for the two isotopologues to 0.106 130 and 0.104 569 cm^{-1} . The corresponding equilibrium distance r_e is 2.246 Å. The usual isotope relationships $\omega'_e/\omega_e = \rho$ and $B'_e/B_e = \rho^2$ can be tested for consistency, where $\rho = \sqrt{\mu/\mu'}$ and μ and μ' are the reduced masses of the isotopologues. The experimental values $\rho = 0.9924$ and $\rho^2 = 0.9853$ are in good agreement with the theoretical mass relations, i.e., 0.9923 and 0.9845, respectively.

V. AB INITIO RESULTS

Figure 3 shows potential energy functions of some spin eigenstates and corresponding spin-orbit states in the ss and sd channels from calculations in the (22,18)-RAS at the MRCI+Q level of theory. Only ungerade states that might contribute to observable transitions from the $X^1\Sigma_g^+$ state are shown, and assignments result from the analysis of the data discussed in the following. The reader is also referred to Table II for additional information on the correspondence of states in Hund's cases (a) and (c). All Hund's case (c) potential functions are also given in a table in the [supplementary material](#).

The dissociation energy in the $X^1\Sigma_g^+$ ground state is $D_e \approx 16\,500\text{ hc cm}^{-1}$ (the MRCI raw value without the Davidson correction is $14\,950\text{ hc cm}^{-1}$), which is close to the experimentally estimated value $16\,530\text{ hc cm}^{-1}$ ¹ (and references therein). Furthermore, the minimum of the potential energy function is between 220 and 225 pm, which also fits well the value estimated experimentally (222 pm³⁴).

The two excited $^1\Sigma_u^+$ levels show a clear avoided crossing between 300 and 350 pm, indicating a change in character.

FIG. 4. Spin-orbit states. Left-hand side: MRCI+Q results $E_{\text{MRCI+Q}}^{(\text{SO})}$ following Eq. (1) (detail of Fig. 3). Right-hand side: raw MRCI results $E_{\text{MRCI}}^{(\text{SO})}$ without the Davidson-correction. See also the caption of Fig. 3 and the discussion of the assignment in the text.

Indeed, inspection of the transition dipole moment indicates that for distances below 350 pm, the lower of the two $^1\Sigma_u^+$ levels has a strong ion-pair character (charge transfer), while the upper level is neutral. This character is exchanged beyond that distance.

Asymptotically, spin-orbit states split by about 2040 cm^{-1} (2043 cm^{-1} from experiment³⁷), and terms are as expected: the first two 1_u levels in the sd separated atom limit and the first 0_u^+ level correlate with the lower $5/2$ D-sublevel, while the last two 1_u levels and the second 0_u^+ level correlate with the higher $3/2$ D-sublevel. The calculated $D_{5/2} \leftarrow S_{1/2}$ excitation energy is $12\,334\text{ hc cm}^{-1}$, and hence about 1000 hc cm^{-1} larger than the experimental energy difference.³⁷

Figure 4 shows a zoomed version of the spin-orbit potential functions of Fig. 3. On the right-hand side of this figure, the spin-orbit states obtained from the direct evaluation of the Breit-Pauli Hamiltonian are shown, i.e., the $E_{\text{MRCI}}^{(\text{SO})}$ energies of Eq. (1). Both Figs. 3 and 4 report results obtained with the AVQZ-DK basis.

It should be noted that the levels $1\,0_u^+$ and $2\,0_u^+$ result from a repulsion of two 0_u^+ levels in the $^3\Pi_u$ and the $^1\Sigma_u^+$ manifolds as a consequence of the spin-orbit coupling. Similarly, the four levels $1\,1_u$ to $4\,1_u$ levels result from the spin-orbit interaction of four 1_u levels in the $^3\Pi_u$, $^1\Pi_u$, $^3\Delta_u$ and the second $^3\Sigma_u^+$ manifolds. While the position of the $2\,1_u$ level is hardly shifted from that of the corresponding $^1\Pi_u$ level, that of the $1\,1_u$ level

FIG. 3. Adiabatic potential functions for the ground state and some ungerade excited states in Cu_2 from MRCI+Q calculations with the AVQZ-DK basis. Relaxed Davidson correction is calculated with respect to rotated reference functions for all levels. Spin eigenstates are shown on the left-hand side, spin-orbit states on the right-hand side. The zero reference energy is the energy of the $X^1\Sigma_g^+$ state, -3307.4167 E_h , at $r \approx 222\text{ pm}$, where $E_h \approx 4.36 \times 10^{-18}\text{ J}$ is the hartree. The legend gives the states in the order of appearance from bottom to top at this equilibrium distance. See also the text for further explanations and a discussion of assignments.

TABLE IV. Experimentally determined electronic and vibrational term values and rotational constants B_0 (in cm^{-1}), equilibrium distances r_e or r_0 (in pm), calculated cross sections $G_{v'v''}$ (in pm^2), and fluorescence lifetimes $\tau_{v'=0}$ (in μs) for some low lying excited states of Cu_2 in comparison with theoretical values from the present work.

Theory (this work)																	
Expt.						MRCI		MRCI+Q								Label	Assignment
T_0^a	$\Delta G_{1/2}^a$	r_e	τ_0	Properties	Reference	T_0^a	$\Delta G_{1/2}^a$	T_0^a	$\Delta G_{1/2}^a$	B_0	r_0	$G_{v'0}$	$(v')^b$	τ_0			
20 100	233	2.246		Q band, middle	This work	19 750	190	21 480	223	0.105	2.26	4.1	(0)	3.0	A'	1 1_u	
20 396	192	2.283	0.115	No Q band, strong	6	19 798	158	21 673	183	0.100	2.32	100.0	(0)	0.04	A	1 0_u^+	
21 748	241	2.328	0.04	No Q band, strong	6	20 984	213	22 506	230	0.100	2.32	190.0	(1)	0.03	B	2 0_u^+	
21 844	218	2.264	0.8	Q band, strong	6	21 344	167	23 132	201	0.103	2.28	44.0	(0)	0.2	C	2 1_u	
25 508	160	2.380	6.5	Weak	6	24 157	127	26 448	154	0.088	2.47	0.15	(6)	4.0	D	3 1_u	
27 136	223			Weak	1	24 988	124	27 736	140	0.074	2.70	≤ 0.001	(c) ^c		E	4 1_u ?	
28 541	246			Weak	6										F	?	
30 678	116	2.730		Middle	6	29 079	124	31 506	117	0.073	2.71	9.2	(26)	0.008	G	3 0_u^+	

^a T_0 defined with respect to the $v = 0$ state in the $X^1\Sigma_g^+$ manifold. $\Delta G_{1/2} = T_1 - T_0$ in the corresponding electronic manifold.

^b $G_{v'v''}$ is the maximal absorption or emission cross section between state v' in the excited electronic level and state $v'' = 0$ in the electronic ground level, the value of v' is given in parentheses.

^cThe maximal absorption or emission cross section lies in the continuum. The value given refers to the cross section to the highest bound state $v' \sim 28$.

is pushed by about 300 hc cm^{-1} below the $^3\Pi_u$ level. The $a 1_u$ level, which relates to the first $^3\Sigma_u^+$ level, is hardly affected by the spin-orbit calculation and essentially coincides with the $^3\Sigma_u^+$ level. The same holds for level $3 0_u^+$, which essentially coincides with the higher $^1\Sigma_u^+$ level shown in Fig. 3 above.

The Davidson corrected MRCI energies are about 1000 to 1500 hc cm^{-1} higher than the raw MRCI values in which the Davidson correction is not included. As will be discussed below, the raw MRCI results are in somewhat better agreement with the experimental transition energies between electronic levels. However, we believe that this is a rather lucky good agreement that could be related to fortunate error cancellations. We shall consider the Davidson corrected results to be more reliable in reference to the whole set of experimental data, despite the larger differences from experimental electronic term values. It is possible that calculations in a larger CAS space would capture electronic correlation better and hence reduce this discrepancy. However, such calculations are outside the scope of the present work. Table IV summarizes the results.

T_0 values in Table IV are defined with respect to the $v = 0$ state in the $X^1\Sigma_g^+$ manifold. Theoretical values were calculated from a Chebychev DVR (discrete variable representation, see Refs. 38 and 39) on a grid of 401 points between 170 and 400 pm, which ensures convergence. A cubic spline interpolation of 13 points calculated *ab initio* was performed to evaluate the potential energy functions on this grid. The copper-63 mass 62.9296 u was used.

While the calculated term values including the cluster correction exceed the experimental ones by about 800 to 1500 cm^{-1} , the uncorrected results underestimate the five lowest observed bands by 400 to 1300 cm^{-1} . Although the latter are somewhat closer to experimental values, we consider the former to be more reliable for two reasons. First, consider the term differences $T_0(Y) - T_0(1 1_u)$ in the manifold of states $Y = 1 0_u^+, 2 0_u^+, 2 1_u, 3 1_u$, and $3 0_u^+$. They are 48, 1234, 1594, 4407, 9329 cm^{-1} , respectively, in the MRCI calculation. In

the MRCI+Q calculation, they are 193, 1026, 1652, 4968, and $10 026 \text{ cm}^{-1}$. Experimentally, if one accepts the assignment proposed in Table IV, they are 296, 1648, 1744, 5408, and $10 578 \text{ cm}^{-1}$, in the respective order, and hence better reproduced by the cluster corrected calculations. Second, as indicated in Table IV, calculated vibrational terms differ from measured values by about 10 cm^{-1} for the MRCI+Q potentials, while differences are a factor of 3 larger for the MRCI results.

Rotational constants B_0 , averaged positions r_0 , and cross sections are calculated as expectation values of the corresponding operators using the vibrational wave functions determined from the MRCI+Q potentials. Cross sections are defined by

$$G_{v',v''} = \frac{2\pi^2}{3hc\epsilon_0} M_{v',v''}^2, \quad (2)$$

where h is the Planck constant, c is the speed of light in vacuum, ϵ_0 is the electric constant, and $M_{v',v''}^2 = \sum_{\alpha} |\langle \psi_{v'} | \mu_e^{(\alpha)} | \psi_{v''} \rangle|^2$ are transition dipole moments using full transition electric dipole moments functions $\mu_e^{(\alpha)}$ ($\alpha = x, y, z$) between the electronic states involved as obtained from the raw MRCI calculations. These functions are also collected in a table in the [supplementary material](#). Only the maximal values for absorption transitions $v' \leftarrow v'' = 0$ are reported in Table IV, where v' is the vibrational quantum number in the electronically excited state and v'' is the vibrational quantum number in the electronic ground level. The corresponding v' of the maximum is also given in the table. The cross sections mirror the weak and strong electronic transitions well.

Using the calculated cross sections, we also report fluorescence lifetimes $\tau_{v'} = 1/A_{v'}$ for several states, where $A_{v'} = \sum_{v''} A_{v',v''}$ and $A_{v',v''} = 8\pi c |\tilde{\nu}_{v'} - \tilde{\nu}_{v''}|^3 G_{v',v''}$ is the Einstein A-coefficient involving states v' and v'' in the corresponding electronic manifolds.

The assignments proposed in Figs. 3 and 4 as well as in Table IV will be discussed in the following.

VI. DISCUSSION

The spectra shown in Fig. 2 demonstrate the strengths of TC-RFWM spectroscopy. For a TC-RFWM signal to be generated, two resonant transitions must share a common intermediate state. Thus, with the use of narrow band nanosecond lasers, single rotational levels can be selected (or labeled) and only transitions from the selected rovibronic level are observed. This selectivity simplifies the assignment of spectra considerably and leads to an *effective* resolution that is much higher than is achievable with standard spectroscopic techniques. As such, the position of individual lines within bandheads can be measured in isolation. TC-RFWM is particularly effective for deciphering overlapping bands and detecting small shifts and extra lines caused by perturbations.

The gas-phase measurements of the electronic structure of Cu₂ were reviewed by Morse in 1993.⁶ Since then, several new states were observed in the UV in absorption⁴⁰ and improved spectroscopic constants for the D state were reported in a study of Cu₂ in supercooled helium.⁴¹ Despite the considerable amount of attention that the copper dimer has received, very few of the excited electronic states have been rotationally resolved and assigned spectroscopic constants.

Aside from the ground state and the lowest triplet state that correlate to 3d¹⁰4s¹2S ground state atoms, the low energy electronic structure of Cu₂ is dominated by states that correspond to the ²S + ²D_(3/2,5/2) (3d⁹4s²) pair of atomic limits. The necessity of describing these “d-hole” excited states in Hund’s case (c) coupling was first proposed by McCaffrey *et al.*² to explain the presence of two ¹Σ_u⁺ states in the visible wavelength range. However, the second ¹Σ_u⁺ state could also arise from an ion-pair state and the influence of ion-pair states in this energy region has been inferred from the very short lifetimes of the A (115 ns) and B (40 ns) states.⁶ The discovery of the A’ state confirms Hund’s case (c) coupling is required to account for the number of low energy electronic states observed (*vide infra*.)

For states in the 20 000–22 000 cm^{−1} energy range, the only reasonable separated atom limits are ²S + ²D_{5/2} and ²S + ²D_{3/2}. The following set of dd separated atom limits consist of a pair of d-hole atoms and have a net bond order of zero if the 3d electrons are considered to be non-bonding. The next highest separated atom limit is ²S + ²P⁰ at 30 535 cm^{−1} above the ground state limit and would require the states to be bound with more than 25 000 cm^{−1}, which is considerably more than the ground state bonding energy of 16 530 cm^{−1}.¹

The states that arise from the ²S + ²D separated atom limits in both Hund’s cases (a) and (c) are covered extensively in the work of Page and Gudeman.⁴² Importantly, under Hund’s case (a), there are only two states that can spectroscopically couple with the ground state via the electric dipole: ¹Σ_u⁺ and ¹Π_u. The C state at 21 843.9 cm^{−1} has already been identified as ¹Π_u in Hund’s case (a) and thus the A’ state cannot be accounted for in this coupling scheme. The A and B ¹Σ_u⁺ states had also presented a problem, but the presence of a second ¹Σ_u⁺ in this energy range could be attributed to the presence of ion-pair states.¹ The same argument cannot be used to explain the presence of an additional ¹Π_u state in this energy range as the lowest ¹Π_u ion-pair states are

expected to lie at least 1 eV above the lowest ¹Σ_u⁺ ion-pair state.¹

In Hund’s case (c), one 0_u⁺ and two 1_u states arise from each of the ²S + ²D_{5/2} and ²S + ²D_{3/2} separated atom limits.⁴² This easily accounts for the A’, A, B, and C states and indicates that two further 1_u states should be spectroscopically accessible from the ground state. One of these states may be the D state, which has so far only been observed in matrices and ultracold helium.^{41,43} The other state could be state E,¹ although the observation of that state might still be questionable.⁶ The assignment of the E and F bands is uncertain. These states could also arise from the dd limit of separated atoms, but the calculation of states belonging to that limit is outside the scope of the present work. If this hypothesis be true, the 4 1_u state would then be a state that has not yet been measured. Apart from the E and F states, our theoretical results in Figs. 3 and 4 as well as in Table IV indeed strongly support these assignments from the overall inspection of relative energies and other calculated properties of the states. From these results, band G can definitely be assigned to the third 0_u⁺ state [or ¹Σ_u⁺ in Hund’s case (a) notation] which would correspond asymptotically to the B_{1u} charge transfer state in the ss limit of separated ions of Table I, confirming thus the conjectures made by Rohlfing and Valentini.⁴⁴

The calculated fluorescence lifetimes reported in Table IV underestimate the observed values for the A and C states by a factor of four but fit rather nicely the values for states B and D. The accuracy of these calculated properties is unknown. Their variance can be rather large even with small changes of the shape of the potential and dipole moment functions. We therefore consider only the qualitative aspect of the calculated cross sections and fluorescence lifetimes in Table IV, which seem nevertheless to contribute coherently to the proposed assignment. As a matter of fact, the intensity ratio of roughly 20:10:1 observed by Bondybey *et al.* for the *v*’ = 0, 1, and 2 peaks, respectively, in the laser excitation spectrum of state A and depicted in Fig. 1 of their paper⁴³ is rather well reproduced by values calculated during this work (15:10:2).

The *ab initio* study of the copper dimer in this work is the first to consider the low energy states in Hund’s case (c) terms. The energy ordering of 0_u⁺ and 1_u terms fits exactly to what has been observed experimentally. The 1 0_u⁺, 2 0_u⁺, 1 1_u, and 2 1_u terms can easily be assigned to the A, B, A’, and C states, respectively. Doverstål *et al.*⁵ assigned the C (1_u) state as correlating with the lower of the two ²S + ²D separated atom limits based upon the measured dissociation energy. Thus, as to not violate non-crossing rules, A’ is also assigned to correlate with the lower of the two separated atom limits.

The study of Witko and Beckmann⁴⁵ is one of the few previous *ab initio* investigations of the excited states of the copper dimer. The case (a) terms that lead to spectroscopically accessible case (c) states are ¹Σ_u⁺ (0_u⁺), ¹Π_u (1_u), ³Σ_u⁺ (1_u), ³Π_u (0_u⁺ and 1_u), and ³Δ_u (1_u). According to Witko and Beckmann, these terms are ordered as such ³Σ_u⁺ < ³Π_u < ¹Σ_u⁺ < ¹Π_u < ³Σ_u⁺ < ³Δ_u. The case (c) ordering then perfectly matches that of the experimentally determined states in the sd separated atom limit: A’ 1_u < A 0_u⁺ < B 0_u⁺ < C 1_u. In addition to being coherent with these previous calculations, the theoretical results from the present work give almost quantitative agreement

with the experimental values. Furthermore they confirm the importance of spin-orbit couplings, which were omitted in Ref. 45.

Support for the aforementioned assignments can be found in the studies of the electronically similar CuAu and Au₂. In the work of Bishea *et al.*⁴⁶ on CuAu, it was shown that despite the small spatial extent of the 3d Cu orbitals, they are indeed split into bonding and antibonding orbitals. By following the example of Bishea and Morse for the case of Au₂⁴⁷ and applying it to Cu₂, it is found that the energy ordering of the 3d orbitals is $d\sigma_g < d\pi_u < d\delta_g < d\delta_u < d\pi_g < d\sigma_u$, which leads to an ordering of the $^2S + ^2D$ excited state terms for each multiplicity of $\Sigma_g^+ < \Pi_u < \Delta_g < \Delta_u < \Pi_g < \Sigma_u^+$. Due to exchange effects, the triplet states are expected to lie below the respective singlet states of the same term. This analytical ordering of states is found to mostly hold for Au₂ with only a very major deviation found in the case of the $^1\Sigma_u^+$ term, which instead of lying highest in energy is found to have the largest binding energy for this set of states,^{47,48} very likely due to strong mixing with ion-pair states.

The *ab initio* calculations of Das and Balasubramanian on Au₂⁴⁸ provide significant insight into the excited electronic states of this species and can be extended to Cu₂. The $A0_u^+$ state of Au₂, for example, was found to have 49% $^3\Pi_u$ ($s\sigma_u \leftarrow d\pi_g$), 21% $^1\Sigma_u^+$ ($s\sigma_u \leftarrow d\sigma_g$), and 12% $^1\Sigma_u^+$ ($s\sigma_u \leftarrow s\sigma_g$) character, where $s\sigma_u \leftarrow s\sigma_g$ corresponds to a charge transfer transition to an ion-pair state. The inclusion of 12% ion-pair state character is significant as it leads to the large oscillator strength observed for this transition.⁴⁷ The even larger oscillator strength of the $B0_u^+ \leftarrow X^1\Sigma_g^+$ transition is in good agreement with the 49% ion-pair character calculated for this state.⁴⁷ The calculations of Das and Balasubramanian also reveal that the lowest two 1_u states have primarily $^3\Pi_u$ and $^1\Pi_u$ character, respectively. Bishea and Morse⁴⁷ assert that these two states correlate with the experimentally measured A' and B' states of Au₂. They also make the observation that the primary $^1\Pi_u$ and not $^3\Delta_u$ character of the second lowest 1_u implies that the energetic splitting of the 5d orbitals in Au₂ is larger than the exchange interactions.

When comparing the experimental and theoretical results for the gold and copper dimers, many similarities are seen. The absorption cross sections of the A and B states in the copper dimer follow a very similar trend and are much larger than for transitions from the ground state to either of the experimentally observed 1_u states. Again, for Cu₂ the B–X transition is the strongest observed in the low energy regime and suggests that the $B0_u^+$ state has significant ion-pair character, which is confirmed by the calculated transition dipole moments in the present work as well as by the *ab initio* calculations of Witko and Beckmann,⁴⁵ who showed that the (ion pair) $\dots 4s\sigma_g 4s\sigma_u$ electronic configuration dominates over $^1\Sigma_u^+$ ($s\sigma_u \leftarrow d\pi_g$) for small internuclear distances. The large cross section of the A–X transition also implies that the $A0_u^+$ state exhibits fractional ion-pair character.

Finally, a discussion on the inability of previous experimental studies to observe the A' state is merited. The first rotationally resolved study of the A state by Pesic and Weniger³ noted the presence of Q-branches, which were not observed in subsequent experimental measurements of this state. Later,

experimentalists assumed that the observation of Q-branches in the spectra of Pesic and Weniger was an error by these workers born from confirmational bias due to the previous assignment of the B state to $^1\Sigma_u^+$, thus leaving only a single $^1\Pi_u$ state to couple spectroscopically with the ground state. Crucially however, the majority of these studies were performed using laser induced fluorescence, an emission-based spectroscopic technique, whereas that of Pesic and Weniger is roughly described as a combination of absorption and emission spectroscopies.³ Given the small separation of the A' and A vibrationless levels of $\approx 300\text{ cm}^{-1}$, the Q-branches recorded by Pesic and Weniger are almost certainly those of the A' state. Indeed the $v' = 1$ level of A' is only $\approx 60\text{ cm}^{-1}$ below the A $v' = 0$ level. We surmise that the A' $v = 0$ state was also observed in the recent two-photon ionisation/hole burning study of Parry *et al.*⁴⁹ There it was assumed to be a hot-band of the A–X system; however, no hot-bands are observed for the stronger B–X system. While a measurement of the lifetime of the A' state was not possible in this work, the calculations yield 3 μs . Such a long lifetime is likely inhibiting LIF studies in a molecular beam. For matrix based LIF studies, the A'–X (0,0) emission would have been buried under the much stronger A–X (0,1) and (0,2) signals. It would then only be observed if the excitation laser frequency were tuned exactly to the transition and no fluorescence from the A–X system were present.

VII. SUMMARY AND CONCLUSION

We report the application of resonant four-wave mixing techniques to the identification of a new low lying 1_u state in the Cu dimer. The highly selective nature of TC-RFWM enabled the separation of the spectra into single J components. The discovery of a second 1_u state in the low energy regime and the present *ab initio* calculations prove the assertion of earlier researchers that spin-orbit or J – J coupling is required to account for the number of observable states from the $^2S + ^2D$ separated atom limits of Cu₂. This work also solves a more than 40 year old mystery in the initial experimental assignment of the A state.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for measured transition wavenumbers by applying double-resonant four-wave mixing spectroscopy, as well as potential functions and transition dipole moments involving the ground and excited ungerade states from the computations. Four tables are included that contain line lists of $v = 0$ and $v = 1$ for the isotopologues $^{63}\text{Cu}_2$ and $^{65}\text{Cu}^{63}\text{Cu}$, respectively. Upper level and transition assignments are listed in addition to the fixed probe lines used for intermediate level labeling of the ground state rotational level in the (1-0) band of the $B^1\Sigma_u^+(0_u^+) \leftarrow X^1\Sigma_g^+$ electronic system. Molecular constants in Table III are obtained by applying non-linear least-square fit algorithms in PGOPHER³⁵ to the observed transition wavenumbers and keeping the constants for the ground state fixed at the values reported by Ram *et al.*³⁴ The supplemental tables contain the residuals for each

transition. Finally, two tables are added listing potential and transition electric dipole moment functions.

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