The ion-pair character of the B0+ state of CuAg

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In order to obtain fundamental insight into the bonding properties of transition metals, the (ν',0) B-X transitions (ν' = 0 – 2) of the heteronuclear CuAg dimer are re-investigated by applying non-linear four-wave mixing and laser-induced fluorescence spectroscopy. The CuAg molecules in a molecular beam are produced by laser ablation of a Cu/Ag alloy target. Rotationally resolved spectra of the B-X transition are recorded. The measurements yield accurate molecular constants for four isotopologues and an equilibrium distance R_e = 2.4577 ± 0.0003 Å for the B state. In particular, the B state is identified as an Ω = 0+ ion-pair state. The results corroborate the important contribution of the charge-transfer state to the metal–metal bond. The results are in good agreement with the recent calculations at the MRCI level of theory (Alizadeh et al., 2014).

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1. Introduction

Among transition metals, the coinage metal dimers (Cu2, Ag2, Au2, CuAg, CuAu, AgAu) exhibit relatively simple electronic structures and provide a unique opportunity to improve our knowledge on the metal–metal bond and, in particular, on the contribution of the d-orbitals to the properties of these diatomic molecules. By performing an accurate spectroscopic characterization of the ground and low lying excited states, detailed information on the electronic configuration of these states is obtained. In addition, such spectroscopic results are essential for the validation of ab initio structure calculations of the diatomics, which in turn provide the basis to model transition metal compounds comprising a larger number of atoms. Therefore, a substantial amount of experimental [1–8] and theoretical work [9–18] has focused on the electronic structures of coinage metal dimers.

It has been realized [2] that the relatively large electron affinity and low ionization potential of the coinage metal atoms might lead to low lying ion-pair states. A typical energy map outlined for CuAg is shown in Fig. 1. The ion-pair limit Cu+(3d10) + Ag+(5s) at r = ∞ follows a Coulomb attraction curve (−e²/R) towards shorter nuclear distance and intersects with several low lying electronic states [19]. In particular, the Coulomb curve intersects the horizontal lines of the neutral atom-pairs at large internuclear distance. For instance, the intersection with the Cu(4s)+Ag(5p) limit is approximately at twice the equilibrium distance of the B0+ state. For such a large separation the ionic bonding characteristics of the B0+ state is expected to be dominant. In contrast, the intersections for the X0+ and A0+ states are in the vicinity of the equilibrium distance and covalent bonding is likely to prevail.

Similar electronic properties are expected for all coinage metal dimers. The separated ions attract one another from the asymptotic atomic limit of the ground states M_A-B[core][d10] + M_B/A [core][10s2], and their potential energy curves towards shorter internuclear distance affect the low lying electronic state properties significantly. They provide additional 1Σ+ (or 0+ in Hund’s case (c) notation) states because of their closed shell structure. The ion-pair state undergoes configuration mixing and avoided crossings with potential energy curves of the same symmetry that correlate with the covalent asymptotic limits [20]. Ion-pair states play, therefore, an important role in the redistribution of electron density. Such charge-transfer processes govern important reaction mechanisms. For instance, recent experiments show that transition metal dimers dispersed on porous carbon nanomaterials emerge as promising catalysts with maximum atomic efficiency and good durability. The basic and fundamental reasons for the enhanced activity is closely related to polarizability in the electronic structure of the bimetallic catalysts and its environment [21–23]. However, a detailed understanding of the underlying mechanisms is still lacking and hinders the development of more efficient and selective catalysts.

In comparison to the homonuclear coinage metal dimers, knowledge about the heteronuclear CuAg is rather limited. In 1956, Ruamps et al. [24] observed the B-X emission spectra of CuAg in a King furnace and reported the origin band at ν0 = 25825 cm⁻¹.
Soon after, Joshi et al. recorded numerous hot bands of the B-X transition in emission and obtained agreement for the origin band and reported vibrational frequencies \( v_{0X} = 178.5 \text{ cm}^{-1} \) and \( 231.8 \text{ cm}^{-1} \) for the B and X states, respectively [25]. Decades later, Bishea et al. [19] investigated the A-X, A'-X, B'-X and B-X band systems of jet-cooled CuAg molecules using resonant two-photon ionization spectroscopy. The determined \((0,0)\) B-X band head position, \( v_{0B} = 25827.63(93) \text{ cm}^{-1} \), is slightly higher than the result from the emission studies [25,24]. Even though the A-X, A'-X and B'-X bands were rotationally resolved, Bishea et al. were not able to analyze the rotational structure of the significantly stronger B-X electronic system by mass-resolved ionization spectroscopy. This transition has a lifetime of \( \tau \approx 14 \text{ ns} \) which implies an oscillator strength of \( f \approx 0.16 \) by assuming that B state fluorescence decays only to the ground state [19]. As discussed in Ref. [2], such a large oscillator strength in coinage metal dimers is indicative of a charge transfer process leading to an ion-pair state.

The CuAg molecule has also attracted the interest of theoreticians [26–30]. *Ab initio* quantum chemical calculations of transition metal dimers are difficult. To obtain reliable data that can be compared with spectroscopic results, electron correlation, relativistic effects and spin–orbit interaction have to be included. The recent work of Alizadeh et al. [30] has investigated the ground and low-lying excited states of CuAg by using the multi-reference configuration-interaction (MRCI) level of theory. The calculated molecular constants for the X, A, A' and B' states are in good agreement with experimental results [19,25]. In particular, the B state has been assigned to the \( 3^1\Sigma^+ \) (00) state which is essentially an ion-pair state at internuclear distances shorter than 3.2 Å. The oscillator strength for the transition from the ground state X0^- is computed to amount to \( f = 0.37 \), indicating a strongly allowed transition with significant charge-transfer character. Please note, as spin–orbit interaction is non-negligible in dicopper [31], states of CuAg are labeled likewise in the following by using their total angular momentum about the internuclear axis \( \Omega \) in Hund's case (c) notation, i.e. X0^- for the CuAg ground state. The B0^- state is computed to mix with other \( \Omega = 0 \) states and undergoes avoided curve crossings as it approaches the Cu^+ + Ag^- separated atom limit. However, to validate the ion-pair character of the B state, further experimental data is required. In particular, rotationally resolved measurements are required to determine the symmetry of this important low-lying state.

In this paper, we report on the high resolution spectroscopy of the B-X electronic system of the heteronuclear transition metal dimer CuAg. The work is based on the recent theoretical and experimental work on the homonuclear dimer Cu2 in our laboratory that revealed the significant ion-pair character of both the B0^+ [31] and G0^+_J [31,38] states. In contrast to the homonuclear species, both 0^- ion-pair states arising from the lowest asymptotic limits (Cu^+Ag^- and Cu^-Ag^+) are, in principle, spectroscopically accessible from the X0^- ground state because the inversion symmetry \( 0^+_\pi \) and \( 0^-_\pi \) states of the homonuclear dimers are no longer present and the selection rules \( g \leftrightarrow g \) and \( u \leftrightarrow u \) lose their meaning. Often, however, strong mixing between the two states might increase the transition strength of one ion-pair state and reduce it for the second. We examine, by applying high resolution spectroscopy, the detailed electronic and structural properties of the B state. The two-color resonant four-wave mixing (TC-RFWM) and laser-induced fluorescence (LIF) methods yield rotationally resolved spectra of the B-X electronic system for the first time. The total angular momentum about the internuclear axis, \( \Omega \), is unambiguously assigned. By considering the determined vibrational and rotational frequencies for four isotopologues, the charge-transfer character of the B state can be further corroborated. In addition, the detailed results allow verification of the applied methods for *ab initio* MRCI and time-dependent density functional theory calculations [30].

### 2. Experiment

The experimental setup is reported in our previous reports [31,32] and outlined briefly in the following. The CuAg molecules are produced by laser ablation of a copper/silver (1:1) alloy disk in a home-built cluster source. The ablation plume is entrained in a helium pulse and expanded into high vacuum. Molecules condense and are internally cooled by the near-supersonic expansion. The collision-free molecular beam contains, among other species, the target molecule CuAg. Two-color resonant four–wave mixing (TC-RFWM) and laser induced fluorescence (LIF) spectroscopy are applied approximately 1 cm downstream of the nozzle exit. TC-RFWM is performed by focusing three parallel propagating laser beams by a lens into the interaction region. If two resonances are addressed in a molecule simultaneously and connected by a com-

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**Fig. 1.** Atom-pair limits of the ground and first excited states (solid black lines) and the lowest lying ion-pair limit (solid line, violet) for CuAg. The determined (0,0) B-X band head position, \( v_{0B} = 25827.63(93) \text{ cm}^{-1} \), is slightly higher than the result from the emission studies [25,24]. Even though the A-X, A'-X and B'-X bands were rotationally resolved, Bishea et al. were not able to analyze the rotational structure of the significantly stronger B-X electronic system by mass-resolved ionization spectroscopy. This transition has a lifetime of \( \tau \approx 14 \text{ ns} \) which implies an oscillator strength of \( f \approx 0.16 \) by assuming that B state fluorescence decays only to the ground state [19]. As discussed in Ref. [2], such a large oscillator strength in coinage metal dimers is indicative of a charge transfer process leading to an ion-pair state.
A signal beam is produced in the forward direction governed by phase-matching conditions [33] and detected essentially background-free by a photo-multiplier tube. Fluorescence emission is sampled perpendicularly to the molecular beam and the main axis of the incoming laser beams and focused onto the slit of a 1 m spectrometer in front of a second photo-multiplier tube.

3. Results and analysis

Fig. 2 shows a TC-RFWM spectrum of the (1,0) band of the B-X electronic transition. Double-resonance spectroscopy is performed by tuning the frequency of the PUMP lasers to the R-branch of the (2,0) A0 + - X0 + transition at 21146.12 cm⁻¹ and scanning the PROBE laser in the wavelength region of the (1,0) B-X band. Four main isotopologues (63Cu107Ag, 63Cu109Ag, 65Cu107Ag, and 65Cu109Ag) are observed in the spectra because the frequency of the PUMP lasers and the applied pulse energy above saturation is simultaneously labeling numerous overlapping rotational levels of all isotopologues. In this range of wavelengths, only transitions are observed by the double-resonance method that exhibit common ground states with the PUMPed lines. Thus, the spectrum in Fig. 2 confirms that the spectral carrier is the CuAg molecule. More importantly, the clear absence of a Q-branch in the spectrum strongly suggests that the B-X transition is in fact a Σ + - Σ (or 0 + - 0 +) type transition. Considering the ground state of 1Σ + symmetry [19,30,34], the B state is unambiguously a 1Σ + state in Hund’s case (a) or Ω = 0 + state in case (c).

An attempt to label specific single J levels of selected isotopologues in order to obtain simplified double-resonance spectra in the B-X spectral region was unsuccessful. Even though well separated transitions in the P-branch of the A-X transition are present and suitable for selective labeling with the PUMP laser beams, scans with the PROBE laser did not result in detectable signals for the double-resonance experiment. The spectrum in Fig. 2 is obtained by exciting several overlapping transitions simultaneously in the band head region of the R-branch. The accessed number density is therefore substantially higher than the one for a well separated P branch transition originating from a single J level in the ground state. Unfortunately, the production of the heteronuclear diatomic from the Cu/Ag alloy disk is not sufficiently efficient. Non-linear spectroscopy in the low density environment of a molecular beam is generally challenging due to the inherent squared dependence of the signal on the number density.

In order to obtain a better knowledge of the B0 + state, LIF spectra have been recorded for the (0,0), (1,0) and (2,0) bands of the B0 + - X0 + transition. A typical excitation scan is shown in Fig. 3 (upper trace) for the (1,0) band. The fluorescence signal of the (1,2) band in the B0 + - X0 + system has been monitored around 3919 Å with a band width of 25 Å. The spectrum shows distinct band heads in the R-branch. The P-branch extends to the red exhibiting relatively large spacings between successive lines. The four band heads between 25985 and 25987 cm⁻¹ are readily identified to originate from the four isotopologues. In addition, a prominent region around 25980 cm⁻¹ is observed where rotational transitions

![Fig. 2](image_url)

**Fig. 2.** The TC-RFWM spectra of (1,0) B0 + - X0 + band. The wavenumber of the pump lasers at 21146.12 cm⁻¹ is resonant with numerous rotational transitions in the band heads of the (2,0) A0 + - X0 + isotopologues. As a result, all four isotopologues are detected simultaneously in the spectrum.

![Fig. 3](image_url)

**Fig. 3.** Excitation scan of the (1,0) B0 + - X0 + band (upper trace, blue). The four distinct band heads of the isotopologues in the R-branch above 25985 cm⁻¹ are formed at J' = 12 - 14. Inverted shown is a simulation of the band by applying the molecular constants determined in this work and including four CuAg isotopologues. A Gaussian lineshape of 0.06 cm⁻¹ and a rotational temperature of 50 K is assumed to model the spectrum. The inset shows the rotational transitions in a Fortrat diagram. Rotational levels (J ≤ 41) are color coded for each isotopologue and shifted on the ordinate for clarity. Underlying black dots mark assigned lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
of the four isotopologues accidentally overlap. Simulations of the spectral regions of the four vibrational bands were performed by assuming reasonable trial values for the vibrational origins and the rotational constants. The spectral features of the overlap region combined with the band head positions were found to be highly sensitive to small variations of the molecular constants. An initial assignment was performed in the (1,0) and (2,0) bands where isotope shifts are sufficiently large to assign transitions to specific isotopologues. The values for the rotational constant \( B_0 \) and the origin position \( T_0 \) of the (0,0) band have been extrapolated and tested for consistency by taking into account isotopic mass relations (vide infra).

The trial constants allowed assignment of 634 transitions. The complete line list is compiled and appended as Supplementary Data. The final molecular constants listed in Table 1 are then obtained by a least squares optimization procedure to the assigned transitions (PGOPHER [35]). A conventional Hamiltonian for a linear molecule is applied by assuming \(^1\Sigma^+\) symmetry for the excited \( B \) and initial \( X \) states. Ground state constants for all isotopologues have been fixed to the reported values from Bishea et al. [19]. The authors reported averaged \( B' \) values for the isotopologues and noted that for the \(^{63}\text{Cu}^{107}\text{Ag} \) isotopologue the rotational constant and thus the equilibrium distance largely deviated from the three other species. It has been argued that the analysis of the mass resolved ionization spectroscopy of this isotopologue has been impeded by the more abundant \(^{65}\text{Cu}^{109}\text{Ag} \) combination occurring at the same mass. For the analysis of the LIF data in the present work, it has been found that the RMS uncertainty of the line fit substantially decreased by replacing the \( B' \) constant with 0.0741 cm\(^{-1}\) for \(^{65}\text{Cu}^{107}\text{Ag} \) isotopologue. The value has been computed by averaging the more precisely determined isotopologues, \(^{63}\text{Cu}^{107}\text{Ag}, \(^{63}\text{Cu}^{109}\text{Ag} \) and \(^{65}\text{Cu}^{109}\text{Ag} \) and accounting for the isotope shift on the basis of the reduced masses (vide infra).

The experimental constants are inspected for consistency by using the usual isotope relations \( \omega' \equiv \omega_0 \rho \) and \( B' = B_0 \rho^2 \) and referencing to the lightest \(^{63}\text{Cu}^{107}\text{Ag} \) isotopologue. The predicted values from \(^{63}\text{Cu}^{107}\text{Ag} \) for \( \omega_0 \) and \( B_0 \) of \(^{65}\text{Cu}^{107}\text{Ag} \) and \(^{65}\text{Cu}^{109}\text{Ag} \) are in excellent agreement with the measured values, further supporting the correct assignment of the observed transitions.

4. Discussion

The results of this study are generally in agreement with the reported values of Bishea et al. [19] from a jet-cooled molecular beam study at lower resolution. A deviation is only observed for their value of \( T_0 = 25827.63(93) \) for the \(^{63}\text{Cu}^{107}\text{Ag} \) isotopologue. The value determined from the vibrational spectra is about 4 cm\(^{-1}\) higher than the rotationally resolved value listed in Table 1. The origin of the discrepancy is unclear. An earlier measurement of Ruamps [24] in a King furnace resulted in \( T_0 = 25825 \) cm\(^{-1}\) which is in better agreement with the value determined by the fit to numerous rotationally resolved transitions between \( J = 3 \) – 49 in this study. On the other hand, the vibrational frequency \( \omega_0 = 163.46(79) \) reported by Bishea et al. [19] compares well with this evaluation leading to \( \omega_0 = 164.2(2) \) cm\(^{-1}\). Furthermore, the equilibrium distance obtained by a Franck–Condon analysis of the vibrational band intensities and resulting in \( r_c = 2.467 \pm 0.028 \) Å is close to the averaged value of \( r_c = 2.457 \pm 0.0003 \) Å, which is based on the equilibrium rotational constant \( B_0 \) evaluated in this work. The averaged fluorescence radiative decay time of all three vibronic bands is 0.02 cm\(^{-1}\).
determined to be $\tau = 13.4 \pm 4.4$ ns in accordance with the value reported by the Morse group [19]. Assuming the B0- state has no further radiative decay channels, the integrated oscillator strength of the B0'-X0' transition is estimated at a value of $f \approx 0.16$ by summation of the spontaneous emission probabilities over the $v'' = 0$–8 levels in the ground state [36].

The CuAg ground state X0'- asymptotically correlates to the ground state separated atom limit Cu(3d$^{10}$s$^1$, 2S$^1/2$) + Ag(4d$^{10}$sp$^1$, 2P$^1/2$). The next higher lying separated atom limits are Cu(3d$^4$s$^2$, 2D$^2$) + Ag(4d$^{10}$sp$^1$, 2P$^1/2$) and Cu(3d$^4$s$^2$, 2D$^2$) + Ag(4d$^{10}$sp$^1$, 2P$^3/2$), which are located at 11202.56 cm$^{-1}$ and 13245.42 cm$^{-1}$ [37] above the ground state limit, respectively. These two excited limits can generate two $\Omega = 0^+$ states in Hund's case (c) and they have been attributed to the A0'- and B0'- states by Bisho et al. [19]. The relatively recent theoretical study confirms these assignments [30] and there is no reason to challenge this conclusion.

Following the discussion of the Morse group in Ref. [19] the assignment of the B0'- state to a covalent electronic structure is unlikely. The next higher energy limit that can generate $\Omega = 0^+$ states is Cu (3d$^{10}$s$^1$, 2S$^1/2$) + Ag (4d$^{10}$sp$^1$, 2P$^1/2$), located at 29552.05 cm$^{-1}$ (3.66 eV) [37] relative to the ground separated atom limit. If the B state correlates to this limit, a dissociation energy of $D_0 = 2.20$ eV for the B state is obtained by considering the X0'- state dissociation energy of $D_0 = 1.74$ eV [19] and the B state term energy of $T_0 = 3.20$ eV. In this case, the B state would be more strongly bound than the ground state, which is implausible because the promotion of the 5s-electron takes place to the diffuse and almost non-bonding 5p orbital. The nearby lying Cu (5S$^1/2$) + Ag (4d$^{10}$5s$^2$, 2D$^2$) asymptotic limit at 30242.30 cm$^{-1}$ (3.75 eV) [37] can also be excluded since it would yield a $\sigma^+\sigma^-$ configuration with a bond order of 1/2 and is thereby expected to be less strongly bound than the ground state.

On the basis of these considerations and the occurrence of the Coulomb potential of ground-state copper and silver ions in the proximity of the B state, Bisho et al. [19] suggested an assignment of the B state to an ion-pair state. Since the rotationally resolved spectroscopy of the B state performed in this study has shown unambiguously a $\Omega = 0^+$ character, this assignment is rather conclusive.

The ion-pair character of the B0'- state can be further substantiated from the determined equilibrium parameters (Table 1). By assuming a Morse-like character of the B0'- state the relatively low vibrational constant of $\omega_v = 164.2(2)$ cm$^{-1}$ would yield a dissociation energy of $D_0 = \omega_v^2/4\omega_v\omega_r = 0.89$ eV [38]. The asymptotic limit for the B0'- state would then be localized at 2.36 eV above the ground state dissociation limit. As mentioned above, in this region of the CuAg energy map further $\Omega = 0^+$ states are not expected. The substantial divergence from a Morse potential is likely due to the small gradient of the Coulomb potential as it ascends slowly toward the separated ion limit at large interatomic distance [20]. In addition, the constant $\omega_r$ is estimated for a Morse potential by the Pekeris relationship [38] as $\omega_r = 6(\sqrt{\omega_v\omega_x}B_0^2 - B_0^2)/\omega_v = 4.8 \times 10^{-4}$ cm$^{-1}$. This value is significantly lower than the theoretically determined value of $\omega_r = 6.4(1) \times 10^{-4}$ cm$^{-1}$ (Table 1).

Thus, in contrast to a conventional valence state, the determined molecular constants strongly deviate from a Morse-like behaviour. Instead, the potential is governed by the $-e^2/R$ term describing the long-range attraction of the ions. Since the B state is of $\Omega = 0^+$ symmetry it undergoes an avoided crossing with an $\Omega = 0^+$ state correlating to the Cu (3d$^{10}$s$^1$, 2S$^1/2$) + Ag (4d$^{10}$sp$^1$, 2P$^3/2$) limit and dissociates at this atomic asymptote (Fig. 1). The resulting bond strength of 2.20 eV is high compared to the ground state (1.76 eV). Combined with the relatively low vibrational constant, a high density of vibrational levels can be inferred which is suggested as the most important spectroscopic characteristic of an ion-pair state [20].

By considering the ionization potentials for Cu and Ag are 7.73 and 7.58 eV [37], and the electron affinities are 1.226(10) and 1.303(7) [39], respectively, the asymptotic limits Cu(3d$^{10}$, 1S) + Ag (4d$^{10}$5s$^2$, 1S) and Cu (3d$^{10}$4s$^2$, 1S) + Ag (4d$^{10}$, 1S) are located at $\approx 6.4$ eV above the asymptotic limit of the ground state. The two ion-pair states are separated by only 0.08 eV. For a homonuclear coinage dimer the two ion-pair states for the identical atoms interact strongly leading to a 0$_u^+$ and 0$_g^+$ state that are degenerate at the asymptotic limit. Similarly there is strong mixing due to the small separation in CuAg leading to an almost complete cancellation of the permanent dipole moments and the accumulation of the full transition strength in one ion-pair state [30]. According to the result of the high level $ab\ initio$ structure calculation, the Cu'Ag' component should be slightly more favored than the Cu' - Ag'. The comparison with the computation shows an excellent agreement with the experimental observations. The evaluated potential minima at $r_e = 3.16$ eV and equilibrium distance of $r_e = 2.47$ Å for the B0'- state are in accord with our findings ($T_0 = 3.17752 \pm 0.00005$ eV, $r_e = 2.4577 \pm 0.0003$ Å). It is interesting to notice, that the MRCl results reveal more evidence for the significant ion-pair character of the B0'- state by considering the computed dependence of the permanent dipole moment on the internuclear separation [30]. The dipole moment is small compared to a pure ion-pair state due to the interaction of almost degenerate ion-pair states mentioned above. Nevertheless, the permanent dipole moment of the B0'- state changes sign at approximately its equilibrium position around 2.5 Å and the dipole moment changes its orientation from Cu'Ag' to Cu' Ag'. The dipole moment is subsequently increasing for distances up to 3.2 Å where an avoided crossing with an $\Omega = 0^+$ state occurs.

5. Conclusion

In summary, the B0'- X0' transition of CuAg has been re-investigated by TC-RFWM and LIF spectroscopy. The rotationally resolved spectra strongly support the assignment of the B state as possessing $\Omega = 0^+$ symmetry. Accurate determination of the molecular constants and the close agreement with recent $ab\ initio$ structure calculations at the MRCl level of theory [30] suggests strongly that the B state is primarily an ion-pair state at its equilibrium position.

For the dicopper molecule, a significant ion-pair character of the B0'- has been found in our recent work by considering the calculated dipole moment at equilibrium distance [31]. At internuclear distances above 3.5 Å an avoided crossing takes place and the B0'- loses its ion-pair character to a higher-lying valence state. In a similar way, according to the MRCl computations by Alizadeh et al. [30], the B0'- state of CuAg undergoes an avoided crossing at approximately the same internuclear distance as a result of interaction with a higher lying $\Omega = 0^+$ state. More experimental and theoretical studies on this heteronuclear diatomic at higher excitation energies are required to clarify these questions and shed more light on the characteristics of these important charge-transfer states of transition metal dimers.

CRediT authorship contribution statement

Qiang Zhang: Conceptualization, Writing - original draft, Visualization, Validation, Investigation. Jiaye Jin: Validation, Investiga-
tion. Peter Bornhauer: Validation, Formal analysis, Data curation. Supervision. Gregor Knopp: Validation, Methodology. Peter P. Radi: Supervision, Resources, Software, Methodology, Formal analysis, Funding acquisition, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

The linelist for the B-X transition of CuAg is tabulated in the file: linelist_CuAg.xlsx. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jms.2020.111326.

References

[1] M.D. Morse, Clusters of transition-metal atoms, Chem. Rev. 86 (6) (1986) 1049–1109. http://doi.org/10.1021/cr00076a005.
[2] M.D. Morse, Chemical bonding in the late transition metals: The nickel and copper group dimers, in: M.A. Duncan (Ed.), Advances in Metal and Semiconductor Clusters, Vol. 1, Spectroscopy and Dynamics, JAI Press, Greenwich, Conn., 1993, pp. 83–121.
[3] R. Ram, C. Jarman, P. Bernath, Fourier transform emission spectroscopy of the copper dimer, J. Mol. Spectrosc. 156 (2) (1992) 468–486. https://doi.org/10.1006/jmsp.2002.2852/9200471. http://www.sciencedirect.com/science/article/pid/00228524/92/00471.
[4] V. Lebedev, P. Moroshkin, J.P. Toennies, A. Weis, Spectroscopy of the copper dimer in normal fluid, superfluid, and solid H4e, J. Chem. Phys. 135 (15) (2010) 154508. http://doi.org/10.1063/1.3497643. http://www.sciencedirect.com/science/article/pii/S00222852/10/00313/1/15/313/10.3497643.
[5] I.S. Parry, A.C. Hermes, A. Kartouzian, S.R. Mackenzie, Imaging the photodissociation dynamics of neutral metal clusters: copper dimer, Cu2, and copper oxide, CuO, Phys. Chem. Chem. Phys. 16 (2) (2014) 458–466. https://doi.org/10.1039/C3CP53214C. http://pubs.rsc.org/en/content/articlelanding/2014/cp/c3cp53214c.
[6] B. Visser, M. Beck, P. Bornhauer, G. Knopp, T. Gerber, R. Abela, J.A. van Bokhoven, P.P. Radi, Unraveling the structure of transition metal dimers using four-wave mixing, J. Raman Spectrosc. 47 (4) (2016) 425–431. https://doi.org/10.1002/jrs.5041.
[7] M. Beck, B. Visser, P. Bornhauer, G. Knopp, J.A. van Bokhoven, P.P. Radi, Rovibrational characterization of high-lying electronic states of Cu2 by double-resonant nonlinear spectroscopy, J. Phys. Chem. A 121 (44) (2017) 8448–8452. http://doi.org/10.1021/acs.jpca.7b08838.
[8] M. Beck, P. Bornhauer, B. Visser, G. Knopp, J.A. v. Bokhoven, P.P. Radi, Spectroscopic disentanglement of the quantum states of highly excited Cu2, Nature Commun. 10 (1) (2019) 3270. http://doi.org/10.1038/s41467-019-11156-2. http://www.nature.com/articles/s41467-019-11156-2.
[9] K. Balasubramanian, Electronic structure of coinage metal clusters, J. Mol. Spectrosc. 107 (23) (2000) 4755–4767. https://doi.org/10.1006/jmsp.2000.5468.
[10] N.E. Schultz, Y. Zhao, D.G. Truhlar, Databases for transition element bonding: metalmetal bonds and length and their use to test hybrid, hybrid metal, and metal density functionals and generalized gradient approximations, J. Phys. Chem. A 109 (19) (2005) 4388–4403. https://doi.org/10.1021/jp0504468.
[11] K.A. Peterson, C. Puzzarini, Systematically convergent basis sets for transition metals. B. Pseudopotential-based correlation consistent basis sets for the group 11 (Cu, Ag, Au) and 12 (Zn, Cd, Hg) elements, Theor. Chem. Acc. 114 (4–5) (2005) 283–296. doi:10.1007/s00214-005-0681-9. http://link.springer.com/article/10.1007/s00214-005-0681-9.
[12] Y. Wang, W. Liu, Benchmark four-component relativistic density functional calculations on Cu2, Ag2, and Au2, Chem. Phys. Lett. 311 (1) (2000) 63–69. http://doi.org/10.1016/S0009-2614(00)01270-7. http://www.sciencedirect.com/science/article/pii/S0009261400012707.
[13] D. Danovich, M. Filatov, No-pair bonding in coinage metal dimers, J. Phys. Chem. A 112 (50) (2008) 12959–13001. http://doi.org/10.1021/jp803667a. http://doi.org/10.1021/jp803667a.00014.
[14] R. Harz, M. Karpinnen, V. Hänninen, L. Holonen, Characterization of the distribution interactions of M2+ and the potential energy parameters for coinage metal clusters, J. Phys. Chem. A 116 (47) (2012) 11685–11693. https://doi.org/10.1021/jp307448n.
[15] S. Sadjadi, C.F. Matta, I. Hamilton, Chemical bonding in groups 10, 11, and 12 transition metal homodimers – an electron density study, Can. J. Chem. 91 (7) (2013) 583–590. http://doi.org/10.1139/cjic2013-025499. http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=PubMed&dopt=Citation&list_uids=237117300737.
[16] S. Radenkovi, D. Danovich, S. Shaik, P.C. Hiberty, B. Braida, The nature of bonding in metal-metal singly bonded coinage metal dimers: Cu2, Ag2, and Au2, Comput. Theor. Chem. 1116 (2017) 195–201. https://doi.org/10.1016/j.jctc.2017.02.013. http://www.sciencedirect.com/science/article/pii/S2211167016600750.
[17] Q. Zhang et al. / Journal of Molecular Spectroscopy 372 (2020) 111326
[35] C. Western, PGOPHER version 10.0, 2017. doi:10.5523/bris.160i6ixoo4kir1jxvawfwo047m.

[36] D. Smith, A.H. Nielsen, B. Stoicheff, G.W. Robinson, 2. Molecular spectroscopy, in: D. Williams (Ed.), Molecular physics, Methods in experimental physics, vol. 3, Academic Press, 1961, pp. 7–264, ISSN: 0076–695X. doi: 10.1016/0076-695X(61)60194-5. http://www.sciencedirect.com/science/article/pii/0076695X61901945.

[37] A. Kramida, Y.Ralchenko, J. Reader, NIST ASD Team, NIST Atomic Spectra Database (ver. 5.7.1)., NIST Atomic Spectra Database (online), Available: https://physics.nist.gov/asd [2020, February 7]. National Institute of Standards and Technology, Gaithersburg, MD. doi:10.18434/T4W30F.

[38] G. Herzberg, J.W.T. Spinks, Molecular Spectra and Molecular Structure: Diatomic molecules, Van Nostrand, New York, 1950.

[39] H. Hotop, W.C. Lineberger, Binding energies in atomic negative ions, J. Phys. Chem. Ref. Data 4 (3) (1975) 539–576. https://aip.scitation.org/doi/abs/10.1063/1.555524.