Spectroscopic disentanglement of the quantum states of highly excited Cu$_2$

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Transition metals, characterised by their partially filled d orbitals, provide the basis for many of the most relevant processes in chemistry, biology, and physics. Embedded as single atoms or in small clusters, they give rise to exceptional optical, chemical, and magnetic properties. So far, it has proven impossible to disentangle the complex network of excited quantum states, which greatly hinders prediction and control of material properties. Here, we apply two-colour resonant four-wave mixing to quantitatively resolve the quantum states of the neutral copper dimer. This allows us to unwind the individual spectral lines by isotopic composition and rotational quantum number and reveals a rich network of bright and perturbing dark states. While this work presents a road map for the experimental study of the bonding between and with transition metal atoms, it also provides experimental reference data for prospective quantum chemical approaches on handling systems with a high density of states.
transition metals are key elements for many applications ranging from high-efficiency white organic light-emitting diodes\(^3\), catalysis\(^2\) and sensors\(^4\), to novel approaches for cancer-cell destruction\(^4\). The usage of transition metals is essential in many chemical reactions. However, even when the atomic structures are known, the underlying quantum chemistry is barely understood. Less is known about processes used in chemical industry, where transition metals are employed as catalysts. While catalysis yields products like fertilisers, which are indispensable to feed the current world population\(^5\), the lack of knowledge about the active transition metal sites obstructs the rational design of new catalysts, which are necessary for the transition towards green chemistry\(^6\).

It has been demonstrated that not only the highest activity, but also the largest adjustability of chemical and physical properties, can be found in the quantum size regime, which spans the size range between a single atom\(^7\) and several nanometres\(^8\). In this regime, the partially filled d orbitals of transition metals lead to a very large number of electronic states. Therefore, perturbation-induced mixing of energetically close states is abundant. Such vibronic coupling, which is neglected in the Born-Oppenheimer approximation, along with spin–orbit interaction combines with coherence phenomena to enhance function in chemical and biophysical systems\(^9\), but obstructs the understanding of such systems. To reproduce these interactions by computation, multiconfiguration self-consistent field and multi-reference configuration interaction methods are required\(^10\).

However, the complexity of an excited transition metal dimer in vacuum can easily exceed the size restrictions of these methods. New approaches strongly depend on experimental verification, which up until now was impossible. The densely packed spectra cannot be resolved with standard experimental methods, as the multitude of overlapping and perturbed bands prevents the assignment of individual spectral features. Here, we provide a solution to this problem by partitioning these spectra into components of defined rotational quantum states, which can be assigned easily.

Such an approach is critical for the study of transition metal dimers given the sheer number of possible transitions in even the low-energy regime and the complex interaction of individual states with one another. The method is demonstrated on a coinage metal, as the density of states at low energies remain manageable, but increases dramatically with the promotion of an electron from the d-shell. Other transition metals have open d-shell ground state configurations, leading to a great number of individual states. An extreme of this is Ti\(_2\) that has almost 5000 states in just the first 1.6 eV above the ground state\(^11\).

The copper dimer is often considered to be the simplest transition metal dimer, with just two molecular states arising from the combination of ground state 2\(\Sigma^+\) (3d\(^{10}\)) atoms. While this has made it a preferred test molecule for numerous computational methods, recent work emphasises the role of dicopper centres in the global carbon and nitrogen cycles\(^12\). The molecular ground state, \(X1\Sigma^+\) (0\(\Sigma^+\)), and the first excited state, \(a^2\Sigma^+_u\) (1\(\Sigma^+\)), are formed by the two electrons in the \(4\sigma_l\) and \(4\sigma_u\) molecular orbitals, respectively, and there is little interaction between the 3d shells localised on the atoms\(^13\).

As spin–orbit interaction is non-negligible in dicopper\(^14\), states are labelled using their total angular momentum \(\Omega\) in Hund’s case (c) notation, i.e., \(X0\Sigma^+\) and \(a1\Sigma^+_u\). Despite its simple ground state, the low-lying states of a copper dimer in vacuum that can be experimentally probed by visible light, were only recently reproduced by computational methods\(^14\). Promotion of an electron from the 3d shell leads to a much larger number of possible combinations, with 40 molecular states formed from the bonding of a ground state atom 3\(\Sigma\) with an excited 2\(\Sigma\) atom. They ensue at low energies since the 2\(\Sigma\) state is only \(~1.5\ eV\) above the atomic ground state. The combination of two 2\(\Sigma\) atoms gives rise to 100 states, which populate the energy range up to 5\(\ eV\).

Gas-phase measurements of the electronic structure of Cu\(_2\) were reviewed by Morse in ref. \(^15\). Since then, several new states were observed in the ultraviolet (UV)\(^16\) and improved spectroscopic constants for the D state were reported\(^17\). Despite a considerable number of spectroscopic investigations, very few of the excited states have been rotationally resolved and molecular constants determined. From the recent investigation of dicopper in this laboratory, low-lying states, including the newly found \(A^{-}\) state, were rationalised by state-of-the-art MRCI computations, including Hund’s case (c) coupling terms. Except for the \(X0\Sigma^+\) and \(a1\Sigma^+_u\) state, the low-energy electronic structure is dominated by states that correspond to the 2\(\Sigma^+\) and 2\(\Sigma^+\) pair of atomic limits. The discovery of the \(A^{-}\) state confirms that Hund’s case (c) coupling is required to account for the number of low-energy electronic states observed. In addition, it was found that the \(G0\Sigma^+\) state can be definitely assigned to a state, which would correspond asymptotically to the ground ion-pair state\(^14\). More recent studies determined molecular constants for the \(J0\Sigma^+\) and \(1\Sigma^+_u\) state and disclosed their symmetry. The \(J0\Sigma^+\) state can be assigned to a promotion of a 3\(\pi\) electron to the 4\(\pi\) molecular orbital thus determining the complete configuration of the \(J0\Sigma^+\) state as 3\(\delta\delta\)3\(\delta\delta\)4\(\sigma\)\(4\pi\)\(4\pi\), a state that dissociates adiabatically to the 3\(\delta\delta\)4\(\pi\) asymptotic limit\(^18\). This state is strongly bound as expected from the promotion of a d-electron to a binding 4\(\pi\) orbital.

In this work, by exciting the copper dimer using deep-ultraviolet light, spectra are recorded in the vicinity of the \(J0\Sigma^+\) state. In this realm, the copper dimer behaves like a typical transition metal dimer possessing open-shell d-electrons: Interactions of close lying states go beyond the reach of any computation and experimental spectra are generally too complex to be assigned. The highly selective and sensitive method applied here quantitatively unravels a rich network of interacting states by assignment of individual rovibronic transitions. The complex bonding features involving ion-pair states, perturbations, and avoided crossings are accessible. Such knowledge sheds light on the electronic structure that governs the functionality of transition metals and provides reference data for advanced computations of these important molecules.

Results

Spectral simplification by double-resonance spectroscopy. The \(J0\Sigma^+\) state can be reached directly from the ground state by a strong transition, which was first described by Powers et al. in ref. \(^19\). However, in that work the bands recorded were seen to be accompanied by unknown features. In 1991, rotationally resolved measurements by Page et al.\(^20\) revealed a (0-0) \(J0\Sigma^+\)-X0\(\Sigma^+\) band that could not be assigned, as no set of contrived molecular constants reproduced it. In light of our results, the reason for this becomes clear.

Figure 1 shows an accurate simulation of the (0-0) \(J0\Sigma^+\)-X0\(\Sigma^+\) band and a Fortrat diagram, which maps the transitions to the individual rotational quantum number \(J\) of the accessed state. There, not only transitions to the bright \(J0\Sigma^+\) state, but also hypothesised transitions into three dark vibronic states are shown. These states exhibit little transition strength from the initial ground state and cannot be accessed directly. However, they gain intensity and experience a line shift where their corresponding branches intersect with the \(J0\Sigma^+\) state. The reason behind this lies in the quantum mechanical mixing of
energetically close bright and dark states, given sufficient overlap of their wave functions. Consequently, both states share part of the same character and level repulsion occurs.

As there is no way to extract the data in the Fortrat diagram from an experimental one-photon spectrum (as in the one simulated in Fig. 1a), the underlying information on the molecular constants of the vibronic states and the interactions among them need to be obtained by a different experimental approach that simplifies the spectrum. In this work, we used Two-Colour Resonant Four-Wave mixing (TC-RFWM)\textsuperscript{21} as a spectroscopic method. While this Optical-Optical Double Resonance (OODR) technique enables us to do spectroscopy on individually addressed quantum states of single isotopologues, the complex process of signal generation\textsuperscript{22} raises substantial requirements on the experimental set-up. In particular, the target dimeric species needs to be provided with both a high and a stable number density, which was only recently achieved\textsuperscript{18}.

**Rotational disentanglement of bands.** TC-RFWM allows spectra to be collected that originate from a single known $J''$ level of the ground $X_0^+$ state. The resulting spectra contain only one R, one P, and sometimes one Q line, depending on the symmetry of the excited state. This capability greatly simplifies the analysis of the spectra, especially in cases where perturbations destroy the regularity of rotational levels in the upper state. When a bright state is perturbed by a dark state, the quantum mechanical mixing of these states causes their energies to shift, but also the strengths of related transitions to redistribute. Hence, the dark state becomes detectable for rotational levels where both states are sufficiently close in energy to perturb each other substantially.

Figure 2a illustrates this effect on transitions from the ground state into the vibrationally excited $J_{0}^{+}$ ($v = 2$) state of the $^{65}\text{Cu}^{63}\text{Cu}$ dimer. Analogous to the computed Fortrat diagram in Fig. 1b, the experimental spectra are arranged as a function of the rotational quantum number $J'$ in the ground state, which was directly provided by the applied method. As a result of the ordering in the ground state, the intersections of perturbing dark states appear shifted by two rotational levels, when comparing the $P$-branch ($\Delta J = -1$) with the $R$-branch ($\Delta J = +1$). For some spectra, additional lines were visible and others remained unassigned, because of spectral overlap in the band used to determine $J'$ in the ground state. Such ambiguities can be resolved by using another transition to access the same $J''$.

Figure 2b depicts the ordering and relative spacing between the rotational levels of the observed vibronic states. Most obvious is the strong interaction between the $J_{0}^{+}$ ($v = 2$) state and the vibronic state preliminarily labelled as $G_{68}O_{10}^{-}$. The label $G_{68}O_{10}^{-}$ was chosen on purpose, as this level is part of a series of vibrational levels that was observed across all measured vibrational levels of the electronic $J_{0}^{+}$ state. Using the isotopic shifts, it can be assumed that $G_{68}O_{10}^{-}$ corresponds to a vibrational level about $v \approx 68$, while its properties (vide infra) suggest an assignment to the electronic $G_{0}^{+}$ state\textsuperscript{12}. At its culmination, between rotational levels $J = 29$ and $J = 30$, the repulsion of these levels increases their separation from 2 to 10 cm$^{-1}$.

The perturbations between the $J_{0}^{+}$ and $G_{68}O_{10}^{-}$ states have been analysed by assuming a homogeneous perturbation on the basis of the observed effective rotational quantum numbers (Supplementary Table 1). Mostly, both P and R branch transitions were observed with sufficient intensity. In contrast, the vibronic state preliminarily labelled $O1$ exhibits a combination of interesting properties. Starting from low rotational levels, the dark $O1$ state just becomes visible at its intersection with the $J_{0}^{+}$ ($v = 2$) state, where it causes a splitting of about 0.4 cm$^{-1}$ at $J = 14$. However, in this range only the P-branch is visible. From $J = 15$ onwards the situation reverses and only the R-branch is visible. Further afield of the intersection, it does not fully disappear as expected from a dark state. Finally, $O1$ approaches the intersection with $G_{68}O_{10}^{-}$, where no significant splitting is added on top of the natural separation of about 1 cm$^{-1}$ between the levels of $O1$ and $G_{68}O_{10}^{-}$, the behaviour of $O1$ changes again and we did not detect a single $O1$ line across the second intersection. Intensity anomalies between $P(J+1)$ and $R(J-1)$ lines have been observed and attributed to the mixing of perturbing states\textsuperscript{23}. The effect can be explained by quantum mechanical interference that comprises information on the perturbation class. For example, parallel and perpendicular transitions (with an orbital angular momentum change $\Delta \Lambda = 0$ or $\pm 1$, respectively) display approximately equal intensities for the $P(J+1)$ and $R(J-1)$ lines for unperturbed states. If a perturbation occurs ($\Lambda$-uncoupling) between two states exhibiting an angular momentum difference of $\Delta \Lambda = \pm 1$, the relative intensity of the branches out of this state can be affected strongly. For parallel transitions the amplitude phases of P and R are identical while for perpendicular transitions they are opposite. As a consequence, P line interference is constructive and the R line interferes destructively and the branch may disappear completely\textsuperscript{24}. Numerous intensity anomalies occurring due to perturbation have been observed and their intensity patterns
contain information on the class of perturbation (ref. 24 and references therein). Additional information on perturbation effects is accessible by considering saturation and polarisation features of the background-free double-resonant method applied in this work. In a simplified spectrum, exhibiting only few transitions owing to the stringent double-resonance selection rules, partially forbidden features (weak “extra lines” obtaining oscillator strength through perturbation) can be observed at high laser intensities. Even though bright transitions might substantially broaden upon saturation, they are in general well separated from the “extra lines” that are made visible at increased laser powers. Furthermore, specific linear and circular polarisation configurations of the two resonant lasers allow further enhancement or discrimination of entire families of rovibronic transitions25 for the characterisation of perturbation effects. Considering the quantum mechanical interference for perturbed levels involving perpendicular transitions, L-uncoupling is suggested for the O1 – G0+u system and consequently a 1u symmetry label for the O1 state. However, the classification of these perturbations requires more detailed experiments and is beyond the scope of this report.

Isotope-selective tracing of dark bands. As the dark states exhibit different properties than the bright states, the resulting mixed states can also act as gateways for perturbation-facilitated studies of other dark regions of the studied system26. For the copper dimer, a good example is provided by the series of vibrational levels that were preliminarily assigned to the G0+g state. In a previous work, we could already affirm computationally that the B0+u state and the G0+g state emerge from the avoided crossing between a covalent bound state and an ion-pair state14. Transitions into ion-pair states are known for their high transition strength. As a consequence, strong emission into the vibronic ground state X0+g (v = 0) is observed from the B0+g state, which has ion-pair character at the inner potential wall (towards low internuclear distance). By implication, the G0+g state should provide similar properties at its outer potential wall. Owing to the shallow potential, this wall is located at a large internuclear distance, so that no vertical transitions into X0+g (v = 0) are possible. On the contrary, strong transitions from the outer potential wall of G0+g would, if they exist, occur into highly excited vibrational levels of X0+g. While scanning the (0-0) J0+u–X0+g band in the deep-ultraviolet range, we indeed found strong blue fluorescence, which corresponds to transitions into the ground state X0+g at vibrational levels starting at v = 83. Further analysis revealed that the vibronic state G620u, which is shown in red in Fig. 1, is responsible for this. Only lines belonging to or perturbed by G620u exhibit this fluorescence. Figure 3 depicts excitation scans in which a spectrometer was used to split the laser-induced fluorescence into individual vibronic bands. In Fig. 3a, the ultraviolet emission close to the excitation wavelength was chosen. Most extra features visible in Fig. 1a disappear and just some particular changes in intensity indicate that this still is a heavily perturbed band. Taking a look at the blue fluorescence around λ=452 and 446 nm in Fig. 3b, c, respectively, it becomes obvious why these features were missing. Already J0+u levels that are sharing only a fraction of G620u character strongly emit in the blue and deplete the excited population rapidly. Therefore, the weaker UV fluorescence is strongly suppressed.

The fast emission of a photon in a totally different spectral range gives these excitation scans a high sensitivity for detecting the dark states. While the nonlinear four-wave mixing discloses the strongly perturbed lines of the dark states close to their intersection with the bright state, the linear, incoherent method is
more suitable for the observation of the weak transitions that are energetically more separated. TC-RFWM intensities depend quadratically on the population whereas laser-induced fluorescence intensities depend linearly, which is advantageous in the low-density environment of a molecular beam. In addition, the nonlinear method depends on different powers of the transition moment as the level of saturation changes and is therefore further limiting the detection of weak transitions.

In Fig. 3b, c numerous rotational levels of the dark $G_{62}O_{6}^{+}$ state are observed that are below the detection limit of four-wave mixing. The excitation scan in Fig. 3b is obtained by monitoring the emission into the highly excited $v = 88$ level of the ground state $X_{0}$ in the $^{65}$Cu$^{63}$Cu isotopologue. The scan displays rotational levels of the $G_{62}O_{6}^{+}$ dark state up to $J = 25$. The isotope shift of $v = 84$ in the ground state is not sufficiently large to separate the emission of the two main isotopologues by the limited resolution of the spectrometer. As a consequence, weak $^{63}\text{Cu}_{2}$ rotational P and R branch transitions up to $J = 33$ of $G_{62}O_{6}^{+}$ are observed in addition as shown in the Fig. 3c. In spite of the complex appearance of the excitation scans, the assignment of the dark states transitions is straightforward on the basis of the more intense transitions to the dark state that are unambiguously defined by double-resonance labelling.

Visualisation and deperturbation. By combining TC-RFWM and excitation scans, we could unambiguously assign approximately 1600 rovibronic lines in the vicinity of the $J0_{u}^{-}$ state of $^{65}$Cu$^{63}$Cu and $^{65}$Cu$^{63}$Cu. While the complete line list is appended as Supplementary Data 1, Fig. 4 illustrates the data graphically by compiling all scans into a single plot. Only non-overlapping line positions were assigned, though some lines appear to overlap in this depiction. Many of the reported lines were assigned more than once. While this improves the statistics in determination of the line position, the invariance of a line on change of the double-resonant excitation scheme also guarantees the correct assignment. As different excitation schemes involve different overlaps in the transition used for selecting the rotational quantum state, only the correctly assigned lines will remain at the same position. Next to transitions into the three lowest vibrational bands of the electronic $J0_{u}^{-}$ state (shown in shades of blue), Fig. 4 is dominated by transitions into two vibrational levels of the $I1_{u}$ state (shown in crimson tones). As the vibrational ground state of the $I1_{u}$ state was never observed, we use preliminary labels for its levels. $I1_{u}$ and $I2_{1u}$ correspond to $v = “x + 1"$ and $v = “x + 2", respectively, in the nomenclature used by Powers et al. While transitions into the $J0_{u}^{-}$ state, and all dark states borrowing intensity from it, only exhibit P and R branches, the $I1_{u}$ state, whose different symmetry we already described in previous work, also exhibits a Q branch. Brought to light by the excitation scans, the $G_{62}O_{6}^{+}$ and $G_{62}O_{6}^{+}$ bands fill significant image area, mostly by their raw spectra plotted in grey. The other $G_{0}^{+}$ bands, as well as the unrelated I1, M1, N1 and O1 bands, were only measured close to their intersection with the electronic $J0_{u}^{-}$ state. The interaction of the $G_{0}^{+}$ levels with the electronic $J0_{u}^{-}$ state increases for higher vibrational excitation, therefore, at higher vibrational levels $v$ of the $J0_{u}^{-}$ state, an increasing number of rotational levels became visible also when employing four-wave mixing spectroscopy. In case of $G_{62}O_{6}^{+}$ some levels became visible even without an actual intersection with the $J0_{u}^{-}$ ($v = 2$) state.
This was additionally favoured by a high thermal population in the observed rotational range. Sufficient $J$-levels were obtained in this system to evaluate the symmetry of the perturber (see methods section). Based on the experimentally obtained line positions, we fitted molecular constants for the involved states. For the $J_0^0$ state and the perturbing dark states, a deperturbation was possible. By this, we were able to not only obtain the molecular constants of these states, but also their interaction strengths, as stated in Supplementary Table 1. For the $GJ_0^+$ and $L$ levels, also the calculated isotope shifts could be utilised for verification. For the $J_0^+$ state, the data of both isotopologues were combined to refine the equilibrium constants. The resulting equilibrium constants for $^{63}$Cu$_2$ are presented in Supplementary Table 2. More details are provided in the methods section. The $I_{1u}$ state is an anomaly in many respects. Only a few vibrational levels have been observed and even these are too weak to be observed by most methods. We previously reported its short fluorescence lifetime and molecular constants of seemingly unperturbed regions\(^\text{18}\). The $I_{1u}$ state seems not to interact with the other states characterised in this work, but nevertheless is subject to a complicated pattern of perturbations. Therefore, the $I_{1u}$ state should be revisited in a subsequent study, so that the perturbing states may be investigated more thoroughly. Such a study can also help to assign the unrelated bands ($L1$, $M1$, $N1$ and $O1$) to specific electronic states. To be used for experimental purposes only, molecular constants that reproduce the observed range were added as Supplementary Table 3.

**Discussion**

TC-RFWM spectroscopy allows overcoming the hindrances that have so far prevented experimental access to systems exhibiting a high density of states. Perturbations identified by this method can be used as gateways for experimental access into otherwise inaccessible regions, including the near-dissociation regime of the ground state. These mixed states oscillate between high- and low-vibrational quanta for large and small internuclear distances, respectively. While at short distance, a model based on the linear combination of atomic orbitals is appropriate, ligand-field theory might be better suited to address the behaviour at long range\(^\text{28}\). The large size of the 4$s$ and 4$p$ orbitals serves to de-shield the atomic-ion cores from each other, leading to a positive point charge perturbing the 3$d$ structures on the other atom. This relates to the foundational concept of “oxidation state”, which could be more properly thought of as the charge on one atom as seen by the atom to which it is bound (Field, R. W. (personal communication (2019))). The features of the nonlinear method open a wide field for future experiments on transition metal systems. The presented data also provide reference data to test new quantum chemical methods for computational handling of systems with a high density of states. Such insights lead to fundamental understanding of the complex electronic structure of transition metal clusters that govern their functionality. Ion-pair states, respectively, the states that originate from their avoided crossings with other states, affect almost all regions of the potential energy landscape of the copper dimer. Considering the commonness of perturbation-facilitated mixing between these and other quantum states, it is unlikely that other transition metal systems, which usually exhibit an even higher density of states, can be understood based on the assumption of pure states and the usage of the Born-Oppenheimer approximation. Even for the copper dimer itself, a glance behind the veil of overlapping lines exposed not only a complex network of perturbations, but also vibronic bands displaying interesting properties to access regions of the energy map beyond the possibilities of more conventional spectroscopic methods.

**Methods**

**Set-up, spectroscopy and deperturbation.** The copper dimers are generated in a home-built laser-ablation source\(^\text{18}\). Upon ablation with a pulsed Nd:YAG laser ($532 \text{ nm, 10 ns, 100 mJ per pulse}$), the plume of copper plasma is entrained in a helium pulse and expanded into high vacuum. In the course of this process condensation and cooling takes place to create a collision-free molecular beam containing sufficient Cu$_2$ for nonlinear spectroscopy. TC-RFWM is performed 1 cm downstream from the nozzle by focusing three parallel propagating laser beams by
a lens (f = 1000 mm) into the interaction region. Doppler broadening is eliminated by probing the molecular beam orthogonally to the direction of propagation. If the ODDR selection is met, a signal is produced in forward direction governed by phase-matching conditions and detected essentially background-free by a photomultiplier tube. The incident laser beams are produced by using Nd:YAG pumped dye lasers with a specified line width of 0.04 cm⁻¹. For II₆X₀⁰⁺ and III₆X₀⁰⁺ transitions the output of the dye-laser frequency is doubled by second harmonic generation and split to provide the two pump beams of ~100 µ per pulse. The (0–0) II-X transitions were assigned a high transition strength of 5.2 × 10⁻⁵ cm⁻¹ to 8.2 × 10⁻⁵ cm⁻¹ per pulse. An additional channel of information is obtained by placing a spherical mirror perpendicularly to both molecular beams and the main axis of spectroscopy. The emitted light is focused onto the slit of a 1 m spectrometer in front of a photomultiplier tube. The measurement of line positions within the raw spectra, as well as the fitting of molecular constants, were performed using the PGOPHER software. Shifted transitions and extra lines caused by perturbations are often revealed by TC-RFWM in a straightforward manner. The stringent double-resonance selection rules yield simplified spectra and allow unambiguous assignments.26–31 The quantification of the perturbation was also based on PGOPHER, where, once the constants were fitted based on the experimental spectra, perturbations can be excluded for comparison. The molecular constants of the ground state of the copper dimer were taken from Ram et al.34.

Equilibrium constants of the J₀ state. Utilising the well-established relationships between the molecular constants of different isotopologues,35 we merged the deperturbed rotational levels of both isotopologues by fitting equilibrium constants. While for most constants, the knowledge of the isotopes’ masses is sufficient, the determination of the electronic term T_e depends on the knowledge of the ground state zero-point energy, as all experimental data is referenced against it. Based on the Dunham coefficients reported by Ram et al.34, we calculated the zero-point contributions for 63CuCu (132,9711(19) cm⁻¹) and 66CuCucu (131,9866(18) cm⁻¹). After merging the isotopologues, T_e, ω_d and α_d were fitted to the T_e values and B_e and a_e were fitted to the B_e values. The equilibrium value for the internuclear distance r_0 was then calculated based on B_e and the isotopic masses. To stay consistent within literature, Supplementary Table 2 presents the equilibrium constants in terms of the lightest isotopologue, 63CuCu. However, by using the same relationships, the constants for any isotopologue can be derived. For 65Cu65Cu, for example, one obtains slightly lower values for ω_d (287.67(17) cm⁻¹), ω_d (1,054 (57) cm⁻¹), B_e (0.1,14276(11) cm⁻¹) and α_e (0.0008913(75) cm⁻¹).

Deperturbation and classification of the Gₓ₀ₓ⁻→J₀ₓ⁻ per- turbation strength listed in Supplementary Table 1 were obtained by assuming a homogeneous perturbation, i.e., independent perturbation of the deperturbed molecular constants. At the scale employed, this does not affect the molecular constants listed in the Supplementary Table 1. The wave functions and the overlap integrals are then obtained by solving the RKR potentials of the J₀ states. This allows the determination of the absolute vibrational quantum numbers of the separated atom limits with double excitation cannot be ignored, and further 0° excited states can be considered. As the avoided crossings and, in addition, v = 0 of the Gₓ₀ₓ⁻ state was never observed, it is still too early to decide if the methods used above are applicable for this system.

Interpolation of missing vibrational origins. Within Supplementary Table 1, only the numbers with a specified standard deviation are directly derived from experimental data. The missing T_e values of Gₓ₀ₓ⁻ states were filled based on the fitted Dunham expansion that was also used to determine the absolute vibrational quantum numbers for the perturbations. The strengths were similar whenever we had experimental access to both isotopologues. Therefore, we presumed a similarity also when only one isotopologue was measured.

Franck-Condon overlaps in the Gₓ₀ₓ⁻→J₀ₓ⁻ systems. Supplementary Fig. 2 shows the RKR potentials of the J₀ states, projected onto the molecule’s equilibrium coordinates. We have already demonstrated that the low-lying electronic states of the copper dimer can be only explained by assuming spin–orbit–states given by Hund’s case (c) coupling.36 In the computational part of that work, only the potential curves of the states that could be computed to separate atom limits with only a single excitation were fully covered. Therefore, only two covalently bound 0° states interact with the 0° ion–pair ground state to bring forth the A, the B, and the Gₓ₀ₓ⁻ states. Taking a look at the experimental determined potential energy curves of Cu₂, which were illustrated, e.g., in a book chapter by Morse,9 it becomes obvious that the separated atom limits with double excitation cannot be ignored, and further 0° excited states can be considered. As the avoided crossings and, in addition, v = 0 of the Gₓ₀ₓ⁻ state was never observed, it is still too early to decide if the methods used above are applicable for this system.

Simulation of perturbed bands. To generate Fig. 1, we used PGOPHER to simulate the (0–0) J₀ₓ⁻X₀⁻ band of Cu₂ based on the constants and interactions reported in Supplementary Table 1. For the spectrum (Fig. 1a), a rotational temperature of 30 K was chosen, in order to achieve a close resemblance of the intensity distribution observed in our experiment. The abundance of the isotopologues was based on natural abundance. As the different statistical weight of symmetrical and asymmetrical rotational levels (3 and 5) in the homonuclear isotope is taken into account in the simulation, an average statistical weight of 4 was chosen for all levels of the heteronuclear isotope to match the average intensity. In the Fortrat diagram, straight lines between the points of each branch were added as a guide to the eye. To emphasise the perturbations that yield some obvious spectral features, the corresponding regions of the Fortrat diagram were copied into the compiled spectra.

Generation of Fig. 2. Parsing the raw list of all assigned lines, the corresponding raw spectra were loaded and normalised. They were then added to the scalable vector graphics file, using the rotational quantum number in the ground state as a vertical offset. Therefore, the peak heights do not scale with the absolute intensity, when comparing different scans. For some rotational levels, different lines were used to select the rotational quantum state. Owing to the different overlaps associated with these lines, only the peaks that belong to the targeted rotational state reproduce. In a second round, windows around the assigned line positions were selected from each raw spectrum. These were redrawn with a coloured background to highlight the assigned peak. To achieve a clearer presentation, a few peaks were manually rescaled and the colorized ranges were slightly readjusted when arranging and formatting the final Fig. 2a. For the corresponding level diagram in Fig. 2b, we used the simulation based on the fitted molecular constant. At the scale reproduced, this does not affect the position of the data points, but improves clarity by extrapolating points missing within the experimental dataset. To further clarify the level repulsion, the levels were plotted as relative wavevector νᵢ₋νᵣₑₐᵢₑₙ = νᵢ − νᵣₑₐᵢₑₙ − 38.000 cm⁻¹ − Bₑ(J + 1) where Bₑ is the rotational constant of the 0° state as reported in Supplementary Table 1. Therefore, the relative values are referenced against an unperturbed, harmonic version of 0°.

Details on the excitation scans. When recording the spectrum in Fig. 3a, some stray light of the UV pump laser passed the spectrometer off-axis. Therefore, we started integration 20 ns after the maximum of the pump pulse to ensure that the electrical response of the photomultiplier had concluded. In contrast, the strong, and therefore short-lived, blue fluorescence shown in Fig. 3b, c was integrated over the complete pulse. This timing difference is responsible for the complete disappearance of the Gₓ₀ₓ⁻ related lines in Fig. 3a.

Generation of Fig. 4. This overview figure was created by reusing the code used for Fig. 2, by applying it on the full line list. As this inevitably produces overlapping spectra, coloured lines (instead of coloured fills) were used to indicate the assigned line positions. For the full spectral range, the represented intensity was composed of the projection of the Bragg peaks, the red square symbol, which is a free fit parameter, denoting T_e, the obtained value v = 62 barely changed (e.g., 62.28 → 62.33). This is in good agreement with recent work by Pashov et al., in which they demonstrated the establishment of absolute vibrational numbering based on four term energies in one isotopologue and one term energy in another. Also when using their method, which is essentially the same as the one using PGOPHER, Gₓ₀ₓ⁻ was also assigned to v = 62. Nevertheless, one should take these values with caution. We have already demonstrated that the low-lying electronic states of the copper dimer can be only explained by assuming spin–orbit–states given by Hund’s case (c) coupling. In the computational part of that work, only the potential curves of the states that could be computed to separate atom limits with only a single excitation were fully covered. Therefore, only two covalently bound 0° states interact with the 0° ion–pair ground state to bring forth the A, the B, and the Gₓ₀ₓ⁻ states. Taking a look at the experimental determined potential energy curves of Cu₂, which were
$^{65}$Cu$^{65}$Cu isotopologue. There, the background is plotted as a completely flat line and the coloured peaks are just visible, because the amplitude was manually increased when comparing the final depiction.

**Data availability**

The raw spectroscopic data that supports the findings of this study and the resulting PGOPHER files are available from the corresponding author upon reasonable request. The authors declare that all other data supporting the findings of this study are available within the paper and its Supplementary Information files.

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