Observation of a *gerade* symmetry state of Cu₂ using two-color resonant four-wave mixing

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Abstract

The first observation of an excited 0_g^+ state of dicopper is reported. “g” inversion symmetry states are not observable by direct one-photon absorption from the $X^1\Sigma_g^+$ ground state. Measurements are performed by applying non-linear two-color resonant four-wave mixing (TC-RFWM) spectroscopy. Cold Cu₂ molecules in a molecular beam environment are generated by applying a pulsed laser vaporization source and subsequent near supersonic expansion of the vaporized metal plume entrained in a helium pulse. Spectra in the wavenumber region of the $[37.5(v)]0_g^+ - B0_u^+$ electronic transition are recorded by using the UNFOLDED double-resonance scheme. Specific rotational levels of the intermediate state $B0_u^+$, $v' = 1$ are accessed from the $X^1\Sigma_g^+$ ground state. Dipole selection rules from the labeled levels define unambiguously the rotational quantum number and symmetry of the final state ($\Delta J = \pm 0, 1$ and $g \leftrightarrow u$). The UNFOLDED scheme is verified by additional measurements *via* the origin level, $v' = 0$, of the intermediate $B0_u^+$ state. Spectroscopic constants of the $[37.5(v)]0_g^+$ state have been determined for both ⁶³Cu₂ and ⁶³Cu⁶⁵Cu isotopologues by analysis of the rotationally resolved spectra. The potential of TC-RFWM to study the unexplored “g” symmetry manifold of Cu₂ is discussed.

KEYWORDS

two-color resonant four-wave mixing, parity symmetry, Cu₂

1 INTRODUCTION

Spectroscopic interest in the copper dimer stems from its closed-shell structure of the ground state where a relatively simple bonding configuration is mainly governed by two 4s electrons and little interaction is implied between the d-electrons residing in the vicinity of the atoms. By opening the d-shell upon excitation of an electron, a

complex electronic configuration is obtained that is typical for transition metals, thus providing an unique opportunity to understand the role of the d-orbitals in chemical bonding.^[1,2] As such, extensive experimental^[3–18] and theoretical work^[19–24] have focused on the ground and excited electronic levels of Cu₂. The electronic ground state has been identified as X¹Σ_g⁺ state in Hund case (a) notation. The subscript “g” (*gerade*, German for even) is used to indicate that the electronic wave function remains unchanged for the inversion operation of the electronic coordinates in the molecular frame. Alternatively, if the electronic wave function changes only the sign for the transformation, the subscript “u” (*ungerade*, German for odd) is added to the term symbol. This parity symmetry must be considered in the spectroscopy of molecules exhibiting centrally symmetric nuclear charges since only g ↔ u electronic dipole transitions are observable. As a result, in the case of Cu₂, only the “u” symmetry excited states can be observed from the X¹Σ_g⁺ ground state by one-photon absorption. Actually, more than ten electronic (“u”) states have been reported for Cu₂. Among these, the A¹1_u, A0_u⁺, B0_u⁺, G0_u⁺, F0_u⁺, I1_u and J0_u⁺ states were high-resolution investigations studied by resolving the rotational structure of the vibronic bands and determined accurate molecular constants.^[4,6,11,12,14,15,18] For excited levels, total angular momentum Ω labeling in Hund case (c) notation is applied, because spin-orbit interaction is not negligible for excited states in Cu₂.^[14] All previous studies have provided much insight into the “u” symmetry electronic structures as well as the d-orbital bonding properties of Cu₂. However, to the best of our knowledge, no “g” symmetry excited states have been reported up to now. In this report, we present a study of the excited “g” symmetry states using the two-color resonant four-wave mixing (TC-RFWM) spectroscopic technique.

In four-wave mixing spectroscopy three input laser beams interact with molecules through the third order susceptibility tensor, χ⁽³⁾, and give rise to generation of the fourth coherent signal beam.^[25] The fully resonant and background free properties render resonant four-wave mixing spectroscopy a sensitive detection technique that is comparable with laser induced fluorescence (LIF) and cavity ring down spectroscopy.^[26] So far, RFWM has been used in numerous spectroscopy studies, including stable molecules such as CS₂,^[27] H₂CO,^[28] Br₂^[29] and free radicals such as C₂,^[30] C₃,^[31] HC₄S.^[32] Apart from degenerate four-wave mixing that yields an absorption-like spectrum, most of these investigations were performed by using a optical-optical double-resonance scheme. Like other two-photon resonance detection techniques, TC-RFWM can significantly simplify complex spectra. As a signal is generated only when both photon energies are resonant with transitions in a selected and isotopically pure molecule that share a common intermediate level, the number of possible transitions is dramatically reduced. In addition, intermediate level labeling allows straightforward assignments of observed lines. When used in combination with narrow-bandwidth nanosecond laser pulses, the selectivity of TC-RFWM can extend to single rotational levels.

The technique has been shown to be favorably suited for the study of small transition metal dimers or clusters, whose electronic spectra are usually very dense and complex due to the high density of states, low vibrational and rotational constants and the frequent abundance of numerous isotopologues.^[14,15,26] Actually, the combination of TC-RFWM and a home made laser vaporization clusters source

yielding internally cold Cu_2 dimers in a molecular beam environment^[15] allowed a systematic investigation of the electronic states of dicopper and resulted in the identification of the $A'1_u$ state and the characterization of the 11_u and $J0_u^+$ states.^[14,15] Furthermore, a recent detailed study of the complex electronic structure of excited “u”-symmetry levels has been performed in this laboratory by applying the same technique.^[33]

In this work, we report on our method to unravel the “g” symmetry electronic states of Cu_2 . Such “g” symmetry states are important for the validation of high-level structure calculations. In addition, “u/g”-symmetry breaking and perturbations have been observed in homo-nuclear diatoms, such as $^7\text{Li}^6\text{Li}$.^[34] A survey in the UV energy region is presented by using the UNFOLDED TC-RFWM scheme. The investigation yields unambiguous assignments and molecular constants for the $[37.5(v)]0_g^+$ state and demonstrates anew the potential of TC-RFWM for the high-resolution spectroscopy of transition metal dimers and small clusters.

2 Experimental setup

The experimental setup has been described in our previous publications.^[15,26] In brief, the copper dimer molecules are produced in a cluster source by laser ablation of a copper target disk. Pure helium gas with a static background pressure of 50 bar is introduced into the source by using a pulsed valve (General valve, series 9), which generates a typical gas pulse of $\approx 250 \mu\text{s}$ width. The ablation laser beam is the 532 nm output of a Nd:YAG laser (Continuum, NY81) emitting an energy of $\approx 40 \text{ mJ/pulse}$. The beam is focused by a spherical lens ($f = 500 \text{ mm}$) and impinges the copper plate at right angle. In order to provide a fresh surface for every pulse, the disk ($d = 50 \text{ mm}$) is mounted on a rotational and translational stage driven by two stepper motors (Maxon). Copper atoms and dimers produced in the laser ablation plasma entrain in the gas pulse and pass through a 50 mm length channel. Subsequent near supersonic expansion takes place into the vacuum chamber at background pressures of $\approx 10^{-6} \text{ mbar}$. About 3 mm downstream from the expansion orifice, Cu_2 molecules are detected by TC-RFWM.

The laser beams for the spectroscopy are setup using a BOXCARs configuration.^[35] Three parallel propagating laser beams are focused by an achromatic lens ($f = 1000 \text{ mm}$ and $d = 50 \text{ mm}$) to pass along the three diagonals of a parallelepiped. The laser beams cross the molecular beam at right angle to minimize the Doppler broadening effect and are focused at the center of the molecular beam. The adjustment of the relative angles of the three incident laser beams is governed by the phase matching conditions, i.e.:

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

In current experiment, the two PUMP beams, with wave vectors $\mathbf{k}_2$ and $\mathbf{k}_4$, are scanned and the PROBE beam, $\mathbf{k}_1$ is fixed at a specific wavenumber.^[4] The signal beam is generated along the fourth (dark) diagonal and re-collimated by using a second objective lens. The signal beam is further separated from scattered light by

remote detection over a distance of ≈ 5 m and by using a lens/pinhole combination ($f=30$ mm, $d=50$ μ m) in front of the photomultiplier detector.

The two pump laser beams are produced by implementing a beamsplitter to separate the output of a dye laser (Radiant Dyes, NarrowScan) that is pumped with the second harmonic of a Nd:YAG (Spectra-Physics, Quanta-Ray 290) laser. DCM/ethanol dye solution is used to cover all wavelength regions of interest. The probe laser beam is generated by another dye laser (Radiant Dyes, NarrowScan) which is pumped by the same Nd:YAG laser but with the 355 nm output. A Coumarin 120/Ethanol dye solution is used to obtain blue laser beam output. During the experiment, the wavelength of probe laser is fixed on individual rotational lines of the (1,0) $B0_u^+ - X^1\Sigma_g^+$ band while the pump lasers are scanned in the wavelength region around 650 nm. To avoid saturation of the (1,0) $B0_u^+ - X^1\Sigma_g^+$ transition, the probe laser beam is attenuated to about 10 nJ/pulse. In contrast, the pump laser beam energy used is about 10 μ J/pulse. A small part of the pump or probe beam is split off and directed to an optical fiber-coupled wavelength meter (High Finesse, WS6), which provides the absolute frequencies of the laser beams online.

The experiment is operated at 10 Hz with the appropriate timings provided by a set of delay generators (Stanford Research Systems, DG 535). Spectra are recorded with an oscilloscope (LeCroy, HDO6104) and stored by using a home-made software (Labview). Typically, 100 pulses are averaged per scan step (0.005 nm/step) of the dye laser on the oscilloscope to improve the signal-to-noise ratio.

3 Results and Discussion

Similar to other optical-optical double-resonance techniques, three different excitation schemes are commonly used in TC-RFWM experiments, namely UP(V), stimulated emission pumping (SEP)(Λ) and UNFOLDED(Ξ) schemes. As mentioned above, two resonances are addressed simultaneously in a molecule that are connected through a common level. The schemes are illustrated in Fig. 1. For the UP scheme the initial state is the common intermediate state and observable transitions are governed by one-photon selection rules. For the SEP and UNFOLDED schemes, the common intermediate state is an excited state, and therefore, possible final states follow two-photon dipole transition rules from the initial state. Consequently, only the latter two schemes can be used to study excited states exhibiting the parity symmetry of the ground state. In present study, we use the UNFOLDED scheme to map the excited “g” manifold states of Cu_2 .

The probe laser is tuned to a strong rotational transition in the (1,0) or (0,0) vibrational band (v',v'') of the $B0_u^+ - X^1\Sigma_g^+$ electronic transition around 455 nm whereas the pump laser is scanned in the vicinity of 650 nm. Primes and double primes denote intermediate and ground states quantum numbers, respectively. Unprimed labels are used for the final state. To avoid excitation of multiple overlapping rotational transitions, mostly P(J'') branch transitions are pumped owing to the larger separation of the rotational lines in $B0_u^+ - X^1\Sigma_g^+$ as compared to the R-branch. Here, J'' denotes the rotational quantum number of the ground state. The total energy of the two-photon excitation is about 4.6 eV and is roughly coinciding

Figure 1: Excitation schemes for TC-RFWM. “g” symmetry states from the initial $X^1\Sigma_g^+$ state are only observable by the SEP or UNFOLDED scheme. See text for details.

with the of $J0_u^+$ state in the “u” symmetry manifold.^[11,15,18] The energy region is chosen owing to the convenient wavelength regions of the dye lasers. Furthermore, the high density of states expected in this energy region facilitates the initial observation of lines to “g”-symmetry levels. Survey scans at low resolution at a stepsize of ≈ 0.01 nm were followed by high-resolution observations at 0.005 nm/step.

Fig. 2a shows a high-resolution TC-RFWM spectra. The measurement is obtained by tuning the probe laser beam to P(10) in the $(1,0)$ $B0_u^+ - X^1\Sigma_g^+$ band of the $^{63}\text{Cu}_2$ isotopologue at 21986.00 cm^{-1} and thus labelling the $J' = 9$ rotational level in the intermediate $B0_u^+$, $v' = 1$ state. Two lines are recorded while scanning the pump wavenumber: a P(9) and a R(9) transition at 15579.85 cm^{-1} and 15582.39 cm^{-1} , respectively. The missing Q(9) line is indicative of a parallel transition ($\Delta\Omega = 0$) and defines the final state term symbol as 0_g^+ . The energy separation between the two lines is of 2.54 cm^{-1} . In order to validate the double-resonance excitation scheme leading to this spectrum, another scan is performed by tuning the probe laser to the rotational P(10) transition of the $(0,0)$ $B0_u^+ - X^1\Sigma_g^+$ band of the $^{63}\text{Cu}_2$ isotopologue at 21744.19 cm^{-1} (Fig. 2b). In this case, $J' = 9$ of the energetically lower lying vibrational origin, $v' = 0$ of $B0_u^+$ is labelled. In order to access the same final 0_g^+ state from $v' = 0$ by the UNFOLDED double-resonance scheme, the P(9) and R(9) transitions are expected to occur in a wavelength region shifted by $+241.81\text{ cm}^{-1}$, which is the energy difference of the $v' = 1$ and $v' = 0$ levels in the $B0_u^+$ state. Fig. 2b. depicts the observed rotational transitions P(9) and R(9) at 15821.63 cm^{-1} and 15824.19 cm^{-1} , respectively. The separation in the rotational branches at $J' = 9$ is 2.56 cm^{-1} in good agreement with the interval in Fig. 2a. Furthermore, the transitions display a wavenumber shift of 241.78 cm^{-1} and 241.80 cm^{-1} , respectively, and reflect therefore accurately the spacing of the vibrational levels $v' = 0$ and $v' = 1$ in the $B0_u^+$ state. The two scans populating the same final levels confirm, therefore, the assignment by using the UNFOLDED resonance scheme, i.e. $[37.5(v)]0_g^+ \leftrightarrow B0_u^+ \leftrightarrow X^1\Sigma_g^+$. The label used to identify the final “g” symmetry state in brackets is a *preliminary* classification indicating the vibronic origin of the observed level in units of 10^3 cm^{-1} . To avoid confusion, the vibrational quantum number variable is added

Figure 2: The TC-RFWM spectra of the $[37.5(v)]0_g^+ - B0_u^+$ transition, **2a)**, is observed by accessing $v' = 1$ of the intermediate $B0_u^+$ state by the rotational P(10) transition from the electronic ground state. **2b)** is obtained by exciting the band origin $v' = 0$ by P(10). **2c)** shows the energy diagram and transitions involved for the UNFOLDED TC-RFWM scheme. Δ indicates the energy interval between levels of $B0_u^+$ $v' = 1$ $J'' = 9$ and $B0_u^+$ $v' = 0$ $J'' = 9$.

in brackets. However, to specify the exact electronic label by this commonly used nomenclature, the vibrational ground state, $v = 0$ has to be determined. Measurements of the ground and further vibrational levels of this state are under way in this laboratory as part of a general mapping of the “g” symmetry manifold. The investigation follows closely the extensive procedure described for the disentanglement of “u” states^[33] and will be subject of a forthcoming publication.

In order to characterize the $[37.5(v)]0_g^+$ state, numerous TC-RFWM spectra have been recorded for both isotopologues. In total, 35 and 34 rotational transitions with quantum numbers from $J' = 9$ to 30 have been recorded for $^{63}\text{Cu}_2$ and $^{65}\text{Cu}^{63}\text{Cu}$, respectively. Tab. 1 and 2 display the unambiguous assignments by intermediate level labeling (first column) and line positions of the final state (second column) which are used to determine accurate molecular constants by applying a least square optimization procedure. A conventional Hamiltonian for a linear molecule is used as implemented in the computer program PGOPHER.^[36] Molecular constants of the ground state have been fixed at the values obtained by a Fourier transform emission study by Ram *et al.*^[4] The two rightmost columns list the rotational lines of the initial excitations to the intermediate, $B0_u^+$, $v' = 1$ state and the correspond-

ing wavenumbers. Column 3 displays the observed transition wavenumbers in the $(v,1)$ $[37.5(v)]0_g^+ \leftrightarrow B0_u^+$ and is followed by the calculated values with the final fit parameters shown in Tab. 3. Column 5 lists the residuals (observed-calculated values). Energies are given relative to the ground state $X^1\Sigma_g^+$, $v = 0$ of the respective isotopologues.

The RMS values of the least-squares fit is 0.03 cm^{-1} , which corresponds roughly to the specified laser line width of $\approx 0.04 \text{ cm}^{-1}$. For these initial measurements power broadening effects have to be considered and may decrease slightly the accuracy of the determined molecular constants. Statistical uncertainties are given in the units of the last significant figure. No allowance is given for systematic errors in the calibration. It is important to notice that the results for the centrifugal distortion constant D_v are effective values and they might contain contributions from vibrational or rotational perturbations by nearby lying electronic states.

To the best of our knowledge, Tab. 3 lists for the first time molecular constants for an electronic level of the “g” symmetry manifold in Cu_2 .

The determined isotope shift of 5.691 cm^{-1} suggest a low vibrational quantum number of the $[37.5(v)]0_g^+$. According to our preliminary survey of this and close lying levels in the UV energy range, $v \approx 4$ by assuming a vibrational wavenumber of $\omega_e \approx 290 \text{ cm}^{-1}$. Interestingly, this value is roughly equal to the vibrational energy of the aforementioned $J0_u^+$ state in the “u”-symmetry manifold with its origin located at $37437.107(95) \text{ cm}^{-1}$.^[15,33] The strong transition moment observed for the $[37.5(v)]0_g^+ \leftrightarrow B0_u^+$ transition further suggests significant ion-pair state character (Cu^+Cu^-) of the observed “g”-symmetry state similarly to the $J0_u^+$ state. However, a substantial difference in the rotational constant of $B = 0.116062(12)$ and $0.067569(60) \text{ cm}^{-1}$, respectively, implies a greatly different equilibrium distance for the $J0_u^+$ and $[37.5(v)]0_g^+$ states. An equal number of “u” and “g” states are formed in the asymptotic limits of homo-nuclear diatomic molecules. Their degeneracy at large internuclear distance is rapidly broken towards smaller radii. As the distance decreases, u/g-symmetry states divide in non-interacting classes with entirely different bonding properties. The only non-Born-Oppenheimer term that breaks this symmetry rule is a coupling between nuclear and electronic angular momenta in near degenerate rovibronic levels of electronic states of opposite parity.

As mentioned above, one-photon selection rules prevents the spectroscopic study of numerous states that might play an active and important role in energy flux processes governing intra- and intermolecular energy redistribution. Also, experimental data on these states are required to validate and improve state-to-the-art *ab initio* structure calculations.^[14]

Thus, to acquire information on the global energy map of homonuclear transition metal dimers, more demanding two-color resonance experiments have to be performed. Fluorescence based methods, such as detection of dispersed fluorescence or stimulated emission pumping by depletion of fluorescence,^[37] have been applied for the characterization of levels accessible by two-photon transitions. Recent examples are found in the literature on Li_2 ,^[34] Na_2 ,^[38] Hg_2 ,^[39] and I_2 .^[40] However, to the best of our knowledge, no optical-optical double-resonance experiments are reported for homonuclear transition metal dimers. Here, we demonstrate the potential TC-RFWM for such studies. The applied UNFOLDED scheme suggests that

Table 1: Line list for the $^{63}\text{Cu}_2$ isotopologue. All values are in cm^{-1} . Energies are given relative to the ground state $X^1\Sigma_g^+$, $v=0$.

Ass.	Level	Obs	Calc	Res	B-X	Probe
P(8)	37570.60	15580.49	15580.53	-0.04	R(7)	21990.09
P(9)	37565.86	15579.86	15579.84	0.01	P(10)	21986.00
P(10)	37564.64	15579.07	15579.10	-0.03	P(11)	21985.57
R(8)	37572.92	15582.81	15582.83	-0.02	R(7)	21990.09
R(9)	37568.39	15582.40	15582.42	-0.02	P(10)	21986.00
P(12)	37563.83	15577.43	15577.44	-0.01	P(13)	21984.66
P(12)	37567.54	15577.43	15577.44	-0.01	R(11)	21990.08
R(10)	37567.51	15581.93	15581.95	-0.01	P(11)	21985.57
P(13)	37562.49	15576.49	15576.52	-0.03	P(14)	21984.17
R(12)	37567.20	15580.79	15580.83	-0.03	P(13)	21984.66
R(12)	37570.95	15580.84	15580.83	0.01	R(11)	21990.08
R(13)	37566.21	15580.22	15580.18	0.04	P(14)	21984.17
P(16)	37563.02	15573.42	15573.39	0.02	R(15)	21989.74
P(17)	37561.86	15572.26	15572.24	0.02	R(16)	21989.60
P(18)	37560.66	15571.06	15571.02	0.04	R(17)	21989.44
R(16)	37567.53	15577.93	15577.88	0.05	R(15)	21989.74
R(17)	37566.64	15577.03	15577.00	0.04	R(16)	21989.60
R(18)	37565.70	15576.10	15576.06	0.05	R(17)	21989.44
P(21)	37546.55	15567.03	15567.02	0.01	P(22)	21979.52
R(21)	37552.44	15572.92	15572.89	0.02	P(22)	21979.52
P(24)	37552.31	15562.58	15562.52	0.06	R(23)	21988.05
P(25)	37537.55	15560.86	15560.90	-0.04	P(26)	21976.70
R(24)	37558.98	15569.24	15569.22	0.02	R(23)	21988.05
R(25)	37544.56	15567.87	15567.89	-0.02	P(26)	21976.70
P(28)	37542.42	15555.71	15555.73	-0.02	R(27)	21986.71
P(29)	37541.92	15553.86	15553.89	-0.03	R(28)	21986.32
P(30)	37539.73	15551.98	15552.01	-0.03	R(29)	21985.92
R(28)	37550.25	15563.54	15563.56	-0.02	R(27)	21986.71
R(29)	37550.02	15561.96	15562.02	-0.05	R(28)	21986.32
P(32)	37534.76	15548.05	15548.08	-0.03	R(31)	21985.04
R(30)	37548.16	15560.41	15560.42	-0.00	R(29)	21985.92
P(33)	37532.32	15546.00	15546.04	-0.04	R(32)	21984.56
R(32)	37543.77	15557.06	15557.06	-0.00	R(31)	21985.04
R(33)	37541.65	15555.33	15555.31	0.02	R(32)	21984.56
R(34)	37539.59	15553.59	15553.51	0.09	R(33)	21984.07

Table 2: Line list for the $^{63}\text{Cu}^{65}\text{Cu}$ isotopologue. All values are in cm^{-1} . Energies are given relative to the ground state $X^1\Sigma_g^+$, $v=0$.

Ass.	Level	Obs	Calc	Res	B-X	Probe
P(9)	37562.08	15576.08	15576.08	-0.00	P(10)	21984.23
R(8)	37565.37	15578.97	15579.03	-0.06	P(9)	21984.63
R(9)	37564.62	15578.63	15578.64	-0.02	P(10)	21984.23
P(12)	37558.40	15573.74	15573.75	-0.02	P(13)	21982.91
R(10)	37563.73	15578.16	15578.19	-0.04	P(11)	21983.81
P(13)	37557.01	15572.84	15572.86	-0.02	P(14)	21982.43
R(12)	37561.78	15577.13	15577.12	0.00	P(13)	21982.91
P(15)	37560.65	15570.91	15570.90	0.01	R(14)	21988.03
R(13)	37560.67	15576.50	15576.50	-0.00	P(14)	21982.43
P(16)	37559.59	15569.85	15569.84	0.01	R(15)	21987.91
R(14)	37565.60	15575.86	15575.82	0.04	R(13)	21988.12
P(17)	37558.50	15568.76	15568.72	0.05	R(16)	21987.78
R(15)	37564.85	15575.11	15575.08	0.03	R(14)	21988.03
R(16)	37564.07	15574.33	15574.29	0.04	R(15)	21987.91
R(17)	37563.20	15573.46	15573.44	0.02	R(16)	21987.78
P(20)	37545.20	15565.03	15565.01	0.03	P(21)	21978.50
P(21)	37543.19	15563.67	15563.66	0.01	P(22)	21977.85
R(20)	37550.72	15570.55	15570.55	0.00	P(21)	21978.50
R(21)	37548.99	15569.47	15569.47	0.00	P(22)	21977.85
P(24)	37547.34	15559.29	15559.27	0.02	R(23)	21986.26
P(25)	37545.43	15557.68	15557.69	-0.01	R(24)	21985.96
R(23)	37543.83	15567.13	15567.15	-0.02	P(24)	21976.50
R(24)	37553.97	15565.91	15565.90	0.01	R(23)	21986.26
R(25)	37552.34	15564.59	15564.60	-0.01	R(24)	21985.96
P(28)	37539.33	15552.62	15552.64	-0.02	R(27)	21984.94
P(29)	37537.12	15550.80	15550.85	-0.05	R(28)	21984.55
P(30)	37534.99	15548.99	15549.00	-0.01	R(29)	21984.15
R(28)	37547.07	15560.35	15560.37	-0.02	R(27)	21984.94
R(29)	37545.14	15558.82	15558.86	-0.04	R(28)	21984.55
P(32)	37530.16	15545.12	15545.14	-0.02	R(31)	21983.29
R(30)	37543.27	15557.28	15557.28	-0.01	R(29)	21984.15
P(33)	37527.80	15543.14	15543.13	0.01	R(32)	21982.82
R(32)	37539.02	15553.99	15553.98	0.01	R(31)	21983.29
R(33)	37536.97	15552.31	15552.25	0.06	R(32)	21982.82

Table 3: Spectroscopic constants (in cm^{-1}) for the $[37.5]0_g^+$ level

	$^{63}\text{Cu}_2$	$^{65}\text{Cu}^{63}\text{Cu}$
T_v	37572.904(14)	37567.213(16)
B_v	0.067569(60)	0.067270(70)
$D_v \times 10^7$	-7.22(49)	-3.56(58)
isotope shift	5.691(15)	

alternatively SEP-type experiments should yield similar favorable signal intensities for the investigation of low-lying “g” symmetry levels. In fact, experiments in this laboratory have shown excellent signal-to-noise ratios for perturbation facilitated double-resonance measurements of high lying vibrational levels ($v \approx 100$) of the ground state of Cu_2 by using the SEP scheme, which is the content of a forthcoming publication. In summary, this study demonstrates a new way to shed more light on inversion symmetry states of homonuclear transition metal dimers that are hidden by stringent one-photon ($g \leftarrow / \rightarrow g$ and $u \leftarrow / \rightarrow u$) dipole selection rules.

4 Conclusion

The application of TC-RFWM spectroscopy for the investigation of an excited 0_g^+ state of the Cu_2 is reported. It is shown that states of “g” inversion symmetry are accessible by using an UNFOLDED double-resonance scheme. Such “g” symmetry states are not observable by direct one-photon absorption from the $X^1\Sigma_g^+$ ground state. Accurate spectroscopic constants of the $[37.5(v)]0_g^+$ level are measured with rotational resolution and reported for both $^{63}\text{Cu}^{63}\text{Cu}$ and $^{63}\text{Cu}^{65}\text{Cu}$ isotopologues. Further studies are under way in this laboratory on numerous “g”-symmetry states in the vicinity of the $[37.5(v)]0_g^+$ state. By intermediate level labelling, rotational transitions appear well separated and unambiguous assignment to single rotational levels is straightforward. The results will yield information on the ‘other half’ of the electronic states ensuing from a specific asymptotic limit. Furthermore, accurate molecular constants of these states are required to validate our recent *ab initio* calculations performed at the Davidson corrected multi-reference configuration interaction (MRCI) level of theory.^[14]

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