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Double-resonance spectroscopy determines highly excited vibrational energy of $^{13}\text{CO}_2$ with kilohertz accuracy

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ABSTRACT

We present a comb-referenced mid-infrared to near-infrared double-resonance (MIR-NIR DR) scheme applied to $^{13}\text{CO}_2$ to achieve high-accuracy rovibrational term values for highly excited, optically dark vibrational states. A single-pass MIR pump drives the strong $\nu_3 = 1 \leftarrow 0$ fundamental transition, while a cavity-enhanced NIR probe interrogates the weak $\nu_3 = 4 \leftarrow 1$ hot band via ring-down detection. Using a ladder (Ξ)-type excitation scheme that links the ground state directly to the $4\nu_3$ manifold, the sum of the two transition frequencies yields the pure vibrational energy of the dark (00 041) state with an uncertainty of 4.0 kHz, providing metrology-grade constraints for theoretical models and line lists. The demonstrated approach offers a practical route to access dark or ultra-weak vibrational manifolds in molecules of atmospheric and astrophysical relevance.

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I. INTRODUCTION

High-precision molecular vibrational spectroscopy constitutes a fundamental link between laboratory-based precision measurements, theoretical quantum-mechanical models, and macroscopic observations and applications. For prototypical small molecules, such as CO_2 , vibrational-rotational transition frequencies, intensities, and line shapes are ultimately governed by the molecular potential energy surface and dipole moment surface. Consequently, high-accuracy spectroscopic data provide not only the most direct and experimentally testable characterization of molecular quantum structure but also indispensable constraints for the construction and calibration of theoretical models. Vibrational transition spectra encode detailed information on chemical potential energy surfaces,^{1,2} enable the assessment of quantum control schemes involving vibrationally excited states,^{3–6} allow the inference of pressure and temperature of target molecules in atmospheric,^{7,8} astrophysical,^{9,10} and combustion-related^{11,12} research fields; and provide stringent benchmarks for effective Hamiltonian models and *ab initio* theories.¹³ For highly symmetric molecules, however, a

significant fraction of the vibrational manifold is optically “dark:” symmetry and selection rules render many transitions infrared-forbidden or extremely weak.^{14–16} Even when not directly observable, these levels couple to bright states via anharmonicity, Fermi interactions, and Coriolis mixing, thereby influencing line positions, intensities, and intramolecular energy flow. Obtaining precise term values for such dark or extremely weak manifolds is, therefore, valuable for improving high-lying models and line lists.

Double-resonance (DR) spectroscopy provides a direct route to these dark manifolds. A strong pump prepares a well-defined intermediate (bright) level, and a second optical field probes a transition originating from that prepared state, thereby converting an otherwise inaccessible target level into an observable DR signal without cooling. In the continuous-wave (cw) regime, the shared velocity class of pump and probe naturally yields sub-Doppler, state-selective features, and comb referencing enables absolute line-center measurements with high resolution. In recent years, several cw optical-optical double-resonance (OODR) techniques have been reported for probing highly vibrationally excited molecular states. Foltynowicz *et al.* presented an OODR

spectroscopy using cavity-enhanced frequency comb probe to record rovibrational transitions of methane in highly excited v_3 vibrational modes, providing valuable data for high-temperature methane spectroscopy and Hamiltonian model validation.^{17,18} However, laser accuracy and residual uncorrected baseline drift limited the achievable precision to the $5 \times 10^{-6} \text{ cm}^{-1}$ level. Hu *et al.* demonstrated comb-locked cavity-enhanced double-resonance (COCA-DR) spectroscopy to measure highly excited vibrational dark states of CO_2 in the near-infrared region, achieving kilohertz-level uncertainties. In practice, the requirement that both lasers be simultaneously locked to cavity modes imposes stringent experimental constraints, and the discrete nature of the cavity modes results in discontinuous molecular velocity selection.¹⁹ MIR-NIR double-resonance spectroscopy has also been demonstrated.^{20,21} The MIR-NIR DR spectroscopic approach was first shown in Ref. 22. Later, Tan *et al.* proposed a MIR-NIR DR spectroscopic approach, which uses cavity-enhanced probe to gain signal, while a collinear pump beam traverses the absorption cell in a single pass.²³ A combined frequency comb and continuous-wave cavity-enhanced double-resonance spectrometer with kilohertz-precision capability was also established.²⁴ Compared with the former two approaches, it significantly reduces experimental complexity while preserving kilohertz-level accuracy and allowing flexible control over the selected molecular velocity classes.

Here, we implement a frequency-comb-referenced MIR-NIR DR scheme for dark manifolds of $^{13}\text{CO}_2$. A ladder (Ξ)-type linkage simultaneously determines absolute line centers of a strong v_3 fundamental and a much weaker step terminating on the $v_3 = 4$ manifold. This provides a kHz-accurate energy link from $v = 0$ to $v = 4$, including the band center of the vibrationally dark (00 041) state, and supplies high-value constraints for modeling $^{13}\text{CO}_2$ and for metrology-grade spectroscopy.

II. EXPERIMENT

The ladder (Ξ)-type DR scheme in $^{13}\text{CO}_2$ is driven by two cw fields: a pump beam at frequency ω_1 and a probe beam at frequency ω_2 , as illustrated in Fig. 1(a). The narrow-linewidth cw MIR pump

selectively excites target molecules from the ground state to an intermediate vibrational level, preparing a velocity-selected molecular sub-ensemble. The NIR probe laser then drives a second transition from this pumped intermediate level.

The NIR probe is resonant with a 0.75 m long high-finesse cavity to enhance sensitivity, while the cavity mirrors ($R = 0.99994$ at $1.5 \mu\text{m}$ and $R \approx 0.5$ at $4.5 \mu\text{m}$; curvature $r = 1 \text{ m}$) are highly transmissive at specific mid-infrared frequencies, allowing the MIR pump to traverse the sample only once. We define ω_{10} and ω_{20} as the MIR and NIR transition center frequencies, respectively, and ω_1 as the locked pump frequency in Fig. 1(b). For a given ω_1 , the pump excites molecules with a velocity V_z along the pump beam direction, and two DR peaks (denoted ω_{21} and ω_{22}) are observed, corresponding to co- and counter-propagating probe beams. By simultaneously fitting the centers of the two DR features together with the stabilized pump frequency and applying the frequency relations given in the following,^{19,23} the intrinsic transition frequencies for both the fundamental and hot-band transitions can be determined using the following equations:

$$\begin{aligned}\omega_1 &= \omega_{10}(1 + V_z/c), \\ \omega_{21} &= \omega_{20}(1 + V_z/c), \\ \omega_{22} &= \omega_{20}(1 - V_z/c).\end{aligned}\quad (1)$$

Note that the recoil shift and second-order Doppler shift are not included in Eq. (1); these effects can be accounted for using formulas provided in Refs. 25 and 26.

The DR cavity ring-down spectroscopy (CRDS) setup is illustrated in Fig. 1(c). The MIR pump is generated as the idler output of a narrow-linewidth optical parametric oscillator (OPO). The OPO design follows our previous work²⁷ and is seeded by a 1064 nm fiber laser. Beat notes between the OPO seed/signal waves and an optical frequency comb (OFC) provide absolute frequency calibration and serve as error signals for OPO stabilization, achieving sub-kHz-level stability (0.5 kHz) of the OPO idler output (used as the MIR pump in DR) via a phase-lock loop (PLL). The OFC is disciplined to an active hydrogen maser calibrated by the National Institute of Metrology of China to guarantee the 14-digit accuracy.

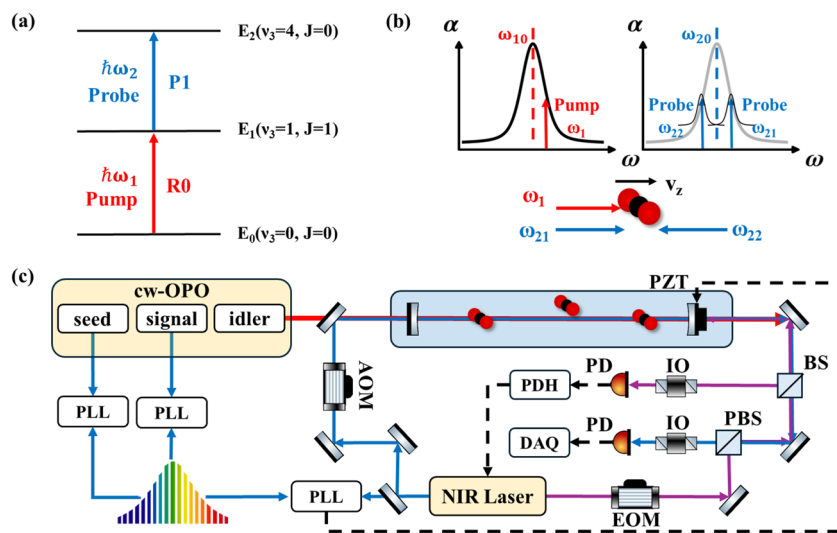


FIG. 1. Experimental principle and setup. (a) Pump-probe ladder scheme of $^{13}\text{CO}_2$. (b) Origin of the doublet in the DR signal arising from the round-trip probe field inside the cavity, yielding two fitted centers ω_{21} and ω_{22} . (c) Optical layout of the DR-CRDS setup. The OPO seed/signal and the NIR laser are phase-locked to an optical frequency comb via PLL. The OPO idler provides the MIR pump ($\hbar\omega_1$, red); the NIR beam is split for PDH locking (purple) and for CRDS probing (blue). Abbreviations: PBS, polarizing beam splitter; PZT, piezoelectric transducer; and IO, optical isolator.

The NIR probe radiation is derived from an external-cavity diode laser (ECDL) and divided into three beams. The first beam is phase-modulated by an electro-optic modulator (EOM) and used for Pound–Drever–Hall (PDH) locking of the probe laser to a selected cavity mode. The second beam is heterodyned with the OFC and the resulting beat signal is used to stabilize the cavity length during spectral scans, providing a frequency stability of 0.2 kHz. These frequency references are essential for obtaining accurate, high-precision spectroscopic frequency information. Because the beat signal between the probe laser and the OFC was fed to a beat-lock servo to lock the cavity length through a piezo-actuator attached to one of the cavity mirrors, the probe laser frequency scan was implemented by changing the beat frequency step-by-step by programming the reference radio frequency.²⁸ The third beam is frequency-shifted by an acousto-optic modulator (AOM) to address an adjacent cavity mode and is then injected into the cavity for CRDS measurements, with a propagation direction opposite to the first beam. Ring-down signals are detected with a photodetector (PD) and recorded by using a data-acquisition system (DAQ). The PDH-locking beam and the probe beam are *s*- and *p*-polarized, respectively, and an optical isolator is placed in front of each detector to eliminate the interference. Further details of the comb-referenced CRDS implementation are available in Refs. 28 and 29. The acquisition rate is 75 ~100 ring-down events per second. For each frequency point, 150 ~200 ring-down events were averaged. The noise-equivalent absorption sensitivity (NEAS) at an averaging time of 1 s was $4 \times 10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$.

Experiments were performed with a MIR pump power of 0.5 mW. The pump was tuned to a strong ν_3 fundamental-band line near $2284.2616 \text{ cm}^{-1}$ —the R(0) line in the (00 011) – (00 001) band, while the probe targeted a much weaker hot-band line near $6709.2457 \text{ cm}^{-1}$ —the P(1) line in the (00 041) – (00 011) band. The Einstein-A coefficients for the pump and probe transitions are³⁰ 125.7 and 0.2002 s^{-1} , respectively. A natural carbon dioxide sample, containing about 1% $^{13}\text{C}^{16}\text{O}_2$, was used in the measurement, and the sample pressure was 3 Pa.

III. RESULTS AND DISCUSSION

Figure 2 shows a representative DR spectrum for the P(1) (00 041) – (00 011) transition. The symbols represent measured data points; the solid curves are Voigt-profile fits used to extract the two peak centers. The corresponding residuals are shown in the lower panel. For $\Delta = \omega_1 - \omega_{10} = +4 \text{ MHz}$, the counter-propagating feature is blueshifted while the co-propagating feature is redshifted, as expected from Doppler-based velocity selection. The final spectrum used for line fitting was obtained by averaging ~50 individual scans, which served as an independent measurement dataset collected over ~40 min. The main baseline contribution came from the optical fringe (FSR ~ 1 GHz) in the CRDS measurement, as shown in Fig. 2. However, within a relatively narrow scanning range (~15 MHz), this fringe, together with the Doppler-broadened feature, can be considered as superimposing a linear baseline on the narrow DR spectrum. During data processing, we applied a linear baseline on the Voigt line profile fitting for ω_{21} and ω_{22} independently for every single-scan spectrum. The statistical values listed in Table I were obtained by linearly fitting the averaged results of six groups of independently repeated experiments.

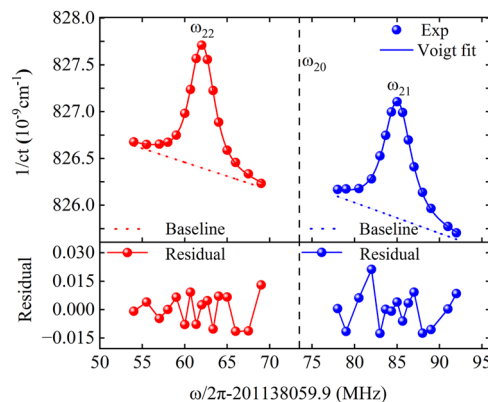


FIG. 2. DR spectrum of the P(1) (00 041) – (00 011) transition. The symbols represent the measured data, and the solid curves represent simulated Voigt profiles centering at ω_{21} and ω_{22} .

We further investigated the effect by varying both the magnitude and sign of Δ . Increasing $|\Delta|$ primarily increases the separation between the two DR peaks (ω_{21} and ω_{22}), whereas reversing the sign of Δ swaps their order. Within statistical uncertainty, the derived intrinsic frequencies remain unchanged. This behavior is expected because ω_{10} and ω_{20} are determined from both peak centers via Eq. (1) together with the stabilized pump frequency ω_1 .

Potential systematic shifts were evaluated by varying the sample pressure (1–4 and 6 Pa) and pump power (0.5, 1, and 1.5 mW) across the accessible range. While these changes broaden the observed profiles, no measurable shift of the fitted DR peak centers was observed. We also assessed the effect of pump–probe misalignment; within the tolerance of visual alignment, the inferred angular contribution to the MIR transition is less than 10 Hz and is negligible at the kHz level.

The fundamental and hot-band transition frequencies ($\omega_{10}/2\pi$ and $\omega_{20}/2\pi$) are derived from the fitted values of ω_{21} and ω_{22} using Eq. (1). Table I summarizes the applied corrections and the associated uncertainty budget. Both optical frequencies are referenced

TABLE I. Uncertainty and correction budget for $\omega_{10}/2\pi$ and $\omega_{20}/2\pi$ (unit: kHz).

Effect	$\omega_{10}/2\pi$		$\omega_{20}/2\pi$	
	R(0) (00 011) – (00 001)	P(1) (00 041) – (00 011)	R(0) (00 011) – (00 001)	P(1) (00 041) – (00 011)
Statistic	...	1.2	...	3.6
Second Doppler	0.04	...	0.1	...
Recoil	0.3	...	–2.0	...
Alignment	<0.01	...	...	...
Others	...	<1	...	<1
This work	68 480 441 334.1(16)	201 138 133 452.5(37)	68 480 441 327(87) ^a	201 138 125 800(294) ^b

^aFrom Ref. 31.

^bFrom Ref. 32.

to the optical frequency comb, and the residual contribution from the pump-to-comb lock is below 1 kHz. The second-order Doppler and photon-recoil corrections are at the sub-kilohertz level and are explicitly included in the uncertainty budget (Table I). Corrections of +0.04 kHz (second-order Doppler) and +0.3 kHz (recoil) are applied to $\omega_{10}/2\pi$, while corrections of +0.1 kHz (second-order Doppler) and -2.0 kHz (recoil) are applied to $\omega_{20}/2\pi$. The alignment-related contribution to $\omega_{10}/2\pi$ is estimated to be <0.01 kHz. Remaining effects (AC Stark, pressure-related shifts, and imperfect overlap) are estimated to be below 1 kHz and are grouped under the “Others” category in Table I.

From the dataset underlying Table I, the extracted center frequency of the MIR R(0) (00 011) – (00 001) transition is $68\,480\,441\,334.1 \pm 1.6$ kHz and that of the NIR P(1) (00 041) – (00 011) transition is $201\,138\,133\,452.5 \pm 3.7$ kHz. These values are in excellent agreement with the most accurate literature data available to date. For the MIR line, Ref. 31 reports $68\,480\,441\,327 \pm 87$ kHz. Prior to this work, the upper vibrational state (00 041) of the $^{13}\text{C}^{16}\text{O}_2$ isotopolog was accessible only through two bands: (00 041) – (00 031) and (00 041) – (00 011). The former was observed in emission,³³ providing 39 line positions of the P- and R-branches (with angular momentum quantum numbers J up to 57) at an uncertainty of 0.0005 cm^{-1} (15 MHz). The latter was measured using cw-CRDS,³² yielding 19 line positions (maximum $J = 39$) with an uncertainty of ~ 30 MHz. In particular, Refs. 32 and 34 report a value of $201\,138\,125.8$ MHz for the P(1) (00 041) – (00 011) frequency. All these earlier data were incorporated into a global fit of effective Hamiltonian parameters. The resulting set of parameters was then used to generate the $^{13}\text{C}^{16}\text{O}_2$ line list in the CDSD-296 data bank,³⁵ which until now represented the most accurate compilation of transition frequencies for this isotopolog. The present measurements reduce the uncertainties for both transitions to the kilohertz level, thereby improving the reference accuracy of the database by several orders of magnitude.

The energy of the $J = 14$ rotational level in the (00 041) state can be determined from previous studies of Tan *et al.*²³ the R(14) line in the (00 011) – (00 001) band is located at $68\,786\,813\,483.4 \pm 2.8$ kHz and the P(15) line in the (00 041) – (00 011) band at $200\,757\,201\,372.4 \pm 4.9$ kHz. In addition, the rotational energy of the $J = 14$ level in the ground state was calculated using the rotational constants reported by Zhang *et al.*;³⁶ the sum of the three energies yields the total energy of $272\,000\,632\,532.2 \pm 5.8$ kHz for the $J = 14$ (00 041) level. Using the purely vibrational energy of the (00 041)

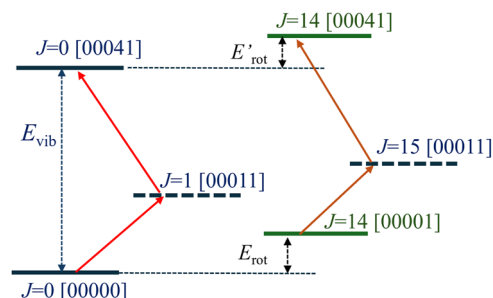


FIG. 3. Diagram of the rotation–vibration energy levels. The red and brown arrows indicate the transitions used in the DR scheme in this work and those in Ref. 23, respectively. The horizontal lines, labeled with rotational and vibrational quantum numbers, represent the respective energy levels.

state obtained in this work, together with the rovibrational energy above, we derived the corresponding pure rotational energy E_{rot} for the $J = 14$ level of the (00 041) state, as illustrated in Fig. 3. These results are summarized in Table II, where they are also compared with the values predicted by the CDSD-296³⁵ and ExoMol³⁷ databases. For the vibrational energy of the (00 041) state, the CDSD-296 and ExoMol values deviate by -7.04 and -6.62 MHz, respectively. Note that the ExoMol value has a 2.2σ deviation compared to the stated uncertainty of 3 MHz. For the $J = 14$ pure rotational energy in the excited state (00 041), the deviations are -0.32 and +0.76 MHz, respectively. As a comparison, for the $J = 14$ pure rotational energy in the (00 001) ground state, the deviations of CDSD and ExoMol are -0.007 and +1.64 MHz, respectively.

Pure vibrational transition energies constitute critical benchmark data for the construction of high-precision potential energy surfaces. Their incorporation into theoretical fitting procedures circumvents the introduction of additional fitting parameters and associated uncertainties arising from rotational level contributions. Although no direct experimental measurements are presently available, spectroscopic databases, such as CDSD and ExoMol, predict the vibrational energy of the (00 041) state with an uncertainty of less than 10 MHz, thereby providing a reliable reference for validating *ab initio* potential energy surfaces and subsequent line-list calculations. Apparently, by taking the correction of the purely vibrational energy using the value determined in this work, the CDSD model

TABLE II. Rotation and vibration energies of $^{13}\text{C}^{16}\text{O}_2$ (unit: MHz).

	$J = 0$ (00 041) E_{vib}	$J = 14$ (00 041) E'_{rot}	$J = 14$ (00 001) E_{rot}
Exp. DR	269 618 574.7866(40)	2 382 057.7456(71)	...
Exp. Ref.	269 618 567.1(294) ^a	...	2 456 617.6764(14) ^b
CDSD ^c	269 618 567.75(3000)	2 382 057.4260	2 456 617.6690
ExoMol ^d	269 618 568.17(300)	2 382 058.5052	2 456 619.3178

^aCombined with values from Refs. 31, 32, and 34.

^bCalculated according to the rotational parameters in Ref. 36.

^cData are from Ref. 35.

^dData are from Ref. 37.

can provide a more accurate description of the rotational structure for this highly excited vibrational state. The CDS vibrational energy deviates from this work by 7 MHz, while the rotational energy deviates by only 0.3 MHz, indicating that most deviations in the effective Hamiltonian model arise from the pure vibrational term. Even using only these two levels ($J = 0$ & 14) of the (00041) band, a satisfying correction can be derived for the entire band. The pure vibrational and rotational energies obtained in this work also provide a benchmark for further verification of theoretical models. The methodology demonstrated herein is sufficiently general and can be readily extended to analogous molecular bands, thereby offering a systematic route toward global spectroscopic validation in related molecular systems.

IV. CONCLUSION

We have demonstrated a comb-referenced MIR-NIR DR-CRDS scheme that enables sub-Doppler, state-selective, and velocity-selective access to high-lying vibrational states of $^{13}\text{CO}_2$. By pumping the strong $\nu_3 = 1 \leftarrow 0$ fundamental transition with a single-pass MIR beam and probing the weak $\nu_3 = 4 \leftarrow 1$ hot band with cavity ring-down spectroscopy, we determined line centers with kHz-level uncertainties. The chosen R(0)-P(1) ladder scheme provides direct access to the pure vibrational energy of the optically dark (00041) vibrational state. Such precise vibrational term values serve as critical constraints for high-lying polyads, where high state density and strong mixing can lead to rapid divergence in effective Hamiltonian models when experimental data are sparse.³⁸

Future work will extend this approach to additional rotational branches and lines, enabling the determination of rotational constants and splitting patterns within dark manifolds through combination differences and network-based closure checks. On the instrumentation side, incorporating pump modulation with synchronous detection and optimized scan strategies should further enhance sensitivity, facilitating measurements of weaker hot bands and rarer isotopologs.

More broadly, cw DR spectroscopy offers tunable control over the selected velocity class via the pump detuning, allowing weak transitions to be isolated with sub-Doppler resolution. In the context of dark-state metrology, varying the pump transition provides access to alternative energy-level linkages and expands spectroscopic coverage. The single-pass pump/cavity-enhanced probe architecture is readily adaptable across different wavelength regions and can be implemented in ladder (Ξ)-, V-, and Λ -type excitation schemes, holding significant promise for a wide range of applications.^{19,39–44}

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

C.-F. Cheng and S.-M. Hu conceived the original idea and supervised the project. T.-H. Liu and Y.-D. Tan designed and built the experimental setup, performed the measurements, and analyzed the data. T.-H. Liu and C.-F. Cheng wrote the original manuscript, and all authors revised and commented on the final version of the manuscript.

Tian-Hu Liu: Data curation (lead); Formal analysis (lead); Writing – original draft (equal). **Yan-Dong Tan:** Formal analysis (equal); Software (equal); Writing – review & editing (equal). **Cun-Feng Cheng:** Conceptualization (equal); Funding acquisition (lead); Project administration (lead); Supervision (equal); Writing – original draft (lead); Writing – review & editing (equal). **Shui-Ming Hu:** Conceptualization (equal); Funding acquisition (equal); Methodology (equal); Project administration (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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