



Mid-infrared–near-infrared double-resonance spectroscopy of molecules with kilohertz accuracy

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Precision measurements of molecular transitions to highly excited states are needed in potential energy surface modeling, state-resolved chemical dynamics studies, and astrophysical spectra analysis. Selective pumping and probing of molecules are often challenging due to the high state density and weak transition moments. We present a mid-infrared and near-infrared double-resonance spectroscopy method for precision measurements. As a demonstration, Doppler-free stepwise two-photon absorption spectra of $^{13}\text{CO}_2$ were recorded by pumping the fundamental transition of R14 (00011)-(00001) and probing the P15 (00041)-(00011) transition enhanced by a high-finesse optical cavity, and the transition frequencies were determined with an accuracy of a few kilohertz. © 2024 Optica Publishing Group

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Introduction. Double-resonance (DR) spectroscopy is a powerful tool for probing highly excited states of molecules, labeling congested transitions [1–3], investigating state-resolved molecular dynamics [4], and analyzing spectral data of astrophysical objects [5,6]. It provides a way to use a known transition to identify transitions with the related quantum state. DR spectroscopy allows us to reach higher excited states which could be hard or forbidden for a single-photon transition. Assigning the transitions would also be much simpler since the intermediate state has been selected by the pump transition. Usually, pulsed lasers are employed in DR measurements to increase the signal, at the cost of reduced resolution and selectivity because of their broad linewidths at the gigahertz level [7,8]. Continuous-wave (cw) lasers with narrow linewidth allow optical–optical DR measurements with a resolution beyond the Doppler limit. The advantage is particularly attractive for molecules with a complicated Doppler-broadened spectrum that has many overlapping transitions [9,10]. However, DR spectroscopy with cw lasers has been only practical to pump and probe strong fundamental transitions of molecules due to the limitation in excitation power and detection sensitivity.

Optical–optical DR has been previously reported by several research groups. Karhu *et al.* [11–13] employed a 3 μm cw laser to pump acetylene and measured its symmetric vibrational states using near-infrared (NIR) cavity ring-down spectroscopy.

Foltynowicz *et al.* [14,15] utilized a 3.3 μm cw pump laser and a 1.67 μm optical frequency comb (OFC) to detect sub-Doppler transitions of methane. The requirements in DR spectroscopy help to reduce the spectral linewidth and label overtone transitions to highly excited energy levels. The accuracy of the measured transitions was limited to a few MHz due to the frequency fluctuation of the pump laser and insufficient detection sensitivity [14]. Hu *et al.* [16,17] have achieved a kHz accuracy using comb-locked cavity-assisted double-resonance (coca-DR) spectroscopy, where both the pump and probe lasers are locked to the same cavity. The method allows for studies of high vibrationally excited states of molecules. The high selectivity of cavity-assisted DR spectroscopy has also been applied in the quantitative detection of trace molecular isotopes, such as $^{14}\text{CO}_2$ ($^{14}\text{C}/^{12}\text{C} \approx 10^{-12}$) in environmental samples [18–20]. Since both lasers with different colors need to be locked with the same cavity but different cavity modes, the technical complexity prevents wide applications of this method.

In this Letter, we present a MIR–NIR double-resonance spectroscopy method for precision measurements. By measuring two DR peaks induced by a standing-wave NIR laser field in a resonant cavity and another unidirectional mid-infrared (MIR) laser beam, we are able to determine center frequencies for both MIR and NIR transitions with kHz accuracy. Since only the NIR probing laser is resonant with the optical cavity, the technical difficulty is considerably released compared to the coca-DR method. As a demonstration, a ladder-type DR spectrum of $^{13}\text{CO}_2$ is measured and both the fundamental transition frequency near 4.3 μm and the overtone one near 1.5 μm are determined with an accuracy of a few kHz.

Experiment. Most molecules have strong fundamental vibrational transitions in the mid-infrared region, making mid-infrared lasers suitable to pump many molecules to vibrationally excited states even with a single-pass configuration. In the MIR–NIR double-resonance spectroscopy method, we use a mid-infrared laser to pump the molecules and a near-infrared laser to probe them. The principle of the method is illustrated in the top right corner of Fig. 1. The pump laser excites molecules with a specific speed along the laser propagating direction, V_z , from the ground state E_0 to the intermediate state E_1 . Subsequently, a near-infrared laser probes the absorption signal of the transition from the E_1 state to the highly excited state E_2 .

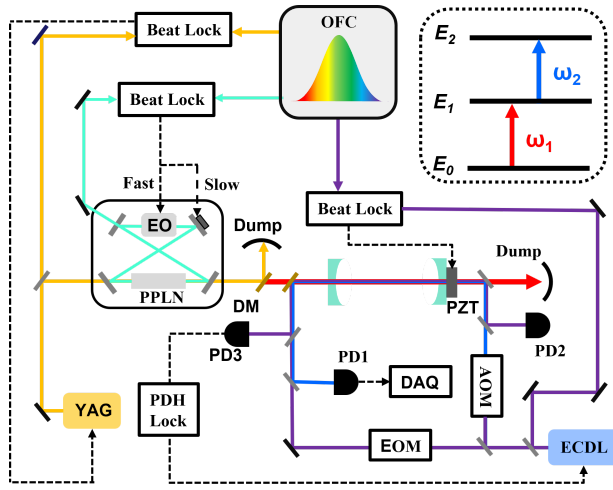


Fig. 1. Schematic of double-resonance spectroscopy. The orange, green, and red lines represent the pump, signal, and idler light beams of the optical parametric oscillator (OPO) light source, respectively. The blue and purple lines represent the different beams of the near-infrared laser. The blue one is used for probing the double-resonance signal, and the purple one is used for PDH locking the laser with the cavity and beating with the comb. Abbreviations: YAG, Nd:YAG laser; EO, electro-optical crystal; AOM, acousto-optic modulator; PDH, Pound–Drever–Hall locking servo; DAQ, data acquisition system; ECDL, external-cavity diode laser; PD, photodiode detector; OFC, optical frequency comb; PZT, piezoelectric actuator; DM, dichroic mirror.

Note that the sample cell is an optical cavity that is resonant with the NIR probe laser but transparent to the MIR pump laser. Consequently, the pump laser passes through the sample cell only once but the probe laser goes back and forth in the cell. Therefore, we could observe two double-resonance spectra with a given pump laser frequency. One is that the probe and pump lasers are resonant to the molecules with the same velocity V_z along the pump laser beam, and the other one is that the probe laser is resonant with the molecules with a reversed velocity of $-V_z$. Double-resonance conditions [17] for these two scenarios are as follows:

$$\frac{V_z}{c} = 1 - \frac{\omega_{10}}{\omega_1} + \frac{V^2}{2c^2} + \frac{\hbar\omega_1}{2Mc^2}, \quad (1)$$

$$\frac{V_z}{c} = 1 - \frac{\omega_{20}}{\omega_{21}} + \frac{V^2}{2c^2} - \frac{\hbar\omega_{21}}{2Mc^2}, \quad (2)$$

$$-\frac{V_z}{c} = 1 - \frac{\omega_{20}}{\omega_{22}} + \frac{V^2}{2c^2} - \frac{\hbar\omega_{22}}{2Mc^2}, \quad (3)$$

where ω_1 represents the frequency of the pump laser, ω_{10} represents the resonance frequency between energy levels E_0 and E_1 for static molecules, ω_{20} represents the resonance frequency between energy levels E_1 and E_2 , ω_{21} is the probe laser frequency when the pump and probe lasers propagate in the same direction, and ω_{22} is the probe laser frequency when the pump and probe lasers propagate in opposite directions. Note that the second-order Doppler shift, $\frac{V^2}{2c^2}$, and the recoil shift, $\frac{\hbar\omega}{2Mc^2}$, are smaller than 1 kHz for infrared transitions considered in this work and could be neglected. Combining Eq. (1) and Eq. (3), we can

determine the frequencies of both MIR and NIR transitions:

$$\omega_{10} = \frac{2\omega_1\omega_{22}}{\omega_{21} + \omega_{22}}, \quad (4)$$

$$\omega_{20} = \frac{2\omega_{21}\omega_{22}}{\omega_{21} + \omega_{22}}. \quad (5)$$

We can see that by fixing the pump laser frequency and measuring both double-resonance spectra in the two propagating directions of the probe laser, both intrinsic transition frequencies of the molecule, ω_{10} , from the ground state E_0 to the intermediate state E_1 , and ω_{20} , from E_1 to the highly excited state E_2 , can be determined simultaneously.

The double-resonance spectroscopy setup is depicted in Fig. 1. The cavity comprises two mirrors with high reflectivity (HR, $R > 99.992\%$) in the range of 1400–1600 nm, and a transmittance of about 50% between 4000 nm and 4800 nm. The MIR laser is the idler light delivered from a home-made narrow-linewidth optical parametric oscillator (OPO) source, the principles and structure of which were detailed in our prior studies [21,22]. The frequency stabilization of the MIR laser is achieved by locking both the pump and signal lights of the OPO source to an optical frequency comb (OFC), enabling kHz-level long-term stability. The NIR probing laser is an external-cavity diode laser (ECDL), which splits into three beams. The first one is used to lock the laser with the optical cavity using the Pound–Drever–Hall (PDH) method. The second one is the beat with the OFC, and the beating signal is used to stabilize the cavity length. The third beam is frequency-shifted by an acousto-optic modulator (AOM) with a frequency equal to the free spectral range of the cavity and then coupled into the optical cavity for cavity ring-down spectroscopy (CRDS) measurements. The details of comb-locked CRDS were elucidated in the previous work [23,24].

Results and discussion. To evaluate the frequency accuracy of the measurement, we first measured the beat frequency between the pump (probe) laser and the optical frequency comb.

The OFC is disciplined by a hydrogen maser with a fractional frequency accuracy better than 1×10^{-13} . The frequency of the MIR laser is determined by measuring the frequencies of the OPO pump and signal lights of the OPO source. The results are shown in Fig. 2(a), and the Allan deviations are shown in Fig. 2(b). Note that the mid-infrared laser frequency, derived from the difference between the measured frequencies of the OPO pump and signal lights, has a fluctuation of less than 0.1 kHz after an averaging time of 300 s. The result agrees well with our previous study [21]. The probe laser frequency was measured by beating with the comb using a transfer lock method [23–26], and the result is shown in Fig. 2(b). The measured frequency drift under 1 s averaging time is within 0.5 kHz, and the frequency uncertainty of the probe laser is less than 0.1 kHz during a spectroscopy scan time of 40 s.

In our double-resonance scheme, the pump laser is locked near the resonance with a frequency detuning $\Delta = (\omega_1 - \omega_{10})/2\pi$ within the Doppler width. The spectroscopy scan is accomplished by actively tuning the beat frequency between the probe laser and the OFC. Two peaks appear while scanning the probe laser, shown in Fig. 3. The sample pressure is 0.5 Pa, and the intra-cavity power for the probe and pump laser is 11 W and 0.35 mW, respectively. One is that the NIR laser and the MIR laser excite molecules with reversed velocity [see Eq. (3)], and the other one is that the NIR and MIR lasers excite molecules with the same velocity [see Eq. (2)]. The spectrum can be well-fitted

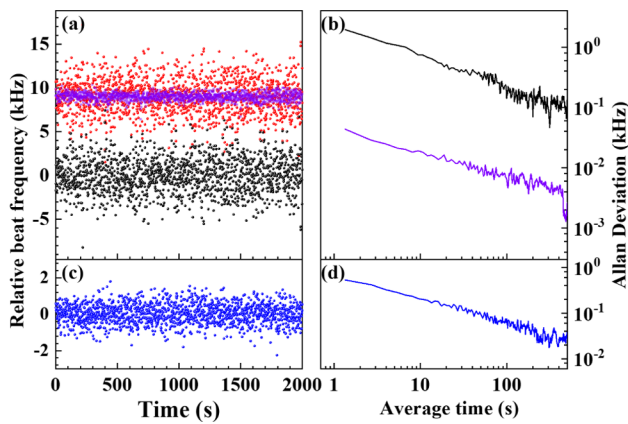


Fig. 2. Frequency drift of the lasers used in the experiment. (a) Beat frequency between the pump/signal light of OPO and the frequency comb. Purple and red colors represent the OPO pump light and the signal light, respectively. The beat frequency data of the OPO pump light has been increased tenfold for better presentation. The black data points represent the difference between the OPO pump light and the signal light, indicating the frequency of the idler light. Data are shifted for better illustration. (b) Allan deviation of the OPO pump, signal, and idler light frequencies given in (a). The frequency fluctuation of the idler light is dominated by that of the signal light; therefore, their Allan deviation curves are overlapping. (c) Beat frequency between the probe laser and the frequency comb. (d) Allan deviation of the probe laser frequencies given in (c).

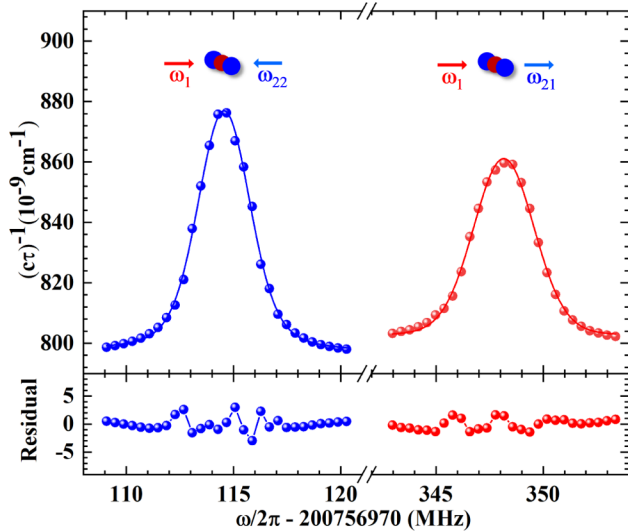


Fig. 3. P15 (00041)-(00011) transition observed by DR spectroscopy. Scattered points are the experimental data, and the solid lines are the simulated spectra using Voigt profiles.

with the Voigt profile, and the linewidth is dominated by the transit-time broadening and power broadening.

The fundamental and overtone transition frequencies ($\omega_{10}/2\pi$ and $\omega_{20}/2\pi$) were derived according to Eqs. (4) and (5), and the uncertainty budget is given in Table 1. The pump laser was locked to the OFC and the uncertainty was less than 1 kHz. The second-order Doppler shift and recoil effects are also below 1 kHz. The imperfect overlapping between the pump and probe lasers could also contribute to a shift of $\omega_{10}/2\pi$. We estimated the possible mismatching angle from the geometric alignments

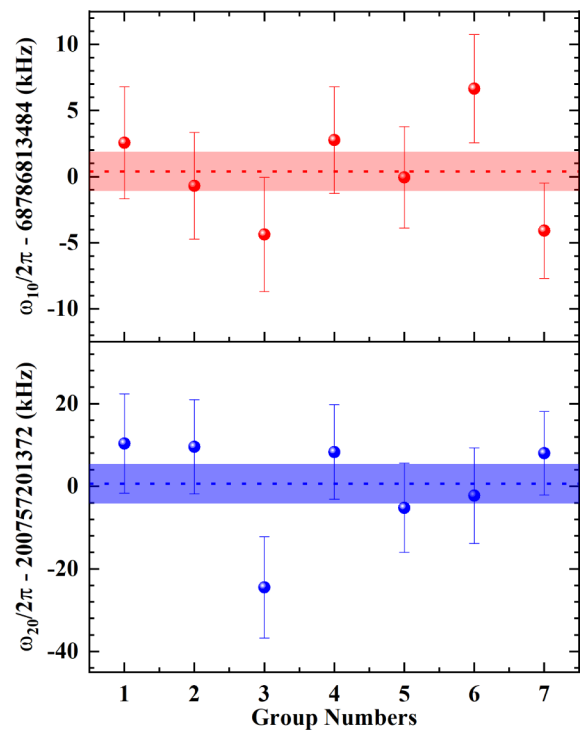


Fig. 4. Frequencies of the R14 (00011)-(00001) (upper panel) and P15 (00041)-(00011) (lower panel) transitions obtained by individual DR spectroscopy measurements. The dashed lines present the mean values, and the shaded areas indicate the standard deviations.

in the experiment and gave an upper limit of 0.01 rad. This mismatching corresponds to a redshift of the $\omega_{10}/2\pi$ value as much as -2.2 kHz. Therefore, we include a systematic shift of -1.1 kHz here. Note that this effect does not contribute to the overtone transition frequency $\omega_{20}/2\pi$ since the back-and-forth NIR probing laser beams could be considered to overlap perfectly inside the high-finesse optical cavity. We have calculated the possible uncertainty contributions from the ac-Stark effect and the pressure-induced effect with the method mentioned in [30], and the values are below 1 kHz, which we have included in the “Others” category in the uncertainty budget table. We repeated the experiment several times, and the transition frequencies determined from different measurements are depicted in Fig. 4. We can see all results agree reasonably with each other. Finally, the fundamental and overtone transition frequencies are determined to be $68,786,813,483.4 \pm 2.8$ kHz and $200,757,201,372.4 \pm 4.9$ kHz, respectively. The corresponding best values in literatures are $68,786,813,426 \pm 87$ kHz [27] and $200,757,194$ MHz, respectively, with an estimated uncertainty between 3 MHz and 30 MHz [28,29]. The results given in this work agree well with them and improve the accuracy by a few orders of magnitude.

Conclusion. In conclusion, we demonstrated MIR–NIR double-resonance absorption spectroscopy of molecules with kilohertz accuracy. We excited molecules with selected velocity along a single-pass MIR laser beam and probed the Doppler-free absorption signal of an overlapping NIR laser beam in an optical cavity. The observed DR spectra show a linewidth of a few MHz, and the rotation-vibration energy in the highly excited vibrational state was determined with an accuracy of a few kilohertz. Although we only demonstrate the ladder-type DR spectroscopy

Table 1. Uncertainty Budget for $\omega_{10}/2\pi$ and $\omega_{20}/2\pi$ (Unit: kHz)

Effect	$\omega_{10}/2\pi$		$\omega_{20}/2\pi$	
	R14 (00011)-(00001)		P15 (00041)-(00011)	
	Correction	1 σ	Correction	1 σ
Statistic		1.5		4.8
Second Doppler	0.04		0.1	
Recoil	0.04		-0.3	
Alignment	-1.1	2.2		-
Others		<1		<1
Frequency	68 786 813 483.4 \pm 2.8		200 757 201 372.4 \pm 4.9	
	68 786 813 426 \pm 87 ^a		200 757 194 000 ^b	

^aFrom Elliott *et al.* [27].

^bFrom Refs. [28,29], uncertainty estimated to be 3–30 MHz.

in this work, the experimental configuration also works for the “V”-type and “ Λ ”-type DR schemes. The method is essentially a coherent pump-and-probe technique and could be implemented in different means and for various purposes. The single-pass pumping scheme allows for a very flexible implementation of the method in different spectral regions. The detection sensitivity has been significantly enhanced by the high-finesse cavity, and further improvement could be expected by modulating the frequency or power of the MIR laser [26]. Owing to the Doppler-free nature of DR spectroscopy, the narrow linewidth observed in this method allows for high-selectivity detection of weak transitions or trace molecular samples [16,18,20]. By changing the off-resonance frequency shifts of the pump and probe lasers, molecules with a specific velocity along the laser beams could be selectively excited. Note that preparing velocity- and state-selected molecules is essential in studying molecular interactions in scattering experiments [31,32]. High selectivity and high precision of the method will shed light on some very challenging experiments, such as trace detection at the part-per-trillion level [20] and testing fundamental physics/symmetry [30,33] in molecules with unprecedented precision.

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Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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