Sub-Doppler Double-Resonance Spectroscopy of Methane Using a Frequency Comb Probe

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Abstract: We use a 3.3 µm continuous wave optical parametric oscillator as a pump and a 1.67 µm frequency comb as a probe to record 36 sub-Doppler double-resonance transitions in the 3v3 band of methane (including 26 previously unreported) with ~1.5 MHz center frequency accuracy.

1. Introduction

Methane has long been a molecule of intense scientific interest. It is a dominant source of the opacity of many of the planets in our solar system [1] and has been detected in hot-Jupiter exoplanets [2]. However, the modelling of the observed spectra is limited by the lack of reference laboratory data. Making measurements at the relevant temperatures is very challenging and provides highly congested spectra at thermodynamic equilibrium. Theoretical spectra can be calculated using line lists obtained from ab-initio calculations [3], but firmly assigned transitions up to highly excited vibrational states, needed to judge the accuracy of the predictions, are still missing in the literature. Double-resonance (DR) spectroscopy is a powerful tool for assignment of highly excited states. It allows the measurement of sub-Doppler transitions from an already assigned state selectively populated by a pump, which dramatically simplifies the spectrum and its assignment. Double-resonance spectroscopy of CH4 was previously reported using dye lasers to produce ns pump and probe pulses in the 1.6 and 3.3 µm spectral regions, and had limited sensitivity and spectral resolution (>0.12 cm⁻¹) [4]. In this work we use a 3.3 µm continuous wave optical parametric oscillator as a pump and a 1.67 µm frequency comb as a probe to record sub-Doppler double-resonance transitions of methane over 200 cm⁻¹ of bandwidth with center frequency accuracy ~1.5 MHz. The probe transitions in the ladder-type excitations [see Fig. 1(a)] reach ro-vibrational states in the ~9000 cm⁻¹ energy region and most of the observed transitions were previously unreported.

2. Experiment

The experimental setup is shown in Fig. 1(b). A sample of 30 mTorr of pure CH4 was contained in an 80-cm-long single-pass cell. The central 55 cm was liquid nitrogen cooled to increase the absorption signal. The pump was a singly-resonant optical parametric oscillator, whose idler frequency (up to 1 W, tunable between 3.1-3.7 µm) was stabilized to the center of a selected CH4 transition in the fundamental v3 band using frequency-modulated Lamb dip detected in pure CH4 in a reference cell. This lock provided a long-term frequency stability of the idler of ~1 MHz. The probe laser was an amplified Er:fiber frequency comb with 400 mW output power around 1.55 µm. The comb spectrum was shifted to cover 200 cm⁻¹ around 1.67 µm (6000 cm⁻¹) using a polarization maintaining Raman soliton microstructured silica fiber.

Fig. 1. (a) Schematics of the energy level structure of the v3 stretching bands of methane with pump (orange) and probe transitions indicated (red: V-type, and blue: ladder-type). (b) Experimental setup. OPO: optical parametric oscillator, BS: beam splitter, DM: dichroic mirror, PM: power meter, HWP: half-wave plate, RSS: Raman soliton self-frequency shift microstructured silica fiber, FTS: Fourier transform spectrometer.
self-frequency shift microstructured silica fiber. The comb was RF-stabilized to a GPS-referenced Rb oscillator. The repetition rate \( f_{\text{rep}} = 250 \text{ MHz} \) was phase-locked to a direct digital synthesizer (DDS) that used the Rb oscillator as a clock. Stepping the DDS frequency allowed stepping the frequencies of the comb modes. The probe light transmitted through the sample was analyzed with a home-built fast-scanning Fourier transform spectrometer (FTS) with auto-balanced detection. The nominal resolution of the FTS was matched to the \( f_{\text{rep}} \) to eliminate the influence of the instrumental line shape [5]. One interferogram was acquired in 5.8 s and yielded a sample point spacing of 250 MHz. The \( f_{\text{rep}} \) was then tuned in steps of 2.78 Hz, which resulted in a 2 MHz shift of the comb modes per step. These resulting 125 spectra were interleaved and averaged (up to 16 times). The noise equivalent absorption coefficient was \( 2 \times 10^{-6} \text{ cm}^{-1} \) after 3.2 h of averaging. The measurement was repeated with the probe polarization turned by 90°. In total, we recorded DR spectra for the pump laser tuned to 9 different transitions in the \( v_3 \) band, viz. R(0), R(1), P(1), Q(1), P(2, E), P(2, F2), P(3, A2), P(3, F1), and P(3, F2).

When the pump was tuned to the R(0) transition in the \( v_3 \) band, we observed one V-type transition [in the R(0) line of the 2\( v_3 \) band, Fig. 2(a)], and five ladder-type transitions in the spectrum. Three of them are shown in Fig. 2(b)-(d) for perpendicular (red) and parallel (blue) relative pump and probe polarizations. The relative line intensities for the two polarizations allow line assignment as indicated in the figure. The assignment is confirmed by comparison to the high-temperature line list from the TheoReTS database [3]. The center frequencies of the DR transitions were found by fitting Lorentzian functions to the data. Their accuracy is confirmed by comparison of the frequencies of the V-type transitions to the results reported in Ref. [6] for the 2\( v_3 \) band, which agree to within 0.4 MHz. In total, we detected 24 V-type and 36 ladder-type transitions for the nine pumped transitions. The center frequencies of all ladder-type transitions are compared to the theoretical predictions from the TheoReTS database in Fig. 2(e). They all agree to within 1 cm\(^{-1}\) (30 GHz), i.e. the estimated accuracy of the theoretical line list.

### 3. Conclusions and Outlook

We report the first measurement of sub-Doppler molecular response using a frequency comb and observe 24 V-type and 36 ladder-type double-resonance transitions in methane, of which 26 are reported and assigned for the first time. The assignment is based on the line intensity ratios for different relative pump/probe polarization, and the TheoReTS line list [3]. The center frequency accuracy is \( \sim 1.5 \text{ MHz} \), limited by the stability of the pump laser, and will be improved by optimizing the Lamb dip lock. We are currently implementing an enhancement cavity for the comb probe in order to significantly increase the absorption sensitivity. DR spectroscopy with a comb probe opens up for accurate assignment of highly excited energy levels that cannot be done using high temperature spectra.

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