

Continuous-Wave Difference-Frequency Generation in Periodically Poled RbTiOAsO₄ Crystal and Application to Isotopic Analysis of Methane

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Abstract: We report on development of a widely tunable infrared (3.4-4.5 μm) continuous-wave laser spectrometer based on difference frequency generation in a periodically poled RbTiOAsO₄ crystal and its application to isotope analysis of ¹³CH₄/¹²CH₄.

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1. Introduction

Quasi-phase-matched (QPM) periodically poled RbTiOAsO₄ (PPRTA) crystal offers several advantages compared to other periodically poled ferroelectric optical materials presently available for continuous-wave (cw) infrared difference-frequency generation (DFG), such as PPLN, PPKTP, and PPKTA. The optical transparency range for PPRTA extends from 350 nm to about 5.8 μm (at the zero transmittance level). It also possesses a high damage threshold of $> 400 \text{ MW/cm}^2$ @ 1064 nm for pulses of 10-20 ns duration, which is \sim five times better than for PPLN, and comparable to that for PPKTP and PPKTA. The nonlinear figure of merit is about 37.5 (pm/V)^2 . PPRTA crystals have been employed for pulsed optical parametric devices [1,2], while cw DFG in PPRTA provides the feasibility of a high spectral purity which is important for applications in high resolution spectroscopy and trace gas sensing [3-4].

In the paper, we report on development of a tunable infrared (3.4-4.5 μm) continuous-wave (cw) laser spectrometer based on different frequency generation (DFG) in a periodically poled RbTiOAsO₄ (PPRTA) crystal. Experimental details of the feasibility of measurements of methane (CH₄) isotopic composition based on laser absorption spectroscopy using this DFG radiation source will be described

2. PPRTA-based DFG laser spectrometer

In the present work, two cw Ti:Sapphire lasers operating from 710 to 720 nm and 847 to 915 nm respectively were used as difference-frequency mixing sources. The two laser beams were collinearly focused onto a PPRTA crystal via a 35-cm-focal length lens. The used PPRTA crystal was 1 mm thick with a 20-mm interaction length and a QPM grating period of 24.1 μm , which allows infrared radiation by quasi-phase-matched DFG tunable from 3.4 to 4.5 μm with a wavelength-tuning bandwidth (FWHM) of $\sim 12 \text{ cm}^{-1}$. Infrared light powers of $\sim 10 \mu\text{W}$ were generated at 4 μm when pumped by total laser powers of 300 mW. These pump conditions yield a power conversion efficiency of $\sim 0.5 \text{ mW/W}^2$ at room temperature. The slope of the temperature-dependent wavelength tuning was found to be $-1.02 \text{ cm}^{-1}/^\circ\text{C}$. The generated mid-infrared laser beam was collimated with a parabolic mirror, and then directed to a multipass White cell for spectroscopic application.

3. Isotopic analysis of ¹³CH₄/¹²CH₄

Measurements of CH₄ isotopic composition were carried out using the QPM-PPRTA based infrared source. The used experimental setup is shown in Fig.1. The used methane sample is buffered in synthetic air with CH₄:N₂:O₂ = 0.3%:79.7%:20%. Two absorption lines of CH₄ were selected for the isotopic ratio measurements: $2885.42096 \text{ cm}^{-1}$ for ¹³CH₄ and $2885.45950 \text{ cm}^{-1}$ for ¹²CH₄, respectively. The corresponding line parameters used in our experiment are given in the HITRAN database [5]. The measurements have been performed at 19 $^\circ\text{C}$. The isotope abundances are typically expressed in the δ -units terms of parts per thousand (or per mil, ‰) relative to a standard. The δ -unit is defined as the isotopic ratio of a sample standardized to the isotopic ratio of a defined reference:

$$\delta = \frac{R_{\text{sample}} - R_{\text{std}}}{R_{\text{std}}} \times 1000 \quad \text{with} \quad R = \frac{{}^{13}\text{C}}{{}^{12}\text{C}}$$

where R_{Sample} is the isotope abundance of the sample, and R_{Std} is the isotope abundance of the standard sample. The standard carbon isotopic ratio value [6] reported is $(^{13}\text{C}/^{12}\text{C})_{\text{std}} = 1.12\%$.

Figure 2 shows an absorption spectrum of methane isotope at 1.65 Torr. The CH_4 isotope abundance can be determined with the ratio of the two lines absorption intensity, which yields a value of 0.0102 ± 0.00012 for the $^{13}\text{CH}_4/^{12}\text{CH}_4$ isotopic ratio, equivalent to an enrichment of $\delta^{13}\text{C} = -89.3\% \pm 1.03\%$. Based on these measurements, we determined also the air-broadening coefficients for the used lines of $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$: $\gamma_{\text{air}}(^{13}\text{CH}_4) = 0.0432 \text{ cm}^{-1}/\text{atm}$ and $\gamma_{\text{air}}(^{12}\text{CH}_4) = 0.0573 \text{ cm}^{-1}/\text{atm}$ (at 296 K), compared to $0.0470 \text{ cm}^{-1}/\text{atm}$ and $0.0540 \text{ cm}^{-1}/\text{atm}$ given by the HITRAN database.

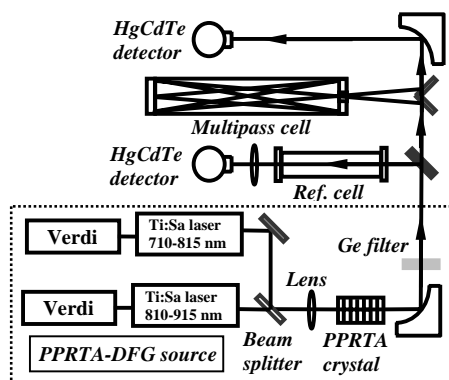


Figure 1 Schematic of a high-resolution PPRTA-DFG laser spectrometer reported in the present work

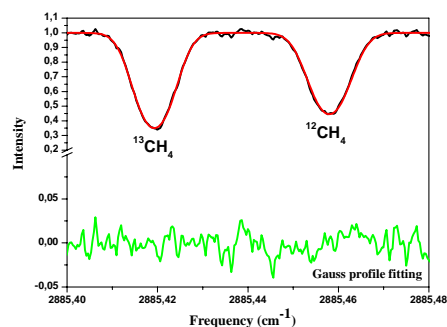


Figure 2 CH_4 isotope absorption spectrum measured at 1.65 Torr and 19°C . The red line is a theoretical Gauss profile fitted to the observed absorption spectrum (black line) and the green line shows the residual.

4. Conclusion

In this paper, we described development of a PPRTA-DFG based mid-infrared laser source for high-resolution spectroscopic application. Isotope abundance measurements of $^{13}\text{CH}_4/^{12}\text{CH}_4$ have been performed based on the DFG laser absorption spectroscopy near $3.466 \mu\text{m}$ with an accuracy of $\Delta\delta^{13}\text{C} = \pm 1.03\%$.

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5. References

- [1] T. J. Edwards, G. A. Turnbull, M. H. Dunn, M. Ebrahimzadeh, "Continuous-wave singly resonant optical parametric oscillator based on periodically poled RbTiOAsO_4 ", *Opt. Lett.* **23**, 837-839 (1998)
- [2] D. L. Fenimore, K. L. Schepler, D. Zelmon, S. Kück, U. B. Ramabadran, P. Von Richter, D. Small, "Rubidium titanyl arsenate difference-frequency generation and validation of new Sellmeier coefficients", *J. Opt. Soc. Am.* **B13**, 1935 (1996)
- [3] K. Fradkin-Kashi, A. Arie, P. Urenski, G. Rosenman, "Characterization of optical and nonlinear properties of PPRTA in the mid-infrared range via difference-frequency generation", *Appl. Phys.* **B71**, 251-255 (2000)
- [4] W. Chen, G. Mouret, D. Boucher, F. Tittel, "Mid-infrared trace gas detection using continuous-wave difference-frequency generation in periodically poled RbTiOAsO_4 ", *Appl. Phys.* **B72**, 873-876 (2001)
- [5] L.S. Rothman, D. Jacquemart, A. Barbe, D. Chris Benner, M. Birk, L.R. Brown, M.R. Carleer, C. Chackerian Jr., K. Chance, L.H. Coudert, V. Dana, V.M. Devi, J.-M. Flaud, R.R. Gamache, A. Goldman, J.-M. Hartmann, K.W. Jucks, A.G. Maki, J.-Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi, G. Wagner, *J. Quant. Spectrosc. Radiat. Transfer* **96**, 139-204 (2005)
- [6] M. Erdely, D. Richter, F. K. Tittle, " $^{13}\text{CO}_2/^{12}\text{CO}_2$ isotopic ratio measurements using a difference frequency-based sensor operating at $4.35 \mu\text{m}$ ", *Appl. Phys.* **B75**, 289-295 (2002)