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Photoacoustic Optical Frequency Comb Spectroscopy of Radioactive Methane in the Mid-Infrared Region

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The standard method for sensitive measurements of long-lived radioactive isotopes, such as ^{14}C , is accelerator mass spectrometry (AMS). The AMS facilities are indispensable for applications like radiocarbon dating, but too expensive and massive for in-situ measurements. Laser spectroscopy, on the other hand, is a promising solution for isotope-selective detection of gas-phase compounds in applications that require low-cost instrumentation and on-site measurement capability. The recent work on laser spectroscopy of $^{14}\text{CO}_2$ has led to impressive detection limits below the natural ^{14}C abundance [1,2], which encourages us to develop similar techniques also for other radiocarbon compounds. Here, we report the first spectroscopic study of radioactive methane, $^{14}\text{CH}_4$. Our work is motivated by a number of important applications, such as determining the biofraction of methane fuel mixtures and in-situ monitoring of radioactive gas emissions at decommissioning sites of light water nuclear reactors.

An essential prerequisite for the development of optical detection of $^{14}\text{CH}_4$ is to compile a spectroscopic database with relevant absorption line parameters. Here, we report the *first* measurement of $^{14}\text{CH}_4$ absorption spectrum. We focus on the fundamental antisymmetric CH-stretching vibrational band (ν_3) of methane in the $3\text{ }\mu\text{m}$ wavelength region. Our results make it possible to locate the absorption lines that are most suitable for $^{14}\text{CH}_4$ detection and quantification while minimizing the spectral interference due to other molecular compounds.

In the measurements of $^{14}\text{CH}_4$ absorption spectrum we have used a recently introduced technology, which combines a broadband optical frequency comb (OFC) light source with Fourier-transform interferometry and cantilever-enhanced photoacoustic spectroscopy (CEPAS) [3,4]. The CEPAS method provides an excellent spectroscopic detection sensitivity with a small sample volume of only a few millilitres, which is particularly advantageous when the sample amount is limited, such as in the case of radioactive species. The mid-infrared OFC light source is a high-power femtosecond optical parametric oscillator, which allows us to perform sensitive (sub 100 ppb) broadband measurements of the entire ν_3 bands of $^{12}\text{CH}_4$ and $^{14}\text{CH}_4$. Not only have we demonstrated the first optical measurements of $^{14}\text{CH}_4$, but also an order of magnitude improvement in trace gas detection sensitivity compared to the best previously reported broadband photoacoustic measurements.

Fig. 1. Photoacoustic spectrum of the $^{14}\text{CH}_4$ sample (about 100 ppm $^{12}\text{CH}_4$ and 1 ppm $^{14}\text{CH}_4$, with residual water content). The inset shows some identified $^{14}\text{CH}_4$ lines (*) which are absent in the HITRAN model of $^{12}\text{CH}_4$ and water. The observed line positions are in agreement with our theoretical calculation of the isotope shift.

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