Advances in laser-based isotope ratio measurements

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The accurate measurement of isotope abundance ratios is an extremely important tool in a wide variety of research fields, including bio-medicine, climatology, and atmospheric physics [1]. In particular, rare isotopologues (that means isotopically substituted molecules) are ideal tracers to study complex environmental processes, such as the global hydrological and carbon cycles. In recent years, laser spectroscopy has been definitively recognized as a valid alternative to isotope ratio mass spectrometry for determining stable isotope ratios. There are already several examples of laser-based instruments that have left the laboratory stage and have been used by isotope researchers for significant advances in their own field of research.

Isotope ratio measurements are usually relative determinations: isotope amount ratios are compared against the value of a reference material, selected by international consensus as the standard for the isotope ratio of interest. This is the way to realize the zero point of what is commonly called the δ value.

The major problem of such differential measurements is the long-term comparability. In fact, reference materials are never stable over long time scales and sooner or later they must be replaced. For instance, the Pee Dee Belemnite (PDB) was agreed to be used as the reference material for the realization of the $\delta^{13}C$ scale. However, since PDB was no longer available, a new common reference was introduced, namely, the Vienna Pee Dee Belemnite (VPDB), which does not exist and will never exist. In order to realize the VPDB-scale, a consensus value of $\delta^{13}C_{VPDB}$ = 1.95‰ was assigned to the limestone material NBS19. Therefore, the current comparability of carbon isotope ratio measurements in CO_2 samples depends on the quality and availability of NBS19. Similar issues involve other elements in other molecules, like sulfur in SO_2 or oxygen in H_2O.

To overcome these difficulties, the development of a highly accurate methodology for the measurements of the ratio of amount-of-substance could be the only valuable solution [2]. Here, I will make an overview of the state-of-the-art spectroscopic techniques for measuring amount-of-substance with the highest metrological qualities [3, 4]. In particular, I will focus on those methodologies employing the most exciting coherent tools of the last two decades, namely quantum cascade lasers and optical frequency comb synthesizers.

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