



Laser ablation molecular isotopic spectrometry of carbon isotopes



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ABSTRACT

Quantitative determination of carbon isotopes using Laser Ablation Molecular Isotopic Spectrometry (LAMIS) is described. Optical emission of diatomic molecules CN and C₂ is used in these measurements. Two quantification approaches are presented: empirical calibration of spectra using a set of reference standards and numerical fitting of a simulated spectrum to the experimental one. Formation mechanisms of C₂ and CN in laser ablation plasma are briefly reviewed to provide insights for implementation of LAMIS measurements. A simulated spectrum of the ¹²C₂ Swan system was synthesized using four constituents within 473.5–476.5 nm. Simulation included three branches of ¹²C₂ (1-0), branches R(0-0) and R(1-1), and branch P(9-8) of ¹²C₂. Spectral positions of the tail lines in R(0-0) and R(1-1) were experimentally measured, since they were not accurately known before. The Swan band (1-0) of the isotopologue ¹³C¹²C was also simulated. Fitting to the experimental spectrum yielded the ratio ¹³C/¹²C = 1.08% in a good agreement with measurements by isotope ratio mass spectrometry. LAMIS promises to be useful in coal, oil and shale exploration, carbon sequestration monitoring, and agronomy studies.

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1. Introduction

Since the beginning of the Industrial Revolution the carbon dioxide (CO₂) levels in the atmosphere have been on the rise and causing noticeable climate change. This increase is mostly due to burning of fossil fuels (i.e., coal, oil, and natural gas), which emit CO₂ into the air. High concentrations of CO₂ can pose an environmental hazard and can be dangerous to human health. In addition, an introduction of massive amounts of CO₂ into the seas can cause acidification, alter water chemistry, and affect the life cycles of many marine organisms, particularly those at the lower end of the food chain [1].

Geologic sequestration of CO₂ has the potential to achieve a significant reduction in the anthropogenic CO₂ emissions. The process relies on capturing the CO₂ from industrial/electrical power generation gas streams, compressing it, and pumping it into storage formations as a supercritical fluid for permanent storage [2,3]. If a leakage pathway develops the CO₂ will potentially escape the containment formation causing elevated levels of the gas in the atmosphere. To ascertain if the increased levels of CO₂ are due to leakage from the storage sites the measurement of CO₂ concentration alone may not be sufficient [4].

Carbon isotope ratios allow an investigator to potentially determine the origin of CO₂ and can distinguish between different sources of feedstock for power plants [5,6]. The CO₂ captured from power plants and

injected underground has unique isotope ratios as compared to other sources and could be identical to the coal used in a particular power plant. Since coal obtained from different sources is likely to have different carbon isotope ratios, by knowing the isotopic fingerprints of each coal reservoir scientists can determine if the increased CO₂ levels in the atmosphere are from the carbon storage sites. Establishing the isotope ratios for the coal used in power plants would allow for the leakage to be easily identified. Therefore, a need arises to quickly and accurately measure the carbon isotope ratios for coal reservoirs, which will not only aid in identifying the leakage source but will also be likely of interest to sequestration site operators and regulators.

Laser Ablation Molecular Isotopic Spectrometry (LAMIS) is a new optical technique for direct isotopic analysis of solid samples in ambient air [7,8]. LAMIS utilizes spectra of diatomic molecules formed in laser ablation plumes in air. Carbon isotope detection in LAMIS has been achieved using C₂ and CN emission [7–10]. This technique is similar to laser induced breakdown spectroscopy (LIBS), although LAMIS measures molecular spectra appearing usually at longer delays after an ablation pulse than what is used in LIBS analysis. Molecular emissions yield isotopic information that is relatively easy to acquire. A spectrometer with modest spectral resolution can be suitable for measuring molecular isotopic spectra. Hence, LIBS and LAMIS techniques can be accomplished on the same instrument. Elemental and isotopic measurements can be performed with minimal sample preparation and benefits of rapid chemical mapping and depth profiling at high spatial definition, in real time at atmospheric pressure. Industrial, laboratory, and field operations are possible, potentially at a standoff distance to the sample [11].

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The ability of combined LIBS and LAMIS for simultaneous elemental and isotopic analysis makes them a useful tool for carbon sequestration monitoring. Real-time monitoring of carbon isotope ratios can lead to a more thorough study and effective way to monitor success of carbon sequestration. LAMIS measurement avoids use of expensive mass spectrometers that require deep vacuum and time consuming sample preparation. In the past, optical emission analyses using the spectra of isotopologue molecules C_2 , CN, CO and N_2 were performed in biochemical and agrochemical studies with stable isotope labels [12,13]. Recently, spectra of C_2 were used to infer rotational temperature as a correction factor for improvement of LIBS precision in coal analysis [14]. Emission intensities of CN and C_2 were also used to correct for matrix effects in LIBS analysis of coal [15].

This paper describes a LAMIS method for determination of carbon isotopes in coal and graphite samples using CN and C_2 spectra. LAMIS will be expedient in investigating whether the increased levels of atmospheric CO_2 originated from the coal mines or coal combustion plants. Establishing the carbon isotope ratios of parent coal mines could develop an isotope library for different coal reservoirs and will aid in identifying the potential environmental problems associated with the subsurface carbon sequestration. Variation of the natural isotopic ratio $^{13}C/^{12}C$ in different materials ranges from 0.96‰ to 1.15‰. These variations can be measured using LAMIS. In general, the paper is aimed at practical applications and analysis of geological samples, while significant part of this work is devoted to accurate characterization of the background in $^{12}C_2$ molecular spectrum, which is critical for measurements of the minor isotope ^{13}C .

1.1. Formation of C_2 and CN species in laser ablation plasma

Different kinetic behavior was observed in laser ablation spectra of native molecular fragments vaporized from organic samples and diatomic molecules formed by association of atomized matter with constituents of ambient air [16,17]. Multiple plasma chemical reactions occurring in ablation plumes with different rates often result in non-stoichiometric distribution of species in laser ablation plasma. Hence, understanding of molecular formation mechanisms and proper selection of experimental conditions are very important for analytical implementation of LAMIS.

In a previous work [9], we concluded that atomization in a plasma plume from solid benzoic acid samples was only partial, revealing preferential ruptures of specific carbon bonds even at relatively high laser irradiance of about $5 \cdot 10^{10} \text{ W/cm}^2$ at 1064 nm. Fragmentation of benzene rings into $^{12}C_2$ dimers observed at delays 1–8 μs after laser pulse was more effective than formation of molecules $^{13}C^{12}C$ involving ^{13}C atom from a carboxylic-acid group $^{13}COOH$. As a consequence, determined isotopic ratios $^{13}C/^{12}C$ deviated significantly from the stoichiometric ratio in the sample. The latter effect was observed relatively close to the sample surface (<2 mm) and therefore, these results can be attributed to preferential evaporation of the native $^{12}C_2$ molecular fragments from a molten spot formed on the surface after laser ablation pulse. At longer distances from the sample (2–5 mm) and delays greater than 4 μs , the observed isotopic ratio $^{13}C/^{12}C$ was close to the real ratio in the sample [10].

Serrano et al. [18] systematically studied an influence of the original molecular structure on the optical emission in laser ablation plasmas of organic solids. They found that electronic distribution within the original organic molecule in the sample has a strong impact on the degree of atomization versus fragmentation during laser ablation. Strengths of various carbon bonds, aromatic structures, functional groups and isomers in the original sample have distinct effects on formation of plasma-phase species. Particularly, this complex interplay of processes influences the resulting optical emission from C_2 and CN radicals in ablation plumes.

Laser pulse duration, irradiance and wavelength also have apparent effects on plume dynamics. Longer laser wavelength (e.g., 1064 nm)

facilitates ejection of polyatomic clusters in a photothermal regime of ablation, while use of laser wavelength at 266 nm or less can result in direct photochemical breaking of bonds [19], particularly because photon at 266 nm has energy 4.66 eV that is larger than C–C bond of 3.59 eV. Therefore, in photothermal ablation the gas-phase C_2 dimers evaporated as native fragments can dominate over those formed by molecular association of atomized carbon. Contrary, a photochemical regime of ablation can result in the opposite relationship with a portion of C_2 formed by association of atomized carbon being larger than that of the vaporized native C_2 fragments.

At near-threshold ablation (laser irradiance 10^8 – 10^9 W/cm^2) of graphite in vacuum, the vapor in the plume dominated by C_2 and C_3 fragments which were directly ejected from ablated graphite as the intact native molecules [20]. Once released from melted graphite surface into the gas phase, they could dissociate only through collisions occurring infrequently in vacuum. At laser irradiance $4 \cdot 10^8 \text{ W/cm}^2$ in helium (1.3 kPa), no atomic carbon emission from graphite ablation was detected but C_2 emission was clearly observed [21]. This is because evaporation of carbon in the molecular versus atomic form is thermodynamically favored. If helium pressure increased up to 80 kPa, collisions in the plume cause sublimation of ejected soot particles that becomes another channel for the formation of C_2 and C_3 [22].

With the increasing ablation laser irradiance ($>7 \cdot 10^9 \text{ W/cm}^2$), molecular emission usually does not considerably change while atomic carbon emission increases dramatically indicating that the prevailing fraction of the plume becomes atomized into free carbon atoms and atomic ions [16]. During ablation in ambient atmospheric air, carbon atomization is also aided by bouncing supersonic shock waves produced after a laser pulse [23]. The laser ablation plume expansion causes a snowplow effect that compresses and moves the background gas in front of the plume, if pressure of the ambient gas is above 1 kPa [24]. In the latter case, most part of the plume is filled with ablated matter from the sample, but ambient gas can anyway entrain through vortexes near the sample surface [25].

Spectra of CN are readily observed during laser ablation of carbon-based samples in air, even if no nitrogen is present in the sample. Multiple reactions of ablated carbon with atmospheric nitrogen occur in plasma plumes. Several competing pathways of CN formation exist including ionic, atomic and molecular reactions. When a snowplow effect dominates, CN can only form at the front of the propagating shockwave [24]. Reactions $C + N_2 \rightarrow CN + N$ and $C_2 + N_2 \rightarrow 2CN$ are both endothermic with activation energies of 1.9 eV and 1.8 eV, respectively [26]. Required initial heating can be obtained from either a forceful shockwave or gas-phase absorption of the ablating laser beam energy. Revealing the latter effect, the direction of CN formation can be inclined toward the incident laser beam, while C_2 radicals propagate either uniformly in a hemisphere or preferentially perpendicular to the sample surface regardless of the angle of the incident laser beam [27]. Density of ejected carbon decreases in time and so does CN, usually with some delay after C_2 . The higher binding energy of CN molecule (7.8 eV) relative to that of C_2 (6.2 eV) increases the chances of CN survival in the plasma plume at longer delays and distances.

Using optical time-of-flight spectroscopy, Al-Shboul et al. observed fast and slow components of both C_2 and CN emission in a plume expanding from graphite into ambient nitrogen at 0.13 kPa [28]. The experiments attested that a fast component was due to initially accelerated C^+ ions, which underwent recombination with electrons and association into molecules forming “clouds” of excited C_2 and CN at distances about 6 mm from the sample surface via multi-body reactions at a plume front: $2C^+ + 2e^- \rightarrow C_2$ and $2C^+ + 2e^- + N_2 \rightarrow 2CN$. The slower component in C_2 emission (1–10 μs) was closer to the surface (within ~5 mm) and was attributed to association of relatively slow neutral carbon atoms accompanied by a longer tail resulting from collisional dissociation of polyatomic carbon clusters.

Plasma chemistry in the gas phase of an ablation plume is obviously complicated (125 species undergoing 1509 processes were included in

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