Article

Isotope Detection in Microwave-Assisted Laser-Induced Plasma

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Abstract: Isotope detection and identification is paramount in many fields of science and industry, such as in the fusion and fission energy sector, in medicine and material science, and in archeology. The isotopic information provides fundamental insight on the research questions related to these fields as well as insight on product quality and operational safety. However, isotope identification with the established mass-spectrometric methods is laborious and requires laboratory conditions. In this work, Microwave-Assisted Laser-Induced Breakdown Spectroscopy (MW-LIBS) is introduced for isotope detection and identification utilizing radical and molecular emission. The approach is demonstrated with stable B and Cl isotopes in solids and H isotopes in liquid using emission from BO and BO_2, CaCl, and OH molecules, respectively. MW-LIBS utilizes the extended emissive plasma lifetime and molecular emission signal integration times up to 900 µs to enable use of low ~4 mJ ablation energy without compromising signal intensity and, consequently, sensitivity. On the other hand, long plasma lifetime gives time for molecular formation. Increase in the signal intensity towards the late microwave-assisted plasma was prominent in BO_2 and OH emission intensities. As MW-LIBS is online-capable and requires minimal sample preparation, it is an interesting option for isotope detection in various applications.

Keywords: LIBS; microwave; isotope; plasma; emission

1. Introduction

Isotopes are widely used in many industries including electronics and semiconductors, medical and forensics science. Isotopic analysis is a challenging task due to the similarities of the analyte. For this reason, the analysis of isotopes is usually preformed in laboratory environment. Isotopes are usually detected based on the mass difference. However, detection of isotopes in plasma provides several advantages due to the presence atoms and molecules in excited forms when the changes in the emission behavior, i.e., the shift of the spontaneous emission either form atoms, radical or closed shell molecules, can be utilized.

Laser induced breakdown spectroscopy (LIBS) is a rising plasma emission-based analytical method that is widely utilized for elemental detection in science and industry [1]. LIBS is a robust, information rich, and online-capable method that requires no or minimal sample preparation. The method generally utilizes the atomic emission produced in a laser-induced plasma plume and its emitted radiation for the elemental identification and quantification. Laser-induced plasma is generated irradiating a sample material, gas, solid, or liquid, with a high-energy laser pulse. The focalized laser pulse absorbing to the sample create a localized area of high temperature vaporizing and ionizing the material leading to the ignition of the plasma plume [2]. The recombining electrons and atoms in the plasma emit radiation on the elemental characteristic wavelengths that is utilized in the elemental identification. In addition, the intensity of the radiation on the respective wavelengths can be further used in the quantification of the elemental composition in the sample material [3]. One obvious advantage of LIBS is the possibility of in situ detection under ambient pressure and temperature conditions. However, the high election density presences a challenge as they tend to

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broaden the emission lines due to stark broadening [2]. To overcome the atomic line broadening issue, isotopic detection based on vibronic transitions in radical shave been used [4]. However, due to the short plasma lifetime in LIBS, the formation of these radicals is usually confined. In addition to the ionic and atomic emission from the plasma, utilization of the radical and molecular emission from the cooling plasma plume has become more popular approach [5-7]. This approach has been shown to be a fruitful tool for isotopic detection [1,2].

The initial laser-induced plasma plume has relatively high temperature and electron density. Therefore, the elemental lines are broadened and the small isotopic shifts in the electronic transitions cannot be resolved in ambient conditions. However, the isotopic shift in the vibronic molecular emission bands tend to be larger than in the purely electronic transitions in atomic species due to the vibrational and rotational contribution. For example, the isotopic shift between ^{11}B and ^{10}B in the $2s2p^2$ ^{2}D transition at 208.89 nm is 0.002 nm whereas the ^{11}BO and ^{10}BO $B^2\Sigma^+ - X^2\Sigma^+$ system's (0-2) band heads at 255.2 nm and at 255.9 nm, respectively, are separated by 0.73 nm [7]. The laser ablation and subsequent plasma formation that takes benefit on the molecular emission behavior has been conceptualized into an isotope detection method called Laser Ablation and Molecular Isotopic Spectrometry (LAMIS) [7,8]. LAMIS approach has been demonstrated for various elements, such as B [7], C [4,9], H/D [4,10], N, O, and Cl [4]. It is also utilized in combination with the isotopic shifts in atomic transitions for detection of U isotopes [11]. Isotope detection and identification is paramount in many fields of science and industry, such as in the fusion and fission energy sector, in medicine and material science, and in archeology. The isotopic information provides fundamental insight on the research questions related to these fields as well as insight on product quality and operational safety. LAMIS is challenging the methods basing on mass spectrometry, e.g., IRMS [12], TIMS [13], SIMS [14], and ICP-MS [15], that are well known for their high resolving power and sensitivity, with reduced need of labor-intensive sample preparation and online isotope detection capability.

LAMIS detects the molecule emission from a cooling plasma using long gate delay of ~10 μs instead of the typical delay of ~1 μs used for atomic emission. To obtain sufficient populations of the excited molecules at the late time of plasma plume, LAMIS applications have used laser powers in the range of 50 mJ to 150 mJ [4,8]. The sensitivity has been improved with a spark discharge (SD) [16] or double pulse (DP) [17,18] that act as an external energy source to the plasma causing reheating and, consequently, re-excitation of the species in the cooling plasma plume. The detection window for LAMIS and SD/DP enhanced molecular emission is still limited being in the range of few tens of microseconds.

Microwave-Assisted Laser-Induced Breakdown Spectroscopy (MW-LIBS) is one of the recent rising techniques to improve LIBS method's analytical performance. It utilizes the microwave radiation as an external energy source to maintain the laser-induced plasma electron temperature and density and, thus, extend the emissive lifetime of the plasma plume up to millisecond range [19]. MW-LIBS can be applied to solid [20-22], liquid [23] and gaseous [24] samples. Up to 100-fold improvements in sensitivity [25] and over 1000-fold improvement in the characteristic elemental plasma emission intensity [26] have been reported with MW-LIBS approach when compared to conventional LIBS arrangement. When microwave-radiation interacts with the laser-induced plasma plume, the plasma front moves rapidly toward the plasma source and the plasma volume increases substantially compared to the initial laser-induced plasma plume. Ikeda et al. have identified three distinct phases in the spatial plasma plume behavior in MW-LIBS: i) laser ablation and initial plasma formation, ii) plasma expansion and microwave sustained breakdown, iii) sustained nonthermal plasma and plasma dissipation [27]. After the first two dynamic phases, the microwave-maintained plasma stabilizes to about 6000 K and the electron density levels to order of 1×10^{16} cm^{-3} that sustains the microwave absorption into the plasma plume. The long relatively cool microwave-maintained plasma period provides environment for molecule formation and, furthermore, enables extended temporal observation window for molecular species [28,29].

This work represents the application of MW-LIBS for isotopic detection and analysis. MW-LIBS can benefit the isotopic analysis in two ways. First, MW-LIBS extend the laser-induced plasma lifetime, enabling for formation of radicals and molecules. Second, the electron density in MW-LIBS is substantially lower than in LIBS [30], which prevent line broadening producing well resolved

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spectra. The molecular emission from the microwave-maintained plasma plume of the MW-LIBS arrangement is used to detect and identify isotopes. As the use of microwave-injection substantially prolongs the plasma lifetime, it enables longer detection window for the molecular emission and, in addition, gives time for the atomic species react into the molecules at excited states. The approach has been demonstrated with detection of ^{11}B and ^{10}B isotopes by emission from BO and BO_2 molecules, ^{35}Cl and ^{37}Cl isotopes by emission from CaCl molecule, and H and D isotopes by emission from OH and OD molecules. To the best of authors' knowledge, this is the first report on the detection and identification of isotopes in MW-LIBS plasma.

2. Experimental Arrangement

A schematic the experimental MW-LIBS arrangement is shown in Figure 1. A pulsed laser Quantel (Brilliant B) emitting at 532 nm with pulse length of 6 ns and repetition rate of 10 Hz was used to ablate the sample and ignite the plasma plume. The laser pulses were focused on the sample surface using a lens with 100 mm focal length. The plasma emission was collected into a fiber bundle Thorlabs (BFY400HS02) that was connected into a spectrometer (Andor Shamrock500i) equipped with an ICCD camera (Andor, iStar). The resolving power of the spectrometer at 332 nm is 10,000 and 16,000 for 2400 and 3600 grooves-per-mm gratings, respectively. The fiber tip was mounted close to the plasma plume enabling direct light collection into the fiber. The microwave pulses were formed with a solid-state microwave source (Sairem) and delivered to the NFA using a coaxial cable (50 U NN cable) with 0.14 dB @ 2.45 GHz. The NFA was manufactured from a semi-rigid silver-plated copper coaxial cable (RG402/U) [31]. The NFA was attached to a precision stage that allowed positioning of the NFA tip 0.5 mm away from the laser propagation path and approximately 1 mm above the sample surface.

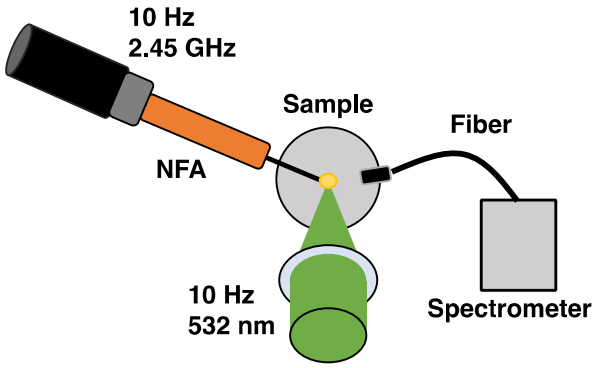

Figure 1. Schematic presentation of the measurement arrangement.

The boron isotope analysis was performed on isotope enriched boric acid samples $H_3{}^{10}BO_3$ (^{10}B 95 at. %), $H_3{}^{11}BO_3$ (^{11}B 99 at. %) and on BN powder with natural ^{10}B/ ^{11}B fraction (^{10}B 19.9 at. % and ^{11}B 80.1 at. %) (Sigma-Aldrich Co., Ltd). For chlorine isotope analysis, the sample was a powder of $CaCl_2$ (Sigma-Aldrich Co., Ltd). Each sample powder was mixed with organic binder and pressed into a pellet. The pellets were placed on a hot surface, at T below ~350K, to form a smooth solid surface. The diameter and the thickness of the pellets are 21mm and 3mm respectively. Hydrogen isotope analysis was performed on liquid samples. The samples were distilled water (H_2O) and heavy water (D_2O) (D 99.9 atom %) (Sigma-Aldrich Co., Ltd). The water was circulated by a peristaltic pump (Ismatec, MWMSC1) which provided 0.26 mL/min [23].

3. Results

3.1 ^{11}B and ^{10}B isotope detection

Boron is an important element in nuclear industry due to its high neutron absorbing efficiency. Therefore, the stable isotopes of boron ^{11}B and ^{10}B are among the most frequently measured isotopes with LAMIS [8]. The BO emission systems $B^2\Sigma^+$-$X^2\Sigma^+$ and $A^2\Pi_I$ - $X^2\Sigma^+$ are well visible in the spectrum

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from a laser-induced plasma in ambient conditions increasing the interest towards this molecule [7]. To demonstrate the isotope separation abilities of the MW-LIBS approach and to enable comparison to previously reported results, the technique is applied for boron isotope analysis. Example spectra of ^{11}BO and ^{10}BO $B^2\Sigma^+$-$X^2\Sigma^+$ (0-2) emission bands are shown in Figure 2. The spectra were collected with 12 mJ of laser pulse energy and 540 W of microwave power in ambient air. The locations and band shapes were identified with using isotope enriched boric acid samples. The applicability of the MW-LIBS method to detection of natural boron isotope fraction was demonstrated using solid BN sample. The observed band head separation of 0.73 nm is similar to the previously reported separation in LAMIS experiments. However, the natural ^{10}B / ^{11}B fraction of about 20% is on the verge of the isotope separation level of MW-LIBS. The separation of the different isotope band heads is not as clear as in previous LAMIS experiments [7,8,17] due to the partial overlap of NO $A^2\Sigma^+$ - $X^2\Pi$ (0-3) and BO $B^2\Sigma^+$-$X^2\Sigma^+$ (1-3) emission bands [32] that are also maintained in the microwave-assisted plasma plume. However, the applications of detection of boron isotope fraction, especially in nuclear power applications, is concentrating on materials with higher ^{10}B / ^{11}B fraction than the natural fraction.

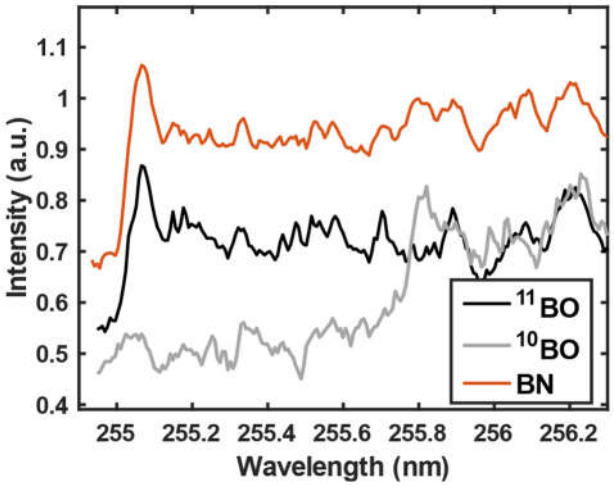

Figure 2. Example spectra of BO $B^2\Sigma^+$ - $X^2\Sigma^+$ (0-2) band head obtained from ^{11}BO and ^{10}BO molecules ablated from boric acid sample and a spectrum from natural ^{10}B/ ^{11}B fraction in solid BN sample. Spectra obtained with 10 μs gate delay, 900 μs gate width, and averaged over 100 shots.

The signal-to-noise ratio (SNR) of the BO emission line as a function of the laser pulse energy and the microwave power was studied. The dependencies are shown in Figure 3. It was found that the SNR improved with stepwise manner when the ablation energy was increased above 10 mJ. However, increasing the laser pulse energy further did not increase the SNR. The increase in microwave power improved the microwave-plasma coupling and slight improvement in SNR was observed when the microwave power was increased from 450 W to 600 W.

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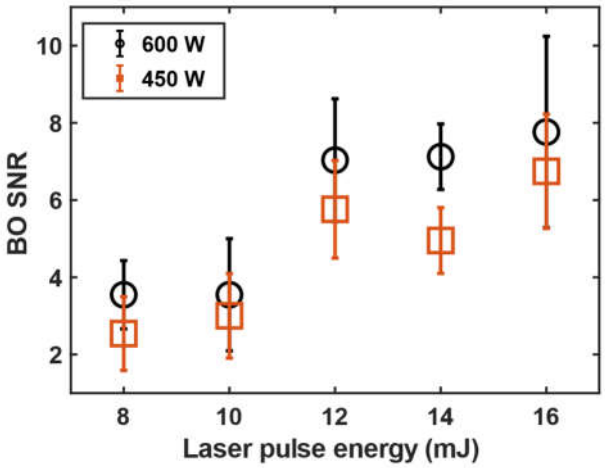

Figure 3. The BO emission dependency on laser energy and microwave power measured with 10 µs gate delay, 900 µs gate width, and averaged over 100 shots.

The BO_2 molecule has also been utilized for detection of the boron isotopes [33]. The isotopic shift in BO_2 $A^2\Pi_u$ - $X^2\Pi_g$ transition's (200-000) band at 493.1 nm has been observed to be 1.93 nm [33], thus, enabling the isotope detection. The spectra obtained of the emission band from isotope enriched boric acid samples are shown in Figure 4. The separation observed in this work between the $^{11}BO_2$ and $^{10}BO_2$ spectra at the $A^2\Pi_u$ - $X^2\Pi_g$ transition's (200-000) band is only 1.05 nm. The BO_2 spectrum was present at laser energies down to 3 mJ that was the consistent microwave coupling threshold in the current arrangement with 600 W of microwave power. However, the intensity approximately doubled as the ablating laser pulse energy was increased to 12 mJ, similar to the SNR increase in BO emission. The BO_2 spectrum in Figure 4 is obtained with 4 mJ of laser pulse energy to reduce the wearing of the sample and to demonstrate the possibility to utilize low ablation laser energies in MW-LIBS isotope detection. The BO_2 emission was not observed without microwave-assistance with the low ablation energy. The atomic boron seems to react efficiently in the microwave-assisted plasma plume with the oxygen molecules originating from air to form BO_2 being visible in the spectrum with substantially lower laser energies than the emission lines from BO providing substantially higher SNR. Thus, the BO_2 signal was not as sensitive to the small variations in ablation and microwave-plasma coupling as the BO signal.

To illustrate the benefit of using microwave to extend the plasma lifetime, the time resolved formation of BO_2 was chosen as an example. This was achieved by setting the microwave pulse to a 600 W with 1.6 ms temporal width and detect the BO_2 emission using a variable gate delay at a fixed gate-width of 10 µs. As shown in Figure 5, the BO_2 emission intensity increases in time up until 200 µs of the microwave-assisted plasma evolution. Despite the low ablation energy, integration over 900 µs of the emissive MW-LIBS plasma lifetime produced improved SNR for BO_2 emission band compared to previously reported signals obtained with conventional LAMIS [33]. Thus, use of microwave-assistance to the laser-induced plasma and consequentially the extended plasma lifetime brings substantial benefit in comparison to the conventional LIBS arrangement.

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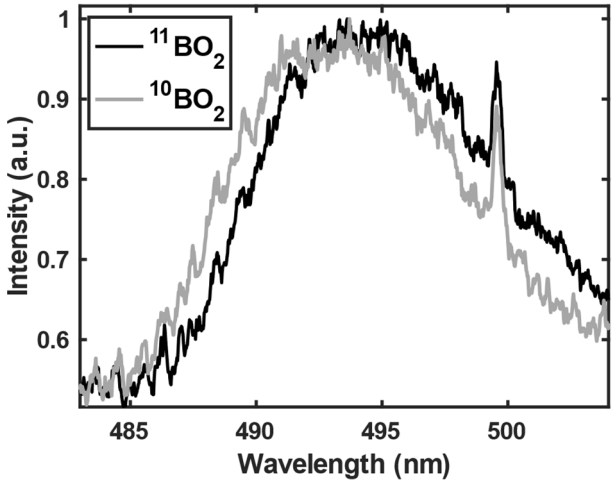

Figure 4. Example spectra obtained from $^{11}BO_2$ and $^{10}BO_2$ $A^2\Pi_u$ - $X^2\Pi_g$ transition's (200-000) molecules. Spectra obtained with 4 mJ, 600 W, 10 µs gate delay, 900 µs gate width, and averaged over 100 shots.

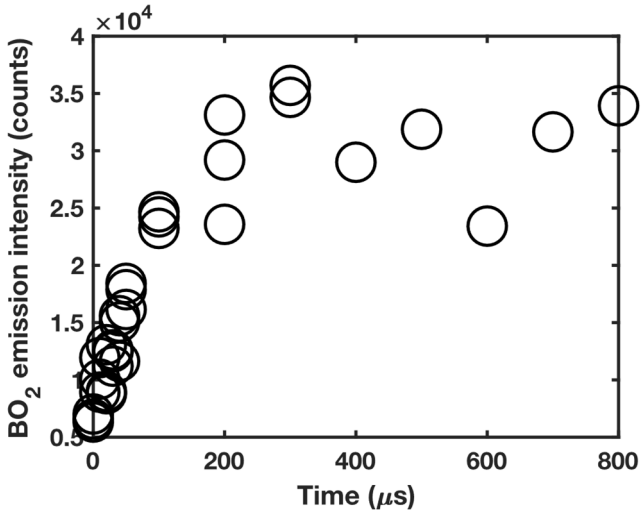

Figure 5. The temporal evolution of BO_2 emission intensity obtained with 10 µs gate width and averaged over 100 shots using 4 mJ of ablation energy and 600 W of microwave power.

3.2 35Cl and 37Cl isotope detection

Chlorine has two stable isotopes ^{35}Cl and ^{37}Cl with natural fractions of 75.76% and 24.24%, respectively [34]. Stable chlorine isotopic variations are observed and utilized as a geological tracing tool for origin and fate of fluids and rock from the Earth's interior parts. Analysis of chlorine stable isotopes have also been suggested to be used in tracing sources, transportation, and transformation of number of natural and anthropogenic organic compounds [35]. Chlorine is challenging element for conventional LIBS analysis that utilizes the atomic emission. Th ground state transitions of atomic chlorine are in deep-UV region and, thus, the excitation of transitions between upper levels requires high excitation energy. Therefore, utilization of molecular emission is an attractive option for chlorine detection [5].

The chlorine is often detected using emission from CaCl molecule. The MW-LIBS spectra of CaCl system $B^2\Sigma^+$-$X^2\Sigma^+$ (Δv = -1) from a $CaCl_2$ pellet with natural isotopic fraction is shown in Figure 6. The spectra are obtained by accumulating 100 shots using 4 mJ of laser pulse energy and 900 W of microwave power. The signal acquisition parameters were 1.2 µs of gate delay and 500 µs of gate width. As can be seen, the peaks in the CaCl emission system experience shift that enables the identification and quantification of the $^{35}Cl/^{37}Cl$ fraction. The spectra obtained with low ablation energy has very similar quality than that reported in previous studies [4]. Thus, the microwave-

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assisted approach enables chlorine isotope identification and quantification in solid samples using low laser pulse energy that enable construction of more compact and cost-efficient isotope detection.

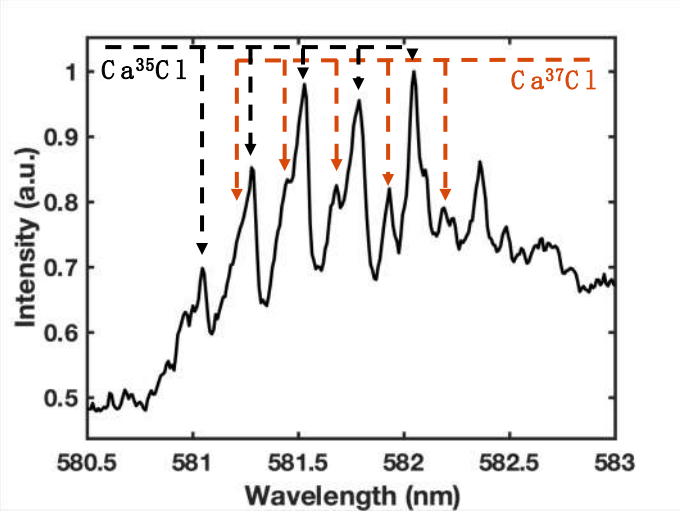

Figure 6. Example spectra obtained from CaCl $B^2\Sigma^+ - X^2\Sigma^+$ ($\Delta v = -1$) system ablated from $CaCl_2$ with natural $^{35}Cl/^{37}Cl$ fraction. The lines associated to $Ca^{35}Cl$ molecule are marked with black dashed arrows and the lines associated to $Ca^{37}Cl$ molecule marked with red dashed arrows.

3.3 ^1H and ^2D isotope detection

Hydrogen has two stable isotopes ^1H and ^2H of which the latter is known as deuterium (D). The natural abundance of deuterium is very small. However, deuterium is used in multiple applications in science and industry. Deuterium is preferable in medical applications due to its non-radioactivity, where it is used as a tracer for pharmaceutical and medical diagnostic applications [36,37]. In addition, deuterium is employed in nuclear plants as a moderator for nuclear reactors due to the heavy nucleus of deuterium [38].

In this work, the hydrogen isotopes are identified using $A^2\Sigma^+ - X^2\Pi$ (0,0) rotational bands R_{11} and R_{22} [39] as this region is interference free from other molecular emission lines. Figure 7 shows example MW-LIBS spectra obtained from H_2O and D_2O streams. The spectra are accumulated over 100 shots using 10mJ laser pulse energy and 900W of microwave power. The OH radical $A^2\Sigma^+ - X^2\Pi$ system's emission intensity was found to increase in time, similarly to the BO_2 emission in section 3.1. Hence, a long gate delay for signal acquisition of 200 µs was used with 600 µs gate width. As the measurement was performed in ambient air, the spectra obtained from D_2O sample has traces of OH signal due to the moisture in air. However, this does not impact on the isotope identification. The separation between the R_{11} and R_{22} branches' band heads are 0.12 nm and 0.24 nm, respectively. The isotopic shift is in agreement with previous studies and the signal intensity and SNR are of similar magnitude as presented on liquid and solid samples with LAMIS [10,40].

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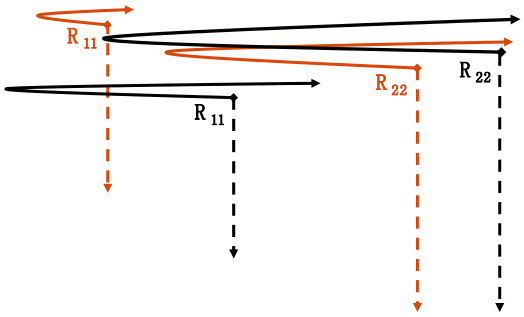

Figure 7. Example spectra obtained from OH and OD molecule ablated from liquid H_2O and D_2O streams, respectively.

4. Conclusions

MW-LIBS is demonstrated for stable isotope detection of B, Cl, and H using molecular emission from the microwave-assisted plasma plume. The B isotopes in solid samples were detected and identified in the plasma using emission from BO and BO_2 molecules. The ^{10}BO and ^{11}BO emission bands were found to be possible to be identified in a solid BN sample with a natural $^{10}B/^{11}B$ ratio. However, the boron isotope detection in ambient atmosphere is limited to samples with high boron content due to spectral interference with NO and other BO emission bands. On the other hand, the BO_2 emission intensity was found to increase substantially towards the end of the microwave-assisted plasma lifetime and has potential to provide sensitive boron detection. The OH/OD emission signal that was utilized for H/D isotope detection in liquid samples was found to increase towards the end of the plasma lifetime with similar trend to BO_2 emission. Hence, it was demonstrated that the use of MW-LIBS gives time for molecular formation in the plasma plume providing increased emission intensity and SNR for various molecular species. In addition, the extended emission lifetime and the consequentially extended signal integration time enabled use of low ablation energies for all samples without compromising the signal intensity or SNR. The low ablation energy is highly beneficial when avoiding sample damage. On the other hand, requirement for low ablation energy can substantially reduce the cost of the experimental arrangement. As demonstrated in this work, MW-LIBS is a promising approach for isotope detection in various applications looking for online-capable method with benefit of low sample damage.

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