

Time-resolved ultraviolet laser-induced breakdown spectroscopy for organic material analysis[☆]

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Abstract

Ultraviolet pulses (266 nm) delivered by a quadrupled Nd:YAG laser were used to analyze organic samples with laser-induced breakdown spectroscopy (LIBS). We present characteristics of the spectra obtained from organic samples with special attentions on the emissions of organic elements, O and N, and molecular bonds CN. The choice of these atomic or molecular species is justified on one hand, by the importance of these species to specify organic or biological materials; and on the other hand by the possible interferences with ambient air when laser ablation takes place in the atmosphere. Time-resolved LIBS was used to determine the time-evolution of line intensity emitted from these species. We demonstrate different kinetic behaviors corresponding to different origins of emitters: native atomic or molecular species directly vaporized from the sample or those generated through dissociation or recombination due to interaction between laser-induced plasma and air molecules. Our results show the ability of time-resolved UV-LIBS for detection and identification of native atomic or molecular species from an organic sample. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is attracting considerable attentions for highly demanding applications such as environmental monitoring and homeland security, due to intrinsic advantages of the technique, *i.e.* capabilities of multi-elemental, *in situ*, real-time or stand-off measurements [1]. Beyond traditional applications of LIBS where inorganic materials are mainly addressed for analytical purposes, recent progresses in broadband LIBS lead to analysis of organic and biological samples. Analysis of organic materials [2] allows

critical applications in homeland defence (landmines [3], explosive [4–6]), forensic (trace of explosive or organic materials), public health (toxic substances, [5] pharmaceutical products [7]), or environment (organic wastes [8]). Even more complicated than organic materials, biological materials such as bacteria, have also been analyzed by LIBS [9–15]. Recent developments of LIBS for organic and furthermore for biological material analysis potentially provide fast sensor systems for explosive trace and pathogen biological agent detection and analysis. From an experimental point of view, a large majority of LIBS applications utilizes a Nd:YAG laser in its fundamental infrared wavelength (1064 nm and several ns duration) for ablation. A few works involved a doubled (532 nm) or a quadrupled (266 nm) Nd:YAG laser [5], or a KrF laser [16] (248 nm) for organic sample analysis.

The challenge for organic or biological material analysis by LIBS is due to the fact that the media to be analyzed are composed of the same elemental substances. For instance four basic elements, C, O, N, and H are omnipresent and provide the

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common basis of the most organic materials. An efficient strategy for detection and discrimination between organic materials is based on determination of ratios between intensities of line emissions from these organic elements, O/C, N/C, or O/N for example. These ratios are related to the chemical composition of the organic compounds [2–7]. For biological materials, it has been demonstrated that a certain number of diatomic molecular fragments, such as C₂ or CN, can provide indications for their speciation [13].

However, detection and identification based on atomic oxygen and nitrogen or their diatomic compounds can suffer from interferences with emission from ambient air when measurements are carried out in the atmosphere. These emissions can be due to air in the vicinity of the impact of laser pulse on sample surface and excited by the plasma. Emission from atomic oxygen and nitrogen can exist due to air molecule dissociation even if the sample is completely free of oxygen and nitrogen. Chemical reactions also can occur between laser-induced plasma and ambient gas, and lead to diatomic compounds such as CN. Atomic as well as molecular species produced after ablation due to interaction between plasma and ambient gas can additionally contribute to the total intensities of specific plasma emission lines. We have previously demonstrated that femtosecond pulses (femto-LIBS) allow identification of native CN bonds directly ablated from a biological sample by observing kinetic behavior of CN band observed in a LIBS spectrum [13,14]. Relative low temperature (hence low continuum emission) of the generated plasma in the femtosecond regime as compared to that generated with infrared nanosecond pulses was crucial for an accurate measurement of the time-evolution of line intensities especially for short detection delays.

It is thus important to study the interaction between plasma plume and ambient gas in order to have a realistic estimation of emission from plasma-excited air. The emission from ambient air depends on plasma properties such as temperature and density. These properties in turn depend on laser parameters (pulse duration, wavelength, fluence) and on physical–chemical properties of the sample. From an experimental point of view, it is important to either minimize emissions of atomic or molecular species (O, N, or CN) due to the interaction between plasma and background gas or make these emissions controllable, in such way their contributions can be removed from the total line intensities of oxygen and nitrogen atoms or CN molecules detected in a LIBS spectrum of an organic material.

In this paper, we present characteristics of time-resolved UV-LIBS for organic material analysis. A sample of nylon is used as typical organic material. A sample of copper and a tablet of aspirin are used as samples with different physical–chemical properties for comparison. Our investigations are focused on emission from atomic oxygen and nitrogen which can originate from either native organic elements or atmospheric air. A kinetic study of line intensities allows us to distinguish contributions of native organic elements from those due to ambient air. For molecular species, kinetic behaviors of the emission from CN bonds are presented. We show that emission from native CN bonds can be distinguished from that due to recombination with ambient air in a time-resolved study of the molecular line emission intensity. We show

also for UV-LIBS, that the laser fluence is a suitable control parameter which allows specifying the regime with predominant native CN bonds or that with predominant recombination CN bonds.

2. Experimental setup

In our experiments, a 10 Hz Nd:YAG laser provided pulses in its fourth harmonics (266 nm, 4 ns). Pulse energy was adjustable from typically 0.5 mJ to 5 mJ. Laser pulses were focused by a quartz lens on the surface of the sample. A single quartz lens was used to collect plasma emission onto the entrance of a fiber which was connected to a spectrometer. LIBS spectra were detected using an ICCD camera. Samples were moved during analysis in order to have a fresh surface for each laser shot.

For atomic species (O, N) (Section 3) a Czerny–Turner spectrometer was used (SpectraPro-2150i, Acton Research Corporation). A sample of nylon and a tablet of aspirin (Aspirine UPSA with Vitamin C) were used as examples of organic materials, although the last one is a mixture of several compounds compressed from powder. A copper sample was used for comparison. Both nylon and copper samples had polished surfaces. Time-integrated spectra were acquired at a central wavelength of 805 nm. The detection gate delay was 150 ns for copper and 100 ns for nylon and aspirin after each laser shot with a width of 1 μ s. Integrated spectra were accumulated over 30 laser shots for copper and 100 shots for nylon and aspirin. Time-resolved spectral measurements were taken in the same spectral range as a function of the detection delay. For each delay, five spectra were taken, which allows calculating mean line intensities and associated standard deviations. Detection windows of 50 ns or 100 ns were respectively used for copper or organic samples in time-resolved spectral measurements.

For time-resolved study of CN band (Section 4) from nylon sample, an Echelle spectrometer was used (Andor Technology, Mechelle). Kinetic spectral series were performed for different laser energies with a detection window of 50 ns width. Each spectrum was accumulated over 100 laser shots. Three identical kinetic series were performed for each energy in order to have a statistics of the measurements. The kinetic behavior of the CN band was compared to that of atomic carbon. The spectral response of the ensemble of Echelle spectrometer and ICCD camera (Andor Technology iStar) was calibrated with a blackbody source in order to compare spectral intensities at different wavelength ranges.

3. Origin of the line emission from atomic oxygen and nitrogen

Fig. 1 shows time-integrated LIBS spectra of copper, nylon and aspirin. The used pulse energy is 5 mJ focalized by a 10 cm focal length lens, resulting in a focused spot of about 100 μ m on the sample, which corresponds to a fluence of about 65 J/cm² and an intensity of about 16 GW/cm². For copper in Fig. 1a, two strong atomic copper lines, Cu I 793.313 nm, and Cu I 809.263 nm lines are observed in the concerned spectral range. Several lines from atomic oxygen and nitrogen are also observed, O I 777/822/823/845 nm and N I 818/820/821/822/824 nm [17]. These lines

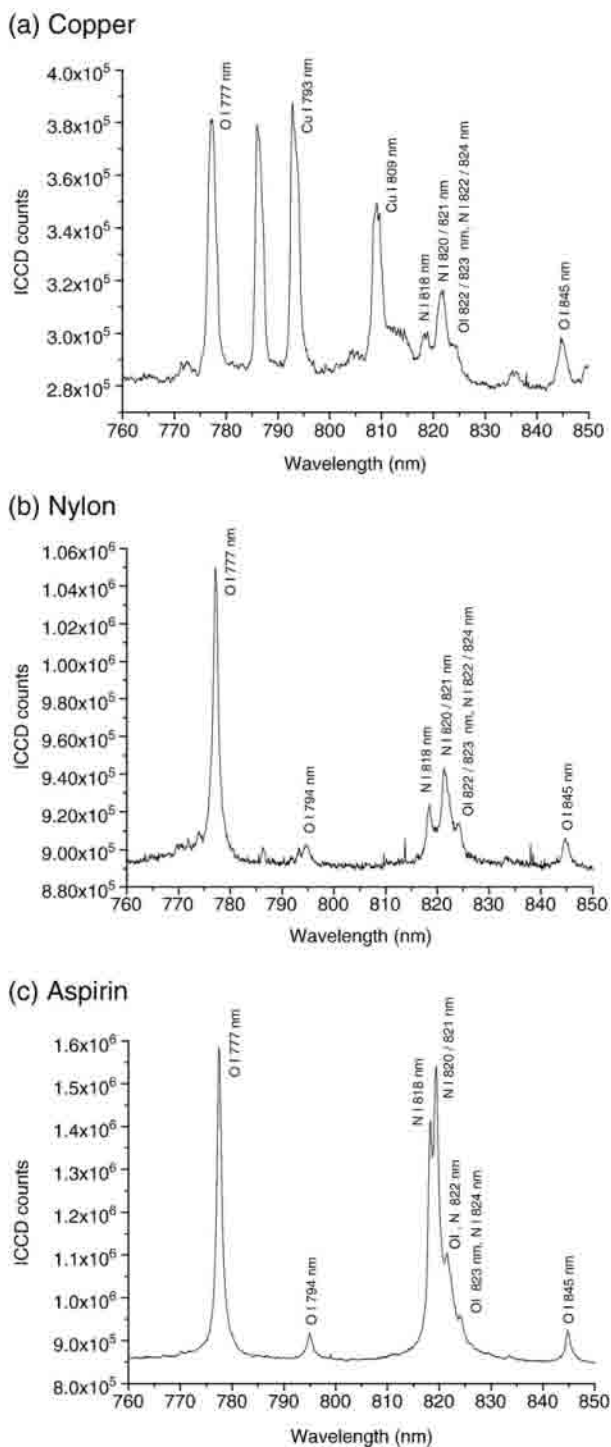


Fig. 1. Time-integrated spectra of (a) copper, (b) nylon and (c) aspirin samples ablated by 226 nm nanosecond pulses.

obviously originate from the gas in the interface between laser plasma and ambient air, since the copper sample does not contain any oxygen or nitrogen. Excitation of ambient air by plasma can lead to air molecule dissociation and subsequent emission from atomic oxygen and nitrogen. We also remark from Fig. 1a relatively weaker emission from atomic nitrogen. That fits the fact that the binding energy is higher for nitrogen molecule (9.8 eV) [18] than for oxygen molecule (5.2 eV) [19]. For nylon and aspirin, the

spectra show intense line emissions of atomic oxygen and nitrogen. The ratio between line intensities, O/N for example, may be correlated to chemical composition of the analyzed sample. The chemical formula of nylon is $C_{12}H_{22}N_2O_2$ (nylon 6–6). However the aspirin tablet contains a mixture of compounds that include active molecules and excipients. For such mixture, one can hardly extract useful information from atomic emission lines. Moreover,

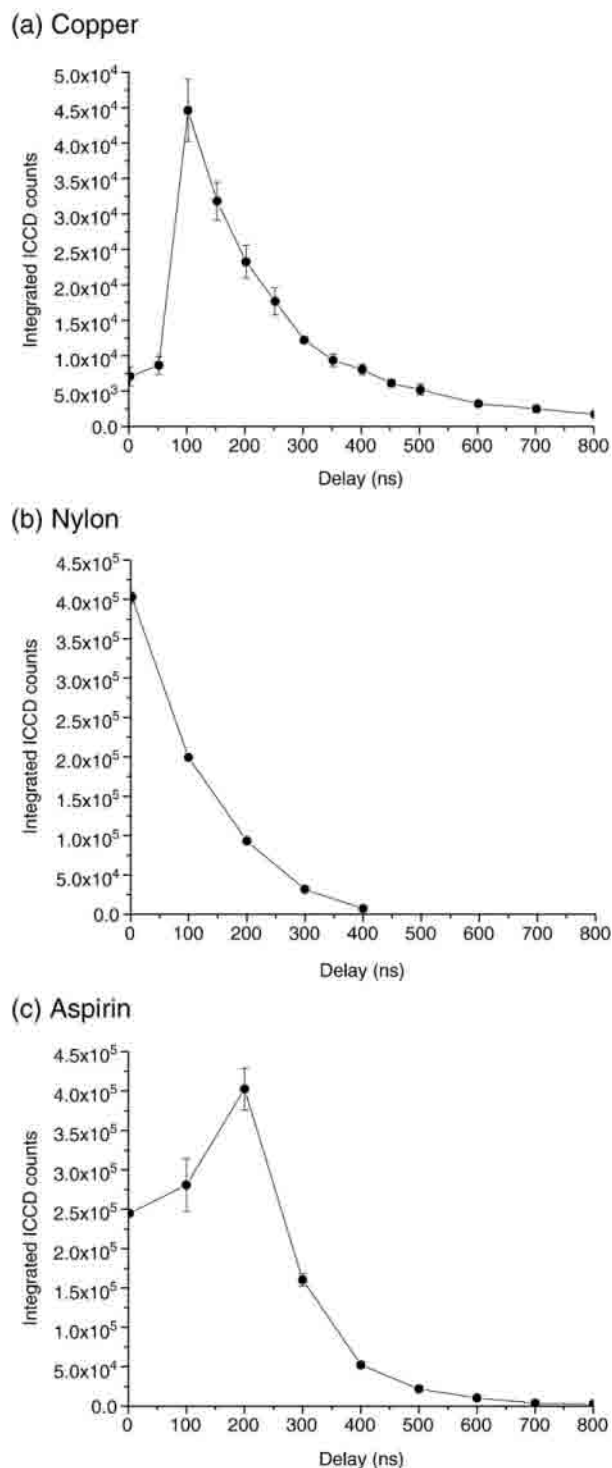


Fig. 2. Time-evolutions of the intensity of atomic oxygen line emission for copper (a), nylon (b) and aspirin (c) sample.

atomic oxygen and nitrogen emissions due to ambient air may contribute to the total emission intensities of these elements in a time-integrated LIBS spectrum. That makes even more difficult to use line ratios from integrated spectra as spectral markers of specific organic compounds.

Kinetic behavior of line emission from atomic oxygen is observed in order to provide information about origins of the

emitters. Fig. 2 shows time-evolutions of the O I 777 nm line for copper (Fig. 2a), nylon (Fig. 2b) and aspirin (Fig. 2c) samples. Experimental data in this figure represent areas under emission lines with background subtracted. For copper, oxygen line intensity increases from a very low level and reaches a maximum at 100 ns with an intensity nearly six times greater than the initial value. This behavior indicates air oxygen molecule dissociation

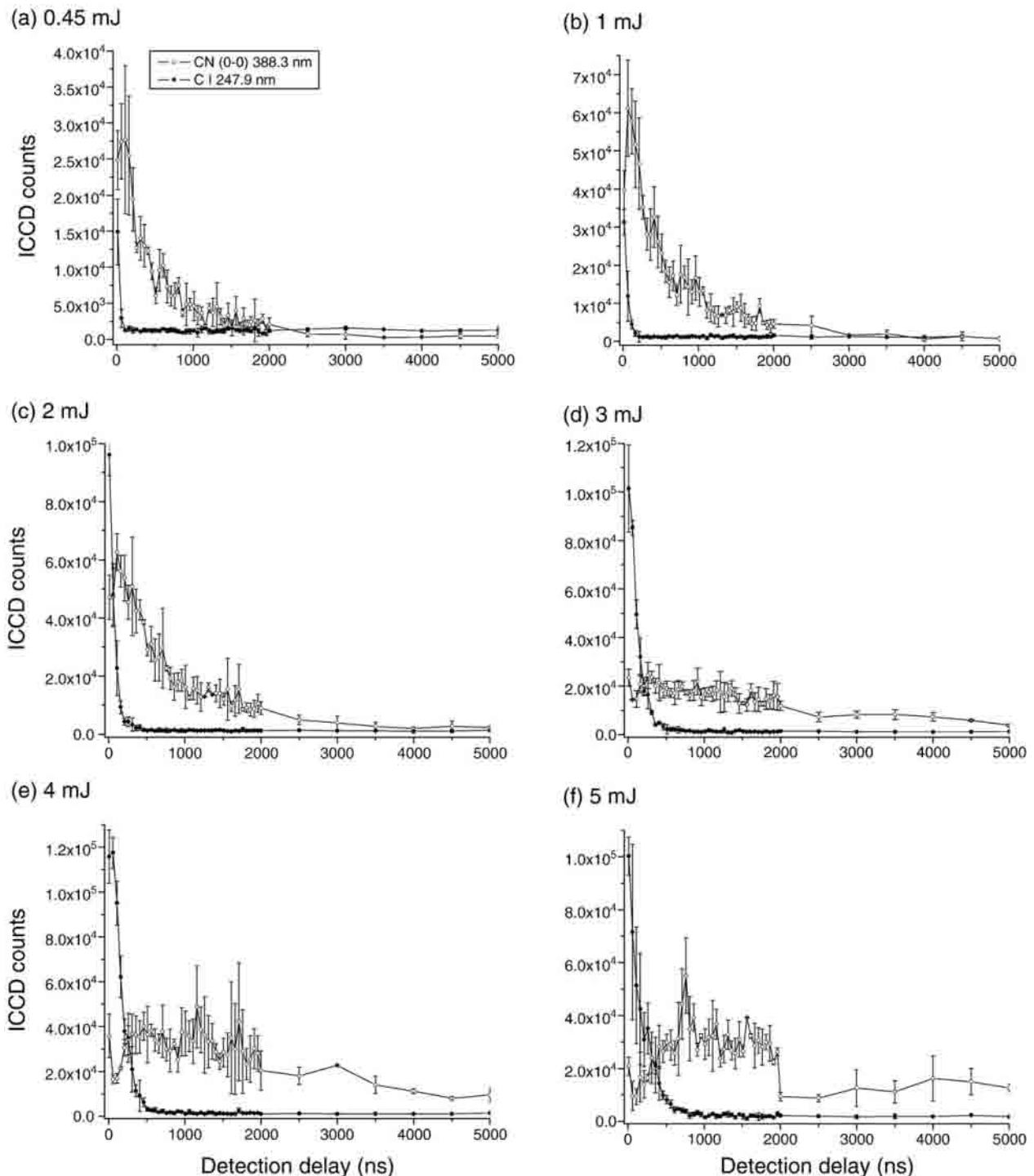


Fig. 3. Time-evolutions of the CN band and atomic carbons emission. The intensity of CN band head (0–0) at 388.3 nm and that of C I 247.9 nm line are presented as a function of detection delay and for different laser fluences of 0.45, 1, 2, 3, 4, and 5 mJ.

induced by the plasma. Quite different behavior is observed for atomic oxygen emission from the nylon sample. A strong emission is initially measured, and line intensity monotonically decreases with the detection delay. This immediate emission from atomic oxygen provides the evidence of emission from native oxygen atoms directly vaporized from the sample. In Fig. 2c, an initial emission intensity is observed. This initial emission intensity increases to reach a maximum at 200 ns before decrease of the signal. This initial increase of line intensity is however different from that observed for copper sample. Here an initial value is measured for the oxygen line which represents 61% of maximal value reached by the line intensity. It is therefore reasonable to consider that in the case of aspirin, we observe a combination of emission from native oxygen atoms and that due to dissociation of air oxygen molecules in vicinity of laser impact. From the comparison between these three different cases, we can conclude that time-resolved UV-LIBS provides distinction between atomic oxygen emission due to native elements vaporized from organic samples and that due to dissociation of air oxygen molecules. However the physical–chemical properties of the sample can sensitively influence the kinetic of atomic oxygen emission. An intermediary situation can occur in which total oxygen emission is contributed by native elements as well as air molecule dissociation. The matrix effect on the kinetic behavior of spectral emission from organic elements has to be taken into account in order to have a correct estimation of native element contribution in LIBS spectrum of organic materials.

4. Time-evolution of the line intensity emitted by CN molecular bonds and its correlation with atomic carbon line

As for all organic materials containing C and N as elemental compounds or CN radicals as intermolecular bonds, emission due to $B^2\Sigma-X^2\Sigma$ transition of the CN molecule around 388.3 nm has been easily detected in UV-LIBS spectra for nylon. However, as it has been pointed out, CN molecules can also be formed through recombination between C_2 available in plasma plume and N_2 in ambient air [13,14,20,21]. We have carried out time-resolved study for different laser fluences in order to determine the origin of the CN radicals observed in LIBS spectra. Time-resolved measurements on the emission intensity of atomic carbon at 247.9 nm are carried out in correlation with the CN band.

Fig. 3 shows time-evolution of the CN band around 388.3 nm for different laser pulse energy (focused by a quartz lens of 5 cm focal distance) ranged from 0.45 mJ (11.8 J/cm² or 2.8 GW/cm²) to 5 mJ (130 J/cm² or 32 GW/cm²). The intensity of the band head at 388.3 nm is presented in Fig. 3, as a function of detection delay for each laser pulse energy. The time-evolutions of the intensity of the CI line at 247.9 nm are presented in the same figures. At low fluences, immediate emission is observed from CN molecules. The band head intensity monotonically decreases. Such temporal behavior indicates contribution of native CN bonds vaporized from the sample. In a correlated way, emission from atomic carbon is rather weak, and quickly damped. As laser fluence increases, a delayed emission of CN bond appears and becomes dominant with respect to the initial

immediate emission which decreases with increasing laser fluence. For high fluences (4 and 5 mJ), the delayed emission becomes maximal 500 ns to 1000 ns after the laser pulse. These time scales fit quite well with the time constants corresponding to the reaction $C_2+N_2\leftrightarrow 2CN$ induced by the interaction between plasma and ambient gas [20,21]. Accordingly, the emission from atomic carbon becomes more intense and having a longer lifetime. This correlation confirms a lower production of native CN bonds and an important contribution due to recombination with atmospheric air in the total emission intensity of the CN band for high laser fluences. This contribution dominates CN band in an integrated LIBS spectrum when high laser fluence is used for ablation. The results presented in Fig. 3 show that for a correct detection of native CN bonds vaporized from the sample, low laser fluence has to be used. And time-resolved study provides a suitable way to distinguish the origins of observed CN molecular bonds.

5. Conclusion

We have demonstrated that time-resolved laser-induced breakdown spectroscopy using ultraviolet nanosecond pulses (UV-LIBS) exhibits several attractive features for analysis of organic samples. Kinetic studies of line emission intensities of atomic oxygen and nitrogen show a regime where emissions are contributed by native oxygen and nitrogen atoms (nylon), as well as a regime where a combination of contributions is observed from native atoms and from atoms provided by air molecule dissociation (aspirin). These different regimes are due to different matrix effects presented by these two types of organic sample. Identification of emissions from native oxygen and nitrogen atoms is important for discrimination and identification of organic materials using line intensity ratios of organic elements. In the case of combined contributions from native emitters and those due to air molecule dissociations, estimation of the contribution from ambient air has to be performed in order to extract intensities corresponding to the emission from native atoms. For the CN molecular band usually observed in LIBS spectra of organic or biological samples, we demonstrate that different kinetic behaviors can be observed which correspond to either native CN bonds vaporized from sample or CN bonds due to recombination with ambient air. A correlation between kinetic behavior of the CN band and that of atomic carbon line emission has been observed, which indicates dominant ablation mechanism for a given laser fluence. This correlation demonstrates the importance of the control of laser fluence for the detection of native CN bonds. UV-LIBS with low laser fluence allows detection of native CN bonds which provide a spectral marker of certain organic materials and an indication of biological materials.

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