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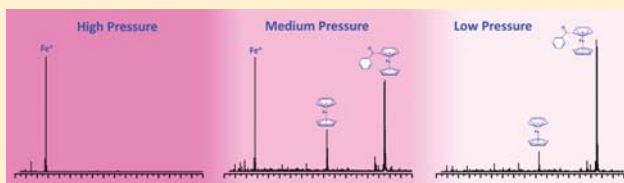
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# Simultaneous Acquisition of Elemental, Fragmental, and Molecular Information on Organometallic Compounds

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**ABSTRACT:** A novel method for obtaining elemental, fragmental, and molecular information of organometallic compounds has been developed using high irradiance laser induced time-of-flight mass spectrometry (LI-TOFMS) with a buffer-gas-assisted ion source. This technique permits direct and matrix-free analysis of solid analyte with minimal sample preparation. In addition, it shows special advantages in integrated acquisition of elemental, fragmental, and molecular information from a single target, on the basis of which identification of organometallic complexes is simplified and expedited.



Inspired by developments in homogeneous catalysis, functional organometallic complexes are currently of growing interest in chemistry. Identification of such compounds has typically been intractable, demanding more effort than that invested in synthetic work especially when the products are sensitive, insoluble, or hard to vaporize. Hence, an appropriate strategy for organometallic analysis has long been needed.<sup>1–5</sup>

Chemical identification can be performed by mass spectrometry (MS) from the acquired mass-to-charge ratios and isotope distributions of the analyzed molecules. The MS technique is applied to different types of compounds by the use of an appropriate ionization source. For example, electron impact (EI) ionization, chemical ionization (CI), matrix-assisted laser desorption/ionization (MALDI), and electrospray ionization (ESI) are widely used in current organic or biological molecule identification, while inductively coupled plasma (ICP) and glow discharge (GD) techniques are suitable for element determination.<sup>6–8</sup> For the analysis of organometallic species, EI, ESI, and MALDI sources are commonly used.<sup>9–12</sup> The analyte must be vaporized for EI, dissolved in a proper solution for ESI, or cocrystallized with a matrix for MALDI, which may induce decomposition of analyte and increase the chance of contamination. Indeed, by focusing a sufficiently bright laser beam onto a solid target, with laser irradiance of  $10^7$  W/cm<sup>2</sup>, some organic molecules can be directly desorbed and ionized without matrix assistance. This is known as laser desorption (LD) which has been used in organic analysis.<sup>13–15</sup> However, this technique can scarcely provide elemental information of the compounds; and, in many cases, special substrates have to be used to obtain intact molecular ions.<sup>5,16</sup>

A novel high irradiance laser ionization (LI) source, which is also known as a laser induced breakdown technique, has been developed and described elsewhere previously.<sup>16,17</sup> Reduction of the ion energy distribution is realized by the introduction of helium into the source chamber.<sup>16–18</sup> Thus, high laser irradiance

( $>10^9$  W/cm<sup>2</sup>) can be applied without losing spectral resolution. With previous developments, an instrument combining the LI source with an orthogonal time-of-flight mass spectrometer (TOFMS) has been used successfully in direct elemental analysis of solids.<sup>17,19–21</sup> Here we report the investigations on the LI-TOFMS analysis of some organometallic compounds, such as ferrocene derivatives and the metal acetylacetonate class. Unique results have been obtained that exhibit the great potential of this technique in organometallic identification. In comparison to other MS techniques, LI-TOFMS shows special advantages in integrated acquisition of elemental, fragmental, and molecular information from a single analyte. Furthermore, most of the samples are characterized in their original solid form without any adduct formation, which greatly simplifies the sample preparation procedure.

## EXPERIMENTAL SECTION

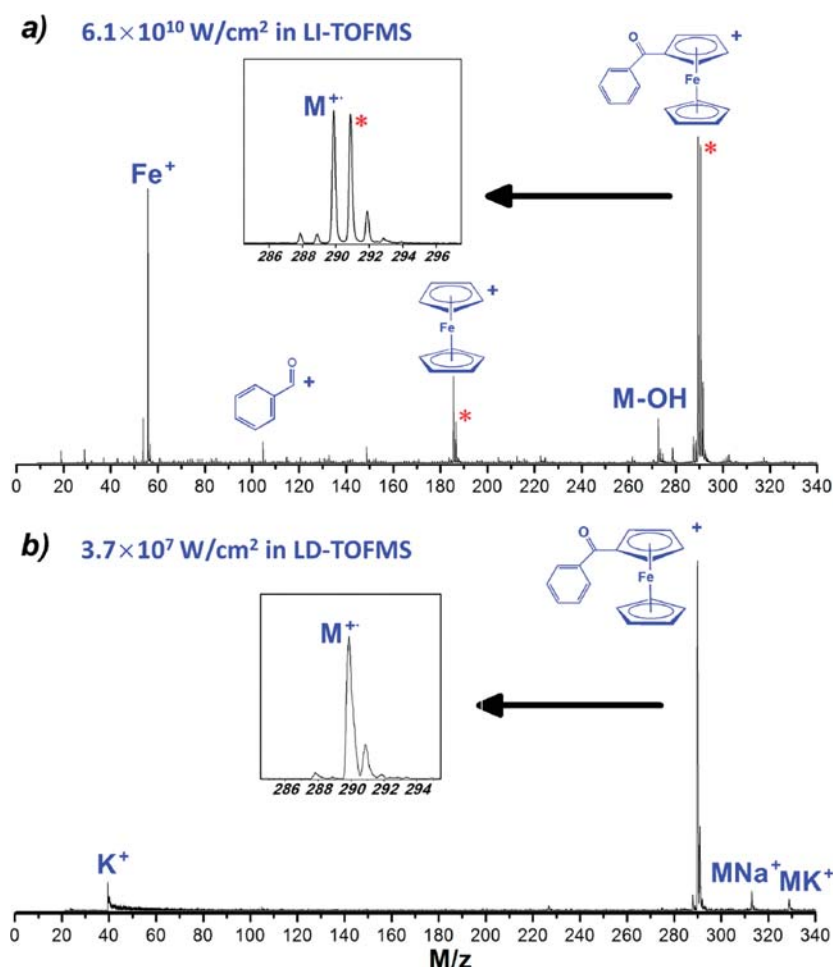
The instrument is as described previously with a few modifications.<sup>16</sup> Briefly, a Nd:YAG laser (NL303G, EKSPLA) with a 532 nm wavelength and a 4.4 ns pulse duration is employed, with pulse energies ranging from 0.04 to 9.6 mJ. The laser beam was focused to produce an ablation spot of 20  $\mu$ m in diameter. The pressure of the injected helium (99.999%) in the source chamber is controlled by a needle valve. In the TOF analyzer, the orthogonal accelerator operates in “pulse train” mode.<sup>17</sup>

Two pure organometallic compounds were purchased from BingQi ChemTech (Shanghai, China) and used in this study. The samples were in powder form and simply pressed into disks under ultrahigh pressure. The sample discs are fixed on a two-dimensional manipulator mounted at the tip of an in-house-built direct insertion probe (DIP). The motion of the manipulator is

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**Figure 1.** Typical mass spectra of benzoylferrocene from (a) high irradiance LI-TOFMS and (b) LD-TOFMS. \* denotes the protonated molecular ions.

set at a frequency of 1 Hz to provide a fresh surface after every 5 laser shots.

The laser desorption experiments were carried out on a MALDI-TOFMS system (Microflex, Bruker Daltonics). The sample was directly mounted onto a modified target plate and analyzed without the use of a matrix. The TOF analyzer was operated in reflectron mode, and each spectrum represents the accumulation of acquisitions from 200 laser shots.

## RESULTS AND DISCUSSION

Figure 1a represents a typical LI-TOFMS spectrum of benzoylferrocene acquired at helium pressure of 180 Pa and laser irradiance of  $6 \times 10^{10} \text{ W/cm}^2$ . The spectrum clearly exhibits dominant signals for both the molecular radical cation  $[M]^{+\bullet}$  and protonated molecular ion  $[M+H]^+$ , which directly provide the molecular weight of the analyte. Moreover, the appearance of fragmentation ions in the mass spectrum including the  $Fe^+$ , benzoyl ( $PhCO^+$ ) and ferrocene ( $FeCp_2^+$ ) ions, offers valuable information for structural identification. Isotopic distribution of the intact molecules and elemental ions can be clearly observed in the spectrum. For comparison, a LD-TOFMS analysis of the same sample has also been carried out. As shown in Figure 2b, the spectrum is dominated by the molecular radical ion  $[M]^{+\bullet}$ , Na and K ions, and their adducted molecular cation. Compared with the spectrum in Figure 1b at an irradiance of  $3.7 \times 10^7 \text{ W/cm}^2$ ,

increasing the laser irradiance in laser desorption does not generate elemental and fragmental ions from benzoylferrocene but yields a spectrum of poorer resolution due to the large kinetic energy spread of ions that cannot be resolved by the on-axis structure TOF instrument. In addition, no element and fragment ions can be acquired in LD-TOFMS analysis even at higher laser irradiance.

At the beginning of this work, much effort was made to evaluate the influence of laser irradiance, since laser power was previously considered to be a dominant factor in regulating the fragmentation of the molecules.<sup>14</sup> However, the change of laser power was proved to have little influence on the spectral pattern at high irradiance in the case of the buffer-gas-assisted source. Modulating the helium pressure in the source chamber was subsequently found to be more effective in transforming the dominant ion generation from intact molecular ions to free metal ions. Mass spectra of benzoylferrocene acquired at different helium pressures are shown (Figure 2), which reveal the effect of pressure on ion formation. At the low pressure (100 Pa in Figure 2), most intact molecules are structurally conserved and form the abundant molecular ion peaks in the spectra, while the intensity of the iron metal ions is relatively small. On the contrary, almost no fragment and molecular species can be found in the spectra when the pressure is high (800 Pa in Figure 2), only elemental ions can be observed unambiguously in the spectrum. Indeed, the result of this latter case accords with the previous study, which demonstrated the capability of LI-TOFMS in elemental analysis

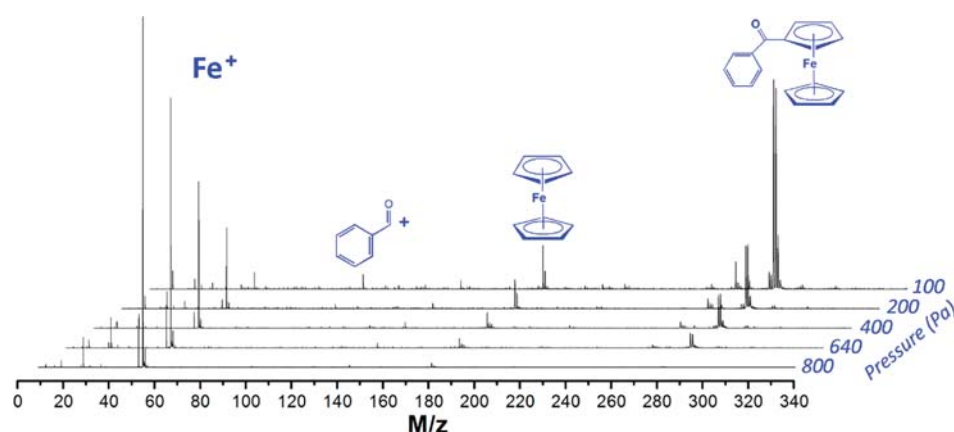


Figure 2. Effect of helium pressure on ion formation in LI-TOFMS analysis of benzoylferrocene.

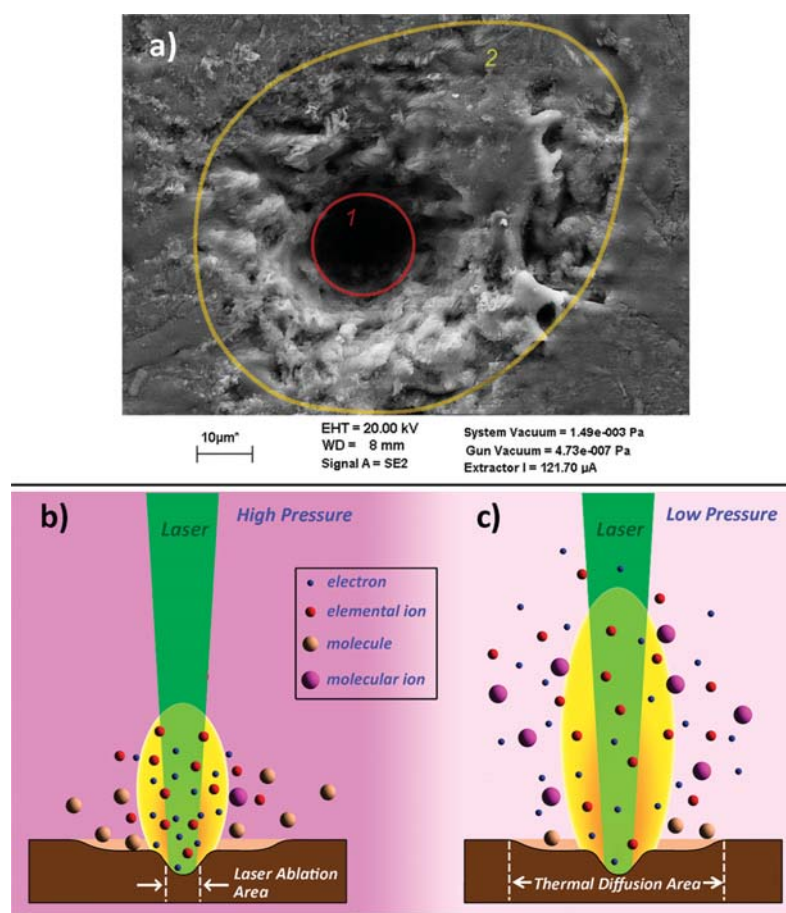
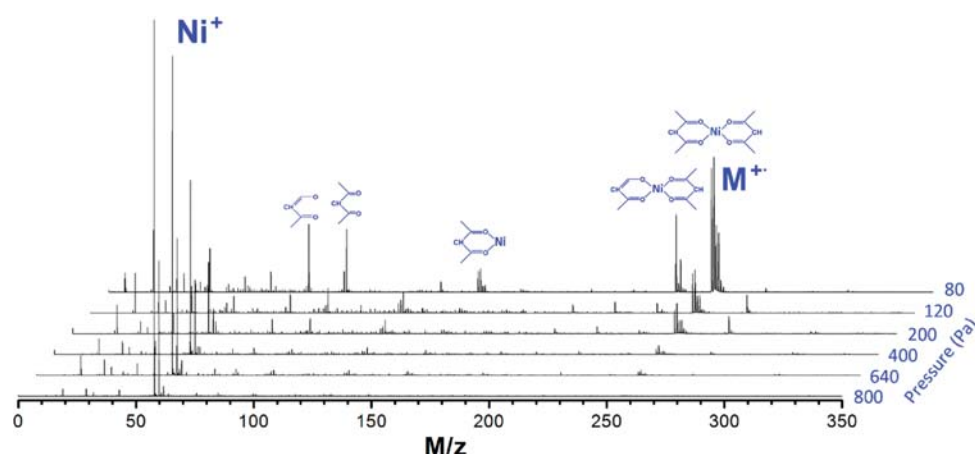


Figure 3. (a) SEM image of laser ablation of a benzoylferrocene sample after 5 consecutive shots. Area 1 (red circle) depicts the ablation surface directly under laser radiation, and area 2 (yellow circle) indicates the thermal diffusion area approximately. Schematic diagrams of laser ablation, ionization, and thermal diffusion desorption under (b) high pressure and (c) low pressure.

using a high helium pressure.<sup>21,22</sup> In this new approach, the molecular and elemental compositions of benzoylferrocene can be acquired separately with appropriate experimental settings, and identification of the analyte is then simplified and expedited from such integrated information.

Laser-solid interaction in a low-pressure inert atmosphere is a complex process, and its essential mechanism has not hitherto

been completely understood. Briefly, high laser radiation on solid surface results in a rapid vaporization of the materials in the irradiated area and directly produces a plasma plume. In the plasma, intense atomization and ionization processes take place. As seen in Figure 3a, a crater is formed in the laser illuminated area of the sample surface after material vaporization (the red circle shown in Figure 3a). When high laser irradiance is applied,



**Figure 4.** LI-TOFMS spectra of nickel acetylacetonate acquired under different helium pressures.

large amounts of energetic free electrons and protons are generated in the plasma whose temperature is as high as  $\sim 50\,000$  K.<sup>23</sup> No fragments and molecular ions can survive in such critical plasma condition. Thermal desorption of the analyte will immediately take place in the area surrounding the crater (roughly within the yellow circle shown in Figure 3a) because the thermal diffusion length is of several tens of micrometers with an irradiance of  $10^{10}$  W/cm<sup>2</sup>.<sup>24</sup> Large quantities of benzoylferrocene molecules are released into the gas environment. When the pressure is high (as shown in Figure 3b), plasma expansion is significantly suppressed by the numerous surrounding helium atoms. Although electrons and protons are generated in the plasma, their mean-free paths are now only several micrometers. They cannot ionize the gas-phase molecules from the thermal diffusion desorption in the surrounding area of the plasma. Even were some fragments or molecular ions to be generated, they would dissociate as a result of the high frequency of collisions with helium atoms. By contrast, under low pressure, electrons and protons will have longer mean-free paths. Collisions of the molecules with the freely expanded electrons and protons can initiate the ionization to produce molecular radical cations and protonated molecular ions (Figure 3c).

To evaluate the applicability of LI-TOFMS in organometallic characterization, a nickel complex was analyzed in the following experiment. As shown in Figure 4, clear elemental spectrum can be acquired at high pressure. Intensities of molecular ions increase with the decrease in pressure, accompanied with the appearance of fragments. The result further validates the influence of helium pressure in transforming the ion composition under high laser irradiance.

## CONCLUSION

High irradiance LI-TOFMS is traditionally realized as a powerful analytical tool for its capability in direct elemental analysis of solids. The present study indicates that LI-TOFMS is also useful for organometallic analysis. Compared with other techniques such as EI, CI, MALDI, and ESI-MS, LI-TOFMS permits direct and matrix-free analysis of compounds with minimal sample preparation. At high source pressure, an explicit spectrum of metal elements in organometallic samples can be provided; while, at low pressure, abundant molecular ions as well as fragments can be generated by a simple adjustment of the buffer gas pressure. In intermediate conditions, elemental,

fragmental and molecular information can be acquired simultaneously, which greatly facilitates the identification of the compounds.

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