Molecular Surface Analysis by Laser Ionization of Desorbed Molecules

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ABSTRACT:While elemental analysis of surfaces has progressed dramatically over the past ten years, quantitative molecular surface analysis remains difficult. This is particularly true in the analysis of complex materials such as polymers and rubbers which contain a wide compliment of additives and pigments to enhance their material characteristics. For mass spectrometric analysis the difficulty is two fold. First, desorption of surface molecules must be accomplished with minimal fragmentation and collateral surface damage. Second, the desorbed molecules must be ionized for subsequent mass analysis with high efficiency and without significant cracking. This paper focuses on the second of these problems.

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1. INTRODUCTION

The two techniques most likely to be used for molecular surface analysis, particularly for complex surfaces, Secondary Ion Mass Spectrometry (SIMS) (see for instance Gardella 1990) and Laser Induced Mass Spectrometry (LIMS) (see for instance Asamoto 1990, Johlman 1990, Li 1990, or Huang 1988), attempt to accomplish molecular desorption and ionization in a single step. Unfortunately molecular analysis often requires careful optimization of both the desorption and the laser ionization step. For instance, the amount of fragmentation of molecular species during the laser desorption depends on many factors including the energy absorbed by the surface, the wavelength of the laser, the pulse length of the laser (Lazare 1989, Feldmann 1987, and Srinivasan 1989). Several authors have shown that separating the ionization and desorption steps can allow characterization of complex surfaces(Grotemeyer 1989, Becker 1990, Lubman 1990). Here we detail studies of complex surfaces where the desorption step and the ionization step are separately optimized. While many problems remain in understanding the desorption of molecules from surfaces, this paper will focus on the ionization step.

The use of laser post ionization has been found to have significant advantages in the analysis of complex materials. First, laser ionization can be efficient, discriminative, and relatively "gentle." (see for instance Hunt 1991, Lubman 1990 or Nogar 1985) Second, the spectral content of the postionization spectrum can provide valuable information to mass spectrum which are always crowded and complex (Hunt 1991, Lubman 1990 or Lustig 1991). Finally the technique can be coupled with a variety of desorption techniques including sputtering, electron stimulated desorption and laser ablation. For molecules of intermediate mass, laser postionization can provide a unique method in the analysis of complex samples.

For high mass molecules laser multiphoton ionization appears to be more difficult. Recent studies suggest, however, that the cross-section for multiphoton laser ionization decreases with increasing mass (Campbell 1991, Schlag 1992, Wurz 1991a,b,1992) . When "large" molecules are photoionized, the ionization process does not necessarily proceed by direct, prompt electronic excitation, but rather involves extensive, rapid internal conversion. The physical process of ejecting an electron from these molecules containing enormous vibrational degrees of freedom is then similar to thermionic emission from solids. In this view rapid excitation by many photons leads to molecular heating. The molecule then "cools" through the ejection of electrons and/or molecular fragments. Thus multiphoton laser postionization of large molecules may not be possible for labile molecules.

2. EXPERIMENTAL

Results from two experimental apparatuses will be discussed in what follows. Because each apparatus has been discussed in detail elsewhere, they will only be briefly described here. The details of the coherent light generation can also be found in these publications.

The first apparatus is a time of flight (TOF) mass spectrometer (see figure 1) which utilizes laser desorption from a sample surface to introduce surface molecules into the gas phase. Following postionization, the photoions are accelerated to 8 KV in one or two steps and then traverse a field free region striking an ion detector. Details of the apparatus may be found in several publications (Hunt 1991, Lykke 1991,1992)

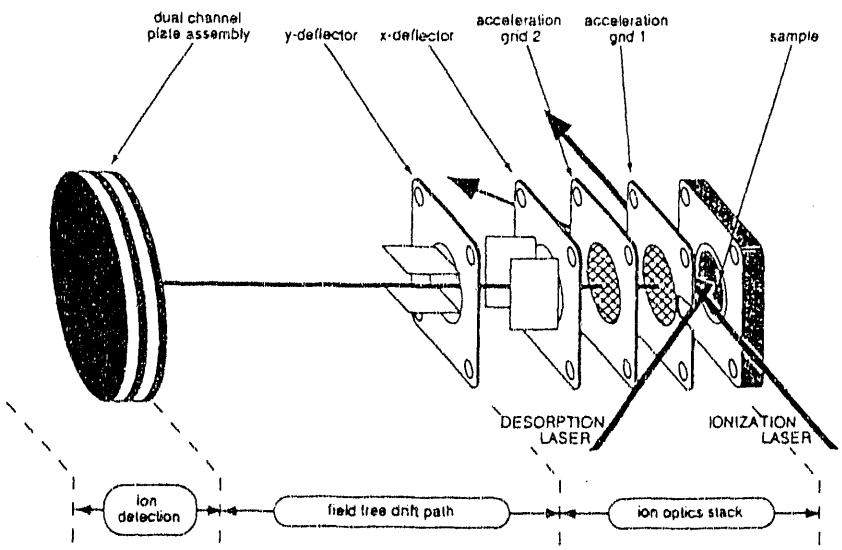

Figure 1. Schematic of the Laser Desorption Time of Flight apparatus. The system is in a ultra high vacuum apparatus which possesses a sample load lock and fused silica windows.

The second apparatus is a laser desorption fourier transform mass spectrometer (FTMS) consisting of a three region vacuum chamber with each chamber separated by differential pumping apertures. This system allows sample introduction through a vacuum interlock. The vacuum system is on a moveable cart allowing the sample and analyzer cell to be placed in the bore of a 7 T superconducting magnet. The FTMS experiments were performed with an Ionspec Omega data acquisition system. RF chirp excitation is used to accelerate photions into cyclotron orbits inside the cell. Detection of the image charge generated by this coherent

motion on the cell walls can be converted to a mass scale. The long transients achievable in this system allows measurements with extremely high mass resolution. A complete description of this apparatus may be found in Parker et al 1992. A diagram of the appartus may be found in figure 2.

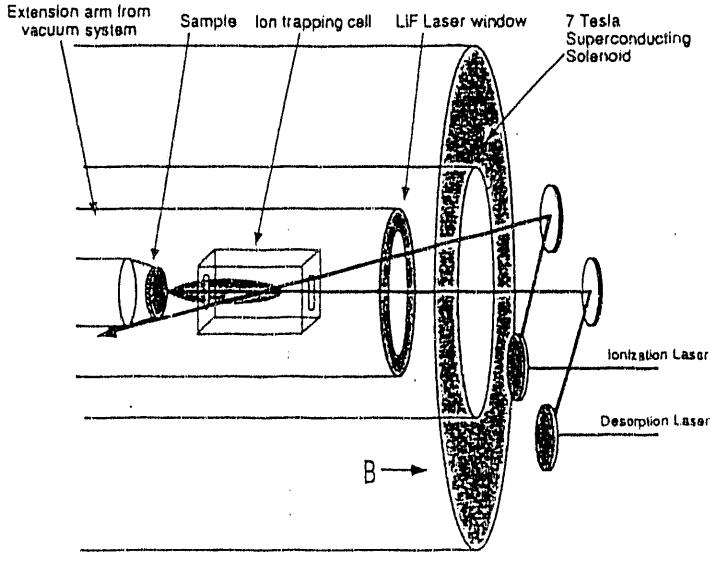

Figure 2. Schematic of the Laser Desorption FTMS apparatus showing the position of the analyzer cell in the 7 T superconducting magnet. The laser entrance port allows access both by a desorption laser and by a photoionization laser.

The principal advantage of FTMS is its ability to achieve extremely high mass resolutions (see for example Li 1990 and references therein). FTMS is a particularly attractive method when postionization is being considered because the mass resolution is not in first order affected by

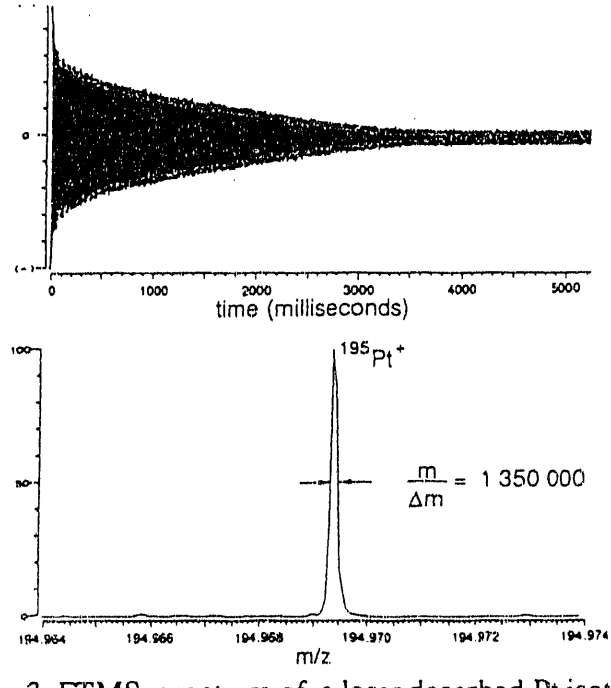

Figure 3. FTMS spectrum of a laser desorbed Pt isotope. The mass resolution displayed exceeds 1.3×10^6.

the formation position of the ions. Thus high mass resolution can be achieved even for large ionization volumes. Figure 3 displays the mass resolution achievable for a Pt isotope. The top panel of figure 3 shows the time dependent image charge signal. This coherent transient lasts nearly three seconds. Fourier transform of this signal yields the mass spectrum shown.

3. RESULTS

Commercially available rubbers are complex mixtures of polymer molecules and various additive molecules. These additive molecules impart certain desirable characteristics of the polymer (Latimer 1989,1988,1986). Detection of polymer additives has been difficult due to the complexity of the mass spectrum. Figures 4 and 5 display laser desorption followed by subsequent laser postionization TOF mass spectra for a vulcanizate rubber sample. While a more complete description of this work can be found elsewhere (Hunt 1991, Lykke 1992) the two mass spectra are illustrative of both the difficulties and the promise of this type of analysis.

Figure 4 shows a mass spectrum utilizing 308 nm desorption and 118 nm ionization. Since 118 nm light is sufficient to ionize in a one photon process all of the molecules in the desorbing flux, this spectrum is representative of the molecules present in the desorbing flux. This flux is dominated by low molecular weight fragments of the rubber polymer and demonstrates some of the difficulties in the desorption step.

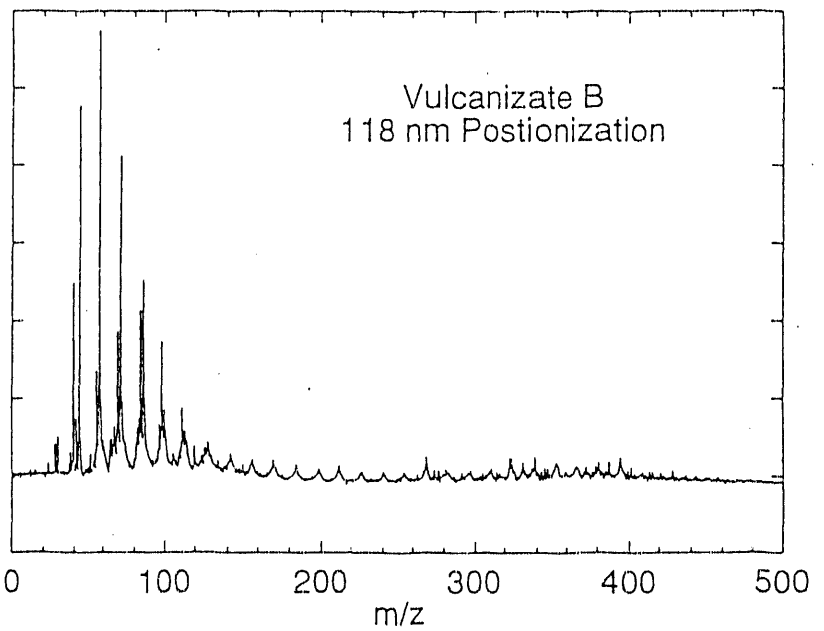

Figure 4. Postionization of a vulcanizate rubber using 118 nm (10.5 eV) radiation. The low mass region represents fragments of the rubber polymer backbone. These molecules appear to dominate the desorbing flux.

Figure 5 shows a wide variety of different ionization experiments following 308 nm desorption. Four different laser wavelengths have been used for postionization - 355 nm, 308 nm, 266 nm, and 212 nm. Even with such a crude spectral analysis it is possible to use

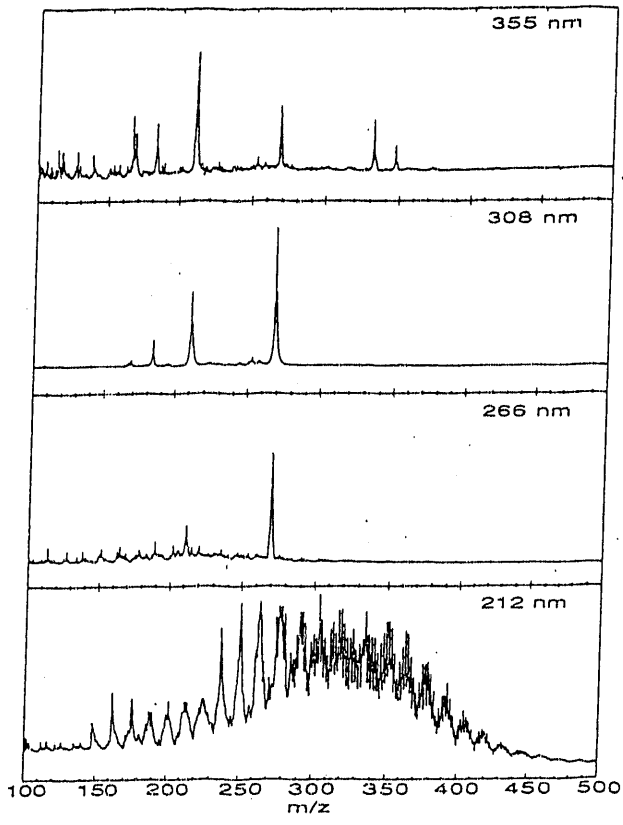

Figure 5. Postionization of a vulcanizate rubber using 118 nm (10.5 eV) radiation. The low mass region represents fragments of the rubber polymer backbone.

this laser wavelength information to gain insight into the molecular content of the rubber surface(Lubman 1990, Lustig 1991). Differnet laser wavelengths access different polymer additives. Radiation at 355 nm selectively ionizes additives that contain aromatic groups, while 212 nm light tends to ionize all but the small ablation fragments of the polymer.

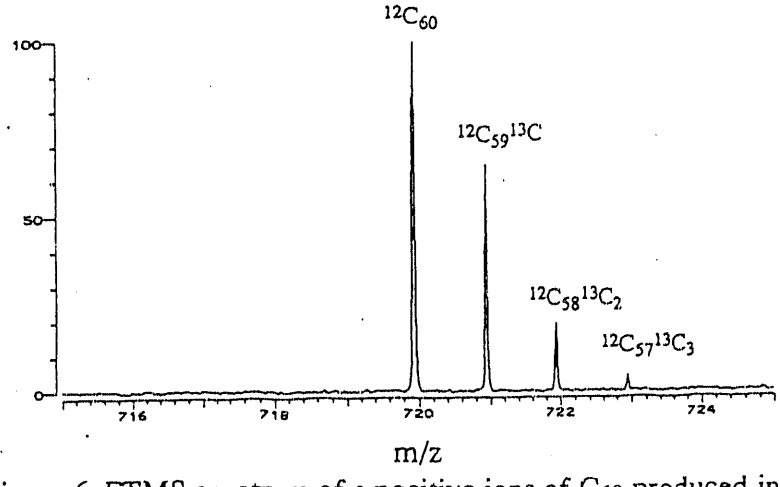

Figure 6. FTMS spectrum of a positive ions of C_{60} produced in the laser desorption process. Clearly evident is the isotopic content of the molecule.

For larger molecules intersystem crossing and subsequent fragmentation make laser multiphoton ionization difficult. In these cases, two schemes are viable. First as in figure 4 one photon ionization can be an effective tool. A second alternative is to use the ions produced in the desorption process itself. An example of the direct ionization of a large molecule is displayed in figure 6. The positive ion of C_{60} is cleanly displayed. Note the isotopic content of the molecule is in accordance with the natural abundance of C.

4. CONCLUSIONS

Laser ionization of desorbed molecules is a sensitive discriminative means for the analysis of molecules on surfaces. Significant work on the understanding of both the desorption and the ionization process of molecules remains, however, before this can be considered a viable method for quantitative surface analysis.

5. REFERENCES

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