Tunable infrared laser desorption and ionization of fullerene films

T.C. Cheng, S.T. Akin, C.J. Dibble, S. Ard, M.A. Duncan[*]

Department of Chemistry, University of Georgia, Athens, GA 30602, USA

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ABSTRACT

Infrared laser excitation/desorption of thin film samples or powders containing fullerenes was observed to produce efficient ionization of both the fullerene and other molecules mixed into the sample. Both cations and anions were produced. The ions produced by this IR laser desorption ionization (IR-LDI) process were detected with a time-of-flight mass spectrometer. The mechanism of this IR-LDI process was investigated with mass spectra under different conditions, delayed pulse acceleration experiments, and IR wavelength dependence studies, employing either a fixed frequency CO_2 laser ($10.6\,\mu m$) or an IR optical parametric oscillator ($2000–4500\,cm^{-1}$; $5.0–2.2\,\mu m$). The mechanism of fullerene IR-LDI was found to involve both direct emission of electrons from alkali-fulleride impurities in the sample and multiple photon-induced thermionic (delayed) emission of electrons from hot fullerenes. In both cases, the electrons produced are accelerated by the source fields resulting in electron impact ionization of, or electron attachment to, neutral species in the outgoing plume of desorbed material. The IR-LDI process is enhanced on resonance with fullerene vibrations, suggesting the possibility of a new kind of laser-thin film spectroscopy.

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1. Introduction

Since its initial discovery by laser ablation cluster growth in a molecular beam [1], the ionization behavior and mass spectrometry of C_{60} have been topics of ongoing interest [2]. Laser desorption ionization (LDI) and mass spectrometry was also employed as one of the first detection methods once fullerenes were produced in macroscopic quantities [3]. Since these early measurements, mass spectrometry, often involving laser desorption ionization methods, has been employed universally to characterize fullerene materials [4–8]. The mechanism of fullerene ionization in these LDI experiments is an interesting topic that has stimulated much discussion [7,8]. Fullerenes have been co-deposited with other analytes to cause fullerene-assisted desorption/ionization [9–15]. The vast majority of these experiments have employed near-UV or visible laser excitation from pulsed nitrogen or Nd:YAG lasers. In the present study, we investigate these issues using *infrared* laser LDI measurements with a pulsed CO_2 laser and with a tunable infrared optical parametric oscillator (OPO) system.

Fixed frequency and tunable infrared lasers have been employed frequently for matrix assisted laser desorption/ionization (IR-MALDI) mass spectrometry measurements, and the mechanism of this process has been investigated extensively [16–26]. Particularly in the case of biomolecules, the lower photon energies in the infrared are believed to minimize fragmentation of desorbed ions [26]. The ionization yield in the infrared is generally much less than in the UV, although the desorption efficiency of neutrals is high. Therefore, IR desorption followed by UV ionization has been investigated [27,28], as have matrix-free methods [12,29]. In all of these cases, the desorption yield follows the infrared absorption spectrum of the matrix or analyte that is absorbing initially. IR absorption leads to energy deposition, and then in the direct IR-MALDI process, proton transfer processes are believed to lead to ionization. IR lasers in the $3\,\mu m$ region produce efficient excitation of O–H stretch vibrations such as those in glycerol or in water ice. Similar observations have been made for IR excitation of liquid water beams [30]. However, the ionization mechanism in matrix-free methods is still open to question. Infrared laser desorption has many attractive features, if suitable substrates can be found for efficient ionization.

Infrared laser excitation of gas phase C_{60} and other fullerenes is well known to give rise to efficient multiple photon absorption leading eventually to ionization in a process completely analogous to thermionic emission [31–37]. This process has been shown to be resonant with the IR-active vibrational transitions, giving rise to resonance enhanced multiple photon ionization (IR-REMPI) [33,34]. To our knowledge, this IR-REMPI process has not been investigated for condensed phase fullerene samples, although it would also be expected to occur in this environment. In this report, we have investigated the ionization of thin film C_{60} samples, and their mixtures, using infrared laser excitation at different wavelengths followed by mass analysis in a time-of-flight instrument.

Wavelength dependence and time-resolved experiments are employed to elucidate the mechanism of the unusual ionization processes detected.

2. Experimental

Films containing C_{60} are prepared by dissolving the powder in toluene and applying a drop of the solution to the insertion probe tip of a laser desorption time-of-flight (TOF) mass spectrometer [6]. The toluene solvent evaporates, leaving behind a film/residue of the fullerene. Sulfur samples or their mixtures with C_{60} are prepared by mixing the powders and packing them together into a 2 mm diameter hole in the same kind of insertion probe tip. Upon insertion into the mass spectrometer, the probe tip surface is flush with the rear acceleration plate of the TOF ion source. Mass spectra are collected in DC mode, in which continuous voltages are applied to the acceleration plates and the laser pulse initiates the time-of-flight measurement, or in a variable delayed-pulse mode in which the acceleration plates are pulsed with high voltage pulsing circuits (Behlke) after the desorption laser firing. Mass spectra are collected with a digital oscilloscope (LeCroy LT342) and transferred to a PC computer with a GPIB interface.

Visible and UV LDI experiments are accomplished with a small Nd:YAG laser (New Wave Research, Polaris II). Infrared laser excitation of samples is accomplished with either a pulsed CO_2 laser (GAM EX10/100 excimer laser modified for CO_2 operation) or a Nd:YAG laser (Spectra Physics Pro-230) pumped optical parametric oscillator (OPO) system (Laser Vision) [38]. The OPO system provides IR radiation with a linewidth of about $1.0\ cm^{-1}$ in the range of 2000–$4500\ cm^{-1}$. In both case the infrared intensity was adjusted to be about 1 mJ/pulse focused slightly to a 1 mm diameter spot size.

3. Results and discussion

Fig. 1 shows the mass spectra of cations and anions resulting from IR-only excitation of fullerene films with a CO_2 laser at 10.6 μm. In the upper trace, the cation spectrum produced from a mixed-fullerene sample is shown, whereas the bottom trace shows the anions produced at the same wavelength from a pure C_{60} film.
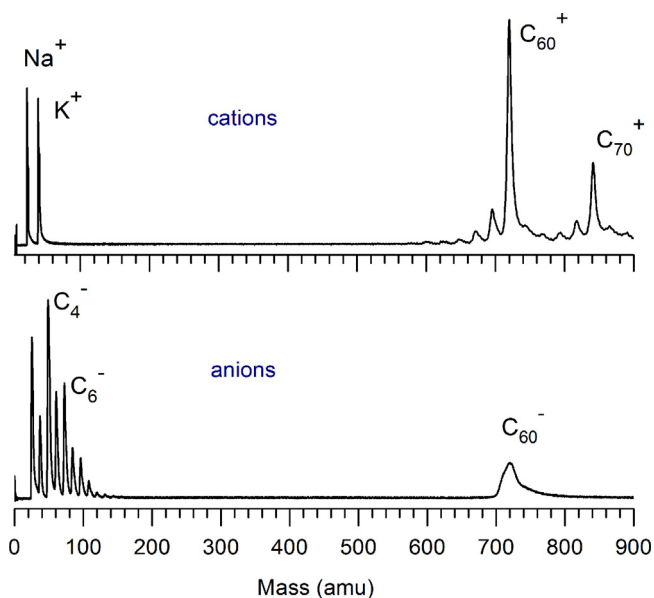

Fig. 1. The mass spectra of cations and anions produced by infrared LDI of mixed fullerene soot (cations) and pure C_{60} samples (anions).

As expected, when C_{70} is present in the sample, it is ionized with efficiency roughly equal to that of C_{60} for both anions and cations. Essentially the same mass spectra are obtained using the tunable OPO laser in the 3 μm region, albeit with lower efficiency. The efficiency of ion production at both wavelengths varies with the laser pulse energy such that no signal is detected below a threshold, then the signal increases with pulse energy, and at the highest values the mass resolution degrades considerably consistent with high kinetic energy release in the desorbed ions and eventual sample destruction.

The formation of ions with infrared excitation energies in the 1 mJ/pulse range is somewhat surprising. Cations could perhaps be formed by multiple photon absorption and thermionic emission of electrons, as this has been observed previously for isolated fullerenes in the gas phase at this wavelength [32]. The 10.6 μm wavelength ($943\ cm^{-1}$) of the CO_2 laser falls close to the energy of the IR-active vibration in isolated C_{60} at $1182\ cm^{-1}$ [4], and this band is power broadened and shifted to lower energy by multiple photon absorption [33,34]. The laser pulse energies used here are at least an order of magnitude lower than those used in the gas phase, but this may be compensated for by the greater density and optical thickness of the sample. The ionization potential of the isolated gas phase C_{60} molecule is 7.58 eV [4] and the work function of its crystalline solid is 4.7 eV [4]. Although we do not yet know the mechanism for the infrared ionization, it is clear that multiple infrared photons must be involved to produce ionization. The underlying surface in these experiments is the stainless steel probe tip. However, tests with plastic and/or teflon probe tip surfaces gave the same results, confirming that the ionization process is intrinsic to the fullerene film and not to the underlying surface.

One clue to the ionization process is the observation of sodium and potassium in the mass spectrum. These impurity ions are detected with abundances roughly equal to that of C_{60}. They come from the fullerene sample; no alkali ions are detected for laser impact on a bare probe tip. However, these ion abundances do not necessarily reflect quantitative concentrations in the sample, as the relative amounts of ions versus neutrals in the desorbed material may depend on many factors. The abundances detected do suggest that there is a significant amount of alkali metal in the samples. This can of course come from glassware contamination, from solvents used and from the initial processing and isolation of the fullerene material. If alkali metals are present in somewhat high abundance, there are likely to be significant amounts of fullerides, i.e., $M_n^+C_{60}^-$ [39], in these films. The desorption process of these species would require less energy to liberate ions or electrons.

The formation of anions indicates that the infrared laser either produces these directly, perhaps by the break-up and desorption of fullerides, or that it produces low energy electrons that can interact with gaseous species in the desorption plume to cause attachment. The small carbon clusters at low mass are likely formed by fragmentation of fullerenes in the LDI process, followed by electron attachment (because the sample here is pure C_{60}, no smaller carbon species should be present with significant abundance). As shown in Table 1, the electron affinities of small carbon clusters are generally greater than that of C_{60} [40], and so it makes sense that electron attachment would occur to produce anions of these species if there is a source of electrons. The broad width of the C_{60} anion mass peak is consistent with metastable behavior in the source, as if the ions are formed over a broad region in space. This is consistent with electron attachment throughout the evolution of the plume. By contrast, the ionization potentials of the small carbon clusters are all much greater than that of C_{60} (Table 1) [41,42]. If these neutral carbon clusters are produced in the desorption plume, they would be more difficult to ionize; if they are produced as cations, and if electrons are present, they would likely attach electrons to form neutrals. Indeed, no small carbon cations are seen, even though