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Strong-field ionization of C_{60} sputtered neutral molecules using 10^{15} W/cm^2 of fs IR radiation

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Implementation of a new high energy, IR laser source for secondary neutral mass spectrometry, is presented. It consists of an 800 nm, 40 fs, 10 mJ, 1 kHz laser pumping an optical parametric amplifier generating 1.2–2.6 μm tunable pulses. The wavelength and intensity dependence of photoionized sputtered indium clusters and gas-phase histamine are presented, exhibiting less nonadiabatic multielectron dynamics (decreased fragmentation) at longer wavelength. Future prospects for secondary neutral bioimaging experiments are explored with a model system consisting of a 400 mesh grid, vapor deposited with adenine, and fixed over indium foil. Copyright © 2012 John Wiley & Sons, Ltd.

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Introduction

Laser ionization of sputtered neutral molecules, which can outnumber the secondary ions by 10^4, has been an invaluable complement to the time-of-flight secondary ion mass spectrometry (ToF-SIMS) experiment for many decades.[1,2] By decoupling ionization from matrix effects and increasing sensitivity, it has provided a route to increased understanding in many experiments of both analytical and fundamental interest. Throughout the years, postionization has implemented a range of light sources, from tunable vacuum ultaviolet (VUV) synchrotron radiation to pulsed near-infrared lasers, interacting with the electrons in neutral particles primarily though the absorption of photons. Recently, however, advances in ultrafast lasers have made readily available pulse intensities exceeding 10^{15} W/cm^2, corresponding to electric field strengths that equal, or even exceed, the Coulomb fields within atoms and molecules. This development raises the prospect of implementing a fundamentally new ionization mechanism for sputtered molecules: strong-field ionization (SFI). Involving either tunneling or barrier suppression ionization, it holds the promise of decreased fragmentation and more general application than previous methods.

A basic explanation of SFI involves the ionization of the most weakly held electron by either tunneling through or escaping over a suppressed potential barrier formed by the superposition of the electric field of the laser and the Coulomb field of the atom or molecule. The experimental conditions conducive to this mechanism, and differentiating it from multiphoton ionization, were first described by Keldysh for atoms.[3] One of the elements of his theory is now popularly known as the Keldysh adiabaticity parameter (γ). It describes the ratio of the laser frequency to the tunneling frequency of an electron. Reformulated, it can also be cast as the ratio of the ionization potential of an atom to the intensity and wavelength of the interacting laser, predicting tunneling behavior when $\gamma < 1$. Theoretical approaches to SFI similar to Keldysh's method, including the work of Perelomov, Popov, and Terent'ev[4] and Ammosov, Delone, and Krainov (ADK theory)[5] have proven highly successful in predicting the ionization of atoms. However, attempts to modify and extend these theories to molecules are less accurate. The atomic theories are based on the adiabatic/quasi-static and single active electron approximations, which means that they ignore any electron dynamics inside the potential well and do not treat the possible interaction of multiple electrons with each other and the laser field. Both become increasingly likely as molecular size increases and can lead to a variety of electronic effects even at laser intensities where ionization is predicted to proceed by tunneling. These phenomena, known as nonadiabatic multielectron dynamics (NME),[6–8] have been shown to produce electronically excited molecules and sometimes severe fragmentation. Fortunately, experimental and theoretical work over the past decade has provided us with guidelines in selecting laser parameters that either minimize or completely avoid these effects in some molecules.

One of biggest factors shown to affect fragmentation is the wavelength of the laser field. In molecules of increasing size, the time scale of electron motion begins to approach the frequency of the laser. As this happens, the electron is not able to adjust adiabatically to the oscillating electric field and becomes excited. In many cases, this effect can be avoided by increasing the wavelength of the laser and thus maintaining the adiabatic behavior of the electron. For this purpose, the use of an optical parametric amplifier (OPA) to extend the accessible wavelength range in SFI becomes imperative.

Our previous work with SFI applied to C_{60}^+ sputtered SIMS yielded very promising results.[9,10] By employing an OPA pumped by our 1.5 mJ, 120 fs, 800 nm laser, we were able to generate light in the 1.2–2 μm wavelength range, at about 10^{13} W/cm^2. These longer wavelengths produced marked reductions in the degree of molecular fragmentation observed in the molecules we investigated. To further exploit the benefits of SFI

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and avoid some of the pitfalls of NME, we acquired a more powerful laser system and high-energy OPA. They allowed us to generate intensities in the 10^{13}–10^{15} W/cm^2 range at wavelengths between 1.2 and 2.6 μm. In the present work, we present some preliminary results investigating several model systems with this laser source-sputtered indium clusters, gas-phase histamine, and the imaging of a 400-mesh grid vapor deposited with adenine.

Experimental section

All experiments were performed using a TOF-MS similar to the one described in detail elsewhere.[11] The sputtering experiments involved a 20 kV C_{60}^+ ion gun (Ionoptika, Ltd.) producing about 50 pA beam current (measured in d.c. mode) in the indium analysis and about 100 pA for the imaging of the adenine grid. The primary ion pulse width was set to 150 ns.

The gas-phase analysis of histamine involved a thick film (≈1 μm) vapor deposited onto a silicon shard (Ted Pella, Inc.). Placed into the analysis chamber, it was allowed to sublime at room temperature, avoiding any thermal excitation induced by heating. Experiments were performed when a constant partial pressure of histamine was reached inside the analysis chamber, monitored by a residual gas analyzer trace of the M-$(NH_2CH_2)^+$ fragment. The vapor pressure of histamine was approximately 3 × 10^{-9} torr.

For the imaging experiments, adenine was vapor deposited onto a 400-mesh copper London finder grid (Ted Pella, Inc.). The grid was mounted directly over indium foil, and the analysis was performed at 100 K.

The laser source employed in these experiments is commercially available. Briefly, a 10 mJ, 800 nm, 40 fs, 1 kHz laser (Legend Elite Duo, Coherent, Inc.) was either directly employed in photoionization or used to pump a high-energy OPA (TOPAS-C-HE, Light Conversion, Ltd.). The OPA generated tunable light between 1.2 and 2.6 μm and was capable of producing a combined signal and idler output of 3.4 mJ at its peak, at 40 fs and 1 kHz. The pump laser's pulse length was confirmed by frequency-resolved optical gating (Grenouille 8-20-USB, Swamp Optics). The laser beam was focused into the vacuum chamber through a calcium fluoride window, using a BK7 lens $f = 125$ mm (Thorlabs). The focal spot diameters ranged from 50 to 200 μm, as determined by optical calculations and Xe gas intensity calibration of each wavelength. Laser intensity was attenuated by rotating a waveplate prior to the compressor grating in the 800 nm experiments and by adjusting the OPA's second delay stage for analysis in the IR. Both methods were not seen to affect any other beam properties besides intensity: the laser's pulse length was maintained, and the OPA's center wavelength and bandwidth remained the same. Xenon gas ionization was studied and compared with the predictions of ADK theory, to calibrate the laser intensity scale.

Indium (99.999%, CAS 7440-74-6), histamine (>97.0%, CAS 51-45-6), and adenine (>99% CAS 73-24-5) were all purchased from Sigma-Aldrich. The indium foil was extensively sputter cleaned prior to the start of experiments.

Results and discussion

We began by studying the ionization of 20 kV C_{60}^+ sputtered indium clusters. They are known to have relatively low ionization potentials of less than 6 eV, to be produced in a large distribution of sizes, and to contain a substantial amount of internal excitation from sputtering.[12]

In Fig. 1, the cluster-to-monomer ratio is plotted, starting at about 10^{13} W/cm^2, an intensity regime where the ionization of the indium monomer is fully saturated. A trend is observed where the relative yield of the dimer and trimer is higher for the 1200 nm light, whereas the yield of the tetramer, pentamer, and hexamer is increased with the 1900 nm beam. This is consistent with increased fragmentation of the higher mass clusters at 1200 nm, which contributes to the greater yield of the dimer and trimer. At 1900 nm, the ionization mechanism is observed to be much softer by comparison because the relative yield of the intact tetramer, pentamer, and hexamer is higher. The indium clusters also allowed checking for the onset of Coulomb explosion as we scanned the intensity from 10^{12} to 10^{15} W/cm^2; none was observed.

We next investigated the wavelength response of gas-phase histamine, revisiting a molecule we had previously studied, but this time with an extra two orders of magnitude of intensity. Experiments at each wavelength were performed on successive days; as such, the magnitudes of the raw signals should not be directly compared. However, clear differences are evident in the ionization of the histamine molecular ion at the three wavelengths employed. In the 800 nm intensity scan (Fig. 2a), the molecular ion signal plateaus around 10^{14} W/cm^2, whereas it continues to increase for both the 1200 and 2000 nm light past this intensity. Such behavior is indicative of NME fragmentation effects at 800 nm, which are avoided at longer wavelength. For 1200 nm light (Fig. 2b), the signal dips around 10^{14} W/cm^2 but continues to rise as the intensity is further increased. This effect may be indicative of a change in the ionization mechanism at this intensity, which prevents the onset of fragmentation. The 2000 nm (Fig. 2c) intensity scan is missing both the plateau and dip observed at the shorter wavelengths, showing a much simpler trace indicative of a softer ionization mechanism relative to the shorter wavelengths. The variation of the ratio of the molecular ion (M^+) to the two main fragments (F = 82 amu + 30 amu) at high intensity (Fig. 2d) provides further evidence of different ionization effects occurring as the wavelength is varied. Farther into the IR, the higher M^+/F ratios observed are evidence of decreased NME fragmentation dynamics and the onset of an overall softer ionization mechanism.

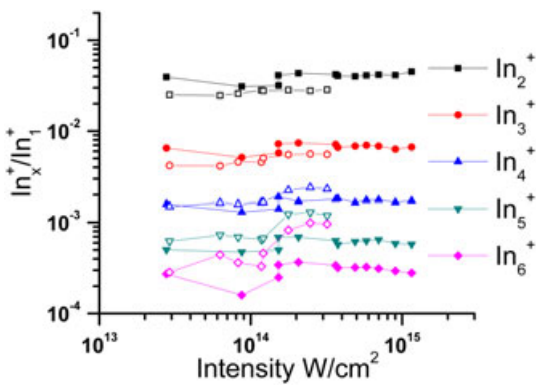

Figure 1. Log–log plot of the ratio of the sputtered neutral indium cluster to monomer as a function of intensity at 1200 nm (solid) and 1900 nm (open).

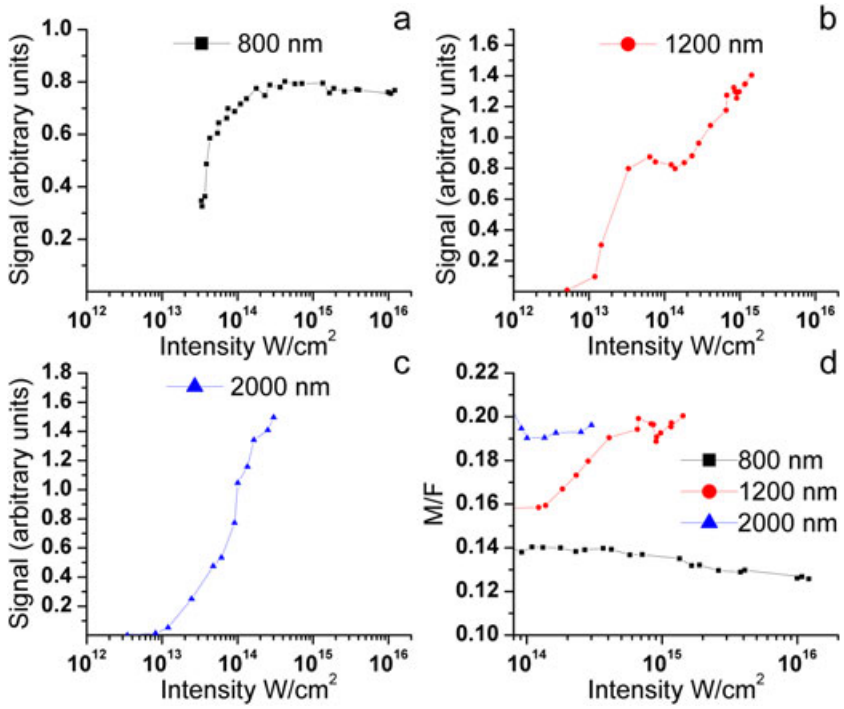

Figure 2. Gas-phase histamine molecular ion signal *versus* log of the laser intensity for 800 nm (a), 1200 nm (b), and 2000 nm (c) light. Molecular ion to fragment ratio (d) plotted *versus* log of the laser intensity at three wavelengths: 800, 1200, and 2000 nm.

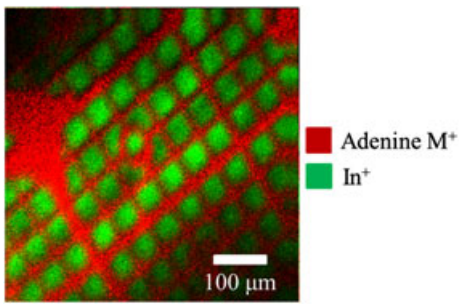

Figure 3. Adenine vapor deposited onto a 400-mesh grid laser postionized neutral's image.

An early example of the application of this new laser system to chemical imaging is shown in Fig. 3. It shows the neutral signal from adenine molecular ion (red) and indium monomer (green), performed by analyzing adenine vapor deposited onto a 400-mesh copper London finder grid and mounted over indium foil. The neutral component represents no loss in resolution over the secondary ion image, showing promise for future bioimaging experiments.

Conclusion

Preliminary results on the implementation of a high-intensity laser system and OPA, capable of generating intensities in the 10^{15} W/cm^2 range, are presented. Studying 20 kV C_{60}^+ sputtered indium decreased NME dynamics, and therefore, more intact ionization of larger metal clusters occurred at a longer wavelength. The same trend toward a softer ionization mechanism farther into the IR was observed in the gas-phase photoionization of histamine. Finally, a simple imaging experiment was performed on adenine vapor deposited onto a 400-mesh London finder grid. It shows promise for the future application of this laser system to bioimaging experiments, where the signal improvements it offers over previous laser postionization experiments and, for some analytes, SIMS, may offer significant insights.

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