The authors thank Referee #1 for their useful comments. Replies and further commentary in response to the comments, including modifications to the submission, are presented below.

1) Mechanism of Ionization:

While the focus of this report is on the applicability of near-IR LDI to AMS, in retrospect, we agree with Referee 1 that some discussion of the ionization mechanism should be presented. We also agree that the important advances to matrix-free IR-LDI that have come out of the laboratory of K. K. Murray (Bhattacharya et al., 2002;Rousell et al., 2004) should be included in the resubmission. However, as we will note in the resubmission, we do not believe it is possible to draw clear correlation between the method of IR-LDI of Murray and our own. Most of Murray's advances to matrix-free LDI have employed silicon surfaces and focused on positive ion formation, with emphasis on high-molecular weight proteins. The current emphasis of our studies is the analysis of oxygenated components of atmospheric aerosols, including organic acids, sterols, and aldehydes all of which are weak acids.

We are hesitant to hypothesize on the most likely ionization mechanism(s) prior to embarking on a detailed systematic study; however, we believe that one possible mechanism yielding negative ions could be as follows:

1) Hydroxylation of the aluminum oxide surface of the aluminum target (via reaction with atmospheric water and water within the aerosol) yielding a surface with a AlOOH coating (i.e. aluminum oxyhydroxide, boehmite) (van den Brand et al., 2004; Alexander et al., 2000).
2) Formation of the complexes at the surface, including those with carboxylates derived from the reaction of organic acids with surface hydroxyl groups forming carboxylate complexes —C(=O)-O-Al, which have been previously identified (Alexander et al., 1998) and may be a high conversion (from the acid to the salt). We hypothesize that other protic analytes form analogous salts with the surface aluminum oxyhydroxide coating.
3) IR energy absorption at the thin film of the sample and/or the interface between the film and the aluminum oxyhydroxide coating. (It is unclear to the authors what the precise absorption band of the 1064 nm radiation is at this time and plan on performing IR analysis of aluminum surfaces including pure aluminum, aluminum oxide and aluminum oxyhydroxide to gain more insight into the NIR-LDI ionization process.)
4) Desorption of the negative ion (derived from the salt) into the gas phase.

It should be noted that the laser energy (ca. 1.2 eV) is far below the work function of aluminum (4.3 eV (Grepstad et al., 1976)) so we do not feel that ionization by a mechanism of photoelectron generation and capture by desorbed organic analytes is a viable mechanism for negative ion formation in NIR-LDI (barring any multiphoton processes). Photoelectron generation has to be accounted for in UV-MALDI and the role of photoelectron generation and recombination and the influence on the efficiency of positive ion formation has been reported (Frankevich et al., 2003).

Precedence for formation of [M-H]⁻ ions from LDI

Most LDI work, including matrix-free methods studies, have focused on the formation of positive ions, $[M+H]^+$, stemming in part from the emphasis given to the LDI analysis of proteins that are conveniently observed in the positive ion mode. There are some notable exceptions to this for matrix-free LDI. Wada and coworkers employed gold and platinum coated porous alumina with submicrometer structures as a potential substrate for surface assisted laser

desorption/ionization (SALDI) mass spectrometry (Wada et al., 2007) for both positive and negative ion mode studies and reported glycine in its deprotonated form, [M-H]⁻. Srivastava and workers have employed matrix-free laser desorption/ionization bioaerosol mass spectrometry (BAMS) with a dual-polarity reflectron time-of-flight spectrometer for positive and negative ion detection (Srivastava et al., 2005). That report included detection of amino acids and nucleobases in the [M-H]⁻ form.

The resubmission will discuss briefly these and other cases of detection of [M-H]⁻ ions from LDI with emphasis on matrix-free methods, which is the focus of our report.

Are any ions other than [M-H]- observed?

Preliminary measurements have shown that [M+H]⁺ ions are formed and measured if the mass spectrometer is configured for positive ions. However, only [M-H]⁻ ions are measured in negative mode.

Types of organic molecules can be detected

To date, we have focused on oxygenated analytes that for the most part contain protic hydrogens, including fatty acids, mono- and dicarboxylic acids and other organic acids, aldehydes, which are weakly acidic in the alpha-position to the carbonyl. In an upcoming report (Geddes et al., 2010) we also report the NIR-LDI spectrum of cholesterol that indicated that this method can ionize alcohols.

2) Experimental Details:

How big is the particle beam compared to the Al wire?

The particle beam diameter (as measured by laser scatter) is 0.3 mm (FWHM) for oleic acid particles. The size of the beam does increase slightly as particle shape deviates from spherical, but for all aerosols measured thus far is always < 0.5 mm (FWHM).

What is the near-IR laser spot size?

The laser spot diameter at the probe surface is 3 mm. Typical energies of the 5 ns pulse were 25 mJ, resulting in a fluence at the probe surface of 80 MW cm⁻². This experimental detail will be added to the revised manuscript.

Is the Al wire biased, floating or grounded? Was any aging of the wire noticed?

The Al wire is floating *(which will be clarified in the resubmission)* and wire aging is noticed after prolonged use, such as employing the same wire for successive chamber experiments. Typically, a decrease in the overall ion signal is observed as the wire ages. We have also noted when using an aluminum wire target for NIR-LDI the progressive appearance in the mass spectra of aluminum oxide and other ions indicative of surface aging. The aluminum wire most likely has an oxide coating when placed in the ionization region of the mass spectrometer. Residual water from the nebulization process (for certain primary particles) as well as that formed in situ (in the case of SOA studies) may adsorb to the aluminum oxide and eventually cause hydroxylation of the surface (van den Brand et al., 2004; Alexander et al., 2000). We believe that adsorption of water and hydroxylation of the aluminum oxide layer of the wire has three possible effects that may influence the ionization process: 1) promotes bonding of organics to the surface of the target (van den Brand et al., 2004); 2) active sites are blocked by

adsorbed water (van den Brand et al., 2004); 3) the surface OH groups may act as IR energy absorbers (akin to OH vibrational absorption by matrix components in MALDI (Sheffer and Murray, 1998)). Clearly the above factors make the role of aging of the aluminum wire on the ionization process complicated, since (1) and (3) may enhance the ionization process while (2) may lower decrease the apparent efficiency of ionization.

How Reproducible are the spectra after repeated use of the wire?

Since submission, we have modified the ionization region such that the wire probe is mounted through a vacuum load-lock that permits changing the probe on a timescale of minutes without breaking vacuum. When doing SOA formation studies we generally change the probe between experiments. This allows us to collect reproducible NIR-LDI mass spectra between different chamber-based experiments. It is clear that a better understanding of the microphysical details of the ionization process, including the role of surface aging of the probe, of NIR-LDI may allow for enhancement of the sensitivity of this method to these and other analytes.

These experimental details will be included in the Experimental section of the resubmission.

Were wires of any other metals tried? How did the spectra and limits of detection compare to Al?

We have made preliminary measurements with other metals (Au, Mg, Cu and In) using oleic acid aerosols. Quantitatively, for all metals tested the performance was similar and the qualitative aspects of the mass spectra were identical. In light of the experience base we had already created, we continued with Al; however, as mentioned above, we are presently undertaking more in-depth systematic studies to better understand the impact of metal properties and surface preparation on NIR-LDI-AMS performance, and further elucidate potential ionization mechanisms.

Does the probe on which the particles are collected even need to be metal?

As stated above, to date we have employed only metal probes. In future experiments, especially for those in positive ion mode, we plan to try silicon and porous silicon (the most commonly employed probes in matrix-free LDI studies (Bhattacharya et al., 2002; Rousell et al., 2004; Okuno et al., 2005; Wei et al., 1999; Finkel et al., 2005; Cuiffi et al., 2001)) as starting points for non-metal probes. Most matrix-free LDI studies to date have employed UV-radiation since this corresponds with a strong absorption band of silicon, however infrared radiation (ca. 3 μm) has been employed successfully in several studies (Bhattacharya et al., 2002; Rousell et al., 2004) and is consistent with energy absorption by hydrogen-bonded OH group (Sheffer and Murray, 1998) and/or a surface film of water on silicon (Yalamanchili et al., 1996). The applicability of 1.064 μm on these surfaces (i.e. silicon and porous silicon) and the overlap with absorption bands for these materials, hydrogen-bonded OH groups, or surface water films will be an important consideration.

Scatter in mass spectral signal at higher deposited masses

In retrospect, the plot in Figure 2 may be misleading. The black squares represent individual measurements (i.e., sampled particle mass followed by AMS analysis). Note that the exact mass sampled is calculated from the total aerosol mass (C_{OA}) of oleic acid measured with the SMPS and knowledge of the sampling rate (through the aerodynamic lens) and sampling time. Therefore, each point in a "grouping" represents a slightly different mass. The red triangles were added as averages for "reasonable" groupings of signals from similar mass depositions. The

triangle at the highest average takes into account only the two highest sampled masses, which, misleadingly, appears to show a greater error. We do not believe that this scatter is due to shot-to-shot fluctuations in the near IR laser. Typically, the instrumental variability (shot-to-shot) is about 10%.

To avoid confusion, the averaged points have been removed from the response curve.

Please explain how the 532-nm laser is used for alignment of the particle beam.

The green laser is used to align the Al probe within the ionization region of the mass spectrometer and the particle beam with the center of the probe. For probe alignment, the green laser is gently focused onto the surface of the probe prior to probe removal. A new probe is then inserted, and its surface aligned to the green laser. Once the probe has been aligned, the laser is moved 2 mm (horizontally) in front of the probe surface. A beam of oleic acid particles is generated and the lens alignment optimized (via vacuum manipulators) to maximize green laser scatter due to the particles crossing the focused cw green laser beam directly in front of the probe. Minimal alignment (if any) of the particle beam is typically required after changing a probe.

Are the particle transmission and deposition efficiencies known? It would be interesting to know how much the limit of detection is determined by these.

We have not determined the transmission or bounce-related collection efficiency on the LDI-probe that would both likely be lower for solid particles compare to liquid ones. It should be noted that the calculated figures of merit are for particles sampled into the AMS and do not account for any sampling or collection losses. Future studies will assess experimental factors, including particle bounce and beam divergence, that may lower particle collection efficiency and how that translates to the instrumental capacity of NIR-LDI-AMS.

Collection of mass spectra and data processing

Below we provide a detailed description of our data acquisition procedure. Although this description could readily be added to the revised manuscript, because it is specific to our oscilloscope and electronics, we do not feel it would be of general utility to the reader and therefore would suggest leaving it out of the published work.

The signal from the MCP plate is passed through a fast pre-Amp (EGG Ortec VT120) then split across two 50 Ω inputs of a digital oscilloscope, one of which is set to a 50 mV/division scale (Channel 1 or C1) thus measuring smaller ion signals and the other at 500 mV/division (Channel 2 or C2) allowing for simultaneous quantitative measurement of any more intense ion signals. The oscilloscope is triggered electronically by the NIR laser q-switch synch (which is also used as the trigger for the delay pulse generator in the ion extraction set-up).

Upon measurement of an ion signal greater than a preselected threshold (to discriminate against noise) the oscilloscope runs a Visual Basic Script to combine the two channel inputs into one output waveform – the output waveform voltage is equal to the higher sensitivity input (C1) at each time point, except when that signal approaches that upper voltage limit of C1, upon which the output switches to the lower sensitivity channel measurement (C2), permitting extension of the linear dynamic range (and resolution) beyond what would be possible with only one channel. This single output waveform is then stored internally and the oscilloscope is ready to collect data again.

Typically for qualitative data collection the output waveform is simply updated as a running average (i.e. each additional output waveform contributes equally to the final spectra), which limits spectra collection speeds to approximately 1 Hz and allows relative sensitivity measurements but no absolute mass loading data to be recorded. For quantitative mass loading data each output waveform is stored and the output spectrum is the integral of all individual stored waveforms. This is currently achieved using the same Visual Basic Script throughout the whole process which requires reading from and writing to an external file upon obtaining each new waveform. Writing to an external file is necessary because the 8-bit resolution of the oscilloscope memory is soon overloaded with multiple passed laser shots. Unfortunately this limits data collection speeds (<1 Hz) and delays increase as the total data stored becomes larger (i.e. more valid spectra recorded for a single particle sampling). This current shortcoming is in the process of being resolved with a more streamlined code.

With low mass sampled ion signals are typically well within the measurement range of the oscilloscope and are present for 1-2 laser shots with subsequent shots showing no measurable signals (above threshold) allowing for high linearity of the mass response. However even with the ion signals being split across two inputs it has still been observed that particularly at higher sampled mass initial ion signals can saturate the lower sensitivity input and therefore artificially lower the recorded intensity. The ion signals can be present for up to 20 laser shots suggesting that improved electronic amplification and data recording may increase the linearity over a greater range of mass loadings.

This is not expected to have a significant effect on measured signal to noise and LOD for extremely low volatility analytes such as oleic acid; however an increased measurement rate may have a dramatic effect on higher volatility species present in typical SOA experiments which are susceptible to volatilization losses under the high vacuum conditions within the ionization region.

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