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Supporting Information

Neutralization Charge Detection Method for Detecting Ions under Ambient and Liquid Phases

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A. General Notes

The sample, grid and detection electrodes of the neutralization charge detector (NCD) are installed horizontally. The detection electrode is a 1 mm thick, 14 mm o.d. washer-shaped electrode with an orifice of 4 mm i.d.. The two hollow plates of the grid electrode have identical shape, with an area of 30×30 mm and 0.5 mm thick. Every hollow plate has a central orifice of 5 mm i.d., and four curved slots to minimize the capacitance between it and other electrodes. The nickel mesh fixed between the two hollow plates is composed of 32 μm thick wires with an aperture width of 1.24 mm (BM0020-03N, Industrial Netting, Minneapolis, MN). The stainless-steel (SS) sample electrode is a rectangular plate fixed on a motorized x-y stage. The detection electrode is enclosed in a grounded SS housing to minimize interferences from ambient electronic noise, except for the sensing surface (bottom). The induction current collected by the detection electrode is amplified with a FEMTO DLPCA-200 fast charge preamplifier (FEMTO Messtechnik GmbH, Berlin, Germany) and monitored by an R&S RTO1004 digital oscilloscope (Rohde & Schwarz Taiwan Ltd., Taipei, Taiwan). For detecting ions in air, the transimpedance gain of the preamplifier is 10^8 V/A and the bandwidth is 200 kHz. For detecting ions in liquids, the transimpedance gain is 10^9 V/A and bandwidth is 1 kHz.

A frequency-tripled Nd:YAG laser beam (355nm, LS-2134UTF, Lotis TII Ltd., Minsk, Belarus) with a pulse duration of 5 ns is used to produce ions. The laser beam probes the sample perpendicularly after passing through the central opening of the detection and grid electrodes. The laser beam is focused by a plano-convex lens to a spot approximately 120 μm in diameter on the sample surface in air. The typical laser energy used for ion generation is 1 to 90 μJ, depending on the observed signal intensity. The pulse repetition rate is 5 Hz for measurements in air. For measurements in liquid phases, the laser is triggered manually after liquid vibration and electronic noise (monitored by splitting the signal to an auxiliary oscilloscope) is small enough to minimize its interference with the presence of a signal. The samples include CsI (Acros Organics, Geel, Belgium), 2,5-dihydroxybenzoic acid (DHB, Sigma-Aldrich Co., St. Louis, MO, U.S.A.), and Ti nanoparticles (30 – 50 nm, UniRegion Bio-Tech,

Hsinchu, Taiwan). The CsI and DHB are dissolved in deionized water before preparation, whereas the Ti nanoparticles are suspended in deionized water through vortexing and deposited to the sample surface before re-precipitation. The amount of CsI deposited on the sample electrode is approximately 0.2 – 5 mg, and the amounts of DHB and Ti deposited are approximately 0.05 – 2.5 mg. Heptane (Merck KGaA, Darmstadt, Germany) is used in experiments under liquid phase.

To analyze ions in the gas phase, the entire device is kept in an ambient environment. To analyze ions in the liquid phase, the sample and grid electrodes are immersed in nonconductive liquids to sustain their electric potentials, while the detection electrode is kept in air. The operation of NCD for detecting ions in liquid is a hetero-phase detection mode, in which the level of liquid is maintained at 2-4 mm above the grid electrode to ensure that the trajectories of ions do not pass through the liquid-air boundary. Under such experimental conditions, the movement of the motorized stages of the sample electrode is slow to prevent severe vibrations in the liquid, which can interfere with ion trajectories and changes spectral patterns. The motorized stages are inactivated during data acquisition to minimize peak fluctuations and noise. The acquisition events without signal and with sever chemical noise are disregarded.

B. Electric field and particle-tracking simulation of the neutralization charge detector

With the experimental conditions used in this study, the electric potential inside the neutralization charge detector (NCD) changes smoothly in most regions except around the mesh. Fig. S1a illustrates equipotential lines within the NCD in one experimental condition simulated using COMSOL Multiphysics v.5.0 (COMSOL Inc., Stockholm, Sweden), with potential difference of 90 V per line. The figure presents the electric potential in two dimensions; the four dots at the center of grid electrode represent the wire mesh. The wire mesh has the lowest electric potential. This attracts positive ions approaching the central-opening toward the wire. Fig. S1b shows predicted trajectory of 50 ions in air in three-dimensional space. The blue lines represent ion trajectories and red dots represent the final position of ions. The result indicates most ions collide with the mesh, and 10% of the ions show a long trajectory and stop at the edge of the central opening of the grid electrode.
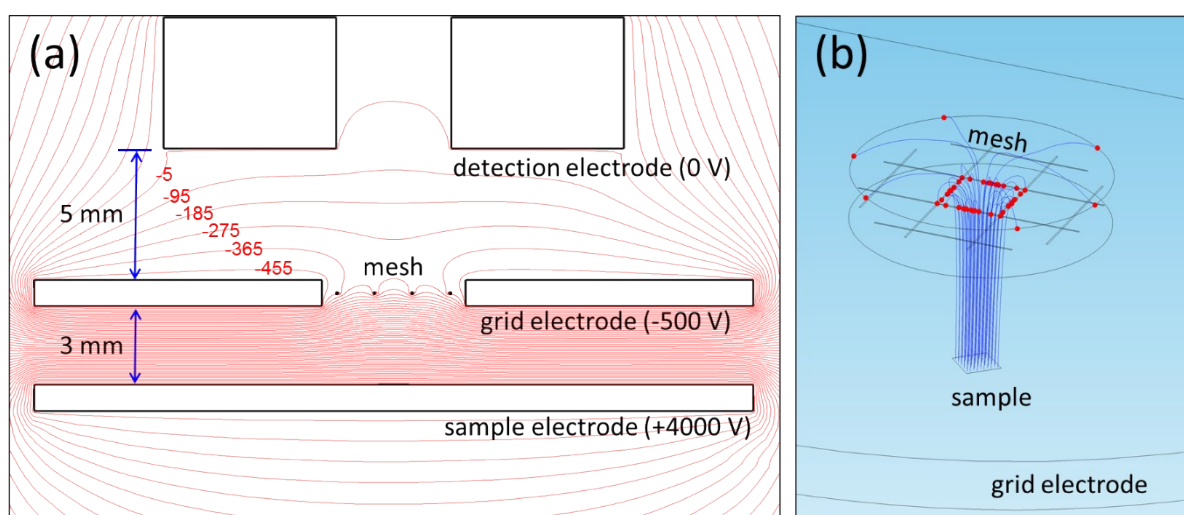

Fig. S1 Simulated equipotential lines around electrodes of neutralization charge detector (a) and trajectories of 50 ions starting from the sample to mesh (b).

According to the simulation, all ions collide with the mesh when they start from a sampling position that is more than 0.25 mm away from the central axis of the grid electrode. Ions starting from within 0.25 mm of the central axis penetrate through the mesh aperture to various extents and return to the mesh or the grid electrode at different times. Fig. S2 displays the result of particle-tracking simulation of 1000 Cs$^+$ ions detected in air and hexane. Because COMSOL simulation is unable to incorporate correction factors relating to the mobility of particles, correction factors to Stoke's equation for air are used to scale the simulation result. The correction was proposed by Cunningham, Knudsen, Weber, and Millikan for charged aerosol particles moving along electric fields in air,[1] including correction factors a = 1.234, b = 0.414, and c = 0.876 for elastic-specular collisions. The corrected mobility (K) has the form:

$$K = \sqrt{1 + \frac{m_g}{m_p} \frac{2.25}{(a+b)[\Omega^{(1,1)*}_{\infty-4}(T^*) + s(r_m, T_\delta) - 1]}} \frac{1 + \frac{l}{\delta}[a + be^{-c\frac{\delta}{l}}]}{6\pi\eta\delta}, \ \delta = r_m + h + r_g(T_\delta)$$

in which m_g is average mass of gas molecules, m_p is ion mass, $\Omega^{(1,1)*}_{\infty-4}(T^*)$ and $s(r_m, T_\delta)$ are correction factors of collision cross section, l is mean-free-path of ion, δ is collision diameter, η is viscosity of medium, r_m is radius of ion, h is the extra distance, and $r_g(T_\delta)$ is average radius of neutral molecules. In this study, the calculation uses typical values: l = 65 nm, η = 1.86×10^{-5} Pa·S, $r_g(T_\delta)$ = 0.125 nm, $\Omega^{(1,1)*}_{\infty-4}(T^*)$ = 1, $s(r_m, T_\delta)$ = 1, and r_m is predicted by theoretical calculation. The collision cross section of Cs$^+$ ions is estimated based on the results of Fernandez-Lima and coworkers.[2] The resultant mobility of C$_s^+$ is about 288.1 times slower than that obtained using an uncorrected Stoke's equation. This factor, 288.1, is used to scale the result of simulation to obtain the predicted spectrum in air. There is no scaling factor used in the result in heptane since a reliable theoretical model is still unavailable.
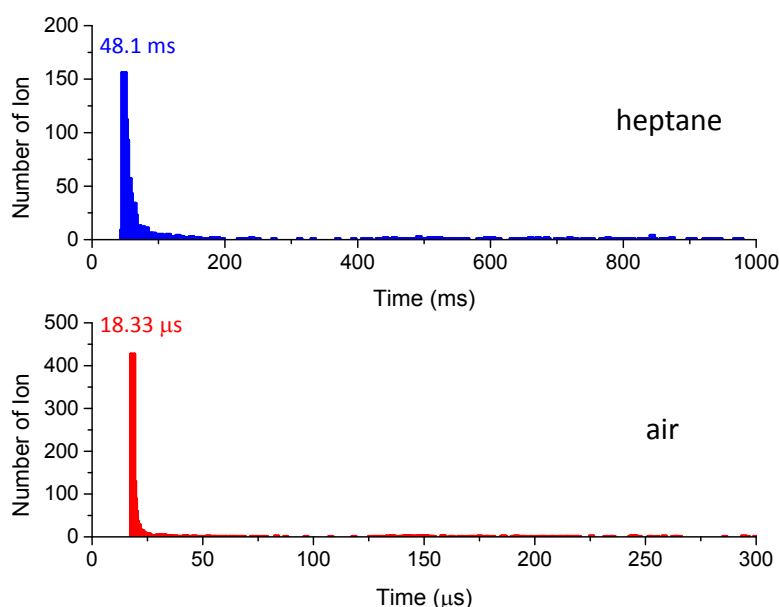
Fig. S2 Simulated spectra of Cs$^+$ obtained in air and heptane.

C.   Experimental tests for confirmation of induction charge detection

The signal observed using NCD is the induction current that corresponds to charge neutralization. Confirmation tests are conducted with a cover slip (ϕ = 18mm, thickness = 0.15 mm, Paul Marienfeld GmbH & Co. KG, Lauda-Königshofen, Germany) installed in front of the detection electrode to prevent the detection electrode from direct contact with ions. Fig. S3 shows the experimental results obtained using Ti in air with similar laser energy. The results show that the peak obtained with the cover slip have similar arrival time and spectral shape as those without the cover slip. The arrival-time difference between the two spectra is within experimental error. This analytical result suggests that direct charge collection is unimportant in NCD. The only noticeable change is peak intensity obtained with the cover slip is slightly lower than that without the cover slip. The lower signal intensity is attributed to the cover slip attenuating laser energy as well the induction current.
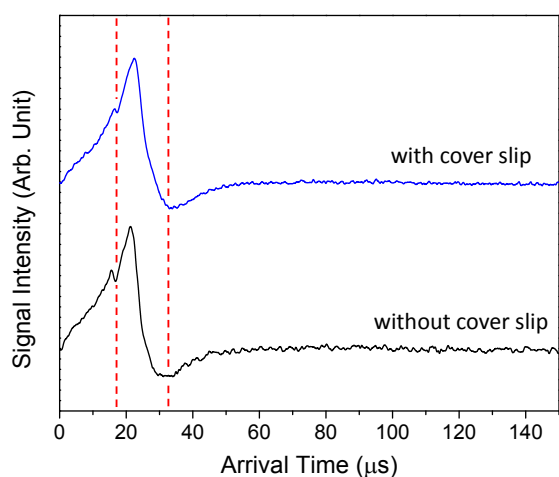

Fig. S3 Induction current obtained with and without a cover slip installed in front of the detection electrode using Ti in air.

D.   Blank tests

To confirm the spectral features observed with NCD are produced from corresponding samples instead of SS material, a series of blank test is conducted. The first test is LDI of a bare SS sample electrode. The results show that no SS-related signal is observed in heptane even with a laser energy of 150 µJ, indicating that the signals in Fig. 3 (main text) do not contain SS-related ions. On the other hand, the threshold laser energy used to produce ions in air is roughly 13 µJ. This threshold energy is significantly larger than the laser energy used to produce Ti ions in air, suggesting the contribution of SS-related ions to the signal in Fig. 2 (main text) is unimportant. Fig. S4 shows a spectrum of bare SS sample electrode in air obtained with a laser energy of 22 µJ. The spectrum shows an intense feature at ~17 µs. Although the arrival time of this feature is similar to the first features in other spectra (Fig. 2, main text), its identity is different from the features obtained with other samples as confirmed by the second test. The second test is performed with CsI prepared on the surface a piece of Scotch tape (Scotch® 3036, 3M Taiwan Ltd.) that is stock on a SS sample electrode. The measurement is conducted under ambient conditions with a laser energy of 24 µJ. The Scotch tape ensures that ion signals are free from contamination of SS-related ions. The spectral features of CsI obtained under this condition are similar to those without the Scotch tape (Fig. 2, main text), as shown in Fig. S4. The

result confirms the ion signal is produced from the sample instead of the bare SS sample electrode. Notably, no detectable ion signal is observed with the Scotch tape in air even with 150 µJ laser energy.
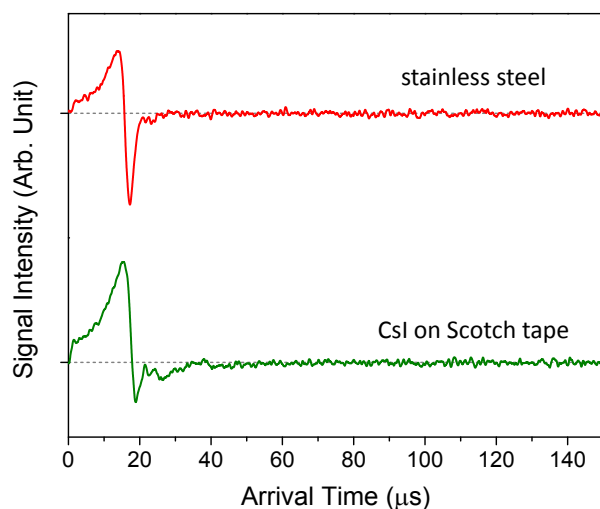
Fig. S4 Induction signal obtained from a bare stainless steel surface and CsI prepared on Scotch tape.

E. Single-shot spectrum of Ti in heptane

The efficiency of NCD for detecting ions in liquid is high enough to observe a clear signal with a single laser shot. Fig. S5 displays a single-shot spectrum of Ti in heptane, which contains numerous sharp peaks. The peaks have high density within 7 – 25 ms. The average width of sharper peaks is roughly 0.29±0.08 ms, and that of the broader peaks is roughly 0.52±0.14 ms.
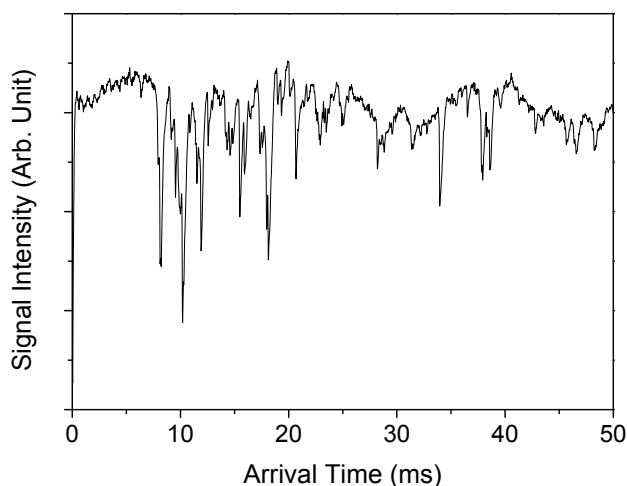
Fig. S5 Single-shot spectrum of Ti in heptane.

References

1.   R. A. Millikan, *Phys. Rev.*, 1923, **22**, 1-23.
2.   F. A. Fernandez-Lima, C. Becker, K. Gillig, W. K. Russell, M. A. C. Nascimento and D. H. Russell, *J. Phys. Chem. A*, 2008, **112**, 11061-11066.