

Supporting Information:

Halogen Radical Chemistry at Aqueous Interfaces

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SI Text

Gaseous methyl iodide, $\text{CH}_3\text{I}(\text{g})$, sparged by ultra-pure (> 99.999 %) $\text{N}_2(\text{g})$ from $\text{CH}_3\text{I}(\text{l})$ maintained at 293 K in a temperature-controlled bath (THOMAS, TRC-4C), was diluted with $\text{O}_2(\text{g})$ (> 99.995 %) before being injected into the spraying chamber of the mass spectrometer (Fig. S1). $\text{O}_2(\text{g})$ was used as effective quencher of excited iodine atoms (see below). Carrier gas flow rates were regulated by calibrated digital mass flow controllers (Horiba, STEC, SEC-400 MARK 3). Conditions in the present experiments were: drying gas flow rate: 13 L min^{-1} ; drying gas temperature: $340 \text{ }^\circ\text{C}$; inlet voltage: + 3.5 kV relative to ground; fragmentor voltage value: 80 V. CH_3I (purity > 99.5 %, Nacalai Tesque), NaI (> 99.5 %, Nacalai Tesque), NaBr (> 99.5 %, Kanto Chemical), H_2^{18}O (97 %, Santa Cruz Biotechnology, Inc.) and D_2O (99.9 atom % D, Sigma-Aldrich) were used as received. All solutions were prepared in purified water (Resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$ at 298 K) from a Millipore Milli-Q water purification system. All experiments were performed at $298 \pm 2 \text{ K}$.

Calculation of $\text{I}\cdot(\text{g})$ concentration

The dissociation of $\text{CH}_3\text{I}(\text{g})$ by 266 nm photons produces into $\text{I}\cdot(\text{g}) + \cdot\text{CH}_3(\text{g})$.¹ We estimate that under present experimental conditions 0.07 ~ 6.6 % $\text{CH}_3\text{I}(\text{g})$ is converted in $\text{I}\cdot(\text{g})$. The concentration of $\text{I}\cdot(\text{g})$ is derived from the $\text{CH}_3\text{I}(\text{g})$ absorption cross sections, laser fluence, and reported gas-phase kinetic parameters. Since the number of photons is always larger than number of $\text{CH}_3\text{I}(\text{g})$ molecules under present conditions, we estimate the initial $\text{I}\cdot(\text{g})$ concentrations from Beer's law:

$$\ln(N_0/N) = I_0 \sigma \Phi_{dis} \quad (\text{E } 1)$$

$$N = N_0 \exp(-I_0 \sigma \Phi_{dis}) \quad (E 2)$$

where σ is the absorption cross section, Φ_{dis} is the dissociation quantum yield, I_0 is the laser fluence in number of photons per unit area, N_0 is the number of molecules before laser irradiation, and N is the number of molecules after laser irradiation.² We derive $N/N_0 \sim 0.934$, meaning $[I \cdot (g)]_0 \approx 0.066 \times [CH_3I(g)]$ at the largest 266 nm laser pulse energy ~ 40 mJ pulse⁻¹. $[I \cdot (g)]_0$ can be varied from 10 ppbv to 40 ppmv under present conditions. $\cdot CH_3$ radicals reacts with excess O_2 to form CH_3O_2 within ~ 50 ns, $k(\cdot CH_3 + O_2 + M) = 4.5 \times 10^{-31}$ cm⁶ molecule⁻² s⁻¹.³ About 70% of the I-atoms from the photodissociation of CH_3I at 266 nm are formed in the excited state $I(^2P_{1/2}), I^*$,⁴ which in the presence of excess O_2 , are quenched to the ground state within ~ 20 ns (from $k(I^* + O_2) = 2.6 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹) under present conditions.⁵ Hence, in our experiments I-atoms colliding with the aqueous microjets are in the ground state. The gas-phase reaction of $I \cdot + I \cdot + (M) \rightarrow I_2 + (M)$ is sufficiently slow ($\tau > 50$ ms)³ and hence negligible.

Calculation of I·(g) uptake coefficient

The rate at which $I \cdot (g)$ are incorporated onto the surface of the microjets is given by the kinetic theory of gases, equation SE1:

$$\dot{n} = \frac{1}{4} n c \gamma = 1.3 \times 10^{18} \gamma \text{ molecules cm}^{-2} \text{ s}^{-1} \quad (SE1)$$

for the experiment of Figure 1, where: $n = 2.3 \times 10^{14}$ molecules cm⁻³, $c = 2.2 \times 10^4$ cm s⁻¹ is the mean speed of $I \cdot (g)$ at 300 K, and γ is the uptake coefficient on 0.1 mM NaBr solutions. Therefore, the number of $I \cdot (g)$ incorporated onto the surface of water during $\tau = 10^{-5}$ s contact times is: $N = 1.3 \times 10^{13} \gamma$ atoms cm⁻². Figure 1 shows that in such

events the concentration of Br^- in interfacial layers of thickness $\delta \sim 10^{-7}$ cm drops by 50%, i.e., the number of Br^- ions consumed per unit area is: $\Delta N = (\frac{1}{2} \times 10^{-4} \text{ mol L}^{-1} \times 10^{-3} \text{ L cm}^{-3}) \times (6 \times 10^{23} \text{ molecules mol}^{-1}) \times (10^{-7} \text{ cm}) = 3 \times 10^9 \text{ ions cm}^{-2}$. By assuming a one-to-one stoichiometry, i.e., by equating $N = \Delta N$, we estimate that $\gamma \sim 2 \times 10^{-4}$.

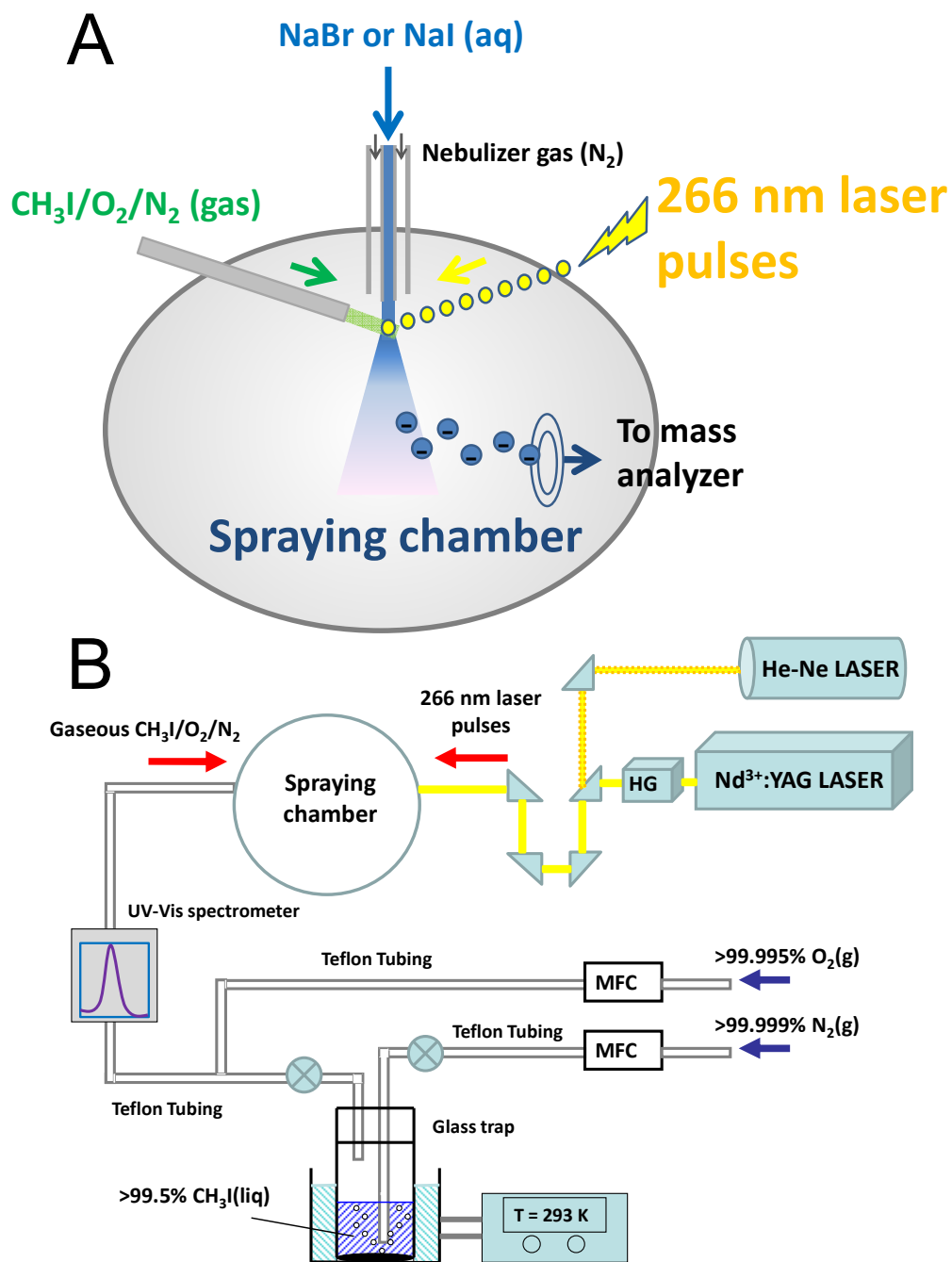


Figure S1 Schematic diagram of an in-situ measurement of laser-induced halogen radical reactions at the air-water interface. HG stands for harmonic generator. MFC stands for mass flow controller.

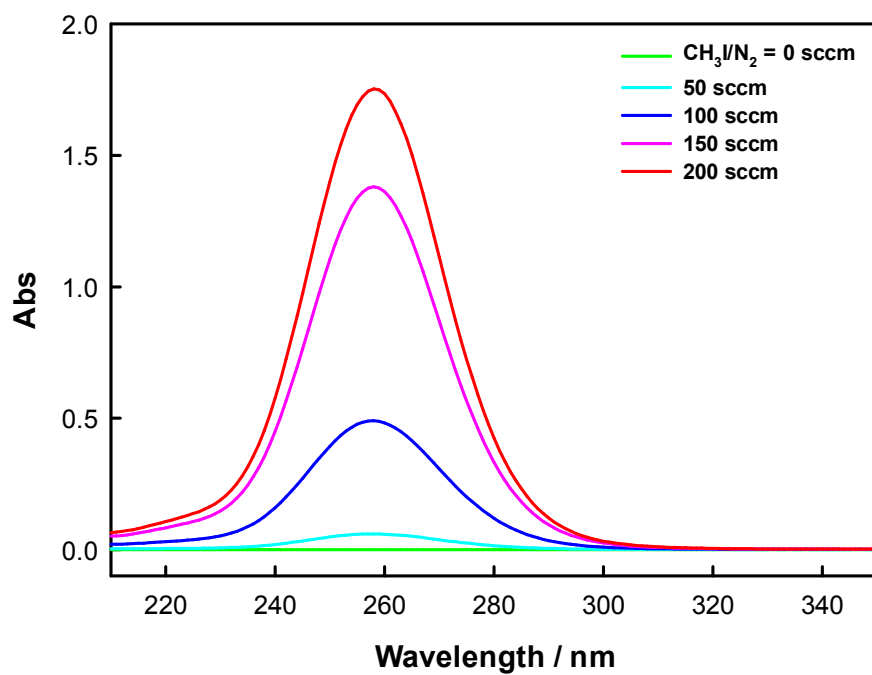


Fig. S2 Ultra-violet absorption spectra of $\text{CH}_3\text{I}(\text{g})$ as a function of flow rate

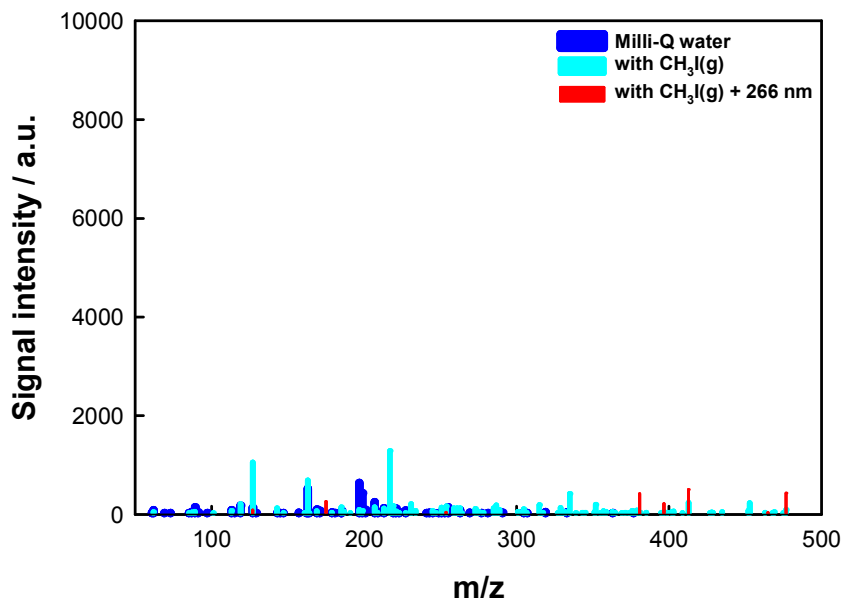


Fig. S3 Negative ion electrospray mass spectra of milli-Q water (resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$) microjets exposed to $\text{CH}_3\text{I}(\text{g})/\text{N}_2(\text{g})$ mixtures at $[\text{CH}_3\text{I}(\text{g})] = 2.0 \times 10^{16} \text{ molecules cm}^{-3}$ with (red)/without (cyan) 266 nm laser beam irradiation. Note that the signal intensities are below background noises.

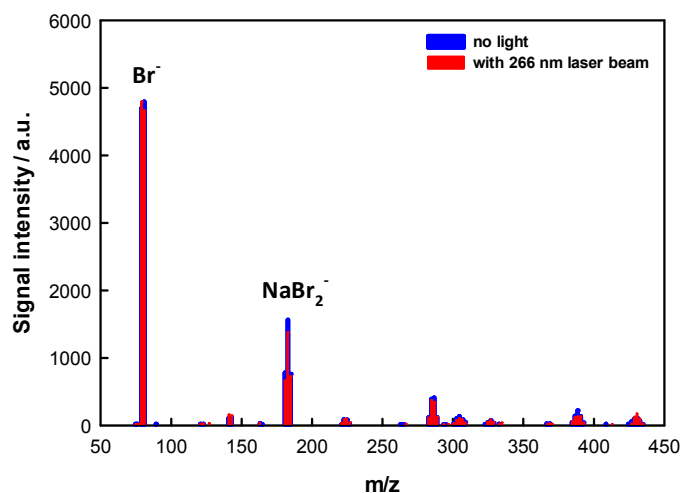


Fig. S4 Negative ion electrospray mass spectra of 0.1 mM NaBr microjets with/without 266 nm laser beam irradiation under N_2 atmosphere. Note that the signal intensities are unchanged within errors upon laser irradiation.

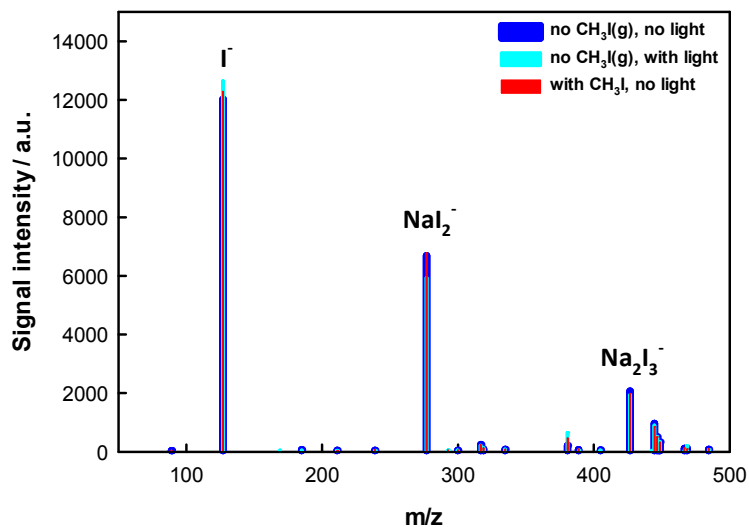


Fig. S5 Negative ion electrospray mass spectra of 0.1 mM NaI microjets with/without 266 nm laser beam irradiation or exposed to $\text{CH}_3\text{I}(\text{g})$. Note that the signal intensities are unchanged within errors upon laser irradiation.

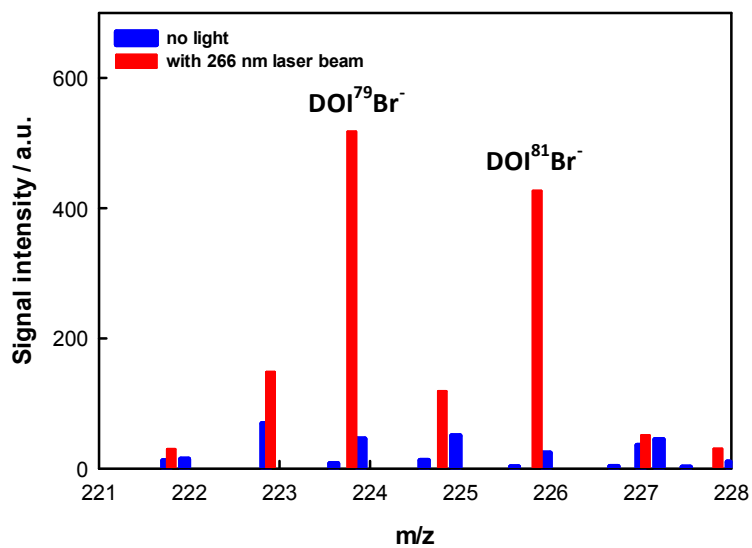


Figure S6 Negative ion electrospray mass spectra of 0.1 mM NaBr in 99 vol. % D_2O microjets exposed to gaseous $\text{CH}_3\text{I}/\text{O}_2/\text{N}_2$ at $[\text{CH}_3\text{I}(\text{g})] = 1.4 \times 10^{16}$ molecules cm^{-3} irradiated by 266 nm laser beams.

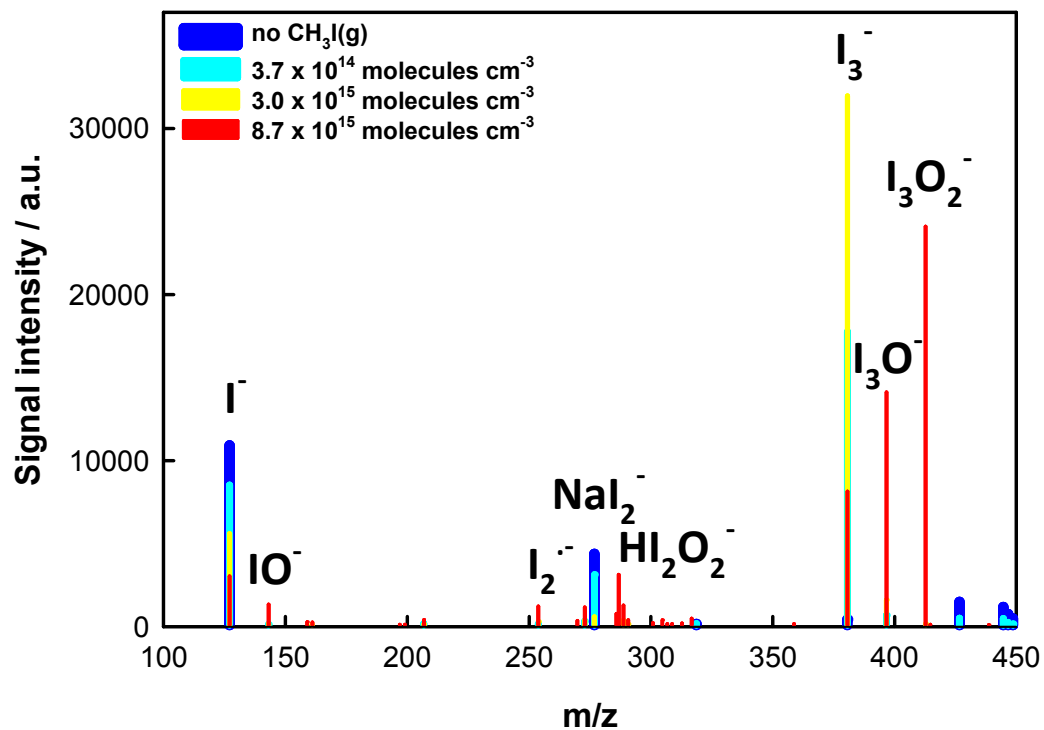


Figure S7 Negative ion electrospray mass spectra of 0.1 mM NaI microjets exposed to CH₃I(g)/N₂(g)/O₂(g) mixtures at variable [CH₃I(g)] under 266 nm laser beam irradiation.

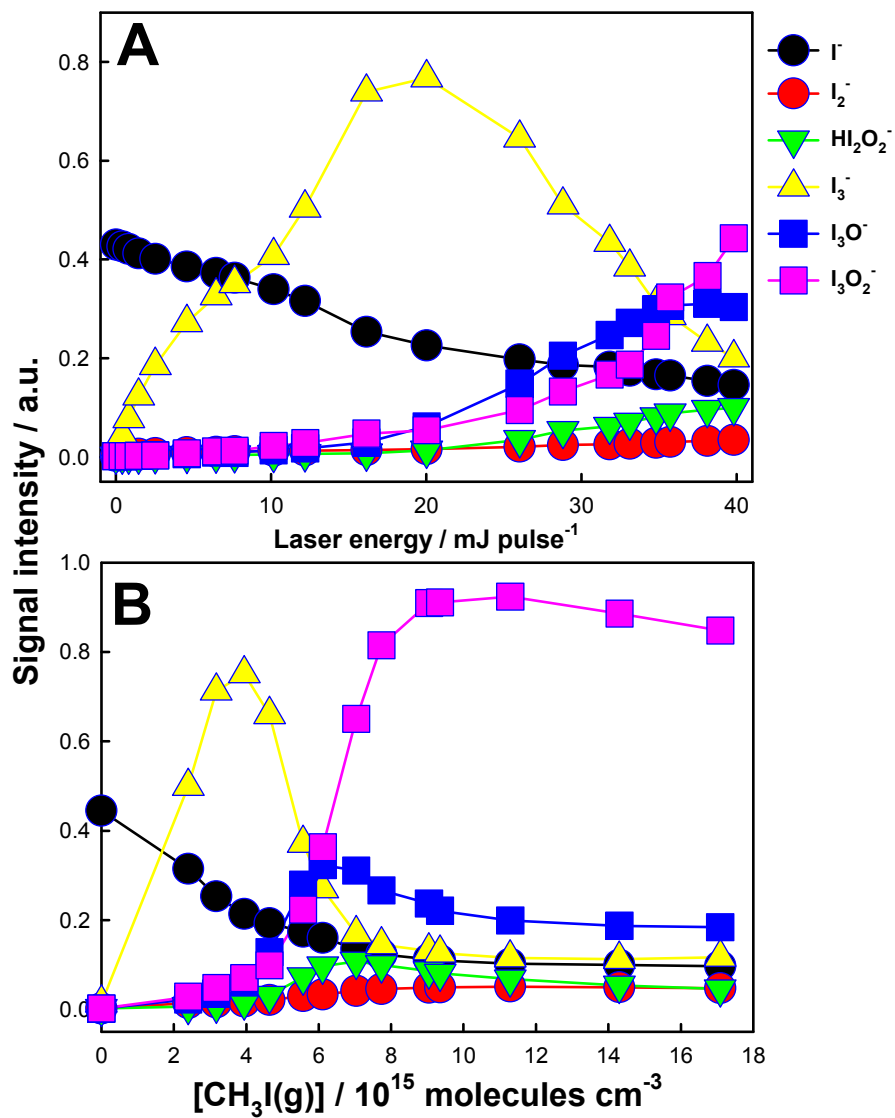


Figure S8 A) Electro spray mass spectral signal intensities acquired from aqueous 0.1 mM NaI microjets exposed to gaseous $CH_3I/O_2/N_2$ at $[CH_3I(g)] = 6.2 \times 10^{15}$ molecules cm^{-3} irradiated by 266 nm laser beams as a function of laser energy $mJ\ pulse^{-1}$. B) as a function of $[CH_3I(g)]$.

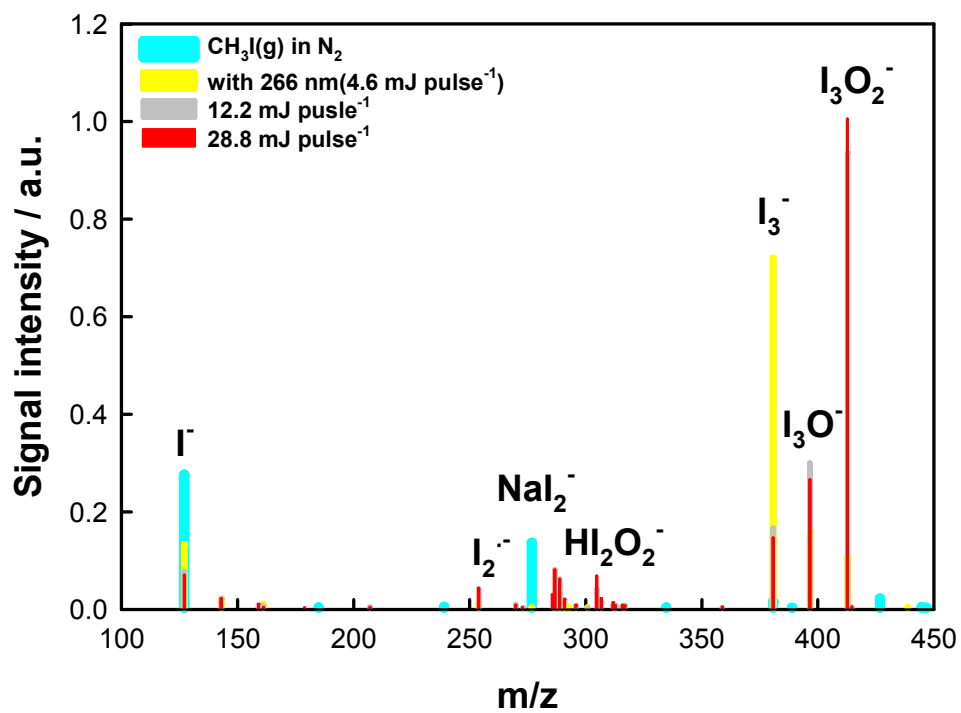


Fig. S9 Negative ion electrospray mass spectra of 0.1 mM NaI microjets with (yellow, gray, red)/without (cyan) 266 nm laser beam irradiation with 2.0×10^{16} molecules cm^{-3} CH₃I(g) under no O₂-flow condition.

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