Supporting Information:

Halogen Radical Chemistry at Aqueous Interfaces

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Gaseous methyl iodide, CH$_3$I(g), sparged by ultra-pure (> 99.999 %) N$_2$(g) from CH$_3$I(l) maintained at 293 K in a temperature-controlled bath (THOMAS, TRC-4C), was diluted with O$_2$(g) (> 99.995 %) before being injected into the spraying chamber of the mass spectrometer (Fig. S1). O$_2$(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 $^\circ$C; inlet voltage: +3.5 kV relative to ground; fragmentor voltage value: 80 V. CH$_3$I (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$_2$O (99.9 atom % D, Sigma-Aldrich) were used as received. All solutions were prepared in purified water (Resistivity $\geq$18.2 M$\Omega$ cm at 298 K) from a Millipore Milli-Q water purification system. All experiments were performed at 298 $\pm$ 2 K.

Calculation of I·(g) concentration

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

$$\ln(N_0/N) = I_0 \sigma \Phi_{dis} \quad (E \ 1)$$
$$N = N_0 \exp(-I_0 \sigma \Phi_{\text{dis}})$$  \hspace{1cm} \text{(E 2)}$

where $\sigma$ is the absorption cross section, $\Phi_{\text{dis}}$ 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. We derive $N/N_0 \sim 0.934$, meaning $[I\cdot(g)]_0 \approx 0.066 \times [\text{CH}_3I(g)]$ at the largest 266 nm laser pulse energy $\sim 40 \text{ mJ pulse}^{-1}$. $[I\cdot(g)]_0$ can be varied from 10 ppbv to 40 ppmv under present conditions. ·CH$_3$ radicals reacts with excess O$_2$ to form CH$_3$O$_2$ within $\sim 50 \text{ ns}$, $k(\text{·CH}_3 + \text{O}_2 + \text{M}) = 4.5 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. About 70% of the I-atoms from the photodissociation of CH$_3$I at 266 nm are formed in the excited state I($^2P_{1/2}$), I*, which in the presence of excess O$_2$, are quenched to the ground state within $\sim 20 \text{ ns}$ (from $k(I* + O_2) = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) under present conditions. Hence, in our experiments I-atoms colliding with the aqueous microjets are in the ground state. The gas-phase reaction of $I\cdot + I\cdot + (\text{M}) \rightarrow I_2 (\text{+ M})$ is sufficiently slow ($\tau > 50 \text{ ms}$) and hence negligible.

**Calculation of I\cdot(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:

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

for the experiment of Figure 1, where: $n = 2.3 \times 10^{14} \text{ molecules cm}^{-3}$, $c = 2.2 \times 10^4 \text{ cm s}^{-1}$ is the mean speed of I\cdot(g) at 300 K, and $\gamma$ is the uptake coefficient on 0.1 mM NaBr solutions. Therefore, the number of I\cdot(g) incorporated onto the surface of water during $\tau = 10^5 \text{ s}$ contact times is: $N = 1.3 \times 10^{13} \gamma \text{ atoms cm}^{-2}$. 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 CH$_3$I(g) as a function of flow rate
Fig. S3 Negative ion electrospray mass spectra of milli-Q water (resistivity ≥ 18.2 MΩ cm) microjets exposed to CH₃I(g)/N₂(g) mixtures at [CH₃I(g)] = 2.0 x 10¹⁶ 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 N₂ 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 CH₃I(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. % D₂O microjets exposed to gaseous CH₃I/O₂/N₂ at [CH₃I(g)] = 1.4 x 10¹⁶ molecules cm⁻³ irradiated by 266 nm laser beams.
Figure S7 Negative ion electrospray mass spectra of 0.1 mM NaI microjets exposed to CH$_3$(g)/N$_2$(g)/O$_2$(g) mixtures at variable [CH$_3$(g)] under 266 nm laser beam irradiation.
Figure S8 A) Electrospray mass spectral signal intensities acquired from aqueous 0.1 mM NaI microjets exposed to gaseous CH$_3$I/O$_2$/N$_2$ at [CH$_3$I(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$_3$I(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 $2.0 \times 10^{16}$ molecules cm$^{-3}$ CH$_3$(g) under no O$_2$-flow condition.
**SI REFERENCES**


