Title: Broadband Deep UV CTTS Spectra of Interfacial Aqueous Iodide

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Supplementary Materials:

Materials and Methods: The laser system (Fig S1) consists of a commercial oscillator (Spectra Physics Mai Tai) seeding a regenerative amplifier (Spectra Physics Spitfire Ace). The output of the amplifier (800 nm, 4.2 mJ/pulse, 1 kHz, 100 fs, horizontal polarization) is split into two separate beams. The first beam ($\omega_1$) is the frequency tripled fundamental (266 nm). The third harmonic generator consists of a BBO crystal which doubles the 800 nm pulse to 400 nm with ~20% efficiency, a calcite delay plate to reestablish temporal overlap between the fundamental and second harmonic pulses, a half-wave plate to match the polarization, and finally, another BBO crystal is used for mixing the 800 nm fundamental with the 400 nm second harmonic pulses to generate 3 µJ of s-polarized 266 nm light with a bandwidth of 2 nm. The tripped pulse is then purified using optical filters and directed through a variable time delay before being focused at a 57° angle relative to normal onto the sample. The 266 nm spot size on the sample is 36 µm on the major axis and 20 µm on the minor axis. This slightly larger than usual spot size serves two purposes: (1) it mitigates heating and sample damage and (2) it ensures a more complete spatial overlap with the larger white light continuum spot.

The second beam ($\omega_2$) is a white light continuum. White light generation is an optical phenomenon wherein a tightly focused ultrafast laser pulse is propagated through a transparent medium, resulting in a superbroadening of the spectrum. This superbroadening is primarily a result of self-phase modulation of the laser pulse, although other factors, such as self-steepening of the pulse, also contribute. Properties of the generated supercontinuum are governed principally by the medium through which the incident laser pulse is propagated, as well as the laser pulse wavelength and pulse duration. In this experiment, water that is constantly flowed through a 5 mm quartz cell serves as the supercontinuum generating medium. An 800 nm, p-polarized beam is focused to a 90 µm beam waist with a 30 mm Rayleigh length. Polarization is conserved throughout the white light continuum generation process, obviating the need for further polarization purification. The long Rayleigh length ensures that the quartz cell will not generate burn spots. After passing through the flow cell, the diverging supercontinuum beam is collimated with a curved mirror before being directed to and focused onto the sample via another curved mirror. Curved mirrors are used to direct the supercontinuum to eliminate chromatic aberrations. The generated white light continuum, which has a spectrum spanning 600 nm to 1400 nm, impinges on the sample at a 50° angle relative to the surface normal with a spot size that is 47 µm on the major axis and 30 µm on the minor axis.

The two incident laser beams are blocked after reflecting from the sample, while the generated s-polarized DUV-SFG signal is collected using a collimating curved mirror and directed into a spectrograph (Acton SpectraPro 300i). Optical filters were used to minimize background light contamination while the spectrum was collected with a CCD (Princeton Instruments, PIXIS). The spectral resolution of this experiment is limited by the bandwidth of the $\omega_1$ pulse (2 nm).

The raw SFG spectrum is normalized with the DUV-SFG output from a reference GaAs sample to account for the intensity of the incident beams and for the inconsistent spectral density of the white light continuum. GaAs was chosen because it has no electronic resonance in the wavelength range being used. The actual $|\chi^{(2)}|$ interfacial spectrum is then obtained by normalizing the SFG spectrum from the sample to that of the GaAs reference, shown in Fig 3.

All glassware in contact with the sample solution is soaked in a Nochromix/concentrated sulfuric acid solution for 24 hours prior to each experiment. All sample solutions are prepared
with ultrapure water (18.2 MΩ cm) from a Millipore system and chemicals of reagent grade (≥99.5%) or better are used. Since the iodide solutions can degrade when exposed to oxygen or light, new solutions were prepared for each experiment, and each individual sample was exposed to laser light for no longer than 60 seconds.

**Fig. S1.** Schematic of the experimental design used for the broadband DUV-SFG experiment. The third harmonic generator is shown first with a BBO, followed a calcite delay plate (Δt), a half-wave plate (½ WP), and finally, a third harmonic generating BBO. The fundamental beams reflected off the sample are physically blocked and optically filtered out so as to not saturate the CCD.