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Pulse-resolved and averaged dynamics of stimulated Raman scattering, plasma emission, and acoustic waves in water and ethanol-water solutions

Zohar Burshtein and Ilana Bar*

Abstract: Laser-induced breakdown (LIB) in liquids involves complex and dynamic processes. This study reports the first pulse-resolved measurements of backward or forward stimulated Raman scattering (BSRS/FSRS), captured synchronously with plasma emissions, and acoustic signals during LIB in water and ethanol-water (EtOH-water) mixtures, using 532 nm nanosecond pulses at 10 Hz. O–H SRS bands show pronounced shot-to-shot variability, revealing transient hydrogen-bond (HB) networks and supporting a continuum of HB configurations, whereas C–H bands, plasma, and acoustic signals remain comparatively stable. Increasing the EtOH concentration reduces the main O–H peak and enhances lower-wavenumber O–H features in the average BSRS spectra, indicating HB structural changes and a transition at 16% EtOH by volume. Plasma profiles vary with EtOH content and laser power, correlating plasma position with self-focusing distance and linking molecular structure to plasma behavior. Acoustic amplitudes decrease with increasing EtOH concentration, due to reduced density and cavitation effects, stabilizing after initial pulses. These findings demonstrate the value of pulse-resolved analysis in revealing dynamic processes masked in averaged data. This approach offers new insights into HB dynamics, plasma evolution, and acoustic responses under intense laser irradiation, with implications for spectroscopy, plasma physics, and fluid dynamics.

Keywords: stimulated Raman scattering; plasma emission dynamics; acoustic waves; water; non-linear optical phenomena; ethanol-water solutions; hydrogen-bonding

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1 Introduction

High-energy pulsed laser beams interacting with various samples can affect laser-induced breakdown (LIB), resulting in formation of plasma (ionized gas)¹. Although this process may seem straightforward, it involves a complex interplay of coexisting phenomena. These include Kerr-induced self-focusing, filamentation, coherent Raman and Brillouin scattering, rapid plasma expansion, shockwave emission, and cavitation bubble generation in liquids^{1–9}. All these phenomena are important for both fundamental studies and practical applications.

Under such conditions, plasma forms through multiphoton and cascade ionization, with free electrons gaining

energy via inverse bremsstrahlung absorption¹. Within tens of femtoseconds, vast ejection of electrons and ions occurs^{1,10}. The remainder of the laser pulse heats the ablated matter, further accelerating electrons through inverse bremsstrahlung. This, in turn, promotes additional ionization via collisions and photoionization, producing a dense plasma. The evolution of this plasma depends on LIB dynamics, material properties, pressure, temperature, and ambient conditions. The plasma emits radiation and launches shockwaves^{6,7}, and in liquids also generates cavitation bubbles, influencing subsequent optical and acoustic responses. Furthermore, when the peak power of the incident laser exceeds the critical power (P_{cr}) for self-focusing, given by $P_{cr} = 3.77\lambda^2/8\pi n_0 n_2$ (where λ is the incident

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wavelength and n_0 , n_2 are the linear and intensity-dependent nonlinear refractive indices), the beam undergoes dramatic changes. For water at 532 nm ($n_0 = 1.33$ and $n_2 = 1.9 \times 10^{-16} \text{ cm}^2/\text{W}^{3,11}$), a $P_{\text{cr}} = 1.68 \text{ MW}$ is obtained. Surpassing this threshold leads to self-focusing, which can cause the beam to collapse and locally intensify the field, thereby enhancing ionization and triggering additional nonlinear phenomena².

These interactions are particularly relevant to stimulated Raman scattering (SRS), mediated by the third-order nonlinear susceptibility, $\chi^{(3)}$, seeded by amplified spontaneous Raman noise^{2,12}. Although spontaneous Raman is weak, its amplification produces SRS signals at molecular vibrational frequencies, propagating backward and forward² (BSRS and FSRS) with spectral features narrower than spontaneous Raman. Because SRS growth depletes the pump, modes with the largest Raman cross sections dominate the spectra. SRS has been widely employed for materials characterization^{2,13–15}, molecular structure analysis^{16,17}, biological imaging^{18,19}, wavelength conversion of pump lasers^{20–28}, and other applications. At the intensities required for SRS, the same laser pulses deposit energy near the focal volume, triggering plasma formation^{1,5,10,13,17} and supersonic expansion that forms high-pressure shockwaves^{6,7}. These shockwaves compress the surrounding fluid before decaying to acoustic speeds^{8,29}, while cavitation bubbles form and subsequently collapse, generating additional shockwaves and acoustic pulses, leading to complex hydrodynamic effects.

Water and ethanol-water (EtOH-water) solutions provide model liquid systems to probe SRS, plasma emission, and acoustics under intense laser excitation. Liquid water and its solutions are key media for LIB and SRS studies since it is ubiquitous across biological, geological, chemical, and physical contexts^{30,31}. In liquid water, each water molecule forms an extended hydrogen-bond (HB) network with its neighbors. This network strongly influences the molecular structure, vibrational spectra, and many physical and chemical properties^{30,32,33}. The structure of liquid water has long been discussed in terms of two main models. The mixture model describes water as a collection of discrete species with intact or broken HBs. In contrast, the continuum model envisions a dynamic, three-dimensional (3D) HB network with a broad distribution of O–H...O angles and bond strengths^{34,35}. While decompositions of broad Raman bands into discrete components^{36–40} can be arbitrary, the continuum model is supported by X-ray absorption^{41,42}, ultrafast spectroscopy^{43,44}, temperature-dependent Raman and infrared studies^{35,45–47}, and theoretical calculations^{35,46}, which collectively indicate continuous structural fluctuations rather than sharp transitions.

Most pulsed-laser studies have largely focused on averaged SRS spectra in water^{13,17,48} and EtOH-water solutions⁴⁸. In contrast, pulse-resolved SRS studies remain limited, despite evidence of shot-to-shot fluctuations^{16,17,48}. To address this gap, we introduce a pulse-resolved, multimodal

synchronization approach. This method simultaneously acquires SRS signals, plasma emission, and acoustic responses for each individual laser pulse under varying experimental conditions. This approach enables quantitative analysis of single-pulse and averaged characteristics, as well as direct examination of correlations across different measurement modalities. Under this approach, we assess whether shot-to-shot fluctuations dominate multimodal responses, whether SRS variability reflects transient molecular structures, and how plasma formation is influenced by non-linear laser-matter interactions. We further examine whether HB networks behave as a continuum of configurations or as discrete structural states, and whether correlations exist between signals on a single-pulse basis. By addressing these questions, we aim to provide new insights into molecular structures and dynamics, the spatial and temporal evolution of plasma, and local pressure variations within the irradiated medium.

2 Experimental setup

Figure 1 shows the setup, which includes an unseeded neodymium-doped yttrium aluminum garnet (Nd:YAG) pulsed laser (Continuum, Powerlite 8010). The laser operates in several transverse modes and delivers a near-Gaussian beam profile (~ 0.95). The output is frequency-doubled via second harmonic generation (SHG) to produce a 532 nm beam with a pulse duration of $\sim 6 \text{ ns}$ (full-width half-maximum (FWHM)) at a repetition rate of 10 Hz. After passing through a half-wave plate, a Glan laser polarizer, and a 4 mm aperture for energy and beam shaping, the beam is focused by a 50 mm focal length lens into the center of a quartz cell ($10 \text{ cm} \times 5 \text{ cm} \times 1 \text{ cm}$) containing water or EtOH-water solutions. The cell was mounted in a fixed holder to ensure precise alignment. The focal spot size was estimated using the aperture-limited diffraction approach⁴⁹, yielding an Airy disk radius of $\sim 8.1 \mu\text{m}$. This method was selected because truncating the original beam introduces diffraction effects that broaden the focal spot beyond the Gaussian prediction. The pulse energies measured after truncation ($12.5\sim 34.0 \text{ mJ/pulse}$) were obtained using a power meter while considering transmission losses from optical elements along the beam path (lens and window). These losses were introduced by Fresnel corrections⁴⁹, while multiplying the measured pulse energy by the transmission coefficients for each optical interface (lens and window) encountered along the laser beam path. By applying a truncation factor of 0.84 to account for the reduced energy and considering both the pulse duration and calculated spot area, the resulting lower-bound estimates for peak power density range from about $0.8 \times 10^{12} \text{ W/cm}^2$ to $2.3 \times 10^{12} \text{ W/cm}^2$. SRS signals emerged above $\sim 12 \text{ mJ/pulse}$, corresponding to a peak power of 2.0 MW, which exceeds P_{cr} for self-focusing^{2,3,11}.

The laser lamps, Q-switch, and camera were synchronized

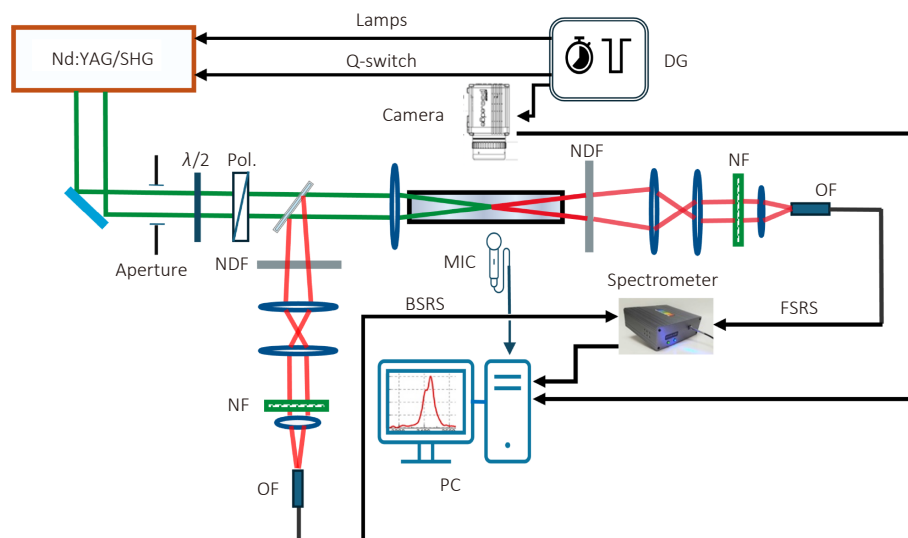


Fig. 1 | Schematic diagram of the experimental setup for backward and forward stimulated Raman scattering (BSRS and FSRS) measurements, plasma imaging, and acoustic detection. The system includes a neodymium-yttrium aluminum garnet (Nd:YAG) laser with a second harmonic generator (SHG), a delay generator (DG), a half-wave plate ($\lambda/2$), a polarizer (Pol.), neutral density filters (NDFs), a 532 nm notch filter (NF), an optical fiber (OF), a microphone (MIC), and a personal computer (PC).

using a time delay generator (DG) (Stanford research systems, DG535), ensuring that the camera was exposed for each pulse. BSRS and FSRS signals were attenuated with neutral density filters (NDFs), then collimated and focused via a microscope objective into an optical fiber (OF) coupled to a spectrometer (StellarNet, EPP2000) with a spectral resolution of 0.3 nm. Before entering the spectrometer, the signals passed through a 532 nm notch filter (NF) (IRID-IAN, ZX000515) with an optical density (OD) > 6. The spectrometer integration was timed to collect SRS spectra for each pulse, which were then correlated with camera images and acoustic data.

A complementary metal-oxide semiconductor (CMOS) camera (PCO.edge 4.2 LT) positioned above the quartz cell captured plasma emission, with DG timing adjusted for optimal exposure. Images were converted to 16-bit ASCII format and processed into 2D intensity maps. Simultaneously, acoustic waves generated by shockwave-cell interactions were recorded using a condenser omnidirectional microphone (Apex Electronics, APEX220; sensitivity: $-63 \text{ dB} \pm 3 \text{ dB}$) oriented toward the focal point and positioned 2 cm laterally from the largest cell facet, 1.5 cm above the laser beam, and 5 cm from the entrance cell wall). Acoustic signals were sampled at 176.4 kHz, converted to ASCII format, and analyzed for root-mean-square (RMS) intensity (see below). Increased pressures within the laser focal volume generated stronger acoustic waves, serving as proxies for shockwaves strength.

Measurements were performed at varying laser pulse energies and in different media, including double-distilled water (DDW), absolute dehydrated EtOH (Biolab Chemicals, AR > 99.9%, water < 0.2% w/w), and EtOH-water

mixtures of different concentrations. EtOH concentration was calculated as the volume ratio of EtOH to total solution. BSRS and FSRS spectra, along with plasma images, and acoustic signals were monitored for 180–200 laser pulses per run, with averages and scatters based on three runs for each condition. This was required since spectra appeared only in some pulses, necessitating a large number of pulses to achieve stable averaging.

3 Results and discussions

3.1 Backward and forward stimulated Raman

BSRS and FSRS spectra were obtained from successive laser pulses in pure water, EtOH-water solutions, and neat EtOH. Figure 2 shows representative single-shot spectra for water, 8%, and 50% EtOH solutions, as well as pure EtOH. For water and dilute EtOH (Fig. 2(a–d)), SRS signals appear in the $3000\text{--}3800 \text{ cm}^{-1}$ region, which is characteristic of O–H stretching^{17,50}. Under our experimental conditions, BSRS signal intensities exceeded FSRS by more than two orders of magnitude at comparable incident energies. This dominance is mainly due to the counter-propagating geometry of BSRS, which improves phase-matching, extends the pump-medium interaction length,⁵¹ and enhances coupling between spontaneous Raman scattering and the more intense propagating pump. Furthermore, plasma formation near the focal region may amplify BSRS by producing high temperatures that rapidly heat the surrounding medium, thereby creating thermal gradients and refractive index variations that alter phase-matching conditions⁵². Because BSRS propagates backward, it samples a wider range of

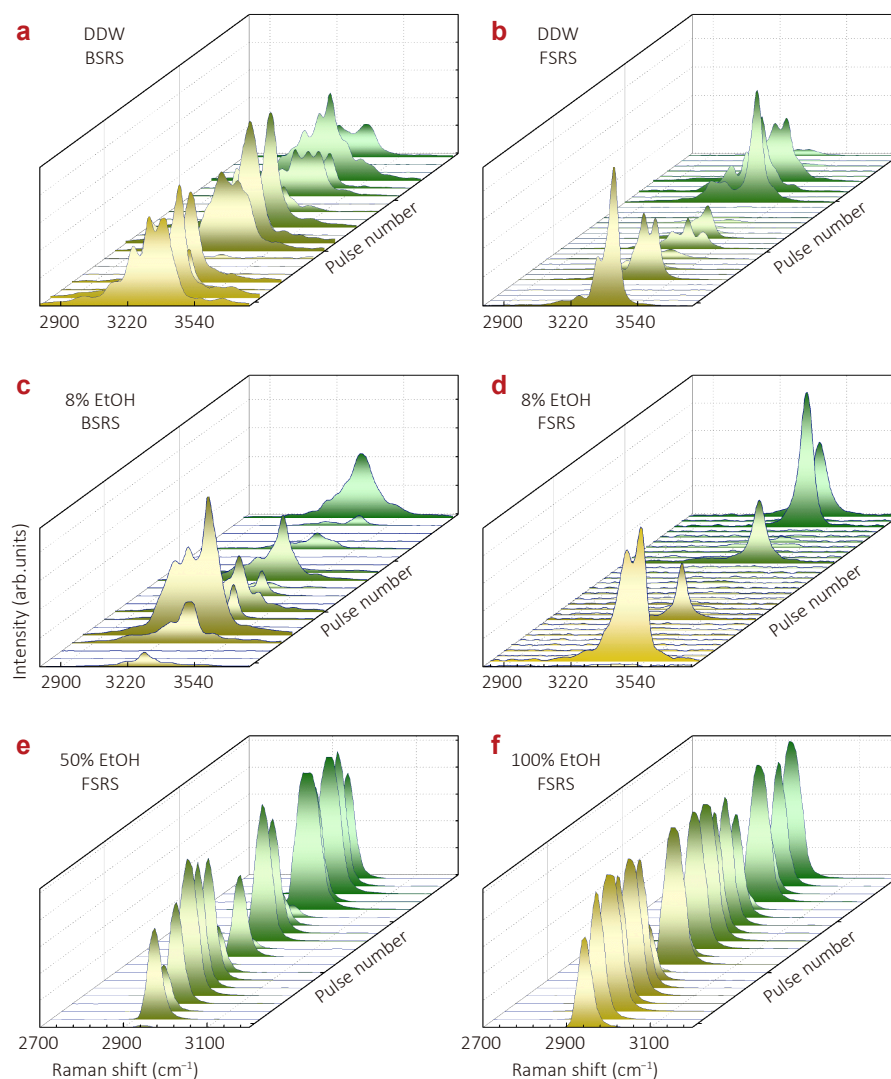


Fig. 2 | Single-shot backward stimulated Raman scattering (BSRS) and forward stimulated Raman scattering (FSRS) spectra showing (a-d) O–H and (e,f) C–H stretching regions for double distilled water (DDW), 8% and 50% ethanol (EtOH) solutions, and neat EtOH. Spectra were recorded at 28.2 mJ/pulse (BSRS) and 30.6 mJ/pulse (FSRS).

environments within the focal region. This results in broader and more complex spectral features that reflect differences in gain dynamics and sensitivity to medium fluctuations. For clarity, the datasets were scaled independently, and the graphs do not reflect absolute intensity differences between BSRS and FSRS.

Single-pulse SRS spectra revealed significant variability in the O–H stretching region ($3000\text{--}3800\text{ cm}^{-1}$) for water and dilute EtOH solutions (Fig. 2(a–d)), with fluctuating peak intensities and profiles. At higher EtOH concentrations, O–H signals became less frequent and weaker, while C–H stretching peaks^{53,54} around 2950 cm^{-1} emerged. Above 40% EtOH (Fig. 2(e–f)), these C–H peaks dominated the spectra and appeared consistently. Under repetitive pulsed excitation, O–H stretch BSRS spectra exhibited broader features than FSRS spectra and both showed distinct pulse-resolved

patterns that have not been previously reported. Earlier studies noted variability in the O–H stretch region^{16,17,48} but mainly focused on averaged spectra rather than individual pulses. Because O–H groups are involved in HB and their stretching modes are highly sensitive to it⁵⁵, unlike the C–H stretch modes, these findings suggest that O–H variability is intrinsic to thermal or structural changes within the dynamic HB network in water and EtOH-water solutions under intense pulsed radiation. Interestingly, although BSRS has been linked to spectral broadening compared to FSRS due to the pump pulse comprising numerous sequential sub-pulses, each undergoing cross-phase modulation through interaction with counter-propagating pump sub-pulses⁵⁶, our results (Fig. 2(a–d) and Fig. S1 of Supplementary information) show that only O–H spectra broaden, not C–H. Thus, broadening and single-shot SRS variability are

attributed to vibrational mode characteristics, requiring analysis that extends beyond simple averaging^{15,17,48}, which can mask rare spectral features related to transient water structures and EtOH solutions.

Figure 2 provides a qualitative view of the variability in pulse-resolved SRS signals. To quantitatively assess this variability, we introduce a metric to characterize the signal position, i.e., the center of intensity (CoI). The CoI is an intensity-weighted mean wavenumber, conceptually analogous to the center of mass and originally introduced for plasma emission analysis⁹

$$k_{\text{CoI}} = \frac{\sum_j k_j I_j}{\sum_j I_j}, \quad (1)$$

where k_j and I_j are wavenumbers and corresponding intensities. Particularly, we calculated CoIs for the O–H and C–H stretch regions using SRS datasets collected for water and various EtOH concentrations. To evaluate signal variability we determined the standard deviation of the CoI (σ_{CoI}) and its normalized value ($\sigma_{\text{CoI}}/\Delta\bar{\nu}$), accounting for the specific wavenumber interval ($\Delta\bar{\nu}$) where the O–H and C–H bands occur (Tables S1–S3 of Supplementary information). For FSRS of water in the O–H stretch region, the CoI is 3385.9 cm^{−1} with a normalized $\sigma_{\text{CoI}}/\Delta\bar{\nu}$ of 4.3%. In dilute EtOH solutions, the CoI is slightly higher with a comparable $\sigma_{\text{CoI}}/\Delta\bar{\nu}$ (Table S1 of Supplementary information). In contrast, for pure EtOH, the CoI in the C–H region is 2947.8 cm^{−1} with a much lower $\sigma_{\text{CoI}}/\Delta\bar{\nu}$ of 0.7% (Table S2 of Supplementary information). These values vary somewhat for solutions with decreasing ethanol content and indicate

that the C–H band is more stable in both shape and intensity than the O–H band.

Relying on the quantitative assessment of signal variability, Table S3 in the Supplementary information presents the averaged CoIs obtained from BSRS pulsed datasets, using the same approach as FSRS. Analysis of these calculated $\sigma_{\text{CoI}}/\Delta\bar{\nu}$ reveals that BSRS signals in the O–H stretch region, measured for pure water and dilute EtOH solutions, present consistently higher variation in signal position compared to the C–H region signals observed in the 24% EtOH solution. Notably, at 24% EtOH, both O–H and C–H stretch signals often appear within the same laser pulse, yet the variation in signal shape and intensity remains lower for the C–H region than for the O–H region. This distinction emphasizes the greater structural dynamics and heterogeneity present in HB environments, as opposed to the more stable C–H configuration under these experimental conditions.

To further quantify the observed variability in SRS signals, we extracted peak positions from single-shot SRS spectra, covering both C–H and O–H vibrational modes. For each spectrum, peaks were identified as local maxima within a 50 cm^{−1} window and required to exceed four times the noise threshold. These positions were recorded using a custom program recorded to generate frequency histograms for BSRS and FSRS (Fig. 3).

The histograms in Fig. 3 show that O–H stretch peak positions span the 3000–3800 cm^{−1} range, suggesting a broad distribution of HB energies. Certain peak positions, related to HB configurations, occur more frequently. For example, water (Fig. 3(a)) exhibits dominant peaks near 3410 cm^{−1}

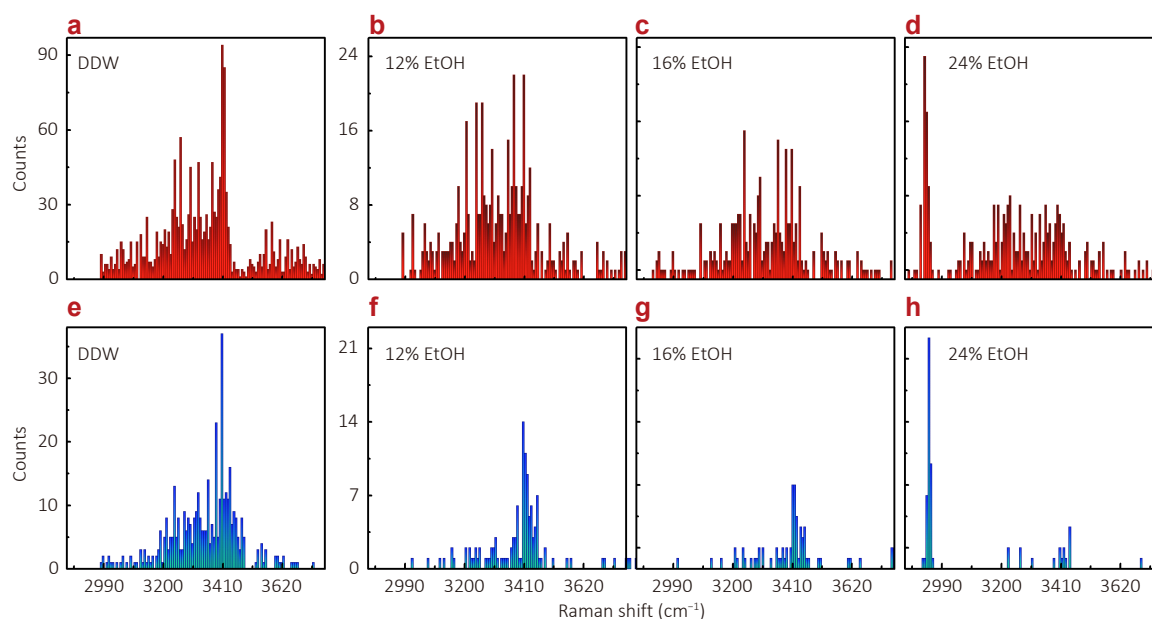


Fig. 3 | Histograms of peak frequency distributions in (a–d) backward and (e–h) forward stimulated Raman scattering (BSRS and FSRS) spectra for double distilled water (DDW) and 12%, 16%, and 24% ethanol (EtOH) solutions. Spectra were obtained with pulse energies of 28.2 mJ (BSRS) and 30.6 mJ (FSRS) and bin size of 7 cm^{−1}; counts represent local maxima in spectra exceeding four times the noise threshold.

(BSRS) and $\sim 3407\text{ cm}^{-1}$ (FSRS) (Fig. 3(e)). In EtOH-water solutions (Fig. 3(b–d) and Fig. 3(f–h)), the appearance of O–H peaks decreases as EtOH concentration rises, while C–H peaks ($\sim 2950\text{ cm}^{-1}$) appear sporadically at 16% and become prominent at 24% EtOH, Fig. 3(d,h), where O–H signals are faint and infrequent. The distribution of peak positions also shifts with EtOH content, with $\sim 3200\text{ cm}^{-1}$ gaining prominence over $\sim 3400\text{ cm}^{-1}$. At 24% EtOH, C–H stretch ($\sim 2950\text{ cm}^{-1}$) dominates, although some residual O–H signals persist.

While the histograms provide information on the positions and relative abundances of peaks in the O–H and C–H regions, they do not include intensity data. This highlights the importance of considering both spectral distributions and signal strength. Hence, averaged spectra serve as statistical representations rather than definitive profiles, especially given the pronounced shot-to-shot variability. As shown in Fig. 4(a), the average BSRS spectrum of water (red line) differs markedly from atypical single-shot spectra (dotted lines), which display distinct peaks or shoulders. These deviations suggest that single-pulse analysis can uncover rare molecular configurations and local microenvironmental fluctuations, highlighting the limitations of simple averaging. Nevertheless, our study is based on a finite number of single-pulse spectra and more extensive statistical sampling would further strengthen these findings.

In addition to quantifying the variability of individual pulse signals, we carried out an analysis of the averaged BSRS and FSRS spectra, measured under different conditions. This analysis, illustrated for selected examples, involved calculating averaged spectra for different numbers of pulses within each subset, as shown in Fig. S2(a–l) in the Supplementary information. Visual inspection shows that the similarity of the O–H or C–H spectra increases as more pulses are averaged. To quantify this convergence, we obtained mean absolute difference (%) as the number of pulses increased (Section S3 of the Supplementary informa-

tion). The results in Fig. S2(m,n) in the Supplementary information confirm that the average O–H or C–H spectra stabilize toward a consistent mean, requiring hundreds of pulses for O–H and only a few tens for C–H. This demonstrates that the C–H average spectra are notably stable even with a small sample size.

Building on this analysis of spectral convergence, we further examined the averaged BSRS (Fig. 4(b)) and FSRS (Fig. 4(c)) at different pulse energies. In both the backward and forward directions, signal strength increases with higher incident energy. When the normalized intensities for BSRS and FSRS are compared (see insets), the overall spectra are quite similar and tend to overlap. However, BSRS consistently exhibits a broader spectral profile than FSRS. This broader shape likely reflects the greater sensitivity of BSRS to slight changes in the molecular environment, which arises from its counter-propagating geometry and the complex dynamics within the focal region.

To further explore these spectral characteristics and the compositional trends of the solutions, we compared normalized averaged BSRS (red) and FSRS (blue) spectra across various EtOH concentrations (Fig. 5(a–f)). These comparisons consistently demonstrate that BSRS spectra are broader, slightly redshifted in the main peak, and exhibit more pronounced shoulders, compared to the narrower FSRS spectra. For example, in water (Fig. 5(a)), the BSRS spectrum shows a peak at 3407 cm^{-1} with a shoulder at $\sim 3270\text{ cm}^{-1}$, while the FSRS spectrum peaks at 3425 cm^{-1} and lacks a shoulder. These differences suggest that distinct interaction mechanisms underlie BSRS and FSRS processes. Importantly, the overall shape and features of the averaged water spectra are consistent with previous findings^{13,16,17,57}, despite differences in spectral resolution.

Averaged BSRS and FSRS spectra of aqueous EtOH solutions (Fig. 5(b–f)) show a consistent decrease in the intensity of the O–H dominant peak as EtOH concentration increases. Single-pulse analysis indicates that this reduction

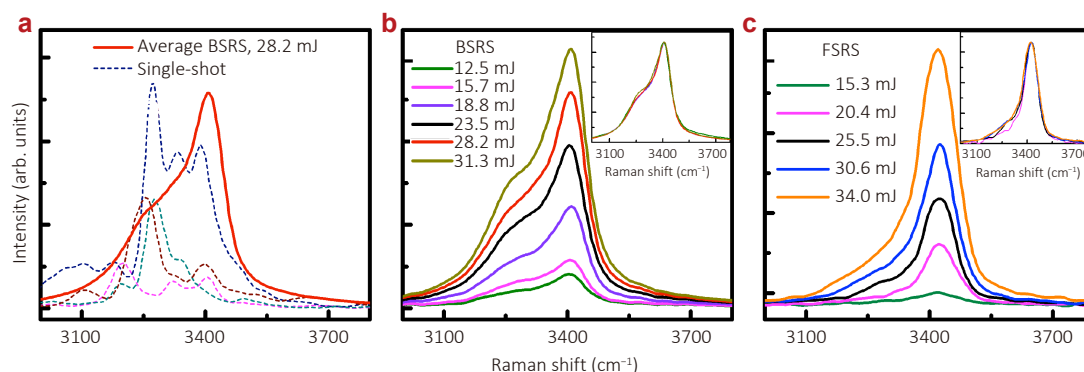


Fig. 4 | (a) Averaged backward stimulated Raman scattering (BSRS) spectrum of double-distilled water (DDW) (red line) with selected single-shot spectra (dotted lines) at 28.2 mJ/pulse; averaged (b) BSRS and (c) forward SRS (FSRS) spectra of DDW at varying pulse energies. BSRS and FSRS intensities are shown on separate scales and not directly comparable. The insets in panels (b) and (c) show the normalized BSRS and FSRS spectra, emphasizing their consistent spectral shapes.

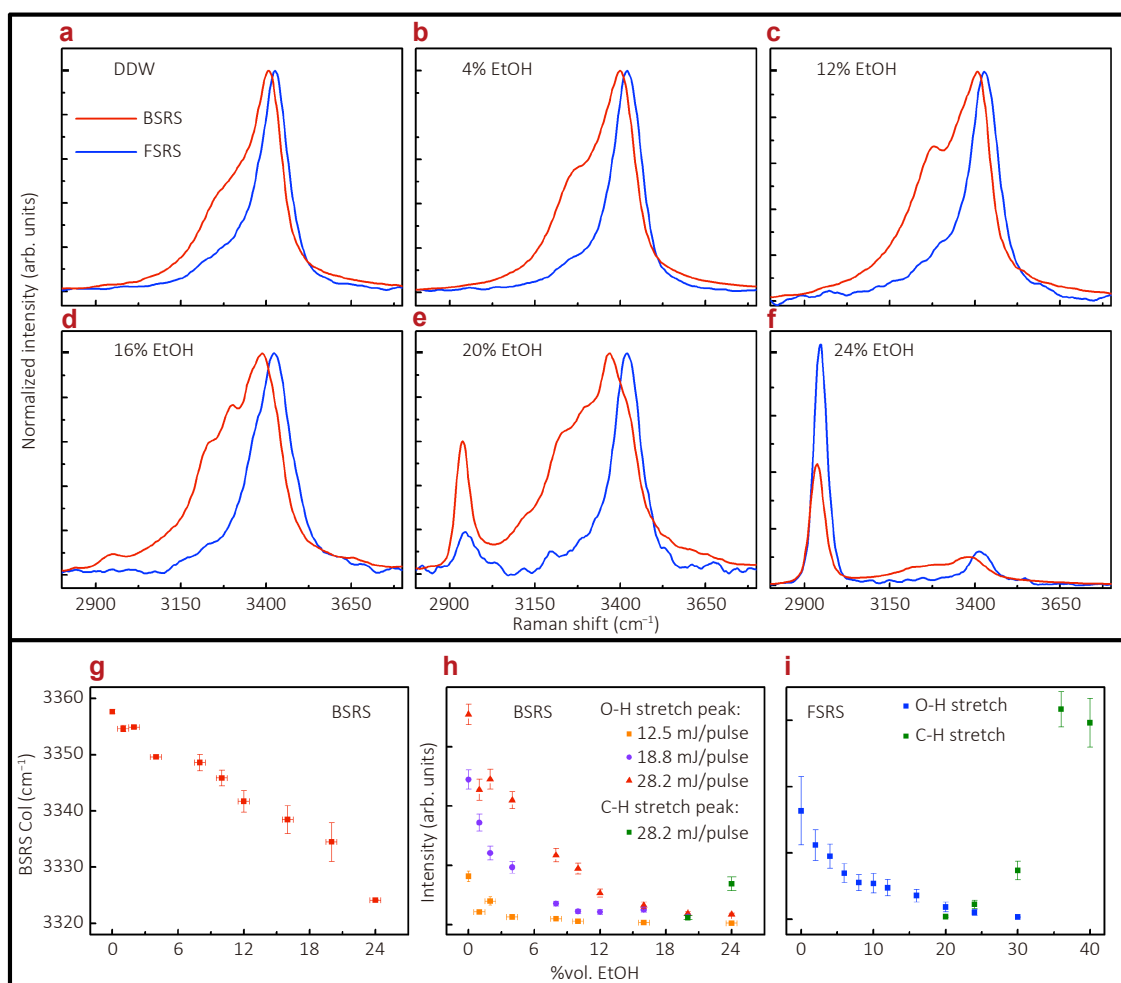


Fig. 5 | (a-f) Averaged backward and forward stimulated Raman scattering (BSRS and FSRS) spectra of double-distilled water (DDW) and ethanol-water solutions, recorded at pulse energies of 28.2 mJ (BSRS) and 30.6 mJ (FSRS). Each spectrum is normalized to the peak. Panels (g-i) show BSRS center of intensity, and maximum BSRS and FSRS peak intensities for O–H and C–H regions vs. EtOH concentration.

results from both fewer occurrences of O–H signals (Fig. 3) and lower intensity. While the FSRS peak shape remains largely unchanged, BSRS spectra evolve with increasing EtOH content. Particularly, the shoulder near 3270 cm⁻¹ becomes more pronounced and splits into two distinct features (~3325 cm⁻¹ and ~3300 cm⁻¹) by 16% EtOH (Fig. 5(d)). This transformation is consistent with the peak distributions in Fig. 3, which show more BSRS peaks in the 3200–3300 cm⁻¹ range. Since the O–H stretching frequency correlates with HB strength⁵⁵, these spectral shifts suggest that EtOH promotes stronger HB structures. This highlights the need for quantitative BSRS analysis. We attempted Gaussian deconvolution of averaged SRS spectra using a limited number of components following previous Raman and SRS studies^{17,39,40,58,59}. However, multiple valid fits and the assumption of linear independence and additive Gaussians proved unreliable, given the strong shot-to-shot variability. These limitations highlight the need for more robust, statistically driven metrics to characterize HB evolution.

To quantify spectral shifts, we treated the spectra as statistical distributions and applied the CoI, an intensity-weighted mean wavenumber (Eq. (1)). The CoI represents the mean position of the spectrum, therefore changes in its value indicate shifts in the mean HB energy within the liquid environment. We calculated CoIs from averaged BSRS spectra for water and EtOH solutions (Fig. 5(a–f)) over 3000–3800 cm⁻¹ range. As shown in Fig. 5(g), the CoI shifts progressively to lower wavenumbers with increasing EtOH concentration, totalling ~37 cm⁻¹ at 24% ethanol. This shift corresponds to an increase of ~1.39 kJ/mol increase in mean HB strength⁵⁵.

We also extracted the maximum O–H and C–H peak intensities from the averaged BSRS and FSRS spectra (Fig. 5(h,i)). In both measurement directions, O–H intensity decreases as EtOH concentration increases, while C–H peaks begin to emerge at 16% EtOH and become stronger at higher concentrations. Unlike a previous SRS report of O–H enhancement up to 10% EtOH⁵⁷, our results align with spontaneous Raman studies^{54,58,60}, which consistently show

O–H intensity attenuation with increasing EtOH concentration. Interestingly, at ~20%–24% (molar fraction ~0.07–0.09) the averaged SRS spectra (Fig. 5(h,i)) show nearly equal O–H and C–H peak intensities. To interpret this, we calculated the gain factor ratio² using

$$\frac{G_{\text{EtOH,CH}}}{G_{\text{water,OH}}} = \left(\frac{N_{\text{EtOH}}}{N_{\text{water}}} \right) \left(\frac{\beta_{\text{EtOH,CH}}}{\beta_{\text{water,OH}}} \right) \left(\frac{\tilde{\nu}_{\text{S,OH}}}{\tilde{\nu}_{\text{S,CH}}} \right)^2, \quad (2)$$

where N is the number density of molecules, β is the differential cross-section for C–H and O–H (1.37×10^{-29} and $4.96 \times 10^{-30} \text{ cm}^2 \text{sr}^{-1} \text{molecule}^{-1}$)⁶¹, and $\tilde{\nu}_s$ represents the peak wavenumbers ($\sim 3407 \text{ cm}^{-1}$ for O–H and 2940 cm^{-1} for C–H). This yields a gain factor ratio of 0.28–0.37. The observation of similar intensities despite differing gain factors suggests underlying structural changes within the HB network and possible signal amplification of the C–H signal.

To probe local changes in the HB network, we generated

difference spectra by subtracting the normalized BSRS spectrum of pure water from those of EtOH solutions, Fig. 6(a–h). These difference spectra provide a detailed view of how spectral features and their variability evolve as EtOH concentration rises. The summary plot (Fig. 6(i)) shows key trends across the data set, including a persistent peak near 3400 cm^{-1} and the emergence of low-frequency features that intensify and change shape with increasing EtOH concentration. While spectral changes are minor at 4%–12% EtOH changes, a sharp decline of the main peak and strong growth of low-frequency features above 16% EtOH indicate a significant transition in the HB network. More specifically, the difference spectra reveal a distinct peak at $3335\text{--}3360 \text{ cm}^{-1}$, attributed to HB EtOH clusters⁵⁸, and another at $3260\text{--}3271 \text{ cm}^{-1}$ in dilute solutions. Notably, above 16% EtOH, the latter feature splits into two components with slight blue and red shifts. These changes, further supported

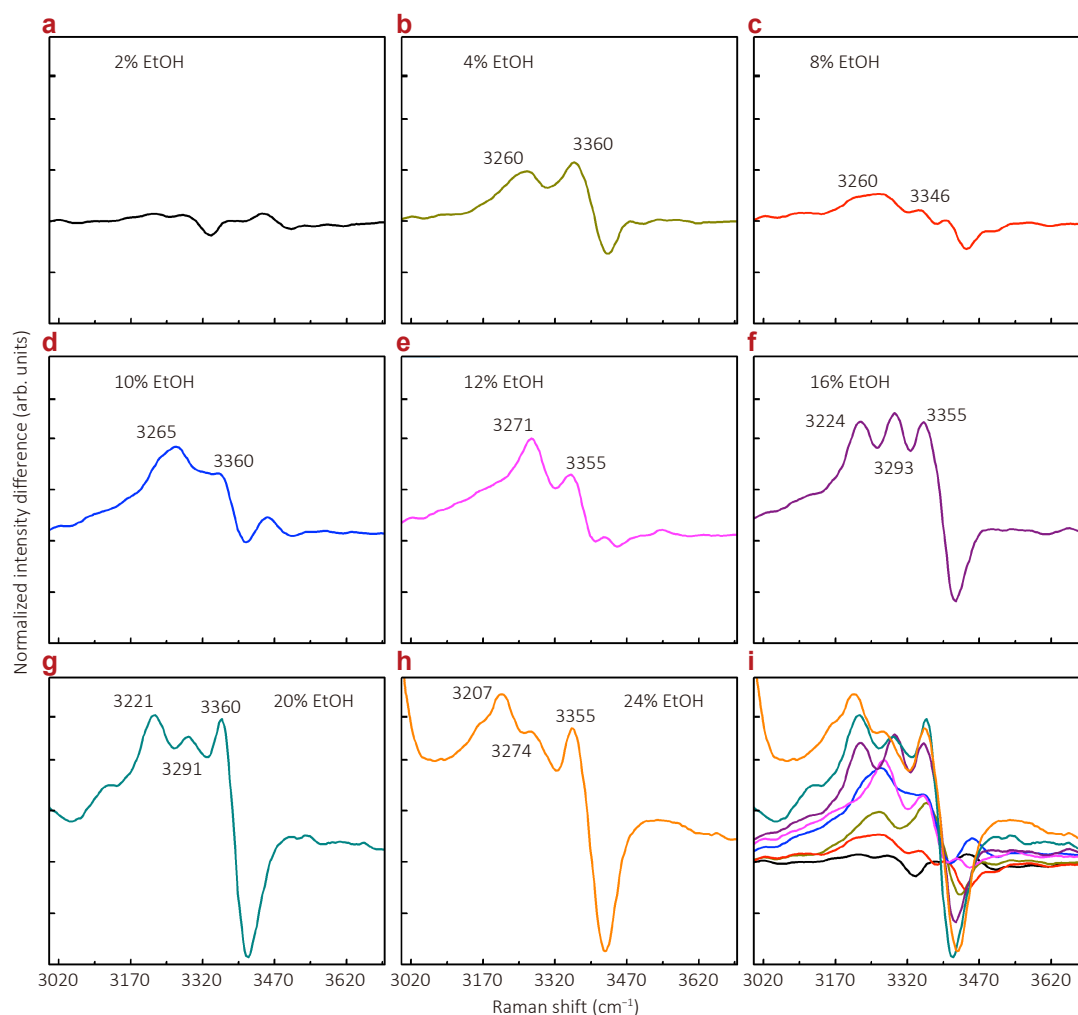


Fig. 6 | Difference spectra of backward stimulated Raman scattering (BSRS) for ethanol-water (EtOH-water) solutions at concentrations from 2%–24%. Panels (a)–(h) show difference spectra obtained by subtracting normalized BSRS of pure water from each solution; (i) summarizes spectral evolution. Key peak positions are indicated.

by peak histograms (Fig. 3) and CoI trends (Fig. 5(g)), indicate redistribution of HB strengths. Although O–H peaks persist, their distribution shifts toward stronger HBs, suggesting that increasing the EtOH concentration modifies the HB network.

Comparison with previous studies has to be made cautiously, as each used different EtOH concentrations and experimental intervals. Nevertheless, our observations qualitatively agree with prior FSRS measurements using ps pulses (10^{13} W/cm² and 20-shot averaging⁴⁸), which reported reduced intensity above 3440 cm⁻¹ and slight enhancement at lower wavenumbers for $\leq 9\%$ EtOH, interpreted as HB reinforcement. In contrast, our FSRS spectra (2.1×10^{12} W/cm²) show only minor shape changes, whereas the BSRS spectra reveal clear structural evolution, likely reflecting the higher sensitivity and the influence of experimental parameters. This trend of HB strengthening and subsequent structural transitions with increasing EtOH concentration is further supported by Raman studies^{54,58}. These studies identified HB strengthening up to $\sim 20\%$ EtOH, followed by weakening. Our findings agree with this trend and are also consistent with results from ¹H nuclear magnetic resonance (NMR)⁶², contact-angle⁶², and compressibility data⁶³ showing changes near 14%–17% EtOH. Additionally, transmission electron microscopy (TEM) imaging at 10% EtOH⁶⁴ and spectroscopic evidence^{54,58} further suggest the formation of clathrate-like structures, where water forms HB cages stabilized by EtOH.

Our CoI analysis (Fig. 5(g)) provides further evidence for the gradual enhancement of HB with increasing EtOH concentration. Specifically, the data supports earlier suggestions^{62,63} that below 16% EtOH, HB-enhanced EtOH-water clusters coexist with a predominantly tetrahedral water. Around 16% EtOH, the emergence of strongly bonded clathrate-like structures become apparent. As the EtOH concentration arises beyond this point (Fig. 6), the observed decline of the 3400 cm⁻¹ peak, together with the pronounced growth of low-frequency features, likely reflects the disruption of weak tetrahedral HBs^{65,66} and a shift toward stronger HB configurations, persisting up to $\sim 24\%$, with another transition near 25%⁵⁸. Although our measurements were performed with a limited set of concentrations and at room temperature, they point to possible structural transitions. Nevertheless, future systematic studies at varying concentrations (especially with finer gradients around 16% and 24%), as well as temperature and pressure should be conducted to obtain a comprehensive mapping of structural transitions and characteristics.

Understanding these spectral changes remains a complex and ongoing challenge. Although average Raman spectra are often deconvoluted into Gaussian or Gaussian-Lorentzian components^{39,40,54,58,59} to infer HB structure, decades of SRS and Raman studies^{13–17,40,54,57–59,65,67} have yet to reach consensus. Assignments vary widely, linking peaks to HB configurations^{58,65}, lattice arrangements^{13,14,68}, or photolysis and

photoionization products^{17,66}. Peaks above 3500 cm⁻¹ typically indicate weakly bonded or free O–H groups^{39,58,65}, while features below 3420 cm⁻¹ remain the subject of ongoing debate. For example, BSRS peaks in the 3360–3380 cm⁻¹ and 3270 cm⁻¹ regions have been associated with anionic water clusters $(\text{H}_2\text{O})_n^-$ ($n = 6, 7$) interacting with hydrated electrons during early irradiation^{66,69}. Additionally, BSRS spectra¹⁷ have also shown multiple shoulders between 3010 and 3900 cm⁻¹, which have been attributed to symmetric O–H stretching of liquid water, free water, and HB structures during electrons hydration and water ionization.

Other studies^{39,58,65} interpret spontaneous Raman peaks at 3200–3250 cm⁻¹ as in-phase vibrations of HB water molecules in tetrahedral structures. Deconvolution into five Gaussians^{39,40,58,59}, links O–H features to specific HB configurations and Fermi resonance effects^{70,71}. *Ab-initio* molecular dynamics (AIMD) simulations based on coupled-cluster (CC) theory⁷² reveal water as a mixture of double-donor (DD), single-donor (SD), and non-donor (ND) molecules in tetrahedral and ring-and-chain-like arrangements. Additionally, previous work proposed that peaks at 3000 – 3300 cm⁻¹ indicate ice VII formation under extreme pressures induced by intense laser irradiation⁷³ and recent BSRS/FSRS peaks^{13,14,74} were interpreted accordingly. However, ice VII formation occurs only after several ns⁷⁵, whereas time-resolved studies show SRS occurs within ~ 100 ps^{13,15,69}, too early for its detection. Furthermore, the broad band of spontaneous Raman spectra includes signals within this range^{39,40,54,58,65}, where pressures are insufficient for ice VII formation, demanding caution in such interpretation.

These varied interpretations reflect two competing models of water structure. The mixture model views water as a dynamic equilibrium of discrete species, forming the basis for Gaussian deconvolution of Raman spectra^{37,39,40}. In contrast, the continuum model, describes water as a 3D HBs network with a broad distribution of O–H $\cdots$ O HB angles and distances^{34,35,55,71}, producing a continuous range of vibrational frequencies. Pulse-resolved SRS complements established techniques such as temperature-dependent Raman³⁵ and infrared spectroscopies^{45,76}, and X-ray absorption spectroscopy⁴² for probing HB structures. Our observations (Figs. 2,3) reveal pronounced shot-to-shot variability in SRS spectra, showing that each laser pulse samples different HB configurations. This variability, along with the distributions shown in Fig. 3, substantiates the presence of a statistical spread of structures and provides further support to the continuum model^{35,42,47,71}, similar to frameworks proposed for spontaneous Raman^{36,71}. Importantly, this statistical continuity does not preclude the identification of distinct structural motifs, highlighting opportunities for more detailed structural analysis. At the same time, mixture models have historically been used to interpret the O–H stretching band in the vibrational spectra of water and aqueous solutions as arising from superposition of distinct

populations⁷⁷. This approach has proven valuable for assigning band components to specific HB environments, and for investigating how temperature, concentration, or solute-induced changes shift the balance between different structural motifs.

3.2 Plasma emission

Plasma emission was observed at the focal region with every laser pulse, occurring simultaneously with SRS and enabling pulse-resolved imaging of the plasma. Digital images (0.0703 mm/pixel) were converted into 2D intensity maps (Fig. 7(a–c)), presenting plasma brightness and axial distribution for the first two pulses at 30.6 mJ/pulse in both water and EtOH-water solutions. These 2D maps reveal notable variations in plasma shape, size, and intensity across samples and between pulses, without any statistical pattern. Importantly, although these maps are derived from the initial pulses of each experimental sets, they do not represent a typical or reproducible profile for the first- or second-pulse. Instead, slight variations occurred even among pulses with the same sequence number across different experimental

runs, as well as between consecutive pulses in the same run. To further quantify the axial emission distribution, the 2D maps were integrated into 1D profiles. Figure 7(d–f) show these time-series 1D profiles for consecutive pulses applied to water and EtOH solutions, providing a clearer view of the temporal evolution and variability of the plasma emission.

Across all conditions, plasma onset generally occurred before the beam reached the focal point (0.0 mm in Fig. 7). In water (Fig. 7(a)), plasma is concentrated near the focus, with discrete regions and minor upstream peaks. In contrast, EtOH-water solutions exhibit more continuous plasma profiles, suggesting altered breakdown dynamics. Analysis of consecutive profiles (Fig. 7(d–f)) revealed moderate variability for water and 12% EtOH, but at 36% EtOH variability becomes severe. Some pulses produced extremely high-intensity plasma, indicating unstable breakdown at elevated EtOH concentrations due to changes in optical and chemical properties.

Plasma characterization relies on 1D profiles, with total intensity calculated as the sum of values within the plasma region and position determined using the CoI concept, previously applied to plasma⁹ and SRS profiles (Eq. (1)).

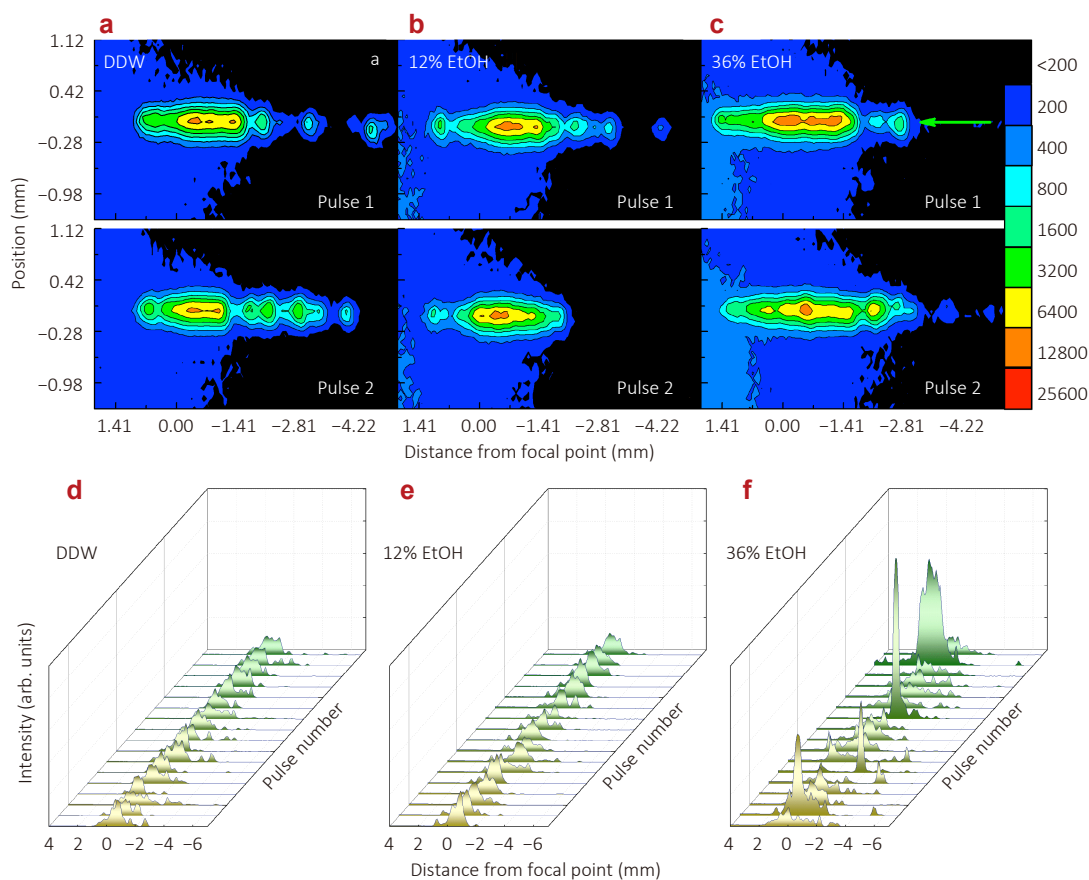


Fig. 7 | Two-dimensional plasma intensity maps for the first two pulses (30.6 mJ/pulse) in (a) double-distilled water (DDW), (b) 12%, and (c) 36% ethanol-water (EtOH-water) solutions. Green arrow indicates laser beam propagation; focal point at 0.0 mm. Color scale shows pixel intensity. Panels (d-f) present pulsed-resolved one-dimensional longitudinal profiles of plasma intensity for each experimental condition.

CoI and total intensity were computed for each pulse, and sequences of consecutive values were analyzed to assess variability. Scatter plots of pulse-resolved plasma intensities (Fig. 8(a–c)) and CoI positions (Fig. 8(d–f)) for water and EtOH-water solutions (12% and 36%) reveal no consistent trend across samples. However, pronounced variability at 36% EtOH is evident in both total intensity (Fig. 8(c)) and CoI distribution (Fig. 8(f)), indicating that higher EtOH concentration introduces instability in plasma formation.

The high variability in plasma emission (Fig. 7(f)) and the fluctuations in the scatter plots (Fig. 8(c,d)) for the 36% EtOH solution, compared to lower EtOH concentration, likely reflect underlying micro-heterogeneity in the solution. Ethanol-water solutions in the 36%–86% range (molar fraction 0.15 to 0.65) are known to exhibit coexistence of ethanol-rich and water-rich domains⁷⁸. This leads to local variations in refractive index and density, which change nonlinearly with ethanol concentration^{79,80}. At intermediate concentrations, these effects cause more structural fluctuations and possible phase separation, ultimately affecting plasma formation, acoustic wave propagation, and signal variability due to local variations.

Unlike the previous study⁹ using water targets and 9 ns (FWHM) pulses at 1064 nm (peak power density 3×10^{11} W/cm²), which reported downstream CoI shifts for the first ~20 pulses before stabilizing at the focus, our data show no systematic relationship between pulse number and either CoI or total intensity. Under our conditions, shorter wavelength (532 nm) and higher peak power density

(10^{12} W/cm²), this discrepancy likely reflects differences in laser-matter interactions and experimental factors. At these intensities, plasma onset occurs earlier along the propagation axis, likely due to increased local energy density from non-linear self-focusing caused by the intensity-dependent refractive index². Additionally, water ionization energy is 12.62 eV⁸¹, while photon energies at 532 nm and 1064 nm are 2.33 eV and 1.17 eV, respectively, meaning different photon numbers are required for multiphoton ionization, influencing plasma dynamics. Future studies should explore whether a threshold in power or wavelength triggers the pulse-number dependence in plasma behavior.

Considering the relatively mild shot-to-shot variability observed in water, profiles were averaged to compare longitudinal plasma intensity (Fig. 9(a)) and total emission (Fig. 9(b)) across different pulse energies. Both metrics increase with energy, reflecting more effective ionization and higher electron density. Notably, the average profiles reveal asymmetry around the focal point, with plasma extending upstream. As the pulse energy increased, both the onset and the peak of plasma intensity shifted upstream [dashed line in Fig. 9(a)], while the termination point remained ~1 mm beyond the focus. This asymmetry likely arises from reduced downstream transmission⁵ and enhanced plasma-induced scattering, probably also contributing to the lower FSRS intensity compared to BSRS. To quantify plasma profiles displacement, we calculated the CoI (Eq. (1)) for each averaged profile in Fig. 9(a) and determined profile width as FWHM. CoI and FWHM values were plotted

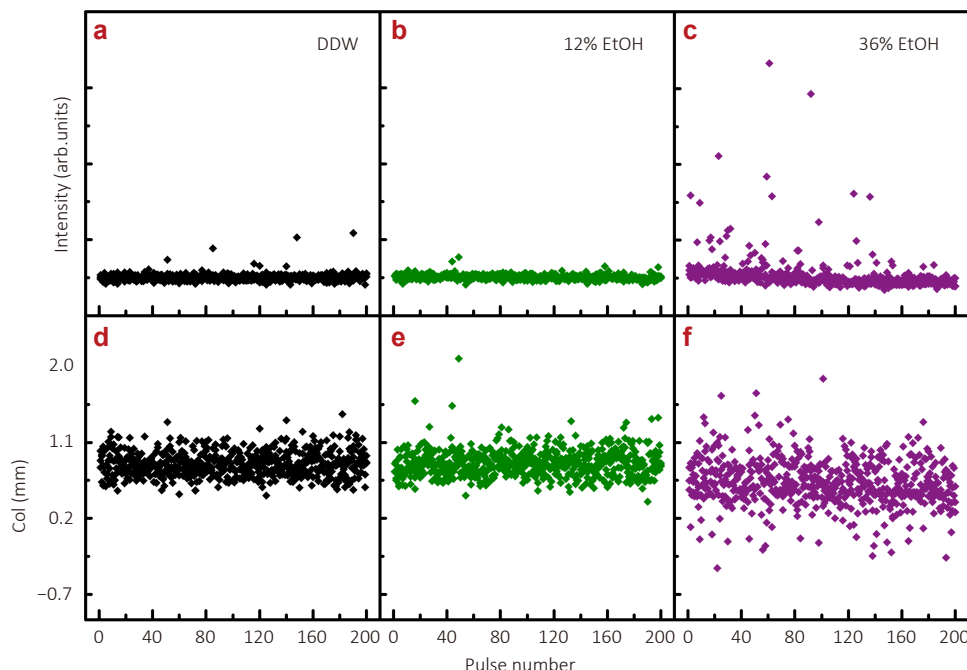


Fig. 8 | Scatter plots of pulse-resolved plasma characteristics: (a–c) Integrated plasma intensity for double-distilled water (DDW) and ethanol-water (EtOH-water) solutions (12% and 36%), and (d–f) corresponding center-of-intensity (CoI) values.

against P/P_{cr} (Fig. 9(c,d)). Increasing P/P_{cr} from 1.2 to 4.0 produced a 0.4 mm upstream shift in plasma position (CoI) with a linear trend across $1 \leq P/P_{cr} \leq 4$; however, linearity is unlikely to hold at higher powers. In contrast, FWHM becomes nonlinear beyond $P/P_{cr} \approx 3.0$, Fig. 9(d).

To assess the spatial displacement of plasma profiles (Fig. 7(a)), we model the effect of self-focusing as a virtual thin lens, with focal length $f_2 = z_{sf}$, positioned in series with the experimental lens (Fig. 9(e)). The effective focal point of

this combined system is estimated by x_{CoI} , which serves a practical marker for the plasma position. The separation between these two lenses is denoted by d . The relationship between the effective focal length (f_{eff}) of the system, and of the experimental lens (f_{lens}) and self-focusing lens (f_2) is given by⁴⁹

$$\frac{1}{f_{eff}} = \frac{1}{f_{lens}} + \frac{1}{f_2} - \frac{d}{f_{lens}f_2}, \quad (3)$$

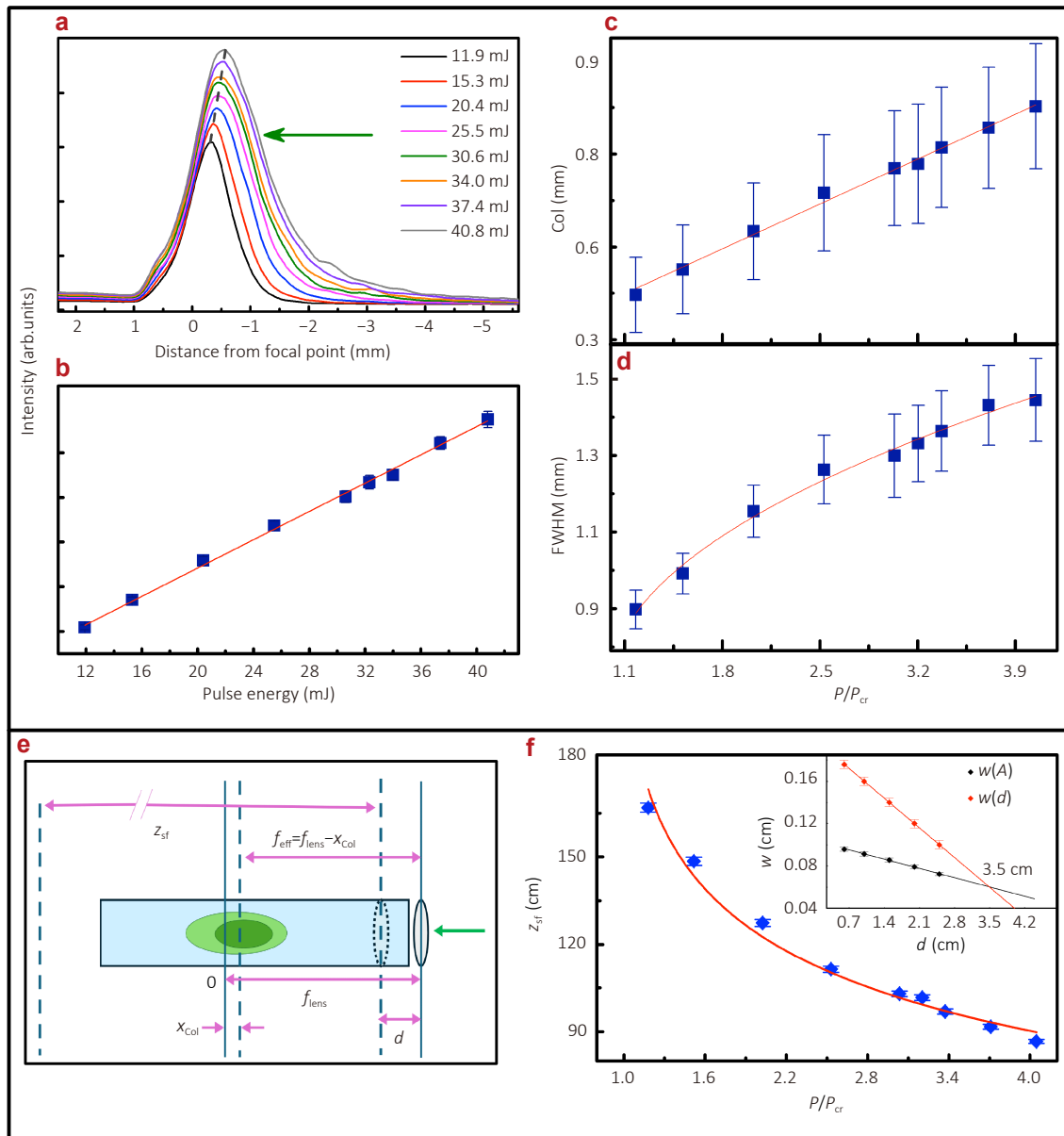


Fig. 9 | (a) Averaged one-dimensional (1D) plasma intensity profiles for different incident pulse energies in pure water; green arrow shows beam direction, dashed line marks upstream shift. (b) Total plasma emission vs. pulse energy; (c,d) Plasma profile dependence on power/critical power (P/P_{cr}): (c) Center of intensity (CoI) and (d) full-width half-maximum (FWHM) (trend line for visual guidance). (e) Schematic of focal distances: solid-lines represent the experimental lens, dotted-lines illustrate effective focusing from self-focusing; green arrow indicates beam direction. (f) Self-focusing distance (z_{sf}) vs. P/P_{cr} , derived from CoI using Eq. (3) and $d = 3.50$ cm; curve fitted with Levenberg-Marquard algorithm ($R^2 = 0.97$). Inset: two linear fits for $w(A)$ and $w(d)$ across five d distances, showing intersection.

where $f_{\text{lens}} = 5.0$ cm, $f_{\text{eff}} = f_{\text{lens}} - x_{\text{CoI}}$ and $f_2 = z_{\text{sf}}$, Fig. 9(e). Solving for z_{sf} gives

$$z_{\text{sf}} = \frac{(5.0 - d)(5.0 - x_{\text{CoI}})}{x_{\text{CoI}}}. \quad (4)$$

By varying d (the distance from the lens to the water cell, ranging from 0.6–5.0 cm) and using x_{CoI} values from Fig. 9(c), we computed z_{sf} via Eq. (4) for each configuration. These values are then plotted against the normalized laser power (P/P_{cr}). Each $z_{\text{sf}}(d)$ dataset was fitted to the nonlinear model²

$$z_{\text{sf}} = \frac{A}{\sqrt{P/P_{\text{cr}} - 1 + B}}, \quad A = \frac{1}{2}kw^2, \quad (5)$$

where A and B are positive fitting parameters, k is the laser wavenumber, and w the beam radius at the virtual lens. Thus, the beam radius at the virtual lens is

$$w_A(d) = \sqrt{\frac{2A}{k}}. \quad (6)$$

Alternatively, geometric optics provides an independent estimate for the beam radius as a function of d

$$w(d) = 0.2(5.0 - d)/5.0, \quad (7)$$

where 0.2 cm is the beam radius at the lens. Using fitted A and k for 532 nm in water, $w_A(d)$ was calculated for each $A(d)$. By plotting $w_A(d)$ and $w(d)$ vs. d , two linear trends emerge, intersecting at $d = 3.50$ cm (Fig. 8(f), inset). This intersection was used to finalize the z_{sf} vs. P/P_{cr} plot, showing strong agreement between the analytic and geometric approaches. The result indicates self-focusing begins after the beam propagates a distance d from the lens, reaching a radius of ~ 0.06 cm.

Plasma formation and self-focusing are competing processes, where self-focusing increases the local energy density, triggering nonlinear effects and plasma generation, while plasma formation dissipates energy through ionization and emission, thereby weakening self-focusing. This interplay likely accounts for the smaller plasma peaks observed prior the main burst (Fig. 7(a)). In the nonlinear fit shown in Fig. 9(f), it is assumed that i) the CoI represents the plasma position and ii) this position corresponds to the effective focal point created by the combined real and virtual lenses. While the CoI may also be influenced by additional factors such as laser and plasma scattering, local refractive index changes, and microbubble formation during breakdown, it remains a practical indicator for the region where the laser intensity exceeds the ionization threshold. The observed dependence of z_{sf} on P/P_{cr} (Fig. 8(f)) together with the agreement with Eq. (5) supports the conclusion that self-focusing is a key driver of plasma generation in water. Thus, the plasma CoI serves as an effective, though not absolute, marker for the self-focusing region, and the applied approximation yields a lower-bound estimate for the self-focusing distance. Future high-power studies could further clarify the

relationship between CoI and self-focusing, as well as the limits of the linear trend in Fig. 9(b).

Introducing EtOH into water alters the density, ionization potential, structure, and both linear and nonlinear refractive indices^{79,82} of the solution, thereby affecting self-focusing and plasma generation. To explore these effects, we measured averaged plasma emissions at 30.6 mJ/pulse for EtOH concentrations up to 50%. The resulting profiles show reduced peak intensity and broader plasma regions (Fig. 10(a,c)) as EtOH concentration increases, reflecting the evolution of the above parameters. These changes, combined with increased absorption, alter both self-focusing and the spatial distribution. Notable, peak intensities from 1D profiles (Fig. 10(b)) show a slight increase at 2% EtOH, a decline beyond 8%, and a secondary rise at 36%, reflecting the interplay of several factors: the lower ionization energy of EtOH (10.2 eV vs. 12.6 eV for water⁸¹) enhances plasma at low concentrations, while refractive index and plasma transmission changes^{5,79,82} affect beam propagation. The anomalous behavior at 36% EtOH likely results from sporadic high-intensity events (Fig. 7(f)), possibly linked to shifts in ionization mechanisms or micro-heterogeneity in the solution. Integrated emission shows no clear trend, except for a rise at 36%, suggesting spatially extended plasma and local instabilities. Moreover, to quantify profile spread, we treated intensity as a distribution and computed the square root of second moment⁸³. Averaged CoI and width (Fig. 10(c,d)) show clear broadening with rising EtOH concentration, while the CoI remains relatively stable up to 24% and shifts downstream beyond 30%, indicating weakened self-focusing, altered ionization dynamics, and changes in the HB network.

Complementing these findings, the spectral signatures in Figs. 5,6 further support the interplay between molecular structure and plasma behavior. Specifically, these spectra reveal that increasing the EtOH concentration not only modifies the HB network in solution but also influences the conditions under which breakdown occurs. Prior Raman studies⁵⁸ identified structural transitions within the 25%–44% EtOH concentration range, characterized by reorganization of the HB network and the formation of molecular clusters and micro-heterogeneity. These changes impact local density and optical properties which in turn can alter the nonlinear optical response of the medium.

3.3 Acoustic signals

Figure 11(a,b) shows two representative acoustic signals generated by 10 Hz laser pulses in pure water and EtOH-water solutions. Each pulse produces a distinct acoustic waveform, where in water, the signals remain relatively consistent, while the introduction of EtOH alters signal intensity and duration. To quantify these effects, RMS intensity was calculated for each pulse. In addition, to further characterize acoustic dynamics, we analyzed the

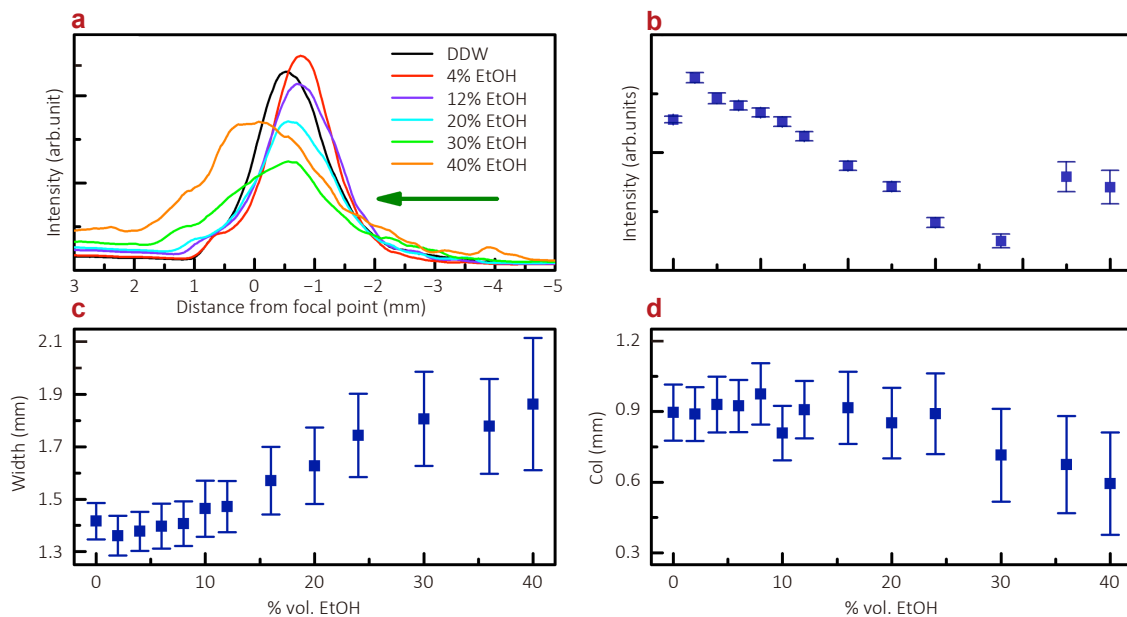


Fig. 10 | (a) Averaged one-dimensional (1D) plasma intensity profiles at 30.6 mJ/pulse for double-distilled water (DDW) and ethanol (EtOH) solutions at varying concentrations; green arrow indicates laser beam propagation. (b) Peak intensity values from profile maxima, (c) Plasma width (σ), and (d) Center of intensity (Col), plotted as functions of % EtOH.

temporal evolution of single-pulse RMS intensity for water and across varying EtOH concentrations. As shown in Fig. 11(c), water produced relatively stable signals, whereas EtOH-containing solutions (Fig. 11(d,e)) exhibit greater fluctuations and a systematic decrease in intensity with successive pulses. Notably, higher EtOH concentrations reach stability more rapidly, suggesting that EtOH accelerates stabilization of acoustic dynamics. This behavior likely arises from changes in physical properties such as density, viscosity, absorption, and ionization introduced by EtOH.

Grouping RMS intensities into 1.4 s time bins (Fig. 11(f)) reveals a gradual decline followed by steady state plateau, with higher EtOH concentrations promoting a faster transition. This trend may be attributed to the formation of cavitation bubbles near the laser focus and their persistence between laser pulses, a phenomenon amplified by the EtOH effect on local density. Similar bubble dynamics have been reported^{9,11}, and are known to influence spectroscopic and plasma measurements. Finally, when averaging RMS intensity across different EtOH concentrations (Fig. 11(g)), a clear decrease is observed with increasing EtOH content. This reduction is most likely due to structural and density changes in the solution, which affect the propagation and characteristics of acoustic waves.

These acoustic signals and their dependence on EtOH concentration raise questions about the relationship between local pressure conditions and spectroscopic features. Previous studies^{13,14,74} have linked specific SRS peaks to formation of ice-VII under the extreme pressures generated by intense laser pulses. In our experiments, the acoustic waves origi-

nate from shockwaves caused by these high-pressure events, suggesting that the RMS acoustic intensity reflects focal pressure conditions. By recording acoustic and SRS signals simultaneously, we were able to pair the acoustic response for each pulse with the corresponding BSRS/FSRS spectra, and plot RMS intensity against both integrated intensity and Col. The resulting scatter plots (Fig. 11(h,i) and Fig. S3 of Supplementary information) show significant shot-to-shot variability. This variability is likely due to fluctuations in plasma formation, phase-matching conditions, and local power density near the focal region. Importantly, our analysis shows no meaningful correlation between acoustic RMS intensity and SRS features, implying that pressure has a limited influence on the spectral shape or intensity of SRS signals under these conditions. While the pressure dependence of ice-VII vibrational spectra⁷³, and earlier discussion in the SRS section raise questions, our findings suggest that SRS may not be a definitive probe for ice-VII formation. Consequently, spectral features previously attributed to ice VII may instead arise from alternative mechanisms, such as transient molecular configurations or dynamic changes in the HB network.

4 Summary

This study introduces a pulse-resolved multimodal synchronization approach for investigating the intricate dynamics of SRS, plasma emission, and acoustic wave generation in water or EtOH-water solutions under intense laser irradiation. By synchronously acquiring these signals for each

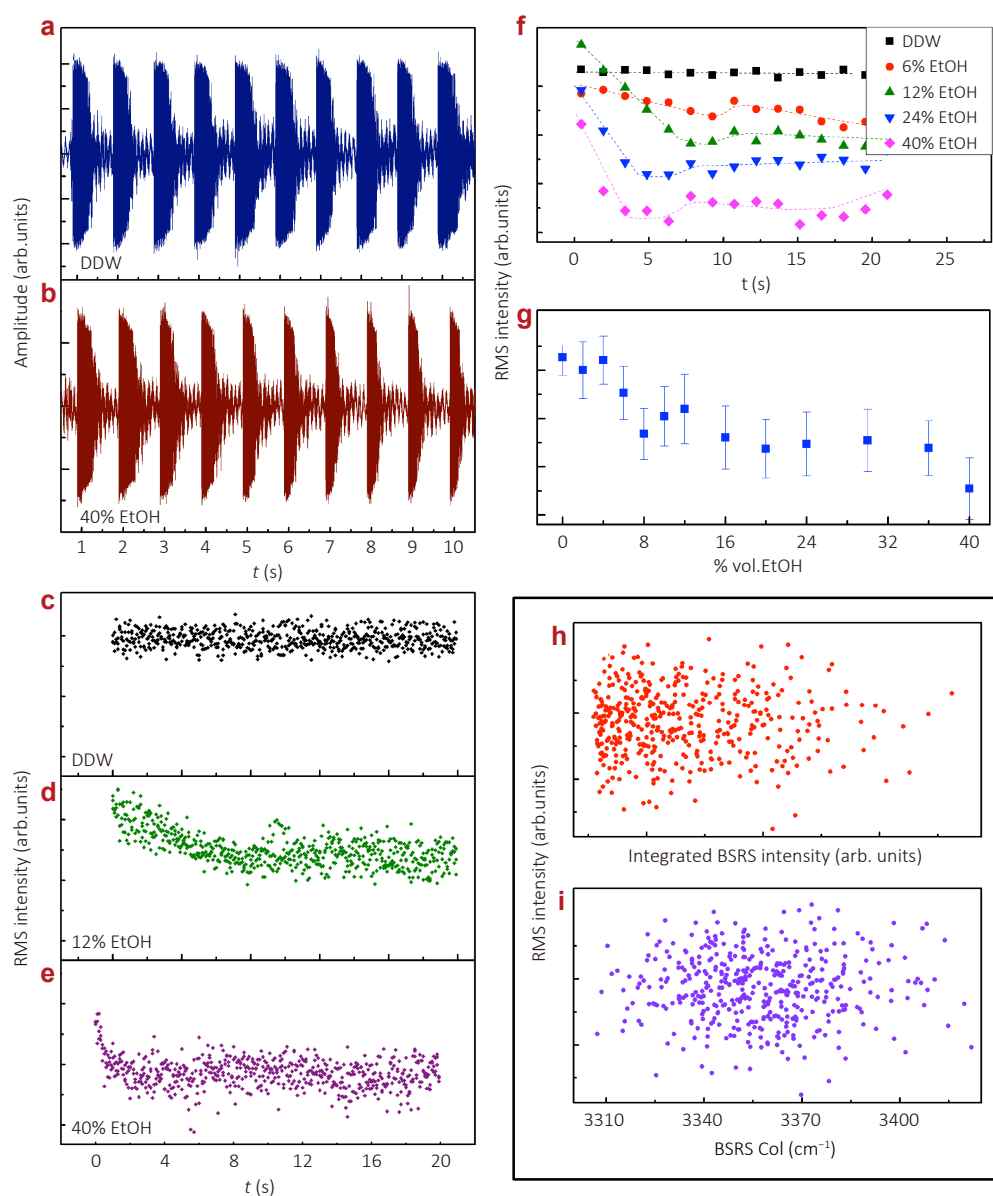


Fig. 11 | Acoustic signals generated by 30.6 mJ laser pulses at 10 Hz in double-distilled water (DDW) and ethanol-water (EtOH-water) solutions: (a,b) first ten consecutive pulses, (c-e) single-pulse root-mean-square (RMS) intensity over time, (f,g) 1.4s (14-pulse) binned averages with dashed lines for visual guidance and mean RMS intensity vs. EtOH concentration; (h,i) Scatter plots showing RMS intensity vs. backward stimulated Raman scattering (BSRS) intensity (water, 28.2 mJ/pulse) and vs. BSRS center of intensity (Col) across the O–H stretch region.

individual laser pulse, we uncover dynamic processes that are often masked in averaged measurements and the interplay between them, offering a more nuanced understanding into nonlinear optical phenomena in liquids.

A central finding is the pronounced shot-to-shot variability observed in the O–H stretching bands in water through both BSRS and FSRS. This variability reflects transient molecular configurations and fluctuations in the HB network. Our approach uniquely employs statistical analysis of single-pulse spectra, which reveals a broad distribution of vibrational frequencies and the presence of molecular configurations and suggesting that averaged spectra reflect

statistical representations rather than definitive profiles. These insights challenge traditional assignment of spectral features to discrete species and rather support a continuum model of HB configurations, highlighting the importance of pulse-resolved analysis for obtaining the molecular dynamics in liquids.

The addition of EtOH to water significantly affects the intensity and distribution of O–H stretching bands in pulse-resolved and averaged SRS spectra, with a transition to C–H dominated features at higher EtOH concentrations. Quantitative analysis of BSRS Col reveals a progressive shift to lower wavenumbers in the O–H stretch region with

increasing EtOH content, corresponding to an increase in mean HB strength. Notable, a structural transition is observed at ~ 16% EtOH, where the HB network reorganizes, favoring clathrate-like and molecular clustering. These changes are corroborated by peak histograms and difference spectra, which show a redistribution of HB strengths and alterations in spectral features shape. Our findings agree with previous Raman and NMR studies, highlighting the complex interplay between molecular structure and spectroscopic response.

Plasma diagnostics provides evidence that, under our conditions, self-focusing is a key nonlinear process driving plasma formation upstream of the geometric focal point. The interplay between self-focusing and plasma generation is modulated by EtOH concentration, which alters the HB network, density, ionization potential, and both linear and nonlinear refractive indices. Analysis of plasma emission profiles and CoI shifts demonstrates that self-focusing begins after the beam propagates a threshold distance from the lens, with the plasma position marking the onset of dominant nonlinear optical phenomena. The spatial displacement and broadening of plasma emission profiles with increasing EtOH concentration reflect changes in optical and chemical properties, as well as the evolution of the HB network. Particularly in EtOH solutions, CoI shifts at 24–30% EtOH suggest structural changes and altered physical properties due to the micro-heterogeneity of the samples. These observations highlight the complex interplay among molecular structure, nonlinear optical effects and plasma behavior in irradiated liquids.

Acoustic measurements reveal further insight into the cumulative effects of repeated pulses on the liquid. In water, acoustic signals remain relatively stable, while EtOH containing-solutions exhibit greater fluctuations and a systematic decrease in intensity with successive pulses, reaching stability more rapidly at higher EtOH concentrations. This is corroborated by grouping of RMS intensities into time bins, revealing a gradual decline followed by a steady-state plateau, with higher EtOH content accelerating this transition. This behavior is attributed to changes in density, viscosity, absorption, and ionization, as well as the formation and persistence of cavitation bubbles near the laser focus. Importantly, no meaningful correlation is found between acoustic RMS intensity and SRS features, indicating that pressure has limited influence on SRS spectral characteristics under these conditions. This challenges previous interpretations that have attributed specific SRS spectral features to high-pressure phases such as ice-VII. The absence of such a link suggests that the observed SRS signatures may instead arise from transient molecular configurations or dynamic changes in the HB network.

Overall, the pulse-resolved, multimodal synchronization approach developed in this study enables capturing both single-pulse and averaged characteristics, and direct examination of correlations between modalities. This analysis

provides new insights into molecular structures, plasma evolution, and local pressure variations in irradiated media. This methodology is a valuable tool for investigating ultrafast processes, phase transitions, and nonlinear optical phenomena in a wide range of chemical and biological systems. Combining this approach with systematic variation of experimental parameters (concentration, temperature, and pressure, as well as laser parameters), statistical analysis, molecular dynamics simulations, and advanced theoretical models is expected to further clarify the fundamental mechanisms and structural transitions in a wide range of chemical and biological systems, opening a window to future innovation in laser-matter interaction studies.

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Author contributions

Conceptualization, I.B.; methodology, investigation, and data analysis, Z.B.; interpretation of results, Z.B. and I.B.; writing—original draft preparation, Z.B.; subsequent writing, review, and editing, I.B.; supervision, I.B. All authors have read and agreed to the published version of the manuscript.

Competing interests

The authors declare no competing financial interests.

Supplementary information

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