ELECTRONIC SUPPLEMENTAL INFORMATION

Materials and Methods: The Vibrational Raman Spectra of Electrical Polarization in Liquid Water

The electric field was produced using a point-plane electrode geometry and is illustrated in Figure 1, panel a. Type I HPLC grade purified water (18.2 MΩ, Cat No. ZMQSP0D01, Millipore Corp., MA, USA) or purified heavy water (99.9% D_2O, DLM-4-100, Cambridge Isotope Laboratories, Inc., Andover, MA, USA) was filled into a glass cuvette (52 mm x52 mm x 1 mm, Cat. No. 704.003, Hellma analytics, Müllheim, Germany), and this was then placed in between the electrodes. The planar electrode is made from copper foil (Cat. No. 1181 3M, MN, USA) and connected to the high voltage output of a DC power supply (HCP 30000-300, FuG Elektronik GmbH, Schechen, Germany). The planar electrode and cuvette were covered with polyethylene film to reduce corona discharge and ion generation, note that this was more effective with positive polarity high potential than with negative, as evidenced by the difference in current draw for the same magnitude of applied potential. The planar electrode was placed directly beneath the bottom of the cuvette. A stainless steel acupuncture needle (SJ.25x40, 40 mm x 0.25 mm, Seirin Corp., Shizuoka, Japan) was used to form the point electrode and connected to the ground terminal of the high voltage source. The electrode was affixed to a rigid insulating armature constructed from polypropylene. The needle was bent at a right angle 5 mm beyond the handle in a manner so as to prevent the electrode from blocking the incident laser beam. For each experiment the electric potential was set to ±20 kV and applied as a step function. During operation a small leakage current 1-10 μA could be measured. Twenty milliliters (12.5 mL) of water were used for each measurement. This brought the liquid surface to a height of 25 mm from the bottom of the cuvette and the tip of the needle was submerged 4 mm below the liquid surface.

For the Raman measurements a collimated and polarization controlled beam from an argon ion laser (Innova 6W Ar+, P=400 mW, 514.5 nm, 1.5 mm beam diameter, 0.5 mrad divergence, Coherent, USA) was guided into the cuvette either perpendicular to the liquid surface. The focal spot size is 150 μm and the confocal parameter is 58.89 mm which is broader than the entire sample cuvette. Thus it is assured that within the interrogated spectral imaging region the illumination power and beam shape are uniform. The Stokes shifted Raman scattered light was collected using a photographic lens (Mamiya Secor SX135 mm F 2.8, Mamiya, Japan) positioned to image the fluid region nearest the tip of the needle onto the entrance slit of a spectrograph (Acton SpectraPro 2300i, 600 lines/mm grating, 30 μm entrance slit, resolution 3.9 cm^{-1}, Acton, NJ, USA). For polarization dependent measurements a linear polarizing filter was placed before the entrance slit. The polarizer was removed for the total scattering measurements. The spectrally dispersed light was imaged using a cooled, intensified CCD camera (NanoStar, LaVision, Göttingen, Germany). Integration time was 100 milliseconds with an intensifier gain of 50. For each experimental configuration 50 frames were collected and summed together. Each frame contained 512 spectra with 640 spectral points each. The sum of the background intensity images recorded with the entrance slit blocked was subsequently subtracted from the experimental images. This effectively removed signal contributions due to thermal, electronic readout, and shot noise and improved the resulting image contrast. All image recording and post-processing was carried out using Lavision DaVis 7.2.1.64 software (Lavision, Göttingen, Germany). The applied electric field intensity was either zero or 20 kV. Voltage was again applied as a step function however, now the system was allowed to equilibrate for at least one minute prior to recording spectra.