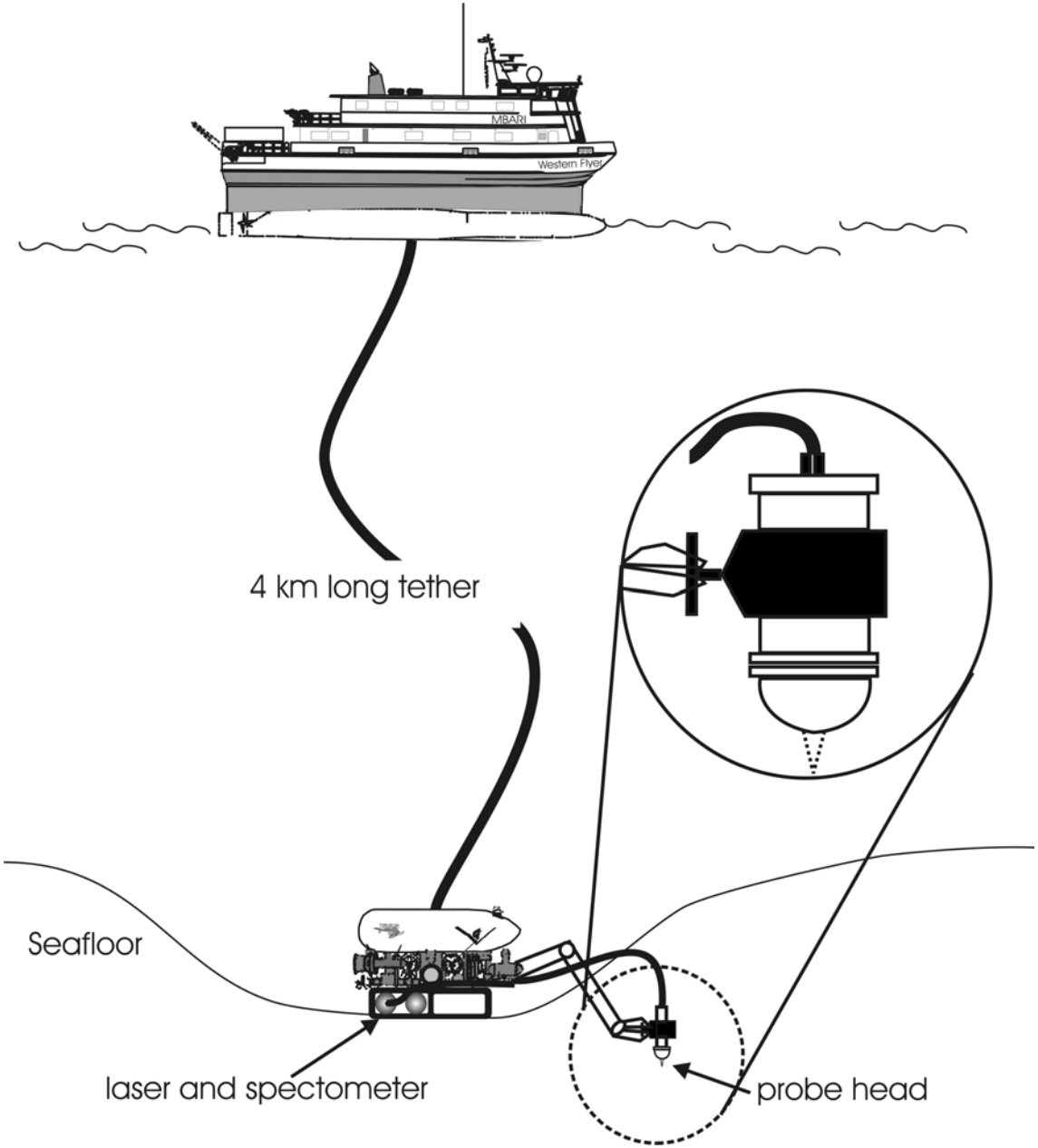

Fig. 1. Schematic overview (not to scale) of the sampling and data-communication systems of the deep-ocean Raman *in-situ* spectrometer (DORISS) system. The remotely operated vehicle (ROV) is tethered by copper wiring (electrical) and fiber-optic bundles (communication) to the research vessel. DORISS' electronics and spectrometer housings remain in the tool sled of the ROV, whereas the probe head is held by the robotic arm and moved to the sampling site.

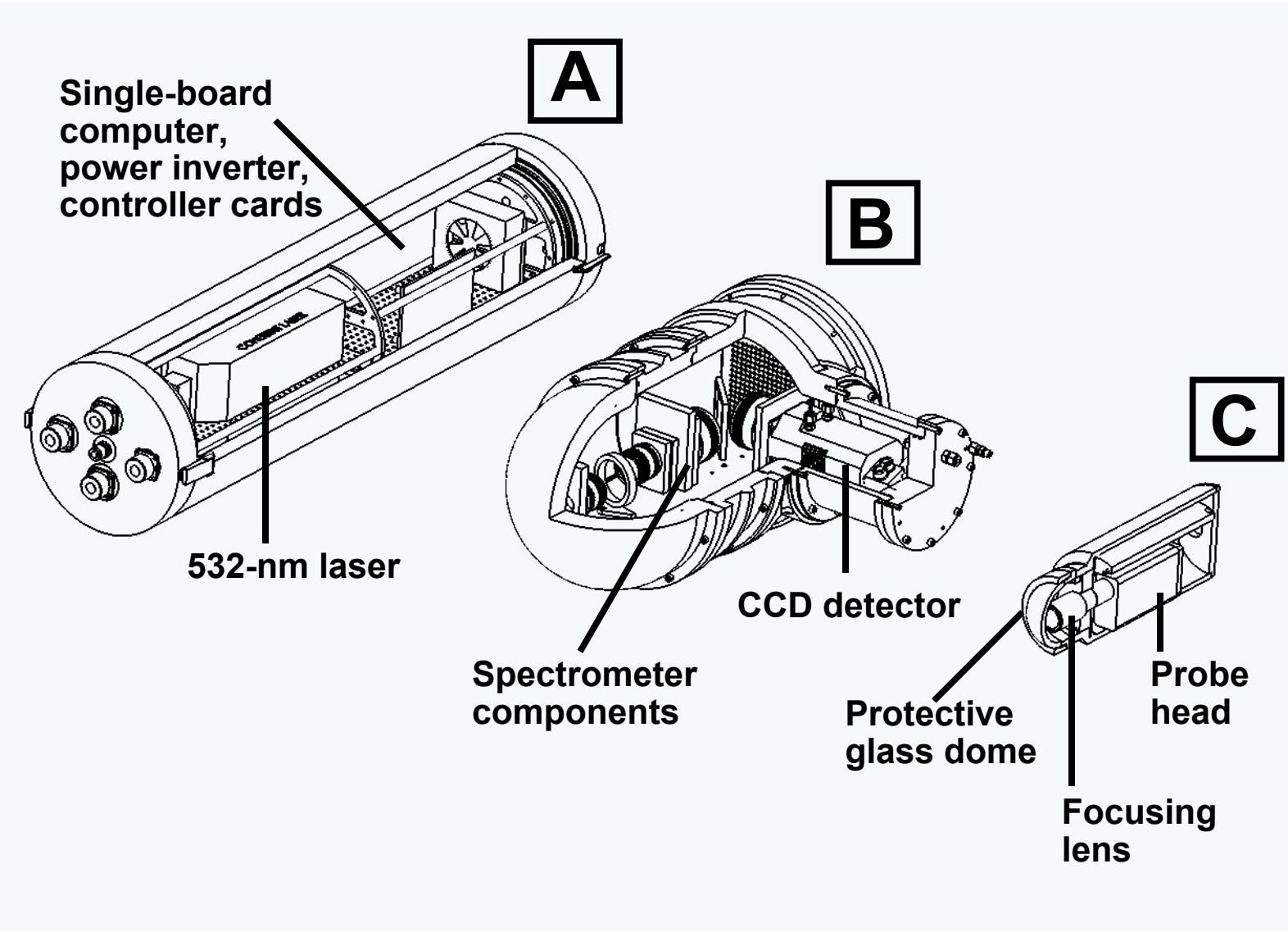

Fig. 2. Schematic view of the distribution of DORISS' components among three pressure-resistant housings: A) electronics, B) spectrometer, and C) probe head. (The handle on the probe head housing and the fiber-optic cables connecting the three housings are not shown here.)

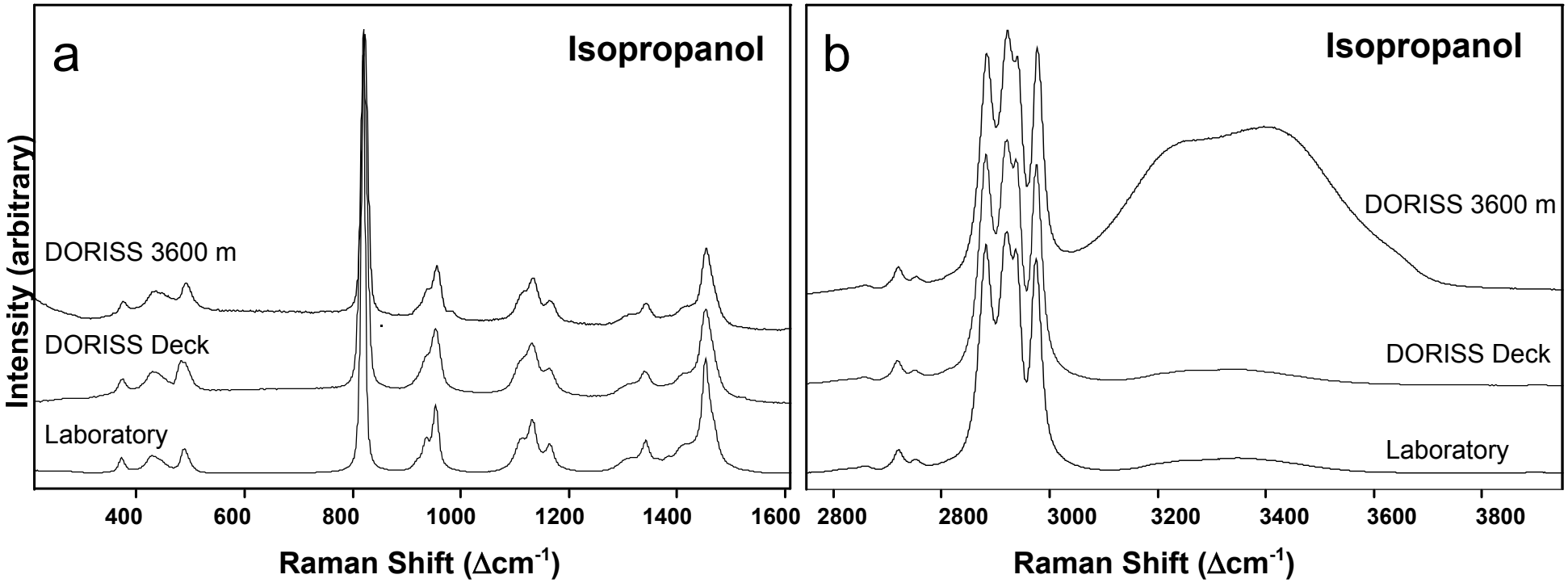

Fig. 3. Comparison of isopropanol spectra acquired with DORISS onboard the research ship in the Pacific Ocean (DORISS Deck), with DORISS at 3600 m ocean depth on the ROV Tiburon (DORISS 3600 m), and with the duplicate laboratory Raman system at Washington University (Laboratory). Data for both the low-wavenumber (a) and high-wavenumber (b) spectral regions. For these spectra, a 100-μm spectral slit was used on the laboratory instrument, but no slit was used on the DORISS. The broad double-band feature at 3200-3500 Δcm^{-1} arises from the intervening sea water.

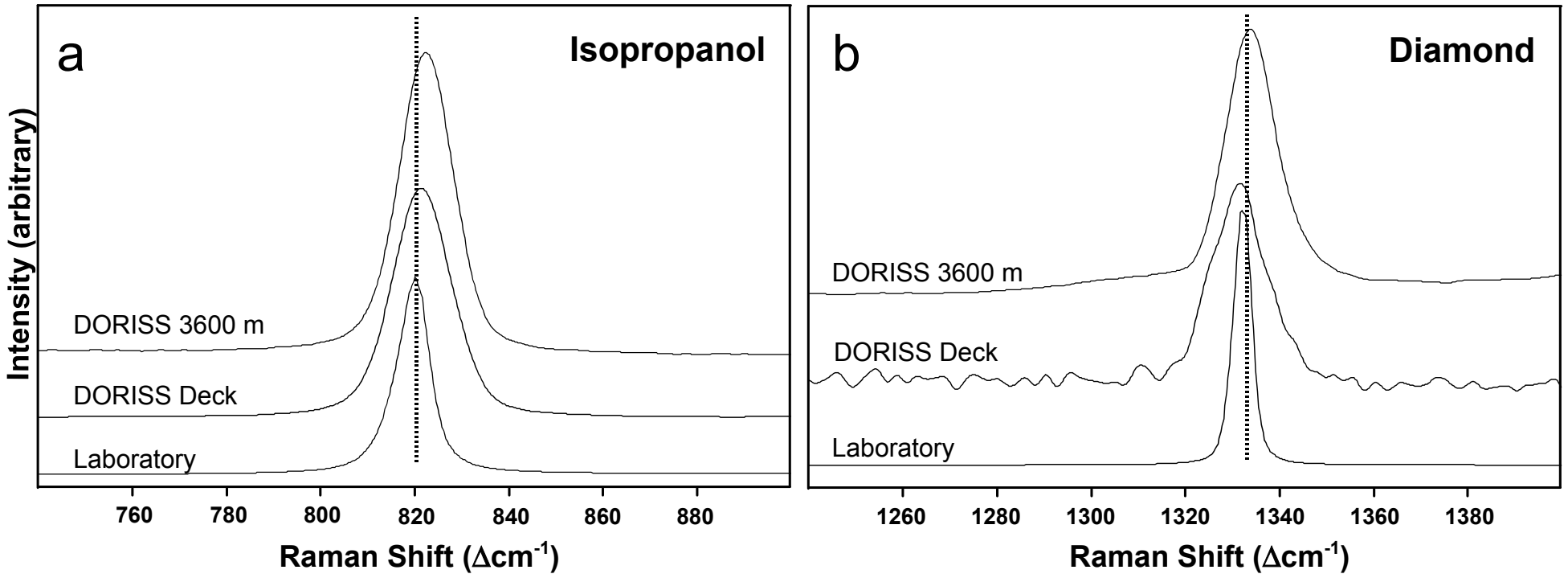

Fig. 4. Comparison of spectral quality and peak positions measured with DORISS and with the well-calibrated duplicate laboratory Raman system at Washington University. (a) Blow-up of one of the many Raman peaks for isopropanol (b) Blow-up of the only Raman-active peak for diamond. The spectra were acquired with DORISS onboard the research ship in the Pacific Ocean (DORISS Deck), with DORISS at 3600 m ocean depth on the ROV Tiburon (DORISS 3600 m), and at Washington University (Laboratory). The laboratory instrument had a 100-μm spectral slit, whereas the DORISS had no slit for the acquisition of these spectra.

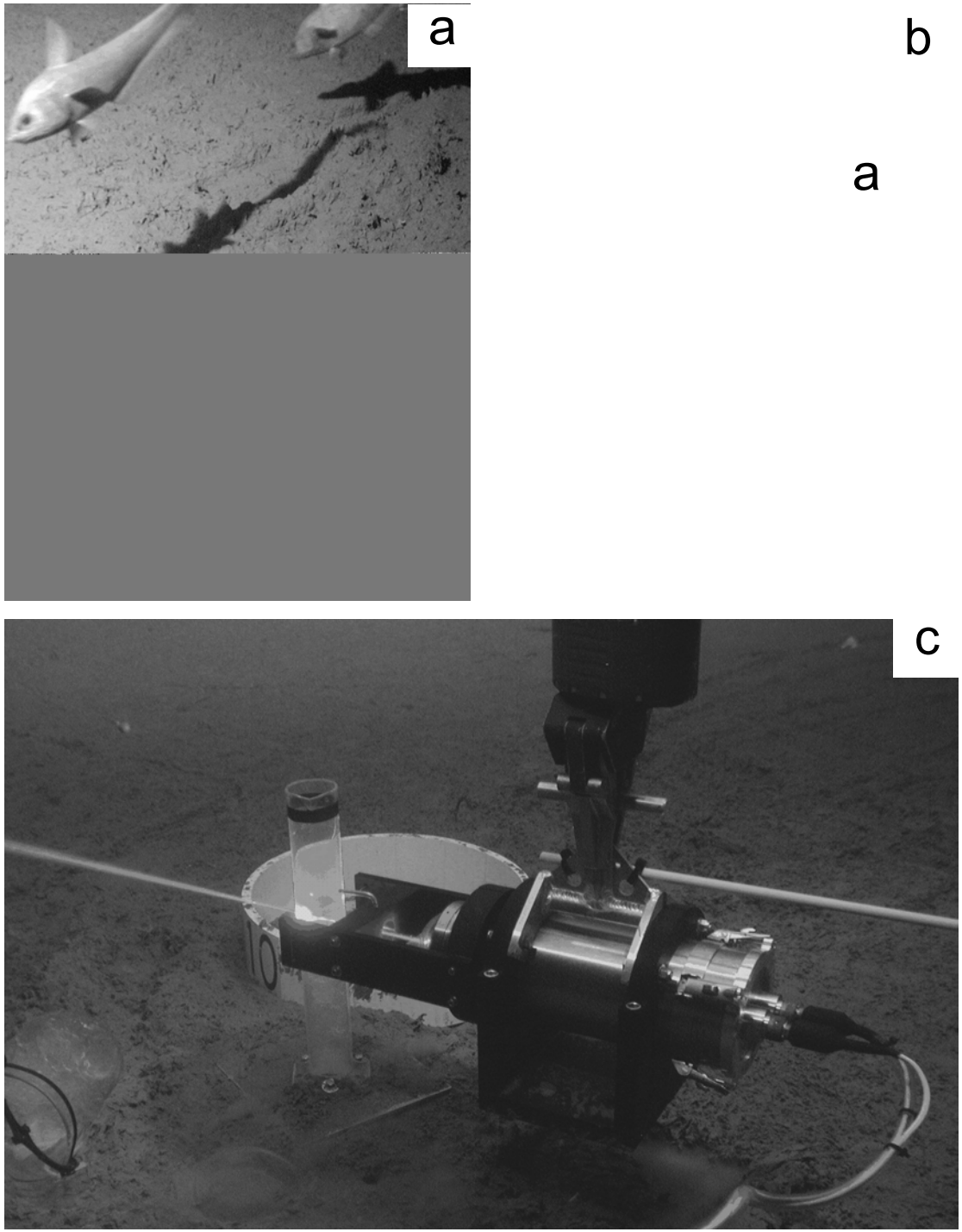

Fig. 5. Laser-sample interaction in three types of experimental configurations during Raman analysis on the deep ocean floor: a) CO_2-water-hydrate "slush" in a beaker on sea floor; probe head focused horizontally into beaker; b) probe head focused vertically down onto large, clear blob of CO_2 that almost completely covers bottom of corral; c) robotic arm (vertical, black) holds probe head and brings the laser into focus on (and through) CO_2-water-hydrate slush in graduated cylinder; large beaker of similar slush lies on its side on ocean floor (bottom, left). The whitish glow, sparkle, and beam seen in Figs. 5a,b, and c, respectively, appear as an intense green color on the ship's monitors.

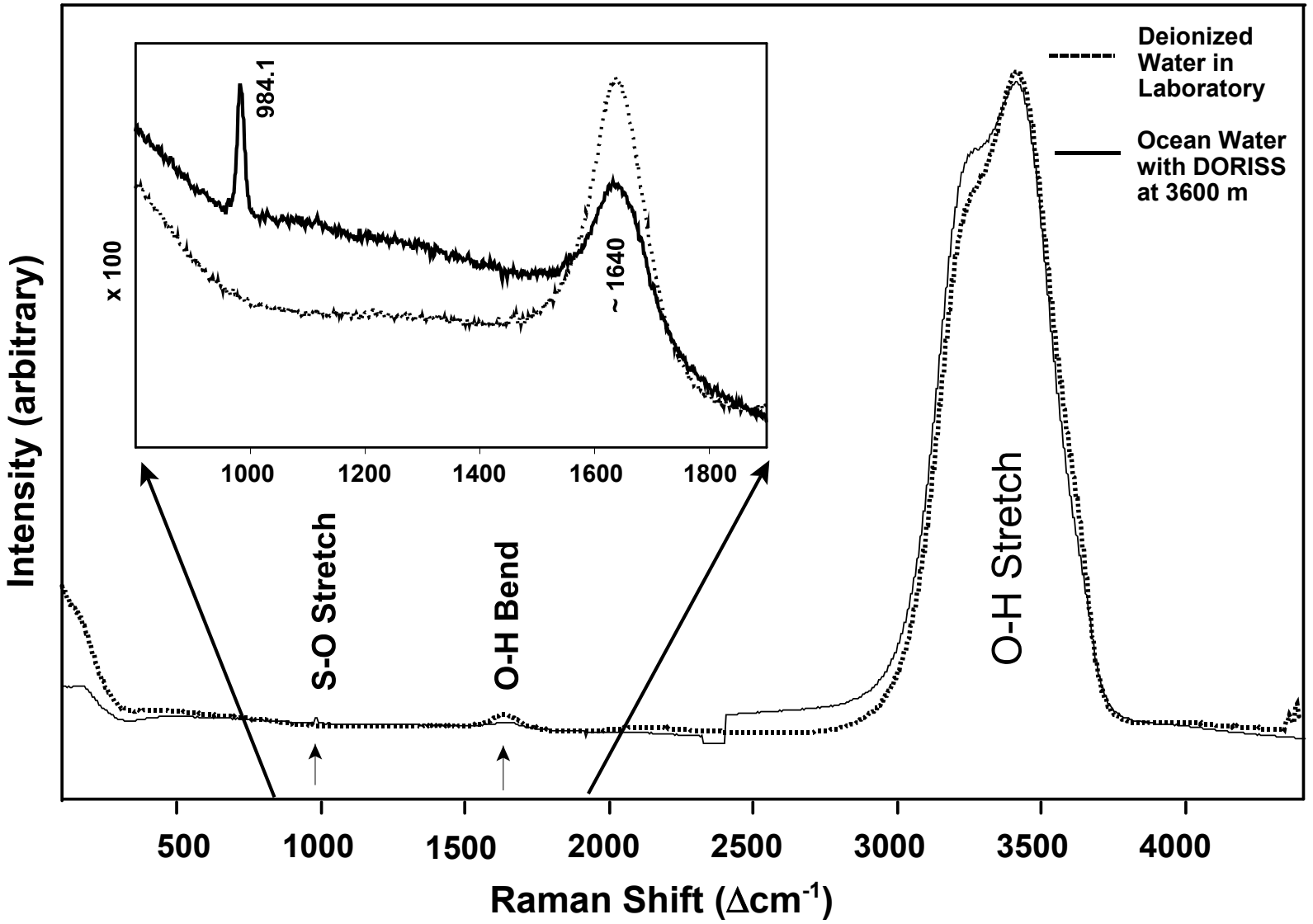

Fig. 6: Comparison of the Raman spectra of deionized water (acquired with the laboratory system at Washington University at room temperature) and ocean water (acquired with the MBARI Deep Ocean Raman System at 3600 m depth and 4 ° C). Inset shows enlargement of 800 to 1900 Δcm^{-1} spectral region. The laboratory system had a 100-μm spectral slit, whereas the DORISS had no slit (resolution imposed by 100-μm collection fiber).

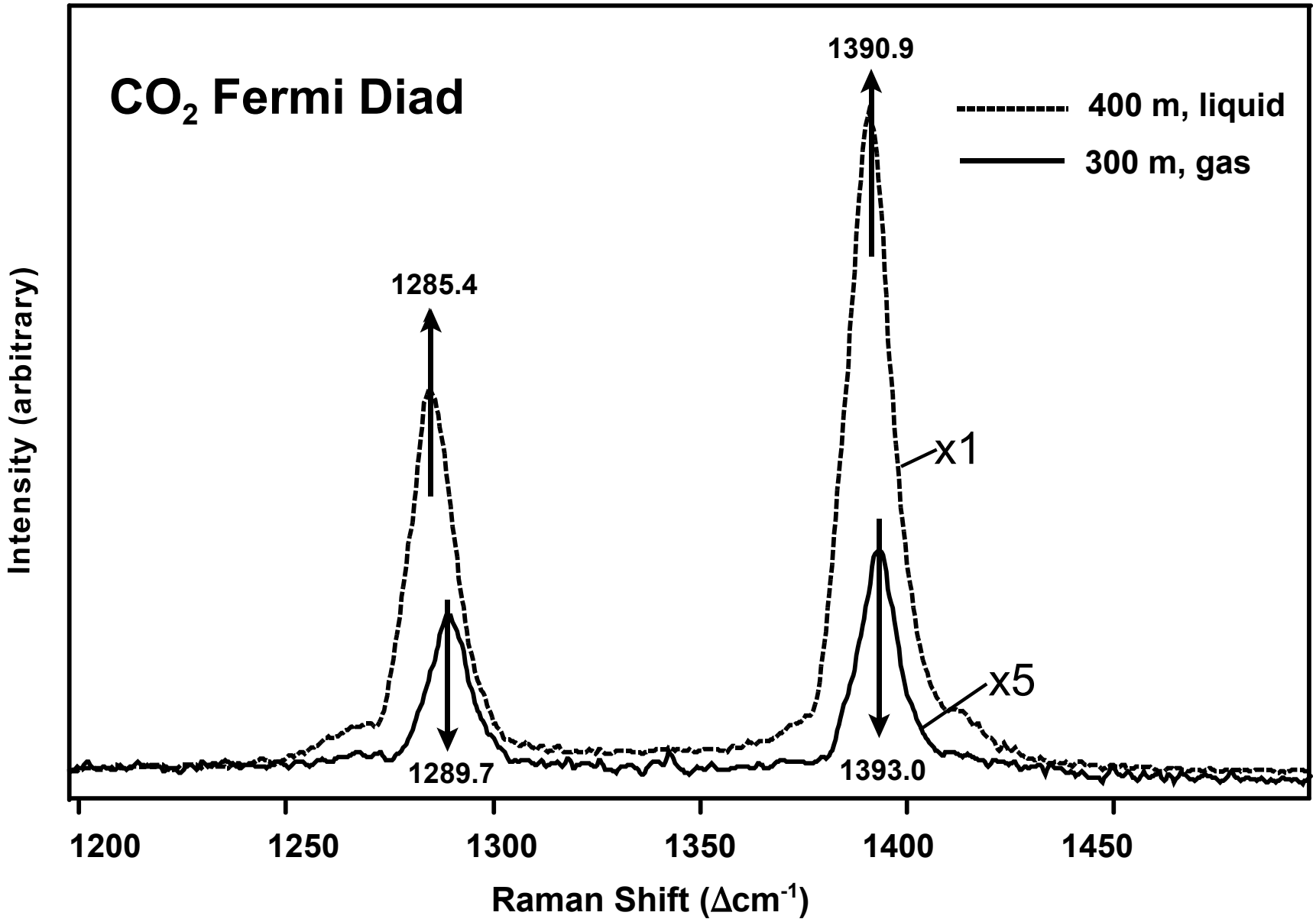

Fig. 7. Raman spectra of liquid and gaseous CO_2 collected during small-scale CO_2 injection experiments on the ROV Tiburon. Raman spectra were acquired during ascent from the ocean floor while DORISS was sitting in the ROV's toolsled. Difference in phase is recognized by strong increase in intensity and spectral downshift in the liquid compared to the gas. In this figure, the peak positions are uncorrected for depth-induced wavenumber shifts. The spectral separation between the two CO_2 peaks (more accurately measurable than the absolute peak positions) is shown in Fig. 8.

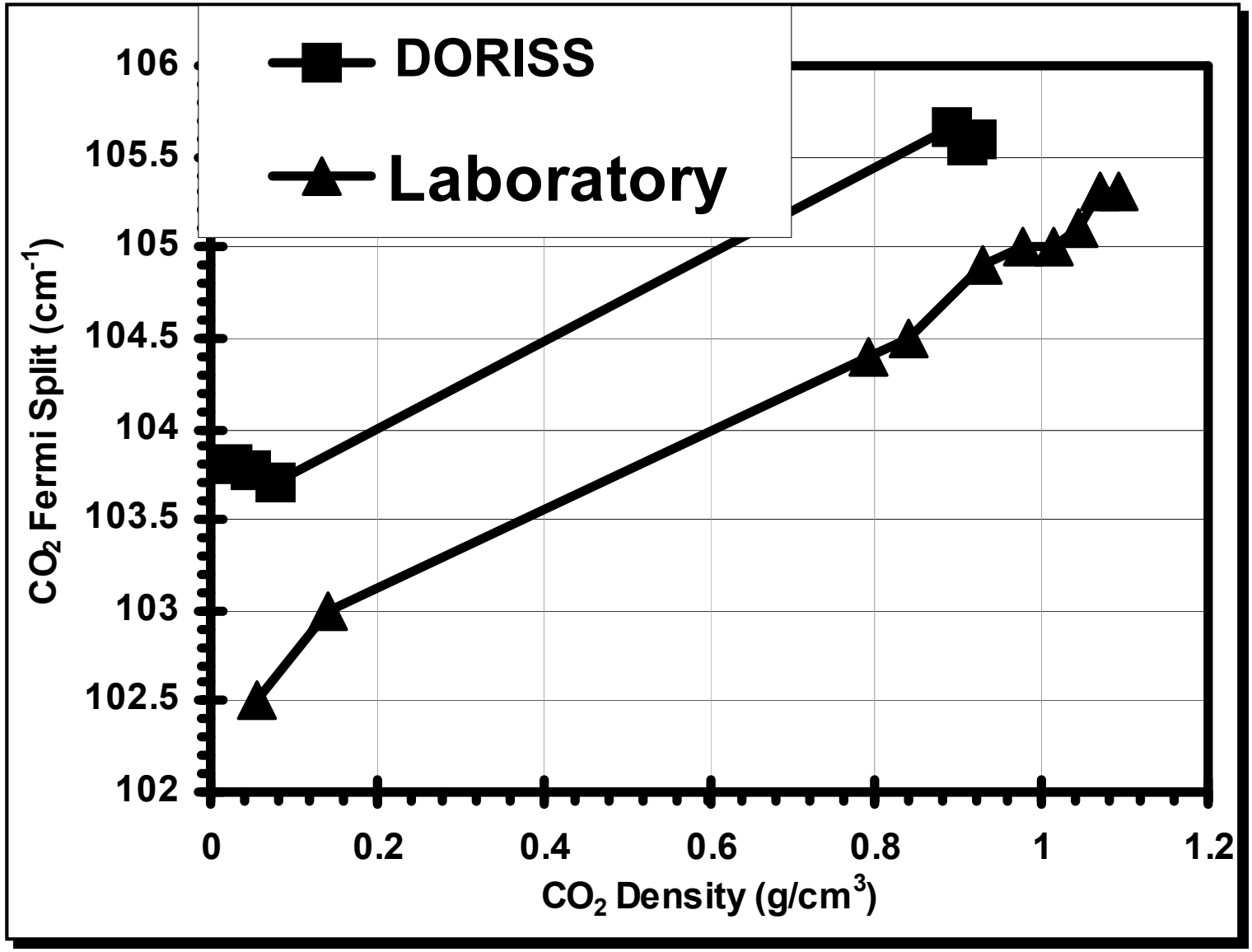

Fig. 8. Plot of the Raman spectral separation between the two peaks of Fermi diad of CO_2 versus CO_2 density (see text). Laboratory data were collected at 23 °C at well calibrated pressures; Raman peak positions were corrected based on gas emission lines from calibration lamps.[22] DORISS data (uncorrected peak positions) were collected in ascent from 664 m depth in the ocean. Parallelism of laboratory and DORISS data indicates appropriate spectral response to changes in density. Offset between the two curves suggests that the dispersion function that was applied to the DORISS was inappropriate under the specific dive conditions.

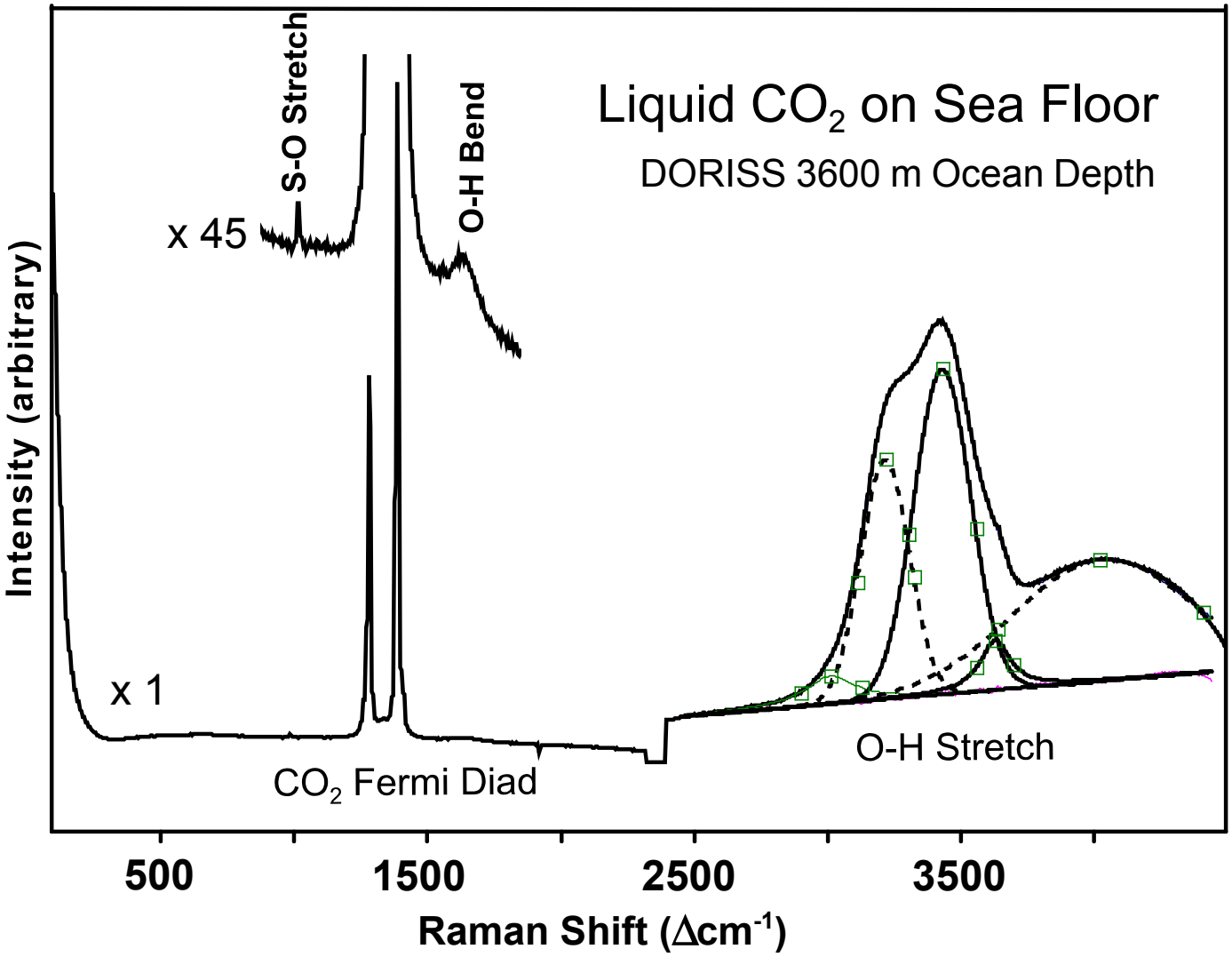

Fig. 9. Raman spectrum taken by DORISS on a large liquid CO_2 blob artificially introduced directly onto the sea floor at 3600 m depth. Although only CO_2 was within the focal volume of the probe head, Raman scattering also was detected from the intervening sea water due to the long focal length of the probe optics.

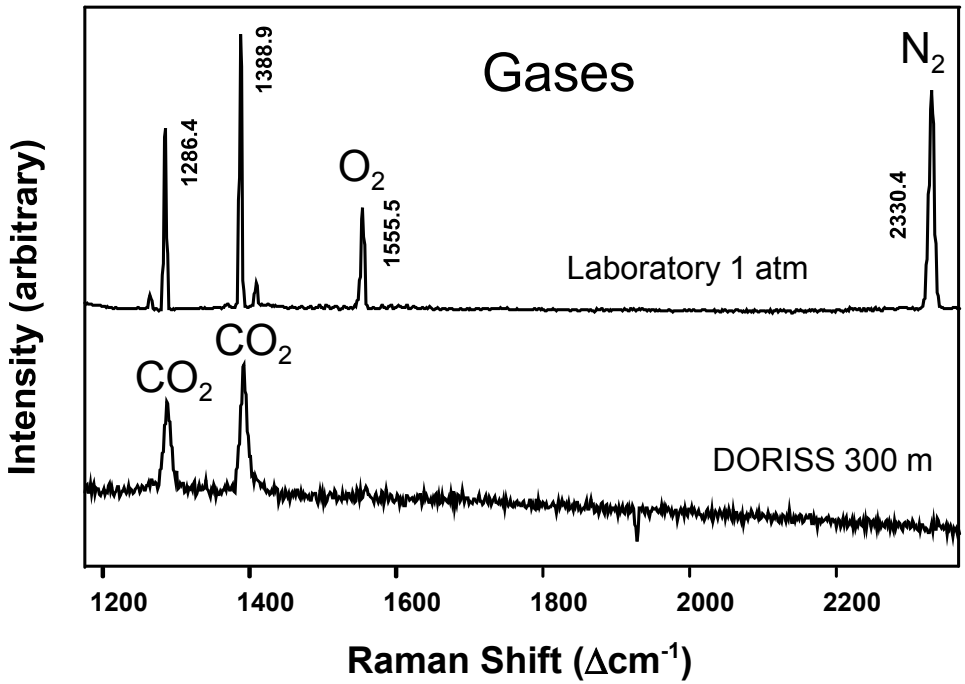

Fig. 10. Raman spectra of CO_2 gas contained at 1 atm in an Erlenmeyer flask in the laboratory (upper trace) and contained in an inverted jam jar in the ocean at 300 m depth (lower trace). Laboratory spectrum also shows signature of air (O_2 and N_2) between flask and probe. Lab spectrum is the average of 64 10-second scans acquired with a 100-μm slit. DORISS spectrum is one 5-second scan acquired without a slit. Small peaks to the low- and high-wavenumber side of the CO_2 Fermi diad are hot bands.[34]

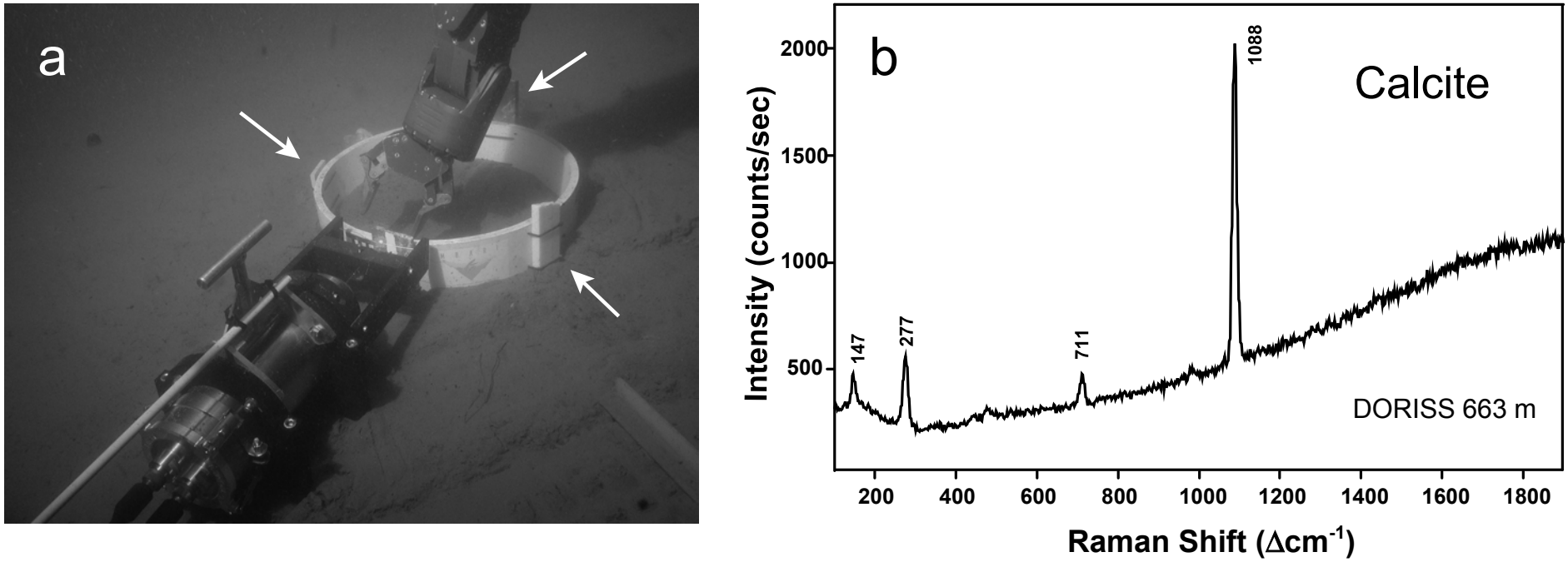

Fig. 11. a) Several sawn slabs of calcite and carbonate rocks (indicated by arrows) are strapped to a PVC corral at 663 m depth on sea floor. Probe head has been guided into focus on the large calcite rhomb painted with a white vertical stripe. b) Raman spectrum of that calcite rhomb (1-second acquisition).

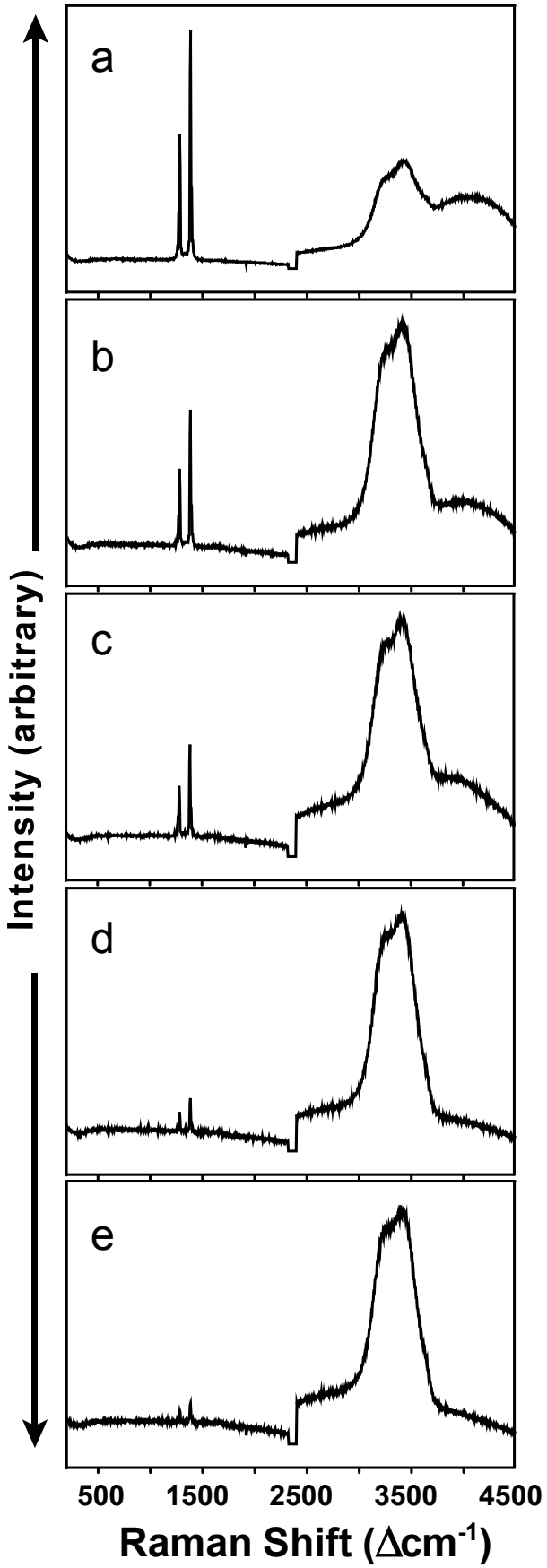

Fig. 12. Series of Raman spectra (each with 1-second acquisition time) as the probe head is moved away from optimal focus of the laser on a CO_2 liquid blob on the ocean floor. As explained in Fig. 9, both sea water and CO_2 are in the laser beam's path. Spectra of both phases are recorded, but the CO_2:H_2O band ratios vary with position of the probe head. The CO_2 blob is in best focus in spectrum a).