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Freestanding sample holder for ultrafast optical spectroscopy at low temperatures

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Ultrafast optical spectroscopy techniques are often employed to gain information about samples that are liquid at room temperature and frozen at cryogenic temperatures. However, the measurements suffer from the presence of unwanted, non-resonant signals originating in the sample cell walls. Most of these artifacts can be avoided in the measurements performed at room temperature by using liquid jet systems, i.e., by removing the sample cell. However, these systems cannot be used in low temperature measurements, when the sample is frozen. Herein we describe a freestanding sample holder that allows low temperature ultrafast spectroscopy measurements free of artifacts caused by the sample cell. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4870277]

I. INTRODUCTION

Ultrafast optical spectroscopy techniques are an invaluable tool for exploring many fundamental physical processes like light and matter interaction, excitation energy transfer, coherent quantum beating phenomena, and others. Quite often the examined samples are liquid at room temperature, requiring the use of a sample cell to perform the experiments. This leads to a mixing of signals from the sample with unwanted, non-resonant signals originating in the sample cell walls.[1–3] These signal artifacts, appearing during the overlap of pulses, are especially strong in the experiments using short wavelength excitation (ultraviolet to green visible wavelength range) and ultrashort laser pulses with duration of less than 20 fs. They can be mostly avoided in the measurements done at room temperature by using a jet system[4] instead of the cell, essentially removing the source of unwanted signals. However, the experiments are quite often performed at low temperatures (e.g., at 77 K in a liquid-nitrogen cryostat) with a frozen sample, where the jet systems cannot be used.[5] To realize low temperature measurements free of the cell walls' signals, we have developed the freestanding sample holder.

II. FREESTANDING SAMPLE HOLDER

The holder (Fig. 1) was designed to be used with the Optistat DN cryostat (Oxford) with the adjustable height sample holder rod and the double sample holder accessory. However, the design can be easily adapted to any top-loading cryostat. The holder consists of a sample slider, slider guides, and glass windows. The slider contains a hole, approximately 5 mm in diameter, to hold the sample. A wire is attached to the upper part of the slider. The front and back slider guides are separated by spacers with the same thickness as the slider. The guides and the spacers form together two grooves, one on each side of the slider, which direct the movement of the slider. The upper part of the front slider guide prevents movement of the slider too far up. The guides were made from polytetrafluoroethylene. The material was chosen based on its low friction, thermal stability, and also because it is easy to work with. The thickness of the guides is dictated by the thickness of used glass windows, which, in turn, is dictated by the mechanical stress that the glass windows have to withstand during sample holder operation. Common microscope slides (with thickness of 1 mm), cut to the appropriate size, can be used for this purpose. The windows can be silanized by applying 5% dimethyl-dichlorosilane in heptane (Sigma Aldrich) to reduce the amount of cracks in the frozen sample.[6] In principle, non-transparent walls can be used instead of the windows. However, transparent windows allow visual inspection of the quality of the formed low temperature sample "glass" (the glassy matrix formed after freezing of the sample). A thin aluminum plate (thickness of 0.5 mm) was used to clamp the front glass.

The thickness of the sample slider controls the thickness of the sample and, therefore, the length of the optical path through the sample. However, it cannot be chosen arbitrarily. Mechanical properties of the slider have to be considered, because it must not deform when moving up as that would lead to cracking of the frozen sample. First, a 1.5 mm thick sample slider, made from polytetrafluoroethylene, was used to successfully test the principle of the operation. However, relatively thick samples are not optimal, because some unwanted signals can also be generated in the solvent. In addition, it was shown that photon echo experiments performed with samples thicker than 1 mm produce some artifacts.[7] Thus, a slider thickness of <0.5 mm would be desirable. Consequently, sliders with thickness of 0.5 mm and 0.2 mm were tested. Both sliders were fabricated from steel. Whereas operation of the 0.5 mm slider was problems free, the sample frozen in the 0.2 mm slider sometimes broke apart and fell off the holder. However, spectroscopic measurements with the 0.2 mm samples were still possible in most cases.

Operation of the holder is as follows.[8] The sample is loaded at room temperature (296 K). The slider is positioned so that a larger part of its hole is covered by the windows,

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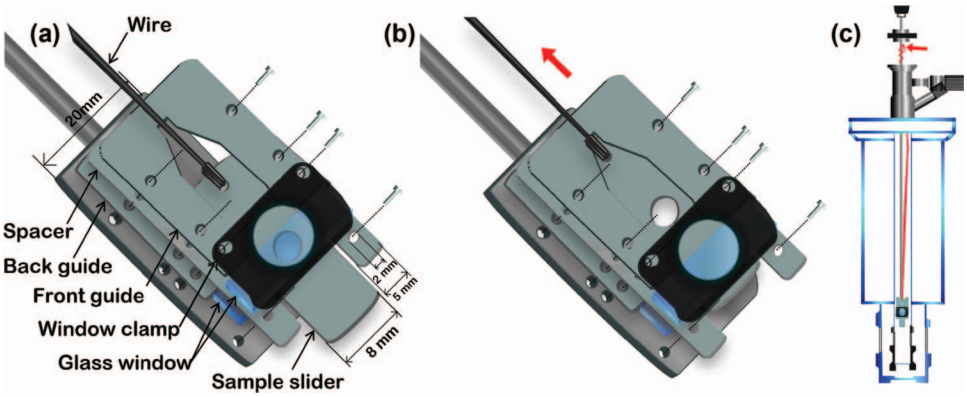

FIG. 1. Freestanding sample holder (shown partially disassembled to ease visualization) with the sample slider in (a) loading position and (b) measurement position. (c) Cross section of a cryostat with the freestanding sample holder in the position for the slider to be moved up (wire, in red, is marked by the arrow).

with a small opening on the top side, forming a "cell." The opening is used to pipette in the sample. Only a small amount of the sample, typically a few microlitres, is needed. Care has to be taken to prevent the sample from leaking in between the slider and the windows and/or between the slider and the slider guides. The holder is then transferred to the cryostat and the sample is left to freeze. Once the sample is frozen, the sample rod is slightly pulled out of the cryostat to access the pulling wire, with the sample still quite low in the cryostat to prevent ice formation by condensation of the atmospheric moisture (Fig. 1(c)). Then the wire is pulled to move the sample slider into the measurement position (Fig. 1(b)). The force needed to pull the slider depends on how much of the sample has leaked and frozen between the slider and the windows. Usually, hand power is enough to lift the sample slider; however, a leaked sample can prevent movement of the slider. The applied force should never be large enough to break the wire since the cryostat can be damaged in recoil. After moving the slider up, the sample is freestanding and can be measured without the influence of the cell walls. Naturally, the glass windows of the cryostat itself are not removed from the beams paths. Therefore, the experiment has to be arranged in such a way that the cryostat windows are outside of both focus and overlap of the beams, which will prevent generation of significant non-resonant signals on the cryostat windows.

It is possible to keep the sample in the slider hole at room temperature by surface tension only, thus foregoing the windows and all moving parts. However, the frozen sample prepared in this way will not have parallel planar surfaces. Most optical measurements are rendered unfeasible with such a sample, because the resulting irregular lens changes direction and collimation of the beams used in the measurements.

III. EXPERIMENT

To demonstrate the effectiveness of the freestanding sample, low temperature coherent two-dimensional electronic spectroscopy (2DES) measurements were performed on a model system (light-harvesting peridinin-chlorophyll-protein complex). 2DES is a powerful four-wave mixing technique for studying molecules and multichromophore systems.[9,10] Recently, we have developed a double-frequency lock-in detection technique for substantially reducing scattering signals in the four-wave mixing experiments.[11] The measurements were performed with the slider in the loading position (Fig. 1(a)), essentially simulating a measurement in a glass sample cell with 1 mm thick cell walls, and in the measurement position (Fig. 1(b)), with freestanding sample. The 0.2 mm thick slider was used in this experiment. Central wavelength of the laser spectrum was at 545 nm. Duration of the used laser pulses was ∼15 fs, full width at half maximum, as measured by the intensity autocorrelation (Fig. 2). Note that although the central part of the pulse is short, its intensity does not go to zero immediately outside of the center. This is often the case for spectrally broad pulses used in ultrafast spectroscopy, where matching the phase of the light over the whole laser spectrum can be a difficult task. Consequently, some contribution of non-resonant signals has to be expected even at population times significantly longer than 15 fs as there will still be some overlap of pulses.

Difference between the data acquired for the sample in the cell and for the freestanding sample is apparent (Fig. 3), especially at early population times. At later population times, completely outside of the pulse overlap region, the

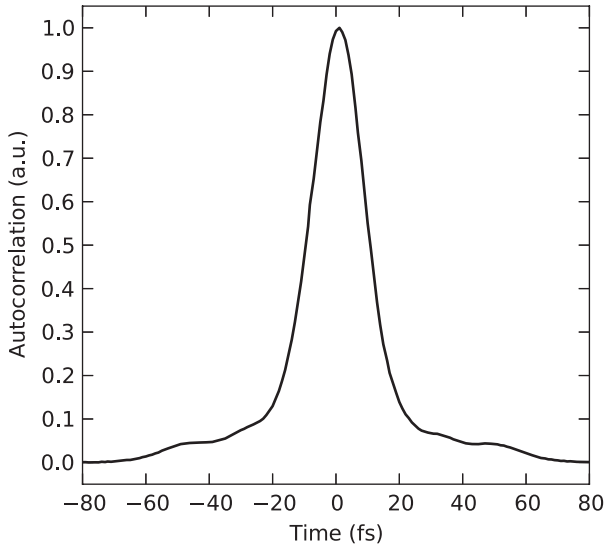

FIG. 2. Autocorrelation of the laser pulses used in the demonstration experiment.

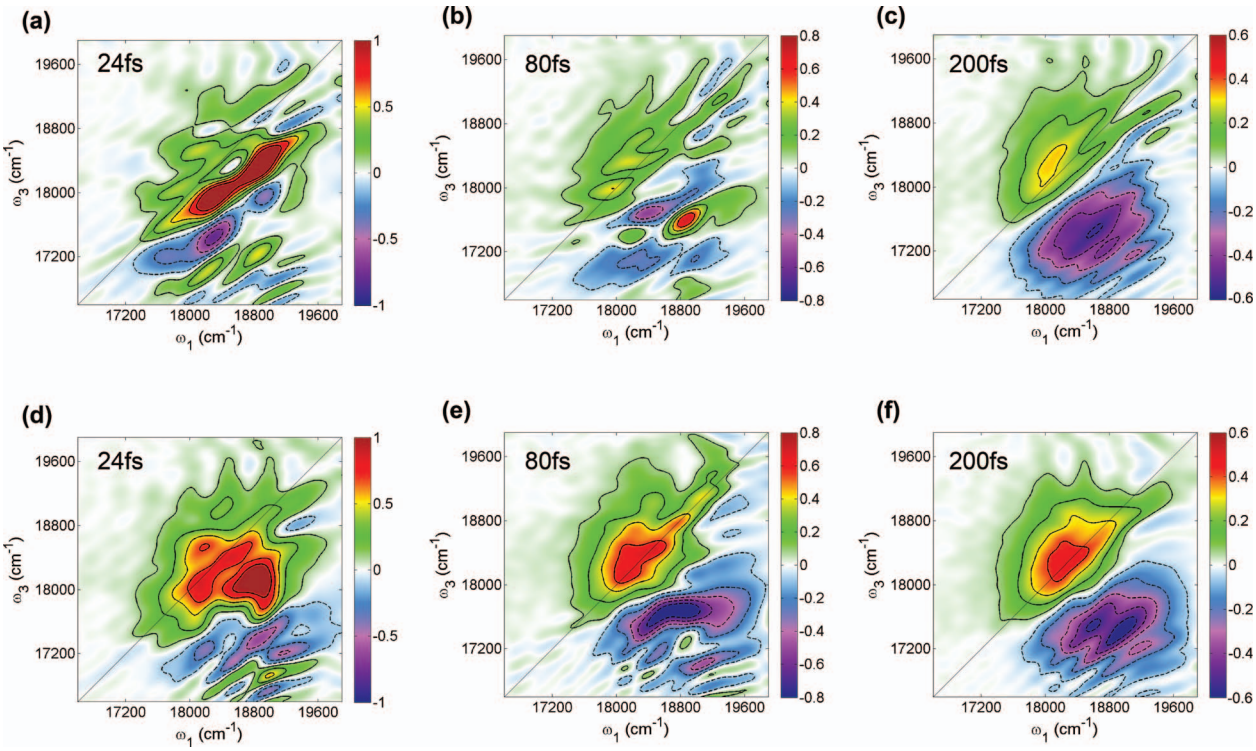

FIG. 3. 2D spectra of a light-harvesting peridinin-chlorophyll-protein complex measured at population times of 24 fs, 80 fs, and 200 fs at 77 K with the slider in the loading position (with 1 mm thick glass windows, top row) and in the measurement position (freestanding sample, bottom row).

non-resonant signals die out and the spectra measured with and without the glass windows match, although the signal is somewhat stronger for the freestanding sample. This is likely caused by the absence of reflections on the windows' surfaces. At a population time of 80 fs, the data measured in the cell deviate significantly from the freestanding sample, although signal originating in the pigment-protein complex can be discerned. At the very early population times, close to the complete pulse overlap (e.g., at 24 fs), the non-resonant signals entirely dominate the measurement in the cell. These signals appear as narrow strong peaks with both positive and negative amplitude, arranged in a semi-regular grid. On the other hand, signals from the sample are much broader. Note, that the wavy pattern visible in the right part of the spectra even at later population times is part of the sample response connected to the vibrational coherences of peridinin-chlorophyll-protein complex. The non-resonant signals, although noticeable, do not overwhelm the sample signal for freestanding sample. These residual non-resonant signals are likely generated in the solvent and cannot be avoided by using the freestanding sample holder. However, the reduction of unwanted signals is clear.

In summary, we developed the freestanding sample holder that allows avoiding unwanted non-resonant signals originating in the sample cell, which are a major problem in the ultrafast spectroscopy experiments at low temperature.

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