Low Temperature Measurements

with Liquid Nitrogen Dewar Accessory

Alex Siemiarczuk Ph.D., HORIBA

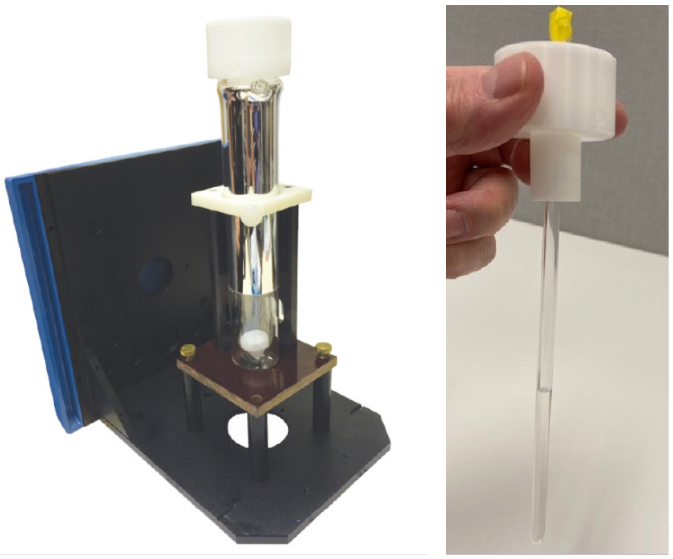
Fluorescence
Technical Note

Introduction

Measurements at low temperatures offer many additional insights into photoluminescence properties of molecular systems. For samples in solutions, cooling down to the liquid nitrogen temperature reveals much finer vibrational structure than that observed at room temperature. This is due to the elimination of rotational degrees of freedom, preventing solvent relaxation effects, and reducing intramolecular structural diversity. For organic molecules, the low temperature measurement is the common method of observing phosphorescence, which is usually undetectable (with a few exceptions) in room temperature solutions due to collisional quenching with solvent and impurity molecules. Fluorescence quantum yield is also often enhanced at low temperatures due to the elimination of intermolecular collisions which contribute to non-radiative deactivation.

The FL-1013 liquid nitrogen dewar accessory from HORIBA allows the user to carry out cryogenic PL measurements at the liquid nitrogen temperature, and is a viable alternative to a cryostat when varying the temperature above or below 77K is not required. This accessory is fully compatible with a broad range of HORIBA fluorescence spectrometers, including Aqualog®-Next, FluoroMax® Plus, Fluorolog®-QM and Nanolog®. The FL-1013 is an affordable and indispensable tool for researchers studying steady-state and time-resolved organic phosphorescence, delayed fluorescence, structural defects and impurities in semiconductors, distinguishing natural and synthetic diamonds, phosphors, etc...

Liquid Nitrogen Dewar Accessory



The liquid nitrogen dewar accessory FL-1013 from HORIBA is a simple and inexpensive option for low temperature photoluminescence measurements. For the best result, the sample should be dissolved in a solvent that forms a glassy medium when cooled down to 77K. The sample solution is placed in a quartz NMR tube, which is then slowly immersed in the liquid nitrogen-filled dewar flask. The upper part of the quartz tube is held by the Teflon cover, which closes the top of the flask. The sample tube position and orientation can be optimized by tightening set screws in the Teflon cover, which will hold the tube in the vertical position. Alternatively, one can use a Teflon cone (included with the kit) to center the tube in the dewar flask. The cone is placed at the bottom of the flask, and the tube should freely rest on it. However, the cone (or any other extra object in the flask) may induce N2 bubbling, so the user should visually inspect the dewar for any excessive bubbling prior to starting an experiment.

Examples of Low Temperature Measurements

Enhanced Spectral Resolution

The electronic spectra of aromatic organic molecules usually exhibit vibrational structure even at the room temperature. Figure 1 shows the excitation and emission spectra of perylene at 293K with a very distinct progression of vibrational bands attributed to C-C stretching vibrations in the aromatic ring (~1400 cm-1).

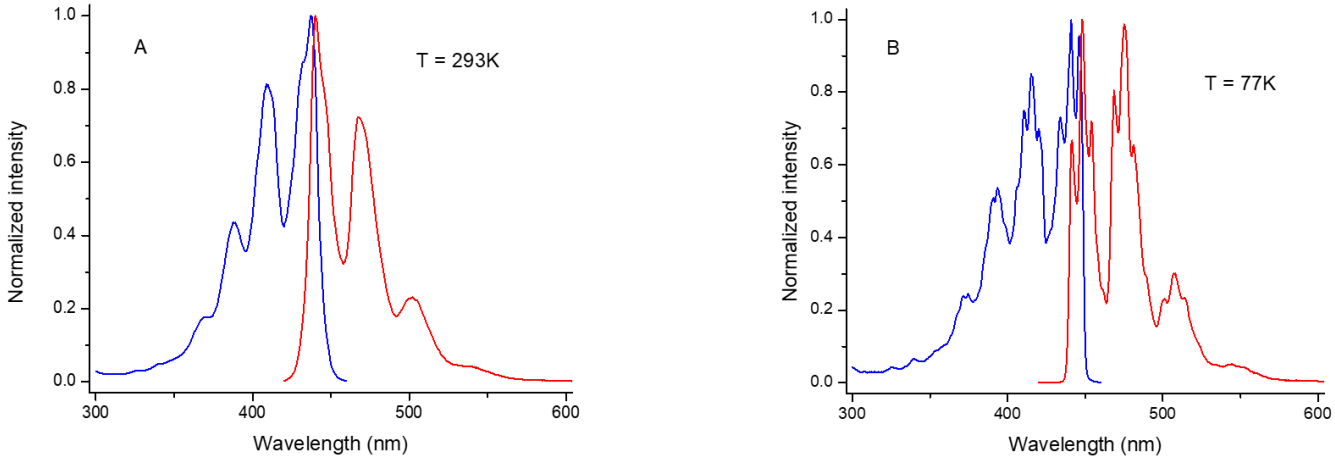


Fig. 1. Normalized excitation and emission spectra of perylene in butanol measured in the FL-1013 LN dewar accessory with a Fluorolog-QM at the room temperature (A) and at 77K (B).

Upon cooling the perylene solution down to 77K (Fig. 2), a much finer vibrational structure is observed. The bands are narrower and a new, lower energy vibrational progression (~700 cm-1) is resolved, corresponding to out-of-plane C-H bending vibrations. Such low temperature emission spectra can be reliably measured with the FL-1013 accessory.

Phosphorescence

One of the main interests in low temperature studies is the phosphorescence of organic materials, which is almost exclusively observed in low temperature glasses.

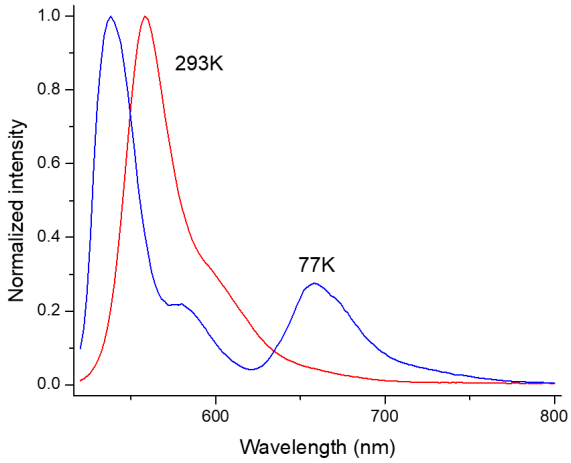


Fig. 2. Emission spectra of erythrosine measured in the FL-1013 LN dewar accessory with a Fluorolog-QM at the room and LN temperatures. A distinct phosphorescence band appears at in the 640 -700 nm range at 77K.

Figure 2 shows comparison of erythrosine emission spectra at the room and liquid nitrogen temperatures in 2-propanol. At 293K, only the fluorescence is present, while at 77K, both fluorescence and phosphorescence spectra are observed.

It should be noted that the fluorescence spectrum of erythrosine is strongly blue-shifted in the glass medium relative to its RT spectrum, since the reorientational relaxation of solvent molecules, which lowers the excited-state energy, cannot take place in the solid medium and, therefore, the S_1 -> S_0 transition energy is higher at 77K than in the liquid solvent.

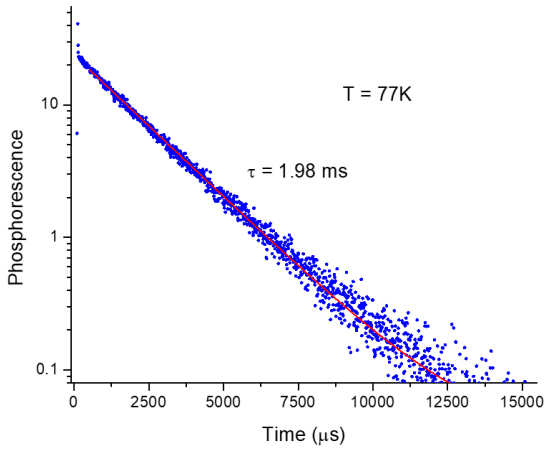


Fig. 3. Phosphorescence decay of erythrosine measured in the FL-1013 LN dewar with using a microsecond Xe lamp excitation and SSTD acquisition mode (ex = 530 nm, em = 650 nm).

The phosphorescence lifetime can be conveniently determined with the LN dewar using a microsecond Xe lamp or other pulsed sources, such as SpectraLEDs, DPSS lasers or a Q-switched OPO laser. Figure 3 shows the phosphorescence decay of erythrosine obtained with a pulsed Xe lamp and HORIBA's proprietary SSTD mode, which is a standard option with each Fluorolog-QM system. Phosphorescence lifetimes from about 1 µs to hundreds of milliseconds can be easily measured with the above configuration using the LN dewar accessory.

Many organic molecules exhibit lifetimes that extend well into seconds. For those, the low temperature spectral and lifetime measurements can be carried out with the FL-1013 LN dewar using exclusively the steady state capability of the instrument, no pulsed excitation source is required.

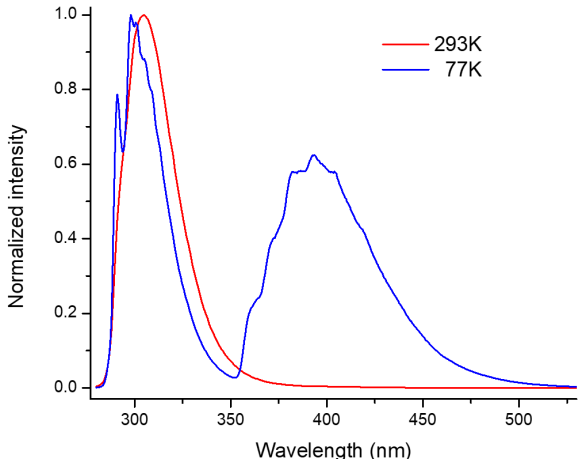


Fig. 4. Emission spectra of 4-ethylnaphtol in ethanol measured in the FL-1013 LN dewar at 293K and 77K.

Such an example is 4-ethylnaphtol, its emission spectra are presented in Fig. 4. It exhibits a strong phosphorescence emission at 77K. The fluorescence spectrum shows a modest blue shift, and both fluorescence and phosphorescence bands reveal some vibrational structure.

The phosphorescence decay of 4-ethylnaphtol can be easily measured using the steady state kinetic mode, as shown in Fig. 5. The trace was acquired in real time with 10 ms integration by closing the automated excitation shutter 28 s after the start of the scan, resulting in a high precision decay curve and yielding a lifetime of 3.44 s. This acquisition mode can be used for measuring phosphorescence decays as low a few tens of milliseconds due to a high temporal resolution of the Fluorolog-QM digitizer.

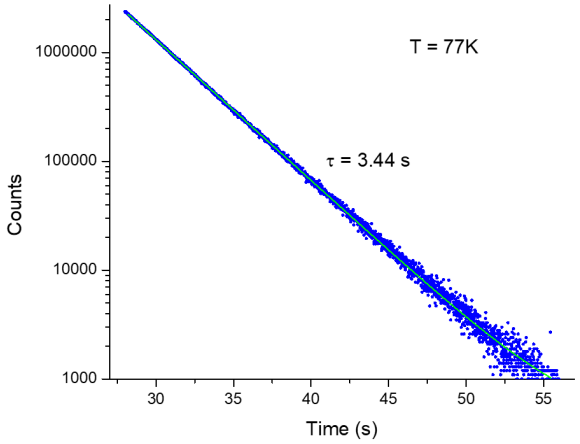


Fig. 5. Phosphorescence decay of 4-ethylnaphtol in ethanol measured in FL-1013 LN dewar with Fluorolog-QM using the steady state kinetic mode acquisition. Ex = 290 nm, em = 390 nm, integration time = 10 ms.

Solid Samples

While the FL-1013 LN dewar accessory is designed to be used with glass-forming solutions placed in an NMR tube, it is possible to adapt it to other types of samples, such as powders, crystals, films, dyes deposited on surfaces, etc….

Powders and small crystals can be placed directly inside the NMR, and the user must adjust the tube position to ensure that the excitation beam is centered on the sample area.

Larger samples, such as slides, can be suspended from the Teflon cover and directly immersed into the dewar flask filled with liquid nitrogen. An example of an anthracene dye deposited on a rectangular piece of a paper card is shown in the picture. The card was suspended with a plastic strap attached to the Teflon cover and slowly lowered into the LN-filled flask. Figure 6 shows fluorescence spectra of the sample measured at 293K and 77K in the FL-1013 dewar.

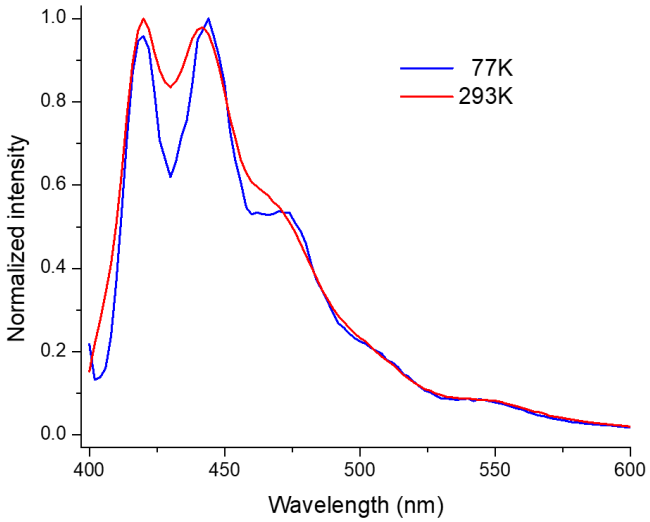


Fig. 6. Fluorescence spectra of anthracene deposited on a paper card measured at the room and LN temperatures in the FL-1013 LN dewar.

Practical Tips

The FL-1013 LN dewar accessory is a very simple and easy device to use. However, since the liquid coolant is used near its boiling temperature (77K), on occasions the user may observe bubbles rising in the volume of nitrogen in the flask. When the bubbles cross the optical path in the sample area, the data may show an increased noise level. This may affect the quality of steady state spectra, but will have no effect on SSTD and TCSPC decay measurements.

There are some simple steps that may prevent or minimize LN bubbling, such as:

- Make sure that the inside of the LN dewar flask is clean and dry. The presence of particles on its surface may cause bubbling.
- Fill the flask with LN. If there are bubbles present, pour out LN and quickly refill with the new coolant. Repeat this process until there are no more bubbles.
- Avoid using the Teflon cone at the bottom of the flask to center the tube for measurements other than TCSPC and SSTD lifetimes. The tube can be centered by tightening the set screws in the Teflon cover.
- If some level of bubbling persists during an experiment, increase the integration time. Figure 7 shows spectral scans carried out in the presence of bubbling with the integration time of 0.1 s and 1 s. While there is a visible effect of bubbling at 0.1 s integration, the increased integration time practically eliminates the noise.

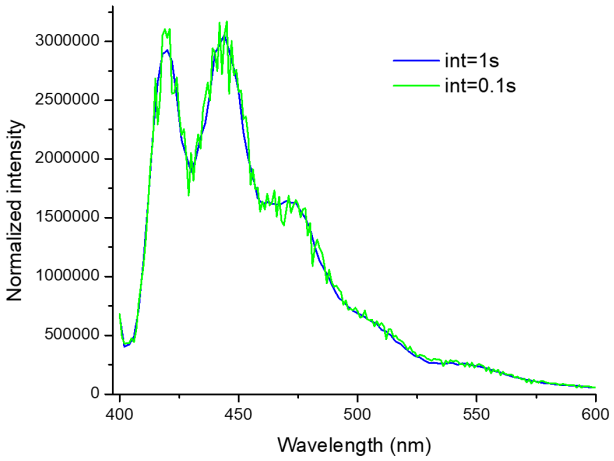


Fig. 7. Effect of the integration time on spectral noise caused by LN bubbling

Conclusion

The FL-1013 LN dewar accessory is an excellent alternative to much more expensive cryostat options for those users who do not require variable temperature. It's a very good choice for a variety of applications, such as measuring steady state and time-resolved phosphorescence, enhancing spectral resolution, eliminating effects of solvent relaxation and diffusion processes, preventing intramolecular conformational changes in the excited states, and many others.

This accessory is compatible with most of HORIBA's fluorescence instruments, such as Fluorolog-QM, Nanolog, FluoroMax Plus and Aqualog-Next.

info.sci@horiba.com

fluorescence.com

USA: +1 732 494 8660
UK: +44 (0)1604 542 500
China: +86 (0)21 6289 6060
Taiwan: +886 3 5600606

France: +33 (0)1 69 74 72 00
Italy: +39 06 51 59 22 1
India: +91 80 41273637
Brazil: +55 (0)11 2923 5400

Germany: +49 (0) 6172 1396 0
Japan: +81(75)313-8121
Singapore: +65 (0)6 745 8300
Other: +33 (0)1 69 74 72 00