**Configuring the Experimental Apparatus for Perovskite Degradation Experiments**

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Different experiments call for different combinations of instruments, and the overall infrastructure was designed to be modular to accommodate these needs. Due to the need to manage several different instruments controlled using scripts written in different programming languages, the structure is hierarchical with most executive functions in a master program written in Python that controls the microscope light source, electronic and transmittance measurements, and coordinates the image acquisition scripts that control the camera and filter cube change wheel. A high-level schematic of the important software, instruments, and information flows is given below. Note that environmental conditions are handled by instruments that are controlled manually or by embedded systems that are not connected to the central control computer.

Diagram

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**Figure 1.** Schematic of the major control software and instruments used in perovskite film & device degradation experiment data acquisition and the information flows between them. Except for illumination, environment control (temperature, humidity, atmosphere) is handled separately by embedded software in the respective instruments.

1. PLVA & Image Acquisition and Microscope Control
2. Photoconductivity Acquisition
3. Transmittance Acquisition
4. Device Data Acquisition
5. Environment Control

**1. PLVA & Image Acquisition and Microscope Control**

Instruments:

* Microscope
* Adjustable-Power Light Source (optional neutral density filters)
* Fluorescence filter cube, or bright or dark field cube
* Additional band or edge filters to shape spectra of incident or detected light as desired
* Objective lens compatible with desired imaging modes
* Camera
* Microscope stage with XYZ control (Z control only necessary if measuring one sample at a time)
* Control computer with MicroManager software

The microscope has two major purposes: i) illuminate the sample with calibrated photon & energy flux; and ii) record optical images and videos in one of several modes: photoluminescence/fluorescence, dark field, or bright field. Calibrated illumination is necessary for calculating PLQY, photoconductivity, and device parameters, as well as providing adjustable-intensity light stress.

1.1. Calibrating Light Source

For quantitative PL measurements and specifying the illumination stress, it is necessary to determine the energy/photon flux distribution in the beam incident upon the sample. This will be a function of the power fed to the light source, as well as the optics between it and the sample (e.g., liquid light guide/fiber optic cable, neutral density filters, filter cube, objective lens). The optics configuration should therefore be carefully chosen to avoid having to redetermine the calibration factors more often than necessary.

Additional instruments needed for this step:

* Beam profiler (e.g., Thorlabs BP209-VIS)
* Power meter (an instrument with a calibrated detector such as an Oriel 70310 is best, but a photodiode with a known responsivity hooked up to a Keithley sourcemeter will work in a pinch)

*1.1.1. Determining Beam Profile*

With the optics in the desired configuration, get the sensing element of the beam profiler into focus beneath the beam. The best way to do this is usually to monitor the beam diameter in the profiler control software, and adjust the height of the profiler to minimize it. (Free software for controlling Thorlabs beam profilers is available from their website.) Once in focus, the profiles may be extracted. It is advisable to acquire several profiles to help average out instrumental noise; data acquisition is generally very fast so there is not a significant time cost of repeat samples. Depending on the operating mode of the beam profiler, the full 2D profile may be given (e.g., with a camera profiler), or it may consist of 1D integral profiles in X and Y directions (e.g., with a scanning slit profiler such as the BP209-VIS). In the former case, no further processing need be done; in the latter, the 2D profile must be reconstructed by assuming a mathematical form of the beam shape and fitting the measured integral profiles against the theoretical ones. Explicitly, the integral profiles can be expressed in terms of the 2D beam shape *z*(*x*,*y*) as:

(Practically, the limits of integration will be constrained by the imaging region of the beam profiler, but as long as the beam edges fit well within this region the distinction is unimportant.)

Reasonable choices for the 2D beam shape are a Gaussian:

or an elliptic paraboloid:

In general, we find that the latter works best in almost all cases; the edges of the beam are generally relatively sharp and the peak relatively wide. Generally, the tails and sharp peak of the Gaussian function do not capture this behavior as well as the elliptic paraboloid, although this is likely to be dependent on the specific light source and optical configuration of the instrument. Other mathematical functions may be possible as well.

*1.1.2. Determining Beam Optical Power*

The beam shape *z*(*x*,*y*) as determined by the profiler is unitless, and provides no information on the overall intensity of the beam. To obtain this information, it is necessary to use an optical power meter. This process is relatively simple but can be tedious. To extract power information, place the power meter beneath the objective such that the entire beam strikes the detecting element. It is also prudent to reduce as much stray light as possible; wrapping aluminum foil around the gap between the objective and the photodetector generally works well, but be careful not to misalign the beam when doing so.

Once the photodetector is set up, vary the power to the light source and record the corresponding photocurrent to obtain a current-power setting curve. If the microscope is equipped with neutral density filters that can be easily moved in and out of the beam path, this can be a very useful way to extend the dynamic range of illumination intensities; in this case, it is useful to record a current-power setting curve for each filter. Depending on how well-shielded the photodetector is from stray light, it is also a good idea to periodically record the photocurrent due to background light so that it may be subtracted from the readings when the light is on. Knowledge of the photodetector’s responsivity in (amps of photocurrent / watts of incident optical power) at the beam wavelength can then be used to convert the photocurrent-power setting curve to an optical power-power setting curve.

CAVEAT: Be careful not to exceed the linear response range of the photodetector! In our experience, photocurrents above 1 mA are suspect for silicon photodiodes, but this be instrument dependent.

*1.1.3. Determining Beam Power Density/Energy Flux/Irradiance*

Having determined both the beam profile and its optical power, it is now possible to synthesize this information to calculate its irradiance distribution *E*(*x*,*y*) – i.e., the power per unit area incident on the sample (which can be converted to an incident photon flux *Φ*(*x*,*y*) via the relation *Φ* = *E/hν*, where *hν* is the energy per photon of the incident beam, assumed to be monochromatic). The beam shape can be normalized by dividing by its integral magnitude:

This normalized beam shape is in turn equal to the normalized irradiance:

where *P*total is the net power in the beam as measured by the power meter. Thus, the irradiance may be expressed in terms of known quantities as

Note that the coordinates *x* and *y* as developed here are referenced to those of the beam profiler. During data acquisition, it is more convenient to work in the grid defined by the pixel array in the camera, so make certain to interpolate the calculated irradiance to this grid. In general, it is best to translate the grid such that the origin corresponds to the beam center, which should also be close to the center of the camera field of view if the optics are aligned correctly.

1.2. Calibrating Detected Intensity

Once the irradiance over the camera field of view is known, the final step in calibration is to use a standard sample with known PL quantum yield to calculate a factor converting the counts detected in each camera pixel to an emitted photon flux from the sample region imaged by that pixel. The easiest way to do this is to use a perovskite sample of the same band gap as those you intend to image, measure its PLQY using an external instrument (such as a confocal PL instrument calibrated with a standard source such as a blackbody), and then collect a camera image of the same sample under a known excitation flux under the microscope (for instance, 1 sun equivalent). For the pixel in the *i*th row and *j*th column of the image corresponding to imaged region of area *A*px, the incident power will then be:

The pixel in the corresponding region of the image will register some number of counts *Cij* during the image exposure time *t*exp, recorded as metadata when the image is saved. This number of counts is proportional to the number of photons emitted by the imaged region in response to the incident beam during the imaging exposure window; we can express a calibration factor *k* that tells how many photons emitted per unit area from the sample correspond to a given number of counts in each pixel:

To determine *k* using a standard of known PLQY *ϕ* such that the emitted photon flux is

we may use the following expression:

Knowledge of this calibration factor thus allows the emitted photon flux (and if the incident irradiance is also known, PLQY) of any image taken using the same optical configuration.

1.3. High-Level Overview of Microscope Control Software

The original microscope control code was developed within the free MicroManager software, written in the BeanShell language. This code covers camera imaging and stage motion, but does not control the light source, which instead requires the Python control scripts discussed below. Due to challenges with synchronizing the Python and MicroManager scripts, the latest version of the control software is run entirely in Python, which calls MicroManager as a subprocess. These scripts can be found in the “bs2py” (**B**ean**S**hell**2Py**thon) folder. “plaq.py” is the main script that executes the subprocess; the others contain important function and class definitions.

When the subprocess is called within the master Python control script (“Film\_Degradation\_DAQ\_script.py” or “Device\_Degradation\_DAQ\_script.py”), it will perform the following major operations: i) move the stage to the desired XYZ coordinate (only if running a composition gradient); ii) automatically determine the optimal camera exposure time to maximize signal to noise ratio without saturating the image; iii) register the stage to compensate for drift by comparing against the last video/image taken at each point (again only relevant for composition gradients); iv) autofocus by adjusting the Z position of the stage; and v) acquire the video or image. Steps ii) through v) will be repeated for each desired imaging mode (PLVA, dark field, bright field). Optimized stage position settings from each cycle are saved to be used as the starting point for optimization in the future cycle.

If dark field and bright field images are desired in addition to PL videos, the filter cube must also be changed. In our instrument, the filter cube wheel can only be moved manually. To automate cube changes, a stepper motor-driven wheel controlled by an Arduino UNO microcontroller was placed in contact with the microscope filter cube wheel. When the Arduino receives a command from the Python master control script to move the cube wheel to a new position, the motor executes the requisite number of steps. Open-loop control was found to be unreliable, with the wheel often losing its position when commanded to rotate through a specific angle. To avoid this, a control scheme was implemented by attaching low-profile but powerful magnets to each position on the filter cube wheel and detecting the spike in the radial component of the magnetic field when one of them approaches a magnetometer mounted close to the wheel. This control scheme enables both relative position control—i.e., how close a filter cube is to being in position—as well as absolute control: by counting the number of spikes in the magnetic field, the controller has a way to remember which filter cube is in position.

**2. Photoconductivity Acquisition.**

Instruments:

* Microscope with illumination source calibrated as above
* Source/measure unit (e.g., Keithley Sourcemeter)
* Waveform generator
* Lock-in amplifier
* Control computer with MicroManager software

2.1 Setting up the Measurement Circuit

Assuming that the light source is calibrated as above so that a sample can be illuminated with a known photon flux, adapting the setup for DC and AC photoconductivity measurements is relatively straightforward. DC photoconductivity measurements are particularly simple; all that is necessary is to hook the positive and negative terminals of a source/measure unit to contacts forming a channel across the sample, apply a voltage, and measure the difference in the channel current when the light is turned on. While attractive in its simplicity, the DC measurement has a drawback of susceptibility to noise due to transient currents that may be particularly prevalent in halide perovskites. AC measurements offer the ability to avoid this complication at the cost of increased instrumental complexity. In this case, the intensity of the light source is varied according to a square wave pattern produced by a waveform generator, causing a strobing effect that generates a square wave photocurrent in the sample. This photocurrent may then be detected by a lock-in amplifier as a voltage across a shunt resistor placed in series between the SMU and the sample. The resistance should be chosen to be large enough to give adequate signal from the lock-in amplifier but small enough to avoid parasitic voltage drop that reduces the bias applied to the sample (and should be significantly smaller than the input impedance of the lock-in amplifier). When the measurement is active, the control program records both the current measured by the source/measure unit (from which the DC photoconductivity can be determined) and the AC photocurrent inferred from the amplitude of the voltage across the shunt resistor connected to the terminals of the lock-in amplifier. Note that this amplitude represents only the first sinusoidal harmonic of the measured signal and is reported as a root-mean-square amplitude. To convert to the peak-to-peak amplitude of the square wave, a correction factor must be applied:

Here, the factor of accounts for the conversion from RMS to peak-to-peak amplitude; the first harmonic in the Fourier series for a square wave has coefficient 4/π. Both DC and AC photocurrent timeseries are saved in the electronic measurement data CSV generated in each run.

Diagram

Description automatically generated

**Figure 2.** Schematic of the AC photoconductivity measurement circuit: the source/measure unit applies a DC bias across the contacts on the sample, while the strobing probe beam modulates the photoconductivity to produce an AC component of the photocurrent. This current is sensed as a voltage drop over a resistor placed across the terminals of the lock-in amplifier.

**3. Transmittance Acquisition.**

Instruments:

* Microscope with illumination source calibrated as above
* Source/measure unit (e.g., Keithley Sourcemeter) attached to photodiode
* Control computer

3.1. Setting up the Measurement Circuit.

Transmittance measurements are completely analogous to DC photoconductivity in terms of the instrumentation and how it is controlled, with the exception that the source/measure unit is connected to a photodiode placed beneath the sample rather than the sample itself. Otherwise, the measurements are conducted in the same way: the difference between the photocurrent through the photodiode when the light is on and off is measured. This can be done at the same time as the DC photoconductivity measurement when two separate source/measure units are dedicated to electronic and optical measurements. The diode photocurrent is, like the raw photoconductivity data, saved in the electronic measurement CSV generated for each run.

Note that the signal read by the photodiode depends not only on the transmittance of the sample, but also the positioning and alignment of the photodiode relative to the beam and the sample. The signal should therefore be understood as providing *relative* transmittance information referenced to the initial signal reading. This may be converted to an absolute value if the transmittance of a pristine sample is known or inferred from UV-vis measurements taken beforehand or on a witness sample.

**4. Device Data Acquisition.**

Instruments:

* Microscope with illumination source calibrated as above
* Source/measure unit (e.g., Keithley Sourcemeter)
* Device measurement stage
* Control computer

Although the device data acquisition script differs considerably from the film DAQ script, the instrumentation is much simpler since transmittance measurements cannot be made, and AC measurements are not customarily made either. Thus, the only electronic measurement instrumentation needed is a source/measure unit hooked up directly to the control computer, with leads attached to the device electrodes.

**5. Environmental Control.**

Instruments:

* Control chamber
* Thermal stage with PID controller, cartridge heaters, and thermocouples
* Ultrasonic humidifier, humidity controller, and fan OR bubbler with water/glycerol bath
* Gas (N2, air, and/or O2) cylinders and mass flow controllers

Environmental control is not part of the centralized control program, and must be set up manually before each experiment. There are several options for control chambers; for experiments on single films with simple electrical connections that do not require XY stage motion, small off-the-shelf environmental control chambers such as the Linkam Scientific LTSE420-P work well. For experiments that require use of the XY stage (composition gradients or devices), a much larger control chamber that fully encloses the stage and partially encloses the microscope is necessary, as well as custom-designed heating stages for films and devices. Implementation of environmental control schemes will therefore depend to some extent on the requirements of a specific experiment.

5.1. Illumination Control

See section 1; as noted there, in general the microscope optics and LED light source are used to control illumination intensity and are independent of the data acquisition scheme. The exception is when performing experiments on compositional gradients, during which the samples spend most of their time outside of the microscope beam. In this case, stress illumination is provided by a large square white LED lamp with a hole in the center that accommodates the microscope objective.

5.2. Temperature Control

Temperature control is achieved using a heating stage with a programmable controller. Different heating stages are used for films and devices, but operate the same way. Programmable PID controllers (e.g., Watlow EZ Zone PM) regulate the current supplied to cartridge heaters inserted into the stage; power is adjusted based on feedback provided from thermocouples attached to the stage. The temperature set point is manually entered into the controller, and maintained for the duration of the experiment. Most controllers can accommodate more complex temperature-time behavior if necessary.

5.3. Humidity Control

Humidity control may also differ depending on the environmental control chamber; if using a small chamber (e.g., the Linkam stage), an incoming dry gas stream is bubbled through flask containing a water/glycerol mixture; by varying the proportion of glycerol to water, a wide range of relative humidities can be attained. The desired humidity can be verified using a hygrometer located downstream of the flask. A drawback to this approach is that humidity control is open loop, and the humidity in the gas feed will gradually reduce over time as water in the flask is depleted. Careful monitoring and replenishment of lost water are necessary to maintain constant humidity.

When using a larger control chamber, humidity can be controlled in a closed loop by connecting an ultrasonic humidifier to a port on the chamber and regulating the power to the transducer using the feedback from a hygrometer. It is also advisable to place a fan in the box to circulate the air and increase measurement accuracy by reducing humidity gradients between the sensor and the sample.

5.4 Atmosphere Control

Control of background atmosphere in the chamber can be set either by connecting a cylinder of the desired gas (if air or pure nitrogen or oxygen) to the box, or using mass flow controllers to achieve intermediate oxygen content.