Investigation of Ultramarine Pigment Excited State Dynamics by Pump-Probe Microscopy and Spectroscopy

by

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Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Chemistry in the Graduate School of Duke University

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Abstract

First mined in Afghanistan nearly 6,000 years ago, lapis lazuli is a blue pigment also known as ultramarine, a material that was highly prized (and corresponding highly priced) by Western painters during the Middle Ages and the Italian Renaissance. Both the mineral lapis lazuli and the synthetic ultramarine can undergo degradation in paintings and other works of cultural heritage, which presents challenges to the preservations of these works. Due to the limitations of many modern analytical techniques, art conservators and conservation scientists often still need to remove a sample of paint in order to understand the layering of pigments in a painting. Femtosecond transient absorption (also called pump-probe) spectroscopy and imaging are here used to explore the effects of depth, polarization, and power on the ultrafast excited state dynamics of ultramarines both natural and synthetic, in order to further understand the photophysics and potential photo-degradation pathways of ultramarine pigments in paintings. Both lapis lazuli and synthetic ultramarine undergo identical forms of photo-induced transformation in the context of these experiments, where it appears that either the lazurite chromophore or the sodalite cage structure of ultramarine is destroyed.
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1. Ultramarine pigments: some background

1.1 History of ultramarine, natural and synthetic

Prior to the discovery and commercialization of modern synthetic pigments, no artist's blue could rival the brilliance of lapis lazuli. In his famous treatise on artists’ materials and craftsmanship during the Renaissance, *Il Libro dell’Arte* (The Craftsman’s Handbook), Italian painter Cennino Cennini calls lapis lazuli “a glorious, lovely and absolutely perfect pigment beyond all pigments.” First used in ancient Egypt, lapis lazuli was particularly important to the artists of the Italian Renaissance, when it acquired the name ultramarine, as it was imported by Venetian merchants from the Badakhshan mines in Afghanistan.

The mineral lapis lazuli generally contains a mixture of other mineral components including diopsides, calcites and pyrites, but the pigment colorant is lazurite, a complex sulfur-containing sodium aluminosilicate. The sodium, aluminum, and silicon atoms form a sodalite-type cage structure, though the exact nature of the chromophore concentrations and occupancies still need to be characterized. Inside this cage structure is a negatively charged radical sulfur chromophore, which is typically either $S^-$ or $S^2-$. The triradical anion is responsible for lazurite’s brilliant blue color, while $S^2-$ provides a more yellow tone and can therefore shift the pigment color into the green.
Figure 1: Sodalite cage structure of ultramarine, containing $\text{S}^5$ (yellow) from ref. 5. Na ions are green, Si atoms are light blue, and Al atoms are dark blue.

In order to achieve the "glorious" color referenced by Cennino Cennini in Il Libro dell’Arte, extensive washing and grinding was necessary to refine the mineral lapis lazuli for use as a pigment; this process frequently produced varying grades of lapis in different shades of grey-blue to blue. Because the only source of lapis prior to the nineteenth century was the Badakhshan mines, natural ultramarine during the Renaissance period was as expensive as gold. Because of this horrific expense, contracts between artists and patrons often specified that the patron would provide both the lapis lazuli pigment and the gold leaf. As such, its use was reserved for figures of especial significance, particularly the Virgin Mary. Artists would sometimes start with a layer of a cheaper but less brilliant blue pigment called azurite, and then for the final layers would cover it over with ultramarine.

In 1824, in a French competition, a prize of 6,000 francs was offered to anyone who devised a suitable and inexpensive method of synthesizing ultramarine. The
competition produced two simultaneous discoveries in 1828: one by Jean Baptiste Guimet and the other by C.G. Gmelin.\textsuperscript{2,6} Two years later, Guimet was producing synthetic ultramarine in his own factory. The process of synthesizing ultramarine required combining finely ground China clay, silica, sulfur, soda ash, wood, and charcoal into a mixture that was heated in a furnace until reaching red heat. As this was a far more cost-effective way of obtaining ultramarine, the synthetic type as produced by Guimet and others quickly came to replace lapis lazuli in Western art.

\textbf{1.2 Conservation issues surrounding ultramarine}

Exposure to acid and/or pollution in the form of SO\textsubscript{2} was recognized by conservators and scientists in the 1960s to have a deleterious effect on the stability and permanence of synthetic ultramarine blue, and was linked to blanching or leaching of the color.\textsuperscript{2} More recently, this blanching of the blue color in acidic media has been linked to destruction of the sodalite cage structure by acid, freeing the sulfur chromophores (which are then potentially converted to H\textsubscript{2}S or elemental sulfur).\textsuperscript{3} The framework degradation has been attributed to the loss of aluminum from the sodalite cage.\textsuperscript{7} This may be the cause of "ultramarine disease," a widespread phenomenon that commonly affects paintings containing lapis lazuli (natural ultramarine), discoloring areas containing the pigment so that they appear grey and dull.
1.3 Previous research with pump-probe microscopy

Both synthetic and natural varieties of ultramarine were among the first to be studied with our group’s pump-probe microscope in both model samples\(^8\)\(^9\) and as part of an *in situ* investigation of a 14th century panel painting by Puccio Capanna (The Crucifixion, c.1330).\(^10\) Previous work on the photochemistry and photophysics of ultramarine has been performed by Dr. Tana Villafana from our group as part of her graduate thesis.\(^11\)

In these early studies, the excited state kinetics appeared to differ in lapis lazuli and synthetic ultramarine samples despite their similar chemistry. The lapis appeared to be characterized by a large instantaneous negative component (potentially as the result of a ground state bleach or stimulated emission) with a long-lived exponential decay (decaying back to zero on the order of tens of picoseconds), while the synthetic ultramarine appeared to consist of a similar instantaneous negative component followed by a slightly slower positive kinetic component. However, as will be shown in this work, by strictly controlling both the focus and the power levels delivered to the sample, the natural and synthetic varieties of ultramarine exhibit similar photophysics. In addition, this thesis will implement polarization controls (by controlling the angle of polarization between the pump and probe) that were not included in the previous pump-probe studies of ultramarine.
2. Pump-probe microscopy and spectroscopy: background and methods

Numerous analytical technologies are available today in museum laboratories and for on-site use in the investigation of cultural heritage; a brief list of the most basic instruments would include Raman, FT-IR, XRF (X-ray fluorescence), XRD, SEM-EDS, GC-MS, and HPLC-MS. Many of these essential techniques are now being complemented by tools such as TOF-SIMS, FORS, OCT, and synchrotron radiation facilities in order to increase the ability of conservators and conservation scientists to understand conservation and material issues of cultural heritage.

A technique for non-invasive three-dimensional imaging has been historically elusive in the field of cultural heritage. Our pump-probe system sidesteps the ethical and physical considerations necessitated by sampling from artworks. In the simplest scenario, the measured signal is directly proportional to the square of the light intensity (or photon density), enabling the collection of microscopic molecular information at a small spatial cross-section. The changes in ultrafast excited state dynamics under investigation here typically involve the third-order susceptibility, \( \chi^{(3)} \) (the second-order susceptibility, \( \chi^{(2)} \), comes into play for second-harmonic generation, a process that does not appreciably contribute to the nonlinear responses of ultramarines), following the equation:
\[ \mathbf{P}(t) = \varepsilon_0 \left[ \chi^{(1)} \mathbf{E}(t) + \chi^{(2)} \mathbf{E}^2(t) + \chi^{(3)} \mathbf{E}^3(t) + \cdots \right], \]

where \( \mathbf{P}(t) \) is the polarization, \( \mathbf{E}(t) \) is the electric field strength of an applied optical field, \( \chi^{(1)} \) is the linear susceptibility, \( \chi^{(2)} \) is the second-order susceptibility, \( \chi^{(3)} \) is the third-order susceptibility and so on.\(^{19} \)

Exploiting this non-linear optical effect enables the collection of images with high axial and lateral resolution at wavelengths in the near-infrared (NIR), which are typically less damaging to cultural heritage samples (particularly those from paintings with poorly lightfast pigments) than optical wavelengths. Pump-probe with NIR wavelengths can be used to image relatively thick samples (100µm or more for paint layers). The fact that our pump-probe microscope can produce three-dimensional virtual "cross-sections" of layers of paint and other artists' materials without any need for sampling provides it with a significant advantage over almost all other techniques available in the field today.

### 2.1 Pump-probe imaging

In pump-probe imaging, the pump beam is the first to arrive at the sample. It induces some change in the electronic states of the sample (for example, promoting or "pumping" electrons to populate an excited energy level) if it has an appropriate energy (wavelength) to interact with the system. The probe beam then follows at some time delay \( \tau \) (which may be on the order of a several hundred femtoseconds to tens of
picoseconds). Excitation and internal conversion typically occur within femtoseconds. In the small amount of time that passes between the arrival of the pump beam and the arrival of the probe beam, the electronic energy levels undergo ultrafast dynamic changes. These changes are monitored by the probe beam, the absorption of which is directly affected by the sample's photophysical properties and interaction with the pump beam. Different ultrafast excited state dynamics, such as ground state bleach (GSB), excited state absorption (ESA), and stimulated emission (SE) will produce either an increase or decrease in absorption of the probe beam (see Figure 2). In a GSB

![Diagram of pump-probe excited state dynamic mechanisms](image)

**Figure 2:** Typical pump-probe excited state dynamic mechanisms. Stimulated emission (SE), ground state bleach (GSD), and stimulated Raman scattering (SRS) are all mechanisms where the presence of the pump decreases the absorption of the probe, which we measure as a negative signal. Excited state absorption (ESA) and sum frequency absorption (SFA) or non-degenerate two-photon absorption (TPA) are mechanisms in which the presence of the pump results in increased absorption of the probe, which is measured as a positive signal.
mechanism, for example, the pump beam (in red in Figure 2) is absorbed by the sample as electrons are promoted from the ground to some intermediate state; however, because the ground state is now depleted, the probe beam absorption decreases in comparison to its absorption when the pump beam is not present.

The pump-probe imaging microscope used for these experiments uses a modelocked Ti:Sapphire Chameleon Ultra II with an 80 MHz repetition rate. The laser

Figure 3: Pump-probe microscope in epi-reflectance mode. The probe beam is generated by a Chameleon Ultra II laser (lower left corner). Part of the probe beam is directed to the microscope; a separated part is sent into the OPO to generate the pump beam, which is modulated at 2 MHz before being sent through the optical delay line. Both beams are raster-scanned over the sample field-of-view and the backscattered light from the probe beam is collected by a photodiode and the modulation change read out by a lock-in amplifier.
beam is passed through a beamsplitter to produce the probe beam and a second beam, which is directed into the optical parametric oscillator (OPO) to generate the pump beam. The pump beam is passed through the time delay line. The time delay (τ) controls the difference in time between when the pump arrives at the sample and when the probe arrives at the sample afterwards. In our pump-probe microscope, the pump modulation (2 MHz) is transferred to the probe beam as the probe passes through the sample. The probe beam measured after passing through the sample typically has a cross-correlation of approximately 220fs. We use lock-in detection to monitor the change in probe modulation following the sample (see Figure 3). The system setup allows for collection of the probe beam in either epi-reflectance or transmission configuration.

By using a pair of scanning galvo mirrors, our system is able to raster-scan an image in the XY plane on the order of several hundred microns in several minutes as our collection time is limited by our SNR (signal-to-noise ratio) and the acquisition time of our lock-in amplifier. In epi-reflectance mode, the backscattered light from the sample is directed back towards the photodiode detector, prior to which we have placed a cut-off filter to eliminate light from the pump beam reaching the detector. In our typical configuration, we generally use a pump beam of 720 nm and a probe beam of 817 nm, so a long-pass filter of 800 nm before the photodiode can be used to eliminate any residual light. The modulation change as transferred from the pump to the probe beam is then read out by the lock-in amplifier. In transmission mode, the pump and probe beams are
collected by a condenser positioned after the sample. The pump beam is once again rejected before the photodiode, so only the transmitted probe signal modulation is measured.

All of the data here were collected using a 40x 0.75NA microscope objective at 720nm pump/817nm probe beam wavelengths in epi-reflectance mode, unless otherwise stated. Power values, measured as an average power in milliwatts (mW) after the microscope objective, are provided with figures and text where appropriate.

2.2 Femtosecond transient absorption spectroscopy

Transient absorption spectroscopy is used as a complementary technique to pump-probe imaging in order to observe excited state dynamics for a continuum of wavelengths of interest (since our pump-probe microscope is limited to acquiring data at one pump wavelength and one probe wavelength at a time).

Our kHz femtosecond transient absorption spectroscopy system (Figure 4) uses a white light (WL) continuum probe. Laser light is generated by an 808nm seed beam provided by a Millennia-pumped Tsunami laser source, which is sent into a Spitfire Ti:Sapphire system for amplification. A portion of this beam is split off and sent into a TOPAS optical parametric amplifier (OPA), which is capable of generating a selected pump beam between approximately 400-2500nm with a bandwidth on the order of 5-10nm (at FWHM). The other portion of the amplified seed beam is sent through a sapphire crystal
to generate the white light continuum probe. The diffuse reflectance from the overlap of the pump and probe beams on an opaque sample is then collected by two parabolic mirrors and sent to an imaging spectrometer via fiber optic cable, where the transient absorption is typically measured between 400-1300nm. A band-pass filter is placed in the pump beam pathway in order to narrow the spectral bandwidth of the pump. A masking pin is also used in the imaging spectrometer in order to block any additional pump light that reaches the detector. The transient absorption ($\Delta A$) at each wavelength across the measured spectrum is determined by

$$\Delta A = \log\left(\frac{I_{\text{sig,off}}}{I_{\text{sig,on}}}\right),$$

Figure 4: Femtosecond transient absorption kHz spectroscopy schematic. The seed beam (red) is used to generate the WL continuum probe (grey) and the pump beam (green), which can be selected to be any wavelength between approx. 400-2500nm.
where $I_{\text{sig, off}}$ is the signal intensity at the detector when the probe is off (the background) and $I_{\text{sig, on}}$ is the signal intensity at the detector when the probe is on.
3. Results & Discussion

3.1 NIR transient absorption spectroscopy results

Transient absorption (TA) spectroscopy data were measured for a powder sample of synthetic ultramarine blue (SUB), shown in Figure 5. A 720nm pump was chosen as this is the typical pump configuration for our pump-probe microscope (with an 817nm NIR probe, see following sections). Figure 5 shows a fast negative kinetic for wavelengths between 800-950nm (cyan trace showing 0.2ps data) with a maximum delta around 850nm. This behavior may represent either a ground state bleach (GSB) or

![Figure 5: NIR transient absorption (TA) data from a powder sample of synthetic ultramarine blue (SUB, Kremer Pigmente #45010). Data collected on kHz spectroscopy system with a 720nm pump beam (0.3mW) and WL continuum probe (60µW measured at 720nm).]
stimulated emission (SE). The kinetic from 800-950nm decays on the order of several
tens of picoseconds into a longer-lived positive kinetic (see purple and magenta traces
for 30ps and 50ps, respectively) that remains positive for the duration of the experiment
(out to 50ps).

3.2 Depth of focus dependence in ultramarine

A comparison was made between two samples of synthetic ultramarine from the
same source (Kremer Pigmente, #45000). Samples were mixed into paint form using a
gum arabic binder (see Appendix A for preparation steps and materials) and applied to
separate glass slides in two different thicknesses: 1) approx. 100-200µm (standard
thickness) and 2) greater than 300µm (thick sample). The “middle” of the sample was
taken to be the point at which the measured pump-probe signal intensity was the
greatest. Pump-probe images and time delay kinetics were then recorded for each
sample at the top of the sample (defined to be the surface or approx. 5µm below it), the
middle of the sample, and the bottom of the sample (taken as approx. 5µm before the
pump-probe signal experiences complete attenuation while traveling through the
sample).

The data, shown in Figure 6, demonstrate the difference in decay kinetics (and therefore excited state dynamics) not only within different depths in the sample but also between samples of different thicknesses. While there is a predictable maximum of pump-probe signal intensity at the middle of the paint film in both samples (red curve in
Figure 6: Pump-probe data from two samples of synthetic ultramarine (top set, a & b – 50-200μm, bottom set, c & d – greater than 300μm). Collected at 720nm pump, 817nm probe wavelengths (1mW of power each).

6a and 6c), the decay kinetics at the top, middle, and bottom z-depths of the sample are not consistent with one another, particularly for the slightly thinner sample (see 6b). At the bottom of the sample in 6b, where attenuation of the pump and probe beams would be the greatest, the pump-probe signal is characterized by an instantaneous negative signal that eventually decays to zero before 20ps. By contrast, the middle layer of the sample exhibits the same instantaneous negative signal, but instead of an immediate decay to zero, the instantaneous response is followed a small, slightly longer-lived
positive signal. This positive signal in 4c appears to include excited state contributions from about 10% of the species that were involved with the instantaneous negative process (which could be either a ground state bleach or stimulated emission).

The appearance of the differences shown in Figure 6 suggested that the pump-probe signal of synthetic ultramarine was highly depth-dependent. To eliminate any potential pump-probe contributions from the gum arabic binder, densely-packed powdered samples of the same synthetic ultramarine were analyzed in order to determine the origin of this possible depth dependence. The same experiment was carried out under the same conditions as above; experimental data are plotted in Figure 7. Here, the difference between the surface (top) layer and the middle and bottom layers of the sample are even more pronounced (see 7b): the longer-lived positive component never fully decays back to zero even after 20ps.

Figure 7: Pump-probe data synthetic ultramarine powder, collected at 720nm pump, 817nm probe wavelengths (1mW of power each).
To complicate the analysis, the pump-probe kinetics from the “thick” synthetic ultramarine blue (SUB) sample shown in Figure 6 above are similar to data from a lapis lazuli paint film prepared in gum arabic binder by a comparable method (thickness approx. 50-200μm), as shown in Figure 8. As stated in Chapter 1, the lack of a similar pump-probe decay response from synthetic ultramarine and lapis lazuli was surprising in previous results because the two pigments are chemically the same. However, the data in Figure 7 suggest that these differences in decay kinetics may not be so much the result of chemical differences but due to a high sensitivity of these pigments to varying experimental conditions such as axial depth of measurement.

Extremely thin, semi-transparent samples of synthetic ultramarine were produced by pressing the paint film between a glass slide and a glass coverslip. Although the exponential decay differs from that of the thicker synthetic ultramarine
sample, the pump-probe signal intensity is once again greatest in the middle of the sample (arbitrarily set to be 15μm in Figure 9). Once again, several z-depth slices were taken at a series of axial focus positions, each 2μm apart. Based on these z-depth measurements, the sample was estimated to be no more than 25μm thick. In all regions of this thin ultramarine sample that were analyzed, the pump-probe kinetics (rather than the absolute intensity) evolved independently of axial focus position within the paint layer. A schematic of where the top, middle, and bottom z-slices of a sample are taken are shown in Figure 10.

Figure 9: Z-depth analysis of thin (approx. 25μm) synthetic ultramarine sample. The middle of the paint film occurs at 15μm (values in the plot are arbitrary). Pu-pr data collected at 720nm pump, 817nm probe wavelengths (1mW of power each).
Because the variance in the pump-probe kinetic shape described above may be the result of varying powers delivered to different parts/depths of the ultramarine sample, a power study was carried out on synthetic ultramarine powder. This was done (as shown in Figure 11) by setting either the pump or probe laser power to a relatively low value that is unlikely to damage the sample – in this case, 0.7mW – and then
changing the power delivered by the other laser. The power values shown in Figure 11 and throughout this thesis are the average powers measured after the microscope objective.

The data shown in Figure 11 were recorded at the approximate center of the sample (where the measured pump-probe intensity is at a maximum) and at fairly low average powers, at or below a combined total of 2.0mW from the pump and probe.

![Figure 11: Pu-pr power study data for synthetic ultramarine (Kremer #45010), measured with 720nm pump and 817nm probe wavelengths. The right side plots show the effect of changing pump power; the left shows the effect of changing the probe power.](image-url)
beams. Based on the data, the sample exhibits greater sensitivity to changes in pump power than to changes in probe power (compare data on the left vs. right sides of Figure 11).

When pump-probe images are collected at the surface (10μm above the middle) and bottom layers (15μm below the middle) of the sample with a constant probe power

![Figure 12: Power study data at surface and bottom layers of sample shown in Figure 9, measured with 720nm pump and 817nm probe wavelengths. Data from the top of the sample is shown in a and b; from the bottom of the sample in c and d. The positive component can be observed to emerge around 2ps with increasing total laser power.](image)
of 0.7mW while increasing the pump power from 0.4mW to 2.0mW, a similar trend emerges (Figure 12). The longer-lived positive kinetic component, which could be a stimulated emission from an intermediate excited state formed following an initial ground state bleach or stimulated emission, appears to “grow in” at higher total average powers. Note that in Figure 12a and 12b, the last pump-probe power pair no longer keeps the probe power constant, but is instead set at 2.0mW pump/1.0mW probe. There is a clear difference in the power-scaling behavior between the positive and negative components here, because the magnitude of the positive kinetic around 2ps is nearly superimposable for both power pairs in both the normalized and raw data sets.

One concern with analyzing these samples is the potential for photo-induced degradation at high laser powers or high photon fluxes, which will be further addressed in Section 3.3.2. However, for the sample analyzed in the case of Figures 11 and 12, the initial pump-probe measurement at 0.4mW pump/0.7mW probe (or vice versa) was repeated at the end of the analysis after the power had been increased to 2.0mW for either the pump or the probe. This is shown in the plots in Figure 12c and 12d: there is ultimately a very small intensity change from the first measurement at 0.4mW pump/0.7mW probe (blue line) to the final measurement after the sample has been subjected to irradiation by four pump-probe power pairs (yellow line).

A similar experiment to study the effect of increasing pump/probe powers on kinetic behavior and signal reproducibility was repeated on a thin sample (<30μm thick)
Figure 13: Thin synthetic ultramarine (Kremer #45010) prepared in gum Arabic with a PVC (pigment-volume concentration) of 20, measured with 720nm pump and 817nm probe wavelengths. Left-hand data plots the effect of changing pump and probe power (probe power is constant at 0.7mW for the first 4 sets of pu-pr power pairs). Right-hand data shows the effect of cumulative irradiation on signal intensity and kinetic behavior following a series of measurements.

of synthetic ultramarine (see Figure 13). Whereas Figure 9 shows no positive kinetic at 2ps for a sample of comparable composition and thickness, Figure 13 clearly depicts the emergence of this positive component at high combined beam powers. However, the appearance of the positive kinetic may also correlate to a loss of total pump-probe signal intensity, as observed in the right-hand side data in Figure 13. Each data set on the right
side of Figure 13 was recorded at the initial 0.7mW/0.7mW pump-probe power. Trace 1 corresponds to the first measurement at 0.7mW/0.7mW pump-probe (dark blue line on left side of Figure 13); Trace 5 was recorded following irradiation with 2.5mW/0.7mW pump-probe (cyan line); and Trace 7 was recorded following irradiation with 2.5mW/2.5mW (purple line). Trace 10 was recorded following Trace 9 to check the reproducibility of the previous measurement.

While the initial absolute intensity fluctuations in traces 1, 5, and 7 (bottom right) appear stochastic, there is a much more dramatic change after higher irradiation powers – see traces 9 and 10, which were recorded following irradiation at the sample with 3.0mW/2.5mW pump-probe power (yellow line on left side of Figure 13). These data could suggest that the intensity of the laser irradiation can cause photo-degradation of the probed excited species. However, any potential photo-degradation does not appear to change the kinetic behavior of the sample (see normalized data, top right of Figure 13). This could indicate that, despite a loss of absorbing/excited species, the fundamental chemistry is not being changed by some photo-induced process.

This power study experiment was repeated on a sample of densely-packed lapis lazuli powder using 0.5mW/0.5mW and 2.0mW/2.0mW pump-probe powers (see Figure 14). There is a clear difference, both in absolute signal intensity and excited state kinetic behavior, between these two low and high power sets. At relatively “high” power pairs – in this case, 2.0mW/2.0mW – the slow positive component that is frequently observed
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in the synthetic ultramarine is finally observed in lapis lazuli. These data prove that the
photophysics of lapis lazuli (natural ultramarine) are not fundamentally different from
synthetic ultramarine, to which it is chemically the same.

A simple experiment was devised in order to demonstrate the power attenuation
that occurs as the pump and probe beams penetrate the paint film, the results of which
are shown in Figure 15. For a powder sample of synthetic ultramarine, an initial pump-
probe kinetic measurement was made in the middle of the sample at an arbitrary power
(0.7mW pump and 1.0mW probe). The focus was then moved to the top of the sample
(approximately 5μm above the middle of the sample) and the measurement repeated
there for 0.7mW/1.0mW and 1.5mW/1.0mW pump-probe power pairs. When the same
power used to measure the excited state dynamics in the middle of the sample is used at
the top of the sample, both the absolute intensity of the kinetic signal and the kinetic

Figure 14: Lapis lazuli powder sample (>300μm thick) from Natural Pigments. Data collected with 720nm pump and 817nm probe wavelengths for varying pump-probe power pairs (shown in legend). Lapis crystals from Natural Pigments are smaller in diameter (~10μm) than lapis crystals from Kremer (20-30 μm). Kinetic time delay curves based on single crystal ROIs.
behavior is changed. However, when the power delivered to the top of the sample is increased (in this case, arbitrarily), the kinetic behavior and absolute intensity can be well-reproduced (compare the near perfect overlay of the red and blue lines in Figure 15). This seems to suggest that the ultrafast excited state behavior of these samples is affected not so much by depth as by power, accepting that the model shown in Figure 10 is true: measuring at the “top” or near the surface of the sample means that the focal volume will be partially outside the sample.

Figure 15: Kinetic data for synthetic ultramarine (Kremer #45010) powder with 720nm pump/817nm probe. An initial measurement was made in the middle of the sample (blue line) at 1.0/0.7mW probe/pump. A second measurement was made at the top of the sample at this same initial power (green line); the power was then increased to 1.0/1.5mW probe/pump in order to see if there was a signal change.
The results of these experiments may, at least in part, explain the depth-of-focus issue encountered in the preceding section. The field-of-view of our microscope may include some crystallites that are slightly out of the plane of focus, causing them to receive a subtle difference in power than those crystallites that are maximally in focus. A shift in focus of as little as 2μm may produce this effect in the case of synthetic ultramarine, as the pigment crystallites are quite small (approx. 5μm or smaller in diameter). However, it appears that the powers needed to generate these kinds of multi-component kinetic behaviors will vary from sample to sample, and therefore further research is needed to understand the physics behind this power thresholding. Since the optical scattering of both types of ultramarine (natural and synthetic) occurs in the Mie regime, the scattering will be proportional to the ratio between particle radius and the wavelength of light. Optical scattering will therefore be more dominant for the larger, rougher lapis lazuli crystallites than the synthetic ultramarine crystallites, which may decrease absorption of the pump and probe beams in the lapis lazuli case and explain this apparent difference in epi-reflectance mode power-scaling.

### 3.3.1 Comparison of lapis lazuli and synthetic ultramarine images

The combined effects of these changes in depth and changes in power are spatially visible in the sample images following phasor analysis. Phasor analysis, as applied here, is a technique that uses a mathematical decomposition of our pump-probe images to generate and plot two phasor components, which are related to the Fourier
transform of the in-phase and out-of-phase pump-probe signals. It is a tool that enables plotting of the spatial distribution of pump-probe components in our images without the need for a model or pre-fitting. More information on the details of how phasor analysis is applied to non-linear optical images and pump-probe images is provided elsewhere.\textsuperscript{20}

The phasor images for both natural lapis lazuli and synthetic ultramarine in Figure 16 support the conclusions drawn in the above section, as well as the schematic proposed in Figure 10 (see Section 3.2). Four samples in total are shown in Figure 16: lapis lazuli samples from two different manufacturers (Kremer and Natural Pigments) and ultramarine samples from the same two manufacturers. In all four cases – but particularly visible in the synthetic ultramarines – the multi-component signal (in green) is seen for crystallites or regions of crystallites in the focal region, whereas the negative signal only (in red) is observed in the out-of-plane crystallites. These phasor images may also explain why the positive component of this excited state kinetic is so difficult to measure for lapis lazuli in comparison to synthetic ultramarine: because the lapis lazuli crystallites are larger than the synthetic ultramarine crystallites, the majority of the lapis lazuli pump-probe signal originates from out-of-plane crystallites or regions of crystallites. In ultramarine, however, the majority of the smaller crystallites are contained within the focal region that is being imaged. A closer examination of the pump-probe images of lapis lazuli and synthetic ultramarine also shows co-localization.
Figure 16: Phasor decomposition (top) of pu-pr kinetic data with corresponding phasors plotted for two types of lapis lazuli powder (middle) and of synthetic ultramarine powder (bottoms). Measured with 720nm pump and 817nm probe wavelengths, 0.8/0.8mW pu-pr.
of the positive and negative signal components. Figure 17 shows images from 0ps and 2ps for both lapis lazuli (17a and b) and synthetic ultramarine (17c and d). Particularly in Figures 17a and b, the lapis lazuli case, the kinetic curves may be misleading as they are the result of averaging over the whole field of view shown in the images to the right of the plots; this means that the longer-lived positive component that normally occurs around 2ps is averaged out due to background noise or from contributions of lapis

Figure 17: Pu-pr kinetic data with corresponding images, measured with 720nm pump and 817nm probe wavelengths. Data on the left (a,b) are from powders of lapis lazuli (Natural Pigments); on the right (c,d), from synthetic ultramarine (Kremer #45010). The pink circle indicates the time point on the kinetic time delay curve that the image was taken from. Red circles in the images indicate particular regions where the two components (positive and negative) may be well observed at different time points. Note that the kinetic curves shown in all cases are the result of averaging over the entire field of view in the image shown above.
crystals that are not receiving enough power to exhibit the positive component, in reference to the depth-of-focus issue discussed above. If the kinetic curve was plotted just for the small regions of interest indicated by the red circles, the positive component would likely appear but would be quite noisy as a result of poor signal-to-noise ratio in these limited area regions (compare data in Figure 16).

The Figure 17 images clearly show that the instantaneous negative signal from a GSB and/or SE mechanism is spatially localized within the same crystallites as the positive excited state component. This rules out the possibility that the positive component is somehow the result of sample impurities; rather, this uncharacterized signal is a fundamental characteristic of the chemistry and photophysics of ultramarine, both natural and artificial.

3.3.2 Damage analysis

In some experiments, increasing the power appears to result in the photo-induced destruction of some excited species, as shown in Figure 18. The order in which the measurements were made by changing the power is shown from top to bottom in the legend at bottom left (i.e., 0.4/0.4mW in blue was made first and 1.0mW/1.0mW in cyan was made last of the four). After increasing the power from 0.4/0.4mW to 1.0/1.0mW pump-probe and retaking the measurement with the initial power configuration of 0.4/0.4mW, a significant loss of signal was observed, likely due to photo-degradation and loss of absorbing species. A final increase to 1.0/1.0mW pump-
probe power shows that some of the probed species do remain and their kinetic behavior is relatively unchanged, but it is clear some kind of photo-damage has occurred.

It would seem that photodamage should be cumulative. However, when a similar sample was subjected to ten consecutive irradiations with 1mW/1mW of pump-probe power (see Figure 19), any changes in the pump-probe signal intensity appear to be stochastic fluctuations and not the result of any trend that points to photo-damage. This seems to indicate that there is some kind of threshold effect in play. Further
investigation is needed here, both to understand the power threshold of photo-induced damage and also to develop a straightforward methodology to analyze samples that may have different damage thresholds.

3.4 Polarization dependence

A polarization study was carried out on the synthetic ultramarine blue powder in epi-reflectance mode. In this experiment, a half-waveplate is placed in the pump beam pathway and the polarization angle of the pump is then set to either 0° or 90° (parallel or perpendicular to the probe beam, respectively). The half-waveplate is adjusted so that the total average power delivered by the pump beam to the sample is...
the same in both polarization configurations (average power measured as
1.5mW/1.5mW for pump and probe, respectively. Based on this experiment, the results
of which are shown in Figure 20, it appears that polarization in epi-reflectance modes
has a slight impact on the absolute signal intensity measured, but not on the kinetic
behavior of these ultramarine samples.

![Figure 20: Polarization study carried out in epi-reflectance mode on SUB power from Natural Pigments (720/817nm pump-probe, 1.5mW/1.5mW power). Blue lines show pu-pr response when the pump and probe beams are parallel; green lines show pu-pr response when the pump beam is perpendicular polarized with respect to the probe beam.](image)

3.5 *Excited state chemistry in ultramarines*

The excited state dynamics of ultramarines appear to feature competition
between an instantaneous negative component with a slow decay (either ground state
bleach or stimulated emission) and a weaker positive component that generally emerges
around 1.8ps (see traces from phasor decomposition in Figure 16). Based on power
scaling experiments performed with the 720nm pump (probe power kept constant at 2mW), it appears that there is a non-linear, roughly quadratic, dependence of the signal intensity on the pump power (see Figure 21). This suggests that pump beam participates in a two-photon absorption into an excited state before the probe beam arrives at the sample. The 817nm probe beam then induces an excited state absorption from this excited energy level.

The instantaneous negative component is most likely the result of either a ground state bleach (GSB) or stimulated emission (SE) mechanism. By switching the wavelengths used for the pump and probe beams from 720/817nm pump-probe to 817/720nm pump-probe, it is possible to establish which of the two mechanisms is responsible for this negative component. Stimulated emission would not be possible with the 817/720nm pump-probe combination as it would violate the law of energy.
conservation (see Figure 2). Preliminary experiments show that the instantaneous negative component is still observed in ultramarine powder when the pump and probe wavelengths are switched (see Figure 22). These experiments appear to confirm the possibility that this is a ground state bleach rather than stimulated emission mechanism, but further power scaling experiments would be needed here due to the interplay between the ESA contribution and the negative (likely GSB) contribution to the excited state dynamics.
4. Conclusions

The experiments described in the previous chapters serve as important engineering controls for further studies of ultramarine photophysical and degradation pathways. We now have a much better understanding of the results that changing focusing depth and/or power affect on our ultramarine model samples; this will ultimately inform how we conduct experiments in situ on paintings and other cultural heritage objects, and also how we potentially design a vigorous pump-probe portable microscope in the future. It is clear from these experiments that we can generally disregard the effect of and/or need for pump-probe polarization control when analyzing ultramarine samples, though this is not necessarily the case for all pigment samples.

The linear absorption spectrum of ultramarine has two well-characterized peaks, one around approx. 360-400nm and the other around 600nm, representing the absorption of the S<sub>2</sub> and the S<sub>3</sub> chromophores, respectively. Having established a three-photon mechanism for the positive component around 1.8ps (a two-photon absorption of the pump followed by ESA of the probe), it seems possible that the two-photon absorption of the 720nm correlates to the linear absorption peak for ultramarine that occurs around 360nm. This suggests that the weaker positive component observed in the pump-probe delay traces may arise from the presence of the S<sub>2</sub> chromophore, which occurs in much lower concentrations in both natural and synthetic ultramarines.
than the dominant $S^-$ species. The negative component, may then correspond to excited state dynamics related to the presence of the dominant $S^-$ species.

### 4.1 Future work

More work is needed to characterize the photophysics of ultramarine, particularly at time delays longer than 2ps, in order to understand if photo-induced degradation mechanisms are occurring in these samples. It seems likely (but has not been definitely confirmed by the experiments here) that the species responding to the pump and probe beams is either the $S^-$ or $S^-$ lazurite chromophores (as opposed to the cage structure). The $S^-$ type chromophore provides the primary blue color in lazurite and has a strong active Raman mode at 548 cm$^{-1}$, as measured with spontaneous Raman.\textsuperscript{11} There is a somewhat competing spontaneous Raman scattering peak of the $S^-$ chromophore at 585 cm$^{-1}$, which is weaker and may appear as a shoulder of the main $S^-$ peak at 548 cm$^{-1}$; this complicates interpretation of dispersive Raman data.\textsuperscript{11}

In her thesis, Dr. Villafana also made an attempt to co-register dispersive Raman images of synthetic and natural ultramarine crystals with images of the same samples collected with our pump-probe microscope (the same as was used for all of the experiments described in this thesis). However, because of differences in resolution and the complication of the $S^-$ Raman shoulder on the $S^-$ peak, we intend to develop a multi-modal stimulated Raman scattering (SRS) and pump-probe microscope that will enable us to compare SRS to other excited state dynamics, such as GSB and ESA,
simultaneously on the same sample with the same axial and lateral resolution. Application of this technique will allow us to further understand if a photo-excited intermediate state is forming on the pathway to photo-induced degradation by providing enhanced spectral resolution and chemical sensitivity.

Since the primary degradation observed with ultramarine is “ultramarine sickness” or ultramarine disease, which is thought to be connected to breakdown of the sodalite cage structure and loss of color in acidic medium (such as oil paint), the photo-induced degradation studied here could potentially represent a secondary ultramarine degradation pathway that could be occurring in alkaline mediums (such as fresco). Experiments on both synthetic ultramarine and lapis lazuli would need to be performed on paint cross-sections from and in situ on fresco, egg tempera, and oil mediums with both pump-probe microscopy and stimulated Raman scattering before further conclusions can be drawn. However, this research shows that pump-probe microscopy and spectroscopy can provide important and useful information on materials used in cultural heritage that might not be scientifically accessible by other modern means.
Appendix A

A.1 Powder samples

Powder samples were prepared by stacking 4 pieces of double-sided Scotch tape (individual thickness of approximately 100μm each) on a glass slide and cutting a square window in the center of the stacked taped. Pigment powder (without added medium) was placed, densely packed, into this rectangular area and covered with a glass coverslip to effectively create a powder cuvette of upwards of 300-400μm powder thickness.

A.2 Gum arabic paint films

Gum arabic medium was prepared by adding approximately 10g of gum arabic powder (Sigma Aldrich G9752) in 30mL of boiling distilled water. The solution was mixed at a temperature of 60°C until the gum arabic powder completely dissolved.

Thin samples were prepared by dropping 2-3 drops of the paint mixture on the center of a glass slide and then pressing down with a glass coverslip. Thick samples were prepared by depositing several drops of the paint mixture on a glass slide, allowing this initial layer to partially dry, and then depositing additional drops on top for several repetitions. PVC (pigment volume concentration) is expressed for samples where known. The PVC of a sample is the percentage of volume of the pigment over the total volume of the paint (including the volume of the binder, the pigment, and any additives).
References


