

UV/Vis/NIR Spectroscopy

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High Resolution Scanning Performance with the PerkinElmer LAMBDA 1050+



Introduction

The LAMBDA 1050+ is the latest in the line of high performance UV/Vis/NIR double monochromator spectrometers offered by PerkinElmer. This instrument incorporates many of the latest technological advances in optical design, including full wavelength range three detector technology, a high resolution, high energy optical system incorporating low stray light holographic gratings, and Indium Gallium Arsenide (InGaAs) sampling modules for enhanced near-infrared (NIR) performance. Ultra-high resolution scanning is one of the achievements in this new instrument. Chemical bonds of small molecules can be studied using high resolution spectroscopy, where fine vibrational structure can be observed. The LAMBDA 1050+ incorporates a true double monochromator of the Littrow design, with custom holographic gratings of 1440 l/mm for the UV/Vis, and 360 lines/mm for the NIR. The resolution (spectral bandwidth) in UV/Vis of the LAMBDA 1050+ is specified to be less than or equal to 0.05 nm. The theoretical limiting resolution of the optical system is less than or equal to 0.03 nm.

The high resolution capability of the LAMBDA 1050+ will be explored in this paper using iodine vapor. Iodine is the heaviest common halogen (atomic number = 53, atomic mass = 127) and exists as a solid at room temperature in sublimation equilibrium with its vapor. The vapor has the appearance of a violet gas, having a visible absorption. This absorption corresponds to a spin-forbidden transition from the lowest vibrational levels of the singlet electronic ground state to high vibrational levels of a triplet excited state.

Experimental

Iodine crystal (ACS) was obtained from Mallinckrodt Chemicals (1008). To increase the sensitivity of the experiment, a quartz 100 mm cylindrical long path cuvette (PerkinElmer #B0631098), and cylindrical cell holder (PerkinElmer #C0550303) was used (pictured below). A few iodine crystals were added to the cuvette, which was then tightly stoppered.



Consumables used in this note:

Iodine crystal (ACS) from Mallinckrodt Chemicals (1008)

Quartz 100 mm cylindrical long path cuvette (PerkinElmer #B0631098),

Cylindrical cell holder (PerkinElmer #C0550303)

Over a period of time iodine vapor visible as a violet gas could be seen forming in the cuvette. The cuvette was slightly warmed to speed the process.

To ensure the most accurate peak positions, a wavelength calibration using deuterium emission lines was conducted prior to measurements. The LAMBDA 1050+ parameters were set to scan from 630 to 500 nm using a 0.05 nm slit setting, 1.00 second response time, and a data interval of 0.01 nm. A background correction was acquired against air (empty beams). When conducting this experiment using a 0.05 nm slit, it should be noted that the energy throughput is greatly reduced. Therefore, a lower integration time was used to ensure that the noise level would be substantially reduced below the actual vibrational transitions that were being recorded. This reduces the possibility of mis-identifying a real transition peak with noise. The peak-to-peak noise level of the baseline under the conditions described above was determined to be less than 0.002 A. (Figure 1).

Results

The acquired iodine vapor scan is shown in Figure 2, along with the baseline for comparison. Note that the vibrational transitions are well above the peak to peak baseline noise under these conditions.

At wavelengths below 550 nm, only $v'' = 0$ type transitions are observed; above 570 nm, only $v'' = 1$ transitions are seen. Between 550 nm and 570 nm, a series of doublet peaks can be seen (Figure 3). The peaks on the long wavelength side originate from the $v'' = 1$ vibrational state, those on the short wavelength side from the $v'' = 0$ state.

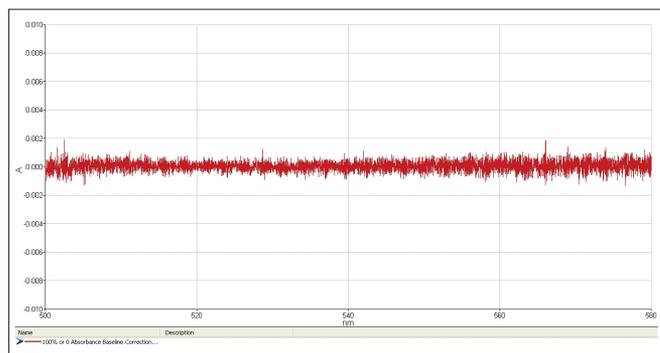


Figure 1. Baseline absorbance plot from 570 nm to 500 nm showing the expanded peak-to-peak noise of a portion of the corrected baseline using a 0.05 nm slit. This noise level is well under the absorbance levels of the vibrational transitions being monitored.

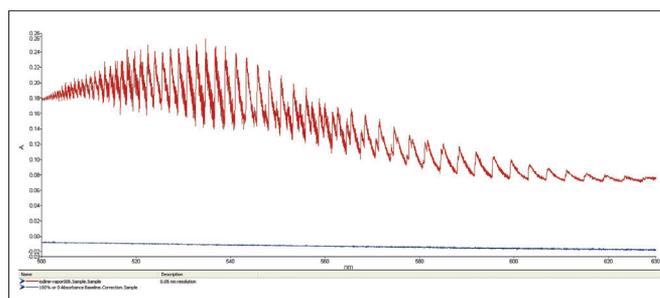


Figure 2. Iodine vapor spectrum (red) acquired with a 0.05 nm slit in a 100 mm pathlength cuvette. The baseline is shown for comparison (blue).

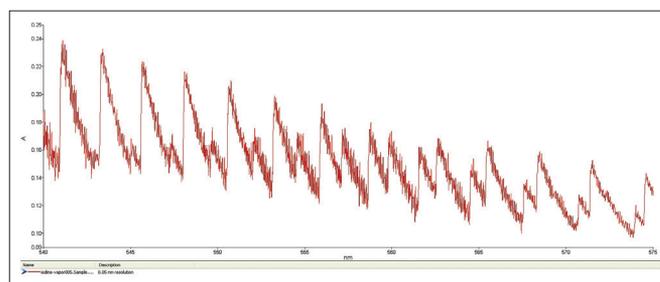


Figure 3. Expanded graph from 540 to 575 nm showing the doublet region. The peaks on the long wavelength side originate from the $v'' = 1$ vibrational state, those on the short wavelength side from the $v'' = 0$ state.

The spectral region from 530 to 500 nm has some of the narrowest vibrational transitions, where a 0.05 nm monochromator resolution is required to fully resolve some of the sharpest peaks. Shown in Figure 4 is an expanded range view of the iodine vapor spectrum from 517.6 to 515 nm. The actual raw data points are superimposed on the graph as green points. Labeled on the graph are adjacent peaks that are fully separated at 0.04 nm. Circled in blue are the narrowest peaks resolved, separated by 0.03 nm. The baseline is superimposed at the same scale as the blue tracing and the bottom of the graph, showing that the baseline noise itself is quite low, eliminating the possibility of contributing false peaks at this absorbance level.

The area between 515.54 and 515.80 was greatly expanded (Figure 5) where peaks defined by the raw data points identify a triplet where two adjacent peaks were actually separated by 0.02 nm (515.73 and 515.75 nm).

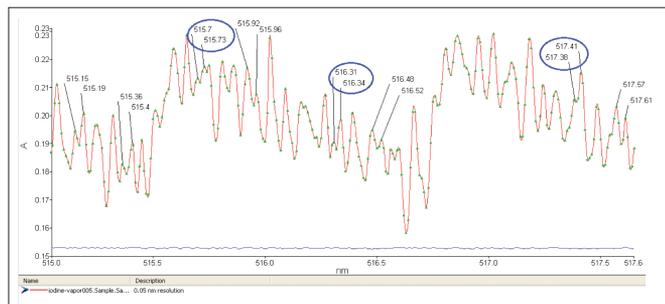


Figure 4. Expanded area of the iodine vapor spectrum (red) from 517.6 to 515.0 nm, showing many sharp vibrational transitions. Superimposed on the graph are the raw data points (green dots) acquired in the scan, and the baseline scan (blue) on the same scale. Peaks were separated fully at 0.04 nm, and are resolved at 0.03 nm in a number of locations.

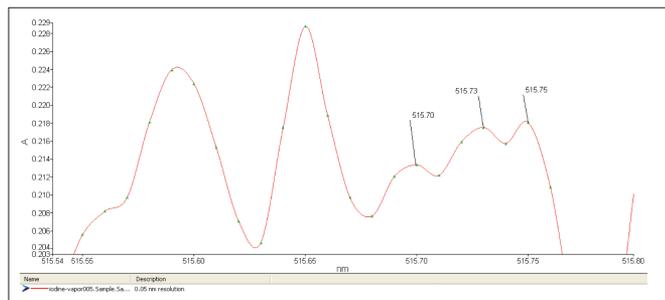


Figure 5. The area between 515.54 and 515.80 was greatly expanded where peaks defined by the raw data points identify a triplet for which two adjacent peaks were actually separated by 0.02 nm (515.73 and 515.75 nm).

Conclusion

The research grade double monochromator PerkinElmer LAMBDA 1050+ is the latest in the line of high performance UV/Vis/NIR double monochromator spectrometers offered by PerkinElmer. This instrument incorporates many of the latest technological advances in optical design, including full wavelength range three detector technology, a high resolution, high energy optical system incorporating high dispersion, low stray light holographic gratings, and Indium Gallium Arsenide (InGaAs) sampling modules for enhanced near-infrared (NIR) performance.

Ultra-high resolution scanning is one of the achievements in this new instrument. A combination of a high energy optical system, a minimum resolution of less than or equal to 0.05 nm, and “best in class” wavelength accuracy (0.08 nm) allows reference quality high resolution data to be acquired with confidence. Using iodine vapor as a case study, it was shown that peaks can routinely be resolved at 0.04 nm, with resolution of peaks still possible at even 0.03 nm, and 0.02 nm!

Because the noise level of the LAMBDA 1050+ when scanning with a 0.05 nm bandpass is very low, the many vibrational transitions of iodine vapor can be identified with reliability. With such demonstrated resolution, the LAMBDA 1050+ is an ideal tool for the study of the quantum mechanics of small molecule vibrational transitions, as well as a wide range of demanding industrial and academic applications.

References

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