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EMISSION SPECTROSCOPY IN SUPERSONIC EXPANSIONS

OSD-107

ELEMENTAL ANALYSIS
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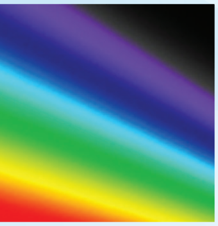

Accurate calibration for narrow spectroscopic lines

Introduction

Supersonic expansions are now common tools in spectroscopy laboratories. They allow molecules, free radicals, van der Waals complexes, and ions to be studied in an ultra-cold collision-free environment. Laser-induced fluorescence (LIF) is often the method of choice for detecting and characterizing such species. In order to obtain additional information about reactive intermediates in supersonic expansions, an emission system with precise wavelength calibration was designed using a HORIBA Scientific scanning monochromator.

Experimental setup

In a pulsed discharge jet, reactive intermediates are readily generated by striking a DC electrical discharge at the exit of a pulsed molecular-beam valve. Stable precursor molecules are seeded in a large excess of an inert carrier gas like helium or argon, and expanded into vacuum in a 10 µs to 100 µs duration gas pulse at a repetition rate of 10 Hz to 20 Hz. The gas pulses are injected between a pair of stainless steel electrodes where a discharge is struck, fragmenting the precursor and producing the products of interest. These species undergo free-jet expansion cooling, and are interrogated down stream with a pulsed, tunable dye laser.

The resulting laser-induced fluorescence is imaged with transfer optics onto the entrance slit of a HORIBA Scientific 500M scanning monochromator equipped with an 1800 gr/mm ion-etched holographic grating blazed at 400 nm. The dispersed fluorescence is detected by a high-sensitivity cooled photomultiplier (PMT); the resulting current pulses are amplified and processed with a gated integrator, and the DC voltages are recorded with a LabVIEW-based multichannel computerized data-acquisition system. Time-gating of the signal discriminates against the strong argon or helium carrier-gas emission lines that would normally obscure the emission spectrum. In practice, the excitation laser is fixed on a strong feature in the LIF spectrum and the monochromator is scanned to obtain a single vibronic-level emission spectrum. Precise wavelength calibration of the instrument while scanning is implemented by including a pair of pulsed rare-gas discharge lamps in the optical path just before the entrance slit.

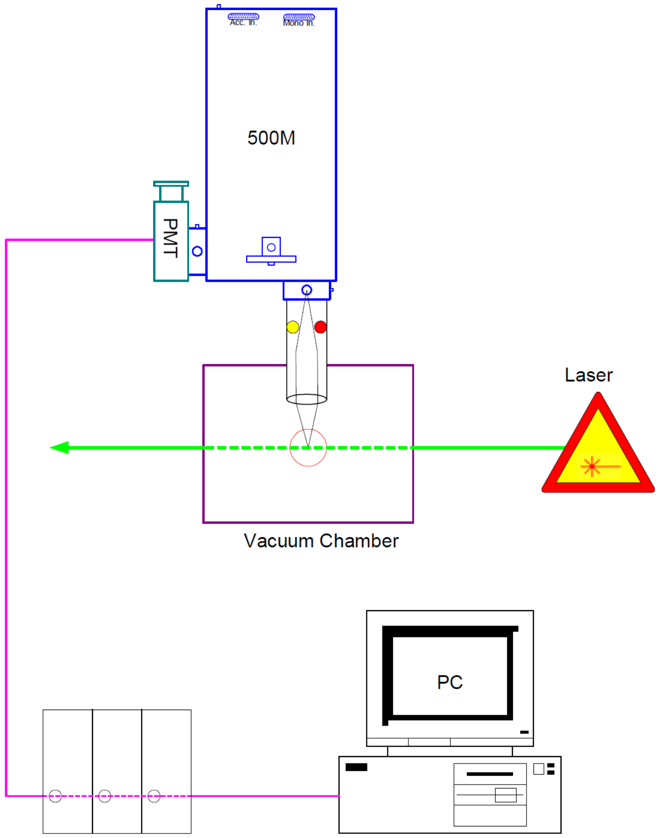

Figure 1. Experimental setup.

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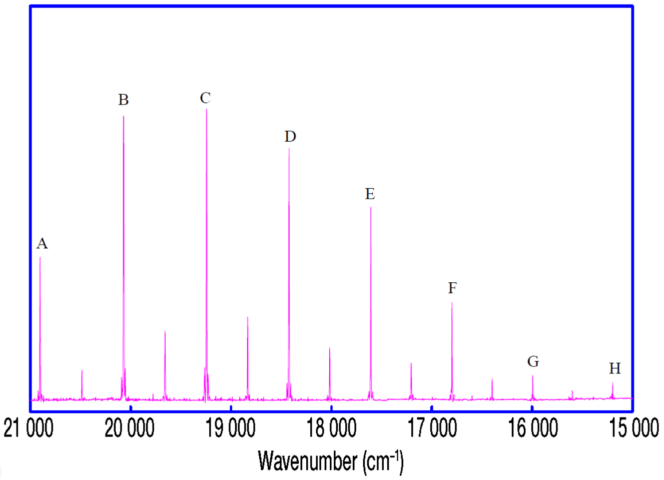

Figure 2. The letters A–H identify the features of the prominent bending progression in the emission spectrum.

These lamps are discharged with a temporal delay of 100 μs to 500 μs after the laser excitation pulse, and their subsequent emission signal is recorded with the same PMT used to detect the LIF signals. Because the LIF and calibration signals are temporally displaced, they can be captured with separate gated integrators with different time-delays, and recorded on different channels of the data-acquisition system. Post-acquisition calibration of the scan is accomplished by fitting the observed wavelengths of the rare-gas emission lines to their accurately known values using a first- or second-order polynomial.

Results

In precise optical emission spectroscopy, measurements in wavenumber units are preferable, for the intervals between features in the spectra are then proportional to molecular energies. The calibration scheme was tested over a wide range of scanning conditions and found to give very precise and reliable calibration with a typical standard error of 1.0 cm^{-1} in the 33 333–20 000 cm^{-1} (300–500 nm) region, and less than 1.0 cm^{-1} between 20 000 cm^{-1} and 12 500 cm^{-1} (500–800 nm). In most cases, a linear function or a quadratic function with a very small second-order term was sufficient to achieve reliable calibration.

A typical example of a single vibronic level emission spectrum recorded with this system is shown in Figure 2. The molecular species characterized is the HPBr free radical; the spectrum was recorded over a period of approximately one hour with slit widths of 0.1 mm, digitizing the signal every 0.5 cm^{-1}.

The spectrum was calibrated to 0.30 cm^{-1}, and a subsequent fit of the peak positions taken from several different spectra to an anharmonic model yielded a standard error of 0.35 cm^{-1}.

Conclusions

A high-accuracy scanning monochromator with subsidiary wavelength calibration provides a precise and cost-effective method of obtaining high-quality single-vibronic-level emission spectra from laser-excited supersonic expansions.

HORIBA Scientific components	Part number
500M monochromator	500M
Photomultiplier tube detector, 190–860 nm	1911
Precision Adjustable Entrance Slit, 3 μm–3 mm	1451N
Precision Adjustable Exit Slit, 3 μm–3 mm	1451X
1800 gr/mm ion-etched holographic grating, 400 nm blaze	18001H-400
LabView VIs	

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