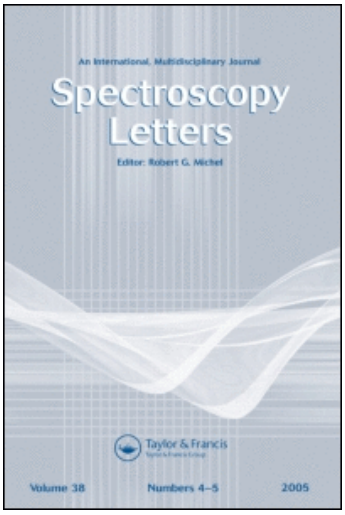

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

A Wavenumber, Intensity, and Resolution Standard for High Resolution Ultraviolet/Visible Fourier Transform Spectroscopy

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To cite this Article Manning, Thomas J.(1996) 'A Wavenumber, Intensity, and Resolution Standard for High Resolution Ultraviolet/Visible Fourier Transform Spectroscopy', Spectroscopy Letters, 29: 5, 959 — 965
To link to this Article: DOI: 10.1080/00387019608001624
URL: http://dx.doi.org/10.1080/00387019608001624

SPECTROSCOPY LETTERS, 29(5), 959-965 (1996)

A WAVENUMBER, INTENSITY, AND RESOLUTION STANDARD FOR HIGH RESOLUTION ULTRAVIOLET/VISIBLE FOURIER TRANSFORM SPECTROSCOPY

Keywords: Fourier transform spectroscopy, ultraviolet, visible high resolution spectroscopy

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Abstract

The Re I (527.55 nm, 18955 cm^{-1}) emission line from a hollow cathode lamp (HCL) is proposed as a standard for wavenumber accuracy and precision, resolution accuracy and precision and intensity precision. The Los Alamos Fourier transform spectrometer measured the HCL emission at high resolution (0.026 cm^{-1}). The advantages of this spectral line to other emission standards is discussed.

INTRODUCTION

Fourier transform spectroscopy (FTS) has several benefits compared to dispersive systems, including the multiplex advantage, throughput advantage, resolution precision and accuracy, wavenumber

precision and accuracy, and intensity precision[1]. Emission from thorium and uranium hollow cathode lamps (HCL's) have been used as standards for wavenumber accuracy for Fourier Transform-atomic emission spectroscopy (FT-AES)[2] and Fourier Transform-Raman (FT-Raman) spectroscopy.[3] These proposed standards emphasize wavenumber accuracy and precision but do not explore the limits of resolving power or intensity precision. Th and U HCL's each emit hundred's of thousands of measurable spectral lines in the ultraviolet and visible (UV/VIS) [2,3], increasing the potential for spectral misidentification.

In this letter, Re I (527.55 nm) HCL emission is proposed as a standard for measuring the quality of spectra obtained with a Fourier transform spectrometer operating in the UV/VIS. The Re I (527.55 nm) line, which has hyperfine structure (HFS) and isotope shifts (IS), offers and excellent reference standard for measuring resolution, intensity, and wavenumber accuracy.

The HCL has several advantages over other common sources such as the ICP, flame, and laser. Specifically the HCL has relatively low shot (no continuum) and flicker noise (1/f) contributions and its low pressure (1 torr) and temperature (500 K) environment serve to minimize collisional and Doppler broadening. Minimizing the contributions from each of those effects allows the physical features of the transition to become discernible.

EXPERIMENTAL

The output of a commercially available hollow cathode lamp (HCL) is used as the standard. An optical filter[4] is used to narrow the bandpass and minimize the multiplex disadvantage. The Los Alamos Fourier transform spectrometer[5,6,7,8] is to acquire this spectra (0.026 cm^{-1}, 2 scans).

DISCUSSION

Rhenium: Spectroscopists have studied the hyperfine structure and isotope shifts of Re I[9,10,11]. Re has two naturally occurring isotopes, ^{185}Re, (37.07%) and ^{187}Re (62.93%). Each of the two isotopes have nuclear spins greater than zero (5/2, 5/2) which lead to hyperfine structure. Both isotopes (185, 187) have similar nuclear magnetic moments (3.172, 3.204 nuclear magnetons), respectively. The clarity and symmetry of the HFS and IS in this transition make it an excellent selection as a spectral standard. The wavenumbers for this transition are listed table 1. The line profile of Re I (527.55 nm) is shown in figure 1.

Resolution: The high resolution capabilities of an FTS can be tested by separating the isotope shifts, which are in the 0.06-0.07 cm^{-1} range. The splittings between the hyperfine components are in the 0.2 to 0.6 cm^{-1} range and serve as a measure for lower resolutions. The full width at half maximum (FWHM) of the individual lines in this study are 0.02-0.05 cm^{-1}.

Quite often FT-UV/VIS instruments claim achieving resolutions ($\Delta\nu$, cm^{-1}) based strictly on mirror displacement (L, cm) where

$$\Delta\nu = 1/(2L) \qquad (1)$$

This relationship does not consider factors such as electronic noise, phase problems, incorrect aperture setting, optical imperfections and mirror jitter which degrade resolution. Imperfections of this nature can also affect wavenumber precision and accuracy and intensity precision and accuracy.

Intensity: The intensity precision of the Fourier transform spectrometer can be measured using the relative intensities of Re I isotopes (see table 1). The peak amplitude ratio of the two naturally occurring isotopes (eq. 1) serve as the standard for intensity precision.

Table 1. Corrected wavenumbers (cm^{-1}), wavelength (nm) Full Width Half Maximum (FWHM, cm^{-1}) and relative intensities of Re I transition illustrated in figure 1.

Wavenumber	Wavelength	FWHM	Intensity	Isotope	#
18950.8035	527.6821	.0432	0.58	185	1
18950.7438	527.6838	.0541	1.00	187	2
18950.2397	527.6978	.0270	0.47	185	3
18950.1756	527.6996	.0391	0.76	187	4
18949.8044	527.7099	.0246	0.33	185	5
18949.7384	527.7118	.0312	0.62	187	6
18949.4877	527.7187	.0220	0.28	185	7
18949.4189	527.7206	.0275	0.38	187	8
18949.3484	527.7226	.0198	0.15	185	9
18949.2811	527.7245	.0234	0.26	187	10

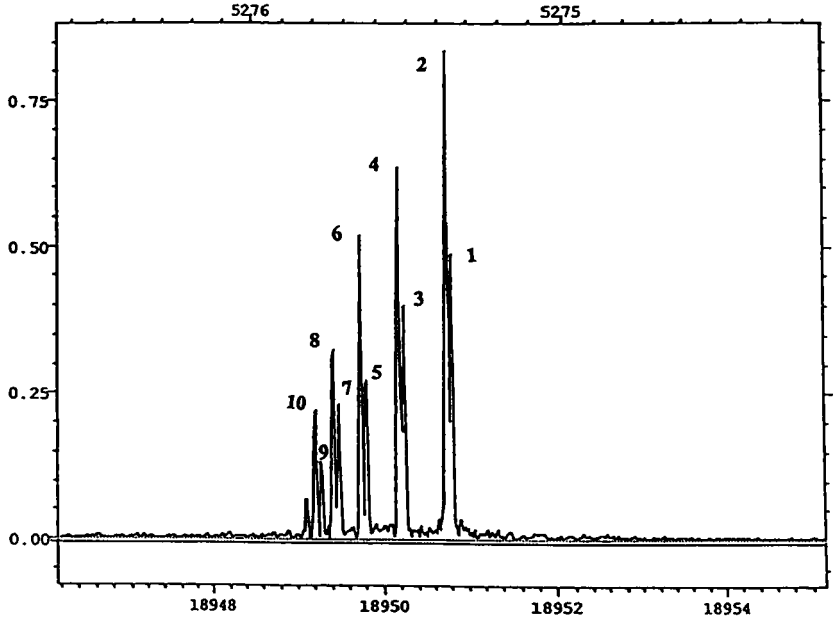

Figure 1. Re I line profile clearly shows hyperfine structure (HFS) and isotope shifts (IS).

For the hollow cathode lamp, the intensity varies 1-2% as a function of time[8]. For the two most intense lines (18950.7397 cm^{-1}, 18950.1715 cm^{-1}), and the accompanying spectral profile for the less abundant isotope (18950.7994 cm^{-1}, 18950.2356 cm^{-1}), there is a systematic error of 1%. The LAFTS has a 0.1% intensity accuracy limit[6] so intensity precision is source limited.

Wavenumber Positions: Spectroscopists routinely use Fourier Transform Spectrometers for high wavenumber precision and accuracy. Several studies have taken advantage of the high wavenumber accuracy of the LAFTS[5,6,7]. This accuracy has typically been greater than 1 part in 10^7. There are two correction factors[12] incorporated in these types of studies: a) aperture corrections b) slight misalignment of instrument. They adhere to the following format:

$$\sigma' = \sigma[1 + (\Omega/4\pi) + \chi/\epsilon\ ] \qquad (2)$$

where $\Omega = \pi D^2/4F^2$ = solid angle (sr)

F = focal length of collimating optics (cm)

σ = measured wavenumber (cm^{-1})

σ' = corrected wavenumber (cm^{-1})

χ = instrumental calibration (cm^{-1})

ϵ = average wavenumber (cm^{-1})

In a previous study[7], the instrumental calibration (χ) was calculated in the following manner. The emission from a uranium HCL was studied with the LAFTS. Twenty five lines were measured in the 385-395 nm range and compared against very accurate (1 part in 10^8) wavenumber values from a uranium atlas[14]. With no correction factors, the values were red-shifted 0.0052 cm^{-1}. With only the aperture correction ($\Omega/4\pi$) applied, this left an average red-shift of 0.0015 cm^{-1} with a standard deviation of 0.0013 cm^{-1}. This value (0.0015 cm^{-1}) is the instrumental calibration (χ). The average

wavenumber, ϵ, is the average of the wavenumbers being studied. For the LAFTS, the misalignment is typically smaller than the aperture correction factor. The correction factors combined are small (roughly 2.2×10^{-7}) but must be considered for high wavenumber accuracy and precision. Table 1 lists the corrected values for the Re I lines. These values are considered accurate to better than 1 part in 10^7.

CONCLUSION

An intensity, wavenumber, and resolution standard for Fourier transform spectroscopy in the visible is presented. It is chosen to evaluate the spectrometer's performance concerning resolution, intensity precision, and wavenumber precision and accuracy. This Re I transition provides narrow, intense lines that are in an easily identifiable pattern. Re HCL's are commercially available and easy to use in conjunction with a FTS. This spectral standard is intense, offers symmetry in HFS and IS, and will clearly tell if the FTS is performing up to claimed specifications.

ACKNOWLEDGEMENTS

TJM would like to thank Byron Palmer, Doug Hof and Jill Angus for help with the LAFTS. TJM would also like to thank Los Alamos National Lab for support.

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RECEIVED: January 11, 1996
ACCEPTED: February 19, 1996