

An Iodine Standard Lamp

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Abstract. We report results of an investigation of a lamp for spectral calibration that is based upon molecular fluorescence. An argon ion laser is used to excite the B state of molecular iodine and the resulting fluorescence provides a series of lines that cover the wavelength range 515 nm to 1340 nm. The intensities of the lines are fixed with respect to one another and are appropriate for determining the relative spectral responsivity of an optical instrument. We discuss a specific example that demonstrates the salient features of this lamp.

1. Introduction

1.1 Background

Optical instrumentation often requires calibration for both wavelength and spectral response. Examples of such instruments include spectrophotometers and remote optical sensors on orbiting platforms. Often, remote sensors are calibrated prior to launch and one must rely upon this calibration. Indeed, it is difficult if not impossible to correct for any drifts in the spectral response function or wavelength accuracy of the remote sensor once it is placed in orbit. At the present time, on-board calibrations are performed using a combination of a low pressure mercury lamp for the wavelength calibration and a quartz-halogen lamp for the spectral response. This is not an optimum solution because the quartz-halogen lamp produces considerable waste heat which can be deleterious to the operation of the satellite.

We are investigating a novel approach for a miniature standard lamp that would be suitable for calibrations of both wavelength and spectral response. Our approach is based on laser-induced fluorescence from molecular species. The approach described here is distinct from other light sources that are commonly used as calibration sources. As mentioned above, spectral responsivity and wavelength calibrations of an optical instrument are accomplished using two distinct light sources. The wavelength calibration is

completed using atomic line sources such as mercury or neon lamps. While these lamps provide a series of known spectral lines, they are not suitable for determining the wavelength-dependent responsivity of the particular instrument that is being examined. The absolute and even the relative intensities of the emission lines are not constant and cannot be used to determine the responsivity.

The responsivity calibrations are performed using a standard irradiance lamp [1]. Such lamps are usually quartz-halogen lamps that can be traced to the National Institute for Standards and Technology (NIST). The major requirement for a source suitable for measuring spectral responsivity of an optical system is that the calibration source must produce light of known spectral irradiance over the entire wavelength range of interest. For the region 250 nm to 2500 nm, a quartz-halogen irradiance lamp is often used. While these lamps are used routinely in a laboratory environment, they require relatively heavy regulated power supplies, are very inefficient since they are incandescent sources, and generate considerable waste heat. They also degrade with use. Consequently, irradiance lamps are not optimal for space applications.

We next describe some of the important differences between atomic and molecular emitters. Atomic spectra arise from radiative transitions between electronic energy levels. Usually these excited states are formed by electron excitation, for example in an electric discharge. The atoms in an excited state, through the process of fluorescence, fall back to a lower level while emitting photons. An example is shown in Figure 1, which gives some of the common

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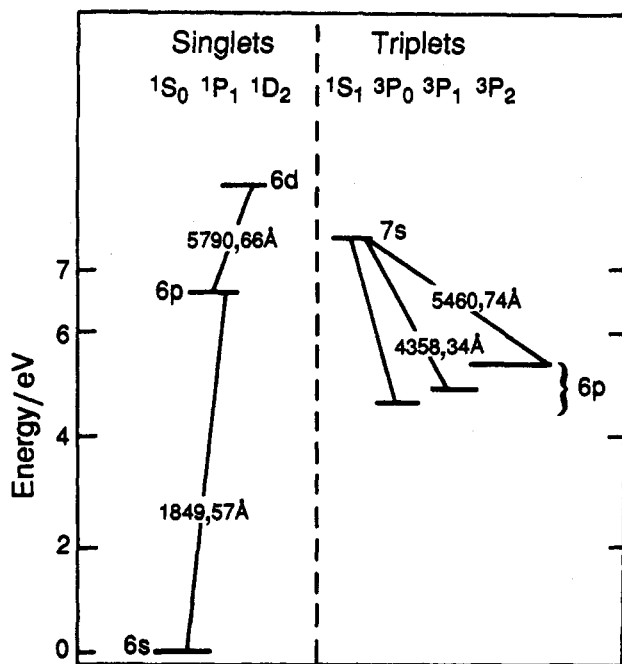


Figure 1. Energy level diagram of Hg (a few intense lines are shown).

Hg emission lines. Note, however, that usually only one or two lines are emitted from any one level. Consequently, one cannot predict the relative intensities of the emission lines because the electron excitation does not populate all of these levels equally. This situation would be alleviated if all the emission lines originated from a common level. Unfortunately, most atoms have relatively few levels, and only a small number of emission lines originate from a single level.

Diatomic molecules possess many additional energy levels, compared to atoms, due to their higher number of internal degrees of freedom. In addition to the electronic energy levels described above for an atom, a diatomic molecule possesses vibrational and rotational energy levels. These additional energy manifolds result from the vibrational and rotational motion of the two nuclei. There is a hierarchy of energy levels: each electronic level has a set of vibrational levels and each vibrational level has a complete set of rotational levels. The energy levels for a molecule are usually displayed as potential curves and we present an example in Figure 2. An individual vibration-rotation state is designated (v, J) where the v and J refer to the respective vibrational and rotational quantum numbers. Levels within an electronically excited state are indicated as (v', J') while those in the ground state are identified as (v'', J'') . We do not show the rotational levels in Figure 2.

In diatomic molecules, radiative transitions in the ultraviolet to near-infrared region of the spectrum occur between two electronic levels. During this process both the rotational level and the vibrational level

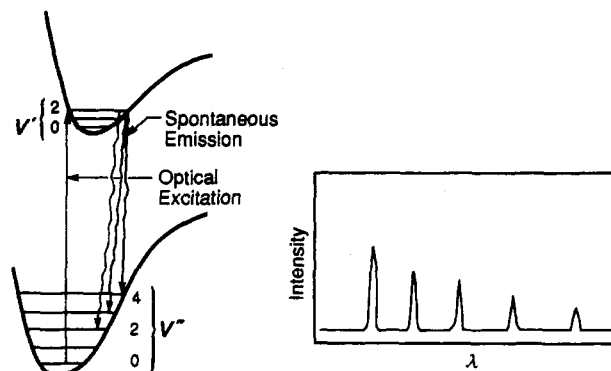


Figure 2. Typical potential curves for a diatomic molecule. Two electronic states are shown. Three of the many transitions that can originate from a single v' are shown. Also shown is a typical spectrum.

can change, and these changes give rise to the rather rich spectra associated with diatomic molecules. Individual spectral features are due to a transition from a v', J' level to a v'', J'' level. There are quantum mechanical selection rules that restrict the changes in the rotational quantum number that can occur during a radiative transition. There are, however, no firm restrictions on the change in the vibrational state during an electronic transition. Thus numerous lines can be emitted from any one vibrational level of an excited electronic state. While there are no prohibitive selection rules for changes in the vibrational quantum number, each $v' - v''$ transition occurs with a well-defined and fixed probability. These probabilities are called Franck-Condon factors, and they are known for many molecules.

The spontaneous emission rate for a rovibronic transition from one $v' J'$ to a v'', J'' is given by [2]

$$A_{v', J' \rightarrow v'', J''} = \frac{64 \pi^4 \nu^3}{3 h} |Re|^2 q_{v', v''} \frac{S_{J', J''}}{2J'+1}, \quad (1)$$

where

ν is the frequency of the transition (in cm^{-1}),
 $S_{J', J''}$ is the rotational line strength (constant for all Δv transitions if only a single J' is excited),
 $|Re|^2$ is the transition moment, and
 $q_{v', v''}$ is the Franck-Condon factor.

If the emission originates from a single v', J' level, then the rotational line strength is constant and the intensity envelope is uniquely determined by the Franck-Condon factors. There is often some variation of the electronic transition moment as a function of v , but in the case of the I_2 transition that we are considering, the variation is known for many $v' - v''$

transitions. Indeed, the relevant spectroscopic parameters that comprise (1) are known for many molecules.

The potential for using diatomic molecules as radiation standards has been recognized by several researchers. Mumma [3] suggested using species such as NO, CO and N₂ as sources for the ultraviolet. Ajello [4] and co-workers developed a laboratory source based on ultraviolet transitions in H₂ and N₂. Although these and similar approaches offer the advantages inherent in molecular emissions as described above, previous workers used electron excitation. Consequently, several energy levels were populated and the emission originated from all of these levels. Although this does not cause any fundamental difficulties, it does complicate the data analysis. In addition, it may require robust and rather massive power supplies.

1.2 Molecular iodine fluorescence

We are investigating the feasibility of an optically excited molecular iodine lamp. This lamp is useful over a broad wavelength range since molecular iodine provides emission radiation covering the wavelength range from 510 nm to 1 340 nm.

We now consider the features of the iodine molecule that are relevant to our approach. We used the

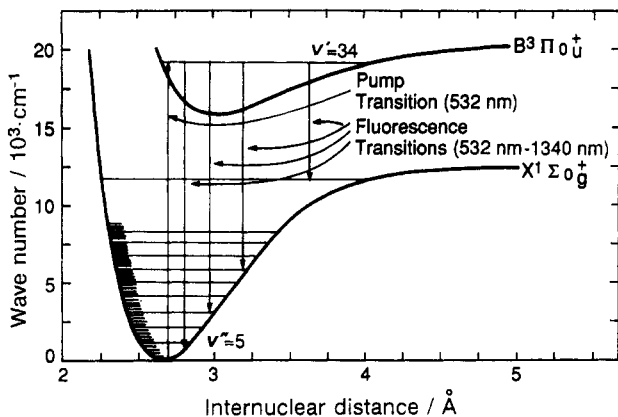


Figure 3. Iodine potential curves showing excitation by a frequency doubled Nd:YAG laser. The laser excites only $v' = 34$ and fluorescence occurs on many $(v' = 34) \rightarrow v''$ transitions. Only a few are shown.

I₂ (B – X) band system shown in Figure 3. This system is perhaps the most extensively studied and best understood of any among diatomic molecules [5-9]. Accurate values exist for the Franck-Condon factors ($q_{v',v''}$) and the variation in the transition moment [9, 10, 11]. In addition, the wavelengths of the transitions are so well known that they are used as wavelength standards [12]. The most important feature, however, is that common light sources such as the

546 nm Hg line can be used to excite a single v', J' level [13, 14]. Laser sources such as the argon ion (514,5 nm) and doubled Nd:YAG (532 nm) can also be used to excite single levels [11, 15, 16]. Consequently, it is relatively easy to produce electronically excited iodine in a pure v', J' level. This single level can emit to numerous vibrational levels in the ground state and thus provide many lines over an extended wavelength range. For example, the argon ion laser 514,5 nm line excites the $v' = 43, J' = 16$ level in the B state and this level emits to all v'' covering the range $0 < v'' < 100$, thus producing emission covering the wavelength range 514,5 nm to 1 340 nm. The lines are spaced approximately 200 cm⁻¹ apart and all are of fixed relative intensity as dictated by the Franck-Condon factors.

2. Experiment

The lamp cells were constructed from Pyrex and a few iodine crystals were placed in the cell prior to sealing. A block diagram of the apparatus is presented

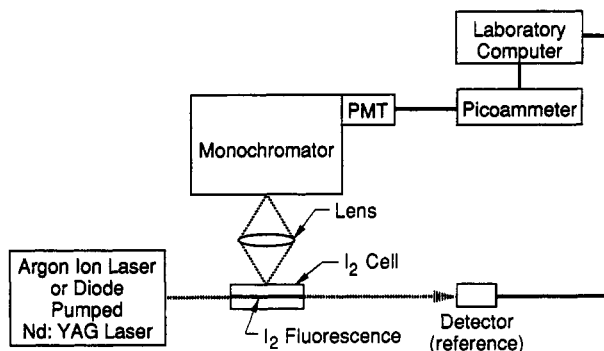


Figure 4. Block diagram of the apparatus used for the initial iodine lamp tests.

in Figure 4. The spectrometer consisted of a McPherson Model 218 monochromator (0,3 m focal length, $f/5,3$), equipped with a 1 200 groove/mm grating blazed at 300 nm. A Hamamatsu R943-02 photomultiplier (PMT) equipped with a gallium-arsenide photocathode was used as the detector. The PMT was cooled thermo-electrically in order to reduce the dark current to negligible levels.

Fluorescence from the lamps was imaged onto the monochromator slit with a single 1,5 inch diameter $f/2$ lens. The image and object distances were the same in this arrangement thus providing an effective $f/4$ input cone to the monochromator. Note that for some experiments no imaging optics were employed: instead the cell was oriented horizontally such that the I₂ fluorescence filled the field-of-view of the monochromator along the axis perpendicular to the

monochromator slit and grating grooves. In either arrangement (with or without an imaging lens) the I_2 fluorescence filled the grating on the axis perpendicular to the monochromator slit. This ensured that all grating grooves were illuminated, facilitating the comparisons with the quartz-halogen lamp. The PMT anode current was monitored using a Pacific Instruments photometer (Model 126) operated as a current meter. The data were recorded with a strip-chart recorder, a laboratory PC equipped with an A/D converter and a commercial data acquisition software routine (LabTech Notebook, Laboratory Technologies Inc.).

Drifts in laser power were monitored with a photodiode. The argon ion laser was equipped with a photodiode that monitored the output power and, through a feedback servo loop, adjusted the plasma current to keep the output constant. We found that the output was constant to within $\pm 2\%$ as measured with a photodiode.

Accurate determination of the spectral response of the spectrophotometer system was a crucial experiment since this would serve as the reference for the response functions generated via I_2 fluorescence. This independent calibration was performed using a NIST traceable irradiance standard in the form of a quartz-halogen lamp (Optronics Laboratories, Model 245C). The standard illuminated a diffuse (Lambertian) high reflector (Spectralon, Labsphere Inc.) positioned to fill the field-of-view of the monochromator. This combination allowed the placement of a known photon flux onto the monochromator entrance slit as required for the calibration.

3. Results

3.1 Calibration using the I_2 lamp

A typical resolved I_2 fluorescence spectrum acquired using an argon ion laser for 514,5 nm excitation is illustrated in Figure 5. The I_2 was held at room temperature (22 °C). This spectrum shows a series of sharp features and an underlying continuum of emission. Each sharp feature is an unresolved pair of rotational transitions, R (15) and P (17) in spectroscopic notation, corresponding to $\Delta J = \pm 1$ transitions from $J=16$ $v=43$ in the upper electronic state of iodine. These transitions originate from the rotational-vibrational level initially populated by the laser.

In (2) we define the observed emission intensity I_{OBS} in terms of the true volumetric emission intensity I_{TRUE} .

$$I_{OBS} = I_{TRUE} R(\lambda) V(\Omega/4\pi), \quad (2)$$

where $R(\lambda)$ is the spectral response of the detection system, Ω is the solid angle subtended by the detection system input aperture, and V is the observed volume.

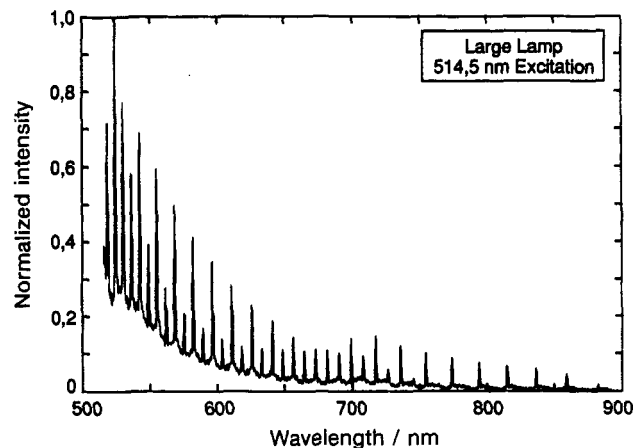


Figure 5. Resolved laser-induced fluorescence from I_2 excited by the argon ion laser 514,5 nm line.

For the present discussion we define the relative spectral response as

$$R_{rel}(\lambda) = R(\lambda) V(\Omega/4\pi). \quad (3)$$

Consequently we can determine $R_{rel}(\lambda)$ from I_{OBS}/I_{TRUE} .

The true volumetric emission rate (W/cm^3) for a $(v', J' \rightarrow v'', J'')$ transition is given by

$$I_{TRUE}(v', J' \rightarrow v'', J'') = N_{v', J'} A(v', J' \rightarrow v'', J'') h\nu, \quad (4)$$

where $N_{v', J'}$ is the number density in (v', J') . The observed volumetric emission rate

$$I_{OBS}(v', J' \rightarrow v'', J'')$$

is defined as the product of the spectral response and I_{TRUE} . Thus we can determine the relative spectral response $R_{rel}(\lambda)$ from

$$R_{rel}(\lambda) = [I_{OBS}(v', J' \rightarrow v'', J'') / [N_{v', J'} A(v', J' \rightarrow v'', J'') h\nu]]. \quad (5)$$

Knowledge of $N_{v', J'}$ is not required for determination of the relative response function since it is constant for excitation by a CW laser. We used data similar to those shown in Figure 5 to determine the relative response $R_{rel}(\lambda)$. In Figure 6 we plot $R_{rel}(\lambda)$ determined from (5). We also show the response curve determined by the quartz-halogen lamp. Both curves are normalized to the response at 580 nm. The agreement between them is quite good. (The feature near 710 nm is due to a Wood's anomaly in the grating.) The largest discrepancies between the average from the I_2 lamp and the curve based on the irradiance standard are only a few per cent. The source of the disagreement between the $R(\lambda)$ is due to the fact that,

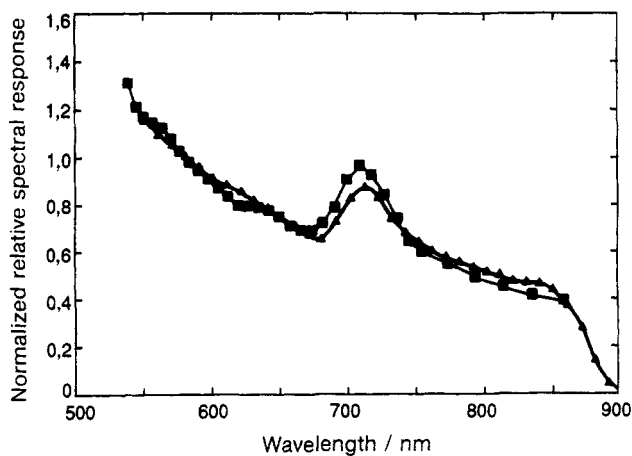


Figure 6. Comparison of response curves for spectrometer measured using a conventional standard lamp and the I_2 lamp (▲: data derived from quartz-halogen lamp; ■: data derived from iodine lamp).

for this initial demonstration, we simply measured emission peak heights for the features in the I_2 lamp. We are performing a more complete analysis at present.

We have also completed a similar set of measurements using a miniature, diode pumped, frequency-doubled Nd:YAG laser. A spectrum of this lamp is shown in Figure 7.

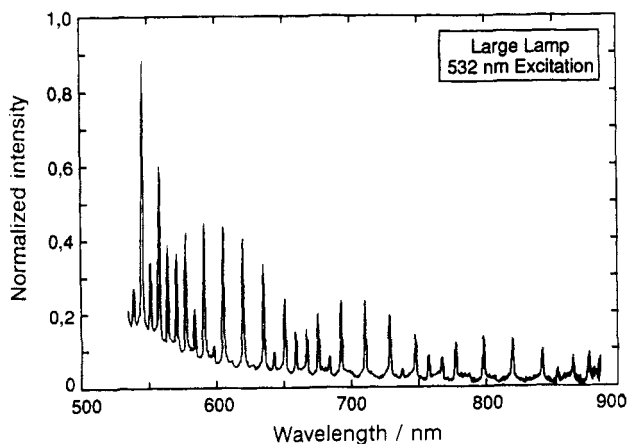


Figure 7. $I_2(B \rightarrow X)$ spectrum for Nd:YAG laser-excited iodine lamp.

3.2 Additional I_2 lamp characterizations

We have also performed miscellaneous tests to characterize more thoroughly the operational parameters of the lamp. In one series of tests we used calibrated neutral density filters to attenuate the excitation laser

beam to study the dependence of the lamp intensity upon the laser power. The results of this study are

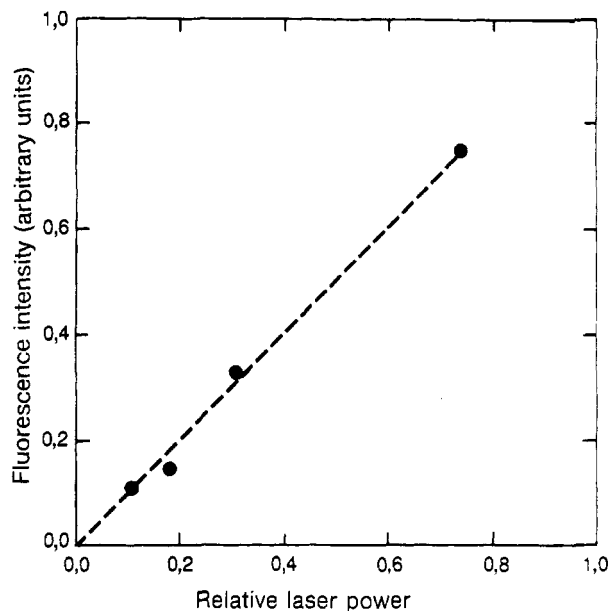


Figure 8. Iodine lamp intensity as a function of excitation-laser power.

summarized in Figure 8. Clearly, the lamp intensity is linear with respect to laser power over a range of approximately one order of magnitude.

We also studied the stability of the lamp over an extended operational time period (~ 2 h) using the argon ion laser as the excitation source. We found that the lamp output was stable to $\pm 2\%$, which followed the stability of the argon ion laser. Consequently, it appears that the stability of the lamp is determined predominantly by the characteristics of the excitation source.

We have described how the fluorescence lamp is used to obtain the relative response for an optical detector. The emission intensity of the iodine lamp can be put on an absolute basis if the excitation rate of the $I_2(B)$ state is known. We are performing these measurements at present.

4. Conclusions

We have presented the results of a preliminary study of optically-excited molecular fluorescence lamps. Using laser-excited molecular iodine as an example, we have demonstrated the feasibility of developing this concept into calibration sources. The lamp has been used to calibrate the spectral response of a spectrophotometer and comparisons were made with a calibration performed using a quartz-halogen lamp. The stability of the lamp is ultimately determined by

the stability of the excitation laser. We are continuing our study with the goal of developing a stable and miniaturized calibration source.

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