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Note: Simple means for selective removal of the 365 nm line from the Hg spectrum using Dy

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The emission spectrum of mercury has a notable line at about 365 nm under both low and medium-high pressure conditions. A simple filter based on a solution of dysprosium ions, Dy^{3+}, is shown to be very useful for applications of Hg-light sources where this line is unwanted. The presented filter is cheap, robust, and stable towards degradation or bleaching – even under intense irradiation. The absorption spectrum for the Dy-filter is presented along with emission spectra from both low-pressure and high-pressure Hg-lamps to illustrate the utility of the technique under best-case and worst-case conditions. Attenuation of the 365 nm spectral line is almost total for the low-pressure source whereas for the high-pressure source the attenuation is about a factor of three. © *2011 American Institute of Physics*. [doi:10.1063/1.3639128]

A plethora of UV light sources exists in the 250 to 350 nm range. However, many of these either have a low luminous intensity (e.g., deuterium lamps), pulsed operation (e.g., most frequency quadrupled Nd:YAG lasers), or high price (e.g., He-Cd gas lasers or XeCl excimer sources).

Within the field of TiO_2-based photocatalysis in general – and TiO_2-based self-cleaning surfaces in particular – it is of interest to explore how activity scales with the thickness of the photocatalytic material.[1] This is especially true when the photocatalytic material is illuminated from the back-side with respect to the reactants since in that case there exists a (wavelength dependent) optimum film thickness.[2,3] In order to obtain an intermediate penetration depth of the photons in such an experiment using a TiO_2-based photocatalyst (band gap of $E_g \approx 3.2$ eV (387 nm)) a photon energy $E = E_g + \Delta$ where $\Delta \in [0.5, \ldots, 1.0]$ eV (335...295 nm) is needed (at 365 nm the $1/e$ penetration depth into a TiO_2 film is on the order of $\sim$1 μm (!)). The 295...335 nm range is also suited for the Pyrex-lids used in our μ-reactors[4,5] in which we wish to perform the photocatalytic measurements. A light source with the following characteristics is therefore sought:

- Main emission between 295 and 335 nm.
- Negligible emission below 290 nm and between 350 nm and 380 nm.
- Delivered irradiance of at least 100 mW/cm^2 over a 10 mm circular sample.
- Continuous illumination (CW source).
- Reasonable cost.

Review of commercially available sources indicate that the simplest solution would be a He-Cd gas laser operating at 325 nm. He-Cd lasers of adequate power, however, are quite expensive. The low throughput of monochromators rule out broadband sources such as Xe-arc lamps. An alternative option would be to use a Hg-arc lamp and use the light at or around the 313 nm line, which is strong in Hg-sources at elevated pressure, but this requires that the (even stronger) broad emission line around 365 nm is filtered away without damping the 313 nm line significantly. While commercial holographic notch filters with an optical density of $\sim$4 are available for 365 nm the holographic medium itself has an unacceptably low transmittance around 313 nm (typically below 10%) which unfortunately precludes such filters from the present application.

The lanthanides are known for their narrow absorption lines arising from *f-f* transitions.[6–9] In particular, holmium is popular as a calibration standard for spectrophotometers. Although Ho^{3+} has a low absorption around 313 nm, its line at 361 nm is too far from the 365 nm line in Hg to be of use for the present purpose.

Dy^{3+}, on the other hand, has an absorption spectrum which is nearly ideally suited for absorbing the unwanted Hg line. Dysprosium triflate ($Dy(CF_3SO_3)_3$) was chosen for the filtering due to the high solubility and the stability of the compound. The salt was prepared by slowly adding 0.445 moles of concentrated triflic acid (100 %) to a suspension of 0.15 moles of Dy_2O_3 in 400 ml of water in a beaker (1000 ml) over a period of $\sim$10 min whereupon the mixture was boiled overnight. The following day, the surplus of dysprosium oxide was filtered off and the supernatant was concentrated under reduced pressure until the salt $Dy(CF_3SO_3)_3 \cdot 9H_2O$ precipitated. The salt was isolated on a sintered glass funnel and washed three times with diethyl ether to remove the remaining water. The product was dried in a desiccator over P_4O_{10}. The purity of the product was checked by an EDTA titration of dysprosium, which confirmed the presence of 9 water molecules.

A cylindrical quartz cuvette of 20 mm optical path length filled with a solution of 0.81 M dysprosium triflate

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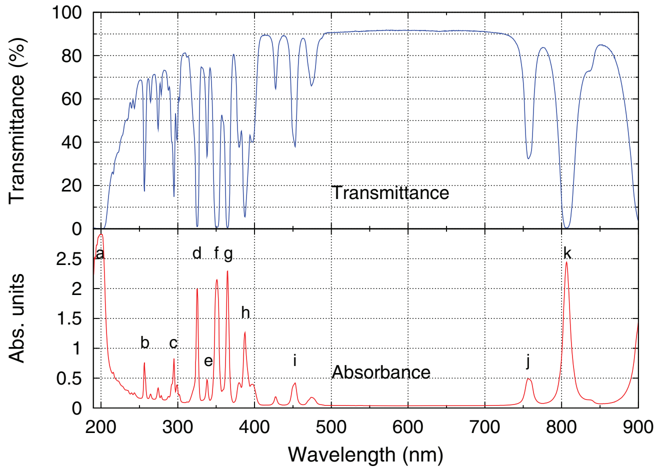

FIG. 1. (Color online) Absorbance and transmission spectrum of $Dy(CF_3SO_3)_3 \cdot 9H_2O$ dissolved in methanol.

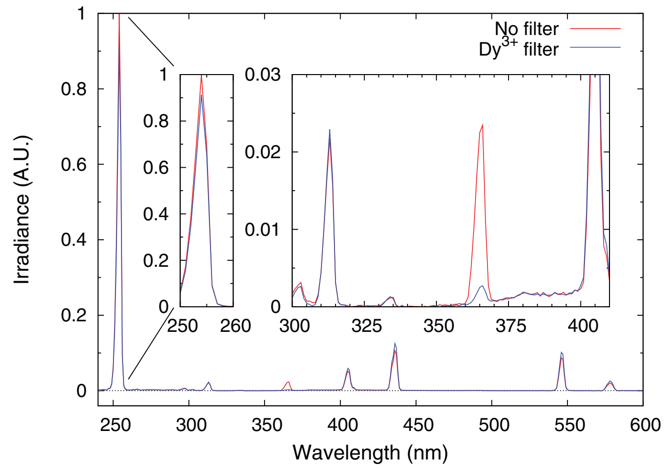

FIG. 2. (Color online) Measured spectra of a low-pressure Hg-discharge lamp with and without the dysprosium filter. The main line at 254 nm is almost unaffected by the absorption of the narrow b line at 256 nm, while the line at 365 nm is significantly dampened.

in methanol was used for the filter. Figure 1 shows the absorbance of a dysprosium triflate filter as measured using a spectrophotometer. Main features in the 190 nm to 900 nm interval are labeled with letters a through k. Also plotted is the transmission spectrum which clarifies where the filter has its absorption lines.

Table I shows quantitative data from the UV-VIS spectrum shown in Figure 1. Columns 3 and 4 show the peak absorbance and the corresponding algebraic damping factor, respectively. The latter four columns show the wavelengths for which the absorbance or damping is half the peak value. This can be used for peak-width estimation (e.g., FWHM values) and peak symmetry estimation. Main absorption lines are a, d, f, g, and k, where g at 365 nm is the one that is useful for the present purpose. The other lines are weaker.

A low-pressure Hg light source is made from an array of 4 low-pressure Hg tubes (8 W each) and Figure 2 shows the measured unfiltered spectrum and the spectrum of the same lamp, when filtered through the dysprosium filter. The irradiance measurement is carried out using a spectroradiometer. The measured data is normalized to the unfiltered Hg-line at 254 nm where irradiance is around 0.624 mW/(cm^2 nm). The integral of the 254 nm peak is 1.96 mW/cm^2 for this lamp.

It is clear from Figure 2, that the dysprosium filter significantly and selectively dampens the line at 365 nm while leaving the other main lines (including the main line at 254 nm) largely unaffected. This makes the filter highly useful for low-pressure Hg-lamps, but the moderate irradiance ($\ll$100 mW/cm^2) makes it unsuited for the purposes of the photocatalytic experiment.

High-pressure Hg-lamps offer much higher radiance than low-pressure lamps and the emission lines at 304, 313, 333, 406, and 437 nm become very intense. For applications where

TABLE I. List of important absorption peaks in $Dy(CF_3SO_3)_3 \cdot 9H_2O$ dissolved in methanol derived from the data shown in Figure 1. A_m, denotes the peak absorption (abs. units) and F denotes the attenuation factor (incident intensity/transmitted intensity). $\lambda_{(A_m/2)}$ values are the wavelengths for which absorption drops to half the peak value (in absorbance units) and $\lambda_{(F/2)}$ values are the wavelengths for which the attenuation factor has dropped to half the peak value.

	Peak[a]	A_m[b]	F[c]	$\lambda_{(A_m/2)}$[a]		$\lambda_{(F/2)}$[a]	
a	198.0	2.90	800	...	...	193.0	203
b	256.5	0.76	5.8	255.5	258.5	255.5	258.0
c	295.0	0.83	6.7	293.0	296.0	294.0	296.0
d	325.5	2.00	98	323.5	327.0	324.5	326.0
e	338.0	0.47	3.0	336.0	340.0	335.0	340.5
f	351.0	2.15	140	348.0	353.5	349.0	353.0
g	365.0	2.30	200	363.0	367.0	364.0	365.5
h	387.5	1.26	18	385.0	391.0	386.0	389.0
i	453.0	0.42	2.6	447.5	455.5	446.0	457.0
j	756.5	0.49	3.0	751.5	763.5	750.5	765.0
k	806.5	2.44	280	801.5	812.0	804.5	808.5

[a]Units are in nm.
[b]Absorbance units.
[c]No unit.

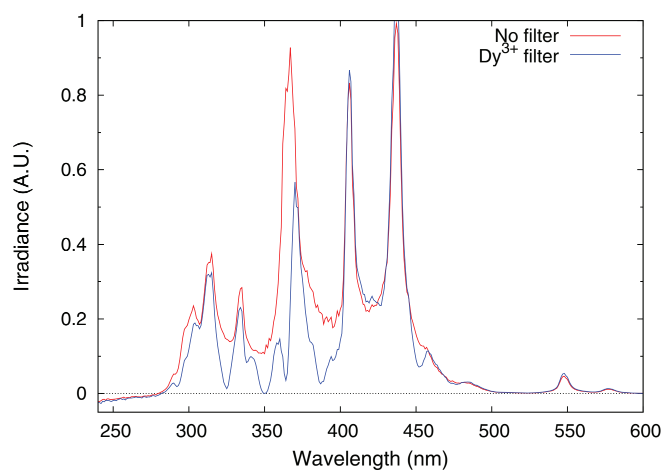

FIG. 3. (Color online) Measured spectra of a high-pressure Hg short-arc lamp with and without the dysprosium filter. The total irradiance in the 300…334 nm interval is dampened by a factor ~0.74 while the interval from 335…370 nm is dampened by a factor ~0.32.

monochromatic light is needed, the very significant line-broadening, which also occurs, is of course unwanted. For the purposes of filtering away the dominant line at 365 nm with Dy^{3+} the broadening of the emission is an important limitation since the absorption line remains quite narrow (see Table I), but nevertheless a Dy^{3+}-based filter may significantly attenuate the 365 nm line.

Figure 3 shows the influence of the Dy^{3+} filter on a high pressure Hg source.[10] Integration of the spectra shows that in the regions of interest (300...334 nm and 335...370 nm) insertion of the Dy^{3+} filter attenuates the light by a factor of ~0.74 in the desired region while the attenuation is a factor of ~0.32 in the unwanted longer-wave region. Thus the overall gain of using the Dy^{3+} filter is a factor $0.74/0.32 = 2.3$. This, relatively cheap, light source provides a total incident power of ~850 mW (300...335 nm), ~500 mW (335...370 nm), and ~4200 mW (370 nm $\leq \lambda$) over a 1 cm^2 area when the Dy^{3+} filter is used. For comparison, we note that when the Dy^{3+} filter is not used the light source provides a total incident power of about ~1150 mW (300...335 nm), ~1600 mW (335...370 nm), and ~4700 mW (370 nm $\leq \lambda$) over a 1 cm^2 area.

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[10] The high-pressure Hg-lamp is a Ushio model SMR-200UV3, 200 W short-arc lamp (1.2 mm arc) fitted with a water/$Cu(ClO_4)_2$ filter to absorb IR and coupled through a deep-UV liquid light-guide (Newport model 76842). The measured spectra have been normalized to the intensity of the 437 nm line without the Dy^{3+} filter. Note that this particular lamp (which Ushio has fitted with an ellipsoid reflector with a selective coating) has almost no intensity at 254 nm. The apparent slightly negative irradiance at very short wavelengths is a measurement artefact which is due to the *very* short integration times used in the measurement of this intense source. We also note that the characteristic fluorescence lines of Dy^{3+} around 480 nm and 572 nm are insignificant compared to the Hg-light.