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The complete UV–visible photoluminescence spectrum of aqueous Ce(III)

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Abstract

In previous work, it has been shown that the Ce-ion catalyzed Belousov–Zhabotinsky reaction exhibits oscillatory photoluminescence. Unfortunately, Ce(III) photoluminescence measurements were performed at a second-order peak. In this Letter, the complete 3-dimensional fluorescence spectrum of Ce(III) is shown including the correct (oscillatory) first-order peak with an intensity 100–700 times higher than the second-order peaks. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The Belousov [1]–Zhabotinsky [2] (BZ) reaction shows probably one of the most complex dynamic behaviors of a nonliving set of chemical reactions. For the classical BZ system [3], the mechanism was elucidated by Field, Körös and Noyes (FKN) [4]. Although, a variety of versions of the BZ reaction have been found, the FKN mechanism with bromide ion control [5–7] is essential in understanding most of the BZ reactions' dynamics, although the role of the organic reactions, especially radical reactions [8–12], are still poorly understood.

A variety of different methods have been used to study the BZ reaction, including electrochemical methods [4,13,14], NMR [15–18], HPLC [19,20], spectrophotometry [21] and fluorimetry [22–27]. The use of fluorimetry has exclusively been concentrated on Ru-catalyzed BZ systems, where Ru is mostly used in the form of $Ru(bpy)_3^{2+}$. Due to a rapid microwave synthesis protocol [28] other Ru-complexes have become more easily available.

In a previous Letter [29] Ruoff has shown that a Ce-catalyzed BZ system can be studied by means of photoluminescence and that the inner filter effect [30] may play an important role in the dynamic behavior of luminescent oscillations. In fact, the predicted dynamics induced by the inner-filter effect were subsequently found in the Ru-catalyzed BZ system [31]. Similar oscillatory behavior has also been reported by Bolletta et al. [32]. Unfortunately, in the Ce(III)-fluorescence work [29] the entire photoluminescence spectrum was not shown and the reported oscillations were recorded on a second-order peak. Bolletta et al. [33] indicated the possibility that the excitation wavelength reported by Ruoff [29] may be a second-order line. Karavaev and Noskov [34] communicated that the weaker peak [29] may be due to trace impurities and that there is probably no relation to the Ce(III) emission. Ruoff originally thought that the reported Ce(III) fluorescence peaks may be due to a multiphoton excitation mechanism,

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causing emission wavelengths shorter than excitation wavelengths.

In this Letter, the entire 3-dimensional Ce(III) UV–visible fluorescence spectrum has been investigated showing that the correct first-order Ce(III) fluorescence peak occurs at an excitation wavelength of ∼260 nm and an emission wavelength of 350 nm. The peaks of the Ce(III) fluorescence spectrum reported earlier [29] are of higher order and the result of using Echellette gratings in the excitation and analyser monochromators.

2. Materials and methods

The BZ reaction was studied under batch conditions in a fluorimetric quartz cell (Hellma Cells, Zeiss, Germany) with a reaction volume of 1.5 ml. The temperature was kept constant by an external circulating water bath at 25°C (±0.1°C). The solution was stirred magnetically from below. The BZ reaction was started by rapidly mixing equal volumes (500 μl) of a 0.9 M aqueous malonic acid (MA) solution, a 0.3 M aqueous $NaBrO_3$ solution and a $Ce(SO_4)_2$ solution in 3 M sulfuric acid. The resulting initial concentrations for H_2SO_4, MA and $NaBrO_3$ were 1.0, 0.3 and 0.1 M, respectively. For preparing the Ce(III) solutions $Ce(NO_3)_3 \cdot 6H_2O$ (Merck, extrapure) was used. The luminescence was studied with a Hitachi F-4500 spectrofluorimeter. The cell and excitation/emission beam arrangement have a standard orthogonal design [30]. The only difference to other commercial spectrofluorimeters is that the F-4500 has a horizontal beam geometry, instead of a vertical beam, which is normally used.

3. Results and discussion

Fig. 1a shows the 3-dimensional fluorescence spectrum of an acidic Ce(III) solution in the range 200–900 nm, for excitation and emission wave-

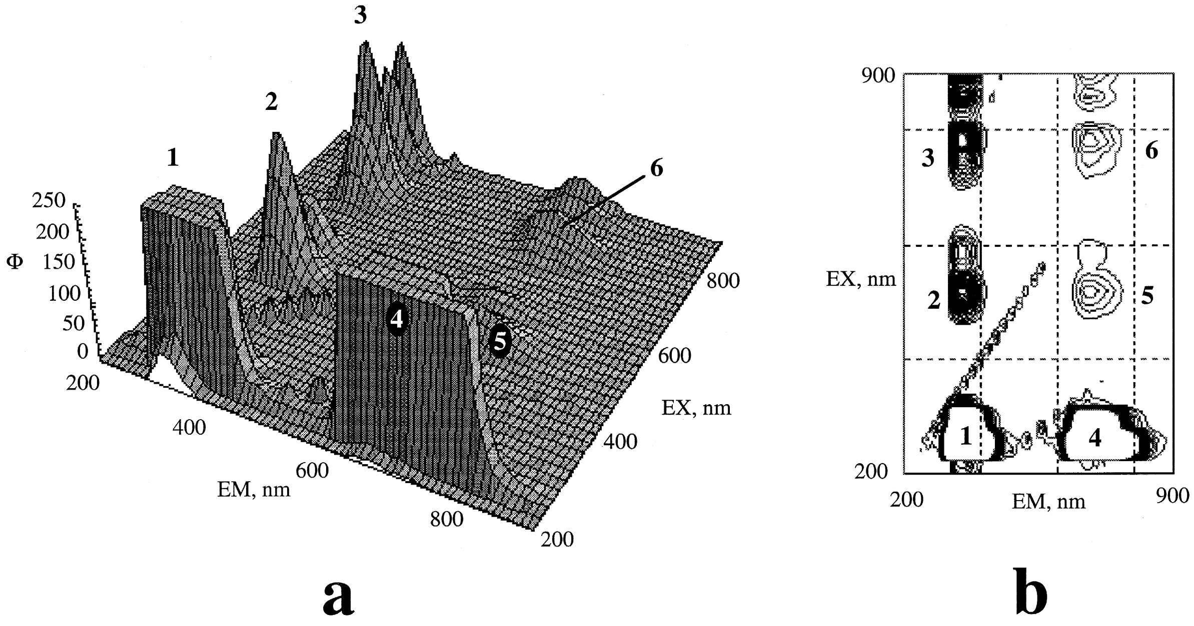

Fig. 1. (a) Fluorescence spectrum of a 2×10^{-5} M $Ce(NO_3)_3$ in 1 M sulfuric acid. Peak 1: 1st-order fluorescence peak. Peaks 2, 3: 350 nm emissions due to excitations by a 2nd-order line at 520 nm and a 3rd-order line at 780 nm, respectively. Peak 4: 350 nm emission line of peak 1 that passes the emission monochromator as a 2nd-order line. Peaks 5, 6: corresponding 2nd-order 350 nm emission lines of peaks 2, 3, respectively. (b) Density plot of the spectrum shown in (a). Scan speed 30000 nm/min; EX: excitation wavelength with sampling interval of 20 nm; EM: emission wavelength with sampling interval of 10 nm: Contour interval: 10 nm. Slit width (EX/EM): 5 nm/5 nm. Photomultiplier voltage: 700 V.

lengths, respectively. Peak 1 is the correct first-order peak with excitation and emission wavelengths at ∼ 260 and ∼ 350 nm, respectively. Peak 2 is a second-order line which has been previously reported [29]. The first-order line 1 has an intensity ∼ 100 times higher than peak 2.

The occurrence of higher-order lines is due to the use of Echellette gratings in the excitation and emission monochromators. The relationship between line order n, wavelength λ, angle of incoming radiation i and angle of reflection r is given by:

$$n\lambda = d(\sin i + \sin r), \qquad (1)$$

where d is the distance between the grooves in the grating [35]. Inspection of the various peaks showed clearly that peaks 2–6 are higher-order lines. Peaks 2 and 3 are the result of exciting Ce(III) with 260 nm by higher-order lines, i.e. $n = 2$ for peak 2 and $n = 3$ for peak 3. Peaks 4, 5 and 6 are second-order lines of the emission peaks 1, 2 and 3, respectively. Since the first-order peak is oscillatory in the BZ reaction, all higher-order satellites should also be oscillatory. This was indeed found, eliminating the possibility that the other peaks are fluorescent trace impurities.

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