“Photochemical Oscillator”: Colored Hydrodynamic Oscillations and Waves in a Photochromic System

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Supporting Information

ABSTRACT: A vertical thermal gradient is generated in a solution of a thermoreversible photochromic spiro-oxygen in methanol or acetone by UV irradiation at the bottom of the solution and evaporation of solvent at the top. When the gradient is sufficiently high, it triggers color oscillations and waves due to hydrodynamic convective motion of the solution. Experiments on such systems in several configurations are presented and simulated with a reaction-diffusion-convection model, which yields good agreement with the experiments. The photoexcitable system described in this work constitutes a prototype of a “photochemical oscillator” which, analogously to an electronic oscillator, converts the continuous UV energy into alternating optical visible and UV signals with periods between 15 and 70 s.

INTRODUCTION

Colored chemical oscillations and waves have been utilized as tools for relaying and processing information in excitable or oscillatory reaction-diffusion media.1–3 In such systems, information is coded in the concentrations of the reactive chemical species, which change in space and time.4–7 When colored oscillations and waves are generated or manipulated photochemically, they can collect, carry, and process the information content of the exciting light.8,9 An interesting class of photoexcitable species is that of photochromic compounds. Photochromic compounds are molecular switches that produce sharp changes of color under irradiation; they are thermally and/or photochemically reversible. Photochromic species and, more generally, chromogenic species have been proposed as multiply configurable “photo-chemionic” Boolean and fuzzy logic elements, based on optical outputs and optical/chemical inputs.10–16 A theoretical analysis suggests that a set of photochromes can give rise to color oscillations if pairs of them with properly matched spectral and dynamical properties are irradiated by white light in a closed isothermal reactor.17

Here we demonstrate that it is possible to produce color oscillations in solution containing a single photochromic species. We show that an irradiated 3 mL solution of a thermoreversible spiro-oxygen (SpO; see Figure 1a) in acetone or methanol produces color oscillations and waves as the result of the interaction between the photoelectrocyclization reaction and hydrodynamic convective motion. This phenomenon can be detected when a sufficiently large thermal gradient is generated across the solution, by heating it at the bottom and/or cooling it at the top. The heating results from UV irradiation of the photochromic species, whereas the cooling effect is achieved by allowing evaporation of the solvent when the cuvette containing the solution is uncapped (see Figure 1b). The thermokinetic origin of the color oscillations and waves is theoretically confirmed by development of a reaction-diffusion-convection model, which we present. Numerical simulations give results in qualitative agreement with the experiments.

The photoexcitable system described in this work behaves analogously to an electronic oscillator. An electronic oscillator is an electronic circuit that converts direct current (DC) from a power supply to an alternating current (AC) signal. In the same way, our photoexcitable system converts the constant intensity of the UV radiation produced by a Xe lamp to an alternating optical signal, i.e., the oscillating intensities of the UV and visible transmitted light. This device can be thought of as a prototype of a “photochemical oscillator”. Just as electronic oscillators find many applications in electronic devices (e.g., producing and decoding radio and television signals; providing clock signals that synchronize the internal operations of computers; keeping time in quartz clocks), so this new “photochemical oscillator” may find application in future generations of computational wetware as a generator of oscillating optical signals and color waves.

EXPERIMENTAL SECTION

1,3-Dihydro-1,3,3-trimethyl-8′-nitro-spiro[2H-indole-2,3′-[3H]napth[2,1-b][1,4]oxazine] (SpO; Great Lakes Chemical Italia S.r.l.) was used as received after checking its high degree of purity.

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of purity by HPLC. Methanol (Sigma, spectrophotometric grade) and acetone (Sigma, distilled before use) were used as solvents. SpO was dissolved in either methanol or acetone in concentrations of the order of $9 \times 10^{-3}$ M.

The absorption spectra, photocoloration and bleaching kinetics were recorded with a Hewlett-Packard 8453 diode array spectrophotometer. A 125 W Xe lamp, filtered by a Jobin-Yvon H110 UV monochromator and focused on the sample through a 0.6 cm diameter silica optical fiber, was used as the irradiation source. The UV radiation ($\lambda_{irr} = 374$ nm) was focused on a 1 cm path length fluorimetric quartz cuvette, perpendicular to the monitoring beam of the spectrophotometer (see the white spot inside the cuvette in Figure 1b). The irradiation intensity was determined by potassium ferrioxalate actinometry to be of the order of $10^{-6}$ mol of quanta dm$^{-3}$ s$^{-1}$, which corresponds to 32 W m$^{-2}$, at the wavelength of irradiation. A Precision Hygro-/Thermo-/Barometer (Greisinger Electronic GmbH) was used to determine the ambient pressure, temperature, and humidity in the laboratory during the experiments. To evaluate the rate of vaporization of the solvent when the cuvette was uncapped, we measured the height of the solution with calipers at various times.

To determine the photocoloration quantum yield, the molar extinction coefficient and the bleaching kinetic constant for the merocyanine in acetone and methanol, 1 mL of SpO solution was uniformly irradiated, taking care to avoid hydrodynamic convective motion. To observe the formation of colored hydrodynamic oscillations and waves, 3 mL of SpO solution was nonuniformly irradiated, with the UV radiation applied only at the bottom of the solution (see Figure 1b). In some experiments, the cuvette containing 3 mL of SpO solution was uncapped; in others it was capped. The goal was to establish the importance of the evaporative cooling at the top of the solution.

Real-time movies of the dynamical evolution of SpO solutions in acetone and methanol were recorded with a digital video camera recorder (Digital 8, DCR-TRV130E, Sony).

**Computational Methods**

For simulating the experimental results, we used a reaction-diffusion-convection model implemented in the software package COMSOL Multiphysics 4.2a. The model is

$$\frac{\partial C_{MC}}{\partial t} = R_{MC} + \nabla \cdot (D_{MC} \nabla C_{MC}) - \vec{u} \cdot \nabla C_{MC}$$

$$\frac{\partial C_{SpO}}{\partial t} = R_{SpO} + \nabla \cdot (D_{SpO} \nabla C_{SpO}) - \vec{u} \cdot \nabla C_{SpO}$$

(1)

where $C_i$ ($i = MC$ or SpO) is a concentration, $R_i$ is a term that describes the reaction kinetics, as detailed below, $D_i$ is a diffusion coefficient and $\vec{u}$ is the velocity of the solution.

To describe the chemical transformations, we assumed that inside the truncated cone both the photochemical reaction (SpO $\rightarrow$ MC, with rate constant $k_1$) and the thermal bleaching process (MC $\rightarrow$ SpO, with rate constant $k_2$) occur. The term $R_{MC}$ in eq 1 is given by $k_1[SpO] - k_2[MC]$, whereas the term $R_{SpO}$ is $-k_1[SpO] + k_2[MC]$. In the rest of the solution, only the bleaching process was taken into account. Therefore, $R_{MC} = -k_2[MC]$ and $R_{SpO} = +k_2[MC]$. The analytical concentration of the photochromic species was fixed at $8.8 \times 10^{-5}$ M. For estimation of the diffusion coefficients of SpO and MC, we used the Stokes–Einstein equation: $D = k_B T/6\pi r$. A reasonable value of the molecular radius is 7 Å (determined by simulation with Hyperchem software). Since the dynamic viscosity of methanol is almost twice that of acetone, the diffusion coefficient in acetone is 2-fold larger than in methanol: $1 \times 10^{-9}$ m$^2$ s$^{-1}$ in acetone, vs $5 \times 10^{-10}$ m$^2$ s$^{-1}$ in methanol.

To run the reaction-diffusion-convection model in COMSOL, it is necessary to specify the values of some physical properties of methanol and acetone. The needed properties of our solvents are listed in Table 1.

The values of the physical properties of silica glass (including thermal conductivity), and their dependence on temperature
were adopted from the Materials Library of the COMSOL software package.

In our model, we assumed that the cuvette, which has an external height and width of 3.1 and 1.2 cm, respectively, and a thickness of 0.10 cm, was surrounded by air everywhere except at the bottom and that there was convective cooling between the air (at a constant temperature of 25.0 °C) and the silica walls of the cuvette. At the bottom of the silica glass boundary, the temperature was fixed at room temperature (25.0 °C unless stated otherwise). This same room temperature was used as the initial temperature of the system. The heating effect due to the UV irradiation at the bottom of the solution (see Figure 1b) was modeled by a heat source having a power of \( P_{\text{ill}} \) and the shape of a truncated cone. This shape simulates the attenuation of the UV radiation due to absorption by the photochromic species, as explained in the Results and Discussion sections.

To model the cooling effect due to evaporation of the solvent when the cuvette was uncapped, we introduced a negative heat source of power \( P_{\text{vap}} \) at the boundary of the solvent (see Figure 2). \( P_{\text{vap}} \) was set to zero in simulations of a capped cuvette.

A standard mesh with 132 484 elements for a 3-D model was used in our simulations.

## RESULTS

Spectral and Dynamical Properties of the Photochromic Spiro-Oxazine in Methanol and Acetone. The spiro-oxazine SpO, dissolved at concentrations on the order of \( 9 \times 10^{-5} \) M in acetone or methanol, has its absorption band between 328 and 425 nm. This band is centered at 355 nm, and since it has just a weak tail in the visible, SpO solutions appear colorless. When SpO is UV-irradiated, a new band in the visible appears. This new band has its maximum at 607 nm in methanol and at 612 nm in acetone (Figures 3a and S1a).

![Figure 2. 3-D model of the silica glass cuvette with 3 mL of solvent (methanol or acetone). The cuvette is surrounded by air, and heat is exchanged between the silica walls and the air (T = 25.0 °C) by convective cooling. At the bottom of the cuvette, a constant temperature is maintained.](image)

![Figure 3. Photochromic properties of SpO in methanol: (a) spectral evolution under irradiation (the black, red, and green spectra show the absorbance values A recorded after 5, 125, and 539 s from the beginning of the irradiation, respectively); (b) PM absorbance at 607 nm during the coloration (UV on) and bleaching (UV off) processes; (c) first derivative of PM absorbance as a function of t for the coloration and bleaching reactions, fitted by the linear functions in eqs 3 and 5 (red straight lines).](image)

### Table 1. Physical Properties of Methanol and Acetone

<table>
<thead>
<tr>
<th>solvent</th>
<th>( \eta = \exp(A + B/(C + T)) ) (Pa s)</th>
<th>( \rho = A/B^{(1+T/C)^D} ) (kg/m³)</th>
<th>heat capacity ( (c_p) ) (J/K kg)</th>
<th>thermal conductivity ( (\kappa) ) (W/m K)</th>
<th>volume expansion ( (\alpha) ) (1/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>( A = -6.7562 )</td>
<td>( A = 54.566 )</td>
<td>2510</td>
<td>0.21</td>
<td>0.00119</td>
</tr>
<tr>
<td></td>
<td>( B = 2337.24 )</td>
<td>( B = 0.233211 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( C = 513.16 )</td>
<td>( C = 84.0853 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( D = 0.208875 )</td>
<td>( D = 0.208875 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acetone</td>
<td>( A = -3.37955 )</td>
<td>( A = 57.6214 )</td>
<td>2150</td>
<td>0.16</td>
<td>0.00143</td>
</tr>
<tr>
<td></td>
<td>( B = 553.403 )</td>
<td>( B = 0.233955 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( C = -46.9657 )</td>
<td>( C = 507.803 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( D = 0.254167 )</td>
<td>( D = 0.254167 )</td>
<td></td>
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</tr>
</tbody>
</table>
respectively); its appearance confers a blue color to the solution. This band is due to the production of the merocyanine MC (see Figure 1a). When the irradiation is discontinued, the merocyanine thermally reverts back to SpO, and the solution bleaches. The change in absorbance over time at the wavelength corresponding to the maximum of this band is depicted in Figures 3b (in methanol) and S1b (in acetone). The first part of these kinetics, where the absorbance grows monotonically, corresponds to the coloration phase seen when 1 mL of solution is uniformly irradiated. The second part is the bleaching stage. Equations 2 and 3 respectively describe the coloration and the decoloration phases\(^1\)

\[
\frac{dA_{MC}}{dt} = \varepsilon_{MC} \Phi I_{abs} - k_A A_{MC} \tag{2}
\]

\[
\frac{dA_{MC}}{dt} = -k_A A_{MC} \tag{3}
\]

where \(A_{MC}\) and \(\varepsilon_{MC}\) are the absorbance and the molar extinction coefficient, respectively, of MC at the maximum of its band in the visible, \(\Phi\) is the photocoloration quantum yield, \(k_A\) is the bleaching kinetic constant, \(I_{abs}\) is the irradiation intensity absorbed by SpO, and \(I\) is the path length of the cuvette (1 cm). At the irradiation wavelength (\(\lambda_{irr}\)), both SpO and MC absorb. Therefore, \(I_{abs}\) is defined by eq 4

\[
I_{abs}^{SpO} = \frac{A_{TOT}^{SpO}}{A_{TOT}} I_0 (1 - 10^{-A_{TOT}})
\]

\[
= \varepsilon_{SpO} (C_0 - [MC]) I_0 F \tag{4}
\]

where \(A_{SpO}\) and \(\varepsilon_{SpO}\) are the absorbance and the molar extinction coefficient, respectively, of SpO at \(\lambda_{irr}\), \(A_{TOT}\) is the total absorbance at \(\lambda_{irr}\), \(I_0\) is the intensity of the lamp at \(\lambda_{irr}\), \(C_0\) is the analytical concentration of the photochromic species, and \(F\) represents the photokinetic factor. When the UV irradiation is performed at an isosbestic point (367 nm in methanol and 379 nm in acetone), \(F\) is constant. Inserting eq 4 into eq 2, we obtain eq 5

\[
\frac{dA_{MC}}{dt} = \varepsilon_{MC} F \varepsilon_{SpO} \Phi I_0 C_0 - (k_A + I_0 \Phi F \varepsilon_{SpO} I) A_{MC} \tag{5}
\]
Equations 3 and 5 show that the first derivative of $A_{MC}$ is linear in $A_{MC}$ for both the coloration and the bleaching stages. Graphical representations of these relations are shown in Figures 3c and S1c. By fitting the experimental data of the bleaching kinetics with eq 3, it is possible to determine the $k_3$ values. On the other hand, by fitting the coloration kinetics with eq 5, we can estimate $\varepsilon_{MC}$ and $\Phi$, with $I_0$ evaluated actinometrically (see the Experimental Section for more details). The results are reported in Table 2. MC has a coloration quantum yield which is more than two times higher in acetone than in methanol, although $\varepsilon_{MC}$ in acetone is half the value determined in methanol. Moreover, MC bleaches more than three times faster in acetone than in methanol, and the interaction with acetone shifts the maximum of the MC band toward the red.

Hydrodynamic Color Oscillations and Waves. When 3 mL of SpO solution in acetone or methanol is UV-irradiated laterally at the bottom of the cuvette (see Figure 1b), it did not change during the experiment.

![Figure 5](image1.png)

**Figure 5.** Oscillations recorded at 612 nm (black trace) and 359 nm (red trace) for the photochromic species dissolved in acetone at a concentration of $8.8 \times 10^{-5}$ M under UV irradiation in an uncapped cuvette.

![Figure 6](image2.png)

**Figure 6.** Oscillations recorded at 612 nm for SpO ($8.8 \times 10^{-5}$ M) in acetone in a capped cuvette. Panel a shows the entire dynamical evolution, consisting of a first stage when the UV is on and a second stage when the UV is off; (b) enlargement of the kinetics showing small, irregular oscillations, whose Fourier analysis (calculated in the time window $[1000, 1195]$ s) is presented in panel c. Ambient conditions: $T_{\text{initial}} = 298.0$ K, $T_{\text{final}} = 298.8$ K; $P_{\text{initial}} = 969.0$ hPa, $P_{\text{final}} = 968.5$ hPa. The initial height of the solution was 3.10 cm; it did not change during the experiment.
If the same UV irradiation of 3 mL of SpO solution is carried out in a capped cuvette, the oscillations are noticeably damped (Figures 6a and S4a). The amplitude of the absorbance variation is ten times smaller than that recorded when the cuvette is uncapped. In fact, \( \Delta A \approx 0.02 \) in closed systems (Figures 6b and S4b), whereas it was \( \sim 0.2 \) in the open system. Moreover, the absorbance values in the capped cuvette are quite irregular, as revealed by the Fourier spectra (Figures 6c and S4c).

The large amplitude oscillations shown in Figures 4, 5, S2, and S3 are observed only when enough (3 mL) photochromic solution is maintained in an uncapped cuvette and UV irradiation is carried out at the bottom of the solution. The chemical mechanism describing the photochromism of SpO does not involve any autocatalytic step, but simply two unimolecular processes evolving toward a stable photostationary state under steady irradiation. From these considerations, we infer that the oscillations of the UV and visible radiation transmitted by the photochromic solution stem from convective hydrodynamic motion of the solvent. In fact, the UV

cuvette is maintained uncapped, the kinetics of coloration, recorded at a height of 0.35 cm from the bottom (that is, inside the cone generated by the UV beam), exhibits surprising profiles. Instead of reaching a plateau at the photostationary state, as occurs when 1 mL is uniformly irradiated, \( A_{MC} \) oscillates (Figures 4a and S2a). The amplitude of the oscillations is quite large: typically \( \Delta A \approx 0.2 \) (Figures 4b and S2b). Fourier analysis of the kinetic traces reveals that the major component in acetone corresponds to a period of 15 s, that is, to a frequency of 0.067 Hz (Figure 4c). In methanol, the main component of the color oscillations is found at a period of 60 s or longer, i.e., a frequency of 0.018 Hz (Figure S2c) or less. The profile of the kinetics is quite sensitive to the environmental conditions (temperature, pressure) of the experiment.

Because \([\text{SpO}] + [\text{MC}]\) remains constant throughout the reaction, in the UV region, where the spectral contribution of SpO overwhelms that of MC, we detect oscillations with the same periodic components as found in the visible, but antiphase to those in the visible region, which are due exclusively to MC (Figures 5 and S3).

Figure 7. Photochromic compound (concentration \( 9.4 \times 10^{-5} \) M) in methanol during the photocoloration stage. The snapshots in the first row are of the uncapped cuvette at 162 (a), 169 (b), 180 (c), 189 (d), 199 (e), and 209 s (f) after the beginning of UV irradiation. The snapshots in the second row show the capped cuvette after 10 (a’), 42 (b’), 196 (c’), 458 (d’), 641 (e’), and 751 s (f’) from the beginning of UV irradiation.
irradiation at the bottom of the solution and the evaporation of the solvent at the top generate a thermal gradient sufficient to trigger a hydrodynamic instability. Similar phenomena have previously been observed in other “photophysical oscillators”, i.e., solutions of luminescent compounds, such as anthracene, 9,10-dimethylanthracene, 21–23 biacetyl, 24 and eriochrome cyanine dyes. 25

There is also an example of damped oscillations of transmitted light induced by laser pulsed shots. 26

We confirmed the involvement of convective motion in our “photochemical oscillator” by recording movies of how the blue color due to MC spreads inside the cuvette when the UV irradiation is on (Figures 7 and S5). It is evident that when the cuvette is uncapped, the UV irradiation coupled to the laminar hydrodynamic motion of solvent molecules gives rise to chemical waves of deep blue. In fact, focusing on the bottom part of the cuvette, at the height of the spectrophotometric probe beam, we see an oscillating strip of deep blue (see snapshots in the first rows in Figures 7 and S5). The spot of deep blue produced at the bottom of the cuvette moves toward the top part of the solution at a speed of about 0.0015 m/s in methanol and 0.002 m/s in acetone. The movement of MC is much slower in the capped cuvette (see snapshots in the second rows of Figures 7 and S5). MC reaches the top of the solution after more than 1 min in acetone and after almost 5 min in methanol. When the cuvette is capped, there is no evaporation of solvent at the top of the solution, and the thermal gradient produced is thus much smaller than that generated by maintaining the system uncapped. The colored MC propagates mainly by diffusion, and the convective motions begin only after prolonged UV irradiation at the bottom of the solution.

Simulations of the Hydrodynamic Oscillations and Waves. To shed more light on the experimental results, we carried out computations after building a three-dimensional model (see Figure 2) of our experimental system using COMSOL software. In our computational model, we introduced both the photochemical and heating effects due to the UV irradiation at the bottom of the cuvette and the cooling effect due to evaporation of solvent at the top of the uncapped cell. The double effect of the UV source was described by assuming that the heating source and the photocoloration reaction are localized in a volume having the shape of a truncated cone located at the bottom of the cuvette. The radius of the larger base of the cone was taken as the radius of the optical fiber (R = 0.3 cm). For the radius of the smaller base, at the opposite side of the cuvette, we chose r = R(0.2)1/2, since the attenuation of the UV intensity after crossing 1 cm of solution was about 80%. Taking into account the actinometric determinations (see the Experimental Section for details), the total heating power associated with the UV irradiation was estimated to be P = 0.1 mW.

To model the chemical transformations, we assumed that the rate constant of the photocoloration process, occurring only inside the truncated cone and given by k = (DF\textsubscript{SpO}/C\textsubscript{SpO}) (see eq 1), was 0.0074 s\(^{-1}\) in acetone and 0.0038 s\(^{-1}\) in methanol. For the kinetic constant of the bleaching process, which occurs everywhere in the solution, we used the values reported in Table 2.

To model the cooling effect due to evaporation of the solvent from the uncapped cuvette, we introduced a negative heat source at the boundary of the solvent. We measured the average rate of solvent vaporization and used the known vaporization enthalpies of methanol and acetone (Table 3) to estimate the power of this heat source as −10 mW.

<table>
<thead>
<tr>
<th>solvent</th>
<th>average rate of vaporization (kg/s)</th>
<th>enthalpy of vaporization (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>−9 \times 10^{-9}</td>
<td>1104</td>
</tr>
<tr>
<td>acetone</td>
<td>−2 \times 10^{-8}</td>
<td>539.7</td>
</tr>
</tbody>
</table>

The COMSOL simulations allowed us to calculate the temperature, velocity and concentrations of SpO and MC in space and over time. Snapshots showing the distribution of [MC] at different times in uncapped and capped cuvettes are shown in Figures 8 and S6 for acetone and methanol, respectively. These snapshots display 2D slices through the middle of the cuvette. They reproduce quite closely what we see experimentally, and the model in general gives results in good agreement with the experiments. The speed at which MC spreads from the bottom to the top of an uncapped cuvette is estimated to be 0.002 and 0.001 m/s in acetone and methanol, respectively. This process is much slower in a capped cuvette. In fact, the time needed by MC to diffuse from the bottom to the top of the solution is almost 3 min in acetone and 5.5 min in methanol, roughly 10 times longer than in the uncapped cuvette.

In Figures 9 and S7 we show how the temperature of photochromic solutions in acetone and methanol changes in time. The thermal gradient (∆T) between the bottom and the top of the uncapped solution, produced by the UV radiation and the evaporation of the solvent, is estimated to be 0.3 K in both acetone and methanol. It is well-known that when ∆T is high enough so that the Rayleigh number (Ra) exceeds its critical value (Ra\textsubscript{c}) convective motion should be observed.

For the geometry of our system, the Rayleigh number is given by


\[
Ra = \frac{g \alpha \rho \Delta T a^4}{\mu \kappa h} \Delta T
\]

where g is the gravitational constant, a is the coefficient of volume expansion, \(\rho\) is the density, \(\kappa\) is the heat capacity, \(\alpha\) is the depth of the column (1 cm), \(\mu\) is the dynamic viscosity, \(\kappa\) is the thermal conductivity of the solvent, and \(h\) is the height of the fluid column (3 cm). Introducing the numerical values of the physical parameters (see Table 1) in eq 6, we find that Ra = (4.93 × 10\(^4\))∆T in methanol and Ra = (1.22 × 10\(^5\))∆T in acetone. Finally, the estimated ∆T = 0.3 K gives Ra = 14790 and 36600 in methanol and acetone, respectively. These values are more than ten times larger than the critical Rayleigh number value (Ra\textsubscript{c}) ≈ 1100. Therefore when the cuvette is uncapped, the thermal gradient generated is large enough to trigger convective motion of the solvent, confirming what we have observed.

For the capped cuvette the estimated thermal gradient was 0.003 K in acetone and 0.004 K in methanol. With these ∆T values the Rayleigh number is 366 and 197 in acetone and methanol, respectively, i.e., Ra < Ra\textsubscript{c}. Therefore, we expect that diffusion of MC and conduction of heat are the main processes of mass and energy transport, and limited if any convection occurs in the capped cuvette. Again, this conclusion is in agreement with our experimental observations.
Figure 8. 3D simulations of merocyanine concentration (in mol/L) in 3 mL of acetone in uncapped (top row) and capped (bottom row) cuvettes. Numbers at the top indicate time from the start of UV irradiation. The snapshots display 2D profiles in the central part of the cuvette. The black wire frame near the bottom depicts the area in which the UV radiation is applied. The temperature at the bottom wall is fixed at 25.0 °C for the uncapped cuvette and at 25.1 °C for the capped cuvette.

Figure 9. 3D simulations of merocyanine concentration (in mol/L) in 3 mL of acetone in uncapped and capped cuvettes. Numbers at the top indicate time from the start of UV irradiation. The snapshots display 2D profiles in the central part of the cuvette. The temperature at the bottom wall is fixed at 25.0 °C for the uncapped cuvette and at 25.1 °C for the capped cuvette.
A further test of the predictive capability of our model comes from extracting the average MC concentration along a line at 0.35 cm above the bottom of cuvette (that is, the height of the center of the UV radiation beam and also of the spectrophotometric white probe beam). The trends of average C(MC) in the case of acetone are shown in Figure 10; those in methanol are depicted in Figure S8. In the uncapped cuvette with acetone as solvent, the increase in the colored species concentration is followed by an interval of irregular oscillations that become regular after about 1200 s. However at longer times the oscillations are damped. This is not surprising, because in the experiments the oscillations died out as well. In the model, the temperature gradient slowly decreases, which affects the flow in the cuvette. Eventually, the flow slows to a level at which changes in concentration resulting from reaction and diffusion balance those caused by convection, and the oscillations cease. In Figure 10c, the regular oscillations of C(MC) are plotted along with those of C(SpO): they are antiphase, as in the experiments. The Fourier analysis (Figure 10d) reveals that their period is about 19 s, quite close to the value of 15 s found in the experiments. When the cuvette is capped, the simulated trend (Figure 10b) of the average C(MC) confirms that the large oscillations seen in (a) are completely suppressed due to the absence of hydrodynamic motion. The time profile shown in Figure 10b depends on the actual location at which the average concentration is evaluated. Profiles with different transients (including the one shown in Figure 6a) can be obtained by moving slightly the coordinate of the line along which the average concentration is evaluated.

**DISCUSSION**

Electronic oscillators, which convert direct current from a power supply into an alternating current signal, are widely used in many electronic devices. As far as we know, the photochemical system we have described in this work is the first example of a “photochemical oscillator” that transforms continuous UV irradiation into oscillating UV and visible transmitted intensities that are antiphase. In the literature there are examples of other photochemical molecular transducers\(^ {28}\) that generate oscillating light signals, but they involve at least one modulated irradiation beam. There are also examples of “photophysical oscillators”\(^ {20-25}\) based on continuous UV irradiation and oscillating emitting light, but they do not show antiphase oscillations for wavelengths belonging to different spectral regions, as our photochromic system does. The working mechanism of our “photochemical oscillator” is based on the thermoreversible photochromism of the spiro-oxazine SpO and the hydrodynamic convective motion of solvent molecules. In our system the chemistry of the photochromic species does not significantly affect the hydrodynamics, because it does not produce enough heat to cause substantial changes in density of the solvent. On the other hand, the cooling effect at the top of the solution, due to the evaporation of the solvent, triggers convective motion of the solution, and this hydrodynamic flow significantly affects the chemistry. Without the flow the conversion of SpO to MC is smaller. The hydrodynamic flow brings fresh solution containing SpO, thereby increasing the amount converted to MC by nearly a factor of 2, as can be seen by comparing Figures 4a and 6a, or as found in our simulations. Thus, the convection
provides a form of feedback, so that the photochromic species becomes an active participant in the wave development rather than a passive indicator. The convection becomes a way to increase the colorability (Col) of a photochromic species, defined as the ability to develop coloration from a colorless or a slightly colored material. Alternative methods have been proposed previously. Since the colorability (Col) of a photochromic compound under stationary irradiation is

\[
\text{Col} = \frac{\Phi}{k_\Delta}
\]  

(7)

one strategy is to reduce \( k_\Delta \) by lowering the temperature of the system, by embedding the photoactive species in a rigid microenvironment, or by hindering the ring closure reaction through the interaction of the zwitterionic merocyanine with amino acids. Other strategies are based on increasing either \( \Phi \) by selection of the irradiation wavelength for photochromic species exhibiting wavelength-dependent quantum yield, or \( k_\Delta \) by careful choice of solvent.

The induction of convective motion provides a novel strategy to increase the colorability, as shown here. The convection is triggered by a thermal gradient generated by the heating effect of UV irradiation at the bottom of the system and the cooling effect of solvent evaporation at the top of the solution. The primary frequency of the oscillations ranges between 0.015 and 0.007 Hz (period between 67 and 15 s), depending on the solvent and the experimental conditions (ambient temperature, pressure and humidity). The oscillating radiation signals are accompanied by colored chemical hydrodynamic waves produced by the convective cooperative motion of solvent molecules dragging the thermally unstable photomerocyanine MC. The color waves propagate rapidly (speeds between 0.0015 and 0.002 m/s) and with a predictable direction due to the coherent laminar thermokinetic movement of the solution. Therefore, like any chemical wave, the hydrodynamic waves we have studied in this work may be useful as a tool to transfer chemical information.

It will be interesting to study the phenomenon described in this paper with other photochromic compounds, dissolved either as single reactive species or combined in pairs. In the latter case, waves of multiple colors might be obtained.

### ASSOCIATED CONTENT

#### Supporting Information

Data on the photochromism of SpiO in acetone and the behavior of colored hydrodynamic waves and oscillations in methanol. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES

24. Epstein, I. R.; Morgan, M.; Steel, C.; Valdes-Aguilera, O. Biacetyl-Oxygen and Other Photochemical Oscillators: The Role of...