

# Reação Oscilante Bromato-Ácido Oxálico- Acetona-Mn(II)-Ácido Sulfúrico, em batelada

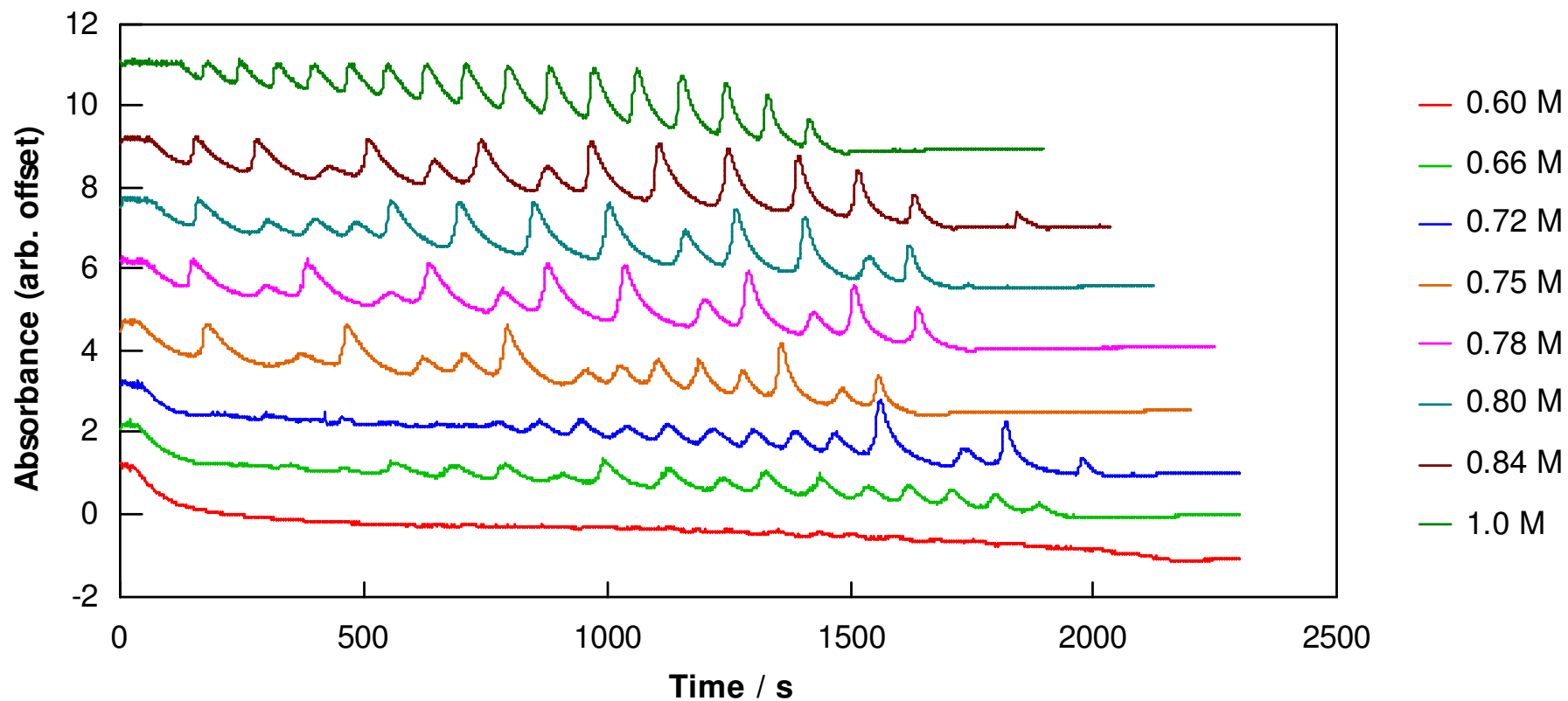
- $[\text{BrO}_3^-] = 0,14 \text{ M}$
- $[\text{ácido oxálico}] = 0,0625 \text{ M}$
- $0,54 \text{ M} < [\text{acetona}] < 1,0 \text{ M}$
- $[\text{MnSO}_4] = 0,0013 \text{ M}$
- $[\text{H}_2\text{SO}_4] = 0,625 \text{ M}$

M. C. Guedes, R. B. Faria, *J. Phys. Chem. A* **1998**, 102, 1973.

# Resultados experimentais em batelada

# Acetone Concentration Effect

Method 1 - Fast Stirring Rate

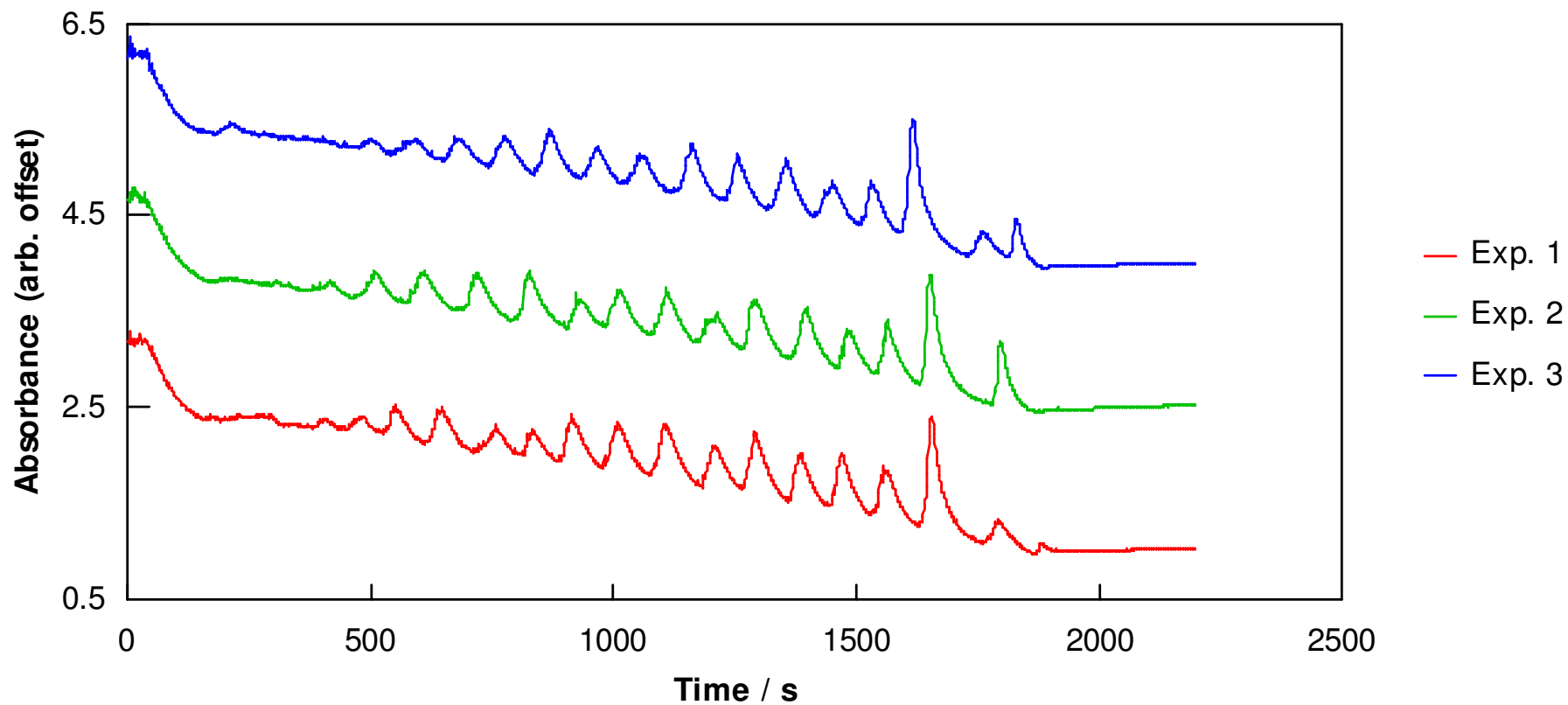


310 nm 20 °C

[H<sub>2</sub>SO<sub>4</sub>] = 0.625 M; [BrO<sub>3</sub><sup>-</sup>] = 0.14 M; [Mn<sup>2+</sup>] = 0.0013 M; [oxalic acid] = 0.0625 M

## Reproducibility - Method 1 - Fast Stirring Rate

[acetone] = 0.72 M



310 nm 20 °C

[H<sub>2</sub>SO<sub>4</sub>] = 0.625 M; [BrO<sub>3</sub><sup>-</sup>] = 0.14 M; [Mn<sup>2+</sup>] = 0.0013 M; [oxalic acid] = 0.0625 M

Resultados teóricos

Modelagem

# Modelagem Bromato-Ácido Oxálico- Acetona-Ce(IV)-Ácido Sulfúrico, em fluxo agitado

- Baseado no modelo de Field & Boyd (*J. Phys. Chem.* **1985**, 89, 3707).
- Integrador numérico escrito por I. Lengyel em Turbo Pascal 6.0 baseado no trabalho de Kaps & Rentrop (*Num. Math.* **1979**, 33, 55).

## REACTIONS

	$k_f$	$k_r$
$\text{Br}^- + \text{BrO}_3^- + 2\text{H}^+ \rightleftharpoons \text{HOBr} + \text{HBrO}_2$	$5.0 \text{ M}^{-3}\text{s}^{-1}$	$1.0 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$
$\text{Br}^- + \text{HBrO}_2 + \text{H}^+ \rightleftharpoons 2\text{HOBr}$	$2.0 \times 10^9 \text{ M}^{-2}\text{s}^{-1}$	$5.0 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$
$\text{Br}^- + \text{HOBr} + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O}$	$8.0 \times 10^9 \text{ M}^{-2}\text{s}^{-1}$	$110 \text{ s}^{-1}$
$\text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \rightleftharpoons 2\text{BrO}_2\cdot + \text{H}_2\text{O}$	$1 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$	$2.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$
$\text{BrO}_2\cdot + \text{Ce}^{3+} + \text{H}^+ \rightleftharpoons \text{Ce}^{4+} + \text{HBrO}_2$	$7.0 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$	$8.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$
$\text{BrO}_2\cdot + (\text{COOH})_2 \rightarrow \text{HBrO}_2 + \text{CO}_2 + \text{HCO}_2\cdot$	$150 \text{ M}^{-1}\text{s}^{-1}$	
$\text{HBrO}_2 + \text{HBrO}_2 \rightleftharpoons \text{HOBr} + \text{BrO}_3^- + \text{H}^+$	$4.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	$2.1 \times 10^{-10} \text{ M}^{-2}\text{s}^{-1}$
$\text{Ce}^{4+} + \text{BrO}_2\cdot + \text{H}_2\text{O} \rightleftharpoons \text{Ce}^{3+} + \text{BrO}_3^- + 2\text{H}^+$	$9.6 \text{ M}^{-1}\text{s}^{-1}$	$1.3 \times 10^4 \text{ M}^{-3}\text{s}^{-1}$
$\text{HOBr} + (\text{COOH})_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{HCO}_2\cdot + \text{Br}\cdot$	$25 \text{ M}^{-1}\text{s}^{-1}$	
$\text{Br}\cdot + \text{Br}\cdot \rightarrow \text{Br}_2$	$1.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	
$\text{HCO}_2\cdot + \text{HCO}_2\cdot \rightarrow (\text{COOH})_2$	$1.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	
$\text{Ce}^{4+} + (\text{COOH})_2 \rightarrow \text{Ce}^{3+} + \text{CO}_2 + \text{HCO}_2\cdot + \text{H}^+$	$27.5 \text{ M}^{-1}\text{s}^{-1}$	
$\text{Ce}^{4+} + \text{HCO}_2\cdot \rightarrow \text{Ce}^{3+} + \text{CO}_2 + \text{H}^+$	$1.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	
$\text{Br}\cdot + (\text{COOH})_2 \rightarrow \text{Br}^- + \text{H}^+ + \text{HCO}_2\cdot + \text{CO}_2$	$2000 \text{ M}^{-1}\text{s}^{-1}$	
$\text{CH}_3\text{COCH}_3 + \text{H}^+ \rightleftharpoons \text{CH}_2=\text{CHOHCH}_3 + \text{H}^+$	$8.3 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$	$21.3 \text{ M}^{-1}\text{s}^{-1}$
$\text{CH}_2=\text{CHOHCH}_3 + \text{Br}_2 \rightarrow \text{BrCH}_2\text{COCH}_3 + \text{Br}^- + \text{H}^+$	$1.03 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	
$\text{BrO}_3^- + (\text{COOH})_2 \rightarrow \text{BrO}_2\cdot + \text{H}_2\text{O} + \text{CO}_2 + \text{HCO}_2\cdot$	$5.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	
$\text{HOBr} + \text{HCO}_2\cdot \rightarrow \text{H}_2\text{O} + \text{Br}\cdot + \text{CO}_2$	$2.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	
$\text{Br}^- + \text{Br}_2 \rightleftharpoons \text{Br}_3^-$	$1.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	$7.5 \times 10^6 \text{ s}^{-1}$
$\text{HCO}_2\cdot + \text{H}^+ + \text{BrO}_3^- \rightarrow \text{BrO}_2\cdot + \text{CO}_2 + \text{H}_2\text{O}$	$2.7 \times 10^3 \text{ M}^{-2}\text{s}^{-1}$	
$\text{Br}_3^- + \text{CH}_2=\text{CHOHCH}_3 \rightarrow \text{BrCH}_2\text{COCH}_3 + 2\text{Br}^- + \text{H}^+$	$2.8 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	
$\text{Br}_2 + \text{BrCH}_2\text{COCH}_3 \rightarrow \text{BrCH}_2\text{COCH}_2\text{Br} + \text{Br}^- + \text{H}^+$	$5.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$	
$\text{Br}_3^- + \text{BrCH}_2\text{COCH}_3 \rightarrow \text{BrCH}_2\text{COCH}_2\text{Br} + 2\text{Br}^- + \text{H}^+$	$5.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$	

Comportamento em

$$[\text{H}_2\text{SO}_4] = 1.0 \text{ M}$$

$$[\text{Ácido Oxálico}] = 0,03 \text{ M}$$

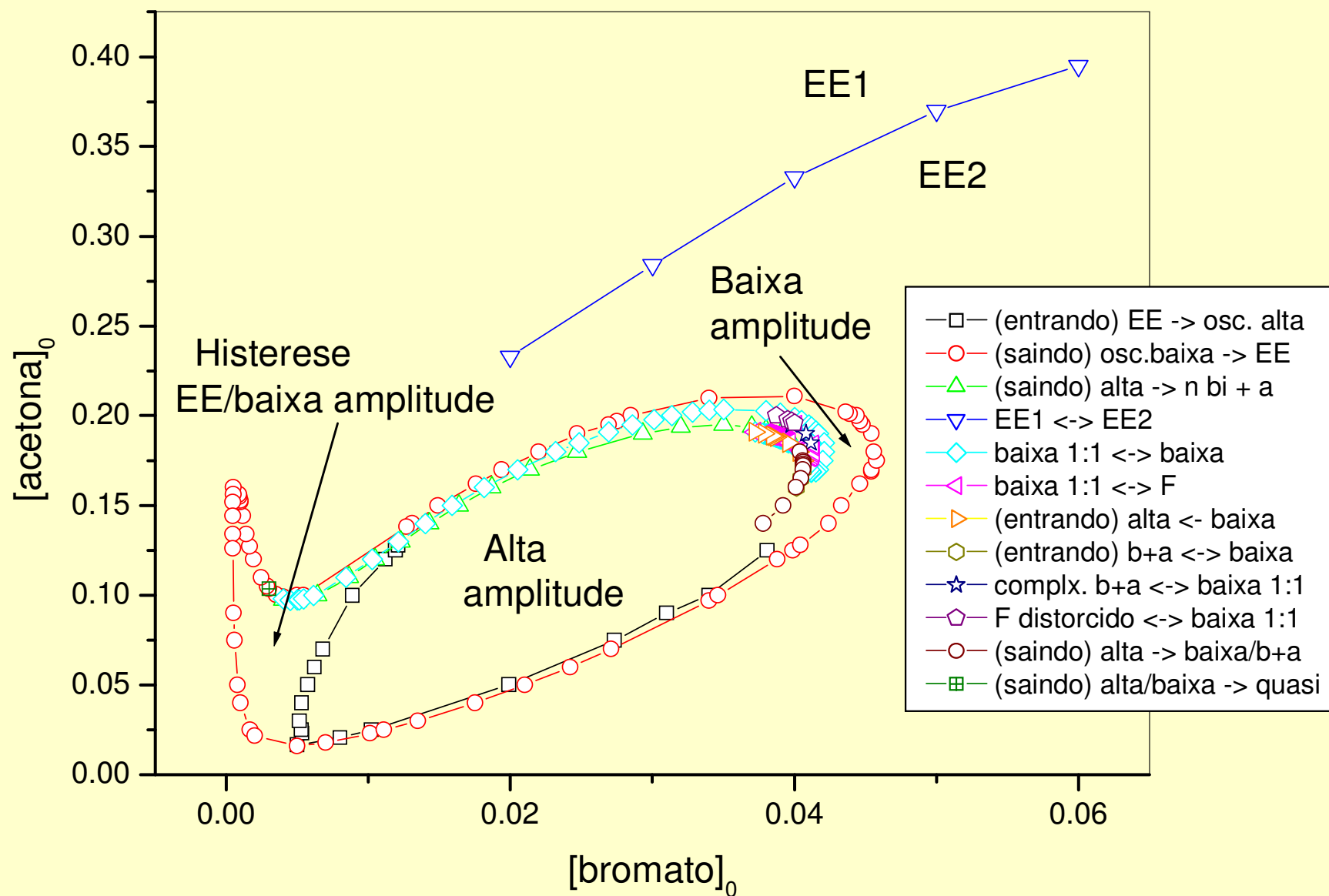
$$[\text{Ce(IV)}] = 0,0005 \text{ M}$$

$$k_0 = 0,005 \text{ s}^{-1}$$

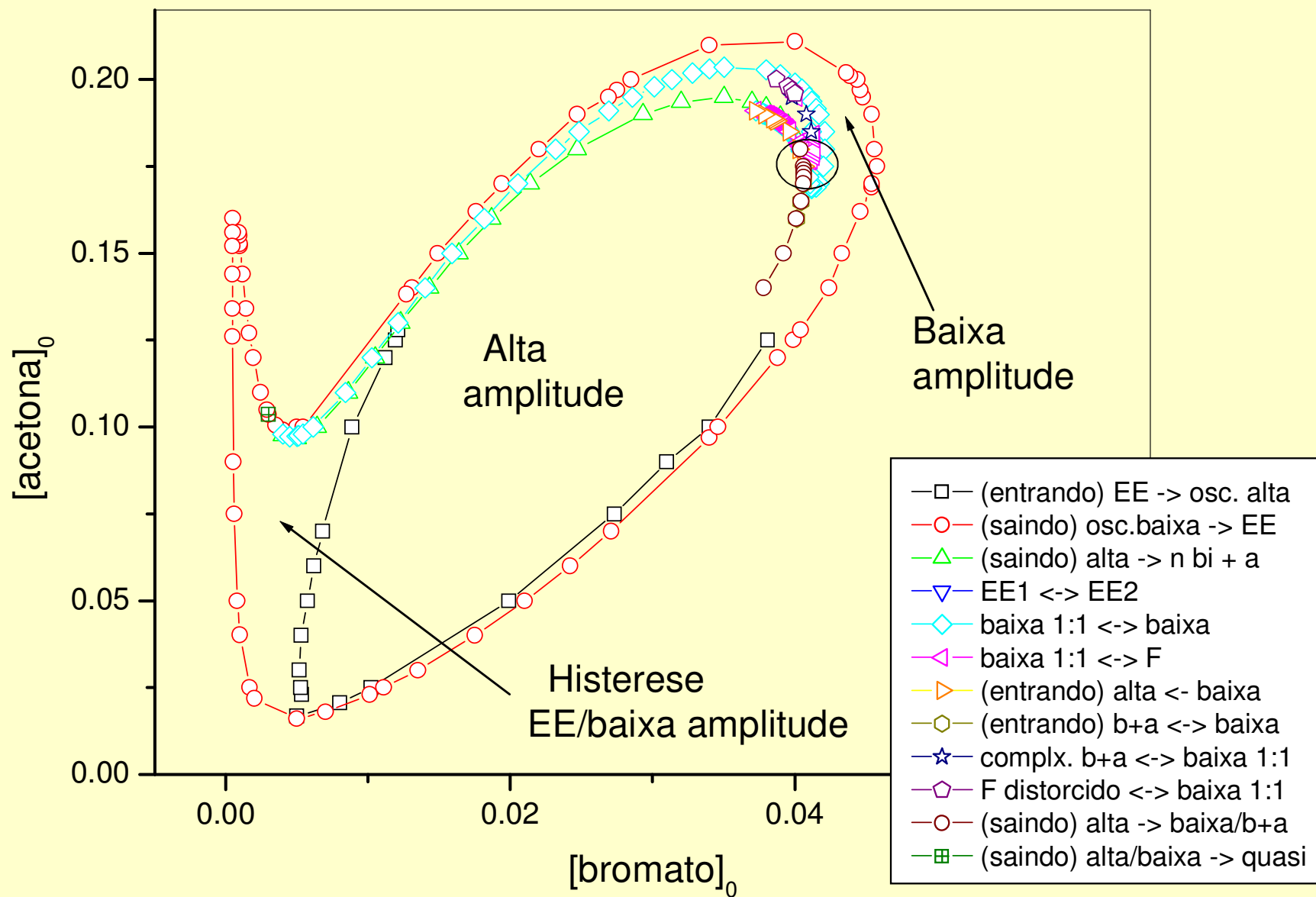


Diagrama de fases  
no plano  
bromato  $\times$  acetona

## Diagrama de fases Bromato x Acetona

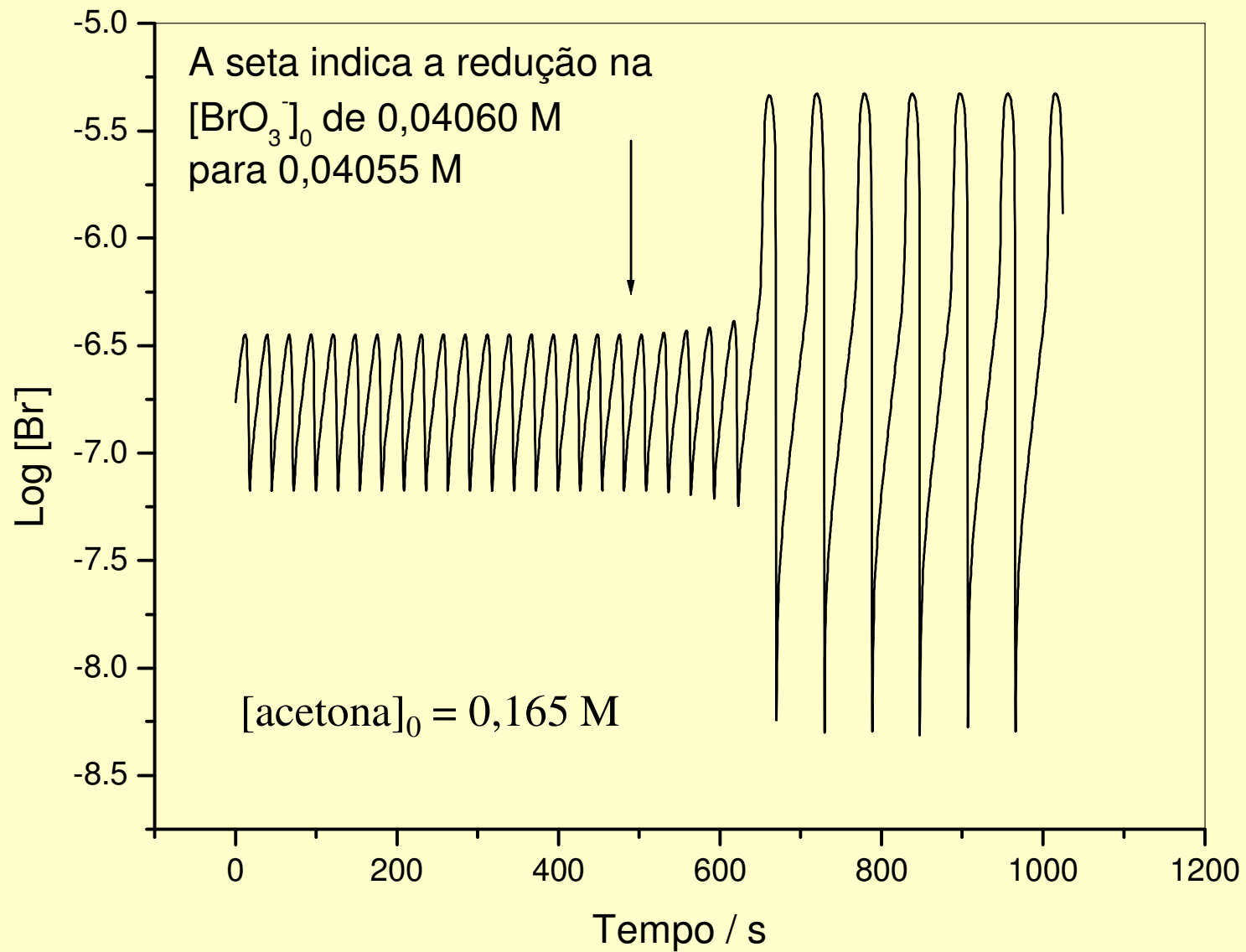


## Diagrama de fases Bromato x Acetona



“CANARD EXPLOSION”

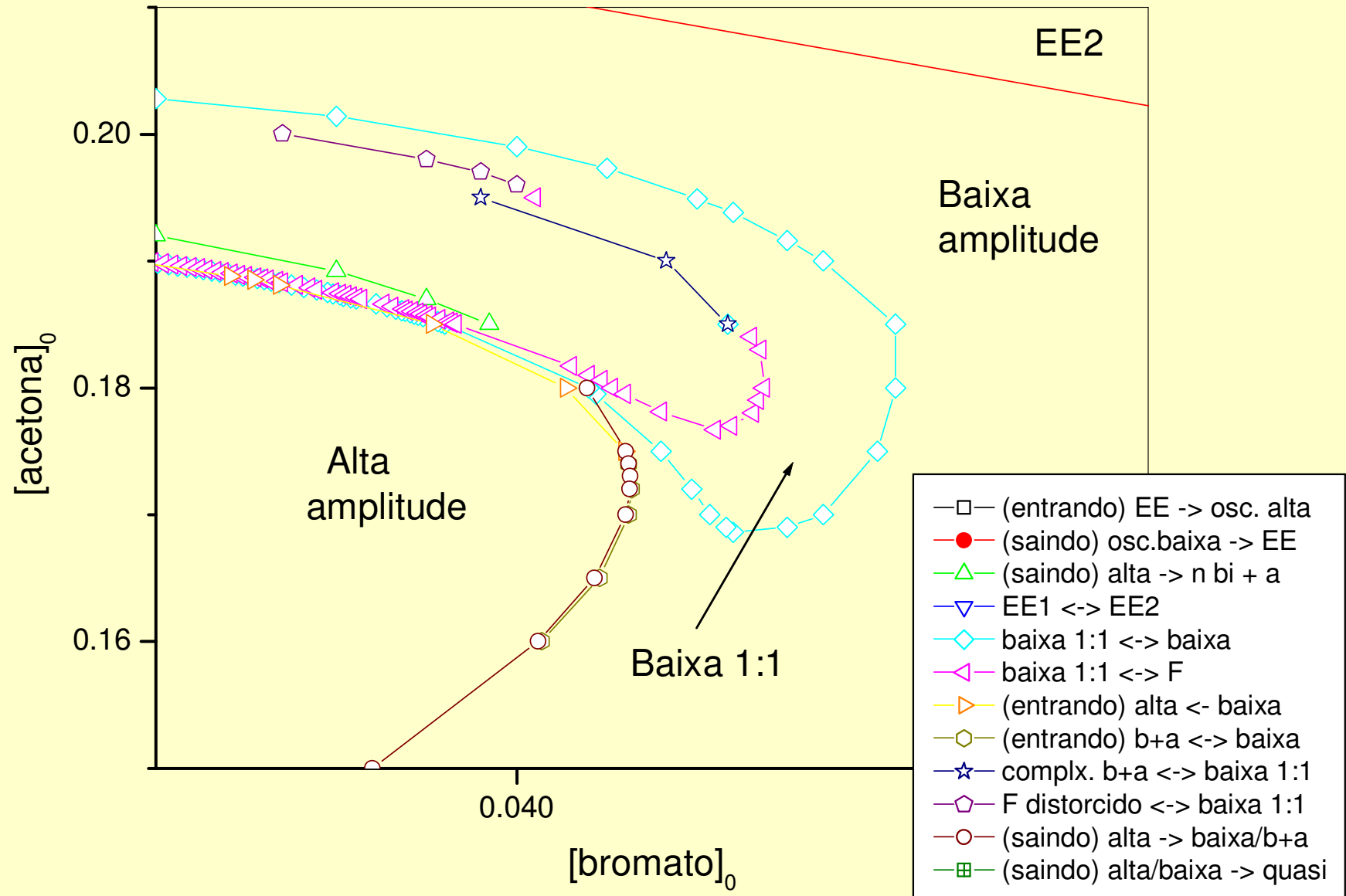
## "Canard Explosion"



Oscilação complexa  
de  
baixa amplitude

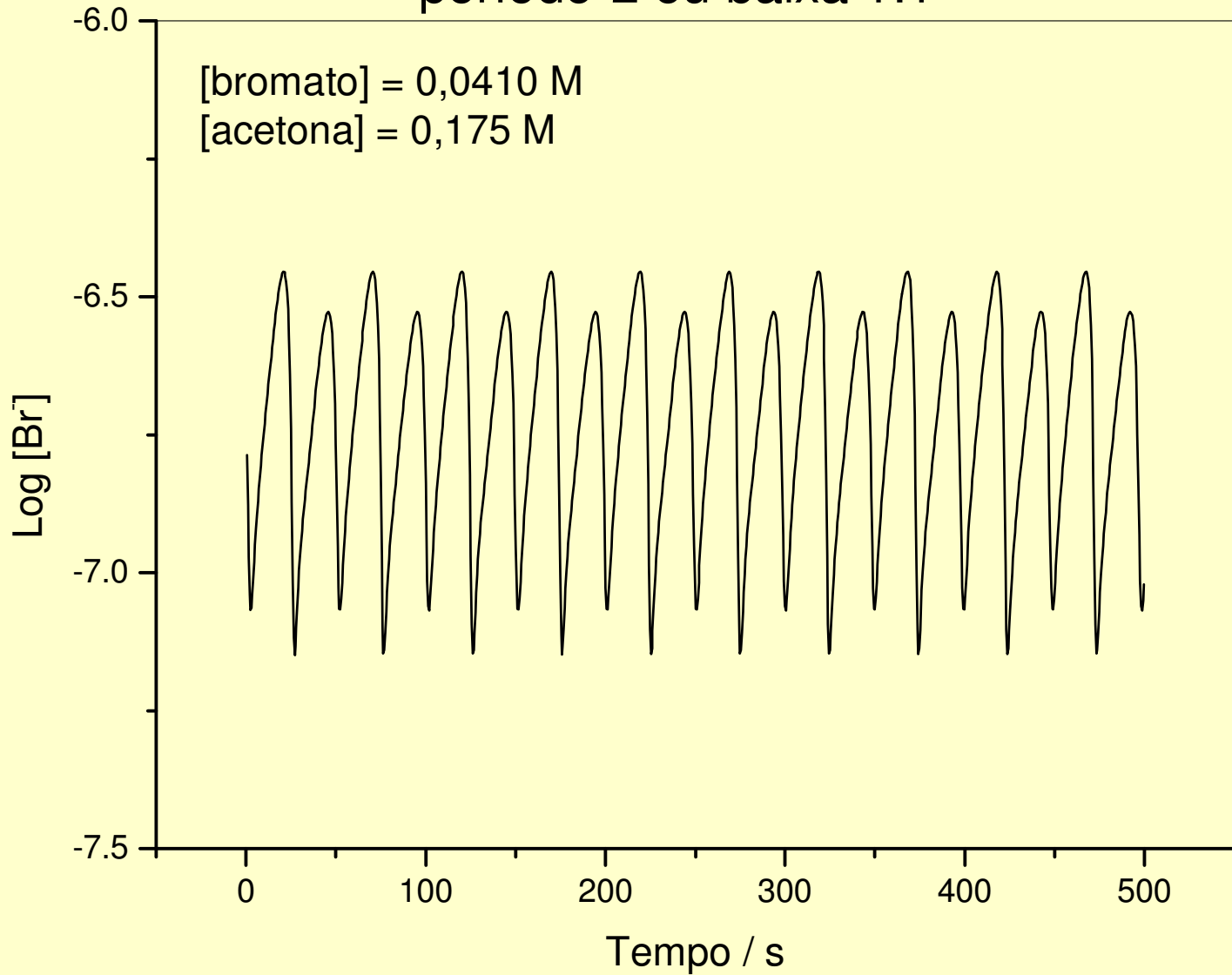
período-2  
(baixa 1:1)

# Diagrama de fases Bromato x Acetona



# Oscilação complexa de baixa amplitude

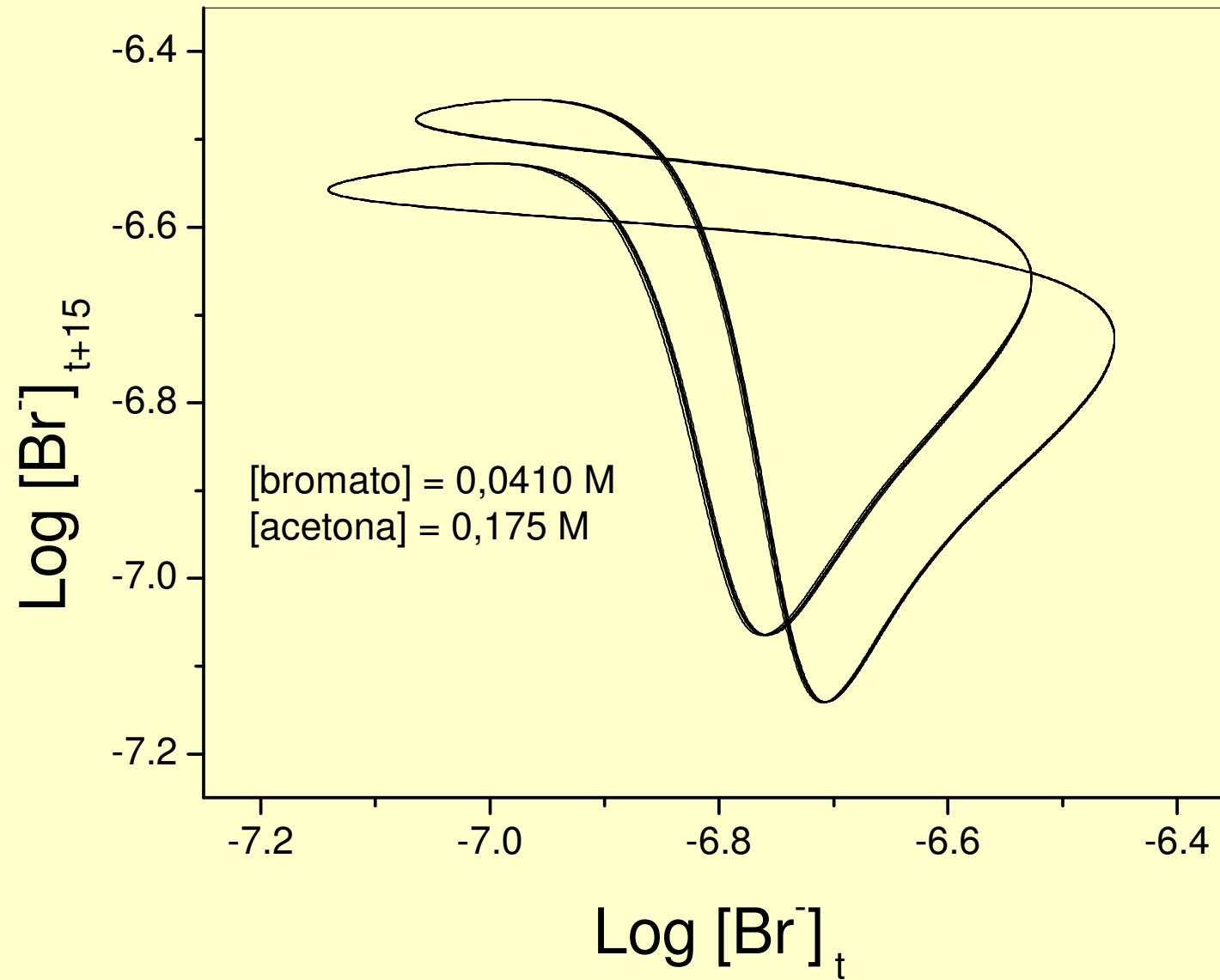
período-2 ou baixa 1:1





ATRATOR

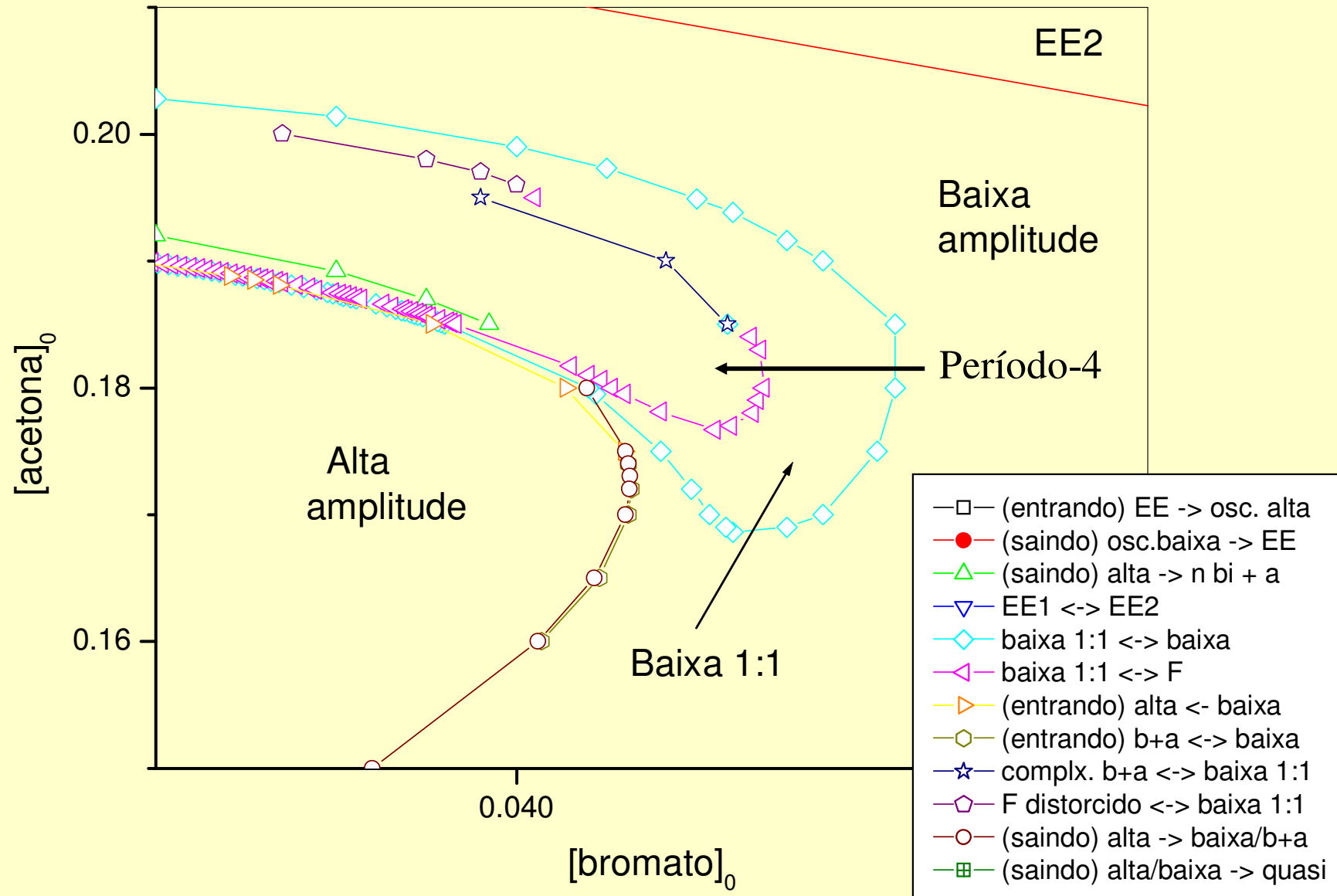
## Atrator para oscilação baixa 1:1



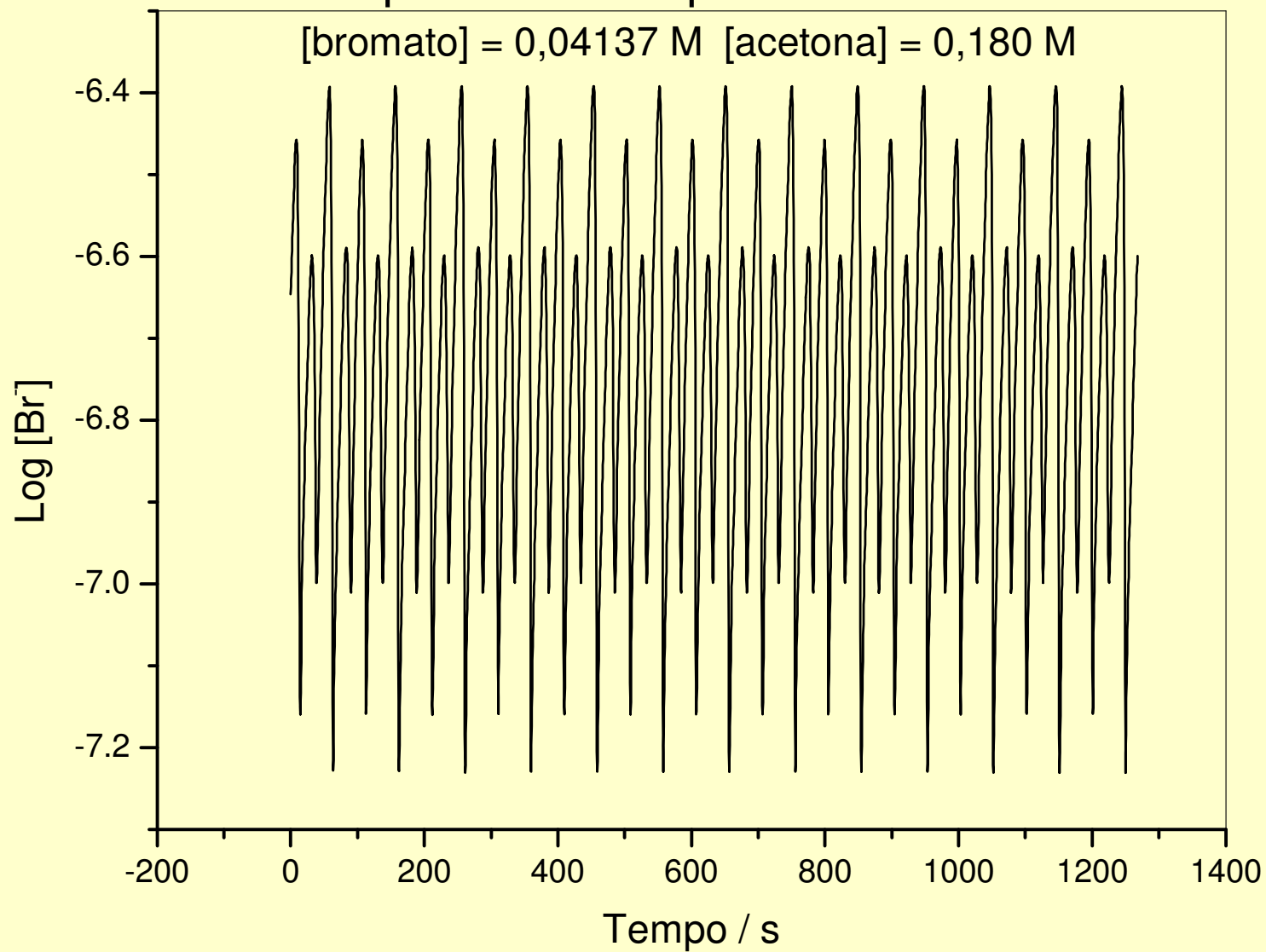
Oscilação complexa  
de  
baixa amplitude

período-4  
(Padrão F)

# Diagrama de fases Bromato x Acetona



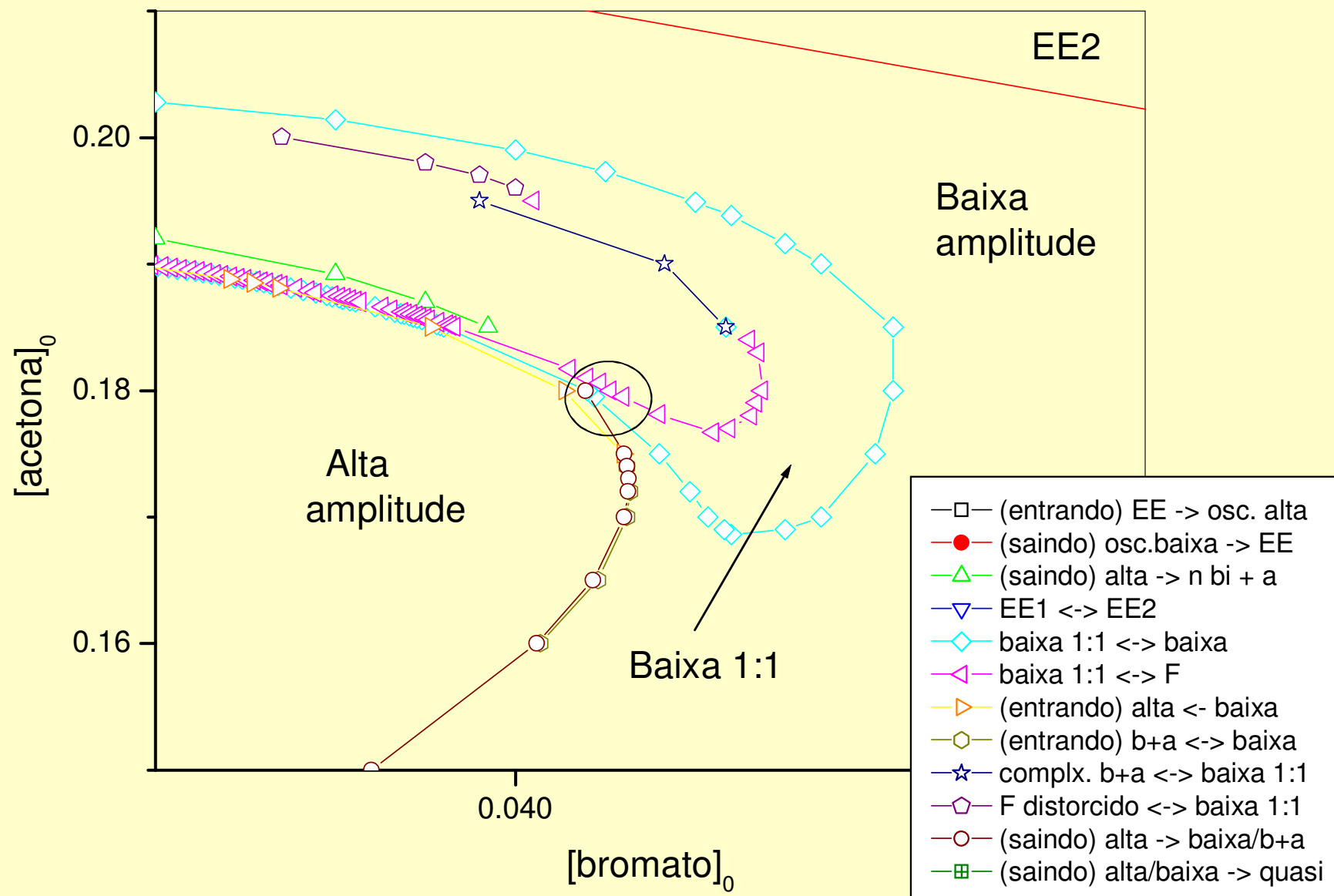
# Oscilação de baixa amplitude período-4 ou padrão F



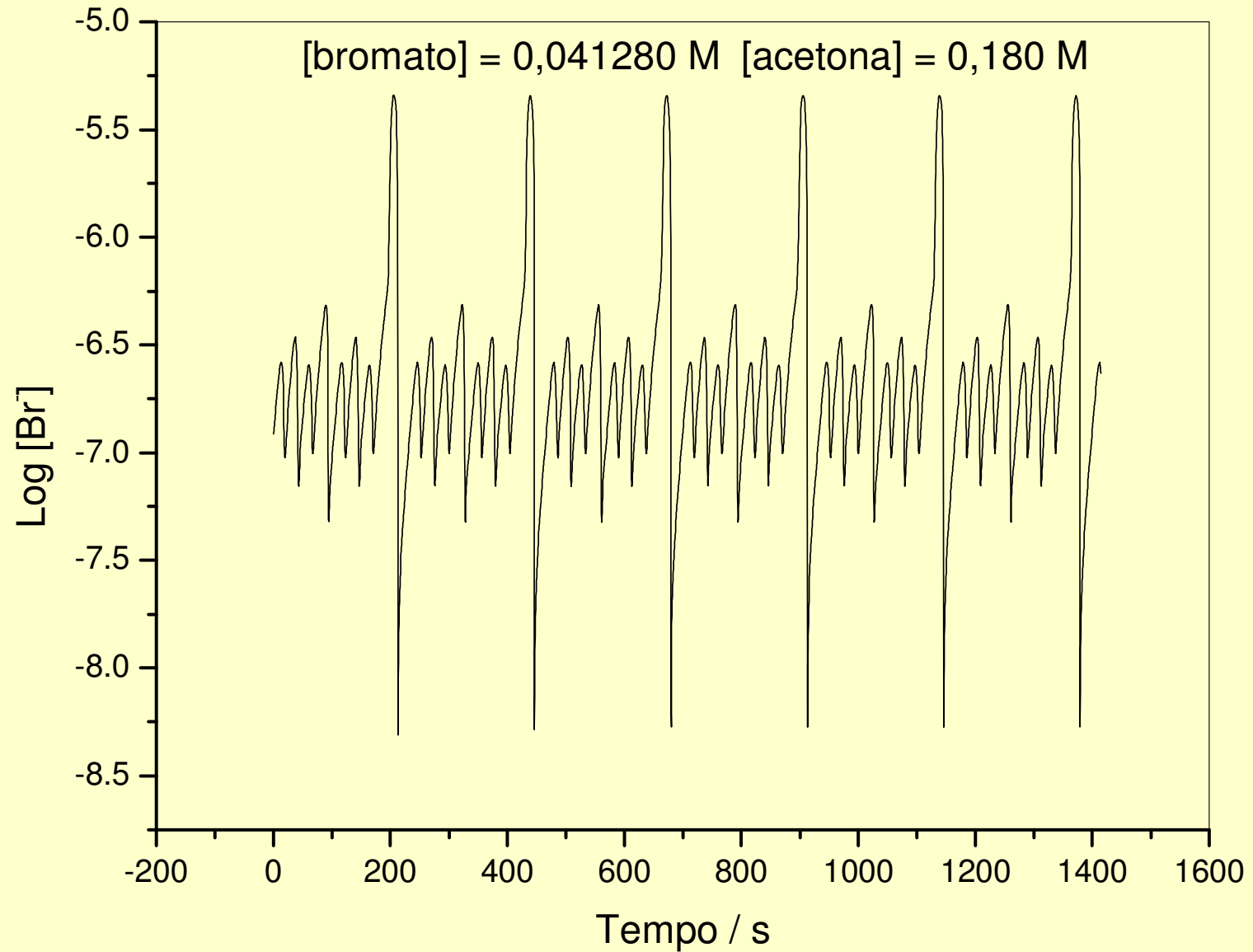
# OSCILAÇÕES MISTAS ESPECIAIS

alta amplitude  
com  
baixa amplitude (período-4)

# Diagrama de fases Bromato x Acetona



## Oscilação mista com alta e baixa-4 amplitude



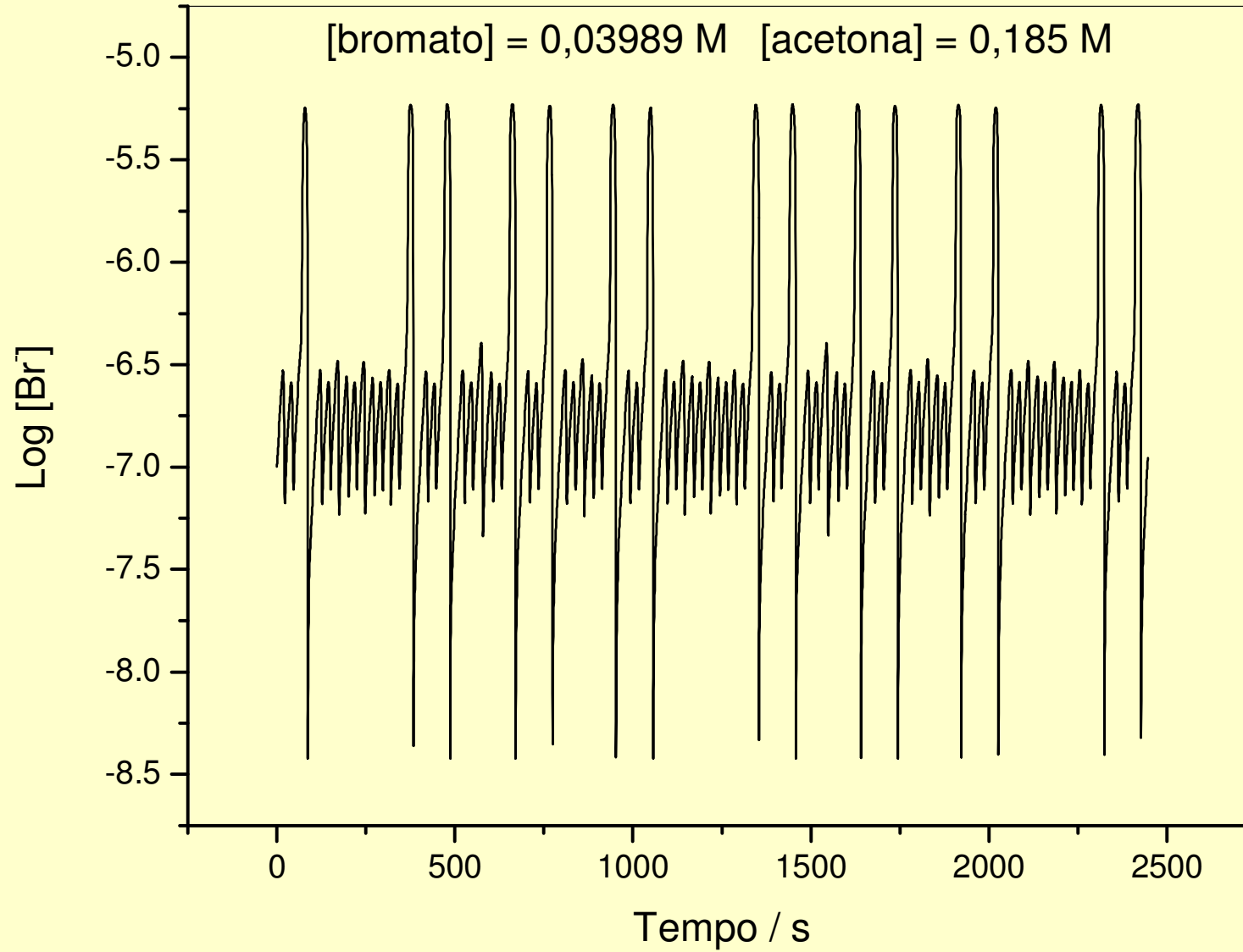


Oscilações complexas  
envolvendo a mistura de 3  
padrões com perfis derivados da  
oscilação período-4 de baixa  
amplitude

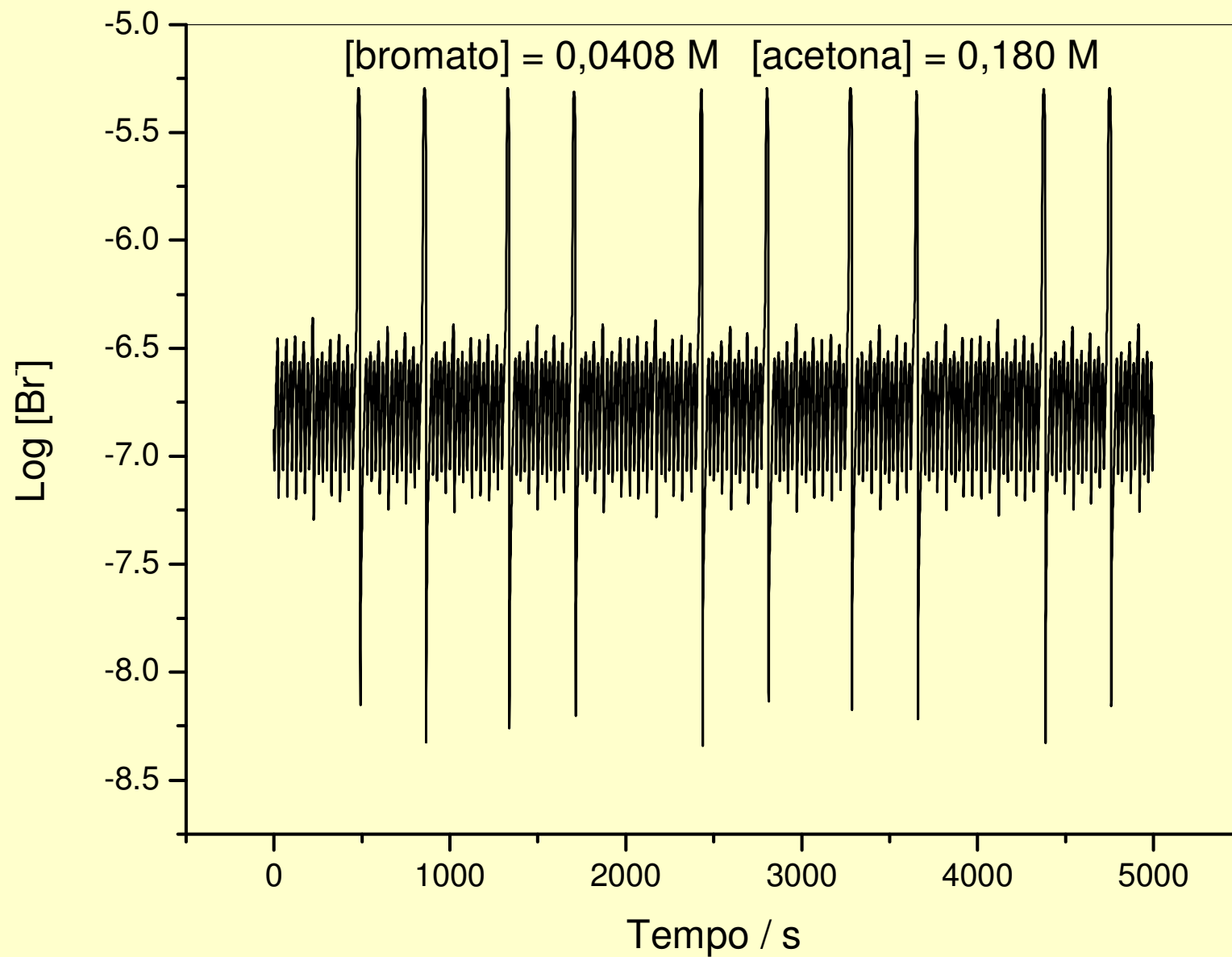
Padrão 10 - 2 - 5 - 2 - 5 - 2

Padrão 27 - 13 - 17 - 13

# Padrão 10 - 2 - 5 - 2 - 5 - 2



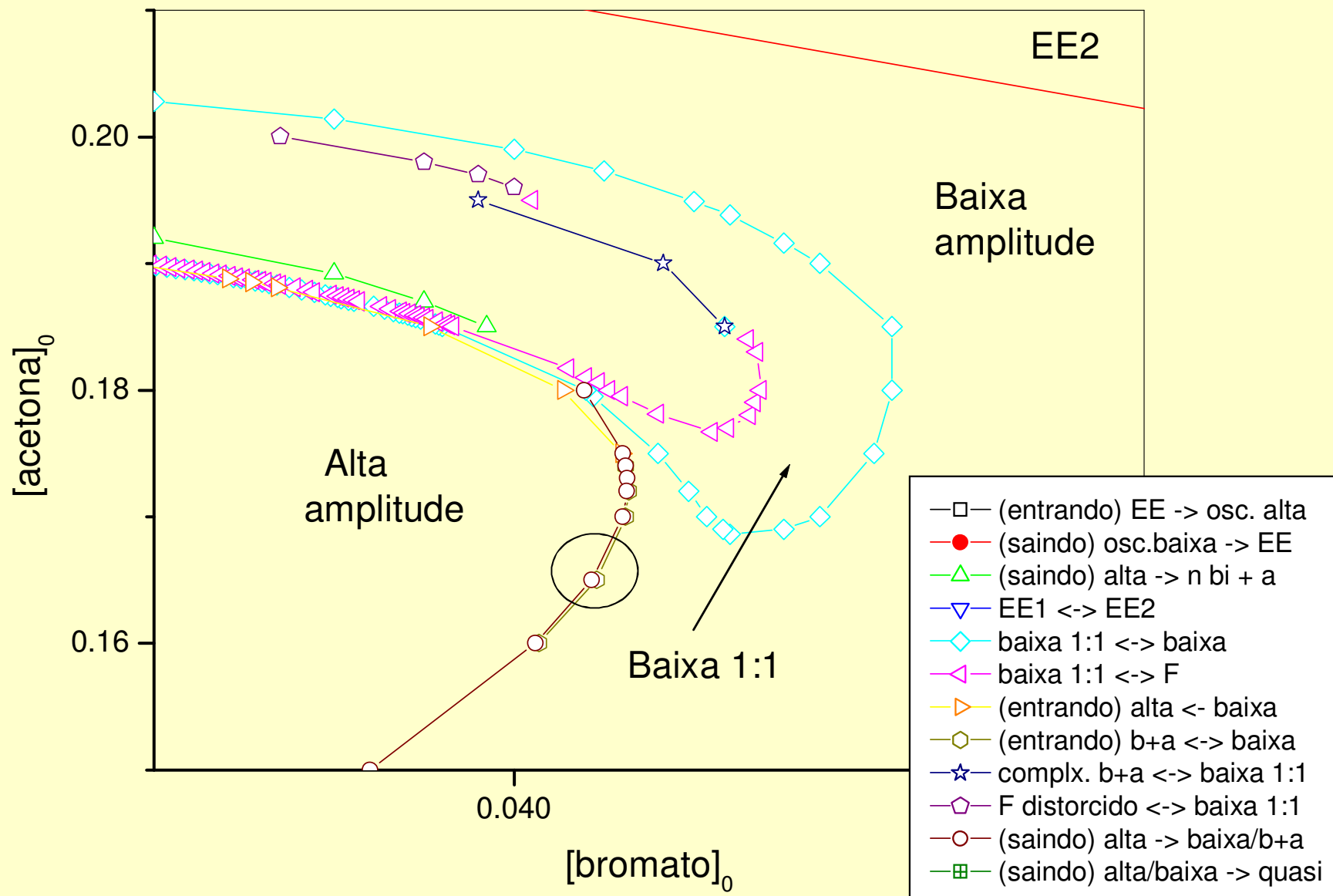
# Padrão 27 - 13 - 17 - 13



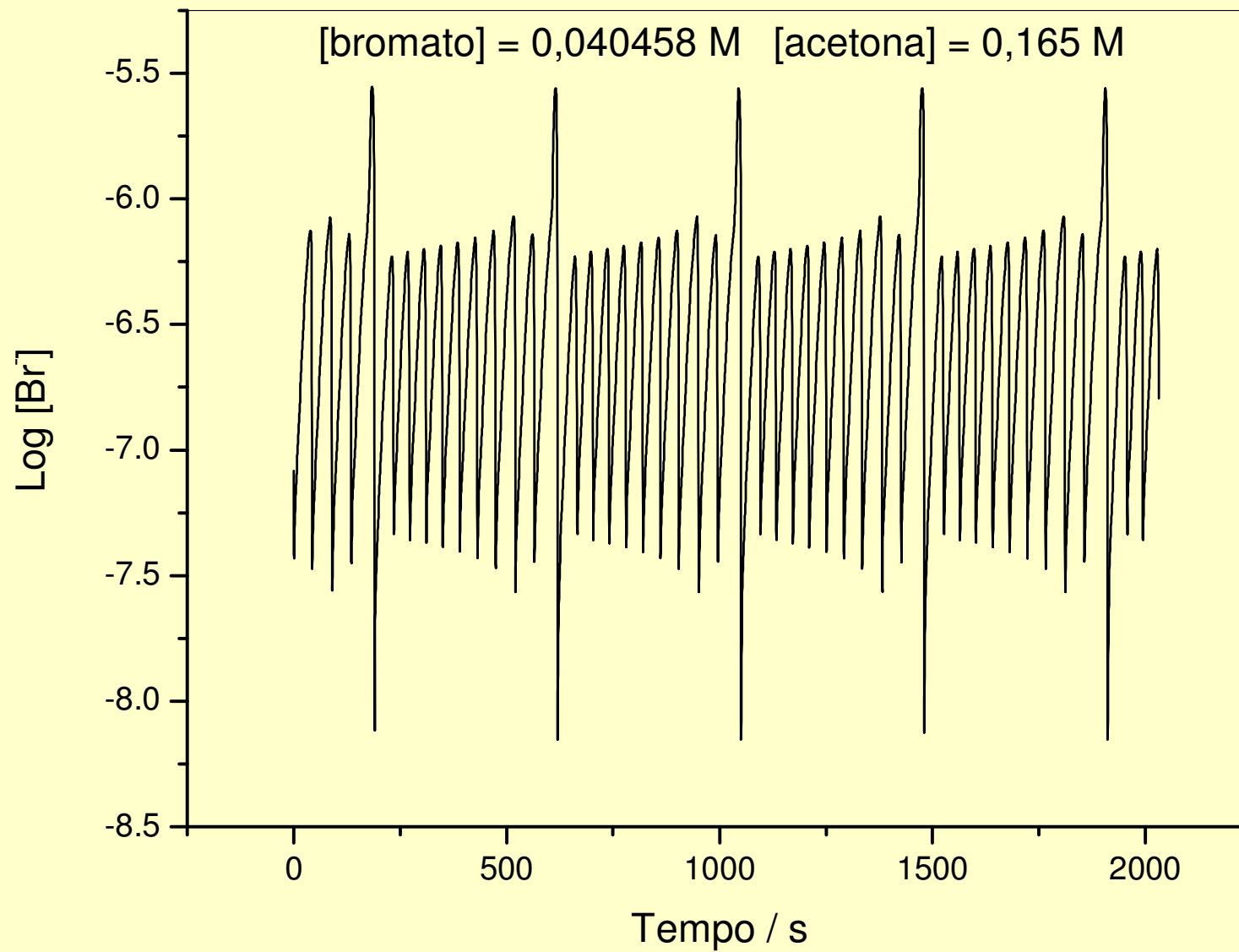
Oscilações mistas  
“tradicionais”  
(mixed-mode oscillations)

$L^s$

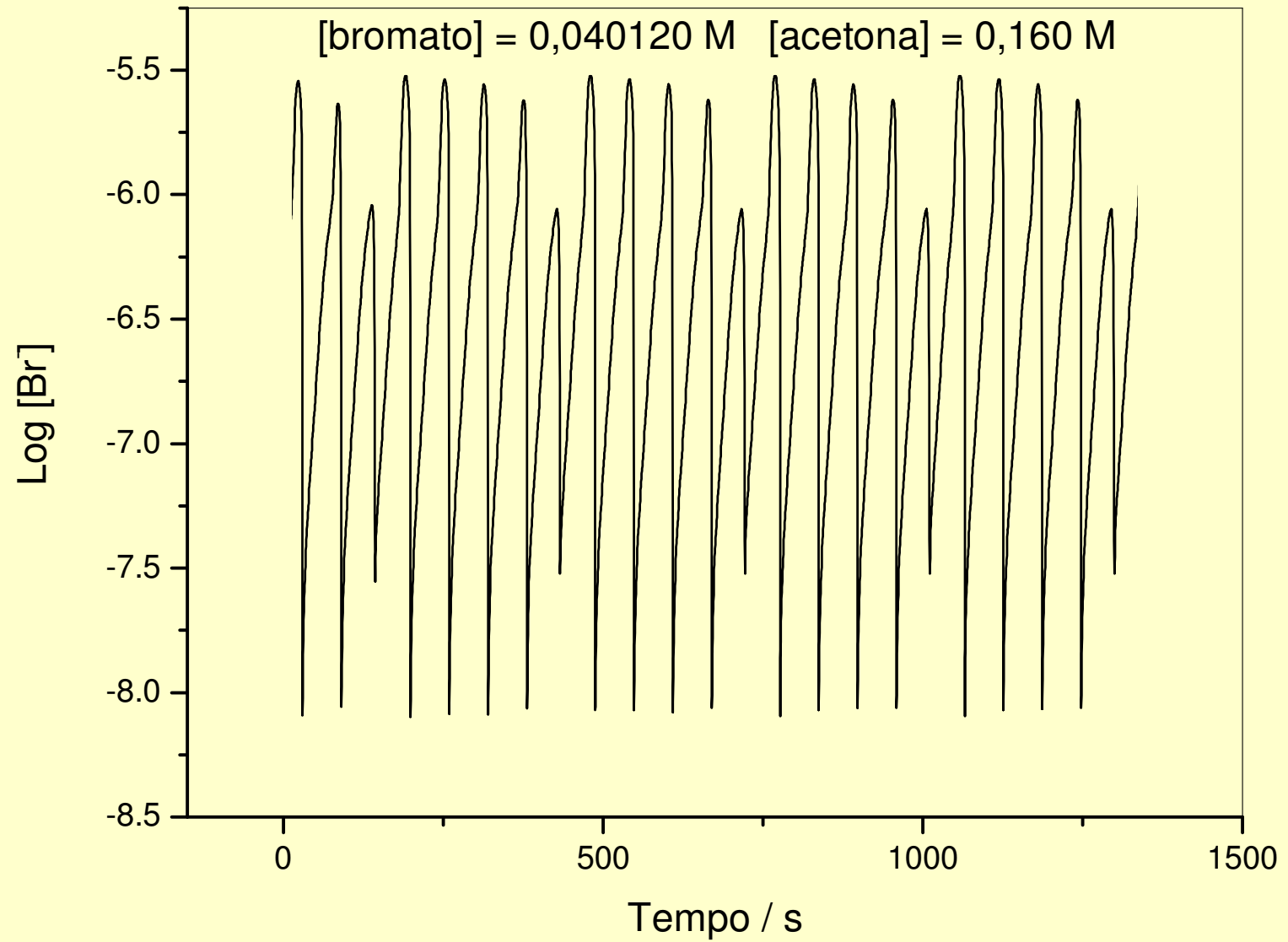
# Diagrama de fases Bromato x Acetona



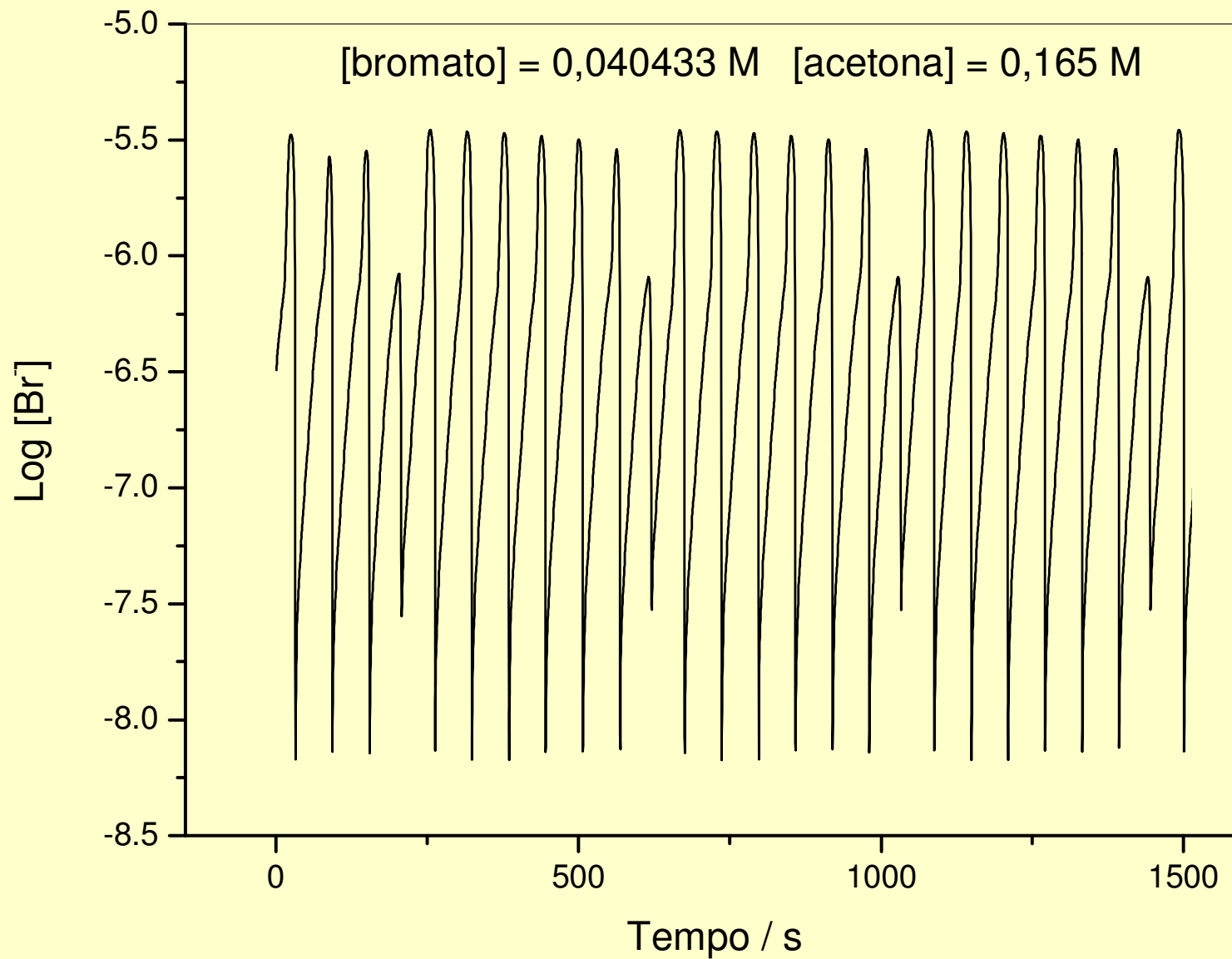
**1<sup>9</sup>**



4<sup>1</sup>



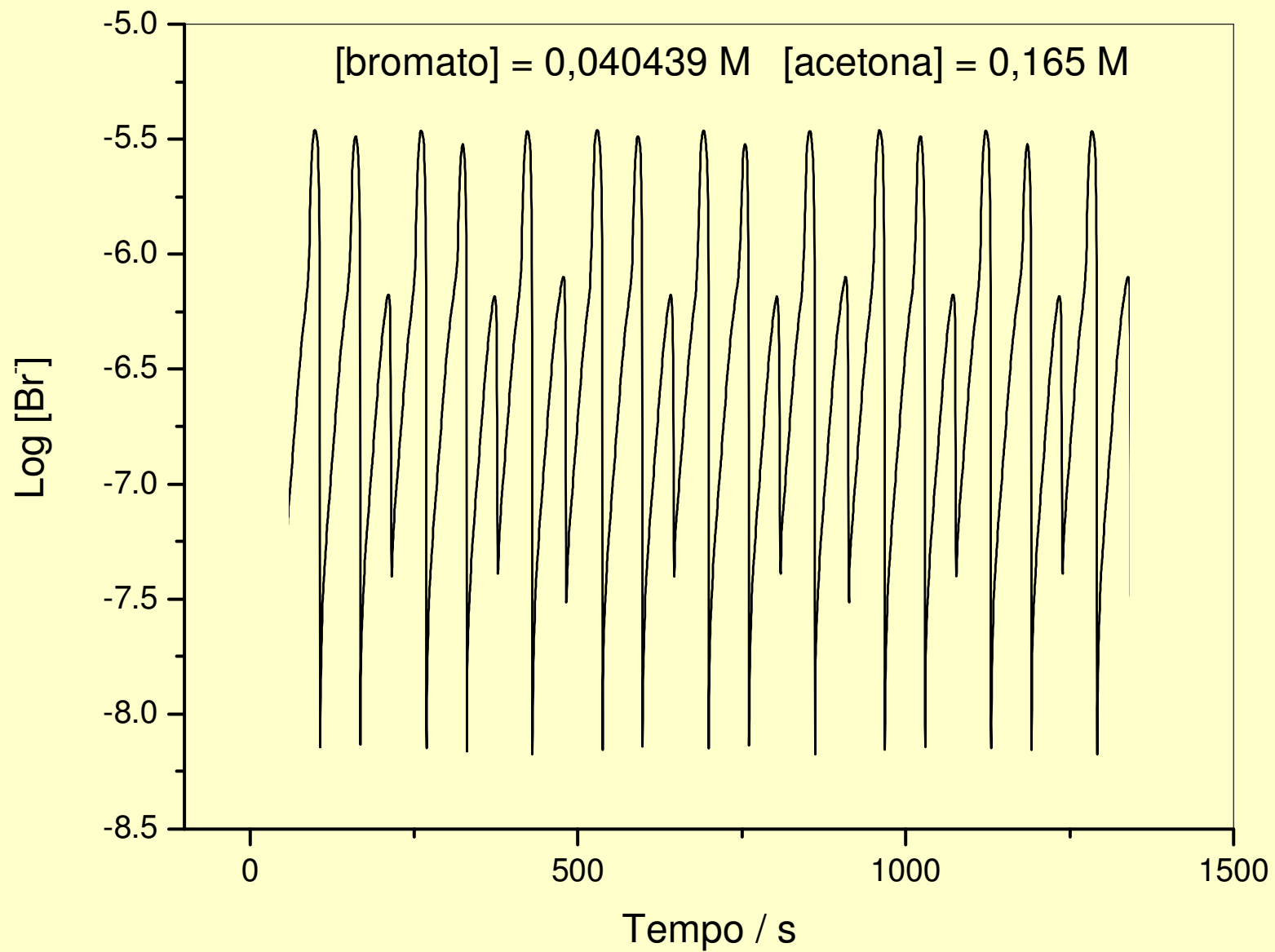
6<sup>1</sup>

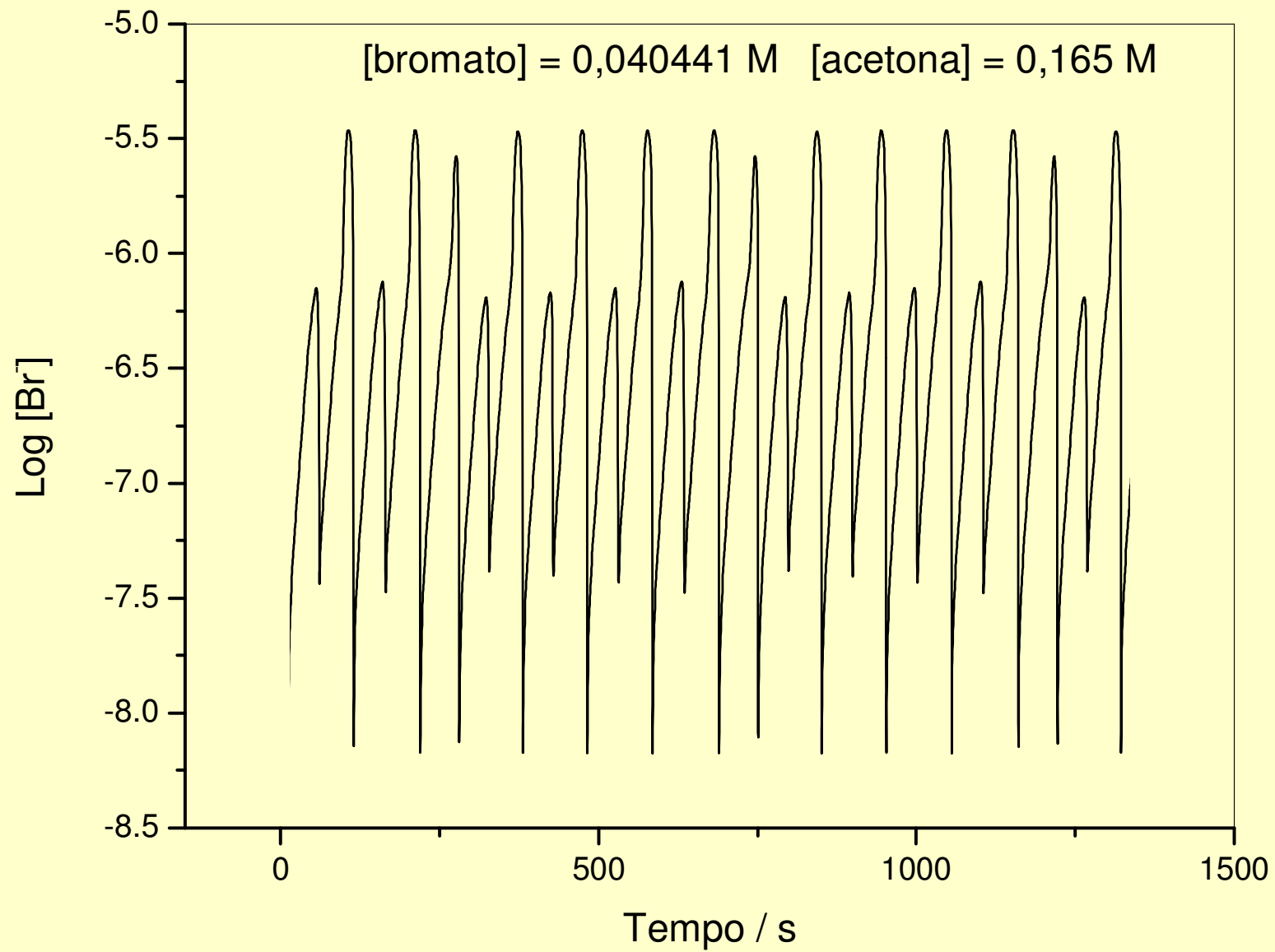
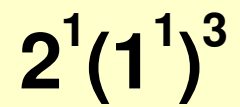




# Combinações de padrões

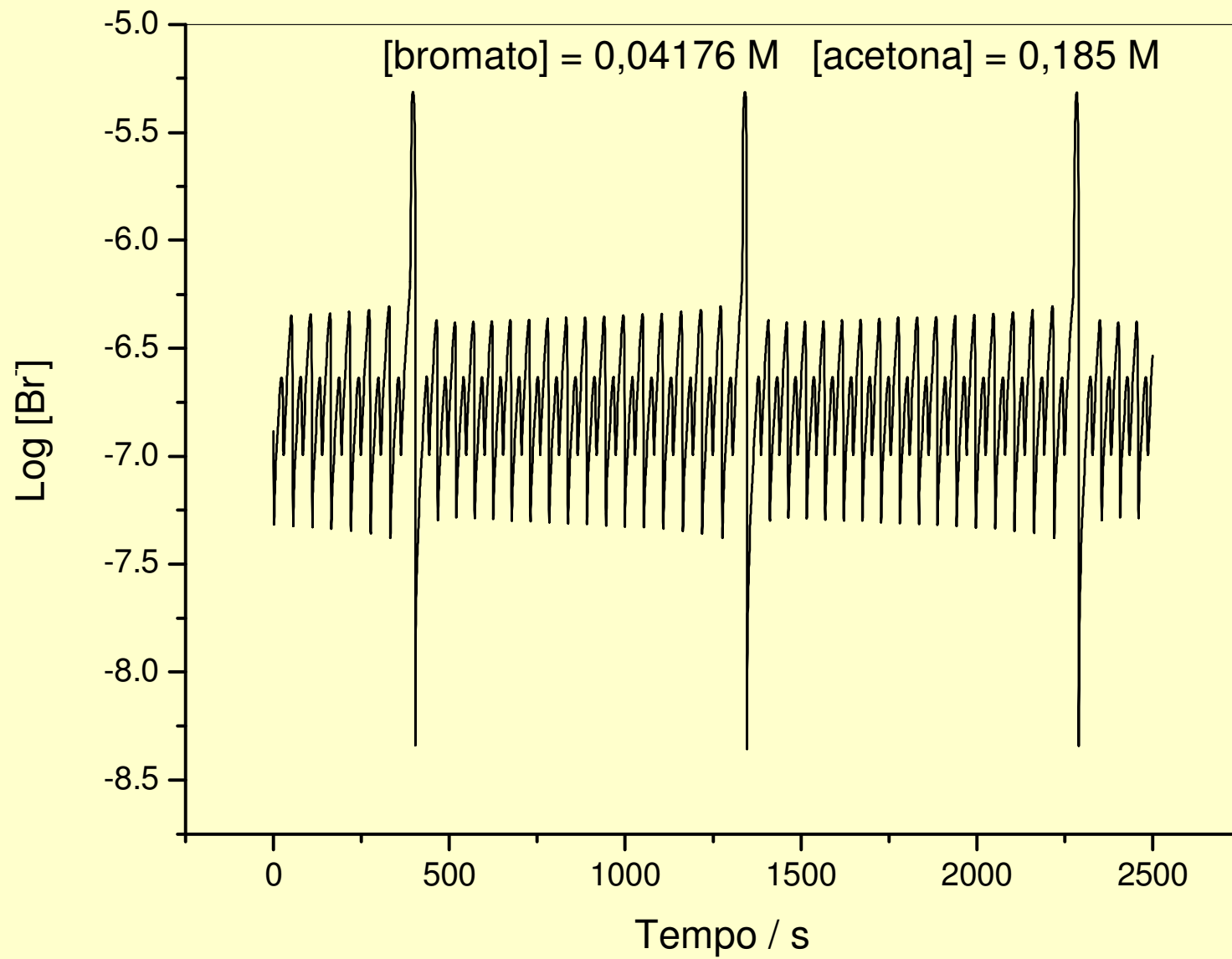
$$1^1(2^1)^2$$





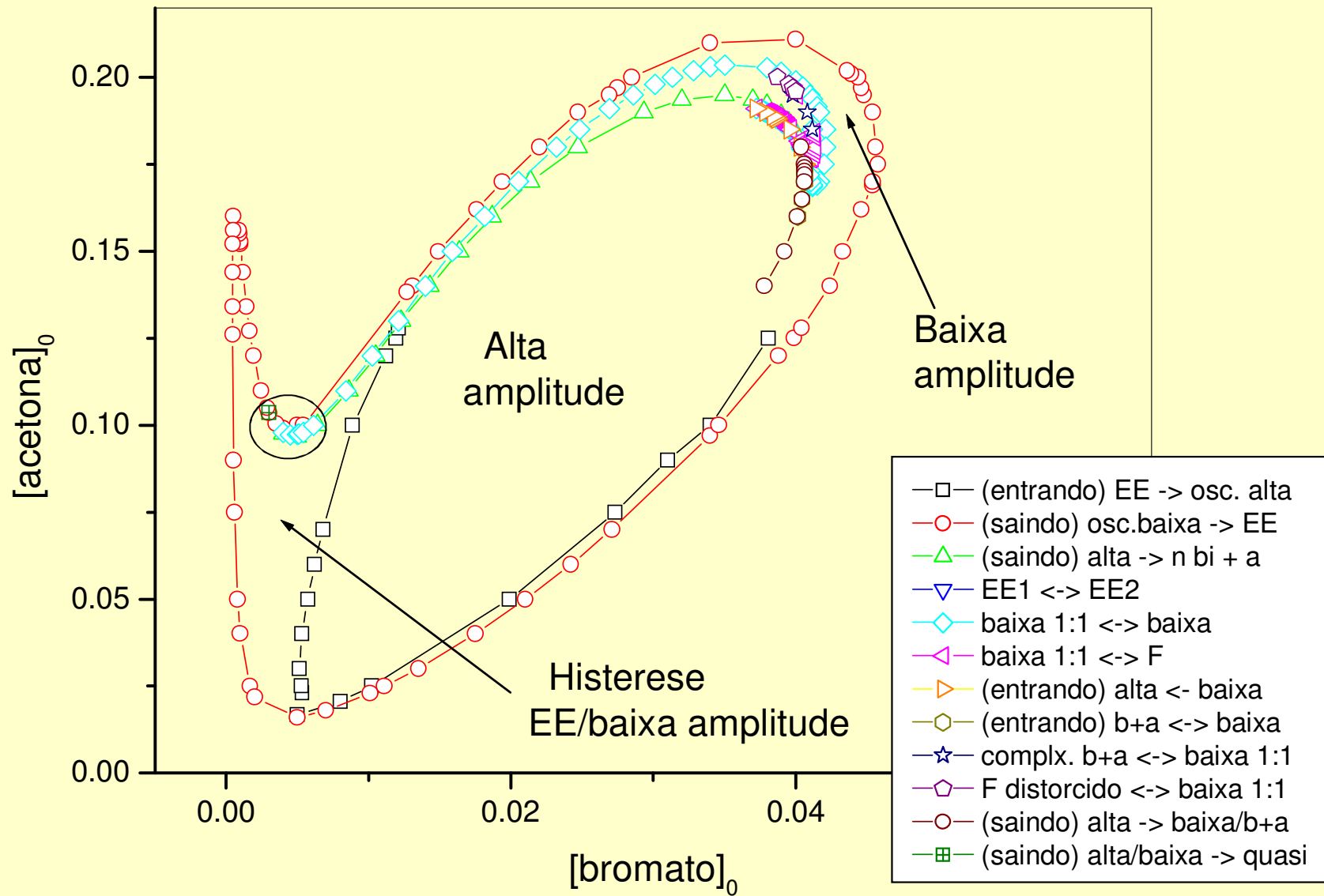
Padrão regular  
de excepcional complexidade  
apresentando  
16  
repetições  
entre oscilações de alta  
amplitude

**1(1<sup>1</sup>)16**

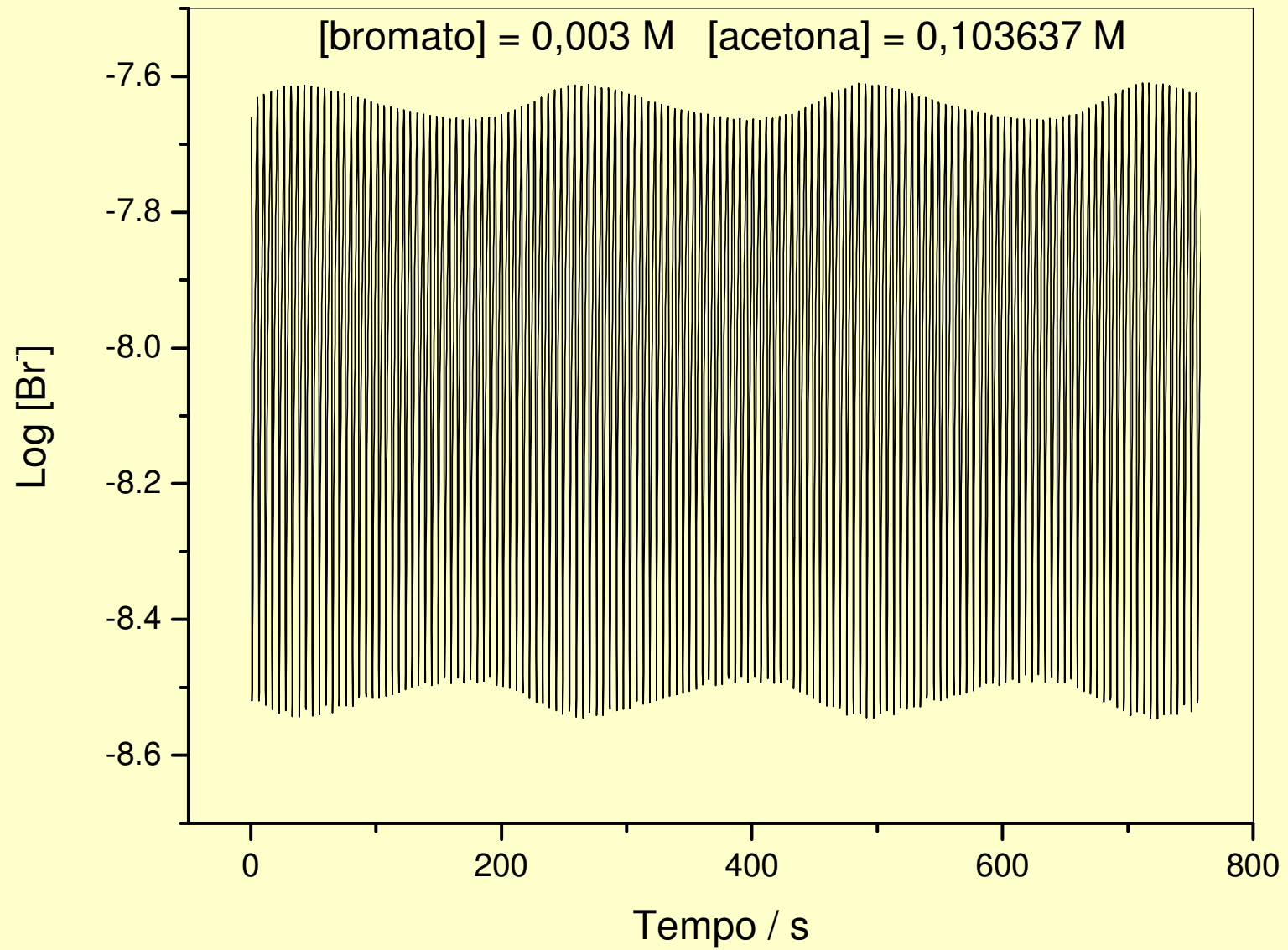


# QUASIPERIODICIDADE

## Diagrama de fases Bromato x Acetona

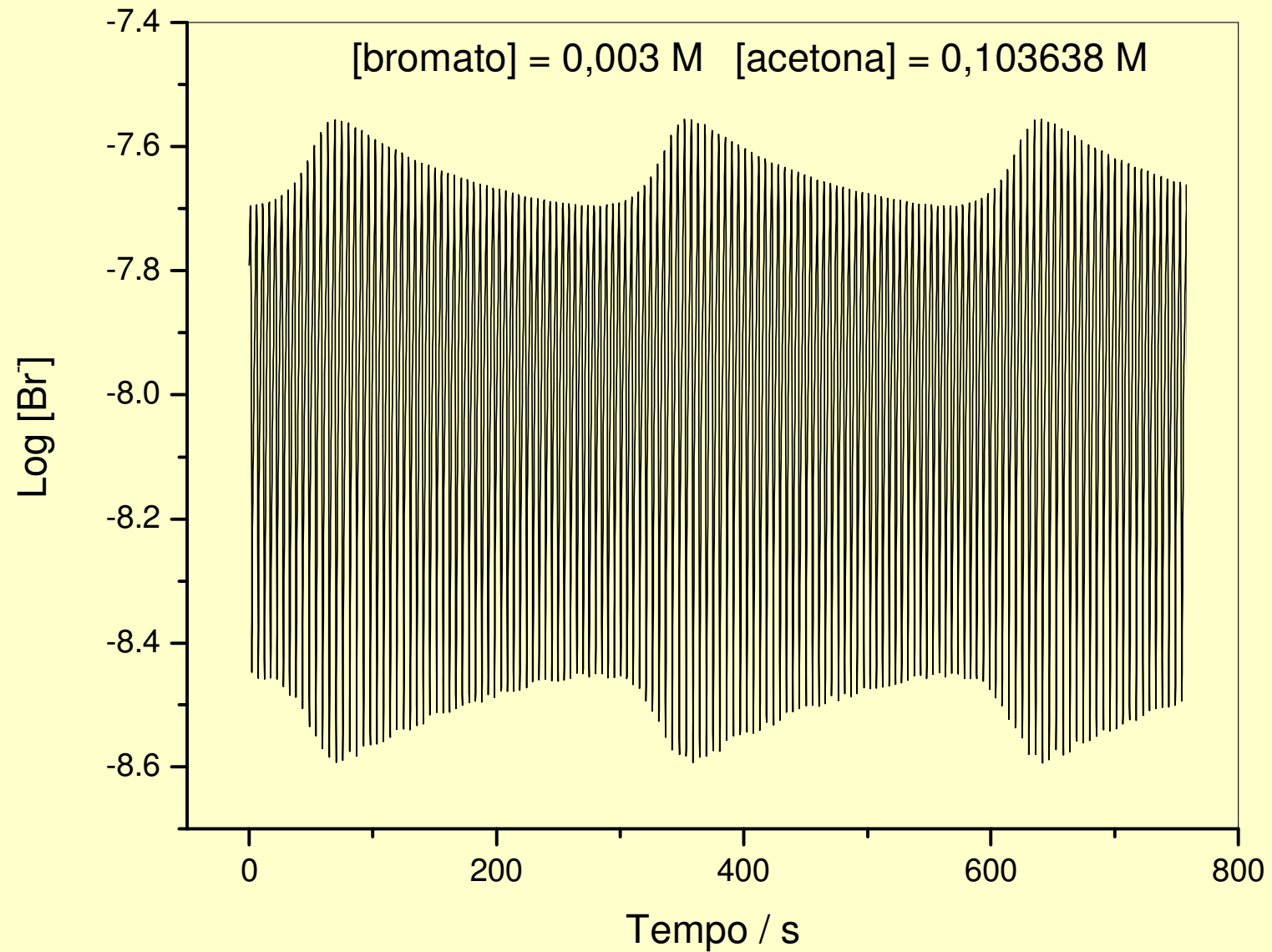


# QUASIPERIODICIDADE





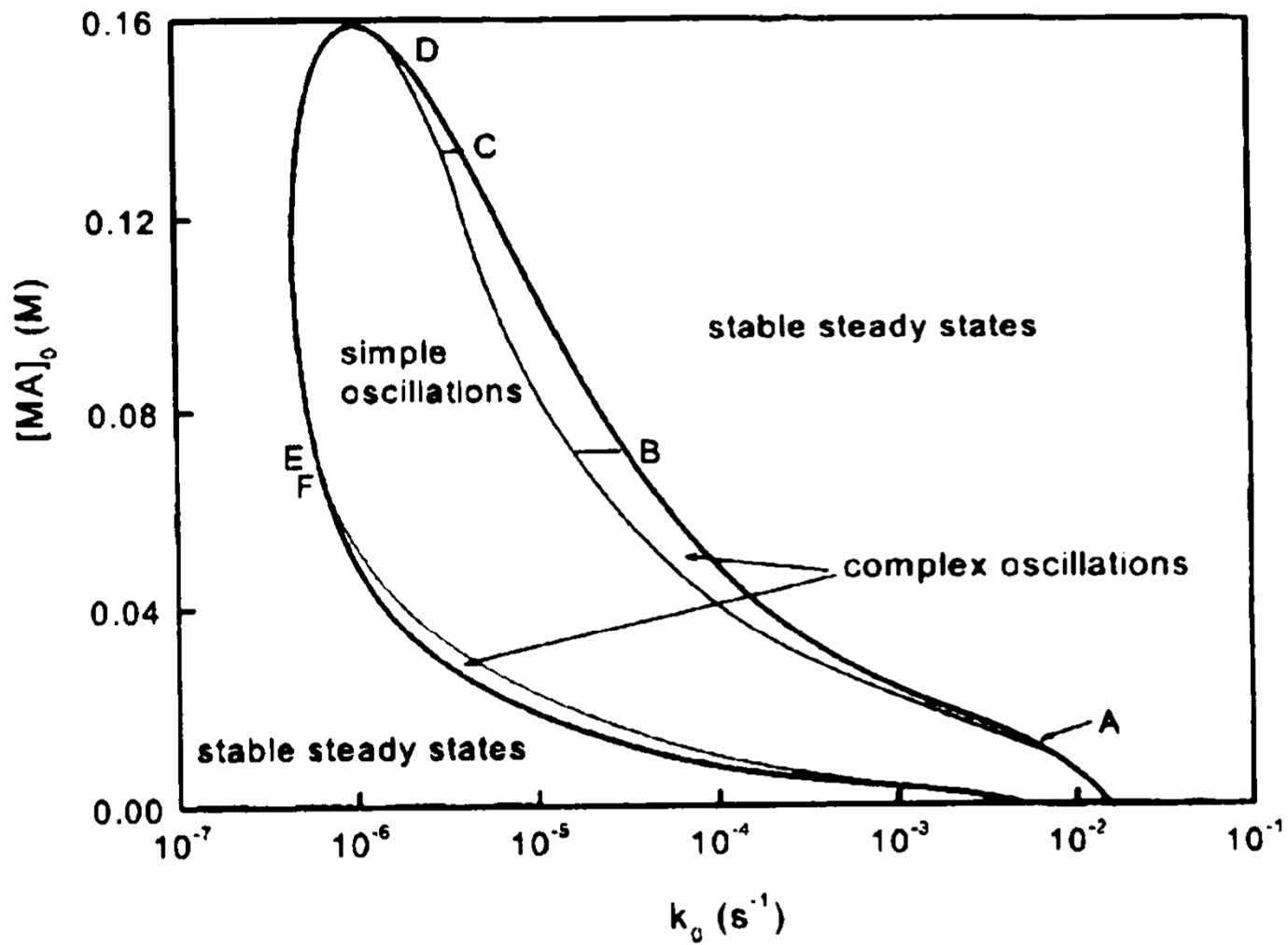
# QUASIPERIODICIDADE



# Modelagem da reação oscilante de Briggs-Rauscher

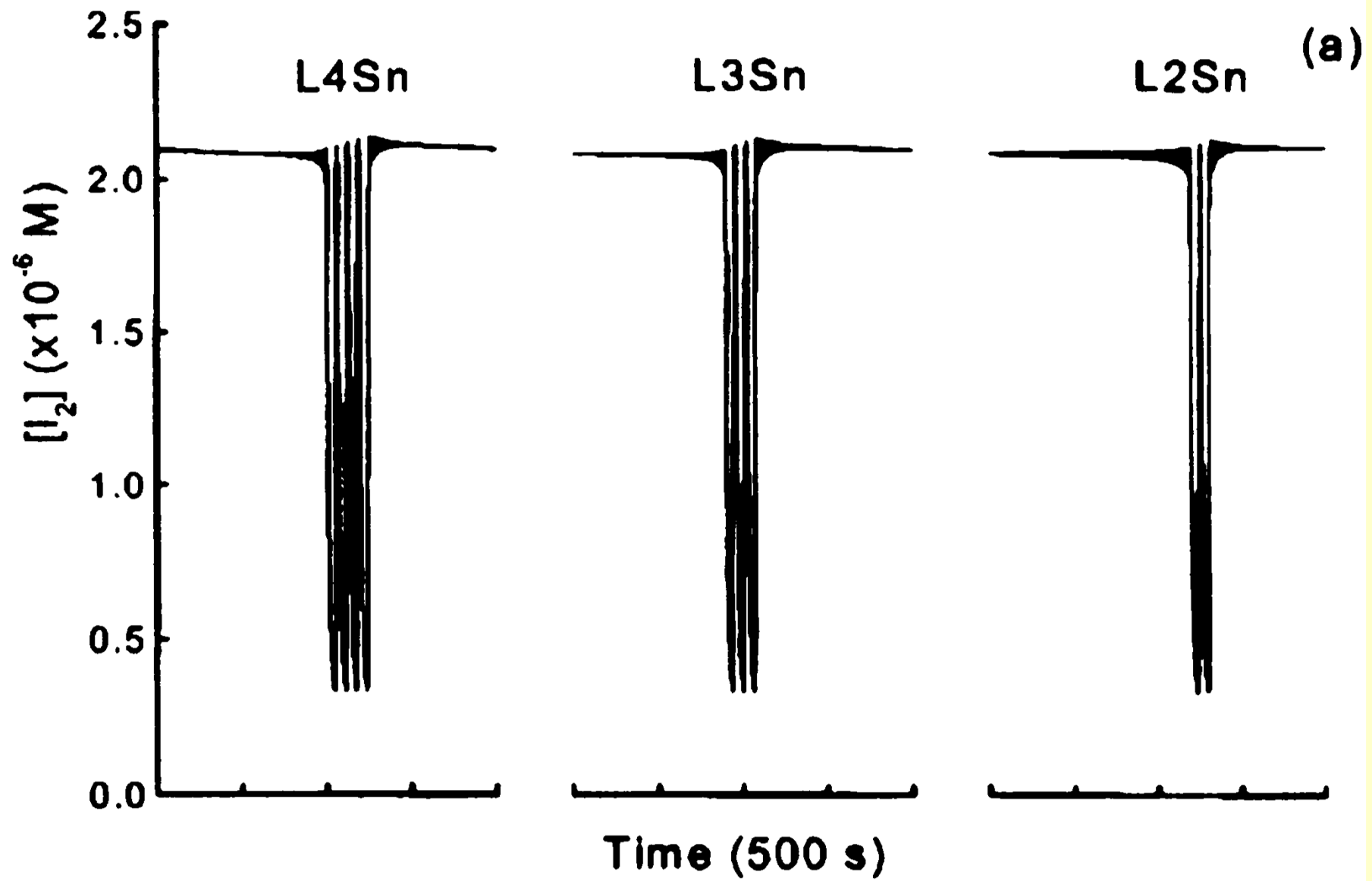
Kim, Shin, Lee

*J. Chem. Phys.* **2004**, *121*(6), 2664

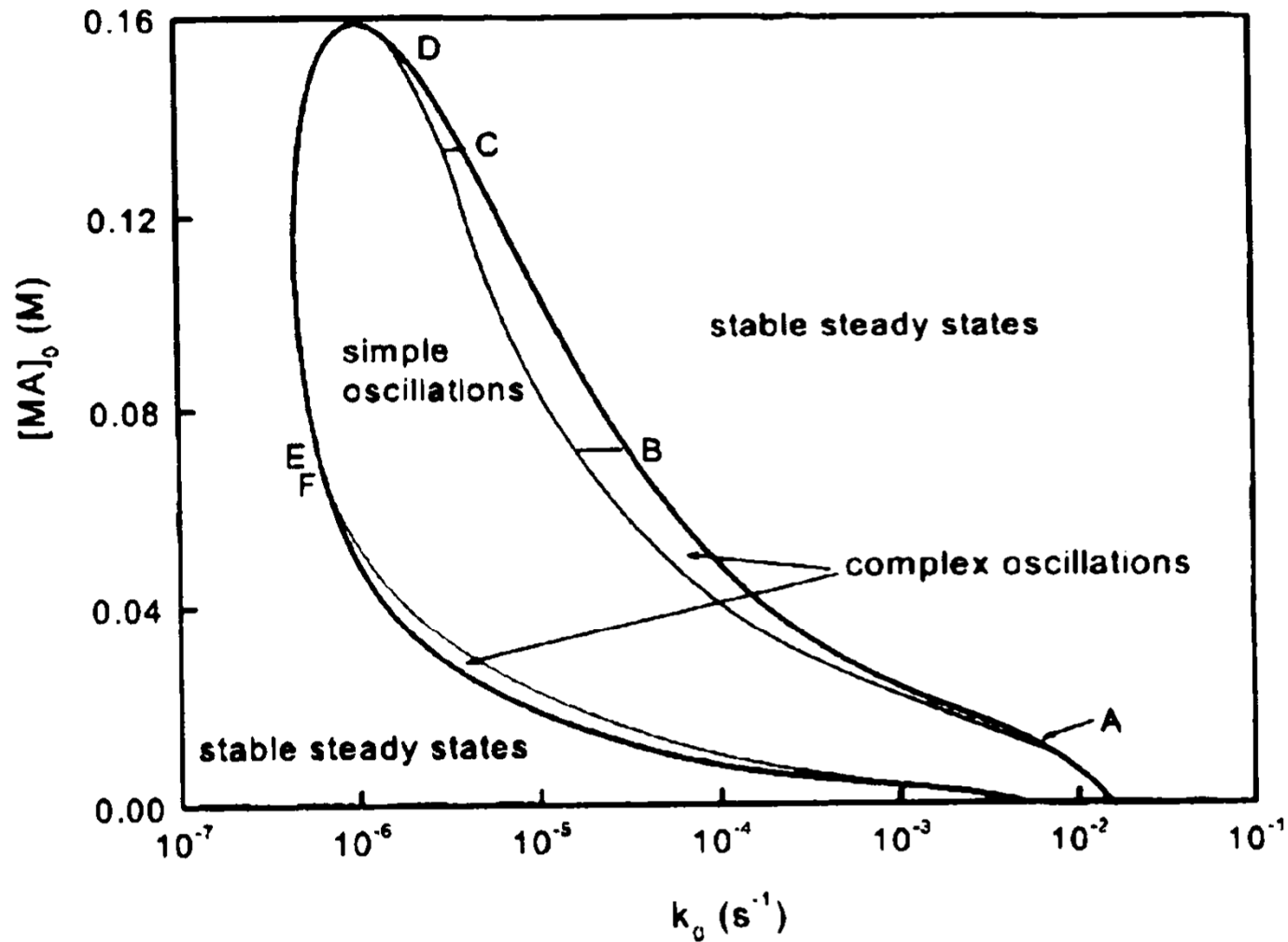


“Burst oscillations”

ao longo da linha B

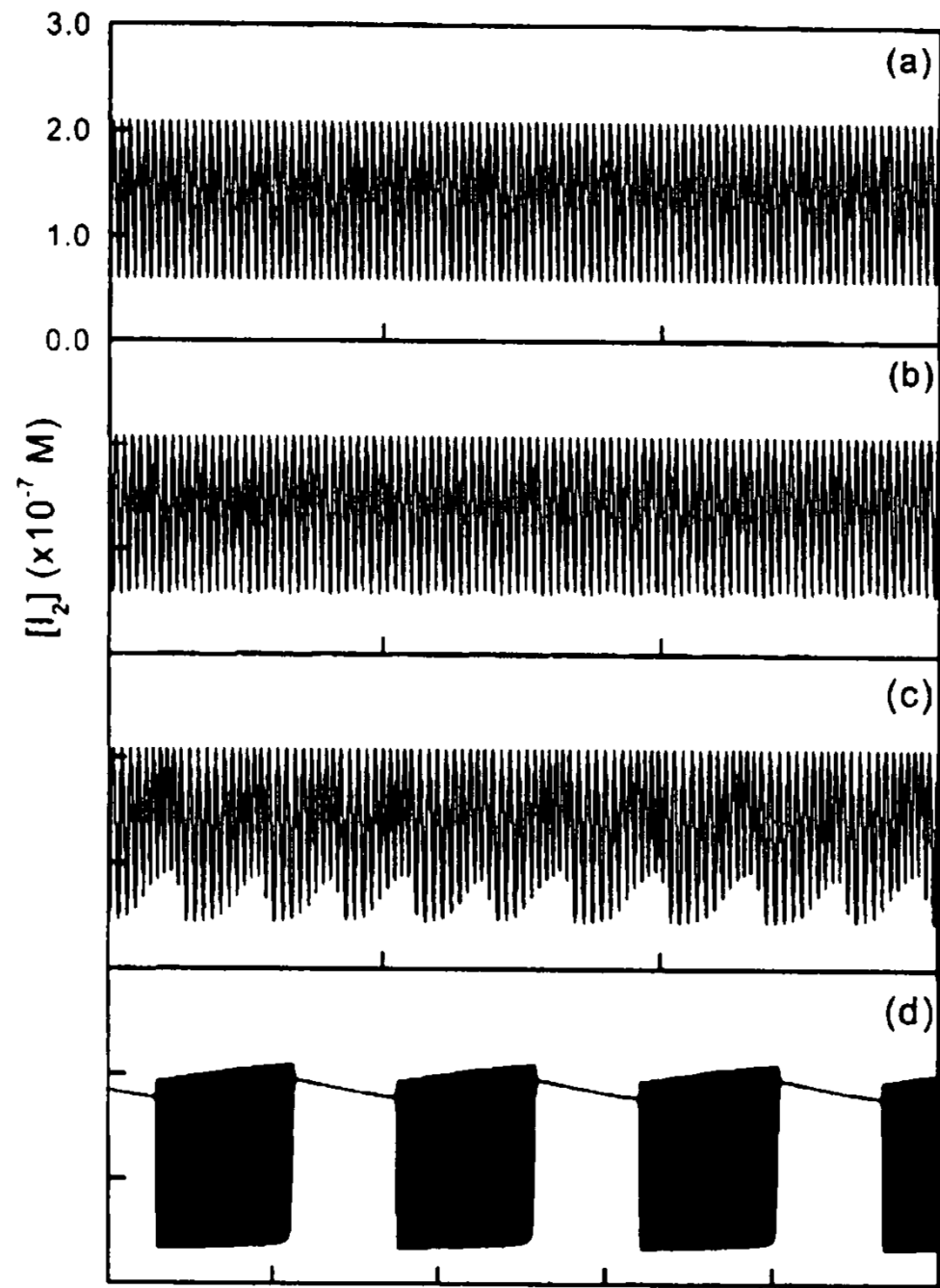


# MMO ao longo da linha C



Oscilações regulares →  
quasiperiodicidade →  
“burst oscillations”

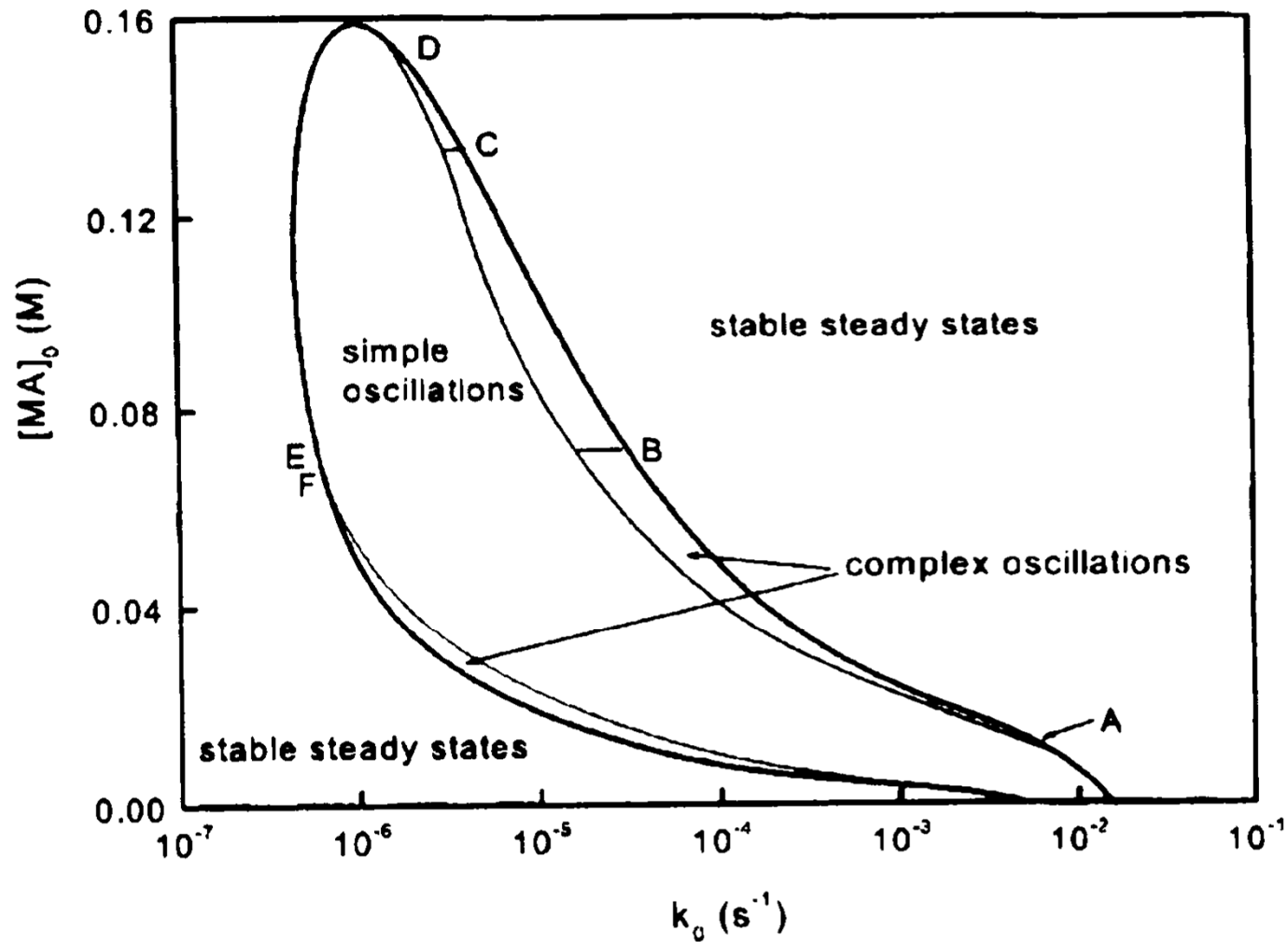
com o aumento de  $k_0$   
ao longo da linha C



Time :  $10^3$  s for (a), (b), (c) ;  $10^4$  s for (d)

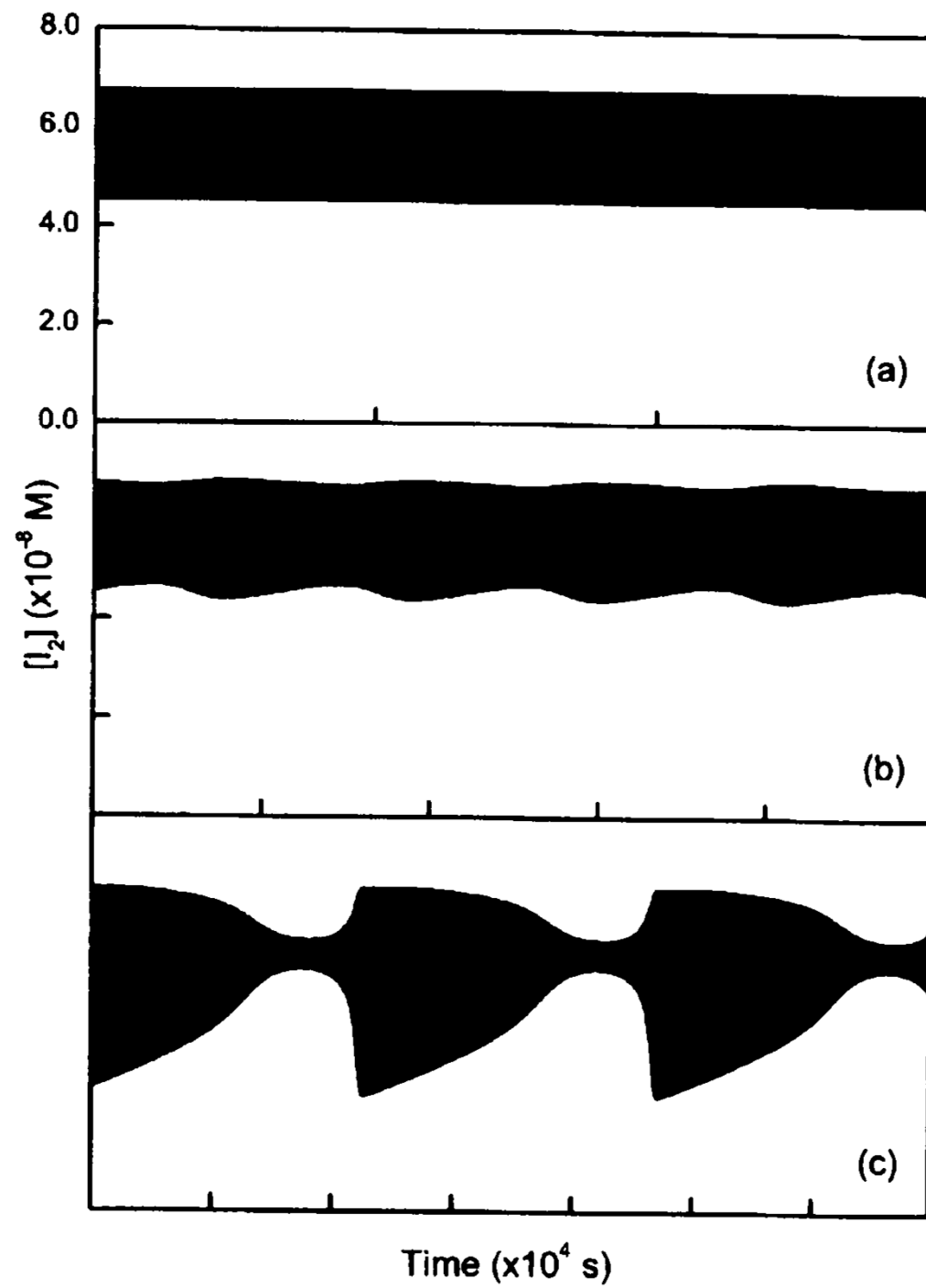


# MMO ao longo da linha D

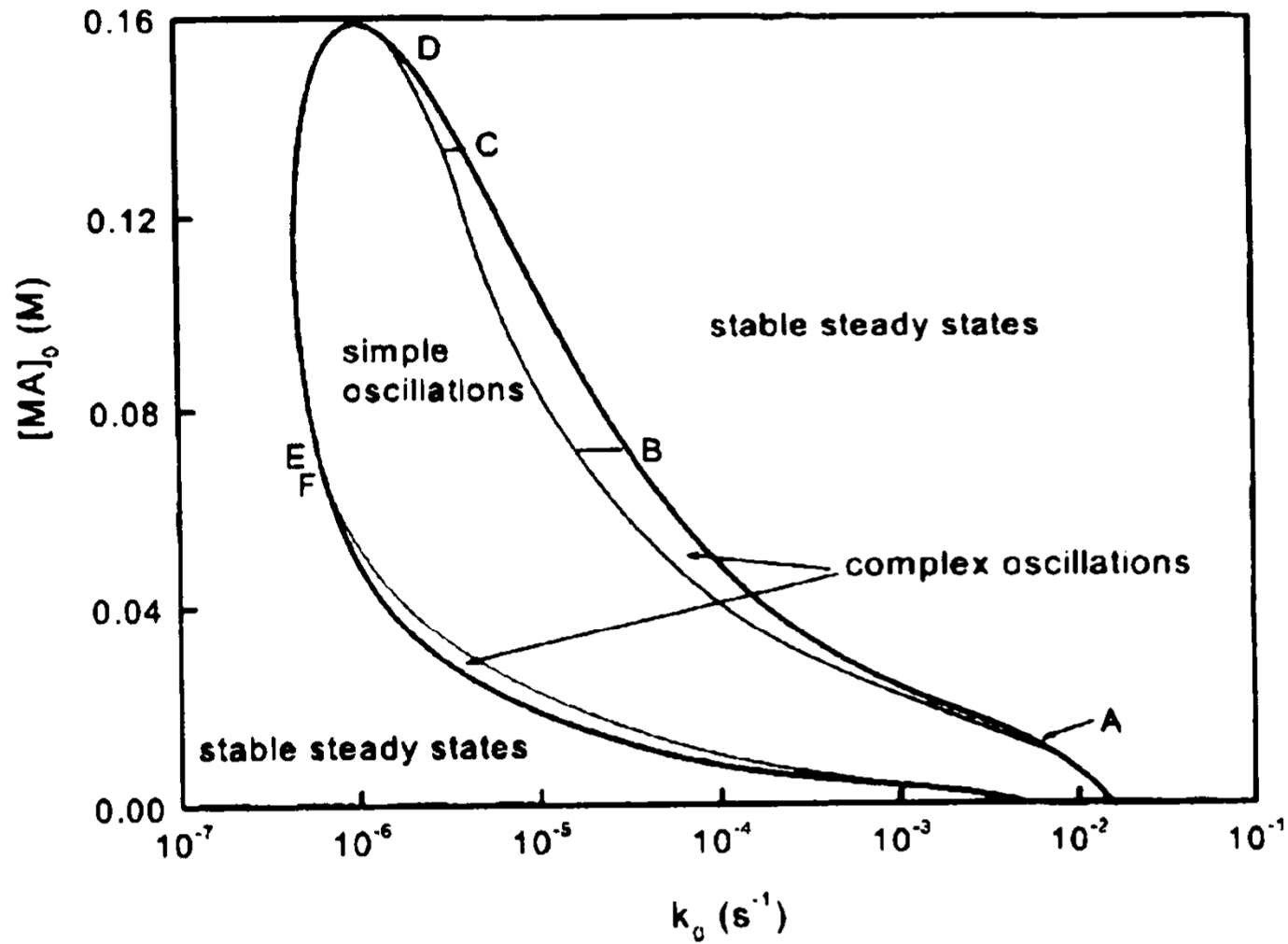


Oscilações regulares →  
quasiperiodicidade →  
“like-fish burst oscillations”

com o aumento de  $k_0$   
ao longo da linha D

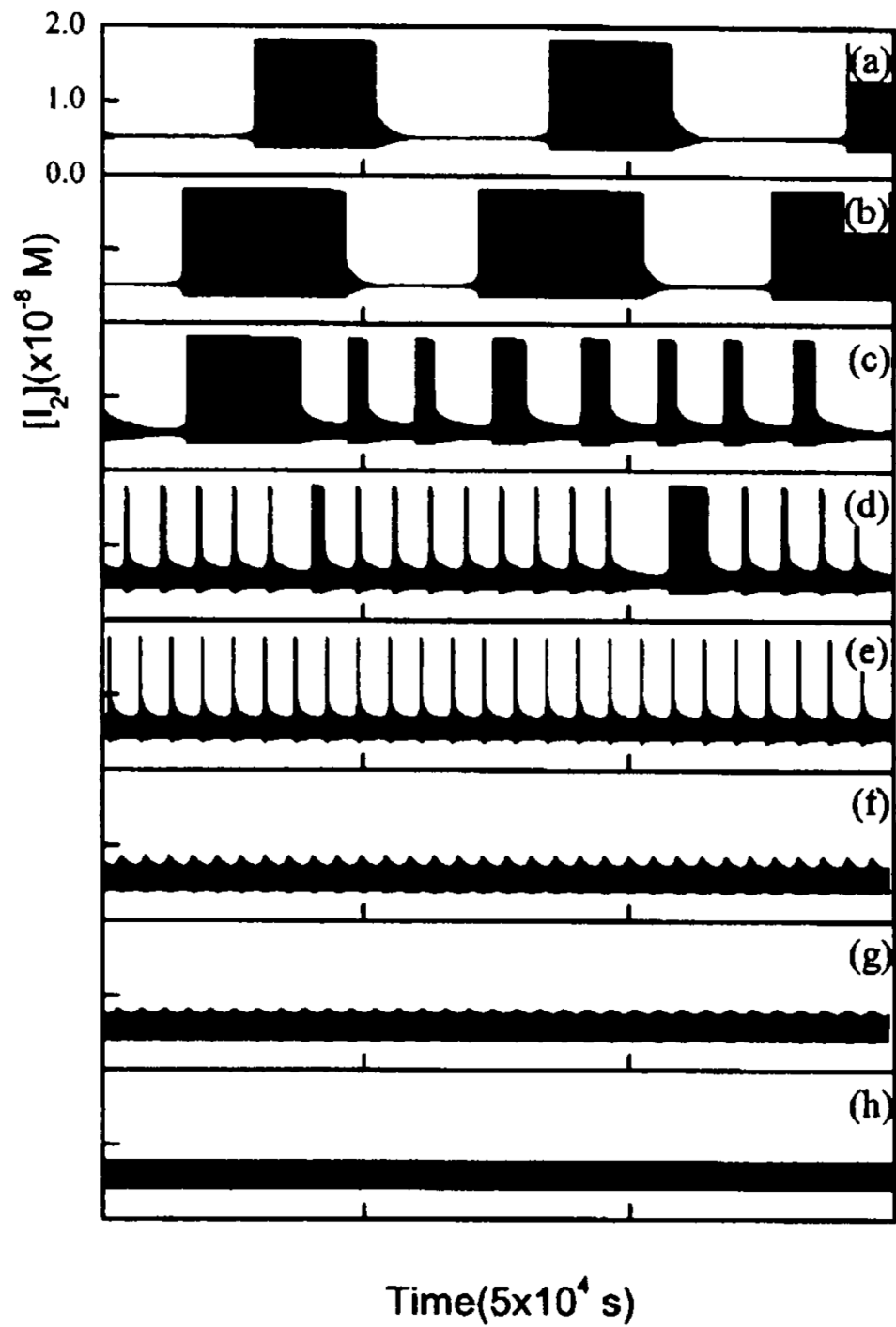


# MMO ao longo da linha E

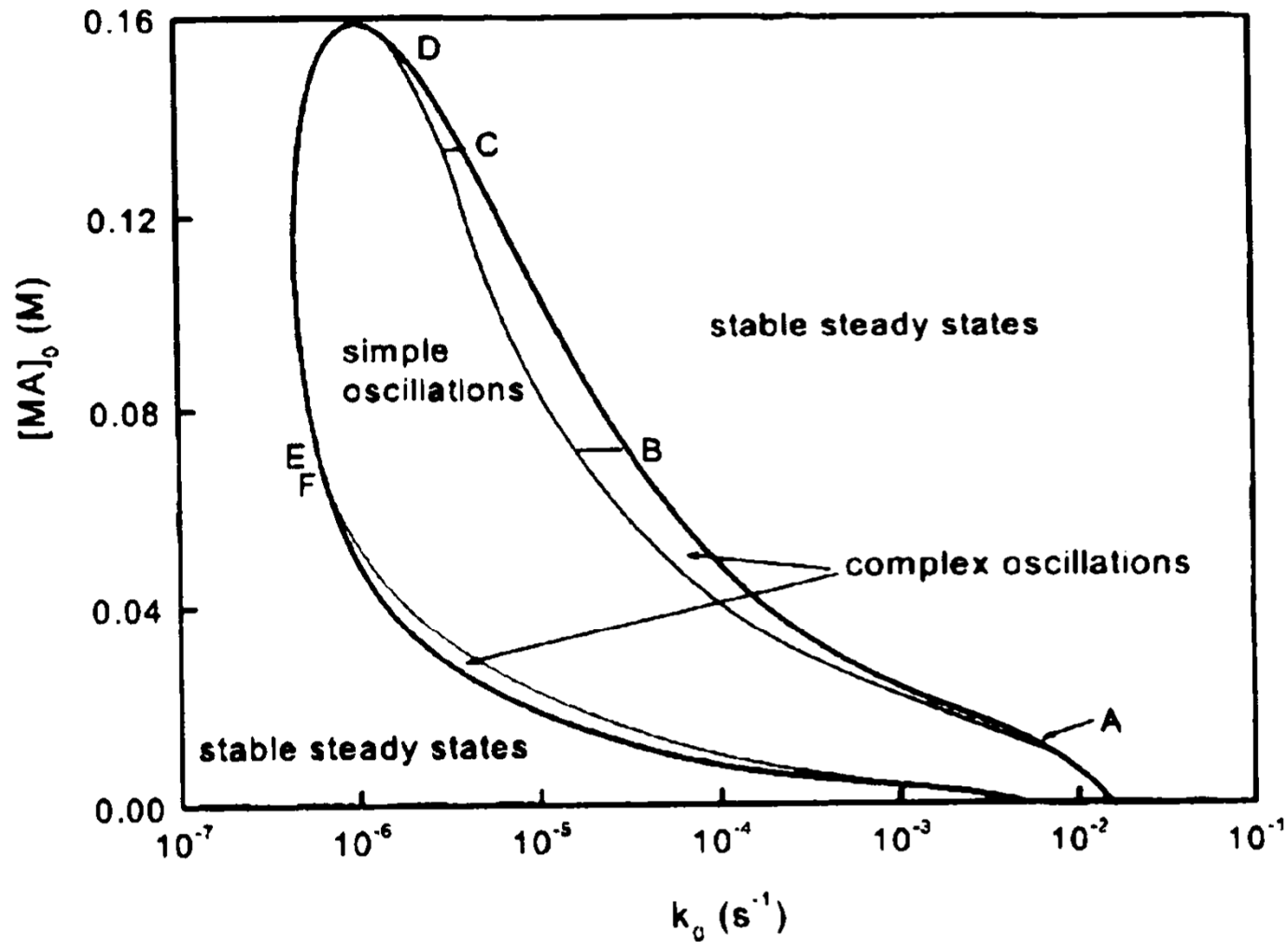


“burst oscillations”  $\rightarrow$   
“burst oscillations” caóticas  $\rightarrow$   
quasiperiodicidade período-2  $\rightarrow$   
quasiperiodicidade (baixa ampl.)  $\rightarrow$   
baixa amplitude regular

com o aumento de  $k_0$   
ao longo da linha D



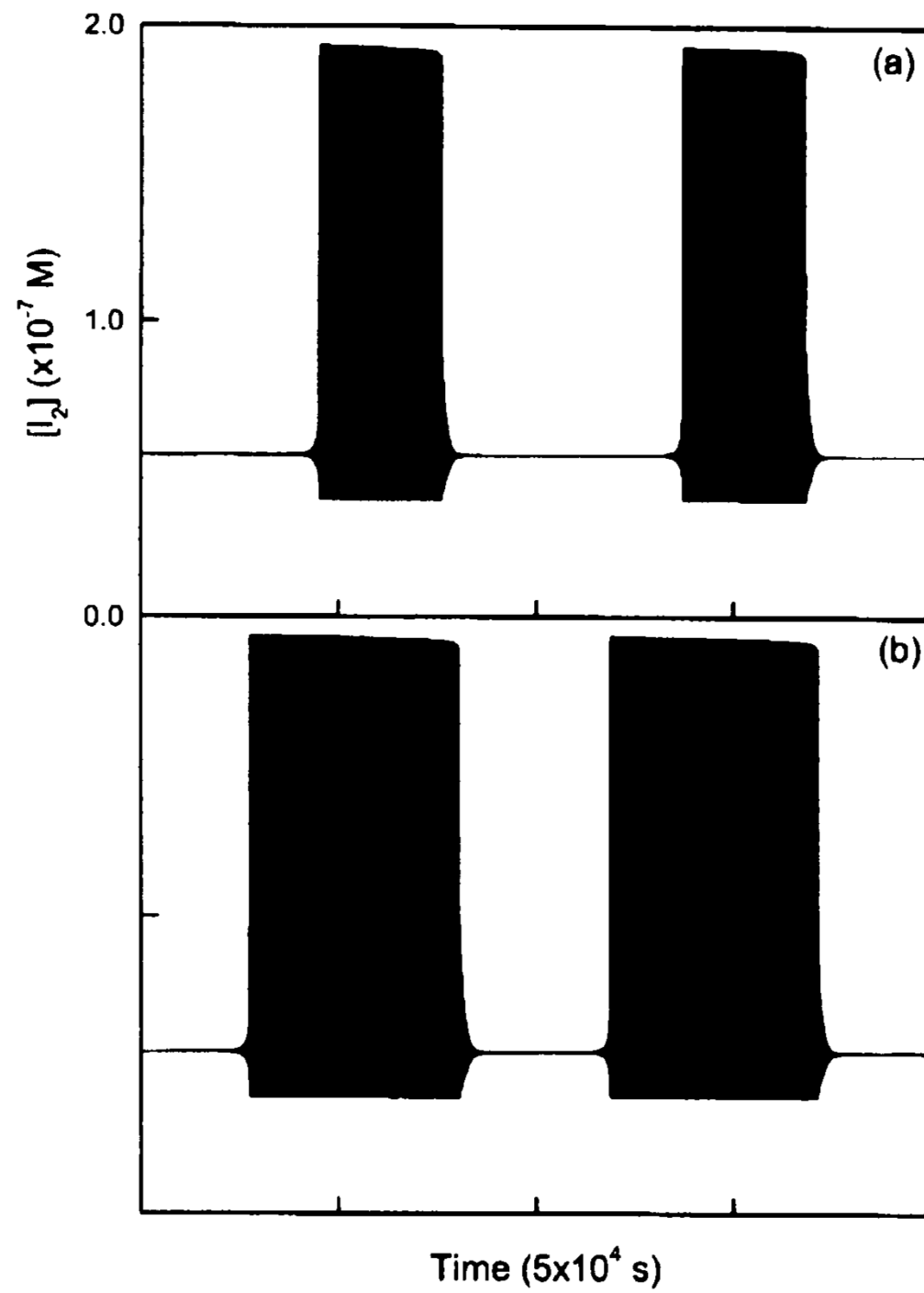
# MMO ao longo da linha F



“burst oscillations”  
ao longo da linha D

O aumento de  $k_0$   
alarga as “burst oscillations” e reduz  
a duração do “estado estacionário”.





voltar