

as the phase III–phase I boundary is approached. Subsequent crossing into phase I is accompanied by transition to full rotational behaviour of the pairs, an almost complete lack of coherence, and destruction of the essential self-consistent and coherent collective structure implicit in a charge density wave.

To compare the measured change in the vibron wavenumber  $\Delta\nu$  with that expected from the transition to a spontaneously polarized state, we have used the frozen-phonon method<sup>16</sup>, taking the structure  $Cmc2_1$  (Fig. 1A) which has the lowest energy of the structures considered here. At  $r_s = 1.47$  (9.6-fold compression), we find  $\Delta\nu = 170 \text{ cm}^{-1}$  for hydrogen, and  $\Delta\nu = 120 \text{ cm}^{-1}$  for deuterium. To determine the effect of librational motion we appeal to the experimentally determined result that  $\Delta\nu$  is directly proportional to the molecular polarization, or dipole moment<sup>12</sup>. We replace  $\mathbf{d}$  with  $\langle \mathbf{d} \rangle$ , estimating the librational amplitude using the calculation by Mazin and Cohen<sup>17</sup>. For an anisotropically polarizable linear molecule, with polarizability tensor components (in a frame in which the molecular axis lies along  $z$ )  $\alpha_{xx} = \alpha_{yy} = \alpha_{\perp}$ ,  $\alpha_{zz} = \alpha_{\parallel}$  (all other components vanishing), which librates in the field  $\mathbf{E} = E_0 \mathbf{z}$ , we have  $\langle \mathbf{d} \rangle = E_0 \mathbf{z} (\alpha_{\parallel} \langle \cos^2 \theta \rangle + \alpha_{\perp} \langle \sin^2 \theta \rangle)$ . Here  $\theta$  is the angle the molecular axis makes with the direction of the field  $\mathbf{E}$ . In the absence of librational motion this reduces to  $\mathbf{d}_0 = \alpha_{\parallel} E_0 \mathbf{z}$ , so that  $\mathbf{d}$  and thus also  $\Delta\nu$  are reduced by a factor  $\langle \mathbf{d} \rangle / \mathbf{d}_0 = 1 - \langle \sin^2 \theta \rangle (1 - \alpha_{\perp} / \alpha_{\parallel})$ . This leads to downward shifts  $\Delta\nu \approx 138 \text{ cm}^{-1}$  for hydrogen, and  $\Delta\nu \approx 103 \text{ cm}^{-1}$  for deuterium, results which are certainly approximate but nevertheless agree well with experiment.

Our results are for hydrogen molecules originally located at the sites of a hexagonal close-packed lattice but undergoing excursions from exact sites. But it is entirely possible that another structure, perhaps with a larger unit cell, may ultimately be favoured, yet which also develops spontaneous polarization; indeed, as we have verified, the off-site behaviour accompanied by spontaneous polarization is not limited to a single structure. The displacement of the molecules shown in Fig. 1 is equivalent to a sliding of alternate layers towards a base-centred orthorhombic structure ( $Cmca$  for the orientations in Fig. 1A)<sup>18</sup>, but with the displacement stopping well short of that configuration. This suggests the possibility that the layering transition discussed in ref. 18 may occur quite gradually.

An issue raised by this physical picture is the ultimate development of the spontaneous polarization at even higher densities. It has been suggested, for example, that molecular hydrogen may become fully ionic with sufficient compression<sup>19</sup>. For densities higher than those corresponding to  $r_s \approx 1.37$ , we find that the charge asymmetry begins to slowly decrease, a trend which is here established only for static protons and for fixed structure, so that further structural transitions are not ruled out. However, the system does not seem to be progressing towards a fully ionic state.

We suggest that phonons other than the vibron may provide further experimental evidence in support of the broken electronic symmetry that we propose, as optical phonons (other than the vibron) and librons must also become strongly infrared-active as the electronic polarization increases. This may provide a very simple explanation for the recent observation of a high-frequency ( $1,600 \text{ cm}^{-1}$ ) infrared-active phonon<sup>20</sup> in solid hydrogen at pressures in excess of 1.5 million atmospheres, and it suggests that detailed infrared studies at these and lower frequencies may offer considerable insight into the structural issues. With respect to other experimental signatures, a straightforward group-theory analysis of the structures considered here indicates the following: first,  $C2/m$  has two vibrons, one infrared-active and one Raman-active, in agreement with experiment. Second,  $Cmc2_1$  has two vibrons, and both are infrared and Raman-active. Third,  $Pca2_1$  has four vibrons; three of these are infrared-active whereas all four are Raman-active<sup>21</sup>. Of course, X-ray or neutron diffraction studies at a level sufficient to determine not only unit-cell parameters but also the contents of the unit cell would provide the ultimate test of the structure. □

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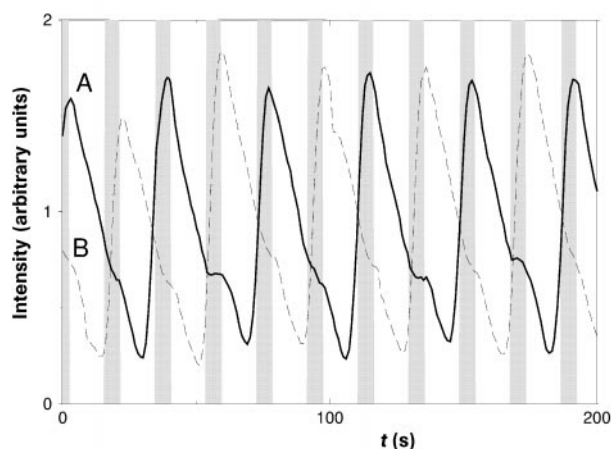
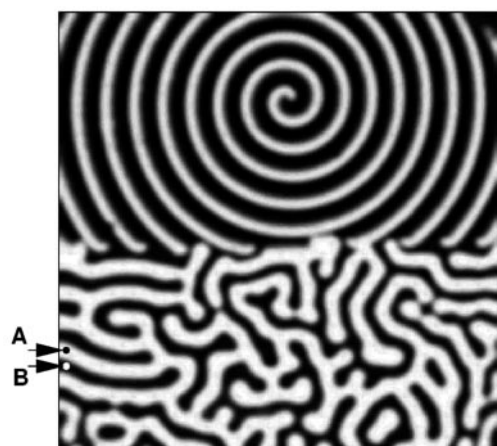
## Resonant pattern formation in a chemical system

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A periodic force applied to a nonlinear pendulum can cause the pendulum to become entrained at a frequency that is rationally related to the applied frequency, a phenomenon known as frequency-locking<sup>1</sup>. A recent theoretical analysis showed that an array of coupled nonlinear oscillators can exhibit spatial reorganization when subjected to external periodic forcing<sup>2</sup>. We present here experimental evidence that reaction–diffusion processes, which govern pattern evolution and selection in many chemical and biological systems<sup>3</sup>, can also exhibit frequency-locking phenomena. For example, periodic optical forcing of the light-sensitive Belousov–Zhabotinsky (BZ) reaction transforms a rotating spiral wave<sup>4</sup> to a labyrinthine standing-wave pattern (Fig. 1). As the forcing frequency is varied, we observe a sequence of frequency-locked regimes, analogous to the frequency-locked ‘tongues’ of a driven nonlinear pendulum, except that in the reactor different frequencies correspond to different spatial patterns. Resonant interactions leading to standing-wave patterns have not been observed previously in chemical or biological media, but periodic forcing (such as circadian rhythm) is abundant in nature and may lead to similar pattern-forming phenomena.

We examine the effect of external forcing on spiral wave patterns in a quasi-two-dimensional reaction–diffusion system with a light-sensitive form of the BZ reaction<sup>5,6</sup>. The reaction medium is a



thin membrane that is sandwiched between two reservoirs of reagents<sup>7</sup>. For the conditions of our experiment (see Fig. 1 legend), the reactor can oscillate homogeneously with the natural frequency  $f_0 = 0.028$  Hz; thus the reaction–diffusion medium can be thought of as a two-dimensional array of nonlinear oscillators coupled by diffusion. The natural frequency is measured by exposing the reaction to bright light for one minute; this resets each point in the reactor to the same initial conditions, and after the light is removed, the medium oscillates homogeneously for several cycles. However, the presence of boundaries and small imperfections in the reactor always leads to the appearance of rotating spirals. The rotation frequency of the spirals ( $f_{\text{spiral}} = 0.045$  Hz) is larger than that of the homogeneous oscillations, and the pattern evolves into a single spiral (top half of Fig. 1), owing to the dominance of the fastest pacemaker in the reactor<sup>8</sup>.

The reaction is perturbed at frequency  $f_p$  with pulses of spatially uniform light from a video projector. The absorption of light by ruthenium molecules causes a temporary shift of the chemical kinetics<sup>6</sup>. The periodic perturbations can destroy the spiral wave pattern and lead to a labyrinthine standing wave pattern, as shown in the (illuminated) lower half of Fig. 1. Black and white domains in the labyrinthine pattern correspond respectively to high and low concentrations of a ruthenium(II) complex. These domains oscillate with opposite phase and are separated by nodal lines that are time-independent. Figure 2 demonstrates that each domain oscillates in synchrony with every other perturbation pulse ( $f_p/f_0 = 2$ )—a 2:1 resonance. The observed effect of forcing on our oscillatory BZ system is different from that found previously in an excitable BZ

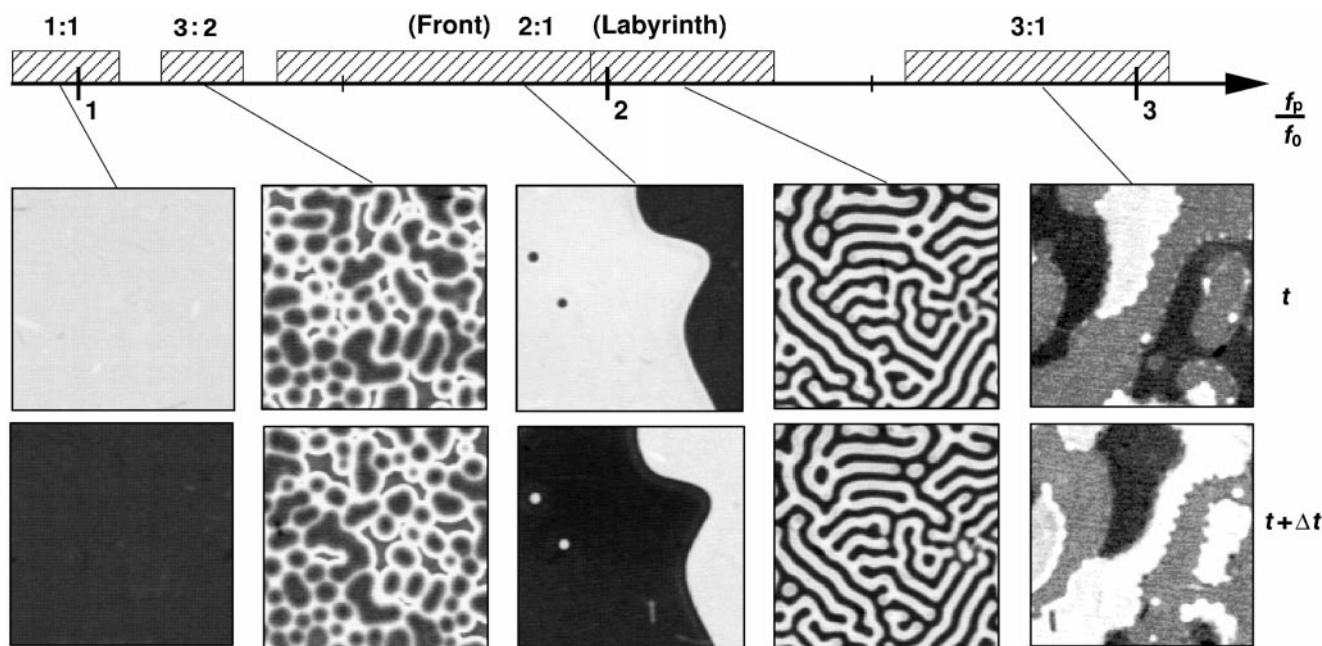
reaction in a Petri dish<sup>9</sup>. Unlike the oscillatory medium, the excitable BZ reaction cannot oscillate homogeneously but can form rotating spirals. Periodic forcing of excitable spirals has been found to lead to a modulation of the rotation frequency and a slow drift of the spiral centre, but not to standing waves<sup>9</sup>.

When we vary the frequency of perturbations, we observe a sequence of resonance patterns, each persisting for a range of perturbation frequency. Figure 3 illustrates the patterns for frequency-locked ratios  $f_p/f_0 = 1, 3/2, 2$  and  $3$ . In the 1:1 regime, the entire reactor synchronizes with the perturbation, oscillating between uniform dark and light. When  $f_p$  is increased, the system is no longer able to synchronize with the perturbation; instead, bubble-shaped structures appear (Fig. 3). The bubbles appear and disappear in a seemingly random fashion, but the temporal spectrum at any spatial point in the pattern has well defined peaks at multiples of  $f_p/3$ , indicating that this is a 3:2 resonance.

Two types of 2:1 resonances are observed: for  $f_p/f_0 < 1.9 \pm 0.1$ , the pattern consists of a stable stationary front separating two oscillating, spatially uniform domains. The shape of the domains does not change; it is determined by the concentration profiles in the beginning of experiment. We also observe localized spots that coexist with the stationary front (Fig. 3); similar localized structures have been found in models of bistable chemical reactions<sup>10</sup> and coupled map lattices<sup>11</sup>. For  $f_p/f_0 > 1.9 \pm 0.1$ , the previously described labyrinthine pattern forms. Once this pattern has grown to fill the entire perturbed region of the reactor, the nodal lines between the two types of domains become stationary. The transition from simple fronts to labyrinthine standing wave is similar to the

**Figure 1** A labyrinthine standing-wave pattern forms in the lower half of the reactor, which is illuminated with light pulsed at twice the natural frequency of the reaction ( $f_p/f_0 = 2$ ), while a spiral wave forms in the upper half of the same reactor, which is in the dark. The reaction occurs in a 0.4-mm-thick porous membrane disk that is placed between two reservoirs (I and II) which are continuously refreshed with BZ reagents. The region shown is a  $13 \times 13$  mm section of the 25-mm-diameter reactor. The patterns in the membrane are determined from light absorption measurements at 450 nm. In the perturbed region, light of  $0.2 \text{ W m}^{-2}$  intensity in the spectral range 430–470 nm is periodically switched on for 6 s and then off for 13 s. Spatially uniform illumination is achieved using a video projector (Sanyo PLC-220N) calibrated by measuring light reflected from a scatter plate and then adjusting each pixel to have the same intensity. The concentrations of the chemicals in reservoirs I and II are:  $[\text{malonic acid}]_I = 0.22 \text{ M}$ ,  $[\text{BrO}_3^-]_I = 0.046 \text{ M}$ ,  $[\text{Br}^-]_I = 0.2 \text{ M}$ ,  $[\text{H}_2\text{SO}_4]_I = 0.8 \text{ M}$ ,  $[\text{Ru}(\text{bpy})_3^{2+}]_{II} = 1.0 \text{ mM}$ ,  $[\text{H}_2\text{SO}_4]_{II} = 0.8 \text{ M}$ ,  $[\text{BrO}_3^-]_{II} = 0.184 \text{ M}$  (here bpy indicates 2,2'-bipyridine). The volume of each reservoir is 10 ml. The flow rate in reservoir I is  $20 \text{ ml h}^{-1}$ ; in reservoir II,  $5 \text{ ml h}^{-1}$ . The system is maintained at a temperature of  $23^\circ\text{C}$ .

**Figure 2** Time series of pattern intensity at the points A (solid line) and B (dashed line) in Fig. 1. The grey-shaded stripes indicate when light perturbations are applied to the reactor. The oscillations at A and B are opposite in phase and synchronized at one-half of the forcing frequency.



**Figure 3** Bifurcation diagram showing different frequency-locked regimes observed as a function of  $f_p/f_0$  where  $f_p$  is the perturbation frequency and  $f_0$  is the natural frequency of the system. Patterns are shown in pairs, one above the other, at times separated by  $\Delta t = 1/f_p$ , except for the 1:1 resonance where  $\Delta t = 1/2f_p$ . Striped boxes on the horizontal axis mark perturbation frequency ranges with the same frequency-locking ratio. The frequency of the pattern

oscillations is determined by analysing time series of single-point measurements similar to that shown in Fig. 2 for the 2:1 resonance. The duration of the perturbation light pulses is fixed at 6 s for all measurements; at  $f_p/f_0 = 1$  the period of the forcing is 36 s, and at  $f_p/f_0 = 3$  the period of the forcing is 12 s. Images are available at <http://chaos.ph.utexas.edu/~lera/forcing.html>

transition from planar fronts to a stationary labyrinthine pattern observed recently<sup>12</sup> in an intrinsically bistable (unforced) reaction. This indicates that in the 2:1 resonance, the BZ reaction behaves as a bistable system with the two states corresponding to the two possible oscillatory phases.

The pattern in the 3:1 resonance regime has three types of domains which oscillate with phases differing by  $2\pi/3$ . After three periods of perturbation, the original pattern is recovered, except for a very slow drift of the domain boundaries. The observed boundary drift supports a theoretical conjecture that such behaviour is a fundamental property of interfaces in tristable systems<sup>13</sup>.

The bifurcation diagram in Fig. 3 has gaps where no resonance was evident. The temporal behaviour in these regions may be quasi-periodic rather than locked, or some of these regimes may be locked at frequency ratios  $m/n$  where  $m$  and  $n$  are too large to be determined in the present experiments, or the fluctuations of the experimental conditions may have shifted the system between adjacent regions. Experiments with a better signal-to-noise ratio are needed to distinguish between these and other possible explanations for the gap regions.

The sequence of resonance regimes observed in the present study is analogous to the behaviour of strongly forced low-dimensional nonlinear dynamical systems<sup>1</sup>, where, as the perturbation frequency is varied, the system can exhibit a sequence of regimes with frequency locking at ratios  $m/n$  (where  $m$  and  $n$  are integers). Unlike the low-dimensional systems that can be entrained by very small perturbations near resonance, the observed standing-wave patterns appear only for a forcing intensity above some critical value. At lower intensity, we observed rotating spirals and other non-stationary patterns.

A transition from travelling to standing waves has been observed previously in several physical systems in the 2:1 locking regime<sup>14</sup>. Our experiments reveal two types of patterns with 2:1 locking. Moreover, we find other frequency-locked regimes which have different types of spatiotemporal behaviour. Patterns similar to

some of those that we have observed have been obtained in a model of a forced weakly nonlinear medium described by a complex Ginzburg–Landau equation<sup>15</sup>. This similarity in the phenomena for a general model and for our experimental system suggests that resonant pattern formation may arise in a variety of chemical, biological and other extended systems where internal oscillatory dynamics are coupled with external periodic forcing. In three dimensions, where spirals become scroll waves<sup>16</sup>, periodic forcing may lead to yet another type of pattern. □

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