Nonlinear Mode Coupling and One-to-One Internal Resonances in a Monolayer WS₂ Nanoresonator

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Supporting Information

ABSTRACT: Nanomechanical resonators make exquisite force sensors due to their small footprint, low dissipation, and high frequencies. Because the lowest resolvable force is limited by ambient thermal noise, resonators are either operated at cryogenic temperatures or coupled to a high-finesse optical or microwave cavity to reach sub aN $Hz^{-1/2}$ sensitivity. Here, we show that operating a monolayer WS₂ nanoresonator in the strongly nonlinear regime can lead to comparable force sensitivities *at room temperature*. Cavity interferometry was used to transduce the nonlinear response of the nanoresonator, which was characterized by multiple pairs of 1:1 internal resonance. Some of the modes exhibited exotic line shapes due to the appearance of Hopf



bifurcations, where the bifurcation frequency varied linearly with the driving force and forms the basis of the advanced sensing modality. The modality is less sensitive to the measurement bandwidth, limited only by the intrinsic frequency fluctuations, and therefore, advantageous in the detection of weak incoherent forces.

KEYWORDS: Two-dimensional materials, transition-metal dichalcogenides, nanomechanical resonator, nonlinearity, internal resonance

T he force sensitivity of a nanomechanical resonator is limited by the thermal force noise (S_F^{Th}) , which according to the fluctuation-dissipation theorem is given by $S_F^{\text{Th}} = 4k_bTm_e\gamma B$; where k_b is the Boltzmann constant, B is the measurement bandwidth, T, m_e , and γ are the temperature, effective mass, and line width of the resonance. Because of their low mass and narrow line width, by employing lowdimensional materials, such as nanowires, nanotubes, and twodimensional (2D) materials, at cryogenic temperatures is an attractive strategy toward the design of resonators with high force sensitivity.¹⁻⁷ However, realizing the thermal force limit in these systems is challenging, as it requires a transduction scheme that can efficiently convert small displacements into a measurable signal.⁸ Consequently, their performance is often limited by noise in the transduction scheme.^{5,9}

An alternative but unexplored approach is to operate the resonator in the nonlinear regime and utilize the sensitivity of bifurcation points that manifest in the frequency-response curve to an external force. The bifurcation points arise on account of nonlinear mode-coupling or internal resonance (IR) in the system. If the linearized natural frequencies are denoted by ω_i ($i = 1, 2, ..., \infty$), IR occurs when some of the

frequencies are commensurate or nearly commensurate, that is, there exist integers k_i (not all of them zero), satisfying $k_1\omega_1 + k_2\omega_2 + ... + k_p\omega_p \approx 0$.^{10–12} Such an approach to force sensing is advantageous due to multiple reasons. First, the method relaxes the requirement of a narrow measurement bandwidth, as nonlinear responses offer a higher signal-to-noise ratio and are relatively simpler to measure. Second, theoretical estimates suggest that a force sensitivity in the attoNewton range can be achieved at room temperature.¹³ Lastly, the shorter integration times may enable the detection of weak, incoherent forces and force jumps.

Nanomechanical resonators that utilize low-dimensional materials can be driven into the nonlinear regime even at modest actuation forces due to their small thickness (bending stiffness) and, therefore, have been the subject of recent research.^{14–20} Among different 2D materials, transition-metal dichalcogenides (TMDCs) with the general chemical formula AB₂ (A = Mo, W and B = S, Se, or Te) are characterized by

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Figure 1. Sample fabrication, Raman spectroscopic characterization, cavity-interferometry setup, and measurement of thermo-mechanical resonance spectra. (a) A pseudocolored SEM image of the monolayer WS_2 nanoresonator that is clamped on two edges using gold electrodes (scale bar: 10 μ m). (b) Raman spectroscopy data (blue, solid line) are fit to a multipeak, Lorentzian line shape (black, dashed line) to identify the peak locations of different phonon modes. (c) A schematic of the experimental setup. A He–Ne laser is used as the probe beam, and a piezo disk is used to actuate the nanoresonator. The sample is housed in high-vacuum conditions (<10⁻⁵ Torr). Different abbreviations: BS, beam splitter; PD, photodiode; ND, neutral density; and LWD, long working distance. (d) The thermo-mechanical resonance spectra of modes 1 and 2 at different probe powers. (e) The Q-factor is lowered with increasing probe power (left axis). The peak-signal intensity is plotted for different probe powers and fit to a straight line (right axis). Data shown are for mode 2.

reduced phonon-phonon scattering²¹⁻²³ and negligible spectral broadening²⁴ and, thus, are better suited to resonator studies than graphene and other commonly employed materials. In this letter, we report a force sensor that utilizes nonlinear mode coupling in a monolayer tungsten disulfide (WS_2) nanoresonator. The driven resonances at a high driving force resulted in multiple pairs of IR. Additionally, some of the modes exhibit exotic line shapes that significantly differ from the standard Lorentzian line shape under low actuation drives as well as the Duffing response under high actuation drives. We posit that the observed line shapes are a consequence of nonlinear coupling between the modes, where the source of nonlinearity is geometric in nature. We utilize a reduced order (RO) model that consists of two Duffing oscillators with commensurate frequencies (i.e., 1:1 IR) and cubic, nonlinear coupling terms to qualitatively replicate the measured line shapes. Bifurcation analysis revealed the exotic line shape to originate from Hopf bifurcation points in the frequencyresponse curve. Although it stems from nonlinear mode coupling, the bifurcation point has a linear dependence on the force magnitude and provides a simple methodology for the

detection of weak forces.¹³ We estimate the force sensitivity as 350 fN in the current implementation and to improve significantly (\sim 500 aN) with the addition of a parametric drive. In summary, the results presented here provide a path forward toward the utilization of nonlinearity for force and mass sensing as well as the synchronization of internally resonant modes in TMDC nanoresonators.

The monolayer WS₂ nanoresonator (Figure 1a) was fabricated using a combination of mechanical exfoliation onto an SiO₂ wafer, potassium hydroxide (KOH)-assisted polymethyl methacrylate (PMMA) transfer of optically identified monolayer flakes onto a pristine Si/SiO₂ wafer, and e-beam lithography/lift-off techniques (see Supporting Information S1 for more details). The resonator was sandwiched between Au electrodes at the top and exposed negative e-beam resist (hydrogen silsesquioxane, HSQ) at the bottom. The cavity depth was determined by the thickness of the spin-coated HSQ, and a value of ~375 nm was chosen as it predicted good responsivity values for monolayer WS₂ based on a thin-film interference model (see Supporting Information S2). Raman spectroscopy was employed to identify the thickness of few-layered TMDC samples.²⁵ Specifically, the Raman spectrum of WS_2 was characterized by the in-plane E^1_{2g} and out of plane A^{1}_{g} phonon modes. It is known that the A^{1} mode undergoes softening as the thickness of WS_2 is reduced, and hence, the spacing between the two phonon modes is indicative of the number of layers. Raman spectroscopy measurement (Figure 1b, also see Supporting Information S3) revealed a spacing of $\sim 66 \text{ cm}^{-1}$ between the two phonon modes, confirming that the nanoresonator is one-layer thick.²⁶ Figure 1c presents a schematic of the experimental setup,²⁵ where a He–Ne laser (632.8 nm, average power <450 μ W) is used as a probe beam and is focused on the nanoresonator, to a spot size of <2 μ m, using a long working distance objective (NA = 0.55). The chip-carrier containing the sample is mounted on a lead zirconate titanate (PZT) disc ($d_{33} \sim 330$ pmV⁻¹) that actuates the different resonance modes of the nanoresonator, and the chip-carrier/PZT disc assembly is housed inside a custom-built vacuum chamber (vacuum level $<10^{-5}$ Torr) with electrical feedthroughs and optical viewports. The underlain Si substrate and the nanoresonator form an optical cavity whose reflectance, modulated by the latter's motion, is measured on a fast photodiode. An RF signal generator provides the driving signal to the PZT disc, whereas a lock-in amplifier measures the photodiode voltage. A spectrum analyzer was used in the thermo-mechanical resonance measurements.

Figure 1d shows the undriven resonance spectrum acquired at room temperature, with a resolution bandwidth of 100 Hz, using different laser powers. The measured data were fit to a Lorentzian line shape composed of two resonance peaks as it improved the fitting. Also, modal analysis (see Supporting Information S4) revealed that the first and second modes have closely spaced frequencies and are characterized by mode shapes whose maximum out of plane displacement occurs near the center of either free-edge. For the case where the probe power was ~180 μ W, curve fitting yielded frequency centroids 1.0429 and 1.0443 MHz and Q-factors of 617 (±500) and 2472 (\pm 750) for the two modes. The lower *Q*-factor of mode 1 is due to poor signal-to-noise ratio (SNR) at this probe power. Increasing the probe power to 450 μ W resulted in a reduction of the second mode Q-factor to $\sim 1200 \ (\pm 110)$, along with a blue-shift of the frequency centroids (1.0462 and 1.0477 MHz). The lowering of Q-factor with increasing probe power reported here (Figure 1e) is consistent with previous measurements on WSe₂ monolayer resonators, where it was shown that the Q-factor decreases due to heating from the probe laser and photothermal back-action from the optical cavity.²² Photothermal back-action is an optomechanical effect that results in a time-delayed force on the resonator and effectively modifies its damping.²⁷ Depending on the sign of the photothermal force gradient (∇F) , the motion of the resonator is either amplified ($\nabla F < 0$) or quenched ($\nabla F >$ 0).²⁷ In our measurements, the peak signal intensity varies linearly with the probe power (Figure 1e); consequently, we rule out any photothermal back-action effects and attribute the decrease in Q-factor to sample heating. We also note that the *Q*-factor reported here (at room temperature) is approximately 1 order of magnitude higher than previous reports on monolayer TMDC resonators with similar sample dimen-sions.^{22,28,29} In order to fully understand the source of this improvement, further measurement of Q-factors at different temperatures is needed to account for both intrinsic and extrinsic damping sources, which is outside the scope of the

current letter. However, we conjecture that the higher Q-factor may partly be due to the robust clamping scheme and the absence of electrostatic damping that is otherwise prevalent in measurements that employ capacitive actuation.²³

Using modal analysis with finite elements (see Supporting Information S4), we first estimated the resonance frequencies of the sample without including any prestress. The Young's modulus of the material ($E_{\rm Y} \sim 270$ GPa) was assumed to be isotropic, which is a valid assumption for strains <10% as shown previously.³⁰ We employed a thin-shell thickness of 0.34 nm that facilitates the use of continuum theory for describing the behavior of 2D WS₂ resonators, while ensuring that the bending rigidity value is consistent with first-principle calculations^{31,32} (see Table S1 in Supporting Information for a complete list of parameters used in the modal analysis). The resonance frequency of the fundamental mode without prestress was estimated to be ~0.47 MHz, which is smaller than the observed value of 1.0462 MHz. For a plate under prestress, the frequency of the fundamental mode can be expressed as $f_0 = \sqrt{f_p^2 + f_m^2}$, where f_p is the resonance frequency of a plate without prestress and f_m is the resonance frequency of a membrane with uniform prestress and negligible bending stiffness. Depending on their relative values, the resonator could be in (1) plate regime where $f_m \rightarrow 0$, (2) membrane regime where $f_p \rightarrow 0$, or (3) in the mixed regime, where both bending rigidity and prestress need to be accounted for. The WS₂ nanoresonator reported here is in the mixed regime, as is evident from $f_p < f_t$ necessitating the inclusion of prestress. We repeated the modal analysis by incorporating a uniform prestress (σ_0) in the plate along the direction perpendicular to the clamped edges. The predicted and measured values for the resonance frequency of mode 1 coincided for $\sigma_0 \sim 45 \ \mu \text{Nm}^{-1}$. For perspective, this value is 3 orders of magnitude smaller than previous reports on MoS_2 drum-head resonators^{33,34} and comparable to H-shaped graphene resonators.8 The smaller value of prestress may partially be attributed to the wet processes in our fabrication workflow as opposed to a purely dry-transfer protocol.^{8,25} From the modal analysis for $\sigma_0 \sim 45 \ \mu \text{Nm}^{-1}$, the predicted frequencies for modes 2 and higher do not line up with the observed values (see Figure S6 in Supporting Information). We briefly comment on the possible reason for this discrepancy. Previous reports on few-layered graphene resonators have shown the possibility of unconventional "edge modes" that arise due to an out of plane deformation profile and/or imperfections in the sample.³⁵⁻³⁷ Further, because the estimated critical buckling load (N_{xx}) is comparable to the prestress ($N_{xx} \sim \sigma_0/2.5 = 16.74 \ \mu \text{Nm}^{-1}$, see Supporting Information S4), the nanoresonator is susceptible to rippling under a nonhomogeneous stress profile. A priori knowledge of both the sample topography and the mode shapes is needed to fully analyze the origin of this discrepancy. The laser spot size in our experimental setup is comparable to the sample dimension, and consequently, we cannot measure the mode-shapes with high spatial resolution.

We measured the driven resonance spectrum of the nanoresonator by sweeping the actuation frequency applied to the PZT disc and recording the voltage on the photodiode with a lock-in amplifier. Unless otherwise specified, the probe power was kept constant at 450 μ W in these measurements. The first four resonance modes are shown in Figure 2a,b at low actuation drives of 0.75 and 1.5 V_{p-p}. The higher order modes



Figure 2. Weakly nonlinear behavior in modes 1 and 2. The driven resonance spectra at low driving voltages is shown for modes (a) 1 and 2 and (b) 3 and 4. (c) Mode 1 displays a mixed-type Duffing response and nonlinear damping with increasing actuation voltages. (d) The effective damping in mode 2 increases with the driving force. In (c and d) the driving voltages used from bottom to top are 0.5, 0.75, 1.5, and 2.0 V_{p-p}.

(>mode 4) had poor SNR at these low actuation drives but were detectable at 2 V_{p-p} and larger driving voltages. Spurious resonances that arise from the motion of the PZT disc were eliminated by measuring the out of plane motion of the adjacent gold electrodes (see Supporting Information S5). Resonances that overlapped in both measurements were categorized as spurious and are not shown. With increasing driving force, mode 1 exhibited the amplitude-frequency effect, that is, the resonance frequency was strongly dependent on the vibration amplitude (Figure 2c). However, the resonance frequency of mode 2 remained stable after initial stiffening (Figure 2d). Further, the resonance line width increased monotonically with the driving force for both modes, which is indicative of nonlinear damping. Nonlinear damping has previously been reported in low-dimensional NEMS such as carbon nanotubes as well as graphene resonators, although its physical origin is currently unclear.³⁸ The weakly nonlinear behavior of mode 1 in Figure 2c can be understood within the framework of a Duffing resonator, viz.,

$$\frac{d^2x}{dt^2} + (\gamma + \eta x^2)\frac{dx}{dt} + \omega_0^2 x + \alpha x^3 + \beta x^4 + \delta x^5 = \frac{F}{m_e}\cos(\omega t)$$
(1)

where m_e is the effective mass, γ is the linear damping coefficient, ω_0 is the resonance frequency, α , β , δ are the cubic-, quartic-, and quintic-order nonlinear coefficients, and η is the nonlinear damping parameter. In Figure 2c, mode 1 undergoes hardening at intermediate drive voltages followed by softening at higher drives. The quartic- and quintic-order nonlinear terms are included to account for this mixed type of nonlinear behavior.^{15,18} The measured data were fit to the Duffing model (given in eq 1) for mode 1 and to a Lorentzian line shape for mode 2 to extract the effective line width at different actuation voltages (see Supporting Information S6).

We investigated mode coupling due to geometric nonlinearity in modes 1 and 2 by driving them at even higher harmonic forces. When the driving voltage was increased to 3 $V_{p-p'}$ we observed a sudden drop in the peak amplitude of mode 1 along with the appearance of a sideband for mode 2 (Figure 3a). This redistribution of energy between the two



Figure 3. Nonlinear behavior at high drive forces is mediated by 1:1 IR. (a, b) The evolution of nonlinearity in modes 1 and 2 is presented for increasing driving voltages. At 3 $V_{p-p'}$, there is a redistribution of energy between modes 1 and 2. The bimodal response of mode 2 suggests 1:1 IR. At a higher driving voltage of 7 $V_{p-p'}$ mode 1 develops a sideband at a lower frequency. Inset in (a) plots the peak intensity (μ V) vs the driving voltage (V) for mode 1. The linear behavior at low voltages is transformed into amplitude saturation at intermediate voltages (red, dashed ellipse), followed by a drop in the intensity at a driving voltage of 3 V (arrow). Mode pairs (c) 3 and 4 and (d) 5 and 6 showed similar behavior with increasing excitation force. Sidebands that appear with increasing drive forces are shown with arrows.

modes at a high actuation amplitude suggests that they are coupled. Further, the emergence of a bimodal line shape for mode 2, which is also referred to as mode splitting³⁹ or an Mshaped resonance curve⁴⁰ in the literature, with increasing actuation amplitude is a telltale signature of 1:1 IR between the two nearly commensurate modes.¹² At even higher driving voltages, mode 1 becomes bimodal and develops a sideband at a lower frequency (Figure 3b, indicated with an arrow). The behavior of mode pairs 3 and 4 (Figure 3c) and 5 and 6 (Figure 3d) was qualitatively similar under high driving forces. For instance, we observed a sudden dip in the peak amplitude of modes 3 and 4 along with an increase in their bandwidth (see Figure 3c) as the driving voltage was increased to 3 V_{p-p} . Mode 6 was bimodal even under low driving forces; as the voltage was increased to 3 $V_{p-p}{},$ a drop in the peak amplitude of the higher frequency branch was accompanied by the appearance of a sideband in the lower frequency branch.

The resonant behavior of modes 7 and 8 as a function of the actuation amplitude is presented in Figure 4. Modes 7 and 8 exhibited a bimodal line shape even at a low driving voltage of 2 V_{p-p} (Figure 4a). Unlike modes 2 and 6 where the two peaks in the bimodal response were well resolved, the line shape for mode 7 is reminiscent of 1:1 IR in taut strings. In the latter, the overshoot is a consequence of amplitude-modulated motion due to Hopf bifurcation.⁴¹ The phase response for mode 7 is



Figure 4. Nonlinear behavior of modes 7 and 8. (a) Resonance spectra obtained under moderate forces; the modes 7 ($\omega_c/2\pi \sim 1.34$ MHz) and 8 ($\omega_c/2\pi \sim 1.37$ MHz) exhibit a non-Lorentzian line shape due to 1:1 IR. (b) The line shape arises from a single mode as confirmed by a total phase change of π (data shown for the case of 2 V_{p-p}). (c) Resonance spectra of modes 7 and 8 at higher actuation amplitudes. (d) Forward and backward sweeps show amplitude modulations of unequal amplitude in mode 7 and softening-type hysteresis in mode 8.

shown in Figure 4b. A total phase shift of π in the frequency span between 1.33 and 1.35 MHz ascertains that the line shape is not due to a superposition of two close-by modes but originates from a single mode. Upon progressively increasing the driving voltage to 6 V_{p-p}, the line shapes for mode 7 remained similar but with better SNR (Figure 4c); whereas for mode 8, the lower frequency portion exhibited softening. Forward and backward swept traces were also obtained (Figure 4d) for modes 7 and 8 at 6 V_{p-p}. In addition to the expected hysteresis (for instance, in the softening portion of mode 8), we noticed that the peak amplitude of mode 7 was smaller during the backward sweep.

The frequency-response curves presented in Figures 3 and 4 are a consequence of 1:1 IR and can be understood using a generalized RO model that consists of two Duffing oscillators with nearly commensurate frequencies and weakly nonlinear coupling terms, given by the following pair of ordinary differential equations (ODEs):

$$\ddot{x} + \omega_1^2 x = \varepsilon [-\mu_1 \dot{x} + k_1 x^3 + a_1 x^2 y + b_1 x y^2 + c_1 y^3 + d_1 y + F \cos(\omega t)]$$
(2)
$$\ddot{y} + \omega_2^2 y = \varepsilon [-\mu_2 \dot{y} + k_2 y^3 + a_2 x^2 y + b_2 x y^2 + c_2 x^3 + d_2 x]$$
(3)

where x and y refer to the modal degrees of freedom and ϵ is a small parameter. The forcing term (F) is present in only one of the oscillators, as it corresponds directly to the experimental situation; however, because of the nature of 1:1 IR, the other mode is automatically excited through the coupling terms. This contrasts with pump-probe experiments, where an additional excitation source (the pump signal) is applied to one of the modes, while its effect on the probe mode is measured. The RO model was derived starting from the Föppl-von Kármán

plate theory, which accounts for geometric nonlinearity (see Supporting Information S7). Using modal expansion composed of only two modes, followed by a Galerkin procedure, it is shown in Supporting Information S7 that the governing partial differential equations reduce the nonlinear ODEs given in eqs 2 and 3. The coefficients in the ODEs are related to the mode shapes and their derivatives; and in those cases where the mode-shapes are known accurately (e.g., circular or square resonator with all boundaries clamped), the experimental observations can be quantitatively explained using the RO model.^{15,42,43} Similar models have been studied previously, with slight variations, for the case of 1:1 IR⁴⁴ and 1:3 IR.⁴⁵ Depending on the nonlinear terms that are retained, the RO model can lead to a diverse set of frequency–response curves such as those shown in Figure 3.⁴⁵

We performed bifurcation analysis (using MatCont, ref 46) on a simplified version of the RO model (given below) to explain the unconventional line shape of mode 7.

$$\ddot{x} + \omega_1^2 x = \varepsilon [-\mu_1 \dot{x} - k_1 x^3 - \Lambda x y^2 + F \cos(\omega t)]$$
(4)

$$\ddot{y} + \omega_2^2 y = \epsilon [-\mu_2 \dot{y} - k_2 y^3 - \Lambda x^2 y]$$
 (5)

The nonlinear coupling terms were restricted to x^2y^2 in the Hamiltonian, and the coupling strength Λ was used as a fitting parameter. Mode-specific parameters such as the linearized frequency ω_i and cubic nonlinearity term k_i were estimated using data obtained with low driving forces and the linear damping parameters were assumed to be equal, that is, $\mu_1 = \mu_2 = \mu$. The book-keeping parameter was taken as $e \sim Q^{-1}$. For simplicity, nonlinear damping terms were not included in the analysis. The different values used in the bifurcation analysis are listed in Table S2 in Supporting Information S8. The method of scales was employed (see Supporting Information S8) to reduce the second-order ODEs to the following set of first-order ODEs in (p_1, q_1, p_2, q_2) space, namely,

$$p_{1}' = -\mu p_{1} - \sigma q_{1} + \frac{3k_{1}}{8\omega_{1}}(p_{1}^{2} + q_{1}^{2})q_{1} + \frac{\Lambda}{8\omega_{1}}(2(p_{2}^{2} + q_{2}^{2})q_{1} - (p_{2}^{2} - q_{2}^{2})q_{1} + 2p_{1}p_{2}q_{2})$$

$$(6)$$

$$\begin{aligned} q_{1}^{\prime} &= -\mu q_{1} + \sigma p_{1} - \frac{3k_{1}}{8\omega_{1}}(p_{1}^{2} + q_{1}^{2})p_{1} + \frac{F}{2\omega_{1}} \\ &- \frac{\Lambda}{8\omega_{1}}(2(p_{2}^{2} + q_{2}^{2})p_{1} + (p_{2}^{2} - q_{2}^{2})p_{1} + 2p_{2}q_{1}q_{2}) \end{aligned}$$

$$(7)$$

$$p_{2}' = -\mu p_{2} - (\sigma - \sigma_{1})q_{2} + \frac{3\kappa_{2}}{8\omega_{2}}(p_{2}^{2} + q_{2}^{2})q_{2} + \frac{\Lambda}{8\omega_{2}}(2(p_{1}^{2} + q_{1}^{2})q_{2} - (p_{1}^{2} - q_{1}^{2})q_{2} + 2p_{1}p_{2}q_{1})$$
(8)

$$q_{2}' = -\mu q_{2} + (\sigma - \sigma_{1})p_{2} - \frac{3k_{2}}{8\omega_{2}}(p_{2}^{2} + q_{2}^{2})p_{2} - \frac{\Lambda}{8\omega_{2}}(2(p_{1}^{2} + q_{1}^{2})p_{2} + (p_{1}^{2} - q_{1}^{2})p_{2} + 2p_{1}q_{1}q_{2})$$
(9)

DOI: 10.1021/acs.nanolett.9b01442 Nano Lett. 2019, 19, 4052-4059 The parameters (p_1,q_1) and (p_2,q_2) are related to the slowly varying amplitudes A and B of the two oscillators by $A = \frac{1}{2}(p_1 - q_1)e^{i\phi_1}$ and $B = \frac{1}{2}(p_2 - q_2)e^{i\phi_2}$. The closeness of the two frequencies is expressed using a detuning parameter σ_1 , where $\omega_2 = \omega_1 + \epsilon \sigma_1$. A different detuning parameter σ denotes the closeness of the excitation frequency to the primary resonance frequency ω_1 by $\omega = \omega_1 + \epsilon \sigma$.

Figure 5a shows the computed frequency response diagram for mode 7 along with the measured data (for 3 V_{p-p}). The



Figure 5. Bifurcation analysis predicts Hopf bifurcations for mode 7. (a) The frequency–response curve obtained from the bifurcation analysis is overlaid on the measured data at 3 V_{p-p} . The stable regions are indicated using solid lines, unstable regions using dashed lines, and Hopf bifurcation points (H_1 and H_2) using arrows. The computed frequency–response curves at increasing drive forces are shown in (b) and (c) along with the measured data at 3.5 and 5.0 V_{p-p} . (d) A bifurcation set is shown with the two Hopf points; the computed curves were extrapolated to lower values of F to identify the critical value below which the Hopf points vanished.

unstable regions in the diagram are shown using dashed lines, whereas the stable regions are shown using solid lines. Points a and c refer to branch points on the diagram, from which additional fixed points could emerge. H_1 and H_2 refer to Hopf bifurcation points along the new branch curve connecting points a and c. The computed frequency response curve differs from the Lorentzian line shape in two aspects: (1) it loses stability along the portion of the curve that connects points a, b, and c; and (2) Hopf bifurcations occur along the new branch curve. To see how the experimentally observed line shape can be explained using the computed diagram, consider a forward sweep. The oscillator moves along the stable branch until it arrives at point a, where there is a bifurcation which causes it to traverse the new branch curve until it reaches the first Hopf point H_1 . According to the Hopf bifurcation theorem, the motion now is no longer periodic but amplitude modulated, which in experiments causes an overshoot from the predicted diagram until it reaches point H_2 .¹² The oscillator then follows the stable branch after traversing the second Hopf bifurcation point H_2 . Frequency-response curves were also computed for increasing forces, as shown in Figure 5b,c along

with the measured data, showing good agreement between the two. The distance between the Hopf bifurcation points increases with the driving force, indicating that amplitude-modulated motion occurs over a wider frequency range. Figure 5d shows a bifurcation set for the coupled system, where at a sufficiently low driving force, both Hopf bifurcation points are predicted to disappear.

MatCont automatically computes the first Lyapunov coefficient for Hopf bifurcation points which can be used to classify them as either sub or supercritical. Because the first Lyapunov coefficient is positive for H_1 , it is a subcritical Hopf bifurcation and may lead to an unstable limit cycle and eventual chaotic motion. However, because the first Lyapunov coefficient is negative for point H_2 , it is a supercritical Hopf bifurcation and is characterized by a stable, limit cycle. This prediction is reflected in the difference between the forward and backward swept data that are shown in Figure 4d. The forward swept trace first passes through the subcritical Hopf bifurcation, and consequently, the peak amplitude is higher when compared to the backward swept trace (which passes through the supercritical Hopf bifurcation first).

Interestingly, the location of the subcritical Hopf bifurcation point H_1 varies linearly with the force magnitude F, and therefore, it could serve as a simple scheme for the detection of weak forces. The supercritical Hopf bifurcation point H_2 has a linear dependence for intermediate force values and plateaus subsequently. As per the bifurcation diagram in Figure 5d, the limit of detection corresponds to the value of the driving force where the Hopf bifurcations disappear. The actuation force on the nanoresonator results from inertial coupling with the motion of the PZT disc. For a harmonic base excitation d = $d_0 \sin \omega t$ of the PZT, the inertial force acting on the resonator is given by $F = Tm_r\omega^2 d_{0}$, where m_r is the mass of the nanoresonator and T is the transmission coefficient. We assume ideal transmissivity (i.e., T = 1) and take the following parameter values: linearized frequency $\omega/2\pi \sim 1.34$ MHz, resonator mass $m_{\rm r} \sim 10$ fg, peak amplitude $d_0 = d_{33}V_{\rm lim}$, where $d_{33} \sim 330 \text{ pmV}^{-1}$ is the piezoelectric coefficient of the PZT disc and $V_{\rm lim} \sim 1.5 V$ is the driving voltage at which the Hopf bifurcation points disappear. The lowest detectable force can be estimated as $F_{\rm min} \sim 0.35$ pN. The sensitivity in the current implementation is limited by the fact that the force of interest is also responsible for driving the resonator into the nonlinear regime, and consequently the bifurcation points disappear at low force magnitudes. Thus, the limit of detection could be further improved by ensuring that the resonator is in the nonlinear regime even without the force of interest, for example, by employing parametric amplification.^{13,47} In parametric amplification, the response of an oscillator can be amplified by applying a pump signal at twice the linear resonant frequency, $\omega_{\rm p} \approx 2\omega_0$, namely,

$$\frac{d^2x}{dt^2} + (\gamma + \eta x^2)\frac{dx}{dt} + \omega_0^2(1 - \lambda \cos \omega_{\rm p} t)x = \frac{F \cos \omega t}{m_{\rm e}}$$
(10)

where λ denotes the amplitude of the parametric drive. When the drive amplitude is increased beyond a certain critical value λ_c , the resonator enters the regime of self-oscillations, even in the absence of a driving force. Such regime can be realized in TMDC resonators using capacitive actuation of the back gate (see ref 48). Further, under parametric amplification, TMDC

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resonators enter the nonlinear regime at relatively small RF voltages (-20 dBm).

To quantify the improvement in sensitivity with parametric amplification, we consider a force as resolvable if the effected change in the bifurcation frequency is greater than intrinsic fluctuations (δf) in the frequency,¹³ that is, $\kappa F_{\min} \geq \delta f$, where κ is the slope of the bifurcation frequency vs force curve (units of Hz/N). By assuming an extremely conservative value of $\delta f = 50$ Hz (for an integration time of 1 s, ref 29) and extracting $\kappa \approx$ 10^{17} Hz/N from the bifurcation diagram for Hopf bifurcation point H_2 , we estimate $F_{\min} = 500$ aN. Taken together, the estimates indicate that force sensitivity in the nonlinear regime can be significantly improved with parametric amplification. We would like to emphasize that this improvement in force sensitivity with a parametric drive is possible only in the nonlinear regime; in the linear regime of operation, a parametric drive would equally amplify both the resonator displacement as well as the thermal noise force, resulting in no net improvement.47

The qualitative implications from the results presented here on the nonlinear behavior of 2D WS₂ are rather general and in line with prior experimental and numerical studies. In macroscale plates, the strongly nonlinear behavior transitions from weakly nonlinear to eventual chaos via energy exchanges between internally resonant modes. The exact nature of IR (i.e., 1:1 or 1:2, etc.) depends on the energy of vibration and imperfections in the plate.⁴⁹ The wide frequency tunability (>10%, using optical or electrostatic means) in 2D nanoresonators should allow a three mode alignment and the engineering of more complex IR phenomena (e.g., 1:1:2 or 1:1:3), which are interesting from a fundamental viewpoint. We also note that the force sensitivity of nonlinear 2D nanoresonators can be further enhanced by increasing the sensitivity of the bifurcation points to the applied force (κ). A first step in this direction would be a systematic analysis of different kinds of IR in well-defined geometries (square or circular, with all boundaries clamped) and the bifurcation points therein. Because the mode shapes agree with theory in these regular geometries, a major advantage is that the coefficients in the RO model can be determined exactly using the formalism presented in Supporting Information S7. An order of magnitude improvement in κ would lead to a force sensitivity that is comparable with the best room-temperature force sensors (see Figure 6).





A hitherto unexplored application of nonlinear mode coupling in 2D nanoresonators is the synchronization of the coupled modes.⁴⁰ The major advantages of using 2D materials, vis-à-vis micromachined Si-based resonators, are (1) the coupled oscillators can be realized in the *same* resonator (the coupled modes shown in Figure 3, for instance), avoiding the need for complex fabrication, (2) the widely tunable resonant frequencies and geometric nonlinearity can be exploited to increase the synchronization range, and (3) the high frequencies involved facilitate signal processing applications in the RF region. Further, synchronization would in turn reduce the phase noise and improve the frequency stability in 2D nanoresonators.⁵⁰

In summary, we have demonstrated the principles for engineering a force sensor that utilizes geometric nonlinearity in a monolayer WS_2 nanoresonator. With the addition of a parametric drive, *attoNewton sensitivity* should be achievable at *room temperature*. We also showed that the room-temperature Q-factor (~1000) in the fabricated monolayer nanoresonator is an order of magnitude higher than prior reports on TMDC resonators. It would be interesting for future work to investigate the improvement of Q-factor at cryogenic temperatures and to identify the different sources of dissipation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano-lett.9b01442.

Device Fabrication; responsivity of the interferometer; Raman spectroscopy; modal analysis using ABAQUS and estimation of critical buckling load; accounting for spurious resonances from PZT disc; curve fitting of weakly nonlinear, frequency–response data in modes 1 and 2; derivation of the RO model from Föppl–von Kármán plate theory; method of scales solution to the RO model; and bifurcation analysis on mode 7 (PDF)

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Notes

The authors declare no competing financial interest.

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