

Surface Adsorbate Fluctuations and Noise in Nanoelectromechanical Systems

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Supporting Information

ABSTRACT: Physisorption on solid surfaces is important in both fundamental studies and technology. Adsorbates can also be critical for the performance of miniature electromechanical resonators and sensors. Advances in resonant nanoelectromechanical systems (NEMS), particularly mass sensitivity attaining the single-molecule level, make it possible to probe surface physics in a new regime, where a small number of adatoms cause a detectable frequency shift in a high quality factor (*Q*) NEMS resonator, and adsorbate fluctuations result in resonance fre-



quency noise. Here we report measurements and analysis of the kinetics and fluctuations of physisorbed xenon (Xe) atoms on a high-Q NEMS resonator vibrating at 190.5 MHz. The measured adsorption spectrum and frequency noise, combined with analytic modeling of surface diffusion and adsorption—desorption processes, suggest that diffusion dominates the observed excess noise. This study also reveals new power laws of frequency noise induced by diffusion, which could be important in other low-dimensional nanoscale systems.

KEYWORDS: Nanoelectromechanical systems (NEMS), surface adsorbate, adsorption-desorption, diffusion, resonator, noise

Physisorption of atomic or molecular species is ubiquitous in virtually all circumstances where solid-gas interfaces exist (e.g., catalysis, adhesion). In physics, directly observing and manipulating individual adsorbed atoms on ultraclean surfaces represents a significant experimental feat.¹ Engineering of atomic and molecular structures on certain surfaces also plays important roles in emerging applications including programmable selfassembly,^{2,3} nanoscale lithography,⁴ and nanotribology.⁵ For solid-state transducers, especially high-precision detectors and sensors, surface adsorbate can have important influences on device performance.⁶ Electromechanical resonators with high quality factor (Q), particularly quartz crystal microbalances (QCMs), are widely used to measure the mass, and other physical and electrochemical properties of the adsorbed layers, by monitoring changes of the QCM resonance frequency, Q factor, or amplitude.^{7,8} Resonant nanoelectromechanical systems (NEMS) sensors have recently demonstrated significantly enhanced mass sensitivities, down to the level of several, or even single, noble gas atoms, 9^{-11} representing an improvement up to 10¹²-fold over a conventional QCM. Such sensitivity levels provide the new opportunity of employing NEMS to directly probe the effects of surface adsorbate, on very small surface areas (typically of the order of only \sim 100 nm \times 1 μ m) and in the submonolayer regime. This approach can effectively complement and advance today's prevailing experimental techniques in surface science (e.g., spectroscopy and ellipsometry for surface thermodynamics, atomic force microscopy, scanning tunneling microscopy, quasielastic atom scattering for surface diffusion, and QCM for interfacial friction).¹² As an initial step toward this new paradigm, in this work we employ a high-Q, very high

frequency (VHF) NEMS resonator to investigate the behavior of physisorbed xenon (Xe) atoms, by performing precise measurements of the excess frequency noise that arises from statistical fluctuations of the adsorbed atoms on the resonator surface.

The core of our experimental apparatus (Figure 1a) consists of a NEMS resonator and a micro gas nozzle, well aligned and in close proximity. The NEMS resonator is a doubly clamped beam with dimensions 2.3 μ m (L) × 150 nm (w) × 100 nm (t). It is surface-nanomachined from a 100 nm silicon carbide (SiC) layer on silicon (Si) substrate, in a process detailed elsewhere.¹³ Metallization and passivation of the device consist of a 30 nm film of thermally evaporated aluminum (Al) capped with 5 nm titanium (Ti). At least part of the top Ti film upon exposure to air turns into native oxide (TiO₂),¹⁴ which is not only an excellent passivation layer but also a popular surface for biochemical species and a remarkable catalyst.^{15,16}

The device is electrically connected onto a dedicated chip carrier (with an embedded circuit board) and mechanically and thermally anchored to a massive sample stage (brass, gold plated). The sample stage is loaded into an ultrahigh-vacuum (UHV) cryostat, first pumped down at room temperature overnight (to $\sim 5 \times 10^{-7}$ Torr) and then cooled down in liquid helium (LHe). The device temperature is precisely measured and regulated by a calibrated on-board thermometer and a closed-loop temperature controller. We employ the magnetomotive scheme^{9,13} to excite the device into resonance and detect its response. The orientation of the magnetic field is such that the

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Figure 1. Adsorbates fluctuations on the surface of a VHF nanoelectromechanical resonator. (a) Illustration of an effusive atomic beam delivering a minute amount of Xe atoms onto the surface of a cold NEMS resonator. (b) Experimental system diagram and schematic of measurement circuits (with acronyms as detailed in Supporting Information). Shown is the closed-loop case; in case of open loop NEMS resonance detection, a network analyzer is connected between nodes (I) and (II). (c) Resonance response near $f_0 = 190.5$ MHz measured via reflectometric network analysis using magnetomotive transduction. The fit (red lines) gives a quality factor $Q \approx 5620$. (d) Calibrated mass responsivity of the device, $\Re \equiv |\partial f_0 / \partial M| = 0.99$ Hz/zg, measured in continuous mass-loading mode. Inset: scanning electron microscope (SEM) image of the VHF NEMS resonator; scale bar is 1 μ m. (e) Illustration of Xe atoms-NEMS interactions with atoms kinetics including adsorption—desorption (out-of-plane) and surface diffusion (in-plane).

out-of-plane flexural modes are excited; the calculated modal mass of the resonator is $M_{\rm eff} \approx 96$ fg. Figure 1c displays the measured response at a temperature $T \approx 58$ K, showing the sharp $(Q \approx 5620)$ fundamental-mode flexural resonance at a frequency $f_0 \approx 190.5$ MHz, corresponding to an effective stiffness $k_{\rm eff} \approx 145$ N/m. We have incorporated the NEMS resonance signal readout (Figure 1b) into a low-noise, frequency-modulation phase-locked loop (FM PLL) circuitry.^{9,17} This enables frequency locking and tracking of the resonance, hence real-time monitoring of the frequency variations that reflect the thermodynamic effects of adsorbates on the device surface. Prior to investigating the real-time behavior of surface adsorbates, we perform extensive tests and careful calibrations of the device response to a steadily increasing mass-load using the FM PLL technique. Figure 1d shows the calibration of the excellent mass responsivity of the device, $\mathcal{R} \equiv |\partial f_0 / \partial M| = 0.99$ Hz/zg [i.e., a resonance frequency shift of ~1 Hz per zg (10^{-21} g) of loaded mass].

Adsorbates are delivered to the NEMS resonator via a micro gas nozzle (Figure 1a) fed by a gas delivery system connected to a buffer chamber. The nozzle has a circular aperture of 300 μ m in diameter. It operates at low gas density as an effusive cell¹⁸ to produce an atomic beam of Xe impinging onto the NEMS surface. The cell's gas kinetics determines the Xe atoms impinging rate I (atoms per unit area per unit time), which can be converted into an effective pressure of the impinging gas phase above the device, via $p = I(2\pi m_{\rm Xe}k_{\rm B}T)^{1/2}$, where $k_{\rm B}$ is the Boltzmann constant and T is the device temperature. In this study, the calibrated constant flux delivered by the nozzle is $I = 2.7 \times 10^{17}$ atoms/(m² · s). This corresponds to a local effective pressure of $p = 6.8 \times 10^{-8}$ Torr at a device temperature T = 60 K. The cross section area of the device exposed to the well-aligned incoming atomic beam is $A_{\rm D} = Lw = 3.45 \times 10^{-13}$ m². A flat surface with this area can accommodate an ideal close-packed monolayer of $N_{\rm a,est} \approx 2.2 \times 10^{6}$ Xe atoms (with a Lennard-Jones diameter $d_{\rm Xe} \approx 0.41$ nm); $N_{\rm a,est}$ is thus the estimated number of available adsorption sites in the limit of an ideal, flat, and clean surface.

We choose to introduce Xe gas to the NEMS surface due to its relatively large atomic mass ($m_{Xe} = 131.3$ amu) and for its record as a classic prototype for studying physisorption in surface science.¹⁹ Existing Xe physisorption studies, however, are primarily limited to ideal, smooth, often specially treated metal surfaces,^{12,19} where a realistic description of the surface processes can be tackled in quantitative analyses or computer simulations.¹⁹ In ordinary and more practical situations involving nonideal, nonmetal, and disordered surfaces, understanding of adsorbates dynamics is particularly poor; quantitative studies and experimental approaches are greatly needed. On the surface of a resonating NEMS device, as sketched in Figure 1e, the behavior of Xe atoms is intriguing and may include both adsorption—desorption (out-of-plane) and



Figure 2. Surface kinetics of adsorbed Xe atoms on the NEMS device via resonant measurements. (a) Measured effective surface coverage (θ , left axis), along with the calculated surface occupation deviation (σ_{occ} right axis) based on measurement data. (b) Measured number of adsorbed atoms (data: blue circles) and the fit to the Arrhenius equation (dashed line). The fit yields $E_a \approx 63.1 \pm 0.23$ meV, and $\nu_a \approx (1.23 \pm 0.05) \times 10^4$ Hz. Inset: the characteristic correlation time assuming a pure adsorption—desorption process, $\tau_r = 1/(r_{ad} + r_{des}) = N/(sIA_D)$.

surface diffusion (in-plane) processes. Because conventional sensors lack the necessary sensitivity, no experiment has been carried out to investigate the contribution of these processes to resonance frequency fluctuations. Note that the frequency variations depend not only on the total number of adsorbed Xe atoms, but also on their distribution and fluctuations on the device surface (e.g., along the length of the device, in this study).

We first measure the adsorption spectrum N(T), i.e., number of adsorbed Xe atoms as a function of the regulated device temperature *T*. As the device is cooled down, N(T) increases. We call this process temperature-programmed adsorption (TPA, see Supporting Information). Such variations are precisely measured as the resonance frequency change $\Delta f_{\rm m}$ due to the mass-loading effect of the adsorbates, $\Delta f_{\rm m} = N(T) \mathcal{R} m_{\rm Xe}$. Figure 2 demonstrates the measured adsorption spectrum and effective surface overage in the temperature range $T \approx 58-80$ K. For a given incoming atom flux, the TPA process is highly repeatable and reversible, by regulating the device temperature back and forth in the appropriate temperature range. Unlike conventional Langmuir isotherm adsorption spectra (i.e., surface coverage versus pressure of the gas phase, at constant surface temperature), the data here are closer to isobars (number of adsorbates versus device temperature, at constant pressure of the gas phase).²⁰ We note that, in our measurements with the above value of the atom flux, when the device is cooled down to a temperature lower than $T \approx 56$ K, the FM-PLL consistently experiences such a sudden and steep frequency shift that it cannot sustain the locking and tracking of the NEMS resonance; we call this phenomenon "PLL runaway". We presume that the inflection point before the onset of this behavior represents an equivalent one-monolayer coverage, beyond which very fast accumulation of Xe atoms occur on the surface, leading to the socalled "wetting"-like behavior (i.e., abrupt formation of multilayer Xe films on device surface, which is dramatic and the associated frequency shift causes the PLL runaway).²¹ The measured frequency shift before PLL runaway is $\Delta f_{
m mon} pprox$ 590 kHz and the corresponding number of atoms is $N_{\rm a,exp} \approx 2.7 \times 10^6$. This value strongly supports our identification of PLL runaway with the completion of a monolayer. The slightly higher value (\sim 20%) compared to our prediction $N_{a,est}$ for an ideally flat surface is very reasonable considering the small but nonzero roughness of the

device surface, and the uncertainty in determining the device geometry and actual surface area. After repeatedly experiencing the PLL runaway and identifying the temperature at which it occurs, we focus our experiments in the range $T \approx 58-80$ K where the TPA is highly reversible and easily controllable.

The measured temperature-regulated surface coverage (Figure 2a), $\theta(T) = N(T)/N_{a,exp}$, helps to reveal the thermodynamics between the surface adsorbates and the gas phase. The adsorbing rate (atoms per unit area per second), $r_a = sI$, is a fraction of the atoms impinging rate, with the ratio s being the sticking coefficient. We take s = 1 as customarily done for Xe impinging on very cold surfaces.²² We model the temperature dependence of the rate of atoms leaving the surface as a thermally activated process following the Arrhenius law, that is, by a surface-detaching rate $r_{\rm d} = v_{\rm a} \exp(-E_{\rm a}/k_{\rm B}T)$, where $E_{\rm a}$ is the activation energy and $v_{\rm a}$ the attempt frequency. The steady-state balance between the gas phase and surface adsorbates dictates $r_a A_D = N r_d$, hence N(T) = $(sIA_{\rm D}/\nu_{\rm a})\exp(E_{\rm a}/k_{\rm B}T)$. As shown in Figure 2b, this simple model neatly fits the experimental data, yielding $E_a \approx 63.1 \text{ meV} (\pm 0.23)$ meV), and $v_a \approx 1.23 \times 10^4$ Hz($\pm 0.05 \times 10^4$ Hz). Note the v_a value from the fit is less reliable than the E_a value (v_a is more sensitive to fitting uncertainties, also depending on accurate determination of several experimental parameters). The extracted $E_{\rm a}$ is substantially smaller than the desorption energy reported for Xe on TiO₂ surfaces,^{23,24} in the range of $E_{\rm des} \sim 200-300$ meV (note that reported desorption energy data for Xe on crystalline metals or graphite are also in this range^{22,25,26}). We recall that atoms can leave the device surface via either desorption into vacuum or lateral diffusion (Figure 1d); both processes can be described by an Arrhenius equation, where however the activation energy of the diffusion process is generally much smaller. Indeed, we find the measured activation energy to be in good agreement with typical reported values of the lateral diffusion energy barrier $E_{\rm diff}$ of Xe on surfaces (e.g., $E_{\rm diff} \approx 52.1$ meV,²⁵ 54 meV,²⁷ moderately higher than the Xe–Xe binding energy, \sim 20 meV). This suggests that in our experiment the dynamic balance of surface adsorbates could be primarily between the adsorbing atoms from the nozzle and the atoms diffusing off the NEMS resonator.

To gain more insight beyond the above steady-state picture provided by the TPA and the initial surface kinetics analysis, we



Figure 3. Frequency instability induced by surface adsorbate fluctuations. Red circles are the measured Allan deviation in the case of constant flux of impinging Xe atoms and blue squares in the case of no Xe flux (system noise floor). In the range of $T \approx 58-80$ K, the excess frequency fluctuation due to adsorbed Xe atoms is clearly visible. The dashed lines are excess Allan deviation due to diffusion (violet with small triangles, see entries in Table 1, last column) and pure adsorption—desorption (dark gray), respectively. The solid lines are total instability levels calculated by adding in quadrature the system instability to that due to diffusion (violet with large triangles) and adsorption—desorption (dark gray), respectively. Allan deviation is measured with an averaging time $\tau_A = 1$ s to ensure adequately dense data with respect to the regulated temperature change. Data symbols are average values and error bars are standard deviations, each computed from ensembles of 500 raw data points.

Table 1. Diffusion Time Constants and Coefficients^a

$T(\mathbf{K})$	N(T)	$ au_{ m D}\left(s ight)$	$D(\text{cm}^2/\text{s})$	$\sigma_{\mathrm{A,diff}} \left(\tau_{\mathrm{A}} = 1 \mathrm{s} \right)$
58.0	2.19×10^6	0.114	1.18×10^{-8}	1.16×10^{-6}
59.2	1.71×10^6	0.064	2.12×10^{-8}	8.86×10^{-7}
60.7	1.27×10^6	0.055	2.44×10^{-8}	7.36×10^{-7}
63.4	$7.69 imes 10^5$	0.053	2.53×10^{-8}	5.69×10^{-7}
^{<i>a</i>} Data dei model) ai	rived from the ond Figure 2 (los	combined a ading curve	analysis in Figure e).	e 4 (diffusion noise

further carefully probe the fluctuations of the surface adsorbates by investigating the noise behavior of the VHF NEMS resonator while tuning the surface coverage via the device temperature. We measure the frequency instability of the NEMS resonator, quantified by the Allan deviation,²⁸ $\sigma_A(\tau_A) = [1/(2(N-1)) \Sigma_{i=1}^N((\overline{f}_{i+1} - \overline{f}_i)/f_0)^2]^{1/2}$, with \overline{f}_i being the average frequencies measured over an averaging time τ_A = 1 s by employing the FM-PLL technique. We first measure the baseline instability without the Xe flux (Allan deviation $\sigma_{A,sys}$); and then again with the Xe flux. Figure 3 shows the measured Allan deviation as a function of device temperature. The axis on the right shows the corresponding mass fluctuations (at zeptogram scale) set by the frequency instability. The instability measured without Xe flux represents the noise floor of the system and slightly decreases as temperature is lowered. This corresponds to the mild but steady increase of the Q factor that we observe upon cooling the device in this temperature range (see Supporting Information). With the introduction of surface adsorbates, excess instability arises, clearly noticeable in Figure 3 for T < 70 K. Also visible are a few small peaks distributed in the Allan deviation plot. The fact that these small peaks appear in the data with surface adsorbates

but not in the noise floor data suggests the existence of some interesting surface processes. We hypothesize that they may be related to the details of certain collective behavior of the adsorbed atoms, which could be dependent on roughness and structural irregularity of the surface (e.g., terraces, defects).

To understand the trend displayed by the measured data in Figure 3, we have developed analytic models for the two processes, adsorption-desorption and surface diffusion, that we consider relevant. We first examine the frequency noise due to adsorption-desorption. The adsorption-desorption noise model (see Supporting Information) deals with nondiffusive (i.e., laterally immobile) adsorbates at submonolayer coverage, in a fashion similar to an earlier work modeling surface contaminants on a quartz crystal resonator.²⁹ Figure 2a shows the measured effective surface coverage $\theta(T)$ and the surface occupation deviation $\sigma_{\rm occ} = [N(N_{\rm a} - N)]^{1/2}/N_{\rm a} = [\theta(1 - \theta)]^{1/2}$ (note that the surface occupation variance is $\sigma_{\rm occ}^2 \equiv r_{\rm ad}r_{\rm des}/(r_{\rm ad} + N)^2$). $(r_{\rm des})^2 = N(N_{\rm a} - N)/N_{\rm a}^2)$, where $N_{\rm a} = N_{\rm a,exp}$ is the number of adsorption sites, and $r_{\rm ad}$ and $r_{\rm des}$ are pure adsorption and desorption rates per adsorption site (in Hz), respectively. Clearly $\sigma_{\rm occ}$ has a maximum at $\theta = 1/2$. Assuming pure adsorptiondesorption, a characteristic correlation time can be defined for this process as $\tau_r = 1/(r_{ad} + r_{des}) = N/(sIA_D)$, which is computed using the measured data and is plotted in the inset of Figure 2b. This leads to the excess Allan deviation $\sigma_{
m A,ad-des}(au_{
m A})$ pprox $0.29\sigma_{\rm occ} \cdot (N_{\rm a})^{1/2} (m/M) (\tau_{\rm A}/\tau_{\rm r})^{1/2}$ in our experimental regime (see Supporting Information). Therefore, considering only adsorption-desorption noise and system noise, the total expected instability is $\sigma_{A,ad,total} = (\sigma_{A,sys}^2 + \sigma_{A,ad-des}^2)^{1/2}$. As displayed in Figure 3 (dark gray lines, note that $\sigma_{A,sys} \gg \sigma_{A,ad-des}$ hence $\sigma_{
m A,ad,total} \sim \sigma_{
m A,sys}$, hardly distinguishable), the estimated adsorption-desorption noise contribution is much lower even than the system noise floor, thus cannot account for the measured frequency instability in the presence of a Xe flux.

This predicted low adsorption—desorption noise and the above kinetics data ($E_a \sim E_{diff} \ll E_{des}$) suggest that desorption cannot be the dominant mechanism of Xe atoms leaving the device surface. Hence we have developed a model to analyze noise due to Xe atoms diffusion on the device surface (see details in Supporting Information). We compute the autocorrelation function $G(\tau)$ of the fractional frequency fluctuations $y(t) \equiv \delta f(t)/f_0$ induced by Xe atoms diffusion

$$G(\tau) = \frac{\langle \delta f(t) \cdot \delta f(t+\tau) \rangle}{{f_0}^2} \approx \frac{aN}{\sqrt{2\pi}} \left(\frac{m}{2M}\right)^2 \frac{1}{\sqrt{1+\tau/\tau_{\rm D}}} \quad (1)$$

with $\tau_{\rm D} = L^2/(2a^2D)$ being the characteristic diffusion time, a = 4.42844 is a constant determined by the shape of the fundamental mode of the device, and *M* is the device's total mass. The associated spectral density of fractional frequency fluctuation is

$$S_{y}(\omega) = \frac{aN}{\sqrt{2\pi}} \left(\frac{m}{M}\right)^{2} \int_{0}^{\infty} \frac{\cos(\omega\tau)}{\sqrt{1 + \tau/\tau_{\rm D}}} \,\mathrm{d}\tau$$
$$= \frac{aN}{2} \left(\frac{m}{M}\right)^{2} \cdot [\tau_{\rm D} \cdot \xi(\omega\tau_{\rm D})] \tag{2}$$

with $\xi(x) \equiv g(\sqrt{x})/\sqrt{x}$, and $g(\sqrt{x}) = \cos(x) + \sin(x) - 2C_1(\sqrt{x})\cos(x) - 2S_1(\sqrt{x})\sin(x)$, where $C_1(x)$ and $S_1(x)$ are the Fresnel integrals³⁰ (see details in Supporting Information), and $\omega = 2\pi f$ is the Fourier (offset) frequency.



Figure 4. Noise spectra of VHF NEMS resonator due to adsorbed Xe atoms. (a) Measured noise spectral density of fractional frequency fluctuation at T = 59.2 K with and without Xe atoms. (b) Excess noise spectral density of fractional frequency fluctuations due to Xe adsorbates, measured at four different temperatures. (c) Least-squares fit of the measured excess noise spectral density data to the predicted function based on the diffusion noise model (see Supporting Information) to extract diffusion time constants and coefficients at various temperatures (results collected in Table 1).

The measured noise spectra of fractional frequency fluctuations (Figure 4a) clearly demonstrate that there is excess noise due to surface Xe adsorbates. In the case of no Xe, the spectrum exhibits 1/fnoise at very low offset frequency ($\sim 0.1-2$ Hz) and flattens out above 2 Hz, indicating the instrumentation noise floor of the system. Figure 4b shows the adsorbate-induced excess noise spectrum, $S_{y,Xe}(\omega) = S_{y,total}(\omega) - S_{y,noXe}(\omega)$, extracted from such measurements performed at four different temperatures in the range of interest. We compute the diffusion time $\tau_{\rm D}$ by numerically fitting the measured spectral density data to eq 2, as shown in Figure 4c. The measurement and analysis yield $\tau_{\rm D}$ \sim 0.05-0.11s, and we obtain the corresponding diffusion coefficient $D = L^2/(2a^2\tau_D)$ to be in the range of $D \sim 1.2 - 2.5 \times 10^{-8} \text{cm}^2/\text{s}$ (we note this is at the same level as reported for Xe diffusion on some other surfaces²⁵). In Figure 4a and b, on the right axis we also show the corresponding adsorbed Xe mass fluctuation noise $S_m^{1/2}(\omega) = f_0 S_y^{1/2}(\omega) / \mathcal{R}$ set by the measured fractional frequency noise.

On the basis of the measured diffusion noise spectra, we estimate the excess Allan deviation due to diffusion, by integrating the fitted noise spectral density (see Supporting Information).³¹ In our experimental regime ($\tau_A \gg \tau_D$), we have $\sigma_{A,diff}(\tau_A) \approx 0.83 \cdot \sqrt{N}$ $(m/M)(\tau_D/\tau_A)^{1/4}$, and the total expected instability due to adsorbate diffusion is thus $\sigma_{A,diff,total} = (\sigma_{A,sys}^2 + \sigma_{A,diff}^2)^{1/2}$. As Figure 3 demonstrates, this model yields excellent agreement in both the temperature dependency and the magnitude of the experimental data. Contrasted with the predictions of the pure adsorption—desorption model, this provides strong support for a surface kinetics dominated by surface diffusion. Very interestingly and importantly, the combined measurements and analyses have revealed a noise process that has new power laws $S_y(\omega) \sim \omega^{\alpha}$ with $\alpha = -1/2$ and instability $\sigma_A(\tau_A) \sim \tau_A^{\beta}$ with $\beta = -1/4$, which to the best of our knowledge have never been documented nor considered in conventional oscillators and clocks (i.e., all known oscillator noise spectra power laws involve an integer exponent $\alpha = 0$, ± 1 , ± 2 ...).³² The revelation of these new weak power laws is possible because for the first time we are now able to tune a very sensitive VHF NEMS resonator to follow in real time the one-dimensional diffusion of adsorbate. It is important to point out the general character of our diffusion noise analysis, which could straightforwardly be extended by means of numerical simulations to account for the properties of different adsorption sites and/or different coverage regimes.

In conclusion, we have investigated the kinetics and fluctuations of surface adsorbate on a high-Q NEMS resonator vibrating at 190.5 MHz. By measuring and analyzing the temperatureprogrammed adsorption spectrum and device frequency fluctuations, we have found that adsorbate diffusion can dominate the observed excess noise. The sensitive measurements have also led to the discovery of new power laws of frequency noise in lowdimensional systems. These first measurements of surface adsorbates dynamics and fluctuations using resonant NEMS may have important implications for at least the following fundamental and technological applications: (i) The surface adsorbates-induced noise translates into equivalent mass fluctuations on the device surface; this imposes limits for the achievable sensitivity of frequency-shift based sensors. (ii) Following this study, it has been attempted to control and engineer adsorbates distribution (e.g., concentration gradient) and surface kinetics to enhance NEMS sensors' functions and performance.³³ (iii) The approach of using NEMS to probe submonolayer surface physics may prove to be a useful supplement to the existing surface science tools, particularly when combined with in situ techniques,³⁴ to pursue, for example, quantitative, real-time measurements of mesoscopic processes such as interfacial damping and atomic tribology.³⁵ Further engineering with innovative device geometries and resonant mode shapes can also help to explore nanoscale Chladni figures³⁶ that may be important for molecular-scale biodetection in fluids and other complicated surface phenomena. This study also opens new opportunities for pushing the limits by investigating surfaces of NEMS made of other emerging materials such as ultrathin nanowires,³⁷ nanotubes,³⁸ and atomically thin graphene sheets.³⁹

ASSOCIATED CONTENT

Supporting Information. Experimental system and techniques employed; supporting theoretical and modeling work. This material is available free of charge via the Internet at http: //pubs.acs.org.

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- Supplementary Information -

Surface Adsorbate Fluctuations and Noise

in Nanoelectromechanical Systems

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This article provides supplementary information to the main text of the title manuscript. We present in Section I the experimental system and techniques employed, along with supporting experimental data. In Section II we present the supporting theoretical and modeling work.

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I. Experimental Techniques and Supporting Data



1. Experimental System and Apparatus

Figure S1. Experimental apparatus. (a) Illustration (design drawing) of the ultra high vacuum (UHV) cryostat with various feedthroughs including very high and ultra high frequency (VHF/UHF) electronics and a gas delivery line. (b) Close-up view of the sample stage area, with VHF/UHF electronic connections, and micronozzle structure. (c) Illustration of the basic principle of the experiment, with the shutter-regulated micronozzle impinging Xe atoms toward the surface of a vibrating VHF NEMS resonator. (d) A picture of the gas nozzle-shutter assembly employed in this work.



Figure S2. The gas nozzle-shutter assembly. (1) Gas line (stainless steel gas tube, outside diameter 1/16", inside diameter 1/32") going to the micronozzle. This supplies the Xe gas flux from the buffer chamber (upstream and outside of the UHV cryostat chamber) to the gas nozzle. (2) Wires for heaters. (3) Mounting holes for heaters. The heaters are resistors, which are wired up and connected to a temperature controller (LakeShore 331, outside of the UHV chamber) for stabilizing the gas nozzle chamber temperature at 200K. (4) Micronozzle gas chamber (gold plated brass). (5) Base/backbone plate (stainless steel). (6) Insulating (Delrin) mounting block for the coil and contacts, and for the counter balance. (7) Counter balance (brass mass). (8) Pivot for the swing arm. (9) Insulating (Delrin) block for contacts and wires. (10) Swing arm (G10 plastic). (11) Close sensing contact (copper-copper). (12) Main gas chamber and house for heaters [gold plated brass, fit and sealed to (4)]. The connection between this main gas chamber block to the base plate (5) has been made via 4 pads with small contact surface, to limit the unnecessary heat transfer to the base plate. (13) Shutter. (14) Micronozzle aperture. (15) Nozzle disk [fit and sealed to (4), disks were made available with different aperture sizes, and we tested disks with aperture diameters of 30, 100, and 300µm]. (16) Coil for electromagnetic actuation of the shutter. The nozzle-shutter assembly is vertically mounted in the UHV cryostat in a strong vertical magnetic field; a small amount of electrical current applied to this coil induces a horizontal magnetic field, hence the electromagnetic actuation and deflection of the swing arm (10) with respect to the pivot (8). (17) Thin wires for sensing contacts. (18) Open sensing contact (copper-copper). (19) Pins for feedthrough wiring of heater and thermometer. (20) Insulating (Delrin) block for contacts and pins. (21) Diode thermometer (LakeShore DT-470) and wires. The scale bar is 1cm.

2. NEMS Resonance Readout



Figure S3. Schematic of the open-loop VHF NEMS resonance signal transduction scheme. The VHF NEMS resonance excitation and detection of electromechanical response are based on magnetomotive transduction in a strong magnetic field (*B*). The two-port measurement uses a HF/VHF network analyzer (HP3577A). The readout circuit is a reflectrometry scheme using a directional coupler (CPL) and a low-noise amplifier (LNA).

3. Real-Time Resonance Frequency Locking and Tracking, and the Noise Measurements



Figure S4. Diagram of the experimental setup and the measurement system. The gas delivery sub-system include Xe gas source (lecture bottle cylinder), a buffer chamber and a specialized gas feedthrough line leading to the micronozzle which is positioned and aligned in the vicinity of the NEMS device; it also includes various accessories such as pressure gauges, regulators, and various coarse and fine tuning control valves. The electromechanical shutter is controlled by a relay circuit. For real-time resonance frequency locking and tracking, the NEMS resonance readout circuit (described in Figure S2) is embedded into a closed loop with feedback, which consists of a frequency-modulation phase-locked loop (FM-PLL).¹ VCO: voltage controlled oscillator, BPF: band-pass filter. As shown, time-domain frequency instability is measured by using a high-precision frequency counter. Noise spectra are measured by using a dynamical signal and noise analyzer. Also, as shown in Figure S2, nodes (I) and (II) here in Figure S3 indicate the alternative configuration for switching back to the open-loop resonance detection circuit.

191.6 Measured Data (No Xe) 191.2 ∆f_{mon}=590kHz *←*T Dependence (No Xe) 0.6 Fit of $f \sim T$ Dependence Measured Data (With Xe) 191.4 Frequency Shift (MHz) 0.5 Frequency (MHz) Frequency (MHz) 191.0 191.2 0.4 191.0 0.3 190.8 Data out of Loc 190.8 0.2 Data out of 190.6 190.6 0.1 PLL Runawa 190.4 0.0 190.4 80 80 70 75 55 60 75 85 55 60 85 20 30 40 50 60 70 80 90 50 65 70 50 65 (b) (c) (a) 7 (K) 7 (K) 7 (K)

4. Temperature-Programmed Adsorption (TPA)

Figure S5. A typical set of measured data for the demonstration of temperature-programmed adsorption (TPA). (a) A fresh measurement of resonance frequency as a function of device temperature when there is no impingement of Xe gas at all. This measurement gives a baseline $f \sim T$ dependence as shown by the fit to the data. (b) Measured frequency trace raw data when there is impingement of Xe gas flux and hence temperature-programmed adsorption. The raw data of measured resonance frequency tracked by the FM-PLL is plotted together with the previously calibrated $f \sim T$ dependence. Here the measured f as a function of T is due to both the pure temperature dependence and the loading of surface adsorbates (Xe atoms). Note the onset of the 'PLL runaway' near $T \approx 56$ K. Beyond this point, the data trace in the lower temperature range is out of lock and not meaningful. In fact, each time this happens, we heat up the device to restore to the fresh surface condition. The Xe gas flux is stopped. We switch to the open-loop resonance detection circuit scheme (Figure S3) with network analyzer to find the NEMS resonance signal again, and we manually bring the FM-PLL back into lock.

5. *Q* Factor Temperature Dependence



Figure S6. Measured device quality factor (Q) as a function of device temperature. No Xe gas impingement in this measurement. There is a mild but steady Q increase as T is decreased in the range of 20~80K. A similar tendency has also been observed in other VHF/UHF NEMS resonators.² Here this measurement verifies the weak temperature dependence of Q. This is also in good qualitative consistence with the observed mild reduction of frequency instability (noise floor without Xe gas flux) as the temperature is decreased (see Figure 3 in main text), because theoretically the frequency instability should be proportional to the inverse of Q.³

II. Theoretical Analyses and Modeling

1. Noise due to Surface Diffusion

Here we describe our treatment of the noise process due to adsorbates diffusion on the surface of NEMS device.



Figure S7. (a) Schematic illustration of mode-shape and location-dependent mass loading response for a doubly clamped beam. (b) The square of normalized mode shape and its optimized Gaussian approximation.

For the doubly clamped beam NEMS resonator operating in its fundamental flexural mode, we first consider its mode shape and the position-dependent frequency shift induced by mass loading effect of an adsorbed atom. As illustrated in Figure S7, the *normalized* mode shape is

$$u(x) = 0.8827 \cos kx + 0.1173 \cosh kx, \qquad (S1)$$

for $x \in [-L/2, L/2]$, with u(0)=1, k=4.73/L and L being the beam length.⁴ For our interest in developing an analytic approach, we have found that approximating the square of the normalized mode shape $[u(x)]^2$ with a Gaussian function and extending the integration interval from [-L/2, L/2] to $(-\infty, \infty)$ considerably simplifies the calculations we present here. Minimizing the 'distance' norm between the two functions by means of a least square technique, we have found

an excellent approximation $[u(x)]^2 = \exp[-(ax/L)^2]$ (see Figure S10) with an optimized parameter *a*=4.42844.

When an atom (or molecule) of mass *m* lands at position *x* on the surface of device (with total mass *M*), and assuming the added mass only changes the kinetic energy but not the potential (flexural) energy of the device, we have the fractional frequency variation (with respect to the initial reference frequency f_0 or ω_0),

$$\frac{\delta f}{f_0} = \frac{\delta \omega}{\omega_0} = -\frac{1}{2} \frac{m}{M} \frac{|u(x)|^2}{\frac{1}{L} \int_{-L/2}^{L/2} [u(x)]^2 dx} \approx -\frac{1}{2} \frac{m}{M_{eff}} |u(x)|^2.$$
(S2)

Here we have $M_{eff} = M \cdot \frac{1}{L} \int_{-L/2}^{L/2} [u(x)]^2 dx \approx \frac{\sqrt{\pi}}{a} M$, which yields the effective modal mass $M_{eff} = 0.40M$. (The effective mass is 0.397*M* if we use the original solution, confirming that the Gaussian approximation is excellent with discrepancy <1%). For a quasi-continuous distribution of adsorbates mass over the length of the NEMS device, we can simply replace $m \cdot |u(x)|^2$ with $mC(x) \cdot |u(x)|^2$, with C(x) being the concentration of the adsorbed atoms (number density per unit length).

We consider pure diffusion of one species in one dimension. The concentration fluctuation $\delta C(x,t)$ obeys the following diffusion equation,

$$\frac{\partial \partial C(x,t)}{\partial t} = D \frac{\partial^2 \partial C(x,t)}{\partial x^2}.$$
(S3)

The Fourier transform $\mathcal{F}_{k}[\partial C(x,t)] = \widetilde{C}(k,t)$ obeys

$$\frac{\partial \widetilde{C}(k,t)}{\partial t} = -Dk^2 \widetilde{C}(k,t), \tag{S4}$$

and hence

$$\widetilde{C}(k,t) = e^{-Dk^2 t} \widetilde{C}(k,0), \tag{S5}$$

where k is the wave number.

The device frequency fluctuation due to the mass fluctuation is given by

$$y(t) = \frac{\delta f(t)}{f_0} = -\frac{1}{2} \frac{m}{M} \frac{\int_{-L/2}^{L/2} [u(x)]^2 \, \delta C(x, t) dx}{\frac{1}{L} \int_{-L/2}^{L/2} [u(x)]^2 \, dx} \approx -\frac{1}{2} \frac{a}{\sqrt{\pi}} \frac{m}{M} \int_{-L/2}^{L/2} \delta C(x, t) [u(x)]^2 \, dx \,. \tag{S6}$$

We can now calculate the autocorrelation function of the fractional frequency fluctuations due to surface diffusion,

$$G(\tau) = \frac{\langle \delta f(t) \cdot \delta f(t+\tau) \rangle}{f_0^2}$$

= $\left(\frac{m}{2M}\right)^2 \frac{a^2}{\pi} \int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} u^2(x) u^2(x') \langle \delta C(x,t+\tau) \cdot \delta C(x',t) \rangle dx',$ (S7)
= $\left(\frac{m}{2M}\right)^2 \frac{a^2}{\pi} \int_{-L/2}^{L/2} dx \int_{-L/2}^{L/2} u^2(x) u^2(x') \phi(x,x',\tau) dx'$

where $\phi(x, x', \tau) = \langle \delta C(x, t + \tau) \cdot \delta C(x', t) \rangle$.

Employing Fourier transform techniques (recall the classical application of Fourier transform and its properties to solving diffusion-type differential equations),⁵ we calculate and carry out transforms explicitly to yield

$$\phi(x, x', \tau) = \frac{N}{L} \frac{1}{2\sqrt{\pi D\tau}} \exp\left[-\frac{(x-x')^2}{4D\tau}\right],$$
(S8)

in which N is the average total number of adsorbed atoms on the device surface. Further, we use the above result for $\phi(x, x', \tau)$ to calculate the double integral in Eq. (S7), again with the integration limits extended to $(-\infty, \infty)$, and we obtain⁶

$$G(\tau) = NL \left(\frac{m}{2M}\right)^2 \frac{a}{\sqrt{\pi}} \frac{1}{\sqrt{2L^2 + 4a^2 D\tau}}$$

$$= \frac{aN}{\sqrt{2\pi}} \left(\frac{m}{2M}\right)^2 \frac{1}{\sqrt{1 + \tau/\tau_D}}$$
(S9)

where we define the characteristic diffusion time $\tau_D = L^2/(2a^2D)$. The advantage of being able to carry out analytically the calculation of the autocorrelation function well justifies the Gaussian approximation of the mode shape. It is interesting and worth noting that $G(\tau)$ is of the form $(1 + \tau/\tau_D)^{-d/2}$ with d=1, the dimensionality of the problem in the present study. In fact, we note that our analysis here is in good analogy to the well-known theory of fluorescence correlation spectroscopy (FCS),^{7,8} in which the correlation function scales as $(1 + \tau/\tau_D)^{-1}$, consistent with the dimension (d=2) of the FCS process.

Now we employ the Wiener-Khinchin theorem⁹ to obtain the corresponding double-sided (DS) spectral density of fractional frequency noise,

$$S_{y,DS}(\omega) = \int_{-\infty}^{\infty} G(\tau) e^{-i\omega\tau} d\tau = \int_{-\infty}^{\infty} G(\tau) \cos(\omega\tau) d\tau$$

$$= aN \left(\frac{m}{2M}\right)^2 \sqrt{\frac{2}{\pi}} \cdot \int_{0}^{\infty} \frac{\cos(\omega\tau)}{\sqrt{1 + \tau/\tau_D}} d\tau$$

$$= aN \left(\frac{m}{2M}\right)^2 \sqrt{\frac{2}{\pi}} \cdot \left[\sqrt{\frac{\pi}{2}} \cdot \tau_D \frac{g(\sqrt{\omega\tau_D})}{\sqrt{\omega\tau_D}}\right]$$

$$= \frac{aN}{4} \left(\frac{m}{M}\right)^2 \cdot [\tau_D \xi(\omega\tau_D)]$$
 (S10a)

The more useful single-sided (SS) spectral density (folding the negative Fourier frequency part over onto the positive side, corresponding to practical measurements)^{10,11} is thus

$$S_{y}(\omega) = 2S_{y,DS}(\omega) = \frac{aN}{2} \left(\frac{m}{M}\right)^{2} \cdot [\tau_{D}\xi(\omega\tau_{D})].$$
(S10b)

In the above calculation the integral for a combined trigonometric-algebraic function⁶ leads to $\xi(x) = \frac{g(\sqrt{x})}{\sqrt{x}}$, $g(\sqrt{x}) = \cos(x) + \sin(x) - 2C_1(\sqrt{x})\cos(x) - 2S_1(\sqrt{x})\sin(x)$; with $C_1(x)$ and $S_1(x)$

the Fresnel integrals,³ defined by

$$C_1(x) = \sqrt{\frac{2}{\pi}} \int_0^x \cos(u^2) du , \qquad (S11a)$$

$$S_1(x) = \sqrt{\frac{2}{\pi}} \int_0^x \sin(u^2) du \,. \tag{S11b}$$



Figure S8. Plot of the function $\xi(x)$ with its asymptotic functions: (i) $x^{-1/2}$ for $x \ll 1$, and (ii) $(2\pi)^{-1/2}x^{-2}$ for $x \gg 1$.

There exist two asymptotic functions of particular interest for the $\xi(x)$ in the spectral density:

(i) for $x \ll 1$, $\xi(x) \approx 1/\sqrt{x}$; and (ii) for $x \gg 1$, $\xi(x) \approx \frac{1}{\sqrt{2\pi \cdot x^2}}$. In Figure S8 we plot the function $\xi(x) \equiv \frac{g(\sqrt{x})}{\sqrt{x}}$ and its asymptotic approximations. These lead to the following results:

(i) For $\omega \ll 1/\tau_D$ (*i.e.*, $\omega \tau_D \ll 1$), the spectral density of fractional frequency fluctuations is

$$S_{y}(\omega) = \frac{aN}{2} \left(\frac{m}{M}\right)^{2} \sqrt{\frac{\tau_{D}}{\omega}}.$$
(S12)

(ii) For $\omega >> 1/\tau_D$ (*i.e.*, $\omega \tau_D >> 1$), the spectral density is

$$S_{y}(\omega) = \frac{aN}{2\sqrt{2\pi}} \left(\frac{m}{M}\right)^{2} \frac{1}{\omega^{2}\tau_{D}}.$$
(S13)

Here we shall clarify and reiterate that these are the *excess* fractional frequency fluctuations spectral densities due to surface adsorbate diffusion. These excess spectral densities are thus additive to other uncorrelated noise spectral densities.

We now turn to discuss the modeling of the time-domain frequency instability. We can convert from the fractional frequency fluctuations spectral density to the frequency instability, Allan *variance*, as follows,^{12,13}

$$\sigma_A^2(\tau_A) = \frac{4}{\pi} \int_0^\infty \frac{\sin^4(\omega \tau_A/2)}{(\omega \tau_A)^2} S_y(\omega) d\omega \,. \tag{S14}$$

Here τ_A is the averaging time and again $S_y(\omega)$ is the single-sided spectral density. τ_A is a characteristic time scale in practical measurements. Specifically, in our time-domain frequency stability measurements, τ_A is the time interval during which each averaged frequency data sample is acquired by the frequency counter. The integral essentially takes all the sideband noise contribution, with an equivalent frequency-domain transfer function set by τ_A . Depending on the time scales and employing the asymptotic functions of $S_y(\omega)$, we have the following cases with interesting power-law relationships:

(i) In the limit of slow measurement, $\tau_A \gg \tau_D$ ($\omega \tau_D \ll \omega \tau_A$), the noise spectrum is dominated by the small-x asymptotic function $\xi(x) \equiv g(\sqrt{x})/\sqrt{x} = 1/\sqrt{x}$ and Eq. (S12), hence

$$\sigma_A^2(\tau_A) = \frac{2aN}{\pi} \left(\frac{m}{M}\right)^2 \left(\frac{\tau_D}{\tau_A}\right)^{\frac{1}{2}} \cdot \int_0^\infty \frac{\sin^4(\omega\tau_A/2)}{(\omega\tau_A)^2} \sqrt{\frac{1}{\omega\tau_A}} d(\omega\tau_A),$$
(S15a)

By computing the Fresnel integrals, this yields the Allan variance

$$\sigma_A^2(\tau_A) \approx 0.6899 \cdot N \left(\frac{m}{M}\right)^2 \left(\frac{\tau_D}{\tau_A}\right)^{\frac{1}{2}},\tag{S15b}$$

and the Allan deviation

$$\sigma_A(\tau_A) \approx 0.83 \cdot \sqrt{N} \left(\frac{m}{M}\right) \left(\frac{\tau_D}{\tau_A}\right)^{\frac{1}{4}}.$$
 (S15c)

(ii) In the limit of very fast measurement, $\tau_A \ll \tau_D$ ($\omega \tau_D \gg \omega \tau_A$), and the noise spectrum is dominated by the large-*x* asymptotic $\xi(x) \equiv g(\sqrt{x})/\sqrt{x} = 1/(\sqrt{2\pi}x^2)$, and with Eq. (S13), thus we have

$$\sigma_A^2(\tau_A) \approx 0.2610 \cdot N \left(\frac{m}{M}\right)^2 \left(\frac{\tau_A}{\tau_D}\right),$$
 (S16a)

$$\sigma_A(\tau_A) \approx 0.51 \cdot \sqrt{N} \left(\frac{m}{M}\right) \left(\frac{\tau_A}{\tau_D}\right)^{\frac{1}{2}}$$
(S16b)

In brief summary, we have two major observations here. First, the Allan deviation is proportional to \sqrt{N} (*N*=*N*(*T*) is the number of atoms on surface, measured as a function of temperature *T*) and mass ratio (*m*/*M*). Second, in different regimes the Allan deviation exhibits distinct approximate power-law dependences $(\tau_A/\tau_D)^{\beta}$ with $\beta = -1/4$, and 1/2.

Most interesting and important, in the regime of $\omega \tau_D \ll 1$, the noise spectrum of fractional frequency fluctuation, $S_y(\omega)$, due to one-dimensional diffusion of adsorbates on surface, has power law $S_y(\omega) \sim \omega^{\alpha}$ with $\alpha = -1/2$ and correspondingly a frequency instability that scales as

 $(\tau_A/\tau_D)^{\beta}$ with $\beta = -1/4$. These power laws are new; they represent the revelation of a new noise process that may become noticeable and important in NEMS resonators and oscillators, and possibly other low-dimension systems. In fact, as we examine the phase noise and frequency stability in various conventional oscillators or clocks (especially those based on electromechanical resonators), the known noise processes are thus far limited to power laws with α in integers ($\alpha = 0, \pm 1, \pm 2$) and β as low as $\pm 1/2$.¹⁴ In the conventional much bulkier, macroscopic electromechanical resonators, the subtlety of surface diffusion noise processes and the relatively weak power laws ($\alpha = -1/2$ and $\beta = -1/4$) are simply not captured due to the device size and often the dominance of other noise processes (those with stronger power laws).

Our measurements of the Allan deviation are in regime (i) as described by Eq. (S15), as also discussed in the main text. We note that Allan variance given by Eqs. (S15)-(S18) is the *excess* variance due to the modeled surface diffusion process. The total frequency instability is thus $\sigma_{A,total}^{2}(\tau_{A}) = \sigma_{A,no-gas}^{2}(\tau_{A}) + \sigma_{A}^{2}(\tau_{A}) \text{ or } \sigma_{A,total}(\tau_{A}) = \sqrt{\sigma_{A,no-gas}^{2}(\tau_{A}) + \sigma_{A}^{2}(\tau_{A})}.$

2. Noise due to Adsorption-Desorption

Here we describe the non-diffusive, pure adsorption-desorption model for surface adsorbates in the sub-monolayer regime. The surface is assumed to be saturated at the completion of the first monolayer, or implicitly equivalent, the atom-atom interaction is assumed to be much weaker than the atom-surface interaction so that only one monolayer can be accommodated. Non-diffusive means the adsorbates are laterally immobile on the surface. These conditions are essentially the same as in the analysis performed by Yong and Vig in dealing with adsorptive-desorptive contaminates on double-side surfaces of quartz crystal resonators.¹⁵

We consider a NEMS device with area A_D exposed to a constant impinging flux I for the incoming gas atoms (here I has the unit of number of atoms per unit area per sec). The number of available adsorption sites on the surface is N_a (ideally $N_a=A_D/A_{ad}$, with A_{ad} the area an adsorbate atom would occupy). The adsorption rate (number of atoms/sec) for the whole exposed area on the device is sIA_D , where s is the sticking probability or sticking coefficient for an incoming atom. Hence for each adsorption site the adsorption rate (in 1/sec, or Hz) is

$$r_{ad} = sI \cdot \frac{A_D}{N_a}.$$
(S19)

Each adsorption site can only accommodate a single atom. Once bound on the surface, the atom may attempt to leave the surface only by desorption (no diffusion). The desorption rate at each site (in Hz) is

$$r_{des} = v_{des} \exp\left(-\frac{E_{des}}{k_B T}\right).$$
(S20)

Here v_{des} is the attempt frequency, and E_{des} is the desorption energy or binding energy, which is the energy the atom is required to gain in order to get free from its adsorption site. When we have N ($N \le N_a$) atoms on the surface, the rate of atom desorption is $r_{des}N$. At the same time, there are ($N_a - N$) available adsorption sites (again, each adsorption site only accommodates one atom), and the rate of atoms being adsorbed is $r_{ad}(N_a - N)$. Therefore, at a given temperature with a surface number coverage N, the steady-state balance is $r_{ad}(N_a - N) = r_{des}N$, which leads to

$$N = \frac{r_{ad}}{r_{ad} + r_{des}} N_a \,. \tag{S21}$$

As we only consider one species of adsorbates and one type of adsorption site, we define an empirical single correlation time τ_r of the adsorption-desorption cycle, $\tau_r = 1/(r_{ad} + r_{des})$, which is essentially the Mathiessen's rule.¹⁶ Hence from Eqs. (S19) and (S21), we have $\tau_r = N/(sIA_D)$.

Assume that the adsorption-desorption induced frequency change on each site is constant, $\delta\omega = -(m/2M)\omega_0$. By examining the frequency variations due to the Bernoulli-type stochastic process associated with each site and the whole ensemble,¹⁵ we obtain the variance of the frequency fluctuation due to adsorption-desorption,

$$\sigma^2 = \frac{r_{ad}r_{des}}{\left(r_{ad} + r_{des}\right)^2} \left(\delta\omega\right)^2 N_a = \sigma_{occ}^2 \left(\delta\omega\right)^2 N_a, \qquad (S22a)$$

with

$$\sigma_{occ}^{2} \equiv \frac{r_{ad}r_{des}}{(r_{ad} + r_{des})^{2}} = \frac{N(N_{a} - N)}{N_{a}^{2}},$$
(S22b)

which we define as the occupation variance. It is evident that the occupation variance assumes its maximum $\sigma_{occ}^2 = 1/2$ when $N = N_a/2$ (*i.e.*, at half coverage); and it vanishes at both N=0 and $N=N_a$ (*i.e.*, zero coverage and completion of one monolayer, respectively). As N and the coverage are generally functions of temperature and pressure, so is the occupation variance. Similar to Yong and Vig¹⁵, the autocorrelation function of frequency fluctuations induced by the adsorption-desorption is

$$G_{ad-des}(\tau) = \sigma^2 \exp(-|\tau|/\tau_r).$$
(S23)

The fractional frequency fluctuations spectrum is thus (again using Wiener-Khinchin theorem)

$$S_{y}(\omega) = \frac{2\sigma_{occ}^{2}N_{a}\tau_{r}}{1+(\omega\tau_{r})^{2}} \left(\frac{m}{2M}\right)^{2}.$$
(S24)

The excess Allan variance due to adsorption-desorption noise is (similar to Eq. (S14))

$$\sigma_A^2(\tau_A) = \frac{2}{\pi} \sigma_{occ}^2 N_a \left(\frac{m}{M}\right)^2 \tau_r \int_0^\infty \frac{\sin^4(\omega \tau_A/2)}{(\omega \tau_A)^2} \cdot \frac{1}{1 + (\omega \tau_r)^2} d\omega, \qquad (S25)$$

We analyze and obtain the following cases:

(i) In the limit of $\tau_A \gg \tau_r$ ($\omega \tau_r \ll 1$), we have

$$\sigma_A^2(\tau_A) = \frac{1}{4} \sigma_{occ}^2 N_a \left(\frac{m}{M}\right)^2 \frac{\tau_r}{\tau_A},$$
(S26a)

$$\sigma_A(\tau_A) = \frac{1}{2} \sigma_{occ} \sqrt{N_a} \left(\frac{m}{M}\right) \left(\frac{\tau_r}{\tau_A}\right)^{\frac{1}{2}}.$$
(S26b)

(ii) In the limit of
$$\tau_A \ll \tau_r (\omega \tau_r \gg 1)$$
, we have

$$\sigma_A^2(\tau_A) = \frac{1}{12} \sigma_{occ}^2 N_a \left(\frac{m}{M}\right)^2 \frac{\tau_A}{\tau_r}$$
(S27a)

$$\sigma_A(\tau_A) = \frac{1}{2\sqrt{3}} \sigma_{occ} \sqrt{N_a} \left(\frac{m}{M}\right) \left(\frac{\tau_A}{\tau_r}\right)^{\frac{1}{2}}.$$
(S27b)

We see that in all cases the excess Allan deviation is proportional to the occupation deviation σ_{occ} , the square root of total number of sites N_a , and the mass ratio (*m/M*). In slow measurements (averaging time considerably longer than the characteristic time of the adsorption-desorption process), the Allan deviation scales with $1/\sqrt{\tau_A}$, similar to that of a thermal noise dominated process. If the measurements can be done much faster than the atoms' adsorption-desorption cycles, the instability will scale with $\sqrt{\tau_A}$, as in the case dominated by random-walk

frequency modulations.¹⁴ Of course, in all cases, the occupation variance σ_{occ} takes into account the effects of the physical parameters (*e.g.*, temperature, pressure, *etc.*) upon the surface.

Note we have assumed that the amount of frequency change due to adsorption-desorption event on each site is constant. If we consider the position dependency due to the mode shape, we ought to convert the picture of two-dimensional discrete adsorption sites to accommodate the one-dimensional continuous mode shape. We can define the adsorption site density per unit length, N_a/L , and integrate over the beam length to calculate the frequency fluctuation variance $\sigma^2 = \sigma_{occ}^2 \omega_0^2 \int_{-L/2}^{L/2} (N_a/L) (m/2M)^2 |u(x)|^4 dx$, and hence the variance in Eq. (S21a), and Eqs. (S24)–(S27) should be corrected by a numerical factor of $1/L \int_{-L/2}^{L/2} (m/2M)^2 |u(x)|^4 dx \approx 0.29$ (and a factor of 0.54 for the Allan deviation).

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