Out-of-Plane Electromechanical Response of Monolayer Molybdenum Disulfide Measured by Piezoresponse Force Microscopy

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ABSTRACT: Two-dimensional (2D) materials have recently been theoretically predicted and experimentally confirmed to exhibit electromechanical coupling. Specifically, monolayer and few-layer molybdenum disulfide (MoS$_2$) have been measured to be piezoelectric within the plane of their atoms. This work demonstrates and quantifies a nonzero out-of-plane electromechanical response of monolayer MoS$_2$ and discusses its possible origins. A piezoresponse force microscope was used to measure the out-of-plane deformation of monolayer MoS$_2$ on Au/Si and Al$_2$O$_3$/Si substrates. Using a vectorial background subtraction technique, we estimate the effective out-of-plane piezoelectric coefficient, $d_{33}^e$, for monolayer MoS$_2$ to be 1.03 ± 0.22 pm/V when measured on the Au/Si substrate and 1.35 ± 0.24 pm/V when measured on Al$_2$O$_3$/Si. This is on the same order as the in-plane coefficient $d_{11}$, reported for monolayer MoS$_2$. Interpreting the out-of-plane response as a flexoelectric response, the effective flexoelectric coefficient, $\mu_{33}$, is estimated to be 0.10 nC/m. Analysis has ruled out the possibility of elastic and electrostatic forces contributing to the measured electromechanical response. X-ray photoelectron spectroscopy detected some contaminants on both MoS$_2$ and its substrate, but the background subtraction technique is expected to remove major contributions from the unwanted contaminants. These measurements provide evidence that monolayer MoS$_2$ exhibits an out-of-plane electromechanical response and our analysis offers estimates of the effective piezoelectric and flexoelectric coefficients.

KEYWORDS: MoS$_2$, electromechanical coupling, flexoelectricity, piezoelectricity, piezoresponse force microscopy.
Piezoelectricity is, however, only one type of electromechanical response possible in crystal lattices. In flexoelectricity, polarization arises from strain gradients as opposed to uniform strain. Thus, a fourth-order tensor describes flexoelectricity, while a third-order tensor describes piezoelectricity. With an even-rank tensor, flexoelectricity is present in every crystal class. Despite this, flexoelectricity has been seldom studied because the strain gradients necessary to cause a noticeable change in polarization in macro-scale materials requires very large strains that can fracture the material. However, in nanoscale materials even small strain can cause large gradients to form.

Investigations of flexoelectricity in 2D materials have mainly focused on either carbon systems or hexagonal boron nitride. These works were performed from the modeling side but since 2D materials are the ultimate nanoscale material and can have large strain gradients they can offer a platform for experimental studies of flexoelectricity.

Another reason for the lack of experimental study of flexoelectricity is because piezoelectricity and flexoelectricity are difficult to isolate from each other. We propose a solution to this problem by utilizing the symmetry of MoS₂ and other TMDs. Their crystal class, $D_{6h} (6m2)$, results in a flexoelectric tensor that has nonzero coefficients in the out-of-plane direction, whereas all out-of-plane piezoelectric coefficients are zero. Flexoelectricity in 2D materials can therefore be studied experimentally if an out-of-plane electromechanical response in MoS₂ is measurable. There have been a few notable experimental studies investigating out-of-plane electromechanical properties of 2D materials, namely on graphene-nitride nanosheets with nonsymmetric holes and graphene forming bonds to the underlying SiO₂ substrate. Neither study suggested an estimate for a flexoelectric coefficient. Interestingly, because 2D materials are essentially only a surface, it becomes ambiguous whether out-of-plane electromechanical effects caused by spatial gradients should be referred to as flexoelectricity or surface piezoelectricity. Nevertheless, it is referred to as a flexoelectric response here.

Piezoresponse force microscope (PFM) is used to measure out-of-plane electromechanical deformation resulting from an applied out-of-plane electric field. Because an electric field is inducing a strain, this is referred to as the converse piezoelectric effect; the direct piezoelectric effect is a strain inducing a polarization. In the measurement, an atomic force microscope (AFM) with a conductive probe is used to apply an electric field through the test material by applying a drive voltage, $V_{drive}$, between the tip and substrate. If there is electromechanical coupling in the material, the AFM tip will be deflected by the expansion and contraction of the material. A lock-in amplifier is used to measure both the amplitude and phase of the response while simultaneously measuring surface topography. (See Figure S1 in the Supporting Information for details regarding the PFM measurement and tip-sample geometry.)

The quantity usually obtained from PFM experiments, $d_{33}$, is the piezoelectric coefficient that represents the out-of-plane piezoelectric response created by an out-of-plane electric field (see Supporting Information Note 1 for details on calculating $d_{33}$ from PFM signals). In actual PFM experiments, the measurement should be referred to as an effective value, $\tilde{d}_{33}$, because of additional possible contributions to the signal including material clamping, inhomogeneous field effects, and other electromechanical effects. Other factors that may affect the measurement and introduce experimental uncertainty include electrostatic effects, topographic artifacts, cantilever dynamics, and instrumental noise.

To help minimize the contribution of nonelectromechanical effects and obtain a quantitative estimate of the true electromechanical response of the test material, a vectorial background subtraction technique is used. PFM measurements taken on nonpiezoelectric substrates or without applying $V_{drive}$ serve as two different measurements of the background contribution to the measured MoS₂ signal. These measurements, which have an amplitude and phase component, can then be made into vectors. Next, by performing a vector subtraction of the background signal from the MoS₂ signal, a more accurate representation of $d_{33}$ can be obtained. The details of this process will be illustrated with data later in this paper.

Samples are made by transferring CVD grown MoS₂ from a growth substrate to either 70 nm gold (Au) or 5.3 nm alumina ($Al₂O₃$) deposited on an n⁺⁺ silicon substrate. Detailed sample preparation steps are described in the Methods as well as Figure S2. The Au is used to concentrate the electric field within the MoS₂ and serves as the bottom electrode. The $Al₂O₃$ serves as a dielectric layer to limit current flow with the n⁺⁺ Si substrate now acting as the bottom electrode. Figure 1 shows a schematic

![Figure 1](image-url)
of the two sample types, along with optical and tapping-mode AFM images of each. The Al2O3/Si sample has very limited optical contrast, resulting in very weak Raman and photoluminescence (PL) signals. In this case, tapping-mode AFM was used to identify locations of MoS2. Figure 2 shows Raman

![Figure 2.](image)

**Figure 2.** Raman measurements of (a) MoS2/Au/Si and (b) MoS2/Al2O3/Si samples. The areas measured are circled in the inset microscope images with corresponding colors. The scale bars are 10 μm. The intensity of the MoS2 Raman signals increases as thicker layers are measured. The peak separation also increases as the thickness increases, as expected. Only the thick MoS2 region on the Al2O3 sample gives a detectable Raman signature due to poor optical absorption caused by the substrate.

data taken at different locations on each sample. On the Au sample (Figure 2a), the separation of the E2g and A1g peaks for MoS2 increases from 19.7 to 25.7 cm\(^{-1}\) from monolayer to thick MoS2, and both peaks increase in intensity, which is consistent with observations reported in the literature. Only the thick MoS2 yields measurable Raman data on the Al2O3/Si sample (Figure 2b) with a peak separation of 26.1 cm\(^{-1}\). The peak near 520 cm\(^{-1}\) is from the underlying silicon. Further discussion of MoS2 thickness and weak Raman and PL data is provided in Supporting Information Note 2 and Figures S3–S5. PL and Raman measurements at different steps of sample preparation are shown in Figure S6, revealing that residual tensile strain caused during growth is released during the transfer process.

Figure 3 shows PFM images of MoS2 on Au. The topographic (Figure 3a), piezoresponse (PR) amplitude (Figure 3b), and PR phase (Figure 3c) channels with V\(_{\text{d}}\) applied show that there is clear contrast between the MoS2 and the Au. When the voltage is not applied, contrast in topography remains (Figure 3d) whereas contrast in piezoresponse disappears (Figure 3e,f), allowing topographic artifacts to be ruled out.

By using the values measured on Au and those measured without the voltage applied as two separate background signals in the vectorial background subtraction process, we obtain the out-of-plane effective piezoelectric coefficient of MoS2. As illustrated in Figure 4, with the amplitude and phase information, the measured PR of MoS2 on Au (black) and the measured PR of the Au background (red) are plotted as two vectors in a 2D x–y graph. In both cases, an average of the amplitude and phase data taken over an area of only monolayer MoS2 or the Au substrate is done to obtain the two vectors. The difference between the two vectors (blue) is taken to be the true PR coming from the MoS2. More details of the vectorial background subtraction method can be found in Supporting Information Note 3. The background-subtracted PR can then be converted to a \(d_{33}\) value using the deflection sensitivity of the cantilever and the drive voltage (details given in Supporting Information Note 1). We finally obtain 0.93 ± 0.23 and 1.12 ± 0.20 pm/V for \(d_{33}\) of MoS2 using the Au and the voltage-off condition as the background, respectively. The two values are consistent within our experimental uncertainty, reinforcing that there are minimal topographic artifacts, that the Au makes little to no contribution to the PR, and that the PR is truly associated with the presence of the MoS2. Detailed analysis of the uncertainty is given in Supporting Information Note 4. In comparison, a piezoelectric lithium niobate (LiNbO3) reference sample has a \(d_{33}\) of 7.5 pm/V, \(d_{11}\) for

![Figure 3.](image)

**Figure 3.** A series of two PFM measurements on the MoS2/Au sample with the drive voltage applied (V\(_{\text{on}}\)) (a–c) and not applied (V\(_{\text{off}}\)) (d–f). The topography images (a,d) show the background Au substrate, monolayer MoS2, and multilayer MoS2 regions. The applied drive voltage does not affect the topographic measurement (color bar is 0–5 nm for both). The piezoresponse (PR) amplitude images (b,e) show that the MoS2 region has contrast against the Au substrate only when the drive voltage is applied (b). The same is true for the PR phase images (c,f). Both amplitude images and phase images share the same color scale.
monolayer MoS$_2$ has been measured$^{13}$ to be 1.85 pm/V, and theoretical estimates for $d_{11}$ of MoS$_2$ range from 2.91 to 3.73 pm/V for clamped- and relaxed-ion cases.$^{11}$

To eliminate the possibility that the observed PR signals are affected by current flow at the tip-MoS$_2$−Au junction, the Al$_2$O$_3$/Si samples were fabricated to limit the potential current flow by introducing an insulating dielectric layer. Figure 5 shows the topographic (Figure 5a), PR amplitude (Figure 5b), and PR phase (Figure 5c) channels of the Al$_2$O$_3$/Si sample while $V_d$ is applied. Similar to the case of the Au sample, there are clear differences in the PFM signal on the MoS$_2$ versus Al$_2$O$_3$ when the voltage is applied, but no differences when the voltage is not applied (Figure 5d−f). In this case, an added complication arises because the voltage is being dropped over a larger distance and over two different materials. Given $V_d$ applied between the AFM tip and the n$^{++}$ silicon substrate, the voltage drop across only the MoS$_2$, $V_{MoS_2}$, can be estimated using a simple planar capacitance model

$$V_{MoS_2} = V_d \frac{\varepsilon_{Al_2O_3} t_{Al_2O_3} + \varepsilon_{MoS_2} t_{MoS_2}}{\varepsilon_{Al_2O_3} t_{Al_2O_3} + \varepsilon_{MoS_2} t_{MoS_2}}$$

where $\varepsilon_{Al_2O_3}$, $\varepsilon_{MoS_2}$, $t_{Al_2O_3}$, and $t_{MoS_2}$ are the permittivity of the Al$_2$O$_3$ and MoS$_2$, and the thickness of the Al$_2$O$_3$ and MoS$_2$, respectively (see Supporting Information Note 5). On the basis of the estimated voltage drop, $d_{33}^{eff}$ is calculated to be 1.34 ± 0.27 and 1.35 ± 0.20 pm/V using the Al$_2$O$_3$ or the voltage-off condition as the background, respectively. These values are slightly larger than the values measured on Au but are still within our experimental uncertainty. Discrepancies could be caused by variability in the separate AFM tips used, variable wear of the AFM tips, changes caused by the presence or absence of current flow, depletion of carriers in the n$^{++}$ Si bottom electrode, or differences in geometries between the two systems. The results for the two different types of samples are summarized in Table 1. The last column compares the signal

Figure 4. A schematic illustration of how the background subtraction method is performed to calculate $d_{33}^{eff}$. The amplitude and phase channels of the MoS$_2$ (black) and Au (red) PFM measurements are used to make two separate vectors. The actual signal is the difference between these two vectors (blue). The dashed circles at the end of the vectors represent the uncertainty of the measured amplitudes and phases.

Figure 5. A series of two PFM measurements on the MoS$_2$/Al$_2$O$_3$ sample with the drive voltage applied ($V_{on}$) (a,b) and not applied ($V_{off}$) (d−f). The topography images (a,d) show the background Al$_2$O$_3$ substrate, monolayer MoS$_2$, and bilayer MoS$_2$ regions. The applied drive voltage does not affect the topographic measurement (color bar is 0 to 3.7 nm for both). The PR amplitude images (b,e) show that the MoS$_2$ region has contrast against the Al$_2$O$_3$ substrate only when the drive voltage is applied (b). The same is true for the PR phase images (c,f). Both amplitude images and phase images share the same color scale.

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measured on the respective substrates to the voltage-off condition, showing that the substrates are not piezoelectric.

| Table 1. \( d_{\text{eff}} \) and Uncertainty Values Calculated from Preforming Background Subtraction with the Indicated PFM Vectors |
|-----------------|-----------------|-----------------|
|                  | \( \text{MoS}_2 \) versus Sub | \( \text{MoS}_2 \) versus \( V_{\text{eff}} \) | Sub versus \( V_{\text{eff}} \) |
| \( \text{Au/Si} \) sample | 0.93 ± 0.23 | 1.12 ± 0.20 | 0.19 ± 0.10 |
| \( \text{Al}_2\text{O}_3/\text{Si} \) sample | 1.34 ± 0.27 | 1.35 ± 0.20 | 0.04 ± 0.15 |

To understand the origin of the measured \( d_{\text{eff}} \) signal in the PFM experiment, including the potential contribution of flexoelectric response, a closer look at the forces involved in the measurement is required. The multiple contributions to the force that acts on the AFM tip can be summarized by

\[
F_{\text{tot}} = F_0 + F_{\text{ES}} + F_{\text{EM}}
\]

(2)

where \( F_{\text{tot}} \) is the total force, \( F_0 \) the elastic force, \( F_{\text{ES}} \) the electrostatic force, and \( F_{\text{EM}} \) the electromechanical force. The different force components can be further written as

\[
F_0 = kd_0
\]

(3a)

\[
F_{\text{ES}} = F_{\text{ES,Tip}} + F_{\text{ES,Cant}}
\]

(3b)

\[
F_{\text{EM}} = F_{\text{EM,Piezo}} + F_{\text{EM,Flexo}}
\]

(3c)

where \( k \) is the spring constant of the AFM cantilever and \( d_0 \) is the deflection set point, that is, the amount of deflection the cantilever experiences while in constant contact with the sample. The electrostatic force is split into contributions from the tip, \( F_{\text{ES,Tip}} \), and the cantilever, \( F_{\text{ES,Cant}} \), and the electromechanical force is split into components from piezoelectricity, \( F_{\text{EM,Piezo}} \), and flexoelectricity, \( F_{\text{EM,Flexo}} \).

The elastic contribution comes from the PFM measurement being a contact-mode AFM technique. The AFM tip is brought into contact with the sample surface and a constant feedback loop attempts to keep the tip and cantilever at a constant level of deflection, \( d_0 \). The constant deflection will create a constant elastic force given by eq 3a. Because the PFM measurement uses a lock-in amplifier which only amplifies signals at the same frequency as the reference signal, the constant elastic force will have no effect on the PFM signal.

However, during the scanning motion, the feedback system will be moving the tip vertically with the topography of the sample to maintain a constant deflection. This gives rise to two possible concerns: (1) the feedback frequencies may interfere with the applied drive frequency, and (2) the tip motion from changing topography could cause topographic artifacts if motion occurs at the same frequency as \( V_g \). A proper \( V_g \) frequency is chosen by taking a frequency sweep of the PR amplitude and choosing a frequency within which gives a largely frequency-independent PR amplitude (Supporting Information Note 6 and Figure S7). In this case, 60 kHz was chosen as the \( V_g \) frequency. Topographic artifacts from tip motion are ruled out by taking two successive PFM scans, one with \( V_g \) applied and one without, as shown in Figures 3 and 5. The voltage-off condition serves as an appropriate background measurement in which any tip motion from topography can be subtracted from the actual PFM signal. Because using the substrate or the voltage-off condition as the background signal gives consistent results, we conclude that the tip motion due to scanning does not have any noticeable effects on the measurement for either substrate.

The next possible contribution to the total force comes from electrostatic forces between the AFM probe and the substrate. These forces can come from the AFM tip or the AFM cantilever, as described by eq 3b. Contributions from the cantilever would act as parallel-plate capacitor-like interactions from the rectangular beam cantilever to the substrate. The dimensions of the cantilever used here are 125 \( \mu \text{m} \) \times 35 \( \mu \text{m} \), so any electrostatic interactions from the cantilever would be averaged over this entire area. Since Figures 3 and 5 show clear variation with submicron resolution, electrostatic interactions from the cantilever are concluded to be minimal.

Similarly, electrostatic forces from the AFM tip can contribute to the total force. This force can be written as

\[
F_{\text{ES,Tip}} = -\frac{1}{2}\frac{dC_{\text{Tip}}}{\text{d}z} \left( V_{\text{DC}} + V_{\text{AC}} \sin(\omega t) + \frac{\Delta \phi}{q} \right)^2
\]

(4)

where \( C_{\text{Tip}} \), \( V_{\text{DC}} \), \( V_{\text{AC}} \), \( \omega \), \( t \), \( \Delta \phi \), and \( q \) are the tip capacitance, applied DC voltage, applied AC voltage amplitude, frequency, time, work function difference between the tip and area under the tip, and electron charge magnitude, respectively. Because the PFM experiment uses a lock-in amplifier to measure tip deflection, it is sufficient to consider only the first harmonic of eq 4, yielding

\[
F_{\text{ES,Tip}} \propto \left( V_{\text{DC}} + \frac{\Delta \phi}{q} \right) V_{\text{AC}}
\]

(5)

This relation provides multiple insights for detecting electrostatic contributions to the PR signal. To determine if electrostatic forces are significant, a DC bias sweep can be performed while measuring the resulting PR amplitude. A linear absolute-value dependence on \( V_{\text{DC}} \) with a minimum at \( V_{\text{DC}} = \Delta \phi/q \) is expected if electrostatic forces are playing a role. Figure S8 shows a piezoresponse amplitude versus \( V_{\text{DC}} \) sweep at a drive frequency of 60 kHz and \( V_{\text{AC}} = 8 \text{ V} \). The piezoresponse amplitude is independent of \( V_{\text{DC}} \) under these conditions, indicating that electrostatic effects and any differences between the workfunctions of the two materials are not significant and can be neglected.

With the elimination of the first two terms in eq 2, the PFM signal must be coming from electromechanical effects. The first effect to consider is piezoelectricity, which is what the PFM was originally designed to measure. The piezoelectric tensor for monolayer MoS\(_2\) can be written as

\[
d_{ij} = \begin{bmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}
\]

(6)

where the indices correspond to those in the following definition of converse piezoelectricity

\[
e_{ij} = d_{ij} E_i
\]

(7)

Here, \( e_i \) is the strain tensor employing Voigt notation and \( E_i \) is the electric field. It is important to note that the piezoelectric tensor for MoS\(_2\) has nonzero components only within the plane of its atoms and has zero components for all out-of-plane responses. This indicates that there should be no piezoelectric effect out-of-plane. However, our experiments yield a nonzero...
value for $\alpha_{31}^{\text{eff}}$ suggesting that this signal could be originating from the flexoelectric effect instead of the piezoelectric effect.

The converse flexoelectric tensor for MoS$_2$ is given by

$$
\text{\boldsymbol{\mu}}_{\text{converse}} = 
\begin{bmatrix}
\mu_{11}^{*} & 0 & 0 & 0 & \mu_{15}^{*} & 0 & 0 & 0 & \mu_{19}^{*}
\end{bmatrix}
$$

where the * indicates that the converse representation is being used and the indices are defined using the converse flexoelectric equation

$$
\sigma_{ij} = \mu_{ij}^{\text{converse}} \partial E_k \partial x_l
$$

where $\sigma_{ij}$ is the stress tensor. The four indices can be transformed to two by using Voigt notation for $ij$ while $kl$ follow $11 \rightarrow 1$, $12 \rightarrow 2$, $13 \rightarrow 3$, $21 \rightarrow 4$, $22 \rightarrow 5$, $23 \rightarrow 6$, $31 \rightarrow 7$, $32 \rightarrow 8$, $33 \rightarrow 9$ to yield $\mu_{ij}^{\text{converse}}$.

To a good approximation, we can assume that the electric field in the MoS$_2$ layer is perpendicular to the surface of the Au and thus the plane of the MoS$_2$ atoms. With this assumption, the contribution of the first six columns of eq 8 to the electromechanical response of MoS$_2$ can be neglected. Also, the first two rows describe stresses created in-plane, which will not influence the PFM measurement. Possible contributions to an out-of-plane electromechanical response from an out-of-plane electric field then include $\mu_{33}^{\text{converse}}$ and $\mu_{39}^{\text{converse}}$. The former is an out-of-plane stress caused by a vertical electric field changing through the thickness of the MoS$_2$. The latter is an out-of-plane shear-stress mode caused by a vertical electric field varying laterally as it spreads away from the AFM tip.

In general, a superposition of both $\mu_{33}^{\text{converse}}$ and $\mu_{39}^{\text{converse}}$ will contribute to a measurable $\alpha_{31}^{\text{converse}}$ value. Although the electromechanical response can be thought of as an effective piezoelectric response, in light of the above analysis it may be more appropriate to refer to the value in this case as an effective flexoelectric response, $\mu_{33}^{\text{converse}}$.

To obtain a rough estimate of $\mu_{33}^{\text{converse}}$ from the measured $\alpha_{31}^{\text{converse}}$, the gradient $\partial E_k / \partial x_3$ is assumed to dominate and is estimated to be $2V/d^2$ (see Supporting Information Note 7 for details). These assumptions combined with eq 9, and $\sigma = Ye$ where $Y$ is Young’s modulus, yield the equation

$$
\mu_{33}^{\text{converse}} = \frac{\Delta \sigma}{V} \frac{t}{2} = \frac{\alpha_{31}^{\text{converse}}}{2} \frac{t}{2}
$$

where $\Delta \sigma$ is the vertical deflection of the MoS$_2$. By taking $Y = 270$ GPa$^3$ and $t$ to be a monolayer thickness of 6.5 Å, our PFM measurements for MoS$_2$ on Au and Al$_2$O$_3$/Si yield values for $\mu_{33}^{\text{converse}}$ of 0.08 and 0.12 nC/m, respectively. These estimates are calculated from measurements only on monolayer MoS$_2$ and further work is needed to analyze how the flexoelectric response would respond with increasing thickness of MoS$_2$ (see Supporting Information Note 8).

Previous studies$^{14}$ have reported that perovskite ceramics in the paraelectric phase have a $\mu_{\text{eff}}$ on the order of 1–100 μC/m while single crystal perovskites are on the order of 1 nC/m. Values of $\mu_{\text{eff}}$ for different measurement techniques and those obtained via experiment versus theory can also vary by orders-of-magnitude but are slowly converging.

A common way to get an order of magnitude estimate of the flexoelectric coefficient of a material is to use an estimate developed by Kogan.$^{39}$ He estimates the flexocoupling coefficient with the equation

$$
f \approx \frac{q}{4\epsilon_{0} \epsilon_{\text{eff}}} \mu_{\text{eff}}
$$

where $a$ is the lattice constant of the material. With the definition

$$
\mu \equiv \chi f
$$

where $\chi$ is the susceptibility of MoS$_2$, an order of magnitude estimate of $\mu_{\text{eff}}$ can be obtained for MoS$_2$. Taking $a = 3.2$ Å$^{40}$ and $\chi$ to be $3\epsilon_{0},^{41}$ the estimate of $\mu_{\text{eff}}$ is 0.12 nC/m. This is remarkably similar to the values derived from our experiments above.

The possibility of contamination on MoS$_2$ causing the measured out-of-plane electromechanical effects should not be overlooked. X-ray photoelectron spectroscopy (XPS) has been performed to detect the presence of various elements on the sample surfaces. Excess carbon, oxygen, and silicon are seen on the surface of the samples (see Supporting Information Note 9 and Table S1). Much of this is likely to be residue remaining on the surfaces after the polydimethylsiloxane (PDMS) transfer process, adventitious carbon that coats most surfaces when exposed to air, potentially other hydrocarbons, or unreacted MoO$_3$ precursor from the CVD process. The residue blankets the surface as it is detectable on the Au surface which contacts the PDMS but does not contain MoS$_2$. The substrate with residue gives little PFM signal, and the background subtraction process should remove most of the contribution to the signal generated from the residue. This does not conclusively rule out that the residue interacts differently with the MoS$_2$ than the substrate or that the slightly higher oxygen content on the sample affects the measurement. Further analysis is needed to definitively rule out contaminations affecting the measurement. However, the current experiment and analysis yields a strong possibility that out-of-plane flexoelectricity is present in monolayer MoS$_2$.

In summary, this work has shown that monolayer MoS$_2$ has an average measurable out-of-plane electromechanical response with a $d_{31}^{\text{eff}}$ of $1.03 \pm 0.02$ μm/V on Au and $1.35 \pm 0.24$ pm/V on Al$_2$O$_3$/Si. There is strong evidence that its origin is from the flexoelectric effect rather than the piezoelectric effect, and an estimate of the effective flexoelectric coefficient $\mu_{33}^{\text{converse}}$ yields 0.10 nC/m. The presence of flexoelectricity in 2D materials has implications across many fields. In 2D material electronics, for example, roughness in the substrate surface could create local curvature and thus local polarization that could affect electronic device performance.$^{42}$ It also opens the door to making new types of nanoscale sensors, actuators, or energy harvesters which could be used in conjunction with piezoelectricity to enhance operation.

**Methods.** Monolayer MoS$_2$ is grown via CVD on SiO$_2$ from solid precursors.$^{43}$ The as-grown MoS$_2$ is under roughly 0.21% residual tensile strain,$^{44}$ which is released during the transfer process. A PDMS stamp and a water bath are used to separate the MoS$_2$ from the growth substrate. The PDMS/MoS$_2$ is then placed on the receiving substrate, Au/Si or Al$_2$O$_3$/Si, and
heated with a hot plate to 50 °C. Slowly peeling away the PDMS transfers the MoS$_2$ to the substrate (see Figure S2 for details).

The Au sample is created via electron beam evaporation onto an n$^{++}$ silicon substrate. A 5 nm titanium adhesion layer is first deposited followed by 70 nm of Au. The Al$_2$O$_3$/Si sample is fabricated by first submerging a n$^{++}$ doped silicon substrate in 80:1 diluted HF to remove any oxide layer. The bare silicon is then immediately transferred into a Fiji ALD system. Using a trimethylaluminum precursor, a 5.3 nm thick layer of Al$_2$O$_3$ is deposited and thickness measured with a J.A. Woollam M-2000 DI ellipsometer.

Raman and PL data are taken using a Renishaw inVia Raman microscope with a 532 nm laser. PL and Raman data of the MoS$_2$ taken on the growth substrate, PDMS stamp, and Au sample show a clear relaxation of strain after the MoS$_2$ is removed from the growth substrate (see Figure S6).

PFM measurements are done on a Bruker (formerly Veeco) Dimension Icon AFM. Conductive cobalt—chromium AFM cantilevers are used (Bruker MESP-RC-V2) for PFM measurements. Tapping mode AFM images were taken using etched silicon cantilevers are used (Bruker TESP). A PFM drive frequency of 60 kHz and a drive amplitude of 8 V is used in all PFM measurements. See Supporting Information for more details.

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