Microsecond photocapacitance transients observed using a charged microcantilever as a gated mechanical integrator

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How light is converted to electricity in blends of organic donor and acceptor molecules is an unsettled question, partly because the spatial heterogeneity present in these blends makes them challenging to characterize. Although scanned-probe measurements have provided crucially important microscopic insights into charge generation and transport in these blends, achieving the subnanosecond time resolution needed to directly observe the fate of photogenerated charges has proven difficult. We use a charged microcantilever as a gated mechanical integrator to record photocapacitance indirectly by measuring the accumulated change in cantilever phase as a function of the time delay between precisely synchronized voltage and light pulses. In contrast with previous time-resolved scanned-probe photocapacitance measurements, the time resolution of this method is set by the rise and fall time of the voltage and light pulses and not by the inverse detection bandwidth. We demonstrate in an organic donor-acceptor blend the ability of this indirect, “phase-kick” technique to record multiexponential photocapacitance transients on time scales ranging from 40 μs to 10 ms. The technique’s ability to measure subcycle, nanosecond charge dynamics is demonstrated by measuring the tens of nanosecond sample electrical charging time.

INTRODUCTION

We introduce a method that significantly improves the time resolution of electric force microscopy (EFM), enabling the rapid acquisition of photocapacitance transients in solar cell films. A light pulse generates free carriers in the sample while a nearby charged microcantilever is used as a voltage-gated mechanical integrator to encode the time evolution of the subsequent carrier recombination as a change in the cantilever’s phase of oscillation. We illustrate the method by using it to reveal a biexponential photocapacitance buildup in a polymer-blend solar cell film, with the fast component having a risetime of 40 μs at high light intensity. We demonstrate the method’s time resolution in a control experiment in which we measure a tip-charging time of 35 ns.

Scanned probe microscopy has allowed researchers to explore spatial variations in charge generation and transport in solar cell films prepared on a conductive substrate (1–4) with a best-case resolution of 2 nm (5). Ginger and co-workers (6–9) introduced time-resolved EFM (tr-EMF), which enabled the study of photocapacitance transients on the microsecond time scale in bulk heterojunction organic blends. These studies revealed that photocapacitance charging rates were proportional to external quantum efficiency in prototypical organic bulk heterojunction blends, raising the exciting possibility of using scanned-probe microscope measurements to help rationally optimize the processing of organic semiconductor donor-acceptor blends.

We seek to extend the time resolution of EFM to study fundamental processes such as photoinduced electron transfer, charge recombination, charge trapping, photocatalysis, and ferroelectric switching at the single-molecule or single-domain level. Such studies would help us understand the mechanism of charge generation (10–21) and recombination (12, 18, 22, 23) in organic donor-acceptor blends, for example—a topic of intense debate. Nanosecond-resolution microwave conductivity measurements of charge generation have recently revealed tantalizing evidence that Marcus theory can be applied to understand charge generation in an organic donor-acceptor photovoltaic film (12, 24). The ability to perform analogous EFM measurements at high spatial resolution on conductive substrates is therefore an extremely exciting possibility. Frustratingly, the tr-EMF experiment’s time resolution is set by the detector and demodulation bandwidth; achieving nanosecond time resolution would seem to require using radiofrequency oscillators digitized at gigahertz sampling rates, which is impractical.

To impart EFM with nanosecond resolution, we must rethink the experiment from first principles. Ultrafast indirect scanning tunneling microscopy (STM) measurements have demonstrated nanosecond to picosecond time resolution on gallium arsenide, but these measurements lack the clear connection to organic solar cell performance demonstrated by Ginger et al. (tr-EMF) (25–32).

Indirect Kelvin probe force microscopy (KPFM) methods can measure surface potential changes with picosecond time resolution (33–37), but these measurements exploit the nonlinear dependence of photovoltage on light intensity and/or the nonlinear dependence of the cantilever frequency $f_c$ on photovoltage or assume that the tip voltage passively observes sample properties. Unfortunately, because photocapacitance generally depends linearly on light intensity, produces a linear change in $f_c$, and depends strongly on tip voltage, the ultrafast methods of previous studies (33–37) are not applicable to the donor-acceptor blends studied here.

Here, we demonstrate a new method to measure the photocapacitance charging rate—“phase-kick” EFM (pk-EMF). The pk-EMF measurement is sensitive to the same underlying photocapacitance dynamics as Ginger’s tr-EMF measurement. Our measurement uses an indirect, nonlinear detection protocol that enables the reconstruction of the full photocapacitance transient while sidestepping detector noise and demodulator bandwidth limitations to the achievable time resolution.

Photocapacitance measurements

We bring a conductive cantilever near an organic donor-acceptor semiconductor film (PFB:F8BT; see Fig. 1A). A voltage pulse is applied to the cantilever while a carefully timed light pulse is applied to the sample.
Because of electrostatic interactions with the sample, the cantilever’s resonance frequency is shifted by

$$\delta f(t) = -\frac{f_0}{4k_0}C''_r(t, \nu)(V_t - \Phi(t, \nu))^2$$  \hspace{1cm} (1)$$

where $f_0$ and $k_0$ are the cantilever resonance frequency and spring constant, respectively; $V_t$ is the tip voltage; $\Phi$ is the sample’s surface potential; and $C''_r$ is the second derivative of the tip-sample capacitance with respect to the vertical direction. We write $C''_r(t, \nu)$ and $\Phi(t, \nu)$ to indicate that these quantities depend on time and light through the sample’s photocapacitance and photopotential, respectively. The change in the curvature of the $\delta f$ versus $V_t$ parabola apparent in Fig. 1B indicates that in the PFB:F8BT sample, light primarily affects $C''$ and not $\Phi$.

To measure the time evolution of the sample’s photocapacitance in Fig. 1, we fixed the tip voltage at $V_t = 10$ V, and the cantilever frequency shift was recorded following the application of a light pulse. The large tip-sample voltage $V_t - \Phi$ makes the measurement relatively insensitive to light-induced changes in $\Phi$. In the representative data of Fig. 1C, the photocapacitance charging time is $t \sim 5$ ms. In Fig. 1D, we show that photoinduced changes in $C''_r$ persist for many seconds, making it difficult or impossible to collect reproducible data and implement signal averaging. As previously observed by Coffey and Ginger (6, 38), we found that $C''_r$ could be induced to recover quickly by returning the tip voltage to zero, which sweeps out the charge accumulated below the tip (text S1 and fig. S1).

**Experimental protocol**

Figure 2 shows our new, indirect photocapacitance measurement. We oscillate the cantilever at its resonance frequency using a commercial phase-locked loop (PLL) controller (Fig. 2A). Because the cantilever resonance peak in vacuum is narrow ($\Delta f_{FWHM} = 2.5$ Hz), we turn off the cantilever drive at $t = -10$ ms so that analysis of the photocapacitance transients is not complicated by PLL phase errors (Fig. 2B).

We apply precisely timed voltage steps and light pulses using a commercial pulse and delay generator. To begin the experiment, we step the tip-sample voltage from $V_t = 0$ to $V_t = 10$ V; light intensity, $I_{\text{light}}$, is $0.1$ kW m$^{-2}$ in (C) and $I_{\text{light}}$, is $20$ kW m$^{-2}$ in (D); light pulse time $= 50$ ms in (C) and $2.5$ ms in (D).

Over the next 50 ms, tip-sample charge equilibrates as additional electrons flow to the sample surface. The additional electrons increase the magnitude of the cantilever frequency shift from approximately $\delta f(-50$ ms) $= -133$ Hz to $\delta f(0) = -150$ Hz (Fig. 2D).

At $t = 0$, we apply a light pulse synchronized to the cantilever oscillation (Fig. 2D). The light pulse initiates charge generation, which causes a change in the capacitance derivative $C''_r$ (Fig. 2E). This change induces a small shift in the cantilever’s frequency of oscillation (Fig. 2F). The frequency shift concomitantly advances the cantilever’s phase of oscillation. At a time $t = t_p$, we arrest the photoinduced advance of the cantilever phase by abruptly stepping the tip voltage back to zero (Fig. 2C).

In these experiments, we simultaneously end the light pulse and the voltage step to limit the sample’s exposure to high light intensities (Fig. 2G). However, this synchronization is not critical for the measurement. No matter when the light pulse ends, $\delta f \approx 0$ after the voltage turns off because $V_t \approx \Phi$. After the voltage turns off, we wait a delay time $t_d$ before restoring the PLL drive. We wait at least 5 ms so that the data used to determine the cantilever phase at the end of the light pulse are not complicated by PLL phase errors ($t_d = 5$ to 15 ms).

Figure 2 (H to M) shows how we calculate the phase shift $\Delta \phi = \phi(t_p) - \phi(0)$. We measure cantilever displacement using a fiber interferometer, digitally sample the displacement at 1 MHz, and save the full transient for later analysis. We first process the cantilever displacement data using a software lock-in amplifier and determine the cantilever frequency before the beginning of the pulse and after the end of the pulse using 3.4 and 6 ms of data, respectively (text S2 to S4 and figs. S2 to S4). We use these frequencies to construct a second software lock-in amplifier with a variable reference frequency set to match the cantilever frequency before and after the pulse. From the in-phase and out-of-phase channels of the lock-in amplifier, we determine the cantilever amplitude, frequency, and phase. Setting the lock-in amplifier to match the cantilever’s...
We fit the measured capacitance transient by the time integral of the light-induced change in capacitance (Eq. 1). Because the capacitance transient is proportional to the integrated photocapacitance transient, the net phase shift is equal to the highlighted area under the cantilever frequency shift curve. The voltage- and light-induced phase shift is calculated using the software lock-in amplifier. The voltage and light turn off simultaneously at $t = t_p$. The software lock-in amplifier outputs the in-phase (solid) and out-of-phase (dashed) components of the cantilever displacement, and the frequency shift is calculated using the software lock-in amplifier. The net phase shift is equal to the highlighted area under the cantilever frequency shift curve.

**pk-EFM theory**

To demonstrate that our new technique is sensitive to subcycle, nanosecond dynamics, we model the cantilever as a harmonic oscillator with position $x$, momentum $p$, mass $m$, and spring constant $k_0$:

$$\dot{x} = p/m$$

$$\dot{p} = -\left(k_0 + \delta k(t)\right)x + F(t)$$

We fit the measured $\Delta \phi$ versus $t_p$ curve to learn about the sample’s transient photocapacitance.

In Fig. 3, we present an alternative view of the pk-EFM experiment. At the top of the figure, we plot versus time the sinusoidal cantilever displacement oscillation and, for comparison, a square-wave reference oscillation. With the light off, the cantilever and reference oscillator evolve in sync. Turning on the light causes the cantilever to begin oscillating at a lower frequency (Fig. 3, top middle) such that, by the time the illumination is halted, the cantilever’s phase of oscillation has shifted relative to that of the reference oscillator (Fig. 3, top right). At the bottom of Fig. 3, we show the evolution of the cantilever and reference oscillator as viewed in phase space and at the outputs of a lock-in detector. At long times (Fig. 3, lower right), the observed phase difference is blurred by phase noise in the cantilever oscillation, but the average phase difference is still retained.

$$F(t) = \frac{1}{2} C_i(t) V_i(t)^2$$

$$\delta k(t) = \frac{1}{2} C_i''(t) V_i(t)^2$$
Fig. 3. Phase space and lock-in detector representation of the pk-EFM experiment. Top: Sinusoidal cantilever displacement “signal” and square-wave “reference” oscillations versus time, initially (left), under illumination (middle), and with the illumination removed (right). Bottom: Evolution of the signal and reference oscillator as viewed in phase space (X, position; Y, momentum) and at the outputs of a lock-in detector (XLI, in-phase channel; YLI, out-of-phase channel) at short time (middle) and at long time (right).

first and second derivatives of the tip-sample capacitance with respect to height, and \( V_t \) is the tip voltage. We neglect dissipation because the experiments described here occur on a time scale much shorter than the cantilever ringdown time. Equations 4 and 5 are two coupled linear equations with time-dependent coefficients.

**Magnus expansion**

Although there is no general analytic solution to Eqs. 4 and 5, we can use the Magnus expansion to obtain a highly accurate approximate solution \(39, 40\). The cantilever’s evolution can be written in terms of the state vector \( x = (\mathbf{x}, p)^T \)

\[
\dot{x} = A(t) x + b(t)
\]

with a state matrix

\[
A(t) = \begin{pmatrix}
0 & 1/m \\
-m\omega^2(1 + \kappa(t)) & 0
\end{pmatrix}
\]

and generalized force

\[
b(t) = \begin{pmatrix}
0 \\
F(t)
\end{pmatrix}
\]

We write \( A \) using the cantilever resonance frequency \( \omega_0 = \sqrt{k_0/m} \) and the normalized spring-constant shift

\[
\kappa(t) = \delta k(t)/k_0
\]

The exact solution for the time evolution of the state vector in Eq. 8 can be written in terms of the system’s propagator \( U \)

\[
x(t) = U(t, t_0) x(t_0) + \int_{t_0}^{t} U(t, t') b(t') dt'
\]

The Magnus expansion writes the propagator as the exponential of a certain matrix \( \Omega \), \( U(t, t_0) = \exp \Omega(t, t_0) \). The first-order Magnus approximation for \( \Omega \) is

\[
\Omega(t, t_0) \approx \int_{t_0}^{t} A(t') dt'
\]

This gives the approximate propagator

\[
U(t, t_0) \approx \begin{pmatrix}
\cos(\bar{\omega}(t - t_0)) & (m\bar{\omega})^{-1} \sin(\bar{\omega}(t - t_0)) \\
-m\bar{\omega} \sin(\bar{\omega}(t - t_0)) & \cos(\bar{\omega}(t - t_0))
\end{pmatrix}
\]

where \( \bar{\omega}(t, t_0) \) is a time-dependent frequency representing the average cantilever frequency between the time \( t_0 \) and \( t \)

\[
\bar{\omega}(t, t_0) = \omega_0 (1 + \frac{1}{t - t_0} \int_{t_0}^{t} k(t') dt')^{1/2}
\]

Likewise, \( \theta(t, t_0) = \bar{\omega}(t - t_0) \) is the cantilever phase accumulated between \( t_0 \) and \( t \). Typically, \( \kappa \ll 1 \), so the phase is well approximated by

\[
\theta(t, t_0) \approx \omega_0 (t - t_0) + \frac{\omega_0}{2} \int_{t_0}^{t} k(t') dt'
\]

Equation 1, the usual KPFM expression for the cantilever’s frequency, is recovered by defining an instantaneous frequency \( 2\pi(t) = d\theta/dt \).

**Experimental protocol**

Consider the experiment of Fig. 2. We abruptly initiate sample illumination at time \( t = 0 \), and the sample’s capacitance begins evolving to a new steady-state value. Simultaneously, both \( C'_s \) and \( C''_s \) will likewise evolve to new values, following the same dynamics. The key to extracting the photocapacitance transient is that we can independently control the tip voltage \( V_t(t) \). At a subsequent time \( t = t_p \), we abruptly turn the tip voltage to zero as in Eq. 2. Inserting Eqs. 2 and 7 into Eq. 11 and inserting the result into Eq. 16 with \( t_0 = 0 \), we obtain

\[
\theta \approx \omega_0 t - \frac{\omega_0 V^2}{4k_0} \int_{t_0}^{t} C'_s(t') dt'
\]

which agrees with the phase shift given in Eq. 3.
Long-time response

For simplicity, let us model the photocapacitance dynamics as a single exponential with a risetime of \( \tau \). In this approximation, \( C'_i(t) = C'_i(0) + ΔC'_i(1 - e^{-t/\tau}) \) for \( t > 0 \). Inserting this \( C'_i(t) \) into Eq. 19, we obtain the cantilever phase measured at \( t ≥ t_p \)

\[
θ(t) ≈ \omega_0 t - \frac{\omega_0 V^2}{4k_0} ΔC'_i(0) t_p + Δφ
\]

(18)

\[
Δφ = -\frac{\omega_0 V^2}{4k_0} ΔC'_{hv}\left\{ t_p - τ + τe^{-t/\tau} \right\}
\]

(19)

The first term in this equation, \( ω_0 t \), is the expected time-dependent phase arising from free evolution of the cantilever. The second term is a pulse-time-dependent phase shift arising from the voltage-dependent force gradient. Because both \( ω_0 \) and \( ΔC'_i(0) \) are easily measured, it is straightforward to extract \( θ \) the additional phase shift \( Δφ \) arising from the transient photocapacitance. The slope of the \( Δφ \) versus \( t_p \) line is \( -ω_0 V^2 ΔC'_{hv}/(4k_0) \), and the intercept is \( τ \), the sample’s sought-after photocapacitance risetime.

Short-time response

At short times, the forcing term \( b(t) \) in Eq. 8 also contributes significantly to the cantilever’s subsequent motion. We model the \( C'_i \) photocapacitance dynamics with the same single-exponential risetime \( τ \): \( C'_i(t) = C'_i(0) + ΔC'_{hv}(1 - e^{-t/τ}) \). For reference, consider the effect of this force in the absence of photocapacitance (\( ΔC'_{hv} = 0 \)). The electrostatic force vanishes abruptly at time \( t = t_p \), so that the cantilever’s position and momentum evolve according to the equations

\[
\left\{ \begin{array}{l}
\frac{x(t > t_p)}{p(t > t_p)} \\
\end{array} \right.
\]

\[
= \left( \begin{array}{c}
A_0 \cos(ω_b(t - t_p) + φ_p) + Δx_0 \cos(ω_b(t - t_p)) \\
- mω_0 A_0 \sin(ω_b(t - t_p) + φ_p) \\
\end{array} \right)
\]

\[
= U(t, t_p) \left( \begin{array}{c}
A_0 \cos φ_p + Δx_0 \\
- mω_0 A_0 \sin φ_p \\
\end{array} \right)
\]

(20)

with \( Δx_0 = V^2 C'_i(0)/(2k_0) \) the DC deflection of the cantilever due to the electrostatic force on the tip and \( φ_p = θ(t_p) \) the cantilever’s phase at \( t_p \) given by Eq. 18. For \( Δx_0 ≪ A_0 \), the effect of \( Δx_0 \) on \( x \) in a voltage-only reference experiment can be written in terms of an equivalent shift in amplitude and phase given by, respectively

\[
ΔA_{ref} = Δx_0 \cos φ_p
\]

(21)

\[
Δφ_{ref} = -\frac{Δx_0}{A_0} \sin φ_p
\]

(22)

In words, the \( V_t \rightarrow 0 \) step leads to either an amplitude or a phase shift depending on the cantilever’s absolute phase of oscillation at the moment when the voltage is returned to zero.

The photocapacitance term \( ΔC'_{hv} \) adds an additional shift to the cantilever position and momentum

\[
\left\{ \begin{array}{l}
\frac{Δx_{hv}(t ≥ t_p)}{Δp_{hv}(t ≥ t_p)} \\
\end{array} \right.
\]

\[
= \frac{δx_{hv} \cos φ_p}{1 + τ^2/ω_0^2} \left( t_p - τ + τe^{-t/τ} \right) V(t, t_p) \left( \begin{array}{c}
0 \\
- mω_0 A_0 \sin φ_p \\
\end{array} \right)
\]

(23)

with \( δx_{hv} = V^2 ΔC'_{hv}/(2k_0) \) the DC deflection arising from the photocapacitance-related force. In writing Eq. 23, we have used the approximation that we are working in a short-time limit, where \( t_p ≪ 1/ω_0 \) and \( τ ≪ 1/ω_0 \). The shifts in position and momentum in Eq. 23 should be added to Eq. 20. The resulting change in cantilever position can be written in terms of an additional amplitude and phase shift. For \( τ_0 ≪ 1 \), the effect of \( δx_{hv} \) on the amplitude and phase is small compared to the effect of \( Δp_{hv} \). In this limit

\[
ΔA = -\frac{Δp_{hv}}{mω_0} \sin φ_p
\]

(24)

\[
Δφ = -\frac{Δp_{hv}}{A_0 mω_0} \cos φ_p
\]

(25)

Writing the amplitude and phase shifts out, we have

\[
ΔA = δx_{hv} \frac{ω_0}{1 + τ^2/ω_0^2} \left( t_p - τ + τe^{-t/τ} \right) \sin φ_p
\]

(26)

\[
Δφ = \frac{δx_{hv}}{A_0} \frac{ω_0}{1 + τ^2/ω_0^2} \left( t_p - τ + τe^{-t/τ} \right) \cos φ_p
\]

(27)

The braced terms in Eqs. 23, 26, and 27 show the same characteristic dependence on \( τ \) seen in the long-time phase shift experiment, Eq. 19. By controlling the timing of the voltage pulse, we can arrange for \( φ_p \) to be \( π/2 \); in this case, the short-time photocapacitance leads to a phase shift. We can instead encode the short-time photocapacitance as an amplitude shift by adjusting the pulse time, so \( φ_p = 0 \) or \( π \). Below, we demonstrate the use of an amplitude shift to verify the effect of short-duration (< 1 μs) voltage pulses on the cantilever. The slope of the \( Δφ \) versus \( t_p \) line is \( ω_0 V^2 ΔC'_{hv}/(2A_0 k_0) \). We observe that \( ΔC'_{hv}/A_0 ≫ ΔC'_{hv} \), making the accumulated phase per unit time in the short-time experiment an order of magnitude larger than one would expect from extrapolating Eq. 18. This fortuitous finding partially mitigates the challenge of observing the small total phase shift accumulated in a sample with submicrosecond photocapacitance dynamics.

RESULTS

See Materials and Methods for a description of sample fabrication, measurement, and data analysis protocols. We directly compared the new phase-kick technique outlined in Fig. 2 to trEFM by consecutively performing both experiments under identical illumination and sample conditions (\( I_{hv} = 100 \text{ kW m}^{-2} \), PFBF88BT on ITO). For the pkEFM experiment, we measured phase shift \( Δφ \) versus pulse time \( t_p \) for \( N = 768 \) data points with the pulse time varied from 0 to 1.4 ms. For each pulse time, we also collected a control data point with the light off. For
The tr-EFM experiment, we calculated the mean and SE of the frequency shift $\delta f$ versus time $t$ from $N = 384$ repetitions. For both experiments, an 87-ms delay (with $V_t = 0$ V) was included between repetitions to ensure that the sample’s photocapacitance was fully recovered. We operated at a tip-sample separation of $h = 250$ nm to limit the effects of tip-sample drift over the course of the 20-min measurement.

To compare the two experiments, we modeled the cantilever’s frequency shift under illumination as the sum of two exponentials

$$
\delta f(t) = \Delta f_1(1 - e^{-t/\tau_1}) + \Delta f_2(1 - e^{-t/\tau_2})
$$

The tr-EFM mean frequency shift data were fit directly to Eq. 28. Because the phase shift during the pulse is the integral of the frequency shift (Eq. 3), we fit the phase to the integral of Eq. 28.

We fit to a biexponential model because the data fit a single-exponential model poorly (text S5 and fig. S5). A biexponential model offers enough degrees of freedom to adequately fit our data. Because we do not yet have a microscopic model for photocapacitance, as explained in Discussion, we will not speculate on the physical origin of the two components. We conclude only that the measured frequency shift has both fast and slow components. A successful microscopic model would explain our observation of a fast initial change in capacitance and continued slow changes in capacitance that extend for much longer than a single-exponential model would predict.

We can nevertheless rule out several possibilities for the observed biexponential frequency and phase transients. At the highest light intensities, the changes in photocapacitance are fast enough to potentially involve our short-time response theory (Eqs. 20 to 27). We do see evidence that light-induced changes in the tip-sample force $F \propto C'_t$ affect the cantilever phase, but the size of the neglected phase shift is only $\sim 0.2$ mV, which is small compared to the total measured phase shift (texts S6 and S7 and fig. S6).

The measured power spectral density of the cantilever displacement signal shows no evidence that multimodal excitation occurs during our experiments (text S8 and figs. S7 and S8). The cantilever’s surface potential $\Phi$ shifted by $+160$ to $+440$ mV under illumination (from an intensity of 0.1 to 100 kW m$^{-2}$). Because we operated at a positive tip voltage, this light-induced surface potential shift would, in isolation, produce a positive cantilever frequency or phase shift. This positive shift is inconsistent with the negative frequency shift of the fast component. Therefore, it is unlikely that the fast component arises from a photovoltage transient.

In Fig. 4A, we compare the data sets by plotting the pk-EFM phase shift experimental and control data along with the integrated biexponential best fit calculated from both the pk-EFM and tr-EFM experiments. The gray points show the control data before correcting for the phase shift caused by the abrupt change in tip-sample voltage at the end of the pulse (Eq. 22; see text S4). In Fig. 4B, the raw tr-EFM data are compared to the biexponential best fit calculated from both the phase-kick and tr-EFM experiments. Although the two fits come from different data sets, they are quite consistent. The agreement between the plots in Fig. 4 (A and B) establishes that both techniques measure the same photocapacitance information.

To further demonstrate the equivalent information obtained with the two techniques, we repeated this direct comparison at light intensities ranging from 0.1 to 100 kW m$^{-2}$. The pk-EFM results are shown in Fig. 4C. The time constant was different at each light intensity. The best-fit time constants $\tau_1, \tau_2$ are found to be comparable for the two methods across the full range of intensities (Fig. 4D and fig. S5). For the fast $\tau_1$ time constants measured at 20 and 100 kW m$^{-2}$, the time constants and error bars are less directly comparable. The tr-EFM model does not account for the fact that the measured $\Delta f(t)$ is a convolution of the cantilever’s actual frequency shift with the lock-in amplifier filter, which explains why it measures longer time constants. The pk-EFM error bars are moreover highly dependent on the pulse times used; to better measure the very fast component of the 20 kW m$^{-2}$ data set, for example, more data points could be taken for pulse times from 0 to 100 μs. Consistent with the study by Coffey and Ginger (6), the time constants decrease with increasing intensity.

In general, the observed frequency shift is the convolution of the lock-in amplifier response function $\mathcal{H}$ and the measured frequency shift $\delta f_{\text{meas}}$. The convolution of the lock-in amplifier response function $\mathcal{H}$ and the measured frequency shift $\delta f_{\text{meas}}$ is given by

$$
\delta f(t) = (\mu \mathcal{G}(t)) = \delta f_{\text{meas}}(t) * \mathcal{H}(t)
$$

In tr-EFM or pk-EFM, we attempt to infer information about sample properties ($G_{\text{samp}}$) from the cantilever’s measured frequency (or phase) shift $\delta f_{\text{meas}}$. The measured frequency shift $\delta f_{\text{meas}}$ or phase shift $\delta \phi_{\text{meas}}$ is the convolution of the lock-in amplifier response function $\mathcal{H}$ and the cantilever’s actual frequency shift $\delta f_{\text{cant}}$.

$$
\delta f_{\text{meas}}(t) = (\mathcal{H} * \delta f_{\text{meas}})(t) = \int \mathcal{H}(\tau) \delta f_{\text{meas}}(t - \tau) d\tau
$$

In a typical direct measurement, it is assumed that sample dynamics are significantly slower than the time scale of the lock-in amplifier response, so that $\delta f_{\text{meas}}(t) \approx \delta f_{\text{meas}}(t)$.

In Fig. 5, we attempt to use tr-EFM to measure the sample’s fast charging time $\tau_2$. We step the cantilever tip voltage from $V_t = \Phi$ to $V_t = \Phi + 10$ V (Fig. 5A). The sample is a property of the sample response function $G_{\text{samp}}$ (Fig. 5B). We signal-average $N = 784$ steps, all precisely synchronized to the cantilever oscillation cycle. We demodulate the signal-averaged data with a wide bandwidth lock-in amplifier filter $\mathcal{H}$ (Fig. 5C; $\omega_4^{-1} = 20\mu$s). We expect that the cantilever’s actual frequency $\delta f_{\text{cant}}$ quickly changes as the sample charges on the microsecond or faster time scale. However, the measured frequency shift $\delta f_{\text{meas}}$ and phase evolve over a time scale of tens of microseconds, reflecting the time scale of the lock-in amplifier filter $\mathcal{H}$. We also observe a significant change in cantilever amplitude (Fig. 5D), which only...
occurs when the charging time occurs on a time scale similar to or faster than the inverse cantilever frequency: $t_c \lesssim \omega^{-1} = 2.6 \mu s \ (eq. \ S13)$. However, the time scale of the change in the cantilever’s measured amplitude is dominated by the response of the lock-in amplifier filter. To demonstrate the difficulty of inferring information about sample properties from the measured amplitude and frequency, we model the expected cantilever amplitude for sample charging time constants of $t_c = 0.1 \text{ ns}$ (orange) and $t_c = 1000 \text{ ns}$ (purple). The residuals for the two models are shown in Fig. 5E. Because $t_c \ll t_L$, there is essentially no difference in the cantilever’s measured amplitude versus time even over this four-order-of-magnitude range of sample charging times. Using the demodulated phase $\delta \phi_{\text{meas}}$ offers no improvement; the phase versus time transient exhibits the same characteristic broadening due to the convolution of the actual phase $\delta \phi_{\text{cant}}$ with the lock-in amplifier filter. The bandwidth of the lock-in amplifier measurement $b_L = 8 \text{ kHz}$ is much lower than the bandwidth of our detector $b_{\text{det}} = 200 \text{ kHz}$. With the results of our short-time response theory available (Eqs. 20 to 27), it is natural to consider measuring the light-induced shifts in cantilever position directly in the time domain. We fit the same signal-averaged displacement versus time data for $t < 0$ (Fig. 5J; blue curve). In Fig. 5K, we plot the difference between the measured displacement data and the blue curve fit. This difference corresponds to the additional cantilever displacement caused by the abrupt change in tip-sample voltage at the end of the pulse. The demodulated cantilever amplitude or phase, depending on the phase of the cantilever at the time of the voltage pulse. The magnitude of the amplitude or phase shift is related to the pulse time $t_p$. For instantaneous sample charging, we would expect $\Delta A_{\text{max}} \propto t_p$. Figure 6F shows that the magnitude of...
ΔA_{\text{max}}/t_p diminishes for short pulse times, consistent with charge being unable to get in and out of the sample on the time scale of the fastest pulses. From \( t_p = 50 \text{ ns} \) to \( t_p = 800 \text{ ns} \), the magnitude of the sample’s response changes by a factor of 2. The two points on the left of Fig. 6F show the measured amplitude response leveling off for \( t_p \) between 400 and 800 ns. However, for tr-EFM, the measured amplitude change only levels off on the time scale of the lock-in amplifier filter, tens of microseconds (Fig. 5D). Even measured directly in the time domain, the cantilever takes an order of magnitude longer (\( \sim 5 \mu\text{s} \)) to fully reflect the effect of the voltage pulse. The key difference is that in pk-EFM, a tip voltage pulse of length \( t_p \) effectively probes the average value of the sample response \( G_{\text{samp}} \) over the interval \( t = 0 \) to \( t_p \). This is markedly different from the tr-EFM measurement of Fig. 5 (D to F), where the measured amplitude, frequency, or phase at a given point in time is always averaged over the width of the lock-in amplifier filter. Crucially, in pk-EFM the measured phase or amplitude shift is independent of the lock-in amplifier or detector. This can be seen clearly in the data of Fig. 6C, where the same data are demodulated with two different bandwidths. Although the shape and smoothness of the traces in Fig. 6C are different, the same data are demodulated with two different bandwidths. Although the shape and smoothness of the traces in Fig. 6C are different, the integrated frequency shift or phase shift shown in Fig. 6D is the same. The only caveat is that the limits of the integral must be extended appropriately to account for the rise and fall time of the lock-in amplifier filter.

To quantitatively describe the experiment of Fig. 6 (A to F), we account for the finite charging/discharging time of the sample in response to a square pulse by writing \( V_t(t) = V (1 - e^{-t/t_c}) \) for \( t \in (0, t_p) \) and \( V_t(t) = V (1 - e^{-t/t_c}) e^{-t/t_p} \) subsequently, where \( V \) is the amplitude of the square pulse, \( t_c \) is the effective sample charging time, and \( t_p \) is the duration of the square pulse. Rewriting the derivative of the amplitude jump from this starting point gives \( \Delta A/t_p = \delta x_c \sin \phi_p (1 - \tau_c t_p^{-1} - \tau_c t_p^{-1} e^{-t_p/t_c}) \) with the phase shift \( \phi_p = 2\pi f_0 d \) controlled by the pulse time delay \( t_d \) and \( \delta x_c = V^2 C_t/(2k_0) \) a DC deflection due to electrostatic forces. The measured cantilever amplitude change in Fig. 6E shows the expected sinusoidal dependence on delay time. Figure 6F shows that the \( \Delta A/t_p \) versus \( t_p \) data are well described by the above equation with \( t_c = 34 \pm 5 \text{ ns} \).

To provide evidence that pk-EFM can likewise measure nanosecond photocapacitance dynamics, we simulated cantilever dynamics using a model similar to Eqs. 4 to 7. The simulations included independently measured effects from (i) near-surface cantilever frequency fluctuations (41–43), (ii) thermal fluctuations in cantilever position (44), (iii) detector noise (42), and (iv) transient force and force gradients arising from the gated photocapacitance signal. Representative numerical simulations assuming 30 min of signal averaging per curve—including realistic millisecond-duration photocapacitance “reset” delays—are shown in Fig. 6D. A photocapacitance risetime of 10 ± 2 ns is clearly resolved.

The data of Figs. 5 and 6 highlight the special ability of pk-EFM to measure fast photocapacitance signals. Another advantage of the pk-EFM experiment is that, in contrast with tr-EFM, time resolution during evolution and sensitivity during detection can be separately optimized. This advantage is explained in Fig. 7. The tr-EFM experiment directly measures the photocapacitance risetime constant by demodulating the cantilever oscillation versus time data using a lock-in amplifier filter with bandwidth \( \omega_0 \) and fitting the resulting frequency shift versus time data. The lock-in filter bandwidth limits the time resolution of the measurement because the measured frequency shift convolves the cantilever frequency shift with the lock-in’s filter function (Fig. 7, A and B). The wide filter bandwidth necessary to obtain improved time resolution also increases noise, as shown in Figs. 1C and 7B. Any such direct
measurement faces the same trade-off: detector bandwidth $b_L$ determines the time resolution $t_r = 1/2\pi b_L$; increasing $b_L$ to reduce $t_r$ leads to a larger mean-square frequency noise.

In contrast, pk-EFM is sensitive to arbitrarily fast changes in photocapacitance during the pulse time $t_p$. Time resolution is obtained by using short pulse times $t_p$. The ultimate time resolution is limited only by the ability to modulate the tip voltage, which can be as fast as picoseconds ($45–47$). We are free to use a phase filter to minimize the effect of surface and detection noise (Fig. 7D and texts S2 and S3). Figure 7E plots the power spectrum of the filtered phase fluctuations. The Fig. 7D filter successfully rejects both low-frequency surface-induced noise and high-frequency detector noise. The Fig. 7D filter—and therefore the mean-square phase noise—is essentially independent of the pulse time $t_p$ for short pulse times.

**DISCUSSION**

Here, we demonstrate a new indirect photocapacitance measurement, pk-EFM. The pk-EFM measurement uses the cantilever as a mechanical integrator and measures cantilever phase shift, a new observable. By measuring phase shift, the average frequency shift during the pulse is inferred without relying on slow modulation and lock-in techniques.

A comparison with the tr-EFM experiment is instructive. In FF-trEFM, the cantilever oscillation is detected, demodulated, and filtered; the measured parameter is the time $t_{FP}$ at which the resulting cantilever frequency transient reaches a maximum. This observed quantity depends not only on the photocapacitance risetime but also on a number of ancillary parameters including the filter parameters and the sample’s steady-state photocapacitance. For this reason, an empirical calibration step is required to relate the measured $t_{FP}$ to the sample’s underlying photocapacitance risetime. This empirical calibration step reduces the entire photocapacitance transient to a single number, $t_{FP}$. It is unclear how this calibration procedure works if the sample’s photocapacitance evolves on multiple time scales, as does the sample studied here. The time resolution of the tr-EFM measurement is limited by the detector bandwidth.

In pk-EFM, the cantilever charge is pulsed, and the cantilever oscillation is detected, modulated, and filtered; the measured parameter is the cantilever phase shift. Like ultrafast STM and KPFM photocurrent measurements, pk-EFM is an indirect measurement. Indirect measurements record only the average detector signal. To build up a picture of the sample’s fast dynamics, we measured the average detector signal for a series of different time-offset electrical or optical pulses. The time resolution is limited only by the duration or jitter of the pulses. Crucially, indirect measurements require a system nonlinearity so that the average detector signal responds to changes in pulse length, delay, or frequency. The phase shift $\Delta \phi$ in the pk-EFM experiment depends on the product of $C_L^*$ and $V_C$, so the limited-duration tip-voltage pulses provide the necessary nonlinearity.

In the pk-EFM experiment, no calibration step is required and the full photocapacitance transient is recovered by measuring the phase shift as a function of the pulse time. In contrast to previous indirect KPFM measurements, pk-EFM makes one phase shift measurement per pulse time, providing crucially important flexibility to include arbitrary wait times and voltage pulses before or after each measurement. This experimental flexibility allows pk-EFM to obtain reproducible photocapacitance measurements in organic semiconductor samples despite lengthy charge equilibration times.

The indirect nature of the pk-EFM method allows it to measure the full photocapacitance transient, not just the photocapacitance risetime. This capability was demonstrated here by uncovering a second, fast photocapacitance risetime not observed before in a nominally well-studied material. The pk-EFM measurement uses well-defined cantilever physics, which enables simulation (including relevant noise sources) of the experiment across a range of time scales. The experiment admits a rigorous signal-to-noise analysis, which details how sample fluctuations, thermal noise, and detection noise affect the measurement’s phase.
resolution. The experiments show that pk-EFM is capable of measuring a photocapacitance transient whose risetime is much shorter than the inverse demodulation bandwidth and the cantilever period. Numerical simulations indicate that pk-EFM is capable of resolving a photocapacitance transient whose dynamics are six orders of magnitude faster than the inverse detection bandwidth (Fig. 6G).

The pk-EFM measurement, with a faster pulsed light source and modest improvements in the time response of the cantilever-circuit charging time, is poised to achieve nanosecond resolution, comparable to what time-resolved microwave conductivity can achieve. Nanosecond-resolution time-resolved microwave conductivity (TRMC) measurements have generated the first evidence that Marcus theory governs charge carrier generation in dilute donor-acceptor films prepared on nonconductive substrates (24). TRMC measures the charge-mobility product. Despite Ginger et al.’s empirical connection between the tr-EFM risetime and device efficiency, it is not yet clear what microscopic material property the tr-EFM photocapacitance experiment is measuring. Ginger and co-workers observe that light affects primarily the risetime, not the magnitude, of the photocapacitance signal in the EFM experiment. This finding suggests to us that the tr-EFM experiment is mainly probing the sample’s photocconductivity. More work is required to test this hypothesis. Tirmzi et al. (48) recently reformulated a theory for the EFM experiment that explicitly incorporates the complex sample impedance. Unifying this improved treatment of the EFM experiment with the pk-EFM theory presented here should allow us to connect the pk-EFM transient signal to materials properties and, ultimately, to microscopic theory. Given its high temporal and spatial resolution, the phase-kick electric force microscope pk-EFM method introduced here clearly opens up many exciting possibilities for studying charge carrier generation and recombination in a wide range of device-relevant semiconductor films.

MATERIALS AND METHODS

Sample preparation
ITO substrates (Nanocs; 10 Ω/sq.) for depositing organic semiconductors were scrubbed with an Aquet liquid detergent/deionized (DI) water solution, rinsed with DI water, and sonicated in a fresh Aquet solution for 5 min. The chips were rinsed, sonicated in pure DI water for 5 min, and dried with high-pressure nitrogen gas. Before depositing the solar cell blend, the chips were plasma-cleaned for 10 min.

To prepare organic bulk heterojunction samples, we separately dissolved 75 mg of PFB [poly(9,9′-dioctylfluorene-co-bis-N,N′-(4-butylphenyl)-bis-N,N′-phenyl-1,4-phenylenediamine)] and F8BT [poly(9,9′-dioctylfluorene-co-benzothiadiazole)] in 5 ml of p-xylene. The solutions were filtered using PTFE (polytetrafluoroethylene) syringe filters, mixed together, and used immediately. Approximately 200 μl was deposited on an ITO substrate and was spin-coated at 2000 rpm for 60 s. All sample preparation was done in a dark room under orange light, and samples were immediately transferred to a nitrogen glovebox. The samples were transferred from the glovebox to the microscope at night, under red light illumination, and exposed to air for less than 15 min.
**Scanned probe microscopy**
All experiments were performed under vacuum (8 × 10⁻⁷ mbar) in a custom-built scanning Kelvin probe microscope (49). The cantilever (MikroMasch HQ:NSC18/Pt conductive probe) had resonance frequency, spring constant, and quality factor, which were determined by measuring the current source (ILX Lightwave LDX-3620), and the current was modulated at radio frequencies using the input on the laser diode mount (ILX Lightwave LDM 4984, temperature-controlled with ILX Lightwave LDT-5910B) (50). The interferometer light was detected with a 200-kHz bandwidth photodetector (New Focus model 2011, built-in high-pass filter set to 300 Hz) and digitized at 1 MHz (National Instruments, PCI-6259). The cantilever was driven using a commercial PLL controller (RHK Technology, PLLPro2 Universal AFM controller), with PLL loop bandwidth of 1.2 kHz (PLL feedback loop integral gain I = 2.5 Hz⁻¹, proportional gain P = 12°/Hz).

For pk-EFM and tr-EFM photocapacitance measurements, the sample was illuminated from above with a fiber-coupled 405-nm laser (Thorlabs, LP405-SF10, held at 25°C with a Thorlabs TED200C). The laser was turned on and off using the external modulation input of the laser’s current controller (Thorlabs, LDC202, 200-kHz bandwidth), and the laser power was measured using a fiber-coupled power meter for each external voltage input. The light was coupled to the sample using a 50-μm core, 0.22-numerical aperture fiber (Thorlabs, FG050LGA) (49). The estimated spot size on the sample was (330 × 120) μm², and the illumination intensity was estimated from the measured power and estimated spot size. The measured switching delay was 3.4 μs, with a 2.5-μs 0 to 100% risetime (fig. S11). The tip voltage was switched off 10 V beginning 50 ms before the start of the light pulse, to allow the sample charges to equilibrate (Fig. 2D). The cantilever drive was switched off 10 ms before the start of the light pulse to avoid complicating the cantilever motion with artifacts from the PLL response (7). A commercial pulse and delay generator (Berkeley Nucleonics, BNC565) was used to generate tip voltage and light modulation pulses, as well as to turn off the cantilever drive voltage. The BNC565 was triggered synchronous with the cantilever oscillation (text S12 and fig. S12). Between individual pulses, the sample was allowed to recover for 87 ms to 4 s with the tip voltage \(V_t = 0 \text{ V}\).

Swept-voltage KPFM curves were taken before and after each pk-EFM or tr-EFM measurement to determine the tip-sample capacitance and surface potential (51). The sample’s voltage (controlled with Leybold Model 2400) was adjusted to the sample’s surface potential (typically 0.2 to 0.4 V), so that \(V_t = 0 \text{ and } \Phi = \text{ constant}\). Measurements were performed 250 ± 10 nm above the surface, determined by measuring the 50% amplitude reduction point before and after each measurement. Data sets with significant tip-sample drift (> 10 nm) over the course of the 1- to 20-min measurement were discarded. Before turning off the PLL drive \((t = -10 \text{ ms})\), the cantilever zero-to-peak amplitude was \(A = 50 \text{ nm}\). At \(t = 0\), the cantilever zero-to-peak amplitude was 42 nm.

The raw cantilever oscillation data (digitized at 1 MHz) was saved along with counter timings (PCI-6259, 80-MHz counter) indicating the precise starting time of the light pulse (synchronized to the cantilever oscillation), allowing the start of the light pulse to be determined to within 12.5 ns. Along with each pk-EFM phase shift data point, a control data point, identical except without turning on the light, was collected.

**Data workup**
The data were processed in Python using a virtual lock-in amplifier technique. First, the data were processed through a fixed-frequency lock-in amplifier, with the reference frequency \(f_{ref}\) equal to the frequency where the data’s Fourier transform was a maximum. The lock-in filter was a modified Blackman finite impulse response filter, as described in text S2, designed to pass frequencies below \(f_{ref} = 2 \text{ and to eliminate frequencies above } f_{ref} = 8 \text{ kHz (3-dB bandwidth, 3.84 kHz). To precisely determine the additional light-induced phase shift in the vicinity of large changes to the cantilever frequency caused by stepping the cantilever tip voltage, we also processed the data with a frequency-variable virtual lock-in amplifier, with**

\[
f_{ref} = \begin{cases} f_1 & t \leq t_p \\ f_2 & t > t_p \end{cases}
\]

The complex output \(z\) of the lock-in amplifier was demodulated into amplitude \(A = |z|\) and phase \(\phi = \arg z\). The frequency was calculated from the phase using a central-difference numerical derivative.

**pk-EFM phase difference filter**
The filtering of the frequency and phase was performed analogously. The frequency \(f_1\) was chosen to be the best estimate of the cantilever frequency before the start of the light pulse, determined by averaging \(f(t)\) out of the lock-in with an exponential weighting with a time constant of 0.67 ms. The frequency \(f_2\) was chosen to be the best estimate of the cantilever frequency after the end of the voltage pulse, using a 1.2-ms exponential time constant. These same time constants were used to determine the phase estimate of the cantilever phase before and after the pulse. The time constants were chosen to minimize the noise, which is determined by the competition between low-frequency surface-induced noise, which needs to be allowed through the filter to better estimate the actual frequency and phase, and high-frequency detection noise, which needs to be rejected to estimate frequency and phase as precisely as possible. The time constants are different because after the pulse, the tip voltage was set to \(V_t = 0 \text{ V}\), reducing the surface noise and allowing the phase and frequency to be determined more precisely by averaging for a longer time (fig. S3). The phase before and after the pulse was determined using a weighted linear fit with the same exponential weighting used to determine the frequency (text S3). The phase difference filter is shown in Fig. 7D.

As illustrated in Fig. 7D and fig. S4, a weighted linear fit, with the same exponential time constants used to determine \(f_1, f_2\), was used to analyze the control data before and after the end of the pulse. To determine the precise cantilever phase at the end of the pulse, we used the 20 displacement data points nearest to \(t = t_p\) to create a Krogh interpolator in Scipy (52, 53). The Krogh interpolator and its first derivative evaluated at \(t_p\) give the cantilever position \(x\) and velocity \(v\). The cantilever phase was calculated from \(x\) and \(v\) using

\[
\phi|_{t=t_p} = \arg \left( x - \frac{v}{2\pi f[k]} i \right)
\]

\[
t_d = 2\pi \phi f[k]
\]

where \(f[k]\) is the cantilever frequency determined by the digital lock-in amplifier at the data point nearest in time to \(t_p\).
The resulting amplitude change $\Delta A$ versus delay time $t_d$ and phase shift $\Delta \phi$ versus $t_d$ plots were fit to sinusoids, and the best-fit phase shift was used to correct the raw phase shift data acquired in the light-on pk- EFM data set (Fig. 4A). The corrected phase shifts are plotted in Fig. 4 (A and C).

The tr- EFM data were processed with a filter bandwidth dependent on the fastest time constant in the sample ($f_{LP1} = 4$ kHz, $f_{LP2} = 15$ kHz for the 20,100 kW m$^{-2}$ intensity data sets). The resulting frequency versus time data were aligned relative to the start of the light pulse and averaged ($N = 32$ to 384). The 100 kW m$^{-2}$ tr- EFM data are shown in Fig. 7B. See text S2 for more information.

**Statistical analysis**

Signal-averaged tr- EFM frequency shift versus time data and processed phase shift versus pulse time data were fit to biexponentials using PyStan (54), a programming environment for Bayesian modeling. In both cases, the data were modeled assuming that the frequency shift versus time data were constant before the light pulse and was characterized by a biexponential decay afterward. The tr- EFM average frequency $ar{f}$ and SE $\sigma_f$ at each time $t$ were used to model the experimental data. The mean frequency shift $\bar{f}$ was modeled as normally distributed with mean $\mu$ and SE $\sigma$, the tr- EFM model was

$$
\begin{align*}
\bar{f}[t] &\sim N(\mu_f, \sigma_f[t]) & t \leq 0 \\
\bar{f}[t] &\sim N(\mu_f + \Delta f_{\phi}, r(1 - e^{-t/\tau_1}) + (1 - r)(1 - e^{-t/\tau_2})), \sigma_f[t] & t > 0
\end{align*}
$$

where $\bar{f}[t], \sigma_f[t]$ were the experimental mean frequency shift and SE calculated from signal-averaging $N$ tr- EFM measurements. The model’s parameters were $\mu_f$, the cantilever frequency before the pulse; $\Delta f_{\phi}$, the steady-state frequency shift caused by the photocapacitance; $r$, the fraction of the steady-state frequency shift attributed to the faster time constant; and $\tau_1$ and $\tau_2$, the exponential time constants, with $\tau_1 < \tau_2$.

The pk- EFM model was more complicated, because more low-frequency phase noise enters the measurement at longer pulse times. We captured this time-dependent phase noise by modeling the phase noise SD $\sigma_{\phi}[t]$ as

$$
\sigma_{\phi}[t_p] = \sigma_0 + \sigma_1 t_p + \sigma_2 t_p^2
$$

with $\sigma_0$, $\sigma_1$, and $\sigma_2$ parameters. We modeled the observed $\Delta \phi[t_p]$ using

$$
\mu_{\phi}[t_p] = \Delta f_{\phi} r \left\{ t_p - \tau_1 + \tau_1 e^{-t_p/\tau_1} \right\} + (1 - r) \left\{ t_p - \tau_2 + \tau_2 e^{-t_p/\tau_2} \right\}
$$

$$
\phi[t_p] \sim N(\mu_{\phi}[t_p], \sigma_{\phi}[t_p])
$$

where $\mu_{\phi}[t_p]$ is the integral of the frequency shift induced by the light pulse (Eqs. 3 and 19).

For both models, weakly informative priors were chosen for $\Delta f_{\phi}$, $\tau_1$, and $\tau_2$. A uniform prior between 0 and 1 was used for the ratio $r$. Noise parameters $\sigma_0$, $\sigma_1$, and $\sigma_2$ used implicit flat priors. The parameter means, SDs, and 15, 50, and 85 percentile best-fit curves in Fig. 4 were calculated using at least $N = 6000$ samples drawn from the posterior. See text S13 and figs. S13 to S15 for more information.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/6/e1602951/DC1

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Citation: R. P. Dwyer, S. R. Nathan, J. A. Marohn, Microsecond photocapacitance transients observed using a charged microcantilever as a gated mechanical integrator. Sci. Adv. 3, e1602951 (2017).
Microsecond photocapacitance transients observed using a charged microcantilever as a gated mechanical integrator
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Sci Adv 3 (6), e1602951.
DOI: 10.1126/sciadv.1602951